Selected papers from the 14th International Conference of the IWA Diffuse Pollution Specialist Group, DIPCON 2010

IWA International Water Association

Specialist Conferences

14th International Conference,
IWA Diffuse Pollution Specialist Group:

Diffuse Pollution and Eutrophication

Agriculture and Agri-Food Canada

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Université Laval

ISSUES AND SOLUTIONS TO DIFFUSE POLLUTION

Eric van Bochove, Peter A. Vanrolleghem, Patricia A. Chambers, Georges Thériault, Beáta Novotná and Michael R. Burkart

Conference sponsored by the OECD Co-operative Research Programme on Biological Resource Management of Sustainable Agricultural Systems

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Preface

On behalf of the Editorial Committee, we are pleased to publish a book of selected papers from the 14th International Conference of the IWA Diffuse Pollution Specialist Group (DIPCON 2010) held in September 12-17, 2010, Beaupré, Québec, Canada. This book entitled "**Issues and Solutions to Diffuse Pollution**" includes 17 keynote papers and 33 session papers selected by the Editorial Committee on the basis of their relevance and scientific merit, as well as the fact that they reflect the international scope of the issue.

Because of the fast-growing knowledge base on identification, fate and management of diffuse pollution, the objective of the DIPCON 2010 conference was to discuss the most recent research findings and information and for the 220 participants from 36 countries to learn and network about Diffuse Pollution and Eutrophication. The DIPCON conferences are a unique venue for these types of interactions as they are attended by a variety of specialists from academic, institutional and consultant organizations from around the world.

Water, air and soil contaminants from diffuse sources include sediment, nutrients, metals, trace elements, pesticides, pathogens, pharmaceuticals and other anthropogenic chemicals. The variety and complexity of processes generating, delivering, transporting and transforming diffuse pollutants concern scientists, economists, policy specialists and stakeholders who are working together to identify new approaches and solutions that protect natural resources. Although most of these diffuse pollution aspects were presented and discussed at the DIPCON 2010 conference, this OECD sponsored book focuses on five topics: 1. Watershed management to reduce diffuse pollution; 2. Managing nutrients in freshwater systems; 3. Policy and economics to manage diffuse pollution; 4. Emerging contaminants and micropollutants; 5. Modelling, monitoring and analytical methods.

We are grateful to all international authors who contributed to the 50 papers published in this book. The success of this international conference was possible with the support of Agriculture and Agri-Food Canada and Université Laval as convenors of the conference; the major sponsorship of OECD through its Co-operative Research Programme *Biological resource management for sustainable agriculture systems*; and special sponsorships by the Government of Québec (MDDEP, MAPAQ), the Government of Canada (NRCan), the International Joint Commission (IJC), Institut national de la recherche scientifique (INRS-ETE) and Institut de recherche et de développement en agroenvironnement (IRDA).

Eric van Bochove
(on behalf of Peter A. Vanrolleghem,
Patricia A. Chambers, Georges Thériault,
Beáta Novotná and Michael R. Burkart)

1 DIFFUSE POLLUTION WORKSHOPS

Communicating Expert Information on Critical Issues

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Abstract

Workshops held during the 14th Diffuse Pollution conference provided a forum to discuss six critical and emerging issues of international interest. Workshops were coordinated with platform and poster session to provide conference participants opportunities to focus on topics by participating in all three presentation styles. Topics discussed included: Nutrient criteria to protect aquatic life of streams and lakes in intensive agricultural watersheds; Watershed management practices to reduce nutrient loss from agricultural systems-- Research results establishing effective and non-effective conservation practices; Water-quality trading-- Pre-requisite analyses; Emerging contaminations in groundwater and surface water-- selected substances, pathogens, sources, monitoring, risk assessment and management; Landscape controls on diffuse nutrient transfers in agricultural catchments; and Managing urban stormwater quality in a changing climate-- Science, engineering and policy. Papers summarizing the discussions and conclusions will be prepared for submission to IWA's *Water 21*. The workshops were largely funded by the Trade and Agriculture Directorate: Organisation for Economic Cooperation and Development, Co-operative Research Programme and the venue and organization was made possible through the efforts of the International Water Association, Diffuse Pollution Specialist Group, Chaired by Dr. Eric van Bochove, as part of the 14th International Conference: Diffuse Pollution and Eutrophication.

Keywords

Agriculture; BMP; Nutrients; Stormwater; Stream Health; Water-quality Trading

The 14th Diffuse Pollution Conference incorporated six workshops that offered opportunities to discuss and contribute to summary papers on critical and emerging issues of international interest. Workshop topics included:

- Nutrient Criteria to Protect Aquatic Life of Streams and Lakes in Intensive Agricultural Watersheds
- Management Practices to Reduce Nutrient Loss from Agricultural Systems: Research Results Establishing Effective and Non-effective Conservation Practices
- Water Quality Trading: Pre-requisite Analyses
- Emerging Contaminations in Groundwater and Surface Water: Selected Substances, Pathogens, Sources, Monitoring, Risk Assessment and Management
- Landscape controls on diffuse nutrient transfers in agricultural catchments
- Managing Urban Stormwater Quality in a Changing Climate: Science, Engineering and Policy

Objectives

Each workshop provided a forum during which two keynote papers were presented with sufficient additional time for discussions from all participants. Workshops schedules were coordinated with platform and poster session themes. This provided conference delegates opportunities to focus on a choice of three themes each day by participating in all three presentation styles.

Structure

Sixty minutes of each workshop was allocated for brief introductory comments, speakers' formal presentation (25 minutes each) and questions of the speakers specifically related to their presentation. The remaining 30 minutes of each workshop were devoted to open discussion of topics not specifically covered by keynote speakers. A Chair and a Secretary shared responsibilities for inviting speakers and participants as well as managing the discussion, recording participants' comments and drafting, editing, and distributing written workshop products.

Products

The results of each workshop will be formulated into a written product that includes a summary of presented papers, participant discussions, and any conclusions reached. Written products will be reviewed by participants before being submitted for publication to the editors of Water 21 by individual workshop chairs and secretaries with the support of the workshop coordinator and the conference organizing committee.

Workshop Descriptions

NUTRIENT CRITERIA TO PROTECT AQUATIC LIFE OF STREAMS AND LAKES IN INTENSIVE AGRICULTURAL WATERSHEDS*

Chair: Michael R. Burkart, Iowa State University, Ames, Iowa, U.S.A.
Secretary: Brook Harker, Agriculture and Agri-Food Canada, Regina, Saskatchewan, Canada

This workshop is the first of two linked workshops to bring together scientists studying the response of aquatic life to excess nutrients (N and P) and those scientists studying methods to reduce nutrient loading from agricultural systems. Discussions included the strategies and methods being developed to identify aquatic ecosystems requiring protection and the range of nutrient levels that limit these ecosystems. Discussions were initiated by speakers having experience with the scientific and regulatory constraints which impact the process of establishing nutrient criteria/targets/standards. Critical questions to which answers were discussed included:

- Are there nutrient levels which indicate an unquestionably healthy aquatic ecosystem regardless of the geographic setting?
- How can the effects of nutrients on aquatic ecosystems be effectively classified and realistically assessed—in terms of water quality, biodiversity, individual species or ecosystem health?
- How can we apply knowledge of trophic conditions for lakes to establishing nutrient criteria for streams and rivers?
- Can we define nutrient criteria that unquestionably indicate an unhealthy aquatic ecosystem?
- How can we apply knowledge of trophic conditions for lakes, to establishing nutrient criteria for streams and rivers?
- Can we define nutrient criteria that unquestionably indicate an unhealthy aquatic ecosystem?
- How do we account for variability in geographic conditions when setting nutrient criteria?
- Do you have existing nutrient targets or criteria for aquatic life in streams and lakes in your region? If so, what strategies were/are being used to define them?
- What are the social, political, and economic barriers to adopting effective nutrient criteria in agricultural regions?

* *The workshop proceedings were published in the February 2011 Issue of Water21 – magazine of the International Water Association, pages 20-22.*

Keynote Speakers

Patricia A. Chambers, Environment Canada, *Development of nitrogen and phosphorus criteria for streams in agricultural landscapes.* See Keynote paper in Chapter 3.

Kenneth S. Lubinski, U.S. Geological Survey, *The scientific basis for designating important aquatic ecosystems and river ecosystem goals in agriculturally dominated watersheds.* See Keynote paper in Chapter 3.

MANAGEMENT PRACTICES TO REDUCE NUTRIENT LOSS FROM AGRICULTURAL SYSTEMS: RESEARCH RESULTS ESTABLISHING EFFECTIVE AND NON-EFFECTIVE CONSERVATION PRACTICES

Chair: Brook Harker, Agriculture and Agri-Food Canada, Regina, Saskatchewan, Canada
Secretary: Michael R. Burkart, Iowa State University, Ames, Iowa, U.S.A.

This workshop brought together scientists studying the response of aquatic life to excess nutrients and those scientists studying methods to reduce nutrient loading from agricultural systems. It specifically discussed conservation practices effective in reducing the loss of N and P to water from extensive and intensive agricultural practices. Speakers were keynote to discuss experiences in the Watershed Evaluation of BMPs (WEBs) project in Canada and the Conservation Effects Assessment Project (CEAP) in the United States. Critical questions to which answers will be discussed included:

- What general strategies (e.g., modelling, hydrologic analysis) can be applied to targeting the location and scale of nutrient-reducing conservation practices?
- Have modelling strategies been effectively calibrated to real field measurements and as to the value of scaling-up, scaling-down findings for policy relevance?
- Are there practices that reduce both P and N or can these nutrients only be reduced using different strategies?
- Are there practices that reduce both P and N or can these nutrients only be reduced using different strategies?
- What practices have resulted in reduced nutrient losses in a variety of climates, landscapes, and agricultural production systems?
- What traditional or novel conservation practices have been shown to be inefficient or ineffective (from either a biophysical or economic standpoint) in reducing nutrient losses from agricultural systems?
- How will a better understanding of watershed-scale landscape relationships help us to better predict the performance of current and possible future nutrient-reducing BMPs?
- What are the trade-offs involved in reducing surface runoff contributions vs. increasing groundwater contamination hazards?
- How important are long-term evaluations to assessing the overall effectiveness of a particular BMP or suite of BMPs at watershed scale?

Keynote Speakers

Mark D. Tomer, U.S. Agricultural Research Service, *Lessons from CEAP: Opportunities and Challenges for Improving Water Quality Performance of Conservation Systems.* See Keynote paper in Chapter 2.

Eric van Bochove, Agriculture and Agri-Food Canada, *Relationships between watershed-scale landscape, hydrology and agricultural practices towards surface and ground water quality improvement: the Bras d'Henri River, Quebec, Canada.* See Keynote paper in Chapter 2.

WATER QUALITY TRADING: PRE-REQUISITE ANALYSES

Co-Chairs: Sean Blacklocke, Environmental Consultant, Dublin, Ireland
Ray Earle, Dublin City Council, Dublin, Ireland
Secretary: John Joyce, Stockholm International Water Institute, Stockholm, Sweden

This workshop brought together researchers and managers from engineering and the natural and social sciences interested in exploring an alternative to achieve cleaner waterways more expeditiously and at less cost. This was the second installment of a three-part series on water quality trading. Water quality trading is a policy option whereby pollution control authorities simultaneously allocate wastewater and diffuse pollution loadings for parameters in an entire water body segment or watershed (river basin or catchment) – they do so only in quantities consistent with maintenance or attainment of water quality standards (i.e., cap) – and wastewater and diffuse pollution dischargers, either individually or collectively as sectors or groups, are allowed to exchange for monetary compensation pollutant reduction responsibilities via permits, consents or contracts (i.e., trade) so long as doing so will not result in violations of water quality standards (i.e., post-trade loadings don't exceed caps). Critical questions to which answers were discussed at this second instalment of the workshop series in Quebec included:

- What is the basic theory underlying the concept of water quality trading and to what extent has it been practiced throughout the world (recap of Instalment 1 of the larger workshop series given in Seoul in 2009)
- What type of effluent monitoring is required as a prerequisite to water quality trading?
- What types of diffuse pollution assessments and monitoring are typically needed in order to qualify diffuse pollution sources as sellers of pollution credits?
- To what degree do end-of-pipe effluent, diffuse pollutant and ambient receiving waters need to be modeled in order to ensure water quality trading does not result in contraventions of water quality standards (i.e., caps aren't exceeded subsequent to trades)?
- What data and algorithms are available to analysts (typically engineers and/or economists) in the various regions throughout the world to do the pre-emptive cost-effectiveness analysis that is usually necessary to assist potential buyers in identifying potential sellers of water pollution control credits?

Keynote Speakers

Barry M. Evans, PhD, Penn State Institute of Energy and Environment at the Penn State University, *Engineering assessments, monitoring and modeling of effluent and diffuse pollution discharges pursuant to establishing a water quality trading program or policy*. See Keynote paper in Chapter 4.

John Joyce, Stockholm International Water Institute, *Conducting cost-effectiveness analysis to identify potential buyers and sellers of water pollution control credits to initiate water quality trades.* See Keynote paper in Chapter 4.

EMERGING CONTAMINATIONS IN GROUNDWATER AND SURFACE WATER: SELECTED SUBSTANCES, PATHOGENS, SOURCES, MONITORING, RISK ASSESSMENT AND MANAGEMENT

Chair: Maria Fürhacker, University of Natural Resources and Applied Life Sciences, Vienna, Austria
Secretary: Graham Wilkes, Agriculture and Agri-Food Canada Ottawa, Ontario, Canada

Hazardous substances in aquatic systems have been under consideration for a long time in the context of different water uses (e.g. irrigation or drinking water) and the increased relevance of pathogens. For a long time nitrate, solvents and selected pesticides, especially lipophilic substances, were the focus in groundwater. Similarly, oxygen depletion and eutrophication were important in surface water. With new detection methods, we are able to identify concentrations of drugs, personal care products (e.g. musk fragrances, repellents). Now we are also able to measure technical products such as bisphenol A, nonylphenol, tributy tin compounds, and detergents (LAS, NPE, and QAC) from construction sources (e.g. pesticides), traffic sources (e.g. heavy metals, oxygenates, PAH, nitro-PAH, mineral oils), or even food ingredients (artifical sweeteners) in the ng- and sub-ng range. Some of these contaminants are mutagenic, genotoxic, toxic for reproduction (CMR substances), endocrine disruptors, or produce allergic responses. Some are less toxic or do not show toxic effects in the measured concentrations. To prioritize potential management measures, a risk assessment for standard-setting and monitoring programmes is necessary. Also, new detection methods for pathogens allows understanding of the links between diseases and well-known or emerging waterborne pathogens. In this workshop scientists, practitioners, politicians and people from administration presented their evaluation methods for new and old pollutants and pathogens. This discussion will facilitate setting targets for quick and long-term responses that use the appropriate best available technologies (BAT) and best environmental practices (BEP) Also, discussions included the required strategies to reach the needed political decisions. Discussion was initiated after a short presentation on emerging contaminants, sources, environmental concentrations and effects and the EU strategy of the WFD (2000/60) including the list of selected substances from 2008. Critical questions to which answers were discussed included:

- How shall we assess and priories “less toxic” substances?
- Which method for pathogen detection shall we choose?
- How can we communicate the risk – especially when it does not exist?
- How can we get necessary political decisions?
- The monitoring of substances is much cost intensive, will it be possible to measure effects in complex samples instead of single chemical substances?
- Will it be possible to select lead parameters?
- Which practices will be appropriate for contamination reduction of diffuse sources?

Keynote Speakers:

Tamara Grummt, PhD, German Federal Environmental Agency, *Risk assessment for emerging contaminants in the water cycle: recent advances and future needs.* See Keynote paper in Chapter 5.

Ed Topp, PhD, Agriculture and Agri-Food Canada, *Fecal contamination of surface waters: Developments in human risk assessment and risk management..* See Keynote paper in Chapter 5.

LANDSCAPE CONTROLS ON DIFFUSE NUTRIENT TRANSFERS IN AGRICULTURAL CATCHMENTS

Chair: Aubert R. Michaud. Institut de recherche et de développement en agroenvironnement, Québec, Canada
Secretary: Deane Wang, University of Vermont, Burlington, Vermont, USA

This workshop brought together scientists studying the transfer of nutrients to surface water from basins predominantly under agricultural use. Studies around the world indicate that there is a considerable spatial and temporal variability in diffuse nutrient transfers to surface waters. This variability largely results from interactions between the spatial distribution of nutrient sources, their quantity and mobility, and the landscape characteristics governing water flowpaths in response to seasonal precipitation trends. Storage and transformation of nutrients along the flow paths, buffer zones and hydrologic networks are also largely governed by the landscape features. From an operational perspective, morpho-pedological pattern and other characteristics of the landscape are thus important factors to identify critical source areas. Understanding these patterns is important to design contaminant-specific best management scenarios. Landscape patterns largely govern how much, how, and when phosphorus and nitrogen inputs eventually reach the water body. From a spatially integrated perspective, the workshop particularly addressed the fluxes of nitrogen and phosphorus in agricultural ecosystems and highlight the landscape controls on their mobility, storage and transformation. Critical questions to which answers were discussed address three components of landscapes, including:

Field, emission zones:

- What are the influences of landscape properties on nutrient exports through runoff?
- What are the effects and interactions of landscape properties and presence of artificial drainage systems on nutrient subsurface transfer to surface water?

Buffer zones:

- How do landscape properties control the efficiency of structural runoff control in providing an efficient P retention along the concentrated surface runoff flow paths?
- What are the influences of landscape properties on permanent or temporary N and P storage and transformation within field buffer strips and field margins?

Hydrologic network:

- Do landscape properties have a determinant influence on when and how the stream acts as a sink or source of N and P?
- How landscape properties influence the efficiency of wetlands and flood plains in storing N and P fluxes?

Keynote Speakers

Jean-Marcel Dorioz, INRA-CARRTEL, *Landscape control on diffuse pollution: a critical review on some investigations on phosphorus -retaining landscape features.* See Keynote paper in Chapter 3.

Mark Dubin, University of Maryland, *Mechanisms of Diffuse Nitrogen Transfers to a Coastal Environment: A Case Study of the Chesapeake Bay, USA.* See Keynote paper in Chapter 3.

MANAGING URBAN STORMWATER QUALITY IN A CHANGING CLIMATE: SCIENCE, ENGINEERING AND POLICY

Chair: Jiri Marsalek, National Water Research Institute, Burlington, Ontario, Canada
Secretary: Jean-Luc Bertrand-Krajewski, Laboratoire de Génie Civil et d'Ingéniere Environnmentale, Lyon, France

This workshop provided a forum for scientists, engineers and policy analysts addressing the issues of managing urban stormwater quality in a changing climate, with considerations for existing facilities (and their adaptation) and future design. A fair amount of literature has been published on quantitative changes in precipitation and air temperature regimes in various parts of the world, as predicted by various types of analysis, including the downscaling of global and regional circulation predictive models and analyses of historical data. Such work has largely focused on changes in precipitation depth and intensities, and their implications for design of urban runoff conveyance and storage facilities. This workshop aimed to reach beyond these limits by examining implications of these changes for performance of existing stormwater management facilities with respect to water quality management, assessment of needs for retrofit of such facilities, and implications for stormwater management policies and future designs. Examples of critical questions discussed in this workshop included:

- How well do we know the performance of existing stormwater management systems (i.e., both, physical systems and policies) for the current climate (as designed)?
- Recognizing the expected changes in the climate (i.e., with emphasis on increased air temperatures and precipitation), what are the expected implications for stormwater quantity and quality? Do the implications for quality vary for various groups of stormwater pollutants of concern? (e.g., total suspended solids and sediment, nutrients, heavy metals, polycyclic aromatic hydrocarbons, fecal bacteria, temperature)?
- Can we define stormwater quality regimes which are predominantly mass-limited and transport-limited?
- Is increased urban runoff providing only higher transport capacity for a mass of pollutants controlled by other land use processes (e.g., traffic density, air pollution, building materials, soil erosion)?
- Assuming intensified urban runoff and runoff quality regimes, will decreases in stormwater management system performance be detectable, and if yes, how should we manage this deteriorating performance?
- How effective are our current stormwater management policies and do we need to modify them to reflect potentially changing stormwater quantity and quality?
- What is the best way of communicating these challenges to the public?

Keynote Speakers

Henry Jun, Ontario Ministry of the Environment, *The Ontario Ministry of the Environment initiative on examining the needs for changes in the existing MOE stormwater management policy and manual in the light of a changing climate.*

Alain Mailhot, Quebec University, *Analysis of urban runoff/stormwater changes due to the changing climate and potential implications for stormwater quality.*

2 WATERSHED MANAGEMENT TO REDUCE DIFFUSE POLLUTION

Critical Source Area Management of Agricultural Phosphorus: Experiences, Challenges and Opportunities

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Abstract

The concept of critical source areas of phosphorus (P) loss, as a result of coinciding source and transport factors, have been studied since the mid 1990's. It is widely recognized that identification of such areas have led to targeting of management strategies and conservation practices that more effectively mitigate P loss from agricultural landscapes to surface waters. Such was the purpose of P Indices and more complex nonpoint source models. Despite their widespread adoption across the U.S., a lack of water quality improvement in certain areas (e.g., Chesapeake Bay Watershed and some of its tributaries), has challenged critical source area management to be more restrictive. While the role of soil and applied P has been easy to define and quantify, representation of transport processes still remains more elusive. Even so, the release of P from land management and in-stream buffering, contribute to a legacy effect that can overwhelm the benefits of critical source area management, particularly as scale increases (e.g., the Chesapeake Bay). Also, conservation tillage that reduces erosion can lead to vertical stratification of soil P and ultimately increased dissolved P loss. Clearly, complexities imparted by spatially variable landscapes, climate, and system response will require iterative monitoring and adaptation, to develop locally relevant solutions. To overcome the challenges we have outlined, critical source area management must involve development of a "toolbox" that contains several approaches that addresses the underlying problem of localized excesses of P and provide both spatial and temporal management options. To a large extent, this may be facilitated with the use of GIS and digital elevation models. Irrespective of the tool used, however, there must be a two-way dialogue between science and policy to limit the softening of technically rigorous and politically difficult approaches to truly reducing P losses.

Keywords

Agricultural landscapes, animal manure, fertilizer phosphorus, leaching, phosphorus indices, surface runoff, water quality.

INTRODUCTION

The accelerated eutrophication of freshwaters and, to a lesser extent, coastal waters is primarily driven by phosphorus (P), predicating P-based management of point and nonpoint sources (Dale et al., 2010; Schindler et al., 2009). While efforts to identify and limit point source inputs of P to surface waters have seen significant progress, nonpoint sources have remained more elusive and more difficult to identify, target, and remediate (U.S. Environmental Protect Agency, 2010; U.S. Geological Survey, 2010). As further reduction in point source P discharge using wastewater treatment technologies becomes prohibitively costly when lower discharge concentrations are achieved, attention has shifted to nonpoint sources, with a strong emphasis on developing strategies to curb agriculture's contributions to surface water P loadings (Duriancik et al., 2008; Hilton et al., 2006).

The attention now afforded to agricultural P management has heightened over the last 10 to 20 years, owing, in part, to highly visible cases of accelerated eutrophication, including the Chesapeake Bay, Florida Everglades, Great Lakes, Neuse River, and Gulf of Mexico (National Research Council, 2008). Compounding concerns derived from these cases is the more recent admission that eutrophication mitigation efforts have not achieved the improvements predicted by watershed models and expected with widespread implementation of conservation strategies (Executive Order 13508, 2009; Kovzelove et al., 2010).

Thus, there has been a strategic shift in agricultural P management strategies from unilateral recommendation of conservation measures to address P loss across a watershed toward specific targeting of particular management practices on critical sources areas within a watershed. This targeting includes both spatial and temporal dimensions. Spatially, the justification for critical source area management derives from findings that the major proportion of P loss from a watershed (~80%) derives from a small area (~20%) of the watershed (e.g., Pionke et al., 1997 and 2000). Critical-source areas within a watershed are essentially P hotspots with active hydrological connectivity to the stream channel (Gburek et al., 2007; Walter et al., 2000). Temporally, the justification for critical source area management derives from observations that the majority of watershed P export is associated with a minority of storm events and that there are critical periods when certain management practices (e.g., broadcast P application and tillage) disproportionately exacerbate the risk of P loss.

Critical source area targeting has become the dominant paradigm for agricultural P management, as reflected by the widespread development and adoption of P site assessment indices (e.g., Sharpley et al., 2003). However, critical source area identification and management is not and cannot be the only tool in mitigating eutrophication related to agricultural sources. There must also be parallel emphasis on long-term factors, such as farm and watershed scale P imbalances, legacy P sources and vertical stratification of P in soils, to realize fundamental, real, and lasting changes in agricultural P losses. This paper reviews the integration of critical source area management into strategies to curb agricultural P losses, highlights a variety of issues challenging critical source and management and reveals opportunities for improved P management.

THE EVOLVING PHOSPHORUS INDEX

In the U.S., a site assessment tool, or P Index, was proposed in 1993 and eventually adopted into the U.S. Department of Agriculture's Natural Resource Conservation Service (NRCS) Conservation Practice Standard for nutrient management (i.e., the NRCS 590 standard). The P Index was designed to identify and rank critical source areas of P loss based on site-specific source factors (soil P, rate, method, timing, and type of P applied) and transport factors (runoff, erosion, and proximity to streams) (Lemunyon and Gilbert, 1993). The fundamental advantage of the P Index is to enable targeting of remedial management to critical source areas where high P source and P transport potential coincide. This approach differed profoundly from other, soil P-based approaches, requiring much more information on site conditions but promising better identification of non-point sources of agricultural P, greater flexibility in remedial options and more cost-effective management recommendations.

Currently, 47 U.S. states have adopted the P Index as a site assessment tool to identify critical source areas and target remedial practices (Sharpley et al., 2003). In addition, versions of the P Index have been proposed for several Canadian provinces as well as several Scandinavian countries (Sweden, Norway). As different versions of the P Index have emerged, ostensibly to account for local topographic, hydrologic, soil, land use and policy conditions, so too have differences in the P management recommendations that are made using the P Index. A survey of 12 P Indices from states in the southern U.S. revealed major differences in the way that the indices, even those from neighboring states, rated site vulnerability to P loss (Osmond et al., 2006). Differences in management inferences derived from those P Index ratings for the same fields ranged from recommending no restrictions on field management (continue status quo or N-based management) to recommending the most restrictive remedial actions (no further P additions allowed). In addition to an obvious absence of cross-border coordination in Index development, some of this disparity may be attributed to the paucity of validation efforts by individual states to fully justify their separate version of the P Index. Some states have pursued rigorous validation of the P Index, or at least quantitative calibration of P Index components using tools such as rainfall simulators and unit source watersheds (e.g., Delaune et al, 2004; Harmel et al., 2005; Butler et al., 2010), but many states have not had the resources, ability or motivation to test the alternative versions of P Indices they have promulgated. Differences in state P Index performance also point to the complex nature of critical source areas and the inherent difficulty in their identification.

The lesson of Osmond et al. (2006), coupled with a poor public understanding of the P Index and public impatience over the slow rate of water quality improvements following P Index implementation, have culminated in a review and revision of the U.S. standard for nutrient management, the NRCS 590 Standard. In regions where P management has been highly politicized (e.g., Chesapeake Bay Watershed), there have even been proposals to supplant the P Index with single, soil-based management guidelines that are easier for the public to understand. These proposals seek to force more restrictive outcomes of site assessment, essentially using site assessment to drive local export of manure to other regions, but have had little to do with the substance of the Index itself, which includes soil P, regardless of its origin, as a principal "source" factor.

Many U.S. state P Indices are currently being revised to address some of the limitations described above. In addition, there has been a movement toward developing versions of the P Index that estimate runoff P loads. A growing number of states (Oklahoma, Wisconsin, Texas) have unveiled tools that estimate edge-of-field or watershed level P load changes with alternative management scenarios. Such load prediction tools directly report the potential water quality outcome of management changes (e.g., kg P ha^{-1} yr^{-1}) and are in particular demand by agencies and end users focused on enumerating watershed management outcomes. However, critics argue that the precision of the load predictions belie the uncertainty in the estimations, and that, at a minimum, are not scalable between field and watershed. Major advances have been made toward representing P source availability in the P Index, even unearthing failings in established P routines used by most fate-and-transport models (e.g., Vadas et al., 2007). However, representation of transport processes has been more elusive. Quantifying flow, a requirement of P load estimation, requires robust models that can reconcile field, landscape and, depending upon the inference scale, watershed hydrologic processes. Thus, debate remains over the appropriateness of using P Indices to predict edge-of-field P loss.

As P Indices evolve to load estimation tools, it is inevitable that they will be applied to the task of reconciling water quality thresholds with watershed management options. One of the first steps in this process is to determine whether the tool should estimate P loads (e.g., kg P ha^{-1} yr^{-1}) or concentrations (mg L^{-1}). This determination requires input by scientists and policy-makers, alike. In the U.S., Clean Water Act regulations for impaired watersheds are based upon load allocations to particular land uses. Therefore, estimating P loads makes sense from the standpoint of regulatory convention. However, trophic response thresholds are generally tied to concentrations in a water body. For instance, in the semi-arid prairie region of Canada, Salvano and Flaten (2006) reported ranges in average P loads of only 0.02 to 0.16 kg P ha^{-1} yr^{-1} for 14 regional watersheds. These loads were very low even though P concentrations in surface waters were well above eutrophication thresholds (from 0.05 to 0.38 mg L^{-1}). Secondly, the interpretive thresholds for determining the degree of change in management required for a critical source area should consider the overall target for P loading or concentrations in the watershed.

CHALLENGES

Challenges facing modern P management have not changed since critical source area targeting became the dominant paradigm. Although the benefits of critical source area management can be readily documented at smaller watershed scales, in-stream processes serve to buffer downstream water quality improvements. In addition, vertical stratification of P in no-till soils and legacy sources of P may overwhelm the short-term benefits of remedial practices applied to critical source areas.

Locally restricted benefits

The local water quality benefit of targeting critical source areas for conservation management within a watershed is shown by work in sub-watersheds of the Little Washita River Watershed (54,000 ha) in central Oklahoma (Sharpley and Smith, 1994). Nutrient export from two sub-watersheds (2 and 5 ha) was measured from 1980 to 1994, while conservation practices were installed on approximately 50% of the main watershed. Practices included construction of flood control impoundments, eroding gully treatment, and conservation tillage. Following conversion of conventional-till (moldboard and chisel plow) to no-till wheat (*Triticum aestivum* L.) in 1983, N export was reduced 14.5 kg ha^{-1} yr^{-1} (3 fold) and P loss reduced by 2.9 kg ha^{-1} yr^{-1} (10 fold; Sharpley and Smith, 1994). A year later, shaping eroding gullies decreased P loss 5 fold and construction of an impoundment decreased P loss from the sub-watersheds by 13 fold (Sharpley et al., 1996). While the benefits of conservation management were observed at a sub-watershed scale (2 – 5 ha), there was no consistent decrease in P concentration in flow at the outlet of the main Little Washita River Watershed (54,000 ha). The lack of remedial success at a larger scale is most likely a result of in-stream processes and the continued release of "legacy P" already stored within the watershed system (McDowell et al., 2002; Meals, 1996; Meals et al., 2009).

Vertical stratification of P with reduced tillage

Within our BMP strategies for controlling P loss, well-intentioned BMPs for reducing one form of P loss may, in fact, increase losses of another form, resulting in little net reduction in P loss and or water quality improvements. For example, in response to deteriorating water quality in Lake Erie, USA in the 1960s and early 1970s, a coordinated but voluntary program was set in place to reduce P loads to the Lake (Baker and Richards, 2002). Phosphorus loads have been monitored since 1975 to determine the effect of adopting BMPs such as conservation tillage (~50% no-till) and nutrient management planning (25% lees P applied) in predominantly row crop agriculture (mainly corn, soybean, and wheat) in two Ohio watersheds with major tributaries to Lake Erie (Richards et al., 2002). As a result, mean annual flow-weighted dissolved P concentrations decreased 86% and total P 44% between 1975 and 1995 (Richards and Baker, 2002). Subsequent to 1995, however, annual flow-weighted concentrations of dissolved P have increased, while total P continued to decline. The trend of increasing dissolved P and decreasing total P may be attributed to a combination of several factors; an accumulation of P at the soil surface with conversion to no-till cropping and an increase in the proportion of fertilizer and manure broadcast, without incorporation, in the fall and winter (Baker and Richards, 2009; Krieger et al., 2010).

One of the most important challenges of using a critical source area approach to manage P is to ensure that the tool correctly accounts for the processes and BMPs that control excess losses in a local situation. For example, similar to their counterparts in Ohio, researchers in Manitoba, Canada have measured increased losses of dissolved P from conservation tillage systems. In this region of the Northern Great Plains, the relatively flat landscapes and semi-arid continental climate results in a high proportion of runoff occurring during snowmelt, over frozen soils, with the majority of P loss in dissolved forms and relatively little loss of particulate P due to erosion (Tiessen et al., 2010). As a result, Tiessen et al. (2010) measured losses of total P that were 12% greater from conservation tillage than from conventional tillage in a twin watershed study near Miami, Manitoba, even though conservation tillage significantly decreased sediment and N loss. Furthermore, in Manitoba, P losses are not predicted accurately using existing critical source area tools that have been designed for land and climates where rainfall-induced erosion of particulate P from sloping landscapes is the main process of P transport (Salvano et al. 2009).

From these two case examples, it is clear that whatever strategies are implemented, they should be done in an adaptive manner. The complexities imparted by spatially variable landscapes, climate, and system response will require iterative monitoring and adaptation, to develop locally relevant solutions. For example, system response can vary from a year to several decades and this time generally increases as spatial scale increases.

Legacy sources of P – interaction of historical additions and hydrology

Few management practices are suited to reversing the effects of historical additions of P to sites that serve as critical source areas. Obvious examples of legacy sources are soils that are highly saturated with regard to P. In the Chesapeake Bay Watershed, the University of Maryland Eastern Shore's research farm occupies the site of a former commercial poultry operation with roughly 30 years of poultry litter application to farm soils in excess of crop requirement. These coastal plain soils are heavily ditched due to shallow regional water tables and possess soil test P concentrations nearly one order of magnitude above the threshold for crop requirement (Kleinman et al., 2007). Because of the ditches nearly all fields may be considered hydrologically active and connected to local surface waters. Annual P loads from field ditches readily exceed 20 kg ha^{-1} yr^{-1} under normal precipitation regimes. Experiments to draw down soil test P by curtailing P application to the soils showed no significant change in soil test P over nearly one decade (Kleinman et al., 2011). Therefore, non-traditional practices may be required to address the overwhelming contributions of P from these critical source areas (e.g., Penn et al., 2007).

Less obvious legacy sources may be found in hydrologically active areas that possess soil test P at or near the agronomic optimum. Buda et al. (2009) monitored contour-cropped fields on a Pennsylvania hillslope, in which the bottom field possessed the lowest relative soil test P (roughly two-fold lower than the other fields), was the only field that did not receive P amendments during the study period, but yielded runoff volumes roughly 50-fold greater than the other fields included in the study. Runoff from the upper fields was largely disconnected from the loads observed from the bottom field. Annual loads of P from this hydrologically active field were > 8 kg ha^{-1}, in comparison to 1 kg ha^{-1} or less from the other fields. This study highlights the ability of site hydrology to overwhelm source factors in determining P loss. More importantly, it points to the ability of hydrology to convert a modest source of P into a major P load. In such cases, careful adherence to critical source area management and non-traditional P runoff remediation practices (e.g., Penn et al., 2007), may be required.

OPPORTUNITIES

Development of a "toolbox" that contain several approaches

Although P Indices were developed as strategic tools for P-based management, they were never intended to provide an easy or complete solution to the problem of increased P runoff brought about by localized P surpluses. Even so, like many simple tools and models, P Indices produced black-and white numbers and color-coded maps, and provided a certain level of comfort that change was forthcoming and P loss would subside. The fact that this has not occurred has renewed the call for stricter guidelines for P application to agricultural land. Given the system buffering (on land and in water bodies) and legacy P effects, how long does it take after conservation measures are initiated before meaningful improvements in water quality can be expected or observed? Part of the current concerns with critical source area assessment and the P Indexing approach is due to unrealistic expectations of how quickly the watershed and the water body can respond to conservation measures.

Clearly, there is an opportunity for a science-based approach to meet this challenge. If the aim is to significantly decrease nonpoint source loading of P to sensitive waters and we acknowledge system buffering and the slow release of P, it will be very difficult to envisage the widespread and continued application of P at levels that exceed crop removal. In effect, this might initiate measures to help farmers address the underlying challenge of localized excesses of manure P and provide cost-effective and practical options that encourage with transport of manure or alternative uses.

Improved identification of critical source areas using LiDAR digital elevation models

Digital elevation models (DEMs) represent a useful geospatial tool to automatically identify potential critical source areas on the landscape, particularly in regions where topography exerts an important control on surface runoff generation. The resolution of DEMs produced from topographic maps (10-30 m) has often been insufficient to identify critical source areas that occupied portions of small fields or hillslopes. However, there have been recent improvements in DEM resolution (< 1 m) through the use of Light Detection and Ranging (LiDAR) technology. These improvements offer new opportunities to identify and map critical source areas and determine if these features are connected to surface waters. This is important because some critical source areas will rarely deliver P to surface waters, while others will frequently deliver P because of their position on the landscape (e.g., near-stream zone) or through other direct connections such as via rills and gullies.

Researchers have demonstrated a number of useful approaches for identifying critical source areas using high-resolution LiDAR DEMs. One of the more common techniques is to calculate the topographic index (Beven and Kirkby, 1979), which is defined as the natural logarithm of the upslope contributing area (*a*) divided by the local slope gradient (tan β). High values of the topographic index represent the potential for saturated areas to develop on the landscape and act as source areas for surface runoff. When information on the topographic index is combined with maps of soil P status, critical source areas can be readily identified (Page et al., 2005). The network index, a recent modification of the topographic index (Lane et al., 2004; 2009), can be used with LiDAR DEMs to identify saturated areas and evaluate their potential to connect to surface waters.

In addition to topographic index approaches, other researchers have mapped potential critical source areas using terrain analysis techniques. For example, work by Heathwaite et al. (2005) summarized the use of multiple flow accumulation algorithms (Quinn et al., 1991) to map surface and subsurface flow pathways for P transport and evaluate their connectivity to surface waters. In the flat landscapes of the Netherlands, Sonneveld et al. (2006) used LiDAR DEMs to estimate internal versus external drainage at the field scale, and determine the potential for externally drained fields to contribute P runoff to surface waters. Finally, efforts to identify and map rill and gully networks using terrain analysis techniques with LiDAR DEMs (James et al., 2007) could eventually aid in determining whether upslope critical source areas directly connect to surface waters.

Clearly, there are a number of promising approaches to identify and map critical source areas on the landscape and assess their connectivity to surface waters using LiDAR DEMs. With an increasing number of states collecting statewide LiDAR datasets, the potential exists to quickly and effectively evaluate critical source areas at relevant management scales.

Establishing critical source area criteria

The act of establishing thresholds for management of critical source areas must balance a variety of considerations. Strategically, there are arguments for varying these criteria by watershed, much as management within a watershed varies by site P loss potential. For instance, watersheds that are severely impaired by excess P may require substantial overall reductions in P loading to reach an ecologically appropriate long term target (e.g., P load reductions of 10% or more). Those substantial reductions will, therefore, require substantial changes to management practices. Conversely, due to a variety of social and economic reasons, targets and management changes in the short term might be much more modest, for example, to moderate further increases in P losses (e.g., 0% increase in P load).

RECOMMENDATIONS

At a field and farm level, research has demonstrated edge-of-field reduction in nutrient and sediment loss can occur within months of changing P-management. However, the spatial complexity of watershed systems increases this response time for P as a function of slow release of legacy P stored in soils and fluvial sediments to surface flow pathways. Critical source area tools are fundamentally sound, particularly when used over the short-term (e.g., a one-year planning cycle), but linkages between the implementation of long-term critical source area management and water quality benefits/improvements are still relatively unknown. Hence the need for long-term validation of critical source area tools, especially in light of potential legacy P effects.

A collection of good tools must be developed, including a practical version of critical source area identification and management based on GIS and DEM technology. Any one of these tools must be linked to effective BMPs and water quality targets in order to effect lasting and meaningful changes. To be successful, the way these tools are developed and implemented will require an honest and forthright two-way dialogue between science and policy to limit the softening of technically rigorous and politically difficult approaches to truly reducing excess P loading.

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The Challenge of Documenting Water Quality Benefits of Conservation Practices: A Review of USDA-ARS's Conservation Effects Assessment Project Watershed Studies

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Abstract

The Conservation Effects Assessment Project was established to quantify water quality benefits of conservation practices supported by the U.S. Department of Agriculture (USDA). In 2004, watershed assessment studies were begun in fourteen agricultural watersheds with varying landscapes, climate, and water quality concerns. This paper reviews USDA Agricultural Research Service 'benchmark' watershed studies and the challenge of identifying water quality benefits in watersheds. Study goals included modeling and field research to assess practices, and evaluation of practice placement in watersheds. Not all goals were met within five years but important lessons were learned. While practices improved water quality, problems persisted in larger watersheds. This dissociation between practice-focused and watershed-scale assessments occurred because: 1) Conservation practices were not targeted at critical sources/pathways of contaminants; 2) Sediment in streams originated more from channel and bank erosion than from soil erosion; 3) Timing lags, historical legacies, and shifting climate combined to mask effects of practice implementation; and 4) Water quality management strategies addressed single contaminants with little regard for trade-offs among contaminants. These lessons could help improve conservation strategies and set water quality goals with realistic timelines. Continued research on agricultural water quality could better integrate modeling and monitoring capabilities, and address ecosystem services.

Keywords

Agricultural watersheds, conservation practice assessment, water quality, watershed modeling.

INTRODUCTION

Agricultural conservation practices in the U.S. are implemented by landowners on a voluntary basis, with financial incentives provided by the U.S. Department of Agriculture (USDA). The incentives include cost sharing for establishing each practice and annual rental payments where lands are contracted to be under perennial conservation cover. These incentive payments were authorized by the U.S. Congress at U.S. $3.5 billion annually (Becker 2002), a level at which cost-benefit analysis is legally required to ensure this taxpayer investment in conservation is being fairly returned in terms of environmental benefits. However, benefits of conservation practices have not been adequately quantified to allow this analysis to take place. The Conservation Effects Assessment Project (CEAP) was undertaken to remedy this knowledge gap and provide information that could be used to improve the cost-benefit balance of USDA conservation programs. The CEAP project (Mausbach and Dedrick, 2004) comprised two components: a national assessment supported by producer survey data and field and simulation modeling, and a series of watershed assessment studies (Richardson et al., 2008). The national assessment results are being published in a series of regional reports; the first one on the Upper Mississippi River Basin was recently released (USDA, 2010). The CEAP watershed assessment studies included ARS Benchmark Watersheds, NRCS

Special Emphasis watershed studies, and CSREES watershed studies (Richardson et al., 2008), and results are being published in a wide variety of journals and reports.

The CEAP watershed assessment studies faced the problem of determining how conservation practices impact water quality in relatively large watersheds, beyond the field scale at which practices are implemented. This was part of the project goal of identifying public benefits of conservation practices, because water is a public resource of vital concern, especially in larger streams and rivers that provide important drinking water, fishery, and recreational resources. At a fundamental level, the scientific challenge of identifying watershed-scale effects derived from a set of field-scale conservation practices is one of scientific control. Large watersheds are not replicable and it is generally not feasible to consistently implement (or withhold) experimental treatments across large areas of private agricultural land. These issues diminish as the scientific approach and objectives are narrowed down to the field scale. Large agricultural watersheds include a mix of practices and it is difficult to isolate the effect of individual practices. Yet, as the CEAP watershed projects progressed, it became clear that more is involved in the question of watershed-scale effects than experimental control and spatial scaling.

This paper provides a review of results from the watershed assessments undertaken in USDA's Agricultural Research Service (ARS) 'Benchmark' watersheds (Fig. 1, and see Richardson et al., 2008), and examines the challenge of identifying water quality impacts in large watersheds. First, we will summarize conservation practice assessments conducted at field and watershed scales, through both modeling and field studies. We then summarize progress made in modeling of agricultural watersheds in these watersheds. Finally, we discuss reasons that conservation practice effects that may be readily identified at the field scale are more difficult to identify at the watershed scale.

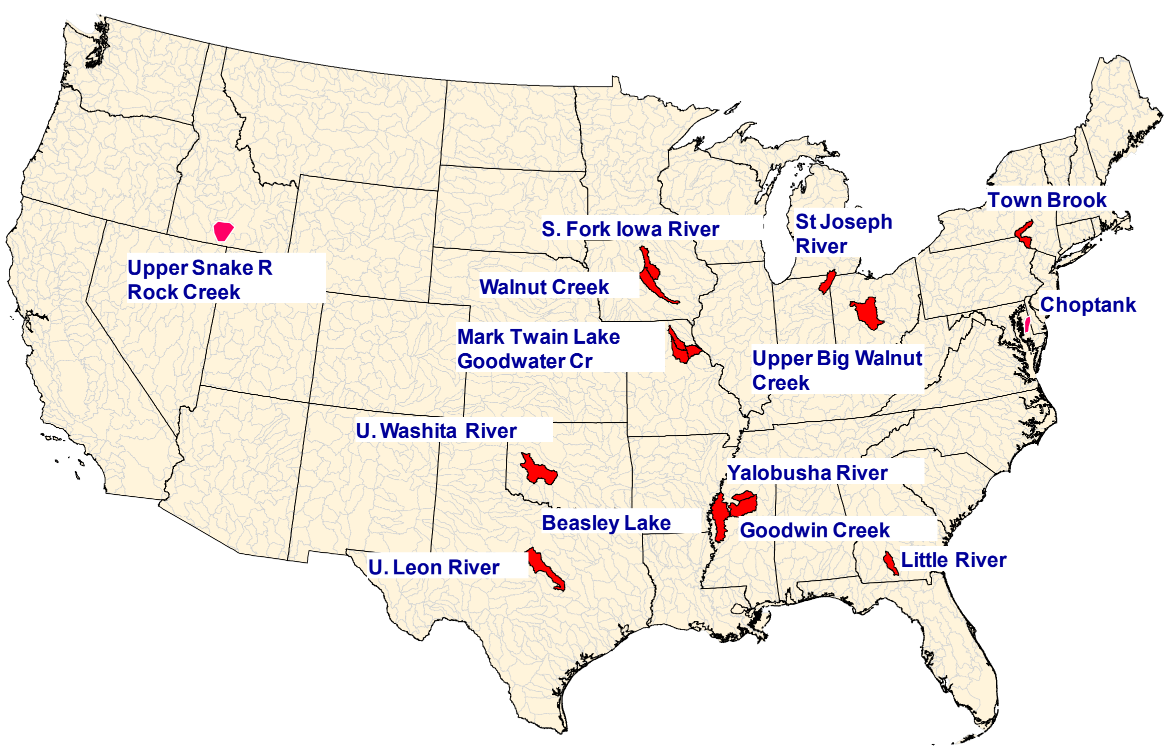

Figure 1. General map of the United States showing Benchmark Watersheds of the USDA-ARS Conservation Effects Assessment Project.

PRACTICE ASSESSMENTS

Assessments of conservation practices can be undertaken through several approaches, including modeling studies, field experiments, edge-of-field monitoring, and watershed scale studies. Watershed scale studies can be conducted either through analysis of an observed time series following practice implementation, or a paired watershed study. Although the paired watershed approach is more powerful statistically (King et al., 2008; Loftis et al., 2001) the single time series approach is simpler to implement and is more common. In this section, we summarize conservation practice assessments that were conducted in the CEAP benchmark watersheds. These practices are listed in Table 1 where CEAP research on each practice is summarized, and a review article is suggested for further reading on each type of practice.

Table 1. Summary results of conservation practices assessment studies undertaken within the CEAP watersheds

Conservation Practice	Pollutant/s (reduction)	Approach (scale[x])	References
Conservation Reserve Program (conservation cover)	Sediment concentration (63%) Sediment (85%), nutrient (>28%) load	Observed time series (W) Runoff monitoring (F)	Kuhnle et al., 2008 Cullum et al., 2010 Hansen, 2007 (R)
Cover crops	Cover crop N uptake (varied) NO3-N leaching load (61%)	Remote sensing calibration (W) Replicated field trial – 4 yrs (P)	Hively et al., 2009 Kaspar et al., 2007 Dabney et al., 2001 (R)
Livestock management: Nutrient management Pasture rotation (fencing)	P loss – farm scale (43-60%) P load (estimated 32%)	Modeling study (B) Field study (W)	Ghebremichael et al., 2007 James et al., 2007 Russelle et al., 2007 (R)
No tillage	Sediment (64-77%)	Modeling study (W)	Yuan et al., 2008 Lal et al., 2007 (R)
Riparian buffers	Sediment, P loads (20%); total N (7%) Sediment load (72%)	Modeling Study (W) Modeling Study (W)	Cho et al., 2010. Moriasi et al., 2010 Lovell & Sullivan, 2006 (R)
Split N application (w spring soil test)	NO_3-N concentration (30%)	Paired watershed (W)	Jaynes et al., 2004 Dinnes et al., 2002 (R)
Engineered hydraulic structures: Flood retarding structures Sediment control structures	Annual max. daily discharge (33%) Sediment load (>15%)	Modeling study (W) Modeling study (W)	Van Liew, et al., 2003 Kuhnle et al., 2008 Vanoni, 2006 (R)

X P = plot scale, F = field scale; B = farm scale W = watershed scale; (R) Review of literature on this practice or set of practices.

Conservation Reserve Program (CRP)

The CRP was initiated as part of the Conservation Title of the 1985 US Farm Bill passed by Congress and implemented by the USDA. Begun during a time of concern about the economic impact of crop surpluses on agriculture's profitability, this program was designed to take highly erodible land out of production and to establish perennial cover for ten years under rental contract. The program was later expanded to encourage establishment of riparian buffers under CRP. The CRP has largely been deemed successful (Hansen, 2007), with quantifiable economic benefits estimated to be about 80% of the program costs (recognizing that not all benefits were quantifiable). Several CEAP benchmark watersheds, in Mississippi and Iowa, documented CRP set aside lands as a key conservation practices on the landscape (Locke et al., 2008; Tomer et al., 2008b; Wilson et al., 2008b), Direct environmental benefit of this practice have been separately estimated in two Mississippi CEAP watersheds. Kuhnle et al. (2008) found about 20% of the Goodwin Creek watershed was converted from cropland to permanent cover between 1982 and 2005; this conversion was largely attributed to CRP and resulted in more than a 60%

reduction in sediment. Establishing CRP within a Mississippi Delta lake watershed reduced total sediments by 85% and nutrients by greater than 28% when compared with adjacent areas under row crop management (Cullum et al., 2010).

Cover Crops

Winter cover crops are a conservation practice that were implemented and are being evaluated in the CEAP watersheds in New York and Maryland (Bryant et al., 2008; Hively et al., 2009; McCarty et al., 2008). Cover crops can increase soil organic matter, and reduce runoff, erosion, and nutrient losses (Dabney et al., 2001). In tile drained areas of the Midwest, cover crops have been shown to decrease NO_3-N leaching by more than 60% with minimal impact on yield when the cover crop is killed 10-14 d prior to planting (Kaspar et al., 2007, and subsequent unpublished data). A remote sensing technique to estimate and map nutrient uptake by cover crops was developed in the Choptank watershed (Hively et al., 2009), providing a technique to help manage agricultural impacts on water quality in the Chesapeake Bay.

Livestock Nutrient/Pasture Management

Livestock, pasture, and manure management were identified as important issues in watersheds in Iowa (Tomer et al., 2008b), New York (Bryant et al., 2008), and Texas (Harmel et al., 2008). In New York, reduced P losses were estimated for excluding of cattle from streams at the watershed scale (James et al., 2007) and precisely meeting feed diet P requirements at the farm scale (Ghebremichael et al., 2007). Manure management practices to minimize P in runoff were evaluated in Texas (Harmel et al., 2008). In Iowa River's South Fork (Tomer et al., 2008a) and in Texas' Leon River (Harmel et al., 2010), *E. coli* populations in stream water would lead to water use impairment in sub-basins with and without large densities of livestock, suggesting that managing bacterial loading in streams through manure and pasture management will remain a vexing issue.

Reduced and No Tillage

No tillage practices or practices that provide year-round residue cover were identified as important practices in CEAP watersheds in Missouri (Lerch et al., 2008), Iowa (Tomer et al., 2008b), Oklahoma (Steiner et al., 2008), Mississippi (Locke et al., 2008), Indiana (Smith et al., 2008), and Maryland (McCarty et al., 2008). No-tillage is an important practice that will reduce amounts of runoff and erosion in most environments (Lal et al., 2007; Yuan et al., 2008). However under some soil conditions there are tradeoffs to consider; for example if surface crusting occurs then runoff can be increased under no tillage (Karlen et al., 2009). Also, in Missouri, no-tillage was associated with increased transport of herbicides in surface runoff, because herbicides are not incorporated into soil under no-tillage management (Lerch et al., 2008).

Riparian Practices

Riparian buffers are installed to encourage infiltration of runoff from cropland and thereby trap sediment, nutrients, and other contaminants to prevent their direct entry into surface waters. This practice was broadly implemented in CEAP watersheds in Indiana and Iowa (Smith et al., 2008; Tomer et al., 2008b). Natural forested buffers, often associated with riparian wetlands, were common in CEAP watersheds in Georgia, Mississippi, and Maryland (Feyereisen et al., 2008; Locke et al., 2008; McCarty et al., 2008). In watersheds where artificial subsurface (tile) drainage is dominant, riparian buffers cannot treat drainage from tile-drained uplands, but do provide a setback that reduces direct losses of nutrients and sediment from cropland adjacent to waterways (Smith et al., 2008). Benefits of riparian buffers have not been measured directly through the CEAP studies, partly because the literature includes many field evaluations (Lovell and Sullivan, 2006). However two modeling studies have been conducted that simulated water quality benefits of buffers in CEAP watersheds (Table 1; Cho et al., 2010; Moriasi et al., 2010).

Natural wetlands are often transition zones between agricultural areas and water bodies and can serve as areas for processing contaminants moving through the system. Placing artificial wetlands in areas where wetlands do not naturally exist can also provide a protective buffer for vulnerable water bodies. A wetland was constructed in CEAP Beasley Lake watershed and its potential for mitigating pesticide in runoff was demonstrated (Moore et al., 2009; Locke et al., 2011). Methods to locate sites most appropriate for installation of riparian buffers and constructed wetlands, based on terrain analysis, were proposed for a tile drained watershed (Tomer et al., 2003).

Ditches have been installed to receive water draining from cropland in many agricultural watersheds, providing a conduit for rapid transport of contaminants to downstream water bodies. Therefore, improving the management of ditches can be an important component of watershed protection. In tile-drained watersheds across the Midwest, drainage ditches are shaped with berms or weirs to prevent runoff from eroding shaped ditch banks (Smith et al., 2008). In CEAP's Beasley Lake watershed in Mississippi, vegetation in a ditch draining agricultural fields was shown to be effective in retaining pesticides (Moore et al., 2001). This and other research (Moore et al., 2008) led to establishment of NRCS guidelines for vegetative ditches in California and Mississippi.

Nitrogen Fertilizer Rate and Timing

A paired watershed study on nitrogen management, which included soil testing in late spring to identify split-N application rates to corn (maize), showed the practice could reduce nitrate concentration in tile drainage by 30% within four years (Jaynes et al., 2004). This study provides a rare example of the use of a control watershed and a pre-treatment calibration period in watershed-scale agricultural research.

Sediment Control Structures

Sediment and floodwater control structures have been evaluated through modeling studies in CEAP watersheds in Mississippi (Kuhnle et al., 2008) and Oklahoma (Van Liew et al., 2003). Erosion and sediment movement are natural geomorphic processes that are impacted by land cover, agricultural practices, and river corridor management, and this is a topic that is revisited below.

WATERSHED MODELING

Models are important tools in watershed management to help assess our understanding of watershed processes and evaluate how proposed changes in land use and agricultural practices might impact hydrology and water quality. Two watershed models, AnnAGNPS (Annualized Agricultural Non-Point Source) (Bingner et al., 2009) and SWAT (Soil and Water Assessment Tool) (Arnold et al., 1998), were employed throughout CEAP, and have seen broad, international application (Gassman et al., 2007; Licciardello et al., 2007; Zema et al., 2010). SWAT was also part of the modeling effort for the CEAP national assessment (USDA, 2010).

Collectively, watershed modeling efforts in the CEAP watersheds have led to a number of advances. In watershed modeling, the issues of calibration and validation in identifying optimal parameter sets and determining parameter sensitivities have received a variety of treatments, and one contribution of the CEAP studies has been a set of recommended guidelines to follow to ensure consistency in watershed modeling efforts (Moriasi et al., 2007). These guidelines, which recommend performance statistics and targets to deem model results "satisfactory", are critical because policy and legal decisions can hinge on realistic modeling results and confidence in the modeling process.

The first goal of watershed modeling is to achieve an accurate hydrologic calibration: water quality responses to management cannot be accurately simulated if hydrologic timings and pathways are not accurately simulated by the model. SWAT was shown to be an effective tool for capturing the dynamics of streamflow and atrazine concentrations of the St. Joseph River watershed (Heathman, et al., 2008; Larose, et al., 2007). In a cross-basin comparison of CEAP watershed SWAT calibrations, Veith et al. (2010) showed that parameters governing surface runoff were most sensitive, and that SWAT appears to perform best in humid environments. In Midwest watersheds, subsurface (tile) drainage has been widely installed, substantially altering watershed hydrology and providing a critical pathway for nitrate losses (Dinnes et al., 2002). A routine to represent tile drainage in the SWAT model was developed and tested (Du et al., 2005), and calibrated for the Iowa River's South Fork watershed (Green et al., 2006). The driving input variable for any hydrologic calibration is precipitation, and the spatial and temporal resolutions of precipitation data can impact the sensitivity of parameters driving key hydrologic processes, specifically groundwater recharge (Starks and Moriasi, 2009). The AnnAGNPS model was used on CEAP Beasley Lake watershed in Mississippi to simulate water and sediment produced on each field and the resulting impact on lake water quality (Yuan, et al., 2008). The model was applied without calibration, and the simulated runoff and sediment yield compared well with observed data. AnnAGNPS was used to identify high sediment-producing areas and to simulate the impacts on water quality of targeting conservation practices to these areas.

Once hydrologic calibration of a watershed model is satisfactorily achieved, simulation of water quality is possible, but progress has been slower than for hydrologic calibration during CEAP's first five years. Water quality assessments of conservation practices through watershed scale modeling in CEAP have dominantly, but not solely, focused on sediment reduction effects (Table 1). Cho et al. (2010) assessed trapping of nutrients along with sediment in simulating effects of riparian buffers in Georgia, and Saleh et al. (2007) demonstrated that SWAT can simulate reduced loadings of nitrate-N in tile drainage resulting from use of split N fertilizer applications, and from winter cover crops. SWAT is undergoing changes to nitrogen cycling and soil phosphorus routines to enable greater progress in this area (Gassman et al., 2007). The SWAT and AnnAGNPS models have been used to quantify the environmental benefits of implementing cover crops and riparian buffers on the Choptank watershed, and data from a sub-basin were used to calibrate and validate the models. The models showed a direct relationship between degree of implementation of cover crops and the reduction in nitrate loading to the stream. SWAT showed marked improvement in load reduction when cover crops were targeted to areas with the greatest nitrate loads rather than randomly applied. AnnAGNPS was used to identify the spatial location for specific pollutant loads within the watershed (McCarty, et al., 2008). The SWAT and AnnAGNPS models were applied without calibration to the Cedar Creek watershed, a 708 km^2 sub-watershed of the St. Joseph River in Indiana, to simulate streamflow, sediment transport, and atrazine losses. SWAT performed better than AnnAGNPS in estimating monthly and annual streamflow, while AnnAGNPS predicted significantly greater sediment loss than SWAT.

As a result of CEAP studies, improvements were identified for both SWAT and AnnAGNPS. Components of subsurface drainage control practices of Midwestern conditions were incorporated into AnnAGNPS to allow evaluations of these improvements for their effect on water, sediment, and chemical loadings in a watershed (Yuan et al., 2006). Enhancements were also completed within AnnAGNPS to account for ephemeral gully erosion sources within a watershed (Gordon et al., 2007), as well as riparian buffer systems (Yuan et al., 2007). New modeling technologies (genetic algorithms) are also being combined with SWAT to evaluate how combinations of practices can be targeted within watersheds, and indeed must be to achieve maximum water quality benefits, as demonstrated in New York's Town Brook watershed (Gitau et al., 2006). Gassman et al. (2007) provide tables summarizing SWAT watershed modeling performance for hydrologic and water quality variables. Arabi et al. (2008) and Gassman et al (2007) provided suggestions of parameter adjustments that best represent a variety of conservation practices, and parameters found to be most sensitive for calibration on different water quality constituents. This progress in watershed modeling has been important in enabling progress in regional modeling efforts for CEAP (USDA, 2010). A remaining challenge is simulating not only water quality responses to conservation, but response of aquatic habitat quality to conservation efforts (Shields et al., 2006).

These modeling accomplishments are consequential but the broad goal of documenting conservation practice effects on water quality at watershed scales has remained elusive. Few efforts have included a field study to quantify a conservation-practice benefit for water quality, followed by a successfully validated model simulation of the same practice and water quality improvement. Demonstration of fertilizer management (late spring nitrate test) benefits for nitrate reduction in a paired watershed experiment (Jaynes et al., 2004), followed by model validation (Saleh et al., 2007) is one example that illustrates a successful effort to combine field and modeling efforts, yet demonstrates the level of effort required to demonstrate and simulate an impact of only one practice on one contaminant in one watershed. Beyond that, watershed modeling remains a semi-empirical process including representational functionality as well as specific governing biophysical processes. Hence watershed simulations may simply estimate the *potential* benefits of conservation based on our understanding of how a practice *should* function to improve water quality. However, design and intent do not necessarily dictate outcome. Therefore, more combined efforts to both measure and simulate benefits of conservation practices accurately will be necessary to improve our confidence in watershed modeling.

MEASURING CONSERVATION EFFECTS IN LARGE WATERSHEDS

Efforts to quantify conservation benefits in the field comprise the minority of practice assessments listed in Table 1, compared to the number of modeling studies. This is a natural consequence of the focus on large watershed studies under CEAP. Assessments of single practices require a level of experimental control that is seldom possible in large watersheds. So what is the point of undertaking these efforts at the large watershed scale? Are there lessons that can be leveraged to move conservation and watershed science forward? This question is apt especially given that watershed and water quality monitoring efforts are subject to gauging, sampling, and analytical errors that are unavoidable and, for stormflow load estimates, combine to become 7-11% under ideal measurement and analytical conditions, depending on the contaminant, and significantly larger if monitoring protocols are not established and adequately followed (Harmel et al., 2006). Yet, measured real world data will be necessary to validate future advances in modeling and ensure we can simulate the effects of changes in land use and climate. In addition, through the CEAP effort, several critical issues that impact watershed water quality dynamics and responsiveness to varying management and climate have been highlighted by these studies, which would remain under-appreciated without them. These issues address the difficulties involved with documenting conservation benefits in watersheds and, at least in part, with validating models that can simulate conservation benefits for water quality. They also help address the basic question of how the USDA could be spending $3.5B per year on conservation efforts and yet not be adequately solving agricultural water quality problems.

Issues that mitigate our ability to measure benefits of conservation practices in large watersheds can be expressed as follows:

First, conservation practices that are implemented may not address critical sources, timings, and pathways of contaminants. Clearly, targeted placement of conservation practices to mitigate contaminant sources is a useful approach for water quality management, based on environmental benefits and cost effectiveness (Gitau et al., 2006; Walter et al., 2007). However, water quality monitoring can reveal the extent of water quality problems in a stream and yet provide very little information about non-point contaminant sources. Making assumptions about contaminant sources without data-based evidence can lead to ineffective recommendations and loss of stakeholder trust in the process of water quality management. Perhaps the clearest example illustrating the need for critical knowledge of contaminant source is that of *E. coli* as an indicator of fecal contamination. Livestock are an obvious source of bacterial contamination, but not the only source, as shown in Iowa (Tomer et al., 2008a) and Texas (Harmel et al., 2010). Measures to reduce fecal contamination by livestock are certainly appropriate in impaired watersheds, but the adequacy of those measures where background levels include multiple sources will be difficult to prove or disprove (Harmel et al., 2010). Another example of complications involved in accurately identifying contaminant source relates to sub-surface contaminant transport in tile drainage systems. Tile drainage is a known source of nitrate loads to streams in the Midwest and has also contributed to phosphorus losses in CEAP watersheds in Indiana (Smith et al., 2008) and Iowa (Tomer et al., 2008a). Some of these losses may be occurring through surface inlets that drain runoff from depressions. Watershed models do not adequately simulate processes governing bacterial transport and survival, nor subsurface movement of phosphorus (Gassman et al., 2009). Conservation practices implemented to improve water quality will need to be supported by flexible policies that allow stakeholders to respond to new information on contaminant sources. Conservation practices also need to be designed and implemented recognizing the importance of timing issues; e.g., the importance of planting date for winter cover crops (Hively et al., 2009).

Second, sediment in streams mostly originated from channel and bank erosion, not from erosion of soil in fields. The importance of natural processes of channel widening and movement for degradation and sediment loads in streams in the context of CEAP research was reviewed by Simon and Klimetz (2008). Many streams in the U.S. are undergoing geomorphic change as fluvial systems respond to hydrologic alterations that accompanied settlement and agricultural development across the North American continent. Downcutting, aggradation, and widening are examples of the processes that keep streambanks unstable over many decades and even centuries. Wilson et al. (2008a) found most (54 to 80%) of sediment loads were derived from channel sources as opposed to eroded surface soils, in a study of five benchmark CEAP watersheds. If erosion-control practices reduce sediment concentration without attenuating hydrologic discharge, then runoff water may enter the stream with a capacity to increase the sediment load by eroding the bed and banks, which may mask the impact of the conservation practice on runoff sediment. Practices that attenuate surface runoff as well as erosion are therefore most effective. Conversion of cropland to perennial cover is one example of a practice that can reduce peak discharge and erosion, and thereby reduce sediment loads, as shown in two CEAP watersheds in Mississippi (Kuhnle et al., 2008; Cullum et al., 2010). Another important cause of bank erosion is past accretion of sediment. Sediment accretion in river valleys has resulted from historical erosion, and has led to channelization, loss of floodplain water storage capacities, and accelerated bank erosion (Yan et al., 2010). Hence sediments derived from bank erosion may be a legacy of pre-conservation (pre-1950) agriculture.

Third, historical legacies and shifting climate combined to mask water quality effects of practices that generally lag practice implementation. As rivers respond to legacy impacts of past erosion through natural geomorphic processes of channel evolution (Simon and Klimetz, 2008), other changes are taking place within our watersheds. Implementation of conservation practices is but one of many changes that are occurring in watersheds simultaneously. Water quality trends need to be evaluated in the context of historical shifts in agricultural land use and the application of new technologies such as improved crop genetics and changing crop rotations, as well as conservation-tillage and nutrient management (Locke et al., 2010). In addition to geomorphic and land use changes, climatic trends and cycles can also have a large effect on water quality observations; in Oklahoma's Ft. Cobb Reservoir, sediment yield increased 183% from dry to wet periods (Garbrecht 2008). Changes in the balance of precipitation and evaporative demand has led to increased stream flows in the Midwest, which increases potential losses of nutrients and sediment if all else is equal (Tomer and Schilling 2009). Against these changes that constantly occur in watersheds, conservation practices often require several years to become effective. The phenomenon of lag effects is critical to understanding how the impacts of conservation practices on water quality need to be evaluated over multiple years, and often decades. This was shown in Walnut Creek Iowa where soil testing and split N-fertilizer applications were trialed in a paired watershed study, in which several years were required to document a response in tile nitrate losses (Jaynes et al., 2004). A significant literature on lag effects has evolved during the past 10 to 15 years, as reviewed by Meals et al. (2010).

Against changing 'background' conditions, how much conservation is required to document water quality change? Those instances where water quality improvement in CEAP watersheds was attributed to conservation practices occurred in Mississippi, where a significant portion of two watersheds (20-33%) was converted to permanent cover (CRP) from cropland (Kuhnle et al., 2008; Cullum et al., 2010). However, Feyereisen et al. (2008) found no trend in water quality during a period when 11% of a mixed land-use watershed in Georgia was converted to conservation practices.

Fourth, water quality management strategies address single contaminants rather than comprehensive approaches including inherent trade-offs among contaminants. This is not an easy issue to address because multiple practices may be required to adequately mitigate a single contaminant, even at a small-watershed scale (Gitau et al., 2004; Gitau et al., 2006). That is, a single contaminant may have several key sources that need to be addressed through a set of targeted conservation practices. While a conservation practice may influence runoff and the contaminants it carries relatively quickly, impacts on other contaminants impacting subsurface water quality may take many years to be detected. Therefore our understanding of tradeoffs among contaminants is evolving slowly. Hydrograph separation studies offer one approach to identify major pathways that each critical contaminant follows; Tomer et al. (2010) concluded that practices to address tile drainage, surface intakes, and riparian management all need to be addressed to comprehensively address water quality in an Iowa watershed. The importance of both upland and riparian management for water quality improvement is therefore highlighted here. While a mix of well targeted practices may be necessary for upland management, well managed riparian buffer can have multiple benefits not only for water quality and bank stability, but for a range of physical benefits for the stream environment that can improve the quality of aquatic habitat (Shields et al. 2006).

CONCLUSION

The Conservation Effects Assessment Project watershed assessment studies have facilitated progress in watershed and conservation science through modeling and observational studies. Progress during the first five years of this effort could be characterized as achieving critical steps in moving watershed modeling capabilities forwards, and recognizing key lessons that begin to capture the complexity and dynamic nature of watersheds through observational studies. Long term studies have demonstrated the impact of climatic variation, and lagged effects of practice implementation. Continued efforts that integrate observational and modeling studies offer the best opportunity to expand on this progress and move conservation science and policy forward, in cooperation and partnership with landowners and other stakeholders who recognize the critical importance of managing water quality. In this effort, it will be important to develop an understanding of linkages between water quality, conservation practices, and indicators of ecological integrity if conservation science is to recognize the full range of ecosystem services that agricultural landscapes and their associated aquatic environments can provide.

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Relationships between watershed-scale landscape, hydrology and agricultural practices towards surface and ground water quality improvement: the Bras d'Henri River, Quebec, Canada

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Keywords

Watershed; pedology, hydrology modelling, agriculture, water quality; BMP

Abstract

Modern agriculture is an important diffuse source of contaminants to stream water as a result of its use of large amounts of fertilizers. Consequently, various beneficial management practices (BMPs) have been adopted to mitigate the degradation of aquatic ecosystems. This paper relates the importance of understanding the relationships between parameters such as the watershed-scale landscape properties (soil, topography, drainage), the hydrological cycle characterizing these landscapes and the agricultural practices that are carried out. This study has demonstrated the considerable impact of soil types have in the landscape capacity to retain nutrients. Equally important are the specificity of the hydrological cycle, such as runoff characteristics and snowmelt. This paper discusses how developing new BMPs to improve water quality needs by addressing specific characteristics of the area where they are implemented.

INTRODUCTION

Modern agriculture has profoundly altered the landscape during the past decades and consequently the concept of agricultural sustainability has become imperative (Pretty, 2008). At the same time, modern agriculture uses large amounts of phosphorus (P) (Cordell et al., 2009) and nitrogen (N) (Smil, 2002) fertilizers to feed a constantly growing human population. As a result, agricultural activity is an important diffuse source of contaminants to aquatic ecosystems and many efforts are deployed to mitigate the resultant environmental impacts (Kronvang et al., 2009; Buczko and Kuchenbuch, 2010). Diffuse source of nutrients, especially P, causes diverse problems such as eutrophication of surface fresh water bodies that seriously degrade aquatic ecosystems and impair the uses of water (Carpenter et al., 1998). To that end, Schindler et al. (2008) have demonstrated that the focus on management should be on decreasing inputs of P to reduce eutrophication. Different approaches to mitigate environmental impacts of nutrient water contamination were limited by the fact that P and N have dissimilar mobility. Nitrogen is highly soluble and readily leached, while P is either insoluble (particulate) or soluble and transported via erosion, surface runoff, and tile drains. Because separate and narrowly targeted strategies for P and N management have lead to mixed results, McDowell et al. (2002) recommended using an integrated approach to manage nutrients by targeting best management practices (BMPs) to watershed areas which contribute most to the P and N exports. Such an integrated approach for addressing nutrient loss control could include: decreased use of fertilizers; containment, treatment and incorporation of manure; tillage practices that conserve soil; vegetated buffers along streams; and maintenance or restoration of wetlands.

In Canada, under the Agricultural Policy Framework, the “Watershed Evaluation of Beneficial Management Practices (WEBs)” project was initiated in 2004 and renewed in 2009 (Harker et al., 2010). The project aims to evaluate the environmental and economic performance of selected agricultural beneficial management practices (BMPs) at several small but intensively farmed watersheds across Canada. In the province of Quebec, the Bras d’Henri-Fourchette watershed project is assessing four group of BMPs of which two are specifically targeted on reduction of nutrient water contamination: animal manure management and surface runoff control measures.

This paper analyzes how critical factors of landscape, hydrology (2006-2009) and agricultural practice (2004-2009) impacted surface and ground waters quality in the Bras d’Henri watershed (2006-2009). This knowledge is necessary to better develop current and future nutrient-reducing BMPs towards water quality improvement at the watershed scale.

METHODS AND MATERIALS

Approach and study sites

A paired watershed approach was used for this study. Two micro-watersheds were selected on a similarity basis. Proximity, available soil characteristics and crops similarities were the main features used for the selection of the paired watersheds. One watershed, thereafter named the “control watershed” was maintained on “*business as usual*” farm management practices, while selected BMPs were implemented in the other watershed, and was named the “intervention watershed”.

In late spring 2004, all sub-watersheds of first and second Strahler stream order (Strahler, 1957) located within the 167 km^2 Bras d’Henri River watershed, downstream of the Chaudière River watershed (6 682 km^2), were investigated. Upon field observations and soil surveys available at that time two watersheds of second order were selected in early summer 2004 for long-term environmental and economical impact assessment of innovative BMPs applied on farms (Fig. 1). Water quality data of the intervention watershed (2.4 km^2), centered at *46°28’49”N – 71°12’55” W*, were compared to those of the control watershed (4.2 km^2), centered at *46°30’42”N – 71°11’34”W*.

BMPs applied in the intervention watershed

Two BMPs were investigated in this study. The first BMP, initiated in 2005, was a nutrient-reducing BMP consisting in an improved application management of hog slurry on agricultural soils cropped in grain and silage corn, and forages. Instead of a single large surface application at sowing, as generally done in the “*business as usual*” practice, this BMP consisted of two split applications of slurry in corn rows using trailing hoses and incorporated below soil surface right after application; the first at sowing and the second at the three-leaf phenological stage three weeks after sowing. In forages, slurry was applied in two or three stages. The second BMP, initiated in 2006, was a series of surface runoff-control BMPs consisting in three main landscape interventions: two grassed waterways (55 and 60 m length), riparian buffer strips (3204 m herbaceous; 3480 m trees and shrubs), and stream bank profiling (800 m).

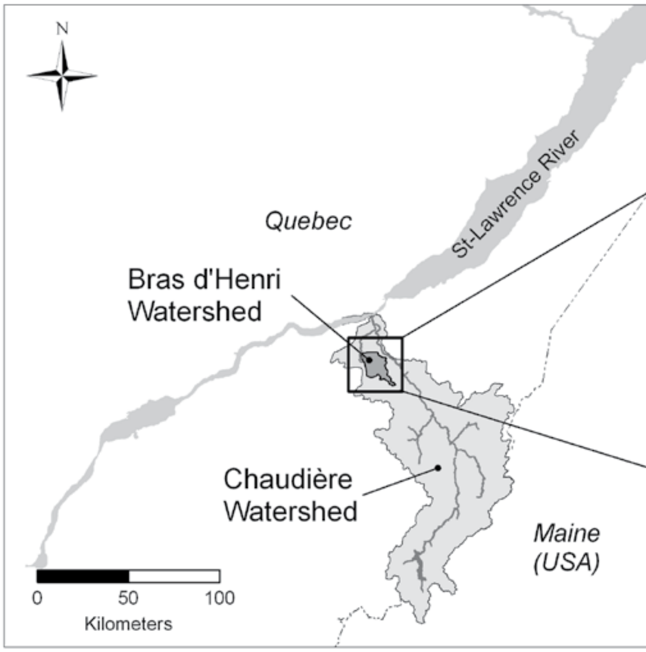

Figure 1. Map of a central south section of the province of Quebec (Canada) showing the Bras d'Henri River watershed confined within the greater Chaudière River watershed. The insert shows the locations of the paired second Strahler order micro-watersheds of this study (control and intervention watersheds).

Site characterization and data collection

Both watersheds exhibited intensive agricultural activity including: high swine and dairy cow livestock density (5.7 animal unit ha^{-1}); crop rotations of cereal, corn, soybean and pasture; and historical applications of mineral and organic fertilizers. In 2005 and 2006, a high precision digital elevation model (GPS-real time kinetic, 2 m resolution) was performed for both watersheds covering fields, streams and ditches. Extensive soil surveys (1: 15 000) were performed in both watersheds to update available soil maps (1: 63 300 and 1: 50 000) drawn between the late 1950' up to 1995. Both watershed outlets were instrumented in 2005 with meteorological, gauging and automatic water sampling stations. In 2006, the intervention watershed was monitored with water quality multiparameter probes (YSI Environmental, model 6820, Ohio, USA). The meteorological stations were used for hydrological modelling purposes and were equipped with data loggers (CR10X, Campbell Scientific, Edmonton, Canada) and Campbell Scientific specific probes to monitor air temperature and relative humidity (Vaisala probe, model HMP45C), wind velocity (wind speed sensor, model 013A, Met-One, Texas, USA), and wind direction (wind direction sensor, model 023A, Met-One, Texas, USA). Other equipments were used to measure liquid and solid precipitations (T200-B precipitometer, Geonor, Olso, Norway) and solar radiation (Radiometer, model CNR1, Kipp & Zonen, Delft, The Netherlands). The gauging stations were monitoring the water height with sonic ranger probes (Sonic Ranger Probes, model SR50A, Campbell Scientific, Edmonton, Canada) overlying the stream and connected to the data loggers. Portable automatic water samplers (model 6712, ISCO, Nebraska, USA) were installed at both watershed outlets. The water quality multiparameter monitoring probes (temperature, pH, electrical conductivity, and turbidity) were fixed to a concrete block laying on the streambed to keep them permanently submerged and were also connected to the data logger.

Ten sites of the intervention watershed were instrumented with twelve open piezometers to study potential groundwater contamination. Two piezometers were installed with their perforated casings at depths of 5.5 and 6.3 m below soil surface to collect deep ground water, while the remaining ten piezometers were installed with their perforated casings at depths ranging from 0.4 to 2.9 m to collect the shallow ground water characterizing the intervention watershed.

Meteorological and water quality parameters were respectively monitored every five and fifteen minutes and hourly averages were calculated, compiled and used for further analysis and modelling purposes. A 150-ml water sample was automatically taken every hour and two composite water samples (3-day and 4-day composite samples) were made on a weekly basis and analyzed for suspended sediments (gravimetric method), total N, total dissolved N, NO_3-N, NO_2-N NH_4-N, total P, total dissolved P, molybdenate reactive P and dissolved reactive P (colorimetric methods). Dissolved organic P was calculated by subtracting the dissolved reactive P from the total dissolved P. The total particulate P was calculated by subtracting the total dissolved P from the total P. Five to six water samples collected from the piezometers during the cropping season were analyzed for the same N fractions listed above for the stream water samples in addition to dissolved reactive P and total dissolved P. Furthermore, piezometer water samples were analyzed for their NO_3^- natural abundance isotope contents. The δ^{15}N and δ^{18}O analyses were determined at the Delta-Lab of the Geological Survey of Canada (Québec) following the detailed methodology described in Savard et al. (2010). Agronomic data were also collected from 2004 to 2007 to estimate the N and P budgets for each watershed. Water samples were collected at the intervention watershed outlet at the main snowmelt event to measure the TSS (total suspended sediments), total P and total dissolved P. Total particulate P was calculated as previously described. In addition, water samples were collected at the watersheds outlets during the months of March and April in 2007 through 2009 to capture potential BMP impacts during the critical period of snowmelt.

Hydrological modelling

The Water Simulation Model (WaSiM-ETH, Schulla and Jasper, 2000) was used to estimate water volumes of the water budget of the intervention and control watersheds during years 2006 to 2008 including the main snowmelt periods. The calibration and validation processes of WaSiM-ETH were identical to those described for the Bras d'Henri watershed in Su et al. (2011). The model outputs of interest for this study are presented in Figure 2. In summary, the model separates total precipitation (snow and rain) into three main water fractions: surface runoff, infiltration flow and water losses. The surface runoff corresponds to a simulated volume of water originating from rain and/or snow cover that does not enter the soil profile as opposed to the infiltration flow. The infiltration flow is subsequently separated into two fractions: the hypodermic flow and the base flow. Together with the surface runoff, the hypodermic flow makes up the volume of water that reaches directly a surface watercourse (direct discharge). Finally, the direct discharge adds up with the base flow, which is a simulated volume of water derived from the seepage of groundwater, and/or through-flow into the surface watercourse, giving the total discharge of the watershed.

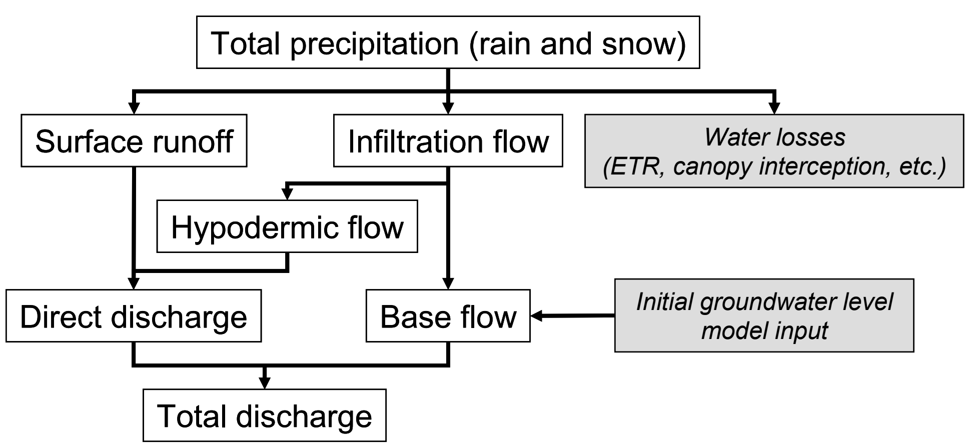

Figure 2. Simplified schematic representation of the WaSiM-ETH model outputs presented and discussed in this study (white boxes) showing their interrelations.

RESULTS AND DISCUSSION

The paired watersheds showed a differing and highly variable pedology after completion of the 1:15 000 scale mapping (Table 1). This contrast was not perceptible on older soil survey maps done at smaller scales (1:50 000 to 1:63 360). More than half of the area of the intervention watershed is covered by podzolic soils compared to the control watershed where gleysolic soils account for 85% of the area. This soil order difference conferred a significantly higher P sorption capacity for the intervention watershed. Estimated from the Mehlich-3 aluminum content, the P sorption capacity for the intervention watershed showed an average value of 1578 mg Al kg^{-1} soil compared to 1411 mg Al kg^{-1} soil for the control watershed. Differences in slopes, textural classes and permeability are responsible for the greater coverage of moderate risks of surface runoff and leaching estimated by the Soil Surface Loss Rating and the Soil Leaching Loss Rating methodology respectively (Robert and Anderson, 1992) in the intervention watershed than in the control watershed. These characteristics indicate a higher vulnerability of the intervention watershed to losses of highly soluble compounds and to losses occasioned by water erosion events. On the other hand, the major soil disparity between the two watersheds indicates a higher risk of P contamination in the control watershed.

The N and P budgets were systematically in excess for both watersheds between 2004 and 2007, except for a negative N budget in 2005 for the control watershed (-9.7 kg N ha^{-1}). The 2004-2007 average excess of P was equivalent for both watersheds (16 kg P ha^{-1}) in opposite to the excess of N much higher in the intervention watershed (35 kg N ha^{-1}) than in the control watershed (7 kg N ha^{-1}). This difference was partially due to the dominance of annual crop, mostly corn, (51% of crop area) in the intervention watershed requiring larger amount of N fertilizers than perennial crops (prairies or forages) covering 41% of crop area of the control watershed. Equivalent P budgets but contrasted P sorption capacities in both watersheds lead to less important soil P saturation (Mehlich-3 P/Al) in the intervention watershed than in the control watershed. In fact, 7% of the cultivated area of the intervention watershed had a soil P saturation value greater than 10% as compared to 19% of the cultivated area for the control watershed (data not shown).

Table 1. Dominant landscape parameters of the Bras d'Henri River paired micro-watersheds

Dominant landscape parameters	Description	Watersheds	
		Intervention	Control
Soil order (area %)	Podzol	55	11
	Gleysol	25	85
Slope (%)	Class	3-8	0-3
Family particle-size	Sandy to coarse loamy	33	22
	Loam	27	63
Soil drainage (area %)	Imperfect	40	12
	Poor	40	80
Soil P saturation (%)	P/Al Mehlich-3	7.0	8.1
Risk of surface runoff (area %)	Moderate	68	38
Risk of leaching (area %)	Moderate	37	8
Annual crop	Area %	50.8	19.4
Perennial crop	Area %	29.3	41.0

The WaSiM-ETH model outputs for years 2006 to 2008 (January 1 to December 31) are presented in Table 2. Results for all three years systematically showed larger total discharge values for the control watershed. The differences in the total discharge values between the control and the intervention watersheds were ranging from 39 mm to 90 mm with an average of 60 mm for the three years. At the same time, although the number of days with surface runoff was substantially less in the intervention watershed, the surface runoff value was comparable between the two watersheds meaning that the average daily runoff was 62% higher in the intervention one. This is in accordance with results presented in Table 1 showing a greater area percentage (68%) presenting a moderate surface runoff risk in the intervention watershed compared to the control watershed (38%). The difference in total discharges in the watersheds can be explained partially by the larger total precipitation and base flow values in the control watershed.

Table 2. WaSiM-ETH model outputs for calendar years 2006, 2007 and 2008.

	2006	2007	2008
Intervention			
		(mm)	
Total precipitation	1000	1004	1119
Precipitation - rain	829	774	786
Precipitation - snow	171	229	334
Evapotranspiration	401	335	419
Surface runoff	31	59	178
Hypodermic flow	404	370	380
Base flow	5	13	19
Total discharge	**440**	**442**	**577**
Number of days with snow cover	83	100	118
Number of days with surface runoff	47	70	97
Number of days without surface runoff	318	295	269
Mean snow water equivalent (mm) *	28	31	80
Air temperature annual average (Celsius)	5,9	4,4	4,6
Control			
		(mm)	
Total precipitation	1027	1069	1150
Precipitation - rain	841	794	793
Precipitation - snow	185	275	357
Evapotranspiration	473	417	476
Surface runoff	65	56	158
Hypodermic flow	440	395	432
Base flow	25	30	36
Total discharge	**530**	**481**	**626**
Number of days with snow cover	86	108	117
Number of days with surface runoff	159	156	191
Number of days without surface runoff	206	209	175
Mean snow water equivalent (mm) *	60	37	85
Air temperature annual average (Celsius)	5,9	4,3	4,6

*The mean snow water equivalent value is covering the period of days with snow cover.

Water quality parameters measured by the submerged multiparameter probes showed relatively constant values during the three year period of 2006 to 2008. The mean water temperature during the monitoring period (mainly from May to November) was 11°C with summer peaks close to 20°C. The pH value remained close to 7.6 which was in accordance with environmental statistics of the main effluents of the St.Lawrence River (MDDEP, 2002). There is no Canadian environmental quality guideline for the protection of aquatic life in terms of electrical conductivity in freshwater streams but there is a maximum increase threshold of 10% for turbidity between background values and increased values (CCME, 1999). The electrical conductivity averaged value of 0.37 mS cm^{-1} was within the range of 0.1 to 2 mS cm^{-1} for freshwater streams published by the Clean Water Team – the Citizen Monitoring Program of the California State Water Resources Control Board (CWT, 2004). The averaged background turbidity value of 400 NTU indicated an inherent turbid water condition at the intervention watershed outlet. Yet, this background turbidity value has rarely increased by more than 10% during high flow periods following rainstorm events. Only few exceptions were observed after unusual severe rainstorms causing excessive soil water erosion and where turbidity values as high as 800 NTU were monitored.

Water quality monitoring results at the two watershed outlets showed differing trends for N and P between the adjacent paired micro-watersheds (Table 3). The intervention-control ratios of the flow weighted mean concentrations of total N and nitrate-N were respectively 1.64 and 2.23. This higher N ratio can be explained by the N balance excess estimated in the intervention watershed as well by sandy loam soils and good drainage soil classes increasing the risk of N leaching in this watershed. However, opposite trends were observed for total and dissolved P for which respective flow weighted concentration values were approximately 2 and 3 times lower in the intervention watershed dominated by podzols (55%) having higher P sorption capacities than the gleysols dominating (85%) the control watershed. The elevated soil P saturation in the control watershed (Table 1) explains its higher median dissolved P concentrations ranging from 0.04 to 0.08 mg L^{-1}. Moreover, median concentrations of the dissolved P were above the total P environmental threshold of 0.03 mg L^{-1} throughout the three years (2006-2008).

The snowmelt event is a major hydrological event and was responsible for large nutrient losses to surface water. Based on stream water nutrient concentrations and WaSiM-ETH total discharge outputs, the estimated loads of total P during the 2006-2008 snowmelt periods (March-April) ranged from 0.10 to 0.79 kg P ha^{-1} of the total P load losses in the intervention watershed. Furthermore, during the growing season only a small number of rainstorm events were responsible for most of the summer losses of total P to surface water in both watersheds. Only the rainfall event of June 25, 2009 in the intervention watershed (data not shown), accounted for 40% of the 0.79 kg P ha^{-1} summer losses while in the control watershed, the rainfall event of June 12, 2009 accounted for 20% of the 0.45 kg P ha^{-1} summer losses.

Table 3. Median concentrations (MC) of water quality parameters and flow-weighted mean concentrations (FWMC) for the period of 2006-2008 (mid-April to end-November).

	Intervention						Control						Intervention/Control	
	2006		2007		2008		2006		2007		2008		Average ratio *	
	MC	FWMC	MC	FWMC	MC	FWMC	MC	FWMC	MC	FWMC	MC	FWMC	MC	FWMC
Total suspended solids	16,07	36,25	16,07	49,20	14,04	72,92	17,72	28,23	8,69	22,28	10,52	62,88	1,36	1,55
Total N	6,21	5,45	5,43	4,53	5,98	6,08	2,42	2,84	3,61	3,51	4,78	3,53	1,77	1,64
Nitrate-N	5,43	4,34	4,73	3,59	4,78	4,82	1,13	1,44	2,42	2,43	3,14	2,20	2,76	2,23
Nitrite-N	0,04	0,03	0,02	0,03	0,02	0,04	0,02	0,03	0,02	0,03	0,02	0,03	1,37	1,09
Ammonium-N	0,09	0,08	0,06	0,10	0,07	0,09	0,09	0,15	0,09	0,11	0,09	0,14	0,82	0,69
Total P	0,08	0,15	0,09	0,13	0,06	0,12	0,15	0,27	0,12	0,19	0,13	0,26	0,59	0,56
Dissolved P	0,02	0,05	0,02	0,05	0,02	0,03	0,08	0,16	0,04	0,10	0,06	0,14	0,33	0,33
Particulate P	0,06	0,10	0,05	0,08	0,05	0,09	0,08	0,12	0,07	0,09	0,06	0,12	0,79	0,84
Sampling period (day)	223		220		205		220		220		199			
Total discharge (mm)**	404		415		344		255		371		198			

* The "intervention/control" average ratios cover the three year period (2006-2008).
** The total discharge covers the water sampling period only.

The isotope analysis of $\delta^{15}N$ and $\delta^{18}O$ revealed that nitrate from ground water samples essentially originated from a mixture of soil organic matter and manure. No mineral N fertilizer (NO_3, NH_4 or urea) isotopic signature was found in the ground water samples suggesting that these sources were rapidly used by the crops and did not leach down to ground water. Based on the $\delta^{18}O$ natural enrichment values, the results have also shown that N from organic sources was nitrified during all seasons including winter and spring melt. Furthermore, most of the isotopic signature values were lying on the denitrification curve where the enrichment of ^{15}N is about twice as high as for $\delta^{18}O$ indicating that denitrification was occurring in the ground water system.

The nutrient-reducing BMP aimed at minimizing ammonia volatilization and nutrient transport to surface waters subsequent to hog slurry applications on agricultural soils. The applied amount of organic fertilizers was first based on the N requirement of the crop. However, for corn, this amount was modulated as per the fertilization grid P recommendations relating to the soil P saturation and for forage, to the soil test P values. In addition, since 2002 Quebec regulation has limited application of P fertilizer on agricultural soils having a soil P saturation value greater than 15 to 20% depending on the soil type. During this study, no soils were affected by this regulation but the historical *modus operandi* has systematically led to excess P application in corn fields. The hog slurry application BMP showed contrasted impacts on the nutrient use efficiency for N and P (data not shown). While no significant difference was observed in the N use efficiencies for both corn and forages between the BMP and the *business as usual* practices during the period of 2005-2007, significantly lower P use efficiencies were observed for corn in the BMP. These observations are in agreement with the observation mentioned earlier that surpluses of P were applied specifically in corn fields. Qualitative water quality measurements in field runoff and leaching waters (data not shown) suggested that the nutrient-reducing BMP had a good potential to minimize transport of nutrients to surface waters so much as the amount of organic amendments applied on soil takes also into account the amount of P applied. In middle or long term perspective, systematic soil P enrichment is not realistic because it will ultimately saturate the soil P sorption capacity and increase P desorption processes and lead to surface water contamination.

The surface runoff-control BMP impact on water quality was not directly assessed at this stage of the project due to the recent onset of the structures. However, positive effects of these landscape interventions should be observed in future water quality temporal trend analysis, particularly on landscape and stream bank sediments loads to the streams.

Relationships between intensive agriculture land use, high livestock density, nutrient surplus and water quality parameters were clearly observed in both micro-watersheds since the monitoring start in 2005. Nutrient transport to surface and ground waters was aggravated by storm events and important snowmelt runoff in both watersheds. Elevated concentrations of nitrate in surface and ground waters of the intervention watershed were mainly attributed to surpluses of manure organic N and higher risks of surface runoff and leaching related to soil and topography properties. In addition, residual soil N was nitrified and leached over winter demonstrating the need to integrate the new BMPs towards all season's hydrology. Above environmental total P threshold concentrations in stream were related to historical excess P balance in both watersheds but more importantly in the control one where soils have a lower P sorption capacity. These combined effects on water quality demonstrated the need to optimize the use of N and P at the source in both watersheds. This should be addressed by adopting nutrient reducing technologies such as new animal precision feeding and manure treatment technologies. N fertilizers should also be better managed in areas at higher risk of leaching, specifically in the intervention watershed. P fertilizer applications should be constrained on saturated and low P sorption capacity soils. Finally, erosion sensitive agricultural soils should be protected from snowmelt runoff by over winter cover crops and vegetated buffer strips should be rendered efficient during spring melt by using alternative plant species acting as a physical buffer such as potentially the switched grass.

CONCLUSION

Achievement of surface and ground water quality improvement in an agricultural area lies on a good understanding of the relationships between parameters such as the watershed-scale landscapes, the hydrological cycle characterizing these landscapes and the agricultural practices that are carried out. This study has showed that the combination of agricultural practices, land use and soil types are well correlated with stream water contamination levels in the two monitored watersheds. It demonstrated that the performance of nutrient-reducing BMPs and structural BMPs aimed at reducing nutrient transport to water bodies can be impacted by the various combinations of the landscape, hydrology and agricultural practices parameters existing in some areas of the Bras d'Henri watershed. Future BMP developments should take these relations into account to reduce the regional impact of agriculture on water quality.

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The Impact of Land Use Change on Stormwater Pollutant Loads from Wachusett Reservoir Watershed

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Abstract

The Wachusett Reservoir is one of the primary drinking water sources for the Boston area in Massachusetts, USA. Major concerns of pollutants in the reservoir include microbial pathogens and nutrients, which can degrade water quality and affect the ecology of the reservoir. Stormwater runoff is one of the major sources of these pollutant loadings to the reservoir, which is greatly affected by land use change and development within the watershed. This study investigated the impact of land use change on the stormwater pollutant loads from the watershed. The estimate was based on a volume concentration model using a GIS analysis. The results show that the watershed was urbanized by approximately 74% and the estimated pollutant loads from the watershed shows positive relations with the extent of development. The results clearly show that the development induces significant increases in pollutant loads that will deteriorate the quality of drinking water sources. The results also show that the management of urban land uses would achieve the reduction of pollutant loads at minimum cost. This study will provide the guidelines to land use planners and environmental regulators in sustainable development of the watershed and systematic BMP implementation to control stormwater pollution.

Keywords

Land use change; Watershed management; Stormwater quality; Pollutant load

INTRODUCTION

The Wachusett Reservoir is one of the primary drinking water sources providing water to over 2.5 million residents of the Boston area in Massachusetts. The reservoir is located in mid Massachusetts (Figure 1), which was built between 1897 and 1908 through damming of the south branch of the Nashua River (DCR a). The drinking water supplied from the reservoir is unfiltered and the quality of drinking water depends primarily on watershed protection and disinfection (Fiedler, 2009). The water quality of the reservoir and tributaries is regularly monitored to quantify the variability of pollutant loads. Major concerns of pollutants in the reservoir include microbial pathogens and nutrients, which can degrade water quality and affect the ecology of the reservoir (Fiedler, 2009). Pathogen monitoring in the watershed is focused on fecal coliforms, which indicates fecal contamination. Nutrients, *i.e.* nitrogen and phosphorus, are of interest because nutrients can cause algal blooms during the summer. Algal blooms often deplete dissolved oxygen in the water and produce compounds that are associated with tastes and odors in drinking water.

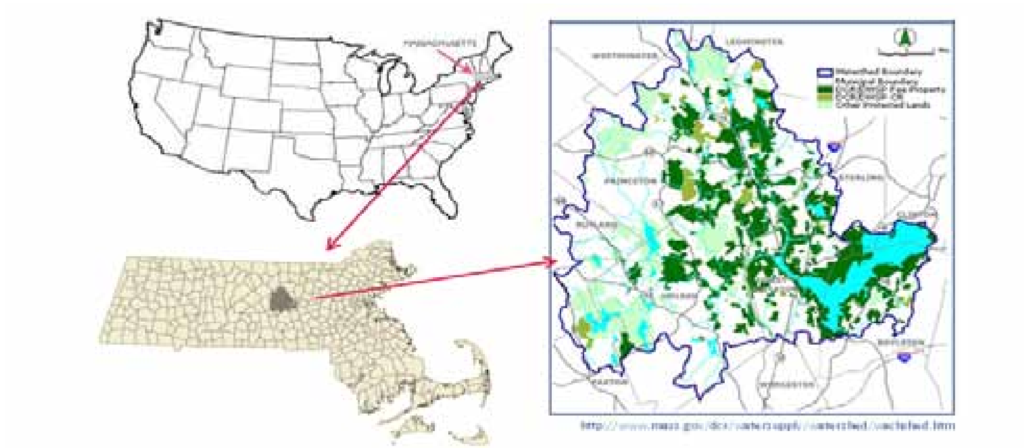


Figure 1. The location of Wachusett Watershed

Stormwater runoff is considered to be one of the major sources of these pollutant loadings to the reservoir because the watershed is undergoing continuous development. The development of the watershed increases impervious surfaces that eventually increase runoff volume and pollutant loads to the reservoir. Stormwater pollutant loads are known to be highly related to land uses (Stenstrom *et al.*, 1984; Young *et al.*, 1996; Ierodiaconou *et al.*, 2004). Therefore, land use information is often used to estimate pollutant loads if accumulated measurements are unavailable (Wong *et al.*, 1997; Park and Stenstrom, 2006).

In this study, we investigated the impact of watershed development on the stormwater pollutant loads discharged to the reservoir and streams. We estimated stormwater pollutant loads and the change in pollutant loads based on land use change in the watershed. Then land use was prioritized in the order of increasing impact on water quality. The results can be used to develop stormwater management strategies and best management practices (BMPs) to maximize water quality at minimum cost. The result will assist future land use planning and sustainable watershed management.

METHODS

The land use data and GIS layers of the watershed were obtained from Massachusetts Office of Geographic Information (MassGIS). The land use data were obtained for three decades (1971, 1985, and 1999). The most recent land use layer from 2005 was not included for the study because its land use classification system and land use collection method are not consistent with others. The land use categories were reclassified to a smaller number of categories: residential, commercial and institutional, public, industrial, transportation, open land, agriculture and forest.

Precipitation data were obtained from Massachusetts Department of Conservation and Recreation (DCR) precipitation database (DCR b). The imperviousness of each land use was calculated using a GIS model (ArcGIS™ version 9.3, ESRI, Redlands, CA) with the imperviousness layer superimposed with the land use layer of the watershed and the runoff coefficient of each land use calculated from imperviousness using the following equation (Driscoll *et al.*, 1990):

$$\mathrm{RC} = 0.7 \times \mathrm{Imperviousness} + 0.1 \tag{1}$$

The event mean concentration (EMC) data of stormwater pollution were obtained from National Stormwater Quality Database (NSQD, v3) (Pitt *et al.*, 2004) since no stormwater pollution monitoring data for each land use are available in the region. The amount of EMC data in Massachusetts or in New England region are not sufficient for statistical analysis and therefore, the EMCs from Northeast Region were used for our analysis. In addition, EMCs for some land uses were not available and therefore, the EMCs for open land use have assigned to the EMCs for forest and agricultural land uses. The fecal coliform EMC for institutional land use also was assigned from the EMC for commercial land use. Table 1 shows the imperviousness, RC, and selected EMC values for each land use in the watershed.

Table 1. Stormwater and runoff characteristics based on based on land uses in Wachusett Reservoir Watershed

Land Use	Imperviousness	RC	EMCs		
			Fecal Coliform (colonies/100mL)	TKN (mg/L)	TP (mg/L)
Forest	0.031	0.12	16331	0.57	0.078
Agriculture	0.055	0.14	16331	0.57	0.078
Open land	0.097	0.17	16331	0.57	0.078
Residential	0.23	0.26	16213	2.0	0.30
Institutional	0.43	0.40	17574	1.80	0.23
Commercial	0.63	0.54	17574	2.0	0.22
Industrial	0.67	0.57	3988	2.1	0.42
Transportation	0.60	0.52	11338	2.4	0.30

Note that RC represents runoff coefficients, EMCs represent event mean concentrations.

The estimate of stormwater pollutants was based on a volume-concentration (Wong *et al*., 1997; Park *et al*., 2006) model because stormwater pollution is highly related to land use activities:

$$PL_i = \alpha \times RC \times RF \times EMC_i \times A \qquad (2)$$

where PL_i is annual stormwater pollutant loading for constituent i (ton/year), α is a conversion factor, RC is the runoff coefficient (dimensionless), RF is annual rainfall (mm), EMC_i is event mean concentration for constituent i (mg/L), and A is the area of land use. Thirty year average annual rainfall (1266 mm) was used for annual rainfall. Selected pollutants are fecal coliform, total Kjeldahl nitrogen (TKN), and total phosphorus (TP). Among these selected pollutant loads, TP loads were compared to the estimate using export coefficient developed by MassGIS as shown in Table 2 (Fiedler, 2009) because the export coefficient of the other pollutants are not available.

Table 2. Massachusetts export coefficient for nutrients (kg/ha/year) (Fiedler, 2009)

Land Use	Nitrate	TP
Forest	2.31	0.08
Agriculture	2.99	0.58
Open land	1.02	0.05
Residential	10.08	2.00
Institutional	8.04	1.51
Commercial	9.81	1.66
Industrial	9.81	2.43
Transportation	2.31	0.08

In order to prioritize land use for stormwater pollution, the concept of leverage is employed (Park *et al.*, 2007). Leverage represents the quantitative effect of stormwater runoff from each land use on the reservoir water quality regardless of the area of each land use.

$$\text{Leverage}_i = \frac{\%\text{PL}_{ij}}{\%\text{A}_i} \tag{3}$$

where PL_{ij} is percentage of the pollutant loading i of land use j and A_j is percentage of the area of land use j.

RESULTS AND DISCUSSION

The Wachusett Reservoir Watershed is approximately 280 km^2. Most of the watershed is not developed and over 70% of the watershed is covered by forest. The watershed was developed from 1971 to 1999 as shown in Figure 2. All urban land uses such as residential, commercial, industrial and transportation areas have increased by approximately 32% to 716% whereas forest and agriculture area have declined by 8% and 16%, respectively. However, the development of urban land use shows a different trend for each decade. Residential and commercial land uses have continuously increased by 16–34% for each decade. However, industrial and transportation land uses dramatically increased between 1971 and 1985 (47 and 823% respectively) but slightly decreased by 10–12% between 1985 and 1999.

The estimated pollutant loads increased during the past three decades as the watershed was developed. Figure 3 shows the estimated annual mass loads of fecal coliforms and nutrients, and their total loads increased by 8% and 33% respectively. The increase in pollutant loads from the watershed is proportional to the increase in urban land use area, which shows that the land use development is a main driver of the increase in mass loads to the reservoir. This demonstrates that increases in urban land uses should be managed to mitigate their adverse impact on the reservoir.

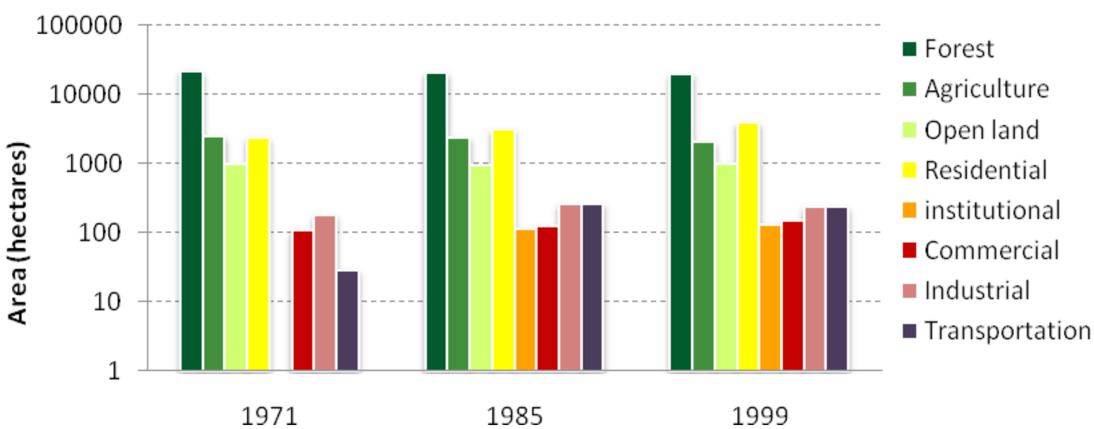


Figure 2. Land use change in Wachusett Watershed

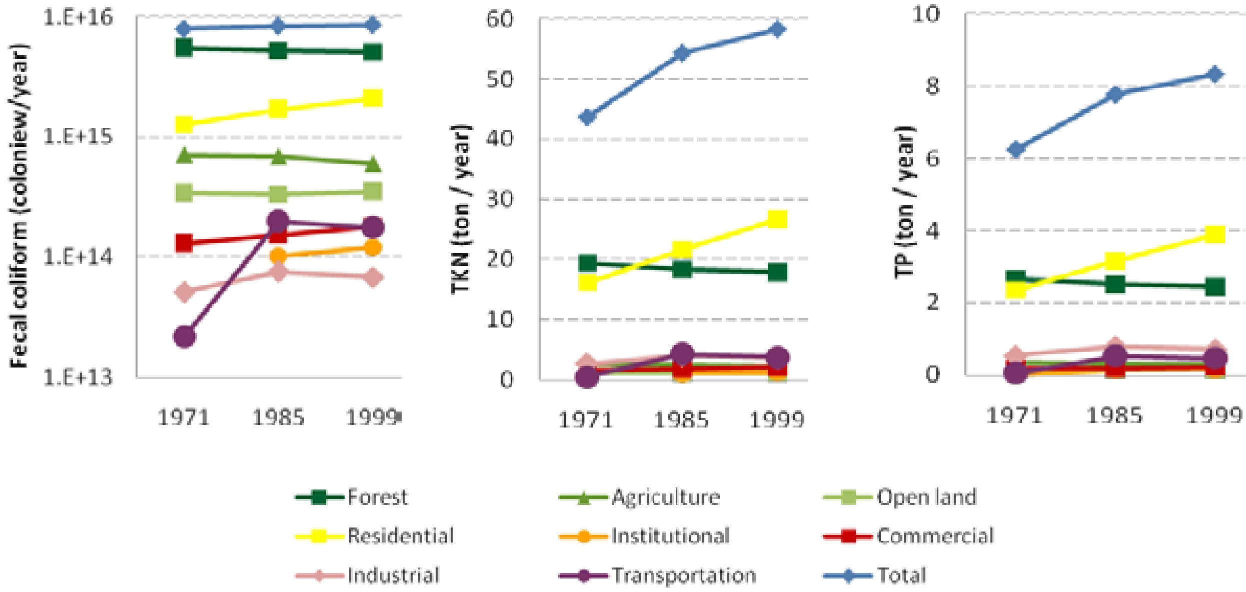
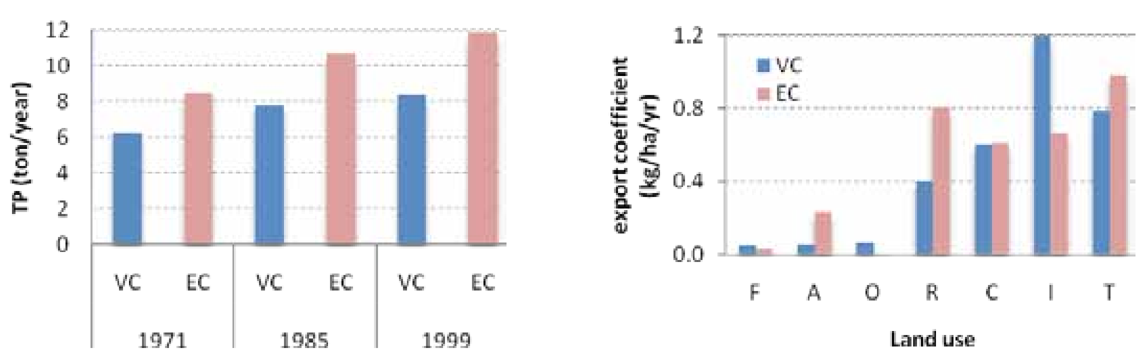


Figure 3. Estimated annual average pollutant loads from Wachusett Watershed

In order to validate the estimates, the estimated TP loads were compared to the estimate using export coefficients as shown in Figure 4 (a). However, the latter include not only stormwater loads but also other non-point source loads such as groundwater discharge. Nevertheless, the magnitude of both estimates are similar, which shows that our estimates of pollutant loads can be confidently derived. Moreover, export coefficients for stormwater runoff from the watershed were calculated. Figure 4 (b) shows the estimated export coefficients of TP for each land use compared with the existing export coefficients developed by MassGIS. Although these export coefficients cannot be directly compared because they refer to stormwater loads and non-point source loads, respectively, this comparison can be used to validate the estimated coefficients. The results show that only the export coefficients of forest and commercial land uses were similar and other coefficients were quite different. The difference between the values indicates that MassGIS values underestimate loadings from industrial and open land uses.



(a) (b)

Figure 4. The comparison between volume concentration (VC) method and export coefficient (EC) methods. (a) mass load estimates using VC and EC. (b) export coefficient esimated from VC method and existing EC values. Note that F is forest, A is agriculture, O is open land, R is residential, C is commercial, I is industrial and T is transportation land uses

The impact of each land use was evaluated using the concept of leverage. If greater pollutant loading can be reduced from smaller areas, then the cost to manage the pollution should be significantly less. Figure 5 shows the leverage for each pollutant, ranged from 0 to 13. For all cases, commercial and transportation land uses showed the highest leverage. Industrial land use also showed high leverage except the case of fecal coliforms. These results suggest that high impervious urban land uses are critical in managing stormwater pollution despite their small coverage area. The map of the watershed in Figure 6 shows these hotspots that should be targeted first. If the cost of implementing BMPs is proportional to area of land uses, the greatest pollutant reduction for a fixed cost will be achieved by managing the areas with high leverage area first. Moreover, the result will be useful for future land use planning to reduce pollution to the reservoir and sustainable water supply management.

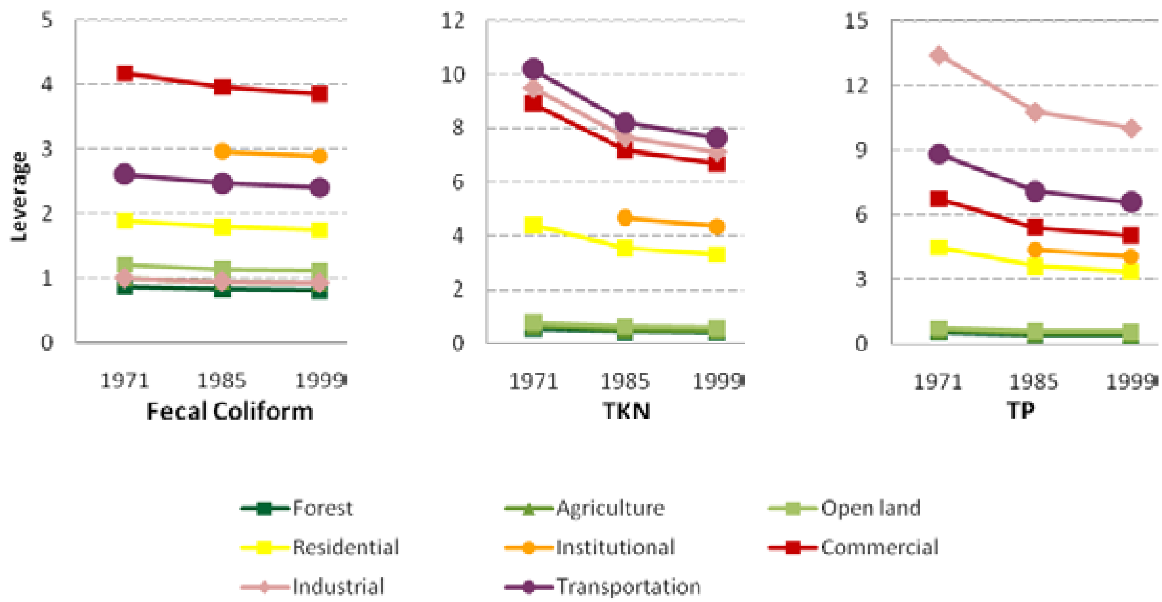


Figure 5. Leverage of each land use for selected pollutants in Wachusett Watershed

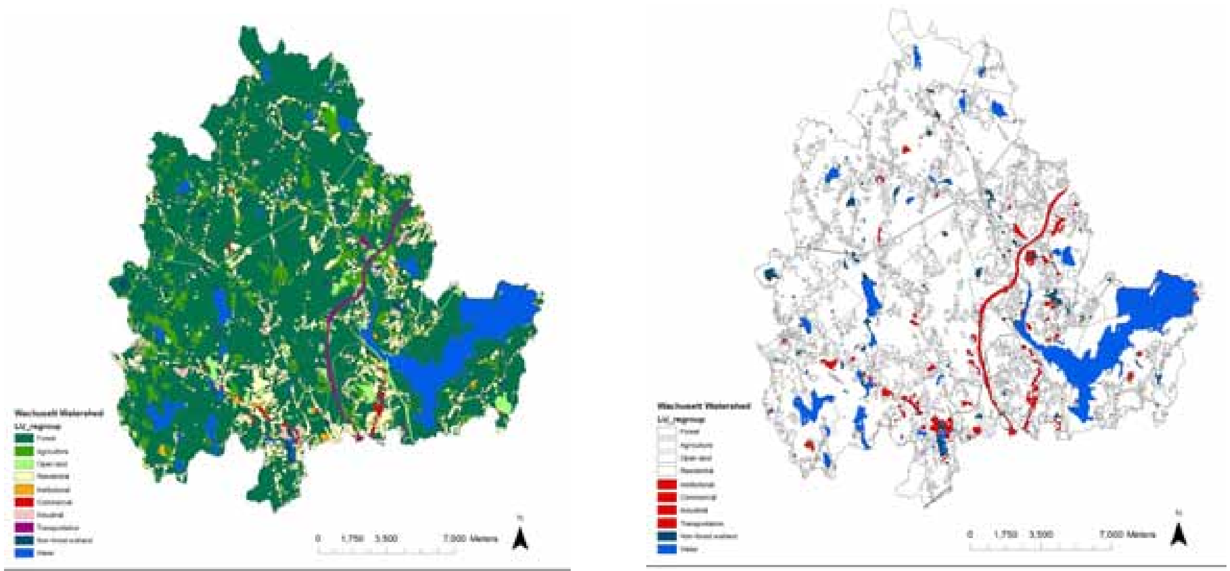


Figure 6. Map of Wachsett Reservoir Watershed (a) land use (b) prioritized land use for stormwater management. Note that red areas are hotspots and blue areas are water bodies in the watershed.

CONCLUSIONS

This study has shown that the land use development of a watershed increases stormwater pollutant loading to the reservoir and the increased urban land uses increases the pollutant loading in the same order of significance. Highly impervious urban land uses such as commercial, industrial and transportation land uses should be prioritized for stormwater management because they have the greatest impact. Treating a small area of these highly impervious urban land uses will achieve significant reduction of the pollutant loads with minimum cost. Therefore, future BMP implementation should target these urban land uses first.

Our approach also shows acceptable estimates of stormwater pollutant loads. However the lack of stormwater monitoring data based on land uses makes it difficult to accurately estimate the loads from the watershed. An effective watershed monitoring strategy is needed to calibrate and validate modeling results. The site-specific information will be valuable for sustainable management of watershed and water resources in an efficient and cost-effective way.

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Identification and Control of Diffuse Pollutants arising from the Eastern Black Sea Watershed of Turkey

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Abstract

This study presents the estimated current diffuse pollution profile of the Eastern Black Sea Watershed of Turkey that has a population density representing the country's average with the dominating sector of agriculture including forestry and fishery. In the estimation of diffuse pollutants, the major factors to be determined are the areal values of each land-use activity, urban and rural population values, and climatic conditions. The paper refers to the methodology used to roughly estimate the diffuse loads based on the two nutrients; Total Nitrogen (TN) and Total Phosphorous (TP). The distribution of the major diffuse pollutants at each of the sharing provinces and at watershed scale is given. The major diffuse N loads are estimated as agricultural activities with 54% followed by livestock breeding that contribute to the N budget with 11% in the watershed. Almost 7% of N loads come from meadows and pasture, and 5% from forests. In the distribution of diffuse P loads, it is estimated that 48% of the loads arise from agricultural activities and 18% from livestock breeding. Almost 14% of the P loads come from septic tank effluents; however, 13% of the loads are due to rural run-off. The future loads for years 2028 and 2039 are also estimated. 30-40% decrease is foreseen in the agricultural pollutants and animal manure through the stepwise application of ecological agriculture and livestock breeding. The basic aim of this study is to put forth a guideline especially for the developing countries facing available data scarcity on identification, estimation and control of diffuse sources of pollutants in a practical manner.

Keywords

Agricultural activities; diffuse loads; land-use distribution; nitrogen and phosphorous; population

INTRODUCTION

Diffuse pollutants enter the receiving water bodies in a diffuse manner at intermittent intervals through precipitation. As waste generation over an extensive area of land is concerned, they are usually in transit with overland and they reach to surface water through run-off or infiltrate through soil. Thus, unlike point sources of pollutants diffuse sources are impossible to monitor at the point of origin and their abatement is rather focused on land and run-off management practices. Compliance monitoring is carried out on land rather than in water. Another important aspect of such sources is that the waste emissions and discharges cannot be measured in terms of effluent limitations (Novotny, 2003).

Extent of diffuse waste emissions expressed by nutrients (nitrogen and phosphorous) is related to certain uncontrollable climatic conditions, geographic, geologic conditions, and may differ from place to place and from year to year (Campbell, 2004). Detailed studies on the determination of diffuse pollutants and to better understand their transportation mechanism on soil till they reach the water media are conducted by means of watershed models. However, such studies need more input data and time for application of the models. Besides, practical estimations can be achieved in a shorter period of time where available data are limited. This study forms an example of how such calculations can also be practiced especially in developing countries with the aim of putting forth the distribution and respective rough loadings of different kinds of diffuse pollutants prevailing in a watershed.

The methodology of estimating the diffuse nitrogen, N, and phosphorous, P, loads based on land-use activities will be discussed in this study. The distribution and estimation of diffuse loads in the study area will be mentioned based on the administrative boundaries to better present the existing situation to the decision makers. Furthermore, control actions that might be considered for the watershed will be referred and outlined.

Such efforts of identifying and estimating diffuse loads and their control in the short and long term forms an important part of integrated river basin action plans that need to be completed sooner according to the EU enforcements. During the accession period, Turkey has to comply with the EU directives regarding Water Framework Directive (WFD). The action plans will then form a basis for the preparation of management plans. The methodology used in this paper is being used in the determination of diffuse loads arising from the river basins of Turkey. Currently, the action plans of the 11 out of total 25 river basins of the country representing the priority ones are being prepared till the end of year 2010. The rest will be prepared next year. The Eastern Black Sea Watershed of the country is among the ones that have not been studied yet (Figure 1). That is the main reason of selecting this watershed as the subject of concern in this study.

Study Area

Eastern Black Sea Watershed is situated at the north eastern part of the country with a surface area of 2.490.320 ha and a population of 2.226.658 according to 2007 figures (Figure 1). 56% of the population constitutes the urban population, whereas the rural population accounts to 44%. The distribution of the urban and rural population of the watershed within years is shown in Figure 2(a). The current population density of the watershed (89 cap./km^2) represents the country's average of 91 cap/km^2 (TUIK, 2008). The watershed consists of land from 10 provinces among which 5 of them have shares between 15-20%. Trabzon and Rize provinces fully take place in the watershed forming a share of 19% and 16%, respectively. Ordu Province has a share of 20%, followed by Giresun with 18% and Gumushane with 15%. The rest of the 5 provinces have minor contribution of land to the watershed varying between 1-5%.

The major economic sector of the watershed is agriculture including the fishery and forestry activities. The identification of diffuse pollutants and the corresponding data inventory stage is the fundamental part regarding the types of human-induced prevailing activities evolving such pollutants (ESCAP, 1997). Therefore, determining the land-use and its distribution within the watershed is the most important initial step to be followed. The watershed is under the effect of typical Black Sea climate. The coastline receives high precipitation varying between 800-2500 mm, whereas the inner part range within 400-800 mm. Precipitation occurs all throughout the year with differences among seasons. The region is the one that receives the highest precipitation values in the country.

The diffuse sources of pollutants in the watershed have not yet been identified and estimated; however, environmental pollutants are rather investigated in a province-based approach in the country. It is mostly a mountainous area with significant agricultural activities in the valleys. The identification of such non-point sources of pollutants is so important and the data inventory stage is the fundamental part regarding the types of human-induced prevailing activities evolving such pollutants. Figure 2(a) indicates the overall land-use distribution of the watershed, whereas Figure 2(c) illustrates the land-use distribution of the watershed based on each of the sharing provinces.

It is important to note that the industry sector in the watershed is not as important as the watersheds around the Sea of Marmara, and in the coastal watersheds situated along the Aegean Sea and the Mediterranean Sea.

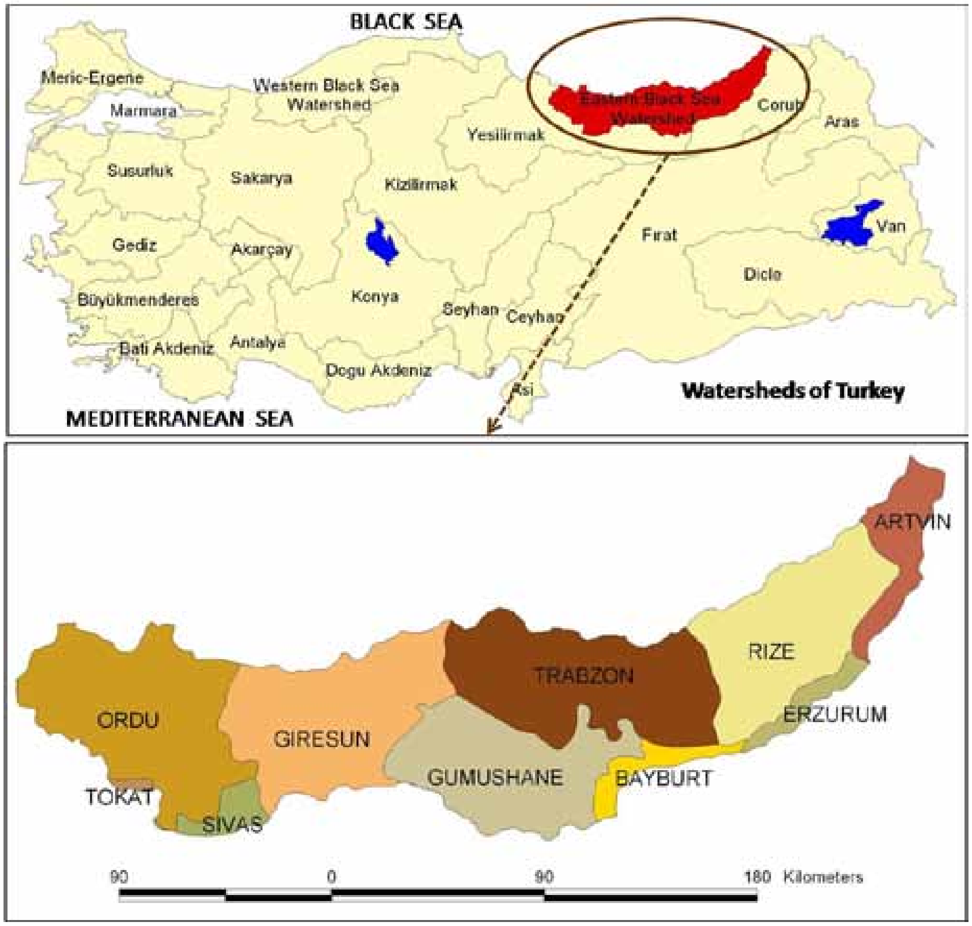
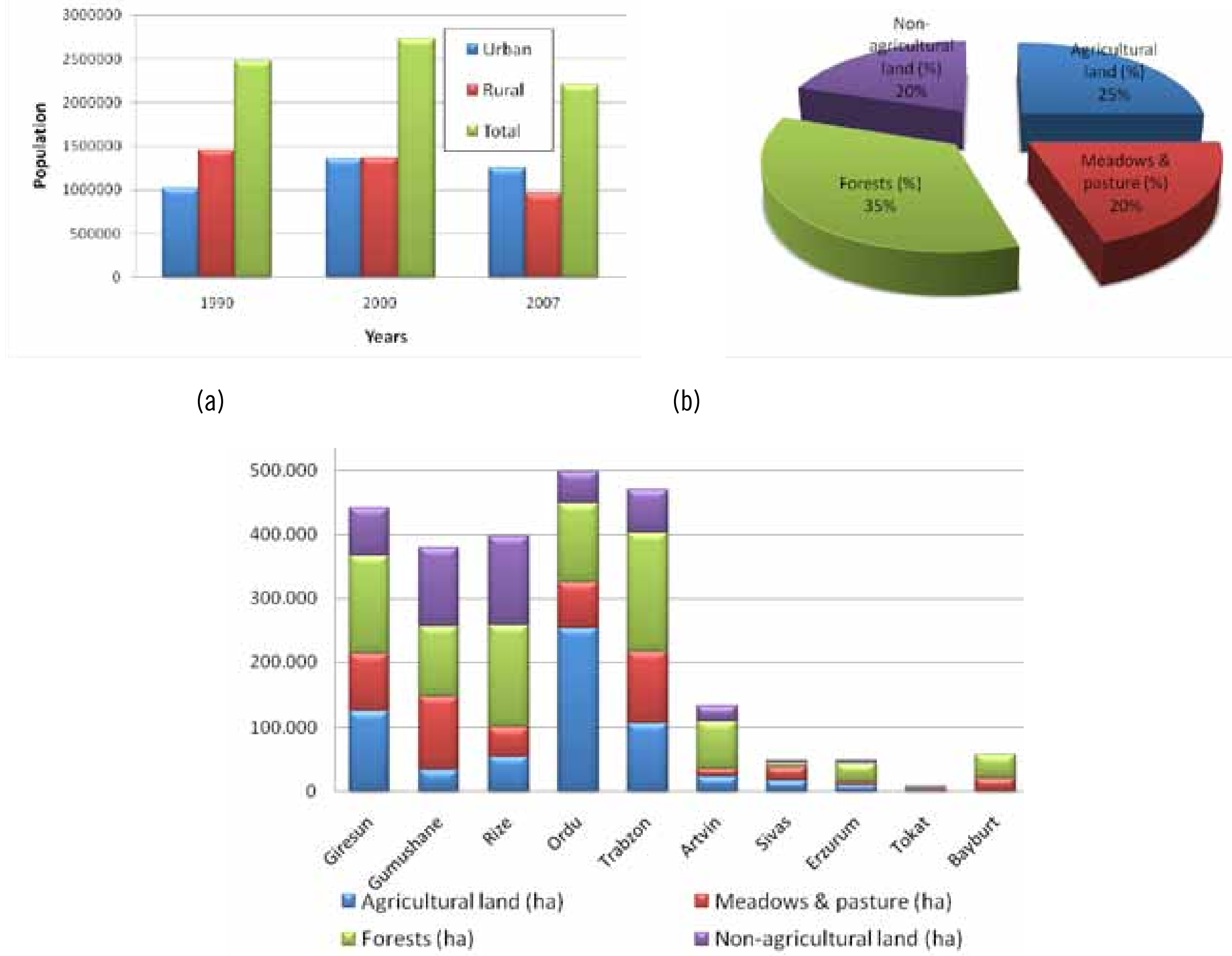


Figure 1. The geographical location of the watershed and the sharing provinces



(a) (b)

(c)

Figure 2. (a) Population trend and its distribution among urban and rural population of the watershed, (b) Land-use distribution of the watershed, (c) Land-use distribution of the watershed according to the sharing provinces

METHODOLOGY USED TO ESTIMATE DIFFUSE LOADS

It is difficult to calculate the diffuse loads of pollutants arising from watersheds as they are distributed in a disperse manner, thus they are estimated based on either unit loads stated in literature or through watershed modelling studies. In this study, the significant diffuse polluting sources arise from agricultural activities, livestock breeding, forests, meadows and pasture, urban runoff, rural runoff, atmospheric deposition including traffic emissions, dumpsite leachate, and septic tank effluents.

Diffuse loads from forests, meadows & pasture, urban and rural areas. The diffuse loads arising from these land-use activities are calculated by multiplying the related areal values with the unit loads cited in literature. In this selection, the similarity of the climatic and geological conditions with the watershed of concern is taken into account. Table 1 refers to the selected unit loads from literature.

Table 1. Unit loads used for various land-use activities (Dahl & Kurtar, 1993; OEJV, 1993)

Land-use activity	Nitrogen (kg/ha. year)	Phosphorous (kg/ha. year)
Forests	2.0	0.05
Meadows and pasture	5.0	0.10
Urban area	3.0	0.50
Rural area	9.5	0.90

Diffuse loads from agricultural areas. The agricultural return flows carry excess fertilizers applied on agricultural land. Thus, as an initial step during the calculation of the diffuse agricultural loads, the annual applied fertilizer amounts are obtained from the official agricultural authorities based on the districts of the provinces forming the watershed (ILEMOD, 2007). As the areal values of each participating district are also given, the active N and P applied per district are calculated and the unit fertilizer application values are calculated. Then, the total application loads are calculated for each of the districts. The crop uptake of nutrients varies within certain ranges; however, it would be ideal if all the nutrients applied are used by the crop. The crop uptakes highly depend on the climatic conditions, soil properties, type of crops produced, form of the fertilizer applied, and the method and frequency of application. In fact uptake rates range from 40-80% of nitrogen applied, and only 5-20% of phosphorous applied. As more fertilizers are applied, uptake becomes less efficient. That is, the percentage of applied fertilizer taken up by plants goes down as application amounts go up, thereby increasing potential nutrient loss through run-off, leaching and volatilization in the form of gaseous nitrogen. Losses from leaching and run-off combined are between 0.5–5% of the phosphorous applied and between 5–30% of the nitrogen applied (Oenema and Roest, 1998; Bottcher and Rhue, 2000). In this study, the crop uptake values are assumed as 50% and 20% for N and P, respectively. Besides, the losses from the soil to the receiving water are assumed as 15% N and 5% P applied. The rest 35% N and 75% P fractions are considered to be lost through transportation reactions such as ammonia volatilization, nitrification, denitrification, and P adsorption on soil. Table 2 summarizes the unit loads and corresponding losses of nutrients per each of the sharing provinces.

Diffuse loads from livestock breeding activities: The animal manure generated from the livestock breeding activities in the watershed is utilized as natural fertilizer in the agricultural activities. Therefore, it is important to know the number of animals and their corresponding manure quantity and quality. The number of livestock breeding animals for the year 2006 is obtained from Turkish Statistical Institute for year 2006 (TUIK, 2006a, b, c).

Table 2. The unit loads and corresponding losses of nutrients arising from the application of commercial fertilizers

Provinces	Unit Loads (kg/ha/year)		Loss of nutrients through overland flow and infiltration (enter the water environment) (15% N and 5% P)	
	N	P	N (kg/year)	P (kg/year)
Giresun	422	147	6.793.480	789.005
Gumushane	19	6.9	64.332	7.689
Rize	952	62.2	7.777.650	169.500
Ordu	62	9.20	2.371.991	116.704
Trabzon	73	7.3	1.154.400	38.350
Artvin	9.82	2.01	215.303	14.722
Erzurum	37.29	16.38	3.142	460
Sivas	37	15.04	16.591	2.239
Tokat	27	33	5.383	2.197
Bayburt	2782	178	1.240.723	26.402

Animal waste is the only output from the breeding activity as a diffuse polluting source. It is collected and rested for a certain period of time prior to its use as fertilizer on agricultural land. The estimation of the respective pollution loads will be performed on the basis of the emission factors derived from literature. The average weight of cow (beef cattle) is stated in MoE (2006) as 636 kg, cow (dairy cattle) 431 kg, sheep as 45 kg, and for poultry. The fate and behaviour of both the natural and commercial fertilizers are almost the same, thus part of the nutrients are passed to the water environment by means of run-off and leaching. Therefore, it is assumed that approximately 5-30% of N, and 0.5- 5%P is lost. If the same percent losses of 15% N and 5% P are assumed as was the case in commercial fertilizers, the unit losses of animal manure through water are calculated for typical manure nutrient ratio.

In the calculations, the weight of various animal categories as cows and cattle is considered as 500 kg, sheep as 45 kg, and poultry as 2 kg, the unit nutrient loads arising from livestock breeding can be calculated accordingly. The nitrogen and phosphorus unit loads emitted by manure highly varies according to the animal category, species of the animal, nutritional habits, weight, and manure characteristics. Therefore, it is quite difficult to fix a deterministic unit load.

Error! Reference source not found.shows the values used in two references cited in literature with the aim of giving an idea on the order of magnitudes of the unit loads, whereas Table 4 demonstrates the selected values and the corresponding losses of N and P losses to the receiving water environment. It can be stated that diffuse nutrient loads vary within certain ranges necessitating uncertainty analysis. This statement is valid for all kind of diffuse nutrient loads arising from the watershed.

Table 3. Production rates for animal wastes

Animal category	Total Nitrogen (kg/ton of animal weight/day)		Total Phosphorous (kg/ton of animal weight/day)	
	Agricultural Statistics, 2001	Andreadakis et al. 2007	Agricultural Statistics, 2001	[Andreadakis et al.,2007
Cows and cattle	0.33	0.45	0.11	0.05
Sheep/goats	0.44	0.41	0.06	0.07
Poultry	0.67	0.33	0.24	0.22

Table 4. Selected manure nutrient values and losses to the water environment

Animal category	Nitrogen (kg/ton of animal weight/day)	Phosphorous (kg/ton of animal weight/day)	N Loss (kg/animal/year)	P Loss (kg/animal/year)
Cows and cattle	0.30	0.10	8.2	0.91
Sheep and goats	0.42	0.06	1	0.05
Poultry	0.52	0.22	0.06	0.008

Diffuse loads from dumpsite leachate, septic tank effluents and atmospheric deposition including traffic emissions: In the watershed, there are no sanitary landfills and thus, leachate arising from the dumpsites adds to the diffuse pollution budget. The capita based solid waste generation for the watershed is calculated as 0.7 kg/capita/day. It is assumed that solid waste generation will differ during winter and summer periods as ash arising from heating practices usually increase waste generation during winter and the winter values are taken as 0.9 kg whereas the summer values are considered to be 0.5 kg in such areas (Ozalp, 2009). The corresponding leachate quantity and quality values are calculated based on some assumptions. It is considered that every province within the watershed boundaries own one dumpsite and that they are under operation since 1990. Another important assumption is that there will be no solid waste arising from rural residents as mostly the kitchen wastes are either buried and/or utilized as fertilizer and other solid wastes are used during heating. Therefore, the solid wastes for the urban residential sites are calculated. During the calculation of leachate quality and quantity the net precipitation values are also considered. Table 5 summarizes the estimated values related to solid waste generation and leachate properties. Details of the calculations are referred in (Ozalp, 2009).

Table 5. Estimated values related to solid waste generation and leachate properties

Unsanitary Dumpsites (Provinces)	Cumulative amount of solid wastes		Leachate	Polluting Loads of Leachate (kg/year)	
	ton	m^3	m^3/day	TN	TP
Giresun	1.572.938	1.693.933	628	91.696	2.292
Gumushane	269.145	289.849	48	353.430	8.836
Rize	605.994	652.608	519	75.788	1.895
Ordu	1.572.938	1.693.933	628	91.696	2.292
Trabzon	1.497.430	1.612.617	598	69.703	1.743
Total	4.021.015	4.330.324	2.421	682.314	17.058
Unit load (kg/ha-year)	-	-	-	8.832	221

Part of the urban areas and the villages are not connected to sewer system. Therefore, the settlements in the unsewered areas use septic tanks whose effluent is considered as part of diffuse pollutants. The rural population of unsewered areas is multiplied by the water demand per capita (50 L/capita/day) to reach to the quantity of the water consumed. 80% of water consumed is assumed to be wastewater discharged from the settlements. The septic tank effluent nutrient loads are then calculated using the typical concentrations depicted in Tchobanoglous and Burton (1991). TKN concentration is 60 mg/L whereas total P concentration is taken as 10 mg/L and so septic tank effluent loads are calculated. TKN is assumed to be equal to total N for the septic tank effluents. Table 6 indicates the raw domestic wastewater unit loads for present and future and septic tank effluent concentrations.

Regarding the atmospheric deposition in the watershed, the unit value of 10.3 kg/ha/year calculated for a similar watershed in the western Black Sea Region of the country with an annual average precipitation value of 836 mm/m^2 is taken as a representative value, and based on a direct proportion, the unit loads of atmospheric deposition for Aras watershed are calculated for each of the sharing provinces (Ozturk et al., 2007). It is important to note that the annual average precipitation values for each of the provinces differ in the watershed. The unit N loads are therefore determined for each province and the corresponding annual diffuse loads are calculation. It is assumed that 5% of the overall surface area is affected by atmospheric deposition. The related calculations are given in Table 7.

Table 6. The raw domestic wastewater unit loads for present and future together with septic tank effluent concentrations

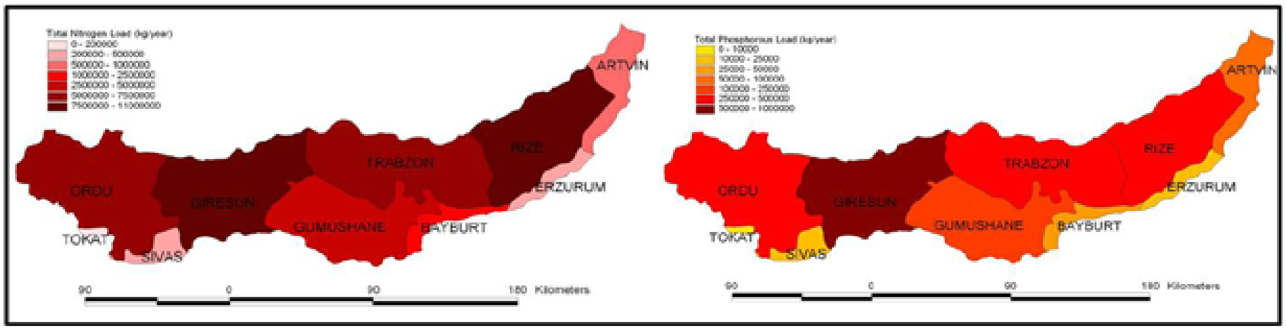
	Unit load for urban population (g/cap.day)	Unit load for rural population (g/cap.day)	Unit load for urban population (g/cap.day) for year 2024	Unit load for rural population (g/cap.day) for year 2024	Unit load for urban population (g/cap.day) for year 2039	Unit load for rural population (g/cap.day) for year 2039	Septic tank effluent concentration (mg/l)
TN	11	8	12	10	13	11	60
TP	1.8	1.3	2	1.6	2.2	1.8	10

Table 7. Estimated unit N loads and corresponding total N load arising from atmospheric deposition

Provinces	Unit Load (kg/ha.year)	Polluting Load (kg/year)
Giresun	16	352.655
Gumushane	6	107.718
Rize	28	544.755
Ordu	13	319.124
Trabzon	10	240.511
Artvin	16	105.665
Erzurum	16	38.746
Sivas	16	38.862
Tokat	16	6.186
Bayburt	16	46.047
Total		1.800.269

Distribution of Diffuse Pollution Loads

When the entire watershed is considered, the dominating diffuse nitrogen loads are estimated to be due to the application of fertilizers by 54% followed by livestock breeding activities where the manure is used as natural fertilizers by 11%. Almost 7% of the diffuse N loads come from meadows and pasture, and 5% from forests. According to the distribution of the phosphorous load, it is estimated that 48% of the loads arise from agricultural activities (commercial fertilizers) and 18% from livestock breeding. Almost 14% of the diffuse P loads come from septic tank effluents; however, 13% of the loads are due to rural run-off. On the other hand, the illustrations given in Figures 3(a) and 3(b) respectively, for N and P loads are for alerting the decision makers and other local authorities. These figures point out the distribution of the total diffuse loads arising from each of the sharing provinces. It can easily be observed that Giresun and Rize provinces dominate over other provinces regarding diffuse N loads whereas Giresun province lead in the diffuse P loads. As such, similar presentations put forth the distribution of total diffuse loads in the participating provinces. It is important to note that the protective actions are currently taken by the administrative units still in the country as watershed management action plans especially for this specific watershed has not been finalized yet.



(a) (b)

Figure 3. Distribution of the (a) diffuse N loads, (b) diffuse P loads within the sharing provinces of the watershed

Control of Diffuse Pollutants in Future

Within the context of this study, the projected diffuse load calculations for future (2028 and 2039) are calculated by considering and proposing a series of protective actions against further deterioration of the watershed.

Leachate appearing as one of the minor diffuse polluting sources in the existing situation compared to other diffuse pollutants is recommended to be further diminished in both quality and quantity as the sanitary landfills in case be designed and constructed in future. The existing dumpsites will then be rehabilitated and sequentially closed in the near future. The leachate generated from the sanitary landfills will act as point sources as they will be collected and treated. The leachate in future will only arise from the already existing solid waste dumpsites as a diffuse source in a decreasing trend (Ozalp, 2009).

Some of the rural areas will still be using septic tanks rather than installing centralized/or decentralized wastewater treatment plants due to the difficulties faced in the geographical situation of the watershed in future; therefore, a certain amount of rural discharges will be accepted as diffuse sources, but as will be observed from the load calculations, their load will be highly reduced due to population decrease in the rural areas.

As mentioned previously, to cope with the diffuse sources of pollutants is a complex task as the pollutants reach to the water environment in a disperse manner. Factors like the soil characteristics, climatic conditions and the intrinsic properties of the fertilizers, manure and forest components (decay material, top soil, etc.) together with the behavior and fate of the nutrients transported on soil highly affect the transportation mechanisms on soil. Rather, in-watershed controls are considered as effective actions to reduce the nutrient loads that might reach to the water environment either through run-off or penetration in soil. It is not possible to completely get rid of diffuse pollutants, however, by taking protective measurements the loads may easily be reduced up to a certain extend. Such actions include application of best management agricultural practices like irrigation techniques, crop selection, time, frequency and amount of fertilizer applications, passing to organic agriculture where no pesticides and commercial fertilizers are used, appropriate reuse of animal waste in agriculture, and controlling non-agricultural areas.

Presently, in the calculations, it is assumed that there will be a 30% decrease in the nutrient loads arising from agricultural activities and from livestock breeding in year 2028, and 40% similar decrease in year 2039 based on international experience (Stolze et al., 2000; FAO, 2002). The most important fact in the reduction of nutrient loads will be through organic agriculture and livestock breeding applications. More detailed surveys need to be conducted at the entire watershed in future to search for the most realistic measures to be taken so as to reduce the diffuse loads. As such, the load estimations for future are presented in Figures 4(a) and (b) for N and P loads, respectively. Apart from the illustrations, the decrease in the N and P loads are also numerically given in Table 8.

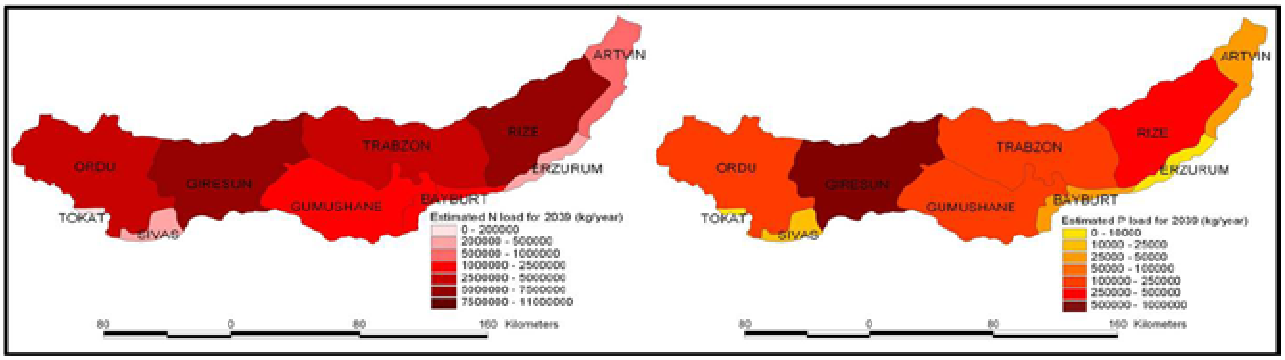


Figure 4. Distribution of the (a) diffuse N loads, (b) diffuse P loads in year 2039 within the sharing provinces of the watershed

Table 8. Diffuse P load distribution for years 2028 and 2039

Years	Total Diffuse Loads (ton/year)			
	N	Reduction (%)	P	Reduction (%)
2007	36.439		2.456	
2028	27.274	25	1.729	30
2039	24.735	32	1.549	37

CONCLUDING REMARKS

This study displays the determination and estimation of diffuse polluting loads in terms of two important nutrients, N and P in a watershed characterized by its low population density and negligible industrial facilities. The methodology of estimating such pollutants are highly dependent on the areal values of different land-use activities, population, and on unit loads for various activities. This approach emphasizes on rough approximation of the diffuse pollutant loads; however more detailed studies can be achieved through watershed modelling applications. In the case of utilizing models, more input data need to be produced which is a tiresome task to handle whenever limited data is available. The benefits of applying such a methodology used in this study is able to display the rough estimated loads per administrative unit composing the watershed which can be demonstrated to the decision makers and other related stakeholders of the watershed including public. Public and state awareness on the subject of concern is an important issue in watersheds regarding diffuse loads. Point pollutants are comparatively easier to cope with as their source origin is observable. As mentioned in this study, the provincial based diffuse pollution can be presented as well as the distribution of loads in the entire watershed. Moreover, some urgent and long term protective measures are referred in the article with the aim of enlightening the decision makers on the actions to be considered in future. This study will act as a road map for similar future studies. The subject of concern is part of Integrated Watershed Management activities in the country that is at the accession stage to join EU.

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Control Approach to Non-biodegradable Organic Matter in Roadway Runoff

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Abstract

Roadway dust includes non-biodegradable organic pollutants such as polycyclic aromatic hydrocarbons (PAHs). The objective of this study was to estimate the non-biodegradable organic matter in roadway runoff using a biodegradability test, and to reveal the effectiveness of its removal using soil infiltration. Total organic carbon (TOC) concentration of roadway runoff was approximately 20 mg/L and 74% was non-biodegradable organic matter. Polycyclic aromatic hydrocarbons were not detected (< 0.050 μg/L) as they usually decompose in an environment with appropriate bioactivity. On the other hand, the non-biodegradable ratio of particulate organic matter (POC) and dissolved organic matter (DOC) were calculated to be 96% and 40%, respectively. Most particulate portions in roadway runoff were organic matter remaining after one hundred days biodegradability test. However, the soil infiltration was able to reduce POC and DOC in roadway runoff to 93% and 55%, respectively. It was nearly one-tenth of the initial TOC concentration. Moreover DOC concentration of the soil infiltration was similar to that of advanced sewage treatment effluent.

Keywords

Biodegradability test; non-biodegradable organic matter; Polycyclic aromatic hydrocarbons (PAHs); roadway runoff; soil infiltration

INTRODUCTION

Despite countermeasures, such as the control of effluents from industrial and domestic sites, the water quality of Lake Biwa has not improved. Its chemical oxygen demand (COD) has been increasing for a few decades and this problem is also seen in other lakes in Japan. This problem makes it difficult to reach environmental standards regarding water quality (MIC, 2004). The COD is an index of the amount of organic matter in water. The organic matter includes both a biodegradable type and a non-biodegradable type. One of the reasons for the increase in COD might be that non-biodegradable organic matter cannot be decomposed by microorganisms. Research on non-biodegradable organic matter is ongoing regarding the source of issues, mechanism and classification (Imai *et al.*, 2007). The focus of the studies is on sample water from the lake, as well as industrial and domestic waste water. The Lake Biwa watershed load has increased as a result of an increase in population and traffic due to urban development and the impervious land surface, the real problem in this watershed is the nonpoint source such as stormwater runoff from urban roadways (Shiga prefecture, 2004). The proportion of non-biodegradable organic matter in roadway runoff is unclear. With an increase in the non-biodegradable organic matter, the concern is that this will have a significant impact on the lake ecosystem. Moreover there are not enough measures taken to prevent urban nonpoint sources in this watershed.

Meanwhile, one of the stormwater management measures for the urban area is groundwater infiltration of rainfall runoff (Furumai, 2006; Okui, 2010). In the paved roadway, rainfall cannot permeate into the soil. This fact indicates that the opportunity of contact with the soil is lost thus the efficacy of the natural self purification process in the watershed is adversely affected. The pollutant loads are purified by the physical-chemical-biological processes in the soil (Tomioka *et al.*, 1998; Wakatsuki *et al.*, 1993). Therefore, infiltration using vegetated buffer and porous pavement has proven to be effective in reducing pollutant load from roadway runoff (USEPA, 2005; Novotny, 2003). This water quality improvement method is able to effectively reduce pollutant loads, especially for total suspended solids, heavy metals and phosphorus (Wada *et al.* 2001, Shinohara *et al.*, 2006; Hatt *et al.*, 2009). In our previous study (Wada *et al.* 2006), we confirmed that the purification system for roadway runoff using soil infiltration is effective to reduce organic matter. The method was described according to the reduction of non-biodegradable organic matter calculated by molecule weight area of Gel Permeation Chromatography – Total Carbon (GPC-TC) analysis, but it was not predicted quantitatively. Although the soil infiltration is proposed as the measures for organic matter in roadway runoff, it was not revealed how much non-biodegradable organic matter can be reduced.

The objective of this study is to estimate the non-biodegradable organic matter in roadway runoff and the effectiveness of its removal using soil infiltration. In this paper, we focused on the non-biodegradable organic matter as chemical speciation of the first flush runoff from urban roadways. The chemical speciation is necessary to assess the treatment effect of soil infiltration, and these data were compared with effluent water from advanced sewage treatment.

METHODS AND MATERIALS

Study site description and sampling

Field surveys of stormwater runoff were set up in two urban roadway stations in the Lake Biwa watershed. The runoff collection was conducted during one rainfall event at St.1 in December 2007, and during one event at St.2 in October 2009. These roadways experienced heavy traffic, with an average of more than 20,000 vehicles every weekday (Shiga prefecture, 2005). The traffic from each survey station was about the average traffic on urban roadways in the watershed. Samples were collected from the first flush runoff of stormwater corresponding to the discharge amount of 2 to 7 mm. Table 1 shows the specifications of the survey stations.

Table 1. Specification of survey station

St.	Catchment area (m^2)		ADT/24h* (vehicle)	Dry weather period (day)	Rainfall Amount (mm)	Rainfall intensity Max (mm/hr)
	Roadway area	Sidewalk area				
1	72	–	20,763	10.5	8	3
2	40	35	25,513	6.4	11	10

* Average Daily Traffic vehicles on Weekdays, Shiga prefecture (2005). Road Traffic Census.

Laboratory experiments

A biodegradability test was conducted on each sample collected at St.1 and St.2 (Run 1 and 2, respectively). In addition, a biodegradability test of the St.1 sample was conducted after permeating the soil (Run 1-2). To assess the soil infiltration treatment, these samples were compared with effluent water from advanced sewage treatment which is one of the point source measurements used in the study. The experimental scheme is shown in Figure 1.

Biodegradability test

With the increasing amount of biorefractory organic matter in Lake Biwa it is important to determine the extremely non-biodegradable amount of material. In this study "biodegradable" was defined as degradable by microorganisms under the best environment for their activity. The “non-biodegradable” material was the remaining material after one hundred days incubation.

The actual conditions for the biodegradability test were as follows: nutrients, minerals and pH buffers were added, and then the sample was kept at 20 with aeration under dark conditions for one hundred days (Fukushima *et al.*, 1995, 1996). As for the physical condition, the container size of 10 L was chosen so that adsorption of the sample through the wall surface was prevented. The activated carbon tank removed any contamination from the oxygen and nitrogen cylinders. The water scrubber protected a loss of the samples by evaporation. The experimental condition and the schematic diagram of the biodegradability test are shown in Table 2 and Figure 2.

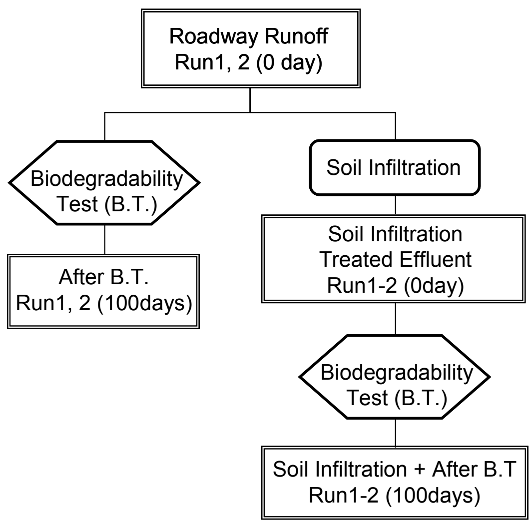

Figure 1. Experimental scheme

Table 2. Experimental condition of biodegradability test

Items	Conditions
Incubation period	One hundred days
Water temperature	20
Light	Continuous dark
Aeration	21 % oxygen and 79% nitrogen gas at a flow rate of 10 mL/min
Seed bacteria	Bacteria preparation for BOD-test (BI-CHEM BOD-Seed, Novozymes Biologicals, Japan)
Additional reagent	K_2HPO_4 21.75 mg/L, KH_2PO_4 8.5 mg/L, Na_2HPO_4 $12H_2O$ 44.6 mg/L, NH_4Cl 1.7 mg/L, $MgSO_4$ $7H_2O$ 22.5 mg/L, $CaCl_2$ 27.5 mg/L, Fe(III)Cl_2 $6H_2O$ 0.25 mg/L
Sample volume of Test	10 L (Unfiltered)

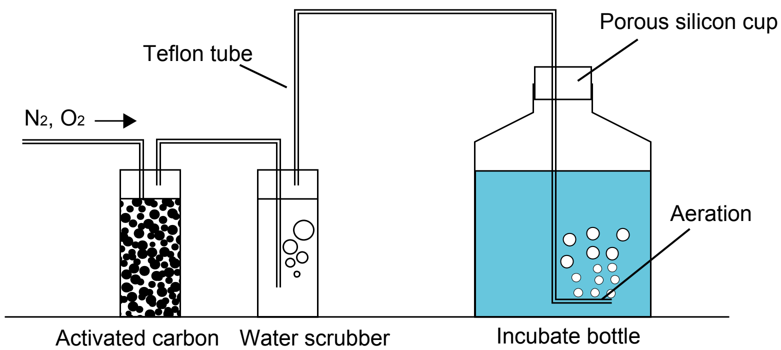

Figure 2. Schematic diagram of biodegradability test.

Soil infiltration

Red soil for infiltration treatment was used during the eight years of our work on the water purification experiment (Wada *et al*., 2001). That is one of the general soils in Japan, and was produced by the Kanto loam layer of volcanic ash soil. This red soil had the aggregate size distribution of 50% diameter (D_{50}) 4.04 mm by drying. As the soil has good permeability, it is used for gardening.

The soil physical property was porosity 45.9%, pH 5.5, ignition loss (IL) 13.7 %, and saturated unit weight (ρ_s) 0.75 g/cm^3. The soil was packed into a column and washed fine-grain fraction off with distilled water. In regard to the soil treatment, the runoff sample (Run 1) was passed through a soil layer of a thickness of 100 cm at the flow rate of 27 mL/min (*L.V.* 1.3×10^{-2} cm/s). This infiltration speed was equal to the coefficient of permeability of sand or the silt and to the speed that water from rainfall goes into the ground. And then, the effluent was supplied for a biodegradability test in the same manner and conditions (Run 1-2). These samples were compared with the effluent water from the advanced sewage treatment process to assess the treatment effect of a non-point source.

The experimental condition and the schematic overview of soil infiltration are shown in Table 3 and Figure 3, respectively.

Table 3. Experimental outline for soil infiltration.

Items	Condition
Column Type	Glass column
Size	10 cm i.d. x 100 cm
Soil	Red soil 50% diameter D_{50} : 4.04 mm
Infiltration Conditions	Flow : downward and saturated Volume : 39.25 L/day Linear velocity : 1.3 x 10^{-2} cm/s

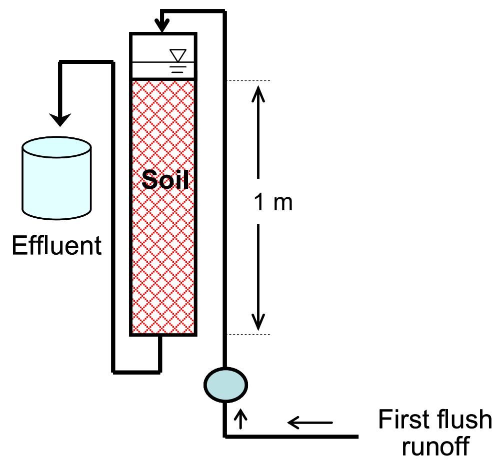

Figure 3. Schematic overview of the column equipment of soil infiltration.

Chemical analysis

Water quality as the index of organic matter instead of COD was total organic carbon (TOC), which was measured as each fraction of the particulate and dissolved portions separated with a 0.45 μm membrane filter. Analytical method of dissolved organic matter (DOC) was JIS K0102-22.1, and particulate organic matter (POC) was measured with a CHN CORDER (Yanagimoto MT-5). Total organic carbon was calculated from DOC and POC.

In addition, the runoff sample of Run 2 measured the Polycyclic Aromatic Hydrocarbons (PAHs) in by gas chromatograph-mass spectroscopy (MOE, 2004). These are well known as pollutant organic matter in roadway runoff. Table 4 shows the chemical analyses of each sample.

Table 4. Analytical substances

Run	Item	Treatment method	Previous biodegradability test (0 day)	After biodegradability test (100 days)
1	Roadway runoff	–	POC, DOC	POC, DOC
2	Roadway runoff	–	POC, DOC, PAHs*	POC, DOC, PAHs*
1-2	Roadway runoff	Soil infiltration	POC, DOC	POC, DOC
Control	Sewerage system effluent	Advanced process**	POC, DOC	POC, DOC

* PAHs: Naphthalene, Acenaphthylene, Acenaphthene, Fluorene, Phenanthrene, Anthracene, Fluoranthene, Pyrene, Benz[a]anthracene, Chrysene, Benzo[b]fluoranthene, Benzo[k]fluoranthene, Benzo[a]pyrene, Indeno[1,2,3-cd]pyrene, Dibenz[a,h]anthracene, Benzo[g,h,i]perylene, Benzo[j]fluoranthene, Benzo[e]pyrene, Perylene

** Nitrified liquor recycles single-sludge nitrification/denitrification process with coagulant addition + sand filtration method

RESULTS AND DISCUSSION

Non-biodegradable organic matter in roadway runoff

The results of the organic matter in the samples of both before and after the biodegradability test are shown in Figure 4.

The TOC of Run 1 and Run 2 before the biodegradability test were calculated to be 21.9 mg/L and 19.0 mg/L, respectively. As the data collected during twelve rainfall events in 2001 to 2005 had an average 28 ± 17 mg/L (Wada & Fujii, 2007), the results were evaluated using a similar concentration. The POC of Run 1 and Run 2 were 13.7 and 10.9 mg/L; and DOC of Run 1 and Run 2 were 8.2 and 8.1 mg/L. Meanwhile, TOC of Run 1 and Run 2 after one hundred days were calculated to be 15.8 mg/L and 14.3 mg/L (average 15.1 mg/L). The POC of Run 1 and Run 2 were 12.9 and 10.6 mg/L (average 11.8 mg/L); and DOC of Run 1 and Run 2 were 2.9 and 3.6 mg/L (average 3.3 mg/L).

Pollutant sources of organic matter in roadway runoff were reported to be atmospheric deposition, pollutants emitted from motor, litter deposits and dead vegetation (Sartor & Boyd, 1972). Around 60% of DOC was reduced by microorganisms and 40% of that was non-biodegradable. On the other hand, POC was found to be extremely non-biodegradable and recalcitrant because of more than 90% (average 96%) remaining after one hundred days. As a lot of rubber litter from tires was included in roadway runoff, it was suggested that the constituents of petrochemical products was equivalent to POC concentration. Compared initial values with values after the one hundred days test, DOC decreased to 22% from 40% of TOC and POC increased to 78% from 60% of TOC (Figure 5). As a whole, the non-biodegradable organic matter accounted for 74% of initial TOC.

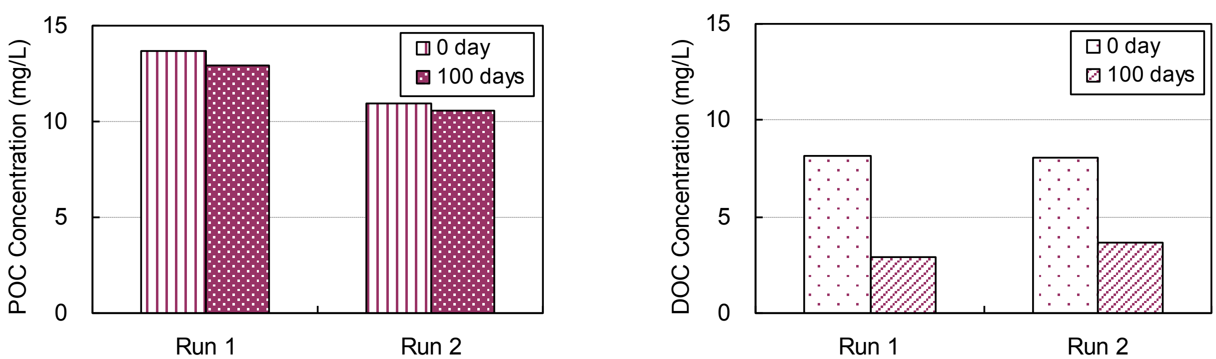

Figure 4. Organic carbon concentrations in roadway runoff before and after the biodegradability test

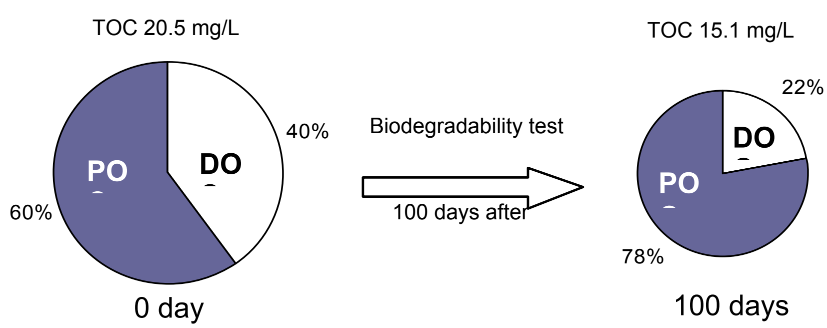

Figure 5. Speciation of total organic matter in roadway runoff

PAHs in roadway runoff

The PAHs in the roadway runoff at St. 2 are shown in Figure 6. The PAHs of Run 2 at the start of the biodegradability test were quantitatively-detected Phenanthrene 0.090 μg/L, Fluoranthene 0.260 μg/L, Pyrene 0.300 μg/L, Chrysene 0.230 μg/L and Indeno[1,2,3-cd]pyrene 0.060 μg/L. The detected substances in Run 2 were similar in that Pengchai's report which indicated a connection between PAHs and tires, street dust and asphalt (Pengchai P. *et al.*, 2002). Polycyclic aromatic hydrocarbons are known to be genotoxic, and carcinogenic pollutants, and are in urban street dust from diesel and gasoline vehicle exhaust (Takada *et al.*, 1990; Ono *et al.*, 1997). Those are adsorbed on the surface of soil particles, fine particles of tire or asphalt. As three to five membered rings PAHs are acutely toxic and releasing these substances into the environment is not recommended (ICSC, 1981). However, the detected PAHs at the start of the test were not detected (< 0.050 μg/L) after one hundred days. This result means that PAHs were included in roadway runoff, but it was found that PAHs decomposed by maintaining appropriate bioactivity in the environment.

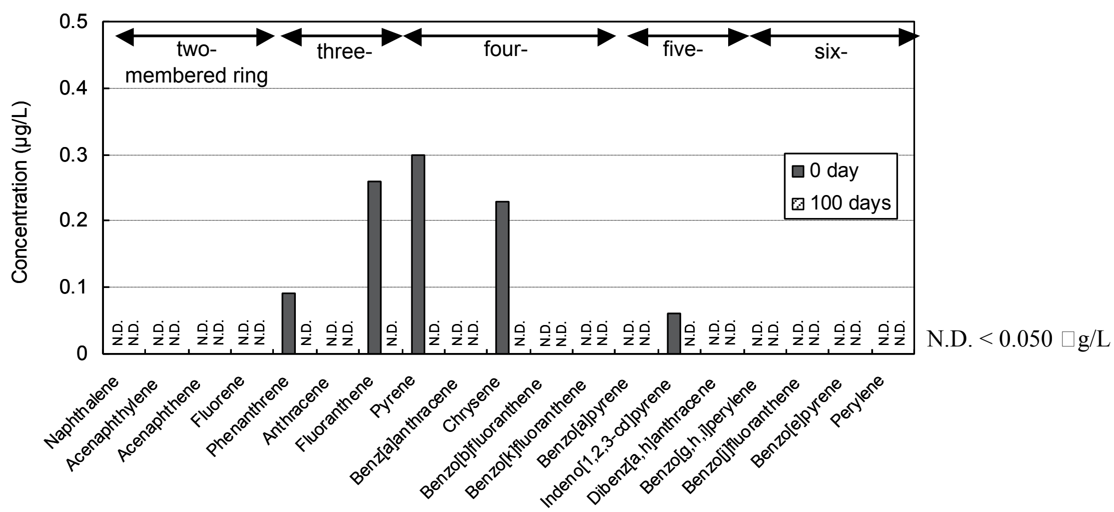

Figure 6. PAHs in roadway runoff of Run 2.
The detected PAHs at the start of the test were not detected (< 0.050 μg/L) after one hundred days

Soil infiltration treatment

To figure out removal ability of non-biodegradable organic matter by soil infiltration, the roadway runoff of Run 1 was poured into a soil column and the biodegradability test was conducted on the soil treated effluent for one hundred days.

By soil infiltration of non-biodegradable organic matter in roadway runoff, the removal efficiency of TOC, POC and DOC were 86%, 93% and 55%, respectively, whereas, the removal ratio of them in the column influent and effluent of the raw water (before the test) were 77%, 89% and 57%, respectively (Table 5).

The removal efficiency of the soil infiltration was evaluated by a comparison with the sewerage treatment water. The sewerage treatment water was not included in POC, because the particulate substances were removed by the treatment process of sedimentation and filtration. By the biological treatment of activated sludge, DOC amounts in that water decreased very little during one hundred days. As shown in Figure 7, TOC and DOC results in Run 1 treated by soil infiltration were lower than the concentration in sewage treatment water (Advanced sewage treatment effluent). Moreover the very high removal efficiency of POC was presented that soil infiltration was effective for non-biodegradable countermeasure. DOC was predicted to be removed by adsorption on soil particles and decomposition by soil microorganisms.

Table 5. Result of non-biodegradable organic matter by soil infiltration treatment with 100cm column. (Unit: mg/L)

	Run 1		Run 1-2		Removal efficiency of NBOM* (B-D)/B	Total removal efficiency of organic carbons (A-C)/A
	0 day (A)	100 days (B)	0 day (C)	100 day (D)		
TOC	21.9	15.8	5.0	2.2	86 %	77 %
POC	13.7	12.9	1.5	0.9	93 %	89 %
DOC	8.2	2.9	3.5	1.3	55 %	57 %

* non-biodegradable organic matter

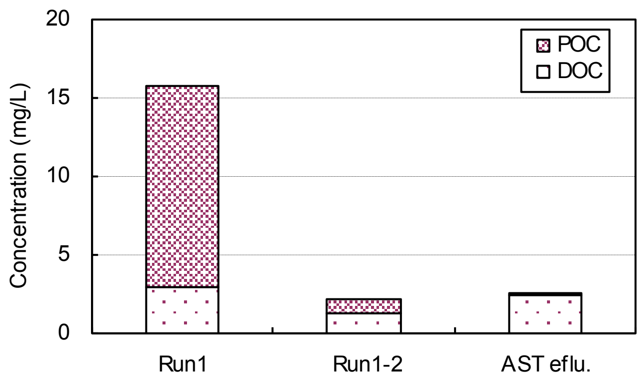

Figure 7. Non-biodegradable organic matter in roadway runoff before and after soil infiltration treatment and effluent from an advanced sewage treatment process

CONCLUSIONS

This study was conducted to estimate the non-biodegradable organic matter in roadway runoff and its removal effectiveness using soil infiltration. The main results obtained were as follows:

- TOC concentration of roadway runoff was approximately 20 mg/L and its 74% was non-biodegradable organic matter. By portion, the non-biodegradable ratio of POC and DOC were calculated to be 96% and 40%, respectively. Most particulate portions in roadway runoff were the organic matter remaining after one hundred days. The non-biodegradable organic matter in roadway runoff is deposited in lake and marine areas, if the rainfall flows out through urban roadways. This fact suggests that the microorganisms, such as zoobenthos and submerged plants, which inhabit the bottom layers are seriously affected.
- However, soil infiltration was able to reduce POC and DOC in roadway runoff to 93% and 55%, respectively. It was nearly one-tenth of initial TOC concentration. Moreover DOC concentration of soil infiltration was similar to advanced sewage treatment effluent. In addition, it was demonstrated that PAHs adsorbed to a soil particulate were decomposed by maintaining appropriate bioactivity in the environment.
- This work found the soil infiltration processing has not only a high removal efficiency on water pollution loads of non-biodegradable organic matter in the roadway runoff, but also accumulation prevention for ecosystems in a water body.

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System design and treatment efficiency of a surface flow constructed wetland receiving runoff impacted stream water

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Abstract

This study reported the efficiency of a free water surface flow constructed wetland (CW) system that receives runoff impacted stream water from a forested and agricultural watershed. Investigations were conducted to examine the potential effect of hydraulic fluctuation on the CW as a result of storm events and the changes in water quality along the flow path of the CW. Based on the results, the incoming pollutant concentrations were increased during storm events and greater at the nearly end of the storm than at the initial time of storm. A similar trend was observed to the concentrations exiting the CW due to the wetland being a relatively small percentage of the watershed (<0.1%) that allowed delays in runoff time during storm events. The concentrations of most pollutants were significantly reduced (p<0.05) except for nitrate (p=0.5). Overall, this study suggests that the design of the system could feasibly function for the retention of most pollutants during storm events since the actual water quality of the outflow was significantly better by 21 to 71% than the inflow and the levels of pollutants were reduced to appreciable levels.

Keywords

Agricultural; design; surface flow constructed wetland; nonpoint source; stream water; water quality

INTRODUCTION

Surface runoff driven by intermittent storm events instigates nonpoint source (NPS) pollution. Recent research has shown that constructed wetlands (CWs) can remove NPS pollutants such as organic content, suspended solids, and excess nutrients including agricultural discharges, thereby diminishing the euthrophication of the adjacent aquatic system and contamination of groundwater used for potable supply (Mitsch, 1995; Comin et al., 1997; Kovacic et al., 2000; Koukia *et al.*, 2009). This could be achieved through various processes including filtration, sedimentation, biological and microbiological adsorption and assimilation (Hammer, 1992; Vymazal *et al.*, 1998). Free water surface (FWS) flow CWs which are shallow and with a combination of emergent, floating and submerged aquatic plants are typically selected for treating agricultural stream water and runoff impacted surface waters in Korea because of their ability to deal with pulse flows and changing water levels. The manner in which the CW design will function during intermittent storm events should be considered because a cycle of high and low flows might affect the pollutant retention of the CW. A wide range of removal efficiencies of CWs receiving agricultural runoff during the high flow periods associated with storm events were reported in some studies. For instance, a small CW in an Australian rural catchment retained only 10 to 20% total nitrogen (TN) and phosphorus (TP) loads (Raisen *et al.*, 1995). The two experimental wetlands of the Olentangy River Wetland Research Park in Columbus, OH flooded with river water attained 80 to 96% nitrate retention (Spieles and Mitsch, 2000). The CW in Lake Dianchi, China received an average inflow TP concentration of 0.87 mg/L and the corresponding removal efficiency is 59% (Lua *et al.*, 2009). Based on the findings of Ham *et al.* (2010), who modelled the effects of CW on NPS pollution, the four sets of 0.88 ha experimental wetland systems attained approximately 50% TN and TP removals. In addition, the study suggested that 0.1 to 1.0 % of the watershed should be allocated to wetlands and a range of 5 to 15 cm/day of hydraulic loading rate to provide adequate nutrient retention and water quality values for the landscape. Indeed, the extent of treatment in CW systems depends upon the wetland design, hydraulic loading, inflow concentration, retention time, water chemistry, mass loading rates, microbial community, etc. (Hammer, 1992; DeBusk, 1999; Carleton *et al*., 2001; Akratos *et al*., 2006; Koukia *et al*., 2009; Kotti *et al*., 2010).

This study reported the efficiency of a FWS CW system receiving runoff impacted stream water from a forested and agricultural watershed. Investigations were conducted to examine the potential effect of frequent hydraulic fluctuation on the CW as a result of storm events by comparing the flow-weighted inflow concentration with the outflow concentration measured during a storm event. In addition, the design of the CW was assessed by examining the water quality changes along the flow path of the CW during the course of a storm event. The collected data and findings from the first operation year of the CW during the storm season were useful to identify trends that could aid in future CW design efforts. Furthermore, the results could provide valuable information during the stabilization stage of the CW and basis of comparison in the succeeding stages of operation.

MATERIALS AND METHODS

Site location and CW design

The FWS CW site was situated in the southern Namsan Town in Kongju City, South Chungnam Province, Korea (36°17’18.52”N, 127°2’9.16”E). It was strategically located at the downstream of a 465 ha watershed composed of 73% forest, 25% agricultural, and 2% urban areas with built livestock facilities to capture the intermittent stream water during dry days and runoff impacted stream water during wet days. The CW represents only a very small portion of the entire watershed, approximately 0.1% of the landscape. In 2009, the watershed received an annual mean precipitation of 1.11 m and the mean annual temperature was 12.6°C. During the monitoring period (storm season) when cultivation activities were high, the average temperature was 22.3°C. The CW was a demonstration project designed by the Environment Management Corporation (EMC) with funding from the Ministry of Environment (MOE). The physical design characteristics of the CW were provided in Table 1. The design flow rate and hydraulic retention time (HRT) were estimated based on the Computational Fluid Dynamics (CFD) model performed by the EMC (EMC, 2008). The design concept was characterized by a series of meanders that enable to hold the water as long as possible within the system especially during period of varying flows due to storm events (Fig. 1). The meandering design was enhanced by the construction of alternating shallow and deep marshes that were sloped as little as possible to avoid high velocities and channelization as the entire system was operated under gravity, including water feed and flow. Figure 2 shows the primary treatment regions in the CW along with the dominant species planted surrounding each region.

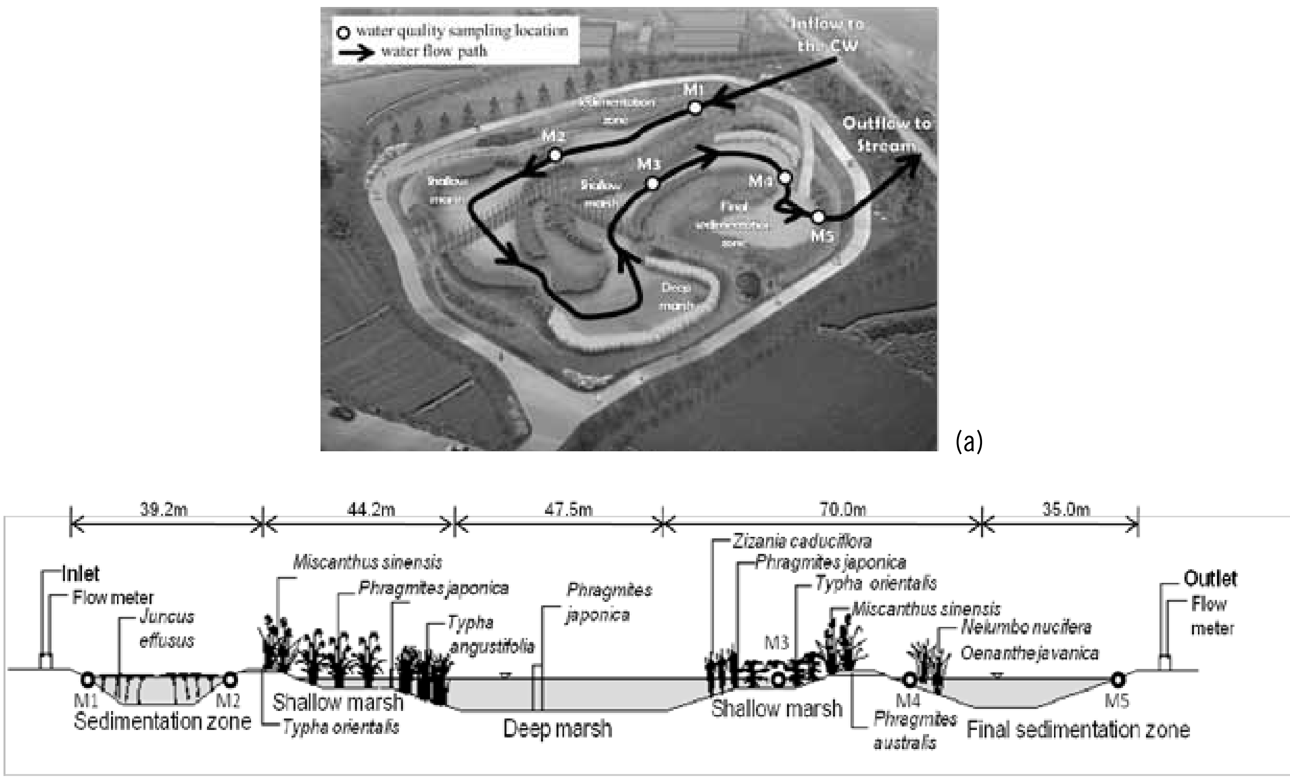
Monitoring of storm events and data analyses

Storm event monitoring was conducted subsequent to the completion of the CW in May 2009. Flow rates at the inflow and outflow of the CW were consistently measured and recorded with an automatic flow meter per minute interval. Considering the large watershed area where runoff was usually delayed, manual grab sampling was employed and initiated once there was an evident fluctuation (rise) on the flow rates. Twelve samples each were collected at the inflow (M1) and outflow (M5), and three samples for each of the other regions (M2, M3 and M4) during a storm event. The first six samples were collected during the first hour at zero minute (initial sampling time) and after 5, 10, 15, 30, and 60 minutes followed by another six samples at every one hour interval. Physical water quality data (e.g. temperature, pH, and dissolved oxygen) were collected along with each sample *in situ*. Conventional water quality parameters that were measured include total suspended solids (TSS), nutrients (TN, TP, nitrate, ammonia, orthophosphate), biochemical oxygen demand (BOD_5), chemical oxygen demand (COD), and dissolved organic carbon (DOC). All the samples were analyzed immediately upon collection in accordance with standard methods.

Table 1. Design characterization of the wetland

Average depth (m)	Storage Volume (m^3)	Surface area (m^2)	Wetland total area (m^2)	Design flow rate* (m^3/hr)	Hydraulic retention time* (hr)
0.9	2,957	3,282	8,861	180	16.8

* Denotes to peak values



(a)

(b)

Figure 1. Representation of the constructed wetland system showing the (a) water flow path and sampling regions and locations; and (b) length dimension and dominant plant species in each region (M# denotes to sampling locations).

The pollutant flow-weighted mean concentration (FWMC) was calculated for each storm event using Eq. 1. The average treatment efficiency was estimated as the percent removal for each parameter calculated by Eq. 2. All statistical hypotheses reported were tested at 5% level (α=0.05) by either an individual t-test or a one-way ANOVA using OriginPro 7.5 SRO v7.5714 (B714) (© OriginLab Corporation, Wellesley, MA, USA, 1991-2003) package software.

$$FWMC\,(\text{mg/L}) = \frac{\sum_{t=0}^{t=T} C(t)\,q_{run}(t)}{\sum_{t=0}^{t=T} q_{run}(t)} \qquad \text{Eq. 1}$$

where: $C(t)$ = pollutant concentration and $q_{run}(t)$ = runoff flow rate discharged at time t

$$\text{Relative Reduction (\%)} = \frac{FWMC_{in} - FWMC_{out}}{FWMC_{in}} \times 100 \qquad \text{Eq. 2}$$

where: $FWMC_{in}$ and $FWMC_{out}$ are the flow weighted event mean concentration at the inflow and outflow, respectively in mg/L.

RESULTS AND DISCUSSION

Storm events and pollutant patterns

Table 2 summarizes the data gathered from a total of six storm events sampled from May to September 2009 monitoring period. The events range in size from 13.5 to 32.5 10^{-3} m of rainfall and the average rainfall duration was 12.4 hr long. The variations of the flow rates at the inflow and outflow during storm events were significantly different (p<0.001) with 0.56 and 0.61 coefficient of variation (CV), respectively. No significant correlations were observed among the antecedent dry period, rainfall and hydraulic loading rate. The hydraulic loading rate (mean±standard deviation) of 29±14.5 10^{-2} m/day during storm events was exceptionally smaller than the designed (peak) hydraulic loading of 130 10^{-2} m/day. This was resulted due to the dominance of low flows as revealed by the median value (52.7 m^3/hr) that was less than the mean value (58 m^3/hr) accompanied by less rainfall during the storm season.

The hydro- and polluto-graphs shown in Fig. 2 reveal the changes in the concentration of pollutants as the storm progressed for low and high flow conditions. It was evident that the inflow concentrations fluctuated relative to the flow while the outflow concentrations remained nearly stable throughout the storm event. Similar to the observations of Fink and Mitsch (2004) which stated that at the inflow, the pulse was more intense and shorter in duration than at the outflow. However, there was no significant correlation between the peaks and flow rates given that the watershed area was large and only a very small portion of the runoff (approximately <1%) were directly flushed to the system during high flow conditions. On the other hand, the concentration peaks during low flow conditions seemed to appear when the flow rate started to increase perhaps at the first two to three hours after sampling commenced.

Water quality changes through the wetland

The polluto-graphs plotted in Fig. 4 illustrate the water quality changes along the various treatment regions in the CW over the duration of the storm event. The pollutant concentrations showed a declining pattern as the water flows through the wetland; more apparently from the middle to the end of a storm event. No significant differences in concentrations were detected except for TSS that varied significantly during the beginning, middle and end phases of the storm. It was observed that at the middle of the storm or during the peak flow, the inflow concentrations were highest as relative to the flows. The incoming concentrations were greater at the nearly end of the storm than at the initial time of storm. A similar trend was observed to the concentrations exiting the wetland. This condition happened due to the wetland being a small percentage of the watershed (<0.1%), which allowed delays in runoff time during storm events. Another factor that might influence the differences in inflow concentration was the rainfall intensity. The detachment, transport and deposition of sediment and associated pollutants were affected by the rainfall drop impact especially when flowing water during a storm exceeded the soil's resistance to erosion.

Table 2. Summary of monitored event data for six storm events for the year 2009

Statistics	Antecedent dry period (day)	Event Rainfall (10^{-3} m)	Rainfall duration (hr)	Hydraulic loading rate (10^{-2} m/day)	Flow rate	
					Inflow (m^3/hr)	Outflow (m^3/hr)
Minimum	3	13.5	4.5	19.3	4.1	0.2
Maximum	9.5	32.5	22.6	57.4	221.4	48.5
Median	4.3	25.75	10.4	23.8	52.7	15.9
Mean±S.D.	5±2.5	25.4±7.1	12.4±6.5	29±14.5	58±33	23±14

The inflow nitrogen was particularly organic in form. Ammonia was predominant in this CW because of moderate pH (6.7–7.2) and temperature (17–25°C) during the storm seasons. Nitrate constitutes to almost 15% of TN, present due to the oxidation of ammonia migrated via storm runoff.

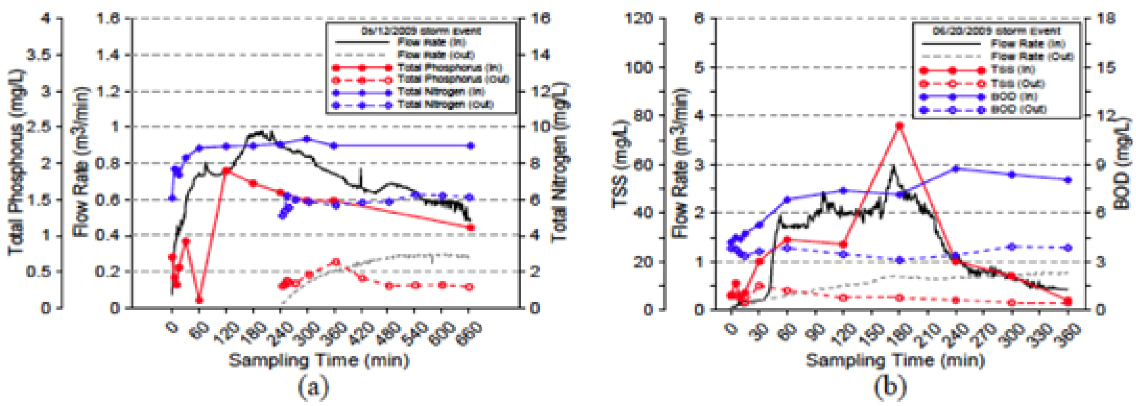


Figure 2. Hydro- and polluto-graphs at the inflow and outflow of the CW during storm events during (a) low flow and (b) high flow condition.

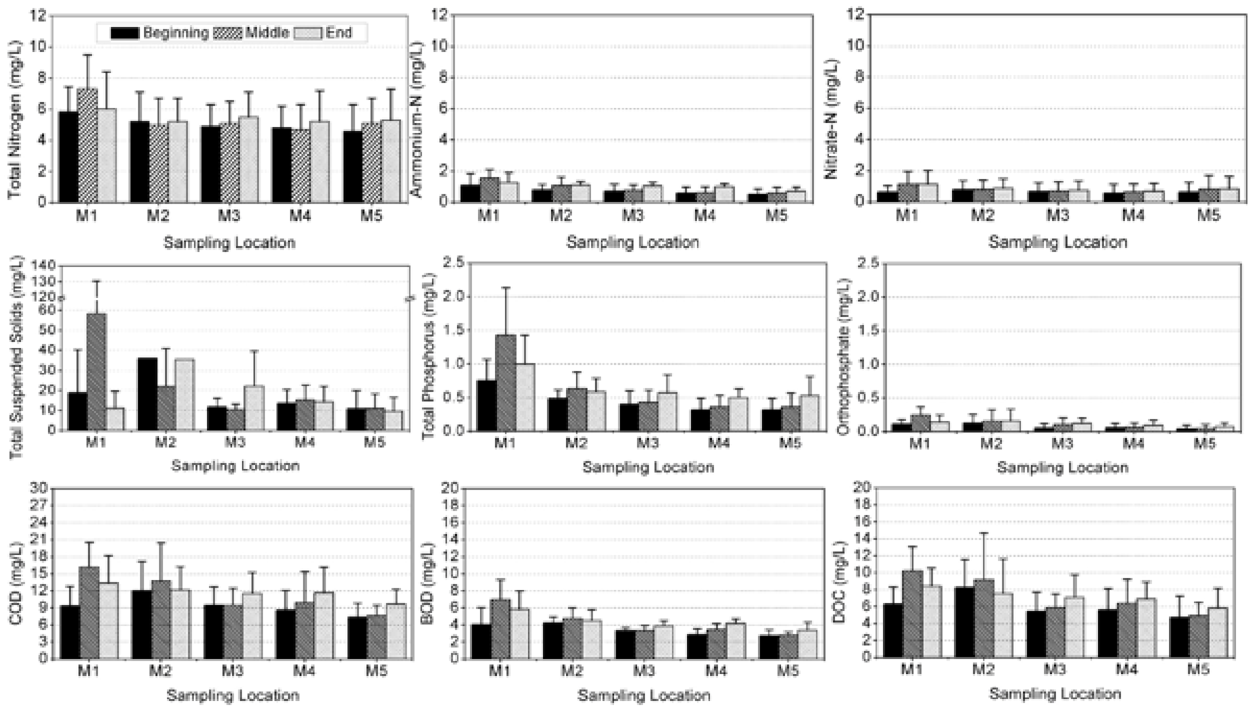


Figure 3. Pollutant flow-weighted mean concentration (mean±S.D.) at each sampling location (M#) in the CW during the beginning, middle and end phases of the storm. (Data averaged from six storm events).

Table 3. Flow-weighted concentration (mean±S.D.) of nutrient, organic and particulates entering and exiting the wetland averaged during the six storm events for the year 2009

Parameter	Baseflow	Storm Events		Relative reduction (%)
	Inflow (mg/L)	Inflow (mg/L)	Outflow (mg/L)	
TSS	8.4±3 [a]	40 ± 33	10±6 [a]	60±26 [b]
TP	0.7±0.4	1.2±0.3	0.4±0.2	67±14 [b]
Orthophosphate	0.1±0.1 [a]	0.2±0.1	0.06±0.06 [a]	76±12 [b]
TN	6.8±1.3 [a]	8.2±0.7	6±0.9 [a]	28±7 [b]
Nitrate-N	1±0.4	1.4±0.9	1.1±0.7	21±10
Ammonia-N	0.9±0.9	1.2±0.6	0.44±0.36	64±23 [b]
BOD_5	3.6±0.94 [a]	6.7±1.7	3±0.5 [a]	53±8 [b]
COD	6.9±2.2 [a]	15±3	7.4±2.2 [a]	50±9 [b]
DOC	5.5±1.2 [a]	9±2.6	5±2 [a]	46±14 [b]

[a] Indicate significant differences between inflow ($p<0.05$)
[b] Indicate significant reductions ($p<0.05$)

As can be seen in Fig. 4, nitrate was not significantly reduced through the CW probably due to the short detention time during storm events. Furthermore, because of its oxidation state, nitrate is chemically stable and would persist unchanged if not for several energy-consuming biological nitrogen transformation processes that occur. However, ammonium was significantly decreased at M2 (after passing the sedimentation zone) and continuously decreased until outflow.

TP was significantly decreased (p<0.001) after passing the sedimentation zone at M2. Dissolved phosphorus (orthophosphate) which corresponds to 20% of TP showed a considerable decrease after passing the deep marsh zone at M3 (p=0.034). While COD was only significantly reduced (p<0.001) at the outflow (M5), BOD_5 reductions were small along the path of the CW and not significant. Typical response data for BOD_5 showed a sharp decrease in concentration to a nonzero fluctuating background with increasing detention time (Kadlec and Wallace, 2009). Therefore, BOD_5 values over short time periods are subject to variation.

Pollutant removal efficiency

It has to be emphasized that the system studied is 'open' and 'natural' wherein the inflows of water are not constant and purely driven by hydrology such as storm events. Therefore, the FWMC was used to quantify the average pollutant load entering and exiting the CW during a sampling event with respect to the runoff volume (Table 3). The findings revealed that the concentration of TSS, TN, BOD_5, COD, DOC and orthophosphate were significantly higher during storm events compared to baseflow inflow concentration. However, a slight increase in TP, ammonia and nitrate inflow concentrations were observed during storm events. The addition of NPS pollutants carried by runoff had caused the dramatic increase in inflow concentration. The CW received almost fivefold increase in TSS, 120–140%, 170–200% and 160–220% increase in TN, TP and organic concentration, respectively.

Based on the analysis of storm events, all constituents were significantly reduced except for nitrate (p=0.5) with only 21±10% reduction rate. Studies conducted by Spieles and Mitsch (2000) reported high nitrate removal of 30–40% for low and high nitrate loading for summer storm events except during periods of drastically increased loading which correspond to major flood events. Overall, the results indicate that the CW was more efficient in reducing TSS (60±26%), total and dissolved phosphorus (67–76%) and ammonia (64±23). CWs are useful for modulation of ammonia because they create circumneutral pH, and may lower water temperatures for warm effluents (Kadlec and Pries, 2004). Greatest variations between inflow and outflow concentrations were observed for TSS, TP and orthophosphate which signifies that the deposition and build-up of sediment during storm events in the CW was highly variable and might be affected by flow rate, retention time, plant uptake etc. which limits the settling process. Fink and Mitsch (2004) concluded that phosphorus retention in CW was variable with retention decreasing steadily as the CW becomes saturated with phosphorus in its sediments and litter. Apparently, outflow concentrations were not always lesser the inflow concentration during baseflow condition. However, no significant differences were found except only for orthophosphate. The orthophosphate outflow concentration during storm events was significantly lower than baseflow inflow concentration, which suggests that orthophosphate was highly retained by the system. It was assumed that the vast amount of algae present in the wetlands during the early summer season was the major contributor to the removal of TP and orthophosphate. Algae will often take up phosphorus and deposit it to the sediment where it becomes buried (Vaithiyanathan and Richardson, 1998).

The inflow BOD_5 and COD concentrations in this study were within the typical ranges for background concentrations of BOD_5 (1–10 mg/L) and COD (10–100 mg/L) from the studies reviewed by Kadlec and Wallace, 2009. They also stated that CWs are efficient users of external carbon sources, manifested by excellent reductions in BOD_5 and COD although CWs possess nonzero background levels of both BOD_5 and COD. The variations in the relative reductions of BOD_5, COD and DOC were small and not significant. However, the outflow BOD_5/COD ratio ranged from 0.32 to 0.49 indicating that the outflow was still rich in usable carbon compounds. Nevertheless, when compared to Korean stream standards set by the Ministry of Environment (MOE, 2004) the BOD_5 and SS outflow quality passed the Level II (fairly good) grade that is below 3 mg/L and below 25 mg/L for BOD_5 and SS, respectively. However, TN and TP outflow quality were poor if compared to the standards for larger water bodies like lakes and rivers. Nutrient input may not be particularly detrimental to aquatic ecology since the receiving aquatic plants and algae possibly uptake the nutrient. In spite of this, reduction of nutrient before reaching the larger waterways is a big contribution to lessen its potential impact and maintain the water quality downstream.

Operational problems and design recommendations

Table 4 shows the summary of observations on the technical and operational problems associated with the design of the CW and some recommendations for future design efforts.

Table 4. Operational problems and corresponding design recommendations for the CW

Operational Problem	Design Recommendation
Majority of sediments, litters and debris from the contributing watershed were often carried by runoff downstream causing excessive clogging at the inlet (Fig.4b-c). The grid at the inlet reduces the hydraulic loading (especially when clogged) during storm events (Fig.4a).	A sediment forebay should be constructed for sediment control and pre-treatment of initial pollutant load. The grid at the inlet should be removed as the water should flow directly to the CW. The sediment could be removed by a routine dredging.
Algae growth was dominant at the open water zones and mostly at the unplanted high water level areas of the CW (e.g. sedimentation and deep marsh).	Algae was also useful in the CW as algae could raise DO to very high levels during bloom conditions and could uptake nutrients; however, removal of algae after the period of high productivity was necessary before it discharged to the stream.
The 'dead zone' areas reduced the water holding capacity of the CW. Also, the decreased in water level during the dry season have caused early death of some wetland plants.	As much as possible the dead zones in the CW should be avoided. This could be done by reconstructing or restructuring the CW to eliminate or reduce the dead zones.
Vegetation in the CW was placed surrounding the perimeter of the water area. The potential of plants in adsorbing the nutrients would not be maximized. Weeds and other non-wetland plants also grew abundantly in the CW (Fig. 4d).	Plants should be placed primarily at the water areas within the CW and not recommended at the first sedimentation zone and final sedimentation zone near the outlet because the plants could not grow well since the water level was highly variable at these areas.

Figure 4. Photographs showing the (a) portion of the stream inlet located 26 m away from the wetland inlet with (b) sediment and litter build-up; (c) stream flow; and (d) deep marsh region.

CONCLUSIONS

This study suggests that the design of the system could feasibly function for the retention of NPS pollutants during storm events. Highest reductions were achieved for TSS, TP, orthophosphate and ammonia with more than 60% removal efficiency rates. Indeed, sedimentation which is a physical process played an important role in terms of the performance of a natural type of treatment system like the CW. While overall mass may not have been removed or retained by the system, the levels of pollutants exiting the CW were reduced to appreciable levels. An important contribution of this study was the prediction of the levels and patterns of NPS pollutants in the watershed area. However, given that the concentration of pollutants were highly variable especially during the storm season, it is difficult to generalize a management strategy. On the other hand, the meandering design of the CW seemed to be functional but the CW was over-designed in terms of hydraulic loading and design flow rate. The incoming flow/volume to the CW was not effectively utilized as much of the CW as possible. It would be recommended to maximize the water holding capacity of the CW especially during storm events. There was a trend for outflow concentrations to remain high when sampling ended. For further investigation, additional number of samples should be collected at the outflow. Nonetheless, if the outflow concentration will not decrease to very low levels, it is possible that the values obtained were the background concentration levels in which the CW operates. Meanwhile, studies are currently underway for seasonal storm events, but storm studies in the succeeding years of operation could also add greatly to this research.

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Development of a GIS Method to Localize Critical Source Areas of Diffuse Nitrate Pollution

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Abstract

The present study aims at developing a universal method for the localization of critical source areas (CSAs) of diffuse NO_3^- pollution in rural catchments with low data availability. Based on existing methods *land use*, *soil*, *slope*, *riparian buffer strips* and *distance to surface waters* were identified as the most relevant indicator parameters for diffuse agricultural NO_3^- pollution. The five parameters are averaged in a GIS-overlay to localize areas with low, medium and high risk of NO_3^- pollution. A first application of the GIS approach to the Ic catchment in France, shows that identified CSAs are in good agreement with results from river monitoring and numerical modelling. Additionally, the GIS approach showed low sensitivity to single parameters, which makes it robust to varying data availability. As a result, the tested GIS-approach provides a promising, easy-to-use CSA identification concept, applicable for a wide range of rural catchments.

Keywords

Critical Source Areas; Diffuse NO_3^- pollution; GIS

INTRODUCTION

Diffuse nitrate (NO_3^-) pollution from intense agriculture adversely impacts freshwater ecosystems, but can also pose a risk to human health, if the water is used for drinking water abstraction. Typical countermeasures, such as the implementation of mitigation zones or changed agricultural practice, are most efficient if they focus on critical source areas (CSAs) of diffuse NO_3^- pollution within a given catchment.

Commonly, numerical models are used for identification of CSAs (e.g Skop & Sørensen 1998, Kuderna et al. 2000). However, in many catchments the application of numerical models is limited, because of their high data requirements (Kuderna et al. 2000, Trepel & Palmeri 2002). Therefore, we reviewed methods with less data and time requirements as alternatives to numerical models for CSA identification (Bugey 2009). Many of these alternative approaches use *Geographic Information Systems (GIS)* (e.g., Soyeux et al. 1993, Jordan 1994, Bae & Ha 2005, Munafo et al. 2005). However, most available GIS methods are site-specific and therefore not transferable to other catchments. The more developed ones focus on the vulnerability of groundwater rather than surface water (e.g. Aller et al. 1987, Vernoux et al. 2007).

The aim of the present work was to assemble a universal GIS-approach for CSA localization based on existing concepts, for application in rural catchments with low data availability. The idea of the method is to provide a ranking of areas within a catchment regarding their potential as NO_3^- sources for surface water, but not to predict actual NO_3^- concentrations or loads in surface waters. The presented approach focuses on small to medium size catchments with fairly homogeneous climate conditions. For a first case study the approach was validated with measured loads and numerical model results for a catchment in Brittany, France. Finally, a detailed sensitivity analysis was performed.

MATERIAL AND METHODS

Approach

General approach. In order to keep the GIS-approach as simple as possible and maximize transferability, existing concepts of catchment analysis and CSA identification (MUNLV 2005; Kuderna et al. 2000; Trepel & Palmeri 2002) were broken down to the most basic and available parameters. The following five parameters were identified:

- Land use
- Soil
- Slope steepness (slope)
- Riparian buffer strips (buffer)
- Distance to surface waters (distance)

In this first approach, all parameters are classified into the three classes of low (1), medium (2) or high risk (3). For the sake of transferability, the risk classes are defined by relating them to the full range of possible values for each parameter, independent from the range of values found in a given catchment. In the following the rationale, as well as the defined classification are outlined for each of the five parameters.

Land use. A number of studies have shown that land use is one of the governing parameters for NO_3^- export from land surfaces (e.g., Crétaz & Barten 2007; Maillard & Pinheiro Santos 2008). The main reason for differences in NO_3^- export between land use types is the N-surplus which is lost to subsurface or surface flow. Agricultural land use typically leads to elevated NO_3^- input on (cultivated) land surfaces, higher share of surface runoff and more erosion, which in turn cause an increase in NO_3^- loss to surface waters (Magdoff et al. 1997).

Based on the performed literature study, the parameter *land use* was classified into the three categories 'unfertilized areas', such as forests or uncultivated grassland (risk class 1), 'other fertilized areas' such as fertilized grassland and grazed pastures (risk class 2) and 'cropland' (risk class 3). The classification agrees with a review by Di & Cameron (2002), who ranked forest as least contributive followed by cut grassland, cropland and horticulture.

Soil. In most catchments subsurface passage is the main NO_3^- pathway to surface water bodies (e.g., Gächter et al. 2004) and soil properties are a major controlling factor of this pathway. Therefore, in the present work soil is considered by using the parameter *root zone available soil water capacity (RZAWC)*, i.e., the soil water available for plants. The higher RZAWC, the more water is retained by plants and consequently less water and NO_3^- leaches to the groundwater. *RZAWC* can be obtained from the soil texture and soil depth, data which are available for most catchments.

An existing RZAWC-ranking by the German Soil-Scientific Mapping Directive (Ad-hoc-Arbeitsgruppe Boden 2005) was reclassified into three classes: loamy silt to clay loam with *RZAWC* ≥140 mm (risk class 1), loamy to silty sand or clay with *RZAWC* between 90 and <140 mm (risk class 2) and coarse to fine sand with *RZAWC* < 90 mm (risk class 3).

Slope. Even though NO_3^- is predominantly lost to infiltration, transport via surface runoff also occurs (Mayer et al. 2005). Moreover, organic N can be transported to rivers via erosion, where it is mineralized to NH_4^+ and oxidized to NO_3^- (e.g., Brunet et al. 2008). In order to account for surface runoff, slope was identified as the most relevant parameter.

The slope parameter is based only on slope steepness, as suggested in the modified Universal Soil Loss Equation (USLE) (Sivertun et al. 1988). For the purpose of this study the full range of the USLE slope steepness factor S by Nearing (1997) was evenly divided into the three classes: 0° to 17.4° (risk class 1), 17.5° to 29.9° (risk class 2) and 30° to 90° (risk class 3).

Riparian buffer strips. An important factor influencing how much NO_3^- reaches the surface waters is the land use within a close distance to the surface waters (Basnyat et al. 2000). If the land around the surface waters is naturally vegetated (e.g., forests), i.e., if a buffer strip exists, the risk that nutrients reach the surface waters is lowered (Pinay & Décamps 1988, Mayer et al. 2005)

Based on a extended review by Mayer et al. (2005) a width of 25 m was chosen, which is likely to lead to a significant removal (~70%) of NO_3^-. Regarding land use of the buffer strip, a forested buffer was found to remove NO_3^- most effectively (risk class 1), followed by a grass-covered riparian buffer (risk class 2) (Mayer et al. 2005). A grassland buffer even has a certain retaining effect, if it is agriculturally used (fertilized or grazed) (Di & Cameron 2002). The highest risk of NO_3^- input occurs when no buffer zone is present, i.e., when agricultural cropland extends all the way to the river (risk class 3). Accordingly, the parameter *riparian buffer strips* represents the risk class for each point on the land surfaces depending on the land use type they drain through immediately before entering the streams.

Distance to surface waters. Many studies assessing pollution risks include the parameter *distance to surface waters* (e.g., Maillard & Pinheiro Santos 2008; Basnyat et al. 2000; Sivertun & Prange 2003). For the present approach, the last two classes of the modified USLE by Sivertun & Prange (2003) were combined to >200 m (risk class 1) while the classes 50 m to 200 m (risk class 2) and <50 m (risk class 3) were adopted directly. Similar to most published approaches, the 'Euclidean distance' function is applied here for the GIS application of the risk classes.

Overlay. The creation of the five thematic maps concerning the risk of NO_3^- export is followed by a combination with equal weight of all five layers. Technically the overlay is performed by averaging raster cells of the GIS layers. The resolution depends on the raster size of available input data. In the following, the term 'overlay' refers to the calculation of the mean risk class for each cell. The results are float values from 1 to 3. In order to make the results comparable the values had to be assigned to low, medium and high risk classes. An equidistant distribution was chosen:

- Low risk class = 1.000 – 1.666
- Medium risk class = 1.667 – 2.333
- High risk class = 2.334 – 3.000

Study Site

General description. The Ic catchment is located in the north of the department Côtes-d'Armor in Brittany, France. It covers an area of 92 km² and the elevation ranges between 206 m a.s.l. in the south and the sea in the north-east (Julich et al. 2009). The predominant soil texture in the Ic catchment is silt loam in the floodplains and sandy silt in the remaining areas with predominantly less than 60 cm soil depth in the north, and more than 60 cm in the south. Land use in the Ic catchment is clearly dominated by agricultural use with 64 % of cropland, while grassland and forests account for about 20 % and 16 %, respectively. Due to the intensive crop production and animal husbandry NO_3^- concentration in the river exceeds 50 mg-NO_3^- L^{-1} almost year-round. Since the area has no major aquifers, river water was used for drinking water production until the beginning of 2009, when waterworks had to be closed down as a result of high NO_3^- levels.

Data. The available spatial data include:

- 50 meter digital elevation model of 2003 (Source: IGN),
- land use map digitized from aerial photographs of 1996/1997 (Source: Conseil Général des Côtes d'Armor),
- soil texture map, 1:100,000 of 1987 (Source: BDPA SCETAGRI),
- soil depth map, 1:100,000 of 1987 (Source: BDPA SCETAGRI),
- stream network map, digitized from aerial photographs of 2008 (Source: SMEGA).

Additionally, discharge and NO_3^- concentrations were measured monthly at monitoring stations at the outlet of the seven subcatchments in Figure 1 from 1996 until 2007. The catchment boundaries were delineated from the DEM 50. Additionally, the results of the numerical catchment model *Soil and Water Assessment Tool (SWAT)* were available (Julich et al. 2009).

RESULTS AND DISCUSSION

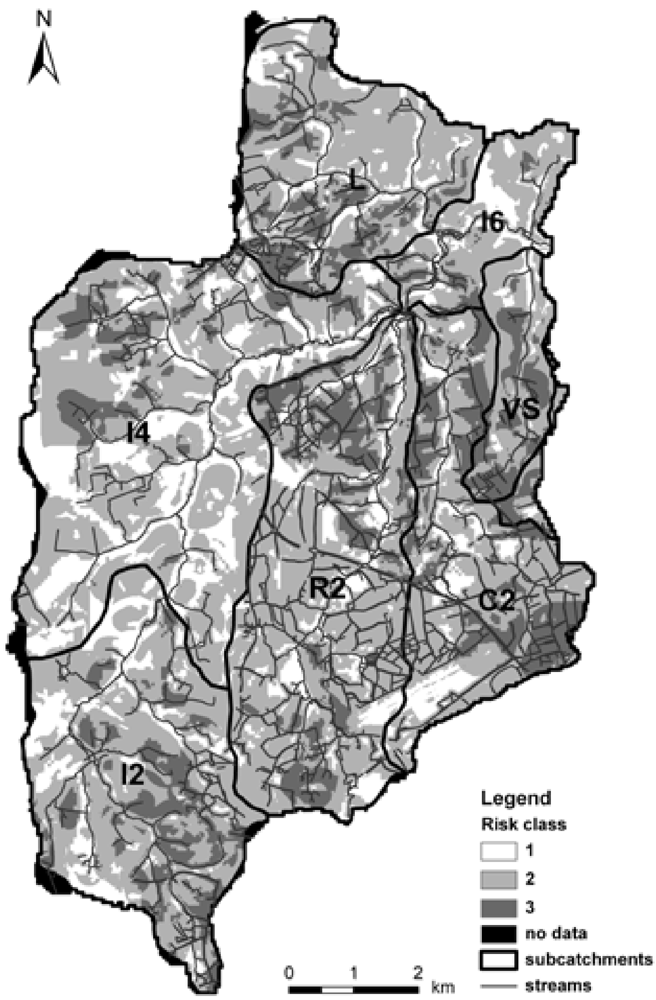

Figure 1. Overlay of five parameters

Application to the Ic case study

The full overlay of the five individual parameters of the Ic catchment has a leveling effect (Figure 1). Most areas belong to medium risk class 2 (63.1 %), high risk class 3 exists mainly in the south-east and east of the catchment (17.6 %), while low risk class 1 can be found along the main rivers (19.3 %). Concerning CSA identification, the full overlay map delivers spatially detailed information compared to other approaches.

Validation

Comparison with measured nitrate loads. In order to validate the applied overlay, the results are compared with average NO_3^- loads obtained from ten years of monthly NO_3^- and discharge measurements at seven monitoring stations in the catchment. It is important to note that the calculation of NO_3^- loads based on monthly measurements can be subject to large errors, since fluctuations during storm events are not accounted for.

A ranking of the seven subcatchments based on measured loads does not correspond to the results for mean risk classes for all subcatchments (Figure 2).

For instance, the subcatchment with the lowest mean risk class (Ic Centre (I4)) shows higher measured NO_3^- loads than some other catchments (Ic Littoral (I6), Lantic(L)) and almost as much as the catchment with the third highest mean risk class (Rodo (R2)).

For a more systematic overview, measured loads are plotted against mean risk classes in Figure 2. Correlation is not significant (p=0.057) concerning a confidence interval of 95 %. Nevertheless, a general trend of higher mean risk class in a subcatchment with higher NO_3^- load can be shown.

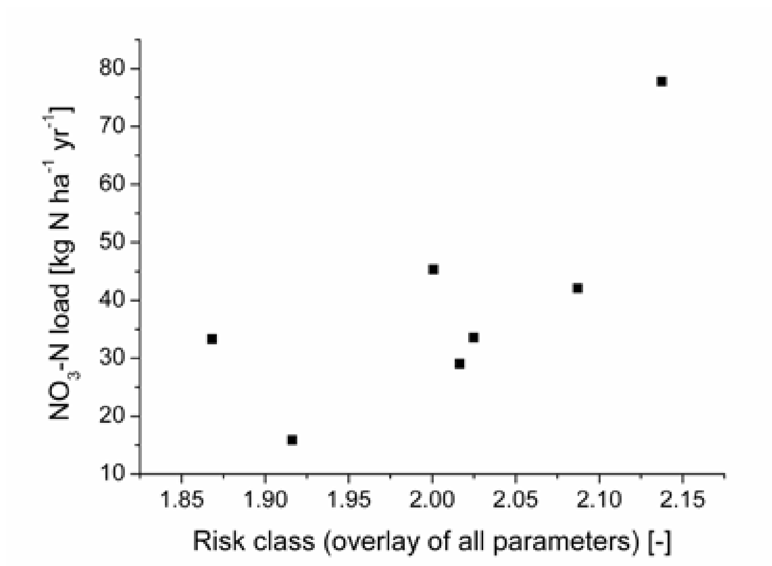

Figure 2. Measured NO_3^- loads against mean risk class of subcatchments after overlay of all parameters

Comparison with SWAT simulation. SWAT aims at predicting NO_3^- loads, whereas the GIS-approach provides a CSA identification. Nevertheless, the results compare relatively well. Both the SWAT model applied to the Ic catchment as well as the GIS-approach predict CSAs in the north-east and in the south of the catchment (Figure 3).

Major differences between the two approaches exist in the north-west where SWAT predicts low NO_3^- loads, whereas the present study expects several CSAs. An explanation can be found in the parameters *buffers* and *distance*, that are strongly influenced by the presence of drainage ditches, which occur in the two subcatchments to a moderate extent, but were neglected in the SWAT analysis (compare river networks in Figure 3a (SWAT) and Figure 3b (GIS)). This example indicates that not only the approach itself but as well the different input data can explain the deviations in the results.

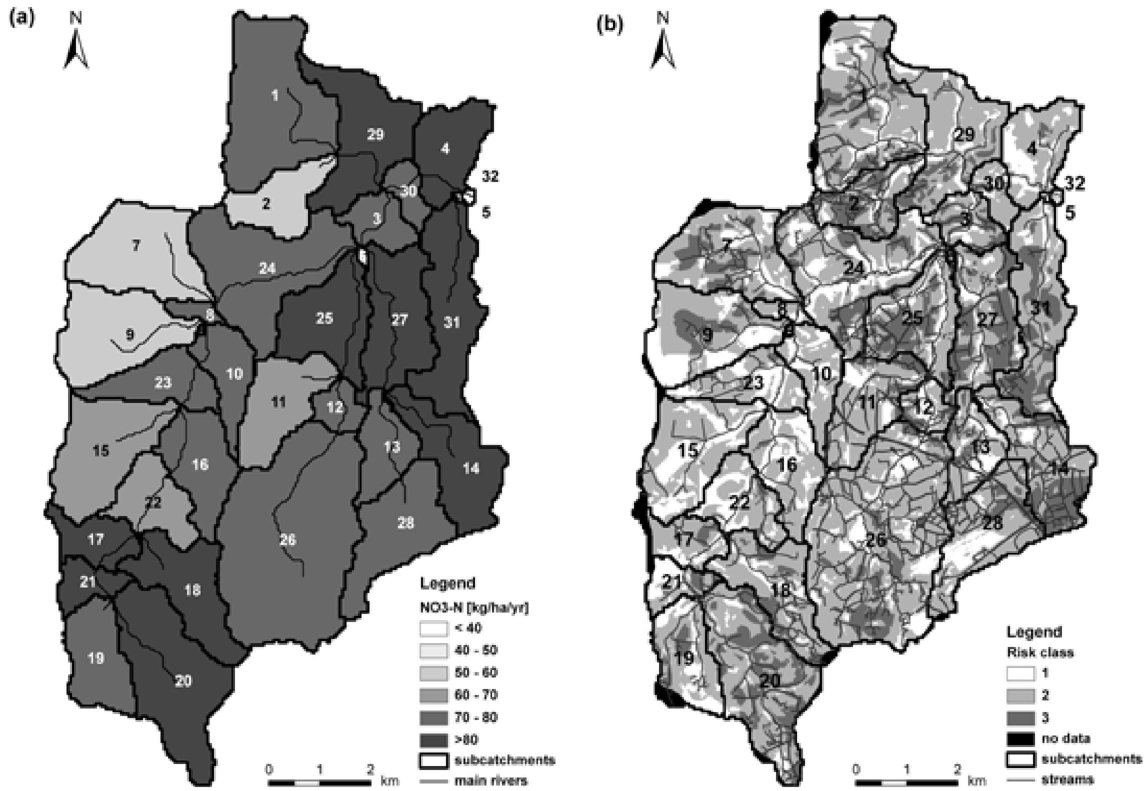

Figure 3. Comparison between (a) the SWAT results (by Julich et al. 2009) and (b) the results of the full overlay of five parameters

Sensitivity analysis

For the applicability of a similar GIS-based approach to catchments with varying data availability, it is important to know its sensitivity to each parameter. In order to assess this sensitivity, overlay was done for each combination of four parameters, i.e. excluding each parameter in turn (Table 1).

Table 1. Ranking of seven subcatchments based on average risk class for full overlay and with each parameter omitted in turn

Sub-Catchment	Ranking					
	Full overlay	Without land use	Without soil	Without slope	Without riparian buffers	Without distance
VS – Ville Serho	1	1	3*	1	1	1
C2 – Camet	2	2	1*	2	2	2
R2 – Rodo	3	4*	2*	3	6*	6*
L – Lantic	4	3*	5*	4	3*	3*
I2 – Ic Amont	5	5	4*	5	4*	4*
I6 – Ic Littoral	6	6	7*	6	5*	5*
I4 – Ic Centre	7	7	6*	7	7	7

* Ranks that differ in comparison to the full overlay of all five parameters

Results of this analysis indicate that the GIS overlay is not very sensitive to the single input parameters. For most parameters no more than two of the seven subcatchments change their position in a ranking according to their average risk class, when one parameter is omitted. Solely the parameter *soil* has a strong effect on the full overlay, leading to a different ranking of all seven subcatchments and a significant shift of CSAs. But even for the parameter *soil* the three subcatchments with the highest mean risk class stay among the top three subcatchments and the four subcatchments with the lowest mean risk class stay among the bottom four subcatchments.

Although sensitivity is lower than expected, it has to be kept in mind that even the change of two subcatchments in the ranking could change the decision on where mitigation measures are considered. Consequently, single parameters can still have a significant influence on the result. The extent of their influence is strongly dependent on the distribution of their risk classes over the considered spatial scale. For example, in the Ic catchment the parameter *soil* shows uniform high risk in the north and uniform low risk in the south. As a result it has a strong impact on risk class distribution on a catchment level. However, if only a northern subcatchment is considered *soil* has a homogeneous character. In this case, the parameter has no impact on the CSA identification, because it only decreases or increases risk classes uniformly.

CONCLUSIONS

The comparably simple GIS approach adopted in this study provides reasonable CSA identification for NO_3^- in a test catchment. The results compare well to CSAs from measured loads and numerical model results. Identified differences to these two approaches cannot be judged directly, since these methods are also prone to significant uncertainties. Surprisingly, the tested GIS approach showed relatively low sensitivity to single parameters, which make it a robust method for catchments with varying data availability.

While the first results are promising, several open points need to be assessed to move towards the development of a future GIS method, universally applicable to catchments, which are affected by diffuse agricultural pollution. In particular it has to be tested on a range of catchments, where similar validation is possible as outlined above to identify shortcomings and need for adaptation. Moreover, possible weighting of the five parameters should be considered.

Regarding application, the tested approach is of interest, given its relatively simple application, its high flexibility to varying data availability and resolution, as well as its high transparency of how final results were achieved. Compared to other approaches, such as river monitoring or numerical modelling, the GIS-method is more time efficient, less costly and can be applied by local engineers. However, it has to be clear that GIS-based CSA identification can only be a first step, which has to be followed by a reality check in the field. For the detailed planning of measures, local information (soil type, topography, cooperation of land-owner, etc.) needs to be collected and cannot be replaced by a GIS-based approach alone.

ACKNOWLEDGEMENTS

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Nutrient Export in Run-Off from an In-Field Cattle Overwintering Site in East-Central Saskatchewan

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Abstract

Wintering cattle directly in the field creates potential concerns with water quality, as nutrients added from urine and fecal material over the winter can end up in runoff water, ground water and soil. In 2008/2009 an experiment was conducted to observe the effect of in-field winter feeding of cows on the nutrients in spring snowmelt run-off water. Low temperatures give little opportunity for organic N, urea and ammonium added in the urine and fecal matter to convert to nitrate, resulting in nitrate-N concentrations in snowmelt run-off water that were similar in the control and winter fed areas. Orthophosphate-P and ammonium-N concentrations were significantly elevated in run-off from the winter feed treatment basins compared to the controls. Surface soil sampled in the spring from the winter feeding site had higher soluble nitrate while soluble forms of phosphorus in the soil were lower compared to the fall soil samples. Caution should be used when utilizing in-field winter feeding systems so that the runoff water does not reach sensitive water bodies.

Keywords

Ammonium, Nitrate, Orthophosphate, Snowmelt Run-off Water, Saskatchewan, Cattle Winter feeding

INTRODUCTION

On the Canadian prairies, many cow-calf producers are adopting an in-field overwintering system. The in-field system can potentially lower cost of production due to reduced yardage and manure hauling costs. The in-field overwintering system was shown in previous research to increase retention and recycling of nutrients contained in feed as the nutrients are applied directly to the field instead of being lost in the pen before being transferred to the field (Jungnitsch, 2008). Increased return of nutrients to the soil and potential loading with high stocking rates in the field raises concern with prospective nutrient transport in runoff water.

Phosphorus, usually in the form of orthophosphate, is a nutrient that is of concern in runoff water from prairie agricultural landscapes. Eutrophication is primarily caused by elevated concentration of phosphorus in the water (Singh et al., 2008). Glozier et al. (2006) worked in a small agricultural watershed on the prairies and proposed a guideline that runoff water should not exceed 0.26 mg total P L^{-1}.

Runoff water with elevated nitrogen concentrations is undesirable and total nitrogen concentrations should not exceed 1.16 mg L^{-1} to ensure a healthy watershed (Glozier et al., 2006). When nitrogen is applied in excess, ammonium-N and nitrate-N can be lost through surface or subsurface flow and nitrate-N can be lost by leaching (Forman, 1995; Larney and Hao, 2007; Freney, 2005). Glozier et al. (2006) proposed a guideline for maximum levels of nitrite, nitrate and ammonium in runoff water at 0.28 mg L^{-1} for NO_2-N/NO_3-N and 0.12 mg L^{-1} for NH_4-N. Above 10 mg L^{-1} NO_3-N, the nitrate-N can become harmful to human health (Forman, 1995; Stumborg et al., 2007).

Jungnitsch et al. (2011) first looked at the soil nutrient content, forms, forage growth and nutrient recovery as influenced by a cattle in-field winter feeding system located on pasture near Lanigan, Saskatchewan. The current study follows the work of Jungnitsch et al. (2011) by providing additional information on nutrient flows in winter feeding systems, with the objective of determining the effect of imposing a cattle in-field winter feeding system on the nutrients in snowmelt runoff water. Our hypothesis is that the concentrations of phosphorus and nitrogen in snowmelt runoff water will be elevated in the winter feeding site watersheds. This hypothesis was tested by collecting surface water samples from catchment basins in paired winter feeding (treatment) versus control (no winter feeding) watershed basins in a pasture field near Lanigan, Saskatchewan, Canada. The water samples were analysed for forms and concentrations of nitrogen and phosphorus. The effect of winter feeding versus no winter feeding on the labile, exchangeable levels of nitrogen and phosphorus in the soil surface (0-10 cm) layer in the spring was also assessed.

MATERIALS AND METHODS

Site. The study was conducted on a Russian wild ryegrass pasture (SE-27-33-21-W2) at the Western Beef Development Center's Termuende Research Ranch located near Lanigan in east-central Saskatchewan (51 51'N, 105 02'W). The pasture site had no cattle present or fertilizer applied in the past five years (2003-2008). The terrain in the field is hummocky, creating ephemeral wetlands (basins) for the runoff water to collect.

Paddock/catchment layout. In the fall of 2008, the pasture was divided into a control area containing 4 basins and a treatment area (cattle winter feeding) with 4 basins (Figure 1). The control area was 6 ha and the winter feeding site was 3 ha in size. Approximately 100 beef cows were baled grazed during the winter of 2008-2009 at a stocking rate of 2218 cow-days ha^{-1} for 88 d in the winter feeding area of the pasture. The cattle fed on 255 round bales weighing 545 kg on average composed of mainly bromegrass with 5 to 10 percent alfalfa. The manure produced by the cattle was approximately 274 tonnes. The cattle were managed within the bale fed area using portable electric fence to control animal access to feed and minimize feed wasting.

The farm yard basins (F1S and F3S) were located on the Termuende Research Ranch where 300 cattle are green feed or bale fed from late January to the end of May. The ranch has been established since the 1970's and the paddocks are located on 32 ha of land. The yard basins were not replicates of the winter feeding basins, F1S and F3S were selected to monitor the snowmelt runoff that drained into the basins during the spring 2009 snowmelt for comparison purposes.

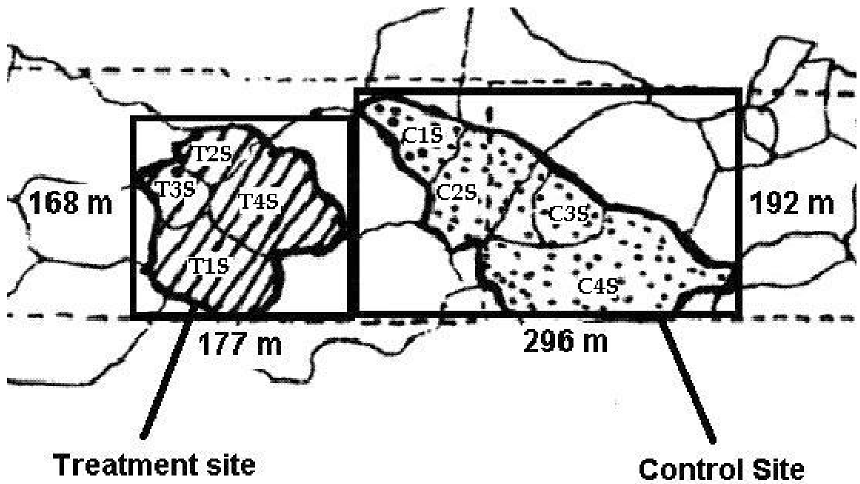


Figure 1. Site map of basins separated into control site and treated (winter feeding) site.

Water Measurements. Data loggers were installed in basins T2S and T1S in the treatment (winter feeding) site, basins C1S and C2S in the control site and basin F1S from the farm yard site (Figure 1). Water Survey of Canada metric staff gauges were installed in basins T3S and T4S in the treatment site, C3S and C4S in the control site and F3S in the farm yard site (Figure 1). The data loggers recorded water depth in basins while the staff gauges were visual markers for manually measuring water depth.

Nutrient Losses. On 31 March 2009 runoff water collection started in the 10 basins from the winter feeding, control and farm yard sites and continued daily until the spring melt was complete on 19 April 2009.

Water samples were frozen at -20 °C until they were thawed and filtered through a 0.45 micron mixed cellulose ester gridded filter paper through Millipore glass apparatuses. The filtered samples were stored in 50 mL vials and analyzed using a Technicon Autoanalyzer II (Keeney and Nelson, 1982) for orthophosphate-P (PO_4-P), nitrate-N (NO_3-N) and ammonium-N (NH_4-N). Orthophosphate-P was measured using the ammonium molybdate blue method (Murphy and Riley, 1962) in an automated analysis system (Technicon Industrial Systems, 1973a). Nitrate-N and ammonium-N were measured using automated colorimetry (Keeney and Nelson, 1982; Technicon Industrial Systems, 1973b).

Soil. Soil was sampled using hand augers to 0-10 cm depth. A sampling grid was utilized during the soil collection. In the fall of 2008 prior to in-field feeding, a total of 50 soil samples were collected across the control and winter feeding watershed locations. After the spring melt in May 2009 a total of 150 soil samples were collected from grids across the control and winter feeding site. Soil samples were spread out and air-dried for 7 days. The samples were then ground to pass through a 2 mm sieve and stored at room temperature in vials until analyzed.

Nitrate-N analysis was completed using the 2M KCl method (Keeney and Nelson, 1982). In this method, 5 g of soil is measured into 250 mL extraction bottles. Then 50 mL of 2M KCl is added to the bottles that are shaken at 142 rpm for 1 hr. The suspension was then filtered through Whatman® #454 filter paper into 50 mL vials. The vials were stored in a cooler until colorimetric analysis was completed using a Technicon Autoanalyzer II (Technicon Industrial Systems, 1973b). Water extractable labile P analysis was completed using the method of Schoenau and Huang (1991). In this method 2 g of soil was weighed into a 100 mL plastic bottle. Then 100 mL of distilled water was added to the containers and they were shaken at 200 rpm for 1 hr. The samples were then filtered through a 0.45 micron mixed cellulose ester gridded filter paper using a Millipore glass filtration apparatus. The samples were stored at 4 C until colorimetric analysis using the Murphy and Riley method (1962).

Statistical Analysis. Soil and water nutrients were transformed using log and square root and then tested for normality using the Shapiro test (Crawley, 2007). Water and soil samples were statistically analyzed using the Mixed Model using the coding lme from the statistical program R (Crawley, 2007). The Mixed Model works well for experimental units that are spread across time and data points that are not independent. Results of the model were summarized by running an ANOVA (Crawley, 2007). The model was set to focus on significant difference between control basin and the winter feeding basin water, and if time measured in days influenced the results. The farm yard (F1S and F3S) was only replicated twice and therefore could not be compared statistically. The soil collected from the control and winter feeding sites in the fall, 2008 and spring, 2009 were analyzed for significant differences. Differences were considered significant when the P value was less than 0.05. The degrees of freedom numerator and denominator are reported to give an idea of the sampling size. The F value or F statistic is shown to better understand the variance of the model.

RESULTS AND DISCUSSION

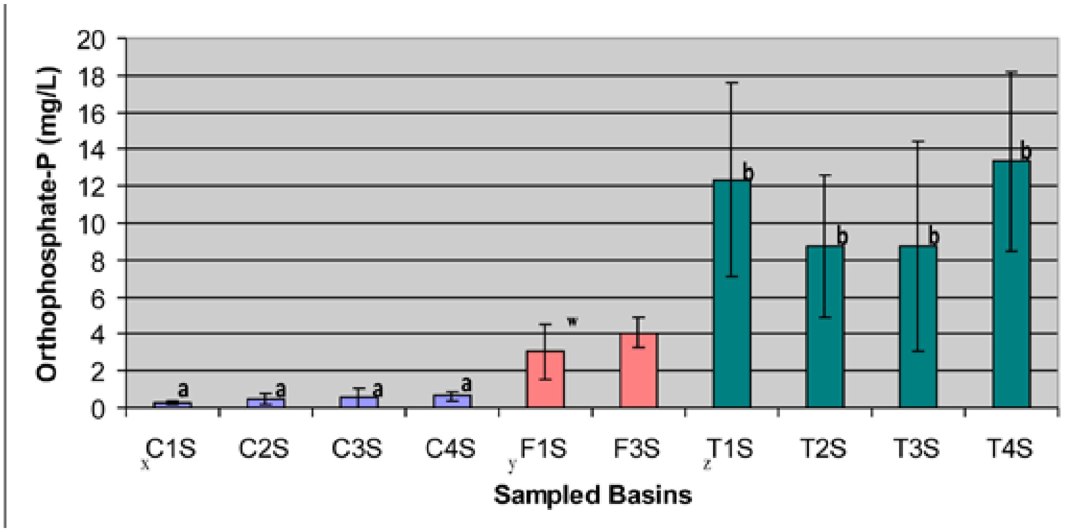
Water

Concentrations of orthophosphate-P collected in the snowmelt runoff water from the in-field overwintering sites were significantly elevated compared to water from the control watersheds (Figure 2 and Table 1). Orthophosphate-P collected in the snowmelt runoff water had an average concentration of 10.72 mg PO_4-P L^{-1} from the four winter feeding basins compared to the control basins' average of 0.47 mg PO_4-P L^{-1} (Figure 2). Ammonium-N in runoff water was also significantly elevated compared to the control water (Figure 3 and Table 1). The average ammonium-N concentration in the run-off water in the four winter feeding basins was 40.17 mg NH_4-N L^{-1} compared to the four control basins' average value of 0.33 mg NH_4-N L^{-1} (Figure 3). There was no significant difference in nitrate-N concentrations in water from the overwintering sites versus the control (Figure 4 and Table 1). The average nitrate concentration in snowmelt run-off from the four winter feeding basins was 0.25 mg NO_3-N L^{-1} and was 0.19 mg NO_3-N L^{-1} for the control basins (Figure 4). The lack of effect of winter feeding on nitrate concentration in runoff water is attributed to dominance of organic N, urea and ammonium in deposited cattle dung and urine (Barrow, 1987). Furthermore, cold temperatures would have limited the conversion of ammonium to nitrate in the process of microbial nitrification (Stark and Firestone, 1996). The nitrate found in the runoff water is likely to have been derived from what was originally present in the pasture soil. This explains the concentration of nitrate in the control and winter feeding runoff water being similar and low.

Table 1. ANOVA results for water ammonium-N (NH_4-N), nitrate-N (NO_3-N) and orthophosphate-P (PO_4-P) from control areas versus the winterfeed areas and the influence of time from the start of the snowmelt until the end of sampling (March 31 to April 19, 2009).

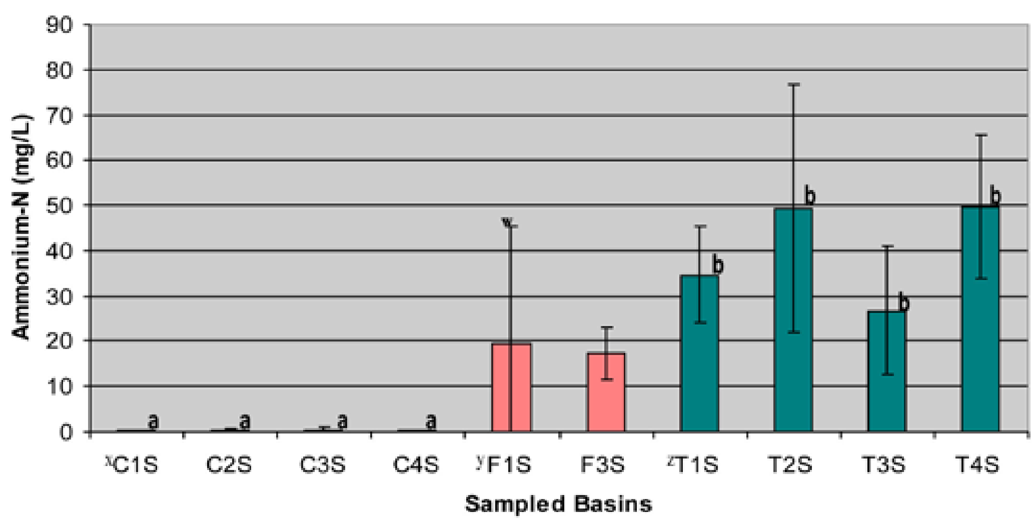
Fixed Factor	numDF[a]	denDF[b]	NH_4-N		NO_3-N		PO_4-P	
			F-value	P-value[c]	F-value	P-value[c]	F-value	P-value[c]
---------- ($\mu g\ mL^{-1}$) ----------								
Plot[d]	1	6	157.28	<.0001	3.824	0.0983	68.972	0.0002
Time	1	106	12.556	0.0006	33.157	<.0001	15.581	0.0001
Plot [d]*Time	1	106	7.7461	0.0064	0.0911	0.7634	10.360	0.0017

[a] Degrees of Freedom Numerator
[b] Degrees of Freedom Denominator
[c] Exact P-value ($P < 0.05$ significant difference)
[d] Control Plot (4 control basins) versus Winter feeding Plot (4 treatment basins)



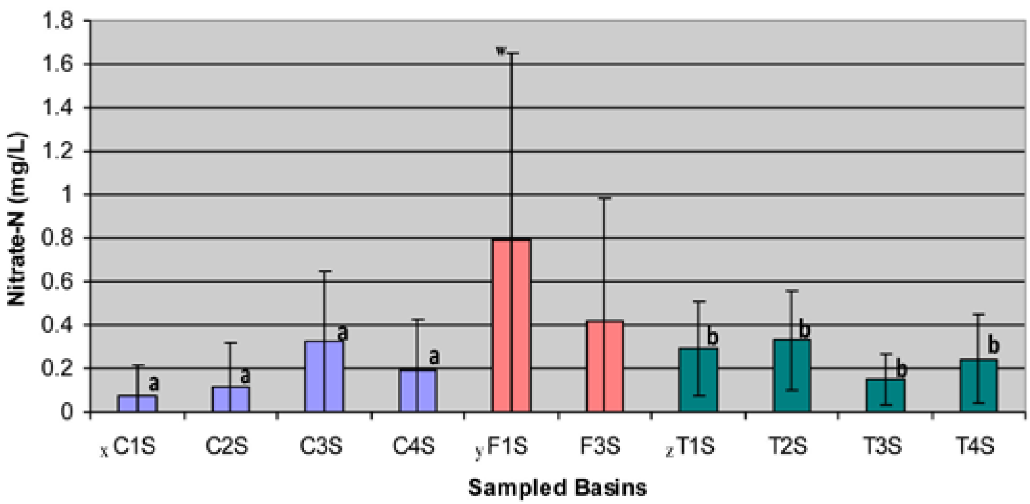
a,b Bars with same letter designation are not significantly different ($P < 0.05$)
w The bars denote standard deviation
x control basin
y farm yard basin
z treatment (winter feeding) basin

Figure 2. Average orthophosphate-P (SRP) concentration from surface runoff water 31 March to April 2009



a,b Bars with same letter designation are not significantly different ($P < 0.05$)
w The bars denote standard deviation
x control basin
y farm yard basin
z treatment (winter feeding) basin

Figure 3. Average ammonium-N (NH_4-N) concentration from surface runoff water 31 March to 19 April 2009



a,b Bars with same letter designation are not significantly different (P < 0.05)
w The bars denote standard deviation
x control basin
y farm yard basin
z treatment (winter feeding) basin

Figure 4. Average nitrate-N (NO_3-N) concentration from surface runoff water 31 March to 19 April 2009

Soil

There was no significant difference in water extractable phosphorus in the soil samples taken from winter feeding and control grids set up across the watersheds in May 2009 (Table 2 and Table 3). Water extractable phosphorus in the surface layer (0-10cm) of the soil was lower in the spring of 2009 than in the fall of 2008 for both control and winter feeding treatments. This likely reflects the rapid uptake of residual manure phosphate by the pasture grass roots and soil microbial populations in the spring when the soil warmed up. Soil nitrate-N had a similar trend to the run-off water nitrate-N, with no significant difference between the control and the winter feeding sites (Table 2 and Table 3). Similarly the soil nitrate-N was not significantly different between the fall and spring sampling. The soil nitrate-N decreased from fall to spring for the control site as was the case with the water extractable phosphorus (Table 2). Uptake of nitrate in spring by grass roots and soil microorganisms is an explanation for this decline. In the winter feeding site the soil nitrate-N did increase suggesting the onset of microbial nitrification, in which ammonium is converted to nitrate-N.

Table 2. Soil nutrient results from fall, 2008 and spring, 2009 sampling of nitrate and exchangeable nitrate

Plot	Nitrate			Water Extractable Phosphorus		
	Mean	Min	Max	Mean	Min	Max
Fall, 2008	------------------ ($\mu g\ g^{-1}$) ------------------					
Control	4.3^a	0.03	7.8	63.2^a	21.1	138.5
Winter feeding	3.8^a	0.4	8.6	60.0^a	19.2	244.7
Spring, 2009						
Control	3.2^a	0.5	9.0	36.5^b	5.2	91.2
Winter feeding	4.9^a	0.2	14.6	53.1^b	0.04	173.3

a,b Numbers within columns with same letter designation are not significantly different (P<0.05).

Table 3. ANOVA results for soil nitrate-N (NO_3-N) and water extractable phosphorus (PO_4-P) from control areas versus the winterfeed areas and the influence of season

Fixed Factor	numDF[a]	denDF[b]	Nitrate (NO_3-N)		Water Extractable Phosphorus (PO_4-P)	
			F-value	P-value[c]	F-value	P-value[c]
($\mu g\ g^{-1}$)						
Plot[d]	1	45	0.4511	0.5052	0.0920	0.7630
Season	1	47	0.0244	0.8765	32.570	<.0001
Plot*Season	1	47	5.6218	0.0219	2.129	0.1512

[a] Degrees of Freedom Numerator
[b] Degrees of Freedom Denominator
[c] Exact P-value ($P < 0.05$ significant difference)
[d] Control Plot (4 control basins) versus Winter feeding Plot (4 treatment basins)

CONCLUSION

Elevation of orthophosphate-P and ammonium-N concentrations in snowmelt runoff water from winter feeding sites indicates that these sites should be located in the landscape to avoid runoff water entering into sensitive surface water bodies. Similar nitrate-N concentrations in snowmelt runoff water from control and winter feeding sites may be explained by cool temperatures limiting microbial conversion of ammonium to nitrate. Lower water soluble soil phosphate in spring compared to fall is attributed to rapid plant and microbial uptake of phosphate in spring as the soil warmed and the pasture began early season growth. Early season growth may potentially reduce further losses from late spring snowstorms and rains when the feeding occurs on pastures with species that utilize nutrients early on in the spring.

There is potential for farmers to use cropped lands for winter feeding as well as pasture land. Future studies should consider looking at composition of snowmelt runoff water from winter feeding sites located on annual cropping land. It would also be beneficial to look at the composition of snowmelt runoff water for a number of years after the cattle winter feeding has stopped to determine how long the runoff water would be a potential source of nutrients.

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Evaluation of Cattle Bedding and Grazing BMPs in an Agricultural Watershed in Alberta

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Abstract

This paper highlights the environmental impacts of implementing beneficial management practices to address cattle bedding and direct access to the creek in a study watershed in southern Alberta, Canada. Approximately 35 cow-calf pairs grazed 194-ha of grass forage and had direct access to the creek in the spring and summer. During winter, the cattle were fed adjacent to the creek at an old bedding site. The practice changes included off-stream watering, bedding site relocation and fencing for rotational grazing. The cost was $15,225 and 60 hr of labour. Four years of data were used in a before-and-after experimental design to evaluate the practice changes. After two years of post-implementation monitoring, riparian assessments showed an increase in plant diversity, but no change in the percent cover of the riparian species *Salix exigua* and *Juncus balitus* and a decrease in *Carex* sp. (P<0.05). Water quality monitoring showed a decrease in the difference between upstream and downstream concentrations of total phosphorus, total dissolved phosphorus, total nitrogen, organic nitrogen and *Escherichia coli* (P<0.10). These results showed that improved environmental changes in riparian and water quality can be measured following the implementation of beneficial management practices for cattle bedding and grazing.

Keywords

Agricultural beneficial management practices; cattle grazing; environmental impacts; riparian assessment; water quality

INTRODUCTION

The effectiveness of beneficial management practices (BMPs) to address environment concerns under Canadian conditions is not well known, and only limited research on BMP effectiveness has been carried out in Alberta (Wuite and Chanasyk, 2003; Stuart et al., 2010). Livestock production is a significant component of the agricultural industry in Alberta and the adoption of BMPs related to environmental issues of livestock management has been of particular concern. This information is needed by producers to make management decisions, and for the development of land management policy. Previously published literature has highlighted the need for improved cattle grazing management near waterways. Many have shown that grazing, especially continuous grazing, corresponded with a flush of sediment, nutrients and *Escherichia coli* (*E. coli*) into nearby surface waters (McDowell, 2006; Sanjari et al., 2009). Cattle management BMPs such as off-stream watering and exclusion fencing have significantly decreased sediments, sediment-bound nutrients and bacteria concentrations (Sheffield et al., 1997; Trevisan et al., 2010; Webber et al., 2010).

A 6-yr Nutrient BMP Evaluation Project was initiated in 2007 to evaluate the environmental effectiveness and economic implications of BMPs at field and watershed scales in Alberta (Olson and Kalischuk, 2010). The project was focused in two agricultural watersheds; however, this paper will be limited to the Indianfarm Creek Watershed in southwestern Alberta. Complete information about the project can be found at Government of Alberta (2010).

The 14 500-ha Indianfarm Creek Watershed is in the Foothills Fescue Subregion (approx. at 49.43° N, 113.87° W). The 30-yr average (1971-2000) annual precipitation for the area is 515 mm (Environment Canada 2009) and estimated runoff is 78 mm (Bell, 1994). Indianfarm Creek is an ephemeral stream and often runs dry after July. Soils in the watershed are predominantly Typic and Entic Haplustolls with textures including clay, silty clay, clay loam and loam. The elevation gradient from the highest to the lowest locations in the watershed is about 500 m, with the land slope ranging from 2 to 9% (Olson and Kalischuk, 2010).

The purpose of this paper is to highlight the environmental impacts of implementing BMPs to address cattle bedding and direct access to the creek. In this paper, one of the ten BMP sites in the Indianfarm Creek Watershed, the Wintering (WIN) site, will be discussed. The WIN site was selected as a BMP site because of the close proximity of a winter bedding area to the creek. The location of the bedding site as a point source was considered as the main focus for BMP implementation. Livestock concentration areas have been shown to be significant point sources of nutrient pollution (Sanderson et al., 2010). In addition to the seasonal bedding area, continued direct access of the cattle to the creek was also a concern. Excess grazing in the riparian area has increased the erosion of the stream bank, and this occurred along the creek throughout the farm management unit.

METHODS

Description of the Wintering site

The WIN site (49.47° N, 113.86° W) consists of approximately 194 ha of pasture, which is part of a larger farm unit including annual crop land (Figure 1). Prior to BMP implementation, approximately 35 cows were wintered and fed from December through April at a bedding site, which was immediately adjacent to the creek. Calving occurred in late February to mid-March at corrals away from the creek. Cattle then used the old bedding site until late May when they were then moved to a pasture, which was distant from the creek, until the end of June. The 35 cow-calf pairs typically grazed the riparian pasture in July and August, accessing water from the creek. Following harvest (September to November), cattle grazed the crop stubble and continued to have access to the riparian pastures and water in the creek.

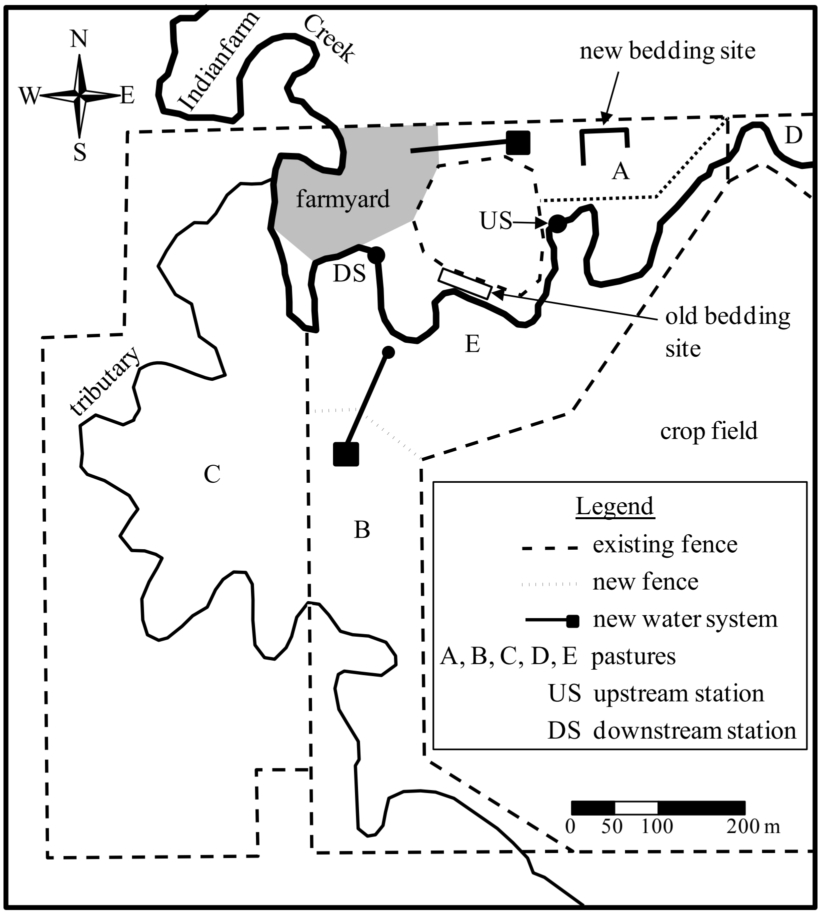

Figure 1. Schematic of the Wintering site along Indianfarm Creek showing the upstream and downstream water quality monitoring stations and the implemented BMPs including a new bedding site, fencing, new watering systems and pastures used for rotational grazing

BMP evaluation design and implementation

A before-and-after experimental design was adopted to evaluate BMPs in this study. The WIN site was first monitored for 2 yr under current management practices in 2007 and 2008 (pre-BMP phase). Then, the BMPs were implemented and monitoring continued for another 2 yr in 2009 and 2010 (post-BMP phase).

The BMPs were implemented at the WIN site in December 2008 and consisted of two main practice changes: (1) relocation of the bedding site and (2) rotational grazing to control access to the riparian area and the creek.

Bedding site relocation. The manure pack at the old bedding site was removed. A new site was constructed away from the creek in a location that was level and accessible from the farmyard (Figure 1). The new bedding site was moved about 200 m north of the old bedding site and on top of the creek bank, about 5 m higher than the creek. The new construction consisted of a permanent windbreak, barbed-wire fencing and an off-stream watering system. The new watering system was an extension from the existing water system in the farmyard.

Rotational grazing. To limit grazing in the riparian pasture and direct access to the creek, additional barbed-wire fences were installed to create three new pastures: Pastures A, B and E. Pasture B was created by the construction of a barbed-wire fence south of the creek (Figure 1) and water was provided with a solar-powered, off-stream water system. The two existing pastures (Pastures C and D), a nearby crop field and the three new pastures were used to implement a rotational grazing and feeding plan. Cattle rotations followed a dynamic schedule in 2009 and 2010 and by using the new A and B pastures, cattle access to the creek was reduced by about 150 days per year (Table 1), compared to the pre-BMP rotations.

The total cost for BMP implementation and maintenance was $15,225 and 60 h of labour. Economic assessment is part of the overall project; however, this component will not be discussed in this paper and the focus will be on riparian vegetation and water quality.

Table 1. Rotations of approximately 35 cow-calf pairs within the five pastures created post-BMP implementation at the Wintering site in 2009 and 2010

2009		
Date	**Days**	**Pasture**
Jan 1–May 11	131	A
May 11–Jun 6	26	B
Jun 6–Jul 11	35	C
Jul 11–Jul 25	14	E
Jul 25–Aug 20	26	B & D
Aug 20–Aug 27	7	E
Aug 27–Sep 19	35	D
Sep 30–Nov 1	30	E & crop field
Nov 1–Dec 31	60	C, B & crop field

2010		
Date	**Days**	**Pasture**
Jan 1–May 15	135	A
May 15–May 25	10	B
May 25–Jun 13	19	C
Jun 13–Jul 27	44	D
Jul 27–Aug 10	14	E
Aug 10–Aug 15	5	B
Aug 15–Sep 18	34	C
Sep 18–Sep 24	6	E
Sep 24–Oct 1	19	D
Oct 1–Oct 20	19	D & crop field
Oct 20–Oct 25	5	A
Oct 25–Oct 26	1	E
Oct 26–Nov 16	21	C & crop field
Nov 16–Dec 31	14	A, E & crop field

Wintering site BMP evaluation

Riparian vegetation. Twenty-four transects bisecting upland, transitional and riparian zones were established in June 2008 at the WIN site, within Pasture E (Figure 1). The transects were arranged in 12 pairs, with a transect on either side of the creek for each pair. The lengths of the transects ranged approximately from 5 to 35 m since the distance between the upland and the edge of the creek was variable. A random sub-set of eight transects were re-sampled in June 2009 and 2010, ensuring transects were paired. Species were identified within 1- by 1-m quadrats placed every 2 m along the transects. The percent cover of each species within each quadrat was recorded. The Wilcoxon signed rank test (Wilcoxon, 1945) was used to compare percent cover within quadrats for three riparian species (*Salix exigua*, *Carex* sp. and *Juncus balticus*) from 2008 to 2009 and 2008 to 2010. The Shannon Diversity Index (Shannon, 1948) was also used to show annual diversity in transects.

Water Quality. Water quality was monitored at the upstream and downstream stations (Figure 1). Monitoring stations were instrumented with Isco 6712 automated samplers (Teledyne Isco, Lincoln, Nebraska) set to sample in response to a rise in flow. In addition, the upstream and downstream stations were regularly grab-sampled as part of a watershed-wide sampling schedule. Flow was monitored at the upstream station using a Level Troll 700 (In-Situ Inc., Fort Collins, Colorado).

Samples were analyzed for total and total dissolved phosphorus (TP, TDP), total nitrogen (TN), nitrate-nitrogen (NO_3-N), nitrite-nitrogen (NO_2-N), ammonia-nitrogen (NH_3-N), total suspended solids (TSS), electrical conductivity (EC), and *E. coli*. Organic N (ON) was determined as the difference between TN and NH_3-N, NO_2-N and NO_3-N.

Statistical analyses of the water samples were completed using SAS (SAS Institute Inc., 2003). Water quality parameters were compared between the upstream and downstream stations using samples that were collected with similar methods on the same day at both stations. Since water quality concentrations at the two stations were not independent of one another, a single population was created by subtracting the upstream concentration from the downstream concentration to create a difference value for each sampling day. Statistical comparisons were made by comparing these differences for each event type and all events combined between the pre-BMP and post-BMP phases. Event types included snowmelt runoff, which typically occurred in March and April with flows of 0.2 to 0.6 $m^3 s^{-1}$; rainfall runoff, which usually occurred in May and June with flows of 0.4 to 50 $m^3 s^{-1}$; and base flows of 0 to 0.3 $m^3 s^{-1}$, which occurred when there was no runoff, typically from July through February. The Univariate procedure was used to test the distribution of the data and the Means procedure was used to generate descriptive statistics. The pre- and post-BMP implementation upstream-downstream differences were tested using the Least Squared Means test in the Mixed procedure with variance components as the variance structure, and the repeated and pdiff options. For the water quality analyses, a significance level of $P<0.10$ was used.

RESULTS AND DISCUSSION

Riparian vegetation

Two years after BMP implementation, there were some observed differences in riparian vegetation. If the BMPs were successful, it was expected that the frequency and the cover of riparian species could potentially increase. However, there were no significant changes in the percent cover within quadrats for the three species examined (*S. exigua, J. balti*cus and *Carex* sp.) from 2008 to 2009 (Wilcoxon value (W_+) = 0.315 to 0.535, $P = 0.593$ to 0.792). Similarly, percent cover of *S. exigua* and *J. balti*cus did not change from 2008 to 2010 ($W_+ = -1.787$ to 1.342, $P = 0.074$ to 0.180); whereas, there was a significant decrease in the percent cover of *Carex* sp. from 2008 to 2010 ($W_+ = -2.097$, $P = 0.036$).

For some species, average percent cover and the number of quadrats they were present in appeared to decrease between pre- and post-BMP phases, particularly *Agropyron dasystachyum* (Northern wheatgrass), *Elymus repens* (Quackgrass) and *Poa pratensis* (Kentucky bluegrass) from 2008 to 2010 (Table 2). The decrease of the native species *A. dasystachyum* is undesirable. However, the decrease in the average percent cover of *E. repens* and *P. pratensis* was positive in that non-native species, such as these, are ineffective at stabilizing creek banks (Hale et al., 2005).

Vegetation diversity increased along several transects at the WIN site from 2008 to 2009 as well as from 2008 to 2010 with the greatest increases in the first post-BMP year of 2009 (Table 3). These changes in the plant community were related to the adoption of the rotational grazing BMP and the wet weather conditions in 2008 (644 mm total precipitation) and 2010 (667 mm total precipitation). Higher diversity has been found to increase the efficiency of resource use and ecosystem resilience during environmental temporal variability (Chapin et al., 2002), and provide habitat for more species and control erosion (Pimentel et al., 1992).

Table 2. Riparian transect comparison at the Wintering site using average percent (%) cover ± standard error (SE) and the number (#) of quadrats where each species was present. The pre-BMP year (2008) was compared to each post BMP year (2009 and 2010) utilizing a different subset of 8 transects each year

	Pre-BMP (2008)[z]		Post-BMP (2009)		Pre-BMP (2008)[z]		Post-BMP (2010)	
Species	% cover ± SE	# quadrats[y]	% cover ± SE	# quadrats[y]	% cover ± SE	# quadrats[x]	% cover ± SE	# quadrats[x]
Agropyron dasystachyum	7 ± 2	3	14 ± 5	11	21 ± 9	7	1	1
Bromus inermis	42 ± 4	30	39 ± 4	35	37 ± 3	45	34 ± 3	48
Carex sp.	17 ± 7	3	14 ± 6	6	8 ± 3	12	5 ± 1	2
Elymus repens	33 ± 9	6	29 ± 16	6	28 ± 5	9	9 ± 4	7
Juncus balticus	5	1	6 ± 4	3	0	0	2 ± 1	2
Poa pratensis	18 ± 4	20	23 ± 4	25	31 ± 4	28	14 ± 2	42
Rosa acicularis	13 ± 3	30	11 ± 3	26	12 ± 2	43	7 ± 1	50
Salix exigua	19 ± 6	8	22 ± 6	8	12 ± 2	5	5 ± 0	3
Solidago canadensis	14 ± 12	6	7 ± 2	7	9 ± 6	7	7 ± 1	21
Symphoricarpos occidentalis	35 ± 4	32	34 ± 4	37	29 ± 3	47	24 ± 3	52
Taraxacum officinale	12 ± 4	17	5 ± 1	29	5 ± 1	27	4 ± 1	34

[z] The pre-BMP year (2008) was compared to each post-BMP year (2009 and 2010) utilizing a different subset of 8 transects each year.
[y] Total number of quadrats was 46 in 2008 and 41 in 2009.
[x] Total number of quadrats was 62 in 2008 and 59 in 2010.

Table 3. Shannon Diversity Index (H) value for Wintering site individual transects measured in 2008,2009 and 2010[z]

Transect	H-value 2008	H-value 2009	H-value 2010	Difference
1a	2.99		2.80	- 0.19
1b	2.65		2.85	+ 0.20
3a	2.70	2.18		- 0.52
3b	2.24	2.90		+ 0.66
5a	1.99	2.12		+ 0.13
5b	2.11	2.21		+ 0.10
6a	2.61		2.46	- 0.15
6b	2.55		2.95	+ 0.40
7a	1.91	2.06		+ 0.15
7b	2.48	2.45		- 0.03
9a	2.07	1.97		- 0.10
9b	2.71	2.71		No change
10a	2.79		2.74	- 0.05
10b	2.49		2.50	+ 0.01
12a	1.98		2.22	+ 0.24
12b	2.42		2.67	+ 0.25

[z] Blank cells indicate the transect was not measured in that year. Transects labelled ‘a’ were on the north side of the creek while those labelled ‘b’ were on the south side.

Water quality

The influence of weather variability on water quality was generally predictable. The pre-BMP years were drier than the post-BMP years with total precipitation of 339 mm in 2007, 644 mm in 2008, 561 mm in 2009 and 667 mm in 2010 (Olson and Kalischuk, 2010; Environment Canada, 2011). Based on precipitation alone, it would have been expected that concentrations in the post-BMP years would have been higher as water quality concentrations in Alberta streams tended to increase in wetter climates and in wetter years (Lorenz et al., 2008). Overall TN, TP, and TSS concentrations tended to be higher in the post- than pre-BMP years, although this trend was not consistently observed throughout the years nor was this trend observed at the downstream station for TSS (Table 4 and 5). The overall *E. coli* concentrations were lower in the post- than pre-BMP years.

Surface water quality showed significant decreases in *E. coli* and certain nutrient concentrations (TN, ON, TP, PP) from pre- to post-BMP phases when comparing the downstream to upstream differences, indicating the BMPs were effective at improving water quality (Tables 4 and 5). These significant changes did not occur year-round, but were often specific to rainfall, snowmelt or base flow.

The difference in *E. coli* concentration between stations during the post-BMP snowmelt events was significantly less compared to the pre-BMP phase (Table 4). The change in *E. coli* concentration differences may have resulted from the relocation of the bedding area and installation of fences as cattle no longer had direct access to the stream during periods of snowmelt. Although the differences between *E. coli* concentrations from upstream to downstream stations appeared to decrease in the post-BMP phase during other events (e.g., rainfall and base flow), this decrease was not significant.

The pre- and post-BMP comparison of the differences between the downstream and upstream concentrations of TN and ON were significant during base flow events (Table 4). As ON was a large fraction of TN, the significant reduction in the ON accounted for similar differences in TN. The reduction of ON may have related to the rotational grazing BMP as the cattle had less direct access to the stream during base flow conditions (July through February) in the post- versus pre-BMP phases.

There was a significant reduction in the downstream-upstream differences from pre- to post-BMP in TP and PP concentrations during rainfall events (Table 5). Particulate P was a large portion of TP during rainfall events. Similar to the influence of ON on TN, the high PP fraction resulted in a significant decrease in TP concentration differences. The reductions of PP could be related to management changes, including the relocation of the old bedding site, which previously contributed to surface runoff during rainfall. The new bedding site was never observed contributing to the creek, even during the very wet year of 2010.

The bedding site relocation and rotational grazing BMPs resulted in the relocation of the pollution source (cattle and manure) and hence, nutrients and *E. coli* away from the creek. The reduction of sediment bound nutrients following the removal of cattle has been reported in other studies (Sheffield et al., 1997). By the design of our study, the relative contributions of the individual BMPs cannot be separated, particularly between the practices that addressed a point source (i.e., removal of the bedding site) and the practices that addressed a non-point source (i.e., direct access along the creek). Both source types exist throughout the Indianfarm Creek Watershed. Often, multiple BMP practices are required at individual sites.

Table 4. Pre- and post-BMP comparisons of average nitrogen and *Escherichia coli* concentrations between downstream and upstream water quality monitoring stations at the Wintering site[z]

	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**
	-- (mg L^{-1}) --								**MPN 100 mL^{-1}**	
	Rainfall (n=5 pre, 27 post)									
Downstream	3.42	2.75	3.06	1.42	0.21	1.22	0.12	0.09	3726	1552
Upstream	2.88	2.78	2.52	1.51	0.21	1.14	0.12	0.10	2329	1031
Difference[y]	0.54	-0.03	0.54	-0.09	0	0.07	0	-0.01	1397	521
	Snowmelt (n=15 pre, 21 post)									
Downstream	1.11	1.52	0.91	1.28	0.09	0.09	0.08	0.13	78	16
Upstream	0.95	1.80	0.77	1.56	0.09	0.09	0.06	0.13	31	15
Difference	0.17	-0.28	0.14	-0.28	0	0	0.02	0	47a	1b
	Base flow (n=6 pre, 18 post)									
Downstream	1.24	0.90	1.16	0.76	0.03	0.08	0.03	0.03	249	92
Upstream	1.17	0.91	1.09	0.77	0.03	0.09	0.03	0.03	242	147
Difference	0.07a	-0.01b	0.07a	-0.01b	0	-0.01	0	0	7	-55
	All events (n=26 pre, 66 post)									
Downstream	1.59	1.86	1.38	1.19	0.10	0.55	0.08	0.09	916	665
Upstream	1.37	1.96	1.18	1.32	0.10	0.52	0.06	0.09	586	467
Difference	0.21a	-0.11b	0.20a	-0.13b	0	0.03	0.01	0	330	198

[z] TN = total nitrogen, ON = organic nitrogen, NO_3-N = nitrate nitrogen, NH_3-N = ammonium nitrogen, *E. coli* = *Escherichia coli.*
[y] Differences between the pre- and post-BMP per parameter and event type that are followed by letters are significantly different at P<0.10.

Table 5. Pre- and post-BMP comparisons of average phosphorus, total suspended solids, and electrical conductivity concentrations between downstream and upstream water quality monitoring stations at the Wintering site[z]

	Pre	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**	**Pre**	**Post**
	-- (mg L^{-1}) --								**(μS cm^{-1})**	
	Rainfall (n=5 pre, 27 post)									
Downstream	0.61	0.52	0.10	0.20	0.52	0.32	725	189	500	492
Upstream	0.52	0.69	0.10	0.16	0.42	0.53	597	331	515	482
Difference[y]	0.09a	-0.16b	0	0.04	0.10a	-0.21b	127	-142	-15	10
	Snowmelt (n=15 pre, 21 post)									
Downstream	0.09	0.26	0.03	0.13	0.06	0.13	29	73	705	502
Upstream	0.07	0.25	0.03	0.13	0.04	0.12	26	66	685	502
Difference	0.02	0.01	0	0	0.02	0.01	3	7	20a	0b
	Base flow (n=6 pre, 18 post)[x]									
Downstream	0.11	0.08	0.04	0.01	0.074	0.067	32	35	523	563
Upstream	0.11	0.08	0.04	0.01	0.070	0.067	31	32	520	559
Difference	0	0	0	0	0.005a	-0.001b	1	3	4	4
	All events (n=26 pre, 66 post)									
Downstream	0.20	0.32	0.05	0.13	0.15	0.19	164	110	624	515
Upstream	0.17	0.38	0.05	0.11	0.12	0.27	137	165	614	509
Difference	0.03	-0.06	0	0.02	0.03a	-0.08b	27	-55	10	5

[z] TP = total phosphorus, TDP = total dissolved phosphorus, PP particulate phosphorus, TSS = total suspended solids, EC = electrical conductivity.
[y] Differences between the pre- and post-BMP per parameter and event type that are followed by letters are significantly different at P<0.10.
[x] Three decimal places were used for particulate phosphorus to show the significant difference.

CONCLUSIONS

After 4 yr of this 6-yr study, conclusions were:

- Mitigating the impacts of the bedding area and direct cattle access to the creek cost $15,225 and 60 hr of labour, which involved readily available cattle distribution tools including fencing, off-stream watering and rotational grazing with appropriate timing to reduce cattle impact on the riparian and water resources.
- The rotation of cattle and subsequent decrease in the number of days cattle spent grazing in the riparian pasture may have improved the vegetative diversity.
- The relocation of the winter bedding site and the reduction of cattle access to the creek likely resulted in decreased average concentrations of *E. coli*, TN, ON, TP and PP.
- Environmental changes in riparian species and diversity and water quality were measured following the implementation of BMPs for cattle bedding and grazing, and results suggested improved environmental quality.

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3 MANAGING NUTRIENTS IN FRESHWATER SYSTEMS

Managing Lakes and their Basins for Sustainable Use: Biophysical Characteristics of Lakes

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Abstract

Lakes and their basins exhibit many biophysical characteristics that are widely studied by various disciplines. The characteristics include basin type, origin and age, climate, salinity, mixing and stratification, species composition, and productivity. From a management point of view, the above features are classified into three broad characteristics, which, all put together, uniquely characterize lakes as lentic (standing or hydrostatic) water systems that are different from all other water bodies. The three characteristics are: 1) long retention time, 2) integrating nature, and 3) complex response dynamics. These three characteristics have significant management implications for lakes. This paper addresses sustainable management of lakes from the point of view of Integrated Lake Basin Management (ILBM). It is argued that the departure point for lake management should be the proper understanding of the biophysical characteristics of lake ecosystems, the interactions between the lake ecosystems and humanity through provision of ecosystem services, and the necessary management measures as dictated by the lake characteristics and the ecosystem-human interactions.

Keywords

Ecosystem services; Integrated Lake Basin Management (ILBM); lentic water systems; world lakes

INTRODUCTION

The importance of lakes needs not be emphasized. Lakes hold more that 90% of all the liquid freshwater that is readily-available on the earth's surface. Lakes provide an important source of water for a wide range of uses such as domestic, industrial, irrigation, fisheries and hydropower. Also, in themselves, lakes are important ecosystems that support a large proportion of the world's biodiversity. It is therefore no wonder that many civilizations have evolved around lakes throughout human history. The development, use and conservation of lakes is thus an issue of major concern at both local and global levels.

It comes as no surprise that the immense value of lakes and hence the many uses to which lakes and their basins are put, combined with the inherent nature of lakes as “sinks”, result in many stresses on lakes that threaten their sustainable use. Globally, the condition of lakes has been deteriorating (Ballatore and Muhandiki, 2002; ILEC, 2005, 2007; Muhandiki and Ballatore, 2007). Table 1 shows problems identified at 28 case study lake basins in a recent global study the state of world lakes (ILEC, 2005). As shown in Table 1, many of the problems facing lakes originate from the basins. It may be said that among all water bodies, lakes are perhaps the most vulnerable to stresses because of the wide range of uses that lakes offer compared to other water bodies. The question that arises is “how then can we manage these very vulnerable water bodies?” This paper addresses this question from the point of view of Integrated Lake Basin Management (ILBM). It is argued that the departure point for lake management should be the proper understanding of the biophysical characteristics of lake ecosystems, the interactions between the lake ecosystems and humanity through provision of ecosystem services, and the necessary management measures as dictated by the lake characteristics and the ecosystem-human interactions. This understanding should provide the fundamental guiding principles for lake management.

Table 1. Summary of problems affecting 28 case study lake basins (ILEC, 2005)

	In-lake					Littoral				Basin origin							Regional/ Global		
Lake Basin	Unsustainable fishing practices	Introduced faunal species	Salinity changes	Weed infestations	Nutrients from fish cages	Shoreline effluent discharges	Shoreline industrial discharges	Shoreline water extraction	Loss of wetlands	Excess sediment inputs	Non-point source nutrients	Agro-chemicals	Water abstraction	Changes in run-off	Effluent and stormwater	Industrial pollution	Atmospheric nutrients	Atmospheric industrial contaminants	Climate change
Aral Sea			→						→				→						
Baikal						↓	→			↓								→	
Baringo	→									↓			↓	↓					↓
Bhoj Wetland				→		→	↓			→	→	→			→				
Biwa									↓		→	→	↑ [2]		↑				↓
Chad									↓	↓			↓						↓
Champlain						↑					↑				↑			→	
Chilika Lagoon			↑	↑						↓	↓	↓	↓		↓				
Cocibolca/Nicaragua						↓				↓		↓			↓				
Constance		↓				↓			→		→	→			→				
Dianchi					↑	→	→		↓	↓ [3]	↓ [3]	↓ [3]	↓		↓			→	
Great Lakes (N. American)		↓				↑	↑				↓	↓			↑	→		→	
Issyk-Kul		→								↓	↓	↓				↓ [4]			↓
Kariba Reservoir					↓	→					↓								↓
Laguna de Bay	→	↓	→	→	↓	→	→			↓	↓				↓	→			
Malawi/Nyasa	↓ [5]			↓						↓	↓	↓		↓	↓		↓		↓
Naivasha	↑	→		↑		↓		→	→	↓							↓		
Nakuru										→	→		↓	↓	↓				
Ohrid	→	↓				→	↓		↓	↓	↓	↓			↓				
Peipsi/Chudskoe	↓			→		→					→ [6]				↓	→ [6]			
Sevan	↓	↓				↓			↓	↓			↓						
Tanganyika	↓ [5]					↓	↓			↓					↓				↓
Titicaca		↓				→	↓			↓					↓	↓			
Toba	↓	↓		↓	↓	→			↓	→	→	↓	↓	→	↓		↓		
Tonle Sap	↓	↓								↑ [7]					↓				
Tucurui Reservoir				→						→									
Victoria	→	↓ [8]		↑		↓	↓		↓	↓	↓				↓	↓ [4]	↓		
Xingkai/Khanka	↓					→	→		↓	↓		↓			↓	↓ [9]			
Total Occurrences	12	11	3	9	4	18	10	1	11	21	16	12	9	4	19	7	4	4	7

Legend — A ↓ symbol means that the problem is not improving significantly; a → symbol means that it has improved somewhat; and a ↑ symbol means that there has been significant improvement.

1 — The lake briefs are not exhaustive in their description of problems; a blank cell in the table does not mean that the lake does not experience the problem. In many lake briefs, there is only limited information on the extent of improvement of a problem; the direction of change shown in the table is based on this information.

2 — Most water abstraction for Kyoto/Osaka/Kobe is downstream of Lake Biwa.

3 — Despite considerable investment, nutrient and chemical concentrations in Lake Dianchi have yet to show improvements. There is some evidence that COD is improving.

4 — Mining in the basin is the source of toxic chemicals reaching the lake.

5 — Includes loss of fish biodiversity through overharvesting for aquarium trade.

6 — Improvements in the nutrient and pollutant status of the lake are the result of a decline in use of nutrients in agriculture and industrial production following the collapse of the Soviet Union rather than from a deliberate policy intervention.

7 — There is a large amount of sediment deposited around Tonle Sap each year, but this is regarded as an essential service rather than as a problem.

8 — Introduced species, particularly Nile perch and Nile tilapia, have contributed to the loss of many native species as well as providing a valuable source of income for the regional community. Here they have been assessed for their effect on the lake's biodiversity.

9 — High copper (Cu) concentrations are recorded in Lake Xingkai/Khanka, but the origins are unknown.

Like many other natural systems that exist with or without the presence of human beings, lakes as ecosystems exhibit a wide range of biophysical characteristics that dictate their functioning. Any attempt by human beings to successfully "manage" lakes therefore would necessarily have to be informed by these dictating features. From a management point of view, the features have been conveniently classified into three broad characteristics, which, all put together, uniquely characterize lakes as lentic (standing or hydrostatic) water systems that are different from all other water bodies (ILEC, 2005, 2007; RCSE and ILEC, 2010). The three characteristics are: 1) integrating nature, 2) long retention time, and 3) complex response dynamics. These three characteristics have significant management implications for lakes and therefore their proper understanding is essential for any lake management program.

With the above three characteristics of lakes as the departure point, the International Lake Environment Committee Foundation (ILEC), based in Japan on the shores of Lake Biwa, in collaboration with many other organizations globally, has been promoting ILBM as a scientifically-sound integrated approach to lake basin management (ILEC, 2007; Muhandiki, 2008; RCSE and ILEC, 2010). ILBM is a way of thinking (conceptual framework) that assists lake managers and stakeholders to manage lakes and their basins in a sustainable manner. The ILBM framework identifies six important pillars of lake basin governance that must be continuously improved to achieve the goal of sustainability. The six pillars are institutions, policies, technology, information and science, participation, and finance. The ILBM framework emphasizes the need to consider the three biophysical characteristics of lakes and the need to focus on maintenance of ecosystem regulating services as a basis for ensuring the continuity of other categories of ecosystem services provided by lakes.

The aim of this paper is to introduce the current thinking on ILBM as a concept for sustainable management of lakes and their basins. The next section introduces the three key features that characterize lakes as lentic water systems and the corresponding implications of the features for lake management. Next, land-water-ecosystem linkages and the ecosystem services concept are introduced. Attention is then focused on the ILBM framework whose departure point is the three characteristics of lakes and the ecosystem services concept. The paper concludes with final observations. The focus of this paper is obviously broader in scope than diffuse pollution concerns, but the concepts introduced are equally applicable to addressing the subject.

CHARACTERISTICS OF LAKES

Lakes and their basins exhibit many biophysical characteristics that are widely studied by limnologists, hydrologists and engineers, among others. Among these features, those with major implications for the use and management of lakes include basin type, origin and age, climate, salinity, mixing and stratification, species composition, and productivity. From a management point of view, the above features are conveniently classified into three broad characteristics, which, all put together, uniquely characterize lakes as lentic (standing or hydrostatic) water systems that are different from all other water bodies. The three characteristics are: 1) integrating nature, 2) long retention time, and 3) complex response dynamics (ILEC, 2005, 2007; RCSE and ILEC, 2010). These three broad features make lakes perhaps the most delicate and difficult water systems to manage. These features have significant management implications for lakes and therefore their proper understanding is essential for lake management. They should be the starting point for any lake intervention program. The three characteristics are described below and summarized in Table 2.

Integrating nature

Lakes are generally located in depressions at the end of the land surrounding them (drainage basin). As a consequence, lakes receive all kinds of inputs from the drainage basin and beyond in the form of direct precipitation on the lake surface, surface flows in rivers and channels, ground water flows, heat- and wind-induced energies that cause waves; thermal energies that affect mixing properties; and land-based and airborne materials, nutrients, and organic substances, both living and nonliving matter (ILEC, 2005). Ironically, depending on the major human values of the lake, the inputs are considered as resources (such as water and fish) or problems (such as pollutants and invasive species). Integrating nature refers to the mixing of inputs within a lake, consequently disseminating both resources and problems throughout the whole volume of a lake. From the point of view of "problem" inputs, their dissemination means that problems are "diluted" over the whole lake and therefore it takes time before they accumulate to levels at which they become visible problems needing management intervention (see also long retention time discussed below). Unfortunately, in most cases, it is often too late to take action by the time the problems become visible.

For lake management, the implications of integrating nature of lakes are that lakes are intrinsically connected to their drainage basin, and that both lake resources and lake problems are shared throughout the lake. Consequently, a lake and its basin have to be managed as one unit irrespective of any boundaries that may exist in the lake and basin, be they political, administrative or social. This is often particularly a big challenge in transboundary lakes and lake basins which are shared by more than one country and therefore whose management requires cooperation of all the countries.

Table 2. Three key characteristics of lakes as lentic water systems

Characteristic	Description	Management implication
Integrating nature	Mixing of inputs (which could be resources or problems) within a lake, consequently disseminating both resources and problems throughout the whole volume of a lake	Lake resources and lake problems are shared throughout the lake A lake and its basin have to be managed as one unit irrespective of boundaries in the lake or basin
Long retention time	Theoretical average time water spends in a lake (it is long for lakes)	Need for long-term institutional and financial commitments
Complex response dynamics	Non-linear response of lakes to changes	Lakes are unpredictable and uncontrollable therefore problems must be anticipated in advance

Long retention time

Retention time refers to the theoretical average time water spends in a lake after entering it and is calculated by dividing the volume of a lake by the total annual inflow or outflow of water into or out of the lake. Long retention time of lakes is a direct result of their process of formation. Lakes are formed by accumulation of water over a long time in depressions at the end of drainage basins. Because lakes have the capacity to accumulate large volumes of water in comparison to the annual flows, the retention times are long. Thus, compared to lotic (moving) water systems like rivers, lakes have long retention times, ranging from a few years (such as 5.5 years for Lake Biwa in Japan) to hundreds of years (such as 1,340 years for Lake Titicaca in Bolivia/Peru). Long retention time gives lakes a large buffer capacity to hold water and pollutants (both resources and problems as discussed above) for a long time. The ability to hold water for a long time means that lakes provide an important storage of water both in times of floods when there are increased flows and in times of drought when there are reduced flows. However, on the other hand, long retention times mean that pollutants build up slowly and stay in lakes for very long times. This means that response of lakes to remedial measures against pollutants takes very long. Long retention times also allows for development of unique and complex ecosystems in lakes. These unique and complex ecosystems may be vulnerable to threats related to long holding times of pollutants in lakes.

The management implication of long retention time is the need for long-term commitments. Problems in lakes build up slowly and take time before they become noticeable, and addressing the problems equally takes long. Lake managers therefore have to be continuously engaged in activities to address lake problems. This calls for long-term institutional and financial commitments.

Complex response dynamics

Complex response dynamics refers to the non-linear response of lakes to changes, in part due to their long retention times and also due to the fact that lakes are not only controlled by physical and chemical processes but also biological process. Examples of complex response dynamics in lakes include biomagnification of toxic chemicals through the food chain and hysteresis behaviour of the trophic status of lakes in response to changes in nutrient concentration. Once the condition of a lake reaches critical levels (e.g. as measured by the level of toxic chemicals in fish or trophic status) restoration of the lake is not achieved by simply reducing or eliminating the inflow of the culprit inputs.

The management implication of complex response dynamics is that lakes are indeed complex ecosystems that are unpredictable and uncontrollable and therefore problems must be anticipated well in advance. This calls for the application of the precautionary principle whenever our understanding of the lake issues is limited (which is often the case). In addition, it calls for continuous development of the knowledge base to understand the complexity of lake ecosystems, through monitoring and scientific studies.

LAND-WATER-ECOSYETM SERVICES LINKAGES

Human life is highly dependent on resources and processes provided by natural ecosystems. These resources and processes are provided by nature essentially free-of-charge and are referred to as ecosystem services. Lakes are an important component of the earth's ecosystem and they provide a wide range of ecosystem services such as water, fish, hydropower, flood and drought regulation, nutrient cycling, aesthetic and scenic values, and educational resources. As was noted in the previous section, lakes are intrinsically linked to their drainage basins. This necessarily implies that ecosystem services provided by lakes are likewise interlinked with the terrestrial ecosystem services provided by the drainage basins. For example, erosion regulation or water regulation provided by vegetation on land have direct bearing the quality and quantity of water in lakes and hence the water provisioning service of lakes. A consideration of ecosystem services provided by lakes cannot therefore be done in isolation of those provided by its drained basin. The consideration of ecosystem services is essential in lake management because of the growing concern that over-exploitation of ecosystem services is compromising the integrity of ecosystems globally, including lake ecosystems. It is not an easy task, however, because land-water-ecosystem linkages are complex since the interactions occur in different spatial and temporal scales.

The 2004 United Nations Millennium Ecosystem Assessment (MEA) provides a useful framework to analyze ecosystem services (MEA, 2005). In the MEA framework ecosystem services are conveniently classified into the following four categories: 1) Provisioning services such as food, water, timber and fiber; 2) Regulating services such as air quality regulation, climate regulation, water purification and waste treatment, and erosion regulation; 3) Cultural services such as spiritual and religious values, aesthetic values, recreation and ecotourism; 4) Supporting services such as soil formation, photosynthesis, and nutrient cycling. It is worth noting that the provisioning services are often valued in monetary terms while the other three categories of services are not easy to value in this way. The result is that the true value of the latter categories of services is often not duly considered in lake basin management. Put otherwise, the general tendency is to over-exploit resource provisioning services provided by lakes and their basins. This over-exploitation is often accompanied by degradation of the other three categories of services, especially the regulating services. Although the degradation is slow as discussed in the previous section (characteristics of lakes), over a long time it can build up to critical levels involving the eventual loss of all the four categories of ecosystem services.

The loss of ecosystem services described above illustrates a case of unsustainable lake basin resource development, which, unfortunately, seems to be the case at many lake basins today as illustrated by the many problems identified in the recent global study on lakes referred to above (Table 1). If sustainability is to be ensured, it calls for a paradigm shift from provisioning services driven lake basin resource development to development that aims at meeting current and future provisioning services needs of lakes and their basins while at the same time not compromising the integrity of the regulating, cultural and supporting services. To this end, it is proposed that attention should be focused on the regulating services of lake basins as a basis for ensuring the continuity of the provisioning and cultural services. In addition, by focusing on the regulating services, and satisfying the required management needs associated with such services, it is proposed that the integrity of the ecosystem supporting services can be maintained. Sustainable lake basin management may therefore be considered as management that ensures maintenance of lake and basin ecosystem services, particularly ecosystem regulating services (Figure 1). This is the ILBM approach that is discussed in the next section.

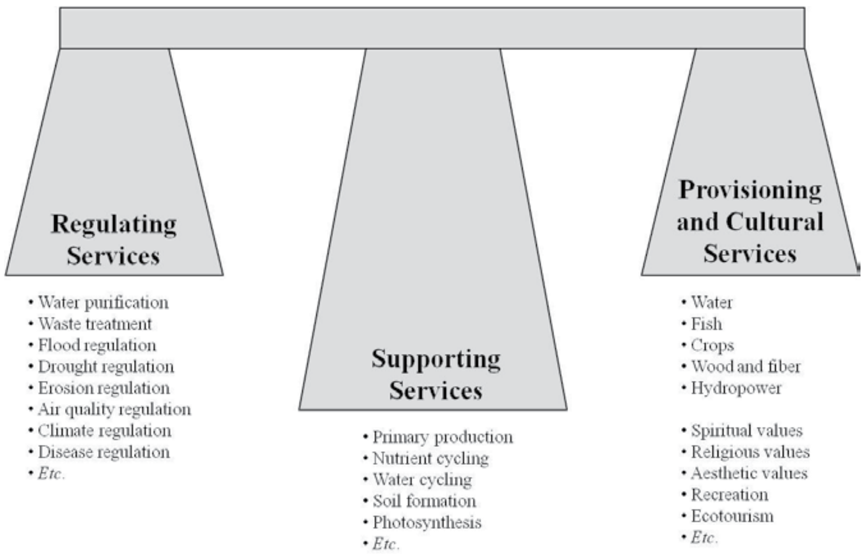

Figure 1. Ecosystem services provided by lakes and their basins

INTEGRATED LAKE BASIN MANAGEMENT FRAMEWORK

The Integrated Lake Basin Management (ILBM) framework was developed in a recent global study on lake basin management (ILEC, 2005). ILBM is a way of thinking (conceptual framework) that assists lake managers and stakeholders to manage lakes and their basins in a sustainable manner. The framework is based on a review of experiences and lessons learned at 28 case study lakes from around the world. The framework identifies six necessary components for effective lake basin management governance, namely, institutions, policies, technology, information and science, participation, and finance.

Experiences learned from the above mentioned global study indicate that good lake basin management requires: 1) Institutions to manage the lake and its basin for the benefit of all lake basin resource uses; 2) Policies to govern people's use of lake resources and their impacts on lakes; 3)Technological possibilities and limitations exist in almost all cases; 4) Knowledge both of a traditional and scientific nature is valuable; 5) Participation of people central to lake basin management; 6) Sustainable finances to fund all of the above activities are essential. These constitute the essential components of basin governance about which ILBM provides the overall framework for application (Figure 2).

The thesis of the ILBM framework is that the challenge of lake basin management is a governance issue and that effective lake basin management will require addressing the six constituent governance pillars. Established on the premise that lake basin management is a continuously evolving process and not a one-time project or program, ILBM emphasizes that the six pillars of lake basin governance must be continuously improved towards the goal of sustainability. The important questions for the lake manager include, among others, the following "What are the strong and weak pillars for my lake? Why are some pillars weak and others strong, and what needs to be done to fix the weak pillars? What are the experiences of other lakes regarding the six pillars and what lessons can my lake learn from the experiences of other lakes? What lessons does my lake offer to other lakes?" These questions, among many other issues, constitute the details of the practical application of ILBM in lake basin management as elaborated elsewhere (ILEC, 2005, 2007; RCSE and ILEC, 2010). The ILBM framework may also be considered as a planning procedure and its use in evaluation of lake basin management is elaborated by Muhandiki *et al.* (2007).

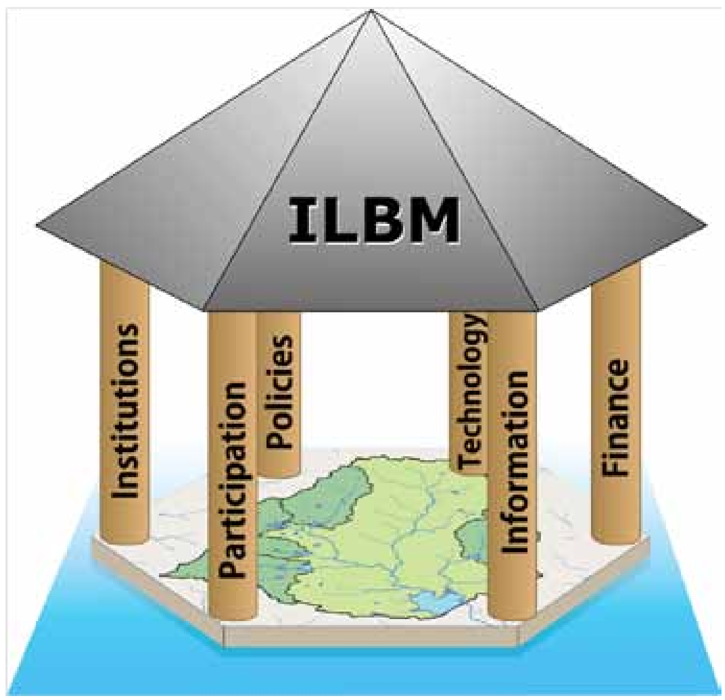

Figure 2. The ILBM framework (ILEC, 2007)

The ILBM framework recognizes that as lentic (standing or hydrostatic) water bodies, lakes have three unique biophysical features that dictate the needed approach for their management (Table 2). Without recognizing these features it is not possible to develop an effective approach to lake management. Building on the MEA classification of ecosystem services discussed in the previous section, ILBM calls for the need to focus attention on the preservation of lake basin ecosystem regulating services, as a basis for ensuring the continuity of other categories of ecosystem services provided by lakes and their basins (provisioning, cultural and supporting services). By focusing on the regulating services, and satisfying the required management needs associated with such services, it is proposed that the integrity of the ecosystem supporting services can be maintained. In this context, ILBM defines sustainable lake basin management as management that ensures maintenance of lake basin ecosystem services, particularly ecosystem regulating services (Figure 1).

It is worth noting that ILBM builds on many existing concepts in resource management such as the Integrated Water Resources Management (IWRM) (GWP, 2000) and Integrated Land-Water-Ecosystem Management (Falkenmark *et al.*, 1999; Falkenmark and Rockstrom, 2004). However, the focus of ILBM is on lakes as lentic (standing or hyrostatic) water bodies, their unique characteristics and the consequent management implications. ILBM argues that the lentic nature of lakes makes them delicate ecosystems needing a special approach. This is not to undermine the fact that lakes are actually part of interconnected lentic-lotic systems on the broader river basin scale. Further considerations of the lentic-lotic connections in the ILBM approach are needed. Indeed, our knowledge of lake ecosystems is still limited and the idealized visualization of ILBM in Figure 2 probably exists only in theory for all lakes in the world. In reality, the ILBM process entails continuous strengthening, reinforcing and redesigning of the six pillars and roof (which are often unbalanced, irregular, collapsed, broken, bent, only partially done, *etc.*). The process is best illustrated as a spiral with Figure 2 as the endless goal.

CONCLUSIONS

Lakes and their basins provide a wide range of resource values for humanity. Among all water bodies lakes provide the widest range of values. This, compounded with the fact that lakes are lotic (standing or hydrostatic) water bodies, makes lakes the most difficult water system to manage. Over-exploitation of lake and lake basin resources, particularly the ecosystem provisioning services has led to the degradation of many lakes around the word and threatens the integrity of many lake ecosystems. This paper introduced the concept of ILBM which has been proposed as the most effective approach to manage lakes and their basins for their sustainable use. Key to ILBM approach are the recognition of three basic biophysical characteristics of lakes as lentic water systems and the focus on ecosystem regulating services of lakes and their basins as a basis for ensuring the continuity of all the other three categories of ecosystems services, namely, provisioning, cultural and supporting services.

ILBM emphasizes that lake basin management is a process, not a one-time project or program. The process will have to continuously evolve in response to changes in the broad range of lake basin management issues and challenges that also continuously evolve in time, space and human conception. Considering that lakes are part of interconnected lentic-lotic systems on the broader river basin scale, further considerations of the inherent lentic-lotic connections in the ILBM approach are needed. Although the paper focused on issues that are broader in scope than diffuse pollution, the concepts introduced are equally applicable to addressing the subject. Commenting on the relationship between poverty and environmental degradation, Dasgupta (2001) observed that "There is an urge…to say that we have adopted wrong values, that if we could only frame the prevailing state of affairs the right way, we would know what should be done to put the world right." Indeed, we believe that to put lake management in the right context, it has to be guided by principles based on the unique characteristics of lakes as lentic water systems. ILBM provides such a framework.

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Diffuse pollution and freshwater degradation: New Zealand Perspectives

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Abstract

Recent opinion surveys point to water pollution, primarily from pastoral agriculture, as the largest environmental issue in New Zealand. With a prognosis for increased land use intensification, further water quality degradation seems highly likely. This paper outlines five major aspects of the diffuse pollution issue: 1. <u>Characterisation of diffuse pollution and the shift from point to diffuse sources.</u> The 'universal' diffuse pollutants: nutrients, fine sediments, and pathogens, all of which are mobilised by livestock, predominate in New Zealand waters. There has been a shift over the last 40 years from point sources to diffuse sources as the major contributors of pollution, with point sources now accounting for only 3.2% of the total nitrogen, and 1.8% of the total phosphorus fluxes to the sea. <u>2. Pathways of diffuse pollutants.</u> Diffuse pollutants move into waters through: overland runoff; direct access to waters by livestock; and leaching to groundwater (often with associated legacy issues reflecting groundwater residence times). These pathways are discussed illustrating the importance of understanding processes – particularly for targeting Beneficial Management Practices (BMPs). <u>3. Attenuation of diffuse pollutants</u> through interception mechanisms and BMPs adjacent to, and in, streams. Attenuation is discussed for riparian zones, and in-stream processing. <u>4. Modelling</u> of diffuse pollution has been done in New Zealand through mechanistic, stochastic and statistical approaches, and management-accessible models are described. <u>5. Managing diffuse pollution</u> needs to recognise that catchments are the most appropriate spatial management unit. Managing diffuse nutrient loads has recently been initiated in New Zealand through regulation by setting load limits (nutrient caps) on catchments, and through identified nutrient concentration targets.

Keywords

Faecal microbial pollution; management; Nitrogen; nutrient loads; Phosphorus; sediments

INTRODUCTION

New Zealand has much natural landscape with mountains and natural forest occupying *ca.*43% of the land surface. These areas contain near-pristine rivers, lakes and wetlands. The remaining land area comprises planted forest (5%) and pastoral and arable land (52%) and the country's lowlands are almost devoid of natural landscape (Elliott, 2005; Davies-Colley, 2009). Given the large area of pastoral farming, it is not surprising that New Zealand suffers considerable diffuse water pollution, and the link between pastoral intensification and declining water quality is increasingly acknowledged by the Government (New Start for Freshwater, 2009). This decline has been rated the country's number one environmental problem in several opinion surveys. Water pollution, now overwhelmingly from diffuse sources, has been well documented and the management of diffuse pollutants is currently receiving considerable attention (Ministry for the Environment, 2009; Land and Water Forum, 2010). There has been government recognition of the "strong link" between land use intensification and water quality decline (Ministry for the Environment, 2009). The reasons for this attention relate to public pressure and changing perceptions of the value of natural waters. Behind these are the continuing drives by international primary commodity markets for the documentation of sustainability practices. A significant pressure for cleaner waters has come from the indigenous Maori (Polynesian) people of Aotearoa/New Zealand. Maori recognise freshwater as a taonga (treasure) and have an obligation of guardianship of the landscape including waters (Land and Water Forum, 2010).

The challenge facing New Zealand is how to cope with the economic drive for increased pastoral production while demonstrably minimising contaminant loss to both freshwater and the coastal zone. Detailed reviews of the extent of, and impacts of, diffuse pollutants on the New Zealand aquatic environment have appeared frequently over the last decade as concern has increased over the impacts of pastoral agriculture on them (McDowell, 2009; Quinn et al., 2009). This challenge is significant. The most recent OECD Environmental Review of New Zealand (OECD, 2007) highlights that water quality in lakes and rivers has declined in those areas dominated by pastoral farming and the OECD has recorded the following changes in the 15 year period, 1990-2005:

- Change in agricultural production: NZ ranked 1st out of 28 OECD countries, with the highest % increase in agricultural production.
- Change in total phosphate fertiliser use: NZ had the 2nd highest % increase in phosphate fertiliser use out of 29 OECD countries, while 23 countries decreased their P-fertiliser use.
- Change in total nitrogenous fertiliser use: NZ had the highest % increase out of 29 OECD countries, while 21 countries decreased N-fertiliser use. (The actual net application of N-fertiliser (2.1 tonnes /km2 of agricultural land) in NZ is now close to the OECD average of 2.2 tonnes/km2 of agricultural land.)

International and New Zealand-specific experience shows that such changes are likely to be accompanied by increases in diffuse pollution (Wilcock, 2009). The New Zealand Office of the Parliamentary Commissioner for the Environment has argued for “a paradigm shift in farming practices for New Zealand to become environmentally sustainable”.

Here we outline five major aspects of the diffuse pollution issue that have wide international relevance: 1. Characterisation of diffuse pollution and the shift from point to diffuse sources; 2. Pollutant pathways; 3. Attenuation of diffuse pollutants; 4. Modelling; 5. Managing diffuse pollution.

CHARACTERISATION OF DIFFUSE POLLUTION

Urban and mining-impacted streams are typically of lowest ‘ecological ‘health’ in New Zealand, as elsewhere, owing to severe physical changes, gross sedimentation, and toxic pollution, but a far greater total length of streams in pastoral agriculture are moderately to severely impacted. The ‘universal’ diffuse pollutants – fine sediments, pathogens and nutrients – all of which are mobilised by livestock, predominate in waters draining the New Zealand landscape.

Fine sediment mostly affects (i) rivers by reducing water clarity and impacting on primary producers and consumers in aquatic food webs, and (ii) coastal areas by reducing water clarity, shoaling by sedimentation and smothering shellfish beds.

Faecal matter (and associated pathogens) affects contact recreation, water supplies and coastal shellfish harvesting from commercial, recreational and traditional harvest sites. In a national study of freshwater swimming sites collated by the Ministry for the Environment 40% of 280 river sites were found to be non-compliant with guideline values for recreation in terms of *E. coli* (http://www.mfe.govt.nz/environmental-reporting/freshwater/recreational/snapshot/freshwater.html#results). Although microbial pollution is of major concern for contact recreation, application of a water quality index for contact recreation to 77 sites in the National Rivers Water Quality Network (NRWQN; Davies-Colley and Ballantine, 2010) suggests that low visual clarity limits contact recreation in NZ rivers more commonly than microbial pollution (high *E. coli*).

In terms of nutrients, New Zealand has a long history of documentation and research on freshwater eutrophication that has affected rivers, wetlands, lakes and estuaries (Burns, 1991; Winterbourn, 1991) with significant deviations from OECD trends (White, 1983). SPARROW modelling calibrated to the NRWQN dataset (Elliott et al., 2005) suggests that point sources account for only 3.2% of the Total N, and 1.8% of the Total P flux to the sea from the New Zealand landmass.

Diffuse pollution has probably been present since widespread land clearance for grazing started in the 19th century in (originally 80% forested) New Zealand, but has gone largely unrecognised until recently. Over the past four decades or so, NZ has been preoccupied with controlling point pollution, with water pollution from diffuse pastoral sources only acknowledged fairly recently – particularly since publication of a landmark paper by Wilcock (1986). Now the gains made from investment in wastewater treatment risk being negated by increasing diffuse pollution from expansion and intensification of pastoral agriculture (Ballantine and Davies-Colley, 2009; Wilcock, 2009; Quinn, 2009). Diffuse pollution (with a few exceptions) seems less amenable than point pollution to control under New Zealand's (effects-based) environmental legislation, the Resource Management Act of 1991.

Correlations between land use and river water quality consistently quantify the relationships between water quality and land use as shown in Table 1. Visual clarity is negatively impacted by land use and is positively related to % native forest in the catchment. Nutrients and *E. coli* concentrations are all positively related to % pastoral land use in the catchment, and negatively to % native forest.

Table 1. Correlation of river water quality variables (medians for the period 2005-08 from NRWQN) and percent of catchment in pastoral, arable and native forest land use types. All correlations are significant at P< 0.05. (From Davies-Colley, 2009.)

Parameter	% Pastoral	% Arable + Hort.	% Native Forest
Visual clarity	- 0.45	- 0.24	0.30
Total Nitrogen	0.85	0.45	- 0.39
Total Phosphorus	0.70	0.24	- 0.32
E. coli	0.80	(0.17)	- 0.34

Of the pastoral land use category, which makes up 42% of New Zealand's land cover, dairy farming has the highest diffuse pollution footprint with 36.7% of the Total Nitrogen load entering the sea originating from the 6.8% of the land area occupied by dairy farming (Table 2), while 'other pasture' (sheep, beef, deer etc) provides 38.9% of the Total Nitrogen from 31.9% of the land area (Elliott et al., 2005). This is not surprising given that the nitrogen loss rates from dairy farms are four times higher than from other pasture (*cf.* 39 kg/ha/yr compared with 8 kg/ha/yr from sheep and beef farms, and 5 kg/ha/yr from forest (MAF, 2008; Quinn et al., 2009).

Table 2. Land use area (%) and Total Nitrogen load to the sea as a % of the national total load (after Elliott et al., 2005). NA = Not Applicable. Total area of NZ = 263 500 km^2; total N load to the coast = 167 700 t/yr.

Pollution Source	Land use area %	Load to Coast %
Point sources	NA	3.2
Dairy	6.8	36.7
Other pasture	31.9	33.3
Trees (Native and plantation forest)	39.2	24.8
Other non pasture (mountains, scrub)	22.1	2.1

A recent study of 112 currently monitored New Zealand lakes (Verburg et al., 2010) found that 49 were eutrophic or worse and 29 were oligotrophic or better. However, bias in the distribution of the monitored lakes was acknowledged in that many lakes in natural areas were not monitored. Statistical extrapolation, accounting for this bias, indicated that 32% of all 3820 NZ lakes of >1 ha in area are eutrophic or worse, while 43% are oligotrophic or better. Of the monitored lakes, 73% of those in the eutrophic or worse category were located in predominantly pastoral land use catchments (Verburg et al., 2010).

Diffuse sources have thus now comprehensively supplanted point sources across the country. For example, at (nitrogen-limited) Lake Rotorua a sewage discharge was diverted in 1991 with an immediate decline in Total N in the lake, but Total Nitrogen levels are now higher than they were in 1991 due to steadily increasing nitrogen loads from catchment streams draining pastoral land (Figure 1).

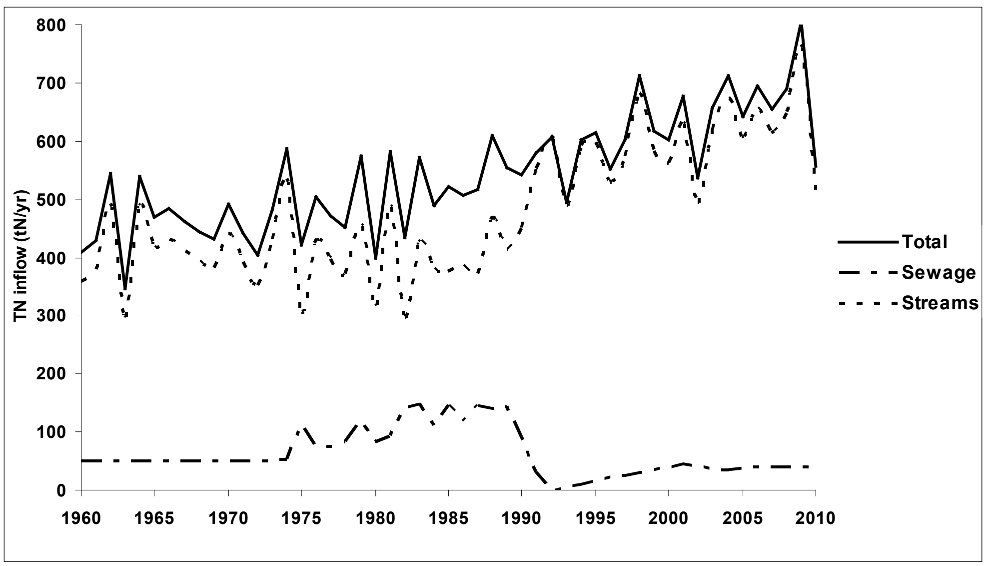

Figure 1. Diffuse pollutants continue to increase as point sources decline. At (N-limited) Lake Rotorua the sewage discharge was diverted in 1991 (Data from Rutherford, 2003 and unpublished) but diffuse inputs from streams continued to increase.

Management of diffuse pollution relies on the estimation for each catchment of the load that has arisen from human activity and is additional to the natural load. We estimate that 75% of diffuse source N & P flux to the sea is from modified landscapes, mostly pastoral and, as such, is theoretically manageable while 25% would be "natural". Lake Taupo, New Zealand's largest lake has a mixed land use catchment with 22% pastoral, 27% as plantation forest and the remaining 51% as native forest, scrub and mountain vegetation. The manageable loads there of Total N and P are only 40% of the natural load as modelled for pre-European times. Nutrient management in the Lake Taupo catchment has been focussed only on that 40%.

New Zealand catchment modelling indicates that the manageable load, as a proportion of the total load, varies not only with time but with distance downstream in rivers. In the case of the Waikato River, the manageable nitrogen load gradually diverges from the 'natural" load as the river progresses downstream to a distance of *ca*. 225 km, and then doubles in the next 50 km while the "natural" load increases by only 16% (Table 3). The manageable load increase is due to the inflows from a major tributary, the Waipa River. The situation for phosphorus is not as clear-cut because the Waipa would have provided a significant natural phosphorus load. In this case the manageable P load doubled below the Waipa junction and the "natural" load also doubled by 0.5 t P/day (Table 3).

Table 3. Waikato River natural nutrient loads and anthropogenic (manageable) loads (tonnes/day) vary with distance downstream from Lake Taupo (0 km). The "natural load" figures are the modelled load for the 1920s before hydropower development but after some limited land use change. 225 km is upstream and 250 km is downstream of the Waipa River inflow

Distance downstream (km)	Total Nitrogen load		Total Phosphorus load	
	1920 'Natural'	2010 Manageable	1920 'Natural'	2010 Manageable
0	1.2	-	0.09	-
75	1.5	3.0	0.2	0.3
170	4.2	6.4	0.4	0.7
225	6.1	9.2	0.51	0.9
Waipa River inflow here				
250	7.1	18.4	1.1	1.8
300	10.5	23.1	1.5	2.5

PATHWAYS OF DIFFUSE POLLUTANTS

Diffuse pollutants move into waters through three main processes:

i. surface runoff as overland from land to water;

ii. livestock direct access to waters (including wetlands and lake margins);

iii. leaching to groundwaters and subsequent re-emergence as springs.

i. Overland flow is probably the largest source of diffuse pollution in New Zealand and comprises mostly particulate diffuse pollutants (fine sediment, microbes and particulate N and P). It is highly flow-dependent as described above, and is mostly derived from critical source areas (CSAs) for runoff representing often only a small proportion of a catchment (Pionke et al., 2000; McDowell et al., 2004). Because surface runoff mainly occurs during and immediately after rainstorms, diffuse pollution from this pathway tends to correlate positively with stream flow – in sharp contrast to livestock access and groundwater seepage (and point source pollution) that tend to be *diluted* with increasing stream flow. In New Zealand rivers water clarity (inversely related to fine sediment) tends to decline with increase in discharge, while microbes, and total nitrogen and phosphorus concentrations increase with discharge – broadly consistent with the inference that overland flow is the dominant source of diffuse pollution in this country (Smith et al. 1996, Davies-Colley, 2009).

In a comparative study of pasture, pine and native forest catchments, Cooper and Thompsen (1988) found that on an areal basis, the pasture catchment exported about 15 times more P than either of the forested catchments and about 3 and 10 times more N than the native and pine catchments respectively. The proportion of TN export that occurred during stormflow in the pasture, pine, and native catchments was 90%, 52%, and 20%, respectively and similar proportions occurred for TP exports.

In any catchment or farm, identification of Critical Source Areas for priority attention to mitigate or ameliorate pollution in runoff is a necessary first step in diffuse pollution control. These areas can then be set aside for management actions that reduce pollutant runoff such as minimising fertiliser application or livestock exclusion or reduction. Beneficial Management Practices (BMPs) that are most appropriate to overland flow are those that act as 'filters' to intercept diffuse pollutants in the surface runoff. These include contour tilling and planting, grassy strips, wetlands and stream-bank vegetation. Other BMPs include the use of slow release fertiliser such as rock phosphate that minimises soluble fertiliser loss in rains (Hart et al., 2004), and livestock stand-off pads that prevent soil damage from treading compaction during wet weather (Table 4).

ii. Livestock direct access. This widespread pollution source is important in NZ and is a significant area for management attention. Direct livestock access to waters or wetlands adversely affects water quality by:

a. Physical damage by livestock treading and browsing to the vegetation, soils and substrates in and on the edges of lakes, wetlands and streams, increasing their susceptibility to erosion, sediment loss and pollutant runoff;

b. Direct dung and urine deposits in waters, which add nitrogen, phosphorus and faecal microbes.

A study in the Sherry River (http://icm.landcareresearch.co.nz/) has shown that river crossings of dairy herds between milking parlour and pasture up to four times daily approximately doubles average faecal pollution levels (Davies-Colley et al., 2004). The microbial quality of the Sherry River has greatly improved since the fords used for dairy crossings were all replaced by bridges, although the river still falls well short of contact recreation guidelines – mainly because dairy cattle continue to access unfenced channels from pasture.

Studies of direct pollution by sporadic access of cattle to streams have been conducted in New Zealand. Bagshaw et al. (2008) found that beef cattle in hill land spent about 2% of their time in stream channels to which they had unrestricted access, and inferred that a proportional amount of faecal deposition would go directly into stream water, with a further 2% deposited in the 'immediate' riparian zone (from which any rise in stream stage would readily entrain faecal matter). Bagshaw and co-workers also studied dairy cow access to unfenced streams (15 separate observational experiments on 5 different farms) and found that cows spent only about 0.1% of time in the channels, but deposited about 0.5% of faeces (Collins et al., 2007). Monitoring of stream water quality upstream and downstream of the dairy paddocks in 10 of the 15 experiments (Davies-Colley and Nagels, 2008) showed that the stream water was highly polluted with *E. coli* concentrations up to 30 000 cfu/100 mL. The faecal bacterial yield agreed well with observations that 0.5% of faecal deposits directly enter stream water, suggesting a 5-fold amplification of defecation rate water *versus* land.

Thus, fencing of stream banks in pastoral landscapes, ideally with a set-back to create a riparian buffer, is increasingly recognised as the most important BMP to arrest this pollutant pathway, with bridged stream crossings also important on dairy farms where cows move usually twice-daily to milking sheds, often crossing streams.

iii. Nutrients leaching to groundwater and their subsequent emergence in seeps and springs, is a particular issue in New Zealand's alluvial soils and porous volcanic soils where groundwater resources are often significant. This is a particular problem for nitrate entering aquifers in aerobic conditions although microbial pollution of groundwaters can also be significant in the near-field. In the intensively-farmed Waikato region 16% of bores exceed this guideline (Quinn et al., 2009). Recently, Hickey and Martin (2009) analysed acute (short-term) chronic (long-term) nitrate toxicity data in order to recommend freshwater guidelines for nitrate concentrations in natural waters. As a result of this analysis recommended guideline values for chronic toxicity were: a) 1.0 mg NO_3-N L^{-1} in pristine environments with high biodiversity values; b) 1.7 mg NO_3-N L^{-1} in slightly or moderately disturbed systems; and c) 2.4-3.6 mg NO_3-N L^{-1}in highly disturbed systems (i.e. with measurable degradation).

Of special note in relation to the management of nitrate pollution are the legacy issues that relate to extended residence times of polluted groundwater. In the Central North Island, nitrate from groundwater-fed springs and seeps is a major contributor to the total nitrogen load of large (nitrogen-limited) lakes. In the Lake Taupo catchment groundwater ages vary from 2.5 to 80 years (Morgenstern, 2007) with a mean age of water of 9 streams being 37 years, so the lake now receives nitrate from farming activities several decades in the past. The effects of current farming will not show up for several decades into the future. The policy response to this legacy of nitrogen in groundwater has been termed "the load to come"

(Vant and Smith, 2004). Lake protection and remediation programmes in the Central North Island have been required to account for the load to come when calculating nutrient input budgets and time scales of change

ATTENUATION OF DIFFUSE POLLUTANTS

Attenuation of pollutants with distance downstream from the source of flow is an important consideration for modelling (Rutherford, 1987; Elliott et al., 2005) and management. Attenuation of overland flow takes place on land through natural interception mechanisms (and BMPs) as mentioned above and it takes place adjacent to, and in, streams where different nutrient attenuating systems have been identified (Downes et al., 1997). These were:

i. streams receiving lateral flow where nutrient processing occurred in groundwater and in surface runoff adjacent to the stream;

ii. Streams with spring sources where nutrients were attenuated in the stream channel.

In the first case, 'Lateral Attenuation', particulate and dissolved inorganic nutrients are removed when surface and subsurface water flows through riparian vegetation before reaching the stream channel. In the second case 'Instream Attenuation', processes such as plant and microbial uptake (denitrification in the case of nitrate) can remove nutrients from waters within the stream channel itself. Other Instream Attenuation processes such as hyporheic exchange, sediment exchange, microbial pollutant die-off in sunlit channels, long-term storage of sediments (infilling) and nutrient transformations (i.e. from dissolved inorganic nutrients to particulate nutrients and vice versa) have also been demonstrated as important. These processes combined reduce fluxes and the concentrations that would otherwise be encountered in downstream water bodies.

i. Lateral attenuation: Attenuation of runoff through riparian vegetation on stream edges has been the subject of long study in New Zealand with one of the seminal works being that of McColl (1978). He showed then the value of riparian vegetation along pasture streams as nutrient traps for overland flow of phosphorus to stream channels during rain storms. The study provided "strong support for the use of buffer strips of vegetation along stream channels as a means of protecting streams from phosphorus losses".

In a study of faecal coliform attenuation in pasture lands, Collins et al. (2004) found that during large runoff events, and where preferential flowpaths occur, buffer strips need to exceed 5 m in length in order to markedly reduce the delivery of faecal microbes to waterways, but during low-rates of water application to pastures, riparian buffers trapped >95% of *E.coli* in the runoff. Cooper et al. (1995) provided a note of caution in the long-term sustainability of riparian strips for lateral attenuation, suggestion that riparian soils can become saturated with P. The results imply that riparian set-asides may lead to the development of a zone likely to supply runoff to the adjacent stream that is depleted in sediment-bound nutrients and dissolved N but enriched in dissolved P.

ii. Instream Attenuation of pollutants has been modelled as a first order decay process (see Cooper and Botcher, 1993; Hearne and Howard-Williams, 1988; Elliott, 2005) so that downstream concentration $C_z = C_0 e^{-Kz}$, where C_0 is the source concentration, K is the attenuation coefficient (m^{-1}) and z is distance downstream (m). In the case of nutrients, the downstream attenuation coefficient for dissolved nutrients in water (K_w) may also be calculated from $K_w=R_w/F_w$ where R_w is the mass of nutrient removed per unit time per meter of stream length and F_w is the nutrient flux (mass per unit time) in the suite of equations describing nutrient spiralling (Newbold et al., 1981). Most diffuse pollution occurs in small (low order) streams that have the greatest attenuation capability. This is demonstrated by the strong dependence of K_w on stream and river discharge (Rutherford et al., 1987; Figure 2). The information suggests that for optimising nutrient attenuation, attention should be paid to streams that have a K_w of greater than 0.0001/m or > 10% loss of nutrient per km of stream length. These conditions are found in streams with a flow rate of < 0.5 m^3/s (Figure 2).

The nutrient attenuation coefficient (K_w) for mid summer periods in the Whangamata Stream in the central North Island was shown to vary fifty-fold, in a cyclical manner, from 0.03/m to 1.5/m.over a 30 year period. This reflected changes in discharge, in-stream vegetation biomass, stream shade by riparian vegetation, and in-stream plant species composition (Howard-Williams and Pickmere, 2010).

In addition to stream attenuation of nutrients there is increasing evidence of high variability in attenuation processes operating in groundwaters particularly for nitrate-N. For instance at Lake Rotorua groundwater appears to be well oxygenated (viz., little denitrification) so attenuation of groundwater N is unlikely. By comparison, at Lake Taupo many groundwaters are anoxic (Hadfield, 2007) and have low nitrate concentrations with an assumption of high denitrification rates on organic-rich layers in the aquifers (Stenger et al., 2009).

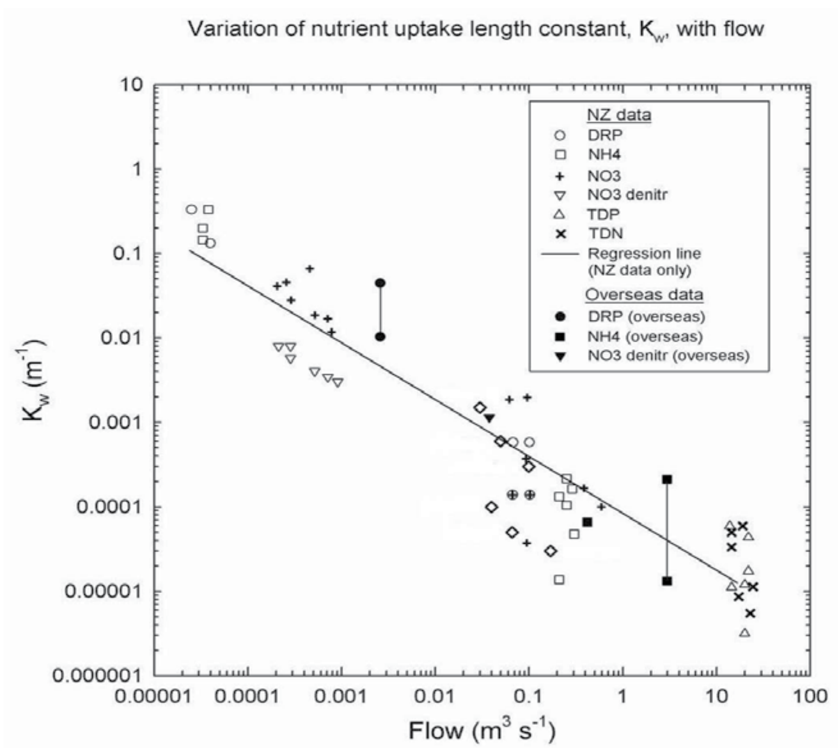

Figure 2. (After Rutherford et al., 1987).
Variation in the downstream attenuation coefficient for dissolved nutrients (K_w) with stream flow

A number of factors affect attenuation (Table 4) and in addition to managing these for nutrient removal, considerable advances can be made by maximising attenuation at diffuse pollution source sites on farms. A comprehensive statement on the effectiveness of on-farm mitigation strategies for managing contaminant sources was provided by Quinn et al. (2009).

Table 4. Mechanisms that enhance attenuation in streams and prevent nutrient loss from farm soils to waters.

Enhancing attenuation in and near waters	Reducing nutrient loss from farms
Riparian strips,	Riparian and farm drain management
Wetland and seep protection	Slow release fertilizers
Maximising aerobic-anaerobic interface for denitrification	Nitrification inhibitors
Constructed wetlands	Constructed wetlands
In-channel vegetation	Nutrient budgets, nutrient mapping
	Feed pads, herd homes, wintering off-site
	Improved weather and climate forecasting
	Nutrient trading/capping

MODELLING

Diffuse pollution modelling in New Zealand has been done through statistical, mechanistic, stochastic and conceptual approaches (e.g. Decision Support Systems and Bayesian Belief Networks) and includes several of the models reviewed for the EU Water Framework Directive (Yang and Wang, 2009). Statistical modelling includes SPARROW (Alexander et al., 2002) which accounts for in-stream attenuation. This has been used to define pollutant loads to the sea across the New Zealand landmass (Elliott et al., 2005) and to focus on more detailed catchment understanding. SPARROW forms the core of a recent model package (Catchment Land Use for Environmental Sustainability – CLUES); which was specifically designed to be used by water managers and combines underlying landuse pollutant spreadsheet approaches such as OVERSEER(TM) with SPARROW to relate catchment pollutant loads on a GIS framework (McBride et al., 2008). The resulting package allows for a map-based delineation of land uses and provides GIS images of seasonal or annual loads of pollutants through the stream network.

Other catchment models that have been used with success are GLEAMS (and GLEAMSHELL) (Cooper and Bottcher, 1993). Catchment nutrient modelling with GLEAMSHELL provided the nutrient inputs to New Zealand's largest lake, Lake Taupo for scenarios that investigated proposals for increased dairy farming in this nitrogen sensitive area. The model, together with an in-lake dynamic ecosystem model (Spigel et al., 2001; Hamilton and Wilkins, 2004), resulted in a Policy Response (Variation 5 to the Waikato Regional Plan) that limits future land-use intensification in the catchment. This includes a nitrogen capping policy that limits inputs to the lake and accounts for "the load to come" of nitrate in groundwater.

Recently the statistical ROTAN model (Rutherford et al., 2009) has been developed to quantify the role of groundwater lags in delaying the response to landuse changes of nitrogen inputs to lakes Rotorua and Taupo. ROTAN is currently being used to calculate how quickly lake inputs will decrease if nitrogen exports from land are reduced in different parts of the Lake Rotorua catchment – so that the mitigations including land purchase and retirement can be targeted where they will be most cost-effective and timely. An empirical approach to modelling diffuse pollution is that of Unwin et al. (2010) who make use of the spatial framework tool, the "River Environment Classification" (Snelder and Hughey, 2005) to model water quality.

Mechanistic models for exploring microbial diffuse pollution have been reported by Collins and Rutherford (2004). These have highlighted the very different 'microbial regime' of baseflows compared to (microbially polluted) stormflows when microbes are entrained by flood currents and washed into waters with overland flow – resulting in polluted storm plumes affecting downstream waters and coasts. A stochastic approach of increasing interest in New Zealand is quantitative microbial risk assessment (QMRA) to investigate health risks to humans of microbial pollution of recreational or drinking waters or bivalve shellfish under different pollution scenarios (McBride, 2007).

MANAGING DIFFUSE POLLUTION

Management of diffuse pollution involves approaches at several levels: reductions of nutrients at source (i.e. by reducing animal stocking rates); retiring, or not permitting certain activities on, sensitive land in sensitive catchments and by widespread application of mitigation methods. It is widely accepted that there is no single mitigation option for diffuse pollution reduction (e.g. Stevens and Quinton, 2009 and Quinn et al., 2009 for arable and pastoral systems respectively). Diffuse pollution management is receiving attention at four levels: i). national government; ii). regional government; iii). rural industry promoted standards and iv). community-led initiatives. Several management instruments are currently being evaluated involving combinations of the above. Regulating for diffuse pollution is not the single answer, even if this were (to become) politically tenable. In the UK, the National Farmers Union rejected regulation as an answer to diffuse pollution stressing the need for advice-based voluntary approaches (Whyte, 2004), a sentiment also strongly expressed by the various agricultural sector groups in New Zealand where a recent Government panel has recommended a matrix of governance and management approaches to the problem (Land and Water Forum, 2010). These approaches range in scale from national to local in the following sequence:

- defining national objectives based on values setting for water quality;
- establishing limits and standards at regional scales but based on spatial frameworks to account for natural landscape and waterway variability; and
- collaborative processes at catchment scales ("integrated catchment management") that involve both industry and local stakeholders.

Key to this last point is strong rural industry engagement to provide credibility, advice and incentives, as well as the introduction of adaptive management and audited self management as tools for promotion and validation of BMPs. Across all these scales in New Zealand are the interests of the indigenous Maori ('first nation') people who have traditional obligations to protect freshwater so as to "leave a worthy inheritance for future generations" (Land and Water Forum, 2010). Negotiations on the role of Maori in freshwater management up to and including full co-management of water bodies (e.g. Collier et al. 2010) are currently underway.

Regional governments in New Zealand have been increasingly active in the last decade in promoting water protection. In Taranaki the Regional Council provides a riparian planning service "to maintain water quality in the region".

Since the late 1990s it has:

- Prepared (free of charge) more than 2 000 farm riparian management plans, focussed mainly on fencing and planting ;
- Promoted 500 km of stream fencing and 425 km of stream bank re-vegetation which, when added to existing fencing and planting means that 60% of stream bank, on the lowland "ring" plain under a riparian plan, is fenced, and 43% is vegetated.;
- Supplied 1.5 x106 plants (300 000 plants in 2010 alone) at cost;
- Detected a 30% improvement in stream ecological health using a Stream health Monitoring and Assessment Kit (SCHMAK), and in this time no negative trends have been detected in the monitored streams.

In two sensitive lake catchments deemed to be of national significance, Lakes Taupo and Rotorua, the last decade has seen national government intervention to assist with lake restoration initiatives that have established nutrient load limits. These have been set following extensive scientific consultation advice and modelling in conjunction with broad community consultation. Thus, in the case of Lake Taupo, the legislated "Regional Plan Variation 5 (Lake Taupo)" imposes a cap (a Nitrogen Discharge Allowance or NDA) on nutrient loads leached from individual farms which is based on the load in their "best" recent farming year. A NDA can be traded between farmers. A 20% reduction in the manageable loads is to be achieved over a 10 year period to accommodate the "load to come" through the purchase and retirement of farms by the Lake Taupo Protection Trust (www.laketaupoprotectiontrust.org.nz).

In the case of Lake Rotorua, a target of 435 t N/yr has been set for the nitrogen input to the lake – the input during the 1960s before there was widespread concern about algal blooms in the lake. Currently nitrogen export within the catchment totals 825 t N/yr, of which >80% originates from pastoral farming. Streams have a large groundwater component and the mean "age" of groundwater ranges from 15 to 110 years which means that even if nitrogen leaching losses from pasture were reduced immediately, it would take several decades for the input to the lake to reduce. Internal releases of nutrient from the lakebed during summer stratification are also likely to delay lake recovery. Measures are currently being considered to reduce nitrogen exports and to reduce internal lake loads.

Significant approaches to water governance at regional and local levels and combining regulation and voluntary action have been proposed in the last few years; Regional government initiatives include the Horizons council's "*One Plan*" that will see the establishment of Water Management Zones with specific controls over landuse intensification of farming activities at catchment and sub-catchment scales, and a mix of 'persuasion, advice and rules to manage water quality within the Management Zones'. Using a similar approach, the Canterbury Regional Council's recent approval of the *Canterbury Water Management Strategy* will see a combination of regulatory action set at regional level, to deal with environmental problems complemented with incentive mechanisms that progressively drive efficiency in the use of water and responsible land management practices. This will be done through ten Water Management Zones sufficiently large to enable the management of surface and groundwater systems to be integrated with the management of the areas where the water is used but also small enough to avoid becoming remote from local catchment issues. Water management zones are seen as spanning the divide at the right scale between regulation and community and industry voluntary action.

As detailed in the water planning frameworks for many countries, catchments are usually the best spatial management unit. In New Zealand, Beneficial Management Practises in dairy farming areas have been quantitatively evaluated over the last decade through a set of five "Best Practise Dairy Monitor Catchments", which demonstrate the efficacy of BMPs (Wilcock et al., 2007) in different dairy-dominated catchments in five regions of the country with varied climate and soils. In the Whatawhata Hill Country experimental farm, retirement of much riparian and steepland in the Mangaotama Catchment has improved water quality and aquatic ecological health in less than a decade (Dodd et al., 2008), although some expected benefits are expected to take longer owing to 'legacy' effects to do with nitrogen in groundwater and stored sediment in streambanks.

As part of the Primary Sector Growth Partnership in New Zealand, "the fertiliser industry is responsible for meeting its commitments to ensuring the sustainable use of freshwater resources in the primary sector. These commitments include: by 2013 80% or nutrients applied to land nationally are managed through quality assured nutrient budgets and nutrient management plans…" (Land and Water Forum, 2010). The dairy industry has signed the voluntary 2003 '*Dairying and Clean Streams Accord*' that had achieved the following by 2008-09: 1. Dairy cattle are excluded from streams, rivers and lakes -80%; 2. Regular race crossing points have bridges or culverts -97%; 3. All dairy farms have in place systems to manage nutrient inputs and outputs -97%; 4. All dairy farm effluent discharge complies with resource consents and regional plans -60%. These data need to be treated with some circumspection as one influential report disputes industry claims about the percentage compliance with the "Accord" (Deans and Hackwell, 2008). Whatever the final numbers, the industry intervention is producing positive environmental outcomes from existing dairy farms. However, of on-going concern is continuing degradation as a result of conversions from sheep and beef farming to dairying (Environment Waikato, 2008).

Managing diffuse nutrient loads through regulation by setting load limits (nutrient caps) on catchments, and through identified nutrient concentration targets (regional planning standards) in downstream waters needs to be directed by government (central and regional) regulatory agencies. This should be combined with co-operative approaches with the rural industry sectors and rural communities to work through voluntary mechanisms (Codes of Conduct, Audited Self Management (ASM) schemes, adaptive management) to implement good management practise.

FUTURE DIRECTIONS

Further improvement in management of diffuse pollution needs attention by science and by government agencies at several scales of policy and regulation, by industry and by communities in catchments.

Science attention should focus on:

- Definition of pollutant pathways,
- Understanding of attenuation mechanisms (including for targeting BMPs),
- Modelling spatial extent, levels and sources of "manageable loads", with user accessibility to models fostered to maximise information transfer,
- Assess effectiveness of BMPs, taking natural spatial variability into account.

Policy, Regulation, incentives and community actions in relation to water resources in New Zealand are currently being re-examined by several agencies (Land and Water Forum, 2010). These include:

- National objective setting, including national environmental standards, is needed to ensure consistency of values and approaches
- Setting of regional standards based on values of receiving waters in a spatial context, and on system time lags. Setting limits (and targets if there is a need to claw back diffuse pollution) is currently a mechanism that regulators have to reduce cumulative impacts of landuse and prevent further diffuse pollution at catchment scales.
- Work with industry landowners and catchment stakeholders, increasingly in ICM-type frameworks, to promote mitigation methods and local-scale management (incentives, BMPs, audited self management, community restoration schemes).

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Landscape control on diffuse pollution: a critical review on some investigations on phosphorus – retaining landscape features

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Abstract

This text focuses on the identification, efficiencies, classification and management of landscape features having a potential buffer function regarding diffuse phosphorus, because of their specific structure (vegetation-soil) and of their location at the interface between sources (farm infrastructures, emitting fields…) and surface water bodies. These buffers are very diverse and correspond to natural landscape features (wetlands, riparian areas…) as well as manmade structures (constructed buffer strips or intermediate cases such as field margins, hedgerows). Their role and efficiency depends on the local factors controlling the retention processes (internal organisation and properties of the buffer), on the position within the watershed, and on the landscape context which reciprocally determines the overall buffer capacity of a watershed. On that basis, we recognize the diversity of the buffers in structure and functioning and thus in the way they attenuate the signal, their limitations (sustainability, side effects) and their hierarchic organisation at the watershed scale.

Key words

Phosphorus, diffuse pollution, buffer strips, landscape, wetlands agriculture

INTRODUCTION

Over the past 2 or 3 decades, the greatest achievement for eutrophication control, has been to obtain a drastic reduction of point sources and begin to implement measures aimed at controlling non-point sources, including agricultural diffuse sources. Diffuse phosphorus (P) has often been identified as a major candidate for pollution control because of the threat of continued P-loading further driving or maintaining eutrophication (Sharpley, 1995; Lake Champlain Management Conference, 1996; CIPEL, 1988…). In Europe, new expectations from aquatic ecosystems, especially lakes (water supply, European water framework directive), new pressures on the watershed combined with the initial effects of climatic change, reinforce the need of a new step in the control of non-point phosphorus. This often led lake managers, to ask scientists operational questions about diffuse agricultural sources of P. An initial set of questions is related to the contribution of P originating from agricultural lands to eutrophication. Another set of questions deals with the achievement of a reduction of P fluxes: which part of watershed P-inputs are controllable? Are the BMPs systems, designed all over the world, implementable in our specific rural context? Should we design a site-specific BMPs system? Can we rely on landscape elements which intercept and retain pollutant ("buffer zones") to reduce fluxes in the specific case of phosphorus.

Given these questions, we developed a set of studies whose general objective was the understanding of the diversity and variability of phosphorus diffuse transfer and transformation at the watershed scale. Our objectives were not to characterize processes and factors involved in P transfer (which are well documented, see e.g. Ryden et al 1973; Sharpley et al 1993; Heathwaite et al 2000, Michaud et al, 2005…), but to understand how landscape features and dynamics distort and organize these processes in space and time, and finally how these factors largely govern the pattern of the P export regime.

We considered mainly medium sized watersheds within a “heterogeneous landscape” which means, presenting a matrix of diverse agricultural fields mixed with patches of non-agricultural land coverage. Heterogeneous landscapes are quite common in Europe and are good models for understanding the importance of landscape structure and organisation, on pollutant fluxes.

In this paper we aim to focus on the buffers as a key aspect of field to watershed scale diffuse phosphorus control and management. Our objective is to review and discuss a series of studies dealing with the mechanisms and assessment of buffer effects at the local and landscape scale. The general questions which form the background to this work are: how do the activities on, and organization of, the landscape contribute to create diverse buffers and thus to attenuate P transfer and export? How can we maximize these effects? How can they be part of a mitigation options strategy?

We use both a theoretical approach, selected bibliography and specific results of our experiments and empirical studies in Lake Geneva (Lac Léman) areas and in Brittany (France), to: 1) conceptualize and categorize buffers effects; 2) classify landscape elements which have the potential to act as buffers; 3) analyse the diversity of conditions and functioning that attenuates P; 4) understand the role of the spatial position of the landscape elements, and of practices that take place within each type (human factors).

CONCEPTUAL FRAMEWORK

Rural landscape as a nutrients transfer system: sources and interfaces.

Transfer system

Rural landscapes are hierarchical mosaics consisting of agricultural fields, non-agricultural lands such as forests or wetlands, and farm infrastructures. All of these components are connected by linear structures such as roads, field margins and riparian strips, and arrayed in the hydrographic network. The landscape components are distributed in space according to natural landscape factors, mainly hydrological and morpho-pedological settings, and to anthropogenic processes, mainly agricultural practices reflecting farm objectives and constraints, and rural development.

The movement of P through the landscape to the outlet of the corresponding watershed is highly variable in space and time. It results in a chain of interacting and cascading processes including, emission from sources, hydraulic transport, storage in landscape sinks and export to receiving water bodies (Wang et al, 2004). The landscape components operating these transfer processes form the “transfer system”.

The P transfer system is characterized by the nature and location of the sources (soil surface), the nature of the flows connecting these sources to the hydrographic network (mainly convergent or sheet surface flows, but also soil matrix flows, piped/ditched flows) and finally by the interaction of flows transporting P with certain types of landscape features. The transfer system regulates the P export regime at the outlet (quantity, quality and timing). This regime is more variable for “particulate-P” (P bounded to particles) than for “dissolved-P” (dissolved forms of P; dissolved- and particulate-P together form “total–P; for P speciation, see Haygarth and Sharpley, 2000)

P sources

In agricultural watersheds, farm fields (mainly tilled fields with some intensive pastures) and farm infrastructures usually represent the main sources of diffuse total-P for water bodies. The P inputs from farm fields are mainly stochastic (from infrequent and sometimes erosive storm events), but secondarily show an annual/seasonal pattern (associated with seasonal precipitation trends, fertilisation timing and biomass decomposition). Dissolved-P is more sensitive to seasonal dynamics (Jordan-Meille and Dorioz, 2004). Fluxes emitted by fields are at a maximum when high-P sources (which depend on practices) coincide with transport factors (erosion, occurrence of surface runoff, local hydrology…). Identifying these "critical source areas" allows the selection of places to preferentially implement mitigation options. Wheel tracks or compacted soil surfaces, which often directly connect crop lands to stream networks, combine to create such high risk areas (Heathwaite et al., 2005).

Mitigation options at the field level are based upon two simple principles (1) control of fertilisation inputs (adjustment of quantity and timing of applications), and (2) development of practices which reduce surface runoff and erosion. The latter corresponds to measures that maintain a high soil infiltrability, avoiding inappropriate practices of soil tillage, crop harvesting or management of inter-crop.

Interfaces and buffers

Non-field farm landscape entities are very diverse and can be classified by their contribution to the transfer system in:

(i) "landscape interfaces", meaning all kinds of landscape structures or sets of structures, situated between phosphorus sources and the hydrographic network; when surface and/or subsurface runoff flows through them, these interfaces act either as sinks, (which attenuate P transfer to varying degrees and are called "buffer interfaces"), or as "connecting media", ensuring a hydraulic connection (fluxes flow through these structures with no major change);

(ii) neutral components, providing a flow of water, which dilutes the concentration of pollutants at the outlet of the watershed.

Landscape interfaces modulate the hydraulic connections within a watershed. The surface runoff enters and flows through the interfaces in a diffuse or concentrated way. Interfaces are very diverse in term of shape, size, and origin. They can be narrow strips, constituting just technical spaces maintained by farmers between their fields and other components (roads, ditches, streams, or other fields). They can be larger landscape elements, made up of fragments of semi-natural landscape (e.g. wetlands, hedgerows…) or vegetative structures constructed intentionally to be buffers.

Buffer and buffer capacity

Concept

The heterogeneity of the landscape has often been considered as a state favourable for trapping diffuse pollutants emitted by farm fields, leading to the concept of buffers and the definition of the "buffer capacity" of a watershed (Haycock *et al.*, 1997; Viaud *et al.*, 2004). The buffer capacity is usually attributed to a few landscape structures, called buffers, which respond to incoming water flows and associated nutrients or contaminants, by temporary and often selective, retention and transformation of some of these pollutants. Buffers play such a role because of their structure and location between water bodies and sources. Interactions between pollutants and these components of the landscape either limit the amount delivered to watercourses or alter the timing of the delivery. The latter effect can be beneficial if it prevents discharges during key sensitive periods of the receiving aquatic ecosystems.

The buffer capacity is universally measured as the ratio between pollutant emissions from the sources (fields) and the amount delivered to the water bodies, with the buffering effect being indicated by a lowering of the pollutant load or an attenuation of the temporal dynamics of the emission, beyond the buffer zone. This measure is applicable from the field to the watershed scale. For total-P, changes in bio-availability should also be taken into account.

Faced with the diversity of structures and processes involved in buffer effects, Viaud *et al.* (2004) proposed a synthetic approach. Inputs and outputs are treated as "signals" (flows and concentrations, or rates). Thus the metrics of the buffering effect is not restricted to mean values, but also include changes in frequency, variability, and range (fig 1a). Regarding total-P the buffer system receives an inflow of surface or subsurface runoff containing particulate- and/or dissolved-P (the "input signal") and releases an "output signal" of a similar nature to down-gradient surface waters. The output signal varies in many ways from the input, with a modified concentration, flux, variation, and/or frequency.

This approach leads Viaud *et al.* (2004) to differentiate several types of buffer according to the signal modulation induced. We will consider only 4 types (fig 1b): “barriers” which stop the propagation (no output signal), “attenuating filters” which decrease the mean level signal and can have a selective effect (e.g. dissolved/particulate), “selective barriers“ which limit the maximum values of fluxes and “retardant filters” which introduce a lag in the transfer. Of course there are mainly of intermediate cases and some temporal variability. Whatever the type of buffer, biogeochemical transformations of P can occur.

Biogeochemical aspects, implications for buffer capacity

The basic processes involved in all buffering effects are well documented (e g. Dillhaha *et al.*, 1997; Uusi-Kampa *et al.*, 1997; Benoit *et al.*, 2004). First of all buffers intercept runoff, retain and store water and/or sediment and consequently the pollutant loads associated. Once pollutants are retained, biogeochemical regulation and transformation may occur.

Particulate-P is easily retained in all kinds of places and structures where the sediment transport capacity of overland flow decreases, promoting particles deposition. Dissolved-P retention is more dependant on contact time, kinetics and soil chemistry (organic matter, Fe oxides etc), thus having some similarities with the behaviour of other dissolved compounds such as NO3. The dissolved-P can be trapped in the solid phase (sorption, precipitation) and consequently the P storage capacity of a buffer will depend partly on the fixation capacity of it soil. These basic processes of the buffer effect for P, can develop in landscape structures that are very diverse in terms of physical state and biogeochemical conditions (marshes, hedges, grass strips etc.). The question is to determine, within a watershed, which non-constructed landscape structures have buffer potentialities and also to assess the efficiency of both non-constructed and constructed buffers?

Other important components of the buffer effect are the processes occurring during storage. Once trapped, pollutants may be stored without transformation or transformed within buffers according to their nature, biogeochemical reactivity and interactions with plants or micro-organisms. For N and C, biogeochemical processes may also result in losses from the watershed in gaseous forms. Regarding P, there is no significant loss but changes to speciation can occur (dissolved-particulate; mineral-organic). Some removal can be achieved by immobilisation in perennial biomass or refractory organic matter. Vegetation and microbiological uptake, however, are often at the origin of further seasonal remobilisation and release of a fraction of the trapped total-P (Dorioz et al 2006). Anaerobic conditions can also create high levels of dissolved-P by the reductive dissolution of ferric hydroxides carrying P.. Thus, the seasonal redox status of a soil, which depends on water residence time, water table depth and fluctuation, is an important determinant of the potential role of a buffer to sustainably retain total-P. It should be noted that soil anoxia has antagonistic effects on N and P dynamics (decreases nitrate but can generate dissolved-P, see Bidois, 1999).

All these basic processes combine to create the buffer effects which are individually as diversified as the factors controlling these processes (vegetation, hydrology, soil, micro-topography, management…)

OVERALL ORGANISATION OF LANDSCAPE INTERFACES AT THE WATERSHED SCALE

Interfaces are important components of the P transfer system (they act as buffers if they are properly structured, located and managed; if not, they ensure direct hydraulic connections between sources and water bodies). Their contribution to the transfer system depends on the objects they “join” together and the water fluxes which flow through them (table 1).

– **Interfaces between farm infrastructures and surface water**. Some landscape structures regulate the surface flow connectivity between sections of farm infrastructures, which mainly consist of impervious surfaces and produces waste water, and surface water. Mitigation options in this case aim mainly to disconnect diverse storage facilities from surface water networks which prevent or reduce the transfer of water polluted by organic matter and nutrients. One possibility for mitigation, among others, (see Stadelmann and Blum, 2005) is to introduce buffers such as a farm pond or grass filter strip.

– **Interfaces between livestock locations, pathways, and surface water**. Free and direct access for livestock to rivers, streams and ditches, is common in many regions and especially in extensive pasturing or rangeland areas. This has many impacts on the P and sediment budgets of rivers:1) direct inputs into the watercourse 2) erosion of river banks and re-suspension of sediment (Lefrancois *et al.*, 2007) and thus generation of a flux of total-P and sediment during both low- and high-flow periods. River bank erosion due to livestock can also allow direct flow connection with hillslope erosion. A manager targeting the protection of water quality aims to transform these interfaces into physical barriers between grazing animals and hydrological network (Meals, 2004). This can be achieved by: 1) fencing off 2) organizing livestock stream and river crossing through specific bridges or paths; 3) relocating gateways of pastures away from watercourses and if possible, from down- to up-slope.

– **Interfaces controlling the connectivity between emitting fields and surface water**. Considering P mobility and dynamics in the environment, interfaces can be differentiated according to the local hydrological and biogeochemical conditions.

(1) **Under saturated conditions** (very shallow groundwater) there are wetlands. They are often located in the lowlands of headwater watersheds, scattered in the rural landscape and often associated with wet meadows. The riparian wetlands, situated along the surface water boundaries, control the inputs from fields to surface water. Some headwater wetlands are in-stream wetlands (inserted within the hydrographic network); they modify the signal emitted by the corresponding watersheds. Maintenance and/or restoration of wetlands are part of the objective of water quality programs, but their attenuating effects on P are still discussed.

(2) **Under unsaturated conditions**, hydrographic network boundaries and field boundaries represent highly diversified interfaces (including constructed buffers, fragments of non-cultivated land, technical spaces…). Under certain conditions they can limit sediment and nutrient transfer from emitting fields to water bodies. Along permanent streams and ditches there are riparian strips (or areas). The objectives are to assess the potential of an individual riparian interface to have a buffer effect and to transform some of them into buffers or to create vegetated buffers instead of ineffective boundaries. The objectives are similar with inter-field boundaries: they control the connectivity of surface runoff, from plot to plot and thus have special importance in the initial step of the propagation of diffuse flow.

BUFFER CAPACITY OF WETLANDS

Small wetlands (typically <10 ha) incorporated into agricultural landscapes, often form interfaces between intensively cultivated hillslopes and plateaux and the water bodies. They often play a major role in the dynamics of exchanges of water and matter between water body compartments and between land and aquatic ecosystems (fig 2).

The efficiency of wetlands at reducing nitrate pollution has been intensively studied (see eg. Machefert and Dise, 2004). Beaujouan *et al.*, (2002) have demonstrated that the length of contact between the wet zone and the contributing area of nitrate, is a major factor in their efficiency regarding nitrogen abatement. Thus a narrow width can be adapted to function as a biogeochemical buffer (Mitsch and Gosselink,1993). Shape, topography and organisation also seem to modify the wetland's effect on total-P transfer, but in a different way.

First of all, all wetlands can trap particles and many individual studies have shown that natural wetlands can, consequently, store some of the total-P emitted from upstream fields (see e.g. Reddy et al, 1999; Uusi-Kämppaä et al 2000). Other experimental results have suggested that wetlands are potential buffers for total-P: P removal has been observed, at least for short term retentions, in natural wetlands used as waste water filtration systems and in artificial wetlands constructed to deal with runoff from fields (Carty et al., 2008).

Three conditions need to combine for total-P retention in a wetland: 1) particulate-P of incoming fluxes decants because of the slowing down of water; 2) dissolved-P is reduced by biological uptake and 3) by some geochemical processes, mainly precipitation (Ca/P and/or Fe/P). Sorption is also mentioned as an important process, particularly in artificial wetlands literature. Absorption by plants and microbes creates short term sinks, with the exception of the incorporation of a fraction of total-P in refractory organic matter of peat (longer sink). Plants in wetlands often have a high P content, and harvesting is a way to remove some P (in some traditional French agricultural systems, biomass from certain wetlands was harvested and used as a litter for livestock, ensuring a return of P from wetlands to the farm fields).

We monitored a very efficient buffer wetland of 2 ha, situated in the Lake Geneva watershed (France, Dorioz and Ferhi, 1994). This case study helped us to understand the key factors of efficiency. At the annual scale, the pilot wetland stored 2/3 of total-P inputs brought by a little stream (Q from 0.1 to 100 $l.s^{-1}$). This represented retention of about 7 kg total-$P.ha^{-1}$. A slight selective effect was observed (60% of retention for dissolved-P and 78% for particulate-P). Considering individual hydro-meteorological periods over a year, we showed that the efficiency tended to be greater with higher-flow event inputs (fig.3) and that the wetland functioning was close to that of an "attenuating filter" (fig.1b). Moreover, transfer within the wetlands led to an important change of particulate-P speciation, as indicated by a comparative study between sediment trapped at the outlet and the inlet (table 2). For the same total-P content, outlet sediments showed a change of the two main P mineral fractions (increase of P extractible by HCl, considered as Ca bounded P, and decrease of P extractable by NaOH considered as Fe bound P), much lower bio-P content, and an exceptionally high fixation power. These drastic differences and the P mass balance, suggest that the wetland introduces a major discontinuity in the total-P transfer dynamic in relationship with: 1) a sufficient water residence time; 2) a diffuse hydraulic connection between inputs and outputs; 3) a consecutive spatial differentiation of functioning within the wetland (sedimentation occurring in the inlet areas, chemical precipitation near the outlet, and biological uptake in the intermediate and largest area). We assume that the efficiency observed in P retention is due to such an organisation and functioning.

The diversity of wetlands in a landscape is very great and as such, individual studies may not be justifiably extrapolated to wetlands in general. Wetland functioning varies with micro-local conditions (shape, vegetation topography, micro-hydrology…) and also with seasonal and hydro-meteorological conditions. In the landscape area including our pilot wetland, we described all of these micro-conditions for wetlands on a gradient from small (<0.1 ha) endoreic wetlands acting as a barrier for surface runoff and total-P, to larger ones acting either as attenuating filters (but more or less leaking during higher flow events). Moreover, despite sedimentation occurring in all wetlands, some of them may be less effective (or sometimes ineffective) in attenuating total-P because of re-mobilisation of particulate-P due to erosion of the wetlands along the flow pathways and/or release and export of dissolved-P (released by reduced iron compounds). This latter phenomenon needs anaerobic conditions which could be permanent or seasonal according to the wetland type (Khalid *et al.*, 1974).

The watershed scale adds complexity: multiple site specificities, interactions between diverse types of functioning, connectivity between wetlands and water bodies (fig 2) and the effect of position within the watershed. Using a landscape approach to study the overall attenuation of diffuse-P pollution in a Lake Champlain sub-watershed (USA, VT), Wang *et al.* (2004) has defined characteristics of the wetland buffer effect on a watershed scale:

(1) wetlands as a whole or as a general land cover type, are significant elements of the landscape buffer capacity for total-P (evaluated to 30%);
(2) P removal is highly variable within a watershed (comparison of a significant set of inlets and outlets during a spring snowmelt, indicated that the net flux was positive for 30% of the sampled wetlands and negative for the other 70%);
(3) landscape position (stream order) modifies the intensity of effects.

The overall message is: although wetlands are diverse in nature, structure and function, their preservation is positive regarding mitigation of P losses. Some management can be done to maintain, improve or restore their efficiencies as buffers. Available knowledge on the working of P-efficient pilot wetlands, gives a framework to advise this management: increasing incoming fluxes from the hillslope (e.g. redirecting drainage water), controlling internal water pathways in order to increase residence time in wetlands and decrease flow velocity and, finally, harvesting biomass to limit P stocks.

Management and artificial transformation of wetlands must also consider some uncertainties concerning the long term saturation of wetland buffers. One can assume that they will be filled with sediment and P, and become ineffective or worst become a source of P. Wetlands used to treat wastewater provide an extreme case of very rapid saturation, turning the sink into a source.

BUFFER CAPACITY OF INTERFACES IN UNSATURATED CONDITIONS

Under unsaturated conditions, vegetative buffers are typically constructed devices along reaches of hydrographic networks, with a strip feature. These constructed vegetated buffer strips have been widely studied and represent a quite well known, tested and calibrated "model". By comparison with this model, it is possible to evaluate the potential buffer effect of non constructed interfaces, particularly of the various landscape entities constituting riparian boundaries or boundaries between farm fields (table 2). If properly structured, managed and situated, all interfaces can contribute to water preservation at the local level. They can also have an effect at the watershed level, modifying the flow regime in the stream, particularly by a decrease of the peak flow and thus the erosion directly related to discharge, such as river bank erosion.

Lessons learnt from constructed vegetative buffer strips

Constructed buffer strips are generally considered to offer an efficient protection against total-P. Hoffmann *et al.* (2009) have reviewed the efficiency of riparian buffers for total-P retention and quantified the reduction of outputs as 41 to 93% (as a percentage of the inputs). The same order of magnitude is given by Dorioz *et al.*, (2006) for particulate-P in grass filter strips. The constructed buffers are rarely 100% effective under experimental conditions (which are generally chosen to be a realistic representation of farming systems). Regarding fluxes, riparian buffers may account for total-P retention rates of up to 128 kgP $ha^{-1}.yr^{1}$, and plant uptake may temporarily immobilize up to 15 kgP $ha^{-1}.yr^{1}$ (Hoffmann *et al.*, 2009). This can be compared to the 1 to 2 kgP $ha^{-1}.yr^{1}$ exported on average by tilled fields. Retention of dissolved-P in riparian buffers is lower, often below 0.5 kgP $ha^{-1}.yr^{1}$, several studies have shown a significant release of dissolved-P of up to 8 kgP ha^{-1} yr^{1} (Hoffmann *et al.*, 2009).

Functioning

The buffering effect of vegetative buffer strips results from a group of phenomena which are triggered during runoff periods, and are the consequences of the hydrological and biogeochemical properties of the zone. Buffer strips have an initial effect on surface runoff flowing downslope over a rougher and more porous surface than upslope, causing it to slow down (fig4a, compartment 1, 2) and infiltrate the soil. Infiltration leads to the injection of dissolved-P and other dissolved nutrients carried, into the soil mass (fig 4 a, compartment 3). Flow through the leafy matrix of grass and herbs covering the soil of the buffer, causes a complementary process of "filtration" (or "turbulent filtration" fig4a compartment) 2) which seems to be efficient in retaining small size particles (Munos-Carpena *et al.*, 1999;). All of these processes combine to reduce the sediment transport capacity (fig4b). Excess particles are progressively sedimented and trapped. Much of the P transported to watercourses being bound to particles, sedimentation is the main physical process occurring within buffer strips.

The specific hydrological properties of buffers are generally linked to: 1) a continuous soil coverage by plants, hence a greater resistance to surface flow and a decrease in flow velocity; and 2) a denser and sometimes deeper root system, which improves soil structure and increases the permeability of the soil. The infiltration, as a result of dense rooting brought about by perennial vegetation and particularly grass species, is often considered to be the main factor in the reduction of overland flow, and thus of deposition of particles.

Particulate-P and sediment are mainly stored in soil surface layers (0-5 cm). The coarser sediments, including soil micro-aggregates (Trévisan and Dorioz, 2001) and a large part of the total sediment, is deposited at the front edge of the filter strip and also accumulate in the final metre of the emitting field (fig 4a, compartment 1). This illustrates the importance of the upper boundary in the functioning of the buffer. Sedimentation through the buffer is selective. Consequently, in some cases, output is made up of the finest fraction of particulate-P, which is also the most bio-available.

Between periods of rainfall, several important processes occur that restore buffer properties (Dorioz *et al,* 2006). Water is evapo-transpirated which renews the water storage capacity of the soil. Deposited sediments are stabilised thanks to entrapment by fine root growth, and/or re-aggregation of fine particles in larger, water stable aggregates. Dissolved-P is actively fixed by soil constituents and biota, and thus remains in the surface layer (these reactions are reduced during cold periods and perhaps universally in the colder climates). Finally, intercepted total-P is partially taken-up by plants and microorganisms and this can lead to release of some portion of P (Stutter *et al.*, 2009). Release processes are regulated by physical and chemical conditions of soils: temperature, drying/rewetting and freezing/thawing, pH and organic matter dynamics (Sharpley and Tunney, 2000).The same kind of processes controls the long-term efficiency of buffer strips. Accumulation of sediment over the years tends to modify the surface state of the soil (micro-morphology and permeability) and increase the P content of the surface soil of the buffer. Finally, the storage compartments (1,2 fig4a), if not properly managed, may be saturated and thus the buffer could become ineffective, or even a source of P.

Key factors controlling effectiveness

Individual buffer strip effectiveness (input/output balance) depends on the interactions between two categories of factor (Schmitt *et al.*, 1999; Eck, 2000): 1) <u>internal factors</u> (size, slope, soil permeability, vegetation) which regulate the residence time and infiltration rate of water, and have been the subject of many of experiments, and 2) <u>external factors</u> (emitting field, location…) which control the properties of incoming flows (surface/subsurface; concentrated/diffuse; P loads).

Dimensions of the buffer. Retention of total-P being the result of phenomena which develop in space, the buffer width, or the width weighted by the slope, are often considered by Extension Services to be the main factor controlling efficiency of vegetated buffer strips. However, experiments have tended to demonstrate that there is no clear universal relationship between total-P sequestration and buffer width. Within a given buffer strip, the effectiveness does not increase linearly with width (e.g. Dillaha *et al.*, 1989; Castelle *et al.*, 1994). Several reviews comparing sets of experiments conclude that the results of effectiveness are very scattered for both sediment and total-P retention (Schmitt *et al.*, 1999; Dorioz *et al.*, 2006; Liu *et al.*, 2008; Hoffmann *et al.*, 2009; Collins *et al.*, 2009). Thus, compilation of experimental results obtained with 10 m strips, gives a retention of total-P ranging from 40 to 100%. Extremes seem more defined: with a width of < 3 m the retention of total-P is rarely more than 60%, and a 100% performance needs generally more than 8 m. Finally very large strips (such as 20-40 m) do not systematically ensure 100% retention (Castelle *et al.*, 1994).

The scatter in the percentage of total-P retained at a given width is the result of several sources of variability: methods (monitoring tends to be different from an experiment to another), other internal factors (most importantly vegetation, see next paragraph) and the nature of the incoming flow. All authors agree that this latter point is critical: an optimal functioning of vegetated buffer strips needs uniformity and regularity of pollutant input flows (Bidois, 1999; Uusi-Kamppa *et al.*, 2000). In most cases where wide buffer strips have been found partially or totally inefficient, the reason were attributed to the conditions of flow entering the buffers; this is generally spatial (concentrated surface flow), but also temporal (high flow velocity, snowmelt…). Inversely, a good retention rate has been obtained even with quite narrow strips, when the input surface flows were diffuse. This suggests that the dimensions of a constructed buffer strip should be modified according to the nature of the input flows, and thus according to the position within the watershed or to agricultural practices encouraging this type of flow.

Vegetation is another source of variability. The plant coverage has a secondary role as long as the minimum requirement of plant coverage (60-70%) is realised (Rogers and Schumm, 1991). It can be grass or a mixture of natural vegetation including grass, and/or trees and bushes: the efficiency of the filter depends more on plant coverage of soil than on the vegetation type (Dorioz *et al.*, 2006). However trees and shrubs are more stable over the long term and signify a more sustainable landscape management (Michaud A. IRDA, Pers. Com.). Management of vegetation is another important factor to consider. A close cut is preferable as it avoids the creation of preferential routes for runoff, and ensures a plant growth dynamic able to stabilise sediment deposits. Enhancing plant uptake of solubilised P would provide a possible loss pathway via vegetation removal. Loss rates of 4-15 kgP $ha^{-1}.yr^{1}$ have been documented through biomass removal (Hoffmann *et al.*, 2009). Buffer biomass harvesting is a recommended strategy for many agri-environmental schemes in America and Europe. Finally, vegetation management could be a critical factor in the long-term, in manipulating buffer conditions to remove stored P, increase buffer strip lifespan and prevent P leaching losses.

Vegetation also means root systems and indirect action on soil properties. Perennial herbaceous vegetation has been recognized to have the best potentiality (Schmitt *et al.*, 1999) because of its well known influence on soil structure and consequently on soil permeability. Roots can also theoretically have an effect on subsurface fluxes but this is not well documented for dissolved-P. The root system of the trees might be more efficient because it can take up water and some chemical compounds from shallow groundwater (up to a few metres deep) and thus have an effect on the subsurface flow in some cases, whereas the grass system cannot. This underlines the specific interest to test hedgerows effects on P.

Design decision. The uncertainties of scientific evidence for effectiveness of buffer strips, in terms of total-P sequestration, makes policy decisions on buffer design rather difficult. The standards should at least include: 1) a continuous perennial vegetation coverage; 2) a vegetation management and harvesting; and 3) a width modulation according to the nature of the surface runoff inputs (in some French regions recommendations indicate a width from 5 to 10 m with diffuse surface runoff and 10 to 15 m for concentrated surface runoff, see Gril *et al.*, 2009; CORPEN, 2007). Because of the extreme variability of the landscape, new buffers, still to be constructed, should be designed within these criteria, but adapted for site-specific conditions (Correll, 2005).

Assessment of buffer capacity of non constructed landscape interfaces

Most of the landscape interfaces are not constructed buffers. Because of the extreme variability of these non-constructed interfaces (table 2) the assessment of their potential buffer effect is never easy. Measuring the individual responses (input/ouput) of all of these diverse elements, for example in a given watershed, is rarely possible. Fields indicators are needed. They can be extrapolated from experiments on constructed vegetated strips considering that the same structure means the same function and that key factors of efficiency are the same for all kinds of interfaces. On that basis,a non-constructed interface which introduces a significant change in conditions for surface runoff and infiltration, due to its roughness, vegetation, permeability and size, can reasonably be considered as a potential buffer for total-P. Table 3 presents the main characteristics used to identify, with a visual and soil expertise, these potential buffers in our pilot areas of Lake Geneva basins.

We applied such expertise in a rural sub-basin of 3000 ha. The studied landscape is heterogeneous (Wang *et al,* 2004) and a range of landscape structures existing in unsaturated areas were identified as potential buffers (semi-natural riparian vegetations, field margins, hedgerows…of varying width). Among them, we observed that well located hay fields (inserted between a source of P and a reach of the hydrographic network) often created very efficient buffer effects (acting as a barrier). This supports the idea that a mixture of land cover and land use is advantageous regarding attenuation of P transfer. Faced with the diversity of landscape interfaces structures, we created a typology which classified them according to their permeability, dimensions, soil, into 3 classes of potential buffer capacity: no buffer effect but protection against stream bank erosion, attenuating filter and barrier.

The typology was also used to categorize all of the landscape interfaces in several sub-watersheds, which were finally characterized by the % of tilled fields buffered by an efficient interface (attenuating filter or barrier). Considering that this % was a reasonable measure of the overall buffer capacity of a given agricultural area, we showed that this property of sub-watersheds was highly variable and mainly related to human factors. Most of the buffer capacity due to interfaces was generated and managed by a few types of farming system (traditional dairy farming systems) while, on the contrary, some more intensive systems tended to increase surface runoff connectivity. Surprisingly, the technical conditions favorable to implementing and constructing new buffer strips were found only in some intensive farm types. Finally, management of non-agricultural land appeared also to be crucial and biophysically induced discontinuities (often corresponding to boundaries of sections of forest) were, overall, a secondary factor.

Efforts will be made to validate our typology locally. This could be accomplished first by a set of experimental studies aimed at calibrating the most typical landscape interfaces identified. Initial results have provided evidence that some hay fields identified as buffers can responded to incoming total-P fluxes by retention (Trévisan and Dorioz, 2001). At the watershed scale, we envisage, using a comparative study of a set of agricultural sub-watersheds, to test the correlation between landscape organization (with descriptors including the typology of interfaces) and some expression of P fluxes at the outlet (similar to the "landscape approach" used by Wang *et al.*, 2004 for wetlands).

Specific buffer capacities of inter-field boundaries

In an agricultural landscape made up of a matrix of small fields, like in our alpine lake basins (mean size of individual fields, 1-2 ha), inter-fields interfaces have a specific importance because they – even the narrow ones – can prevent the concentration of surface runoff and thus: 1) contribute to limiting cascading effects of erosion from field to field; and 2) increase the performance of the down-gradient vegetated buffers. Consequently in our landscape system, they were considered as a critical location for buffers.

Whatever their initial detailed features, inter-field boundaries can be managed to become efficient filter strips. Recommendations for improvement and maximisation of existing interfaces are based upon the same kind of diagnostics as the assessment of interfaces, previously presented. Gateways often represent a specific point of interest because they are breaks in the boundaries and thus are critical areas for surface runoff in all kinds of fields (tilled fields or pastures). Ruts from tractor wheels tend also to converge and can channel surface water to these areas. At the landscape level gateways, livestock and tractor pathways represent a network of preferential flow pathways that hydrologically connect fields situated up-slope to down-slope and finally to the water course. Relocation of gateways, if possible, from down to up-slope is a simple way to decrease local and global hydrological connectivity, thus reducing this source of P pollution.

In some regions, the networks of interfaces between fields are made up with hedgerows ("bocage" in Brittany France) which means planted with trees, with or without a bank. Intense watershed studies have shown that the influence of these structures at that scale on the flow regime of streams and rivers (Mérot 1999; Viaud *et al.*, 2005) decreases the peak flow by modifying surface, subsurface, and inter-storm flows, and modifying evapo-transpiration from the watershed, therefore contributing to a decrease in the erosion of the river bank and flooding. We can reasonably assume that this will also reduce total-P transfer, at the watershed scale.

DISCUSSION – CONCLUSION

Diffuse-P transfer is a landscape-level phenomenon involving the complex diversity of landscape components that governs flow paths and the spatial distribution of sources, connections and buffer effects that make up the transfer system (Wang *et al.*, 2004). Buffer effects influencing total-P transfer occur in many kinds of natural or semi-natural landscape entities and in constructed devices. All buffers have the capability to both, decrease the suspended-matter transport capacity of surface water flows and to store water and particles, thus increasing their residence time and allowing further biogeochemical processes to develop. This potential for attenuation is obtained each time surface or subsurface water flows through hydrological discontinuities due to certain types of soil-vegetation and/or topography. Total-P can be easily and efficiently trapped, even during short and relatively rapid transfer, via sorption of dissolved-P and physical retention of particulate-P. Dissolved-P is more sensitive to contact time, kinetics and soil chemistry. Trapping generates storage in sediment, soil, and biomass, preventing or delaying, the export to sensitive water bodies.

Construction of buffers has been largely promoted as an efficient tool for reducing the transfer of suspended matter, pesticides and nitrogen to waters bodies (Patty *et al*., 1997) and, in Europe, often sustained by financial compensation. Recommendations to employ constructed buffers to control diffuse total-P transfer have also become very popular among lake managers. But there are several issues for the assessment of the buffer effects on total-P, and this contributes to some uncertainty in the capacity and design of buffers. Moreover, land managers has not paid enough attention to non-constructed landscape buffers (particularly hedges, field margins, hay fields) whose beneficial effects on total-P transfer exist but are difficult to quantify. All this illustrates the need for better conceptual and operational tools.

Since the long-term functioning and eventual saturation of constructed buffers are not yet well documented, there is an initial uncertainty about the sustainability of buffers regarding total-P. As no loss pathway exists for P, it is unlikely that retention can be infinitely sustained (Stutter *et al*., 2009). Sustainability is driven by the processes occurring after the initial trapping phase and can limit, over the relatively long term (years), further mobility of accumulated total-P. That limitation depends largely on the management of vegetation and soil surface and conditions. Anoxia and/or dead organic matter accumulation on the soil surface (corresponding to plant uptake), leads to dissolved-P releases, which can limit or nullify the buffer capacity. In the same way, the accumulation of diverse contaminants within the same storage location is not necessarily positive. As an example, dissolved-P release has been observed in wetlands receiving excessive fluxes of NO_3 (Paludan, 1995).

Diversity and common denominators. Buffers usually appear to provide useful short-term functions in the attenuation of diffuse phosphorus pollution, despite the extreme diversity of landscape contexts and structures, which explains the variability of individual performance. The performance of buffers varies largely according to a set of interactive, internal and external factors – a complexity which limits our capability to extrapolate the buffer capacity of a given landscape buffer from experimental results. In fact, the multiplicity of factors driving buffer capacity being thus, each study of an individual buffer tends to be site-specific and scale-specific even for quite well-known and tested models like the grass vegetated buffer strips (Dillaha and Inamdar, 1997). However, fortunately there are only a few common limiting factors. These can be used to indicate whether a buffer effect can, or cannot, be reasonably expected in a given landscape structure. For example, in unsaturated areas, buffer effects, require first of all, a minimum width, permeability and soil coverage, with these dimensions having to be modulated according the nature of flow inputs (diffuse/concentrated). This latter characteristic controls the eventual existence of preferential pathways for surface water flows within the buffer. This characteristic is also an important indicator of the functioning of wetlands.

Watershed scale. The watershed scale adds a lot of complexity, and our understanding of the overall buffering capacity for P is limited. Firstly, the transfer system includes not only sources (emitting discharge/concentration inputs signals) and buffers (transforming these signals): many landscape elements between sources and water bodies function just as connecting media. These are generally and implicitly considered as neutral components, transferring the input signal without modifying it. But we should pay attention to other situations: 1) some connecting interfaces can become critical areas for erosion, if not minimally vegetated and managed (e.g. banks damaged by tilling); and 2) direct field-to-field connections can facilitate concentrated runoff and consecutive cascading erosive effects. In the latter case, the absence of a buffer is not neutral, but rather means an increase in the signal intensity and difficulties in controlling diffuse transfer.

Buffers have also to be evaluated with respect to scale and landscape connectivity (e.g. Verstraeten *et al*., 2006). Within a watershed, buffer interfaces represent very diverse entities but with similar function with regard to total-P attenuation. In heterogeneous landscapes, they are often organized as a network characterized by: 1) connectivity; 2) distribution related to slope, vegetation and local hydrologic gradients; and 3) management practices applied on these pieces of land (a given structure acts as a buffer only if properly managed).

Within this network, the efficiency and nature of buffer responses tend to be distributed spatially as a function of the organisational level of the watershed. Fig 5 illustrates this idea using as a reference the landscape organisation observed in the Lake Geneva rural area. Buffers acting as real barriers (as defined by Viaud *et al*., 2004) tend to be located in places corresponding, to short and relatively rapid transfers, which means sheet surface flows, temporary inputs, and to unsaturated areas (no release). Such efficient buffers (no ouput signal exept background level), constructed or otherwise, are usually located at field boundaries (often vegetative strips or hedgerows). Once the surface water flow is concentrated, barriers are rare (they might be very wide); consequently the buffers existing at this level of organisation mainly function as attenuating filters (leaking vegetative strips or riparian wetlands), with different degrees of efficiency for total-P, and a selective effect for bio-available P and dissolved-P. At the upper level of organisation (sub-watershed, stream order 1 and 2) in-stream wetlands functioning as attenuating filters are the only type of buffer possible. Finally at the basin level, buffer effects become limited to trapping particulate-P in flood areas (an "attenuated barrier" according our classification). The in-stream processes associated with biota and sediment delay the transfer but their environmental benefit has to be demonstrated (Dorioz et al 1998). Thus the buffer network has a hierarchical organisation typical for P transfer system and corresponding to a decreasing gradient of efficiency from the fields up to the basin level (the dynamic would be inverse for NO_3).

Maximizing the buffer effect: "critical buffers". Since the position of the buffer interfaces within the watershed is one of the major drivers of their efficiency, it is generally considered that the placement of improvements of buffer capacity of interfaces or/and the construction of new buffers, must be done in hot spot locations, such as in bottom field corners, gateways…. This means that careful selection of buffer features is required in critical areas, depending on the local hydrological situation. An example of the latter point would be the selection of grassed buffer strips for sheet flow, but bunds and constructed wetlands for convergent flow paths. Other decisions also have to be made, such as whether to target hot spots with wider buffers (Vidon *et al.*, 2010), or a uniform system of narrower buffers applied everywhere (e.g. 2 m riparian buffer strips) preventing surface flows to be concentrated. This can be solved differently according to the rainfall regime and thus climate. Special attention should also be paid to situations where no buffer would mean a cascading effect (e.g. inter-field buffers).

In the limited space of many European agricultural areas, buffers still need to be proven to work, to ensure their existence and implementation. However, the lack of data and models that we have mentioned is not sufficient to deter the incorporation of all categories of buffers into landscape management. Buffers should be maintained, constructed and used despite their limitations and as part of the general strategy for the control of phosphorus diffuse pollution.

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Mechanisms of Nitrogen Diffuse Transfer to a Coastal Environment: Case Study of the Chesapeake Bay, USA

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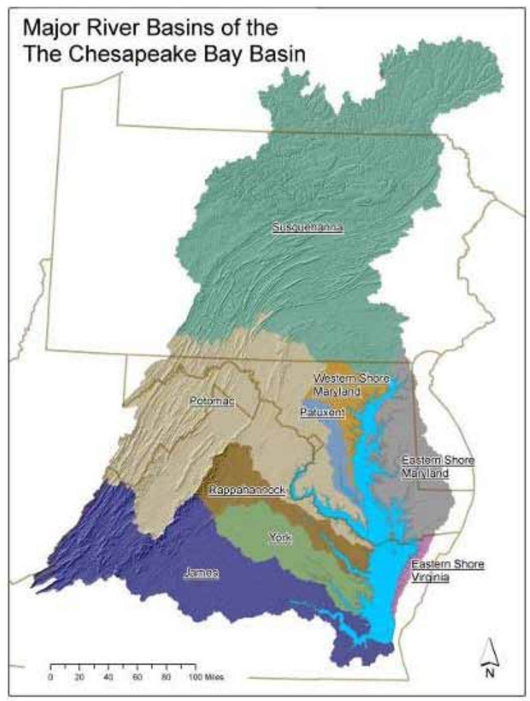
Abstract:

The Chesapeake Bay watershed is the largest coastal estuary in the United States of America. Approximately one-half of the Chesapeake's water volume originates from a 64,000 plus square-mile watershed encompassing parts of Delaware, Maryland, New York, Pennsylvania, Virginia, West Virginia and the District of Columbia (Figure 1: Chesapeake Bay Watershed). The land-to-water ratio (14:1) is the largest of any coastal water body in the world, causing the additive effects of human interactions with the natural landscape to contribute to an unhealthy estuary.

Nitrogen and phosphorus are the primary nutrients of concern, which in association with sediments, annually cause water quality impairments within the Bay and its tributaries. Agriculture is estimated to be the single largest contributor of nutrients and sediments to the tidal Chesapeake on an annual basis. According to the EPA Chesapeake Bay Program Office (CBPO), nitrogen losses from agricultural lands represent more than 38 percent of the total contribution of nitrogen to the Chesapeake.

The mechanisms of nitrogen diffusion within the Chesapeake are significant and diverse, including surface and subsurface losses from stormwater runoff and infiltration respectively, as well as vitalization losses and atmospheric deposition. The application of targeted Best Management Practices (BMPs) is a critical tool to minimize nitrogen losses to the Chesapeake.



Keywords

Chesapeake Bay, Coastal Environment, Nitrogen

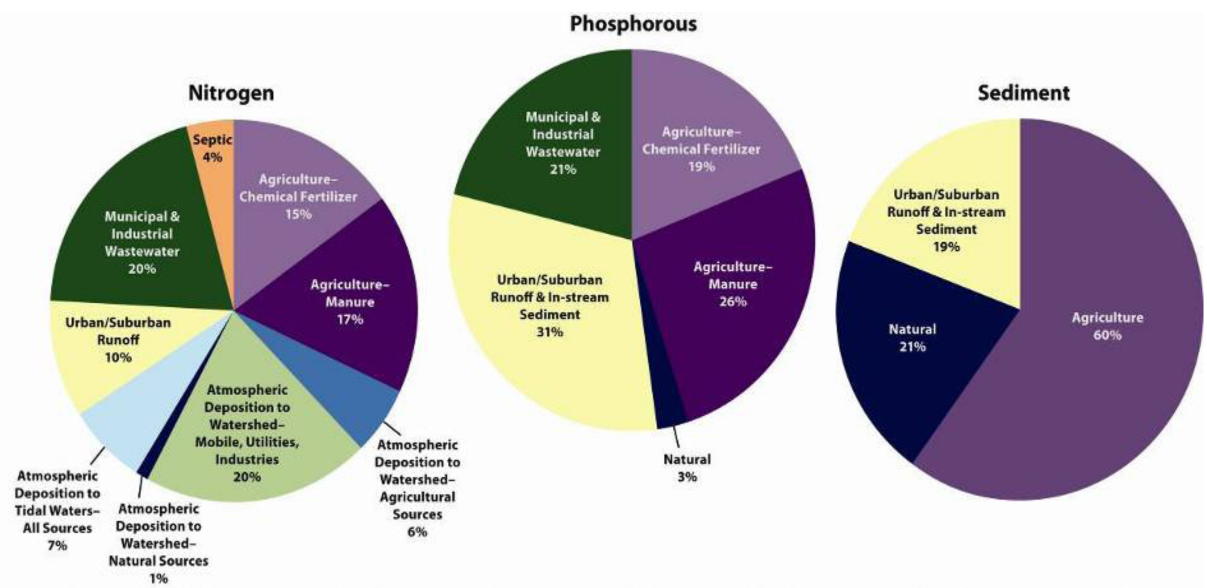
INTRODUCTION

The Chesapeake Bay watershed is the largest of 130 coastal estuaries in the United States of America and the third largest in the world. Approximately one-half of the Chesapeake's water volume originates from the Atlantic Ocean, with the remainder being provided from a 64.000 plus square-mile watershed encompassing parts of six states (Delaware, Maryland, New York, Pennsylvania, Virginia and West Virginia) and the District of Columbia. There are approximately 50 major tributaries that flow into the Chesapeake, but only three deliver nearly 80 percent of the estuary's fresh water; the Susquehanna River (48 percent), the Potomac River (19 percent) and the James River (14 percent).

The Chesapeake's significant land-to-water ratio (14:1) is the largest of any coastal water body in the world. The watershed is also home to almost 17 million people with nearly 156.000 additional new residents annually. Thus, the human interactions with the natural landscape, in combination with more than 100.000 streams and rivers serving as conduits threading the watershed, annually contribute an unhealthy excess of nutrients and sediments to the estuary. The additive effects of which can negatively impact the more than 3.600 species of plants, fish and animals to be found with the Chesapeake and its surrounding watershed.

Nitrogen and phosphorus are the primary nutrients of concern, which in association with sediments, cause water quality impairing levels of dissolved oxygen, chlorophyll a, and water clarity. Thus, the Chesapeake has been identified as an impaired water body under the federal Clean Water Act (CWA).

In consequence of the impaired designation under the CWA, the federal Environmental Protection Agency (EPA) is currently under litigation agreement and court order to prepare and implement a Total Maximum Daily Load (TMDL) plan for the tidal Chesapeake and its contributing watersheds by December 31, 2010. For the first time since the partnership restoration efforts began in earnest in the mid 1980's, the Bay TMDL will set federal mandatory loading limits for nitrogen, phosphorus and sediments to the tidal waters by contributing basin. Due to the size and complexity of the Chesapeake and its watershed, the Bay TMDL will be the largest TMDL ever developed, and will set a new national standard for future TMDLS in other major water bodies across the United States.



Note: Does not include loads from tidal shoreline erosion or the ocean. Urban/suburban runoff loads due to atmospheric deposition are included under atmospheric deposition loads. Wastewater loads based on measured discharges; other loads are based on an average hydrology year using the Chesapeake Bay Program Airshed Model and Watershed Model Phase 4.3 (CBPO, 2009).

The major land uses of the Chesapeake's watershed are principally forest (65%) agriculture (23%) and developed (12%). According to the USDA National Agricultural Statistics Service's (NASS) 2007 U.S. Agricultural Census, approximately 83.700 farms exist in the watershed, representing the largest single managed land use at over 12.826.000 acres in total acres. Over 7.193.000 acres of these acres are in crop land production while 1.925.000 acres are in pasture management, the remainder being predominantly wood land and operational facilities (Figure 2: Chesapeake Bay Nutrient and Sediment Contributions by Sector).

Consequently, agriculture is not only the largest managed land use, but is also estimated to be the single largest contributor of nutrients and sediments to the tidal Chesapeake on an annual basis. According to the analysis by the EPA Chesapeake Bay Program Office, nitrogen losses from agricultural lands represent more than 38 percent of the total contribution of nitrogen to the Chesapeake. The sources of nitrogen from agricultural lands include losses from inorganic fertilizers (15%), organic nutrients (17%) and atmospheric deposition to the watershed attributed from agriculture (6%). In addition, agriculture is partially responsible for the atmospheric deposition to tidal waters (7%).

Methods

The EPA Chesapeake Bay Program Office relies on multiple sources of information for gauging current water quality and habitat conditions within the Bay and its tributaries, as well as modelling future potential conditions through the implementation of nutrient and sediment management practices and land use changes. A suite of national and regional models are utilized to analyze and interpret the data, calibrated to several decades dedicated collection.

An important source of water quality information is obtained through the US Geological Survey's Tidal and Non-Tidal Water Quality Monitoring Networks, consisting of an extensive array of automated real-time monitoring stations (Figure 3: Chesapeake Bay Water Quality Monitoring Sites). Non-Tidal monitoring sites obtain both flow as well as concentration for not only the major tributaries, but also increasingly for the sub-watersheds. Base flow conditions are monitored at all sites, with storm flow sampling being typically conducted at stations with automated sampling equipment.

Water Quality data obtained from the monitoring networks is analyzed by the US Geological Survey's SPARROW Model to attribute measured nutrient loads to documented human activities and land uses throughout the watershed. This analysis allows the allocation of measured nutrient loads to the non-point sectors, such as forests, developed areas and agricultural land uses.

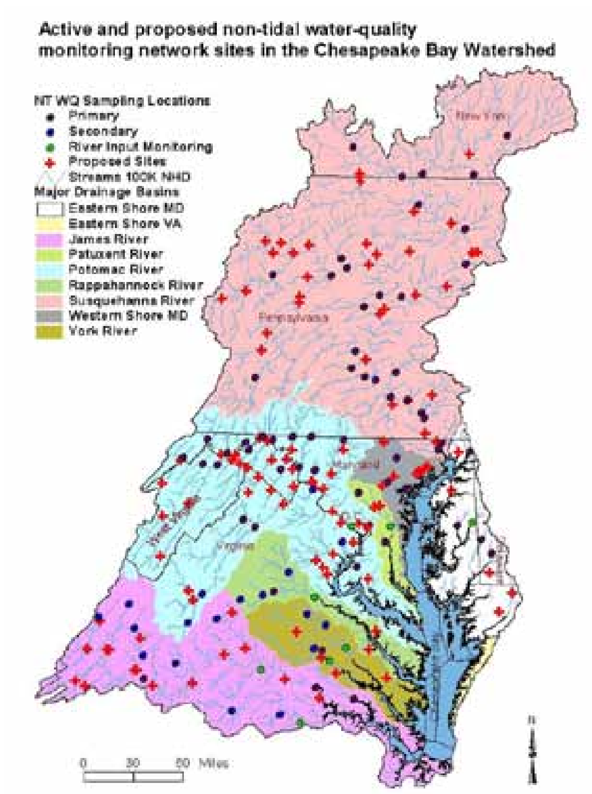


Figure 3. Chesapeake Bay Water Quality Monitoring Sites, CBPO

Management implementation data is provided by each of the Bay jurisdictions electronically through the National Environmental Information Exchange Network (NEIEN). Consisting of permitted point source discharge data and applied management practices, the information is used to inform the Chesapeake Bay Program models for implementation progress reporting.

The Chesapeake Bay Program's Scenario Builder Model (SB) is used to create simulations of the past, present and future states of the watershed gauge potential effects of management actions and to evaluate alternatives. In addition, the model produces inputs for the Chesapeake Bay Program's Watershed Model through the calculation of nutrient mass balances for non-point sources. This is especially relevant for agricultural land uses for incorporating specific nutrient generation, update and loss calculations for diverse livestock and crop production systems.

The Chesapeake Bay Program's Land Change Model analyzes current conditions and forecasts the effects of future developed and agricultural land uses and population on the Chesapeake Bay watershed. The model bases forecasts on US Census Bureau information, land cover trends from satellite imagery, sewer service area and county level projections.

The Chesapeake Bay Program's Airshed Model analyzes data on nitrogen emissions from permitted sources such as power plants, and non-permitted sources such as agriculture, vehicles and other sources to estimate the amount and location of atmospheric depositions on the tidal Bay and the watershed. National and jurisdictional air quality initiatives are utilized by the model to forecast future reductions in nitrogen emissions.

The Chesapeake Bay Program's Watershed Model (WSM) incorporates information from multiple sources, including Scenario Builder, the Land Change Model and the Airshed Model to estimate the source and amount of nutrients and sediments reaching the tidal Chesapeake on an annual basis. Within the structure of the model, the watershed is divided into more than 2,000 modelling segments representing political and physical boundaries. Several sub-models are used to calculate surface runoff and sub-surface flows for all land uses, to simulate soil erosion and the transport of nutrients and sediment loads from land uses to watershed tributaries, and to simulate the transport and attenuation of those nutrients and sediment loads from the tributaries to the tidal Chesapeake.

The Chesapeake Bay Program's Estuary Model analyzes the water quality effects from the tidal nutrient and sediment loads generated by the Watershed Model. The tidal Chesapeake is sub-divided into more than 57.000 modelling cells and is built on two sub-models to simulate the mixing of waters within the Bay as well as its biological, chemical and physical attributes.

Through the combined analysis of water quality data and other sources with the Chesapeake Bay Program's suite of models, the present and future effects of national and partnership actions can be assessed and evaluated. This ability is especially critical to the development of a Chesapeake Bay wide TMDL.

Results/Discussion

The mechanisms of nitrogen diffusion within the Chesapeake are significant and diverse, including surface and subsurface losses from stormwater runoff and infiltration respectively, as well as volatilization losses and atmospheric deposition (Figure 4: Nitrogen Cycle). Approximately two-thirds of the Chesapeake's nitrogen pollution originates from human activities leading to surface and subsurface losses from the watershed, while atmospheric deposition accounts for the remaining one- third.

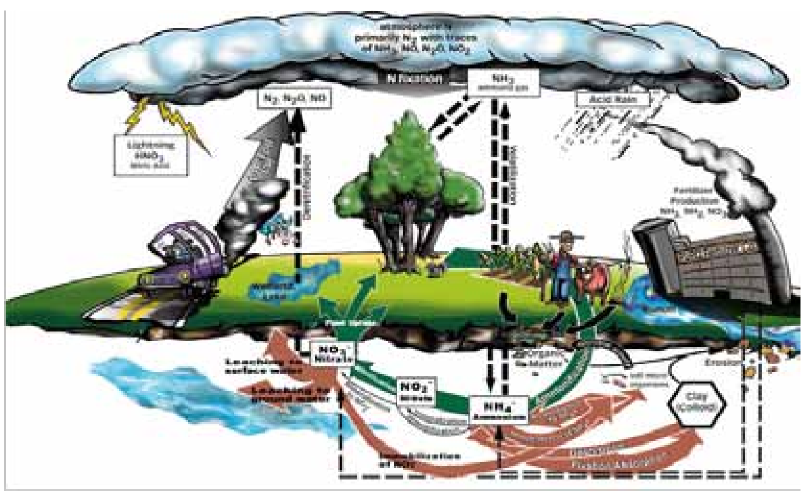


Figure 4. Nitrogen Cycle

Nitrogen pollution impacts the health of the Chesapeake through the increased growth of algae, at times encouraging dense algae blooms on the water's surface or on the leaves of submerged aquatic vegetation (SAV). These algae blooms can have a detrimental effect on the growth of SAV from diminished sun light penetration through the water column as well as reduced photosynthesis. Compromised SAV beds also impact a diversity of species which rely upon them as a critical food source and habitat.

A secondary effect of algae blooms can occur when their growth exceeds the capacity of algae-consuming organisms, resulting in dead algae descending to the Bay floor. There bacteria decompose the dead algae, which consumes available dissolved oxygen. Reduced dissolved oxygen levels can negatively impact bottom dwelling organisms, causing dead zones especially in deep water channels. (Figure 5: Nitrogen Impacts on Bay Water Quality)

To reduce nitrogen losses from agricultural land uses, the Chesapeake Bay Program partnership has developed an extensive menu of management options known as Best Management Practices (BMPs) that continues to be re-evaluated and enhanced through adaptive management. The application of targeted BMPs is a critical tool to minimize nitrogen losses to the Chesapeake and achieve the partnership's restoration goals which supporting a sustainable agricultural community.

Chesapeake Bay Program Best Management Practices (BMPs)

Nutrient Management
Nitrogen Based Nutrient Management Plans (application reduction)
Phosphorus Based Nutrient Management Plans (application reduction)
Enhanced Nutrient Management (7% TN)
Precision/Decision Agriculture (4% TN)

Conservation Plans (3-8% TN)

Residue Management
Conservation Tillage (land use change)
Continuous No-Till (10-15% TN)

Cover Crops
(Early, Standard, Late Planting Options)
Cereal Cover Crops (10-45% TN)
Commodity Cover Crops (5-17% TN)

Pasture Management
Prescribed Grazing (9-11% TN)
Prescribed Intensive Rotational Grazing (9-11% TN)
Horse Pasture Management (0% TN)
Stream Access Control w/ Fencing (13-46% TN)
Alternative Watering Facility (5% TN)

Riparian Management
Grass Buffers (13-46% TN)
Forest Buffers (19-65% TN)
Non-Urban Stream Restoration (0.02 lb/ft)

Feed Management
Poultry Phytase (0% TN)
Swine Phytase (0% TN)
Dairy Precision Feeding (reported lbs. TN)

Animal Waste Management
Animal Waste Storage Structure (80% TN)
Barnyard Runoff Control/Loafing Lot Management (20% TN)
Manure Transport (reported lbs. TN)
Liquid Manure Injection♦ (25% TN)
Poultry Litter Injection♦ (25% TN)
Manure Processing Technology* (reported lbs. TN)

Animal Mortality
Mortality Composting (40% TN)
Mortality Incineration♦ (40% TN)

Land Conversion
Tree Planting (land use change)
Wetland Restoration (7-25% TN)
Land Retirement (land use change)
Vegetative Environmental Buffers♦ (land use change)

Ammonia Emissions Control (50-60% TN)

Carbon Sequestration/Alternative Crops (land use change)

Water Control
Water Control Structures (33% TN)
Cropland P-absorb Materials♦ (0% TN)
Cropland Irrigation Management♦ (4% TN)
Container Nursery/Greenhouse Runoff Control♦ (75% TN)

Notes: Total Nitrogen Effectiveness Factors (TN) are included for selected BMPs
♦ Indicates Interim Approved BMP

Figure 6. Chesapeake Bay Program BMPs

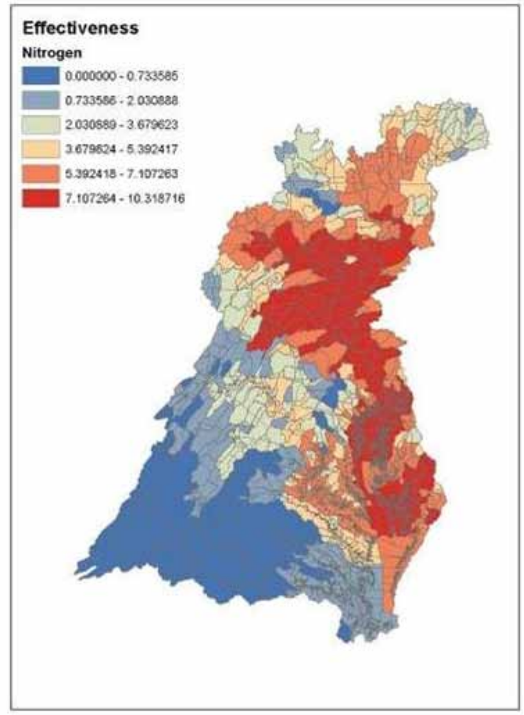


Figure 5. Nitrogen Impacts on Bay Water Quality, CBPO

Although available agricultural BMPs are numerous, they can be grouped into the following broad categories: nutrient management, conservation plans, residue management, cover crops, pasture management, riparian management, feed management, animal waste management, animal mortality, land conversion, ammonia emissions control, carbon sequestration/alternative crops, and water control. These BMPs and their associated nitrogen reduction effectiveness values are included in Figure 6: Chesapeake Bay Program BMPs.

Through extensive research and literature analysis, coupled with scientific and professional judgement, agricultural BMPs utilized by the partnership have been codified by definition and effectiveness at managing nutrient and sediment losses in typical production systems.

Despite the successes achieved by the Chesapeake Bay Program partnership in implementing BMPs since the mid-1980's, the Chesapeake remains an impaired water body under the federal

Clean Water Act (CWA). After an official acknowledgement by the partnership that the water quality goals to enable delisting of the Bay could not be achieved by 2010, EPA began to prepare for developing the largest Total Maximum Daily Load (TMDL) plan ever attempted.

The Phase I Chesapeake Bay TMDL process was officially initiated by EPA in 2009 which would culminate in a completed TMDL plan by December 31, 2010. Utilizing the existing data and modeling analysis resources of the EPA Chesapeake Bay Program Office, allocations of nitrogen, phosphorus and sediment were provided to each of the Bay jurisdictions on a basin basis in mid-2010. These load allocations formed the nutrient and sediment caps in which the Chesapeake could receive on an annual basis while not impairing the Bay's resources.

The creation of nutrient and sediment allocations to the Bay jurisdictions was based on a complex formula weighing water quality and living resource goals. Watersheds that contributed most to the "downstream" water quality issues were responsible for achieving the most pollution reductions. However, past achievements in reducing nutrient and sediment loads were credited towards obtaining their TMDL cap loads.

Figure 7. EPA Phase 1 TMDL Nitrogen Allocations by Basin, CBPO

Although EPA set the nutrient and sediment allocations for the jurisdictions (Figure 7: EPA Phase 1 TMDL Nitrogen Allocations by Basin), the Bay states and the District of Columbia could decide how to divide the allocations between point and non-point sources sectors within their boundaries. Each jurisdiction was responsible for developing a Bay TMDL Watershed Implementation Plan (WIP) for submission to EPA in preparation for the final Bay-wide TMDL plan. The WIPs included eight primary elements.

1. Interim and Final Target Loads
2. Current Program Capacity
3. Mechanisms to Account for Growth
4. Gap Analysis
5. Commitment to Fill Gaps: Policies, Rules, Dates for Key Actions
6. Tracking and Reporting Protocols
7. Contingencies for Failed, Delayed, or Incomplete Implementation
8. Appendix:
    a. Loads divided by 303(d) segment drainage and source sector
    b. 2-year milestone loads by jurisdiction –EPA will use to assess milestones
    c. No later than November 2011: Update to include loads divided by local area and controls to meet 2017 interim target loads

The initiation of the Chesapeake Bay TMDL also brought about a significant change in the partnership's approach to implementing water quality goals. Previously, the partnership operated in a voluntary manner with none or very minimal consequences if the jurisdictions fell short in achieving their restoration plans. The federal TMDL process also included the threat of future federal consequences if a jurisdiction did not succeed in implementing their objectives through the WIPs. Consequences could now include the expansion of NPDES permit coverage to currently unregulated sources, increased federal oversight of NPDES permits, the requirement of net improvement offsets, the revision of the TMDL allocations to a finer scale, the requirement of additional reductions from regulated point sources, increased federal enforcement of the CWA, the redirection or conditioning of federal grants, and the promulgation of local nutrient standards.

One fundamental aspect of the Chesapeake Bay Program that will not change with the implementation of the TMDL is that agriculture will play a key role in assisting the states in achieving significant nutrient and sediment reductions under their WIPs. In addition, the states will rely on agriculture to create offsets for future developed growth in order to maintain the caps loads.

How will this new "demand" for nutrient and sediment reductions be met by agriculture? One new initiative currently under development is the tracking and reporting of non-publically funded "volunteer" conservation practices, also known as non-cost shared BMPs. In these times of state economic hardships, these "new" BMPs may be critical in leveraging limited public resources to meet part of the nutrient reduction goals.

Another area of interest is through creating access to agricultural management information between landowners/operators and private, county, state and federal partners to insure greater accountability and confidence. An increasing reliance on "advanced" management practices built on "core" principles could also encourage new innovations and opportunities for information sharing.

The ever-present option for the states continues to be the expansion of state regulatory and permitting authorities which could further incentivize well managed versus poorly managed operations. Faced with limited public funds, this option may appear economically feasible; however, increased oversight and enforcement will be required to achieve actual nutrient and sediment reductions.

On the federal level, President Obama signed the Chesapeake Bay Protection and Restoration Executive Order on May 12, 2009, which recognized the Chesapeake Bay as a national treasure. In addition, it also provided EPA with additional authority in implementing the Bay TMDL. One element of the Executive Order stipulated that EPA should evaluate the current federal NPDES Concentrated Animal Feeding Operation (CAFO) permitting program to potentially expand its coverage within the Chesapeake watershed. In the future, additional animal feeding operations (AFOs) could be re-designated and subsequently permitted under CAFO program. Existing CAFO permitted operations could also face more stringent federal permit standards for on-site manure management, as well as expanded federal CAFO permit standards for off-site manure management could be included.

CONCLUSIONS

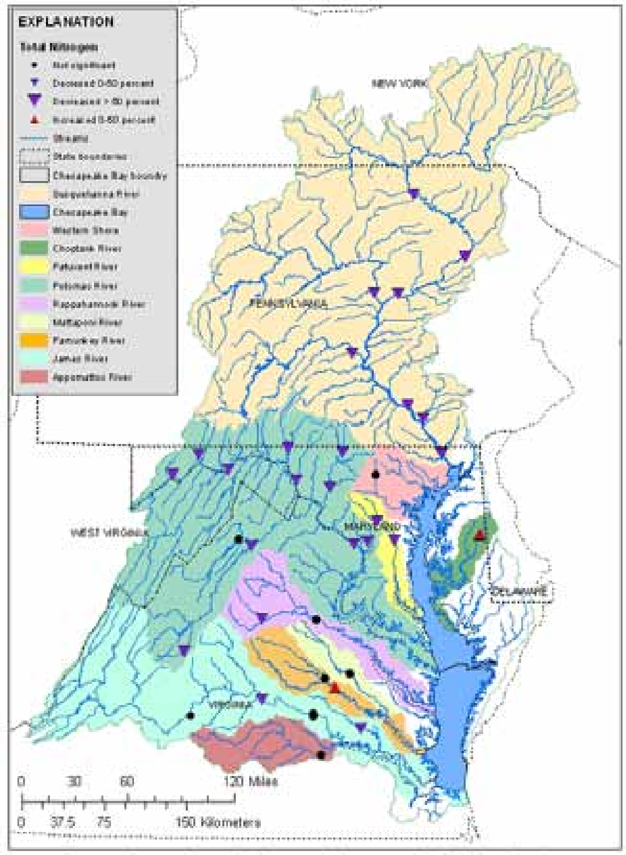
In conclusion, the Chesapeake Bay represents not only the largest estuary in North America, but also focal point of a national effort to restore the water quality and habitat of this unique natural treasure. The combined and coordinated efforts of the Chesapeake Bay Program partnership through over a quarter of a century have achieved positive results for reduced nutrient and sediment loads to the Bay and its tributaries. With a few exceptions, flow-adjusted trends for total nitrogen across the watershed indicate a declining annual load to the Chesapeake (Figure 8: Total Nitrogen Trends). Unfortunately, the Bay remains an impaired water body under the federal Clean Water Act (CWA).

Nitrogen and phosphorus are the primary nutrients of concern, which in association with sediments, annually cause water quality impairments within the Bay and its tributaries. The mechanisms of nitrogen diffusion within the Chesapeake are significant and diverse, including surface and subsurface losses from storm water runoff and infiltration respectively, as well as vitalization losses and atmospheric deposition.

In conjunction with the development of the federal Chesapeake Bay TMDL, each of the watershed jurisdictions are required to simultaneously develop supporting Watershed Implementation Plans (WIPs) by major tributary initially in 2010; and by county and/or sub-watershed in 2011. The WIPs will describe in detail the following eight critical elements: nutrient and sediment target loads; current implementation capacity; accountability for growth; identification of implementation gaps and commitments to fill them; tracking and reporting protocols; and contingencies for delayed or incomplete implementation.

Agriculture is estimated to be the single largest contributor of nutrients and sediments to the tidal Chesapeake on an annual basis. According to the EPA Chesapeake Bay Program Office, nitrogen losses from agricultural lands represent more than 38 percent of the total contribution of nitrogen to the Chesapeake. Although agriculture contributes a significant level of nutrients to the Chesapeake from the over 83.700 farms in the watershed, this land use also represents the largest single managed land use in the watershed at approximately 12.826.000 acres.

The application of targeted Best Management Practices (BMPs) is a critical tool to minimize nitrogen losses to the Chesapeake. Through the implementation of a diversity of conservation practices over the past quarter of a century, and the unfortunate loss of agricultural lands to development, significant gains have been achieved in reducing the annual nitrogen contributions to the Chesapeake, a trend that the Bay jurisdictions are counting on to meet their new EPA TMDL allocations by 2025.



Flow-adjusted trends for total nitrogen for 34 sites in the Chesapeake Bay Watershed, 1985-2008.

Figure 8. Total Nitrogen Trends, CBPO

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Development of nitrogen and phosphorus criteria for streams in agricultural landscapes

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Abstract

Efforts to control eutrophication of water resources in agriculturally-dominated ecosystems have traditionally focused on managing on-farm activities to reduce nutrient loss; however, another management measure for improving water quality is adoption of environmental performance criteria (or "outcome-based standards"). Here, we review approaches for setting environmental quality criteria for nutrients, summarize approaches developed in Canada for setting "ideal" and "achievable" nutrient criteria for streams in agricultural watersheds, and consider how such could criteria could be applied. As part of a "National Agri-Environmental Standards Initiative", the Government of Canada committed to the development of non-regulatory environmental performance standards that establish total P (TP) and total N (TN) concentrations to protect ecological condition of agricultural streams. Application of four approaches for defining ideal standards using only chemistry data resulted in values for TP and TN spanning a relatively narrow range of concentrations within a given ecoregion. Cross-calibration of these chemically-derived standards with information on biological condition resulted in recommendations for TP and TN that would protect aquatic life from adverse effects of eutrophication. Non-point source water quality modelling was then conducted in a specific watershed to estimate achievable standards, i.e. chemical conditions that could realistically be attained using currently available and recommended management practices. Our research showed that taken together, short-term achievable standards and ultimate ideal standards could be used to set policy targets that should, if realized, lower N and P concentrations in Canadian agricultural streams and improve biotic condition.

Keywords

Nitrogen; phosphorus; nutrients; streams; thresholds; criteria

INTRODUCTION

Agricultural activities add nitrogen (N) and phosphorus (P) to surface and ground waters as a result of runoff or seepage of manure and fertilizer, discharge of milk house or greenhouse wastes to surface waters, defecation by cattle allowed access to streams, and erosion of stream banks due to livestock trampling or tillage. The addition of bioavailable N and P to surface waters can cause prolific aquatic plant growth, depletion of oxygen due to decomposition of excessive plant biomass, and changes in abundance and diversity of aquatic invertebrates, fish and, possibly, birds and mammals dependant upon these habitats (Carpenter et al., 1998; Smith, 2003). In addition, elevated concentrations of un-ionized ammonia, nitrate and nitrite may be toxic to humans and aquatic life (Camargo and Alonso, 2006).

Management of N and P in agricultural landscapes has focused on controlling nutrient loss to surface or ground waters (by minimizing the source, mobilization, and transport of nutrients) and assessing ecological impacts (water chemistry, condition of aquatic biota, and/or changes in ecosystem services). One management measure for improving environmental quality is the adoption of environmental quality criteria (e.g., guidelines, standards, objectives, targets or benchmarks). These criteria are recommended levels for a given parameter which, if not exceeded, should result in negligible risk to biota (including humans), their functions, or any interactions integral to sustaining health of ecosystems and designated resource uses. Application of environmental quality criteria in the management of agricultural watersheds can improve decision-making by serving as benchmarks for assessing potential or actual impairment of a watershed, identifying priority sub-watersheds requiring action, evaluating efficacy of best management practices, and tracking progress in remediation of impaired watersheds.

The goal of this paper is to provide a brief review of approaches for setting environmental quality criteria for nutrients, summarize approaches developed in Canada for setting "ideal" and "achievable" nutrient criteria for streams in agricultural watersheds, and consider how such criteria could be applied.

APPROACHES FOR SETTING ENVIRONMENTAL QUALITY CRITERIA

Historically, the development of criteria to reduce water pollution focused on setting limits for water-borne pathogens and toxic chemicals. These criteria are based on toxicological endpoints (death, behavioural change, etc.) typically determined from laboratory experiments. In contrast to pathogens and toxic chemicals, other stressors (e.g., nutrients, turbidity, flow, and temperature) can change the structure or function of ecosystems by affecting such properties as productivity, biodiversity, and species numbers. Because these non-toxic stressors do not necessarily result in death or a chronic condition, identification of criteria associated with a deleterious change in environmental quality has been difficult. Where criteria have been identified for nutrients as agents of eutrophication, these values have usually been determined on the basis of best professional judgement or evaluation of minimally-disturbed conditions (i.e., the water quality potential for a geographic area through current assessment of minimally-disturbed sites, analysis of historical data from sites that would have been minimally disturbed reference at the time, or modeling to predict historic conditions; Stoddard et al. 2006). Many countries have had some form of nutrient criteria since the 1960s or 1970s, the most common being maximum allowable concentrations of N or P in water (Table 1).

Table 1. Examples of N and P criteria for various jurisdictions and rationale for their adoption. TN is total nitrogen; TP is total phosphorus: SRP is soluble reactive phosphorus.

Jurisdiction	N (mg/L)	P (mg/L)	Rationale
USA – Florida	TN: 0.67, 1.03, 1.54, 1.65 or 1.87 mg/L for 5 watershed regions [a]	TP: 0.06, 0.12, 0.19, 0.30 or 0.49 mg/L for 5 watershed regions [a]	90th percentile for biologically healthy sites
New Zealand	TN: 0.295 mg/L for upland and 0.614 mg/L for lowland rivers [b]	TP: 0.026 mg/L for upland and 0.033 mg/L for lowland rivers [b]	80th percentile for reference sites
Australia	TN: 0.15 - 0.45 mg/L for upland rivers; 0.20 - 1.20 mg/L for lowland rivers, depending on region [b]	TP: 0.01 - 0.02 mg/L for upland rivers; 0.01 - 0.065 mg/L for lowland rivers, depending on region [b]	80th percentile for reference sites
Sweden	Not developed because no general relationship between TN and diatom index	TP: 0.0125 mg/L [c]	Boundary between good and high ecological status
UK	Total ammonia: 0.2 mg/L (high quality) or 0.3 mg/L (good quality) for upland, low alkalinity rivers; 0.3 mg/L (high quality) or 0.6 (good quality) for lowland, high alkalinity rivers [d]	SRP: 0.050 mg/L (high quality) or 0.12 mg/L (good quality) for high alkalinity rivers; for low alkalinity rivers, 0.020 mg/L (high quality) or 0.040 mg/L (good quality) for upland systems or 0.030 mg/L (high quality) or 0.050 mg/L (good quality) for lowland systems[d]	90th percentile for sites of high or good biological quality

[a] USEPA 2010
[b] ANZECC 2000)
[c] Naturvårdsverket 2007. Note that in the European Water Framework Directive, assessment class boundaries are defined as deviation from reference conditions. The concentration given in the table is an additional required value for high status waters.
[d] UK Technical Advisory Group on the Framework Directive 2008

The goal of N and P criteria based on maximum allowable concentrations is usually stated as protection of aquatic ecosystems from deleterious consequences associated with eutrophication. Yet historically, concentrations were rarely quantitatively linked with ecological condition. Because the goal in setting criteria for nutrients is not simply to reduce N and P concentrations in water but, ultimately, to protect and provide suitable conditions for a diverse community of aquatic and riparian organisms, many water management agencies and scientists are now investigating biological indicators of trophic status and their relationship with N and P loads or concentrations. This is particularly evident in the agri-environment sector where programs with themes such as "sustainable agriculture" aim to explicitly integrate environmental health and farm viability. Yet there are several challenges in defining nutrient criteria for agro-ecosystems:

1. few if any portions of agricultural landscapes are undisturbed, or even minimally disturbed. Thus, it is difficult to identify the ecological conditions that existed in the absence of agriculture or prior to intensive agriculture.
2. even if such conditions could be defined, the goals of sustainable agriculture are to maintain, or restore, good ecological condition, not necessarily the unmodified condition.
3. multiple stressors (nutrients, suspended sediments, pesticides, climate change) are often present in agricultural watersheds, necessitating consideration of the interactions of nutrients with other stressors.

As part of a “National Agri-Environmental Standards Initiative” (NAESI), the Government of Canada committed to the development of non-regulatory environmental performance standards for N and P to protect ecological condition of agricultural streams. Two types of standards were recognized under NAESI:

1. Ideal Performance Standards (IPS), specifying the desired ecological condition needed to maintain ecosystem health, and
2. Achievable Performance Standards (APS), specifying environmental conditions that could realistically be achieved using currently available and recommended best available processes and technologies (i.e., beneficial management practices or BMPs).

Hence, the former standard (IPS) defines the maximum concentration of N or P at which no known or anticipated adverse effects on ecological condition would occur, whereas the latter standard (APS) defines the level of a chemical, physical or biological condition that is technically feasible to achieve. Thus, if a number of watersheds within an ecoregion were assessed and these watersheds had varying concentrations of N and P, the theoretical relationship is such that as N or P increases, the impact (i.e., proliferation of blue-green algae, changes in benthic invertebrate composition, etc.) on the environment is also amplified (Figure 1). The ideal situation (i.e., IPS) would be one in which N and P are maintained at concentrations that are unlikely to degrade ecological condition. However, for technological and economic reasons, it may not be possible to achieve the IPS in the short term and interim objectives can be based on implementation of technologically-feasible BMPs (APS) or even technologically- and economically-feasible BMPs.

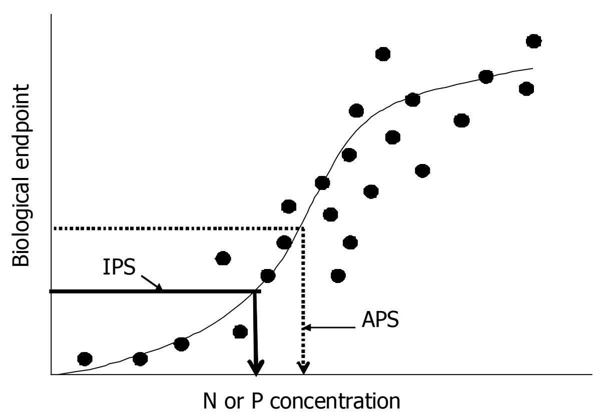

Figure 1. Conceptual diagram showing the relationship between biological endpoints (e.g., algal abundance, benthic invertebrate composition, stream metabolism, etc.) and N or P concentration. The Ideal Performance Standard (IPS) defines the maximum nutrient concentration at which no known or anticipated adverse effects on ecological condition would occur. The Achievable Performance Standard (APS) defines the level of a chemical and ecological condition that is technically feasible to achieve in a given watershed.

DEVELOPMENT OF NUTRIENT CRITERIA FOR CANADIAN AGRICULTURAL WATERSHEDS

Ideal Performance Standards (IPS)

As the first step in developing IPS, we applied four approaches for identifying criteria for TN and TP, all of which utilize water chemistry data but no ecological data:

(1) the median of the 25th percentile of nutrient concentrations (stations medians) for each season from both reference and non-reference streams (USEPA, 2000);
(2) the 80th percentile of nutrient concentrations from least-disturbed streams (i.e., streams with < 25% agricultural land cover in their watershed) from flow periods conducive for algal growth (summer and fall) (after ANZECC & ARMCANZ, 2000);
(3) an upper bound set to either a predefined trigger range (defined according to the reference trophic status) or a value of 50% above baseline nutrient concentrations whichever is less (CCME, 2004). The predefined trigger ranges are: oligotrophic: ≤ 0.025 mg/L TP and ≤ 0.70 mg/L TN; mesotrophic: 0.025 - 0.075 mg/L TP and 0.70 - 1.5 mg/L TN; eutrophic: ≥ 0.075 mg/L TP and ≥1.5 mg/L TN (TP ranges from CCME, 2004; TN ranges from Dodds et al., 1998).
(4) a change-point in the relationship between nutrient concentrations and agricultural land use, determined by regression-tree analysis (Breiman et al., 1984). The median value of TP or TN for all stations below the change point in percent agricultural land cover is the calculated threshold.

Data were obtained from provincial agencies (see Acknowledgements) and usually collected monthly (for details, see Chambers et al, in press). Because each of these four approaches has its own shortfalls, the most conservative approach for calculating provisional chemical criteria was to average values from these four approaches (Table 2).

Table 2. Comparison of provisional chemical criteria for total nitrogen (TN) and total phosphorus (TP), calculated as the average of four approaches (described in the text). If the provisional chemical criteria lay within the range (≈) of the biological criteria, the recommended nutrient criteria were the chemical criteria. Where provisional chemical criteria were greater (>) than biological criteria, further data analysis was undertaken to determine whether the biological or the provisional chemical criteria should be adopted.

	Region of Canada	Provisional chemical thresholds (mg/L)	Chemical compared to biological thresholds	Recommended Nutrient Criteria (mg/L)
TN	Okanagan Basin, British Columbia	0.21	≈	0.21
	Southern Alberta	0.98	≈	0.98
	Southern Manitoba	0.39	≈	0.39
	Southern Ontario	1.06	≈	1.06
	Chaudière-Appalaches, Quebec	1.19	≈	1.19
	North-west New Brunswick	0.87	≈	0.87
	Prince Edward Island	1.21	≈	1.21
TP	Okanagan Basin, British Columbia	0.020	≈	0.020
	Southern Alberta	0.106	>	0.106
	Southern Manitoba	0.102	>	0.102
	Southern Ontario	0.026	≈	0.026
	Chaudière-Appalaches, Quebec	0.042	>	0.032
	North-west New Brunswick	0.013	≈	0.013
	Prince Edward Island	0.048	>	0.032

We then cross-calibrated these provisional chemical criteria with criteria identified by analysis of relationships between biological condition and nutrients (i.e., "stressor-response" relationships). In the case of benthic and sestonic algal abundance, where recommended limits are available (although still debatable), we related chlorophyll *a* (chl*a*) to TP and TN. For significant linear regressions ($p < 0.05$), the 80% prediction interval for 5 µg/L sestonic chl*a* or 100 mg/m^2 benthic chl*a* was calculated for each regression (after El-Shaarawi and Lin, 2007). For metrics without pre-defined limits of acceptable ecological condition (i.e., 7 metrics describing benthic algal and invertebrate composition), regression-tree analysis was used to identify concentrations of TP or TN where the biotic metric showed the greatest degree of change (Breiman et al., 1984). For TP, the biological criteria ranged from 0.014 mg/L (sestonic chl*a*) to 0.063 mg/L (Diptera+non-insect relative abundance) with the other criteria between 0.022-0.032 mg/L TP (Chambers et al., in press). For TN, the biological criteria ranged from 0.59-2.83 mg/L TN (Chambers et al., in press).

Next we compared our provisional chemical and biological criteria. For regions where chemical criteria fell within the bounds of biological criteria, we recommended using the chemical criteria as the recommended nutrient criteria because our chemical criteria were more rigorous, generally being based on large, multi-year datasets (Table 2). Moreover, in cases where a chemical criterion is less than the lower range of biological criteria, adoption of the chemical criteria defuses the argument that additional pollution can occur until a biological criterion is reached. For regions where chemical criteria exceeded biological criteria, further exploration of the data was warranted to determine if the region had least-disturbed sites that met the biological criteria. Applying this argument for TN resulted in adoption of provisional chemical criteria as nutrient criteria for all regions because for every region, our provisional TN chemical criteria lay within the bounds of all biological criteria (Table 2). In the case of TP, provisional chemical criteria fell above the bounds of biological criteria for 4 regions. Further analysis led to acceptance of biological criteria for 2 regions (Table 2).

Achievable Performance Standards (APS)

To develop APS, scenario modelling was undertaken based on optimal implementation of BMPs across a watershed, without consideration of economic feasibility. In this analysis, the Soil and Water Assessment Tool (SWAT) was used to estimate APS for NO_3-N and soluble P with combinations of selected BMPs in the Black Brook Watershed (BBW), north-western New Brunswick. BBW is a primarily agricultural watershed (~65%) that is dominated by intensive potato production. Four commonly used BMPs, namely flow diversion terraces (FDT), fertilizer reductions, tillage methods, and crop rotations, were considered individually and in combination. Results indicated that crop rotation and fertilizer application rate were the most effective in reducing NO_3-N concentrations, whereas soluble P concentrations showed the greatest decrease in response to implementation of FDT (Figure 2). At the watershed level, the best achievable reduction in NO_3-N loading was 49.7 kg ha^{-1} yr^{-1} with a BMP-combination of fertilizer reduction (20%) and crop rotation (potato-hay); the best achievable reduction in soluble P loading was 0.5 kg ha^{-1} yr^{-1} with a BMP-combination of crop rotation (potato-hay), FDT (100%), and fertilizer reduction (20%) (Yang et al., in press). These loading reductions resulted in APS for Black Brook (at the outlet) of 2.13 mg/L NO_3-N and 0.01 mg/L soluble P. When compared to IPS values specifically calculated for BBW, the APS is 3.5 times higher than IPS for NO_3-N and 1.5 times higher for soluble P.

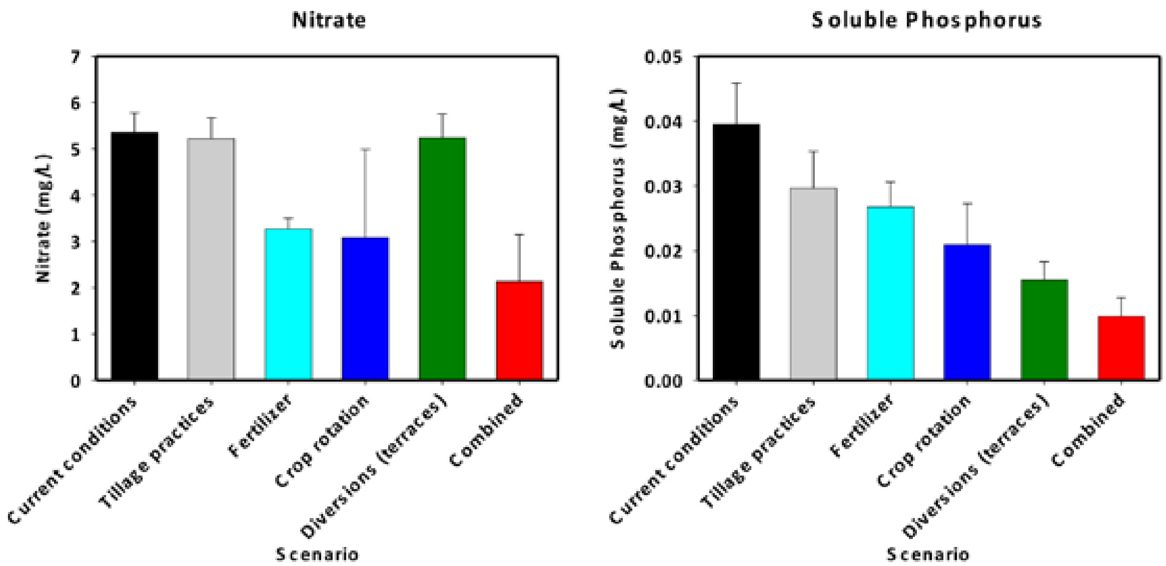

Figure 2. Results of SWAT model scenarios for the determination of APS for nutrients (NO_3-N or nitrate and soluble P) in the Black Brook watershed, New Brunswick, Canada.

APPLICATION OF ENVIRONMENTAL QUALITY CRITERIA

Our research showed that for streams within agricultural regions of Canada, it is possible to define N and P criteria to protect aquatic life from the adverse effects of eutrophication. Moreover, interim APS can also be defined that permit step-wise progress to the ultimate goal of achieving the IPS. Together, these two types of criteria can be used to inform management decisions now and in future: while the IPS is the ecological condition that is the ultimate objective, APS will identify what is currently achievable and contribute to the development of evidence-based policy targets. Adoption of such policy targets should, in the long term, result in achievement of the desired IPS (Figure 3).

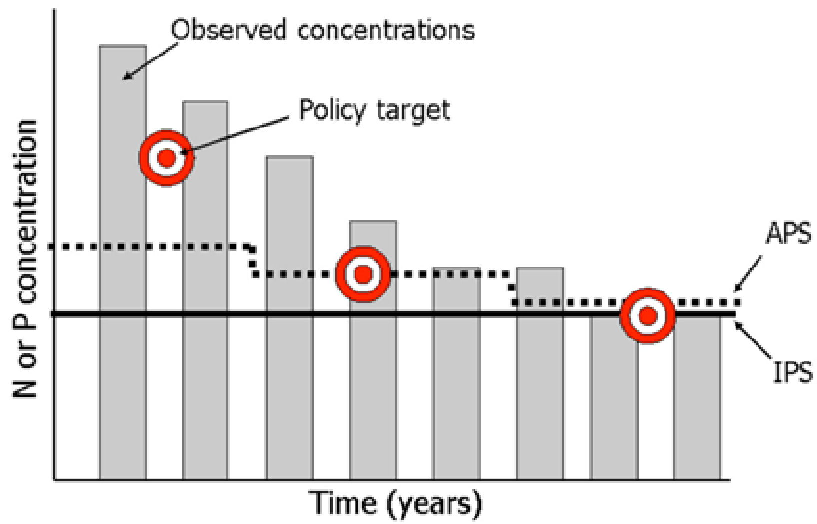

Figure 3. Conceptual diagram showing the relationship between observed concentrations of N or P in a stream draining an agriculturally-managed watershed, the Ideal Performance Standard (IPS) for N or P, the Achievable Performance Standard (APS) for N or P, and the policy target for N or P. Over time, observed concentrations will decrease in response to application of policy targets. These policy targets would be set on the basis of information on the N and P concentrations that could be achieved following adoption of currently available BMPs (i.e., APS) and economics. Eventually, the policy target would match the IPS.

Future research on criteria development will benefit from consideration of interactions of nutrients with other stressors. This is particularly relevant for streams in agricultural watersheds where multiple stressors (nutrients, suspended sediments, pesticides, climate change) are often present.

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The scientific basis for designating important aquatic ecosystems and river ecosystem goals in agriculturally dominated watersheds

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Abstract

Over the last several decades aquatic resource management programs have emphasized the development of conservation strategies at increasingly larger scales. Broader strategies are especially necessary to address the impacts of diffuse agricultural pollution that are difficult to quantify at the scale of an individual farm, but that gradually accumulate downstream. Implementing conservation strategies across multiple spatial scales complicates stream or river management decisions in at least two important ways. The first complication, common to almost all large-scale programs, is that these strategies require establishing a clear relationship between conservation practices implemented at individual sites (through "projects") to desired outcomes across a large system. The second complication is that it is difficult to define stream and basin health across multiple scales. Stream scientists have produced a wealth of information leading to a consensus about the fundamental attributes (flow, water quality, energy, biota, and habitat) that comprehensively reflect stream health and explain how streams respond to human activities. Each of these two complications can be influenced just as much or more by social and economic conditions than by the state of the science. Strategizing across large watersheds and ecological goal-setting do, after all, require subjective valuations based on not just the best available science, but also the practical consideration of public perceptions and desires. The increasingly held concept of accountability for conservation programs designed to reduce the impacts of agriculture will require greater attention to the ways by which we measure, individually and collectively, the success of projects and programs. While shifting to address larger scales managers need to avoid the implication that doing so will reduce the importance of ongoing project- or site-scale efforts. An objective and detailed understanding of exactly how and how much science is needed to support future decisions can increase the probability that the right questions are asked and answered as future mitigation programs are implemented.

INTRODUCTION

Over the last several decades aquatic resource management programs in the U.S. have increasingly emphasized the development of conservation strategies at larger (greater than individual farms or 12-digit hydrographic units) spatial scales. This shift from farm-scale conservation planning has, in part, followed a gradual acceptance of the principles of ecosystem management (summarized by Grumbine, 1994), which promote strategies that are not strictly tied to public lands but instead include all areas that exert some control over natural resources and processes of interest. In the area of water resources management, the shift has been especially valuable in addressing cumulative, downstream flow and water quality problems. Examples include the vision and plans of the Gulf Hypoxia Task Force (2001), which eventually led to strategies across the entire Mississippi Watershed, and the development of National Fish Habitat Partnerships (Association of Fish and Wildlife Agencies, 2006). One of these partnerships, the Fishers and Farmers Partnership for the Upper Mississippi River Basin, includes goals for fish habitat restoration over an area of 189,000 square miles including more than 30,000 miles of streams (Fishers and Farmers Partnership Steering Committee, 2009). The needs for river science to become more interdisciplinary, integrative, and relevant at such spatial scales were key points made recently by the National Research Council to the U.S. Geological Survey (National Research Council, 2007).

A scientific basis (the organized collection of relevant facts, including biological responses to diffuse pollution and its mitigation) for supporting management across multiple spatial scales (on individual farms, and within stream reaches, networks and landscapes) is clearly necessary, perhaps even more so than the scientific basis required since the 1950's for establishing water quality standards for point sources of pollution. Many more obstacles, however, stand in the way of applying science in this context. Perhaps the most practical problem is the extra funding, energy and commitment needed to succeed, either through regulation or conservation, across the areas included in large basins. Associated with this problem is the difficulty of avoiding the implication that greater attention placed on larger spatial scales reduces the importance of ongoing project- or site-scale efforts. Adequately supported efforts at both scales will continue to be necessary.

In this paper, the emphasis is on non-financial issues, and in particular the question of what science can contribute to developing management programs that attempt to address diffuse agricultural pollution impacts at large scales. I present two major groupings of constraints: those associated with spatial strategy development (designating important aquatic ecosystems), and those associated with ecosystem goal setting. The constraints associated with spatial strategy development are typically the first set of issues a developing program attempts to address. In the real world these constraints interact with each other, forming what appears to be an impenetrable web of obstacles.

SPATIAL STRATEGY DEVELOPMENT

Early in the development of large spatial scale programs, water resource planners face the questions "Where in a basin should we start?" and "What patterns of spatial growth should the program follow?" These questions surface because few large scale programs are funded and staffed with a long-term commitment of adequate resources to accomplish the purpose of the program across the entire basin, however long that might take. As a result, program planners must develop one or more spatial strategies that foster immediate local successes linked to desired long-term outcomes. Unfortunately, few programs last long enough to allow serious evaluation of large-scale success. This situation is especially problematic for programs designed to address agricultural impacts that have resulted from decades of incompatible practices, accumulating across hundreds or thousands of farms and ranches. Never the less, at this point, program planners find themselves seeking scientific information to designate a small subset of "important" aquatic ecosystems within the larger set that exists within a basin.

So what is an "important" aquatic ecosystem within a large basin? The following two criteria are perhaps the most common ones that have been used to answer this question.

System condition

Streams that exhibit better water quality or biological condition (i. e. retaining most of their native species and ecological processes) are designated as more important during the initial stage of a conservation program. This follows what is sometimes known as the "Save the best first." philosophy.

System risk

Streams that are more at risk (those whose basin landscapes are dominated by agriculture rather than by diverse covers and uses) from the impacts of a particular stressor or practice are considered more "important" than others, within programs designed to mitigate the practice.

While these criteria are among those most commonly used to evaluate stream or sub-basin "importance" from a planning perspective, other non-traditional criteria are being incorporated into some newer programs. For example, the Fishers and Farmers Partnership for the Upper Mississippi River Basin includes criteria that recognize the influence of a stream reach on downstream reaches, and the conservation opportunities (including collaborative efforts with partners) available within a stream and the drainage basin as factors that are equally valuable in designating "important" aquatic systems (Fishers and Farmers Partnership Steering Committee, 2009). The concept of using the existence of "conservation opportunities" in a stream or sub-basin as a stream-selection criterion by the Fishers and Farmers Partnership stems from the desire of its partners to engage farmers as active leaders of local conservation projects. If the Partnership is successful in accomplishing this, the number of stream conservation practitioners and the number of conservation projects within the Upper Mississippi River Basin could increase dramatically.

The addition of relatively new spatial decision criteria to the process of designating "important" aquatic ecosystems will certainly come with additional challenges for the scientific community. It seems very possible, for example, that the need to evaluate non-traditional criteria could quickly require economic and social science expertise that has often been missing from these kinds of planning efforts.

Further, the increasingly held concept of accountability for conservation programs designed to reduce the impacts of agriculture will require greater attention to the ways by which we measure, individually and collectively, the success of projects and programs. A recent review of stream restoration projects in the Upper Mississippi River Basin suggested that only a small fraction of the projects received even a minimal level of monitoring or evaluation (O'Donnell and Galat, 2007). In order to understand both the local and downstream effects of conservation projects, the scientific community, and agencies responsible for agricultural conservation practices are going to have to take up the challenge of monitoring stream networks across large scales (Figure 1).

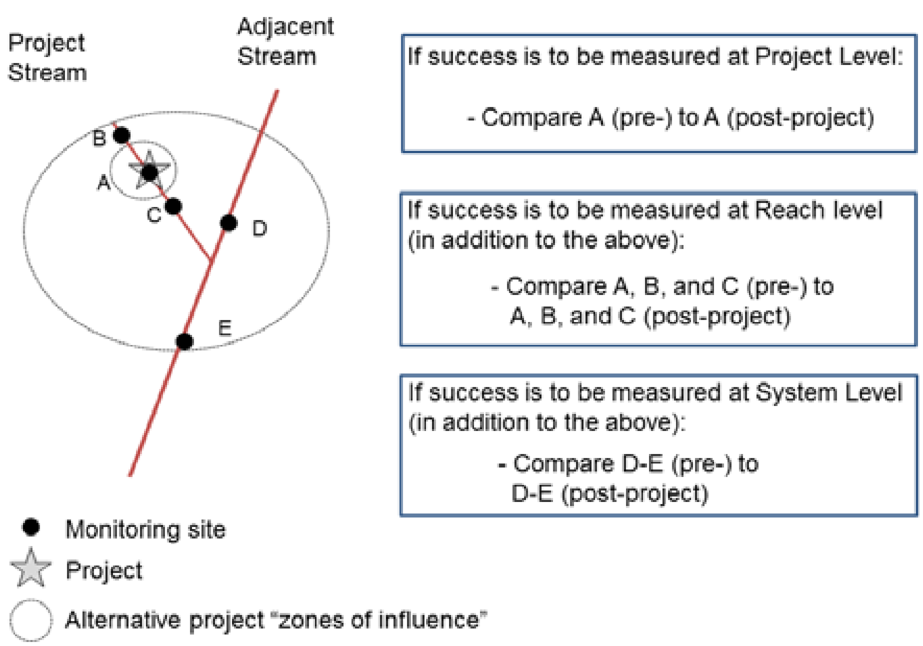

Figure 1. Alternative monitoring scenarios for evaluating the local and downstream effects of conservation projects, and quantifying the "zones of influence" of such projects in agricultural basins.

A final scientific issue relates to how data from different stream reaches and their individual sub-basins can be organized in a hierarchical fashion, similar to the layout of a stream network, to progressively but accurately portray conditions at each level of spatial extent. Within a basin, sample size decreases with increasing stream order, and it is risky to assume that simple equations can predict cumulative downstream dependencies. The sharing of experiences with this problem among stream scientists from many disciplines is especially important now.

ECOSYSTEM GOAL SETTING

In addition to spatial issues applicable to the designation of "important" aquatic ecosystems, are several issues related to the quality of the desired systems. Stream scientists have, over the last 4 decades, produced a volume of research that is directly applicable to supporting ecosystem goal setting in a large basin context, and relevant to the diffuse impacts of agriculture.

The concept of stream or river health has become valuable as a general goal for river management (Constanza et al. 1992: Cairns et al. 1993: Karr 1999: Norris and Thoms 1999). On a continuous scale of condition, river health occupies a position between undisturbed and degraded. The concept resonates well with policy makers and the public, and the phrase portrays a self-sustaining river reach or sub-basin that supports native species and ecological processes, even though the river and basin may be heavily used. The definition is useful for any river, but especially for large rivers, which commonly occupy downstream positions in a stream network, and are therefore exposed to the cumulative effects of diffuse pollution.

The concept of ecosystem health can be adequately defined using a small set of essential ecosystem characteristics (Harwell et al. 1999). Such characteristics for stream and river ecosystems include stream flow, water quality, energy flow, habitat, and biota (Karr 1999). When these general characteristics are used to establish an assessment system for a single river, however, slight modifications are frequently made to customize the definition based on the physical, hydrologic, ecological and human use history of the river. On the Upper Mississippi River for example, the characteristics have been slightly modified to emphasize sediment and nutrient elements of water quality, and to establish management priorities related to biological processes and native species (Figure 2). As yet, however, the metrics used to quantify the definition for decision purposes have not included stakeholder input or review.

River health, being a comprehensive concept, provides a suitable context within which more specific management objectives can be established. On the Upper Mississippi River for example, management objectives are currently being proposed to protect aquatic macrophyte (vascular plant) communities. The objectives are based on scientific understanding of the conditions required by macrophytes, as well as how and why macrophytes and algae have alternately dominated off-channel habitats in the floodplain in recent decades. The temporal patterns of macrophyte/algae dominance have been related to natural (floods, droughts) and anthropogenic disturbances in the floodplain and basin. Macrophytes are preferred, especially over cyanobacteria, because the large plants promote favorable water quality, habitat conditions, and food chains that are more typical of the river during undisturbed, low water periods.

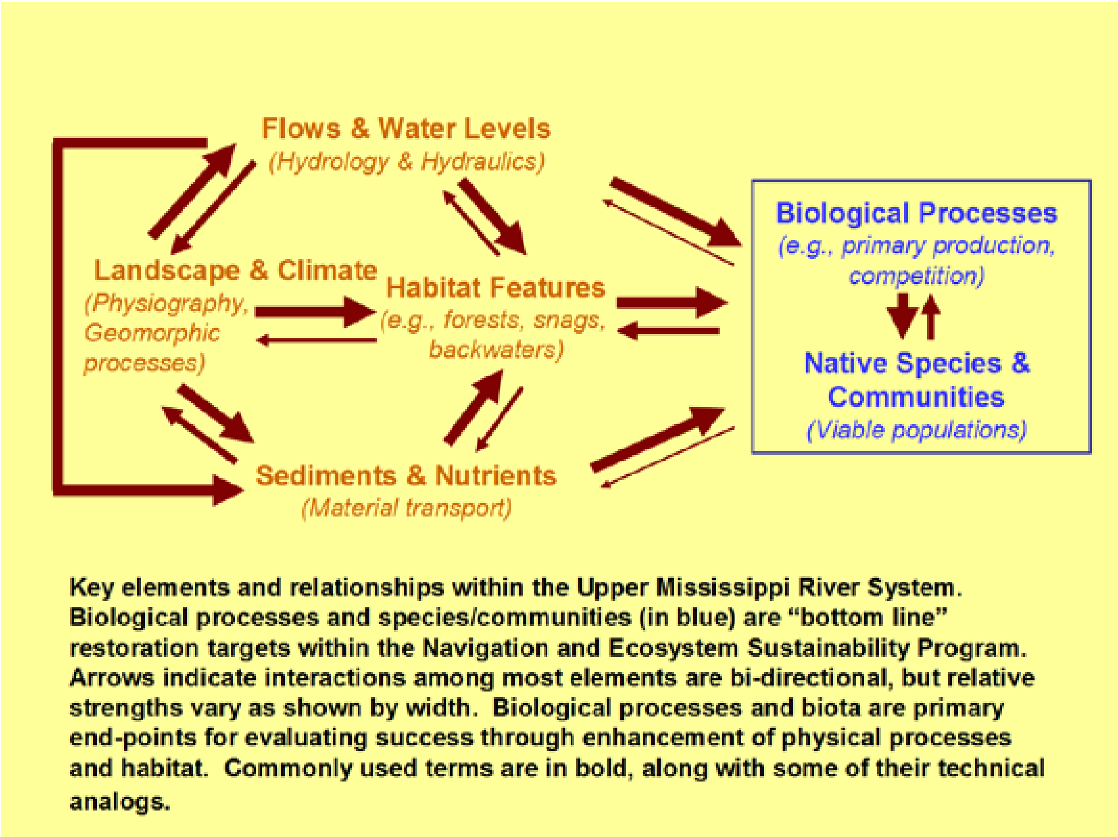

Figure 2. Essential ecosystem characteristics of the Upper Mississippi River (Galat et al. 2007).

The macrophyte/algae relationship in this "downstream" section of the larger river network may be the one of the most scientifically credible and socially relevant metrics available to measure the positive biological benefits derived from upstream conservation measures to reduce sediment and nutrient loads. Further upstream, however, where macrophytes do not naturally occur, different measures would be required.

CONCLUDING REMARKS

It is likely that more management programs to mitigate the diffuse effects of agriculture will be designed and created in the future. Such programs are necessary to address the widespread but difficult to quantify responses of downstream aquatic ecosystems to upstream land uses. Many newer programs are taking more of a spatially- targeted approach to regulation and conservation, thus avoiding some of the problems that past shot-gun like programs have had in demonstrating desirable outcomes and accountability.

We can expect that these programs will be expensive and that they will only be able to show results after many years of implementation. An objective and detailed understanding of exactly how and how much science is needed to support future decisions can increase the probability that the right questions are asked and answered as these programs are implemented.

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Snowmelt and its role in the hydrologic and nutrient budgets of Prairie streams

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Abstract

Watersheds in the Canadian prairies are characterized by seasonally disconnected hydrologic networks whereby stream channels are hydrologically connected during snowmelt but have disconnected reaches throughout the remainder of the year. Snowmelt is therefore the most significant hydrological event in the Canadian prairies, yet few studies have investigated the role of snowmelt in the nutrient budget of prairie streams. We quantified hydrologic and nutrient dynamics during snowmelt for ten agricultural subwatersheds distributed along a gradient of human activity in the Red River Valley, Canada, to evaluate the timing of nitrogen (N) and phosphorus (P) export. Elevated concentrations of total P (TP) and total N (TN) were observed during the snowmelt peak, with maximum stream concentrations reaching 3.23 mg TP L^{-1} and 18.50 mg TN L^{-1}. Field observations also revealed significant runoff from flooded fields adjacent to streams during this critical period. Dissolved P and N dominated the total nutrient pool throughout snowmelt, likely due to reduced erosion and sediment transport resulting from the combination of the flat topography, frozen soil and stream banks, and gradual snow cover melt. Significant correlations were observed between snowmelt N load ($r= 0.900$; $p<0.05$) and both agricultural land cover and fertilizer usage, with a weaker correlation between snowmelt P load ($r= 0.794$; $p<0.05$) and agricultural area. Our results showed that snowmelt plays a key role in nutrient export to Prairie aquatic ecosystems. These quantities of nutrients may have serious impacts on downstream ecosystems, as they represent a large potentially bio-available nutrient source. Land use management practices need to consider the critical snowmelt period to control nutrient loads to Lake Winnipeg and other waterbodies in the Great Plains.

Keywords

Nutrient; load; subwatershed; snowmelt; Canadian Prairies;

INTRODUCTION

Prairie streams and rivers represent a dwindling resource of unpolluted freshwater in North America (Dodds *et al.* 2008). They are also critical components of the Great Plains ecosystem, providing a hydrological connection between the terrestrial grasslands and downstream rivers and lakes. This hydrological connection governs the timing and magnitude of nutrient loads and their export to downstream ecosystems. However, much of the Canadian and USA Great Plains ecosystem has been fundamentally altered by conversion to agricultural and urban land cover. These land-use changes, as well as stream manipulations (e.g., channelization and riparian and instream vegetation removal), have contributed to increased nutrient export by reducing nutrient retention and storage in upland and riparian soils and vegetation (Bourne *et al.*, 2002; Dodds *et al.*, 2008; Ensign and Doyle, 2005; Wiley *et al.*, 1990). The result has been excessive inputs of nutrients into aquatic ecosystems, contributing to eutrophication of prairie lakes, toxic algal blooms and loss of sensitive species (Bourne *et al.*, 2002; Hall *et al.*, 1999).

In Canada, deterioration of water quality in Lake Winnipeg, the tenth-largest freshwater lake on Earth (at 24,514 km^2), has raised concerns about the role of point versus non-point sources in contributing to eutrophication of Great Plains waterbodies. Over the last three decades, total nitrogen (N) and total phosphorus (P) loads to Lake Winnipeg have increased by 13 and 10%, respectively (Jones and Armstrong, 2001). Algal blooms have increased in frequency, duration and intensity in the last twenty years. Preliminary estimates of total N and total P loads from Lake Winnipeg tributaries have clearly identified the Red River as a major contributor of nutrients to Lake Winnipeg (Bourne *et al.*, 2002), with 27.1 and 41.4% of the Red River total P and N contribution derived from point sources, notably the city of Winnipeg and other municipal and industrial effluents. The Canadian portion of the Red River watershed encompasses an area of 12,900 km^2 and is characterized by a wide range of human activities, making it difficult to ascribe the portion of the nutrient load derived from agricultural versus urban sources. Typical of prairie watersheds, the Red River watershed features a nearly flat topography dissected by small wetlands and channelized streams and rivers, many of which have been altered as a result of intensive drainage for agriculture. This landscape, combined with the continental semi-arid climate of the Canadian Prairies, results in hydrological disconnects along stream networks. During snowmelt, stream channels are hydrologically connected (and, depending upon snowpack depth and rate of snowmelt, may flood extensively) whereas for the remainder of the year all streams except mainstem rivers have disconnected reaches as a result of low or no flows caused by high temperatures, limited precipitation and increased evaporation (summer and fall) or frozen channels (winter). Snowmelt is therefore the most significant hydrological event in the Canadian prairies, contributing 56 - 95% of the annual flow volume (Glozier *et al.*, 2006). Yet, despite the nutrient significance of snowmelt to the hydrologic cycle of prairie water courses, few studies have export during this time period. One water quality study conducted on a Canadian prairie stream reported that snowmelt contributed to 40 – 95% and 51-97% of the total P and N annual loads, respectively (Glozier *et al.*, 2006). Hence, hydrological connectivity of subwatersheds during snowmelt may exert a strong influence on annual nutrient exports to the Red River, and ultimately to the Lake Winnipeg.

The goal of our study was to quantify hydrologic and nutrient dynamics in prairie streams in the Red River watershed of MB, Canada during snowmelt. Specifically, we aimed to 1) quantify nutrient export during snowmelt from 10 subwatersheds representing a gradient of human activity; 2) evaluate the timing at which agriculturally derived nutrients are exported from subwatershed to the Red River main tributaries. An improved scientific understanting of the contribution of headwater streams to nutrient export during snowmelt is essential to designing land use management practices to control nutrient loads to Lake Winnipeg.

MATERIAL AND METHODS

Study sites

The Red River Valley of south-western Manitoba is dominated by agricultural land used for grain, oilseed and livestock production. As part of a larger continuing study on nutrient losses from prairie watersheds, water quantity and quality were monitored throughout snowmelt at the outlet of ten subwatersheds located within an 8500 km^2 area of the Red River Valley (Figure 1, Table 1). These sites were selected to span a gradient in agricultural land cover (Table 2) for estimation of nutrient emissions in relation to a human activity. In addition to the site criteria defined by Yates *et al.* (in review), our selection of subwatersheds was constrained by the need to have outflows located near a main road to ensure site accessibility during snowmelt.

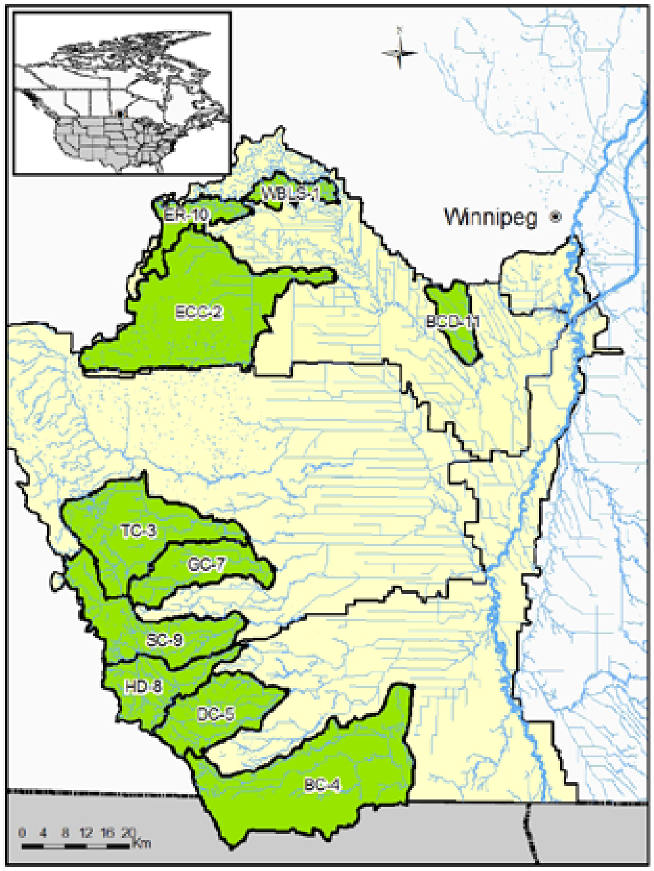

Figure 1. Location of the ten study subwatersheds in the western part of the Red River Valley in Manitoba, Canada.

Table 1. Sites, stream names, watershed area, outlet coordinates and nearest Water Survey of Canada (WSC) stations

Site	Stream	Area (km^2)	Longitude	Latitude	WSC station
WBLS-1	West Branch La Salle River	64.54	-97.7752	49.9308	05OG008
ECC-2	Elm Creek Channel	602.24	-97.7779	49.8125	05OG005
TC-3	Tobacco Creek	350.94	-98.0018	49.4032	05OF024
BC-4	Buffalo Creek	626.28	-97.5499	49.1766	05OC019
DC-5	Deadhorse Creek	217.54	-98.0017	49.2368	05OC016
GC-7	Graham Creek	183.55	-97.9306	49.3564	05OF024
HD-8	Hespeler Drain	180.36	-97.8861	49.1677	05OC016
SC-9	Shannon Creek	279.39	-98.0016	49.2744	05OF014
ER-10	Elm River	105.32	-98.0101	49.9124	05OG008
BCD-11	Big Coulee Drain	83.69	-97.3792	49.6947	05OG001

Water Data

Stream discharge at all sites was estimated using an indirect approach. A pressure transducer logger (HOBO, Onset Computer Corporation, MA) was deployed in each stream from October 2009 to May 2010. Water level and temperature were monitored at 30-minute intervals throughout winter and snowmelt. For all sites, the reference water level was measured at logger deployment and retrieval. Atmospheric pressure and temperature were also monitored at four of the ten sites. The barometric data combined with the measured reference water levels were used to correct the raw water level data and obtain net water level at all sampling sites. Daily net water levels were then related to the product of daily discharge, measured at stations located within 50 km of each of our sampling sites, and the drainage-area ratio between the sampling site and the discharge station (Daily provisional discharge data were obtained from Water Survey of Canada (WSC); www.wateroffice.ec.gc.ca.). Daily discharge for each site could be predicted from net water level using a power or a polynomial relation. For all 10 sites, predicted discharge values were significantly correlated with observed discharge values ($0.734 < r < 0.971$; $p < 0.05$; $n > 10$ for each site). Grab water samples at all sites were taken daily during the rising limb and peak of the snowmelt hydrograph (March 13 to 22, 2010) and weekly during the falling limb (March 28 to April 25 2010), with a total of 10 - 15 samples collected per site between March 13 and April 25 2010. All water samples were collected from a bridge (upstream side) or from the shore in 500 mL high density polyethylene (HDPE) bottles, stored at 4ºC in a cooler and transported to Environment Canada's National Laboratory for Environmental Testing in Saskatoon (SK). Samples from all sites were analyzed for total N (TN) and total P (TP); dissolved nitrogen (TDN) and phosphorus (TDP) were analysed at four sites (TC-3, BC-4, HD-8 and BCD-11). TN and TDN were determined colorimetrically as nitrite after automated cadmium reduction of nitrate to nitrite (Eaton *et al.*, 2005). TP and TDP were determined colorimetrically as orthophosphate by reduction using stannous chloride (Eaton *et al.*, 2005). Analyses for TDN and TDP were performed on filtered sub-samples (< 0.45 µm). Daily site concentrations were estimated by interpolating between sampling days. Daily TP and TN loads (L_i) were calculated using Eq. 3.

$$L_i = (Q_i\, C_i)K \qquad \text{Eq. 3}$$

where Q_i is the daily discharge ($m^3\, s^{-1}$), C_i is the daily concentration ($mg\, m^{-3}$) and K is the number of seconds in a day. The load (L) for a given snowmelt period was the sum of the daily loads of that period, Eq.4.

$$L = \sum_{i=1}^{n} L_i \qquad \text{Eq. 4}$$

where n is the number of days for that period.

Land cover data

Detailed information on data sources and calculations used to estimate land cover, fertilizer usage and population served by wastewater lagoons are given in Yates *et al.* (in review). In brief, watershed boundaries were delineated using the ArcGIS 9.3 (ESRI 2008) extension Arc Hydro 1.4 (ESRI 2010) based on a 30 m digital- elevation model and a 1:50,000 stream network. Information on the application of synthetic fertilizers was summarized from records of fertilizer application maintained by the Manitoba Agricultural Services Corporation (www.mmpp.com/mmpp.nsf/mmpp_publications.html). Wastewater lagoon information was obtained from Manitoba Conservation who provided locations of wastewater treatment lagoons, and the receiving environment, as well as the estimated number of people served by the lagoon within the subwatershed.

RESULTS AND DISCUSSION

Temporal variation in nutrient export during snowmelt

Stream discharge and nutrient export during snowmelt varied considerably both within (i.e., temporal variation) and among (i.e., spatial variation) the 10 study streams. In 2010, snowmelt initially started in mid-March, about two weeks earlier than normal. Water sampling began as soon as open flowing water was observed, with the earliest site initially sampled on March 13 and the latest on March 19. Although snowmelt hydrographs varied among sampling sites (Figure 2), a general pattern was observed with a main snowmelt (March 13 - 29) followed by a secondary snowmelt and a post-snowmelt period.

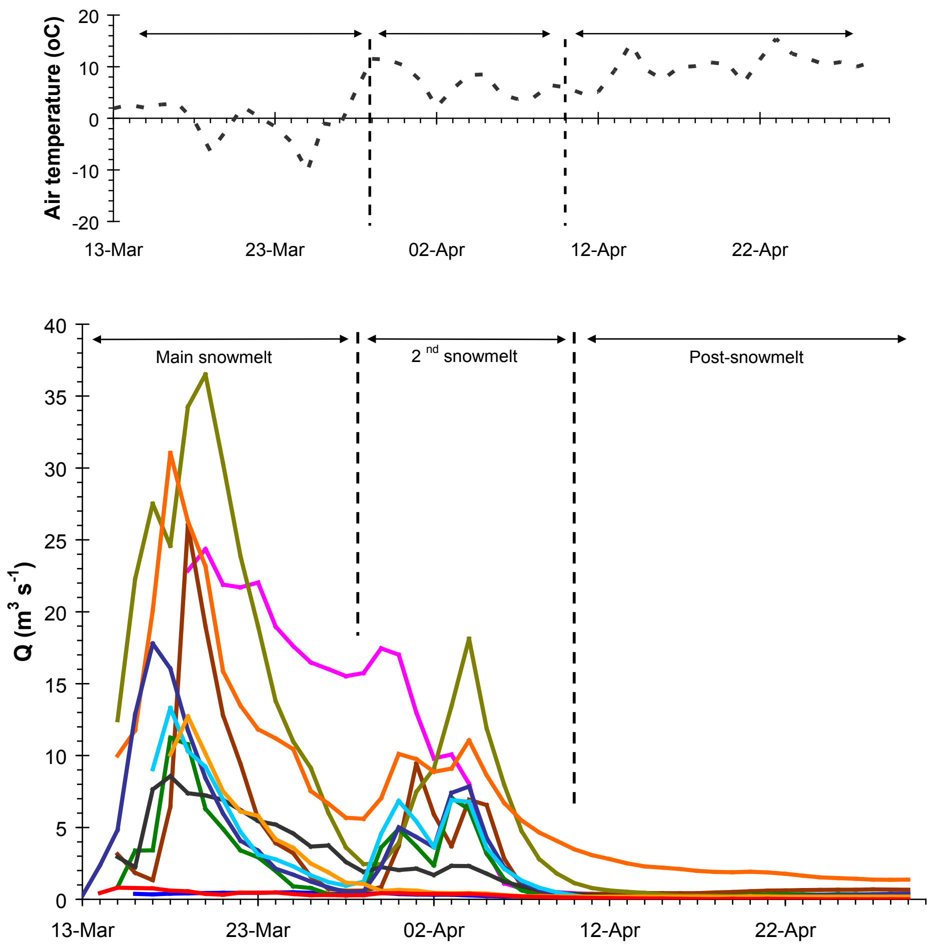

Figure 2. Air temperature from Environment Canada weather station located at Morden (south Manitoba) and hydrograph showing the change in discharge (Q) through snowmelt for all sites.

For most of the sampling sites, discharge peaked during the main snowmelt period and coincided with visible runoff from flooded fields adjacent to the streams. This overland flow likely generated significant nutrient-enriched runoff to streams due to prolonged water contact with soil. Air temperature dropped below zero after March 19, reducing and/or stopping snowmelt processes and inducing discharge recession. A subsequent temperature increase induced a second melt from March 30 to April 10. The rising limb and discharge peak were less than during the main snowmelt because most of the water from melted snow had already drained to the streams. The post-snowmelt period was characterised by a recession limb reaching base flow discharge at all sites. Although data are not yet available for the remainder of 2010, our results to date are consistent with findings of others that snowmelt in the Canadian Prairies is the most significant hydrological time period, replenishing streams, rivers, lakes and reservoirs (Norum *et al.*, 1976). In fact, a study of streams in southern Manitoba reported that snowmelt may account for 56 to 95% of annual flow (Glozier *et al.,* 2006).

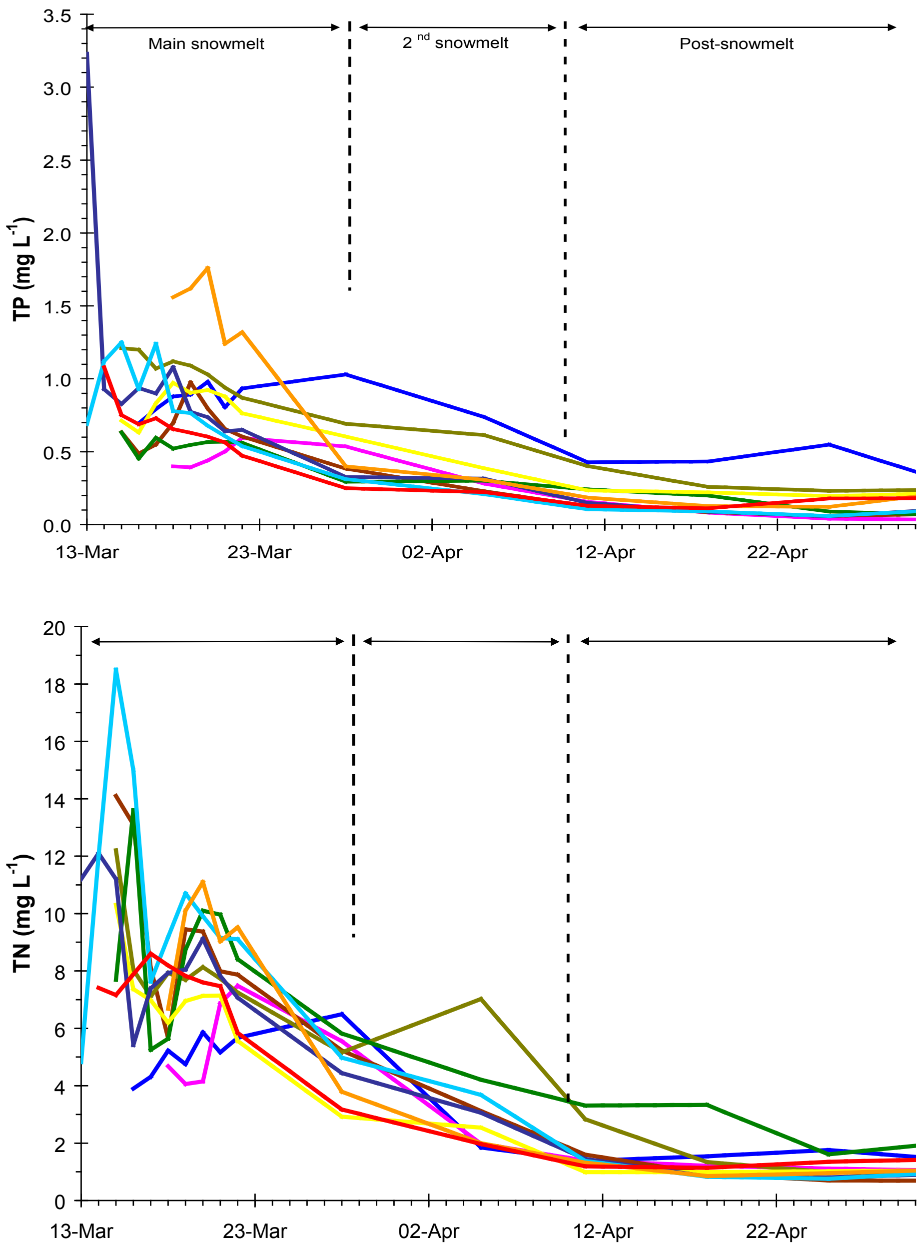

Figure 3. Concentrations of TP and TN during different phases of snowmelt 2010.

Concentrations of P and N at all sites varied greatly through the snowmelt and post-snowmelt periods, with average for the 10 sites ranging from 0.343 - 0.864 mg L^{-1} TP and 3.85 - 7.84 mg L^{-1} TN. Maximum concentrations were 3.23 mg TP L^{-1} at HD-8 and 18.50 mg TN L^{-1} at SC-9. In general, TP and TN concentrations were greater during the main snowmelt and lower during post-snowmelt discharge recession (Figure 3). Discharge was generally correlated with TP ($0.370 < r < 0.969$; $p<0.05$) and TN ($0.515 < r < 0.935$; $p<0.05$) concentrations, although the strength of the associations varied among the sites. For the four sites where water samples were analysed for dissolved nutrients, dissolved forms comprised 81.7 - 87.2% TP and 94.0 - 95.7% TN (median values), indicating that dissolved forms dominated snowmelt. Ratios of dissolved to total nutrients tended to be relatively stable throughout the snowmelt and post-snowmelt periods, with slightly higher values during peak discharge. Our observation that much of the N and P transported during snowmelt in Canadian prairie streams is in the dissolved phase agrees with other prairie studies on water quality in streams or field runoff that reported high proportions of dissolved nutrients during snowmelt (Glozier *et al.*, 2006; Hansen *et al.*, 2000; Little *et al.*, 2007; Sheppard *et al.*, 2006; Tiessen *et al.*, 2010). The combination of flat topography, frozen soil and stream banks, and a gradual melt appears to considerably reduce erosion and sediment transport during snowmelt (Hansen *et al.*, 2000; Glozier *et al.*, 2006; Tiessen *et al.*, 2010). Nutrients delivered during snowmelt represent a critical component of the nutrient budget of both proximal and downstream aquatic ecosystems.

Table 2. Loads of total phosphorus and nitrogen for all subwatersheds during different phases of snowmelt (SN) 2010.

Site	Phosphorus				Nitrogen			
	Main SN	2nd SN	Post-SN	Total	Main SN	2nd SN	Post-SN	Total
	(kg)			(kg P km^{-2})	(kg)			(kg N km^{-2})
WBLS-1	467	223	37	11.3	2817	896	124	59.5
ECC-2	9636	2809	30	20.7	109848	25536	356	225.4
TC-3	6137	976	72	20.5	71365	13280	822	243.5
BC-4	23679	4497	131	45.2	181223	46372	810	364.9
DC-5	2383	864	59	18.3	36727	13703	1021	285.3
GC-7	14724	3270	687	101.8	112244	18825	3154	731.3
HD-8	6858	1068	30	36.6	62365	11576	321	341.4
SC-9	4146	884	2	18.0	51054	14852	27	236.0
ER-10	7714	132	46	75.2	49316	1014	316	482.3
BCD-11	381	68	6	5.4	4300	695	59	60.2

Nutrient loads from the subwatersheds ranged from 456 – 28 308 kg TP and 3738 – 228 406 kg TN (Table 2). The main snowmelt contributed the majority of nutrients (64.3 - 97.8% of TP and 71.4 - 97.4% of TN) compared to only 0 - 5.1% of TP and 0 - 3.2% of TN post-snowmelt. Statistical analysis revealed a significant correlation between TP and TN loads during snowmelt ($r=0.959$; $p<0.05$). To compare nutrient export measured in this study to other Prairie snowmelt studies, TP and TN loads were normalized to watershed area. Loads per unit area for our 10 subwatersheds varied from 5.4 - 101.8 kg TP km^{-2} and 59.5 - 731.3 kg TN km^{-2} (Table 2). Similar snowmelt export coefficients have been reported for South Tobacco Creek, an agricultural watershed located in the south-western part of the Red River Valley, with values ranging from 36 - 91 kg TP km^{-2} and 133 - 307 kg TN km^{-2} (Glozier *et al.* 2006). By comparison, several other studies of Prairie rivers have reported much lower nutrient export: 1.73 kg km^{-2} TP during snowmelt for a small tributary of the Assiniboine River, MB (Neil, 1992); 0.464 kg TP and 1.334 kg TN km^{-2} during spring high flows, which includes snowmelt, for the Souris River (Chacko 1986); and 1.329 - 10.237 kg km^{-2} TP annually for five Canadian Prairie streams (Fortin and Gurney 1998). The extent of human activity could potentially explain the observed differences between the different studies. However, non-fertilized lands in southern Manitoba have naturally high soil fertility and differences in the portion of native grassland in the watershed may also explain difference in nutrient export. Although several studies have investigated the ecological relevance of nutrient export in the Great Plain ecosystem (Tate, 1990; Chambers *et al.*, 2005; Dodds *et al.*, 1996; Dodds, 2000; Dodds and Oakes, 2006; Dodds *et al.*, 2008; Banner *et al.*, 2009), only a few studies on the Canadian prairies have highlighted the role of snowmelt in nutrient delivering nutrients to downstream ecosystems.

Human Activity Gradient and Nutrient Export

Human activity plays a key role in the introduction of nutrients to the environment. Analysis of human activity in our 10 subwatersheds showed that agriculture was the dominant land cover in all basins, covering 55 - 88% of the area (Table 3). Fertilizer was applied to 31.3 - 76.0% of the watershed areas at rates ranging from 11 – 27 kg P ha^{-1} and 28-71 kg N ha^{-1}. The density of people served by wastewater lagoons (WWL) was fairly low for the 10 watersheds, indicating that WWLs are unlikely to be a dominant factor influencing snowmelt loads (Table 3).

Table 3. Land use cover, fertilizer application and wastewater lagoon (WWL) information for the ten subwatersheds.

Site	Land Use (%)			Fertilizer			WWL*
	Agriculture	Deciduous Forest	Grassland	Land treated (%)	P (kg ha^{-1})	N (kg ha^{-1})	(pop.km^{-2})
WBLS-1	82.5	1.5	6.2	73.6	26.9	65.7	2.32
ECC-2	54.7	13.7	22.6	31.3	10.8	28.0	1.06
TC-3	70.3	13.4	11.3	68.9	18.0	61.3	1.88
BC-4	82.6	4	5.9	71.3	17.7	42.4	0.91
DC-5	69.4	7.7	13.3	55.1	12.4	38.9	n.a.
GC-7	81.6	4	7.8	58	16.7	50.1	n.a.
HD-8	66.2	7.6	15.6	49.2	16.2	44.1	n.a.
SC-9	65.4	10.4	14.9	62.4	17.3	52.0	0.89
ER-10	57.1	15.5	12.3	48.9	17.8	36.9	n.a.
BCD-11	88.3	0.8	3.8	76	24.1	71.3	n.a.

* Population served by wastewater lagoons by km^2
n.a. = not available

Comparison of nutrient export from our subwatersheds with measures of human activity showed that snowmelt N was better correlated with land use than was snowmelt P. Snowmelt TN was strongly correlated with both agricultural land cover (r= 0.91; $p<0.05$) and the estimated quantity of N fertilizer applied in the watershed (r= 0.80; $p<0.05$); snowmelt TP was also correlated with agricultural land cover (r= 0.81; $p<0.05$). The stronger relationships between land use and TN as compared to TP are surprising given that snowmelt TP and TN loads were correlated (r=0.97; $p<0.05$), resulting in similar gradients in TP and TN export amongst subwatersheds (Figure 4). The only sites not showing similar ranks for TP and TN export were ECC-2 and DC-5. Nevertheless, our findings agree with several other Prairies studies that demonstrate stronger relationships for N concentration and/or load, as compared to P, with land use (Dodds and Oakes, 2006; Little *et al.*, 2003). In contrast, Banner *et al.* (2009) found a strong relationship (R^2=0.79) between median TP concentration and riparian land use along Prairie streams. However, TN data were not presented to assess whether N or P was better predicted by land cover. Observations that streams and ponds in southern Manitoba often have high nutrient values (Pip, 2005) and that agricultural activities were the major source of N and P to southern Manitoba streams (Bourne *et al.* 2002) also attest to the important role of agriculture as a nutrient source of prairie surface waters.

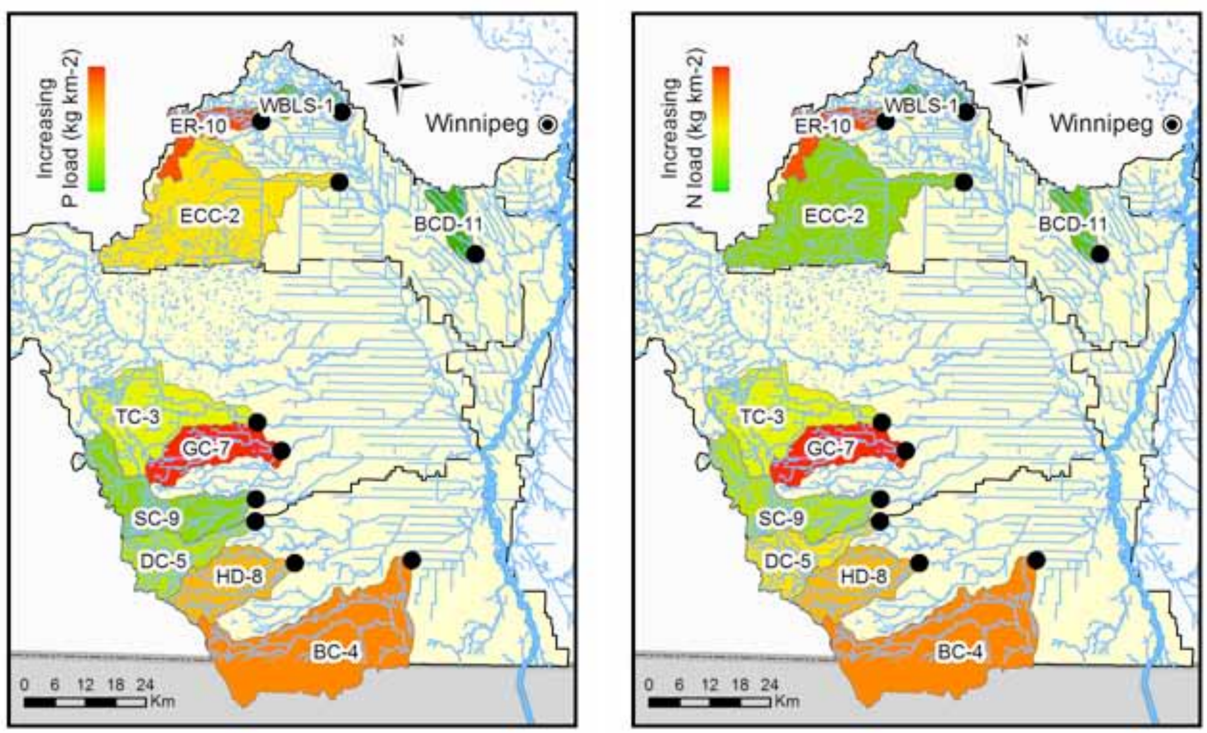

Figure 4. Gradient of total phosphorus (left) and nitrogen (right) loads normalized to watershed area for snowmelt 2010 in the south-western Manitoba.

CONCLUSION

Snowmelt is the most significant time period in the hydrologic cycle for streams and rivers in the Canadian prairies. Although the contribution of snowmelt to annual water budgets has been examined for prairie watercourses, few investigations have been conducted on stream nutrient export during snowmelt. Characterization of nutrient loads in 10 subwatersheds in the Red River Valley of south-western Manitoba, Canada provided important observations of nutrient concentrations and loads during snowmelt. Although concentrations of TP and TN at all sites varied considerably through the snowmelt and post-snowmelt periods, concentrations were typically greater during the snowmelt peak and lower during post-snowmelt discharge recession. Much (> 80 %) of the TP and TN exported was in the dissolved phase, thus posing significant risk to proximal and downstream ecosystems with respect to eutrophication. Nutrient export was correlated with agricultural land area in the watershed; this observation and results from other studies in the region suggest that agricultural activities are a dominant source of nutrients to southern Manitoba streams. Our results suggest that an improved scientific understanding of the contribution of snowmelt to the nutrient budget of Prairie aquatic ecosystems is essential for designing land use management practices to control nutrient loads to Lake Winnipeg and other waterbodies in the Great Plains.

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Use of shading equipment for eutrophication control in a Brazilian water reservoir

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Abstract

The paper describes the use of shading as a lake restoration technique in order to limit cyanobacteria growth. The experiments, which have a pioneer character in the country, were carried out in a man made lake situated in the State of Espirito Santo, Brazil. A plastic material, with 70 % of shading efficiency, was installed over the surface, at the deepest point of the lake. Results of the first year, based on a monthly monitoring program, show that cyanobacteria growth has been partially controlled. The most striking result refers to a dominance shift from the genus *Microcystis* (potentially toxic) to *Merismopedia* (nontoxic). However the available data cannot indicate if this change is due exclusively to the installation of the shading equipment. The intense phytoplankton productivity dynamics is a typical feature of warm water bodies and the influence of unknown forcing factors may contribute to frequent oscillations in the structure of the phytoplanktonic community. Weekly temperature and dissolved oxygen profiles did not show any negative effect from the artificial shading. The redox potencial remained positive in all samples, indicating the absence of phosphorus resuspension from the sediments. The shading technique has a low cost/benefit value and can therefore be used in the restoration of tropical as well temperate lentic waters.

Keywords

Cyanobacteria; eutrophication; shading

INTRODUCTION

Eutrophication of lentic systems is one of the major issues regarding environmental problems in aquatic systems. This problem is potentialized in the case of warm water reservoirs, where all methabolic processes develop in a more accelerated form. This is specially true for nutrient assimilation performed by the phytoplankton. Another drawback of the onset of algal blooms is the possible presence of cyanobacteria. Blooms of cyanobacteria (or Cyanophyceae algae) are a serious concern for Brazilian authorities, since the worldwide first reported deaths of human beings caused by the ingestion of water contamined with cyanotoxins have been registerd in this country (Azevedo et. al., 1996). Cyanobacteria present an array of characteristics that give them a clear competitive growth advantage over planktonic algae under specific environmental conditions. They are not favoured by high light intensity and require little energy to maintain cell structure and function (Mur et. al., 1999). There are evidences that cyanobacterial blooms may be minimized by limiting the light availability for these organisms. The use of shading of surface waters as a lake restoration technique is discussed in Cooke et.al. (2005). The shading can be performed by installing floating polyethylene sheeting or using dyes to suppress plant growth. In this case the dye is added as a concentrate and wind disperses it throughout the lake. Moreover some experiments have shown that light limitation may effectively act for limitation of cyanobacteria growth (Mullineaux, 2001).or even for establishing competition between toxic and nontoxic strains (Edwin, 2007).

METHODS

Barragem Norte is a man made lake located inside the industrial area of SAMARCO Mining Co., in the State of Espirito Santo, Brazil. The main industrial activity is the production of iron pellets. The reservoir acts as water supply source for the company, as well as a buffer for hydrological and water quality purposes. As the reservoir is situated adjacent to a natural lagoon (*Maimbá)* the local environmental agency has determined the maximum load of contaminants that could be discharged into the lagoon in rainy periods. The reservoir has an area of 36 ha, a volume of 1,131,000 m^3 and a maximum depth of 5.5 m. In order to limit the intensive algal growth a shading experiment was implemented in a part of *Barragem Norte.* In our knowledge this is a pioneer example in Brazil for lake restoration through the shading of surface waters. The shading is obtained through the use of a plastic material (*Sombrite®*) with a light retention of 70 %. and installed in 6 cells of 20 m x 30 m (Fig. 1). A consistent monitoring program has been implemented since the beginning of the experiment (June/08). This program is specifically designed for the evaluation of the efficiency of the shading process.

Figure 1. Shading experiment in Barragem Norte

RESULTS AND DISCUSSION

The results of the first year of the shading experiment are shown in Figure 2. It can be seen that, in the initial phase, a marked drop in algae densities has been recorded. Afterwards the phytoplankton rose again, but a light trend in obtaining lower densities can be inferred.

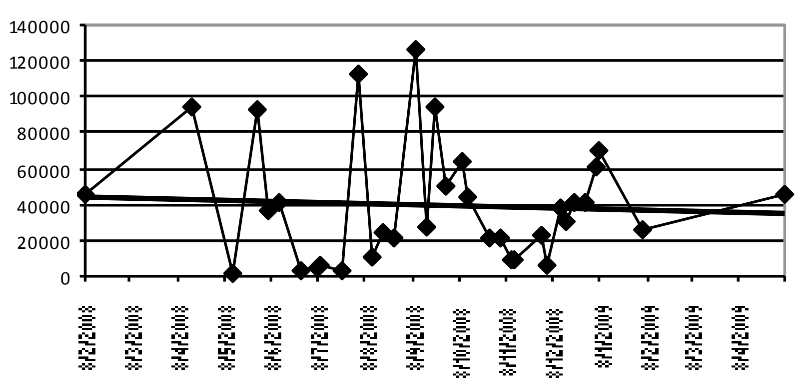

Figure 2. Phytoplankton densities (ind/mL) in the period Feb/08-May/09

With respect to the cyanobacteria percent in the whole algal population (Fig. 3), it can be seen a drastic drop immediately after the installation of the shading structure, which has been followed by a senoid behaviour. It seems that the prevalence of cyanobacteria oscillates according to the influence of possible forcing factors (radiation, temperature, winds, hydrodynamics) which present a marked stochastic nature and therefore cannot be modeled.

It should be stressed that tropical lakes, due to their geographical localization and the inherent climatic conditions, present some typical features, which may be summarized in the following points (von Sperling, 1997):

- The intense solar radiation and high water temperatures accelerate nutrient uptake by the algae;
- Phytoplantonic population peaks are less frequent in comparison with temperate aquatic systems;
- High nutrient assimilation capacity, associated with enhanced recycling rates, lead to the prevalence of an intense degree of productivity;
- Since nutrient concentrations, specially dissolved phosphorus contents, are usually low, many water bodies can be classified as oligotrophic in spite of their high productivity;
- Sometimes low phytoplankton densities may be associated with high growth rates;
- High mineralization rates lead to an accelerated oxygen depletion and to the formation of sediments that are very poor in organic matter; consequently there is no direct connection between hypolimnetic oxygen deficit or content of organic matter in the sediment and the water body productivity.

In the present case a general trend in the reduction of the amount of cyanobacteria in the total phytoplankton population can be expressed by following numbers: average % of cyanobacteria in 2006: 98,3: 2007: 97; 2008: 81,6; 2008 after shading: 79,2; 2009: 86,8 %. The comparison of the general average of cyanobacteria before and after shading (96,2 %, n=18 and 80, 3%, n=28) indicates a concrete lowering in the marked dominance of cyanobacterial groups

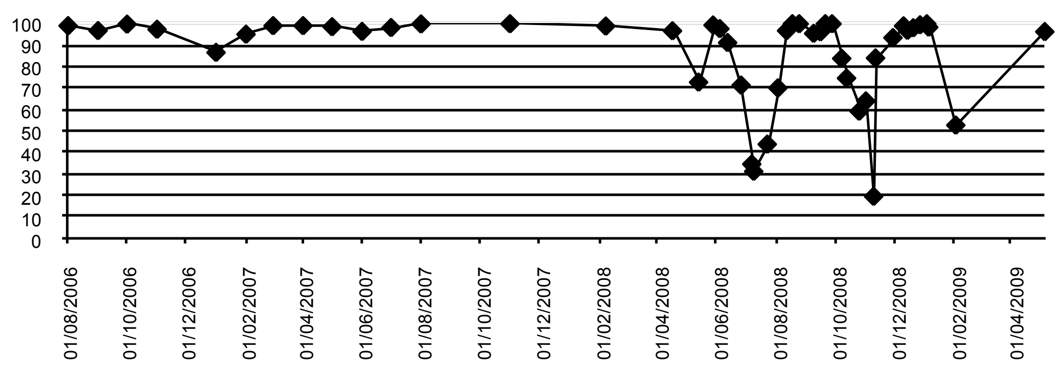

Figure 3. Percent of cyanobacteria (period August/06-May/09)

At a first look the results may give the impression of a disappointing amount of reduction, but it should be taken into account that the massive presence of cyanobacteria in stressed warm waters is so strongly established that most restoration efforts would effectively promote only a mild reduction in the degree of dominance of these organisms. In spite of the possible influence of temperature on cyanobacteria growth (Whitton and Potts, 2000) no correlation could be found in the present case, i.e., high cyanobacteria populations have been registered in low (around 20 ^{0}C) as well in high temperatures (around 30 ^{0}C).

With respect to changes in the phytoplankton after the onset of the shading experiment, some considerations should be expressed regarding the hydrodynamic aspect of the dam, which is strongly dependent on the water body morphology. These morphometric features play a relevant role in the distribution of particles (including organisms) and dissolved material (Håkanson, 1981). *Barragem Norte* dam presents a low value of relative depth (0,81 %), which is defined as the relationship between lake maximum depth and the mean diameter of the lake (i.e., diameter of a circle that has the same area as the lake). This means that the water column is easily subject to vertical circulations, which generally happen during the winter time. This mixing process accelerate hence the distribution of suspended and dissolved matter in the liquid mass. On the other hand the shoreline development is high (3,6), what indicates a dendritic morphology of the water body. This parameter represents the degree of irregularity of the shoreline. Its value is given by the ratio between shoreline length and the perimeter of a circle that has the same area as the lake. This means that some accumulation of suspended and dissolved matter may take place in the several arms or re-entrances of the aquatic system. Moreover the dam presents a concave form, which is indicated by a volume development value higher than 1 (in this case 1,7). The volume development is a measure used to illustrate the form of the lake basin. It is defined as the quotient between the lake volume and the volume of a cone whose base area is equal to the lake area and whose height is equal to the maximum depth.

The morphometry of the dam points out to an intense exchange of water among the several compartments of the ecosystem. This characteristic surely limitates the informations related to the real effect of shading on the reduction of phytoplanktonic biomass. However the consideration of the temporal behaviour of the algae groups, particularly the cyanobacteria, at the deepest point of the dam, where the shading equipment has been installed, may give some insights about the influence of light limitation on phytoplankton growth and on the prevalence of cyanobacteria. In this sense the most remarkable result of the shading experiment is related to the shift in cyanobacteria dominance, which moved from the potencially toxic strains of *Microcystis sp.* and *Pseudoanabaena galeata* to the nontoxic species of *Merismopedia tenuissima.* In spite of the eventual prevalence of other potentially toxic genus, such as *Aphanocapsa* and *Planktonlyngbia,* specially in the period from December/08 to May/09, there are clear evidences that *Merismopedia* blooms occurred after the beginning of the shading experiment. However there are no sufficient statistical data that may associate this algal shift exclusively to the artificial shading. Other unknown forcing factors may have also contributed to this change in the cyanobacteria populations. The genus *Merismopedia* is generally found in association with some salinity in the water body, with low orthophosphate concentrations and in low altitude lakes (Livingston, 2006). All these conditions are found in the aquatic system of *Barragem Norte.* All analysis carried out for the determination of cyanobacteria toxins (microcistin) in the period January06-May09 showed no detectable values.

CONCLUSIONS

The evaluation of the experiment points out to a general reduction in the phytoplanktonic population as well as in the percent of cyanobacteria. A shift in the population dominance, favouring here the prevalence of nontoxic strains, has been also observed. The potentially toxic genus *Microcystis* and *Pseudoanabaenaceae* have been partially substituted by the non-toxic genus *Merismopedia.* There are no registers of any ecological damage to the aquatic life as a consequence of the installation of the shading equipment. Due to intense productivity dynamics in tropical lakes, the reduction of cyanobacteria populations has not achieved high values. It may be estimated that the use of shading as a restoration technique may be more successful in the case of temperate water bodies.

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Trophic state assessment in warm-water tropical lakes and reservoirs of the central region of Mexico

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Abstract

The overall water quality of lakes and reservoirs in Mexico continues to deteriorate. At 1981, the Center for Sanitary Engineering and Environmental Science (CEPIS), coordinated an international study of the eutrophication in warm-water tropical lakes. The importance of this regional effort was the development of a reliable model, which is now applied in the management of water bodies. The objective of this document is to review and evaluate the trophic state issues of various water bodies located in the central region of Mexico. Five lakes and seven reservoirs were included in this assessment. These tropical lakes and reservoirs are generally high altitude and nutrient-rich. The total nitrogen (TN) to total phosphorus (TP) ratio of 9:1 was utilized. With the use of this ratio, the majority of Mexican lakes were limited by nitrogen, and also the observed levels in Mexican water bodies of both NT and NP were relatively high and surpassing levels that are traditionally considered to be limiting. Other factors, such as light and residence time, could also be limiting. The studied lakes and reservoirs suggest an accentuated effect of diffuse pollution inputs from the catchment area, due to the tropical/semi-tropical/semi-arid intrinsic characteristic of these water bodies. The classification of lakes, according to water quality and trophic state assessment, is useful for its inclusion in the management projects and future rehabilitation goals.

Keywords

Applied limnology; eutrophication; Mexico; reservoirs; tropical lakes; warm-water lakes.

INTRODUCTION

Over the past years, the explosive population growth in Latin America affected many of the reservoirs and lakes in the region which have suffered the consequences of the eutrophication process, therefore has interfered with their designated uses. According to various studies, the overall water quality of lakes and reservoirs in many regions of Mexico continues to deteriorate (Olvera *et al.*, 1998; Lind *et al.*, 1992; Bravo *et al.,* 2008). At the decade of the 80's, the Pan American Center for Sanitary Engineering and Environmental Science (CEPIS) in Peru, coordinated an international study of the eutrophication of warm-water tropical lakes (Salas and Martino, 1991). The data set used in this study where from about forty lakes/reservoirs and the studies were generated mainly by the following countries: Argentina, Brazil, Colombia, Ecuador, Mexico, Puerto Rico, USA and Venezuela. The importance of this regional effort was consolidated with the development of a reliable simplified mathematical model, to be applied in the evaluation and management and study of lakes and reservoirs.

In the case of Mexico, two government institutions collaborated with the international eutrophication assessment: a) The *Centro de Estudios Limnológicos (Center of Limnological Studies, CEL)*, who was responsible of the study of three water bodies: Chapala (1983-1984 and 1986-1987), Zirahuén (1986-1987) and Laguna de Cajititlán (1981-1982 and 1986-1987); and b) The *Instituto Mexicano de Tecnología del Agua (Mexican Institute of Water Technology, IMTA)*, cooperated with the study of two water bodies: Tequesquitengo (1986) and Requena (1986-1987) (Salas and Martino, 1991).

Later on, the methodology and the mathematical model obtained in the CEPIS Regional Program were applied by IMTA in Mexico for: Reservoirs Valle de Bravo (1987 and 1992-1993), Nabor Carrillo (1987), Madín (1988), Villa Victoria (1988), Guadalupe (1993); and later, Zimapán Reservoir (2002-2006) and Lake Pátzcuaro (2006- to date); in other words, with the addition of six reservoirs and one lake.

In Mexico there are notably more reservoirs than lakes. There are only 17 water bodies greater than 100 km^2 and only three of them are natural: Lakes Chapala, Cuitzeo and Pátzcuaro. That is why it is evident that Mexico is not internationally remarkable in lake diversity; and maybe, because of this fact, the limnological studies have mainly focused in these water bodies, like Chapala and Pátzcuaro, the first and third largest lakes in Mexico (Arredondo-Figueroa and Aguilar-Díaz, 1987; Bernal-Brooks, 2002). In contrast, Aldama (2002) reported 4500 reservoirs in Mexico, 840 of which are classified as large impoundments, according to the International Commission on Large Dams (ICOLD).

These reservoirs fulfil the definition of warm water tropical lake, which is based on a minimum temperature of 10°C under normal conditions, minimum annual average of 15°C. Nevertheless, extremely high altitude tropical lakes ($\geqslant$ 3000 m above sea level) were not included in the program (Salas and Martino, 1991). It is frequent that tropical systems develop extremely low TN:TP ratios, thereby favoring the dominance of cyanobacteria (also termed blue-green N2-fixing algae). It is generally believed that nitrogen is the most common primary nutrient which limits the maximum algal biomass levels in tropical/subtropical systems (Ryding and Rast, 1989; Lind et al., 1992).

Mexico's geographical position covers tropical and subtropical areas between two oceans (Pacific and Atlantic), including remarkable mountainous topographies, with a wide variety of climatic conditions. The Tropic of Cancer lies across the northern and central zones of Mexico (it passes close to the southern peninsula of Baja California) at 23°26'16" north of the equator. An under researched region consists of high latitude (15-23°N or S) tropical lakes. Because of the meteorological conditions of these global belts make them semiarid, Lind *et al.* (1992) suggested that these lakes may be different from the equatorial lakes as well as of temperate lakes. In the central part of Mexico, the physiographic systems include the Trans-Mexican Volcanic Belt and the Sierra Madre del Sur, which leads to a complex topography and high altitude lakes and reservoirs; this also gives to this country a high biodiversity value like a high amount of aquatic endemic species, because it is located on the borderline of the neartic and the neotropical biota. This document covers high altitude lakes and impoundments exceeding the height of 1500-m, with an exception: Lake Tequesquitengo which is located at just 900 m. The altitude factor put together these case studies with those of subtropical Florida (e.g., Lake Okeechobee, located in South Florida, is at 27°12'-26°40'N) or Texas (e.g. Lake Livingstone, a man-made lake about 100 km N from the city of Houston, at 30°44'24'N;. this last U.S. reservoir was included as the northernmost water body, in the international warm-water tropical lake study), but this two water bodies are not really in the tropical area of the world. In spite of this fact, in the case of Mexico, solar radiation and two distinct climate seasons (rainy and dry seasons), remain the same as at the tropical geographic latitude (Alcocer and Bernal-Brooks, 2010).

Man-made lakes in the high-hill semi-arid zone perform the same socioeconomic functions as natural lake in the developed countries, and can be considered even more valuable resources, due to the general and increasing scarcity of water (Thornton and Rast, 1993). Moreover, generally, most tropical lakes and reservoirs are situated in developing countries, where there is a chronic lack of financial resources for the establishment of long term and consistent monitoring programs (Von Sperling and Sousa, 2007).

The main objective of this study is to review and evaluate the trophic state issues of various water bodies located in the central region of Mexico, including lakes, as well as reservoirs, and because of the 'apparent' lack of papers related to their study in our country.

METHODS

Table 1 shows the key features of five lakes and seven reservoirs included in this article, for their comparison and trophic state assessment; this table also displays, in first place, the national information obtained by the CEPIS Regional Program and, in second place, with the use of that experience and methodology, it includes the water bodies information, done later by IMTA. The water sampling methods used in this study were described by Castagnino (1982) with modifications proposed by Olvera-Viascán *et al*. (1998). These methods are based on the CEPIS protocols (Salas and Martino, 2001).

Based on the lake/reservoir morphology, three to six water surface sampling stations were established, with sampling frequencies varying from monthly to bimonthly. All data cited were from studies of at least ones year. In every station, Secchi disk readings were made and water samples were taken at two levels: an integrated one using the hose method from the surface to twice the Secchi disk depth, and a second one, using a Van Dorn bottle at 1-m from the lake bed. Each water sample was analyzed for: TP, TN, chlorophyll *a* (Chl *a*). Laboratory analysis were made according to Standard Methods (1998 [20th ed. and previous]). Chl *a* samples were determined using the spectrophotometric method described by the Standard Methods (*op. cit.*); in samples obtained by the hose method; samples were filter through Whatman 1.2 μm GF/C glass fiber filters. This method corrects the presence of degradation products, like pheophytin *a*; Chl *a* was extracted by macerating filters in a tissue grinder in a solution of 90% acetone.

Profiles were performed for temperature, dissolved oxygen, pH and conductivity, using field multi-parameter YSI models No. 6000 and 6600 (in the first studies, temperature and DO were measured using a YSI meter model 58; pH was measured with a Cole-Parmer 612 PH-meter, and conductivity with a YSI SCT-meter model 33); these profiles were taken at 0.5-m from the surface, at 1 or 2-m intervals and at 0.5-m above the lake bed.

Trophic State Index (TSI, Carlson, 1977) for Secchi disk, chlorophyll *a* and TP were used, and the TN index calculation was taken from Kratzer and Brezonik (1981). The simplified total phosphorus model for trophic classification (CEPIS Regional Program; Salas and Martino, 1991; equation 16) was used.

The key parameters used for the trophic state assessment are shown in Table 2.

Table 1. Lake / reservoir list, morphological and hydrological data, mixing classification and consulted references. Note R. Nabor Carrillo is called *Lago Nabor Carrillo (Lake Nabor Carrillo)*, but it is a constructed water body.

Lake (L.)/ Reservoir (R.)	Years of study	Symbol	Latitude N	Longitude W	Altitud (m)	Catchment area Ac (km^2)	Lake area Al (km^2)	Ac:Al Ratio	Average depth (m)	Max. depth (m)	Residence time T_w (yr)	Mixing classification	References (& leading institution)
Waterbodies included in the CEPIS Regional Program													
L. Cajititlán	1981-1982	Ca_1	20°25'06"	103°19'08"	1549	280.0	10.6	26.4	0.69	4	**a**	Polymictic	Salas and Martino, 1991 (CEL)
L. Cajititlán	1986-1987	Ca_2	20°25'06"	103°19'08"	1549	280.0	14.3	19.6	1.69	4	**a**	Polymictic	Salas and Martino, 1991 (CEL)
L. Chapala	1983-1984	Ch_1	20°06' 20°20'	102°41' 103°25'	1520.7	52,500.0	1,061.0	49.5	4.20	7.5	11.05	Polymictic	Salas and Martino, 1991 (CEL)
L. Chapala	1986-1987	Ch_2	20°06' 20°20'	102°41' 103°25'	1524	52,500.0	1,078.5	48.7	4.43	7.5	15.94	Polymictic	Salas and Martino, 1991 (CEL)
R. Requena	1986-1987	R	19°57'00"	99°18'52"	2110	759.0	4.8	158.1	5.0	13	0.26	Polymictic / Oligomictic	Salas and Martino, 1991 (IMTA)
L. Tequesqui-tengo	1986	T	18°37'06"	99°16'05"	900	28.9	8.0	3.6	16.0	25	98.5	Monomictic	Salas and Martino, 1991 (IMTA)
L. Zirahuén	1986-1987	Zir	19°25' 19°27'	101°43' 101°46'	2075	260.8	11.23	23.2	20.64	40	**a**	Monomictic	Salas and Martino, 1991 (CEL); Chacón-Torres and Rosas-Monge, 1998
Waterbodies done following the CEPIS methodology, by IMTA & the National Autonomous University of Mexico (UNAM).													
R. Guadalupe	1993-1994	G	19°37'51"	99°15'29"	2300	271.9	3.5	77.7	11.09	21	0.28	Monomictic	Lugo *et al.*, 1998 (IMTA and UNAM-Iztacala)
R. Madín	1988	M	19°31'24"	99°15'33"	2346	105.0	0.85	123.5	17.4	36	0.39	Monomictic	Bravo-Inclán, 1995 (IMTA)
R. Nabor Carrillo	1987	N.C.	19°28'00"	99°58'17"	2236	1,700.0	9.17	185.4	2.29	3.65	56.3	Polymictic	No reference available (IMTA's internal report).
L. Pátzcuaro	2006-2008	P	19°32' 19°41'	101°32' 101°42'	2035	929.0	97.0	9.6	4.7	10.9	**a**	Polymictic	Sánchez-Chávez *et al.*, 2008
R. Villa Victoria	1988	V.V.	19°28'07"	100°00'31"	2605	617.7	27.5	22.5	6.5	12.5	1.62	Polymictic / Oligomictic	No reference available (IMTA's internal report).
R. Valle de Bravo	1987	V_1	19°11'45"	100°09'26"	1830	546.9	17.3	31.6	19.4	35	2.2	Monomictic	Olvera-Viascán, 1990 (IMTA)
R. Valle de Bravo	1992-1993	V_2	19°11'45"	100°09'26"	1830	546.9	17.3	31.6	19.4	35	1.8	Monomictic	Olvera-Viascán *et al.*, 1998 (IMTA)
R. Zimapán	2002-2006	Zim	20°39'29"	99°30'07"	1548	11,978.0	17.4	688.4	52.40	110	1.16	Meromictic	Bravo-Inclán *et al.*, 2008 (IMTA)

[a] Without outflow, or the residence time tends to be extremely high.

Table 2. Lake/reservoir key parameters used in the CEPIS simplified model. Water bodies are listed in accordance with increased average total phosphorous concentration. Underlined TN:TP ratios show the possibility of being TN limited; Bold N:P ratios could present TN and TP colimitation.

Lake (L.) / reservoir (R.)	Symbol	Secchi disk (m)	Chlorophyll *a* (µg L^{-1})	Average total phosphorus (mg L^{-1})	Average total nitrogen (mg L^{-1})	TN:TP ratio	Trophic state
Lakes							
L. Tequesquitengo, 1986	T	2.23	26.4	0.023	0.645	28.0	M (E)
L. Pátzcuaro, 2006-08	P	0.28	31.8	0.143	2.206	14.5	E (HE)
L. Zirahuén, 1986-87	Zir	6.50	1.67	0.250	0.730	<u>2.9</u>	E
L. Cajititlán, 1986 -87	Ca_2	---	22.38	0.400	2.400	<u>6.0</u>	HE
L. Chapala, 1983-84	Ch_1	0.70	5.02	0.426	0.876	<u>2.1</u>	M
L. Cajititlán, 1981 -82	Ca_1	---	---	0.470	4.240	**9.0**	HE
L. Chapala, 1986 -87	Ch_2	---	8.9	0.680	1.130	<u>1.7</u>	E
Reservoirs							
R. Valle de Bravo, 1987	V_1	1.84	29.2	0.006	0.607	101.2	M (E)
R. Villa Victoria, 1988	V. V.	0.57	54.2	0.029	1.150	39.7	M (E)
R. Valle de Bravo, 1992-93	V_2	2.67	8.5	0.040	0.434	**10.9**	E (M)
R. Madín, 1988	M	0.32	56.1	0.249	1.111	<u>4.5</u>	E (HE)
R. Requena, 1986-87	R	0.79	35.2	0.383	1.740	<u>4.5</u>	E
R. Guadalupe, 1993-94	G	0.63	54.9	0.887	4.530	<u>5.1</u>	HE
R. Zimapán, 2002-06	Zim	1.94	38.3	0.959	5.977	<u>4.3</u>	E (HE)
R. Nabor Carrillo, 1987	N. C.	0.16	189.1	9.530	11.912	<u>1.2</u>	HE

--- Not available.

RESULTS AND DISCUSSION

Comparing the morphometric data of Table 1, it is clear that the reservoirs have a bigger catchment area (Ac) in relation to their water body surface area (Al; reservoirs show high mean Ac:Al ratio = 213.2 ± 223.4 units); and lakes are not as much affected with less extended basins (mean Ac:Al ratio = 25.8 ± 21.5 units). Zimapán Reservoir stands out as having an enormous basin, with an Ac:Al ratio of 688.4 units, which is more than three times the mean average Ac:Al ratio; also, the Ac:Al ratio for Lake Chapala stands out (with 49.5:1 for Ch_1, and 48.7:1 for Ch_2); in the case of Cajititlán Lagoon and between the first and second studies, the lake had a surface increase which was beneficial for the 1986-1987 period. Summarizing, the area ratio is an index that is directly proportional to the degree of potential effects of diffuse pollution (Von Sperling and Sousa, 2007), and the contribution of clay that limits the photosynthesis and the nutrients which stimulate this process (Lind *et al.*, 1992). Thornton and Rast (1993) suggest that semi-arid highlands are generally comprised of well-leached, organic poor soils, which are extremely susceptible to erosion; this is aggravated by the seasonal nature of the rainfall events, which commonly occur in the form of important storm events, which have a high erosive potential.

The total nitrogen (TN) to total phosphorus (TP) 9:1 ratio, proposed by Vollenweider (1983; cited by Salas and Martino, 1991) was utilized. Consequently, lakes with TN to TP ratios less than 9 were potentially nitrogen limited. As can be observed in Figure 1, the majority (*circa* two thirds, 60%) of the trophic studies in Mexican lakes/reservoirs were nitrogen limited. Furthermore, data with the probability of P limitation can be observed in four cases (26.7% of the total); and Valle de Bravo Reservoir (V_2) and Cajititlán Lagoon (Ca_1) could be either limited by TN and/or TP. This nitrogen limitation was not found in the CEPIS study of warm-water lakes. They founded that the majority of the tropical lakes/reservoirs were phosphorus limited, as in the classical temperate water bodies. These findings are in accordance to what Ryding and Rast (1989) stated: "it is generally believed that nitrogen is the primary nutrient which limits the maximum algal biomass levels in tropical/subtropical systems…"; "…The available evidence, however, produces a less clear picture of specific nutrient limitation in such systems." Also, a low N:P ratio could be related to various factors: a) The nutrient inputs of treated or untreated waste water discharges and agricultural wastes to the lake are sources of soluble phosphate; b) Tropical and semi-arid lakes and reservoirs are characterized by highly variable seasonal rainfall; and c) the degree of basin human impacts due to changes in soil uses, modifying forested zones into pasture, agriculture or urban ones. This is supported by the issue that both nutrient concentrations in Mexican water bodies were relatively high, surpassing levels that suggest neither nutrient is the algal growth-limiting factor.

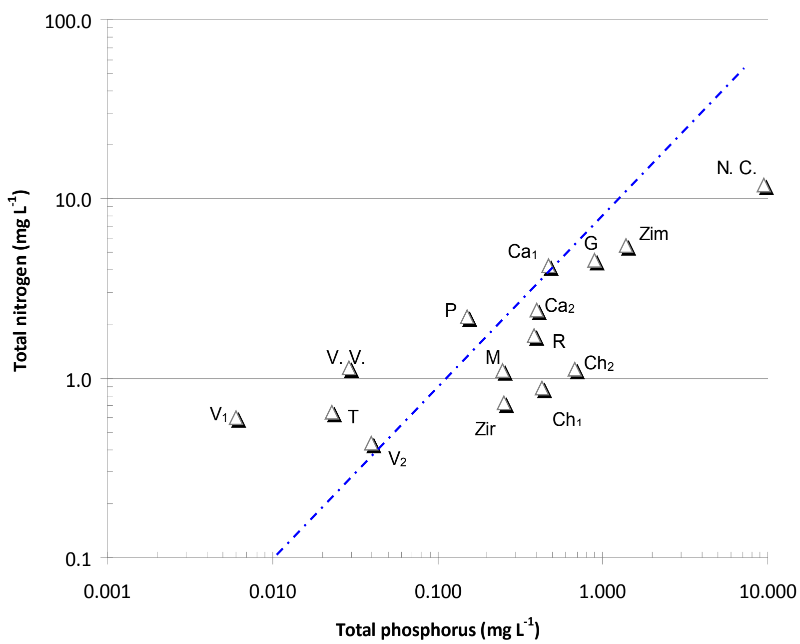

Figure 1. Nutrient limitation for 12 water bodies in Mexico.

Using the nitrogen to phosphorus ratio concept, the majority of the Mexican warm-water tropical lakes and reservoirs were determined to be nitrogen limited, although in various cases another factors, such as light, could be limiting in view of the high observed levels of both TN and TP. Two examples of this possibility are related to light limitation, which is present in Lakes Chapala (Lind *et al*., 1992) and Pátzcuaro (Sánchez-Chávez *et al*., 2008). Both lakes contain a remarkable turbidity caused by sediments constantly kept in suspension by wind-driven forces over the relatively shallow lakes. For Pátzcuaro, the high nutrient concentrations in the lake have led to degradation of water quality, resulting in cyanobacteria blooms, as well as significant floating aquatic macrophytes of water hyacinth, mainly located in an embayment, on the south-eastern zone of the lake.

The trophic state of lakes is the result of complicated multivariable processes (Nürnberg, 1996). Both for lakes and reservoirs, the TN to TP ratio is inversely correlated with the Ac:Al ratio. In Table 2, it is often observed a relationship in the data of: Secchi disk – Chl a – TP – TN, which tend to be maximum – minimum – minimum – minimum for lakes, and tend to be minimum – maximum – maximum – maximum, for reservoirs. This statement is often modified or changed by various factors established by Salas and Martino (1991; equation 16), which include: a) a high external P load, or in the case of shallow lakes, a high internal loading impact on the photic zone; b) a low average depth (a shallow lake has an average depth of about 3-m or less), shallow lakes are often polymictic, and thus, with a high probability of sediment disturbance. In general, it appears that shallow lakes tend to have higher phosphorous concentration than deeper lakes; and c) a high residence time (T_w), lakes tend to have higher residence times than reservoirs. For example, Lakes Pátzcuaro, Chapala, Cajititlán Lagoon, and Nabor Carrillo Reservoir had very low average depth, which could enhance the probability of eutrophication, but also, this shallowness could enhance a high abiotic turbidity, rather than primary productivity (see above). Also, high residence time affects the trophic state of Lakes Pátzcuaro, Chapala, Zirahuén, and Nabor Carrillo and Tequesquitengo Reservoirs, this later impoundment and located in a close basin, had an extreme retention time (T_w = 98.5 yr), thus reflecting an intense sensitivity to P-loadings enrichment.

Based on the data base of Table 2, Figure 2 shows the lake and reservoir results of the Trophic State Index (TSI). Values presented by the TSI, clearly show the eutrophic or hipereutrophic (only few times mesotrophic) state for the majority of the Mexican water bodies. In Figure 2, the data obtained from Lake Chapala to the left part of this plot, the bars show a notable increase in the values of TSI TP, also shown by the low TN:TP ratio which are underlined in Table 2. In the same table, Secchi disk data, except for five exceptions (above 1.84 to 6.50 m), were notably very low; and Chl *a* shows a non very clear picture of the trophic state limit of Eutrophic – Hipereutrophic set by Nürnberg (1996), of 25 µg L^{-1}, this is because, even two mesotrophic water bodies (Lake Tequesquitengo and Villa Victoria Reservoir), have a mean annual Chl *a* above this line (with 26.4 and 54.2 µg L^{-1}, respectively; see also discussion of trophic state limits for water bodies in Bravo-Inclán *et al*, 2008). Nevertheless, experience shows that the TSI of Chl *a* (and also TSI TN) represent a more trustful picture of the trophic state of the lakes/reservoirs found in the central part of Mexico. Carlson (1977) remarked that the TSI derived from Chl *a* is best for estimating algal biomass in most lakes (and reservoirs) and, therefore, that priority should be given for its use as a trophic state indicator. The TSI range found, from 48 to almost 100 TSI units, indicates the remarkable productivity dynamic of the warm tropical Mexican water bodies.

We found inconsistencies of Zirahuén TP annual concentration (250 µg L^{-1}) against the trophic state proposed by Salas and Martino (1991), because other authors like Chacón-Torres and Rosas-Monge (1998) and Arredondo-Figueroa and Aguilar-Díaz (1987) point out that, during the decade of 1980, this lake was oligotrophic. These first authors reported a mean value of TP of 8.7 µg L^{-1}, which is very low, but more congruent with a low trophic state (oligotrophic), and with the average values of 6.50-m of Secchi disk depth and 1.67 µg L^{-1} of Chl *a* (Table 2). Also, it is important to emphasize that TSI derived from Chl *a* in Lake Zirahuén is the lowest value of all (equal to 35.6 TSI units).

The results of the trophic state assessment of tropical lakes are shown in Figure 3. This plot includes the limits which approximately separate oligotrophic mesotrophic state at 0.030 mg L^{-1}, and the mesotrophic-eutrophic state at 0.070 mg L^{-1}. It is important to comment that the simplified methodology malfunctions with lakes that have a prolonged retention time (low flushing time; e.g., Lakes Chapala, Zirahuén and Tequesquitengo).

In Figure 3, Valle de Bravo Reservoir shows a coherent picture, because in the periods of study (from V_1 to V_2), it has changed from mesotrophic to eutrophic. Requena Reservoir is located in the right-upper zone, and it stands as having the lowest residence time of all (Tw = 0.26 yrs). Cajititlán Lagoon studies (Ca_1 and Ca_2), were not included in Figure 3, because they report an extremely high residence time ($Tw \approx \infty$); the same situation applies for Lake Pátzcuaro which is located in a closed (endorheic) basin. Chapala Lake points (Ch_1 and Ch_2), were located in a high position due to the high concentrations of TP; and it shows the same trend as Valle de Bravo Reservoir: as time passes, it changes from mesotrophic to eutrophic. But Ch_1 is located high and separated from the mesotrophic-eutrophic limit. Thornton and Rast (1993) suggested that primary production in turbid lakes and reservoirs is greatly compressed into the upper few centimetres of the surface waters; and also, they cite evidence of enhanced bacterial activity in turbid lakes at the expense of phytoplankton. These observations may explain the discrepancy between the evident trophic state (mesotrophic), and the calculated one (eutrophic). Besides, according to Lind *et al*. (1992) and Ryding and Rast (1989), Lake Chapala also appears to exhibit nitrogen limitation, which could be problematic to deal right, with a P-based trophic model.

Trophic state assessments should also have the consideration of other factors, such as:

- Climatic conditions. The ratio of evaporation *versus* precipitation dictates whether a lake will become more concentrated with time, and also, become more saline and eutrophic. In the central region of Mexico, the mean annual evaporation is generally higher than the precipitation.
- Summer dissolved oxygen depletion in the hypolimnion (related to number of days and extension of the anoxic status).
- Algal blooms frequency; undesirable macrophyte prevalence, such as water hyacinth.
- Warm-water exotic species of fish predominance (e.g. Tilapia and carp).

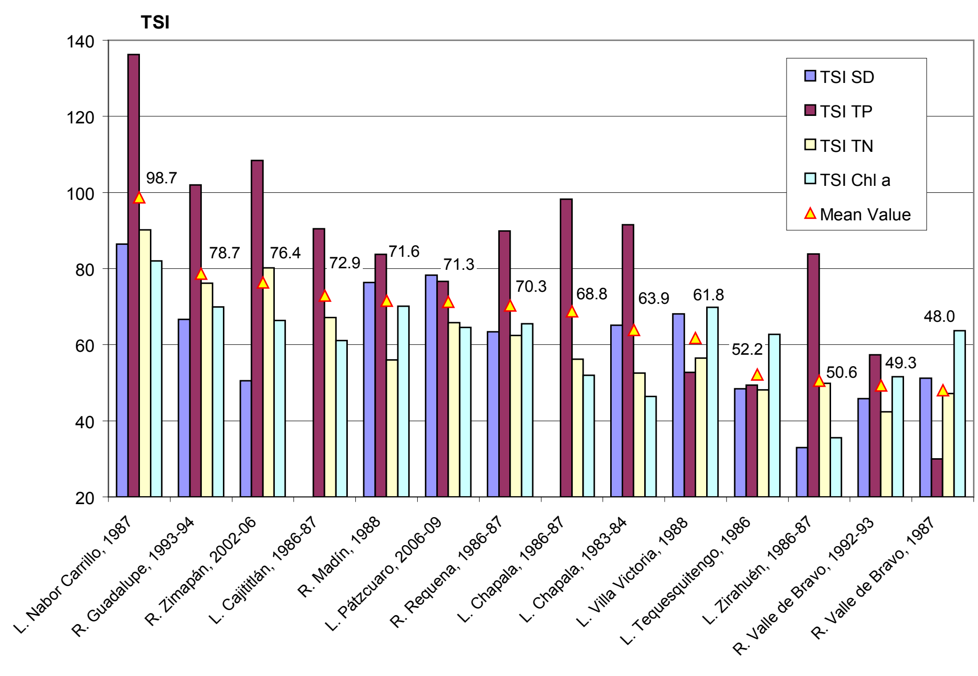

Figure 2. Trophic State Index (TSI) for 12 water bodies in central Mexico. The numbers beside the triangles specify the average TSI values. Cajititlán Lagoon (Ca_1) was not included in the graph, because it lacked data of Chl *a* and Secchi disk.

CONCLUSIONS

The classification of lakes, according to water quality and trophic state, as well as the use of simplified methodologies, are useful for the assessment of eutrophication, and justify its inclusion in the management projects and the setting of future rehabilitation goals.

The lakes and reservoirs of central Mexico are located in a band of 19-23°N, and in the majority of the cases, they are high altitude water bodies (>1,500-m), these characteristics derive in a special climatic semi-arid situation that makes them quite different from typical warm tropical lakes, as well as the temperate ones.

The TN:TP ratio suggests that the water bodies included in this paper are possibly more limited by both nitrogen and/or light, than the classical temperate water bodies concept of the dominance of the phosphorous limitation.

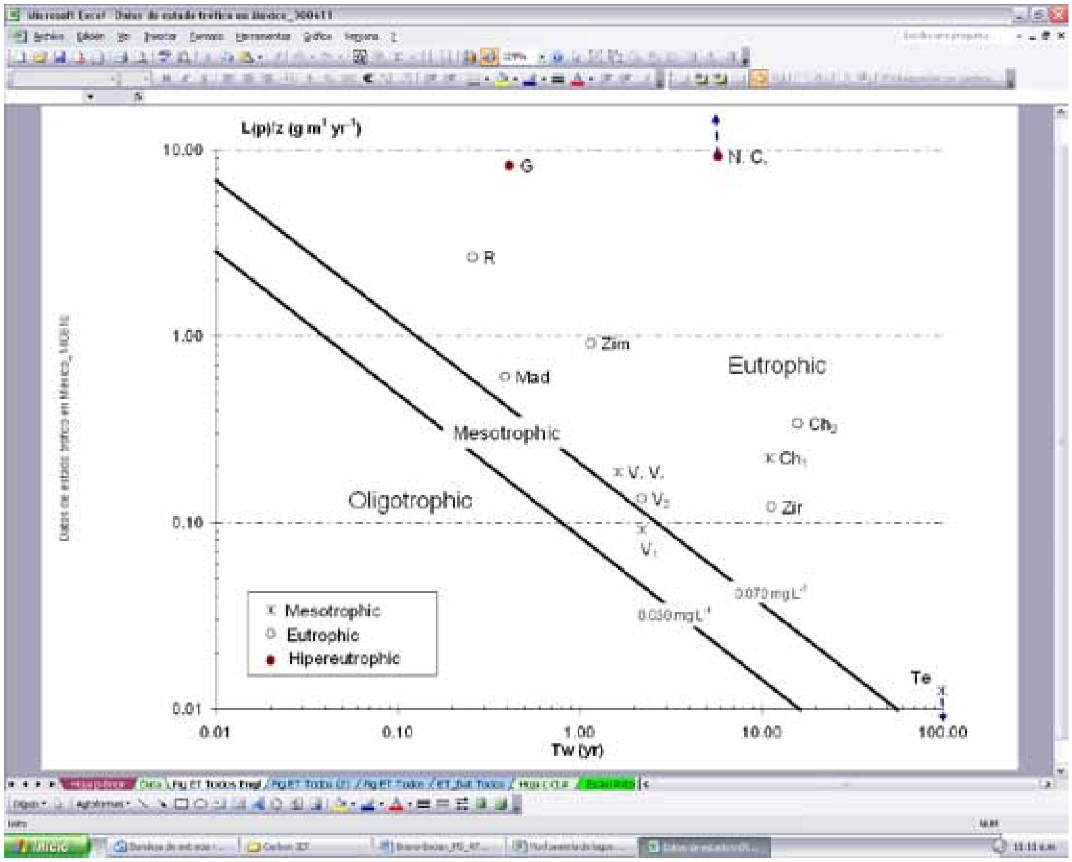

Figure 3. Trophic state classification for 12 water bodies in central Mexico, using the simplified methodology of warm-water tropical lakes (Salas and Martino, 1991). Note that Lake Tequesquitengo (Te) and Nabor Carrillo Reservoir (N.C.) fall out of the plot limits (marked by the arrows).

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Characteristics of Pollution Load in a Polluted Lake Basin Taking into Account Rain-Fall

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Abstract

In this research, we investigated the characteristics of pollution load from a half-sewered semi-urbanized area including the seasonal variation of the water quality and runoff characteristics during rainfall events. The results suggest that the concentrations of particulate and organic forms of nutrients were high during the rice field plowing season and the subsequent temporary drainage (midseason drainage). NH_4^+-N was detected throughout the year, indicating the inflow of untreated or incompletely treated domestic wastewater. From the results of L-Q equations with data including rain fall events, it became clear that nutrient loads tended to runoff in the flood stage more than in the normal stage though the main sources are point sources in this basin, with the calculated ratios of the runoff load in the flood stage to the yearly total pollution loads being 56.1% for T-N and 41.3% for T-P.

Keywords

Pollution load; Half-sewered Area; Nutrient; Seasonal Variation; L-Q Equation; Rain Fall

INTRODUCTION

Lake Aburagafuchi is a small and shallow brackish lake situated in Aichi prefecture in the central area of Japan. The size and location of Lake Aburagafuchi are shown in Table 1 and Figure 1, respectively. It has two inflow rivers, the Osada River and Hamba River, which flow through agricultural and urbanized areas, and two outflow rivers. Figure 2 shows the land use in the basins of the two inflow rivers. Here, “others” in the graph means urban areas. Approximately half of each basin is covered by agricultural areas including rice fields and dry fields, and the other half is covered by urban areas. The Hamba River basin has a little higher percentage of agricultural areas than the Osada River basin. Water quality in Lake Aburagafuchi has deteriorated under the impact of the development of urbanization and the delayed implementation of countermeasures against wastewater in the basin (Council for Promotion of Water Purification in Aburagafuchi, 2010). In this area, the sanitation coverage is 58.0% (Aichi prefecture, 2010).

Many researches about runoff characteristics of nutrients from nonurban areas such as forest area or agricultural area have been performed (Kato et al., 2009, Shinme et al,. 1999, Yamada et al., 1998), but few researches have dealt with urbanized areas (Gunes, 2008). In a river basin where pollution loads consist mainly of domestic and industrial loads and unsatisfactory sewerage systems are provided, it has been unclear how the pollutants from the point sources are transported to the river. In this research, we investigated the characteristics of pollution load from half-sewered semi-urbanized areas including the seasonal change of the water quality and runoff in rainfall events in two inflow rivers in Aburagafuchi basin. In addition, we made L-Q equations with data including rainfall events, yearly total pollution were loads calculated based on the resulting L-Q equations, and the importance of the rainfall events was discussed.

Table 1. Size of Lake Aburagafuchi

Surface Area	Shore length	Average depth	Volume	Basin area	Basin population	Lake type
0.64km^2	6.3km	3m	2.0million m^3	58.3km^2	96,508	Brackish

*Basin population is as of March 2005

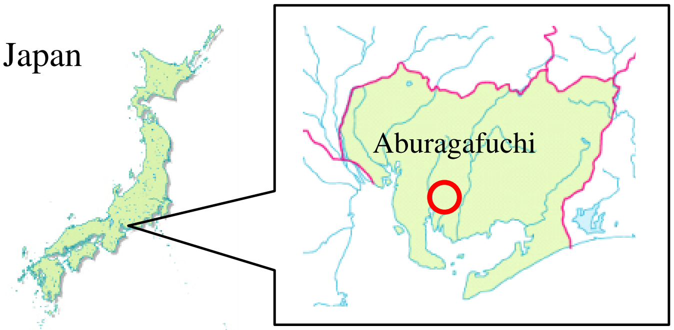

Figure 1. Location of Lake Aburagafuchi

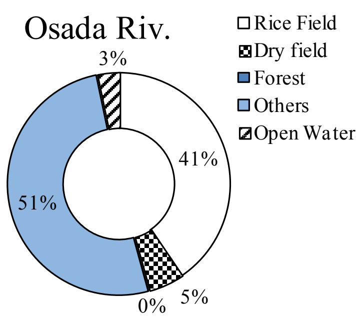

Figure 2. Land Use in Osada River Basin and Hamba River Basin

Figure 3. Sampling Points

METHOD

Water Samplings and Flow Rate Measurement

Figure 3 shows the sampling points. The samples were taken by bucket from the surface. To clarify the seasonal variation of nutrient concentrations, we carried out periodic sampling at 11:00 am every month from May, 2008 to March, 2009, and water flow was calculated based on the H-Q equation proposed by the river management authority and on the water level. Additionally, we carried out water sampling and flow rate measurement in January, March, May, July, September, and November in 2008. In September, we sampled data in the flood stage. The sampling in the flood stage was carried out 12 times in 15 hours. Water samples were filtered with a 1μm pore glass fibre filter and dissolved items were analyzed. We measured the flow rate in the Osada River and Hamba River with an electromagnetic flow meter (ALEC ELECTRONICS AEM1-D).

Water Quality Analysis Items

Concentrations of nitrogen and phosphorus were analyzed with a Bran-Luebbe TRAACS 2000 auto-analyzer to obtain the data representing ammonium nitrogen (NH_4^+-N), nitrite nitrogen (NO_2^--N), nitrate nitrogen (NO_3^--N), dissolved nitrogen (D-N), total nitrogen (T-N), phosphate phosphorus (PO_4^{3-}-P), dissolved phosphorus (D-P), total phosphorus (T-P).

RESULTS AND DISCUSSION

Seasonal Variation of Water Quality

Figure 4 shows seasonal variation of nutrient concentrations obtained by periodic sampling in the Osada River and Hamba River. Figure 5 shows the ratio of discharged nutrient loads calculated from unit load and statistical amount. Particulate phosphorus (PP) and dissolved organic phosphorus (DOP) were calculated by subtracting DP from TP, and by subtracting PO_4^{3-}-P from DP, respectively. Particulate nitrogen (PN) and dissolved organic nitrogen (DON) were calculated by subtracting DN from TN, and by subtracting NH_4^+-N, NO_2^--N, and NO_3^--N from DN, respectively.

As for phosphorus, the ratio of PO_4^{3-}-P to TP was high at both points. In the Osada River, concentration of PO_4^{3-}-P fluctuated wildly. This may be caused by factory-derived water. Since Lake Aburagafuchi basin is located near Toyota city, famous for its automobile industry, it has many automobile parts factories and plating factories which use zinc phosphate or manganese phosphate in surface treatment processes. Concentrations of PP and DOP were almost constant throughout the year in both rivers. However, in May and June, rice field plowing season, concentrations of PP and DOP became high. This was caused by rice field plowing and temporary drainage after plowing. (Ito et al., 2007; JA Aichichuo, 2008; Kondoh et al., 1993). And in March, concentrations of PP and DOP also became high. In this area, some fields have adopted a new farming method called the V-furrow No-Till Direct Seeding of Rice (Aichi Agricultural Research Center, 2003, Ito et al., 2008). In 2002, about 500 ha of 31200 ha rice field areas were cultivated by the method throughout Aichi prefecture (Aichi prefecture, 2007; Hamada, 2004). Although rice field plowing is usually carried out in late April to May in Japan, with this method, it is carried out in November to March. And in this area, it is carried out in March.

As for nitrogen, the ratio of NO_3^--N to T-N was high in both rivers. In the summer, concentration of nitrogen was low, as a result of the increase of water flow for irrigation. In this area, there is a large-scale irrigation network called the Meiji Irrigation Canal from Yahagi River (Meiji irrigation Land Improvement District, 2010). Characteristically, NH_4^+-N was detected throughout the year. Although the concentration of NH_4^+-N was lower in the summer, its load did not fluctuate very much. This means the source is a constant load point source such as untreated domestic wastewater, though the factory load occupies a large part in Figure 5 which was calculated from the goods productions amount and unit load. Concentrations of PN and DON were high in May and June, also as a result of rice field plowing and drainage.

So it can be said that concentrations of nutrient in this area are influenced constantly by domestic wastewater, seasonally by agriculture and additionally to a great extent by factories.

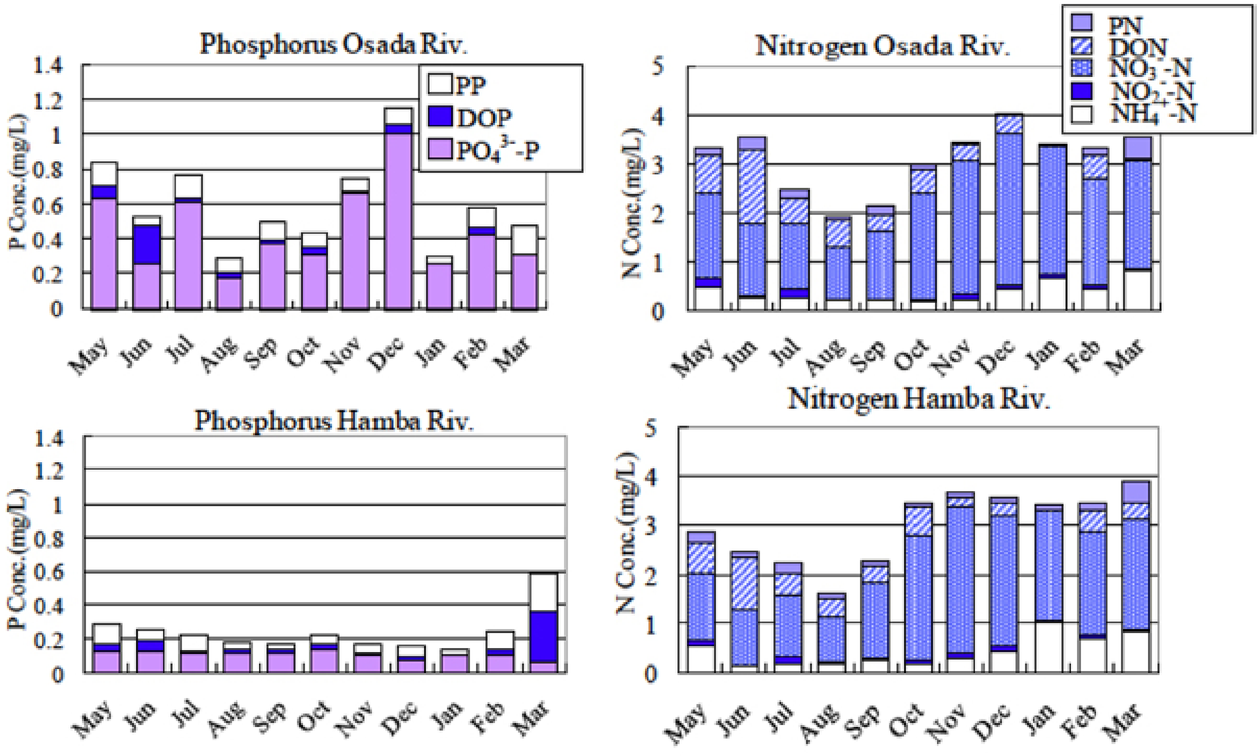

Figure 4. Nutrient Concentrations in Inflow Rivers

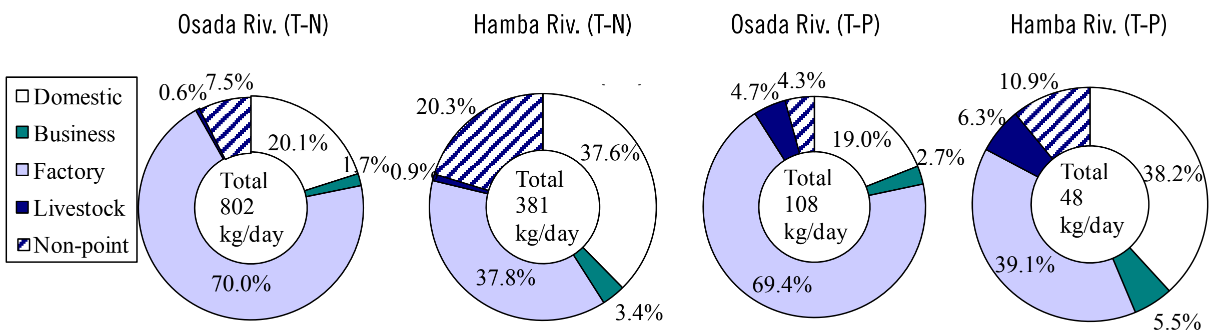

Figure 5. Sources of Discharged Nutrient Loads

L-Q Equation

To clarify the characteristics of nutrient loads from the Osada River basin and Hamba River basin, we used the L-Q equation. The following is the L-Q equation.

$L=c*Q^n$

L: Nutrient load (kg/day)

Q: Flow rate (m^3/day)

c, n: Constant value

The value of n indicates the effect of flow rate on nutrient load, and it is the parameter of runoff characteristics (Yamada et al., 1998).

n>1: runoff type, nutrient load increases greatly with the increase of the flow rate.

n=1: constant concentration type, concentration of nutrient is kept constant with the increase of the flow rate.

n<1: dilution type, nutrient in the water is diluted with the increase of the flow rate.

Figure 6 shows L-Q equations for the normal stage and flood stage. The normal stage and flood stage were separated by the 95th largest daily average flow in a year (Nakatsugawa et al., 2005). As for T-N, the load increased mildly with the increase of water flow in the normal stage in both the Osada River and Hamba River. But in the flood stage, n approached 1 or the load increased in proportion to the increase of flow rate. As for T-P, in the Osada River, the load showed a trend similar to that of T-N, while in Hamba River the load increased in proportion to the increase of the flow rate in both the normal and flood stage. The results show that although the main source of nutrient load is point sources in the Aburagafuchi basin, nutrient loads showed significant increase in the flood stage, which might be caused by the accumulated nutrients in ditches and rivers during the normal stage. In addition, the ratio of nutrient loads to the flow rate is high in the rice plowing season.

Yearly Total Nutrient Loads in the Normal Stage and Flood Stage

Yearly total nutrient loads divided by the normal stage and flood stage were calculated based on the resulting L-Q equations and daily average water flow, which is shown in Table 2. As for T-P, the load was 18.5 tons/year in the normal stage, while 13.0 tons/year in the flood stage. As for T-N, the load was 96.4 tons/year in the normal stage, while 123.2 tons/year in the flood stage. Therefore, 41.3 % of yearly total pollution load of T-P is runoff in the flood stage, and 56.1 % of yearly total pollution load of T-N is runoff in the flood stage. So it can be said that total number of days is only 95 days, but a large amount of pollutants are discharged.

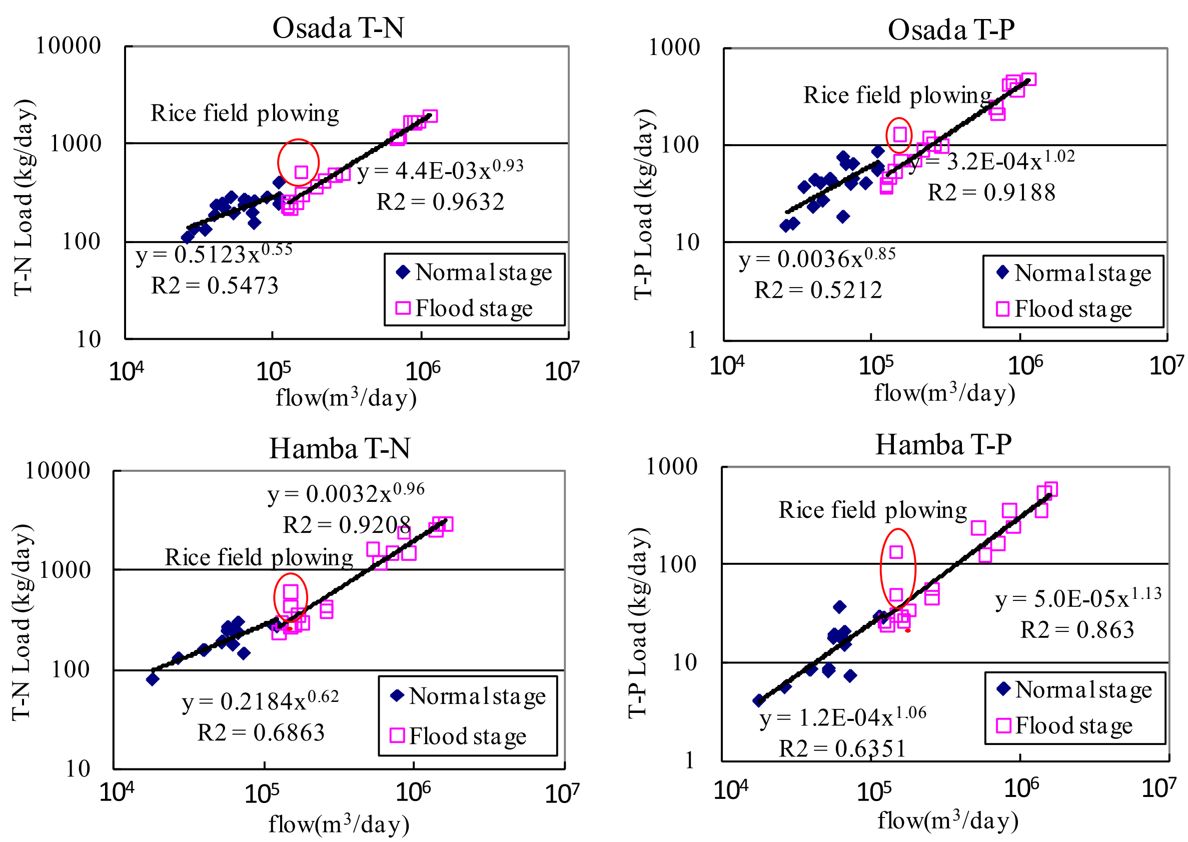

Figure 6. L-Q Equation of Nutrients

Table 2. Nutrient Loads in the Normal Stage and Flood Stage

tons/year	T-N	T-P	Number of days
Normal stage (**Normal/Total ratio**)	96.4 (43.9%)	18.5 (58.7%)	270 (74%)
Flood stage (**Flood/Total ratio**)	123.2 (56.1%)	13.0 (41.3%)	95 (26%)
Total	219.6	31.5	365

CONCLUSION

This research was a survey carried out to clarify the characteristics of pollution load from half-sewered semi-urbanized areas. The results of the periodic sampling suggested that concentration of PO_4^{3-}-P was high and fluctuated wildly in the Osada River, and concentration of suspended and organic forms of nutrients became high in the rice field plowing season in both of the inflow rivers. The existence and constant load of NH_4^+-N indicated pollution by domestic wastewater. It became clear that concentrations of nutrients in this area are influenced constantly by domestic wastewater agriculture and factories.

The calculation of yearly total pollution loads clarified that 56.1% of T-N and 41.3% of T-P is runoff in the flood stage, which might be caused by the accumulated nutrients in ditches and rivers during the normal stage.

ACKNOWLEDGMENT

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Groundwater Exchanges of Pollutant Loads (Macro- and Micropollutants) To Surface Waters: A Source Apportionment Study

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Abstract

The EU Water Framework Directive (WFD EC60/2000) requires that quality-flow compliance at a particular surface-water reach entail consideration of all upstream inputs, including contaminated land and groundwater contributions. Besides European Union, many other governments are now stimulating a more integrated approach to managing the soil-groundwater-surface water system. The interactions between groundwater and surface water are complex. Surface-waters and groundwaters are, in fact, linked components of a hydrologic continuum. During rainfall events surface runoff phoenomena, at the net of the plant uptake or soil retention, may concentrate pollutats in the aquifers. A fraction of these loads through sub-surface runoff pathways may reach the surface waters after a certain time lag. Very rarely such sub-surface pollution can be directly correlated to a specific source. Multivariate statistical techniques may improve our understanding of these sub-surface runoff phoenomena. Aim of this study was to analyze the source apportionment and the groundwater contribution to the total pollutant load of Mella river, located in the Northern Italy and characterized by a groundwater discharge area. Factor Analysis (FA) was applied to a series of water quality measurements at three monitoring sites: respectively located upstream, in the middle and downstream the groudwater discharge area of the Mella river basin. FA results in the upstream sites were different from the other two stations that were influenced by the groundwater discharge contribution. In the upstream site, in fact, the major pollutant source (i.e. about 45% of the total variance) resulted to be the contribution of the Gobbia tributary which collects the industrial loads of the Val Trompia metallurgic consortium. On the other hand the groundwater was found to be the most significant pollutant source (i.e. > 25% of the total variance) in the other two sites. FA proved also useful to distinguish between sources of metals and tetrachloroethylene.

Keywords

Diffuse loads; groundwater interactions with surface waters; source apportionment; macro- and micropollutants.

INTRODUCTION

The European Water Framework Directive (WFD: 2000/60/CE) defines a new logic in surface- and ground- water quality management for the European Union, promoting a river basin-approach rather than a local scale approach. Besides European Union, many other governments are now stimulating a more integrated approach to mitigate and managing pollution at watershed scale. This is the reason why the analysis of water quality requires today more complex investigations and the identification of all the emission sources affecting water quality at catchment levels. The monitoring and quantification of point and non point sources contributions to the global pollutant load is therefore a key issues for the implementation of management strategies. Diffuse loads may be significant either in wet-weather conditions (i.e. pollutants transported by surface runoff) or in dry-weather conditions (i.e. pollutants trasnported by subsurface runoff or due to the groundwater exchanges with surface waters). In this respect, the understanding of the interactions between surface waters and groundwaters (SW-GW) may be the basis for effective water resource management (Sophocleous, 2002). To fully understand the SW_GW interactions, a sound and robust monitoring of surface- and groundwater quality data is required. Instream measurements, that are very often instantaneous, can provide information about the total load amount in a specific watershed, but do not provide insights about the source apportionment of pollutants. Therefore, the monitoring data need to be integrated with other investigative tools, such as mathematical models or statistical techniques. However, up to now only few experiences are reported concerning the source apportionment of micropollutants (e.g. Simeonov et al., 2003, Pekey et al., 2004, Gevaert et al., 2009, Ki et al., 2009, Chon et al., 2010), most of the available literature concerning the monitoring either at the emission source (Chon et al, 2010) or in water bodies (JRC 2006) of these substances. On the other side, many conceptual models have been developed for the SW-GW system (Cho et al, 2010, Schilling et al., 2007, Ebel et al., 2009, Martin et al., 2004, Sulis et al., 2010). Nevertheless, the effect of the SW-GW interactions on surface water quality is hard to quantify. Multivariate statistical techniques (e.g. Factor Analysis) may help for the understanding of the GW-SW interactions at watershed scale (Menció and Mas-Pla, 2008, Azzellino et al., 2008). Aim of this study was to apply Factor Analysis (hereinafter FA) to series of water quality measurements collected at three monitoring sites, located within the Mella river watershed (Figure 1), in order to assess the source apportionment of different macro- and micropollutants.

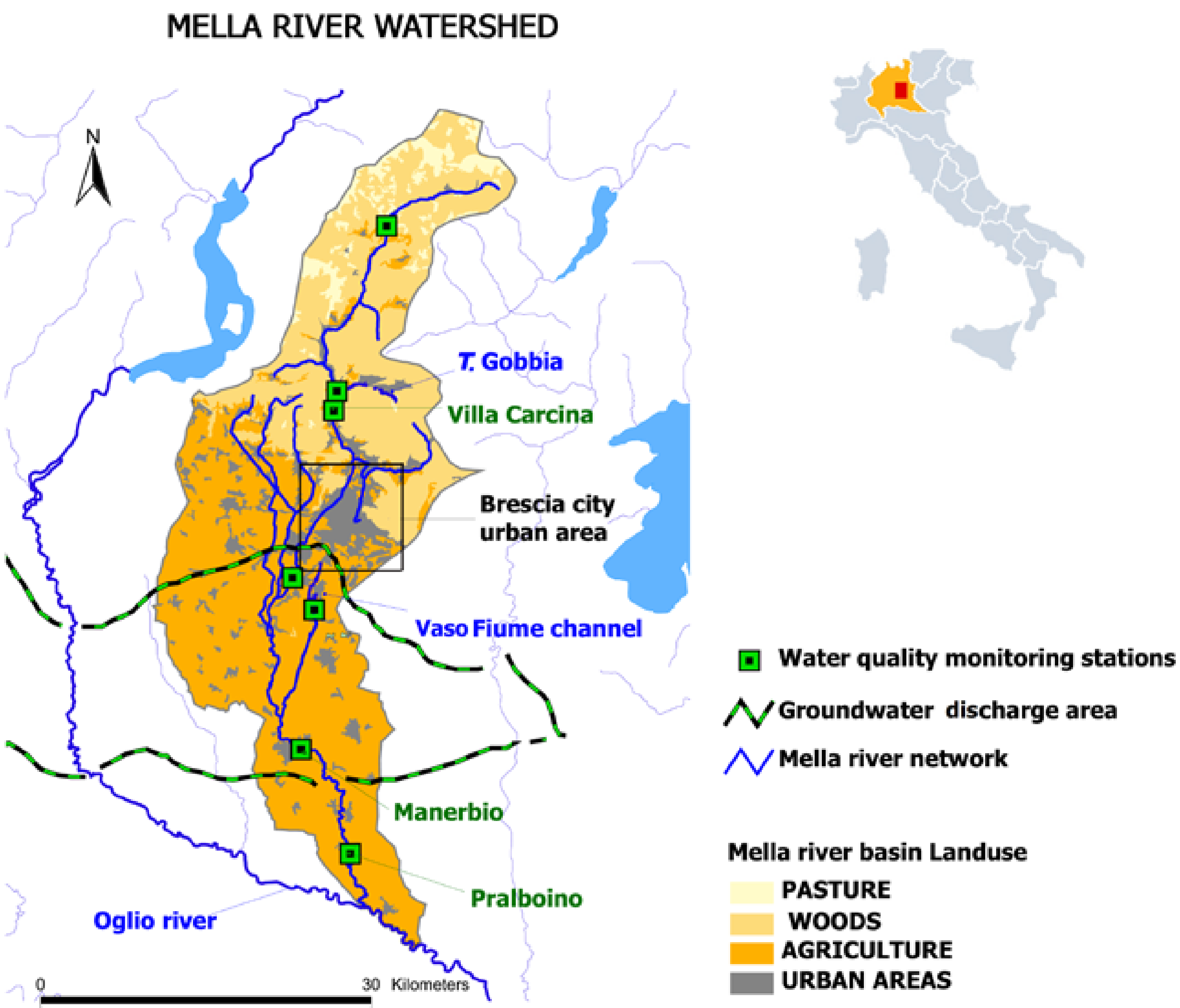

Figure 1. Mella river watershed study area. The water quality monitoring stations and the groundwater discharge area are shown.

MATERIALS AND METHODS

Study Area

The Mella river watershed is a basin of 1022 km^2 located in Northern Italy. The catchment is characterised in the upland portion by streams with relatively steep slopes and deep-incised channels, flowing across a largely forested region with some agricultural areas. On the contrary in the lowland region the Mella river passes through an urban area (Brescia city, about 200,000 inhabitants) and, downstream, through a very productive agricultural region (see Figure 1) characterised by the groundwater discharge area. At the basin closure, the Mella river mean flowrate is of about 30-40 m^{3}s^{-1}.

Input Data

Factor Analysis was applied to the instream measurements of several water quality parameters, analysed both during dry and wet weather conditions (see Table 1).

All the measurements came from to the monthly monitoring activity, conducted by ARPA, the Italian Regional Environmental Protection Agency, during the biennial 2003-2004 at 3 sampling stations within the Mella river watershed: *Villa Carcina*, located in the upland region at about 33 km from the headwater, *Manerbio* located at about 70 km from the headwater in the watershed portion where the water table is at surface and constitutes a groundwater discharge point, and *Pralboino* located at 87 km from the headwater and at few km to the river confluence into the Oglio river.

Table 1. Summary statistics of the water quality measurements available for the three monitoring stations.

	Mean	Std. Deviation	Median	Minimum	Maximum	N
Temperature	13.23	6.06	12.45	.80	26.30	60
pH	7.40	.40	7.24	6.74	8.60	59
Dissolved Oxygen (mg l^{-1})	9.68	1.71	9.50	5.50	13.70	60
Conductivity (μS cm^{-1})	574.45	169.66	581.00	268.00	882.00	60
Hardness (mg l^{-1})	280.85	75.72	282.74	147.00	437.03	60
Suspended material (mg l^{-1})	19.49	41.60	8.52	.90	282.00	60
BOD (mg l^{-1})	3.93	3.44	2.90	.00	18.90	57
COD (mg l^{-1})	16.80	33.66	10.85	2.50	265.00	60
Echerichia coli (l^{-1})	91608	67981	91780	88	161000	60
N-NH4 (mg l^{-1})	.67	.78	.51	.00	4.90	60
N-NO3 (mg l^{-1})	4.48	2.61	4.84	.79	8.92	60
Total phosphorus (mg l^{-1})	.53	.61	.30	.01	2.80	60
Orthophosphate (mg l^{-1})	.15	.13	.11	.00	.56	60
Total Nitrogen (mg l^{-1})	5.28	2.45	5.93	1.39	9.51	60
Cl^- (mg l^{-1})	28.35	15.43	31.90	.49	53.30	60
SO_4^{-2} (mg l^{-1})	47.39	13.51	50.85	20.70	71.00	60
Tetrachloroethylene (μg l^{-1})	.75	.95	.49	.00	6.00	60
Fe (μg l^{-1})	143.40	139.93	90.50	.00	548.00	54
Cu (μg l^{-1})	38.90	172.56	8.00	2.38	1336.00	60
Zn (μg l^{-1})	106.58	473.79	33.00	2.56	3687.00	60
Total Cr (μg l^{-1})	21.20	71.52	4.90	.00	466.00	60
Pb (μg l^{-1})	10.92	25.01	4.90	.00	134.60	60
Ni (μg l^{-1})	15.39	12.35	15.39	.00	82.35	60

Statistical Analysis

Factor Analysis (FA) was performed on the correlation matrix of the measurements (according to Afifi and Clark, 1996). All the statistical computation were made using the statistical package SPSS 15.0. Factor Analysis was obtained through a preliminary Principal Component Analysis (PCA) which extracted the eigenvalues and eigenvectors from the covariance matrix of the original variances. Factor analysis was chosen to reduce the contribution of the less significant parameters within each component, by extracting a new set of varifactors through rotating the axes defined by the PCA extraction. The Varimax rotation criterion was used to rotate the PCA axes allowing to maintain the axes orthogonality. The number of factors to be retained was chosen on the basis of the "eigenvalue higher than 1" criterion (i.e. all the factors that explained less than the variance of one of the original variables were discarded). That allowed to select few factors able to describe the whole data set with minimum loss of original information.

RESULTS AND DISCUSSION

Factor Analysis was applied to the three data subset. The extractions of varifactors is summarized in Table 2. As it can be observed, although with different number of varifactors the three FA explained approximately the same amount of variance.

By looking at the factor loadings matrix (i.e. the list of the correlation coefficients of the original variables with the extracted varifactors see Tables 3 to 5) it is possible to identify the most meaningful parameters within each component. Parameters that lie on the same component are reasonably believed to share the same origin.

Table 2. Summary of the FA extraction from the three data subset

Monitoring station	Number of varifactors	Total explained variance	Sample size
Villa Carcina	5	87.3 %	20
Manerbio	7	86.5 %	20
Pralboino	6	86.3 %	20

Villa Carcina FA

As shown in Table 3 the first varifactor for the *Villa Carcina* subset is able alone to explain about 45% of the total variance and is strongly correlated to pollutants typical of urban raw wastewaters (i.e. BOD, COD, N-NH4, Suspended materials) and to the metals Fe, Cu, Zn, Cr and more weakly to Pb. The *Villa Carcina* monitoring station is in fact strongly influenced by the confluence of the Gobbia tributary which carries the pollutant load of the Val Trompia area, characterized by several raw civil wastewater discharges and by the pollutant load of one of the major metallurgic consortium of industries in Northern Italy. In this respect it is worthwhile to mention even a weapon production activity that dates back to the 16th century. With such a dominant source of pollution is also interesting is to observe the second and the third varifactors which are respectively loaded by temperature, dissolved oxygen, P-PO_4 and tetrachloroethylene, and by hardness, sulphates, Pb and Ni. Also to be remarked are the relationships of temperature with dissolved oxygen ($r: -0.793$, $P < 0.001$) and with tetrachloroethylene ($r: 0.523$, $P < 0.05$) concerning the second varifactor and the relationship between Pb and Ni ($r: 0.759$, $P < 0.05$) concerning the third varifactor. The fourth varifactor is loaded by pH, total phosphorus and N-NO_3. The fifth varifactor accounts for a 5% of the total variance and is not significantly loaded by any specific pollutant.

Table 3. Factor loadings matrix of the *Villa Carcina* subset. The highest factor loadings are shown in bold.

	1	2	3	4	5
Temperature	0.320	**0.647**	0.271	0.481	-0.178
pH	-0.370	0.033	0.064	**0.829**	0.142
Dissolved Oxygen (mg l^{-1})	-0.473	**0.627**	-0.145	-0.040	0.460
Conductivity (μS cm^{-1})	**0.628**	0.560	0.401	-0.097	0.101
Hardness (mg l^{-1})	0.115	0.571	**0.683**	0.261	0.162
Suspended material (mg l^{-1})	**0.935**	-0.260	-0.114	0.122	0.080
BOD (mg l^{-1})	**0.930**	0.011	-0.184	-0.145	0.045
COD (mg l^{-1})	**0.924**	-0.240	-0.102	0.122	0.139
Echerichia coli (l^{-1})	-0.434	0.440	-0.393	0.143	-0.324
N-NH4 (mg l^{-1})	**0.944**	-0.020	0.029	-0.151	-0.137
N-NO3 (mg l^{-1})	-0.411	-0.132	-0.298	**0.595**	0.205
Total phosphorus (mg l^{-1})	0.511	0.055	-0.022	**0.793**	0.051
Orthophosphate (mg l^{-1})	0.143	**0.579**	0.049	-0.276	-0.275
Total Nitrogen (mg l^{-1})	**0.927**	0.184	-0.006	0.079	-0.149
Cl^- (mg l^{-1})	**0.750**	0.525	-0.129	-0.154	0.182
SO_4^{-2} (mg l^{-1})	-0.046	-0.288	**0.620**	-0.431	0.516
Tetrachloroethylene (μg l^{-1})	0.162	**0.886**	-0.143	-0.186	0.144
Fe (μg l^{-1})	**0.853**	0.152	-0.274	-0.054	-0.114
Cu (μg l^{-1})	0.944	-0.201	-0.119	0.110	0.115
Zn (μg l^{-1})	**0.934**	-0.252	-0.125	0.112	0.096
Total Cr (μg l^{-1})	**0.947**	-0.153	-0.084	0.115	0.112
Pb (μg l^{-1})	**0.563**	-0.207	**0.692**	-0.060	-0.250
Ni (μg l^{-1})	-0.114	-0.177	**0.879**	0.256	-0.182
Eigenvalue	**9.488**	**3.615**	**2.624**	**2.439**	**1.913**
% of Variance	**44.2**	**15.4**	**12.2**	**10.9**	**4.6**
Cumulative % of Variance	**44.2**	**59.6**	**71.8**	**82.7**	**87.3**

Manerbio FA

As shown in Table 4 the first varifactor for the *Manerbio* subset explains a little less than 30% of the total variance and is strongly correlated to pollutants which suggest a strong link with groundwater (i.e. conductivity, nitrates, sulphates and chlorides). In this respect it should be reminded that at *Manerbio* site, the water table is at surface so this monitoring station is right in the middle of the groudwater discharge area. The second varifactor explains the 12% of the total variance and it accounts for the direct relationships between COD and total phosphorus (r: 0.624, $P < 0.01$) and the inverse correlations of COD and phosphorus with Cr (respectively r: -0.445, $P < 0.05$; r: -0.458, $P < 0.05$). The third and the fourth varifactors explain comparable fractions of variance and separate $P\text{-}PO_4$, Pb and E.coli from Cu and Ni which are themself strongly correlated to each other (r: 0.747; $P < 0.05$). From the fifth to the seventh varifactor, the explained variance significantly decreases. However, these varifactors outline the fact that Zn, tetrachloroethylene and dissolved oxygen as not correlated to the other pollutants. Concerning oxygen it should be remarked also that at Manerbio site it accounts for only the 6.9% of the total variance.

Pralboino FA

The first varifactor concerning the *Pralboino* subset explains the 26% of the total variance (see Table 5) and it appears similar to the first varifactor extracted for the *Manerbio* subset, even though the pollutants that can be associated with groundwater (e.g. conductivity, nitrates, sulphates and chlorides) are in this case also inversely correlated with dissolved oxygen and total phosphorus.

Table 4. Factor loadings matrix of them *Manerbio* subset. The highest factor loadings are shown in bold.

	1	2	3	4	5	6	7
Temperature	**0.504**	0.410	-0.076	-0.263	-0.296	0.459	0.225
PH	**-0.696**	0.428	-0.284	0.117	-0.241	-0.150	-0.036
Dissolved Oxygen (mg l^{-1})	-0.133	-0.077	0.157	0.044	-0.025	-0.082	**0.927**
Conductivity ($\mu S\ cm^{-1}$)	**0.829**	-0.108	-0.083	-0.120	0.063	0.445	0.058
Hardness (mg l^{-1})	**0.611**	0.183	0.307	-0.187	0.373	0.156	-0.250
Suspended material (mg l^{-1})	-0.465	-0.039	0.162	-0.270	**-0.769**	-0.103	0.030
BOD (mg l^{-1})	-0.365	0.000	0.568	-0.348	-0.220	0.200	-0.424
COD (mg l^{-1})	-0.107	**0.807**	0.016	-0.292	0.060	-0.205	-0.177
Echerichia coli (l^{-1})	0.006	0.263	**-0.722**	0.249	0.008	-0.047	-0.303
N-NH4 (mg l^{-1})	-0.247	-0.417	-0.016	**0.547**	0.413	0.174	0.013
N-NO3 (mg l^{-1})	**0.939**	-0.019	-0.217	-0.123	-0.096	-0.084	-0.135
Total phosphorus (mg l^{-1})	-0.417	**0.866**	-0.059	0.016	-0.032	-0.037	0.066
Orthophosphate (mg l^{-1})	0.141	-0.139	**0.649**	0.212	0.480	0.289	0.143
Total Nitrogen (mg l^{-1})	**0.947**	-0.075	-0.210	0.024	-0.055	-0.027	-0.120
Cl^- (mg l^{-1})	**0.948**	-0.036	0.046	-0.053	-0.138	0.205	0.101
SO_4^{-2} (mg l^{-1})	**0.947**	-0.094	-0.085	0.050	0.057	0.004	-0.037
Tetrachloroethylene ($\mu g\ l^{-1}$)	0.273	-0.165	0.099	-0.117	0.113	**0.839**	-0.300
Fe ($\mu g\ l^{-1}$)	-0.028	-0.314	0.498	0.007	0.178	0.502	0.227
Cu ($\mu g\ l^{-1}$)	0.003	-0.184	-0.052	**0.910**	-0.057	-0.155	-0.091
Zn ($\mu g\ l^{-1}$)	-0.250	-0.173	0.291	0.072	**0.787**	0.002	-0.005
Total Cr ($\mu g\ l^{-1}$)	-0.160	**-0.689**	0.498	-0.076	0.326	-0.031	0.035
Pb ($\mu g\ l^{-1}$)	0.247	-0.157	**-0.736**	-0.397	-0.084	0.128	0.103
Ni ($\mu g\ l^{-1}$)	-0.161	0.093	0.118	**0.824**	0.351	-0.028	0.272
Eigenvalue	**6.258**	**2.781**	**2.757**	**2.531**	**2.272**	**1.721**	**1.585**
% of Variance	**27.2**	**12.1**	**12.0**	**11.0**	**9.9**	**7.5**	**6.9**
Cumulative % of Variance	**27.2**	**39.3**	**51.3**	**62.3**	**72.2**	**79.7**	**86.5**

On the other hand, the second, the third and the fourth varifactor explain approximately the same amount of variance (ca. 14%) but they do not exactly correspond to the *Manerbio* varifactors. In particular, the second varifactor in this case accounts for the inverse relationship of Cr and Ni with phosphorus and is weakly loaded also by COD and tetrachloroethylene. The third varifactor is loaded by pollutants associated with the presence of raw civil wastewaters (i.e. COD, BOD, $N\text{-}NH_4$, $P\text{-}PO_4$) and is inversely loaded by Pb. The fourth varifactor is loaded by Fe, Cu and Zn. The fifth varifactor outlines the inverse relationship of E.coli and tetrachloroethylene (r: -0.522, $P < 0.05$) and explains the 9% of the total variance whereas the sixth varifactor is strongly correlated with pH and hardness and it explains little less than 8% of the total variance.

CONCLUSIONS

Factor analysis applied as a tool for studying the pollution source apportionment in the Mella river was proven useful to distinguish between anthropogenic and geogenic sources.

The FA results for the three monitoring stations outlined the effect of the highly dominant pollution source of the Gobbia tributary for the *Villa Carcina* site and the effect of the groundwater discharge area for the other two sites. *Manerbio* and *Pralboino* FA reust confirm that groundwater is a significant source of N-NO_3 for Mella river although it does not appear to be a source for other pollutants. On the other hand, heavy metals were found to behave differently in the three sites. Fe, Cu, Zn, Cr and Pb and Pb and Ni respectively showing high factor loadings in the first and in third varifactor, were highly clustered in the *Villa Carcina* site, suggesting that in this area they are probably discharged from few and distinct sources. On the contrary, with the exception of Cu and Ni, all the metals were found uncorrelated at the *Manerbio* site suggesting a relative absence of common sources. In addition the differential binding behaviour in sediments of these metals may be a possible explanation of the observed lack of correlations. At *Pralboino* site Fe, Cu and Zn were correlated again as Cr and Ni suggesting again the presence of common sources. Concerning tetrachloroethylene it is worthwhile to remark that if at *Villa Carcina* site its variability was found correlated to that of the dominant source of pollution (i.e. the first varifactor), its behavior on the other hand was found almost uncorrelated to the pattern of all the other pollutants at the other two sites, suggesting a different source for such a pollutant. The presence of contaminated land sites in the Mella river basin may suggest these sites as a potential source of tetrachloroethylene.

Table 5. Factor loadings matrix of them *Pralboino* subset. The highest factor loadings are shown in bold.

	1	2	3	4	5	6
Temperature	0.479	-0.163	-0.232	**-0.530**	-0.046	-0.503
PH	-0.285	-0.292	-0.020	-0.121	-0.328	**0.760**
Dissolved Oxygen (mg l^{-1})	**-0.649**	0.386	-0.313	0.296	0.176	-0.328
Conductivity (μS cm^{-1})	**0.902**	0.196	0.014	-0.240	0.091	-0.024
Hardness (mg l^{-1})	**0.572**	0.241	-0.166	-0.119	0.356	**0.581**
Suspended material (mg l^{-1})	-0.508	**-0.779**	0.019	0.084	0.122	-0.155
BOD (mg l^{-1})	-0.075	-0.042	**0.762**	0.366	-0.085	-0.117
COD (mg l^{-1})	-0.102	**-0.571**	**0.598**	0.078	-0.185	-0.014
Echerichia coli (l^{-1})	0.067	-0.129	0.272	-0.066	**-0.804**	0.143
N-NH4 (mg l^{-1})	0.257	-0.127	**0.803**	0.337	-0.257	0.117
N-NO3 (mg l^{-1})	**0.929**	0.004	-0.140	0.174	-0.105	0.097
Total phosphorus (mg l^{-1})	**-0.611**	**-0.633**	0.192	-0.086	-0.043	0.171
Orthophosphate (mg l^{-1})	0.246	0.076	**0.648**	0.551	0.272	0.293
Total Nitrogen (mg l^{-1})	**0.923**	-0.040	0.089	0.240	-0.159	0.091
Cl^- (mg l^{-1})	**0.912**	0.038	0.216	0.037	0.204	-0.176
SO_4^{-2} (mg l^{-1})	0.880	0.171	-0.074	-0.019	-0.021	-0.328
Tetrachloroethylene (μg l^{-1})	-0.003	**0.552**	0.030	-0.068	**0.695**	0.115
Fe (μg l^{-1})	0.113	0.217	0.063	**0.600**	0.467	-0.194
Cu (μg l^{-1})	-0.053	-0.042	-0.026	**0.937**	0.068	-0.076
Zn (μg l^{-1})	0.102	0.103	0.336	**0.839**	-0.199	0.003
Total Cr (μg l^{-1})	0.001	**0.820**	-0.031	0.087	0.245	-0.053
Pb (μg l^{-1})	0.097	-0.106	**-0.897**	0.224	0.001	0.043
Ni (μg l^{-1})	-0.206	**0.763**	0.197	0.300	0.334	-0.260
Eigenvalue	**6.049**	**3.393**	**3.335**	**3.214**	**2.116**	**1.748**
% of Variance	**26.3**	**14.8**	**14.5**	**14.0**	**9.2**	**7.6**
Cumulative % of Variance	**26.3**	**41.1**	**55.6**	**69.5**	**78.7**	**86.3**

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Impact of critical source area (CSA) on AnnAGNPS simulation

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Abstract

The objective of this paper is to study the impact of critical source area (CSA) within an Annualized AGricultural Non-Point Source pollution models (AnnAGNPS) simulation at medium- large watershed scale. The impact of CSA on terrain attributes is examined by comparing six sets of CSA (0.5, 1, 2, 4, 6, and 8 km2). The accuracy of AnnAGNPS stimulation on runoff, sediment and nutrient loads on these sets of CSA is further suggested in this paper. The results are as followed: (1) CSA has little effect on watershed area, and terrain altitude. The number of cell and reach decreases with the increase of CSA in power function regression curve. (2) The variation of CSA will lead to the uncertainty of average slope which increase the generalization of land characteristics. At the CSA range of 0.5 km2 to 1 km2, there is little impact of CSA on slope. (3) Runoff amount does not vary so much with the variation of CSA whereas soil erosion and Total Nitrogen (TN) load change prominently. An increase of sediment yield is observed firstly then a decrease following later. There is evident decrease of TN load, especially when CSA is bigger than 6 km2. Total Phosphorus (TP) load has little variation with the change of CSA. Results for Dage watershed show that CSA of 1 km2 is desired to avoid large underestimates of loads. Increasing the CSA beyond this threshold will affect the computed runoff flux but generate prediction errors for nitrogen yields. So the appropriate CSA will control error and make simulation at acceptable level.

Keywords

Critical source area (CSA); terrain attributes; AnnAGNPS simulation; non-point source pollution loading

INTRODUCTION

Non-point source pollution is complex and occurs on the land surface. Prominent discrepancies in model simulation can occur with scale change of watershed subdivision in models (Vieux and Needham, 1993; Bloschl and Sivapalan, 1995; Arnold *et al.*, 1998; Ahmadzadeh and Petrou, 2001; Chen *et al.*, 2006). In the AnnAGNPS model, a cell is the basic unit for watershed runoff and pollutant load calculation. The discretization of watershed network is determined by the critical source area (CSA) and minimum source channel length (MSCL). In general, the critical source area (CSA) is defined as the minimum catchment area required by a channel for permanent exist where is considered as the source area of rivers (Beven *et al.*, 1979; Quinn P, *et al.* 1991; Brannan *et al.*, 1998). The critical source area (CSA) is commonly presumed as constant when extracting stream network by using Digital Elevation Model (DEM). It has been recognized that discretization scale significantly affects watershed model results, with respect to both hydrology and water quality (Brown *et al.*, 1993; Farajall *et al.*, 1995; Brasington *et al.*, 1998; Callow *et al.*, 2007; Tian et al. 2009). In fact, there are many factors influencing the critical source area (CSA), such as slope, soil, land use, climate and vegetation. Theoretically, the small CSA as possible is required to represent the practical situation and to assure the precision of model stimulation. However, the smaller CSA will lead to the more cells and the more calculated amount for model. So, the suitable CSA will balance the accuracy of stimulation and calculated data amount. The spatial extent of input parameter aggregation has been studied previously to have substantial impact on model outputs (FitzHugh *et al.*, 2000; Jha *et al.*, 2004; Huang *et al.*, 2009). Such results have attributed to the impacts of increasing amounts of aggregation on the distribution of overland soil, land use, and terrain parameters (Zhang *et al.*, 1994; Chaplot *et al.*, 2002, 2004, 2005; Chen *et al.*, 2004; Kang *et al.*, 2004; Xu *et al.*, 2007). The objective of this paper is to study the impact of critical source area (CSA) within an AnnAGNPS Model applied to simulate runoff, sediment, total nitrogen (TN), and total phosphorus (TP) loads for a small watershed – the Dage subwatershed of the Chaohe river basin, China.

THE STUDY AREA

Miyun Reservoir is the most important source of drinking water supply for Beijing. It is situated in Miyun County, which is within the northern mountain area of Beijing Autonomous Municipality. Its upper watershed includes two perennial rivers (Chaohe River and Baihe River) and five seasonal ephemeral rivers. The watershed flows across nine counties of Beijing Autonomous Municipality and Hebei Province. The total watershed area is 14,871 km^2 of which 1,400 km^2 is in Miyun County (Fig. 1). Due to strict control of point source pollution by banning any kind of plant effluents in the second-class protection areas, nitrogen and phosphorus loads are mainly from non-point sources. The eutrophication trend has become an important factor in the degradation of the water quality of Miyun Reservoir. Currently, the water quality of Miyun Reservoir is mainly mesotrophic.

Research revealed that non-point sources contributed 75 % TN and 94 % TP, respectively (Wang *et al.,* 2003). The region has a continental climate. The average annual precipitation is 660 mm and of this amount, 76.5% usually falls from July through September (Wang *et al.*, 2001).

The studies area—Dage watershed is situated at the headwater of Chaohe River, with a total area of 1876 km^2. The elevations are from 623 m to 2,213 m with a decreasing trend from northwest to southeast. Forest and grass land are two major land use types in the watershed, accounting for 44.24 % and 27.64% of the total land area, respectively. Major soil types on the watershed are brown earth (over 50%) and umber.

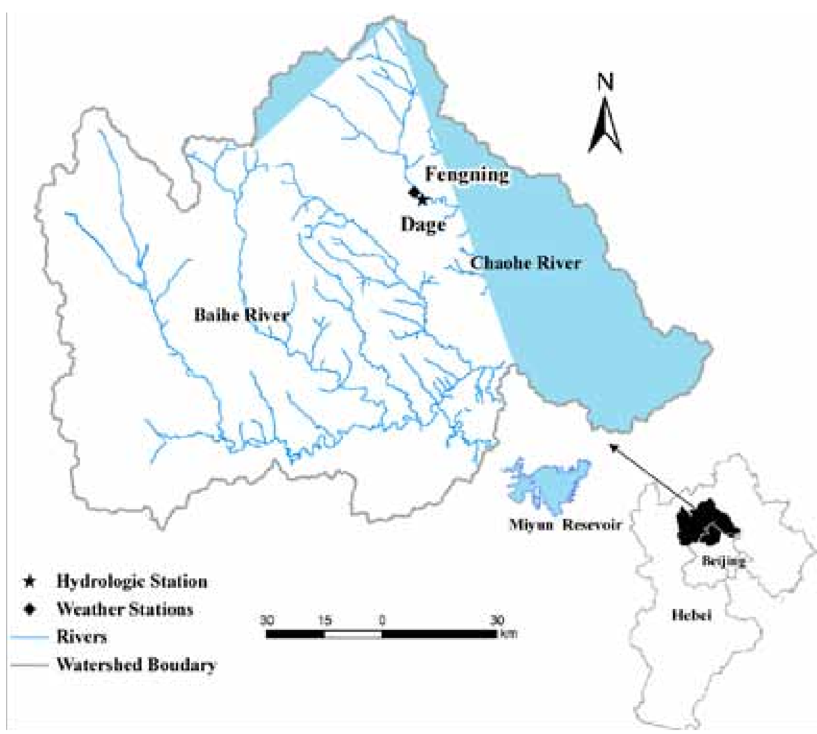

Figure 1. Map of research area

MATERIALS AND METHODS

Brief description of AnnAGNPS model

AnnAGNPS model is a parameter distributed model at watershed scale developed by USDA – ARS (United States Department of Agriculture – the Agricultural Research Service) and NRCS (The Natural Resources Conservation Service) including runoff, soil erosion and chemical transport models. The calculation of Hydrological model is based on water balance equation (1) and the Soil Conservation Services Curve Number (SCS-CN) equation (2) and (3) (Bingner, *et al.*, 2005). Sediment load is calculated by Revised Universal Soil Loss Equation (4).

$$SM_{t+1} = SM_t + (WI_t + Q_t + PERC_t + ET_t + Q_{lat} + Q_{tile}) / Z \tag{1}$$

where SM_t is moisture content for each soil layer at beginning of time period (fraction), SM_{t+1} is moisture content for each soil layer at end of time period (fraction), WI_t is water input, consisting of precipitation or snowmelt plus irrigation water (mm), Q_t is surface runoff (mm), $PERC_t$ is percolation of water out of each soil layer (mm), ET_t is potential evapotranspiration (mm), Q_{lat} is subsurface lateral flow (mm), Q_{tile} is tile drainage flow (mm), Z is thickness for soil layer (mm), and t is the time period.

$$Q = (WI - 0.2S)^2/(WI + 0.8S) \tag{2}$$

$$S = 25400/CN - 254 \tag{3}$$

Where Q is runoff (mm), WI is water input to soil (mm), S is the potential maximum retention; CN is curve number which is a function of land use, soil, management, and hydrologic condition. In SCS model, soils are defined by 4 groups based on their runoff potential-low, moderately low, moderately high and high.

$$A = R \cdot K \cdot L \cdot S \cdot C \cdot P \tag{4}$$

Where A is estimated average soil loss in tons per acre per year, R is rainfall-runoff erosivity factor, K is soil erodibility factor, L is slope length factor, S is slope steepness factor, C is cover-management factor, P is support practice factor.

Parameters of model and data analysis

Some parameters are influenced strongly by CSA, such as watershed area, cell number, cell slope, and cell elevation. In this paper, reach number, reach slope, reach elevation and reach length, runoff, sediment yield and TN, TP loading are selected to study the impact of CSA on model simulation.

The studied area has nearly sole soil type, and uncomplicated geomorphic characteristics and land use; The CSA is set as 7 conditions from 0.5 km^2 to 8 km^2 (see Table 1).

DEM data is from 30 m × 30 m raster data of 1: 50000 topographic map. By running TopAGNPS module of AnnAGNPS Arcview Interface, the converged networks including cells and reaches are divided according to different CSA settings and the studied parameters are calculated. Based on land use data of the year 1995, soil data and metrological data (from the year 1990~2000), the impact of CSA on nonpoint source pollution loading are studied.

Calibration and validation of model

The hydrological flow and sediment data from the year of 1980~1990 at Dage gauge station are used for model calibration and validation by adjusting some parameters. Table 1 is the comparison of simulated load of flow and sediment and measured ones.

Regarding to hydrological simulation, the simulated values of annual mean flow are much closer to measured ones during the normal flow years and high flow years. In the year of 1984 with very low flow, the stimulated flow varies greatly. There is similar trend for sediment simulation. During the normal flow years and high flow yeas, there are better simulated results. However, the contributions of sediment and nutrient loads during low flow periods are very small for annual load. So AnnAGNPS model may be used for simulation of non-point source pollution in this research area after calibration and validation.

Table 1. Comparison of simulated and measured load of flow and sediment

Year	Measured flow (mm)	Stimulated flow (mm)	Measured sediment (t)	Stimulated sediment (t)	Precipitation (mm)
1980	33.25	10.82	20.80	25.38	398.60
1981	29.87	10.33	62.60	62.65	384.10
1982	70.15	83.13	142.00	96.50	532.60
1983	28.18	13.91	38.90	29.91	385.80
1984	24.18	4.08	86.60	20.53	293.00
1985	29.44	21.37	134.00	86.81	433.90
1986	51.08	62.91	240.00	165.24	534.70
1987	46.26	59.92	145.00	67.50	557.40
1988	46.49	48.84	62.70	57.11	409.30
1989	28.55	18.77	45.30	53.73	416.50
1990	39.68	51.25	109.00	84.03	624.30

RESULTS AND DISCUSSION

Impacts of different CSA on terrain parameters of cells and reaches

According to the values of CSA and MSCL of AnnAGNPS model (Table1), the watershed delineation is shown in Fig. 2.

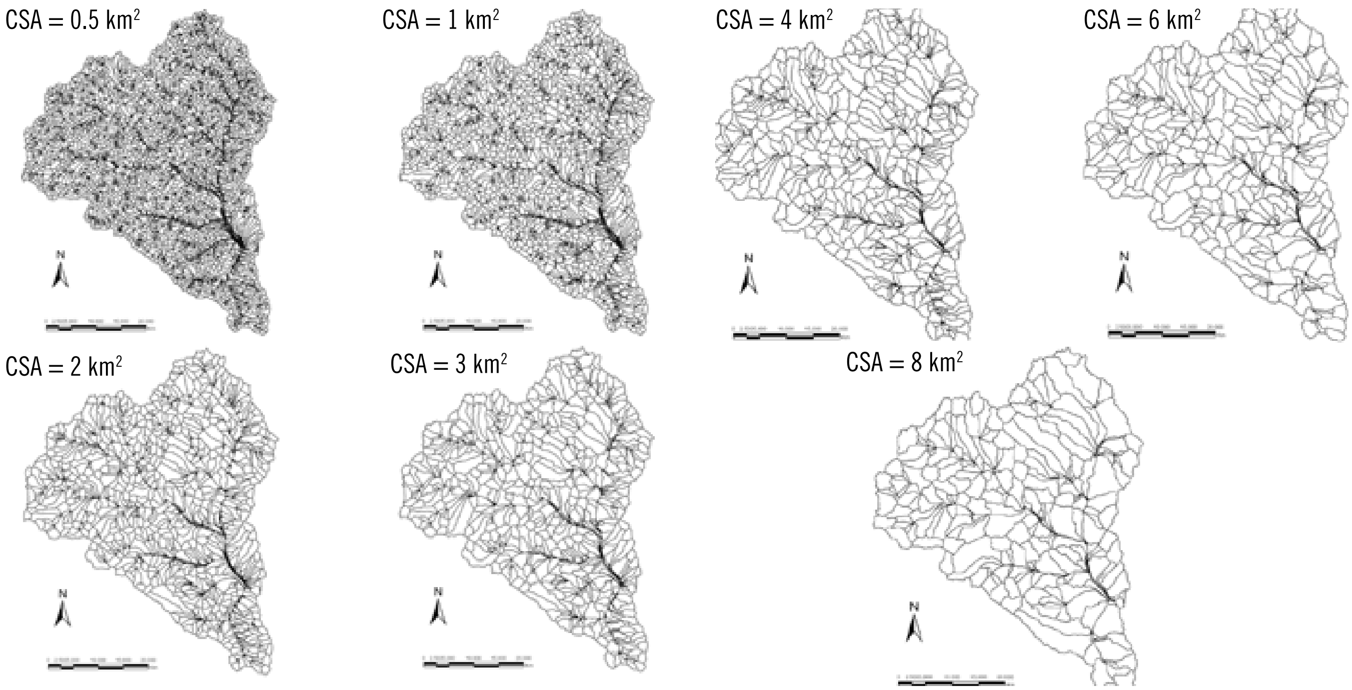

Figure 2. Stream network of different CSA and MSCL value

Compared on the area of watershed at different CSA settings, the result is shown in Table 2.

Table 2. Number of cell and reach of different CSA and MSCL

CSA (km^2)	0.5 km	1 km	2 km	3 km	4 km	6 km	8 km
MSCL (m)	100	200	300	400	500	600	800
Area (km^2)	1876.12	1876.12	1875.34	1876.06	1876.12	1876.12	1876.12
Number of cell	4936	2530	1200	798	617	422	282
Number of reach	2026	1029	485	321	247	169	113

It shows that there is little impact of CSA on watershed area. The area is almost same at different CSA settings, except the little variance at CSA = 2 km^2 and 3 km^2. These tiny differences may be explained by the selection of outlet, but unrelated with CSA and MSCL.

Statistics analysis on the elevation of cells and reaches from different CSA indicates that there is little impact on the minimum elevation whereas there is decreasing trend of maximum elevation with CSA. There is a slight variance of average elevation of cells and reaches (see Table 3).

Table 3. Elevation variance of cell and reach at different CSA

	0.5 km	1 km	2 km	3 km	4 km	6 km	8 km
CELL							
Minimum	638.00	631.00	638.00	640.00	640.00	640.00	640.00
Maximum	2077.00	2051.00	1929.00	1914.00	1875.00	1855.00	1810.00
Mean	1107.05	1091.97	1091.73	1071.50	1080.58	1083.90	1098.44
SD	254.42	254.31	250.36	255.70	246.24	248.90	252.29
REACH							
Minimum	623.50	624.38	628.11	627.94	627.94	627.94	627.94
Maximum	1786.16	1625.74	1471.31	1459.09	1439.26	1433.77	1411.57
Mean	1019.93	991.44	971.56	939.92	943.58	935.76	932.88
SD	213.68	205.44	199.05	195.36	189.76	187.32	190.58

As seen from Fig. 2, the stream network becomes sparser with the increase of CSA value. That means the number of catchment became fewer.

There is regular variance of CSA and the number of cell and reach (See Table 2). The fitted regression equation is as followed:

$$y_1 = 2473.702x - 1.0179 \qquad R^2 = 0.9987$$

$$y_2 = 1006.725x - 1.0272 \qquad R^2 = 0.9988$$

In which, y_1, y_2 represents the number of cell and reach after regression, x is the value of CSA. The determination coefficient R^2 are more than 0.998, which means these regressions can represent the varied pattern of the number of cell and reach with CSA.

Table 4. Variance of cell slope at different CSA

	0.5km	1km	2km	3km	4km	6km	8km
Number	4936	2530	1200	798	617	422	282
Minimum	0.17	0.19	0.01	0.22	0.22	0.22	0.33
Maximum	40.02	38.32	31.19	32.28	32.28	30.37	29.37
Mean	15.68	15.19	14.46	15.14	15.25	15.04	15.80
SD	8.20	8.17	7.23	7.83	7.40	7.42	7.08

Table 4 shows the variance of cell slope at different CSA. It can be seen that the maximum slope of cell decreases firstly with the increase of CSA, and then tends to steady. The mean slope has tiny variance whereas the minimum slope varies greatly.

For further clarification on the effect of DEM resolution on different slope grades, seven grades of cell slope such as ～5° (grade 1)， 5～10° (grade 2), 10～15° (grade 3), 15～20° (grade 4), 20～25° (grade 5), 25～30° (grade 6), 30～35° (grade 7) and > 35° (grade 8) are classified according to the critical slope grading (Tang, *et al.,* 2005). The area percentages of different slope grades are recalculated according to this classification and shown in Fig. 3.

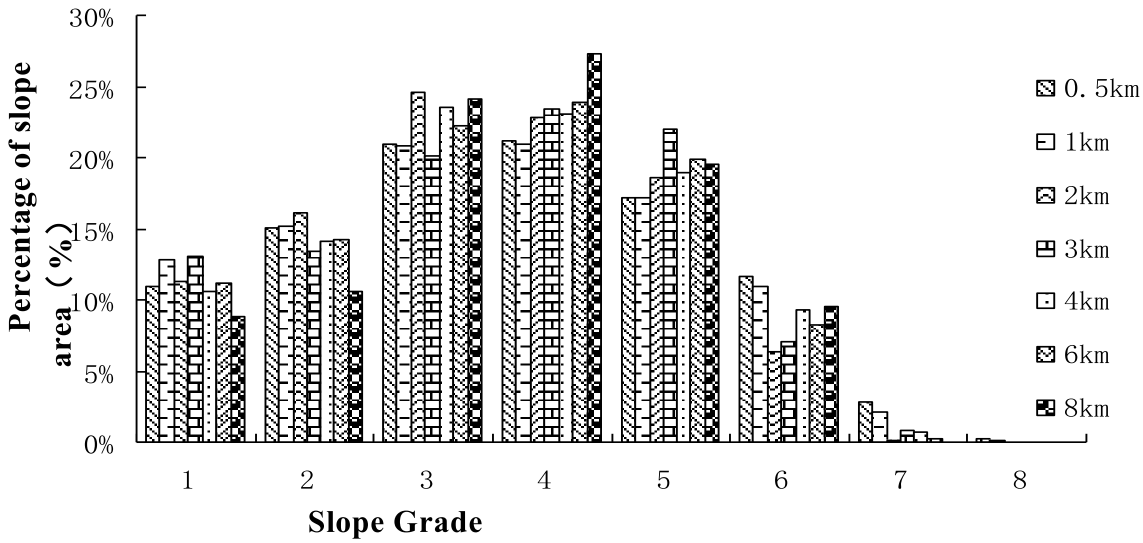

Figure 3. The percentage of slope areas from different CSA

As shown by Figure 3, the percentage of lower slope (grade 1, 2) and higher slope (grade 7, 8) are smaller than the medium slope (grade 3~5), especially for grade 4; There is clear increase of slope area with CSA. The cell number decreases sharply when cell slope >30° . It indicates that steep slope is generalized with increase of CSA. In general, the increase of CSA causes the area loss of steep and gentle slope whereas the area addition of medium slope.

With the increase of CSA from 0.5 ~ 1 km^2, the percentage of lower slope (grade 1, 2) and higher slope (grade 7, 8) increase slightly; While the percentages of the medium slope (grade 3~5) keep almost the same. That means that there is little effect of CSA to cell slope at CSA range from 0.5~1 km^2.

From Fig.2, we can seen that the smallest CSA as possible may represent the practical situation and to assure the precision of model stimulation. However, the smaller CSA will lead to the more cells and the more calculated amount for model. So, the suitable CSA will influence the accuracy of stimulation.

In this study, CSA＝1 km^2 and MSCL＝200 are chosen for AnnAGNPS model stimulation so that the predicted results can represent the practical situation closely and the calculated amount of model stimulation is lessened as well.

Impacts of different CSA on stimulated results of non-point source pollution

After the calibration and validation of AnnAGNPS model, the stimulated results are showed on Table 5 based on the hydrological data of the year 1988.

Table 5. Simulated results of AnnAGNPS model at different CSA

CSA (km^2)	Runoff (mm/yr)	Sed (mg/ha/yr)	TN (mg/ha/yr)	TP (mg/ha/yr)
1	46.05	3.82	7.88	0.61
2	45.51	4.05	7.83	0.60
3	45.59	4.16	7.70	0.62
4	45.06	4.11	7.49	0.61
6	45.15	3.79	6.90	0.58
8	46.66	3.75	6.08	0.59

There is little influence on stimulated runoff whereas simulated sediment increases firstly, then with a decreasing trend. That may be resulted from two factors. Slope of cell and reach decrease gradually while CSA increases. That will lead to decrease of the sediment loading. In addition, the length of stream is getting short with CSA increase, so the transfer route of sediment becomes short which lead to the increase of sediment loading. TN loading decrease with the increase of SCA and TP has slighter variance. That may be related with the slope generalization.

CONCLUSIONS

The results are as followed: (1) CSA has little effect on watershed area, and terrain altitude. The number of cell and reach decreases with the increase of CSA in power function regression curve. (2) The variation of CSA will lead to the uncertainty of average slope which increase the generalization of land characteristics. At the CSA range of 0.5 km^2 to 1 km^2, there is little impact of CSA on slope. (3) Runoff amount does not vary so much with the variation of CSA whereas soil erosion and TN load change prominently. An increase of sediment yield is observed firstly then a decrease following later. TN load decreases evidently especially when CSA is bigger than 6 km^2. TP load has little variation with the change of CSA. Results for Dage watershed shows that CSA of 1 km^2 is desired to avoid large underestimates of loads. Increasing the CSA beyond this threshold will affect the computed runoff flux but generate prediction errors for nitrogen yields. So the appropriate CSA will control error and make simulation at acceptable level.

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Model based assessment of the effectiveness of groundwater protection measures in groundwater bodies on surface water quality improvement

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Abstract

An integrated macroscale model is used to simulate the reactive nitrogen transport from the intake into the soil through the transport through the soil and groundwater up to the outflow into surface waters by the pathways surface runoff, drainage runoff, interflow and groundwater runoff. The model is applied to three agriculturally intensive used catchments in Lower Saxony with sizes ranging from 1500 km² to 3500 km². The nitrogen loads and concentrations in the surface waters were modelled for 35 monitoring stations and compared to the observed values, showing a good agreement. The total N-loads amount from 3300 t N/a up to 8100 t N/a, dominated by the direct runoff components, in particular the artificial drainages.

Areas showing predicted nitrate concentrations in percolation water above the EU groundwater quality standard of 50 mg NO_3/l, have been identified as priority areas for implementing nitrogen reduction measures. The model was used to quantify the requirements to reduce the N-surpluses from agriculture in these areas to fulfil this environmental target and to estimate the reduction effects on the N-loads and the nitrogen concentrations in rivers. It could be shown that these measures would lead to a significant reduction of the N-loads up to 15 % or 1300 t N/a. Although these measures have been developed mainly for groundwater protection, they would also lead to a significant reduction of the outputs from direct runoff components. The effects on the resulting nitrogen concentration in the rivers were shown to be very heterogeneous and amount to reduction levels between 0.3 mg N/L and 2.6 mg N/L. This would lead to a slight improvement of surface water quality, but most of the surface waters in the investigated areas would still be classified as critically polluted.

Keywords

Catchment management; diffuse source pollution; mitigation methods

INTRODUCTION

The implementation schedule for the EU Water Framework Directive requires the establishment of river basin district management programmes until 2009. In Germany, the reduction of nitrogen load into groundwater, mostly caused by diffuse emission from agriculture, is one of the most challenging tasks. Within the EU-Life project WAgriCo (Water Resources Management in Cooperation with Agriculture) and its follow-up project WAgriCo2 nitrogen management options are developed and implemented on a farm level.

Starting point of the analysis of the actual nitrogen surpluses in the soil are N-surpluses as a result of an N-balancing approach (Schmidt *et al.*, 2007), which considers the most important N-inputs to the soil and N-removals from the soil through crop harvest The most important pathways for diffuse nitrogen inputs into the groundwater systems and the surface waters are modelled with the water balance model GROWA (Kunkel & Wendland, 2002). The time-dependent nitrogen degradation along the nitrogen pathways in soil and groundwater is modelled using the DENUZ and WEKU models (Kunkel & Wendland, 1997; Wendland *et al.*, 2009).

Three catchments areas were investigated, each located in the North German Lowland within different large European river basins and cover approximately 300 000 hectares of agricultural land (see Figure 1). The size of the catchments ranges between 1500 km² and 3500 km², their aquifers consist mainly of Pleistocene sand and gravel deposits. According to the first review of the status of the groundwater bodies in Lower Saxony, the achievement of the good status is unclear or rather unlikely for all of the three pilot areas. In all three areas 55 % or more of the land surface is used agriculturally. Therefore, the natural conditions in groundwater and surface waters are significantly influenced by anthropogenic interferences into N-balance and runoff regimes.

In the WAgriCo-project, we focused of measures particularly directed to groundwater protection. As a target value for groundwater protection measures a nitrate concentration in percolation water of 50 mg/l has been defined. With the model the actual nitrate concentrations in percolation water as well as the tolerable N-surpluses needed to meet the environmental target have been calculated, which allows to quantify the required reduction of N-surpluses by measures. As a result, the required reduction by agriculture is very significant and amounts between 25 $kg \cdot ha^{-1} \cdot a^{-1}$ and 60 $kg \cdot ha^{-1} \cdot a^{-1}$ (Kunkel *et al.*, 2008a). The follow-up WAgriCo2-project, which is in the focus of this paper, extends to nitrogen transport from the intake into the soil up to the outflow into surface waters with respect to different transport pathways for diffuse pollution. Thus, the model was used to calculate the nitrogen loads transported by the pathways surface runoff, drainage runoff, interflow and groundwater runoff and the resulting nitrogen concentrations in surface waters. Beneath an analysis of the current situation, the effects of the implementation of the required N-surpluses reduction on the N-concentration at 35 monitoring stations and the N-load in the surface waters are investigated.

Figure 1. Location of the investigated areas.

METHODOLOGICAL APPROACH

The nutrient load at a certain location in a river, e.g. a monitoring station at the outlet of a subcatchment, is calculated under consideration of the nutrient inputs, the water balance and the denitrification processes in the soil, the groundwater and the river:

$$L_{MS} = d_{river} \cdot \left\{ \sum_{i=1}^{catchment} d_{\mathrm{soil}\,i} \cdot a_N \cdot \left(N_{AA,i} + N_{Atm,i}\right) \cdot \left[r_{D,i} + r_{I,i} + d_{\mathrm{Aquifer},i} \cdot r_{b,i}\right] + \sum_{s=1}^{catchment} L_{\mathrm{Point},s} \right\} \quad \text{eq. 1}$$

with:	L_{MS}	=	Nitrogen load in the river at a monitoring station	[t/a]
	d_{river}	=	Nitrogen losses in the river relative to the inputs	[-]
	d_{soil}	=	Nitrogen losses in the soil relative to the inputs	[-]
	a_N	=	N-storage changes in the soil relative to the N-surpluses	[-]
	N_{AA}	=	N-surpluses from agriculture	[kg N/(ha a)]
	N_{Atm}	=	atmospheric net N-deposition	[kg N/(ha a)]
	r_D	=	amount of drainage runoff relative to total runoff	[-]

r_z	=	amount of interflows relative to total runoff	[-]
$d_{Aquifer}$	=	Nitrogen losses in the aquifer relative to the inputs	[-]
r_b	=	amount of base runoff relative to total runoff	[-]
L_{Point}	=	punctiform N-inputs into the river	[t/a]

Starting point is the nitrogen input into the soils. The most important diffuse nitrogen sources are the atmospheric N-inputs (N_{Atm}) and the N-surpluses from agriculture (N_{AA}). Whereas the atmospheric N-inputs into the soils may be estimated by a constant net deposition rate (15 kg N ha^{-1} a^{-1} and 30 kg N ha^{-1} a^{-1} in forestal areas), nitrogen supplies and extractions for the agricultural area are calculated from agricultural statistics on the municipality level from data, e.g. on crop yields, livestock farming and land use by balancing the nitrogen supplies and extractions. As a rule, the difference between nitrogen supplies, primarily by mineral fertilizers and farm manure, and nitrogen extractions, primarily by field crops, leads to a positive N-balance. Thus, nitrogen surpluses from agriculture represent a risk potential since they indicate the amount of nitrogen potentially leaching into groundwater and surface water.

A certain amount of the mineral N-surpluses in soils is denitrified to molecular nitrogen. Denitrification losses in the soil (d_{soil}) are calculated using the DENUZ model as a function of the diffuse N-surpluses, denitrification conditions and the residence time of percolation water in the soil according to a Michaelis-Menten kinetics. The reaction kinetic parameters were assessed on the basis of observed denitrification rates in German soils (NLfB, 2005) according to the geological substrate, the influence of groundwater and perching water of the soils and the average residence time of perching water in the soil (Kunkel & Wendland, 2006; Kunkel *et al.*, 2010). In pasture and forestal areas nitrogen intakes may be accumulated to a certain extent in the soil or the plants. This is considered by landuse dependent accumulation factors (a_N), which were set from observed values and literature data.

The displacement of N-surpluses into surface waters is coupled to the different runoff components. These are calculated by the water balance model GROWA (Kunkel & Wendland, 2002). The model has been developed to support practical water resources management issues of large river basins and was already applied to different regions (Bogena et al., 2005; Kunkel et al., 2005; Tetzlaff *et al.*, 2007; Wendland *et al.*, 2003; Wendland *et al.*, 2005; Wendland *et al.*, 2007). It employs an empirical approach with a temporal resolution of one or more years. Annual averages of the main water balance components are quantified as a function of climate, soil, geology, topography and land use conditions. Beneath percolation water rate the portions of drainage runoff (r_D), (natural) interflow (r_I) and groundwater runoff (r_B) to total runoff are determined as temporal averages depending on the site conditions using a hierarchical approach (Bogena *et al.*, 2005; Kunkel *et al.*, 2008b). Whereas the direct runoff components (drainage runoff and interflow) reach the surface waters within short time periods (within about a week), groundwater runoff needs much more time (years) to percolate into surface waters.

Denitrification processes may significantly reduce the nitrate inputs into the aquifer during the passage in the groundwater ($d_{Aquifer}$). This reactive nitrate transport in groundwater was modelled using the stochastical WEKU model (Kunkel & Wendland, 1997). According to extensive field studies by (Böttcher *et al.*, 1989; Walther *et al.*, 2003) in a catchment area in the North German Lowlands and (van Beek, 1987) for a site in the Netherlands a first order denitrification kinetics depending on the nitrate inputs and the residence time in groundwater with a reaction constant of 0.17–0.56 a^{-1} is considered. Rather simple indicators, such as the presence of Fe(II), Mn(II) and the absence of O_2 and NO_3 can be used to decide whether denotrifcation in the aquifer is possible or can be neglected (Wendland *et al.*, 2002).

The nitrogen load at a certain monitoring station is calculated by the integration of the diffuse nitrogen inputs into the surface waters via the different pathways calculated for each grid cell over the catchment area of the considered station plus the sum of the inputs from point sources (L_{Point}), mainly municipal and industrial waste water treatment plants. Nitrogen processes in the river itself have to be considered, since they may reduce the nitrogen loads in the rivers significantly (by about a factor of two). Nitrogen conversion in the rivers (d_{River}) is calculated on the basis of an approach by (Behrendt *et al.*, 1999) using the size of the catchment area and the total runoff as inputs.

INPUT DATA

A digital data basis for the study region has been compiled and harmonized from a number of existing data sets. The results of the N-balancing model has been provided for the time period of 1999-2003 by the State Agency for Mining, Energy and Geology (LBEG) of Lower Saxony. The input data for the GROWA, DENUZ and WEKU models, i.e. data on climate, topography, soil cover, soil parameters, hydrogeological parameters, water quality and point sources, have been provided by the Lower Saxony Water Management, Coastal Defence and Nature Conservation Agency (NLWKN) and the State Agency for Mining, Energy and Geology (LBEG). Most of these parameters are derived from digital maps, with scales from 1:50,000 to 1:200,000. Modelling was done using raster cells with a spatial resolution of 50x50 m^2. This size is adapted to the data set which displays the highest spatial differentiation, in this case the land use data set. For the climate data we used the time period of 1961-1990 as a temporal reference period.

RESULTS

Analysis of the current situation

In the first step, the model is used to analyze the present state of the nitrogen pressure to the model areas. Figure 2 illustrates the potential nitrate concentration in the leachate, which has been calculated from the nitrogen surpluses, the percolation water rate and the consideration of the denitrification in the soil (Wendland *et al.*, 2009). The map shows that especially in the Hase and the Große Aue catchment nitrate concentrations in the leachate of more than 50 mg/L, often more than 150 mg/L occur. This is due to the intensive agriculture in these catchments, leading to N-surpluses of 75 $kg \cdot ha^{-1} \cdot a^{-1}$ combined with relatively poor denitrification potential in the soils. The concentrations in the Ilmenau/Jeetzel catchment are generally lower due to the more extensive agriculture and the lower N-surplus levels.

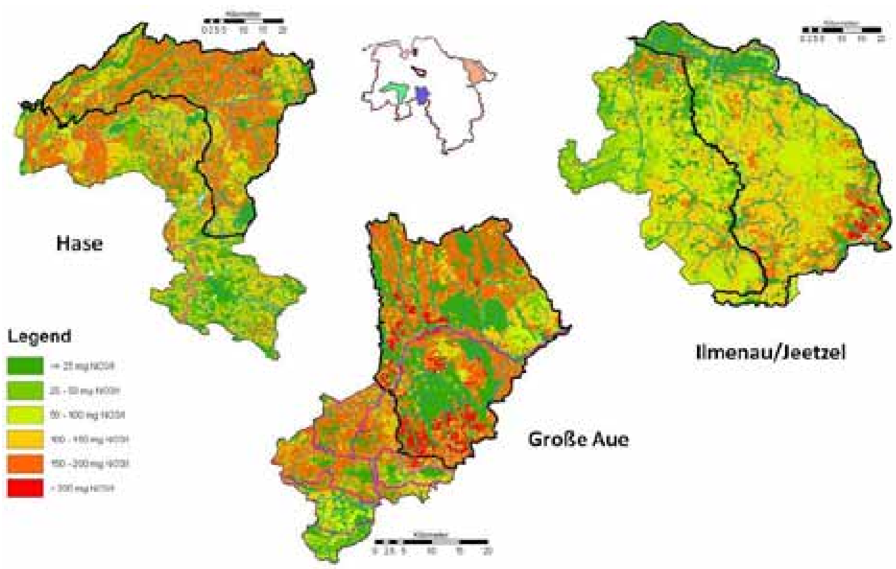

Figure 2. Calculated nitrate concentration in the leachate.

Figure 3 shows the total diffuse N-outputs to surface waters as calculated from the sum of the outputs from the individual pathways drainage runoff, interflow and groundwater runoff. In the vicinity of surface waters rivers elevated N-outputs arise from the short travel times of nitrate in the aquifer, which are not long enough to enable complete denitrification. Artificial drainages in the central part of the Hase and large areas of the Große Aue catchment are leading to a high portion of direct runoff and therefore to high N-outputs to the surface waters. In the areas, which are dominated by groundwater runoff, e.g. in most parts of the Ilmenau/Jeetzel catchment and the Geest areas in the northern parts of the Hase and Große Aue catchments, long groundwater residence times and good denitrification conditions in the aquifers lead to an effective denitrification in groundwater and to small N-outputs into the surface waters.

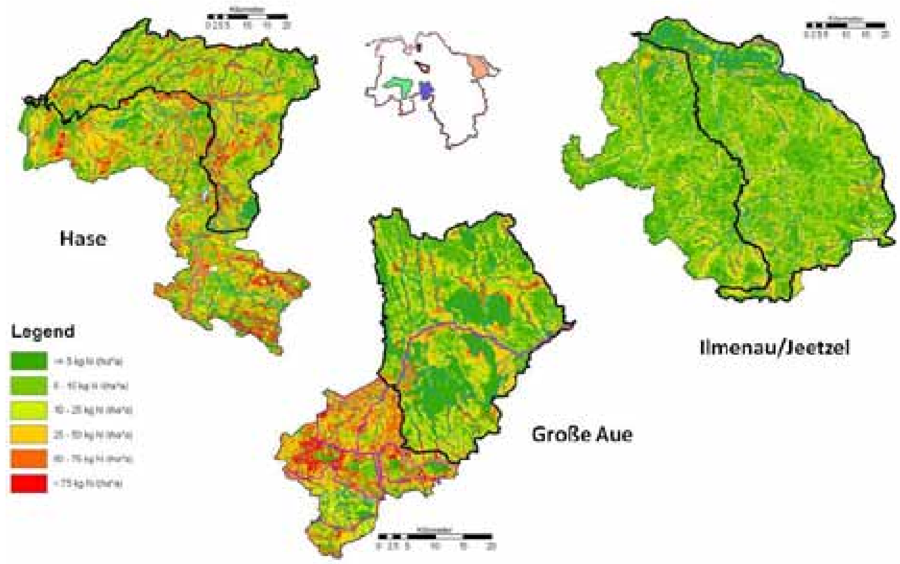

Figure 3. Nitrogen outputs into surface waters from diffuse sources (artificial drainage, interflow, groundwater runoff).

Figure 4 shows the calculated total N-loads of the surface waters in the modelled areas differentiated to the different sources. The total N-Loads amount to 3300 t/a up to 8100 t/a. Although Ilmenau/Jeetzel is the largest catchment area, the N-loads are much smaller than those out of the smaller Hase catchment due to the less intensive agriculture. The direct runoff components (interflow and drainage runoff) dominate the N-loads. In the Hase and the Große Aue artificial drainages have a high impact on the N-loads, whereas the natural interflow is more important in the Ilmenau/Jeetzel catchment. The relative small contribution of N-loads from groundwater runoff (600-800 t/a) indicates the importance of denitrification in the aquifers. Point sources have only a small influence on the total N-loads.

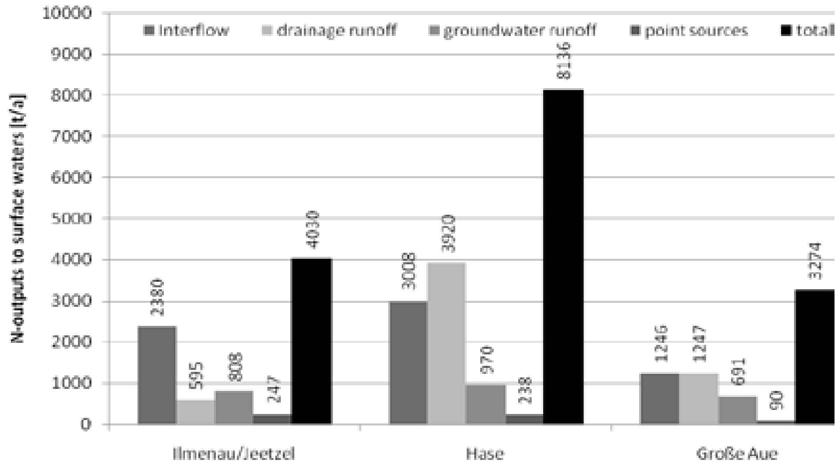

Figure 4. N-outputs to surface waters of the model areas differentiated to output pathways.

Validation of model results

The water balance calculated with the GROWA model was validated using runoff records from 14 gauged sub-catchments. The grid-wise calculated runoff levels are integrated for the catchments of the individual monitoring stations and compared to the measured mean runoff levels (total runoff) and the mean monthly low flow runoff (groundwater recharge). The comparison of the total runoff levels, for instance, leads to a regression coefficient of 0.993, indicating that the derived mean long term total runoff levels are quite good represented by the model. The separation of total runoff into the different runoff components included calibration steps and therefore shows a quite good correlation to the observed runoff data. The nitrate concentrations in the leachate have been compared to nitrate concentrations in soil profiles observed at permanent soil observation sites in Lower Saxony (Bartels *et al.*, 1991) showing a good correlation (Wendland *et al.*, 2009).

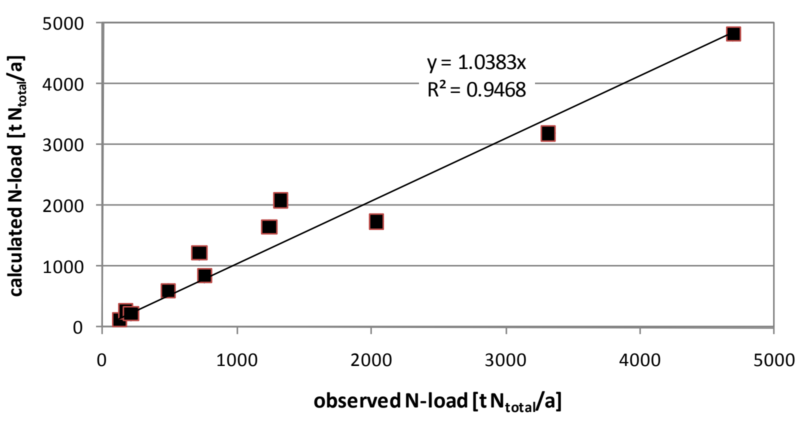

Figure 5. Comparison of measured and modelled N-loads.

The Nitrogen loads in surfaces waters calculated according to equation 1 was compared to the measured loads at the 14 monitoring stations with usable data. The result (figure 5) illustrates that the measured N-loads are very good represented by the model. Finally it can be concluded that the model results compare good to measured long-term data, represent the current situation quite good and can therefore be used to analyse the effects of land use change scenarios.

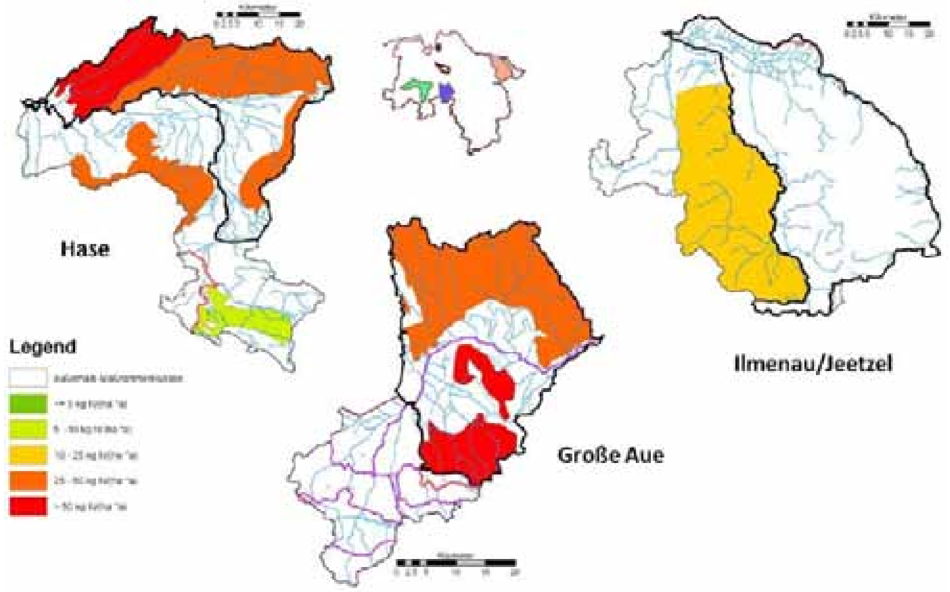

Figure 6. Reduction requirements of N-surpluses from agriculture to meet the environmental target of an averaged nitrate concentration in the leachate of 50 mg NO3-N/L (Kunkel *et al.*, 2008b).

Nitrate reduction requirements

The EU Water Framework directive requires the nitrate concentration in all groundwater monitoring wells to be less than 50 mg NO3-N/L. The nitrate concentration in groundwater is very difficult to assess by large scale models mainly because of lack of data. If the focus of agro-environmental measures is particularly directed to groundwater protection, the effects of measures are to be judged against another environmental target value. In the WAgriCo-project a mean long term nitrate concentration in percolation water of 50 mg NO3-N/L was defined as a suitable environmental target for protecting groundwater against an exceeding of the EU quality standard for nitrate. This value, however, is not to be applied to each individual site, but is regarded as an average value for a larger area defined by the groundwater bodies and their hydrogeological subdivisions. The average value for the actual situation is calculated on the basis of the modelled nitrate concentrations in the leachate (see figure 3). Additionally, the tolerable N-surpluses needed to meet the environmental target are calculated, which allows to quantify the required reduction of N-surpluses by measures. The required reduction by agriculture is very significant (see figure 6) and amounts to be between 25 kg·ha-1·a-1 and more than 60 kg·ha-1·a-1, values which are hardly realizable (Kunkel et al., 2008a).

Influence of agro-environmental measures on surface water quality

Existing monitoring stations in the model areas show averaged nitrogen concentrations above 1 mg N_{ges}/L and up to 7 mg N_{ges}/L. According to the classification of Germany's Working Group of the Federal States on Water Problems (LAWA, 1998) in most of the monitoring stations a class II-III (3-6 mg N_{ges}/L, polluted) is observed. In the Hase and Große Aue catchments, the concentrations in the surface waters are between 4 and more than 7 mg N/L, indicating the high pressures of agriculture to the nutrient pollution of surface waters. In contrast to groundwater, no common threshold values for nitrate concentrations in the surface waters are available. Therefore, the influence of a potential full implementation of the reduction requirement of the N-loads and the nitrogen concentrations in the surface waters of the three catchments is investigated.

In Figure 7 these effects on the N-outputs to surfaces waters are shown differentiated for the different outtake pathways similar to figure 5. For all model areas, a significant reduction of the N-loads up to 15 % or 1300 t N/a may be achieved. This reduction is mainly attributed to the direct runoff components. Because of the high denitrification potential in groundwater, however, the total load reduction is relatively small and amounts to about 200 t N/a. The effects of these measures on the resulting nitrogen concentration in the rivers are heterogeneous and amount to 0.3 mg N/L up to 2.6 mg N/L. This would lead to a slight improvement of surface water quality, but in no case a better classification of the surface water could be achieved; most of the surface waters in the pilot areas would still be classified as critically polluted.

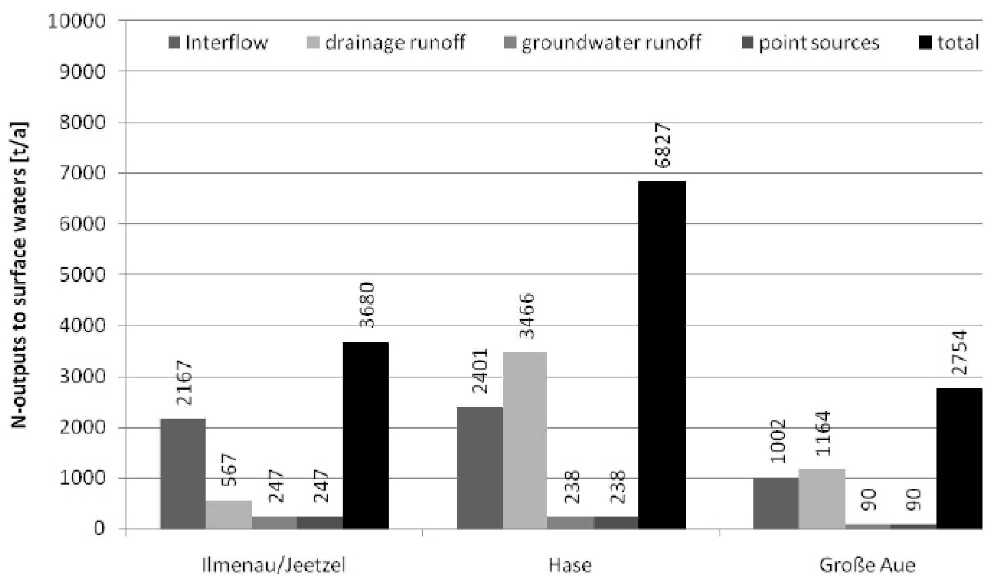

Figure 7. N-outputs to surface waters of the model areas differentiated to output pathways after implementation of the N-reduction measures to reach an averaged nitrate concentration in the leachate of 50 mg NO_3-N/L.

CONCLUSIONS

An integrative model is used to simulate nitrogen transport from the intake into the soil up to the outflow into surface waters with respect to the transport pathways for diffuse pollution drainage runoff, interflow and groundwater runoff for three catchment areas in Lower Saxony. Starting from the N-surpluses from agriculture, the most important pathways for diffuse nitrogen inputs into the surface waters are modelled with the water balance model GROWA. The time-dependent nitrogen degradation along the nitrogen pathways in soil and groundwater is modelled using the DENUZ and WEKU-models. The Nitrogen concentrations at 35 monitoring stations and the N-loads via the different pathways in the surface waters are calculated and compared to the observed values. The modelled and observed values are in very good agreement. Relatively high nitrogen concentrations between 4 and more than 7 mg N/L are present in the rivers, indicating the high pressures of agriculture to the nutrient pollution of surface waters.

The model results show that the total N-loads, amount from 3300 t N/a up to 8100 t N/a, are dominated by the direct runoff components, in particular the artificial drainages. The influence of groundwater borne nitrogen intakes into surface waters is relatively small, although the intakes into groundwater are often higher than the loads transported by the direct runoff components. This is due to a very effective denitrification in the sand and gravel aquifers.

We used the model to quantify the effects of agricultural measures to reduce the nitrate concentration to 50 mg/L in percolation water on the nitrogen loads from the different transport pathways and the resulting nitrogen concentration in the surface waters. Although these measures have been developed mainly for groundwater protection, they would also lead to a reduction of the total N-load to the surface waters by up to 1300 t N/a or 15 %. This reduction is mainly attributed to the direct runoff components. The load reduction from groundwater runoff would be about 50 %; because of the high denitrification potential in groundwater, however, the total load reduction is relatively small and amounts to about 200 t N/a. The effects of these measures on the nitrogen concentration in the rivers are very heterogeneous and amount to reduction levels between 0.3 mg N/L and 2.6 mg N/L. This would lead to a slight improvement of surface water quality, but most of the surface waters in the pilot areas would still be classified as critically polluted.

This investigation demonstrate that the integrated model can be used to predict nitrate loads for different nutrient transport pathways and nitrogen concentrations in the surface waters of mesoscale and macroscale catchments. The model results can be used to derive effective measures to reduce the diffuse nitrate intakes into the groundwater and the surface waters and to identify the hot spot areas, where reduction measures would be most efficiently. Therefore, the model results can support the development of surface water monitoring programmes, since it is possible to identify those sub catchments, which are dominated by a certain transport pathway. The efficiency of reduction measures on that particular transport pathway can then be targeted monitored.

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Water Quality Trends (non flow-adjusted) in the Last Decade for Ten Watersheds Dominated by Diffuse Pollution in Québec (Canada)

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Abstract

The aim of this work is to evaluate river water quality trends (non flow-adjusted) over the last decade in watersheds in Québec where diffuse pollution is dominant. Ten watersheds where diffuse sources represent more than half of the annual load of phosphorus (P) and nitrogen (N) were chosen for this evaluation. Trend analyses results indicate a significant reduction of contaminant concentration for total P in seven rivers, for ammonia N in five rivers, for nitrite and nitrates in three rivers, for total filtred N in two rivers and for fecal coliforms in one river. However, they show a significant increase for turbidity measurements in nine rivers and for suspended solids (SS) concentrations in two rivers. In spite of the encouraging P reduction observed in most of the rivers studied, for seven of them median concentrations remain at least two times greater than the Québec water quality guideline for water protection. These results indicate the need to continue the efforts to further reduce P pollution. The increasing trends in turbidity and SS measurements command some efforts too. Future trend analyses should consider flow data and quantify actions taken to reduce the diffuse sources over the last decade at the watershed scale when data will be available.

Keywords

Water quality trend; diffuse pollution; agriculture

INTRODUCTION

In the province of Québec, efforts have been made over the past 30 years to reduce river pollution. Legislation and water pollution abatement programs initially focused on municipal point source pollution and manure storage but were only partially successful in correcting water quality problems (Gangbazo and Painchaud, 1999). For many watersheds, diffuse pollution sources, mainly from agriculture, have been identified as the main source of phosphorus (P) and nitrogen (N) in many rivers exceeding water quality guidelines (Gangbazo et Babin, 2000; Gangbazo *et al.*, 2005).

Over the last decade, new regulations on agricultural pollution, supported by financial programs (Boutin, 2004; Prime-Vert Program, 2009), have focused on diffuse P control. The *Regulation respecting the reduction of pollution from agricultural sources* (GOQ, 1997) introduced the obligation of agro-environmental fertilization plans (AEFP) and spreading registers for the majority of farms. It also prohibited manure and mineral fertilizers spreading outside the period of 1 April to 30 September. The AEFP, based on a balance between crop requirements and nutrients supplied from all sources, must take into account the P richness of soils and indicate the reduction measures when they are too rich. The modernization of the 1997 regulation that came into force in 2002 has permitted to intensify its control. Additional measures, like restriction of animal access to watercourses enforced in 2005, were also introduced (MDDEP, 2010a).

In the province of Québec, these measures have contributed to reduce the P budget (difference between nutrients supplied from all sources and crop uptake) from 14.4 kg P/ha in 1998 to 8.3 kg P/ha in 2007. In spite of a 6% animal unit (AU) increase, improvements in animal feeding like the generalized use of phytase and a 32% decrease in the use of mineral P fertilizer have helped improve the P budget and to respect the AEFP. The N budget and mineral N fertilizer sales in Québec, however, remained relatively stable over this period. Manure spreading after fall harvest also decreased, passing from 46% to 34% of manure volume for annual crops and from 69% to 24% of manure volume for grasslands. Some point source improvements like the increase from 68% to 74% of total AU with watertight manure storage and a decrease in dairies untreated wastewaters volume from 58% to 33% of total cow AU also occurred (BPR, 2008).

The aim of this work is to evaluate water quality trends (non flow-adjusted) in the last decade, in river watersheds where diffuse pollution is dominant, for total P, filtered N forms, fecal coliforms (FC), turbidity and suspended solids (SS).

METHODS

Studied watershed

Ten watersheds located in the St Lawrence Lowlands and the Appalachians, with drainage area ranging from 20 to 550 km^2, were chosen for the evaluation (figure 1). Five of them were not affected by any municipal point source of pollution. The other five did receive effluent from wastewater treatment plants but these facilities did not undergo any treatment upgrade in the last decade. One watershed (number 8) also received untreated municipal wastewater. Diffuse sources in these ten watersheds represent more than half of the annual load of P and N measured in rivers.

Water sampling and analysis

Water quality validated data from MDDEP (2010b) database were used. River water was sampled monthly or bi-monthly and samples were sent to the Centre d'expertise en analyse environnementale du Québec to be treated in less than 48 hours and analysed with standard methods (CEAEQ, 2004). Samples were filtered (0.45 µm) for N forms and SS, and not for total P, and analysed with the procedure described in Gangbazo et al. (2002, 2003). However, for watersheds 1, 6, 7, 8, filtration differed (1.2 µm) and was used for P too. In these watersheds, total P was obtained from the sum of separately analysed particulate and dissolved forms. These analyses and FC counts for all watersheds were made as described in Gangbazo and Painchaud (1999).

Statistical methods

Trends in water quality variables (non flow-adjusted) over the period of 1999 – 2008 were analyzed using the Statistical Analysis Software (SAS) 9.1 (SAS Institute, 2003). The Mann-Kendall test was used when both seasonality and autocorrelation were not detected. The seasonal Mann-Kendall test was selected when data showed seasonality without autocorrelation (Helsel and Hirsch, 2002; Gilbert, 1987). Finally, Hirsch and Slack (1984)'s approach was used when seasonality and autocorrelation occurred. Monthly median concentrations were used for trend tests. In presence of autocorrelation, missing data were replaced by the monthly median value calculated over the whole period. For stations with many missing values, the SAS ARIMA procedure (ARMA(1,1) process with linear trend and cyclic component), which support missing data, was used for validation of the trend results. For this work, trends were not considered significant when probability values (p) were greater or equal to 0.05.

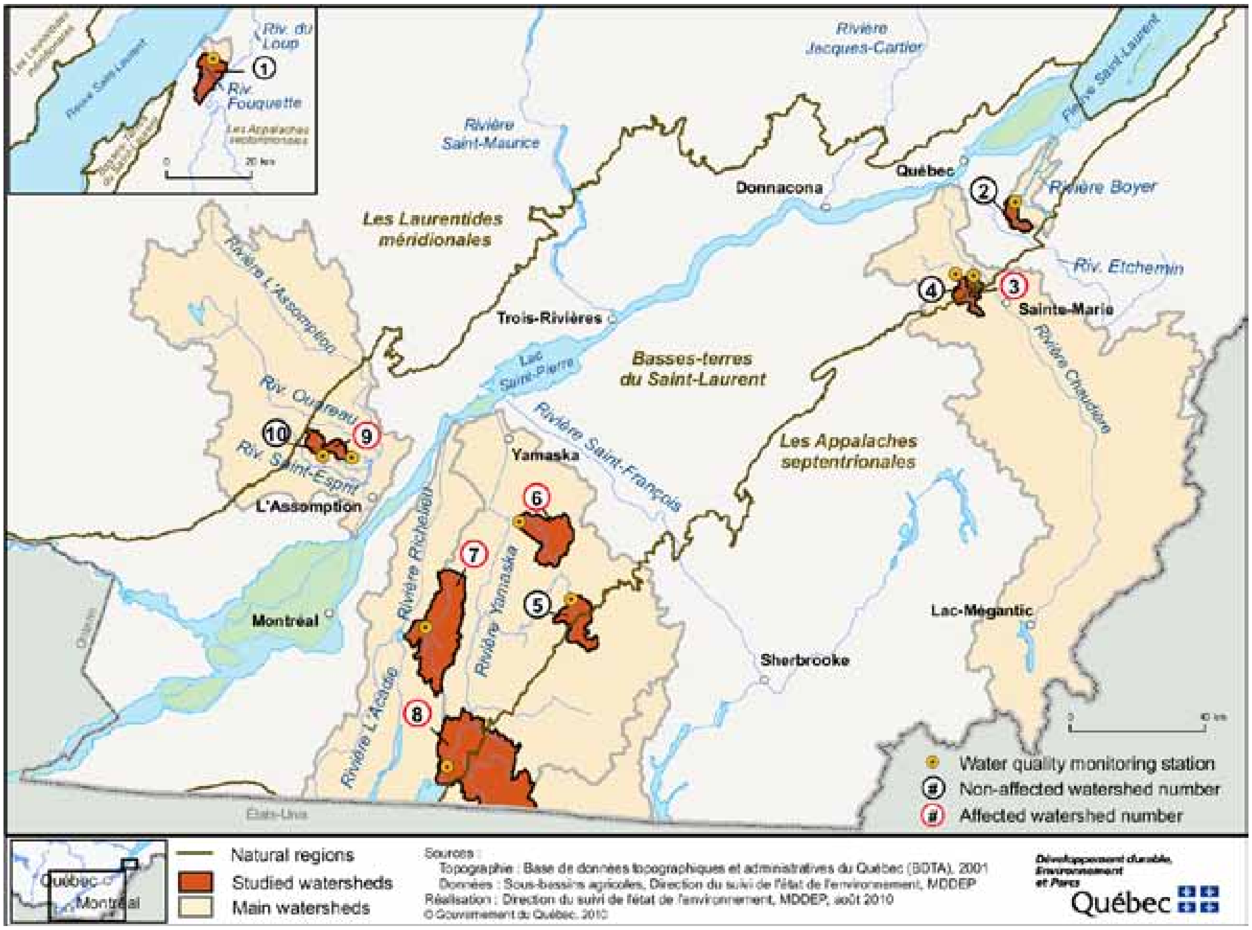

Figure 1. Watersheds and monitoring stations location

RESULTS AND DISCUSSION

Trend analyses results indicate a significant reduction of contaminant concentration for total P in seven rivers, for ammonia N in five rivers, for nitrite-nitrates in three rivers, for total N in two rivers and for FC in one river. However, they show a significant increase for turbidity measurements in nine rivers and for SS concentrations in two rivers. These results are presented and discussed in this section. They are also put in the context of limited availability of validated discharge data and of watershed scale inventoried actions taken to reduce the diffuse sources.

The trend lines in figures below were established with the Sen's slope estimator when Mann-Kendall test was used and with the seasonal Kendall slope estimator for other cases (Gilbert, 1987), and positioned using median concentrations based on monthly median data and median time of observed values.

Phosphorus

Trends for total P concentrations in the ten rivers over the last decade are illustrated in figure 2. The significant P reduction in seven of them suggests that the efforts to reduce P pollution were efficient. However, in spite of the encouraging observed

P reduction in most of the rivers studied, for seven of them median concentrations remain at least two times greater than Québec's water quality guideline for preventing eutrophication (MDDEP, 2009). These results indicate the need to continue the efforts to further reduce P pollution.

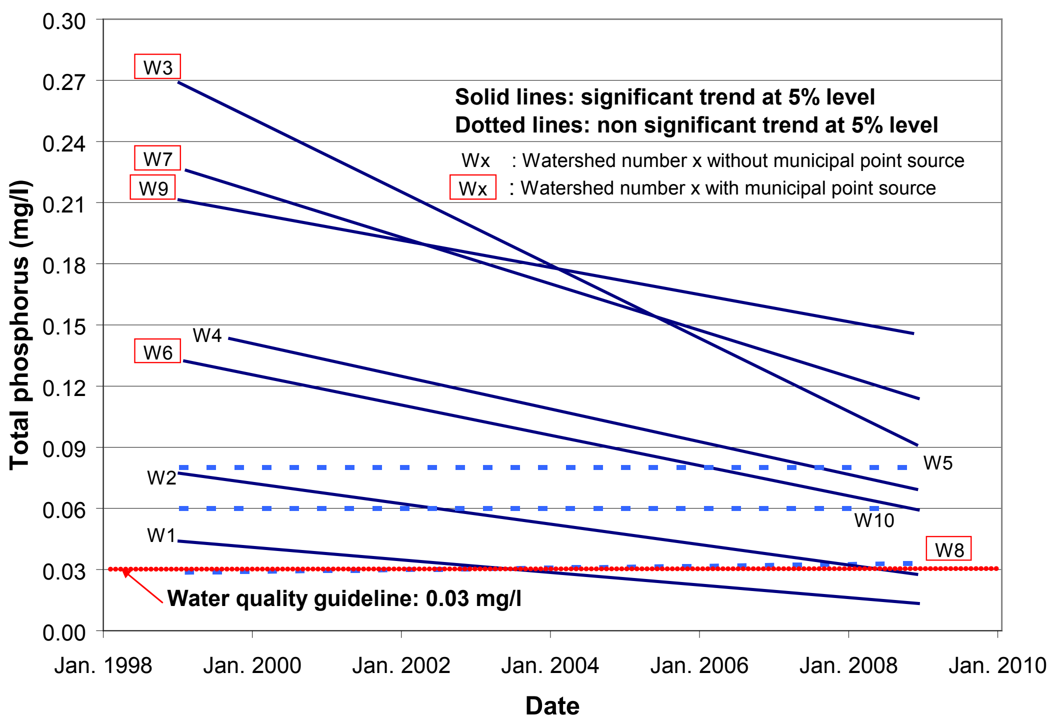

Figure 2. Trends of phosphorus concentrations in ten rivers over the last decade

Nitrogen

Ammonia N Trends for ammonia N concentrations in the ten rivers over the last decade are illustrated in figure 3. After the encouraging observed ammonia N reduction in half of the rivers studied, median concentrations remain greater than the Québec water quality guideline for raw water disinfection efficiency (MDDEP, 2009) in one of them. These results suggest that the efforts to reduce diffuse pollution over the last decade, such as reducing fall manure spreading, had a positive effect to reduce ammonia N concentrations in many watersheds.

Nitrates-nitrites Trends for nitrates-nitrites concentrations in the ten rivers over the last decade are illustrated in figure 4. After the encouraging nitrates-nitrites observed reduction in tree of the rivers studied, median concentrations remain greater than the Québec water quality guideline for aquatic life protection (chronic effect) (MDDEP, 2009) in one of them. These results suggest that the efforts to reduce diffuse pollution had a positive effect to reduce nitrates-nitrite concentrations in some watersheds.

Total filtered N Trends for total filtered N concentrations in the ten rivers over the last decade are illustrated in figure 5. There is no Québec water quality guideline for total N. However, observed reduction in two of the rivers studied suggest that the efforts to reduce diffuse pollution had a positive effect to reduce total filtered N concentrations in some watersheds. As a rule of thumb, the Ministère du Développement durable, de l'Environnement et des Parcs (MDDEP) considers that total filtered N concentrations above 1 mg N/l in a watercourse are significant and indicate the impact of human activities.

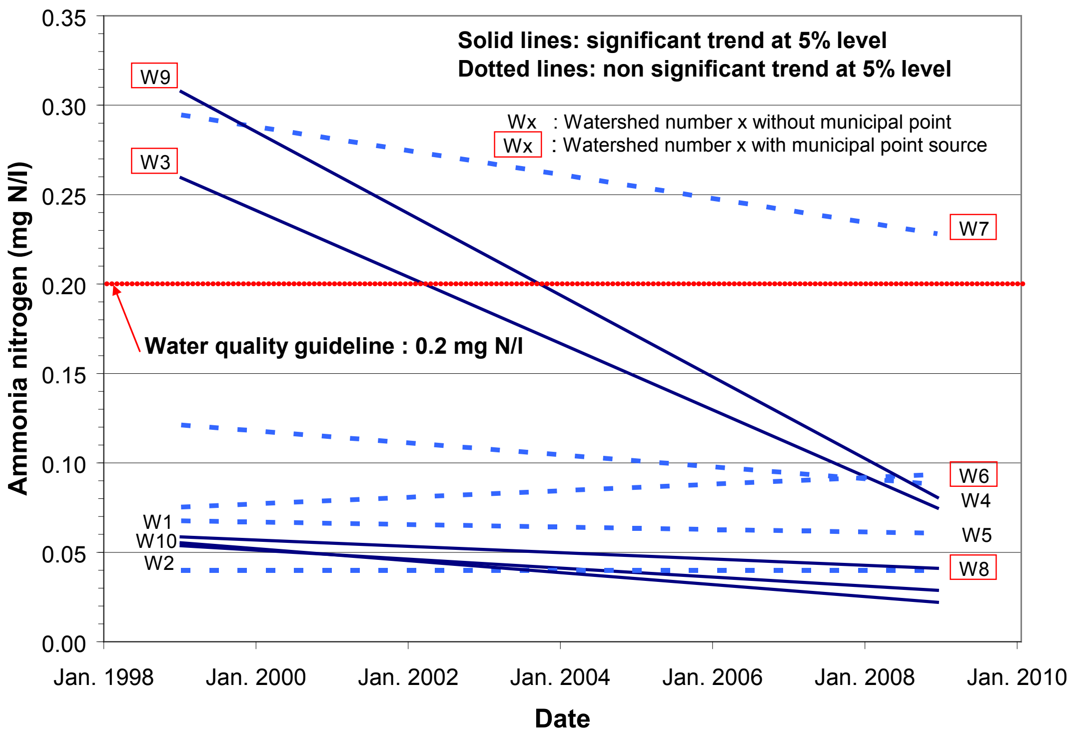

Figure 3. Trends of ammonia N concentrations in ten rivers over the last decade

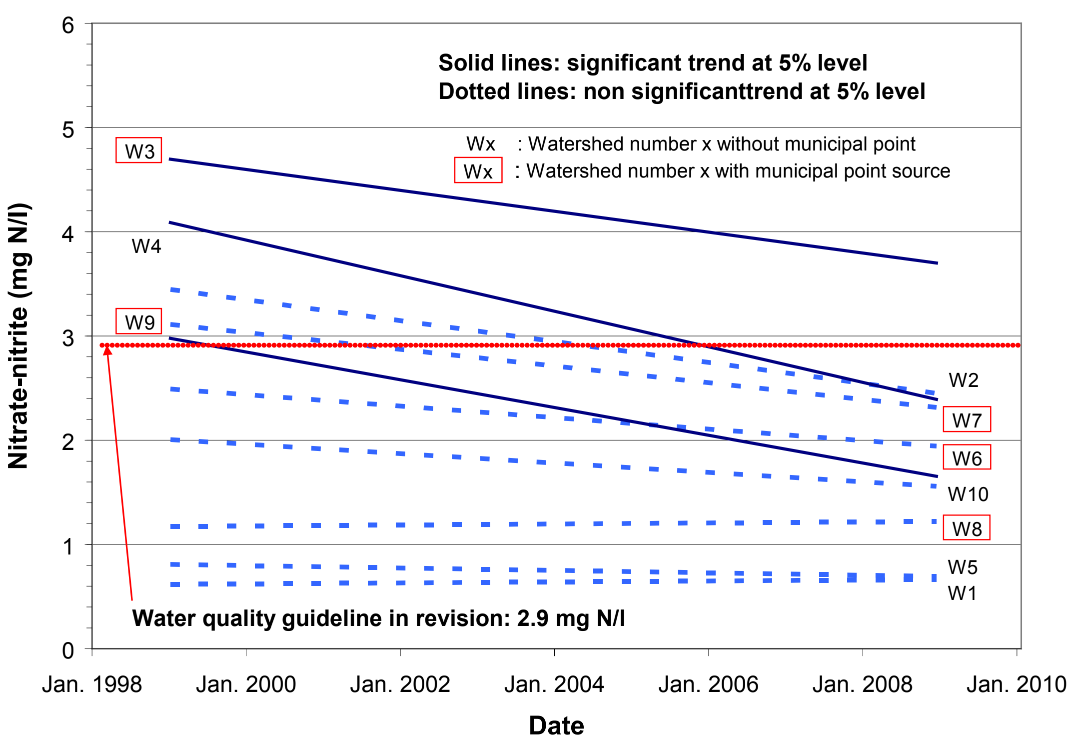

Figure 4. Trends of nitrate-nitrite concentrations in ten rivers over the last decade

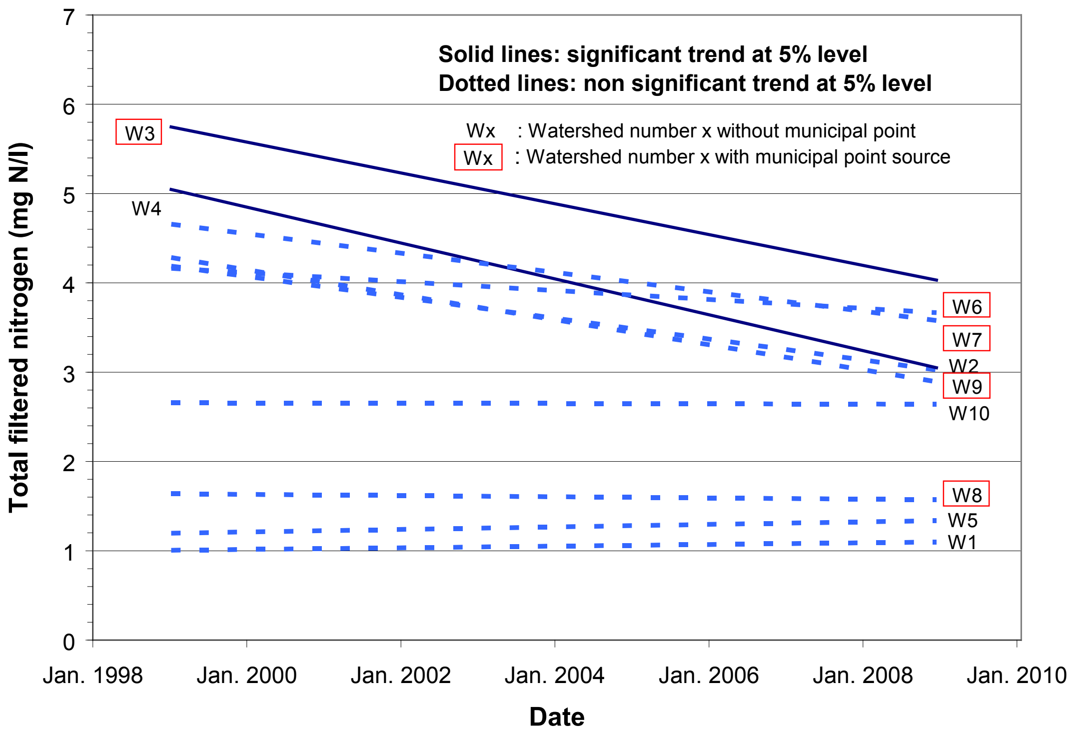

Figure 5. Trends of total filtered N concentrations in ten rivers over the last decade

Fecal coliforms

Trends for FC concentrations in the ten rivers over the last decade are illustrated in figure 6. In spite of the encouraging observed FC reduction in one of the rivers studied, in seven of them median concentrations remain greater than the Québec water quality guideline of 200 CFU/100 ml for protection of direct water contact recreational activities such as swimming (MDDEP, 2009). For one river, more than one half of the measured FC concentrations remain greater than the Québec guideline for indirect water contact activities like boating and fishing (1 000 CFU/100 ml). However, it should be stressed that direct water contact activities were not among the water uses that were targeted for recuperation by the Québec pollution abatement programs in agricultural watersheds.

These results suggest that the measures to reduce diffuse pollution over the last decade, mainly oriented on P pollution, had a limited effect on FC concentration and indicate the need to continue the efforts to further reduce FC pollution. The increasing proportion of cattle AU with controlled access to watercourses, raising from 49% to 81% in Québec in the last decade, and manure treatment, adopted by 2% of AU (BPR, 2008), are examples of measure that should be continued.

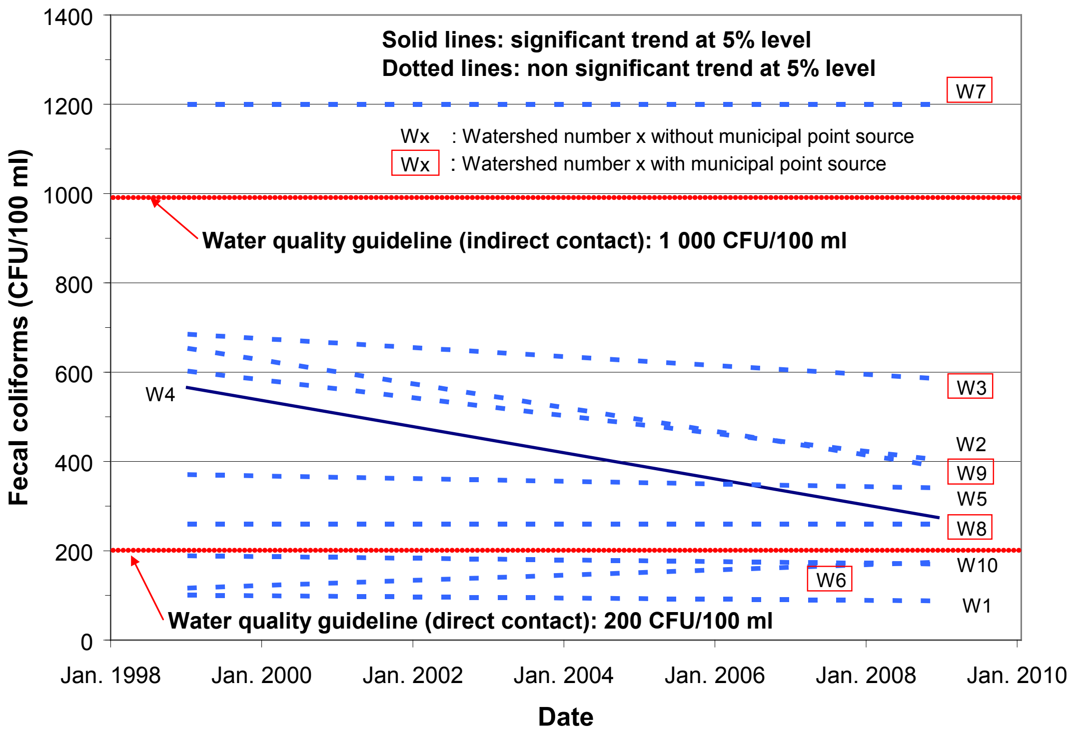

Figure 6. Trends of fecal coliform concentrations in ten rivers over the last decade

Turbidity and suspended solids

Turbidity Trends for turbidity values in the ten rivers over the last decade are illustrated in figure 7. Observed turbidity increases in eight of the rivers studied suggest that the measures to reduce diffuse pollution in the studied watersheds were not effective to reduce turbidity in these rivers.

Suspended solids Trends for SS values in the ten rivers over the last decade are illustrated in figure 8. Observed SS increases in two of the rivers studied and absence of change in others suggest that the measures to reduce diffuse pollution in the studied watersheds were not effective to reduce SS in these rivers.

Even if some soil conservations actions such as increasing no till crop areas, which raised from 36% to 48% of annual crops in Québec in the last decade (BPR, 2008), should have contributed to reduce the turbidity and SS concentrations in some of the studied rivers, other factors such as the proportion of annual crop, which increases of 8% in the last decade (BPR, 2008), can have had a reverse effect. Moreover, we can not exclude the effect of a possible increasing trend in river flows to explain the increasing trends in turbidity and SS measurements. River discharge validated data should be integrated in the analysis to see if these trends are caused by hydrologic factors. However, the results suggest the need of more efforts to reduce this type of pollution.

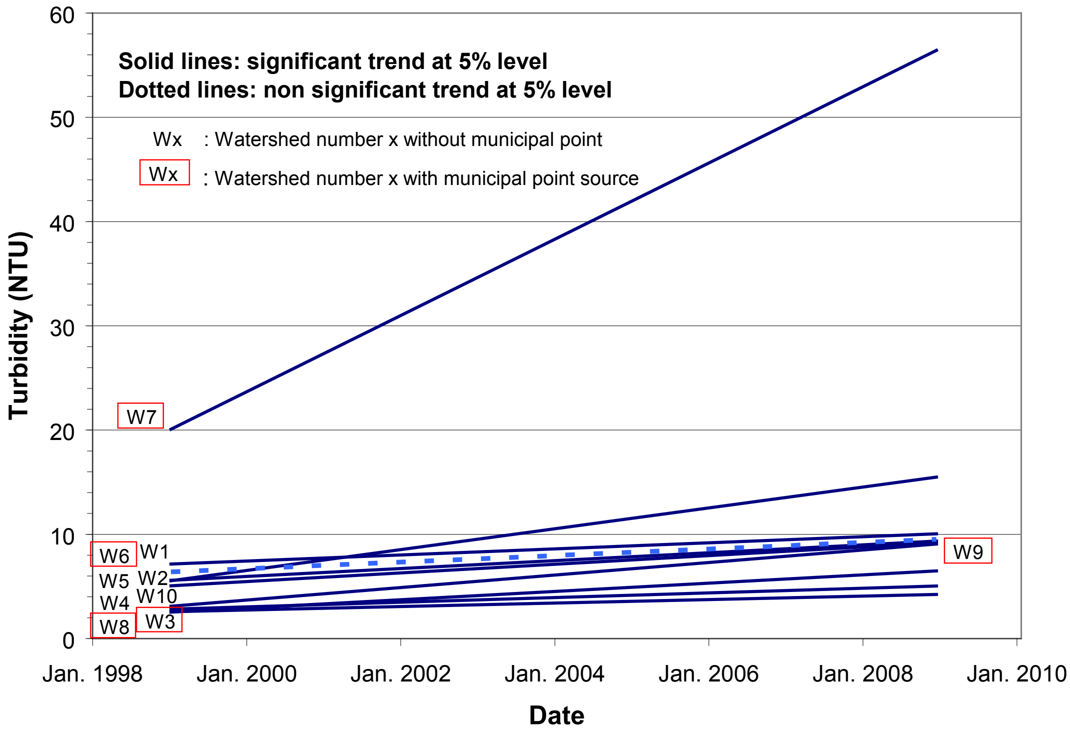

Figure 7. Trends of turbidity values in ten rivers over the last decade

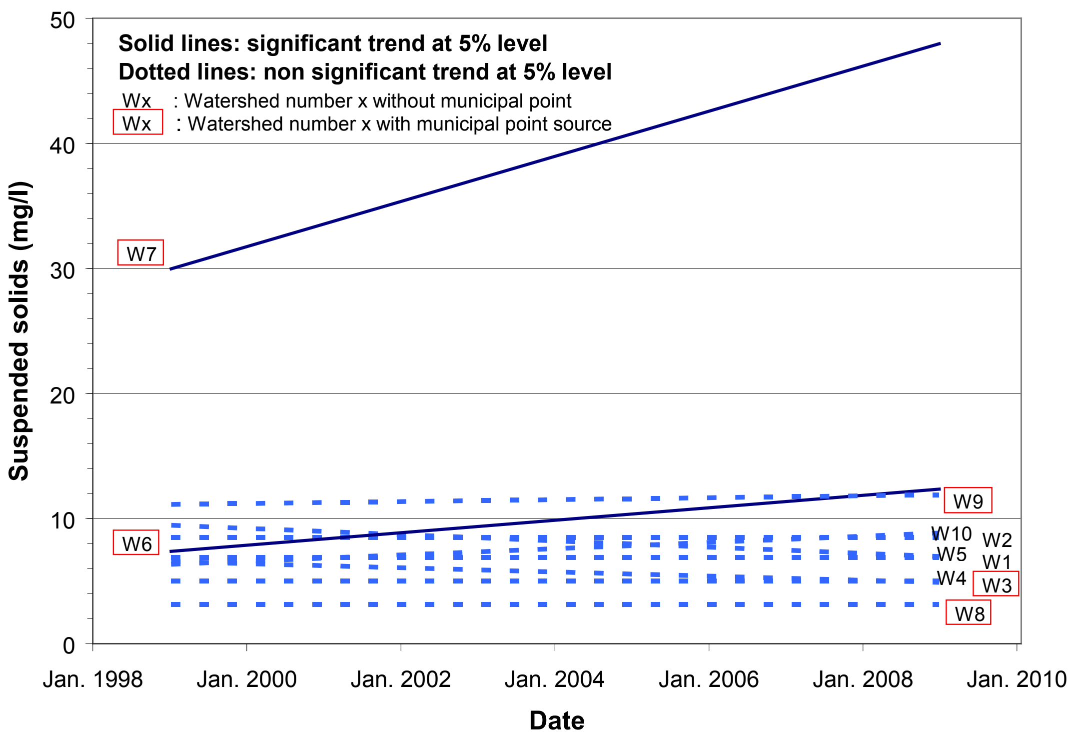

Figure 8. Trends of suspended solid concentrations in ten rivers over the last decade

Effects of discharge and measures to reduce diffuse pollution sources

The significant trends observed in water quality can be explained either by changes in agricultural practices, by upgrading of septic systems or by hydrological factors. We did not take into account flow in the trend analysis because of data availability. Preliminary river flow data analysis suggests an increasing trend in discharge over the last decade for five of the seven rivers with discharge data. However, non validated data at the end of the decade include possible presence of ice effect that would overestimate discharge values and generate a false positive trend. Furthermore, there is little available quantitative information at the studied watershed scale on changes in agricultural practices or septic systems improvements.

As a real increasing trend of river flow over the last decade could explain the turbidity increase observed in most rivers and the SS increase in some, one would expect as well an increase in other parameters related to river flow like P. So, the observed P reduction in spite of turbidity increase suggests an important effect of measures to reduce diffuse P sources. Widespread source reduction measures such as phytase in animal food and mineral fertilizer P reduction can have effects on river P, but not on turbidity, and can explain the opposite trend obtained for these two parameters.

In the near future, trend analysis on flow adjusted data could permit to confirm that measures to reduce pollution from diffuse sources over the last decade have been effective for improving water quality, particularly for P. In these watersheds, actions taken to reduce the diffuse sources over the last decade should also be inventoried in order to quantify the extent of the changes that did take place and identify the more efficient ones.

CONCLUSIONS

River water quality trends in the last decade in ten watersheds in Québec where diffuse pollution is dominant were evaluated. Results suggest that the measures to reduce diffuse pollution, mainly oriented on P sources, permitted to improve water quality, in most studied rivers for P and, for some rivers, for N and FC. However, P concentrations remain higher than the Québec guideline for most of the rivers, indicating the need to continue efforts. The increase trend in turbidity measurement for most rivers suggests a possible effect of discharge. Future work should take into account validated discharge data and watershed scale information on measures adopted to reduce diffuse pollution when they will be available. A paper including these improvements has been submitted to *Water Science and Technology*.

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4 POLICY AND ECONOMICS TO MANAGE DIFFUSE POLLUTION

Emerging economic instruments for addressing diffuse pollution

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Abstract

This paper seeks to assist non-economist diffuse pollution managers interested in better understanding the fundamentals of a select group of economic instruments that are currently emerging in water pollution control policy environments in developed countries throughout the world. Four such marginal modifications to existing diffuse pollution control base policies are explained: competitive best management practice implementation grants, conservation easement purchase initiatives, water pollution mitigation banking or 'offsets' systems; and water quality trading projects and programmes. It is concluded that application of these economic instruments, where institutions and technology permit, can likely improve upon the economic efficiency and/or cost effectiveness of addressing diffuse pollution problems. This is attributable mainly to these instruments' influence on the incentives dynamics for diffuse pollution abatement.

Keywords

Competitive diffuse pollution BMP grants, conservation easements, water pollution mitigation banking, water quality trading

INTRODUCTION

There is a rich body of theoretical and empirical research on the comparative merits of various 'economic instruments'[1] to address diffuse pollution. Among these instruments is the dissemination of the research itself, which aims to educate and inform people of the social costs of diffuse pollution in an effort to persuade them to curb their polluting activities. But perhaps more common in the literature are explorations and evaluations of the relative theoretical performances of more direct 'carrots' and 'sticks' approaches, sometimes referred to as 'mechanism design theory' (Baerenklau, 2002). In other words, much of the social scientific research into influencing human behaviour to reduce diffuse pollution compares instruments that punish polluting activities – i.e., sticks (e.g., common law liability, statutory regulations and standards, pollutant discharge taxes) – with those that reward actions taken to reduce or eliminate diffuse pollution – i.e., carrots (e.g., competitive grants for installing best management practices, water quality trading programmes).

As an effort to adequately cover the broader topic of 'economic instruments' to address diffuse pollution is well beyond the scope of this paper, its focus is rather to explain some of the instruments within the smaller subset of 'carrots-based' approaches, and within that subcategory, illuminate a few that seem to be growing in popularity and promise around the world. In so doing this, in no way are the authors attempting to make the contention here that these instruments are universally superior to 'sticks-based' approaches in delivering more economically efficient levels of in-stream diffuse pollution or even more cost-effective in achieving government-mandated diffuse pollutant loadings reductions. Nor are we conceding their inferiority in these regards. And we are not even attempting to address the parallel and very important issues of equity

1. It should be noted here that many researchers reserve the use of the term 'economic instruments' for those associated with harnessing market forces to effectuate the achievement of generally desirable social objectives such as diffuse pollution reductions (i.e., 'carrot' approaches), while using the terms 'regulatory instruments' or 'coercive instruments' (i.e., 'stick' approaches) when referring to the more traditional government interventionist measures aimed at internalising social costs on the producers and consumers that generate those costs (i.e., correcting for 'market failures'). The authors of this paper use the modifier 'economic' and thus also the term 'economic instruments' in the broader sense, where any system of incentives, whether negative or positive, with the potential to influence an economic agent's behaviour is 'economic' in nature. Thus a tax on diffuse pollution and a subsidy to prevent diffuse pollution are both considered 'economic instruments' by the authors of this paper.

and fairness in the implicit assignments of diffuse pollution control responsibilities via the introduction of these or other economic instruments. The intent of this paper is to simply provide readers with a better understanding of the fundamentals of some of the increasingly popular 'carrots-based' economic instruments to address diffuse pollution that are emerging in various regions throughout the world.

The following four emerging economic instruments are described in the most general terms:

- Competitive best management practice implementation grants;
- Conservation easement purchase initiatives;
- Water pollution mitigation banking or 'offsets' systems; and
- Water quality trading projects and programmes.

It is important to note that these economic instruments are not wholly distinct from or necessarily mutually exclusive to one another or to sticks-based approaches (e.g., management practice technology standards requirements). In fact, all are predicated in actual practice on some form of commonly observed statutory or common law (or at least customary) system for allocating initial water pollution control responsibilities (i.e., system for allocating shares of streams' waste assimilative capacities). This is the reason the term 'market-based' instruments is avoided here, as typically such instruments are marginal modifications to policies that are based in government regulations and/or government financing systems and a centralised process for allocating shares of assimilative capacities amongst all dischargers in a common water body or catchment.

COMPETITIVE BEST MANAGEMENT PRACTICE IMPLEMENTATION GRANTS

In Europe, the Common Agricultural Policy Single Farm Payment system awards monetary payments[2] to farmers from government if certain codes of practice are implemented on their farms, including Best Management Practices (BMPs) to reduce or eliminate agricultural diffuse pollution. Similarly, in the United States (US), the US Environmental Protection Agency's (EPA) Clean Water Act Section 319 program provides States with grant funds to address their respective diffuse water pollution problems, which includes awards to enterprises that generate diffuse water pollution for the purposes of implementing mitigating measures. Among these enterprises, of course, are farms of various natures and sizes, which can also draw from Federal cost-share funds for mitigating agricultural diffuse pollution (e.g., Environmental Quality Incentives Program). The US also now provides grant funds to address industrial and municipal diffuse pollution out of a program (Clean Water Act State Revolving Fund) originally intended to finance exclusively the construction or improvement of wastewater treatment plants and collection systems.

This government-sponsored 'economic instrument' – paying enterprises that generate diffuse pollution to voluntarily install or employ mitigation measures – is arguably the universal historic status quo in addressing the diffuse pollution problem. It is in no way unique to the US or European Union (EU), nor is it the only means by which US States, EU Member States or other countries such as Australia, New Zealand and Canada attempt to manage diffuse pollution. But it has arguably been, in the most general sense, the predominant approach historically. These basic schemes are thus not 'emerging' in any real policy innovation sense in most developed nations, albeit they are generally increasing in scope and complexity.

What has been emerging in the past couple of decades in the US, EU and some other developed parts of the world is new regulation to control diffuse pollution. Introduction of the of the Nitrates Directive to EU Member States and the phased National Pollutant Discharge Elimination System Industrial and Municipal Stormwater Regulations serve as good examples.

2. The distinction between subsidies and grants are ignored in this paper, as the concept of the competitive BMP grant instrument's intent to compensate the diffuse pollution source for all or part of its costs of mitigation measure implementation is what is critical to this cursory level of comparison between instruments. However, it is acknowledged that the mechanism by which a source is compensated can be a program administration performance factor.

This relegation to incrementally introduce regulatory 'sticks' to policies for addressing diffuse pollution, which were historically dependent mostly on public education and voluntary implementation of measures (usually financed in large part by government payments), is likely due to several factors. Perhaps first and foremost is the fact that the proportion of waterways reported by States as impaired due to diffuse pollution versus wastewater effluents has increased. This is likely due to the relative success of point-source pollution control measures over the past several decades, which incidentally, has resulted in marginal pollution abatement costs at end pipes escalating to the point in which they are well in excess of many of the marginal costs of diffuse pollution abatement options yet to be employed. It is probably also due to improvements in watershed/catchment-based monitoring and modelling, which has allowed water pollution managers to better detect diffuse pollution and better quantify the extent to which these dischargers are contributing to the contraventions of ambient standards on waterways receiving both point-source and diffuse pollutant loadings. Regardless, what is clearly 'emerging' in every sense at the current time is a global geographic patchwork of mixed carrot and stick approaches to addressing diffuse pollution, with each respective strategy having a different balance of self-funded regulatory compliance by sources and government-sponsored subsidy and grant schemes to ameliorate some or all of this cost burden. And emerging out of this transforming status quo are marginal carrot-oriented modifications to these base policies. One such modification is the *competitive* BMP implementation grant.

Sometimes also described as uniform or discriminative price auctions for diffuse pollution BMP implementation funds (Cason and Gangadharan, 2003), competitive BMP implementation grants are distinct from the traditional government payment schemes (e.g., Single Farm Payments or Section 319 Grants) in that each diffuse source that is awarded funds does more than simply propose and implement a one-size-fits-all mitigation measure for their source category (scaled of course to the size of their enterprise). In order to be awarded competitive BMP implementation funds, sources must propose measures tailored to their respective enterprises' operations and impacts on their proximal receiving waters. This must generally also be accompanied by adequate supplementary information (e.g., engineering and opportunity cost estimates, etc.) indicative of the extent to which proposed measures will be economically efficient (i.e., evidence that marginal benefits to water users exceed marginal costs to cost-sharing government and source) or at least cost effective (i.e., evidence that the proposed BMP implementation strategy is a relatively low-cost means of contributing to the attainment of a government-mandated ambient water quality standard).

The emergence of this marginal modification to the diffuse pollution base policy of mixed regulatory requirements and government implementation funding, at least in the US and Europe, is likely attributable to the increased pressure diffuse sources are under to implement BMPs now that doing so is no longer entirely voluntary. At least two things should be different from the perspective of the diffuse sources. First, there should be added curtailment to their ability to exaggerate their costs to make implementation of the measures profitable to their enterprises rather than just budget-neutral or net costly. Second, the threat of fines for noncompliance with the new regulations, as opposed to simply the threat of the introduction of costly new regulations, should have an enhanced coercive effect on sources. Complete inaction (i.e., noncompliance and no grant-fund proposal or the proposal of a non-competitive BMP implementation strategy) can result in both fines and unsubsidised compliance costs.

CONSERVATION EASEMENT PURCHASE INITIATIVES

Many competitive BMP implementation grant schemes include grant funds to finance the most technically simple diffuse pollution BMP of all – the cessation of polluting activities on certain high-impact land parcels. This can be done via initiatives that provide for the purchase or leasing of the land use rights associated with the polluting activities themselves, i.e., conservation easement purchase initiatives. Before the wave of new diffuse source regulations emerged over the past two decades, and before the development of catchment/watershed-scale geographic information system (GIS)-based water quality modelling, agricultural diffuse pollution was addressed in large part by government purchases of temporal use rights to riparian planting and/or grazing land. Although farmers would have likely known a great deal about the costs and perhaps even the effectiveness (and sometimes resulting benefits) of any diffuse pollution mitigation measures they could have implemented at that time, they had limited or no positive incentives to communicate this information to water pollution control authorities administering non-competitive BMP implementation grant programs. In fact, to do so might have provided a regulatory authority with the rationale to introduce new regulations. It could have also exposed the information-sharing sources to liability for damages to other water users. Thus, due to both the incentives dynamic and the absence of modelling tools and monitoring networks to estimate the source, transport and fate of diffuse pollutants, this blunt instrument for addressing diffuse pollution was quite common.

Two decades later, however, these conditions have changed in many developed countries due in part to reasons noted in the preceding section of this paper. Under for instance the US Conservation Reserve Program and Australia's National Heritage Trust, a competitive tendering process is administered by government to award diffuse pollution BMP implementation funds based on the estimated relative cost-effectiveness or economic efficiency of any one proposal (US General Accounting Office, 1992; Heaney and Baer, 2002; Gordon, 2003). New applicants don't automatically qualify based simply on the business attributes of their enterprise. Still common amongst the BMPs is the simple cessation of polluting activities on lands draining to surface and/or infiltrating groundwaters, as engineering and maintenance costs of this type of measure can often be much lower than those of new structural or operational measures. In most general terms, if the opportunity cost of pulling that land out of production for a set period of time can be covered in part or in full by government payments, a mutually beneficial exchange between the land-owning enterprise and the other relevant water users (represented in this example by government) is a strong possibility. The enterprise suffers an opportunity cost (and perhaps some maintenance and small engineering costs) less than or equal to the amount of the government compensation, and the other water users gain marginal benefits from the diffuse pollutant reductions with a total value in excess of this government expenditure.

Unlike the larger economic incentives category of competitive BMP implementation grants, conservation easement purchases are not limited to government authorities. Private-sector entities and non-profit organisations such as the Nature Conservancy are steadily emerging as alternatives to strictly public-sector remedies to diffuse pollution problems. Like the Conservation Reserve Program and National Heritage Trust, diffuse source enterprises can sell or lease to these private or non-governmental groups the use rights to the lands they own that contribute the most to any given diffuse pollution problem. As the owners or more personally proximal stewards of these scarce financial resources, the purchasers have an obvious added incentive over governments to make purchases that better maximise the effectiveness or efficiency of achieving their conservation objectives. Like government purchasers of conservation easements, private and non-governmental sector purchasers often optimise across multi-objective conservation criteria (e.g., habitat restoration, recreational resource provision) rather than focus exclusively on more narrowly defined water quality improvements.

WATER POLLUTION MITIGATION BANKING OR 'OFFSETS' SYSTEMS

Progressing along the complexity spectrum of economic instrument policy add-ons, water pollution mitigation banking – also commonly referred to as 'offsets' systems (Rolfe et al., 2004) – harness market-driven forces for further economic development to create *quid pro quo* proffers that can eventuate into net water quality improvements. In water pollution control policy environments in which ambient water quality standards and wasteload allocations amongst all dischargers are established and accepted by all water users, water pollution mitigation banking is an option on water bodies or in catchments in which current wasteload allocations consume the entire assimilative capacity of the water body or catchment. **Figure 1** is a simplified schematic of water pollution mitigation banking.

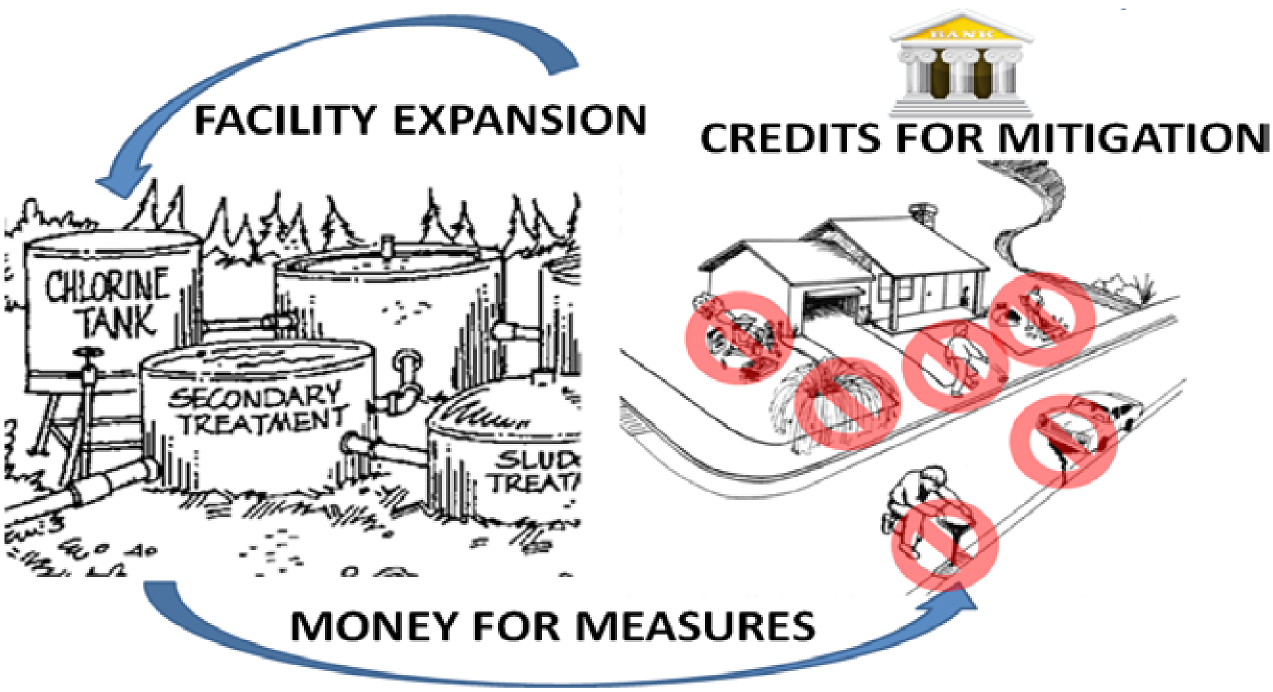

Figure 1. Simplified schematic of bi-lateral water pollution mitigation banking

A municipal wastewater treatment plant discharging to a water body with no available assimilative capacity to accommodate the plant's potentially desired expansion to accept wastes from the collection system of a recently annexed service area will not be able to obtain a permit (i.e., discharge consent) for this expansion from the pollution control authority charged with achieving or upholding the ambient water quality standard. This is unless the treatment plant agrees to install highly and perhaps prohibitively expensive tertiary treatment for the water-quality-limiting pollutants it discharges. If an older residential development is not subject to regulations requiring the installation of relatively low-cost storm sewer pollution mitigation measures such as storm drain filters, or if such regulations simply have not and likely will not be enforced to any significant degree in the near term, the operators of the wastewater treatment plant may create an opportunity to simultaneously increase its loadings and stay within its budget constraints via mitigation banking. By paying for the older residential development's storm drain filtration system, the pollutant reductions yielded from this measure can earn 'credits' for the treatment plant to be held in a mitigation bank. If the resultant pollutant reductions associated with these credits are equal to or in excess of the reductions needed to lower total water body loadings to the point in which the water body can safely assimilate the treatment plant's proposed increase in discharge at secondary treatment levels, the credits can be used by the treatment plant to offset its increased loadings.

In cases in which the ambient standard is not being met due to total loadings in excess of the water body's assimilative capacity, the pollution control authority will likely require the treatment plant to generate and redeem credits in excess of those needed to cover its proposed increase in loadings. This will have the ultimate effect of either maintaining the water quality standard more cost effectively in the face of increased loadings from the treatment plant or making net pollutant reductions toward the achievement of the water quality standard. If all stakeholders (i.e., treatment plant, residential development association, other water users, pollution control authority) have no other eminent plans to alter the status quo of water use (which includes of course the use of the water body's assimilative capacity), the mitigation banking option presents a win-win scenario for all relevant parties.

If the treatment plant's plans to treat the annexed area's discharge are foiled for some reason after the plant has invested in the storm drain filtration system, it can sell the credits it has earned to other potential dischargers wishing to expand or locate along the water body. In fact, as illustrated in **Figure 2**, if pollutant reductions from the storm drain filtration system are well in excess of those needed to offset the treatment plant's expansion and its commensurate increase in loadings, the surplus in credits can be used to offset both the treatment plant's expansion as well as accommodate the development of a new parcel of land along the water body (one with the potential to contribute to new diffuse pollutant loadings).

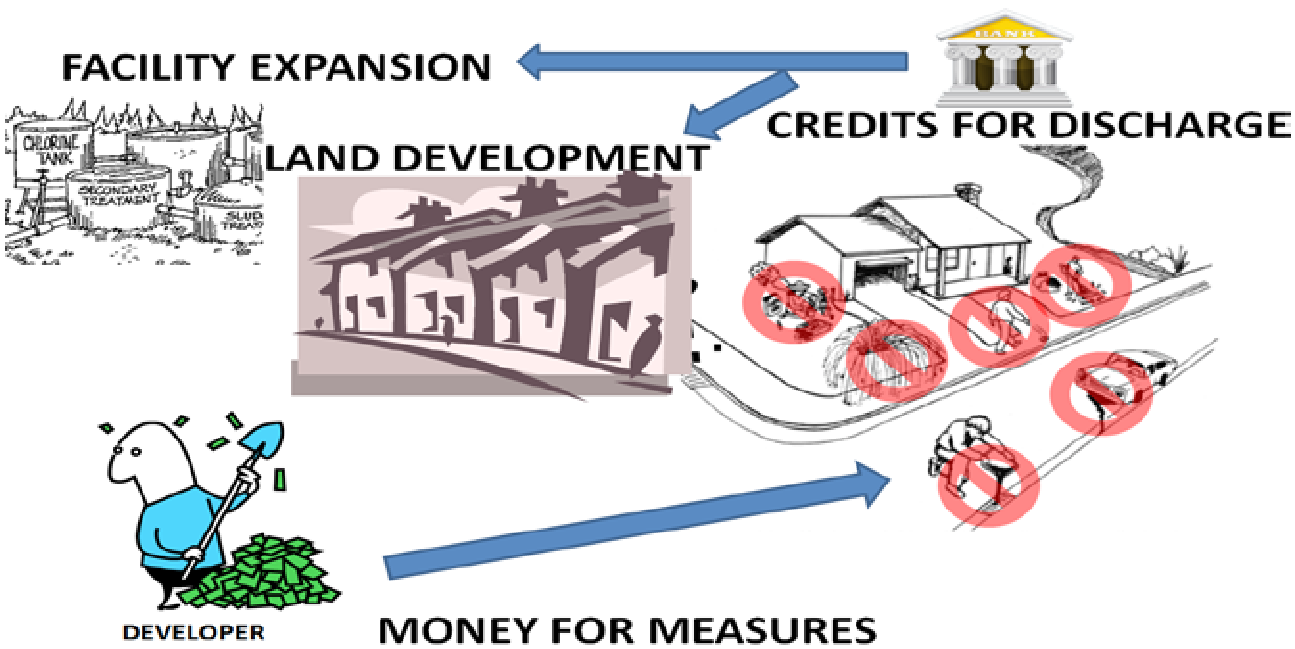

Figure 2. Simplified schematic of multi-party water pollution mitigation banking

The same conditions imposed by the pollution control authority will typically apply for bi-lateral as well as this type of multi-party diffuse pollution mitigation banking – existing or new sources of point-source or diffuse pollution can increase their respective loadings as long as the redistributed total loading to the water quality limited segment of the water body is either the same or net negative[3].

A water pollution mitigation banking system such as the oversimplified theoretical one explained here *does not* accommodate new discharges at the expense of jeopardising the maintenance or achievement of water quality standards. Such systems create new positive incentives for water quality standards to be achieved (or maintained) more expeditiously and cost effectively while accommodating certain economic development initiatives that often come with new discharges.

Experimentation with and implementation of water pollution mitigation banking systems or derivations of such systems are ongoing in multiple watersheds/catchments throughout the world, including in the US, Australia, Canada, New Zealand and Europe (Selman et al., 2009). Much of the literature doesn't make a distinction between mitigation banking, offsets and 'water quality trading' applications, as none seem to have a commonly observed definition, and the distinctions

3. It is important to note that most water bodies do not assimilate wastes originating from various sources in various locations uniformly, nor are all segments of a water body homogenous with respect to their respective abilities to assimilate these wastes. Thus, unlike some air emissions offset systems that assume a homogenous 'bubble' over the relevant sources, transfer coefficients have to be developed for each sources' pollutants via water quality modelling and applied to end-of-pipe or edge-of-field (or atmospheric depositional or groundwater infiltration) loadings in order for stream segment loadings to be standardised into bankable credits.

between them can be quite subtle. For the purposes of this paper, the main distinction made between pollution mitigation banking (or offsets) and water quality trading is that banking/offsets systems typically require *ex ante* measures implementation and evidence of the effectiveness of the measures before credits are banked and redeemable. In contrast, a water quality trading application (as described in the proceeding section and at least as typically regarded in the US), permits trades between dischargers without a banking instrument *per se* and without observable *in situ* evidence of the effectiveness of the measures to be applied. In the US, water quality trades can be made on the basis of modelled mitigation measures' estimated effectiveness in contributing to the pollutant reductions needed for ambient standard attainment or maintenance. This is due to the fact that the new US system of five-year watershed-based permitting, in conjunction with the well-established wasteload allocation process and Total Maximum Daily Load development process, provides relative assurance that trading will not result in contraventions of ambient standards.

WATER QUALITY TRADING PROJECTS AND PROGRAMMES

As the US has more applications of water quality trading than any other country and arguably has the most well-established water quality trading policy in the world, it's perhaps simplest to explain the fundamentals of water quality trading applications within the context of the US water pollution control policy environment.

In the US, each point-source discharger has a set of regulatory requirements that either specifies the amount of pollution they can contribute to a stream or that specifies or recommends required pollution control measures. This holds true for some diffuse sources as well, although certain agricultural facilities in some states are still effectively not subject to such regulation. Applications of the US Environmental Protection Agency's (EPA) Water Quality Trading Policy *do not* dismiss these point-source or diffuse-source pollution mitigation measure regulatory requirements.

Water quality limited streams in the US are ones in which full compliance with the sector-specific regulatory requirements for wastewater and diffuse pollution (where applicable) mitigation measures are inadequate to achieve one or more of its ambient water quality standards. In other words, when modellers simulate conditions of critical flow and maximum permitted pollutant loadings pursuant to the TMDL development process for these water bodies, they show that less than 100% of the required pollutant reduction is achieved with these mandatory requirements. In the theoretical scenario presented in **Figure 3**, only 85% of the 100% of necessary pollutant reduction is achieved through full implementation of existing regulatory requirements.

Supplementary Measures	Necessary Pollutant Reduction	Costs
AGRI Buffer Strips	5%	$10K
AGRI Retention Ponds	5%	$20K
AGRI Manure Storage Facilities	5%	$30K
MUNI Tertiary Treatment	5%	$100K
MUNI Septic System Tie Ins	5%	$200K
INDR Tertiary Treatment	5%	$300K
Supplementary Measures Total from MUNI	10%	$300K
Supplementary Measures Total from INDR	5%	$300K
Supplementary Measures Total	15%	$600K
Waste = ($300K + $300K) - $60K = $540		

Figure 3. Hypothetical US wasteload allocation scenario

In this scenario, some or all dischargers will have to employ supplemental measures to achieve ambient standards on their water body. For instance, an agricultural facility (AGRI) might have to install riparian buffers, retention ponds, or manure storage facilities. A municipality (MUNI) may be required to tie houses on septic tanks into the city sewer or may have to upgrade the treatment works from secondary to tertiary treatment for certain water quality limiting pollutants. Industrial dischargers (INDR) may also have to upgrade treatment beyond best available technology or even beyond new source performance standards. Each of these supplemental measures will have some degree of effectiveness toward achieving the 100% pollutant reduction required to achieve the ambient standard for any given pollutant limiting the water quality of the water body. In this example, respective implementation of each supplemental measure would get the water body 5% closer to 100% of the necessary pollutant reduction.

Each of these supplemental measures also has a marginal cost, and neither the effectiveness nor the cost of each measure implemented at the various sources will likely be exactly the same. For instance a retention pond or buffer strip on a farm is often more effective and less costly in removing nutrients from runoff than an upgrade from secondary to tertiary treatment of effluent. When lining up all of the supplementary measures that can be applied at each pollution source, typically some are significantly more cost-effective than others. This is due predominantly to the differences in marginal costs of measures implementation at each source coupled with the variability amongst each source's distinctive impacts on the water quality limited segments of the receiving waters. So the wasteload allocation scenario with which pollution control authorities often find themselves faced when allocating loadings on water quality limited streams can often be similar to the one shown in **Figure 3**. Here 15% of the total required pollutant reduction is not addressed with existing regulations. So some combination of supplemental measures must be applied, at some cost. And again, the 85% loading reduction requirement pursuant to existing regulations *is not* on the negotiating table – it's a given.

It may seem obvious that the EPA (or its state delegate) should allocate loading reduction responsibilities such that the most cost-effective supplemental measures will be employed up to the point of achieving the 15% remaining required reduction. In this oversimplified example, this would essentially entail the EPA assigning full responsibility to the agricultural facility, with it reducing the remaining 15% pollutant reduction needed at a total cost of $60K. But for the reasons stated already, and also for probably the most significant reason, at least in the US – protection of use rights on private property – it is sometimes the case that the cost-effective allocation of pollution control responsibilities is foregone in favour of targeting the deep pockets of industrial enterprises and the many pockets of rationally ignorant municipality taxpayers. Quite simply, a non-cost-effective wasteload allocation can often prove much more politically expedient.

In the example here, if municipalities and industry pick up the tab for the 15% remaining reduction requirement, it costs an order of magnitude more: $600K. In simply subtracting that $60K from $600K in the hypothetical scenario in **Figure 3**, it is obvious that this politically expedient wasteload allocation results in a total waste of pollution control efforts totalling $540K. It is important to note that the EPA may have some sense of which combinations of measures are most cost-effective, but as mentioned before in the section on competitive grants, the best knowledge about the respective cost effectiveness of individual measures typically lies with the dischargers themselves.

In the simplified schematic of a hypothetical water quality trading application given in **Figure 4**, the municipality is assigned 10% of the reduction responsibility and the other 5% has been assigned to the industrial discharger. In the absence of water quality trading or some other marginal economic instrument application, the wasteload allocation process ends here. If water quality trading is accommodated, it can continue.

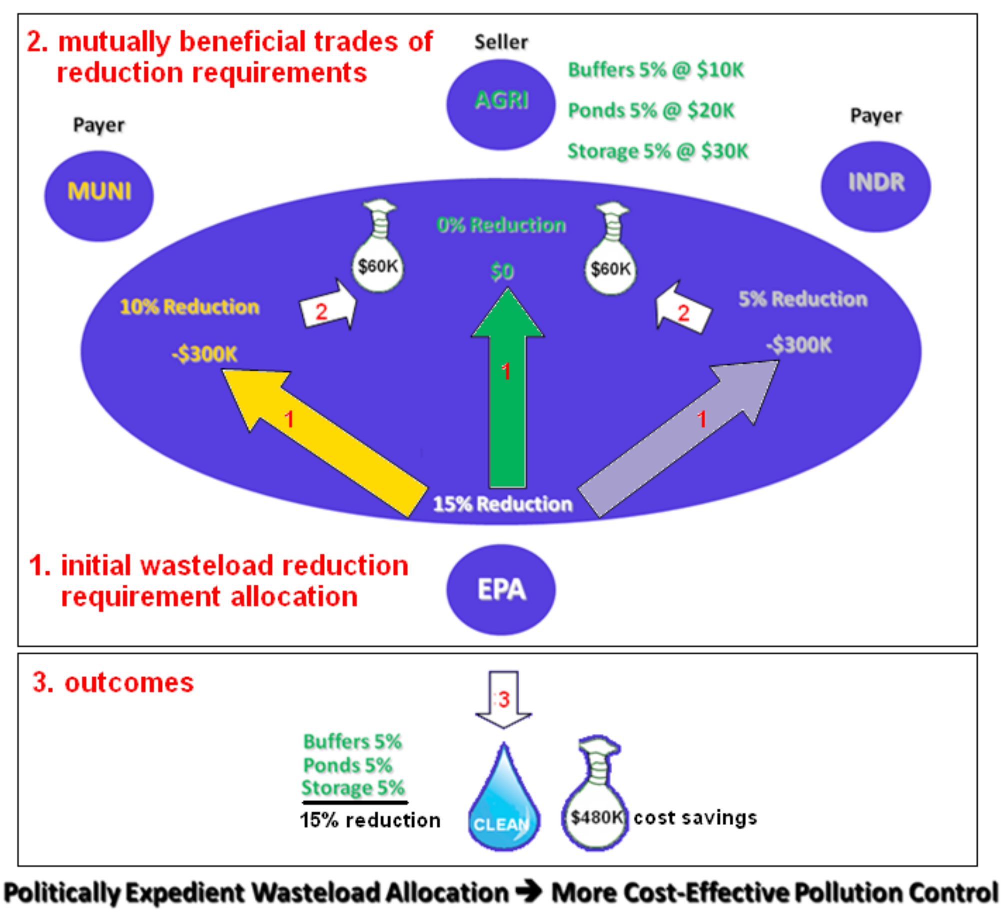

Figure 4. Simplified schematic of hypothetical water quality trading application in the US

If the municipality is unable to immediately come up with the $300K it is now facing, but it can get its hands on $20K right away, it might choose to pay the agricultural enterprise perhaps double the cost of installing the buffer strips to avoid reducing 5% of the loading through septic tank tie ins, which was going to cost $100K. The municipality will not know exactly how much the farmer's cost will be, so the farmer might very well build in such a profit. The municipality might also pay the farmer to install retention ponds for the same reason – to avoid a treatment plant upgrade that would have cost $200K.

Similarly, the industrial facility is facing a secondary-to-tertiary treatment upgrade to meet its new 5% reduction requirement, and it's going to cost $300K. Faced with such a prospect, the industrial discharger may choose to cover the cost of manure storage for the agricultural facility. Not knowing exactly what this cost will be, it too could likely end up paying the farmer an amount in excess of the full measure implementation cost.

In the post-trading scenario illustrated in **Figure 4**, the same water quality target set prior to trading is still scheduled to be met, and perhaps it might be met much more expeditiously now that the municipality can for instance forego a bond issue or rate increase and the industrial discharger has an altered economic incentive dynamic that may not include litigation for a larger allocation of wasteload. The farmer has a strong new incentive to implement relatively cost-effective supplemental measures due to the fact that doing so could actually earn profits for the enterprise (as if the farm was in the business of 'producing' water quality in addition to its conventional agricultural commodities). Regardless, the hypothetical application detailed in **Figure 4** yields water quality standard attainment with $540K cost savings to dischargers.

Obviously, throughout the trading process, impartial water quality modellers must be on hand to predict the various proposed reallocations of wasteload and reduction requirement responsibilities to ensure no trade will result in a contravention of a water quality standard anywhere along the water body. Due to the relatively high degree of uncertainty with which these predictions must often be made, typically the EPA will build in a margin of safety at the point of trade so that the reallocation is certain not to result in a contravention of an ambient standard.

CONCLUSIONS

It is noted again that the authors make no attempt to achieve the following with this paper:

- Prove that the four economic instruments highlighted here are universally superior to 'sticks-based' approaches in delivering more economically efficient levels of in-stream pollution or more cost-effective in achieving government-mandated pollutant loadings reductions;
- Attempt to address the issues of equity or fairness in the implicit assignments of diffuse pollution control responsibilities via the introduction of these economic instruments (i.e., answer the question of whether the 'polluter pays' when these instruments are applied);
- Provide a comprehensive accounting of international applications of the four highlighted economic instruments or even explain in detail the mechanics and nuances of any one application;
- Apply mechanism design theory to compare the relative theoretical performances of the four highlighted economic instruments.

This was avoided here for four main reasons:

1. Addressing any one of these relevant and important items is well beyond this paper's scope.
2. Superior resources are already available that address these elements (see REFERENCES).
3. It is the opinion of the authors that no single economic instrument or combination of economic instruments are likely to be (or at least can be proven to be) universally optimal in delivering more economically efficient or cost-effective water pollution control, as each potential application area is likely to have different base policies, incentives dynamics, available technologies, etc.

4. Focusing on any one of these aspects of the highlighted emerging economic instruments for addressing diffuse pollution would have significantly compromised the main objective of the paper, which is to assist non-economist diffuse pollution managers in their efforts to better understand the fundamentals of a select group of emerging economic instruments to address diffuse pollution – instruments the authors believe these managers are likely encountering with increasing frequency in their reviews of professional literature and in their collegiate and public discourse on diffuse pollution management.

What should be concluded from this work are the following key points:

- There seems to be a general international consensus amongst diffuse pollution managers and researchers that often water pollution control policies as implemented stand to be improved with respect to the extent to which they yield economically efficient or cost-effective water pollution control.
- In many developed countries, it is widely suspected that often the industrial and municipal sectors implement mitigation measures that are comparatively less cost-effective than those that are technically feasible but foregone in the agricultural sector, due in part to unique political constraints that are inherent in regulating agricultural enterprises.
- Many diffuse pollution managers and researchers, and water pollution control professionals in general, including the authors of this paper, believe the attainment of water quality standards currently jeopardised in part by diffuse pollution might be expedited via experimentation with applications of the marginal economic instruments highlighted in this paper.
- The four economic instruments highlighted in this paper, if applied at appropriate times, in appropriate areas and in an appropriate manner, hold the potential to create new private-sector incentives for the expedited remediation of diffuse pollution problems and hold the potential to advance the more rapid development of the management tools needed to better understand the source, transport and fate of diffuse pollutants.

Figure 5 is an illustrative summary of the overall key message of this paper:

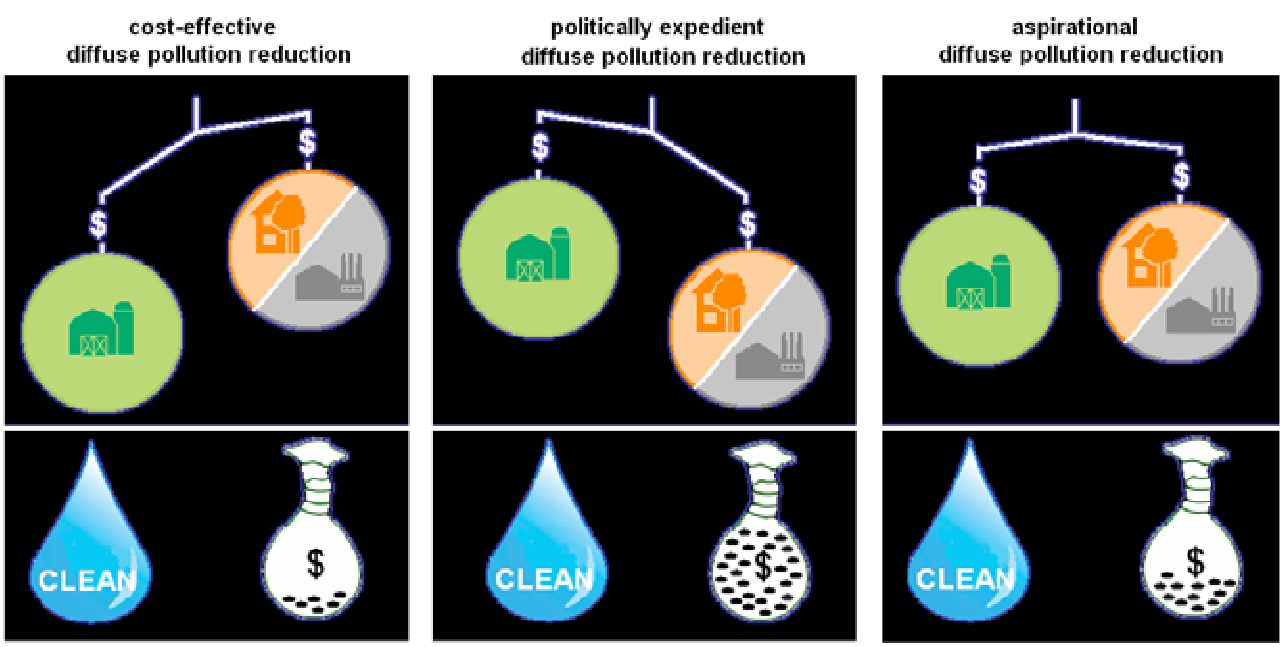

Figure 5. Illustration of overall key message of paper

If:

- Cost-effective diffuse pollution reduction in any given waterbody or catchment entails heavy cost impacts on sources with relatively low marginal mitigation measure implementation costs (e.g., agricultural enterprises) – sources that are unwilling and/or unable to absorb these costs; and
- Political forces are influencing the wasteload allocation process for the water body or catchment such that highly non-cost-effective allocations of pollution reduction requirements are suspected;

Diffuse pollution managers that aspire to achieve or protect ambient water quality standards on the waterbody or within the catchment should consider further investigating the potential for pilot testing and ultimately applying one or more of the many emerging economic instruments that are increasingly modifying base diffuse pollution control policies throughout the world, including and perhaps especially the four detailed in this paper.

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Regulatory and Voluntary Programs to Control Nonpoint Source Pollution in the United States

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Abstract

Nonpoint Source Pollution is the cause and source of the majority of water quality impairments in the United States. Under Section 319 of the Clean Water Act, the U.S. Environmental Protection Agency implements the national NPS program. Unlike the case for point sources, the CWA does not provide EPA with direct authority to implement NPS programs. The States are the primary implementing agencies and receive funding and program direction from EPA. States rely primarily on voluntary programs, but some States have begun in recent years to introduce some regulatory components into their NPS programs. In addition, there are important areas of overlap between the nonpoint source and point source programs, giving rise to a trend to regulate through the point source program some sources that previously had been treated as NPS – most notably larger animal feedlots and significant urban stormwater sources. During the past ten years, EPA has provided program leadership that has helped propel significant progress in three particular areas – the development and implementation of watershed-based plans; the use of low impact development (LID) techniques to infiltrate, evapo-transpire and use/reuse rainfall; and the identification, assessment, and protection of healthy watersheds. However, a great deal more work remains to be done to assure the protection and achieve the restoration of all waters affected by nonpoint source pollution.

Keywords

Nonpoint source pollution; runoff

BACKGROUND

The United States has implemented an active and evolving nonpoint source (NPS) pollution control program since enactment of Section 319 ("Nonpoint Source Pollution") of the Clean Water Act (CWA) in 1987. Section 319 does not define the term "nonpoint source"; EPA has informally interpreted the term to refer to sources that are not defined and regulated as "point sources", which in turn generally refers (through detailed statutory terminology and a considerable number of court decisions) to discharges through pipes and channels. Although not formally defined, NPS pollution is generally regarded to include runoff from agricultural operations (except for concentrated animal feeding operations of certain sizes, which are subject to regulation as point sources); forestry (again with certain exceptions, particularly for forest roads); urban runoff (subject to significant and growing exceptions as the point source program has gradually expanded to address large cities, moderate-sized cities, and an increasing number of small cities, as well as various site-level construction and development activities); hydrologic modification; (e.g., dams, channelization, and stream/streambank modification) and septic/decentralized wastewater treatment systems.

Statutory Background

In the U.S., since 1972, all point sources have been required by Section 402 of the CWA to have permits; they may not discharge without one. The permits are issued by states or EPA. Permits typically include numerical discharge limitations based upon both technology-based requirements (e.g., "best available technology economically achievable") and water quality standards (e.g., discharges may not result in water quality exceeding X ug/l). Violators of these permits are subject to a range of fines, civil enforcement, and criminal enforcement, depending on the circumstances.

In contrast to point source regulations and permits, Congress did not provide to EPA any regulatory authority when it enacted Section 319 of the CWA in 1987. Rather, States developed NPS management programs, which were to include, per Section 319(b)(2)(B), "nonregulatory or regulatory programs for enforcement, technical assistance, financial assistance, education, training, technology transfer, and demonstration projects." In short, they were not required to include regulatory components, and almost all State NPS programs do in fact rely primarily on nonregulatory approaches. A few States, however, have increased their use of regulatory approaches in recent years (e.g., California, Florida, North Carolina, and Washington, Wisconsin), as will be discussed below.

Scope of Nonpoint Source Pollution in the United States

Thus we have the conundrum, undoubtedly shared by many other countries represented at this conference, of having the least authority to manage the most prevalent sources of pollution in the United States. National statistics published in the National Water Quality Inventory show that 44% of assessed river and stream miles are impaired, and the leading sources of the impairments are notable for the prevalence of nonpoint sources. Taken in order, and omitting the category "Unknown/ Unspecified", the leading sources of impairment are agriculture, hydromodification, habitat alteration, natural/wildlife, municipal discharges/sewage, unspecified nonpoint sources, atmospheric deposition, resource extraction, and urban runoff/stormwater. Note that traditional industrial sources do not even make the "Top 10" list. Moreover, data from lakes and reservoirs tell a similar story. The good news is that the generation-old regulatory focus on cleaning up both industrial wastewater discharges and municipal sewage discharges in the U.S. has achieved considerable success. However, it now is clear that to achieve water quality standards in the tens of thousands of waterbodies that remain impaired, we will need to implement an equally effective nonpoint source program.

Early Program Implementation Efforts

In the 1990's, following enactment of Section 319, the national NPS program could accurately be regarded as largely a demonstration program -- demonstrating practices and program implementation methods that could effectively reduce NPS pollution. Through a grant program established under Section 319, States began to implement their programs with $40 million (U.S. dollars) and gradually grew to $100 million in the late 1990's. States also added almost $60 million to match the Federal contribution. However, divided among 50 States, several Territories, and Tribes, these funds were too small to enable the States to solve significant watershed-wide NPS pollution problems.

UPGRADING NPS CONTROL IN THE FIRST DECADE OF THE THIRD MILLENIUM

Beginning in 1999, Congress doubled the Section 319 appropriation to $200 million in Section 319 and has maintained that funding level ever since. As a result, funding levels became sufficient to implement at least some projects not only at a site (e.g., a farm, parking lot, or streambank) but also on a watershed basis. In other words, these funds could now be used not only to implement individual demonstration projects, but rather could be used to demonstrate real water quality improvement at the watershed level. This led to a considerably more ambitious and accomplished program.

Watershed-Based Planning and Implementation

Beginning in 2002, EPA's grant guidelines have required States to devote one-half of their Section 319 funds to remediating impaired waters by developing and implementing "watershed-based plans". The plans must include nine components, including detailed identification and quantification of pollutants and stressors in the watershed; estimates of the pollutant load reductions that are necessary to achieve water quality standards; identification of the practices that will need to achieve those load reductions; and other planning information. In addition to the grants guidelines, we also have published a 400-page *Handbook for Developing Watershed Plans to Restore and Protect Our Waters* and presented many training programs ranging from one hour to five days.

Our planning approach generally begins with a Total Maximum Daily Load (TMDL), which provides the pollutant load that the water body is capable of receiving without violating water quality standards. Once that numerical goal is established, the watershed-based plan fills in the details regarding which practices need to be implemented by which sources or set of sources in order for the TMDL to be achieved and for the waterbody to meet water quality standards.

We at EPA believe that a watershed-based planning approach to defining and solving water quality problems is an absolutely critical step in the process of successfully implementing a watershed-wide project and achieving water quality standards. If you have not yet clearly identified and quantified the sources of the water quality problem, and then clearly identified and quantified the relevant set of on-the-ground practices needed to achieve your goal, you will have sharply limited your ability to reach that goal.

While the concept of watershed plans is not at all new, the more rigorous and quantitative approach established in EPA's guidelines is new and has certainly presented technical challenges to some States. However, we have observed that, increasingly over time, States are proving themselves to be up to these challenges and are developing sophisticated, detailed plans that are establishing a clear path for successful implementation. Most states at this point are proudly posting their watershed-based plans on their websites. Here are a couple of examples:

Mill Creek, Pennsylvania. This 120-kilometre creek lies in a 76 square-kilometre watershed that is dominated by dairy operations which pose both manure and streambank erosion issues, and consequently the creek fails to meet water quality standards for nutrients and siltation. The watershed-based plan maps 200 farms and 600 sites that need to be remediated and includes a 20-page chart identifies the needed practices and their associated costs, culminating in a plan that will achieve water quality standards at an estimated cost of $5.5 million.

Blacks Creek, Pennsylvania. This is a much different type of environmental setting, although it is located in the same Commonwealth of Pennsylvania, this time on the western side. It is an old coal mining region, and many years after the active mining operations have ceased, it suffers from a legacy of severe impacts, including acid mine drainage that includes iron, aluminum, and other metals along with acidity. The Blacks Creek watershed-based plan was developed jointly, with Section 319 funds, by two consulting firms, BioMost, Inc. (a for-profit corporation) and Stream Restoration Incorporated (a non-profit corporation), but the plan was managed by Slippery Rock Watershed Coalition. This collection of Federal and State government, local citizen-led watershed groups, both public and private firms exemplifies the wide range of coalition-building that is possible when projects are focused at the watershed level. On the technical side, the plan describes all significant sources of mine drainage that impacts the watershed; develops treatment recommendations and cost estimates for each one; prioritizes the projects; and provides an implementation timeline.

This rigorous, detailed approach to developing and implementing watershed-based plans has enabled States to begin to make inroads on their huge lists of impaired waters. EPA publishes a Section 319 Success Stories summary of every watershed project that has successfully restored water quality on our Section 319 Nonpoint Source Success Stories website. We are currently achieving such reportable successes at the rate of about 50-68 Success Stories annually in the past three years. Most of these successes involve the participation of many landowners (e.g., agricultural producers) and/or other actors in the watershed, each taking appropriate actions to reduce the runoff of pollutants or to remediate physically damaged streambanks and streambeds.

This rate of success, however, needs to be measured against the scope of the problem. In the United States, the States are required by Section 303(d) of the Clean Water Act to identify waterbodies that are impaired. To date, over 44,000 TMDL's have been developed for impaired waters, and NPS pollution is a dominant cause or impairment in most of these. As impaired-waters lists continue to be refined based on additional data and TMDL's continue to be developed for those impaired waters, it would not be surprising to find over time that the U.S. has at least 50,000 waterbodies in the U.S. that are impaired solely or to a significant extent by nonpoint source pollution. At a remediation rate of 50 waterbodies per year, it would take 1,000 years to achieve water quality standards in all U.S. waters, which indicates that our current efforts and tools are inadequate to the task of remediating impaired waters.

Actions to Pick Up the Pace of Watershed Restoration

Short of statutory change, EPA is pursuing several avenues in our efforts to improve the pace of progress:

1. Cooperative Efforts with the U.S. Department of Agriculture: While EPA works with many governmental and non-governmental partners, the U.S. Department of Agriculture is our most significant partner in our efforts to reduce the large contribution by the agricultural sector to NPS pollution. During the past decade, USDA, like EPA, has received significant funding increases for its conservation programs; however, the amount is much larger than EPA's. A combination of conservation funds managed and distributed to agricultural producers by USDA currently provides approximately $4 billion annually to farmers across the country to implement practices to protect soil, water, air, and wildlife and to set aside particularly vulnerable lands. We are currently working closely with USDA in several key geographic regions to jointly focus our funds on solving specific water quality problems through concerted actions.

2. Increasing the Use of Point Source Authorities Where Applicable and Appropriate: The Clean Water Act authorizes EPA and the States to regulate "concentrated animal feeding operations" (CAFO's), and EPA defines that term to apply to animal feeding operations (AFO's) that have a certain number of animals (depending on type; e.g., dairy cows or swine); have a lower, mid-level number of animals but meet certain other attributes related to direct contact with water or mode of discharge to water (e.g., a flushing device); or are designated on a case-by-case basis based on a determination by the responsible State permitting agency (or in some cases USEPA) that the AFO is a significant contributor of pollutants to the water. In some States, the State and/or EPA are exercising their respective authorities to more closely monitor activities and determining whether certain AFO's should be regulated and permitted as CAFO's.

3. Raising the Technology Bar: EPA has recently begun to raise the technology bar through the promotion of more rigorous practices than in the past; these newer practices have been shown to be necessary in order to meet water quality goals in many watersheds. These practices have been set forth in a major new (and very large) guidance document, "Guidance for Federal Land Management in the Chesapeake Bay Watershed", which addresses all significant categories of nonpoint pollution. Thus it begins with a very large chapter on agriculture, which is the leading source of impairment in the Bay. http://www.epa.gov/nps/chesbay502/. This guidance makes recommendations intended to assure that nutrients are applied to the land only when and in the amounts needed. For example, if soil phosphorus exceeds a certain level, manure should not be applied to that cropland at all. This raises difficult questions regarding the management of excess manure, which in turn lead to exploration of alternative management and use of the manure. Other issues addressed include the need to restrict or tightly manage farming on highly erodible cropland; the need for close management of agricultural drainage systems; and the preservation and/or restoration of stream buffers.

4. Making Funding Contingent Upon Performance and Progress: EPA has focused recently on means to achieve a more expeditious pace of implementation in particular high-priority watersheds. It is critical that EPA and States use federal taxpayer funds as effectively as possible to achieve water quality improvement. Therefore, in the high-priority Chesapeake Bay, which is impaired primarily by NPS pollution, EPA has recently established specific short-term numerical pollutant-reduction goals for the States that contribute pollutants to the Bay. EPA has stated that its goal is to work closely with the States to assure that States meet these goals. However, if the States fail to meet those goals, EPA may as a last resort act to use available authorities to limit or prohibit new point source discharges of nutrients and sediments in the impaired waters and/or to withhold, condition or reallocate federal grant funds to achieve greater water quality improvement.

In addition to these efforts, some States have gone beyond the minimum requirements of the national program to develop regulatory components in their NPS programs. These include the States of California, Florida, North Carolina, Washington, and Wisconsin. For example, California has broad authority to regulate nonpoint source pollution and, while using it sparingly in earlier years, has in the past decade used it effectively to require farmers in the Central Valley of California and elsewhere to control their practices to, e.g., reduce off-site runoff of selenium. Similarly, it has used this authority to impose strict controls on forestry operations in particular watersheds in order to minimize any impacts on water quality. Wisconsin has established requirements to restrict livestock access to waters of the State and to require tillage setback from waterbodies, as well as other requirements. North Carolina regulates animal feedlots that are smaller than those regulated at the Federal level. However, even States that have some regulatory authority usually have processes that are intended to place initial emphasis on voluntary approaches unless and until these appear to be ineffective.

Radically Modernizing Urban Stormwater Thought and Practice

While the watershed-based approach is the fundamental approach EPA has been implementing to restore waters that have been impaired by NPS pollution and especially by agriculture, as described above, EPA has also focused increased attention during the past decade on protecting water quality from the ever-present threats of impairment presented by development in our urban areas, suburbs, and even exurbs. Together with EPA's point source program, which currently regulates some significant (and increasing) aspects of development and post-development runoff, EPA's NPS program has put a great deal of emphasis on low impact development ("LID") and green infrastructure ("GI"). See www.epa.gov/nps/lid and www.epa.gov/greeninfrastructure, as well as the previously cited "Guidance for Federal Land Management in the Chesapeake Bay Watershed".

It is worth pausing for a brief nomenclature discussion. Low impact development generally refers to systems and practices that mimic natural processes to infiltrate, evapo-transpire (return water to the atmosphere through evaporation or through transpiration by plants), or use/reuse stormwater or runoff on the site where it is generated. "Green Infrastructure", a term coined in the 1990's, has been defined as "an interconnected network of natural areas and other open spaces that conserves natural ecosystem values and functions, sustains clean air and water, and provides a wide array of benefits to people and wildlife". However, it has more recently also come to be used more narrowly in the context of stormwater programs, having roughly the same meaning as "low impact development", though both of these terms tend to be expressed with different scopes or shades of nuance depending on the user. I will use the term LID/GI for the remainder of this discussion.

LID/GI concepts grew out of frustration with the inadequacies of the previous generation of proposed solutions to stormwater problems. After a generation of inadequate efforts to control stormwater runoff through such mechanisms as off-site wet ponds and dry ponds, EPA as well as many states, local governments, and expert nongovernmental organizations have concluded that the preservation of pre-development hydrology should be the principal means of protecting or restoring water quality in the face of stormwater impacts.

In the natural, undisturbed environment, rainfall is quickly absorbed by trees, other vegetation, and the ground. Most rainfall that is not intercepted by leaves infiltrates into the ground or is returned to the atmosphere by the process of evapotranspiration. Significant runoff generally only occurs in larger precipitation events. Traditional development practices cover large areas on the ground with impervious surfaces such as roads, driveways, sidewalks, and buildings. Under developed conditions runoff occurs even during small precipitation events that would normally be absorbed by the soil and vegetation. The collective force of the increased runoff scours stream bottoms, erodes stream banks, and cause large quantities of sediment and other entrained pollutants to enter the water body each time it rains.

As watersheds are developed and impervious surfaces increase in area, the hydrology of the watersheds fundamentally changes over time, which results in degraded aquatic ecosystems. In recognition of these problems, stormwater managers employed extended detention approaches to mitigate the impacts of increased peak runoff rates. However, according to the National Research Council (an arm of the United States' National Science Foundation), wet ponds and similar practices are not fully adequate to protect downstream hydrology because of the following inherent limitation of these conventional practices: poor peak control for small, frequently occurring storms; negligible volume reduction; and increased duration of peak flow. Moreover, detention basins create higher runoff temperatures as they trap, hold, and then discharge runoff.

Detention storage targets relatively large, infrequent storms, such as the two and 10-year/24-hour storms for peak flow rate control. As a result of this design limitation, flow rates from smaller, frequently-occurring storms typically exceed those that existed onsite before land development occurred and these increases in runoff volumes and velocities typically result in flows erosive to stream channel stability. Indeed, the U.S. National Research Council (an arm of the U.S. National Academy of Sciences) published a study in 2008 that confirmed that current stormwater control efforts are not adequate and found that (1) stormwater control measures such as product substitution, better site design, downspout disconnection, conservation of natural areas, and watershed and land-use planning can dramatically reduce the volume of runoff and pollutant load from new development, and (2) stormwater control measures that harvest, infiltrate, and evapo-transpire stormwater are "critical" to reducing the volume and pollutant loading of small storms.

EPA is strongly promoting this approach of retaining rainwater onsite through infiltration, evapo-transpiration, and use/reuse. For example, in December 2007, in Section 438 of the Energy Independence and Security Act of 2007, Congress required Federal development and redevelopment projects to achieve predevelopment hydrology to the "maximum extent technically feasible". A Presidential Executive Order required EPA to write guidance for all federal agencies to implement this provision, and EPA's guidance used an approach of approximating predevelopment hydrology through the on-site retention of rainfall events up to the 95th percentile storm event (which, for example, is 1.7 inches, or 4.32 cm, in Washington, DC). EPA also used the same approach in the previously discussed Chesapeake Bay guidance. The latter document in particular contains a great deal of information on practices that are available to achieve this goal, along with many real-world examples that show how to achieve the goal in the context of different site conditions, including redevelopments of highly urbanized areas.

The most prominent LID/GI practices, many of which were until recently virtually unheard of or relatively unknown, have become much better known in the past decade. The most prominent practices fall under the general categories of bio-swales, bio-filters, or "rain gardens"; pervious pavements, including pervious concrete, pervious asphalt, and pervious paver; green roofs; trees that are provided adequate space and enhanced technique that greatly increase access of roots to air and water (e.g., Silva cells); and storage devices such as cisterns and rain barrels.

Studies to date regarding the cost-effectiveness of these practices show that they often save money when compared to traditional stormwater infrastructure that relies on pipes and ponds. Implementing well-chosen LID/GI practices saves money for developers, property owners, and communities while protecting and restoring water quality. Prime reasons for these costs savings are the ability to eliminate or reduce the size and/or number of storm sewers and ponds.

Perhaps even more impressive than the cost-effectiveness of LID/GI approaches is the fact that they provide many environmental and societal benefits that are not provided by traditional stormwater infrastructure. These include:

- Replenishment of ground-water supplies
- Cleaner water through the use of plant media to reduce pollutant discharges
- Cleaner air through filtering by trees and vegetation of many airborne pollutants, resulting in reduced respiratory illness
- Reduced urban temperatures, which increases comfort as well as reducing ground-level ozone concentrations
- Moderated impact of climate change by conserving and harvesting water and through carbon sequestration
- Increased energy efficiency through reducing air conditioning and heating costs and by reducing the amount of stormwater that needs to be conveyed and treated
- Enhance community livability and aesthetic benefits thanks to trees and plants
- Higher property values as the result of greener environment
- Crime reduction and reduced stress of urban living

Cities in the United States have begun to analyze and estimate the net benefits of LID/GI as compared to traditional stormwater infrastructure. The most prominent example to date is the City of Philadelphia's study, "A Triple Bottom Line Analysis of Traditional and Green Infrastructure Options for Controlling CSO Events in Philadelphia's Watersheds. This study found that the benefits of using green infrastructure in Philadelphia would be large and substantially outweigh the costs.

Identifying, Assessing, and Protecting Healthy Watersheds

Finally, EPA is placing increased emphasis on the protection of good quality waters and their habitat through a new Healthy Watersheds initiative. See www.epa.gov/healthywatersheds. An increasing number of states are identifying their most valuable aquatic resources by assessing not only the chemical and physical properties of waterbodies but also such critical factors as the varied ecological flows needed throughout the year; green infrastructure provided throughout the contributing watershed; landscape condition; and geomorphological attributes. The Healthy Watersheds Framework addresses the complexity of watershed ecosystems through an integrated assessment of all of these relevant attributes. This integrated assessment then provides the information needed to identify those areas within a State or watershed that have the best overall condition and that should therefore form the basis for protection priorities and strategies.

EPA's Healthy Watersheds Initiative was motivated in significant part by the sad story of past failures to protect good water quality condition. Here are a few of the documented ill effects of past failures (references for all statistics below are documented, and linked to, in the Healthy Watersheds website provided immediately above):

- Over the last 50 years, coastal and freshwater wetlands have declined; surface water and groundwater withdrawals have increased by 46%; and non-native fish have established themselves in many watersheds.
- A recent national water quality survey of the nation's wadeable streams showed that 42% of the nation's stream length is in poor biological condition and 25% is in fair biological condition.
- Nearly 40% of fish in North American freshwater streams, rivers, and lakes are found to be vulnerable, threatened, or endangered; this is nearly twice as many as were included on the imperiled list in a similar survey conducted in 1989.

Actions to protect healthy watersheds can help arrest this state of decline and avoid the costs of restoring impaired waters. Furthermore, protecting and conserving healthy watersheds provides many other economic benefits. Healthy watersheds provide habitat for fish, amphibians, birds, and insects, and they contain stream corridors which provide a key connection across the landscape for animals and birds. They preserve recreation opportunities such as fishing and water-related recreation (e.g. boating) and contribute to tourism (e.g., hiking and birding). They reduce vulnerability to invasive species, floods, fires, and other natural disasters. Healthy watersheds with natural land cover and soil resources also provide vast carbon storage capabilities, offsetting greenhouse gas emissions. Similarly, by protecting aquifer recharge zones and surface water sources, the costs of drinking water treatment may be reduced. A survey of 27 drinking water utilities' treatment costs and watershed characteristics found that for every 10% increase in forest cover of the source area, chemical and treatment costs decrease by 20%.

EPA has drafted a guidebook to help States and communities protect their healthy watersheds. Tentatively named "Identifying and Protecting Healthy Watersheds: A Technical Guide", this guidebook will set forth a recommended process for developing an assessment of watersheds within a defined geographic area (e.g., a State) that includes consideration of a range of relevant factors and attributes described above; using appropriate criteria to delineate those watersheds (or portions of watersheds) that are "healthy", and developing an implementation plan to protect the healthy watersheds. Ultimately, the goal of a holistic water quality program should be to protect those waters that are healthy while restoring those areas that are not. Thus EPA regards its Healthy Waters Initiative and its impaired-waters-restoration activities as complementary. Both are necessary to provide good water quality for future generations.

CONCLUSION

The United States has achieved great progress in reducing water pollution from point sources. Nonpoint source pollution remains a considerable challenge. Solutions to urban runoff problems appear to be within reach, while slow progress is being made in addressing agricultural sources. EPA will continue to pursue a range of funding and programmatic solutions to water quality impairment, while at the same time improving its programs that protect waters that have not yet been impaired.

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Diffuse water pollution and AGRICULTURE: Policy approaches and outlook across oecd countries[1]

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Abstract

High quality water resources are vital not only in securing human health and maintaining ecosystems, but also in providing amenity, recreational, visual and other benefits. With the achievement in reducing industrial, sewage and other 'point' sources of pollution, focus has switched in many OECD countries to lowering agricultural pollution. This is because water pollution from agriculture mainly originates from diffuse sources with many crop and livestock farms spread across agricultural landscapes. With structural changes in the livestock sector toward larger more intensive units, however, agriculture is also increasingly contributing to point source pollution This paper explores the policy linkages between agriculture and diffuse water pollution across OECD countries. Following the introductory remarks, the paper continues in Section II by: describing the principal policy and management concerns; examining the main water quality trends; and outlining the medium term outlook, including the likely consequences of climate change for agricultural and water quality linkages. Section III describes which policy instruments and mixes OECD countries use to address water quality issues associated with agriculture. In the final Section IV opportunities to move toward more sustainable management of water quality in agriculture are identified.

Keywords

Agriculture; diffuse water pollution; policies; outlook, OECD countries

THE CHALLENGE

During the past 20-30 years in addressing water pollution in agriculture governments have provided substantial support to the sector, introduced regulations and provided farmers with technical advice. While these efforts have resulted in some progress in lowering agricultural pressure on water systems, they have generally fallen short of what is required to meet policy goals. Among these goals include the need to improve the natural environment, lower drinking water treatment costs and reduce costs to farmers through the lost of nutrients, pesticides, and soil into water bodies.

SETTING THE SCENE: PRINCIPAL CONCERNS AND FUTURE OUTLOOK

The organising framework for this paper is captured in Figure 1, which summarises the complex interactions and linkages between policies, markets and environmental conditions on farming systems, farm practices and farm input use, which in turn impacts the state of water quality from streams, groundwater to deep seas. Depending on the trends in the state of water quality this will feed back into possibly provoking a policy response. Agriculture can also be subject to pollution itself from other sources. Irrigated agriculture is particularly prone to this problem, where it may draw water polluted upstream by urban and industrial sources.

1. This paper is published under the authorship of Kevin Parris and does not necessarily reflect the views of the OECD or its member countries. The paper largely draws from a forthcoming OECD publication (late 2011), *Sustainable Management of Water Quality in Agriculture,* www.oecd.org/water.

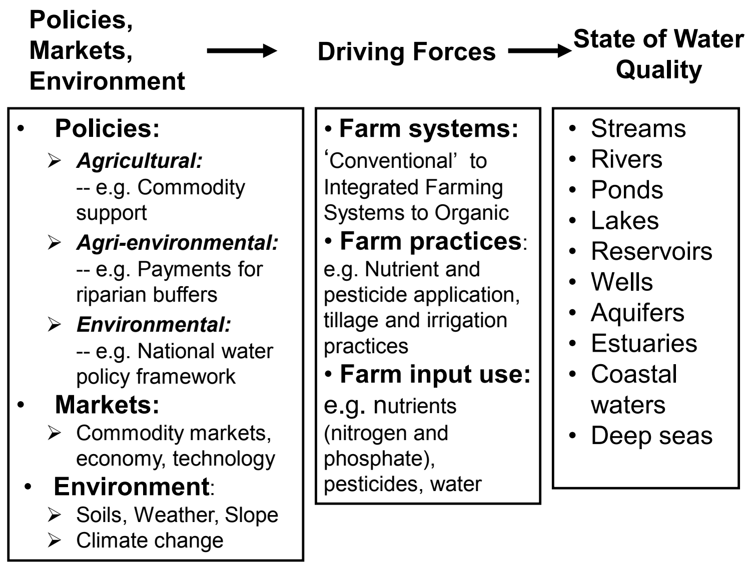


Figure 1. Linkages between policies, agriculture and the state of water quality
Source: OECD Secretariat.

In response to the mix of policies, market and environmental influences shown in Figure 1, a growing number of OECD farmers are adopting environmental ***farm management practices*** that seek to minimise the impact of agriculture on water systems. To encourage more farmers to adopt such practices governments are providing incentives through payments to offset the cost of adopting these practices (e.g. establishing riparian buffers), supported through farmer advice and enforced through regulatory measures. Farmers are also changing their farming practices in response to voluntary private led initiatives, often led by water treatment companies and interests in the agro-food chain (e.g. input suppliers and food retailers).

While the uptake of environmental farm management practices across OECD countries to address water quality issues has been increasing there remain on-going challenges common to most countries. Addressing these challenges, discussed below, would help develop policy approaches that encourage farmers to adopt management practices beneficial to improving the quality of water systems.

There is considerable evidence from farm survey data across many countries that ***farmer awareness or recognition that agriculture makes a contribution to water pollution is low*** (Blackstock *et al.,* 2010; National Audit Office, 2010). This might reflect a lack of understanding of the science of the transport and fate of pollutants on farms to water systems, especially groundwater. Raising farmer awareness and acceptance of water quality problems is an important first step in getting uptake of mitigation measures (Blackstock *et al.,* 2010). Many policy interventions to control diffuse source pollution tend to proceed on the basis that the links between farming activities and water pollution are understood by farmers (Blackstock *et al.,* 2010). But there is evidence that farmers are willing to accept further education and advice on nutrient and pesticide management on their farms in the interests of protecting the environment and that overall awareness is increasing and leading to improved management practices to control pollution (European Commission, 2010).

The pathways by which pollutants reach surface, groundwater and marine waters are often complex and not fully understood. The impacts of diffuse source pollution depend on the quantities of pollutants released; how easily the pollutants are transported into water systems; and how sensitive the water environment is to pollution (Environment Agency, 2007). `Further improvements in scientific understanding and knowledge of these processes and linkages are critical to help highlight the most appropriate mitigation actions to alleviate water pollution pressures from agriculture.

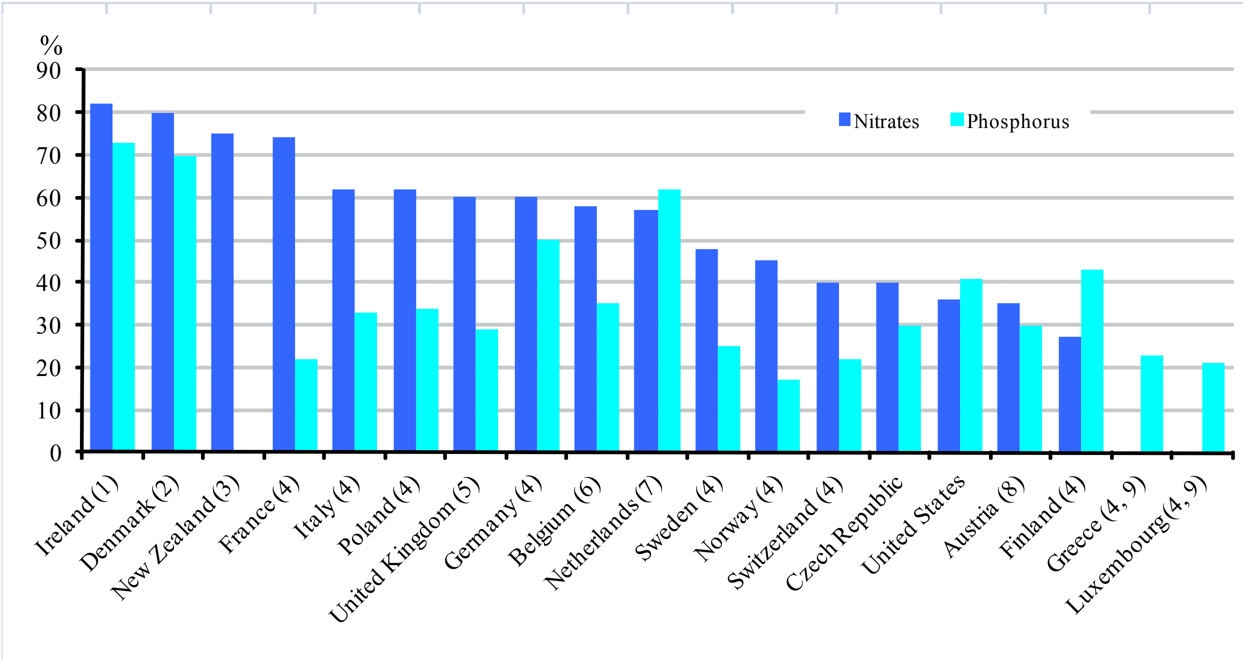
Over recent decades programmes aimed at reducing diffuse source pollution from agriculture have often reported little or no improvement in water systems. While there are many causes for this an important reason is ***time lags***. Time lag (sometimes referred to as the legacy problem) is the time elapsed between adoption of management changes by farmers and the detection of measurable improvement in water quality of the target water body, which can range from hours to decades (Kronvang, Rubaek and Heckrath, 2009; Meals, Dressing and Davenport, 2010).

Underlying the difficulties of insufficient knowledge, time lags, and stochastic processes that pervade policy related diffuse source pollution problems in agriculture, is the issue of ***information failure*** (Borisova *et al* 2003; Cabe and Herriges, 1992; Doole and Pannell, 2009). The lack of information that hinders efficient policy making relates to the: high number of polluters; asymmetric information between farmers and policy makers; temporal and spatial variation in pollution concentration; and the high cost of data collection for this kind of environmental issue. Given growing interest in more comprehensive water catchment based approaches to address water pollution, this requires a broader set of information to support policy making that more traditional approaches. But because information is imperfect, decision making under uncertainty will be unavoidable.

Given the large natural and agricultural variation across water systems, water management is in most cases more efficient at the catchment or sub-catchment level (also referred to as water basins/sub-basins), with management initiatives best integrated across the different users and needs of the catchment (Land and Water Forum, 2010; Ministry of Infrastructure and Environment, 2010). ***Integrated catchment management*** refers to the process by which stakeholders can develop a common vision, agree shared values, make collective informed decisions and manage together the catchment. This process involves integration of water users, polluters, scientists, policy makers and other interested stakeholders where tradeoffs are made between these various interests, in an open and transparent way and where the focus is on synergy and win-win solutions (Collins and Anthony, 2008).

Farmers choice and changes in farm management practices and systems, discussed above, ***impact on water systems*** (Figure 1). The state of water quality in surface waters, groundwater and marine waters are monitored by all OECD countries, although national water monitoring networks vary in their detail and coverage of agricultural water quality impacts.

For many countries the share of agriculture in the total pollution of surface water by nitrates is over 40% (Figure 2). Evidence of the contribution of agriculture in groundwater pollution is limited, but some information suggests it may be lower than for rivers and lakes but increasing. Agriculture is a major source of phosphorus in surface water (Figure 2) and coastal waters accounting for a share of over 40% in some OECD countries.



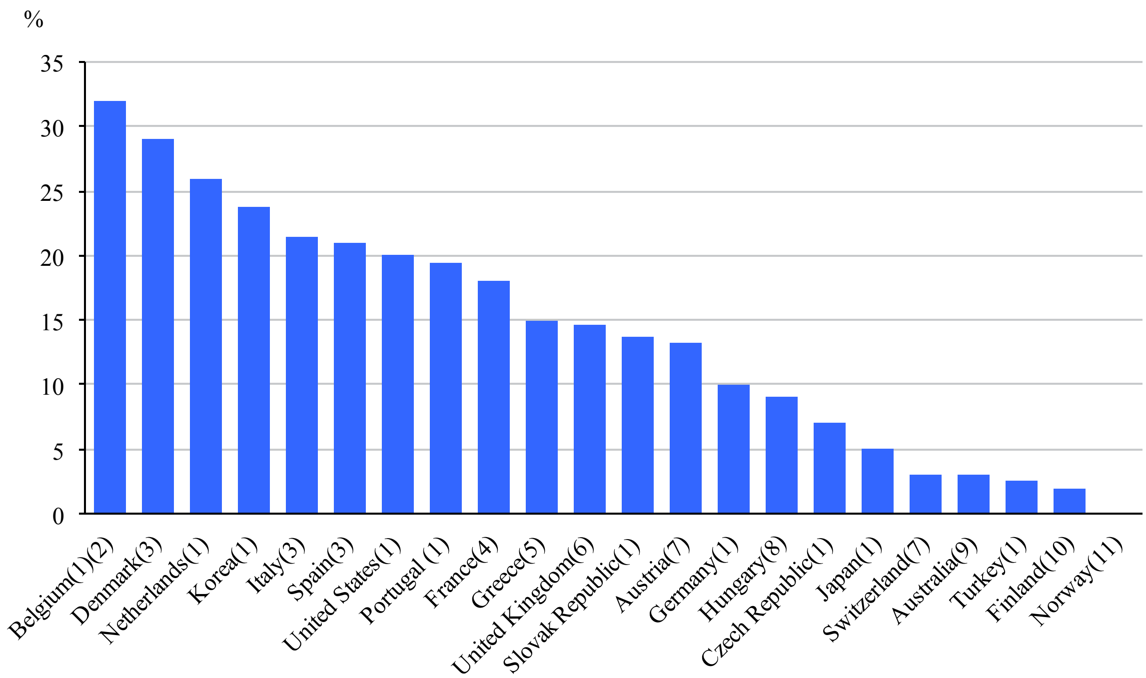
1. 2004, see Ireland
2. Phosphorus (2002), percentage refers to Danish lakes only.
3. Data for nitrate contamination of rivers and streams, total input to surface waters from agriculture non-point source pollution. Data for phosphorus not available.
4. Data for mid-1990s for Finland, France, Germany, Greece, Italy, Luxembourg, Norway, Poland, Sweden, Switzerland.
5. United Kingdom.
6. Flanders only, 2001.
7. The Netherlands, 2002.
8. Value for 2000.
9. Data for nitrate emissions are not available.

Figure 2. Agriculture's contribution of nitrates and phosphorus in surface water: mid-1990s to mid-2000s[1]
Source: OECD (2008).

The overall pressure of agriculture on water quality in rivers, lakes, groundwater and coastal waters has eased since the early 1990s due to the decline in nutrient surpluses and pesticide use and improvements made in soil conservation leading to a reduction in soil erosion rates. The absolute levels of agricultural pollutants, however, remain a challenge to achieve further reductions for most OECD countries, especially diffuse source pollution.

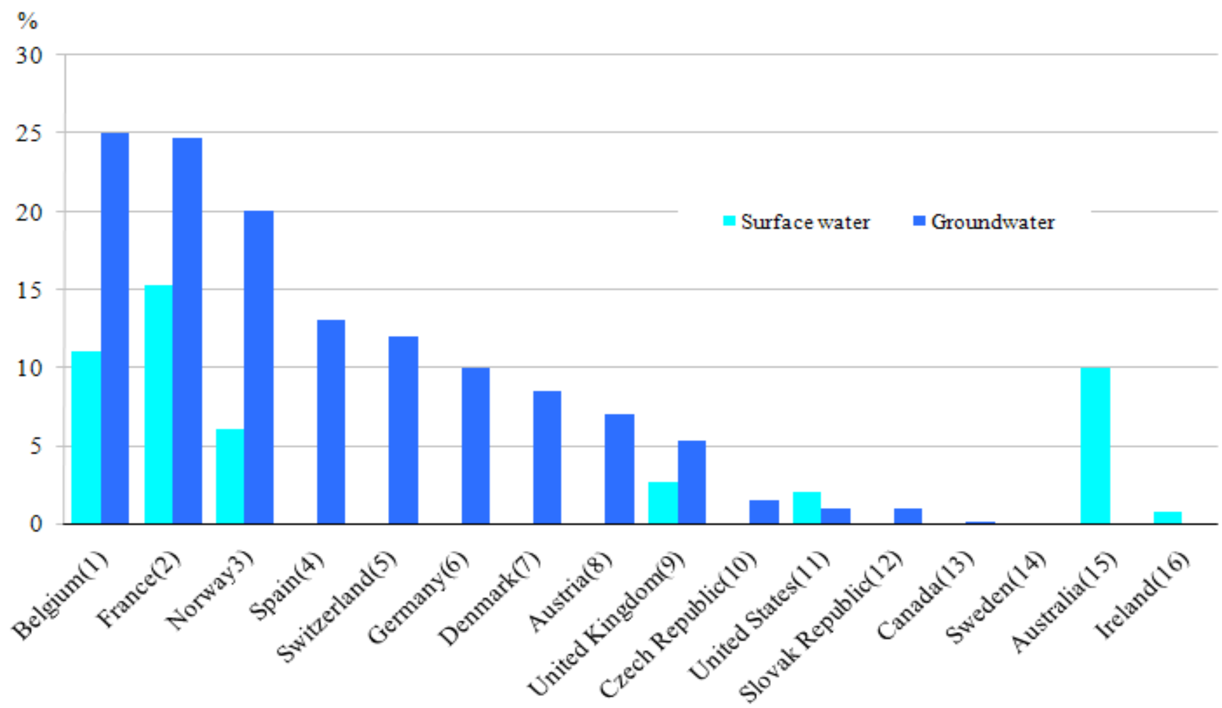
Nearly a half of OECD countries record that nutrient and pesticide concentrations in surface water monitoring sites in agricultural areas exceed national drinking water limits for these contaminants. But the share of monitoring sites of rivers and lakes that exceed recommended national limits or guidelines for environment and recreational uses is much higher, with agriculture a major cause of this pollution in many cases.

With respect to groundwater (shallow wells and deep aquifers), agriculture is now the major and growing source of pollution across many OECD countries, especially from nutrients and pesticides, although evidence of groundwater pollution is limited (Figures 3 and 4). This is a particular concern for countries where groundwater provides a major share of drinking water supplies for both human and livestock populations, and also as natural recovery rates from pollution can take many decades, in particular, for deep aquifers. There is also some evidence of increasing pollution of groundwater from pesticides despite declining use of pesticides in many cases, largely explained by the long delays pesticides can take to leach through soils into aquifers.



1. Data refer to average of 1995-2005.
2. Belgium (Flanders only).
3. Data refer to average 2002 and 2003.
4. Data refer to 2001.
5. Data refer to average 2001-02, with a range of 10-20%.
6. Data refer to 2004.
7. Data refer to 2002.
8. Data refer to average 2000-02, applies to all surface water monitoring points.
9. Groundwater in intensively farmed areas of north-eastern Australia.
10. Data refer to 2002, estimated for shallow wells at 2% and for aquifers 1.5%.
11. Norway (National environmental monitoring programme) reported 0% for 1985-2002.

Figure 3. Share of monitoring sites in agricultural areas that exceed recommended drinking water threshold limits for nitrates in groundwater: 2000-04
Source: OECD (2008).



1. Data 2000-02. Flanders region only. Atrazine only for surface water. Regional variation show concentrations ranged between 13% to 32%, with 10% of monitoring sites in excess of 0.5µg/l compared to drinking water standard of 0.1µg/l.
2. National data. Average poor and poor status.
3. Data applies only to monitoring locations in high risk pollution sites. Data 1995-2002, with concentration levels for surface water declining in most locations. For groundwater % share for pesticide presence applies to farmer's drinking water wells, while pesticide concentration in groundwater is 2% for those aquifers supplying more than 100 people.
4. No data for surface water.
5. Data 2002, applies to water catchments under arable farming. No data for surface water.
6. Data 1995. No data for surface water.
7. Source EEA (2005), data 2000. No data for surface water.
8. Data 1990-2001. Atrazine only. In 1992-94 share of monitoring sites with pesticide concentration above drinking water standard for groundwater was 20%. No data for surface water.
9. For surface water data applies to England and Wales, average 2000-02 for atrazine samples over 100mg/l. For groundwater data applies to average 2000-02 for monitoring sites in arable land areas, the percentage is 4% for managed grassland.
10. Data refer to 2003. No data for surface water.
11. Data 1992-98. Value for surface water (figures in brackets apply to groundwater) show 1-2 pesticides present in 8% (29%) of monitoring sites; 3-4 pesticides in 18% (11%) of sites; and more than 5 pesticides in 74% of sites.

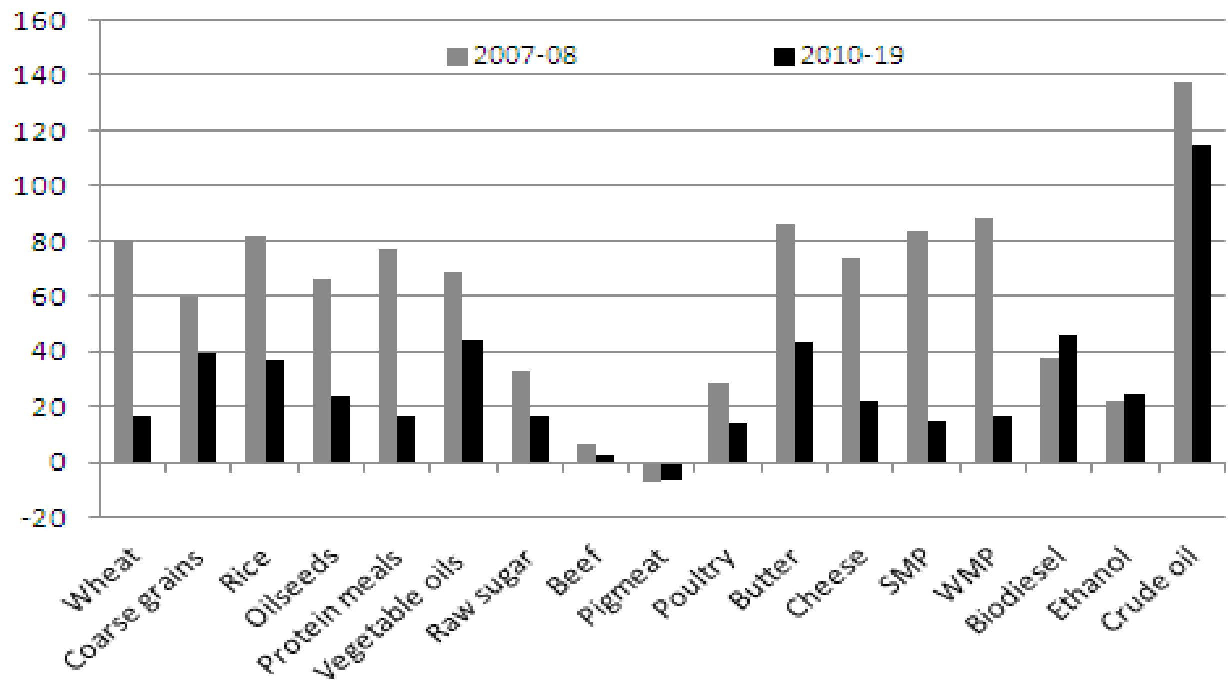
For surface water (farmland streams) 80% of monitoring sites have concentrations above aquatic life water guidelines.

12. Data 1985-2002. No data for surface water.
13. Rural wells. No data for surface water.
14. Data 1998-2002, measurement for only one region Vemmenhög, 0% for groundwater. No data for surface water.
15. Cotton growing areas of Eastern Australia only. No data for groundwater.
16. 2004. Applies to exceedence levels in public water supplies.

Figure 4. The share of monitoring sites in agricultural areas where pesticide concentrations in surface water and groundwater exceed recommended national drinking water threshold limits: 2000-02
Sources: OECD (2008).

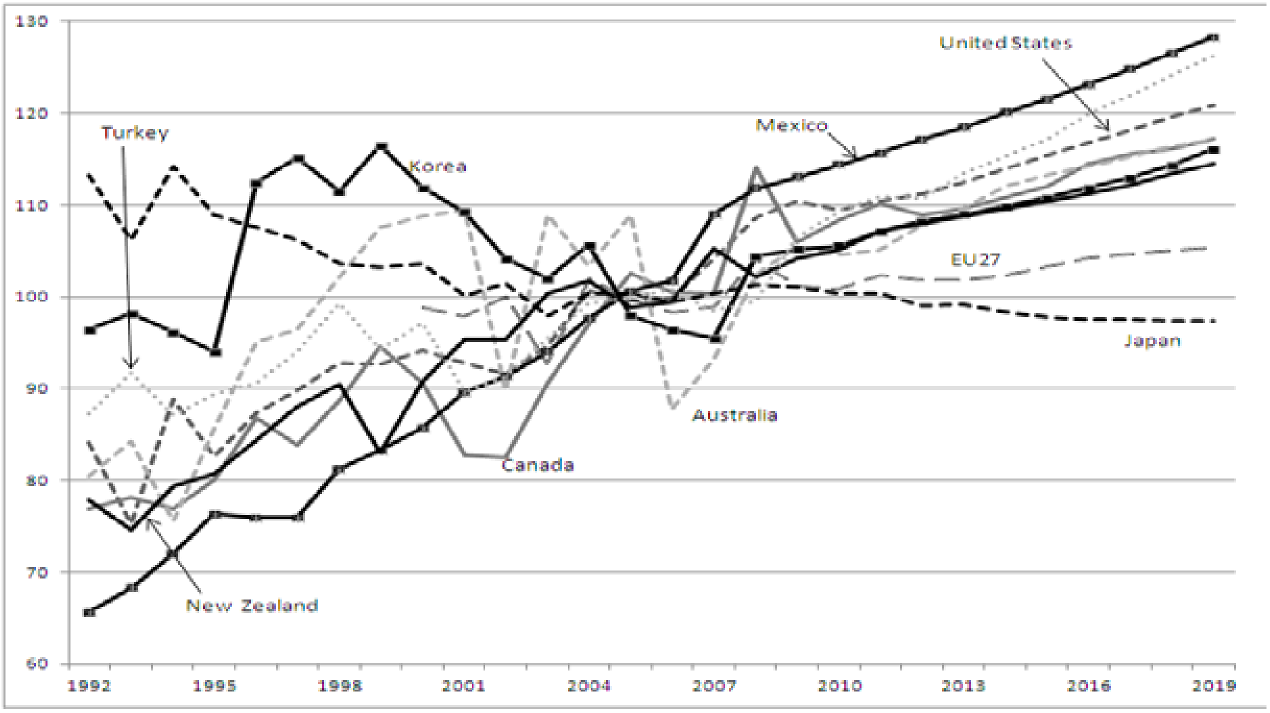
The OECD-FAO Agricultural Outlook (OECD, 2010a) projects over the next 10 years to 2019 a trend of sustained crop, sugar and vegetable oilseed product prices, in nominal and real terms (allowing for inflation). These commodity price projections are expected to remain well above the levels observed prior to the 2007-08 price peaks*, i.e.* during the 1997-2006 period (Figure 5).

Projections also indicate a similar trend to crops for bioenergy, with rising real prices for biodiesel and ethanol. More modest increases are expected for livestock prices, other than pig meat, over the coming decade, but average dairy prices (shown in terms of dairy products in Figure 5), are expected to be 16-45% higher in 2010-2019 relative to 1997-2006 (Figure 5) (OECD, 2010a).



Note: SMP – Skim Milk Powder; WMP Whole Milk Powder; For biodiesel and ethanol the base period is 2001-06.

Figure 5. OECD projections for international commodity prices in real terms to 2019
Source: OECD (2010a), OECD-FAO Agricultural Outlook 2010-2019, www.agri-outlook.org



Note: Net agricultural production measures gross value of product produced, net of "internal" feed and seed inputs to avoid double counting (for example maize and livestock production), so that the production measure approximates a value added concept. There are no projections for Chile, Iceland, Israel, Norway and Switzerland.

Figure 6. Index of net agricultural production trends for selected OECD countries, 1992-2019 (Index 2004-06 = 100)
Source: OECD (2010a), OECD-FAO Agricultural Outlook 2010-2019, www.agri-outlook.org

The outlook for agricultural commodity prices translates into projected growth in agricultural production for nearly all OECD countries over the coming decade (Figure 6). From the trends in national agricultural production projections in Figure 6 it is possible to discern two broad groupings of OECD countries in terms of their potential pressure on water systems over the coming decade:

- Group 1: Countries which are projected to continue with strong growth in production over the coming decade, such as Canada, United States, Mexico, Turkey, Australia and New Zealand. For this group of countries the potential consequences for water systems of the projected growth in agricultural production might include (trends may vary within and across countries):
   i. heightened pressure on water quality from the increased use of fertilisers and pesticides, and greater quantities of livestock manure, although absolute levels of pollution for many of these countries is below the OECD average;
   ii. elevated soil erosion leading to greater siltation of water systems as a result of farming more intensively environmentally fragile lands and/or expanding production onto marginal land not previously cultivated;
   iii. expanded production of bioenergy, especially using cereals, oilseeds and sugar crops as feedstocks for manufacturing biofuels, which may lead to a rise in fertiliser and pesticide use; and,
   iv. regionalised pressures on water systems could alter as a result of the continued structural changes in livestock production toward larger and more concentrated livestock operations, notably in the pig, poultry and dairy sectors.

- Group 2: Countries where projected production growth over the coming decade is expected to be modest for the EU 27 or decline in the case of Japan. For this group of countries the potential consequences for water systems of the projected low growth or decrease in agricultural production might include (trends may vary within and across countries):
    i. reduced overall agricultural pollutant loadings into water, although the absolute levels of pollution for many of these countries might remain above the OECD average; and,
    ii. localised increases in water pollution, with structural changes in the livestock sector towards larger concentrated operations.

For all OECD countries over the medium term there are a number of developments that may generally help toward lowering the pressure of agriculture on water systems, including:

i. efficiencies in farm chemical input use per unit of output, partly induced by higher prices for inorganic fertilisers and pesticides due to the projected increase in crude oil prices (Figure 5), which might also encourage greater use of livestock manure as a bioenergy feedstock;
ii. improvements in farm management practices, and pollution related technologies, especially biotechnologies and use of global positioning systems (GPS);
iii. increases in public pressure to reduce the health and environmental costs of water pollution from agriculture, likely to result in strengthening of environmental pollution policies, especially those policies addressing diffuse source pollution from agriculture; and,
iv. reforms likely to continue with agricultural policies leading to further declines in overall OECD agricultural support and a continued shift towards decoupled support.

The medium and long term outlook for agriculture is expected to be increasingly impacted by ***climate change and climate variability***. Changes in climate and climate variability that affect the profitability of agriculture will in turn lead to changes in locations of crop and livestock production, and technologies and management practices used to produce individual crops and livestock (Abler *et al.*, 2001). These economic responses to climate change could lead to indirect consequences in changing pollutant run-off and leaching rates as well as soil erosion rates, which may increase or diminish pollution from agriculture assuming no economic or policy response.

Relationships between climate change and pollution from agriculture are likely to be complex, as increased flooding, for example, could mobilise sediment loads and associated contaminants and exacerbate impacts on water systems. On the other hand, more severe droughts could reduce pollutant dilution, thereby increasing toxicity problems (Collins and McGonigle, 2008). But the expectations are that whatever the impacts on water quality, the task of achieving water quality objectives in agriculture will become more difficult in the coming years as a result of climate change. These conclusions are tentative, not only because of the overall uncertainties of current climate change research, but more specifically that the linkages between climate change, agriculture and water quality are not yet extensively researched.

OECD POLICY INSTRUMENTS AND MIXES TO ADDRESS WATER QUALITY IN AGRICULTURE

There are three broad policy types that affect farmer decision choice on management practices and systems and their use and management of farm inputs and waste, which in turn impact on the state of water quality (Figure 1), including: overall agricultural policies; environmental policies and agri-environmental policies.

Reform in ***agricultural support policies*** across most OECD countries over the past 20 years have had a significant influence in lowering the overall pressure on water quality than would otherwise be the case in the absence of these policy reforms, including:

i. *Reduction in the overall level of support to farmers*. In 2007-2009 support to producers in OECD countries was estimated at almost USD 260 million or EUR just over180 billion, as measured by the Producer Support Estimate (PSE) (OECD, 2010b). The PSE fell from 37% of farmers' total receipts in 1986-88 on average to 22% in 2007-09 (Figure 7). Policies that increase producer prices or subsidise input use (e.g. pesticides) without restricting output encourage farmers to increase production, use more inputs, and farm more fragile lands (Shortle forthcoming).

ii. *Change in the way support is delivered toward support more decoupled from production*. The ways in which support is provided to farmers have also changed (Figures 7). OECD governments are gradually shifting to support that is more decoupled from current production and which gives greater freedom to farmers in their production choices. Support is increasingly being tied to parameters other than commodity output, such as area or animal numbers, and with respect to historic levels of these parameters (OECD, 2010b).

iii. *Development of environmental conditionality* (cross compliance). Support is becoming increasingly conditional, as well as decoupled from production and input use. Producers, if they want to receive support, are now more often obliged to contribute to improvements, for example, in the environment, rural amenities, or better treatment of animals. In 2006-08, over 30% of support to OECD farmers had some such conditions attached, whereas in 1986-88 this share was only 4% (OECD, 2010b).

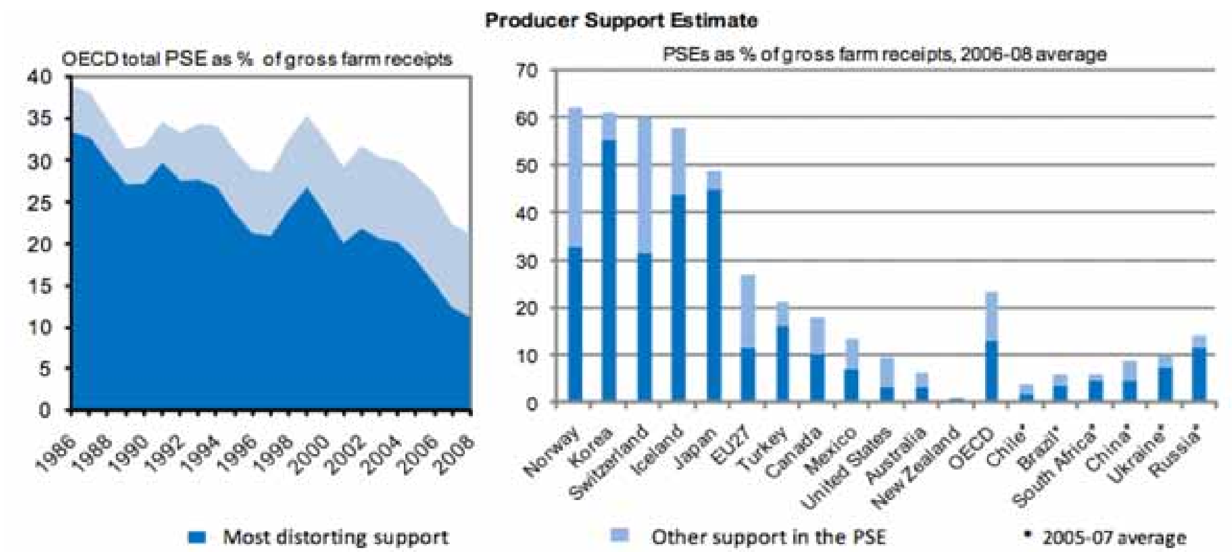


Figure 7. Trends in total support and the composition of support
Source: OECD, PSE/CSE database 2010, www.oecd.org/tad

Environmental policy across OECD countries has historically largely resorted to regulations to control water pollution through emissions limits applied to industrial and municipal point sources of pollution. In most instances this regulatory approach achieved considerable success in reducing point sources of pollution, with the same type of approach extended to agricultural point sources of pollution, especially intensive livestock operations (Shortle forthcoming). Environmental policies have also generally provided the regulatory framework for registration, handling and disposal of pesticides and some emerging contaminants in agriculture (e.g. pharmaceutical products for livestock), as part of broader and long standing environmental policies focusing on chemicals.

With the reduction in point source pollution, policy focus is shifting to lowering the impact of diffuse sources on water quality has become more prominent (Graham, Schempp and Troell, forthcoming). As a consequence environmental agencies are increasing their attention to addressing diffuse source pollution in agriculture.

Agricultural policy reforms in OECD countries have seen a shift toward more decoupled support, as noted above, including the use of ***agri-environmental policies*** (AEPs). There has been a substantial increase across most OECD countries in the application of agri-environmental and natural resource management policies, commonly with the use of payments supported by regulatory instruments and technical advice to farmers. This is illustrated with the expansion in agri-environmental payments in the United States; the development of environmental conditionality within the European Union's *Common Agricultural Policy*; and the increasing budgetary expenditure under Australia's *Natural Resource Management* measures.

AEPs, among other environmental objectives, are widely used to control water pollution, both directly, such as payments for riparian buffer strips and livestock manure storage facilities, and indirectly, including programmes aimed at soil conservation and extensification of farming. The use of AEPs has generally been in contrast to national environmental policies to address water pollution, with the emphasis on voluntary uptake of measures, with farmer adoption encouraged by payments. This relates, in particular, to the difficulties of developing policy approaches to address diffuse source pollution in agriculture.

Typically OECD countries have addressed agricultural water pollution by using a mix of economic instruments (*stimulation*), environmental regulations (*regulation*), and communicative approaches (*persuasion*) (Oenema *et al.,* 2009; Vojtech, 2010). A large array of measures has been deployed at the local, provincial/state through to national and transborder scales, with many initiatives that emphasize voluntary adoption of pollution control practices encouraged by payments (Shortle forthcoming).

Table 1. Overview of policy instruments addressing diffuse sources of water pollution

	National level				State/provincial level				Total
	Nutrients	Pesti-cides	Both	Total	Nutrients	Pesti-cides	Both	Total	
Policy objectives	44	35	14	93	–	–	–	–	93
Policy instruments	137	78	25	240	61	41	4	106	346
Regulatory instruments	54	37	7	97	28	20	0	48	146
Economic instruments	37	8	9	54	17	7	1	25	79
Thereof taxes	2	4	0	6	2	1	0	3	9
Thereof subsidies	32	1	7	40	13	7	1	21	61
Information instruments	32	25	7	64	11	14	2	27	91
Other instruments	14	10	2	26	5	0	1	6	32

Source: OECD, 2007.

Application of the *Polluter-Pays-Principle* (PPP) in agriculture, such as by using a ***pollution tax***, can produce efficient and effective economic and environmental outcomes (OECD, 2010c). Where taxes or charges have been applied in OECD countries they are usually applied to fertiliser and pesticide inputs. But application of the PPP in agriculture is difficult and rare across OECD countries, mainly because diffuse source pollution from agriculture into water cannot be measured at reasonable cost with current monitoring technologies (this does not generally apply to point sources of pollution in agriculture), and also due to property right, institutional and other barriers (Blandford, 2010).

Most OECD countries offer ***monetary payments*** (including implicit transfers such as tax and interest concessions) to farmers and other landholders to address environmental problems (*e.g.* to reduce pollution) and/or to promote the provision of environmental amenities associated with agriculture (Vojtech, 2010). These payments are mainly provided on a voluntary basis, however, there are payments (mainly investment subsidies) provided to farmers to assist them to comply with environmental regulations. In practice, many agri-environmental payments tend to be linked to land or other factors of production.

Water quality trading (WQT) refers to the application of emissions trading to water pollution control. Traditional air and water pollution regulations entail imposing periodic (*e.g.* annual) maximum limits on emissions sources (*e.g.* smokestacks, outfalls), and requiring that those limits be met at the source. The requirement that limits are met at the source prevents emissions reductions from one source being used to meet the requirements of another.

Overall, WQT can be viewed as a promising innovation for water quality management in agriculture rather than a mature technique. There have been some notable successes, but there are also cases where little has been accomplished. Trading experiences will provide lessons to help determine the best applications and designs, but additional research on the science of trading for fully capped agricultural sources will be needed if water quality policy makers choose to make significant use of trading for managing agricultural diffuse source pollution (Shortle forthcoming).

Since the 1980s there has been a general expansion in ***regulatory measures*** affecting agriculture to protect water systems. These measures are usually compulsory or the producer faces penalties, such as fines and, where eligible, withdrawal of agri-environmental payments. Regulations are the most widespread and common policy measure used across OECD countries to limit the environmental impacts of agriculture on water systems. Regulations range from very broad prohibitions (e.g. the blanket ban on DDT pesticide) to intricate details about specific farm management practice (e.g. pesticide spraying distance from a river) (OECD, 2003; 2010d).

The historic reliance on a mix of payments and regulations supported by technical incentives for producers to address water pollution in agriculture outlined previously, is encountering growing difficulties in many countries. This is because of inefficiencies and failures in the development, implementation, and enforcement of these policy approaches; the rising budgetary cost of providing payments; the problems with administering and enforcing regulations; and also the diminishing efficiency of these policy approaches to achieve continued and significant reductions in the impairment of water quality resulting from agricultural practices (Gouldson *et al.,* 2008).

Because of these difficulties there is growing interest and experimentation with developing ***communicative policy approaches***, such as information based instruments, voluntary or private regulations and support mechanisms, and capacity building approaches (Barnes *et al.*, 2009; Dowd *et al.*, 2008; Gouldson *et al.,* 2008; Kay *et al.*, 2009). Some of these approaches are already well developed in many countries, especially developing research and diffusing knowledge to farmers through advisory services, but others are not so widespread and less developed, such as private and voluntary regulation in the area of water pollution control. A key consideration in the interest and increasing uptake of communicative approaches is their focus on changing the behaviour of farmers, the agro-food chain and other stakeholders (Blackstock *et al.,* 2010; Gouldson *et al.,* 2008).

OPPORTUNITIES FOR MOVING TOWARD SUSTAINABLE WATER QUALITY MANAGEMENT IN AGRICULTURE

Policy measures have had varying success, within and between countries, in changing farming practices and systems leading to measurable improvements in water quality. But the mix of payments and regulations, supported by technical advice for producers to address water pollution in agriculture is encountering growing difficulties in an increasing number of cases. This is because of inefficiencies and failures in the development, implementation, and enforcement of these policies; the rising budgetary cost of providing payments; and problems with administering and enforcing regulations.

Policy reforms to improve the economic efficiency and environmental effectiveness of the current policy mix to lower agricultural pressure on water systems are important steps toward the sustainable management of water quality in agriculture. But in addition to undertaking these reforms, there is mounting interest in many countries in exploring and establishing new policy opportunities and market approaches to address diffuse source pollution from agriculture because of the:

i. limitations with traditional rigid regulatory frameworks, when the public sector might draw on the more dynamic and less costly capacities of the private (e.g. water companies, agro-food chain) and civil sectors (e.g. farmer and environmental groups) to achieve water quality goals;
ii. frustration with the protracted time and institutional complexities to adopt new policy approaches, when non-legislative approaches might be quicker and easier to apply;
iii. realisation that environmental issues, such as improving water quality, are complicated because of the stochastic interaction of human activity with the natural environment;
iv. comprehension that scale and context are important, so that common national policy frameworks need to be targeted and tailored to suit water catchment and sub-catchment scales; and,
v. consideration that effective and legitimate public policy requires a more comprehensive and inclusive public consultation process and stakeholder involvement, whereas regulatory approaches may be perceived by individual farmers as not applying to them.

The success in executing the policy reforms and new policy opportunities, will greatly depend on governance structures and processes, as well as property rights, to implement and govern policy changes. The complexity of agricultural and environmental policies, coupled with the unique characteristics of diffuse source water pollution, makes it difficult to create unambiguous incentives, governance structures, and property right arrangements to internalise pollution costs. Generally, each institution or water quality programme relevant to agriculture pursues its own goals without reference to the environmental incentives (or disincentives) it creates.

A further complication is the relative speed with which the structural change in agriculture can intensify and exacerbate diffuse source pollution problems, such as structural changes in the livestock sector and the disposal of manure. Political and regulatory change usually happens at a much slower pace, so that by the time the problem is recognised and solutions are proposed, more intensive farming practices are well established.

Addressing water pollution from agriculture at the catchment level, not only facilitates the involvement of all the relevant stakeholders, including the farming and non-farming community but also offers scope for better targeting of mitigation efforts. Hence, as policies to reduce diffuse pollution from agriculture evolve, this can be integrated with efforts targeting other diffuse and point sources of pollution, such as from intensive livestock facilities, urban and industrial sources.

Integrated water catchment management refers to the process by which stakeholders can develop a common vision, agree shared values, make collective informed decisions and manage together the catchment. This process involves integration of water users, polluters, scientists, government institutions and other interested stakeholders. Tradeoffs can then be initiated between these various interests, in an open and transparent way and where the focus is on synergy and win-win solutions.

While policy making needs to focus at the water catchment level to address diffuse source agricultural water pollution, this should also be accompanied by efforts and linkages at both the sub-catchment level, but also through to the national, and where relevant the trans-national boundary level.

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Engineering Assessments, Monitoring and Modelling of Effluent and Diffuse Pollution Discharges Pursuant to Establishing a Water Quality Trading Program or Policy

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Abstract

Water quality trading programs require the estimation of pollutant loads before and after the implementation of various best management practices (BMPs). Depending on the complexity of the program, they may also require fairly precise estimates of site-specific pollutant delivery rates across a watershed, as well as the pollution reduction effectiveness of BMPs. Both watershed modelling and monitoring can provide such information, and various web-based applications and databases have recently been developed that can support the nutrient trading process.

Keywords

Water quality monitoring, water quality modelling, water quality trading

INTRODUCTION

Water quality trading is essentially a process by which a given party required to reduce a pollutant load generated by them by a specified amount achieves this reduction by paying another party to reduce their pollutant load by an equivalent amount. Such trading, typically accomplished via the purchase of "pollution reduction credits", is usually done at a cost savings to the payer. It most commonly involves trades between point sources and non-point (diffuse) sources (e.g., between wastewater treatment plants and farmers), but trades between point sources are also common. In rare instances, organized trading between various non-point sources at the watershed level has also occurred; as, for example, credit purchases between dairy farming operations in New Zealand (Selman et al., 2009).

Evidence to date suggests that one of the fundamental prerequisites to establishing a viable water quality trading project or program is a relatively sophisticated foundation of scientific knowledge on the sources and sinks of point-source and diffuse pollutants. More specifically, and notwithstanding a variety of other social, legal and economic prerequisites, key *scientific* pillars typically supporting water quality trading initiatives include:

- Relatively advanced understandings by facility engineers of the pollutant removal efficiencies of their currently employed and potential alternative pollution abatement technologies and practices;
- Spatially and temporally comprehensive and detailed ambient stream and discharge monitoring networks and a centralised repository for these data; and
- Reasonably accurate and precise models to predict the transport and fate of both point-source and diffuse pollution discharge constituents – ones which estimate how those constituent loadings affect the concentrations of pollutants subject to ambient water quality standards along the various stream segments they impact.

Further, general observation of water quality trading initiatives to date suggests that even in the presence of these prerequisite scientific inputs, full exploitation of the water quality improvements and cost savings inherent in water quality trading is not achieved due, perhaps in part, to the absence of an easily-accessible forum in which buyers and sellers can evaluate their potential trading partners' capacities to engage in mutually beneficial trades. In other words, another important determinant of the volume of trading in a pollutant reduction credit market (i.e., participation in a water quality trading program) may be the look and feel of the 'marketplace' itself. It is suggested that water quality trading programs that are supported by user-friendly decision support systems – ones in which all trading partners have equal access to and clear interpretations of the scientific underpinnings of initial and post-trade waste-load allocations – may prove to develop faster than those lacking such welcoming virtual marketplaces.

In a survey recently completed by the World Resources Institute (Selman et al., 2009), fifty-seven water quality trading programs were identified world-wide. Of these, all but six were in the United States, with the remaining ones located in Australia, New Zealand, and Canada. At the time the survey was completed (late 2008), twenty-six were active, ten were inactive, and twenty-one were being considered for implementation. Of the ones still active, the key success factors attributed to their success include the following:

- Strong regulatory and/or non-regulatory drivers which helped create a demand for water quality credits;
- Minimal potential liability risks to the regulated community from meeting regulations through trades;
- Buy-in from local and state stakeholders
- Robust, consistent and standardized estimation methodologies for nonpoint source actions; and
- Standardized tools, transparent processes, and online registries to minimize transaction costs.

This current paper focuses on activities related to the last two factors.

METHODS

All water quality trading programs rely on the use of one or more estimation methodologies and these methodologies can vary significantly in their complexity. This paper first provides a review on these methodologies for estimating tradable credits, along with real-world application in watersheds in Pennsylvania. In addition, the paper summarizes various commonly-used water quality models and advancement of GIS technology in watershed modeling for evaluating pollutant loads delivered to receiving waterbodies.

Furthermore, the paper prompts the use of integrated water quality modeling and monitoring approach, which can greatly facilitate the evaluation of BMP effectiveness and the estimation of key factors critical to trading calculations such as baseline pollutant loads and attenuation rates.

The paper concludes by highlighting some of the water quality support systems that have been employed around the world in an attempt to bring this type of highly technical scientific information together in an integrated and user-friendly manner.

RESULTS AND DISCUSSION

Estimating Tradable Credits

With any viable water quality trading program, it is necessary to establish a value for pollutant credits that may subsequently be sold or purchased in some type of market or exchange program. Although the details of various trading programs set up to date differ considerably, most of them include in some form the following basic procedures:

- Establish a current load for one or more pollutants;
- Calculate the potential load reduction(s) that might occur as a result of the application of specific control technology(ies)/field practice(s);
- Apply various "trading ratios" as required; and
- Set price(s) via established protocols.

As alluded to earlier, trades may occur between various combinations of point and non-point sources. Point source load and reduction estimates are generally easier to accomplish since they involve direct "end-of-pipe" measurements. Non-point source loads and reductions, on the other hand, are much more problematic due to their diffuse nature. With point sources, various loads (e.g., TN, TP and BOD) are typically measured via periodic effluent monitoring (sampling). In the United States and Canada, for example, such monitoring is dictated by permit/regulatory requirements, and is frequently conducted on a monthly or weekly basis. In the absence of an existing requirement, for water quality trading purposes, such loads should probably be measured on at least a weekly basis (particularly in the case of point-to-point trades).

In the case of non-point sources, the estimation of tradable credits is often done via use of one of three commonly-used approaches:

- Direct measurement through monitoring;
- The use of pre-determined reduction coefficients for various field practices regardless of location within a given watershed or other site-specific conditions; and
- Calculations based on site-specific load estimates and implementation characteristics.

The first approach, direct measurement through monitoring, is potentially the most accurate, but it also may be the most costly. For example, a fairly extensive "in-stream" sampling network might be required to monitor the multiple pathways associated with many different types of non-point sources of pollution (e.g., large farms, logging operations, mining operations, residential areas, etc.) in a typical watershed (see Figure 1). The number of potential monitoring sites would likely increase as both watershed size and landscape complexity increase. Also, since non-point source pollution is inherently a "wet weather" process, and watershed loads vary as a function of variability in precipitation, such monitoring would have to be conducted over many years in order to adequately establish "typical" loads for any given pollutant. An equally important potential drawback to this approach is that a high degree of uncertainty may exist with the value of purchased or sold credits until extensive monitoring is completed. In some instances, this may mean that the value of such credits may be negatively impacted by the high cost of the "up-front" monitoring.

With the approach involving the use of pre-determined reduction coefficients, a simplified method is typically used for both estimating loads from various non-point sources and for calculating the associated reductions that might be obtained via the implementation of best management practices (BMPs). In this case, pollution reduction credit values are based on "average" reduction coefficients found in the literature. For example, with the Red Cedar River, Wisconsin (USA) water quality program, a 12 lb/acre credit is given whenever conventional tilled land is converted to no-till, regardless of site conditions or geographic location within a given watershed. One of the primary advantages of this approach is that it is relatively easy to administer.

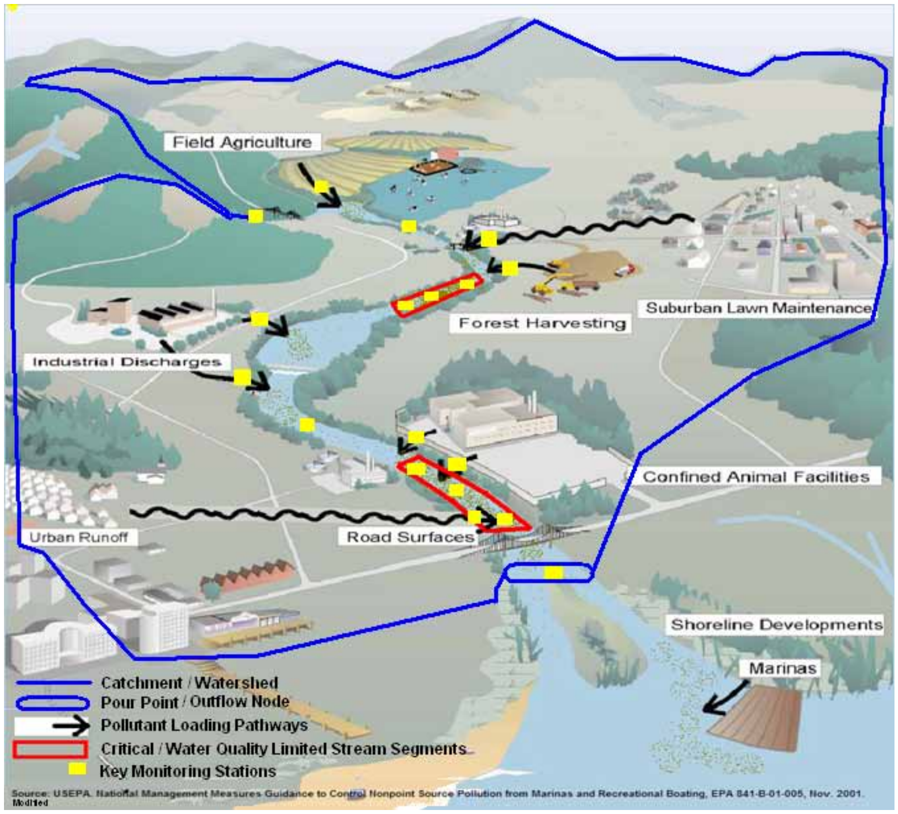

Figure 1. Watershed with potential monitoring sites.

With the third approach, calculations used for estimating both pollutant loads and potential reductions are typically based on the results of detailed watershed modelling. The initial (baseline) loading rates used as the basis for future reduction estimates are allowed to vary across the watershed according to differences in both site conditions and the manner in which BMPs are implemented. As described below, a variation on this approach is currently being used by the State of Pennsylvania in its' Nutrient Trading Program to meet its' obligations with respect to reducing nutrient and sediment loads being delivered to the Chesapeake Bay.

About a third of the land area within Pennsylvania is contained within the Chesapeake Bay watershed situated on the east coast of the United States (see Figure 2). Based upon the results of EPA's comprehensive Chesapeake Bay Watershed Model (USEPA, 2009), different nutrient and sediment loading rates and "in-stream" attenuation factors have been developed for different watershed "segments" (sub-basins) located throughout the region, including the twenty-five sub-areas located within Pennsylvania. (Attenuation factors relate to pollution reduction by various in-stream processes prior to being delivered to some "end-point"; in this case, the Chesapeake Bay). To support this modelling effort, an exhaustive BMP evaluation study has recently been completed for the purpose of establishing pollutant reduction efficiency values for different landscape settings throughout the region (Simpson and Weammert, 2009). This prior work has facilitated the development of a streamlined approach for estimating both loading rates and BMP reduction efficiencies in support of Pennsylvania's trading program.

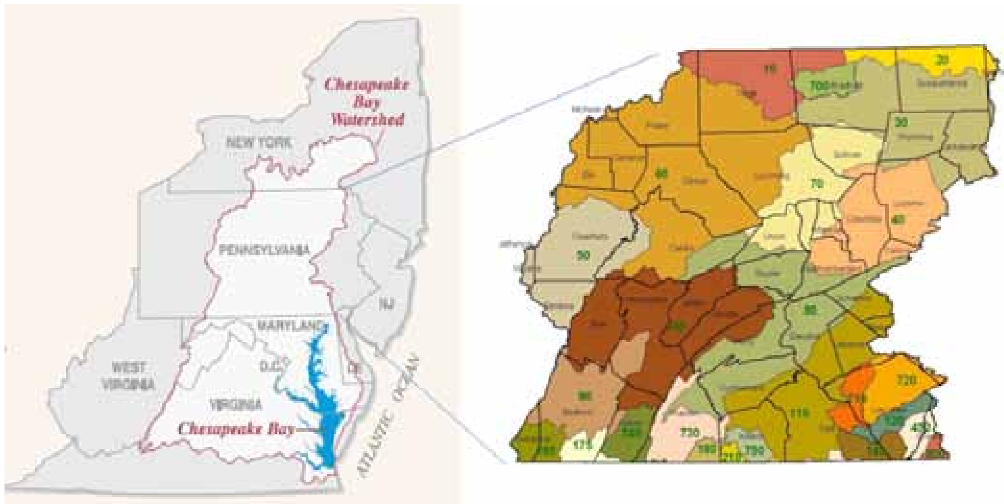

Figure 2. Pennsylvania sub-basins within Chesapeake Bay watershed.

In Pennsylvania, the general approach used for calculating nutrient credits can be described by the equation:

CP = (BL P * RFP * DFP)

where

CP = Pollution credits generated (in lb or kg per year)
BLP = Baseline load (in lb or kg per year)
RFP = Reduction factor (%) which varies by pollutant and practice/control approach
DFP = Delivery factor which varies by pollutant and geographic location

Based upon the Chesapeake Bay modeling work described earlier, each of the watershed sub-basins shown in Figure 2 have been assigned "baseline" nutrient and sediment loading rates for a range of land use/cover types (e.g., conventional till land, conservation till land, hay/pasture, woodland, etc.), as well as delivery factors (ratios) for each pollutant.

As an example of how nutrient credits are established under this scheme, various calculations are provided in Figure 3 for a situation in which a nutrient management BMP (reduced fertilization based on crops needs and soil testing) is used on 150 acres of conventional till land located in sub-basin 60. In this case, the model-based loading rates for nitrogen and phosphorus in sub-basin 60 are 32.3 and 1.86 lbs/acre/year; and the model-based delivery ratios (or delivery factor – DF) for nitrogen and phosphorus are 0.93 and 0.436, respectively (i.e., 93% and 43.6% of the nutrient loads delivered to large steams in this sub-basins are expected to be ultimately transported to the Chesapeake Bay). Also, for the Chesapeake Bay Watershed Model, the BMP reduction efficiency values (or reduction factor – RF) for nutrient management for nitrogen and phosphorus have been set at 11% and 20%, respectively. Therefore, for this scenario, the baseline loads (BL) are calculated to be 4,845 and 279 lbs/year for nitrogen and phosphorus, respectively; and the load reductions (or credits – C) are calculated to be 496 and 24.3 lbs/year, respectively. These nutrient credits may subsequently be certified as being available for purchase by Pennsylvania's Nutrient Trading Program at a mutually agreed upon price between the seller and buyer.

As evident from the above example, a prerequisite for performing the nutrient credit calculations illustrated is having reasonably accurate estimates for key variables including initial baseline loading rates, attenuation/delivery factors, and BMP-specific pollutant reduction coefficients. The first two variables are typically established via the use of detailed watershed simulation modelling (as illustrated by the Pennsylvania example given), and the latter variable is usually based on best available information drawn from previous studies and on-site testing.

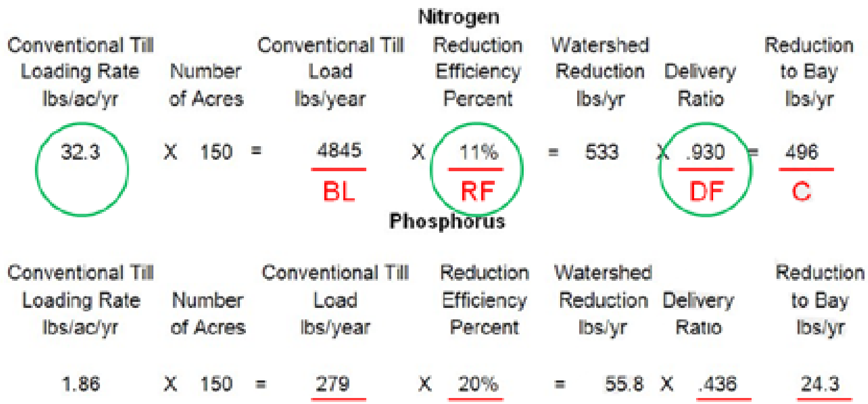

Figure 3. Example derivation of water quality credits in Pennsylvania

Water Quality Modelling

Over the last several decades, many different types of computer-based simulation models have been developed for the purpose of evaluating pollutant loads delivered to surface water bodies such as streams, lakes, estuaries, etc. At a basic level, these models can generally be described as being either watershed (landscape) models, or receiving water models. Due to the combination of these two types in many instances, however, this distinction has blurred somewhat over time. In the case of watershed or landscape models, such models can be described as being used primarily to simulate the movement of pollutants (e.g., nitrogen, phosphorus, sediment, pathogens, pesticides, heavy metals) over and through the land surface. The primary pathways/mechanisms by which pollutants might move in such models (although not always at the same level of detail) include dissolved or washed-off solids in surface runoff, pollutants attached to eroded soil in surface runoff, pollutants leached and transported via subsurface flow, streambank erosion, and direct disposal in surface waters. The typical hydrologic processes simulated with such models include precipitation (P), surface runoff (R), evapotranspiration (ET), infiltration (I), baseflow (BF), and deep groundwater recharge (GWR); all for the ultimate purpose of simulating flows and loads (Q) at the watershed outlet (see Figure 4). Examples of some watershed models commonly used in North America, Europe and elsewhere include, SWAT (Rosenthal et al., 1995), GWLF (Haith and Shoemaker, 1987), AGNPS (Young et al., 1989), HSPF (Bicknell et al., 1993), MONERIS (Venohr et al., 2010), and HBV (Lindstrom et al., 1997).

Receiving water models, by contrast, are typically used to simulate the various changes in flows and pollutant loads/concentrations that might occur as a result of a range of processes (e.g., deposition, plant uptake, chemical/biological transformations, etc.) over time and distance. A typical use of a receiving water model might entail an analysis of changing pollutant concentrations in different stream reaches or segments of a large lake depending upon changing input loads and water levels through time (or distance, in the case of riverine models). Some examples of popular receiving water models include QUAL2K (Chapra and Pelletier, 2003), Bathtub (Walker, 1996), StreamPlan (De Marchi et al., 1996), SWAT, HSPF, and SHE (Abbott et al., 1986).

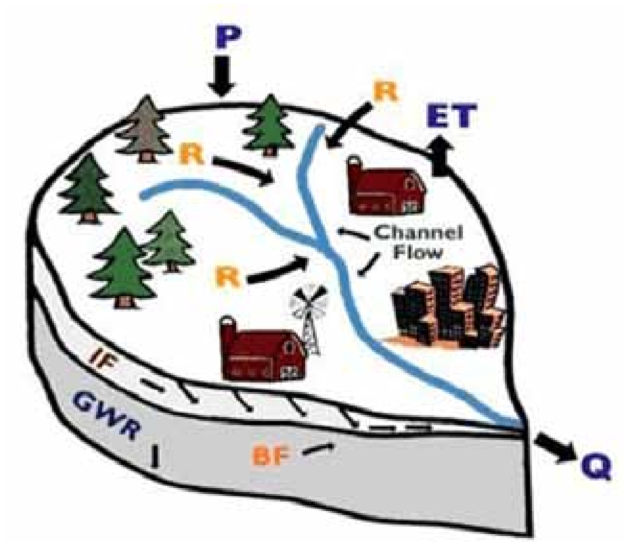

Figure 4. Primary processes simulated in a watershed model.

Input pollutant loads to receiving water models are oftentimes compiled or estimated separately by the user. However, there are many “combined” models that provide a linkage between “landscape” and “surface water” sub-models to facilitate analysis of the entire process of pollutants moving from areas in the watershed to receiving water bodies such as streams, lakes and estuaries, and subsequent transformations (i.e., attenuation) as a function of time and distance. Examples of some linked models include SWAT, HSPF, WAM (Bottcher et al., 2002), and MONERIS.

With watershed models, an important model characteristic that affects the accuracy at which loads are simulated is whether a “lumped” parameter or “distributed” parameter approach is used. With the former approach, data pertaining to such input parameters as soil type, land cover type and land slope are often generalized to simplify modelling algorithms. With a distributed approach, however, model input data are spatially organized at a much finer level of detail. Figure 5, for example, illustrates the use of both approaches with respect to estimating available water-holding capacity of soils. With the lumped approach, an average value of 14.4 cm of water per cm of soil is used; and with a distributed approach, this parameter value is allowed to vary spatially by sub-area. With respect to watershed modelling, this latter approach often provides better approximations of local landscape conditions, and hence, better simulations of loads originating from specific geographic locations. This has important ramifications with regard to nutrient trading in that better estimates of potential load reductions can subsequently be made if “localized” pollution loads are more accurate (i.e., the “BL” factor in Figure 3).

Another important model characteristic than can affect the utility of simulation results for calculations associated with nutrient trading is the capacity for estimating load attenuation as a function of travel time and distance. Since the attenuation rate is the inverse of the delivery factor (DF) shown in Figure 3, the estimation of this factor can be critical for use in supporting nutrient trading programs. With some models such as SWAT, MONERIS and SPARROW, the ability to estimate attenuation rates (and therefore, delivery rates) is handled by internal algorithms that can be calibrated using available in-stream water quality data. With other models, such rates may have to be calculated empirically. For example, attenuation/delivery rates within the Chesapeake Bay region have been estimated based on SPARROW modelling conducted by the U.S. Geological Survey (Preston and Brakebill, 1999). A graphic representation of delivery rates for nitrogen in this region is shown in Figure 6. In another example (see Figure 7), attenuation factors for point sources and diffuse sources of pollution in the Connecticut River Basin on the east coast of the United States were independently estimated via a process of iteratively reducing loads from both until they matched in-stream loads monitored at multiple in-stream sampling locations (Evans, 2008).

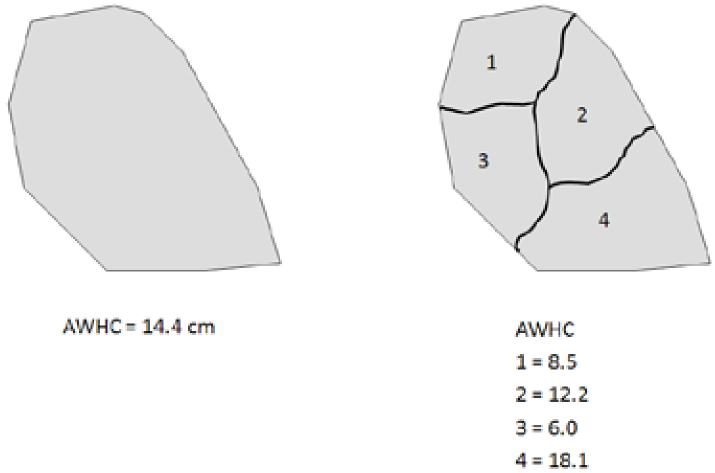

Figure 5. Lumped vs. distributed parameter approach.

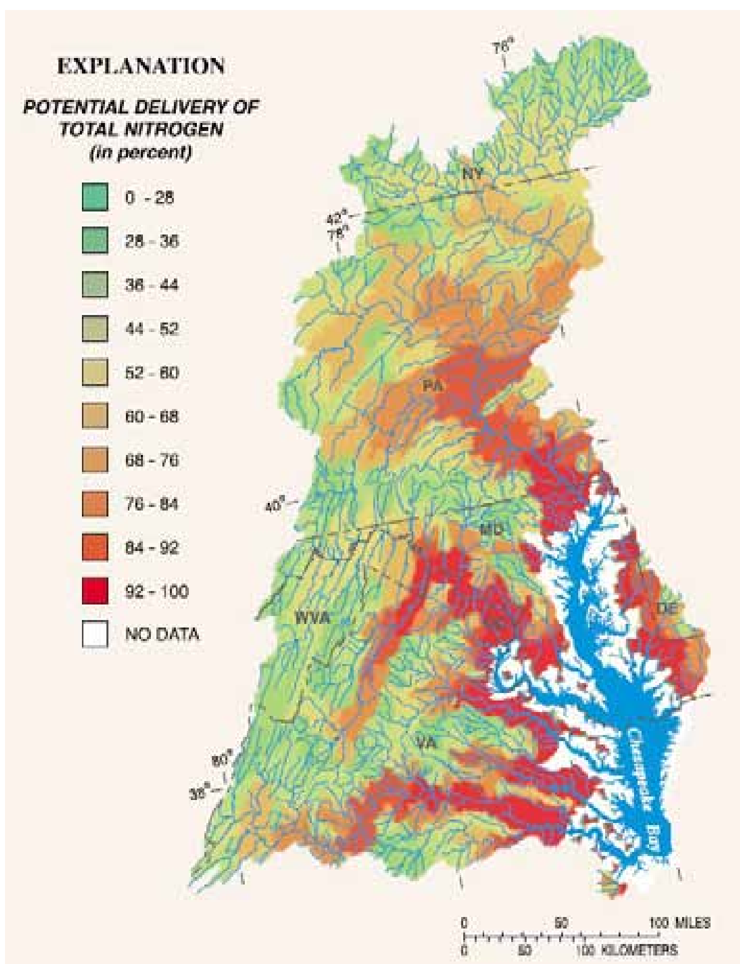

Figure 6. Estimated delivery rates for nitrogen in the Chesapeake Bay region (from Preston and Brakebill, 1999).

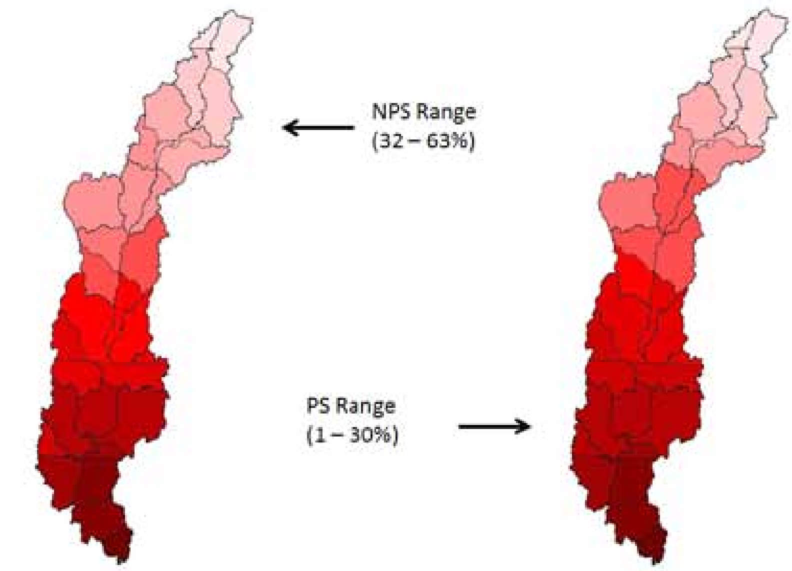

Figure 7. Estimated nitrogen attenuation rates for the Connecticut River Basin (from Evans, 2008)

GIS-Based Watershed Modelling

Significant improvements to watershed models and modelling techniques have been made over the last few decades. One of the most important improvements has been the development of assorted linkages to geographic information (GIS) software. Such linkages have greatly enhanced the estimation of the many parameters typically needed for these models, as well as the visualization of simulated results. In fact, digital data pertaining to soil types and characteristics, land use/cover, land slope, climate, and other model-related parameters is so prevalent that the utilization of watershed models without GIS linkages is fast becoming outdated. The use of digital GIS data sets allows more accurate representation of the spatial variation that exists across most watersheds, and such data are more easily modified to reflect changing (and future) conditions. Examples of watershed models with some level of GIS interface or linkage include:

- BASINS (linkage with HSPF, SWAT and GWLF models with either ArcView or MapWindow GIS software)
- AVGWLF, MapShed, CANWET (interface for customized GWLF model with either ArcView or MapWindow GIS software)
- SWAT (AGWA, AvSWAT)
- MIKE-SHE (linkage with ArcView)
- MONERIS
- HBV (Scandanavia)
- WAM (ArcView)

Such GIS interfaces typically allow a user to load in various GIS data sets, select one or more watersheds for subsequent data extraction/model parameterization, and then execute a model for watershed simulation (see Figure 8). In many cases, additional modelling and analysis tools also exist for further examination of watershed loads and conditions. For example, the PRedICT tool included with AVGWLF and MapShed provides for the generation of various “load scenarios” in which the effects of different levels of implementation of mitigation strategies such as the use of agricultural and urban best management practices (BMPs) can be explored. Other tools or models that provide some degree of “BMP evaluation” include STEPL, MONERIS and WAM.

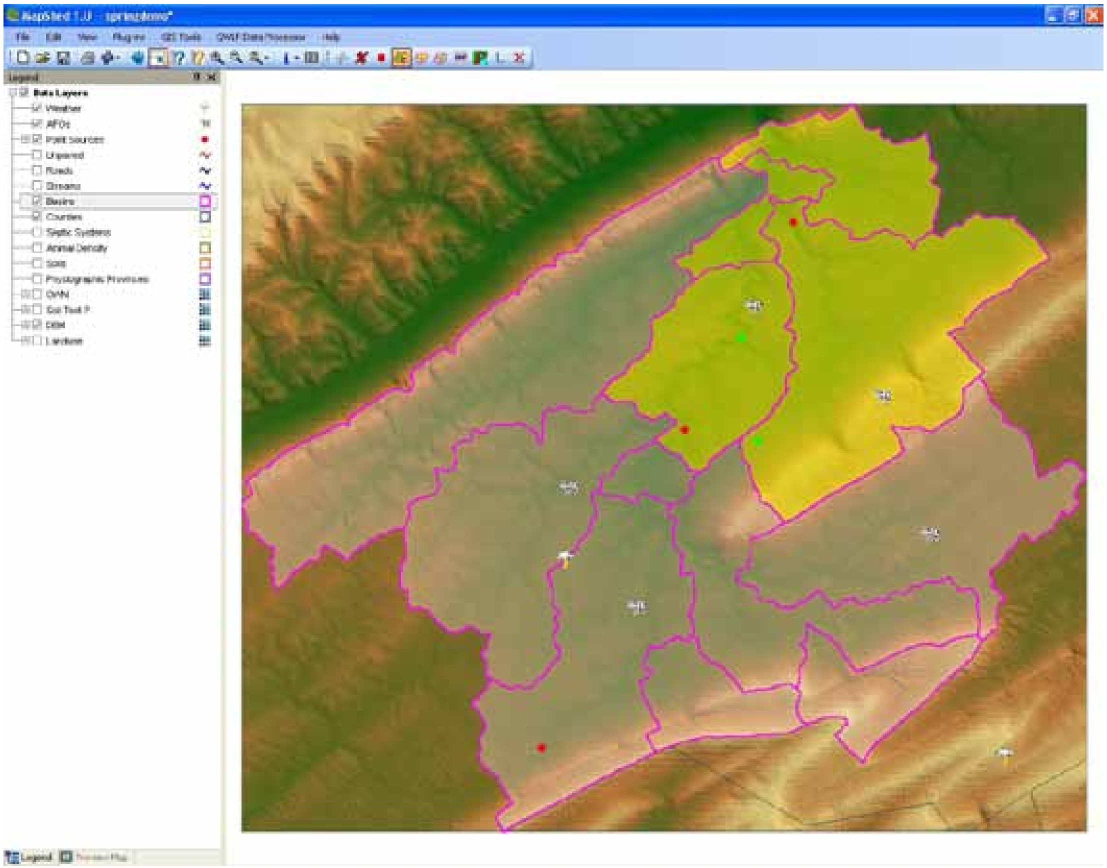

Figure 8. Example GIS/model interface (from Evans et al., 2010).

Basic Integrated Monitoring/Modelling Approaches

For use in support of nutrient trading programs, there are several basic approaches which incorporate some level of water quality monitoring and/or modelling that can be used, including:

- Intensive monitoring of the entire watershed (including intensive in-stream sampling at multiple locations to capture loads from many diffuse and point sources of pollution).
- Selective monitoring of key sources, and use of a low-level watershed model to simulate loads from remaining sources.
- Use of a higher-level watershed model in combination with an in-stream model to estimate loads and attenuation actors.

Other approaches similar to these, as well as various permutations of each, are also possible.

With the first approach, many samples at many locations over many years may be required in order to adequately measure loads (see above discussion related to Figure 1). As watersheds increase in size, the amount of sampling utilized may increase to levels that are not economically sustainable. The second and third approaches may involve comparisons of model-simulated loads against in-stream water quality data, whereas the first approach would be entirely based on in-stream sampling. Supplemental estimation of attenuation/delivery rates may be required for the second approach, whereas this may not be needed with the third approach depending upon the higher-level model used. All of the above approaches would also likely involve estimation or direct measurement of point source loads.

In each case, other "trading ratios" in addition to attenuation/delivery factors may also be required. Examples of other such ratios include "uncertainty ratios", "equivalency ratios", "retirement ratios", and "insurance or reserve ratios" (Selman et al., 2009; Zhang, 2008). Uncertainty ratios are primarily used to compensate for the uncertainty of the effectiveness of various mitigation measures, as well as the uncertainty associated with watershed modelling and weather variability. These ratios are often set around 2:1 (i.e., two units of non-point source reduction are required for each unit of point source load). Equivalency ratios are often used when two or more pollutants are traded to obtain an equivalent environmental result. For example, one unit of phosphorus reduction may have the same effect as eight units of BOD reduction, and one unit of nitrogen reduction may have the same effect as four units of phosphorus reduction. Retirement ratios (sometimes called "environmental benefit ratios") are used to ensure that a net water quality benefit is achieved beyond what can be achieved solely via regulation. For example, Michigan's trading program requires a 1:1.1 retirement ratio for trades between point sources. In other words, 10 percent of the credits generated and sold are retired and cannot be used to offset future loads. Finally, insurance or reserve ratios are used to set aside a portion of all generated credits into an insurance fund or "reserve pool". For example, in Pennsylvania's trading program, a 10 percent reserve ratio is applied to all generated credits. These excess credits are held in a special fund and serve as insurance in case regulated sources should default on any purchased credits.

Evaluation of BMP Effectiveness

A primary requisite with the BMP evaluation tools mentioned above, as well as in the calculation of nutrient trading credits as reflected in Figure 3, is the utilization of reasonable estimates for the pollution reduction effectiveness of various BMPs and other mitigation strategies. Unfortunately, there is no single source of universally-accepted effectiveness values. This, in part, is due to the wide differences in climate, landscape settings, and agricultural practices that exist throughout the world. However, a vast number of reports, databases and web sites exist from which useful information can be obtained.

For example, because of the extensive technical work that has been completed to support watershed modelling efforts in the Chesapeake Bay, many reports are available from www.chesapeakebay.net, including several on the implementation and effectiveness of a wide range of urban and agricultural BMPs. One excellent recent example is the report prepared by Simpson and Weammert (2009), which provides updated information on BMPs currently used in the Bay watershed model. Two other useful web sites include www.sepa.org.uk/bmp maintained by the Scottish Environmental Protection Agency, and www.sera17.ext.vt.edu, a site developed by a large group of agricultural researchers in Canada and the United States.

Another excellent source dedicated to urban BMPs is the International Stormwater BMP Database (www.bmpdatabase.org). This database is a joint effort involving many government agencies, non-profit organizations, and private companies in the United States. Currently, the database includes performance analyses, assorted BMP tools, monitoring guidance, and other publications based on over 300 BMP studies in North America.

Water Quality Trading Support Tools

As policies and regulations pertaining to water quality trading have been developed over the last decade, a number of useful tools (many web-based) have emerged to help promote and sustain this type of activity. Some examples include:

- Nitrogen Trading Tool developed by the U.S. Department of Agriculture (http://199.133.175.80/nttwebax/)
- Spreadsheet Tool for Estimating Pollutant Loads (http://it.tetratech-ffx.com/stepl)
- NMAN developed by the Ontario Ministry of Agriculture, Food, and Rural Affairs (www.omafra.gov.on.ca/english/nm/nman/default.htm)

Although these tools differ in their specific purpose and functionality, they are generally used to calculate initial and reduced loads at the farm level using site-specific input on such things as crop type, amount of area cultivated, fertilizer and manure use, and proposed BMP(s).

Another tool that takes this type of analysis one step further is the “Nutrient Net” web site recently developed by the World Resources Institute. The intent of this particular web-based application is to calculate existing pollutant loads and potential reductions, translate any reductions into “saleable” nutrient credits, and provide a means of communication between potential buyers and sellers of such credits (see www.nutrientnet.org). Among other things, this site provides a sophisticated map-based approach for characterizing local site conditions (e.g., soils, slope, climate, etc.) and deriving reasonable loading rates based upon these conditions.

SUMMARY AND CONCLUSIONS

The recent development of water quality trading programs around the world has focused attention on various technical requirements needed to support and sustain them. All trading programs rely on the use of one or more calculation methodologies for generating credits to be sold and purchased, and these methodologies can vary significantly in their complexity. Over the last two decades, vast improvements in watershed modelling techniques (including improvements in computers, GIS linkages, and the availability of digital map data) has greatly facilitated the estimation of key factors critical to nutrient trading calculations such as baseline pollutant loads and attenuation rates. Similar improvements have also been seen in the development of reasonably accurate BMP effectiveness estimates and the availability of web-accessible BMP databases and tools for estimating potential pollutant reductions based on various BMP implementation scenarios. The above advances have been supplemented by increasingly sophisticated web-based applications that incorporate site characterization and load estimation tools with other tools that promote interaction between potential sellers and buyers of water quality credits.

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Conducting cost-effectiveness analysis to identify potential buyers and sellers of water pollution control credits to initiate water quality trades

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Abstract

This paper explains the general concept of water quality trading and an overview of the mechanics of a cost-effectiveness analysis and how such analysis can be used to assist buyers and sellers of water quality credits.

Keywords

Buyers; Sellers; Credits; Water Quality Trading; Cost Effectiveness Analysis

INTRODUCTION

Government intervention into market-based production and consumption of goods and services that cause water pollution ultimately results in the redistribution of activities which generate and mitigate water pollution. The degree to and nature by which the redistribution of these activities takes place is obviously a function of the particular policy instrument employed (e.g. common law liability, regulations-based technology standards, effluent taxes, diffuse pollution mitigation grants and subsidies, etc.).

Among the policy instruments available to modify the most common system of water pollution control – government-determined water quality standards and centrally allocated water pollution control responsibilities – is water quality trading. Water quality trading (WQT), also commonly referred to as effluent trading, transferable discharge permits (consents), and water emissions trading.

The WQT concept is a simple one: water pollution control authorities simultaneously allocate wastewater and diffuse pollution loadings for pollutant parameters for an entire waterbody, catchment or river basin. They allocate in quantities consistent with maintenance or attainment of water quality standards (i.e. the cap) – and wastewater and diffuse pollution dischargers, either individually or collectively as sectors groups, are allowed to exchange for monetary compensation pollutant reduction responsibilities via permits, consents or contracts (i.e. trade) as long as doing so will not result in violations of water quality standards (i.e. post-trade loadings don't exceed caps).

The objective of WQT is to achieve water quality standards faster, fairer, and cheaper. It is similar to that of the carbon cap-and-trade scheme. The role of cost-effectiveness analysis in WQT is to identify the least-cost combination of measures needed to achieve a water quality objective, thus setting out the potential opportunities for trading. In essence, such an analysis is often the necessary starting point for WQT to commence. Without this information at the advent of a water quality trading initiative, the potential buyers and sellers of water quality credits are unlikely to be able to identify one another.

The objective of this paper is to:

1. Explain the general concept of WQT and provide an overview of the mechanics of a cost-effectiveness analysis conducted for application to a newly formed WQT initiative; and
2. Illustrate how such an analysis can be used to assist buyers and sellers of water quality credits in their efforts to identify one another.

WATER QUALITY TRADING: THE GENERAL CONCEPT

A potential buyer of emission credits is identified as a source that exceeds a socially acceptable level of discharge defined not only on the basis of environmental damage but also available technology, relative alternatives and production techniques. The lower the threshold for discharges and the more extensive a permit system is, the higher will be the interest in purchasing credits from other sources. This is because all discharge sources face increasing marginal abatement costs. As the level of abatement increases for any source then the cost per unit of reduction will increase. In addition, the more competition there is for control credits then the higher the price paid for these credits will be and the more constrained sources will implement own abatement measures. Diagram 1 depicts total reduction abatement costs for each source (A, B, C…).

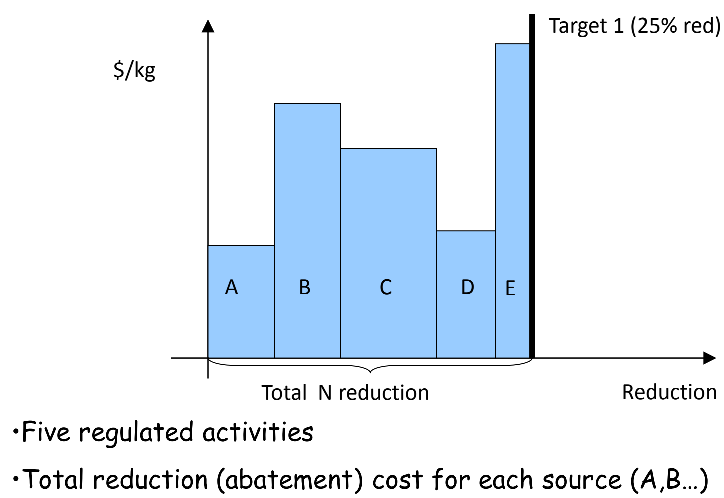

Diagram 1. Potential buyers: Regulated sources
Source: Author's

Creating demand for discharge sellers is critical. Sellers of credits will be sources that through their actions can provide a reduction in nutrients compared to current practices. These sources include both constrained and unconstrained dischargers. For constrained sources such as Waste Water Treatment Plants (WWTP) investment in abatement measures may result in reductions that are in excess of the permitted discharge, allowing constrained sources to sell credits would increase the cost efficiency of abatement.

Unconstrained sources which are able to reduce emissions through management practices may also be sellers of credits. These include best management practices (BMP) in the agricultural sector. The quantification of effectiveness remains a key challenge. The necessary step for the transformation of BMP programs into credits lies in the quantification of the expected effect of the BMP on discharges by the adopting source.

The evidence to support the 'effectiveness' component relies heavily on a range of professional inputs, such as modellers, hydrologists and soil scientists. Modelling offers a possibility for site-specific quantification of the effect of BMPs when adopted by individual producers. In essence, the use of modelling transforms the nonpoint source (NPS) discharge into a quasi-NPS discharge or what perhaps may be best described as a model generated point source. This enables agreement on equivalency. Diagram 2 depicts total reduction costs for each measure (I, II, III…).

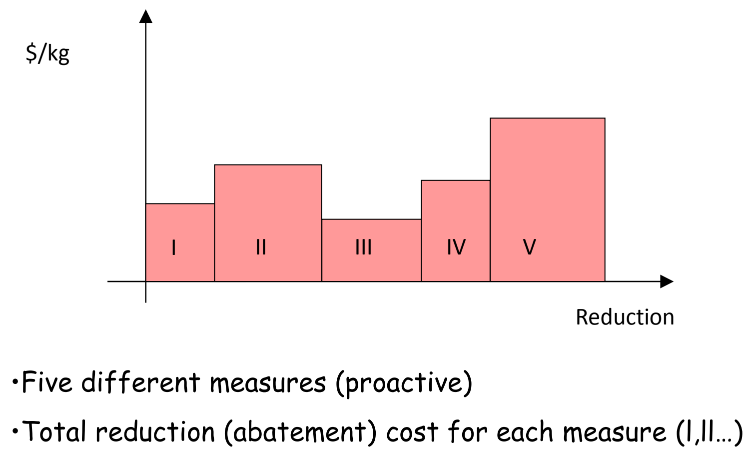

Diagram 2. Potential sellers: Abatement sources
Source: Author's

The constrained discharger demands pollution control credits to comply with regulation. The discharger can abate internally or purchase corresponding load reduction. The discharger faces two types of abatement costs: high abatement costs – with a corresponding large demand for other reduction sources, or low abatement costs – with a corresponding low demand for other reduction sources. Constrained discharger with low abatement costs will engage in few trades. Diagram 3 depicts the marginal abatement opportunities and constraints against a number of targets.

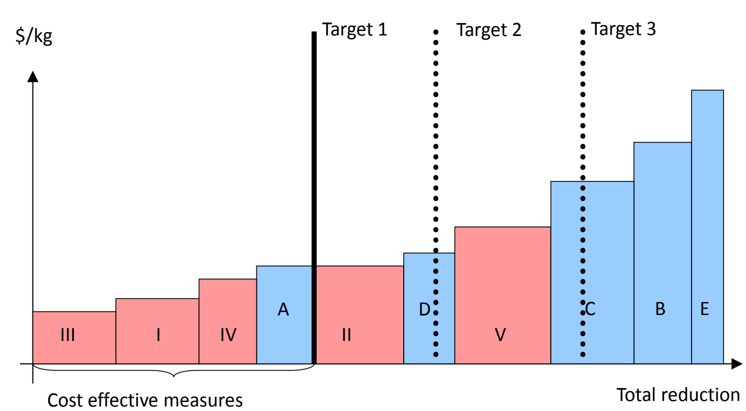

Diagram 3. Marginal Abatement opportunities and constraints
Source: Author's

The larger the spatial scale and the more stringent the target, the more opportunity for cost effective trades. The quantification of effectiveness remains a key challenge and agreement of sufficient equivalency is required to determine effectiveness. The type of measure and the location determine effectiveness.The smaller the scale the greater the chance for equivalency.

THE MECHANICS OF COST EFFECTIVENSS ANALYSIS OF WATER POLLUTION CONTROL MEASURES

A cost-effectiveness analysis in the context of the application described in this paper is simply a determination of the least-cost combination of water pollution control measures available to achieve some pre-determined water quality objective, which in most applications will simply be an ambient standard concentration for a regulated pollutant. In true market-based political economies (i.e. non-centrally-planned economies), the cost-effective provision of most goods and services is not contingent on a cost-effectiveness analysis. Producers in market economies must exploit the least-cost combination of input factors to stay competitive (subject to government interventions to protect human rights, private property rights, natural resources held in the 'public trust' etc.). Cost-effective production of most commodities occurs in such societies automatically (subject to interventions) – no cost-effectiveness analysis by a central authority or trading broker is necessary.

Cost-effectiveness analysis is, however, sometimes prepared in the water pollution management realm at the treatment facility level to minimise the cost of achieving effluent permit limits. It is also commonly applied to discharger categories (e.g., metals manufacturers) across multiple waterbodies in a single political jurisdiction. This in fact is the case in the United States (US), where cost-effectiveness analysis is a required step in the National Pollutant Discharge Elimination System Effluent Limitations and Standards regulations promulgation process. The application of cost-effectiveness analysis across all discharger types in a single waterbody (or watershed) is also a regulatory requirement in certain situations in the US (under Section 208 of the Clean Water Act) and in Europe (under Article 3 of the Water Framework Directive).

The information needed for a cost-effectiveness analysis of this nature consists of estimates of relative effectiveness (relative to attaining the pre-determined water quality objective) and marginal costs associated respectively with the implementation of each potential measure. In absence of bespoke costs estimates, literature-based ranges of estimates are obtainable and can be applied to a particular area of interest if the types of sources impacting the water bodies can be identified and some assumptions can be made as to their current water pollution control measures. However, the effectiveness any given measure from an impacting source may have in contributing toward attainment of a water quality standard objective cannot be estimated without area-specific monitoring data (which can typically be supplemented with water quality modeling data). As such, cost-effectiveness analysis of water pollution control measures cannot be done in the absence of quantitative information about current levels of pollutant loadings in water bodies of interest and the respective sources of those loadings.

With water quality modeling data in hand, cost-effectiveness analysis of water pollution control measures is done via a simple constrained cost-minimization calculation. The calculation takes account of the exact levels of employment of each measure at each impacting source and their coinciding marginal costs, thus allowing the levels that coincide with the minimum marginal cost to achieve the pre-determined water quality objective to be identified.

Expression 1, (taken directly from Blacklocke, 2007) is a generalized version of the algorithm typically used to conduct a cost-effectiveness analysis of water pollution control measures.

Expression 1 – Generalized Algorithm for Cost-Effectiveness Analysis of Water Pollution Control Measures

$$\min \mathrm{TOTAL\_COST}\ P_{REQRED} = \sum_{x=1}^{X}\sum_{y=1}^{Y}(\mathrm{MARGINAL\_COST}_x)(P_{REDy})$$

$$\mathrm{s.t.} \sum_{x=1}^{X}\sum_{y=1}^{Y} P_{RED_{xy}} \geq P_{REQRED}$$

where;
MARGINAL_COST = additional cost of reducing additional pollutant (P)
P_{REQRED} = required reduction of P loading to water body
P_{RED} = reduction of P loading to water body
x = P loading reduction management measures
y = P units reduced

The four distinct cost categories that are typically included in a cost-effectiveness analysis of pollution control measures include:

- Engineering and construction (i.e., capital);
- Operation and maintenance;
- Administrative and regulatory; and
- Opportunity (i.e., lost profit).

A generalized algorithm for discounting and summing these cost components through any given time period is given in **Expression 2**.

Expression 2 – Generalized Algorithm for Discounting and Summing Cost Components

$$\mathrm{MARGINAL\_COST}_x = \sum_{t=1}^{n}(1+r)^{t-1}\left(MC_{EC_x} + MC_{OM_x} + MC_{AD_x} + MC_{OP_x}\right)$$

where;
$\mathrm{MARGINAL\_COST}_x$ = total additional cost of reducing additional pollutant (P) unit via measure x
MC_{ECx} = additional engineering and construction cost of reducing additional P unit via measure x
MC_{DMx} = additional operation & maintenance cost of reducing additional P unit via measure x
MC_{ADx} = additional administrative cost of reducing additional P unit via measure x
MC_{OPx} = additional opportunity cost of reducing additional P unit via measure x
x = P reduction measures
r = discount rate
t = time periods of expenditures on measures (e.g., number of years expenditures are annualized)

In order to take account of the dynamic nature of such estimates, a cost-effectiveness analysis such as this should be undertaken frequently. Changing information influencing measures might include:

- Changes in measure-specific funding procurement;
- Changes in total pollution control program budgets;
- Changes in the operations and resultant discharges of the impacting sources;
- Improved estimates of measures' effectiveness and costs;
- Revisions to regulatory water quality objectives; and
- Changes in measure-specific regulations.

It is important to note that although point estimates are typically used in the optimization calculations described in **Expressions 1 and 2**, in reality, for *ex ante* estimations, those estimates would typically be medians of ranges constituted by literature-based derivations of values.

EXAMPLE OF APPLICATION OF COST-EFFECTIVENSS ANALYSIS TO ASSIST WATER QUALITY TRADING

Presented here for the purpose of illustrating the concepts presented in the previous section of this paper is a hypothetical cost-effectiveness anlaysis of water pollution control measures. For simplicity, the application requires only simple visual optimisation.

Assume water quality modelling of available monitoring data for a catchment or waterbody has generated estimates of respective phosphorous (P) loadings from four different sources: manure fertilised land, chemical fertilised land, septic systems, and domestic WWTPs (see Figure 1).

P Loads (kg/yr)	
Manure fertilised land	2,186
Chemical fertilised land	2,255
Septic Systems	35
WWTP	811
Total Current	5,288
Good Status	2,299
Target Reduction	2,989

Figure 1. P loading estimates to a hypothetical catchment

In terms of economic sectors, the water quality pressures from P are agricultural and domestic in nature, and P loading to the river from agriculture dominates.

With this estimate of current total P loading at average flow, and an estimate of the total P loading that is consistent with 30 micrograms of P per litre at this same flow (which is the ambient standard), by simple subtraction the P reduction target can be identified. It is 2,998 kg/year.

Table 1 shows a list of measures for each P source for which estimates of P reduction effectiveness and costs were generated. Also shown in Table 1 are the estimates of each measures' effectiveness and costs associated with only that one increment of implementation.

Table 1. Simple visual cost-effectiveness analysis of water pollution control measures (Source: Author's)

Sources of P	Management Measures	Effectiveness (P kg/yr reduction)	Costs (E/yr for 10 yrs)	Cost- effectiveness (E/kg P reduction	Rank
Manure fertilised land	Manure management plans	437	250,000	572	06
	25% stocking reduction	546	22,800,000	41,758	15
	Sheltered manure storage	218	150,000	688	07
	1,5 km2 riparian buffers	328	580,000	1,768	09
	Feed optimisation plans	219	3,200	15	01
	500 m3 retention ponds	164	60,000	366	05
Chemical fertilised land	Fertiliser manegement plans	564	82,500	146	03
	50% grassland conversion	1128	408,500	362	04
	1,5 km2 riparian buffers	338	580,000	1,715	08
	500 m3 retention ponds	451	60,00	133	02
Septic systems	Inspections and upgrades	32	652,408	20,388	14
	Treatment plans tie-ins	35	244,678	6,991	12
	Education programme	9	75,000	8,333	13
WWTP	MLE without filtration	561	2,649,000	4,722	10
	MLE with filtration	686	3,788,000	5,522	11
Totals		3181	1,014,200		

Assume that the costs are annualised over ten years and include regulatory agencies administrative costs; the sources engineering and construction costs, operation and maintenance costs, and opportunity costs. An example of the latter would be the lost profit on cattle that might result from a stocking reduction management measure.

Determining the most cost-effective means by which the P reduction objective can be attained and thus the P standard can me met involves simply singling out the management measures, one after the other in rank order of cost-effectiveness. The cost-effectiveness score is calculated by dividing the cost estimate by the effectiveness estimate. Measures are selected until the total P reduction target is met or exceeded.

Now assume this allocation of water pollution control responsibilities is not politically practical, perhaps due to the imbalance in the distribution of new costs between the agricultural and domestic dischargers relative to their respective abilities to absorb these costs without severe economic implications (e.g. farms go out of business).

If the government authority, in making its allocation of pollution control responsibilities, takes such considerations into account in making its assignment of new measures, the effect will be to increase the total cost across all dischargers of meeting the P standard (See Table 2). In this example, the same objective is met, but at a cost of 3.3K instead of 1.0K.

Table 2. Allocation of water pollution control responsibilities accounting for cost-impact equity (Source: Author's)

Sources of P	Management Measures	Effectiveness (P kg/yr reduction)	Costs (E/yr for 10 yrs)	Cost- effectiveness (E/kg P reduction	R A N K
Manure fertilised land	Manure management plans	437	250,000	572	06
	25% stocking reduction	546	22,800,000	41,758	15
	Sheltered manure storage	218	150,000	688	07
	1,5 km2 riparian buffers	328	580,000	1,768	09
	Feed optimisation plans	219	3,200	15	01
	500 m3 retention ponds	164	60,000	366	05
Chemical fertilised land	Fertiliser manegement plans	564	82,500	146	03
	50% grassland conversion	1128	408,500	362	04
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	500 m3 retention ponds	451	60,00	133	02
Septic systems	Inspections and upgrades	32	652,408	20,388	14
	Treatment plans tie-ins	35	244,678	6,991	12
	Education programme	9	75,000	8,333	13
WWTP	MLE without filtration	561	2,649,000	4,722	10
	MLE with filtration	686	3,788,000	5,522	11
Totals		3,087	3,263,200		

Alternatively, the government authority, with no readily available cost or effectiveness estimates and no water quality models, may choose to ignore all costs and cost impacts and forego any effectiveness estimation and simply continue to ramp up pollution abatement requirements on the already highly regulated sources. An example of the outcome of this approach is shown in Table 3, where in this hypothetical scenario, the discrepancy between the cost-effective allocation of P reduction responsibilities and the centrally allocated one is 3K. And further, the P standard is not attained.

Sources of P	Management Measures	Effectiveness (P kg/yr reduction)	Costs (E/yr for 10 yrs)	Cost- effectiveness (E/kg P reduction	R A N K
Manure fertilised land	Manure management plans	437	250,000	572	06
	25% stocking reduction	546	22,800,000	41,758	15
	Sheltered manure storage	218	150,000	688	07
	1,5 km2 riparian buffers	328	580,000	1,768	09
	Feed optimisation plans	219	3,200	15	01
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	50% grassland conversion	1128	408,500	362	04
	1,5 km2 riparian buffers	338	580,000	1,715	08
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Septic systems	Inspections and upgrades	32	652,408	20,388	14
	Treatment plans tie-ins	35	244,678	6,991	12
	Education programme	9	75,000	8,333	13
WWTP	MLE without filtration	561	2,649,000	4,722	10
	MLE with filtration	686	3,788,000	5,522	11
Totals		1941	4,368,378		

Table 3. Information-limited or simple technology based allocation of pollution control responsibilities (Source: Author's)

Under a water quality trading system, such politically practical and/or information-limited water pollution control allocations can be made, and the trading policy instrument can serve as a means by which some cost savings may be recaptured.

Consider how the information in the most rudimentary cost-effectiveness analysis presented in Table 1 could be used to enable the initiation of water quality trading. Assume that regulations were enacted that required that 50% of chemically fertilised cultivated land area be in grassland in order to lower the level of intensive agriculture, or that compensating reductions be purchased in lieu of the regulations. The regulations would lead to a reduction of 1,128 kg P (Table 1). The regulated landowners could purchase reductions from cheaper sources of measures in Table 1; feed optimisation plans, fertiliser management plans and retention ponds. These sources could provide up to 1,234 kg reductions at a cost of $145,700 compared to the $408,500 that this would cost if the regulated landowners undertook the reduction themselves. While the level of reduction is the same the cost saving is $262,800 compared to achieving the regulation by changing crop production. Including a mandatory 25% reduction in stocking ratios would change the distribution of measures but the results would still be cost effective. The total reduction would increase to 1674 kg P with 1,234 coming from the sources identified above and the additional amount (440 kg P) coming from grassland conversion. The cost for the total reduction is around $305,000 which can be compared to the total cost if there was no possibility to trade ($230,490,000).

CONCLUSIONS

The objective of water quality trading (WQT) is to achieve water quality standards faster, fairer and cheaper. The potential buyer of emission credits is identified as a source that exceeds a socially acceptable level of discharge defined not only on the basis of environmental damage but also on available technology, relative alternatives and production techniques. The constrained discharger demands pollution control credits to comply with regulation. The discharger can abate internally or purchase corresponding load reduction. The discharger faces two types of abatement costs: high abatement costs – with a corresponding large demand for other reduction sources, or low abatement costs – with a corresponding low demand for other reduction sources. Constrained discharger with low abatement costs will engage in few trades.

Cost effectiveness analysis in WQT allows for the identification of the least-cost combination of measures to achieve the water quality objective, which in most applications will simply be an ambient standard concentration for a regulated pollutant. The information needed for a cost-effectiveness analysis of this nature consists of estimates of relative effectiveness (relative to attaining the pre-determined water quality objective) and marginal costs associated respectively with the implementation of each potential measure.

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Developing a Community-based Approach to Diffuse Pollution Control in the Loweswater Catchment (UK)

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Abstract

Diffuse pollution is a significant problem in the UK which affects compliance with very demanding water quality and ecological targets established under the European Union Water Framework Directive. Although a number of management initiatives have already been implemented by government agencies to reduce diffuse pollution, the majority operate at a very large spatial scale with a minimum of stakeholder engagement. This paper reports on a project which has aimed to develop an alternative community-based approach to catchment management at the local scale which is capable of tackling diffuse pollution through collaborative research and problem-solving. A new institutional mechanism has been created for Loweswater in the English Lake District which involves members of the local community, researchers and institutional stakeholders. Working together, the participants have aimed to improve understanding of the catchment and to identify practical actions to reduce the algal blooms which affect the lake. A substantial body of knowledge has been generated and some land owners and others interests have voluntarily made changes to their practices. Nevertheless, the community-based mechanism is not connected to the formal institutional structures and processes for resource planning and management operated by local municipalities or government agencies. As a consequence, implementing proposals and recommendations developed collaboratively by the group remains a considerable challenge.

Keywords

Community, collaboration; watershed management; Loweswater

INTRODUCTION

There have been significant improvements in the quality of UK surface waters during the last twenty years which are largely due to increased investment in sewage treatment and tighter regulation of point-source discharges. However, new and more stringent standards established under the European Union (EU) Water Framework Directive (WFD) now mean that many surface waters previously considered to be in a 'healthy' condition are now at risk of failing water quality and ecological targets. As a result, the control of diffuse pollution has become a major focus of concern for science, policy and management. In comparison to point-sources, the effective control of diffuse pollution is a much more complex and intractable problem. Typically, numerous potential sources and pollutant pathways are involved and there is often a great deal of uncertainty regarding their relative influence on aquatic conditions and risks such as toxic algal blooms. Furthermore, it is often unclear whether water quality problems are the result of past or present land-use and management practices, or possibly a combination of both. There are also significant institutional challenges associated with diffuse pollution, as the problem often spans the jurisdictions and interests of many different organisations, agencies and groups. Governance arrangements for agriculture, other types of land and also water use are generally complex, multi-layered and poorly co-ordinated. As a consequence, changes in policy and practice that are required to deal with diffuse pollution can be very difficult to achieve. It is not surprising therefore that diffuse pollution has been characterised as a 'wicked' or 'messy' problem which is beyond the capacity of any single organisation or agency to effectively control on its own (Lachapelle et al. 2003, Watson et al. 2009a). The implication is that new and innovative institutional arrangements are required (Jaspers, 2003; Mitchell, 2005). In particular, collaborative institutional mechanisms are needed to bring different forms of expert and lay knowledge together and to generate effective management responses through collective debate and action (Warner, 2007; McDonnell, 2008).

This paper is concerned with the question of how collaborative management responses to diffuse pollution can be developed, and analyzes one such initiative developed in the Loweswater catchment in the English Lake District. A short description of the Loweswater catchment is provided in the next section, followed by an explanation of the philosophy and the specific approach adopted for this catchment project. Attention is then turned to assessing how collaboration has worked in practice at Loweswater and to the benefits, costs and challenges associated with this type of approach. Finally, conclusions regarding the value of collaborative institutional platforms for managing diffuse pollution at the catchment scale are presented, and lessons for future policy and practice are outlined.

UNDERSTANDING AND ACTING IN LOWESWATER

Loweswater is a small shallow lake with a surface area of 0.64 km^2 and a total catchment area of 8.9 km^2 to the west of the town of Keswick in the English Lake District. Land use in the catchment is dominated by economically marginal sheep farming, with some additional beef and dairy production on the improved grassland around the edges of the lake. The lake itself, which once supported a valuable trout fishery, is owned and managed by a charitable conservation organisation called the National Trust (NT). The surrounding landscape is classed as a 'quiet valley' by the Lake District National Park Authority, and as a result only very low levels of tourism development have been permitted. The local population is a mix of farming families plus 'off-comers' who are typically retired people with professional employment backgrounds. In the last few years, members of the local community and some of the management agencies have expressed concern about the quality of the lake, and in particular the sight of toxic blue-green algal blooms which have resulted in warning signs being posted around the perimeter footpaths. The blooms occur erratically and do not appear to follow the patterns shown in similar lakes in the area. As a result, the algal blooms have become a local 'knowledge controversy' with questions being asked about the seriousness of the problem, the likely causes and actions which can be taken to improve the condition of the lake (Waterton et al. 2006).

Philosophy and approach

With funding from the Rural Economy and Land Use (RELU) programme, researchers from Lancaster University and the Centre for Ecology and Hydrology (CEH) have been working since June 2007 with members of the local community and the various agencies to address these questions by conducting research, engaging in debate and attempting to put ideas into action. As such, the project has provided a rare opportunity to develop a collaborative approach to integrated catchment management at a very small 'local' scale. In order to bring the different individuals, groups and organisations in the catchment together, a community forum (named the Loweswater Care Project) was created by the research team. The LCP is open to anyone with an interest in Loweswater and functions as a 'knowledge collective' whereby information from many different sources can be gathered together, shared, scrutinized and debated in a series of bi-monthly meetings held in the local village hall. The LCP has developed a distinctive 'philosophy of practice' which is designed to encourage constructive, open debate and the sharing of information and ideas: First, different understandings of the problem(s) in the lake and the surrounding catchment which participants may subscribe to are recognized, respected and valued within the LCP. Second, the LCP accepts that knowledge and expertise related to the catchment need to be openly debated rather than taken for granted or assumed to be accurate. Third, it is acknowledged within the LCP that there will always be gaps in knowledge and understanding, and that decisions will inevitably have to be made in the face of uncertainties. Finally, the LCP recognizes that the development of a shared understanding and commitment among the participants is essential as a basis for future collective action.

Problems related to the use of water, land and other natural resources, including diffuse pollution, are often characterised by complexity, change, uncertainty, and potential conflict. Collaborative decision making and problem-solving is particularly suited to these kinds of conditions and challenges (Innes and Booher, 1999). As such, a collaborative approach was adopted for the Loweswater project. One of the most widely cited definitions of collaboration was provided by Gray (1985):

> "By collaboration we mean: (1) the pooling of appreciations and/or tangible resources, e.g. information, money, labour etc., (2) by two or more stakeholders, (3) to solve a set of problems which neither can solve individually."

Collaboration clearly means much more than simply multi-party participation, co-operation or co-ordination. It is conceived as an emergent and iterative process where differences in interest, values, preferences and capabilities are recognised and used in a constructive way to enhance the problem-solving capacity of a multi-party group. Various models of the collaborative process have been proposed in the literature (for example, McCann 1993, Selin and Chavez 1995, Hudson et al. 1999). Although there are some differences, most models typically focus on role of contextual conditions, problem-setting, direction-setting, structuring and finally outputs and outcomes (Figure 1).

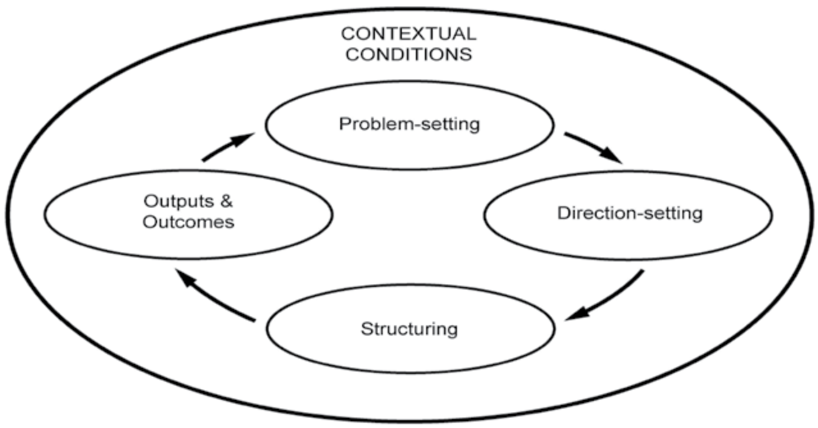

Figure 1. Conceptual framework for collaborative working

Contextual conditions draw attention to the fact that collaboration can be very difficult to initiate among a diverse mix of organisations and interests because differences are likely exist, at least initially, in terms of power, human and financial resources, authority/jurisdiction and knowledge/expertise. In addition, some organisations may perceive collaboration as an opportunity to extend their influence or gain additional resources to further their individual aims and objectives. In contrast, conditions tend to favour genuine collaboration when organisations appreciate their interdependencies and realise that acting alone will not resolve the problems they face. The implication is that collaboration has greater potential in some situations than others. Prior to commencing the process, advocates may need to work with potential participants on an individual basis in order to actively generate sufficient support and commitment.

The process of collaboration itself involves four phases of activity (Watson, 2004). During problem-setting, attention is focussed on establishing a joint understanding of the identity of the problem(s) and the stakeholders who occupy the problem domain. In the context of diffuse pollution control, questions such as 'what is the current state of the catchment or river basin', 'who is affected and in what ways' and 'is the current state less than desirable' are collectively addressed by the participants so that social recognition of the problem's existence is developed. Successful problem-setting also helps to strengthen the links among the participants and may also help to draw in additional groups that previously had resisted collaboration, or possibly sought to use it solely for their own ends. In the direction-setting phase, attention is turned towards the identification of desirable future conditions and establishing a common direction for action. This is often referred to as 'ends legitimacy' – the process of gaining support for super-ordinate and feasible goals which reflect the concerns and aspirations of the collaborating organisations. In practice, the establishment of long-term goals and actions is often a difficult and time-consuming process because of the diversity of understandings, values, attitudes and aspirations that exists among the people who are involved. In the structuring phase, attention shifts towards the establishment of arrangements to guide subsequent collective action. In effect, roles and responsibilities are allocated regarding the implementation of agreed actions and the regulation of future interactions among the collaborators. According to McCann (1993), this phase in the process is particularly important for ensuring that agreed plans are fully implemented. If responsibilities are vague or unclear, it is likely that a significant implementation gap between 'planning' and 'action' will emerge. The ultimate purpose of collaboration is to make a set of problems less severe and more manageable. In this sense, collaboration should be viewed as a means to an end and not an end in itself. The fourth phase is therefore concerned with the generation of outputs and outcomes. Outputs refer to joint policies, programmes and projects that are developed and implemented by the participants. Outcomes refer to changes in the scale or significance of the shared problem or problems identified at the beginning of the collaborative process. The generation of demonstrable outputs and outcomes is extremely important, as this is likely to encourage the participants to remain committed to the process in the future.

Although the conceptual framework implies that collaboration is a tightly structured and cyclical process, in practice the phases of activity may not follow the suggested sequence and several repetitions of the cycle may occur during the lifetime of a particular management initiative. Furthermore, given that knowledge is likely to be incomplete and understandings are likely to change during the process, it may be necessary to go back to a previous phase and re-consider the nature of the problem, the definition of goals, the structure of the initiative or the types of outputs and outcomes which are judged to be necessary or desirable.

Research Findings and Insights

Although the Loweswater project is not due to finish until December 2010, some findings and insights regarding the value of a collaborative approach to catchment management and diffuse pollution control have already emerged. Some of the key findings as they relate to the five aspects of the collaborative model presented in Figure 1 are summarized below. A combination of favourable contextual factors enabled a collaborative process to be initiated. Loweswater is a small and isolated place where community spirit and social relationships are very important. In addition, the algal blooms provided a highly visible indicator of poor water quality which had generated public concern and comment for several years prior to the start of the project. In 2003, eleven local farmers had established their own Loweswater Improvement Project and had worked with CEH and the NT on a programme of lake and stream sampling to improve understanding of possible links between land use and water quality. As such, the situation was therefore well 'primed' for this type of approach, but nevertheless working collaboratively was still a new experience for many local people and institutions. As such, the researchers had to work hard during the first few months to explain the underlying philosophy of the project and the value of opening-up the scientific questions, rather than continuing under the widely held assumption that the problem was solely a direct consequence of the intensification of farming in the catchment since the 1950s.

A great deal of the LCP's effort has been devoted to developing a better understanding of the identity of the problem by investigating conditions and processes affecting both water and land. This has included surveys of farming practices, terrestrial ecology and fish populations plus automatic monitoring of water quality and meteorology from a buoy anchored on the lake. In addition, studies of local history and management arrangements have been conducted. Many different types of information and data have been utilized, including old photographs, personal recollections and field observations in addition to the results of the science-based surveys. While some of the initial work was conducted by members of the research team, opportunities were also presented for other members of the LCP to become involved. For example, £35,000 was made available for additional small research projects to be conducted by local people in conjunction with the institutions and full-time research team. Funded small projects covered a wide range of topics, including the condition of septic tanks and the use of household detergents in the catchment, the analysis of historical land-use data and palaeolimnological records of nutrient change in the lake, a hydro-geomorphological survey, modelling of nutrient leaching from soils and a study of local attitudes to the use and future development of the area for tourism and outdoor recreation. The results from the various strands of research have been presented and debated at LCP meetings with the aim of developing a fuller and more sophisticated collective understanding of the catchment and possible links with the algal bloom problem.

Some of the research has shown very clearly that there have been significant changes in the catchment during the last 200 years and, despite the local perception of a very static and unaltered landscape, future changes are inevitable. This has helped to focus the LCPs attention on direction-setting and the identification of management goals and objectives. A key step in this process was the development and adoption of a vision statement by the LCP:

> "The LCP is a grassroots organisation made up of local residents, businesses, farmers, ecologists, sociologists, geographers, agronomists, environmental agencies and other interested parties. We work collectively to identify and address catchment-level problems in an inclusive and open manner. The LCP's vision is to gain a better understanding of the diverse challenges faced by the Loweswater catchment and together to seek economically, socially and ecologically viable ways forward and put them into practice."

Although the vision statement has helped to articulate the long-term aspirations and goals of the LCP, questions relating to the future of the catchment have been among the most difficult and challenging. In part, this reflects the higher levels of uncertainty compared to questions related to the past and the present. However, it is also a reflection of composition of the local population which includes a significant number of elderly people, many of whom are quite wealthy and have retired to the area because of the quiet and 'unspoilt' environment it offers. As such, there is some resistance to the need for change in the use and management of the catchment, although there is nevertheless a broad consensus that improving water quality in order to reduce the risk of algal blooms is a worthwhile objective. The LCP has not resolved these tensions, but it has nevertheless drawn attention to the connections among environmental, economic and social goals and the need for balance and compromise in decision making. As a result, the future of farming has emerged as one of the main topics for debate in the LCP. On the one hand, the evidence points towards agriculture as a key contributor to nutrient enrichment in the lake, but on the other hand it is also recognized that agriculture has produced much of the landscape which is valued by the members of the LCP.

Structuring has primarily involved the establishment and maintenance of the LCP over a three year period. Despite there being some different expectations, local people and representatives for the institutions have regularly attended the LCP meetings. By June 2010, a total of twelve LCP meetings had been held, with 25-35 people attending on each occasion. While it was hoped that the LCP would develop some self-organising qualities, in practice the meetings have been largely arranged and facilitated by the full-time researchers. However, a community-based researcher, who is also a well-respected local farmer, has been instrumental in maintaining communication with members of the community and sustaining their interest and support for the project.

Key organisations such as the Environment Agency, Lake District National Park Authority, National Trust, and Natural England have participated in the project over the last three years and have been willing to explain their catchment management roles and responsibilities to the LCP. However, specific links between the LCP and the formal decision-making structures and procedures of these organisations have not emerged. The organisations appear to be interested in and supportive of the LCP, but in terms of their management policies Loweswater itself is not a high priority compared to the larger lakes in the region such as Bassenthwaite and Windermere. In addition, Loweswater is not very 'visible' in terms of government-sponsored management initiatives such as the Water Framework Directive and the Catchment Sensitive Farming Initiative, which are being implemented at much larger spatial scales. The lack of connection between the LCP and the formal decision making structures and procedures operated by the institutions has been both an advantage and a disadvantage. One advantage has been that the LCP has created its own 'space' which is free from direct pressure or interference by the institutions. The main disadvantage, however, has been that the LCP has lacked direct routes or mechanisms which might otherwise allow ideas or recommendations to be put into practice.

The outputs and outcomes of collaboration are usually regarded as the most important indicators of 'success'. The LCP has generated a vast amount of research evidence and other information related to the condition, use and management of water and land in the catchment both at present and in the past. None of the evidence, however, can be regarded as definitive or entirely conclusive. In addition, a substantial list of desirable actions related to farming, septic tanks, the use of low phosphate products, population decline, economic opportunities, improving institutional inter-relationships, communication, and further research has been generated. Relevant organisations, groups and interests and the obstacles which will need to be overcome in order to implement each action have also been identified. Given the long-term nature of many of the LCP's goals and objectives and the fact that the project has been running for only three years, tangible outcomes are more difficult to identify. The lack of links between the LCP and more formal institutional arrangements has had an adverse impact on outcomes but nevertheless two farmers have reduced applications of fertilizers to their land on the basis of agronomic surveys commissioned by the project. In addition, land owners and the institutions have co-operated at a practical level by clearing some of the streams and channels in the catchment where sedimentation problems were identified. Arguably the most significant outcome to date has been the 'collaborative capital' created by the individuals, groups and agencies involved in the LCP. The trust and mutual respect which has been generated along with the improved understandings of land-water-people relationships have enhanced the problem-solving capacity of this small community.

CONCLUSIONS

The control of diffuse pollution is as much an institutional problem as it is a scientific or technical problem and often involves many different agencies and organisations operating in different jurisdictions and at different spatial scales. Overlapping institutional powers and responsibilities related to agriculture and other land uses as well as water resources planning and management frequently result in fragmented, piecemeal and ineffective policy and management responses. In addition, private property rights can mean that land uses such as agriculture are extremely difficult to regulate or influence, and often fall outside the remit of catchment planning and management initiatives. In the UK, diffuse pollution is starting to receive greater attention from policy makers and resource managers, particularly due to the more stringent targets and requirements developed as a result of the EU Water Framework Directive. Nevertheless, many of the new catchment planning and diffuse pollution control initiatives have been applied at very large spatial scales with very limited stakeholder engagement (Watson et al., 2009b). As a result, these initiatives are not capable of addressing the specific circumstances and nuances of individual catchment and sub-catchment systems, or of providing meaningful opportunities for stakeholder engagement and the utilization of local knowledge.

The Loweswater catchment management project has provided useful insights and lessons regarding how some of these institutional constraints can be overcome, and how a more collaborative approach to diffuse pollution control can be developed at a local scale. One of the main benefits of the Loweswater project is that it has brought a very diverse group of people and interests together and enabled them to improve understanding of the catchment by sharing existing knowledge, undertaking new research and debating the results and findings in an open forum. However, it is also important to recognize that collaboration is not always possible, and that a considerable amount of time may be required in order to nurture sufficient local interest and commitment before this kind of approach can be successfully initiated. In the case of Loweswater, collaboration emerged after several years of interaction among researchers and members of the local community, and followed earlier initiatives undertaken by local farmers. In addition, the visibility of the algal blooms and the posting of warning signs around the perimeter of the lake helped to galvanize public concern and to establish the legitimacy of the diffuse pollution problem in the catchment.

It is also clear the expectations regarding what can be accomplished through collaboration need to be carefully managed. Even at a very small local scale, the development and implementation of a collaborative catchment plan or strategy to address diffuse pollution can take several years. In the three years since the Loweswater project began, most progress has been made with respect to the problem-setting and direction-setting phases of collaboration. The complexity of the diffuse pollution problem has become much more apparent as a result of the research and the open discussions and debates which have taken place. This has confirmed the need to take multiple potential sources and pollutant pathways into account, to accept the uncertainty that surrounds causal links and to develop a diffuse pollution strategy that utilizes a mix of land use, land management and water management interventions and controls. Significant progress has also been made in specifying goals, objectives and desirable actions along with the identification of organisations with the potential to take responsibility for implementation. Nevertheless, progression from planning to management and the actual implementation of measures to tackle diffuse pollution and improve conditions in the catchment has been a challenge. Three particular factors have contributed to this situation. First, the project has operated outside formal institutional structures and channels in order to create and maintain a collaborative environment where different forms of knowledge can be combined. As a consequence, however, direct links to the agencies and other organisations with the power and authority to implement the agreed measures were not established and the LCP has had to rely on informal relationships and persuasion. Second, from the perspective of the management agencies, Loweswater is a relatively minor lake which does not warrant the same level of management attention as others such as Bassenthwaite and Windermere which are extremely important for the regional tourism economy. Third, most of the formal institutional arrangements for land and water operate at much larger spatial scales and therefore a small rural catchment management initiative such as Loweswater does not easily connect or 'fit' with them. A final insight concerns maintaining and demonstrating progress during collaboration, particularly when the achievement of ultimate goals such as the reduction or removal of toxic algal blooms may take many years to accomplish. Sustaining the interest and support of the participants over an extended period of time can be difficult, but is more likely to succeed when channels for clear communication are created, when regular updates and progress reports are provided, and when public attention is drawn to small but significant developments such as voluntary changes in farming practices or the completion of a piece of research.

Overall, the Loweswater project has shed some new light on the potential benefits and advantages of adopting a collaborative approach to catchment management. While collaboration is needed to overcome the institutional constraints and the scientific challenges of understanding problems such as diffuse pollution, collaboration itself is a complex process which needs to be carefully understood and managed. A particularly important lesson concerns the importance of ensuring that collaborative initiatives are clearly linked to, although not controlled by, the formal institutional arrangements for land and water so that agreed policies, plans and actions can be implemented effectively.

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Integrating the Implementation of the European Union Water Framework Directive and Floods Directive in Ireland

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INTRODUCTION

Centuries of land development, whether for human settlement, energy production, materials extraction, navigation, transportation, fishing, agriculture or other industrial manufacturing, has left Ireland's River Basin Districts (RBDs) with a legacy of modified waterbodies – ones that must provide a wide variety of water services and uses to a population currently in excess of four million people. The River Basin Management Plans (RBMPs) developed over the past few years in accordance with the European Union (EU) Water Framework Directive (WFD) (European Parliament and Council, 2000) indicate that approximately 84% of all Irish surface waterbodies require enhanced implementation of mitigation measures to attain the WFD-established objectives.

Artificial Waterbodies (AW) and Heavily Modified Waterbodies (HMWB), both totalling 37 each throughout Ireland (South Western River Basin District, 2008), are required to meet Good Ecological Potential (GEP) by 2015 via adequate implementation of these measures, whereas the generally more stringent Good Ecological Status (GES) standard is the objective for all other waterbodies. The actual metrics for GES were established in 2009, but the precise means by which the attainment of GEP objectives will be judged has yet to be agreed. Less Stringent Objectives (LSO) or time extensions on the established 2015 objectives are permitted for selected waterbodies under the Directive upon demonstration by Member States that adequate implementation of mitigation measures to achieve 2015 objectives is either a) technically infeasible, b) disproportionately expensive (i.e., marginal costs of measures implementation significantly outweigh the marginal social benefits), or c) disproportionately costly (i.e., likely to inflict costs and/or cost impacts on a certain stakeholder group or groups in a widely disparate manner). Temporary derogations or 'exemptions' are also allowed for in certain circumstances.

As implementation of the RBMPs gets underway by way of continuing or introducing the measures required for each waterbody to attain the 2015 WFD objectives, some of the focus of water resources policy makers and regulators in Ireland is now turning towards integrating the wide array of inextricably linked water resources management issues such as efficient energy production, climate change, bathing water quality and flood risk management.

The EU Floods Directive (European Parliament and Council, 2007) in particular serves as a topical example of this emerging need to harmonise the intersecting and sometimes competing objectives of EU water resources management Directives.

The WFD is driven largely by ecological considerations whereas the FD is geared primarily towards protecting physical property and preventing human mortality (e.g., drowning deaths from flash floods).

Thus the same waterbodies, and in particular current or potential HMWBs, arguably have somewhat competing policy objectives put upon them via these two Directives – hence the need perhaps for some additional pre-emptive thinking in Ireland regarding the means by which these objectives will be set and ultimately met.

THE EUROPEAN UNION WATER FRAMEWORK DIRECTIVE EC/60/2000

The WFD introduces modern concepts intended to shift EU water governance away from a uni-disciplinary, one-dimensional focus on water pollution control and towards the application of principles and practices associated with catchment-based 'Integrated Water Resources Management' (Ker Rault, P. A. and P. J. Jeffrey, 2008). Thus, signatory EU Member States such as Ireland, in adopting and transposing this modernized legislation into State statutory constructs, has committed to carefully balancing environmental, economic and cultural considerations in carrying out the implementation of the measures identified in its RBMPs.

The WFD is to be implemented via a series of three six-year planning cycles, the first of which concludes in 2015. Among the key requirements of river basin management planning under the WFD are:

1. Characterisation of RBDs (i.e., inventory of the distinct physical, economic, institutional and cultural characteristics of each of the RBDs);
2. Definition and identification of significant water pressures in each catchment or subcatchment (e.g., agriculture, urban runoff, septic tanks, etc.);
3. Classification of waterbodies (e.g., designated protection area waterbody, AWB, HMWB, etc.) and establishment of measurable objectives for each class of surface and ground water;
4. Analysis and subsequent identification of cost-effective combinations of mitigation measures needed to achieve the 2015 objectives for each waterbody and a schedule of implementation actions adequate to meet these objectives by 2015 (i.e., Programme of Measures (POM)); and
5. For waterbodies meeting the conditions required for 'derogations' or 'exemptions' (i.e., WFD 2015 objective exemptions) – whether they be permanent exemptions on water status objectives (i.e., LSOs), exemptions on timelines (i.e., time extensions for objective achievement to 2021 or 2027), or exemptions due to 'new modifications' – required is further analysis and full and transparent disclosure to the public of the specific technical and/or financial constraints and considerations that are projected to impede implementation of the measures identified as necessary for 2015 objective attainment for each waterbody.

The currently ongoing process being undertaken by Ireland pursuant to WFD Articles 4.8 and 4.9 to classify and thus designate certain waterbodies as HMWBs has particular relevance to the implementation of the FD. The agreed nature of the cost-effectiveness analysis of mitigation measures and the analysis of costs and benefits used to justify any potential AWB and HMWB exemptions under the WFD is similarly critical to the implementation of the FD. In interpreting the WFD requirements for exemption justifications for *all* waterbodies, the European Commission has been clear and unwavering:

> *"Common to all these exemptions are strict conditions to be met and a justification to be included in the River Basin Management Plan[s]."* (European Commission, 2009).

More specifically, and again per the WFD text in Article 4.4 and all relevant Common Implementation Strategies (CIS) published to date explaining this text (European Commission, 2009), all time extensions are to be grounded in some degree of substantive analysis that explains why 2015 objective attainment is either technically infeasible, disproportionately expensive, or significantly inhibited by natural conditions. Further, the EC and Member State Water Directors have agreed that "when applying the 'disproportionality justification', the reasons, underlying data and assessments should be made public" (European Commission, 2009). According to the Eastern RBD RBMP (Eastern River Basin District, 2010) and an internal document recently circulated enumerating the exemptions for Ireland's remaining six RBDs (RPS Consultants, 2010), nearly 1,700 time exemptions on 2015 WFD objectives are being sought in Ireland.

Article 4.5 of the WFD requires even more stringent criteria and more rigorous analysis for LSOs to be permitted, including demonstration that the environmental and socio-economic needs served by the activity making the LSO necessary cannot be achieved by a "better environmental option not entailing disproportionate costs". To date, Ireland has only identified one waterbody for which LSO derogation will be sought – a groundwater body in the Avoca River Basin. The Eastern RBD RBMP includes the stated intent to complete a cost-benefit analysis of this LSO before 2015.

For waterbodies to be modified by 'new sustainable human development activities' to the extent that WFD objectives will not be met or maintained, it must be demonstrated (again, in the RBMPs) that these modifications are of overriding public interest and/or benefits. More specifically, the EC states that "an analysis of the costs and benefits of the project adapted to the needs of the Directive is necessary to enable a judgment to be made on whether the benefits to the environment and to society of preventing deterioration of status or restoring a water body to good status are outweighed by the benefits of the new modifications or alterations to human health, to maintenance of human safety or to sustainable development" (European Commission, 2009). The planning of a significant 'new modification' of this nature and scope must also be accompanied by an analysis of its costs and benefits pursuant to the Environmental Impact Assessment Directive.

Again, in effect this means that justification for not meeting WFD objectives by 2015 on any waterbody requires presentation to the public of clear evidence that doing so is either:

- technically infeasible,
- likely to yield low social benefits at relatively high additional costs, and/or
- likely to induce disparately distributed implementation costs or cost-impact burdens amongst community stakeholders.

There seems to be disagreement presently between Member State Water Directors and the EC on whether constraints on State water resources management budgets can be used to justify failures to meet 2015 WFD objectives, with the EC apparently still holding firm that they cannot (European Commission, 2009).

The European Union Floods Directive EC/60/2007

The EU Parliament re-entered Ireland's water resources management arena more recently with the Floods Directive (FD) (European Parliament and Council, 2007), which is the key constituent of the EU Flood Action Programme of 2005. The EU Member States are henceforth responsible for, among other things, evaluating, preventing and managing flood risks. The FD states:

> "Floods have the potential to cause fatalities, displacement of people and damage to the environment, to severely compromise economic development and to undermine the economic activities of the Community (Preamble 1).
>
> Floods are natural phenomena which cannot be prevented. However, some human activities (such as increasing human settlements and economic assets in floodplains and the reduction of the natural water retention by land use) and climate change contribute to an increase in the likelihood and adverse impacts of flood events (Preamble 2).
>
> It is feasible and desirable to reduce the risk of adverse consequences, especially for human health and life, the environment, cultural heritage, economic activity and infrastructure associated with floods. However, measures to reduce these risks should, as far as possible, be coordinated throughout a river basin if they are to be effective (Preamble 3)."

In introducing a "framework for the assessment and management of flood risks, aiming at the reduction of the adverse consequences for human health, the environment, cultural heritage and economic activity", the FD is effectively instituting measures which can contribute to the prevention of deterioration of water status as provided for by the WFD.

The FD is to be implemented in Member States such as Ireland in three phases. During the first phase, the EU Member States must carry out a preliminary assessment of flood risks for river basins and for coastal zones by 2011. During the second phase, they must draw up flood hazard maps and risk maps by 2013. These must identify high, medium and low-risk areas, including those where occurrences of floods would be considered an extreme event. The maps will also have to include details on expected water depths, economic activities that could be affected, the number of inhabitants at risk and the potential environmental damage. The third phase will require member states to produce catchment-based Flood Risk Management Plans (FRMP) by 2015, thereby harmonizing with the WFD RBMP cycle.

The FRMPs are required to include measures to:

- reduce the probability of flooding and its consequences;
- prevent unsustainable land use practices (by discouraging building in flood-prone areas);
- protect such areas from the likelihood of floods (restoring natural flood plains); and
- inform and prepare the public.

The FRMPs are to be informed directly by detailed analysis in Catchment Flood Risk Assessment and Management Planning Studies. In essence, the analyses (including socio-economic analysis) upon which the plans published in the RBMPs and FRMPs are to be justified, must be conducted in a substantively coordinated fashion, as must the procedures for 'actively involving interested parties' in the generation and communication of the findings of these analyses. S.I. 122 of 2010, which is Ireland's statutory transposition of the FD, makes it clear that in Ireland, "Flood risk management plans shall take into account relevant aspects such as costs and benefits…"

The required timeline for implementing the key elements of both the WFD and FD described here is illustrated in Figure 1.

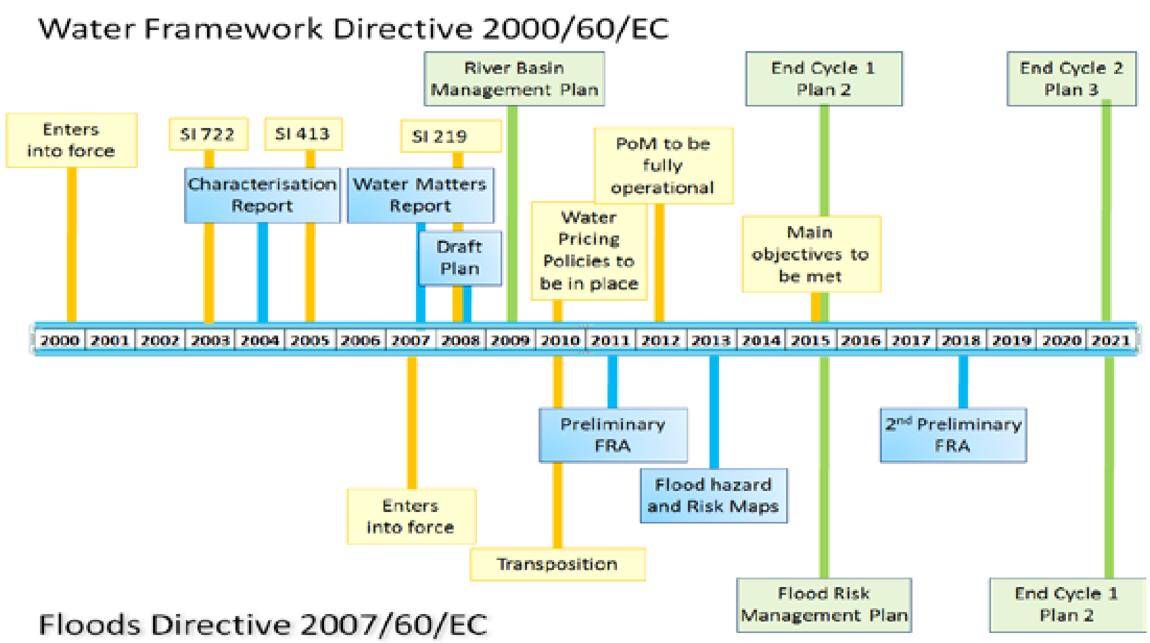

Figure 1. Schedule of Implementation Requirements of the WFD and FD

INTEGRATING THE IMPLEMENTATION OF THE WFD AND FD IN IRELAND

The WFD was transposed into Irish law primarily by Statutory Instrument Nos. 722 of 2003 – basic transposition; 413 of 2005 – advisory council; 218 of 2009 – RBMP deadline extension; 272 of 2009 – surface water objectives; 9 of 2010 – groundwater objectives; and 90 of 2010 – RBMP second deadline extension. The FD was transposed into Irish law by Statutory Instrument No. 122 of 2010 – basic transposition. Both sets of Directive transpositions implicitly embrace the concept of catchment-based Integrated Water Resources Management in a variety of ways, as illustrated in Figure 2.

Plan / Programme	WFD	FD
Flood Risk Management Plans	✓	✓
Arterial Drainage and Flood Relief Schemes	✓	✓
Conservation Plans (Biodiversity Plans)	✓	?
Water Services Strategic Plans	✓	✓
Pollution Reduction Plans	✓	
Sludge Management Plans	✓	
Major Accident and Emergency Plans	✓	✓
Forest Management Plans	✓	?

Figure 2. Integrated Components of WFD and FD Implementation in Ireland

As shown in Figure 3, many familiar implementation applications of both of the Directives illustrate the potential for achieving common objectives simultaneously.

Water Framework Directive		Floods Directive
Reduce Pollution Catchment Management	↔	Reduce Flooding Mitigation of Flooding
Subject to WFD Analysis For good status etc	←	Actions from CFRAMS e.g., morphological
Remove Culverts	→	Model to see if flood moves d/s
Space for Rivers Allow flooding on flood plains	→	Development Planning Zones A, B, C
Morphological Change E.g., if a flood weir removed	→	Flooding Implications Move upstream?
Article 4 Allows certain works under FD	←	FRMP

Figure 3. Integration of WFD and FD in Ireland to Achieve Common Social Objectives

Per Article 9 of the FD, the Competent Authorities for the FD "shall take appropriate steps to coordinate the application of this Directive [FD] with that of Directive 2000/60/EC [WFD] focusing on opportunities for improving efficiency, information exchange and for achieving synergy and benefits having regard to the environmental objectives laid out in Article 4 of Directive 2000/60/EC [WFD]". The respective Competent Authorities for WFD and FD implementation and other directly relevant authorities in Ireland are listed in Table 1. A similar degree of cooperation with bodies implementing other environmentally-oriented Directives, e.g. the Bathing Water Directive, is also desirable.

Table 1. Ireland's WFD and FD Implementation Authorities

	WFD	FD
Sponsoring Dept.	DEHLG	DoF
Competent Authorities	*EPA* for the purposes of reporting to the European Commission and assigned other functions *Local Authorities acting jointly* for setting objectives, making and implementing RBMP	OPW
Relevant Public Authorities	33 in ERBD	All Government Departments, All Local Authorities, All semi-state bodies, All WFD Competent Authorities
Advisory Council	48 in ERBD	-
Specified Public Bodies	-	Constituent Local Authorities, OPW, ESB, WI
Specified Organisations	-	All government departments, All Local Authorities, ESB, EPA, WI, Marine Institute, Met Eireann, GSI

The WFD Competent Authorities in Ireland are the lead Local Authorities for each RBD with the Department of Environment, Heritage and Local Government (DEHLG) responsible for funding their implementation activities. The Office of Public Works (OPW) is the Competent Authority in Ireland for the FD, and they are sponsored by the Department of Finance in this capacity.

Article 14 of the WFD and Articles 9 and 10 of the FD address how the respective Competent Authorities are to jointly effectuate the "active involvement of all interested parties" throughout the coordinated WFD and FD implementation process. In Ireland, the administrative arrangement for accomplishing this also includes public participation procedures pursuant to Ireland's Planning and Development Regulations of 2001. Although S.I. 122 of 2010 enumerates the many administrative steps leading to the final submission of FRMPs to the Minister for Environment, Heritage and Local Government for approval, as does S.I. 722 of 2003 for the WFD RBMPs, the details of the actual sequence and means by which this RBMP/FRMP 'coordinated active involvement of all interested parties' will realistically be accomplished is less clear at present.

SOME CONSIDERATIONS FOR FUTURE WFD AND FD INTEGRATED IMPLEMENTATION IN IRELAND

In taking into account our current understanding of Ireland's WFD/FD integration strategy as highlighted in the preceding text, the authors wish to raise some considerations with the aim of potentially contributing to the ongoing improvement of the new integrated WFD/FD implementation process.

1. In attempting to understand the process of classification of Ireland's waterbodies, and in particular the provisional classification of HMWBs, lacking currently in the available reports is a clear presentation of evidence that HMWBs (or any other waterbodies) would be put to their highest valued uses under their current or current-provisional classifications. It is noteworthy that in other developed countries, it is not uncommon for flood control structures and even viable hydroelectric dams to be removed in response to cost-benefit analyses indicating that restoration of these waterbodies to natural conditions is more cost-beneficial.

2. In trying to discern from the available reports the actual combinations of mitigation measures that are being pursued to cost-effectively achieve WFD objectives on any given waterbody (or even in any given catchment), apparent becomes an analytical disconnect between the cost-effectiveness analysis, the exact mitigation measures to be employed, and the waterbodies on which these measures are to yield cost-effective attainment of WFD objectives. The Economics Background Report (RPS Consultants, 2010 – unpublished) in particular appears to be the document that will ultimately serve as the required cost-effectiveness analysis to accompany six of the RBD's RBMPs in Ireland. However, it does not examine in detail measures that are already mandated by existing legislation and concentrates on only three areas of implementation (i.e., unsewered areas, river channelization and wastewater treatment plant upgrades). The analysis makes a number of broad assumptions, particularly about the implementation, effectiveness, costs and benefits of the proposed measures, so that establishing the optimal approach and its actual effectiveness, costs and their cost distributions for any specific waterbody (or in any given catchment) is difficult. Many of the building blocks for a cost-effectiveness analysis are in this report, but the actual identification of the most cost-effective combination of measures specific to each waterbody required to meet 2015 or extended-timeline objectives for any given waterbody is absent.

   In contrast, the Eastern RBD RBMP references ongoing efforts to do this waterbody-level or subcatchment-based comprehensive cost-effectiveness analysis via the Eastern RBD River Basin Management System. Also in contrast, the Eastern RBD RBMP expressed the clear intent to ultimately provide the actual identification of the cost-effective combination of measures required to meet WFD objectives for each of its waterbodies. However, even these outputs are not currently available for public review. All RBDs may find that in the absence of this final distillation to the local level of measures, effectiveness, costs and cost distributions and impacts, many interested parties will not be able to fully comprehend the reasons for and consequences of the decisions that are being taken on the management of their communities' waterbodies.

3. Several of the proposed timeline exemptions were justified in the available reports nominally as 'technically infeasible' or they indicated that 'technical constraints' or 'practical constraints' would prevent 2015 WFD objective attainment. In reviewing the actual descriptions of the circumstances underlying some of these characterizations, though, it appears that in reality 2015 objective attainment is clearly within the *technical* realm of possibility. For instance, time to design and install wastewater treatment plant upgrades and budget cycles needed to procure the necessary funding for these upgrades are cited as time-exemption justifications in the Extended Deadlines Background Document (RPS Consultants, 2010). These exemptions seem to suggest administrative or *fiscal* constraints (i.e., inadequate near-term financing to achieve objectives on time) rather than technical constraints. Such criteria may not be considered by the EC as appropriate for 2015 WFD objective exemptions.

4. The Regulatory Impact Analyses (RIA) that were done for both the WFD and the FD, respectively, were to serve in part as higher-level administrative checks on the costs and cost impacts of the transpositions of these Directives. Both documents provide little in the way of assisting their readers in understanding the full suite of costs, cost distributions or cost impacts of the respective measures to be implemented in Ireland. The WFD RIA (Environmental Resources Management, 2007) consists mostly of national-level water services and septic tank installation costs, whilst the FD screening RIA (Office of Public Works, 2009) estimates consist mainly of past flood damage costs. Although such estimates are potential components of a thorough cost-benefit analysis on

WFD and FD implementation strategies for HMWBs or watebodies potentially qualifying for exemptions, they do little in and of themselves to communicate the tradeoffs between catchment-level or waterbody-level implementation alternatives. For many 'interested parties', the *interest* is likely be in the costs and benefits of WFD and FD decisions as they affect their local waterbodies or catchments.

5. The current deficiencies in analyses of the costs and benefits associated with the implementation of the measures set forth in Ireland's RBMPs and the one draft FRMP completed to date (Cork City Council, 2010) may be symptomatic of the institutional arrangement under which Ireland is to implement the WFD and FD. Again, under the WFD in Ireland, the Competent Authorities for RBMP implementation are the lead Local Authorities for each RBD. But funding for this implementation, including for the analysis of costs and benefits under various implementation alternatives, comes from Central Government via the DEHLG. The funding arrangement for WFD implementation in Ireland adds to the institutional tension between Local Authorities and their preference for locally-based decisions and local funding autonomy and the DEHLG and its natural inclination towards national authority and centralized funding mechanisms. The potential under this arrangement for differences in estimating and interpreting costs alone for the Local Authorities (on the receiving end of funds) and Central Government (on the awarding end of funds) is difficult to ignore.

   Further, with the OPW serving as the Competent Authority for implementing the FRMPs within each RBD, and funding coming directly from the Department of Finance, another layer of potential institutional discontinuity in the WFD/FD implementation process seems evident. Again, the primary objective of the FD is to protect human life and property from flood events, whilst of course harmonizing with the often competing primary objective of the WFD, which is, to the extent practicable, to restore waterbodies to "good" or better ecological status (whilst of course harmonizing with competing human development needs). One might reasonably anticipate that a cost-benefit analysis done by the OPW of either the initial designation of a HMWB or the appropriate extended timeline for restoring to natural conditions this HMWB might, because of different priorities, produce a higher estimate of net benefits than a cost-benefit analysis of the same waterbody conducted by analysts whose primary focus is expediting the achievement of the WFD's primary objectives. This is because a cost-benefit analysis done primarily from the viewpoint of flood control is likely to look more favourably on a HMWB than a cost-benefit analysis done by analysts more versed in or focused on the many intrinsic and other ecological values that are characteristic of pristine waterbodies.

   The reality, however, is that the cost-benefit analyses for WFD and FD measures implementations need not be done multiple times in tandem by institutions with inherently potential competing objectives and motivations. Further, a potential future reality in Ireland does not have to include the ultimate decisions regarding WFD and FD to be taken (and justified in these analyses) and submitted to the Ministerial level of government for final approval by these respective Competent Authorities directly. At a minimum, joint WFD/FD cost-benefit analyses could be conducted on multi-objective implementation measures by a single, independent and more technically diverse institution. With some amendments to Irish statutory law, the potential for institutional biases could be addressed even more comprehensively by the creation of a higher-level body charged simply with ensuring that all of Ireland's waterbodies are put to their highest valued social uses subject to meeting a baseline of human and ecological health criteria not entailing disparate costs and cost impacts, as this is effectively the common, ultimate objective in all of the modern integrated water resources management legislation in Ireland.

6. Finally, the actual details of the public participation process that has been established for the 'coordinated active involvement of all interested parties' in Ireland, and that is required for the compliant joint implementation of the WFD and FD, is somewhat unclear at present. This is understandable given that this process is an unavoidable by-product of the multi-institutional arrangements described above, but further clarification or development of the details of this process would be welcomed.

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Watershed Evaluation Of Beneficial Management Practices: On-Farm Benefits And Costs

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Abstract

The main objectives of the Watershed Evaluation of Beneficial Management Practices (WEBs) research project are to determine effectiveness of Beneficial Management Practices (BMPs) in improving water quality in rural Canada, and to evaluate the potential on-farm costs and benefits of adopting these BMPs. This report addresses the economic on-farm benefits and costs of BMP adoption on farms in the Lower Little Bow River (LLB) watershed of southern Alberta, Canada.

Climate in the LLB watershed is semi-arid and land use is diverse. Farms are very large and tend to have relatively little debt. A stochastic and dynamic farm-level simulation model is developed to assess net farm benefits for a mixed crop and cow-calf operation, one of the dominant farm types in the watershed. The model incorporates significant bio-physical and economic relationships, and accommodates for production and market risks.

Model results indicate that implementation of these BMPs significantly reduces farm cash flow. Depending on the desired level of riparian protection, increasing calf productivity and/or improving pasture utilization might, in theory, off-set off-stream watering costs. But such improvements do not occur overnight. Fencing cost is prohibitive. Moreover, preliminary results from ongoing experiments in the LLB watershed indicate no change in water quality due to BMP implementation. Given the vagaries of the cattle business, uncertainty about international border closures, the high cost of fencing and no clear on-farm benefits to adoption, use of fencing should be targeted to very sensitive riparian niches. Financial incentives may also be required for voluntary BMP adoption.

Key Words

Beneficial Management Practices (BMPs); water quality; on-farm costs; Gross Margin or cash flow; Net Present Value (NPV)

INTRODUCTION

There is growing public concern among Canadians about the quality of water in Canada's streams, rivers and lakes. Agriculture is identified as one of the contributors to declining water quality. Research studies in the USA and Canada have shown that intensive cropping and traditional livestock management practices in riparian areas can damage riparian vegetation and degrade water quality. Degraded riparian areas and contaminated water have negative consequences for biodiversity as well as animal and human health.

Governments, federal and provincial, recognizing public concern, have identified and are actively promoting a number of Beneficial Management Practices (BMPs) to reduce surface and ground water contamination in agriculture, and to improve water quality. Effectiveness of these BMPs on farms in specific watersheds has not been determined. Further, the benefits and costs of implementation have not been assessed. Consequently, a 5-year research project was launched in 2004 to test the effectiveness of specific BMPs and suites of BMPs, and to evaluate the on-farm benefits and costs of adoption

The Watershed Evaluation of Beneficial Management Practices (WEBs) research is proceeding on several fronts. Research scientists from Agriculture and Agri-Food Canada are conducting field experiments to measure effectiveness of BMPs to reduce contamination and to improve water quality. Soil scientists are documenting the hydrology of the watershed. One group of economists is conducting market experiments to measure social benefits. Results from these latter initiatives are reported elsewhere (Miller et al, 2009; Agriculture and Agri-Food Canada, 2010). This report is confined to assessing on-farm benefits and costs of implementing BMPs in the Lower Little Bow River (LLB) watershed of southern Alberta and identifying potential barriers to adoption (Koeckhoven, 2008).

LLB watershed is a sub-watershed of the Oldman River Basin (ORB) in southern Alberta. It is located mainly in County of Lethbridge, in Census Division 2, about 40 kilometres northeast of the City of Lethbridge. It is approximately 55,664 ha. (22,537 acs.), >2% of the ORB. It is semi-arid with net moisture deficit of 350 mm/year. Strong Chinook winds are common in the watershed and average daily temperatures range from -8ºC in January to 18ºC in July. Land use is very diverse ranging from extensive cow-calf farms on native pasture, to dry land farming, intensive irrigated row crops and intensive confined livestock feeding operations. Stream flow in the LLB is controlled mainly by an upstream dam, the Travers Dam, and, to a lesser extent from irrigation runoff and irrigation return flows. Monitoring trends have indicated declining water quality downstream. As most of livestock feeding activity is concentrated in this county, north of Lethbridge, it is believed that run-off from agricultural lands is a major cause of the water contamination in the watershed.

METHODS OF APPROACH AND RESEARCH

The main objectives of this economic study are to assess direct **on-farm** economic and financial benefits and costs of adopting selected BMPs to improve water quality in the LLB watershed in southern Alberta, Canada, and to identify potential barriers or impediments to adoption on farms Koeckhoven (2008). Broadly defined, BMPs are those farm management practices which federal and provincial governments promote to reduce production risk, market or financial risk, environmental risk, and risk to food quality and safety. The BMPs being assessed in the LLB watershed are cropland conversion to permanent grass cover, vegetative buffers, off-stream watering and fencing, and manure management.

The research tools employed in this study include enterprise and whole farm budgets, and stochastic simulation analysis. Representative farm analysis was used to estimate firm-level gross margins or net cash flows. Stochastic parameters, prices and yields, covered elements of production and market risks. Combined simulation and present value analyses generated estimates of current value of net cash flow over project life. Net present value (NPV) can be represented as follows:

$$NPV = \sum_{t=1}^{N} \frac{C_t}{(1+r)^t} - I_0.$$

Where

t = year (t=1, 2, 3… N); N = number of years; ***Ct*** = gross margin or net cash flow in year *t* (C = difference in cashflow with BMP and without BMP); ***r*** =market interest rate or discount rate; and $\boldsymbol{I_0}$ =initial cash outlay of the investment. Investments in Cropland Conversion and Riparian Fencing are spread over years 1 to years 3. Off-stream investment in watering system occurs in year 1.

Seven cow-calf farms were surveyed in the study area, Census division 2, by Alberta Agriculture and Rural Development (AARD) as part of its AgriProfit$ Business Analysis Program. Using a detailed questionnaire, field staff interviewed farmers on their farms in 2006 and 2007. Once questionnaires were processed, individual results were mailed to participants. Field staff followed up with telephone calls to validate that the data and information processed were consistent with farm records. These survey results were supplemented with 2004-2006 land use survey data in the micro watershed by the County of Lethbridge and other historical data. Other sources of data included census data, Alberta provincial enterprise and farm budgets, published farm statistics and research reports, fact-sheets and personal communication.

Mixed beef cow-calf farms represent one of the dominant farming types in the watershed. A 400 head mixed beef cow-calf farm was selected as the representative model farm. It is comprised of 5,115.3 ha. (12,640 acs.). Seventy two per cent of the land is in pasture, 18% in cereals and oilseeds, and 10% forages; just over 1/3rd of the land is irrigated. The riparian area is assumed to occupy 2% of the land.

MODEL RESULTS

Field survey data indicated that beef cow-calf farms were marginally profitable in the base period. Gross Margin NPV was estimated at $\$4.6075 \times 10^6$ (s.d. 15%) or (\$901/ha; \$11,520/cow). Over the 20 year project life, converting a 20 m (66 ft) strip of **cropland** to 9m (30 ft) of vegetative buffer and 11m (36 ft) of hay land cost \$1,008/ha. (\$408/ac.). Reduction in farm cash flow ranged from \$14,591 to \$53,055 depending on the proportion of riparian area converted. The addition of cattle exclusion fencing significantly reduced farm cashflow. Without fencing, cash-flow from cropland fell 1.2% at 100% protection; with exclusion fencing, and potential loss of hay and grazing, cash-flow fell by up to 4.4%.

Estimated opportunity cost of installing the off-stream watering system (OWS) on **pastureland** was \$33,465 or \$84/cow. This BMP reduced farm cash-flow by <1% or \$62/cow. When the OWS was combined with exclusion fencing for controlled grazing or total cattle exclusion, farm cash flow fell by 2-7% depending on reach of shoreline protected.

Effects of streambank fencing on water quality and riparian health in LLB watershed were monitored by Miller et al. (2009). Preliminary results indicate no significant difference in water quality at up- and down-stream stations. However, there was noticeable improvement in riparian health. There was also greater nutrient enrichment at the cattle off-stream watering sites further away from the streambank than watering sites located near the streambank. These findings suggest that the OWS has potential to divert cattle away from the streambank and also to reduce direct drinking from the river (Miller et al.)

Review of scientific research literature indicates that cattle prefer to drink water from a trough instead of drinking directly from a river, stream or pond (Miner et al. 1992; Veira and Liggins, 2002). Given a choice, cattle prefer high quality to low quality or contaminated water (Willms et al. 2002; Lardner et al. 2005). Moreover, cattle with access to clean water from a trough spend more time grazing and less time resting than cattle drinking pond water. Furthermore, calves with access to aerated and coagulated water pumped to a trough, gained more weight than calves drinking directly from the pond (Lardner et al 2005). Cows and calves with access to off-stream water and salt gained more on pasture than cattle with direct stream access. Finally, once cattle are trained to drink from a trough, they tend to avoid drinking in the river and spend more time grazing the uplands (Godwin and Miner, 1996; Porath et al., 1997). In short, water quality increases water intake, feed consumption, grazing and feed intake thereby improving beef cattle performance (Willms et al; Willms et Colwell, 1994). Redistributing faeces and urine away from the streambank and depositing same on the pasture can improve nutrient cycling.

Indirect benefit estimation was beyond the scope of this economic research. However, sensitivity tests related to two indirect benefits of BMP adoption were explored, viz., increasing average daily gains of calves on pasture due to increased calf productivity and increased pasture utilization. An increase in average daily weight gain of 5% was just sufficient to recover the cost of the OSW, but not the combined cost of OSW and fencing. Of the two scenarios considered for pasture utilization, a 3% increase in pasture utilization achieved a net gain of \$32,155 or \$82/cow, and a 6% increase created a net gain of

$95,151 or $238/cow. Except at the 25% level of riparian protection, the 6% increase in pasture utilization was insufficient to offset fencing costs.

CONCLUSION AND POLICY IMPLICATIONS

Cropland and pastureland taken out of production to protect riparian health and water quality directly reduce farm cash flow. The off-stream watering system (OSW) installed on pastureland to protect riparian health and water quality while very costly, had only a marginal negative effect on farm cash flow. Farms may be able to absorb less costly OSWs without creating a negative cash flow. Given the size of these southern Alberta farms, fencing costs are prohibitive and have a bigger negative impact on farm cash flow. Therefore targeting fencing to very sensitive riparian areas such as stream entry points can reduce implementation cost, reduce stream contamination and improve riparian health.

By exploring the indirect benefits such as increased daily weight gains, increased pasture utilization, healthier cattle and reduced mortality due to cattle stuck in mud or drowning, ranchers may be persuaded to voluntarily adopt these BMPs. It bears noting that ranchers in the study area have limited debt. Given the vagaries of the cattle business, BSE and trade issues, minimal debt is a probably a direct strategy to manage production and market risk. Therefore **voluntary** adoption of these BMPs will greatly depend on measuring direct as well as indirect farm benefits, and availability and applicability of farm-level technical BMP information. Financial incentives may also be necessary in some circumstances such as high up-front capital investment and uncertain or negligible on-farm benefits.

These initial results of the WEBS LLB watershed study can inform producers of potential impacts of BMP adoption on farm performance. Results also provide guidance for policy-makers regarding potential incentives that may be required to encourage timely adoption of BMPs.

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How effective is the implementation of controls on diffuse pollution under the Water Framework Directive in Scotland? Answers and questions from the Lunan Diffuse Pollution Monitored Catchment project

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Abstract

Scotland is at the initial stages of implementing a coordinated strategy to mitigate rural diffuse pollution based on a national and catchment scale programme of guidance, awareness raising and inspections. To support this strategy, the Lunan Water Diffuse Pollution Monitored Catchment (a typical mixed arable farmland catchment, containing two eutrophic lochs) has been established since 2006. The focus of this paper is on assessment of effectiveness of measures to reduce total P inputs to the lochs. A target of 40% reduction of total loads, achieved from external sources, has been identified, to restore long term good ecological status. Using a before-after-control-intervention (BACI) design, we are seeking evidence of the impact of differential implementation of measures across 5 sub-catchments monitored for discharge, turbidity and water chemistry (including storm events). Statistical methods and data analysis are still under development, but the indications are that to observe impacts of change for a 40% reduction in event mean turbidities, around 130 pre- and 130 post-intervention storm events would be needed,. Subcatchment TP load estimates show the monitored sub-catchments generating areal loads of 0.48-0.79 kg TP/ha catchment/year.

Keywords

Eutrophic; diffuse pollution mitigation; turbidity; cost:effective; Lunan Water

INTRODUCTION

Diffuse pollution is the most significant pollution pressure leading to failure of the water environment in Scotland to achieve Good Ecological Status (GES), as required by the EU Water Framework Directive (WFD). The Scotland River Basin Management Plan (SEPA, 2009) sets out programmes of measures to achieve improved compliance with GES. Scotland is at the initial stages of implementing a coordinated strategy to mitigate rural diffuse pollution based on a national and catchment scale programme of guidance, awareness raising and inspections. This strategy is summarised in Figure 1. It recognises, a number of key principles, such as the need for a partnership approach involving stakeholders at catchment scale; a sound evidence base to assess sources and transport of diffuse pollution, accurately target measures and get stakeholder buy-in; one-to-one advice and farm visits to identify hotspots, target measures and cost-effectively change management practices; and a combination of regulatory, economic and voluntary mitigation measures.

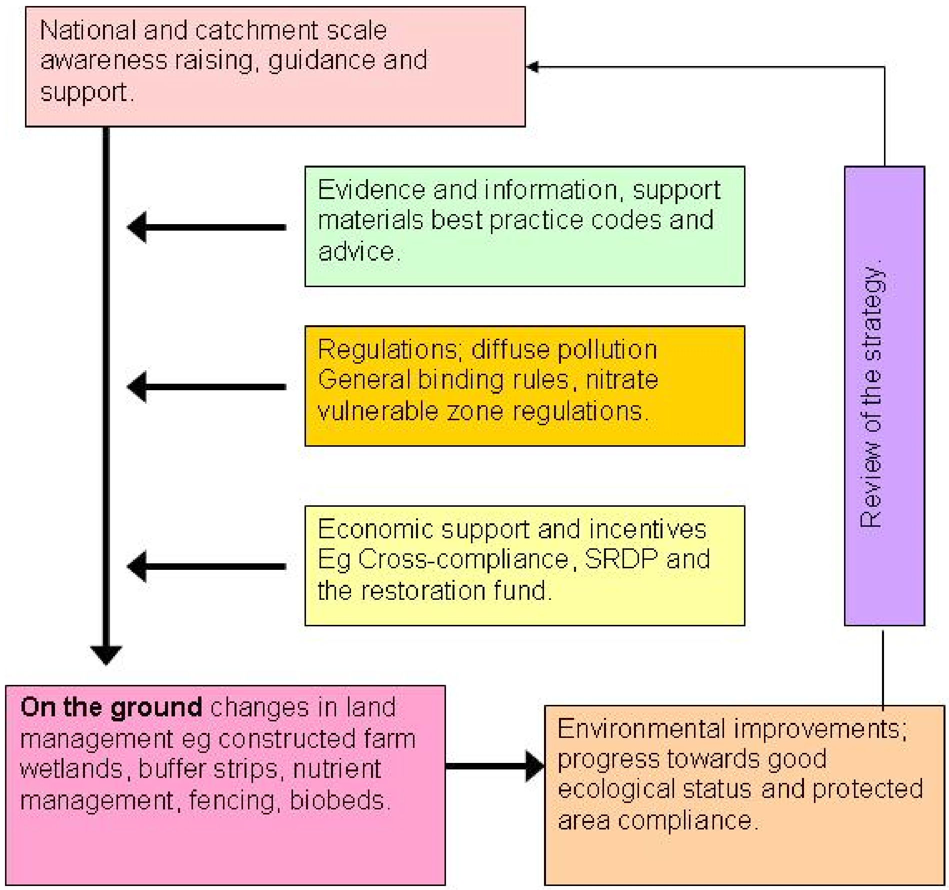

Figure 1. Implementation of national and catchment scale strategies for diffuse pollution management in Scotland.

As part of this process, a group of 14 Priority Catchments (PCs) for catchment wide implementation of pollution control measures have been identified using a risk-based approach by the Scottish Environment Protection Agency (SEPA) and partner organisations. To support this strategy, evidence is needed of policy effectiveness and efficiency, and Diffuse Pollution Monitored Catchments (DPMCs) have been established to assess these measures at catchment scales, using a level of monitoring that would not be possible across the 14 priority catchments. One of these DPMCs is the Lunan Water, a 134 km^2 catchment in Angus, Eastern Scotland. It is a typical mixed arable farmland catchment, containing water bodies currently at less than GES. Within the catchment are two Lochs, Rescobie and Balgavies, which have been designated as an SSSI covering 1.78 km^2. These lochs suffer from over-enrichment with P leading to serious eutrophication in summer, which also affects the Lunan Water downstream. In addition, much of the catchment is underlain by porous groundwater bodies, vulnerable to nitrate pollution, the river drains to a designated bathing water, and a previously healthy population of salmon and sea trout is now in serious decline. While a number of regulatory, voluntary and economic measures have been promoted since the start of the project, several questions need answering for example: what is the impact of these measures on water quality and achievement of GES in the catchment? What level of monitoring is needed to obtain evidence of improvements due to diffuse pollution control in the DPMCs and PCs? What is needed to achieve catchment scale uptake of effective diffuse pollution mitigation measures on the ground?

DIFFUSE POLLUTION MITIGATION TARGETS: RESCOBIE LOCH

The focus of this paper is on assessment of measures to reduce P inputs to the two Lochs. Figure 2 shows the fluctuation of total P in Rescobie Loch. Using the arithmetic mean of the annual geomean values (2003-2006) of 70.1ug/L TP, and the OECD equation (Vollenweider and Kerekes, 1982) to calculate implied TP loads from the catchment, we estimate current mean TP loading of 0.27 kg/ha/year of catchment (or 9.3 kg/ha of Loch or 550 kg P overall). Using the Loch specific SEPA good/moderate boundary of 27 ug/L TP (Fozzard, pers.comm) this gives a target TP loading of 0.10 kg/ha of catchment or 3.6 kg/ha of Loch or 210 kg P overall. By difference, the required reduction in TP loading is: 0.17 kg P/ha of catchment or 5.8 kg/ha of Loch or 339 kg P overall.

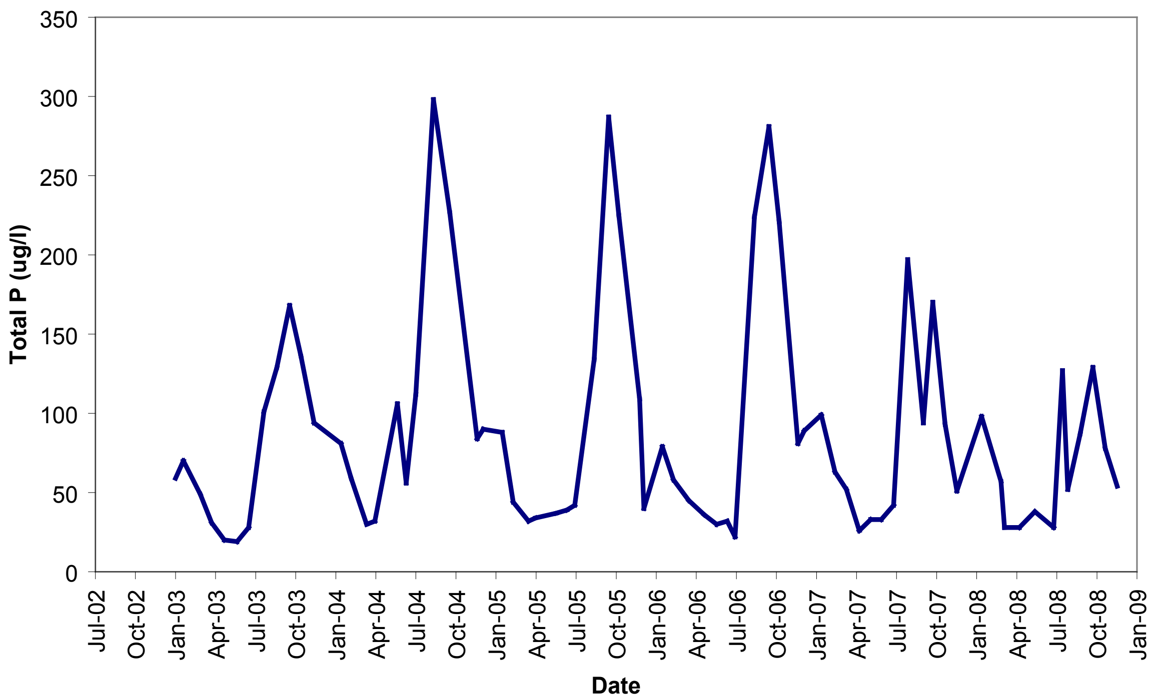

Figure 2. Time series of Total P concentration in Rescobie Loch, 2002-2009.

DIFFUSE POLLUTION CONTROL MEASURES

Voluntary measures. Engagement of land users in the catchment has been developed through an Environmental Focus Farm (Mains of Balgavies) and regular farmer focus groups, run by Scottish Agricultural College (SAC). Interaction with these and other water users (eg Rescobie Loch riparian owners) has occurred through further focus groups and an annual Lunan science update meeting. Through such regular engagement, it has been possible to raise awareness about measures, and this has led to changing practice, such as modified cereal tramlines and reduced cultivations to catch soil erosion, improved nutrient budgeting and liming practices to promote more efficient and uniform nutrient uptake by crops, conversion from winter to spring cereals, and to obtain support for pre- and post-implementation monitoring of watercourses. In addition, a major septic source in the Burnside sub-catchment (a caravan site) has had its sewage treatment system upgraded, and improved fish passage in the main stem has been established.

Regulatory measures. Since the start of the project, the requirements of the WFD have been transposed into the national Controlled Activities Regulations (CAR, 2008). These provide for three tiers of regulation: licensing, registration and general binding rules, depending on risk. Diffuse pollution is controlled by General Binding Rules (GBRs), whereby activities posing a risk, such as cultivation of land, need to follow rules to protect the water environment. These rules are based on good practice and provide a level playing field for land managers. Examples include the establishment and maintenance of a 2m buffer between watercourses and cultivated land (part of GBR20-cultivation of land), avoidance of poaching within 5m of a watercourse (GBR19-keeping of livestock) and maintaining a minimum distance of 10m from watercourses for storage of manures (GBR 18 – management of fertilisers and manures). More details are available on http://www.sepa.org.uk/water/diffuse_pollution.aspx

Diffuse pollution auditing by SAC on representative farms in two sub-catchments (Balgavies (2007) and Baldardo (2009/10)), and river walks by SEPA (on the Lemno in spring 2010) is assessing to what extent these GBRs are being complied with.

Economic measures. The Scottish Rural Development Programme (SRDP, 2010) (http://www.scotland.gov.uk/Topics/farmingrural/SRDP) funds measures to control diffuse pollution, including adoption of riparian wetlands, farm ponds etc. Some of these are competitive funds, and some are guaranteed funding under a "land management options" scheme. These include use of 6m grass margins,which currently attract £473/ha and retention of winter stubbles (£96/ha).

Septic sources. In addition to the agricultural sources of pollutants, septic tanks are a significant factor, and it has been estimated there are over 800 in the whole catchment, contributing up to 30% of the estimated annual P load. Awareness raising through a leaflet about dseptic tank maintenance, through annual science update meetings and through several focus groups has taken place. In addition, it is known that a caravan park in the Burnside sub-catchment has had an improved sewage treatment system installed.

DIFFUSE POLLUTION CHARACTERISATION

In order to characterise inputs into the Loch and assess the effects of control measures, five sub-catchments typical of land use in the upper Lunan catchment (though not necessarily feeding into the Loch itself) were identified for monitoring of discharge and pollutant concentrations. These are shown in Figure 3.

The strategy has been to monitor (from 2007) these subcatchments before the impact of the above changes in diffuse pollution management took place, and then promote changing management differentially across these subcatchments (from 2009), as set out in Table 1. The precise timing of the differential treatment varies, as does the level of farmer engagement and support for the process. By comparing "treated" and control" catchments and applying the statistical approach of "Before-After-Control-Impact (BACI)" analysis (eg Bishop et al., 2007; Murtagh, 2000, 2002; Stewart-Orten et al., 1986), the sub-catchment scale impact of measures as they were implemented, can be assessed.

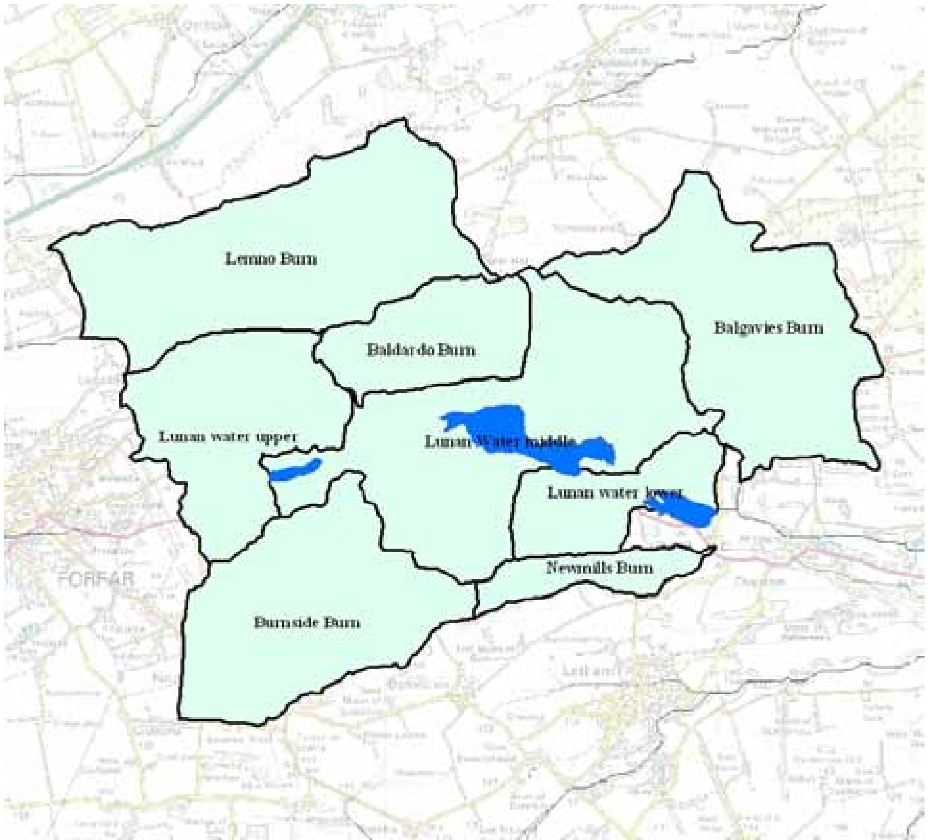

Figure 3. Subcatchments in the upper Lunan Water Catchment. Note that Lemno Burn feeds another river, the South Esk, but is included as this was originally acting as a control subcatchment, and that Balgavies Burn flows directly into the Lunan Water below the loch. The 5 monitored subcatchments are: Balgavies(590 ha), Baldardo (238 ha), Lemno (710 ha), Newmills (105 ha) and Burnside (538 ha).The total catchment area of Rescobie Loch (the larger of the two main lochs shown) is 2016ha.

For the purposes of BACI assessment we assume:

1. Balgavies catchment can be considered a "moderate compliance control" (in that the diffuse pollution audit which took place on the Environmental Focus Farm in 2007 showed broad compliance with the general binding rules, but other farms had unknown compliance);
2. Baldardo catchment can be considered a "treated" catchment in that based on farm walks which took place in March 2008 the compliance was poor, but farmers began to implement voluntary measures from this point. Across the sub-catchment, a stream culvert, avoidance of winter cereals, adoption of a 6m grass margin for arable crops, and development of in-wintering facilities for livestock have been the main measures as of June 2010;
3. Lemno catchment can be considered a "poor compliance control" catchment in that no intervention took place till autumn 2009, when awareness raising under the Priority Catchment work began, and riparian surveys in spring 2010 showed poor compliance; as of spring 2010, this catchment can be considered as a "treated" catchment, due to the awareness raising programme undertaken.
4. Newmills catchment can be considered a "poor compliance control" as no intervention and limited engagement with the farmer focus groups has taken place;

5. Burnside catchment can be considered a "poor compliance control" as no intervention and no engagement with the farmer focus groups has taken place. However, a caravan site in the catchment, had an improved treatment system installed in spring 2010.

MONITORING OF SUBCATCHMENTS

The loading of P to the Lochs from the monitored sub-catchments is being estimated using a combination of continuous discharge estimation, real time turbidity monitoring, and storm event sampling using Rock and Taylor autosamplers and weekly or fortnightly spot samples.

MMG barodivers were used to measure water levels and ISCO Acoustic Doppler and manual propellor based systems were used to provide a stage discharge relationship. The relationships developed were:

Lemno:
$Q = 2288s^3 + 1213s^2 - 287s$

Baldardo (Birkel et al., 2010)*:*
$Q = 2500s^3 + 1s^2 + 0.001s$

Where Q = discharge in l/s and s=water level in m.

Turbidity was measured using YSI Hydrodata 6136 Nephlometric Turbidity Probes with 90 degree scatter, automatic, mechanical wipers, and a range of 0-1000 or 0-400 NTU. Eight storms were sampled at 4 hourly intervals using Rock and Taylor automatic water samplers, during Dec 2008 to Mar 2010 at Wemyss on the Baldardo Burn. Storm event samples were analysed for a wide range of chemistry (TP, SRP,DOC, NO_3, NO_2, NH_4, alkalinity, pH, EC), and samples were also filtered (with GFC and 0.45 μm filters) to provide sediment samples for total P determination by persulphate digestion.

Start and end times of discharge events were estimated using the following procedure for the Baldardo and Lemno catchments. First the local gradient of the discharge vs. time relationship was calculated, using four-hourly means to provide some smoothing. The start and end points of each event were identified by a change of this slope from negative to positive, while peak discharges were identified where the gradient changed from positive to negative. Paired events across the two catchments have been defined as those where the peak discharges fall within five hours of each other. In order to avoid identifying too many minor turns in the discharge time series, the average gradient for the first 7 out of 10 hours before the peak must be positive and the average gradient for the last 7 of 10 hours after the peak must be negative. This procedure identified 130 paired events between 2007 and 2010 in the Baldardo and Lemno catchments. The event discharges are very strongly correlated between catchments, so any comparison of loads in a BACI analysis is at risk of being dominated by this correlation. It was therefore felt better to use the mean turbidity per event to assess the impacts of changing management. The paired data were fitted to an equation of the form shown in eq. 1:

$$\ln(T_{treat\ i}) = a + b\ln(T_{notreat\ i}) + e(treat_i) + \varepsilon_i \qquad (1)$$

Where

$T_{treat\ i}T_{treat\ i}$ is the log-transformed mean turbidity in the treated catchment (for event *i*)

$T_{notreat\ i}T_{notreat\ i}$ is the log-transformed mean turbidity in the untreated catchment (for event *i*)

$treat_i treat_i$ is the treatment index variable (0 before treatment, 1 after treatment)

Table 1. Summary of diffuse pollution measures in 5 subcatchments.

catchment	DP control activity	2007	2008	2009	2010
Balgavies focus farm catchment (pre-compliant) 3 farms	Farmer focus group	yes	yes	yes	yes
	GBR awareness	compliant	Compliant	compliant	compliant
	Farm DP audits	1 farm			
	DP mitigation measures	Minimum tillage	yield maps vs liming	nutrient budgets, erosion risk assessment	Erosion detention bunds
Baldardo intervention catchment 4 farms	Farmer focus group	yes	yes	yes	yes
	GBR awareness			non-compliant	non-compliant
	Farm DP audits			2 farms	1 farm
	DP mitigation measures		Economic measures (SRDP) planned	stream culvert erosion risk ->no winter cereals riparian wetland	In-wintering of stock Erosion detention bund planned 6m grass buffers (1 farm planned)
Lemno control catchment 1 estate,3 farms	Farmer focus group	no	No	no	DP awareness raised (S.Esk CMG)
	GBR awareness				non compliant (70%)
	Farm DP audit	no	No	no	river walks to assess GBR compliance (SEPA)
	DP mitigation measures				septic tank project planned
Newmills control catchment 2 farms	Farmer focus group	yes	yes	yes	yes
	GBR awareness			Assumed non-compliant	Assumed non-compliant
	Farm DP audits	No	no	no	No
	DP mitigation measures	pond already present in corner of one field			
Burnside control ca. 15 farms	Farmer focus group		Invited but no participation		
	GBR awareness				Compliance rate unknown;
	Farm DP audits	no	No	no	no
	DP mitigation measures				septic tanks improvements at caravan site

RESULTS

Does the BACI paired catchment method have the power to detect change in management?

Figure 4 shows a plot of the 130 paired event mean turbidities across the two sub catchments. If we consider these as one dataset, we can assess what level of change in mean turbidity would be needed across the "treated" Baldardo catchment, in order to be able to say with confidence that change has occurred. Data have been normalised to give a zero intercept (necessary to allow the intercept to be estimated independently of the slope, so that an appropriate estimate of the standard error of the intercept can be obtained).The SE of the intercept is 0.05. With a similar post-mitigation dataset the SE for detecting change = 0.071. A 30% reduction in turbidity load would corresponds to a change of –0.155 in the intercept on the log scale, while a 40% reduction corresponds to a change of –0.222. The power to detect a change may be approximated using the standard normal distribution function (Φ). For a one-sided test at the 5% significance level, $\Phi^{-1}(0.95)=1.645$, so the power to detect a 30% reduction may be approximated

$$\text{by } 1-\Phi\left[1.645-\frac{0.155}{0.071}\right]=0.7$$

while for a 40% reduction the power is 0.93. This tells us that to have a good chance of finding a statistically significant treatment effect, with an average turbidity reduction per event of 40%, we need around 130 events to be captured both before and after the intervention. These calculations assume that events are independent, whereas in reality there is likely to be autocorrelation between successive events, which will mean that a larger number of events will need to be captured.

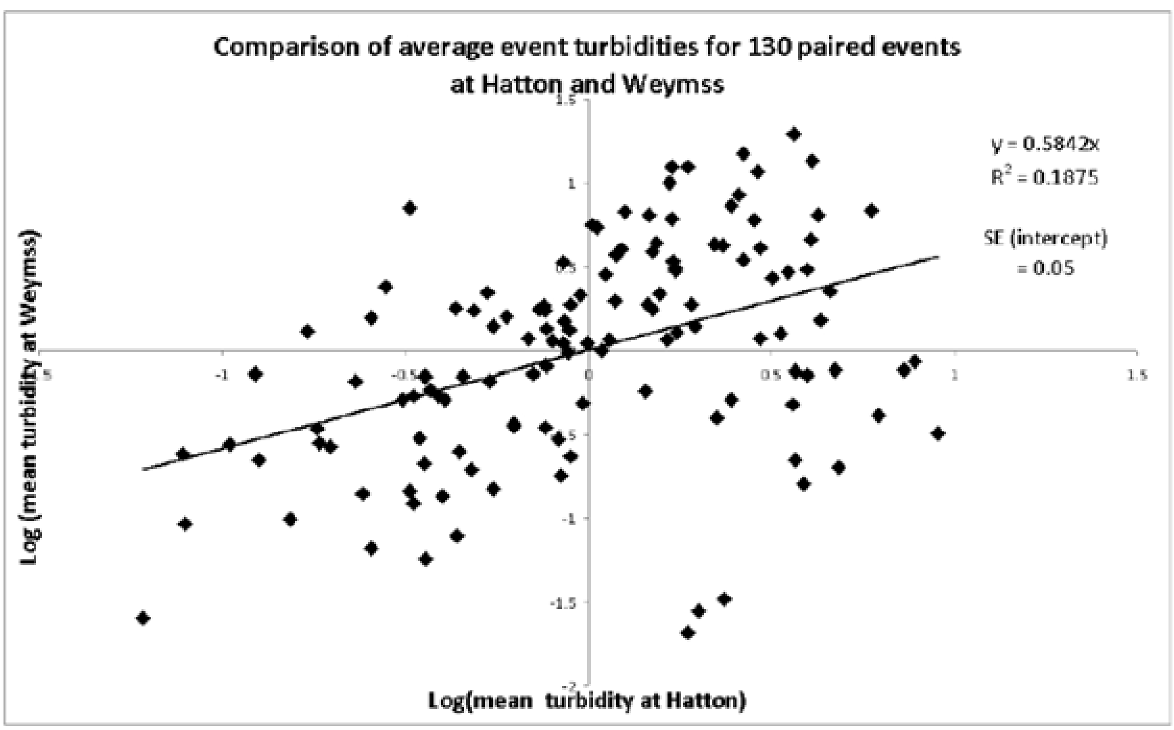

Figure 4. Comparison of average event turbidities for 130 paired events at Wemyss (on the Baldardo catchment) and Hatton (on the Lemno catchment). Data have been normalised to give a zero intercept (necessary to allow independent assessment of whether a change in the intercept has occurred, as a result of management intervention).

Bearing in mind that the “treatment” in the Baldardo catchment is assumed to start after March 2009, this dataset also includes some results from a post-treatment dataset, so it may over-estimate the error in the intercept. However there are not really sufficient pre-and post data to make a statistically valid analysis at this stage. The result above can be used to assess the likely cost-effectiveness of alternative methods of capturing event data, given the relative expense of turbidity measurement and capture and chemical analysis of storm event samples (see below).

Estimation of total P loads

Table 2 shows a summary of the total P vs turbidity relationships for the eight events sampled on the Baldardo catchment.

Table 2. Events sampled on Baldardo sub-catchment.

event	start	end	mean discharge (l/s)	mean [TP] (mg/l)	mean turbidity (NTU)	Total P load (kg)
1	03/12/2008 13:30	09/12/2008 01:30	61.5	0.14	24	4.2
2	24/01/2009 23:45	28/01/2009 07:45	107.5	0.17	120	5.3
3	14/02/2009 20:30	17/02/2009 16:30	42.3	0.14	87	1.4
4	11/03/2009 11:15	12/03/2009 23:15	18.9	0.08	55	0.2
5	14/05/2009 17:45	19/06/2009 22:00	13.1	0.16	82	6.6
6	20/10/2009 09:15	05/11/2009 08:15	273.0	0.37	78	138.4
7	18/11/2009 10:45	23/11/2009 10:45	209.0	0.21	83	19.2
8	11/01/2010 11:15	21/01/2010 01:15	146.8	0.36	43	43.7

Currently there are only paired events for chemistry captured on the Lemno for the summer period, so for estimation of total P loads from turbidity data, we have used the relationship between sample [TP] and turbidity over all events captured at the Baldardo site:

$$\ln([TP]) = 0.4231 \ln(NTU) - 3.3489 \qquad r^2 = 0.453, n=386.$$

Where NTU = turbidity and [TP] = total P concentration in mg/L.

Using this relationship for both the Lemno and Baldardo sites, gives estimated loads and mean [TP]. Back-transformation bias is accounted for using the method of Gilroy et al. (1990) and Cooper and Watts (2002), which takes allows for the fact that the parameters from the regression equation have been estimated. Standard errors are calculated assuming that discharge is known. However, in reality the uncertainty will be greater than this because discharge has also been estimated using a stage-discharge relationship.

The estimated total P loads for the period from July 2007 to March 2010 are given in Table 3, on a quarterly basis. For the year prior to intervention (April 2008 to March 2009), these loads correspond to estimated losses per unit area of catchment of 0.46 kg P/ha and 0.48 kg P/ha for the Baldardo (pre-treatment) and Lemno (control) catchments respectively. For the year after intervention (April 2009 to March 2010), the estimated loads are 0.74 kg P/ha and 0.73 kg P/ha for the Baldardo (treated) and Lemno (control) catchments respectively.

Table 3. Estimated TP loads, using [TP] vs turbidity relationship.

Baldardo	Lemno							
	TP	SE	Discharge mean		TP	SE	Discharge mean	
Quarter until	Kg		mm	[TP] mg/l	kg		mm	[TP] mg/l
01/10/2007 00:00	25.8	1.7	52.8	0.21	68.8	3.7	69.7	0.14
01/01/2008 00:00	27.5	1.7	66.0	0.18	142.3	9.1	98.6	0.20
01/04/2008 00:00	22.9	1.4	51.2	0.19	107.7	6.4	92.2	0.16
01/07/2008 00:00	6.1	0.3	20.0	0.13	24.4	1.3	21.5	0.16
01/10/2008 00:00	10.5	0.6	27.9	0.16	39.7	2.3	35.6	0.16
01/01/2009 00:00	42.8	3.1	88.1	0.20	122.8	8.4	86.8	0.20
01/04/2009 00:00	51.1	4.3	95.0	0.23	153.4	10.2	113.6	0.19
01/07/2009 00:00	5.6	0.3	16.6	0.14	19.3	1.1	21.8	0.12
01/10/2009 00:00	26.6	2.1	62.6	0.18	102.9	11.5	79.2	0.18
01/01/2010 00:00	108.7	11.0	204.9	0.22	279.5	17.1	208.4	0.19
01/04/2010 00:00	34.9	2.4	102.7	0.14	118.5	6.4	123.7	0.13
Total/Mean	362.4		787.6	0.18	1179.3		951.3	0.17

DISCUSSION

We return to the three questions posed at the end of the introduction.

What is the impact of measures on water quality in the catchment and achievement of GES?

There is no evidence to date of significant differences between intervention and control catchments, following intervention. There is a much larger difference between years and seasons, than between catchments. However, it is to be expected that as the project continues, with more post-intervention activity on the ground, that treatment effects will be more significant. Moreover, the statistical analysis is still under development and several improvements in the approach, including the use of different turbidity vs total P calibrations for winter and summer, and rising and falling hydrographs, the use of log-log relationships to improve normality of the fits, the correction and use of turbidity data using an instrument with a maximum reading of 400 NTU (data collected prior to July 2007), and the use of land cover data to correct expectation of soil loss due to erosion.

What level of monitoring is needed to obtain evidence of improvements in the DPMCs and PCs?

The target reduction in TP loading to achieve GES in Rescobie Loch is around 60% (339 kg TP). An unknown component of the load comes from internal sources within the Loch, which will gradually decline as external inputs are mitigated. It seems reasonable to aim at 40% reduction in loading from external sources (216 kg TP). Evidence from the paired event sampling is that capturing around 130 events both pre- and post-intervention would give a very high probability (0.95) of finding a significant effect with a 40% reduction in loading, although the true probability is likely to be lower than this due to autocorrelation.. With chemical analysis at a conservative £10/sample and 10 samples/event, the chemical analysis costs alone for a chemical event based method would be £52,000/ pair of sites, counting both before and after catchment improvements. Add to this the transaction costs of maintaining autosamplers and triggering them prior to events, and it is clear that a turbidity-based method (cost of turbidity probes plus loggers around £4,000/pair of sites) is very attractive for generating evidence of change in stream quality.

This analysis is relevant to the needs of initiatives such as the mitigation of diffuse pollution in priority catchments project, where SEPA and partners need to demonstrate the efficacy or otherwise of programmes of measures from the River Basin Management Plan, to achieve compliance with the requirements for GES, or at least to show improvements in this direction. If monitoring to achieve the above levels of uncertainty were required across the 14 Priority Catchments, with 5 pairs of monitoring sites in each catchment, the "pollutant analysis" budgets for the two approaches are £3.6m for chemical analysis as against £280k for the turbidimetric approach. Note that similar hydrometric data will be needed with each approach.

What is really needed to achieve uptake of effective diffuse pollution mitigation measures on the ground, in an equitable and cost:efficient way, and to ensure the catchment wide approach required?

The evidence of river walks undertaken by SEPA in the South Esk catchment (including the Lemno) suggests that non-compliance rates with the GBRs are about one per km of river. On the Lunan Water, farmer focus groups running from 2007-2010 have been attended by a relatively small number of farmers. Good compliance levels, and continued improvement in environmental management, can be partially attributed to this in the Balgavies catchment (where the Environmental Focus farm was located). Several other farmers who attended the focus farm meetings have undertaken specific improvements, but as these are scattered across a range of watercourses, it is difficult to assess their impact. Evidence suggests that voluntary participation in awareness raising is not sufficient to achieve the catchment wide coverage required to see improvements in water quality. The extent of catchment coverage required is a question for further research. Can awareness raising activity be targeted to high-risk areas within the catchment? It is questionable whether the actions undertaken in the Baldardo catchment would have happened without the farm walks undertaken in March 2009 and the subsequent diffuse pollution audits. Awareness of the requirements of the GBRs was low, prior to these one-to-one visits, despite the focus farm groups, so the qualitative evidence suggests that such one-to-one environmental advice and scrutiny is crucial. If such discussions can be accompanied by some realistic evidence of pollutant loading, and targets for reducing this loading, we found this helped engagement with farmers. On the other hand, if obtaining evidence of change using chemistry only is expensive, and changes are delayed, these are likely to generate reluctance to participate in diffuse pollution control management. This work contributes to the development of a method to assess the effectiveness of measures to mitigate diffuse pollution. Based on the combined quantitative (intensive chemical load measurements) and qualitative evidence collected so far from the DPMCs, the best approach to assessing change in the PCs may well be to use a more input-focused approach, ie. assess changing land use/management and compliance levels on the ground and estimate impacts of non-compliances directly. In catchments representative of typical land uses however, loads and concentrations of diffuse pollutants coupled to ecological status are essential. This information could then potentially be extrapolated to other, similar catchments. More evidence to develop and improve methods to assess change is required.

Summary of other research work in the Lunan water catchment

For the groundwater work, a catchment model has enabled better understanding of the links between surface and groundwater to be made. Water balance data indicate that groundwater leakage occurs at the sub-catchment scale, but is subsequently returned to the river at the main Lunan catchment scale. The groundwater appears to contribute between 25 and 50% of the total stream flow (Birkel, pers.comm., LeFeuvre and Fitzimmons, 2010). The groundwater dating work has provided evidence that, in some areas, reductions in nitrate pollution will not be effective in ameliorating groundwater nitrate concentrations for a number of years (Birkel et al., 2010). Rapid ecological appraisals (riparian and aquatic vegetation, hydromorphology, diffuse pollution, aquatic invertebrate ecology, and migration barriers) of 5 reaches of the main stem of the river have also been carried out. For further information, see Vinten et al. (2008, 2009).

CONCLUSION

Turbidity monitoring may be a more cost-effective way of achieving evidence of change than storm event chemistry samples, but it may be that, from a catchment management perspective, coupling this data to qualitative evidence, using river walks and/or farm walks and audits, is more cost:effective as this may promote change in behaviour as well as gathering evidence.

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5 | EMERGING CONTAMINANTS AND MICROPOLLUTANTS

Risk Assessment for Emerging Contaminants in the Water Cycle: Recent Advances and Future Needs

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Abstract

The increasing worldwide contamination of freshwater systems with thousands of industrial and natural chemical compounds is one of the key environmental problems facing humanity. Anthropogenic impacts on ecosystem and human health are both an urgent and international issue. In the area of sustainable water pollution control, the monitoring programme does not envisage inclusion of new effects. The large number of circumstances that require regulation, together with the limited availability of personnel and financial resources, necessitate the setting of priorities and focusing on risks, which are perceived from a scientific perspective to require precautionary action and which, at the same time, are highly topical in terms of health and environment policy.

Keywords

Emerging contaminants, biological test strategy, toxicological safety, science based risk management

INTRODUCTION

The multiplicity of newly detected substances and the complexity of unwanted effects require a reorientation in environment-related toxicology concerning methodical concepts for the ascertainment of possible harmful effects and the assessment of their significance for the environment and humans.

Substances such as pesticides, drugs, nanoparticles and transformation products represent just a small selection of groups of substances whose toxicological effects have to be described with respect to environment-related exposure, and for which a risk assessment has ultimately to be undertaken. Whereas, for example, harmonized test strategies and OECD guidelines on prioritized toxicological endpoints exist for the authorization of chemicals, the use of biological test methods for the assessment of environmental contaminants depends, in the main, on the spectrum of often coincidentally available methods of the laboratory involved in the investigation. The result is that data is neither appropriate nor sufficient for reasonably sound risk assessment. This gives rise to the demand for systematic acquisition and assessment of toxicological data also on environmental contaminants. The corresponding investigative programme should at the same time be determined primarily on the basis of statutory requirements.

Contrary to the widespread opinion that the involvement of toxicological methods would result in more stringent regulation, numerous examples could be cited that disprove this claim. In terms of the principle of precaution, the lack of toxicological knowledge leads to greater insecurity, which in turn results in practice in extensive and often very costly packages of measures. The appropriate employment of biological test methods creates greater toxicological safety in the setting of limit values as well as greater trust among the general public, and it also helps to avoid unnecessary costs.

Environmental and human exposure

The increasing worldwide contamination of freshwater systems with thousands of industrial and natural chemical compounds is one of the key environmental problems facing humanity. Emerging contaminants can be defined as contaminants that are currently not included in routine monitoring programmes and that may be candidates for future regulation, depending on research on their human toxicity and ecotoxicity, potential health effects, public perception, and monitoring data revealing their occurrence in different environmental compartments (Petrovic and Barceló, 2006).

Environmentally hazardous substances are more often released from diffuse sources and consumer-related municipal (point) sources than from production-related industrial point-sources. Diffuse sources are agriculture, traffic and landfills, but also consumer-related releases that are becoming more and more important, such as household chemicals, personal care products, construction materials and technical chemicals. In groundwater, nitrate, solvents and selected pesticides – especially lipophilic substances – were for a long time the focus of attention, while in surface water, oxygen depletion and eutrophication were important. With the application of new detection methods, we are able to find concentrations of drugs, personal care products (for example, musk fragrances and repellents), technical products (for example, bisphenol A, nonylphenol, tributyl tin compounds, detergents (linear alkyl sulphonates (LAS), alkylphenol ethoxylates APE, quaternary ammonium compounds (QAC)), contamination from construction materials (for example, pesticides), contamination from traffic (for example, heavy metals, oxygenates, PAH, nitro-PAH and mineral oils), and food additives (artificial sweeteners) in the ng- and sub-ng range.

Pharmaceuticals and Personal Care Products

Pharmaceuticals are chemicals formulated into drugs for treatment of diseases, such as chemo-preventatives or drugs that enhance health or structural functioning of the human body. This group of compounds comprises large, diverse arrays of chemicals that can occur in the environment as unregulated contaminants and possibly give rise to known or suspected adverse ecological and/or human health effects (Giger, 2009; Richardson, 2009), but its significance has gone largely unnoticed (Daughton and Ternes, 1999).

Many of the compounds are water soluble, only slightly absorbing to top soil, and may be quite stable in the soil and groundwater environment (Heberer, 2002; Stuer-Lauridsen, et al., 2000). It is thus very likely that some emerging groundwater contaminants may be concealed within this class of compounds. Reviews on the occurrence and fate of pharmaceutical substances in the environment has been published by Daughton and Ternes, (1999), Giger (2009), Heberer, T. (2002), Kolpin et al. (2002), Loraine and Pettigrove (2006), Stumpf et al. (2006) and Zuccato et al. (2000). Pharmaceutical drugs and PPCP have been measured in surface water, groundwater and drinking water at trace levels that are in the 1 ng/l to 1 µg/l concentration range (Daughton and Ternes, 1999). Among the pharmaceuticals, the most frequently detected compounds were clofibric acid, ibuprofen, carbamazepine, diclofenac, phenazone, propylphenazone, diazepam, gemfibrozil, sotalol, tylosin and triclosan.

Detergents, surfactants and perfluorinated compounds

Alkylphenol polyethoxylates (APEOs) are non-ionic surfactants discharged into wastewater treatment plants and into the receiving water bodies of these plants, since their degradation and removal from wastewater is incomplete (Birch, 1991; Manzano et al., 1999). In oxidative conditions, APEOs decompose through the progressive loss of ethoxylate groups to form short-chain APEOs such as NP3EO, NP2EO and NP1EO (Maguire, 1999; Manzano et al., 1999). In anoxic conditions, these short-chain NPEOs and NPECs can further degrade into nonylphenol (NP) (Ike et al., 2002). In rivers, according to Jonkers et al. (2001), carboxylation takes place rapidly on the long ethoxylate chain and the shortening of this chain proceeds more slowly. NP, short-chain NPEOs and short-chain NPECs are degradation by-products of the parent nonylphenolic substances, and are now frequently detected in various water bodies in Europe, North America, Japan and Asia (Bennie, 1999; Ying et al., 2002).

Studies have confirmed the presence of nonylphenolic compounds in drinking water processed from surface waters (Kneeper and de Voogt, 2003; Petrovic et al., 2003). Laboratory tests have demonstrated the toxicity of various nonylphenolic compounds in invertebrates, fish, mammals and algae (Servos, 1999). These substances are also recognized as endocrine disrupters, and short-chain ethoxylated or non-ethoxylated degradation by-products have more endocrine activity than their parent products (Soto et al., 1992; White et al., 1994; Jobling et al., 1995; Blom et al., 1998).

Several studies by Loos et al. (2007; Loos et al. (2009) and Richardson, (2009) have identified nonylphenol and its carboxylates and ethoxylates, perfluorinated compounds (PFCs), including perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) in surface, ground and drinking waters. They can be transferred, bioaccumulated, and biomagnified along food chains, and their presence has been found in various tissues of many wildlife species and even in the human body (Richardson, 2009). Due to their persistent character in water and the recent interest in the scientific community, two of these PFCs, PFOS and PFOA, are currently receiving a great deal of attention as emerging contaminants in EU rivers and in the USA (Richardson, 2009; Loos et al., 2009).

PFOS, PFOA, NPE1C, NPE2C and NPE3C were among the most detected contaminants (around Lake Maggiore, Italy) in lake, river, rain and tap water samples confirming the persistent character of these substances (Loos et al., 2007). An EU-wide survey of PFCs from over 100 European rivers in 27 European countries produced a mean concentration of PFOS (6 ng/l) and PFOA (3 ng/l) in all river samples. Similarly, Saito et al. (2004) reported elevated PFOA and PFOS concentrations (4.5–67,000 ng/l PFOA and 1.5–526 ng/l PFOS) in river water from the Osaka region in Japan. The occurrence of nonylphenolic compounds (NP1EC, NP2EC, NP1EO and NP2EO) in raw surface waters, which receive (directly or via their tributaries) effluents from waste water treatment plants (WWTPs), was reported by Petrovic et al. (2003).

Pesticides and biocides

Pesticides and biocides are among the anthropogenic organic compounds that contaminate surface and groundwater bodies, are often used in urban areas as a material protection agent, in renders and paints for exterior facade coatings, in bitumen sheets for roof waterproofing, as well as for wood treatment, concrete, paints and in-can preservatives (Burkhardt et al. 2007; Schoknecht et al. 2009; Wittmer et al., 2010). Pesticides can be applied on gardens, lawns, or even on sealed surfaces (Wittmer et al., 2010). Mecoprop is widely used in bitumen sheets to prevent roof penetration through plant growth, and is released from flat roofs. It is one of the most frequently detected pesticides in surface waters (Bucheli et al., 1998b; Gerecke et al., 2002; Burkhardt et al., 2007). Studies on artificial rainfall applications on different model roofs as well as a number of field studies under natural conditions have confirmed that the roof protection agent biocide (for example, R, S-mecoprop and Preventol B 2) was the source of these compounds (Bucheli et al., 1998). Investigation on the leaching of biocides from a render under UV irradiation revealed the release of high concentrations of diuron, terbutryn, cybutryn and carbendazim (Burkhardt et al., 2007). Gerecke et al. (2002) reported the presence of pesticides (for example, atrazine, diuron and mecoprop) in effluents of WWTPs and in rivers, suggesting that effluents are the specific sources of pesticides in surface waters. Comparisons of the relative importance of WWTPs and diffuse sources revealed that farmers who did not properly comply with 'good agricultural practice' caused at least 14% of the measured agricultural herbicide load in surface waters. Pesticides, used for additional purposes in urban areas (that is protection of materials, conservation, etc.), entered surface waters in up to 75% of cases through waste water treatment plants. Burkhardt et al. (2007) investigated several biocides at different scales: facades and roofs, effluent and sludge from wastewater treatment plants and receiving waters, in which higher specific loads of biocidal products were observed in WWTPs where stormwater and domestic/industrial wastewater were treated on account of a combined sewer system.

Artificial sweeteners in source water

Besides "well-known" potential contaminants, food additives are also detected in river waters. The use of artificial sweeteners in the food industry has grown rapidly in recent years, but little attention has been paid to additives in food and beverages with respect to occurrence and fate in the aquatic environment. These chemicals pass through the human metabolism largely unaffected, and are excreted via urine and faeces. Now they are found in environmental waters, and being persistent, they could potentially enter the aquatic environment (Buerge et al., 2009). These compounds, which are frequently detected in ground and surface water samples (ng/l to µg/l concentration), include acesulfame, cyclamate, saccharin, and sucralose (Buerge et al., 2009; Giger, 2009; Loos et al., 2008¸ Scheurer et al., 2009). In German surface waters, for example, acesulfame was the predominant artificial sweetener with concentrations exceeding 2 µg/l; but other sweeteners were also detected at levels of up to several hundred nanograms per litre in the order saccharin ≈ cyclamate > sucralose (Scheurer et al. 2009). The presence of acesulfame in tap water and processed drinking water was also reported by Buerge et al. (2009). The chemical sucralose was detected in most samples collected from rivers in 27 European countries.

Nanomaterials

Nanomaterials are natural and man-made (engineered) structures, ranging in size from 1 nanometre (nm) to 100 nm, and belong to a new and expanding class of chemicals (emerging contaminants) whose environmental hazard is poorly determined. They are widely used in areas such as cosmetics, sunscreens, clothing, paints, car tyres, tennis rackets, lubricants, electronics, soaps, shampoos, detergents, fabrics, lubricants, chemotherapy and even recreational equipment such as golf balls and (Richardson, 2008; Wiesner et al., 2006). Releases of nanomaterials may come from point sources (for example, landfills), non-point sources (for example, wet deposition and stormwater runoff) and attrition from products containing nanomaterials (Wiesner et al., 2006). Research to date indicates that many non-organic nanomaterials (ceramics, metals, and metal oxides) are inherently non-biodegradable, and are stable and persistent (EPA, 2007). They are also capable of bioaccumulation in the food chain (Biswas and Wu, 2005). A number of researchers have reported acute and chronic toxicity of various nanomaterials (Cattaneo et al., 2009; Lovern and Klaper, 2006; Shvedova et al., 2009; Fortner et al., 2005).

Quaternary ammonium compounds (QACs)

Quaternary ammonium compounds (QACs) are an important class of industrial chemicals widely applied as disinfectants, wood preservatives, antistatic agents, corrosion inhibitors and detergents among a variety of other applications. As a result, QACs are ubiquitous contaminants found worldwide in both engineered and natural systems. QACs are toxic to aquatic organisms (Boethling, R.S., Lynch, 1992; Grillitsch et al., 2006). As hydrophobic cation exchangers, QACs sorb strongly to soils and sediments (Gaze et al., 2005), and many tetraalkylammonium QACs, including benzyldimethylammonium compounds, alkyltrimethylammonium compounds and dialkyldimethylammonium compounds are persistent enough to be found at appreciable concentrations in receiving waters (Ding and Tsai, 2003; Martínez-Carballo et al., 2007) and sediments (Fernandez et al., 1996; Kreuzinger, et al., 2007; Martinez-Carballo et al., 2007). In several studies, didecyldimethylammonium chloride and benzalkonium chloride have been selected as some of the best representatives of QACs (Grillitsch et al., 2006; Martínez-Carballo et al., 2007). Based on consumption, toxicity and degradation criteria, Martínez-Carballo et al. (2007) selected several dialkyldimethylammonium chlorides, benzalkonium chlorides and alkyltrimethylammonium chlorides to be determined in surface water samples. The target substances were detected in most surface waters at ng/l concentrations. Due to relevant adsorption onto suspended matter, it was also established that surface waters with a high content of suspended matter exhibit significantly higher concentrations of QACs. Environmental risk characterization and evaluation of QAC in Austrian rivers revealed that small rivers with high particulate matter were contaminated with QAC, and concluded that a QAC-derived risk to sensitive aquatic non-target organisms could not be excluded (Grillitsch et al., 2006).

Polyaromatic hydrocarbons (PAHs)

Polyaromatic hydrocarbons (PAH) are a group of organic contaminants derived from both natural and anthropogenic sources. The main anthropogenic sources of PAHs are coal combustion and vehicle emissions (tyre wear, asphalt, tar, small engine exhaust and leaching of sealants) (Dickhut et al., 2000; Mahler et al., 2005). PAHs tend to accumulate on roads, car parks, rooftops, and other impermeable surfaces. Rainfall runoff from motorways, roads and car parks contributes significant quantities of PAHs to surrounding surface water bodies and road debris (Aryal et al., 2005; Brown and Peak, 2006; Diblasi et al., 2009; Krein and Schorer, 2000).

Because of their hydrophobicity, PAHs show high persistence in the water-soil environment, posing a threat to human health and the environment. As a result, PAHs are ubiquitous persistent organic contaminants, and are considered to be highly hazardous to the environment and human health (Fang et al., 2004). The European Water Framework Directive established a list of priority hazardous substances in the field of water policy, in which PAHs were among the identified chemicals (2000/60/EC). Several PAHs are known to be cancer-causing agents, may act as synergists, or are mutagenic (Wenzl et al., 2006). Risk assessment of PAHs associated with stormwater pond sediments showed that sediments from commercial and residential ponds have the potential to pose moderate to high risks for adverse, chronic effects to benthic organisms and an increased risk of cancer for humans following excavation and on-site disposal (Weinstein et al. (2010). PAHs from coal-tar-based paving sealants in car parks ended up in sediments and were the most likely cause of decreased community health of benthic macroinvertebrates; and it is also reported that macroinvertebrate densities downstream were only half those upstream (Scoggins et al., 2007).

RISK ASSESSMENT

Theoretical concept

The term “emerging” contaminants is, to begin with, non-judgemental and characterizes differentiation compared to classic industrial chemicals, for which risk assessment and the setting of standards has been concluded on the basis of current knowledge. The specific question as to why these new environmental contaminants are nevertheless toxicologically significant can be answered as follows:

The new environmental contaminants impact complex protected goods. Protection targets include the human being, particularly in crucial phases of development (for example, in childhood). Extensive exposure is possible via water pathways. New environmental contaminants generally possess problematical properties. Due to their for the most part high polarity and low sorption tendency, these substances easily enter drinking water. In addition, they dispose of relatively high biological and chemical persistence. Some of their adverse effects – for example, endocrine disruption in surface water – can be detected ecotoxicologically at a very early stage. Extrapolation of such warning signals to humans is, however, questionable. At the same time, there are initial indications of adverse effects from an epidemiological point of view. There is largely a lack of knowledge of the temporal course between exposure and possible effect, and about the number of persons and/or organisms that are in fact affected by exposure via the water pathway. Our knowledge of precise relationships within the chain of cause and effect is presently completely inadequate [Figure 1].

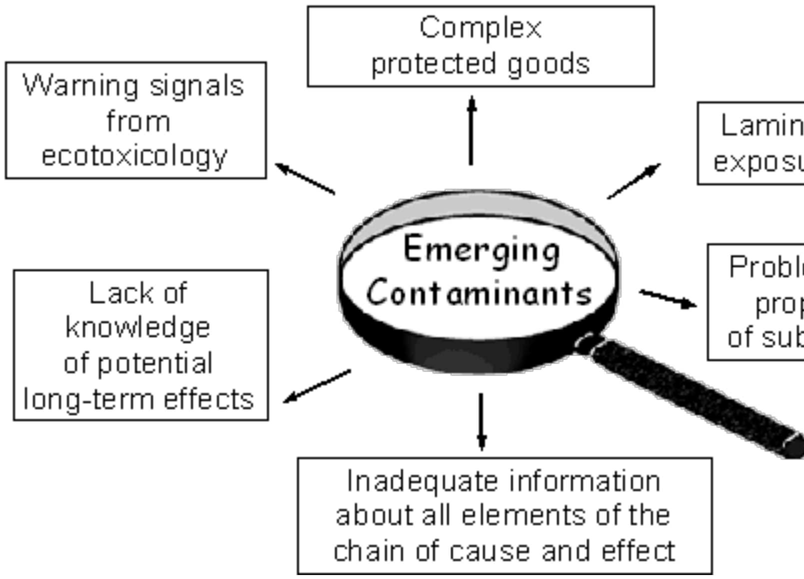

Figure 1. Emerging contaminants

In other words, lack of toxicological knowledge currently prevails as far as new environmental contaminants are concerned. There are grounds, however, for granting the new environmental contaminants a special status. One of these grounds is the ambivalence of the conducted debate. The intended benefits of the new environmental contaminants for life and health (the economic factor) have to be seen alongside the potential endangerment of the environment and, via the environment, of healthy humans (the ecological factor). Against this background, it is necessary to develop new concepts for the scientific assessment of new environmental contaminants.

Substance patterns of new environmental contaminants detected up to now provide consistent evidence of exposure in the low-dose range. From this, it can be reasonably deduced that toxicological high-dose mechanisms are irrelevant; a conclusion, which might initially appear to be insignificant, but, with respect to the orientation of test strategies and, as a consequence, assessment strategies, is still too little considered. This is not surprising, since they were initially developed for the testing of chemicals and drugs. Adaptation of these test strategies to the detection and assessment of new environmental contaminants should be based on the precept that it is primarily the toxicological safety of a substance that should be characterized, and not its toxicological risk.

For practical implementation of this principle this means providing proof of primary key mechanisms under realistic exposure patterns (low-dose range) at a cellular and molecular level. In the choice of appropriate biotests, their prognostic predictive value in relation to long-term effects and the form of adverse effects (for example, cancer) should be a decisive criterion.

Due to its biological position in the causal chain of "exposure and effect", genotoxicity occupies the prime position among assessment-relevant parameters. There are two basic reasons for this:

1. According to the WHO World health Report 2006, more people die worldwide of cancer than of an infectious disease. That is not least a result of the high degree of regulatory density for the hygienic-microbiological sphere.

2. The conservation of biodiversity is a key issue of international environment policy. The aim will be to indicate causalities concerning possible causative noxae and the loss of biodiversity. Here, the substance-based approach must be ranked equally with other parameters (for example, water engineering).

Anthropogenic impacts on ecosystem and human health are both an urgent and international issue. The economic scale of the problem is indicated by the findings of several economic studies.

In the area of sustainable water pollution control, the monitoring programme does not envisage inclusion of new effects. Nevertheless, there are an increasing number of scientific studies, in which a cause is established between substance-related, genotoxic load and its effect at the ecosystem.

It is increasingly recognized that assessment of the impact of emerging contaminants on ecosystems requires understanding of effects throughout the hierarchy of biological organisation. Long term exposure to emerging contaminants will not result in rapid change. The impact will be gradual and over a long time without visible changes in the ecosystem.

Furthermore the timescale from exposure up to adverse effects are often of the order of decades. The solution lies in the detection of early signals, which are relevant and prognostic to adverse effects.

The large number of circumstances that require regulation, together with the limited availability of personnel and financial resources, necessitate the setting of priorities and focusing on risks, which are perceived from a scientific perspective to require precautionary action and which, at the same time, are highly topical in terms of health and environment policy.

Real exposure scenarios, in particular, necessarily require that besides classic elements of water pollution control other important parameters be embraced, which have proven to be relevant in studies (such as, for example, the effect of genotoxicity at the population level). The situational implementation of modern experimental concepts in water pollution control enables early recognition and assessment of new hazard potentials, and the formulation, where required, of recommendations for action. As to biological methods, it can be said that a large number of standardized and sufficiently sensitive test methods are available.

The objective of future endeavours in water pollution control must be the development of harmonized test strategies for hazard-based risk management of anthropogenic trace substances. These form the basis for scientific risk assessment, which in turn guarantees legal certainty in the administrative area, also concerning cost-benefit analysis. An initial step in this direction has been taken in Germany with regard to drinking water. The theoretical concept is based on the recommendation of the Germany Federal Environment Agency entitled "Assessment of the presence of partly appraisable or non-appraisable substances in drinking water from a health point of view", in which a health-related indicator value (*gesundheitlicher Orientierungswert – GOW*) is recommended as an assessment criterion [Figure 2].

The GOW is a health-related precautionary value for human-toxicological substances that are only partly or not at all assessable. The gradual deduction of the GOW is based on the effect mechanisms of substances and corresponding available toxicological data. This theoretical concept designates biological endpoints, but mentions no procedural method for experimental collection of toxicological data. Since the respective measures in risk management arise from the GOW level (dependent on available data in the 0.1 to 3 µg/l), methodical instruments for acquisition of toxicological data have to be stipulated. On the basis of experiences with chemicals law, for reliable assessment a harmonized test strategy is necessary for every endpoint mentioned in the GOW concept.

For those substances possibly present in drinking water with increasing density of data the following maximum (safe) *values for health for lifelong consumption* in drinking water can be expected.

≤ 0.1 µg/l:	there are only inadequate or no toxicological data at all available, the substance is genotoxic or is suspected to be *genotoxic*;
≤ 0.3 µg/l:	the substance has been proven to be *non-genotoxic*, but otherwise there are no significant experimental toxicological data available;
≤ 1 µg/l:	the substance has been proven to be *non-genotoxic* (see above). In addition, there are significant in vitro and in vivo data on the *oral neurotoxicity* of the contaminant. However, these data do not produce a value lower than 0.3 µg/l;
≤ 3 µg/l:	the substance is neither genotoxic, nor neurotoxic (see above). In addition, there are significant in vivo data from at least one study on subchronic-oral toxicity of the contaminant. However, these data do not produce a value lower than 1 µg/l.

Figure 2. Evaluation of partly or non-assessable substances in drinking water based on the GOW concept (UBA, 2003)

The theoretical concept links Science-based information to setting limit values. Furthermore, it allows realtime decisions for risk management. Due to the ecotoxicity and environmental impact of emerging contaminants the practical approach should be also transferred on environmental risk management.

Methodical developments concerning the mechanism of genotoxic effect are sufficiently advanced, so that a first step in genotoxicity testing can be established. Figure 3 displays the hierarchical test strategy, whose proposed inclusion in water pollution control programmes and employment in the assessment of environmental contaminants and/or degradation and transformation products are currently the subject of discussion. The hierarchical test strategy covers the characterization of cytotoxic effects by means of 2 to 3 in vitro tests. The Ames test and the induction of micronuclei in the mammalian cell culture are employed for detection of genotoxic hazard potential. Standard protocols are available for both procedures.

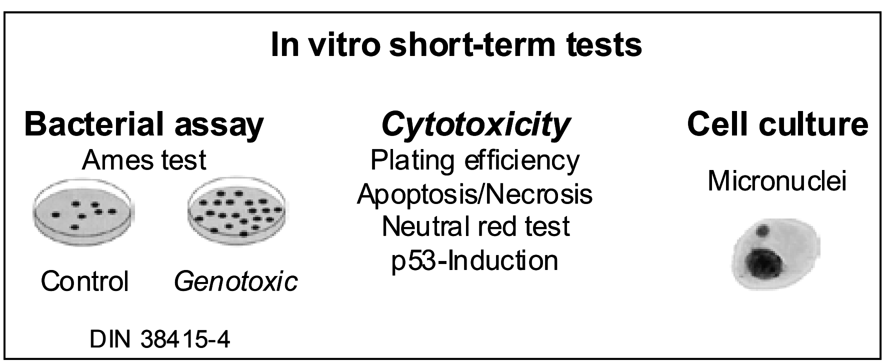

Figure 3. Test strategy in genotoxicity testing

In vitro genotoxicity testing enables initial statements on the effect mechanism of substances in the form of a yes/no answer (genotoxic or non-genotoxic). With in vitro tests primary effect mechanisms can be sufficiently reliably identified.

CONCLUSION

The risk management of anthropogenic trace substances lies in the area of conflict involving risk (undesired effects for the environment and humans) and innovation/benefit (for example, for health through drugs and quality of life through nanomaterials). The question therefore arises as to how real risks can be reliably assessed, and how the balance between risk and benefit can be communicated to the public, bearing in mind that not all population groups that are potentially affected (for example, through drinking water) also benefit from the use of substances.

For this question, assessment strategies for the derivation of normative values are the main element in health-related environment policy. In this context, the scientific debate is presently conducted very inconsistently. This leads, in turn, to insecurity among the public, and not infrequently to overestimation of the risks and, due to the pressure for action, to highly costly and mostly unnecessary measures. Basic regulation of assessment concepts is therefore essential; a demand that also arises from new regulations in the environmental area (EU Water Framework Directive and daughter directives) and in chemicals law (REACH).

A fundamental criterion for the specification of limit values is the inclusion of substance-related effect mechanisms, which have to be identified and quantified by means of biological tests. This paradigmatic change in evaluative toxicology, away from theoretical safety factors and towards exposure-related hazard potentials, leads to science-based risk management, which, as a result, enjoys greater authority among the public.

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Fecal contamination of surface waters: Developments in human risk assessment and risk management

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Abstract

There are several developments in water microbiology that will undoubtedly help define and manage risks to water quality from diffuse fecal pollution. A toolbox of 'microbial source tracking' methods in combination with geostatistical methods can be used to elucidate the significance of these sources with spatial and seasonal sensitivity. The correlation between 'traditional' indicators of water quality (e.g. abundance of *Escherichia coli*) and the abundance of human pathogens is often weak, suggesting that new metrics of water quality risk and methods for detecting pathogens are desirable. New molecular methods are becoming available to quantify specific microorganisms in environmental matrices, detect traits that distinguish pathogenic types, and help establish the role that waterborne pathogens play in the epidemiology of enteric disease. There are a number of emerging microbial pathogens whose significance to acute and chronic disease remains to be defined, and the significance of waterborne transmission determined. Conceptual advances in physical exposure modelling and in Quantitative Microbial Risk Assessments (QMRAs) are helping to better predict how water quality will vary with land use practices, and the likely outcome for public health. Furthermore these tools will become indispensable for validating risk mitigation strategies, Better Management Practices in the agricultural context.

Keywords

Agriculture, diffuse pollution, pathogens, risk assessment, risk management; water quality

INTRODUCTION

A direct causal link between unclean water and outbreaks of cholera was established over a hundred and fifty years ago, a seminal discovery in the relationship between environmental quality and human health. Even though this knowledge subsequently resulted in the development and adoption of water treatment and sanitation technologies and practices, fecal contamination of surface water still remains a very significant public health challenge. Globally, an estimated 3.2% of deaths are attributable to unsafe water caused by poor sanitation and hygiene, a problem particularly acute in rural areas in the developing world (WHO 2009). In the developed world considerable money is spent on protecting water quality, ideally through a "multi-barrier" approach integrating methods and policies for source water protection, water purification and safe distribution to the consumer. Within this context, this brief review considers several 'emerging' issues related to the assessment of source water quality, and strategies for mitigation of diffuse fecal pollution. Specifically, we consider here molecular technologies to identify, quantify and characterize microbial pathogens; the development of strategies to identify sources of fecal pollution at a watershed scale; and the development of physically-based exposure models and quantitative microbial risk assessment (QMRA) frameworks to analyze and predict water quality data and extrapolate potential impacts on policy-relevant human health outcomes. The perspectives in this paper are largely informed by our own research on assessing and managing the impacts of agricultural activity on water quality within the Canadian context.

TOOLS TO QUANTITATIVELY DETECT AND CHARACTERIZE MICROORGANISMS THAT POSE A THREAT TO HUMANS

Many jurisdictions evaluate and mandate compliance with drinking and recreational water quality standards on the basis of the presence and the abundance of *E. coli* (National Research Council 2004). For example, Canadian Recreational Water Quality Standards recommend that *E. coli* densities in excess of a geometric mean of 200 Colony Forming Units per 100 ml indicate that the water is unsuitable for swimming and bathing (Health and Welfare Canada 1992). The correlation between 'traditional' indicators of water quality (e.g. abundance of *E. coli*) and the presence or abundance in water of bacteria, viruses and protozoa that are pathogenic for humans is often weak (Yates 2007; Wilkes et al. 2009; Edge et al. In Press). Therefore in many circumstances indicator microorganisms may be less efficacious than desired as a metric for water management, and it would be far preferable to actually measure pathogen abundance directly. To this end, a number of pathogen-detection technologies are under development. Pathogen-specific signature DNA sequences can be detected by quantitative PCR. PCR methods have been used to quantify various bacteria (Khan et al. 2009), viruses (Fong and Lipp 2005), protozoa and toxic phytoplankton (Humbert et al. 2010). Bacteria of "emerging" (cryptic) importance and those that are recalcitrant to culture-dependent enumeration such as *Campylobacter* spp. (Inglis et al. 2010) *Legionella* spp (Parthuisot et al. 2010), *Arcobacter* spp. (Gonzalez et al. 2010), and *Helicobacter* spp. (Yáñez et al. 2010) are amenable to detection by PCR-based methods. These PCR-based methods require extraction of DNA from samples and can have problems with poor detection limits, interference with contaminants and, most importantly, the inability to discriminate between viable and dead pathogenic cells (Girones et al. 2010). Biosensors combining detection of microorganisms with specific antibodies or antimicrobial peptides coupled with microelectrodes or nanotubes to provide an electronic signal are examples of developments in technology that could revolutionize the availability of economical, high throughput, real-time pathogen quantitation systems (Mannoor et al. 2010; Garcia-Aljaro et al. 2010).

Distinguishing with confidence waterborne microorganisms that are truly pathogenic for humans can be a challenge. In some cases ascribing identity suffices. However, even for pathogens such as *E. coli* O157:H7, which are associated with outbreaks of severe human disease, differences in virulence among the three lineages and various clades of the organism have been noted (Zhang et al. 2010). On the other hand many pathotypes of *E. coli* that can cause diarrhea and extraintestinal infections are less well characterized and isolates from water are only considered "potentially" pathogenic on the basis of the virulence gene complement of these strains. The distribution of virulence genes in bacterial isolates can be elucidated by DNA-DNA hybridization with microarray technologies (Hamelin et al. 2007). Cryptosporidia are typically enumerated using immunofluorescence following immunomagnetic separation of oocysts. This method does not distinguish the many varied *Cryptosporidium* species, only a few of which are human infective. Further analysis using DNA-based typing methods is required to determine if the water carried human-infective or benign (or both) types of oocysts (Ruecker et al. 2005, 2007). Some pathogens can also transform in a viable but non culturable state when entering a hostile environment such as surface water, and thus will only be detected by molecular techniques. It is hypothesized that cells in this form retain their pathogenic potential and can infect organisms after resuscitation (Oliver 2010), as it has been shown with *Helicobater pylori* (Cellini et al. 1994; She et al. 2003). However, *Listeria monocytogenes* cells in this state were shown not to be infective (Cappelier et al. 2005), showing that exceptions occur. Finally, distinguishing viable pathogenic microorganisms from dead (and therefore) non-pathogenic microorganisms is a challenge when using molecular methods because the DNA can persist once the cell is dead (Rudi et al. 2005).

Some waterborne organisms can induce sequelae and chronic disease following infection (Fratamico et al. 2009). For example, *Campylobacter jejuni* infections have been associated with arthritis, Reiter's syndrome and Guillain–Barré syndrome (Snelling et al 2005). *Helicobacter pylori* colonizes more than half of the world's population, and is the main cause of gastric ulcers in humans. Furthermore, a fraction of those infected by *H. pylori* may also develop distal gastric adenocarcinoma, and B cell mucosa-associated lymphoid tissue (MALT) gastric lymphoma (Atherton 2006). There is also an increased risk of developing an inflammatory bowel disease (IBD) following an episode of gastro-enteritis (Rodriguez et al 2006; Gradel et al 2009). While IBD may result from a combination of genetic and environmental factors (Braus and Elliot 2009), it has also been hypothesized that there may be a role for persistent infection by enteric pathogens. *Mycobacterium avium* subsp. *paratuberculosis*, non-pylori *Helicobacter*, adherent-invasive *E. coli* and *Campylobacter concisus* are all possible candidates (Hansen et al. 2010). It is also suspected that irritable bowel syndrome (IBS) is triggered by enteric infections, since an increase in the incidence of IBS was observed among the citizens of Walkerton after the 2000 outbreak. In this case, 36% of the population who had gastro-enteritis while the outbreak was ongoing subsequently developed IBS, while only 10% of the population who were not infected during the outbreak developed the syndrome (Marshall et al 2006; Kalischuk and Buret 2010).

METHODS TO IDENTIFY SOURCES OF FECAL POLLUTION IN WATERSHEDS

In the typical North American context, sources of fecal pollution in mixed activity watersheds can include human sewage and septage, storm water discharge, effluents from land receiving animal manures, roaming mammalian wildlife, and highly mobile avian wildlife. Methods to distinguish and identify these varied point and non-point pollution sources could help guide the implementation of targeted mitigation measures (Health Canada 2002; International Joint Commission 2004; USEPA 2000). There has thus been significant interest in identifying source-specific attributes of the enteric flora that can distinguish the host source in fecally contaminated water (USEPA 2005). These can variously include bacteria, viruses and epithelial cells shed by the host (Edge and Schaefer 2006). A variety of molecular and phenotypic methods are available to compare water and fecal isolates of indicator bacteria (*E. coli*, enterococci) and infer source (Santo Domingo and Sadowsky 2007). These "library dependent" microbial source tracking methods have the disadvantage that the robustness of the source assignation is dependent on the size and representativity of fecal collection obtained in the study (Lyautey et al. 2010; Stoeckel and Harwood 2007). Furthermore, the 'reference' library is only useful for the area under investigation from which it was isolated. In contrast, 'library independent' methods that detect source specific signatures in DNA extracted directly from water are not limited by the cost and the tractability of obtaining large numbers of representative fecal isolates from within the area of investigation. Quantitative PCR can be used to estimate the relative significance of each marker in fecal or water samples. Source-specific variation in the sequence of the 16S rRNA gene of *Bacteroidales* can be detected by PCR, and on this basis markers have been developed to detect fecal contamination of ruminant, human, and anserine origin (Bernhard and Field 2000a; 2000b; Field et al. 2003; Mieszkin et al. 2009; Fremaux et al. 2010). Host mitochondrial DNA in fecal material is another useful marker for assigning fecal source (Kortbaoui et al. 2009; Baker-Austin et al. 2010). Source assignation studies in watersheds with abundant and varied avian and mammalian wildlife will in particular benefit from an increased availability of diverse markers in the microbial source tracking "toolbox". Recently, it has been shown that highly discriminatory genotyping methods applied to *Cryptosporidium* and to bacterial pathogens such as *E. coli* O157:H7 and *Campylobacter jejuni* are very useful in pinpointing many wild and domestic animal sources of fecal contamination in watersheds (Ruecker et al., 2007; Jokinen et al., 2010). MST methods have been used to elucidate fecal pollution sources in numerous published studies that vary in size and setting including surface water impacted by agricultural effluent and sewage (Fremaux et al. 2009), recreational beaches impacted by birds (Edge and Hill 2007), and marine shellfish beds impacted by agriculture or sewage (Gourmelon et al. 2010).

The conclusions are particularly compelling when surface water fecal source pollution assignations based upon molecular microbial methods are coherent with land use and hydrology within the watershed. These results may then be very valuable in communicating with the public and contributing towards resolving debates between stakeholder communities. Detection of presumptive human pollution downstream of a sewage outflow, or a ruminant marker downstream of an area with many cattle on pasture is consistent with common sense. In many watersheds different potential fecal sources (livestock, wildlife, human) will be in close proximity and thus landuse should be defined rigorously. This can be done by combining various methodologies including discrete (point observations from land use survey) and continuous (raster satellite imagery land use) Geographic Information System (GIS) data. Satellite imagery can be used to produce land use data sets, and discrete land use observation techniques (e.g., road side surveys) can be used to delineate locations of specific farming operations and other point data. These types of data can be combined with a digital elevation model (DEM) to define distances upstream to a particular land use, percent coverage of specific land uses, and their densities within watersheds (e.g. Lyautey et al., 2010).

MODELS TO PREDICT EFFECTS OF SOURCE WATER PROTECTION MITIGATION MEASURES ON WATER QUALITY AND PUBLIC HEALTH RISK

Many watershed scale hydrological models are commonly used to simulate the fate and transport of agrochemicals and bacteria in surface waters by considering a vast array of environmental and land use variables that impact surface water pollution (e.g. SWAT; Baffaut and Sadeghi 2010). Predicted trends in surface water concentrations and loads can be evaluated in terms of pathogen (presence, density) distribution and temporal hotspots. The microbial contaminant module in SWAT allows simulation of transport, growth and decay of two distinct bacteria species that vary widely in their survival characteristics for example. Fate of micro-organisms deposited on land by manure applications or by grazing animals, and transport in surface runoff into streams or lakes is considered. Specific partitioning coefficients determine the relative amount of bacteria in soluble and adsorbed phases. Bacterial decay is modelled with first order kinetics and a provision is made for re-growth. In addition to transport by runoff, infiltration and incorporation through tillage are considered. Common tillage practices incorporate a portion of the applied bacteria into the soil profile.

In 2000, following the events of the waterborne outbreak of *E. coli* O157:H7 and *Campylobacter* in Walkerton, Ontario, leading to the death of seven people and over 2300 cases of illness, public health officials and the drinking water industry were forced to re-evaluate Canadian water safety practices (Hrudey et al. 2002). For many years, the water treatment industry and public health have relied on compliance with end-product standards to ensure the protection of population health and water safety. Since 2000, this approach has been challenged by the proposition that a risk assessment approach is better than rule compliance for informing water safety decision-making and improving public health protection. Internationally, a risk analysis framework (which includes risk assessment, risk management and risk communication) has been incorporated into international guidance documents on drinking water safety, under the broader umbrella terms "water safety plans", "multiple barrier approach" and "source to tap" (WHO, 2004). As the World Health Organisation's guidelines for drinking water quality note, "the most effective means of consistently ensuring the safety of a drinking-water supply is through the use of a comprehensive risk assessment and risk management approach that encompasses all steps in water supply from catchment to consumer…such approaches are termed water safety plans (WSP)." (WHO, 2004).

Traditional epidemiological tools are often not sensitive enough to detect a small number of cases of illness arising from environmental exposure to pathogens (Eisenberg et al., 2006). Large outbreaks are more frequently detected, but the existing passive nature of traditional enteric surveillance systems limits the ability of public health practitioners to detect sporadic, endemic cases of disease in the community (Shuster et al. 2005). Few data are available to evaluate the role that environmental transmission routes of various enteric pathogens have on endemic levels of disease in a population. While risk assessment was first designed to assess chemical risks from environmental exposures (including food, water, air and the built environments), the tool began to be applied to the field of microbial risk assessment in recreational water in the late 1970s and early 1980s (Dudley et al., 1976; Fuhs, 1975; Haas, 1983a; 1983b). Quantitative microbial risk assessment (QMRA) is a structured, integrative, quantitative, multi-disciplinary method, specific to microbial risks, and is rapidly becoming an accepted tool in the risk management of a number of key policy issues in public health and the management of environmental issues (Fewtrell and Bartram, 2001; Haas, 2002; Pruss et al., 2002). The use of risk assessment as a basis for decision-making or agenda setting has evolved rapidly in the past ten years. Most importantly, risk assessment provides a mechanism for the systematic collation of knowledge (and data) about an identified risk (or problem). Not only is it useful for ranking risk settings and prioritizing actions or policy development to mitigate risks; it is also useful for identifying research needs and data gaps in the science of waterborne pathogens (or chemicals).

QMRA is currently used on an international level to establish standards, guidelines, and other public health provisions for drinking water safety at the community level in the United States, the United Kingdom, Australia, and many European countries. This originated from its initial application in food monitoring and guideline development. The tool has been used to assess the risks of waterborne viruses (e.g. Soller et al., 2006), multiple waterborne pathogens (eg. Rose and Gerba, 1991) and protozoan pathogens, including *Cryptosporidium* and *Giardia* (Gofti-Laroche et al., 2003; Haas, et al., 1996; Haas, 2000; Perz et al., 1998; and Teunis et al., 1997). QMRA studies have also been performed to assess the public health risk of exposure to microorganisms in recreational water (Ashbolt et al., 2010; Craig et al., 2003; Roberts et al., 2007; Soller et al., 2010; Steyn et al., 2004; and Schets et al., 2008).

QMRA is increasingly being applied to support traditional drinking water safety verification through indicator monitoring. In 2001, Eisenberg et al. used the QMRA approach to evaluate the reliability of both water and wastewater treatment plants for public health protection in the United States. In 2003, Havelaar and Melse, representing the World Health Organisation's Collaborating Centre for Risk Assessment of Pathogens in Food and Water, published guidelines for the use of QMRA to quantify public health risks in an integrated manner, to develop health-based targets for drinking water quality. In 2006, Soller used the QMRA framework to inform the national estimate of acute gastrointestinal illness attributable to microbial contamination of drinking water in the United States. In 2007, Astrom et al used the tool to evaluate the efficacy of selective closure of a raw water intake to protect public health in Sweden. These are just some examples of how the international drinking water community has incorporated the QMRA tool to inform local, state level and national practices to protect public health. Overall, QMRA is an important tool for risk managers at many levels to predict and quantify the benefits of risk management "multi-barriers" approaches, i.e., to simulate pathogen removal and identify potential intervention points along the "source to tap" continuum, based on source water quality and treatment performance indicators.

Understanding the uncertainty and variability in pathogen concentrations in source waters, which are used for recreation, drinking, or irrigation, is essential to appropriately quantify and mitigate human health risks. Decisions related to the drinking water treatment required to consistently ensure adequately safe drinking water, or the change in land use practices to better protect public health, depend on pathogen concentration data (Haas et al., 1996). A more recent development in the QMRA field involves the recognition that measurement error can be an important, yet often unrecognized, factor in the assessment of risk. It is recognized that environmental sampling and microbial detection methods are uncertain, and without incorporating this uncertainty in the final risk models, the final risk estimates are biased (Schmidt and Emelko, 2010). Understanding this uncertainty and variability in pathogen or indicator concentrations in time and space is critical in these efforts and must be explicitly addressed in the risk analysis framework.

With considering exposure from agricultural sources, QMRA uses stochastic risk assessment models to estimate the probability of risk of acquiring enteric infections (including protozoan, viral, and bacterial pathogens) by contact during or after land application of sewage biosolids and manures, swimming in a river or lake impacted by agricultural runoff, as well as consumption of drinking water drawn from the area of investigation. Pathogen datasets are fitted to appropriate distributions and used as input into a conceptual static model (i.e., primary transmission) of health effects. Probabilistic QMRA models are developed using published dose response relationships for the various pathogens (e.g., Hass et al., 1996), and literature values are applied for human exposure (by direct ingestion) to soil and water during environmental exposures. Monte Carlo simulations are conducted (using, for example, MSExcel with @risk or Crystal Ball software) and risk outcomes generated as probability density functions. The influence of different pathogen genotypes on final risk estimates can be considered. Percentiles of risk probabilities of infection or illness are generated, depending on the metric used in the original dose response studies. Risk estimates can then be ranked by exposure route and pathogen type, to help identify and elucidate existing data gaps and refine and prioritize future research needs. Results from different QMRA scenarios can be compared for a variety of nutrient management practices (e.g., application method, storage and pathogen reduction treatments) to provide a quantified, risk-based context to comment on the impacts of beneficial management practice implementation at a watershed scale. This information can then be used to inform source water protection and recreational water policies.

CONCLUSIONS

Protecting the quality of water used for drinking or recreation is the first crucial step in protecting human health from waterborne disease. This imperative constrains how and where agricultural activities are undertaken, and guides mandated practices for the management of sewage and septage. A variety of technical innovations are permitting more rapid quantitative detection of pathogens. New knowledge concerning the molecular basis for the pathogenic potential of waterborne microorganisms will help refine an understanding of human health risk from waterborne disease. Finally, new more robust modelling approaches will be used to predict the consequences of specific practices on water quality, and the impact of land use change with respect to human health risk.

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Mathematical Modeling of Heavy Metals Contamination from MSW Landfill Site in Khon Kaen, Thailand

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Abstract

Kham Bon landfill site is one of many unsanitary municipality waste disposal sites in Thailand. The site has been receiving municipality wastes without separating hazardous waste since 1968. Heavy metals include, Pb, Cr and Cd were found in soil and groundwater around the site, posing health risk to people living nearby. In this research, contamination transport modeling of Pb, Cr and Cd was performed using MODFLOW. In addition, 20 years prediction of heavy metals contamination using the model was performed. Model results showed that heavy metals especially Pb and Cr migrated toward the north-eastern and south-eastern direction. The 20 years prediction showed that, heavy metals tends to move from the top soil to deeper aquifer. The migration would not exceed 500 m radius from the landfill center in the next 20 years which is considered a slow process. From the model simulation, it is recommended that mitigation measure should be performed to reduce the risk from landfill contamination. Hazardous waste should be separated and disposed in proper landfill. Groundwater contamination in deeper aquifer should be closely monitored. Consumption of groundwater in 500 m radius must be avoided. In addition, rehabilitation of the landfill site should be undertaken to prevent further mobilization of pollutants.

Keywords

Landfill; Contamination; Heavy Metals; Landfill leachate

INTRODUCTION

Kham Bon Landfill site is located at Kham Bon village, Khon Kaen Province, Northeast Thailand (Figure 1). This site received MSW approximately 200 tons/day of waste from Khon Kaen municipality along with 15 nearby communities. Waste disposed at this site consists of food, plastic, paper and cardboard, wood, glass, metals and related municipal garbage. In addition to the MSW, hazardous waste such as batteries, used fluorescent lamp, used aerosol spray cans, insecticide containers and paint containers has also been disposed in the site (Kirathithorn, 2004). The landfill was not designed for hazardous waste disposal, therefore, pollutants from this site has potential of leaching into the soil, surface water and groundwater to nearby area. The contamination has been clearly identified (PCD, 1998). Heavy metals include cadmium (Cd), chromium (Cr) and lead (Pb) were found in monitoring wells, private wells, wells used for community water supply (Kayandee, 1999; Boupan, 1999; Chuangchum et al., 2008) and soil around the site (Promlao et. al. 2007).

Since Kham Bon landfill site is a potential source for metal contaminants, this research focuses on employing groundwater and heavy metals transportation model for prediction of heavy metals concentration in groundwater. The results are used to explain contamination pathway and to predict heavy metals concentration in groundwater in the future.

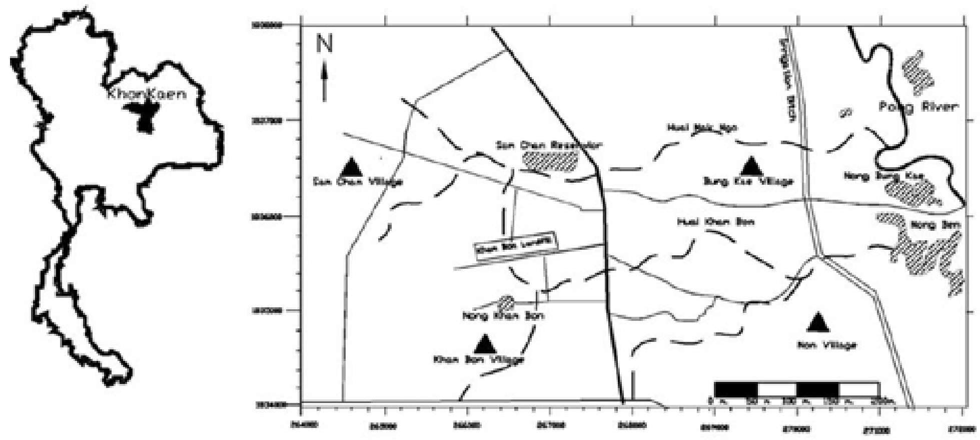


Figure 1. Location of Kham Bon site

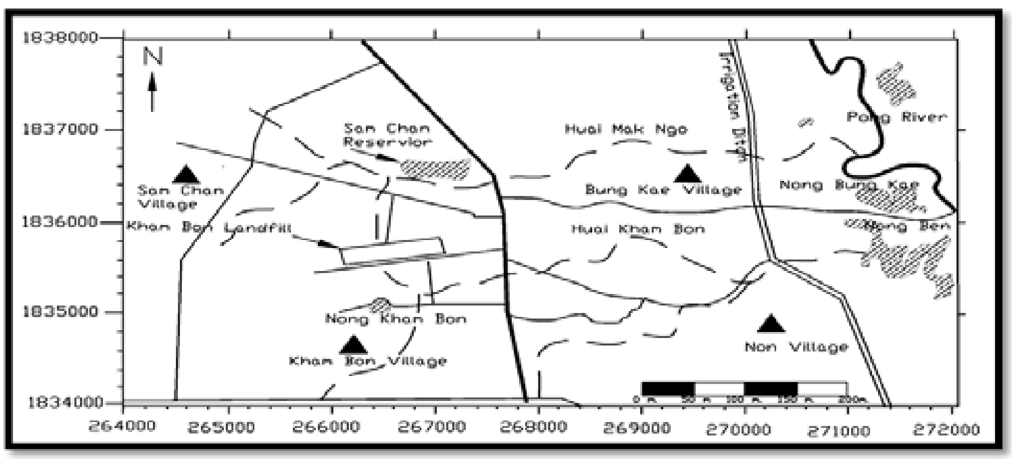


Figure 2. Location of Kham Bon landfill site

SITE DESCRIPTION

Site Characteristic

The study area lies within the boundaries of the Kham Bon Sub District, Khon Kaen Province, Thailand. It is about 17 km north of Khon Kaen city along national highway A2 (Friendship Highway) as shown in Figure 2. The site covers area of 156 800 m^2. The landfill has been operated by Khon Kaen Municipality. The community closet to the landfill is Kham Bon Noi community with approximately 70 households and population of 200. It locates about 20 m south of the site. The community does their living by sorting garbage in the landfill to collect and sell recyclable items to recycle shops nearby.

Site Geology

The site is on Khorat plateau. The geological features are Khorat group of sedimentary rocks, Phu Phan and Khok Kruat formation. Phu Phan formation consists of conglomeratic sandstones. Khok Kruat consisted of red silt stones, sandstones and conglomerates. Alluvial sediments of Quaternary age are also found on top of Phu Phan formation in some area.

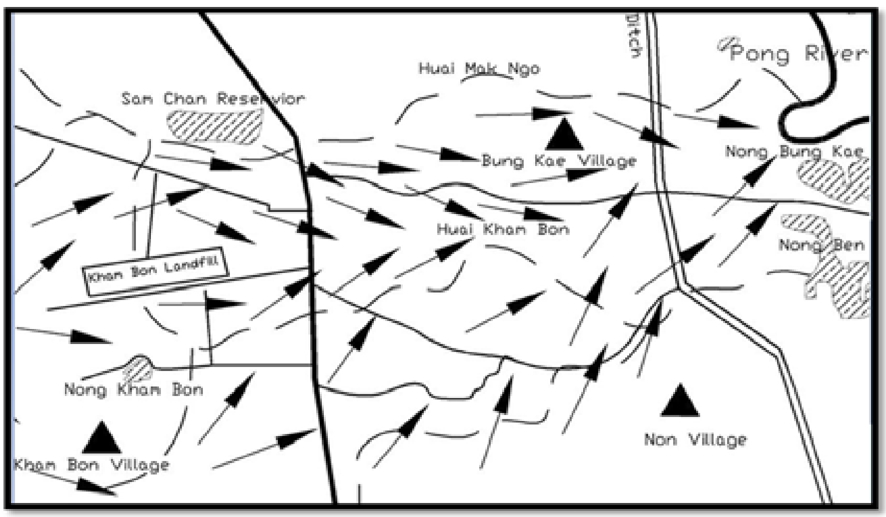


Figure 3. Groundwater flow directions

Surface and Groundwater Direction

The site is situated on top of elevated land, surrounding with crops cultivation, typically cassava, sugar cane, eucalyptus and rice. It is located on a ridge about 180 to 220 m above mean sea level between Mak Ngo Creek at the North and Kham Bon Creek at the South. Soil surface slopes gradually down eastwards to the Phong River at the east.

Surface water drains in 2 pathways. First, surface runoff drains northwards from the site into Sam Chan reservoir and then flows eastwards to Mak Ngo Creek before discharging to Pong River. Second, runoff drains southwards into Kham Bon Creek and then flow to Bung Kae Reservoir and Pong River. Groundwater aquifer depth in the area is less than 1.0 m in some area during wet season and about 3-8 m during dry seasons. Groundwater flows from east to west toward the Phong River as shown in Figure 3.

GROUNDWATER MODELING

In this research, 3D groundwater flow and transport models were selected based upon the hydro geological characterization and model conceptualization. Computer program, Visual MODFLOW 3.1 developed by Waterloo Hydrogeologic Software (WHS), was used to determine the contaminant distribution pathway and to assess the possible impact of heavy metals contamination to groundwater. Study area covered 2 km radius of landfill center. Groundwater flow model was calibrated under steady-state condition. Details about parameter input, model calibration and contamination prediction results are as follow.

Parameter Input

Topographic Data: Topographic data used was based on Thai's Military map scale 1:50 000. The map was digitized using AutoCAD program. AutoCAD file extension was changed from .dxf file to text file before imported to Visual MODFLOW.

Geologic Data: Soil type input in this model was divided into 3 layer followed the soil characteristic in the study area. The soil mainly compose with 3 soil types; sand, clayed sand, sandstone. Details of soil types are shown in Table 1.

Table 1. Layer of Soil

Layer	Types of Soil	Characteristics of Soil	Thickness (m)
1	Sand	Medium grained, well sorted, well roundness, loose, non-plastic	10
2	Clayed Sand	Medium to coarse rained, well sorted, well roundness, moderately to highly plastic, soft.	15
3	Sandstone	Very fine to fine grained, well sorted, well roundness, calcareous cemented, moderately hard, composed of micas	25

Hydrologic Data: Precipitation data from Thai Metrologic Department for 30 years from 1978 – 2008 was used. Base on topography and land use, recharge in this model divided in 2 zones which are general area (15% of precipitation values) and landfill area (85-90% of precipitation values). Hydrology data from field measurement in 7 monitoring wells used for the model input is shown in Table 2.

Table 2. Hydraulic head of 7 monitoring wells

Name.	UTM-m.		Borehole Elevation (m)	Groundwate Level (m.)	Observation Head (m.)
	East	North			
KK1	265705	1835893	194.627	5.6	189.027
KK2	266119	1836284	182.399	1.35	181.05
KK3	266113	1836087	185.103	2.24	182.86
KK4	266192	1836060	190.393	7.55	148.89
KK5	266317	1836110	192.507	4.7	187.807
KK6	265911	1835899	192.876	7.3	185.576
KK7	266185	1835931	187.702	3.25	184.452

Dispersivity: Dispersivity values in longitudinal, horizontal and vertical transverse ratio were obtained from the value recommended by Karlheinz (1996). Different type of soil has different value as listed in Table 3.

Table 3. Dispersivity of layer used in model

Layer No.	Longitudinal Dispersivity	Horizontal Dispersivity Ratio	Vertical Transverse Dispersivity Ratio
1	3	0.1	0.1
2	1	0.1	0.1
3	1	0.1	0.1

Distribution Coefficient: This parameter affects the mobility of contaminant in soil. It depends on type of soil and is site specific. In this research, distribution coefficient values reported by Chuangcham et al. (2008) as shown in Table 4 were used.

Table 4. Distribution Coefficient (K_d) of Kham Bon Soil

Heavy Metals	**K_d (l / kg)**		
	Silty Clay Loam	**Sand**	**Silty Loam Sand**
Pb	83.4	8.8	30.8
Cr	16.5	4.4	9.7
Cd	32.3	10.7	17.2

Constants: Hydraulic conductivity of soil specific storage (S_s), specific yield (S_y), total porosity (n) and effective porosity (n_e) were obtained from the value recommended by Karlheinz (1996). Input parameter, hydraulic conductivity of waste is from PCD (1998) in the Kham Bon landfill site. Constants for input parameter used in the model are shown in Table 5.

Table 5. Constants Used in Groundwater Model

Parameters	**Unit**	**Value**		
		Layer 1	**Layer 2**	**Layer 3**
1. Hydraulic Conductivity of soil				
1.1 K_x	m / d	1	0.01	1
1.2 K_y	m / d	1	0.01	1
1.3 K_z	m / d	0.1	0.001	0.1
2. Hydraulic Conductivity of waste layer K_x=K_y=K_z	m / d	0.864		
3. Specific storage (S_s)		0.01	0.001	0.001
4. Specific yield (S_y)		0.2	0.2	0.15
5. Total porosity (n)		0.33	0.29	0.2
6. Effective porosity (n_e)		0.22	0.2	0.15
7. Recharge				
7.1 General Area	mm / yr	0, 35.73		
7.2 Landfill Area	mm / yr	100, 426		
8. Evapotranspiration				
8.1 General Area	mm / yr	100, 120		
8.2 Landfill Area	mm / yr	50, 70		
9. Extinction Depth	m.	3		
10. Contaminated Area	m^2	2.36 x 3.11		
11. Simulation time	Years	20		

Initial Concentration: Initial concentrations form filed sampling during February 2010 as shown in Table 6 were assigned in the model cell. Other boundaries are convective flux boundaries and adjusted until concentration of contaminants in model equal to real concentration from field data. The transport model was run at 180-day time interval for a total of 20 years.

Table 6. Metals Concentration for Contaminant Transport Model

Location of samples	Recharge concentration for (mg/l)		
	Pb	Cr	Cd
KK1	0.04	0.018	0.01
KK2	0.24	0.027	Name.
KK3	0.08	0.027	N/D
KK4	0.21	0.026	N/D
KK5	0.32	0.038	N/D
KK6	0.17	0.027	0.01
KK7	0.17	0.028	0.01
Recharge Concentration	0.001		

Discretization: The study covered area of 2.36 x 3.11 km^2. The area was divided into 118 rows, 155 columns that followed soil characteristic of the site. The location and width of the constant head boundary were designated based on an aerial photograph of the site, coupled with elevation data from direct surveys that imported into Visual MODFLOW.

Model Calibration

Model calibration was done by adjusting parameters until the degree of fit between the simulated and observed water levels is less than 10%. Average differences between simulated and measured head is commonly expressed by standard error, the root mean squared (RMS) and correlation coefficient. From the calibration, the maximum residual obtained was 1.65 m and the absolute residual mean obtained was 0.908 m. The normalized residual mean square error of the model was 13.11 %. The normalized residual mean was 0.675 m. The observation versus predicted head values had a correlation coefficient of 0.995 m. In general, the model-simulated heads were slightly higher than the observed heads. Results of ground water flow model after are shown in Figure 4. From the Figure, dark area is surface water body where no water flows in and out. Arrow indicates direction of flow. Model results reveal that groundwater flow direction from landfill is from west to east.

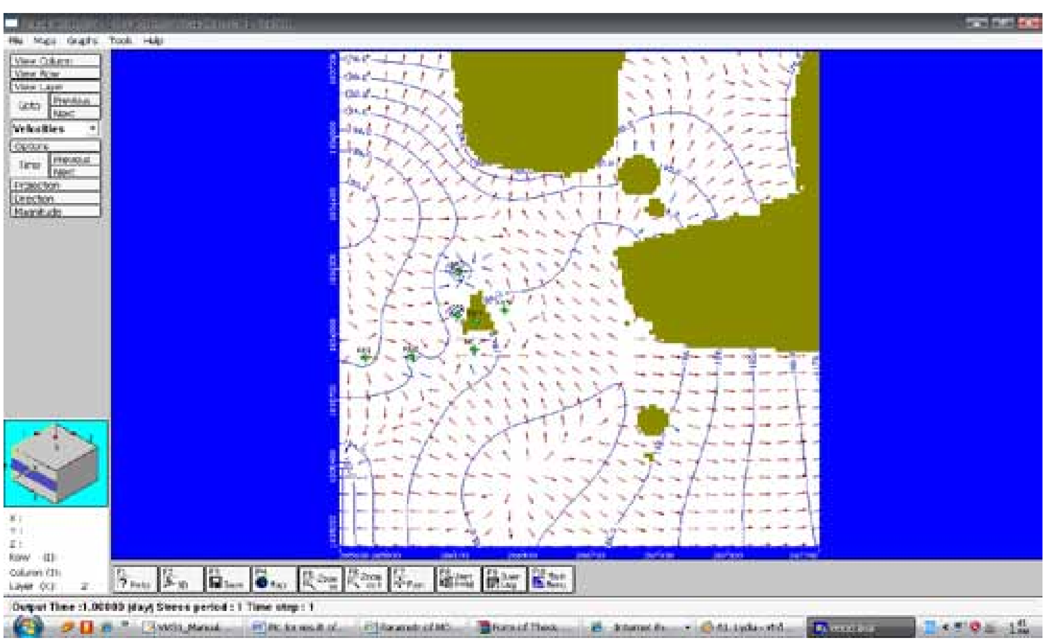


Figure 4. Groundwater flow direction under steady-state flow obtain from model

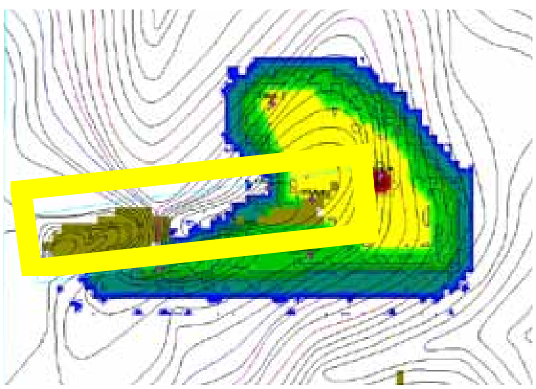
Contamination Prediction Results

After calibrated, the model was used to predict contaminant transport condition in the future. Migration pathway and concentrations of contaminants in groundwater was elucidated using the model. Results are shown in Figure 5, 6 and 7.

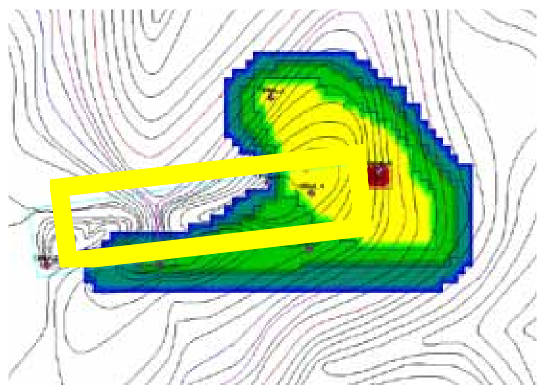
Figure 5, “a” and “b” showed contamination of Pb in the present. From the Figure, contamination of Pb is higher in the northeast direction. This is due to the site geology where water drains northwards from site into Sam Chan reservoir and flow eastwards to Mak Ngo Creek. Concentration in Layer 1 (0-10 m from surface) is higher than in Layer 2 (10-25 m from surface). Figure 5, “c” and “d” are prediction of Pb contamination in the future, 20 years from now. From the results, heavy metals tend to move from the top soil to deeper aquifer. The horizontal distance does not expand while vertical distance goes further down. The migration does not exceed 500 meters after 20 years and consider a slow process which corresponds to similar prediction previously reported by Tiwary et al. (2005).

Contamination plums of Cr and Cd are displayed in Figure 6 “a”, “b” and 7 “a”, “b”, respectively. The directions of Cr and Cd migration are the same as Pb. Cd migration covers smallest area due to the low solubility. The 20 years prediction of Cr and Cd demonstrated similar results as shown in Figure 6 “c”, “d” and 7 “c”, “d” respectively.

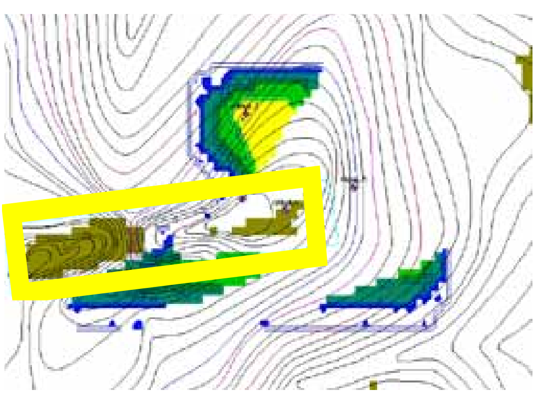
From the filed survey, it was found that contamination was occurred mainly from surface runoff. The 20 year simulation was run under the assumption that leachate collection system is constructed and well operated. From the assumption of the simulation, it can be concluded that even the leachate collection system is applied, contamination still migrates to aquifer. Thus, the mitigation measured is required.



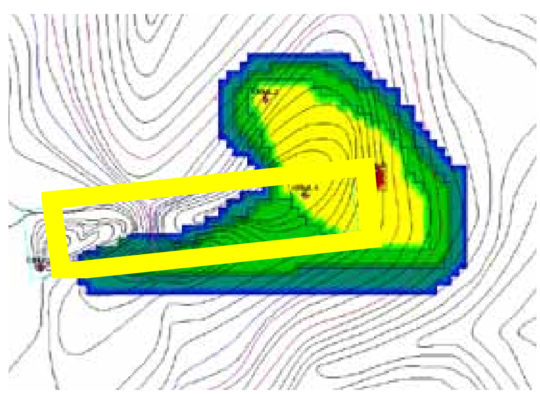
a. Plume of Pb in layer 1 in the present



b. Plume of Pb in layer 2 in the present

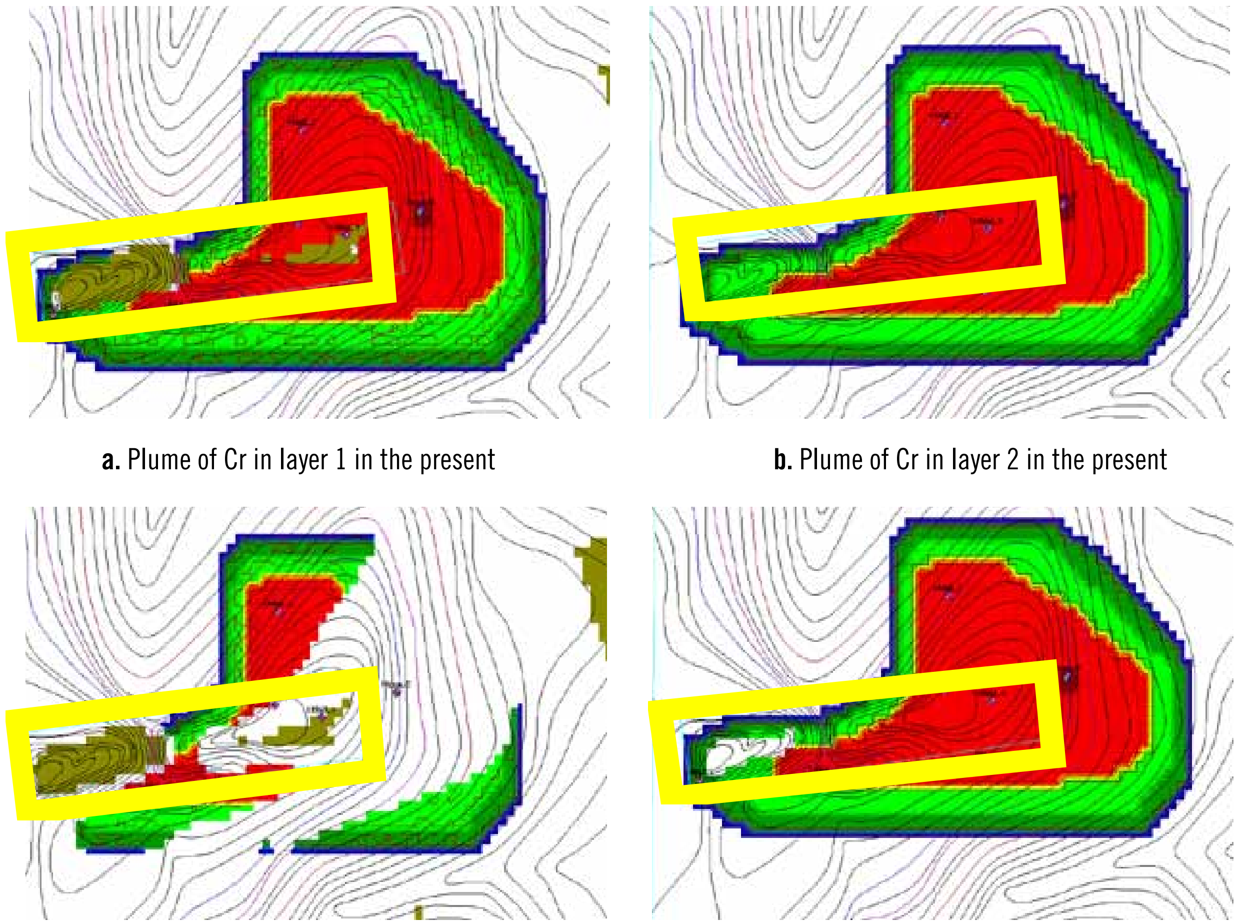


c. Plume of Pb in layer 1 (20 years)



d. Plume of Pb in layer 2 (20 years)

Figure 5. Plume of Pb from MODFLOW simulation



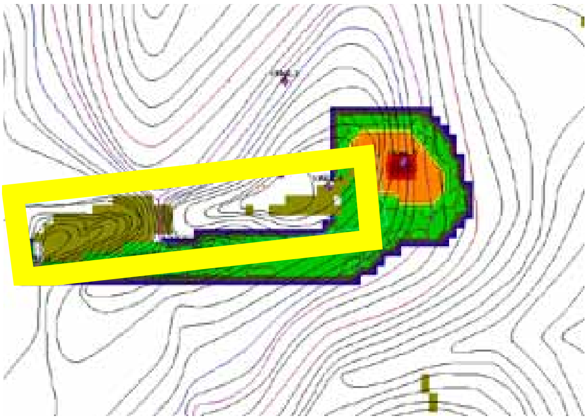
a. Plume of Cr in layer 1 in the present

b. Plume of Cr in layer 2 in the present

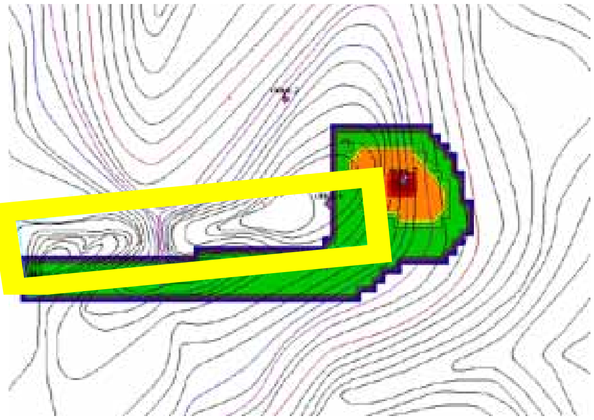
c. Plume of Cr in layer 1 (20 years)

d. Plume of Cr in layer 2 (20 years)

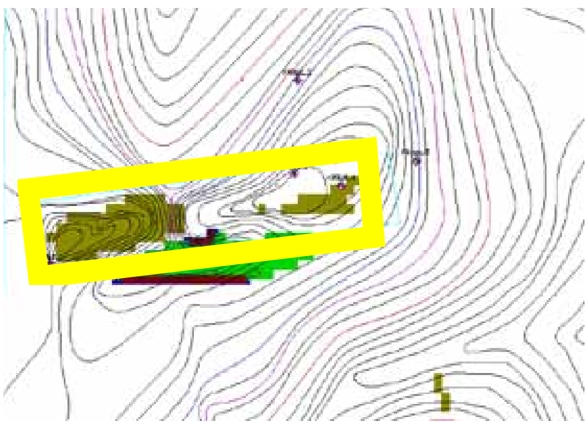
Figure 6. Plume of Cr from MODFLOW simulation



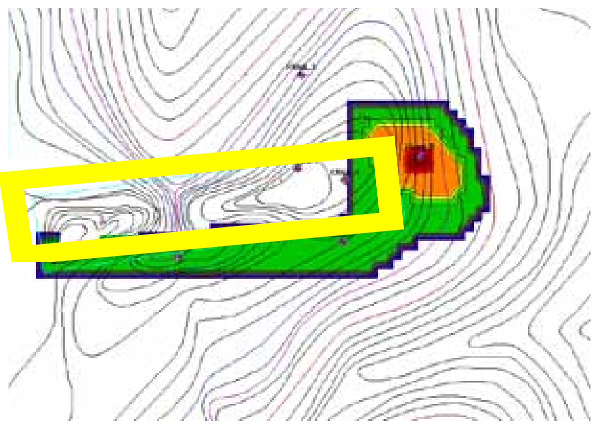
a. Plume of Cd in layer 1 in the present



b. Plume of Cd in layer 2 in the present



c. Plume of Cd in layer 1 (20 years)



d. Plume of Cd in layer 2 (20 years)

Figure 7. Plume of Cd from MODFLOW simulation

CONCLUSIONS

In this study Visual MODFLOW model was used to predict the distribution pathway of heavy metals contamination from Kham Bon landfill site in the next 20 years. Hydrology model calibration provided maximum residual is 1.65 m and the absolute residual mean is 0.908 m. The normalized residual mean square error of the model is 13.11%. The normalized residual mean is 0.675 m. The observation versus predicted head values has a correlation coefficient of 0.995 m. Model results reveal that groundwater flow direction from landfill is from west to east.

The model was generated to show Pb, Cr and Cd migration pathway which showed that heavy metals especially Pb and Cr migrate to northeastern and southeastern part more than other parts. Because of site geology and water drains northwards from the site into Sam Chan reservoir and flow eastwards to Mak Ngo Creek. The degree of migration was Pb>Cr>Cd. In the next 20 years, heavy metals predictions tend to move from the top soil to deeper aquifer. The horizontal distance does not expand while vertical distance goes further down. The migration would not exceed 500 m after 20 years and the migration is considered a slow process. Even the leachate collection system is applied, contamination still migrate to aquifer. Thus, mitigation measure is required.

It is recommended that hazardous waste sorting and ground water contamination in deeper aquifer should be closely monitored. In addition, consumption of groundwater in 500 m radius should be avoided because it was contaminated with high level of heavy metals. During rainy season, the material to cover the waste from leaching with runoff should be applied. In the future, rehabilitation of the landfill site should be undertaken to prevent further mobilization of pollutants.

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Screening of Organic Contaminants in Urban Snow

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Abstract

Snowmelt is known to cause peak concentrations of pollutants which may adversely affect receiving water quality. High concentrations in snow have been shown for e.g. metals and suspended solids, whereas studies on organic pollutants are rarely reported. This study aims at investigating the occurrence of anthropogenic organic compounds in urban snow, and at identifying sources of the pollutants. Snow from sites in Gothenburg, Sweden, was sampled and a range of organic substances was analysed. The most frequently detected organic pollutants in urban snow were polycyclic aromatic hydrocarbons, high molecular-weight phthalates, 4-nonylphenol and 4-octylphenol. Brominated flame retardants and chlorinated paraffins were only sporadically detected. In several snow samples, the concentrations of specific PAHs, alkylphenols and phthalates were higher than reported stormwater concentrations and European water quality standards. Pollutant source identification and sustainable management of snow are important instruments for the mitigation of organic contaminants in the urban environment.

Keywords

Alkylphenols; PAHs; perfluorinated compounds; phthalates; sources; urban runoff

INTRODUCTION

In the beginning of 2010, southern Sweden experienced unusually cold weather and a winter with extraordinary amounts of snow. To manage these masses, many municipalities were forced to dump urban snow into watercourses and coastal waters. This led to a debate on the contamination of snow, and it was concluded that the occurrence of hazardous substances in snow is, to a large extent, unexplored.

Urban snow accumulates pollutants emitted from human activities and acts as a temporary storage of contaminants during sometimes month-long periods. Snowmelt generally occurs during a short time period, which often results in concentration peaks of contaminants in surface runoff and in receiving waters (Meyer and Wania 2008). The transport of pollutants from the snowpack shows distinct peak loads where the dissolved pollutants are released with the initial melt-water fractions and the particulate pollutants at the end of the snowmelt. Snowmelt studies show that levels of metals and suspended solids may be several orders of magnitude higher than pollutant loads in rain-induced runoff (Westerlund and Viklander 2006). Organic contaminants in urban snow have, however, not been studied to the same extent. The occurrence of e.g. perfluorinated compounds (Liu *et al.* 2009), and polycyclic aromatic hydrocarbons (PAHs) (Reinosdotter *et al.* 2006) in urban snow has occasionally been reported. Screening studies of snow, where several groups of organic contaminants are investigated, are even more infrequent. Screenings of organic substances have earlier been performed on e.g. river water (Dsikowitzky *et al.* 2004) and landfill leachate (Paxéus 2000). These studies illustrate the broad spectrum of organic contaminants emitted from urban areas.

This study aims at investigating the occurrence of anthropogenic organic compounds in urban snow in Gothenburg (Sweden). Initially, non-target screenings of semi-volatile organic compounds (SVOCs) were performed, and thereafter target analyses of specific compound groups. These target compounds were selected according to their potential to reach the urban stormwater system and their potential effects in the aquatic environment. The study also aims at identifying sources of the detected pollutants in urban runoff.

MATERIALS AND METHODS

Sampling

Sampling of snow was conducted during both 2009 and 2010. Snow sampled in February 2009 had fallen during one day, five days prior to sampling, and was used for the non-target screenings and for analyses of phthalates and alkylphenols. Samples were collected from three sites in Gothenburg: Kärra – suburban area, estimated annual average daily traffic (AADT) 500 vehicles; Gårda – motorway area, AADT 90 000; and Järnbrott – access road to residential and industrial area, AADT 59 000. The samples were collected from snow banks in direct proximity of the road. In 2010, Gothenburg experienced several snowfall occasions (Figure 1) and the sampled snow was used for target analyses of organic contaminants. Samples were collected from Kärra, Gårda and Järnbrott, and at the end of the snowmelt period, samples were also collected at three centrally located snow deposits (Gårdamotet, Heden and Vallhamra). An urban background sample was collected in the Delsjön forest area, circa two kilometres from the city centre. The snow was collected in solvent-rinsed glass containers with Teflon-lined caps or in stainless steel containers. The snow was thawed in room temperature and samples analysed by the accredited laboratories were sent in coolers as soon as possible.

Non-target screening

The thawed samples (~ 1.5 l) were spiked with internal standard (phenanthrene-d_{10} and 2-fluorobiphenyl) and extracted by solid phase extraction using C_{18} discs (3M Empore). The contaminants were eluted with isopropanol and *n*-heptane. The extracts were dried with Na_2SO_4 and evaporated before analysis on an ion-trap GC-MS (CP-3200 and Saturn 2200, Varian), equipped with a fused silica (VF-5ms) capillary column (30 m × 0.25 mm × 0.25 µm). Chromatographic conditions were: 1 µl split/splitless injection (290°C), initial oven temperature 50°C, 5 min hold, programmed to 290°C at a rate of 5°C/min. Helium was used as carrier gas (1 ml/min), and the transfer line and trap temperatures were set to 250°C and 220°C, respectively. The mass spectrometer performed a full scan from m/z 40 to 450. Identification was based on a comparison of chromatographic retention times and mass spectra of analytes with those of reference compounds and spectral databases (NIST/EPA/NIH Mass Spectral Library 2005). For quantification of analytes, three-point calibration curves were used. Procedural blanks were treated identically with the snow samples, from extraction to analysis.

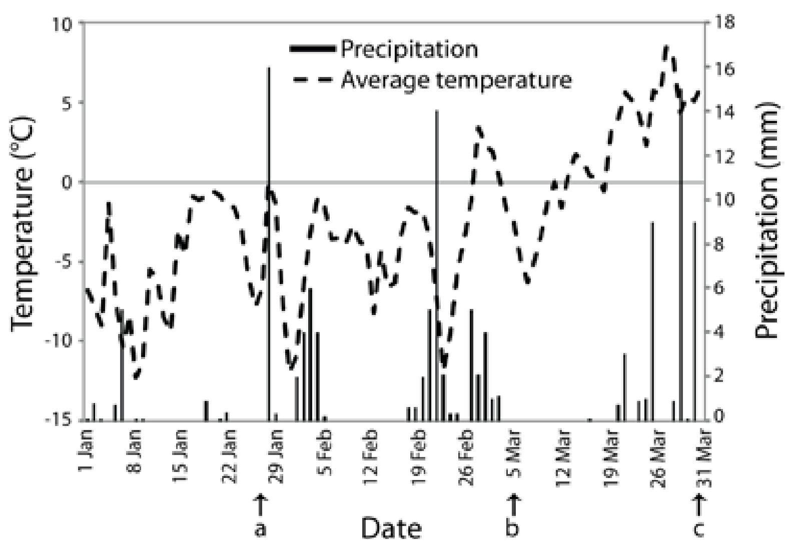

Figure 1. Weather data for Gothenburg during the winter 2010. The sampling occasions are marked with arrows: (a) road side snow in Järnbrott; (b) road side snow in Järnbrott, Gårda, Kärra; and (c) snow deposits in Gårdamotet, Heden, Vallhamra and background snow in Delsjön

Target analysis of organic contaminants

Analyses of alkylphenols, brominated flame retardants, chlorinated paraffins, perfluorinated compounds, phthalates and PAHs were performed by accredited commercial laboratories. The methods for extraction, clean-up and analysis are summarized in Table 1.

RESULTS AND DISCUSSION

Non-target screening

The original aim of the non-target screening was to identify and quantify the most abundant pollutants in each snow sample. The identification was, however, obstructed by the large number of peaks in the total ion chromatograms, implying that the samples contain a multitude of different compounds, presumably of anthropogenic origin. All samples also showed an unresolved complex mixture (UCM), often used as an indication of petroleum-derived contamination, which prevented identification and quantification of peaks in the latter part of the chromatogram. We could, however, clearly identify specific phthalates (DiBP, DnBP, BBP and DEHP [full names of analysed substances are found in Table 1]), benzothiazole, several phenols (e.g. *tert*-butylphenol, butylated hydroxytoluene [BHT] and 2,4-di-*tert*-butylphenol) and PAHs in the snow samples. In addition, concentrations of SVOCs and total petroleum hydrocarbons (TPHs) were determined. The highest concentrations (6.0 mg TPHs/l and 8.0 mg SVOCs/l) were detected in the motorway area (Gårda), and the lowest concentrations (1.6 mg/l for both TPHs and SVOCs) were found in the residential area (Kärra).

Table 1. Chemical names, analytical methods and detection limits for the target compounds

Substance group	Included compounds	Extraction, clean-up, analysis	Reported detection limit
Alkylphenols* (APs)	4-*tert*-octylphenol (4-OP); 4-nonylphenol (4-NP); 4-*t*-octylphenol and 4-nonylphenol mono-, di-, tri-, tetra-, penta-, and hexa-ethoxylates (OP1-6EO and NP1-6EO, respectively)	Liquid liquid (LL) extracted with *tert*-butyl methyl ether, cleaned with silica gel and derivatized using N-Methyl-N-(trimethyl-silyl) trifluoroacetamide. GC-MS	10 ng/l for OPs; 500 ng/l for NPs. Up to 0.8 µg/l for OPs and 2 µg/l for NPs in samples with large matrix effects
Brominated flame retardants* (BFRs)	tetrabrominated diphenyl ether (tetraBDE); pentaBDE; hexaBDE; heptaBDE; octaBDE; nonaBDE; decaBDE; tetrabromobisphenol-A (TBBA); decabromobiphenyl (DeBB); hexabromocyclododecane (HBCD)	Extracted with toluene, followed by several clean-up steps. GC-MS	0.0003–0.10 µg/l
Chlorinated paraffins (CPs)	C_{10}-C_{13} short-chain chlorinated paraffins (SCCP); C_{14}-C_{17} medium-chain chlorinated paraffins (MCCP)	Extracted with toluene. GC-NCI/MS	0.20–0.50 µg/l
Perfluor-inated compounds* (PFCs)	perfluorooctane sulfonate (PFOS); perfluorooctanesulfonamide (PFOSA); perfluorooctanoic acid (PFOA)	Solid phase extraction, eluted with methanol. LC-MS/MS	1.5–2.0 ng/l
Phthalates*	dimethyl (DMP); diethyl (DEP); di-*n*-butyl (DnBP); di-*iso*-butyl (DiBP); di-*n*-octyl (DnOP); di-(2-ethylhexyl) (DEHP); butylbenzyl (BBP); di-*iso*-decyl (DIDP); di-*iso*-nonyl phthalate (DINP)	LL extracted with *n*-hexane. GC-MS	0.1–2.0 µg/l
Polycyclic aromatic hydrocarbons* (PAHs)	naphthalene (NAP); acenaphthylene (ACY); acenaphtene (ACE); fluorene (FL); phenanthrene (PHE); anthracene (ANT); fluorantene (FLR); pyrene (PYR); benzo[*a*]anthracene (BaA); chrysene (CHY); benzo[*b*]fluoranthene (BbF); benzo[*k*]fluoranthene (BkF); benzo[*a*]pyrene (BaP); dibenzo[*a,h*]anthracene (DBA); benzo[*ghi*]perylene (BPY); indene[1,2,3-*cd*]pyrene (INP)	Extracted with *n*-hexane. GC-MS	0.01 and 0.1 µg/l

* Analysis accredited by Swedac (The Swedish Board for Accreditation and Conformity Assessment). Measurement errors have been reported (no included in table).

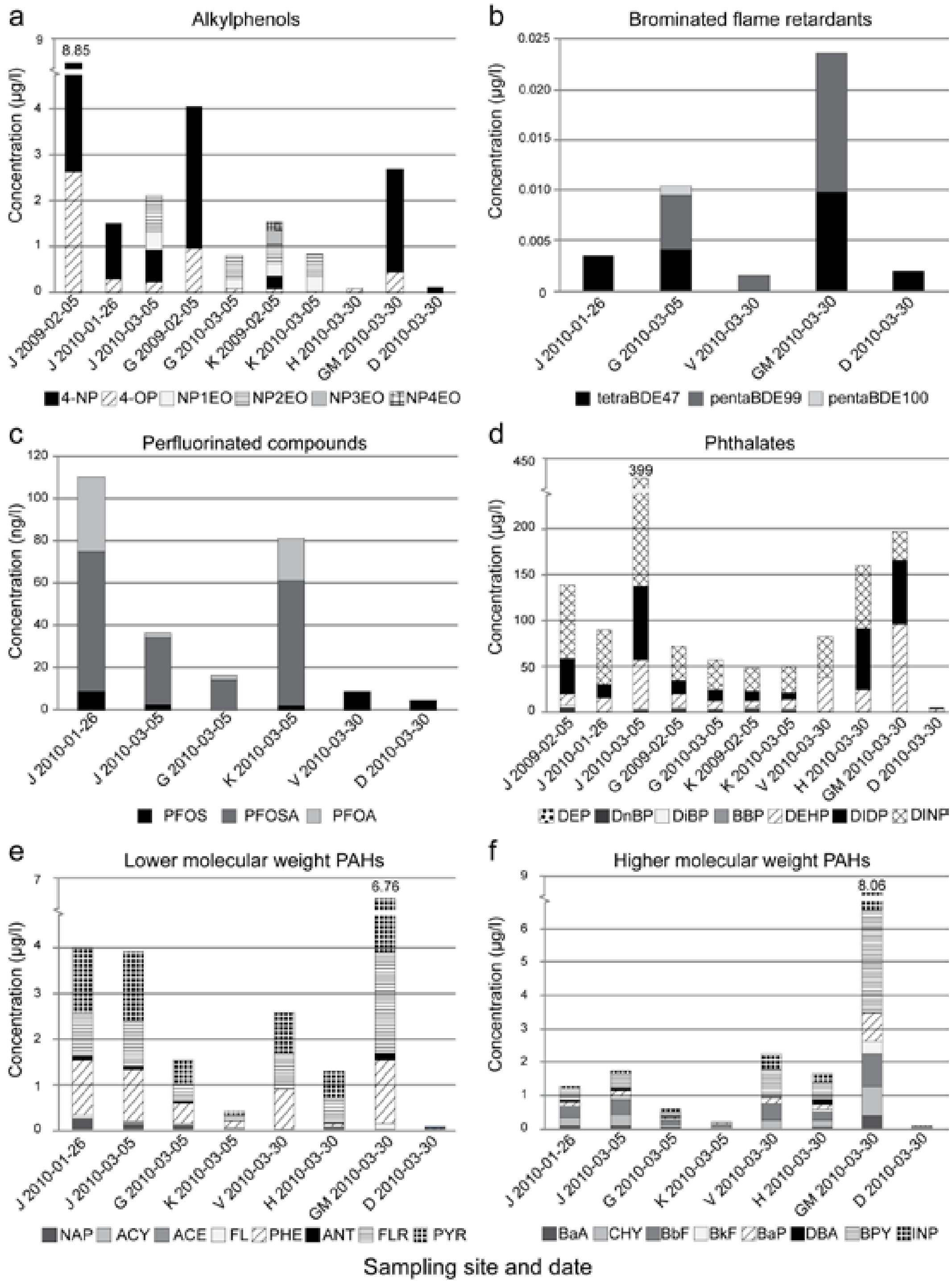

Figure 2. Detected concentrations of (a) alkylphenols; (b) brominated flame retardants; (c) perfluorinated compounds; (d) phthalates; (e) lower molecular-weight PAHs; and (f) higher molecular-weight PAHs. Sampling occasions where concentrations of all APs, PFCs and BFRs are below the detection limits are not shown in the graphs. Sampling sites: J – Järnbrott; G – Gårda; K – Kärra; V – Vallhamra; H – Heden; GM – Gårdamotet; D – Delsjön

Alkylphenols

Alkylphenols were analysed in snow sampled in both 2009 and 2010. The highest maximum and median AP concentrations (Figure 2a) were observed for 4-NP (6.2 and 0.27 µg/l, respectively), whereas 4-OP showed the highest detection frequency (82%). Nonylphenols are used in larger amounts than octylphenols, and the trend with higher NP concentrations have been observed in environmental matrices world-wide (Ying *et al.* 2002). The octylphenol ethoxylates were below the d.l. in all samples, whereas NP1EO and NP2EO were detected in four of the samples, and NP3EO and NP4EO in one sample (Figure 2a). For the snow deposit samples (Heden, Vallhamra and Gårdamotet), the detection limits (d.l.) were elevated up to 2.0 µg/l for 4-NP and 12 µg/l for NP4EO due to large matrix effects, and all APs were below the d.l. in the Vallhamra sample. The varying detection limits render data analysis difficult and it has not been possible to identify clear trends. There is only weak concentration correlation between samples collected on the same day, and between samples from the same site. It can be concluded, though, that the 4-NP and 4-OP concentrations found in snow exceeded most reported stormwater values from Sweden (maximum 1.2 and 0.35 µg/l, respectively; $n = 13$ [Björklund *et al.* 2009]). In addition, the European environmental quality standard for surface water (EQS [Directive 2008/105/EC of the European Parliament and of the Council]) for 4-NP – maximum allowable concentration (MAC) 2.0 µg/l – was exceeded in three of the samples and the EQS for 4-OP – annual average (AA [considered protective against short-term pollution peaks]) 0.1 µg/l – was exceeded in five of the snow samples.

Nonylphenol is the precursor in the production of ethoxylates, and also a major degradation product of NPEOs, which are used in industrial applications of surfactants. Abiotic degradation of NPEOs is considered to be negligible in comparison to biodegradation (Langford *et al.* 2005), which is likely to be inhibited by the prevailing temperatures at the time of snow sampling. The high concentrations of 4-NP in snow, compared to NPEOs, and the expected low degradation of NPEOs into NP, suggest that 4-NP may be emitted directly to the urban environment. In a substance flow analysis vehicles, where nonylphenolic compounds are used in lubricants, fuel and car care products, air-entraining additives in concrete and tyre wear, were identified as the most important NP and NPEO sources in stormwater (Björklund in press). The ethoxylates may also be used in de-icing products and have been suggested as additives in diesel, but reports on the use of 4-NP in such products have not been found. In conclusion, we have not found an explanation of the relatively high 4-NP concentrations found in some of the snow samples. Octylphenol sources are of different character than nonylphenols sources since only 2% of the total use of OP is used for producing ethoxylates and the remaining part is used in the manufacturing of resins (DEFRA 2008). Circa 80% of the resins are used in the production of tyres, which suggests that the octylphenol in urban snow mainly originates from tyre rubber. Other applications of octylphenolic compounds include paints, polymers and cleaning products.

Brominated flame retardants

The most used BFR in Sweden is currently TBBP-A, followed by decaBDE and HBCD (KemI 2010). The use of decaBDE is, unlike penta- and octaBDE, not regulated in Sweden. It is therefore somewhat surprising that the BFRs detected in urban snow (Figure 2b) were pentaBDE-99 ($n = 3$; 0.0015–0.014 µg/l), pentaBDE-100 ($n = 1$; 0.001 µg/l), and tetraBDE-47 ($n = 4$; 0.0019–0.0097 µg/l), the latter being the most occurring congener in pentaBDE. The commercial mixtures of pentaBDE include tetra-, penta- and hexa congeners; octaBDE includes hexa-, hepta-, octa- and nonaBDE; whereas decaBDE only includes small amounts of nonaBDE (de Wit 2002). A phase-out of the production and use of pentaBDE in Sweden started in 1999 (KemI 2003). Since 2004 the use is restricted within the European Union (Directive 2003/11/EC) and pentaBDE is currently found only in imported goods. The main application of pentaBDE is in polyurethane foam found in e.g. furniture and car headrests and ceilings, and to minor extent in textiles, building materials and packaging. Historically, tetraBDE-47 has been the most occurring congener in environmental matrices from areas generally affected by pollution (de Wit 2002). Studies from the past decade indicate, however, that decaBDE-209 is currently the most occurring congener in the Swedish environment (ter Schure *et al.* 2004). This congener was, however, not detected in urban snow. It should be noted that the analytical detection limit was higher for decaBDE (up to 0.10 µg/l) than for tetra- and pentaBDE (up to 0.010 µg/l).

Background concentrations of polybrominated diphenyl ethers (PBDEs [varying number of congeners included]) in rain and bulk precipitation in Sweden have been detected in the low nanogram-per-litre-range (ter Schure *et al.* 2004). The PBDE concentrations in urban snow are similar to Swedish precipitation levels, which suggest that the PBDEs in snow may originate from atmospheric deposition. No other studies on the occurrence of BFRs in urban snow or stormwater have been found. The detection limits of HBCD and TBBP-A (up to 0.10 µg/l) in the current study are presumably too high compared to expected environmental concentrations (Remberger *et al.* 2002; 2004), and the substances were below the d.l. in all snow samples.

Chlorinated paraffins

The use of CPs has decreased by 80% in Sweden since 1994, but a substance flow analysis revealed that the largest emissions into the environment derive from large stocks of CPs in the urban area (Fridén and McLachlan 2007). Short-chained and medium-chained CPs were detected in two snow deposit samples (Heden and Gårdamotet) at 0.33 and 32 µg/l, respectively. The analytical detection limits of SCCPs and MCCPs were 0.20–5.0 µg/l (the higher value in one sample with large matrix effects), whereas many reported concentrations found in natural waters are in the nanogram-per-litre-range (Bayen *et al.* 2006).

Perfluorinated compounds

Perfluorinated alkylsulfonates (PFASs) and perfluorinated carboxylates (PFCAs) are two major PFC classes of environmental concern (KemI 2006; Kim and Kannan 2007; Fromme *et al.* 2009). The most studied PFAS is PFOS, which is considered to be the final degradation product of many commercially used sulfonated fluorochemicals, including PFOSA, and is shown to be exceptionally persistent in the environment. The most studied caboxylate, PFOA, is also persistent and have shown carcinogenicity and reproductive toxicity.

PFOA and PFOSA were detected in four and PFOS in five out of eight snow samples (Figure 2c). PFOS and PFOA are the most frequently detected PFCs in many environmental studies and concentrations found in this study (<d.l.–9.0 and <d.l.–36 ng/l, respectively) are lower or in the same range as those reported in stormwater in Japan (Murakami *et al.* 2009; Zushi and Masunaga 2009); rain and snow-induced runoff in the US (Kim and Kannan 2007); and comparably lower than concentrations found in fresh snow in China (Liu *et al.* 2009). The median concentrations of PFOS and PFOA in urban snow (0.81 and 2.3 ng/l, respectively) are similar to concentrations detected in precipitation in Sweden (median 2.2 and 3.1 ng/l, respectively [Woldegiorgis *et al.* 2006]). On the contrary, the PFOSA concentrations in snow (maximum 66 ng/l) are, when detected, one magnitude higher than most reported concentrations in stormwater and rain (Woldegiorgis *et al.* 2006; Kim and Kannan 2007; Murakami *et al.* 2009). In addition, PFOSA concentrations being occasionally several times higher than PFOS and PFOA concentrations have not been observed in the referred studies.

Kim and Kannan (2007) found high concentrations of PFCs in runoff from parking lots and areas with high traffic intensity, and studies by Zushi and Masunaga (2009) revealed positive correlation between high PFCs concentrations in stormwater and transportation-related land use. The PFCs are added to several transportation-related products, such as car care products, water and dirt repellant car-seat textiles, upholstery and windshield washer fluids (KemI 2006; Murakami *et al.* 2009). Other potential sources in snow and runoff include impregnated snack and food wrappings, and water- and dirt-resistant products for shoes and clothes, which is the major application area for PFCs in Sweden (KemI 2006). The high PFOSA concentrations, compared to PFOS and PFOA, may be an indication of PFOSA point sources. It is a major metabolite of N-alkylperfluorosulfonamides, which have been used in paper and packaging applications and surface treatment of e.g. carpets and textiles (Fromme *et al.* 2009). Specific point sources of PFOSA have, however, not been identified in the sampling area.

Phthalates

Phthalates were analysed in snow sampled in both 2009 and 2010. The most frequently occurring phthalates in urban snow were DnBP, DiBP, DEHP, DIDP and DINP (detection frequency 55, 55, 100, 91 and 91%, respectively [Figure 2d]). The DEHP concentrations in snow (2.3–96 µg/l) all exceeded the EQS of 1.3 µg/l in surface waters. The highest phthalate concentrations were found in snow sampled in Järnbrott in March 2010, with maximum concentrations at 260 µg/l for DINP and 81 µg/l for DIDP. Compared to studies on urban stormwater from Sweden and Austria (Björklund *et al.* 2009; Clara *et al.* 2010), the snow samples show higher maximum concentrations of all phthalates, except DMP and DEP.

The contribution of DINP to total phthalate concentrations exceeded 40% in all samples, except the samples from Gårdamotet and Delsjön. Björklund *et al*. (2009) and Clara *et al*. (2010) showed similar results; high detected concentrations of DIDP, DINP and DEHP compared to most low molecular-weight phthalates. Within the European Union, the use of DEHP is currently restricted due to the substance's toxic effects and DIDP and DINP have replaced DEHP in many applications (KemI 2010). Björklund *et al*. (2009) showed strong correlation between the relative phthalate distribution in stormwater sediment and the prevalent phthalate use in Sweden, which is dominated by DINP and DIDP. The current study further strengthens the theory that DIDP and DINP are the phthalates occurring at the highest concentrations in urban matrices in Sweden.

A substance flow analysis of phthalates revealed that traffic is an important source to these substances in stormwater (Björklund in press). Phthalates may be emitted from applications of soft PVC, which is the main use for the high molecular-weight phthalates, car undercoating, adhesives, sealants, rubber, and paints. Other phthalate sources include coated roofing and cladding, tarpaulins, cables, shoe and textile wear. Coated roofing and cladding materials are believed to be minor sources of phthalates in the road side snow, since all samples were collected from sites where the snow has no contact with buildings.

Polycyclic aromatic hydrocarbons

The PAHs could be detected in all road side snow samples (Figure 2e and f); the highest total concentrations were found in Järnbrott (5.6 and 5.2 µg/l), followed by Gårda (2.1 µg/l). The Gårdamotet snow deposit showed, however, the highest total PAH concentrations of all samples at 15 µg/l, which is at least 2.5 times higher than the concentrations found in the other samples. A study on stormwater quality in Gårda showed total PAH concentrations that are comparable to the concentrations found in snow in this area (Pettersson *et al.* 2005). The snow concentrations found in the current study are generally within the range of other reported snow studies (Viskari *et al.* 1997; Lindgren 1998). The European EQS for BaP in surface waters – MAC 0.1 µg/l – was, however, exceeded in five samples; the EQS for BbF+BkF – AA 0.03 µg/l – was exceeded in all samples, except the background sample; and the EQS for BPY+INP – AA 0.002 µg/l – was exceeded in all samples.

The PAHs generally detected at the highest concentrations, and also the most frequently occurring, were PYR, PHE, FLR and BPY (Figure 2e and f). The maximum detected concentration was found for BPY (3.1 µg/l) in the Gårdamotet deposit sample, whereas PYR generally showed higher concentrations in other samples. Among the US EPA classified carcinogenic PAHs, the most frequently occurring, and also the substances detected at the highest concentrations, were BbF, INP and CHY. The highest concentration was found for INP (1.5 µg/l) in Gårdamotet, whereas BbF generally showed higher concentrations in other samples. Similar trends in occurrence of PAHs have been observed in other studies of road side snow (Viskari *et al.* 1997; Reinosdotter *et al.* 2006).

Ravindra *et al.* (2008) have reviewed PAH source studies and summarize that PYR, FLR and PHE – the most abundant PAHs in the current study – are suggested as source markers for both incineration and vehicular emissions, including both diesel and petrol. Other suggested markers include oil combustion and wood burning as possible sources to the PAHs observed in our study. In addition, PAH profiles for petrol and diesel, lubricating oil, bitumen and asphalt, and tyre rubber were compared with the PAH content in urban snow. Moderate to strong correlations were seen between road side snow and tyre rubber ($r \sim 0.7$–0.9 [Lindgren 1998; Edeskär 2004]) and lubricating oil ($r \sim 0.6$ [Wang *et al.* 2000]).

CONCLUSIONS

The snow samples contain a large amount of analytes with varying properties. Further fractionation and clean-up are therefore necessary steps to successfully identify specific pollutants in a non-target screening of SVOCs.

The most frequently detected pollutants in urban snow were PAHs, high molecular-weight phthalates, 4-nonylphenol and 4-oktylphenol. Brominated flame retardants and chlorinated paraffins were only sporadically detected in urban snow.

Strong correlation was generally observed for phthalate and PAH concentrations between sampling occasions, implying that the substance composition is similar in most samples. Within other substance groups and between substance groups, the correlation was generally moderate to weak. The snow was grab sampled and pollutant concentrations from different years and sites may not be comparable due to different climatic conditions, land use, snow-handling activities and changes in traffic intensity. In addition, the generation of pollutants in road side snow and snow deposits is not comparable.

Due to the high snow concentrations of APs, DEHP, and PAHs, compared to water quality standards (no joint European EQS for other substances), urban snow should be deposited at sites were the meltwater is controlled and treated prior to discharge into natural waters.

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Xenobiotics in Stormwater Run-off and Combined Sewer Overflow

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Abstract

Stormwater runoff contains a broad range of heavy metals and xenobiotics. A number of these substances are in Europe regulated through the Water Framework Directive (WFD) establishing Environmental Quality Standards (EQSs) for surface waters. Knowledge about discharge of these substances through stormwater runoff and combined sewer overflows is important in order to ensure compliance with the EQSs in the receiving waters. Results from a screening campaign including more than 50 substances at four stormwater discharge locations and one combined sewer overflow in Copenhagen are reported here. Heavy metal concentrations were found at levels similar to earlier findings, with Cupper found at concentrations 10 times higher than the national regulation for surface waters. The concentration of PAHs in the samples exceeded the EQSs with factors between 1 and 2,000 showing that PAHs in stormwater can pose a potential risk for receiving waters. Glyphosate was found in all samples, but EQS has not yet been established for this substance. Diethylhexylphthalate (DEHP) was also found at all five locations and in concentrations exceeding the EQS. The results give a valuable background for designing monitoring programmes focusing the effort to ensure good water quality in receiving surface waters.

Keywords

Run-off; Measurement; Occurrence; Urban water; Water Framework Directive

INTRODUCTION

The European Water Framework Directive (WFD) (EU, 2000) requires the establishment of monitoring programmes in all EU member states in order to provide an overview of the chemical status of the aquatic environment. This includes monitoring of the 41 priority substances (PSs) defined in the context of the Environmental Quality Standard Directive (EQSD) (EU, 2008). The aim is to reduce the pollution associated with these PSs to a level not exceeding the established environmental quality standards (EQSs) and to phase out the emissions of selected PSs, which are denoted as priority hazardous substances PHSs. Both annual average (AA) EQSs and when relevant maximum annual concentration (MAC) EQSs have been established (EU, 2008). According to the WFD EU member states have recently submitted their river basin management plans (RBMPs) and the second generation RBMPs have to be submitted in 2015. These plans must ensure the good ecological and chemical status of the European water courses within the year 2015 and outline what has to be improved and how it can be improved. The means to reach this status are manifold, ranging from legislation towards the use of a PS over information campaigns to reduce the use of a PS or the correct way of disposing of products containing a PS to improvements of treatment technologies. As part of the legislation, EU decided to establish the EQSs for a range of substances, but application of best available technology or best environmental practice or emission permits, i.e. emission limit values (ELVs), also need to be considered in the abatement of pollution. These various measures need to be controlled by monitoring programmes. How detailed the monitoring should be depends on earlier substance findings and pollution source inventories for the focal catchment. In Denmark, historical and recent national surveillance programmes have contributed with an in-depth knowledge about the emissions of nutrients, but the WFD does not only focus on the nutrients.

For some of the PSs information on concentrations found in stormwater discharges and combined sewer overflows (CSOs) exists but for many substances such information is scarce. The aim of these screening campaigns was to study the occurrence of a broad range of xenobiotics in stormwater discharges including a CSO facility. For this purpose samples have been collected from five locations in Copenhagen during 2008 and 2009 using spot sampling, precipitation or volume proportional sampling.

MATERIALS AND METHODS

Sampling and sampling locations

Five sampling locations in the greater Copenhagen area were selected for this study of which four catchments are served by separate sewer systems and the remaining catchment by a combined sewer system. Figure 1 shows the catchments on a map and the individual locations are described below.

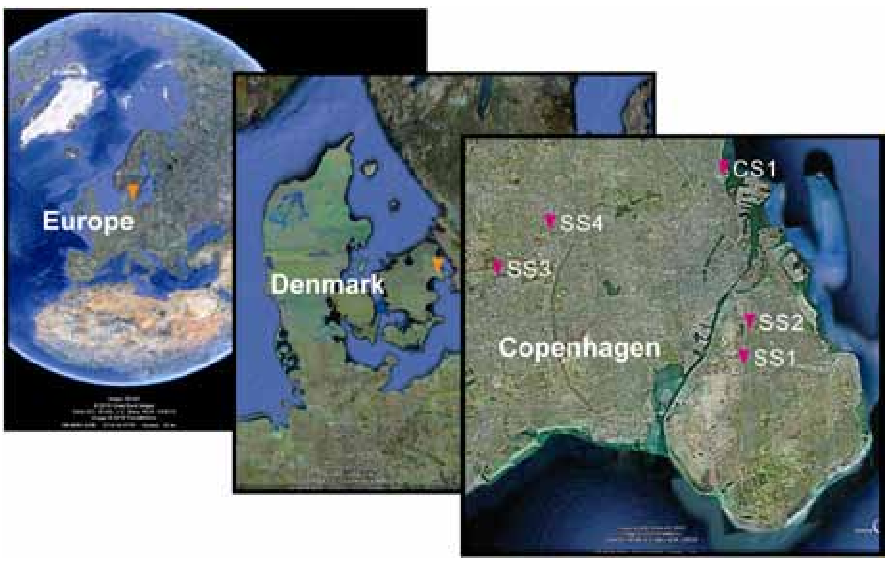

Figure 1. Map of greater Copenhagen (Google earth, 5.1.3535.3218) indicating the five sampling locations, two of them (SS1 and SS2) in Tårnby situated at the island Amager and three of them (CS1, SS3 and SS4) in Gentofte, Albertslund and Glostrup, respectively, situated in the surroundings of Copenhagen, see text for details.

Byparken (Tårnby), separate storm sewer 1 (SS1). Stormwater from 1.3 reduced hectare (red ha) of roads is collected and treated in a grit chamber and a pilot plant using dual porosity filtration (Jensen and Bisballe, 2005). Grab samples were collected from the inlet to the pilot plant (SS1-1) and at the outlet from the filter (SS1-2) on 15OCT2008 after a 3-hour rain event of 2.3 mm.

Digevej (Tårnby), separate storm sewer 2 (SS2). Stormwater from a residential area of 9.4 red ha including a metro station is treated in a grit chamber prior to discharge. A grab sample from the grit chamber was sampled 18NOV2008 after a 30-min rain event of 1 mm.

Fabriksparken (Albertslund), separate storm sewer 3 (SS3). Stormwater from a residential area and an industrial area of a total of 56 red ha is treated in oil separators and collected in a stormwater retention basin. A grab sample from the inlet to the retention basin was sampled 18NOV2008 after a 3-hour rain event of 5.7 mm.

Ejby Mose (Glostrup), separate storm sewer 4 (SS4). Stormwater from three separately sewered catchments is discharged to a bog in Glostrup after passing through oil separators. These discharges count for the majority of the water discharged into the bog, whereas a minor part originates from a smaller catchment including a landfill, which however has been protected and equipped with a fend-off drain in order to minimise pollution. Catchment 1, SS4-1, is a residential area of 56 ha. Catchment 2, SS4-2, is an industrial area of 87 ha (e.g. car repair shops, machine factories, construction companies whole sale companies, and office buildings) including a heavily trafficked road. Catchment 3, SS4-3, is a green area of 12 ha including a residential area, roads and a smaller part of the same heavily trafficked road as in catchment 2.

Precipitation proportional samples were taken from the three catchment discharges 02-03SEP2009 during a longer rain event of about 10 mm. From the middle (SS4-4) and the outlet (SS4-5) of the bog grab samples were taken in connection with this rain event.

Scherfigsvej (Gentofte), combined sewer (CS1). Combined sewer overflow from a large residential area of the Northern part of Copenhagen of 1,100 red ha including heavily trafficked roads and drains is collected and treated in a mechanical treatment plant (Godsk and Arnbjerg, 2006). A volume proportional sample was sampled from the inlet 30SEP-01OCT2008 during a 16-hour rain event of 4.5 mm.

Samples were all kept at 5°C in the darkness before analysis which was done within 24 h after sampling.

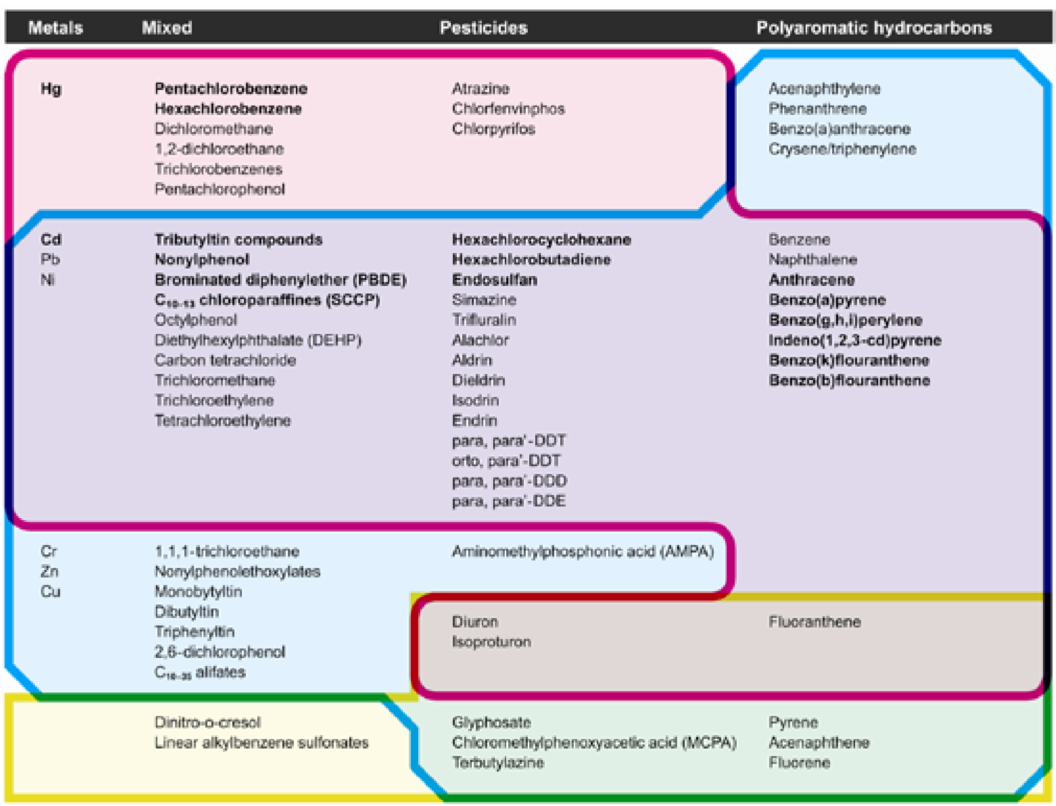

Figure 2. EU priority substances and **priority hazardous substances** are shown in the red rounded shape. Substances shown in the yellow squared shape were selected in an earlier risk assessment of a catchment in Copenhagen. Substances shown in the blue shape were selected for analysis in this work and based on the other two groups as well as potential sources in the catchments.

Analysis

Chemical analysis was performed for more than 50 xenobiotics. The substances were selected based on the list of substances within the WFD (EU, 2008). Earlier studies of xenobiotics in surface runoff have also been considered (Kjølholt et al., 1997; Danish EPA, 2006; Godsk and Arnbjerg, 2006; Jensen, 2009) as well as a risk assessment of substances found in a watercourse in one of the catchment areas (Eriksson et al., 2007). Furthermore sources to the compounds have been looked at (e.g. some are intermediates in industrial processes and not used in Denmark), and available analytical packages and prices have affected the final choice of substances. The selection process is illustrated in Figure 2. As the results reported here come from two different studies, minor differences exist in the substances chosen for analysis. All analyses were performed by Eurofins Miljø A/S, except for the heavy metals in the samples from SS1, SS2, SS3 and CS1 which were analysed at DTU Environment's own laboratories.

RESULTS

All results obtained in this study are shown in Table 1. In the following paragraphs the findings for the individual substance groups will be discussed and when possible compared with earlier findings and the existing EU EQSs or similar standards related to Danish law.

Heavy Metals

Heavy metals occurring in stormwater originate from building materials, e.g. metal roofs, gutters, drainpipes, roofings etc., and from traffic due to abrasion of asphalt, tyres, brake linings and exhausts. The presence of heavy metals in the samples corresponds well with the earlier measurements in separate stormwater and the expected concentration range in CSO in Denmark, a range which has been assessed based on earlier measurements.

The concentrations of nickel measured here are not expected to be problematic in relation to the EU EQS. No MAC-EQS has been established for nickel and in only one of the measurements the total concentration exceeded the AA-EQS. It is not expected that nickel concentrations in general will exceed the set EQS, not only because the EQS values refer to the dissolved concentration and the set EQS is an annual average, but also because dilution in the recipient will lower the concentration further. This is confirmed from the measurements from the bog and from the outlet of the bog, where the concentrations are about 20 times lower than the EQS. Lead and cadmium are heavy metals that strongly bind to particulate matter suspended in the aqueous phase. So even though the total concentrations in almost all the samples exceed the EQS, these metals are expected to meet the EU EQS as the EQSs refer to the dissolved concentration. This is further confirmed by the measurements from the bog and from the outlet of the bog, which are a factor 10 and 100 less than the EQS, respectively. This shows a considerable removal of heavy metals in the bog where sedimentation of particulate matter is taking place. Copper is not listed in the EU WFD, but Danish legislation sets a standard for surface water for copper to a dissolved concentration of 12 µg/L. Copper has similar association constants with humic material as lead and cadmium, however, pH will influence the distribution between the bound and dissolved fraction (Schnoor, 1996). Even though the measured outlet concentrations of copper in the stormwater cases exceed the set limit, in one case with more than 10 times, it is expected that the dissolved concentration will be below the set environmental criteria. In the bog and in the outlet from the bog and in the outlet from the dual porosity filtration system, the measured total concentrations are at the level of or below the environmental criteria.

Table 1. Presence in μg/L of the analysed xenobiotics and heavy metals in water samples from the sampling locations SS1-SS4 and CS1, see the Materials and methods section for details.

					PAH						
Naphthalene	<0.01	<0.01	0.072	0.021	na	na	na	1.4	<0.02-0.59	0.05-5	2.4/-
Acenaphtylene	<0.01	<0.01	0.039	0.028	0.013-0.024	<0.01	<0.01	0.029	<0.01-0.23		
Acenaphthene	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01-0.054	0.01-1	
Fluorene	<0.01	<0.01	0.028	0.014	na	na	na	0.13	<0.01-0.27	0.01-1	
Phenanthrene	0.017	<0.01	0.29	0.11	na	na	na	0.82	<0.01-3.1	0.01-0.5	
Anthracene	0.012	<0.01	0.084	0.037	na	na	na	0.22	<0.01-0.38	0.01-0.3	0.1/0.4
Fluoranthene	0.025	<0.01	0.55	0.18	na	na	na	2	0.016-3.9		0.1/1
Pyrene	0.034	<0.01	0.56	0.27	0.044-0.19	0.03	0.019	2.1	0.02-4.1		
Benzo(a)anthracene	<0.01	<0.01	0.21	0.066	<0.01-0.042	<0.01	<0.01	1	<0.01-0.54		
Chrysen/triphenylene	<0.01	<0.01	0.38	0.25	0.052-0.14	0.015	<0.01	0.76	0.016-1.9		
Benzo(b+j+k)fluoranthene	<0.01	<0.01	1	0.26	0.046-0.12	0.016	0.011	3.1	<0.01-2.0	0.01-0.5	0.03/-[c]
Benzo(a)pyrene	<0.01	<0.01	0.31	0.06	<0.01-0.064	<0.01	<0.01	1.6	<0.01-0.59	0.01.0.5	0.05/0.1
Benzo(g,h,i)perylene	<0.01	<0.01	0.47	0.16	0.026-0.085	<0.01	<0.01	1.4	<0.01-0.96		}0.002/-
Indeno(1,2,3-cd)pyrene	<0.01	<0.01	0.39	0.12	0.016-0.044	<0.01	<0.01	2.6	<0.01-0.42	0.02-0.5	
Dibenzo(a,h)anthracene	<0.01	<0.01	<0.01	<0.01	na	na	na	0.19	<0.01-0.086		
Total PAH	0.088	<0.01	4.383	1.576	0.197-0.707	0.061	0.030	17.35			
					Pesticides						
Glyphosate	1.2	0.26	0.043	0.17	0.59-0.94	0.35	0.088	1.3	0.1-9.0		
AMPA	0.32	0.42	0.077	0.13	0.06-0.33	0.84	0.95	1.3	0.2-0.9		
Diuron	0.055	0.027	<0.01	<0.01	na	na	na	0.48			0.2/1.8
Isoproturon	0.044	0.035	<0.01	<0.01	na	na	na	0.20	<0.05-0.079		0.3/1.0
Terbutylazine	<0.01	<0.01	<0.01	<0.01	na	na	na	0.20	<0.05-0.16		
MCPA	<0.01	<0.01	<0.01	0.018	na	na	na	<0.01	<0.05-0.13		
Monobutyltin	0.035	0.018	0.048	0.072	na	na	na	<0.01			

Dibutyltin	0.008	<0.005	0.009	0.009	na	na	na	<0.005			
TBT	<0.004	<0.004	<0.004	<0.004	na	na	na	<0.004			0.0002/0.0015
Other xenobiotics											
C_{10-13} chloroparaffins	na	na	na	na	<0.4	<0.4	<0.4	na			0.4/1.4
Benzen	na	na	na	na	<2	<2	<2	na	<0.2		10/50
C_{10-25}	na	na	na	na	37-99	42	<8	na			
C_{25-35}	na	na	na	na	15-250	110	22	na			
NP	<0.1	<0.1	0.32	0.1	0.17-0.43	<0.01	<0.01	<0.1		0.1-5	0.3/2.0
NPEs	<0.1	<0.1	na	na	<0.01	<0.01	<0.01	<0.1			
NPE_2s	<0.1	<0.1	na	na	<0.01	<0.01	<0.01	<0.1			
OPE_ns	na	na	na	na	<0.5-12	<2.0	<2.0	na			0.1/-
DEHP	3	<0.5	8.5	3.5	2.9-8.4	<0.5	<0.5	57	1.1-160	1-20	1.3/-
PBDE	<0.005	<0.005	<0.005	<0.005	na	na	na	<0.005			0.0005/-
Trichloroethylene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.17	<0.05-0.62		10/-
Tetrachloroethylene	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	<0.02	0.58	<0.03-2.6		10/-
Chloroform	0.02	0.034	<0.02	<0.02	na	na	na	<0.02	<0.1		2.5/-
Heavy metals											
Pb	17.6	0.3	72.4	23.3	9.8-37	2.6	0.95	19.2	3.6-76	10-70	7.2/-
Cd	0.2	0.1	0.63	0.34	0.11-0.32	0.019	0.0045	0.28	<0.1-0.8	0.1-1.5	0.08-0.25 /0.45-1.5[d]
Cr	41.2	2.3	na	na	0.41-1.8	0.35	0.83	na	<1-140	0.5-40	50[f]
Cu	67.5	7.8	154.6	52.1	22-57	15	12	75	4.4-310	4-200	12[e]
Ni	12.6	1.5	40.5	11.7	0.93-2.4	1.4	0.91	13.4	1.4-27	1-20	20/-
Zn	244	28	na	na	74-180	19	4	na	<5-790	100-500	

AMPA: Aminomethylphosphonic acid; MCPA: Chloromethylphenoxy acetic acid; TBT: Tributyltin; NP: Nonylphenol; NPEs: Nonylphenol ethoxylates; NPE_2s: Nonylphenol diethoxylates; OPE_ns: Octylphenol polyethoxylates; DEHP: Diethylhexylphthalate; PBDE: Polybrominated diphenylether; na: no analysis; <: concentration below the limit of detection; CSO: combined sewer overflow; AA: annual average; MAC: maximum annual concentration; -: not applicable; [a]: Kjølholt et al. (1997) and Danish EPA (2006); [b]: Arnbjerg-Nielsen et al. (2002); [c]: EQS is only for b and k; [d]: depending on the hardness of the water; [e]: Danish legislation; [f]: WHO provisional drinking water guideline.

So far, no EQSs have been decided for chromium and zinc. However, the World Health Organisation (WHO, 2008) has mentioned both metals in their drinking water guidelines. A provisional drinking water guideline value of 50 µg/L has been set for chromium, a value the samples from this study at no point exceed. No value has been set for zinc, as the metal is not of health concern in concentrations normally observed in drinking water.

Polyaromatic hydrocarbons

PAHs in stormwater originate mainly from combustion of fossil fuels and wood but also from oil-products, asphalt, tyres, spillage etc. (Ledin et al., 2004). For the CSO outlet (CS1) the concentrations of the individual PAHs exceed the EQSs for all but naphthalene. The concentrations exceed the EQSs with a factor of 2-2,000 depending on the individual PAH. The presently found concentrations are high compared with findings in CSOs in existing national monitoring programmes in Denmark (Arnbjerg-Nielsen et al., 2002). Especially regarding the PAHs consisting of 5-6 aromatic rings (benzo(b+j+k)fluoranthene, benzo(a)pyrene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene) the concentrations are found above the earlier observed intervals of PAHs in CSO in Denmark (Arnbjerg-Nielsen et al., 2002). Even with a dilution factor of 10 the CSO water will exceed the MAC-EQS for benzo(a)pyrene and a dilution factor of 2,000 is needed to bring the concentrations of benzo(g,h,i) perylene and indeno(1,2,3-cd)pyrene below the AA-EQS.

In the separate stormwater samples the different PAHs exceed the EQS with factors of 1-500 and generally the pollution level is in the following order: SS2>SS3>SS4-3>SS4-2>SS4-1. Stormwater outlet SS1 only receives small concentrations of PAHs, which during dual porosity filtration is removed to below the LOD. The bog received water with concentrations of the high molecular weight PAHs above EQS, but in the bog and in the outlet from the bog they were below the EQSs or below the LODs. With respect to benzo(g,h,i)perylene and indeno(1,2,3-cd)pyren the EQSs are below the LODs. This emphasises, that PAHs in CSO as well as stormwater discharges can pose a potential risk for the receiving waters.

Pesticides

Both the public and the private use pattern of pesticides with respect to pest abatement highly influences the occurrence in stormwater from the individual catchment. Other sources to pesticides are atmospheric deposition and leaching from building materials and paints during rain events (Ledin et al., 2004). Alachlor, aldrin, DDT, DDE, DDD, dieldrin, endosulfan, endrin, isodrin, lindane, simazin, trifluralin and hexachlorobutadiene, all of which are regulated under the EU WFD, were not found in this study, mainly because they are not used in Denmark.

The CSO sample contained the highest concentrations of pesticides. Glyphosate and the degradation product aminomethylphosphonic acid (AMPA) were found in all samples, with the highest concentrations in the CSO (CS1) and two of the stormwater sites, the dual porosity filtration treatment facility (SS1) and the bog (SS4). From the inlet to the outlet of the treatment facility (SS1) as well as from the inlet to the outlet of the bog (SS4) the concentration of glyphosate decreased and the concentration of AMPA increased, indicating the consecutive degradation throughout the two systems.

Both diuron and isoproturon were found above and around their respective EQSs in the CSO samples, but well below in the stormwater samples. Terbutylazine and chloromethylphenoxy acetic acid (MCPA) were only at one site each found at levels slightly above their LODs.

Other xenobiotics

Diethylhexylphthalate (DEHP) is a softener which is found in plastic products and other building materials, from where it can be emitted to the receiving waters during rain. DEHP was the only organic substance found in all non-treated samples and at the same time exceeding the EQS. However, it was found below the LOD in the outlet from the dual porosity filtration system (SS1-2) as well as in the bog (SS4-4) and in the outlet from the bog (SS4-5). This indicates that removal of particulate matter, sorption and dilution are efficient in reducing the concentration of DEHP. However, the concentration in the CSO was 40 times above the EQS, thus requiring a substantial dilution of untreated CSO in order to reach EQS.

Nonylphenols and octylphenols are precursors for older detergents but also found in various building materials (Ledin et al., 2004). Nonylphenol was found in several of the stormwater discharge samples, however only at the level of the EQSs, and was not found in the bog and in the outlet of the bog. Octylphenolpolyethoxylates were found in two of three inlets to the bog, but not in the bog or in the outlet of the bog. No nonylphenolethoxylates were found.

C_{10}-C_{13} Chlorinated parafines (SCCPs), chlorinated solvents and benzene were nearly all found below their LODs, which, except for the chlorinated parafines, are well below their EQSs. For the solvents this was expected, as they easily evaporate, however, traces of trichloroethylene and tetrachloroethylene were found in the CSO. Chloroform was found in increasing concentrations throughout the dual porosity filtration treatment facility. All of these were below the EQS.

Alifates, for example found in petroleum products for vehicles, having up to 10 carbon atoms were found below the LOD, whereas alifates having from 10 to 40 carbon atoms were found much above their LODs in the three inlets to the bog. In the bog and in the outlet from the bog, the concentrations undergo a reduction. At the outlet from the bog the concentration is about 10 times lower than at the inlet, resulting in a concentration below or just at the level of the LOD. There are no EQSs for these substances.

The brominated diphenylether (PBDE) flame retardants in for example electronic equipment and the tributyltin (TBT) anti-fouling and wood preserving agent were found below their LODs, however, the LODs are 10 and 20 times higher than the corresponding EQSs, and thus there is no guarantee that the PBDEs and TBT are not present at critical concentrations in the sampled waters. DBT and MBT, mainly originating from being used as polyvinyl chloride stabilisers, but also as degradation products of TBT, were found at similar levels of about 0.005-0.05 µg/L in both CSO and stormwater.

DISCUSSION

This work focussed on a broad screening to gain knowledge on the presence of a large number of xenobiotics in run-off. Therefore it was decided to use the spot sampling technique where equipment for volume or precipitation proportional sampling was not installed. The different sites were also not sampled during the same rain event. The samples must therefore be considered as random checks. These methods resulted in a number of reasons for differences in concentration levels across the sampling campaigns: the sources at each location, the length of the preceding dry weather periods and the duration and intensity of the rain event. It is evident, that if detailed knowledge about the concentration time profile of a particular discharge, is desired, it is necessary to apply one of the volume or precipitation based sampling techniques. If the main interest is the total load of dissolved xenobiotics to the studied system, a more thorough sampling technique is needed. In this respect sampling using a passive sampling technique would be more adequate. To the best of our knowledge, passive sampling of xenobiotics has not yet been used in sewer systems with success, though measurements of nitrate and phosphorous in drains and surface water from agricultural fields have been taking place (Rozemeijer et al., in press). The spot sampling technique in this case only provides a snapshot of the presence of xenobiotics in the water under study. The outcome of a spot sample could be that no substances would be detected, even though the entire rain event provides a range of substances. Nevertheless, the concentration levels from the current work give a good insight into the presence of a large number of xenobiotics on these selected locations.

The present and earlier measuring campaigns show, that stormwater discharges contain a range of xenobiotics, of which especially heavy metals, PAHs and DEHP can be found in concentrations exceeding the EQSs established in the WFD. The pesticides listed in the WFD were all found at concentration levels below their corresponding EQSs, except for diuron in CSO, which were 2,5 times as high. However, other pesticides, e.g. glyphosate, used locally and not included in the current range of substances in the WFD, were found and may pose a risk to the environment. Glyphosate can be bought in any home and garden care shop and is regularly applied in residential areas as a pest control. Diuron, on the other hand, is not sold from Danish shops with the purpose of private application for pest control. However, diuron and other pesticides (e.g. terbutryn) are known to be present in façade building materials and paints (Burkhardt et al., 2007) from which the substances are washed off upon rain events. In a environmental risk assessment performed for the stream Harrestrup Å in the greater

Copenhagen area, it was concluded that glyphosate, diuron, isoproturon, terbutylazine and MCPA are the pesticides that potentially pose a risk to the aqueous environment (Eriksson et al., 2007). The measurements performed in this study confirm that these pesticides are the ones being used in the greater Copenhagen area and that stormwater as well as CSOs contributes to the pesticide pollution load to the stream.

Substances like the PBDEs were not found in this study. This is most likely because the sources to PBDEs are electronic equipment and e.g. car seats that need flame retarding properties. These sources will not immediately release substances to stormwater, but the intensive use of products with such substances may in the long run result in measurable concentrations in the urban environment.

Whether stormwater discharges pose a risk to the aqueous environment depends on local conditions (base water flow, amount and frequency of discharged water etc.). Never the less, stormwater discharges, especially CSOs, that are not treated are a considerable source to pollution (Eriksson et al., submitted). For the Danish RBMPs, submitted for revision during spring 2010, the influence of xenobiotics on the water quality has only been included when monitoring data allow doing so. There is however a severe lack of data on the presence of xenobiotics in Danish surface waters, lakes and streams, why it is difficult to exempt these substance for deteriorating effects on the water courses. It is therefore anticipated, that water courses receiving large amounts of stormwater discharges will be at risk and the WFD's aim of achieving good ecological and chemical status will therefore also be at risk. However, a focused effort has been put on the reduction of nutrients like nitrogen and phosphorous (Jørgensen, 2010).

Another way to limit the environmental presence of xenobiotics would be to establish ELVs. Compared with the EQSs, ELVs limit how much a particular discharge is allowed to emit to the recipients. In this way a higher pressure to meet given standards would be put on the individual polluter compared with the EQS approach. Using the EQS approach also raises the question about dilution factors and mixing zones. How close to the discharge point is it allowed exceeding the EQSs? The WFD also operates with other measures to reduce the pollution. Whether it should be the application of best available technology (BAT) for industry or the best environmental practice (BEP) for instance regarding how to handle large amounts of stormwater, e.g. infiltration, retention, are options to be discussed and decided on by the local authorities. According to the WFD, even though the receiving waters meet the EQSs the authorities are obliged to introduce at least one other abatement approach than the EQSs. Whether it is to restrict the emissions, i.e. ELVs, or the use of BAT or BEP is up to the local authority.

The high costs associated with sampling and analysis of xenobiotics is mainly responsible for the lack of knowledge regarding the contents of xenobiotics in stormwater discharges. More knowledge in that respect obtained through efficient measuring campaigns, for instance the use of a passive sampler in order to better estimate the total load of xenobiotics, would be a great advantage in order to target the efforts towards reducing the emissions of xenobiotics from stormwater and CSO discharges to the receiving waters.

CONCLUSIONS

The results from these investigations show that EU WFD PSs and other identified xenobiotics including degradation products are found in various stormwater discharges around the greater Copenhagen area. In some cases the concentrations are reduced at treatment facilities, but in other cases the concentrations of xenobiotics remain at levels that are exceeding EU EQS values and thus potentially would result in adverse effects. Among the heavy metals, copper is found to be problematic, as the discharges exceed the Danish standard with up to 13 times, and even in the outlet from the bog, the concentration is at the level of the Danish standard. Especially the discharges of PAHs require a substantial dilution, sometimes up to a factor of 2,000, in order to bring the concentrations below the EQSs. Glyphosate was found in all samples. Diuron was the only pesticide found in concentrations exceeding the EQSs, thus requiring some degree of dilution. The softener DEHP requires removal or dilution factors of 2-45 in order to reach the EQS. Neither alkylphenols, SCCPs, alifates, PBDEs nor alkyl-tin substances were found to exceed the established EQSs.

ACKNOWLEDGMENTS

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Solid and Liquid Phase of Perfluorinated Compounds (PFCs) in Chao Phraya River, Thailand

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Abstract

Perfluorinated compounds (PFCs), especially Perfluorooctane sulfonate (PFOS) and Perfluorooctanoic acid (PFOA), are fully fluorinated organic compounds, which have been used in many industrial applications. The purposes of this field study were to determine solid and liquid phase of PFCs contamination in Chao Phraya River and to compare the changes of PFCs concentration in Chao Phraya River. Surveys were conducted in industrialized area in the lower reach of Chao Phraya River. A solid phase extraction (SPE) coupled with HPLC-ESI-MS/MS were used for the analysis for ten PFCs. Ten PFCs were analyzed to identify the contamination in both suspended and dissolved phases. The average concentration of PFCs were ranged 0.89 – 14.07 ng/L on 2008/5/26. On 2008/8/4, lower concentration of PFCs was detected, <LOQ – 5.93 ng/L. PFOA was the most dominant PFCs, while PFPA and PFOS were also highly detected in most samples. The solid phase of PFCs was also analyzed. The ratio of solid:liquid PFPA (0.1:1.0) was lower than PFOA (0.7:1.0) and PFOS (0.96:1.0) indicating that the shorter chain (more hydrophilic) PFCs was better to dissolve in water rather than adsorb onto suspended solids. To compare among PFOS and PFOA, PFOS had more potential to attach in the suspended solids than PFOA.

Keywords

Micro pollutant; Perfluorinated compounds (PFCs); PFOS; PFOA; Surface water; Thailand

INTRODUCTION

Perfluorinated compounds (PFCs) are one of the emerging contaminants in our environmental system. They have been noted as one of the important environmental problems in recent years due to their occurrences and properties. PFCs are man-made surfactant, which are formed by the replacement of hydrogen bond in the hydrocarbon chain by the fluorine atom. The carbon-fluorine bond is one of the strongest in nature, which makes them highly stable against extreme physical, chemical and biological conditions (3M, 1999; Key et al., 1997). These specific compounds have a special oil and water resistant property that have been used in many applications such as surface treatment, paper protection, performance chemicals, coating materials, emulsifiers and surfactants (Key et al., 1997; Kissa, 2001). The most commonly used PFCs are Perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), which have been used in many kinds of products. These two chemicals have been used in many applications for many years (Alexander et al., 2003). Once PFOS and PFOA are released into the environment, these chemicals persist and are distributed throughout nature. They have been found in surface water and tap water in both developed and developing countries from around the world including North America, Europe and Asia (Berger et al., 2004; Saito et al., 2004; Sinclair and Kannan, 2006; Sinclair et al., 2004).

Not only in water environment but PFOS and PFOA have also been detected in livers, bladders and blood samples of human and many kinds of animals including fish, birds, and marine mammals (Renner, 2001). Animals in the higher food chain such as mink and bald eagles (fish-eating animals) contained higher concentration of PFOS representing bio-accumulative properties (Giesy and Kannan, 2001). PFOS has also been shown to be toxic in rats and rabbits in the laboratory (3M, 2003;

Renner, 2001). Recently, due to their persistence, bio-accumulation, long range transportation and toxic effects; PFCs control regulations (EC, 2006; USEPA, 2006) have been released. PFOS was also categorized as one of the persistent organic pollutants (POPs) in the 4th meeting of the conference of the parties to the Stockholm Convention in May 2009 (Earth Negotiations Bulletin, 2009).

In Thailand, PFCs was detected in Chao Phraya River (PFOS 1.9 ng/L, PFOA 4.7 ng/L) and Bangpakong River (PFOS 0.7 ng/L, PFOA 0.7 ng/L) (Kunacheva et al., 2009) in 2006 and 2007. Chao Phraya River passes through the urban area and receives wastewater from both industrial and domestic activities. Since many regulations have been applied, it is better to understand the changes of PFCs level in this river. The aims of this field study were to determine solid and liquid phase of PFCs contamination in Chao Phraya River and to compare the changes of PFCs concentration in the river.

MATERIALS AND METHOD

PFCs Standards

In this study, ten PFCs were selected as target chemicals. Standard reagents were obtained from Wellington Laboratories, Canada, with purities of >99% (Table 1). PFCs stock solution was prepared by dissolving Perfluorocarboxylic acids mixed solution (PFC-MXA) and perfluorosulfonates mixed solution (PFS-MXA) into 100 mL acetronitrile (LC/MS grade) and stored in polypropylene (PP) bottles at 4ºC. PFCs standard solutions were prepared by diluting different volumes of single stock solutions together into 40% acetronitrile solvent. These multi component standards contained same concentration of each PFC.

Sampling Location

Chao Phraya River basin is the major river system in Central Thailand, which supplies water to a major metropolitan region. It covers 160,000 km^2, representing 30 percent of the country's total area and is the source water for 23 million people (ONWRC, 2003). The Chao Phraya basin is on a mountainous range with agriculture valleys found in the upper region, while the middle region contain terrestrial plains that are highly productive for agriculture. This study focused on the lower reaches of Chao Phraya River (65 km. to Gulf of Thailand), which flows through Bangkok city. There are dense residential, commercial and industrial areas along both sides of the river through the Gulf of Thailand. The possibility of detecting PFCs in this area was highly expected especially around the industrial activities (Prevedouros et al., 2006). The sampling in Chao Phraya River was conducted on 2008/5/26 and 2008/8/4. Six sampling points in Chao Phraya River mainstream (CH1-CH6) and eight points from the tributaries (CS1- CS8) were selected as in Figure 1. The tributaries of Chao Phraya River receive wastewater from both domestic and industrial activities.

Sample Collection

Samples were collected by grab-sampling using a polypropylene container. New 1.5 L narrow-neck Polyethylene terephthalate (PET) bottles with screw caps were used as sampling containers. PET bottles were washed with methanol and dried prior to use. Bottles were rinsed three times before collection of river water with samples. After sampling, the samples were brought back to the laboratory and were pre-treated in the same day.

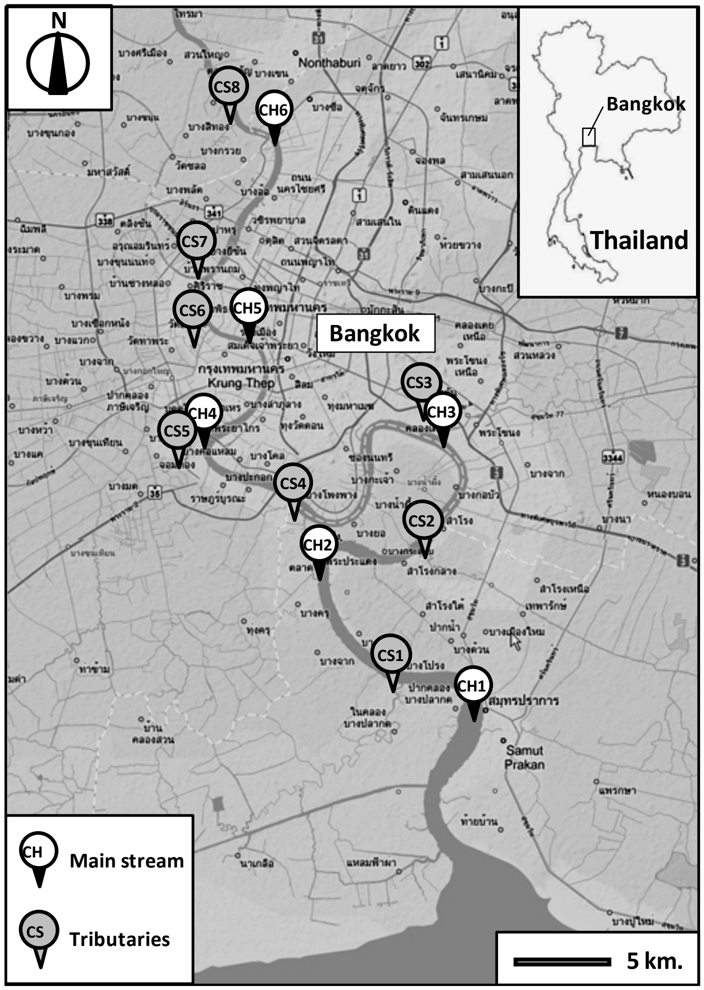

Figure 1. Sampling location in Chao Phraya River

Sample Pre-treatment

Liquid phase samples. Collected samples were filtered by 1 µm GF/B glass fiber filter to separate suspended solids. The filtrate 500 mL was loaded to a PresepC-Agri (C_{18}) cartridge, which was used for concentrating PFCs, at a flow rate 10 mL/min (Kunacheva et al., 2009). The cartridge was preconditioned by 10 mL of methanol (LC/MS- grade) followed by 2×10 mL of ultrapure water (LC/MS- grade) before use. The above procedures were completed in Thailand and the cartridges were brought back to Japan for further analysis. In Japan, each cartridge was air dried for one hour, eluted by 2×2 mL LC/MS-grade methanol, evaporated to dryness with nitrogen gas, and reconstituted into 40% LC/MS-grade acetronitrile to a final volume of 2 mL. PFCs in filtrates were concentrated by a factor of 250 times. PFCs standards were spiked (10 ng/L) into a duplicated sample before loading to the cartridge to find their recoveries.

Solid phase samples. The suspended solids phase sample that was separated by GF/B filter (Filtered volume: 500 mL) was further analyzed by using Accelerated Solvent Extraction (ASE-200). The filters were air dried and inserted to ASE cells for extraction. The standard 10 ng/L was spiked into the duplicated cell before extraction. The extraction was done by using LC/MS-grade methanol as a solvent. The extraction ran three cycles (15 min/cycle) by using pressure 2,000 psi and temperature at 100ºC. Then, the extracted sample was diluted with LC/MS-grade ultrapure water into 1 L, loaded to a PresepC-Agri (C_{18}) cartridge and the same procedure as liquid phase samples were carried out.

Instrumental Analysis and Quantification

Separation of PFCs was performed by using Agilent 1200SL high-performance liquid chromatography (HPLC). Extract 10μL was injected to a 2.1×100 mm (5 μm) Agilent Eclipse XDB-C_{18} column. Mobile phase consisted of (A) 5mM ammonium acetate in ultrapure water (LC/MS grade) and (B) 100% acetronitrile (LC/MS-grade). At a flow rate of 0.25 mL/min, the separation process started with initial condition of 30% (B), increased to 50% (B) at 16.5 min, then to 70% (B) at 16.6, held at 70% (B) for 3.4 min, increased to 90% (B) at 21 min, maintained at 90% (B) for 1 min, and then ramped down to 30% (B). The total running time was 34 min for each sample. For quantitative determination, the HPLC was interfaced with an Agilent 6400 Triple Quadrupole (Agilent, Japan) mass spectrometer (MS/MS). The mass spectrometer operated with an electrospray ionization (ESI) negative mode. Analyte ions were monitored by using multiple reaction monitoring (MRM) mode. The analytical parameters of each PFC are shown in Table 1.

Table 1. Analytical parameters of each PFC by HPLC/MS/MS analysis

Compound	No. of Carbon	Parent ion (*m/z*)	Daughter ion (*m/z*)	CE (eV)	Retention time (min)	LOQ (ng/L)	Recovery
PFPA	C5-A	263	219	-15	2.1	0.5	0.79
PFHxA	C6-A	313	269	-15	3.2	0.4	0.82
PFHpA	C7-A	363	319	-15	5.4	0.3	0.91
PFOA	C8-A	413	369	-15	8.1	0.5	1.02
PFNA	C9-A	463	419	-15	10.9	0.4	1.01
PFDA	C10-A	513	469	-15	13.8	0.2	1.02
PFUnA	C11-A	563	519	-15	16.7	0.3	1.05
PFDoA	C12-A	613	569	-17	19.1	0.2	0.90
PFHxS	C6-S	399	80	-90	8.9	0.4	0.96
PFOS	C8-S	499	80	-90	15	0.2	1.08

Note: CE = Collision Energy, LOQ = Limit of quantification
A = Perfluorinated carboxylic acids (PFCAs)
S = Perfluorinated sulfonates (PFCSs)

Calibration and Validation

The calibration curves for quantification, consisting of seven points covering 0.05 to 10 μg/L, generally provided linearity with determination coefficients (R^2) more than 0.995 in every compound. Limit of detection (LOD) for HPLC/MS/MS was defined as concentration with signal to noise ratio (S/N) of 3:1. Practically, limit of quantification (LOQ) was used for quantifying analyte, which was defined by S/N 10:1 (Saito et al., 2003), (Table 1). The duplicated analysis was also performed on all samples and coefficients of variations (CV) of concentration were below 20%. During the collection of samples and analysis, analytical blanks were performed by using ultrapure water (LC/MS-grade) to identify the contamination during the analytical procedures.

RESULTS AND DISCUSSION

PFCs Concentration

Sampling was conducted in Chao Phraya River, which is located in the urban area (Bangkok City) receiving wastewater from both industrial and domestic activities. Six sampling points in Chao Phraya River mainstream (CH1-CH6) and eight points from the tributaries (CS1- CS8) were selected. Table 2 shows statistics of PFCs concentration in Chao Phraya River on 2008/5/26 and 2008/8/4. PFCs were detected in all samples along the river indicating that most of areas were contaminated by PFCs. Ten PFCs were detected on the average of 29.2 ng/L (2008/5/26) and 12.6 ng/L (2008/8/4) along the river.

Table 2. PFCs concentrations in Chao Phraya River on 2008/5/26 and 2008/8/4

Date	*n*		PFCs Concentration (ng/L)									
			PFPA	PFHxA	PFHpA	PFOA	PFNA	PFDA	PFUnA	PFDoA	PFHxS	PFOS
2008/5/26	14	Ave	5.24	0.89	1.71	14.07	1.71	0.59	0.64	0.58	1.09	3.09
		SD	6.23	0.41	1.02	7.68	0.51	0.29	0.18	0.20	1.08	3.51
		Range	<LOQ-26.36	<LOQ-2.10	<LOQ-4.56	1.05-36.75	0.78-2.66	ND-1.28	ND-0.92	ND-1.04	<LOQ-4.46	0.90-14.09
2008/8/4	14	Ave	1.24	<LOQ	0.59	5.93	<LOQ	<LOQ	<LOQ	ND	<LOQ	3.84
		SD	1.52	-	0.35	6.08	-	-	-	-	-	8.54
		Range	<LOQ-5.61	<LOQ-0.52	<LOQ-1.56	1.05-22.42	<LOQ	<LOQ	<LOQ	ND	<LOQ-1.07	<LOQ-33.06

Note: *n* = Number of Sample, Ave = Average, SD = Standard Deviation,
<LOQ = Less than Limit of Quantification, <LOD = Less than Limit of Detection

The average concentration of PFCs were ranged between 0.89 – 14.07 ng/L on 2008/5/26. The increase of PFCs concentrations along the river continuously indicated point and non-point source pollution along this river stretch comparable to the previous sampling in 2006 and 2007 (Kunacheva et al., 2009). PFOA was the most dominant PFCs which contributed 48% (Figure 2), while PFPA and PFOS were also highly detected with 18% and 10%, respectively. Other seven PFCs accounted for less than 10% of ten PFCs. The large portion of PFPA contamination in this area was unique comparing to Japan, where PFHpA and PFNA were the main detected PFCs besides PFOS and PFOA (Murakami et al., 2008). This might be due to the usage of PFPA in Thailand was generally higher than other countries. PFOA and PFOS were ranged between 1.05 – 36.75 ng/L and 0.90 – 14.09 ng/L. These levels of contamination were comparable to the geometric mean of PFOS and PFOA in surface water in Japan (Saito et al., 2004). The highest concentration of both PFOS (14.09 ng/L) and PFOA (36.75 ng/L) were found at CS3, where industrial zones and a port was located in this area. The same location also detected the highest PFOS and PFOA concentration in 2006 and 2007(Kunacheva et al., 2009). Industrial area has been reported as the major source of PFCs contaminated in surface water in many countries such as USA (Hansen et al., 2002; Sinclair and Kannan, 2006), Japan (Saito et al., 2004) and Singapore (Yu et al., 2009).

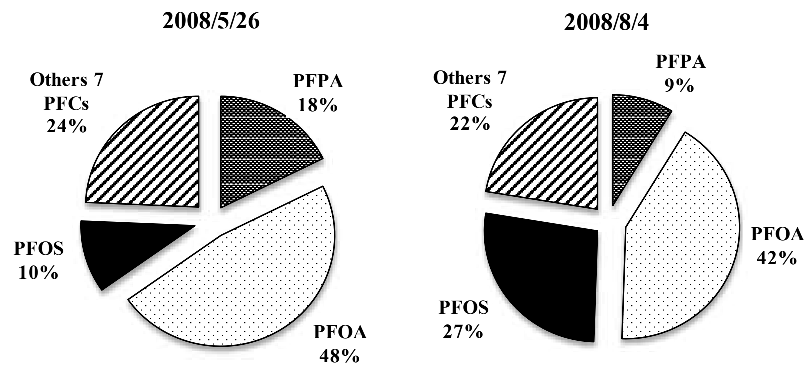

Figure 2. Relative abundance of PFCs in Chao Phraya River

On 2008/8/4, lower concentrations of PFCs were detected, <LOQ – 5.93 ng/L. Only four (PFPA, PFHxA, PFOA and PFOS) out of ten PFCs were detected higher than LOQ. PFOA, PFOS and PFPA were the major PFCs as on 2008/5/26 which accounted for 42%, 27% and 9%, respectively. Lower concentration of PFPA and PFOA were found during this sampling with an average of 1.24 ng/L and 5.93 ng/L, respectively. However, PFOS were comparable to the last sampling with average concentration of 3.84 ng/L. Comparable relative abundance of PFCs with the previous sampling on 2008/5/26 confirmed that PFOS, PFOA and PFPA are the major PFCs contamination in this area.

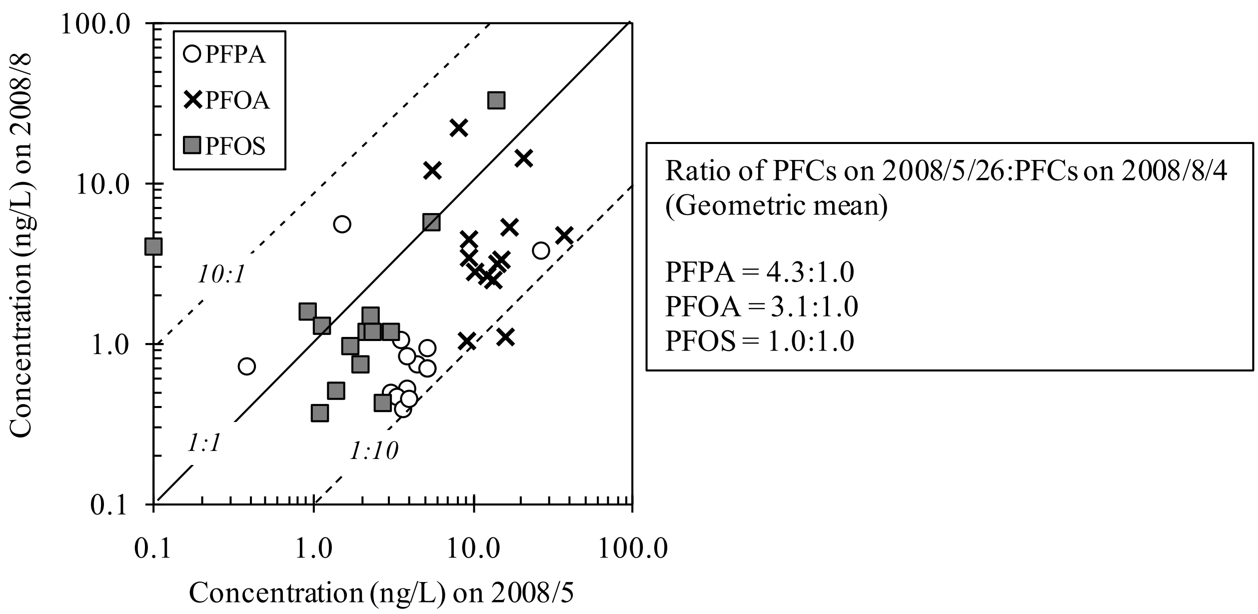

Figure 3. Comparison of PFPA, PFOA and PFOS concentrations on 2008/5/26 between those on 2008/8/4

Figure 3 shows the comparison of PFPA, PFOA and PFOS concentrations on 2008/5/26 between those on 2008/8/4. Most of the plots are below the 1:1 linear line. Ratio of PFPA, PFOA and PFOS concentrations on 2008/5/26 to those on 20008/8/4 were calculated as 4.3:1.0, 3.1:1.0 and 1.0:1.0, respectively. It showed that PFPA and PFOA on 2008/5/26 were detected much higher than those on 2008/8/4; in contrast to PFOS which were detected in comparable levels during both sampling. Decreasing levels of PFPA and PFOA contamination might be due to the changes of usage which were fluctuating. Furthermore, to calculate mass loading, flow rate data were obtained from Royal Irrigation Department, Thailand (Royal Irrigation Department (Thailand), 2008). Flow rate (monthly average) of Chao Phraya River were reported to be at 30.2×10^6 m^3/d in 2008/5 and 24.3×10^6 m^3/d in 2008/8. The average loadings of PFPA, PFOA and PFOS in two samplings were at 94.3 g/d, 284.6 g/d and 93.4 g/d, respectively. This PFOA contamination was comparable to those in Yodo River, Japan in 2004 and 2005 (Lien et al., 2008); however, the PFOS loading were much higher in Chao Phraya River than those in Yodo River.

Solid and Liquid Phase PFCs Concentration

In this study, the solid phase of PFCs was also analyzed in all samples. Figure 4 shows the solid and liquid phase concentrations of PFPA, PFOA and PFOS in Chao Phraya River. The ratio of solid:liquid of PFPA (0.1:1.0) was lower than PFOA (0.7:1.0) and PFOS (0.96:1.0) indicating the shorter chain (more hydrophilic) PFCs were better to dissolve in water rather than adsorbing onto suspended solids. To compare between PFOS and PFOA; PFOS had more potential to attach in the suspended solids than PFOA. These results show that PFCs concentrations in suspended solids could not be negligible. To calculate and compare the results of PFCs contamination, it is essential to analyze both solid and liquid phase samples.

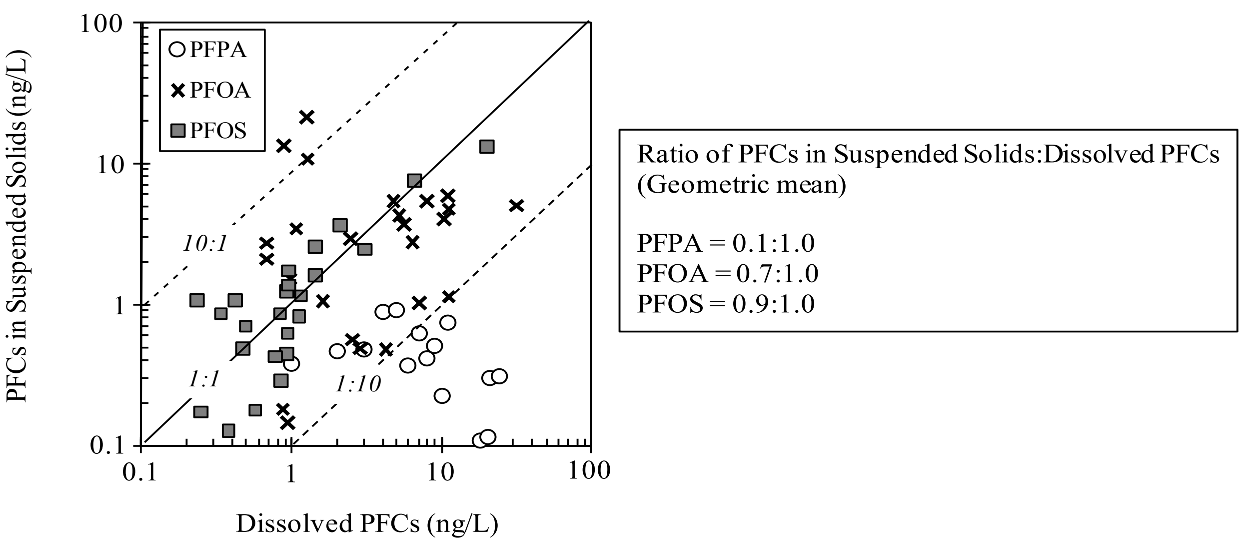

Figure 4. Solid and liquid phase PFPA, PFOA and PFOS concentrations in Chao Phraya River

Comparing PFOS and PFOA concentration with previous study

Figure 5 shows geometric mean of PFOS and PFOA concentrations in Chao Phraya River in this study comparing with those from 2006 and 2007 (Kunacheva et al., 2009). PFOS were detected about 2 ng/L during 2006 to 2008. PFOS concentration which was comparable indicated that PFOS was still used in the manufacturing even after the major PFCs producing company began to phase out their usage of PFOS in 2000. For PFOA, the concentration was increased in 2008 about 2 fold higher than in 2006 and 2007. It showed that the usage of PFOA was increasing during the past few years. The regulation to control the production and usage of both PFOS and PFOA is needed not only in developed countries but also in developing countries. In 2009, PFOS was categorized as persistent organic pollutants (POPs) (Earth Negotiations Bulletin, 2009). The decrease of PFOS contamination in surface water will be expected in years to come. It is essential to continue the monitoring of PFOS and PFOA concentration in the future.

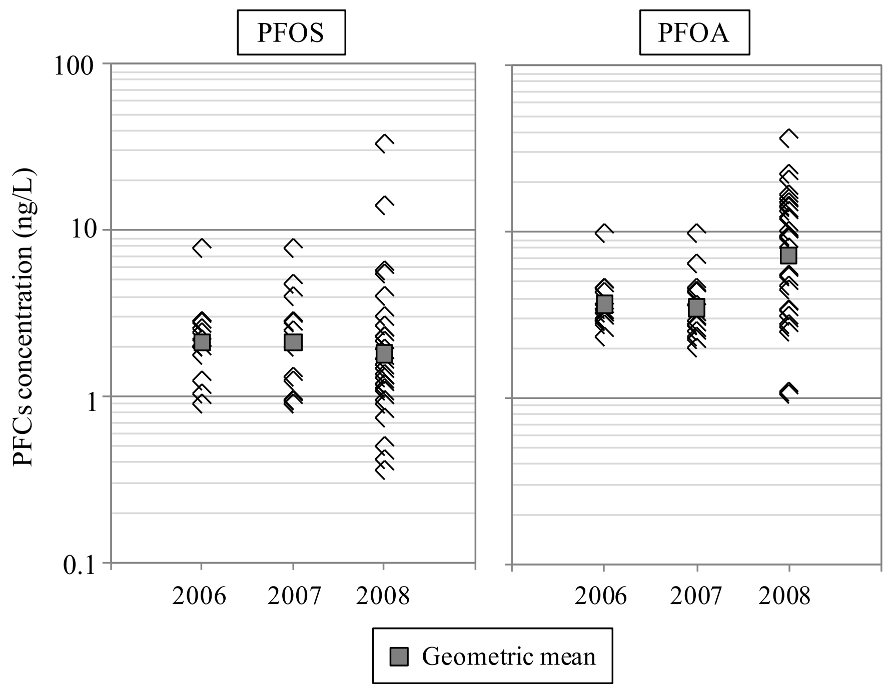

Figure 5. PFCs concentration in 2008 (this study) and in 2006, 2007 (Kunacheva et al., 2009)

CONCLUSIONS

Sampling was conducted in industrialized area in Chao Phraya River, Thailand. Ten PFCs were analyzed to identify the contamination in both suspended and dissolved phases. The average concentration of PFCs ranged between 0.89 – 14.07 ng/L on 2008/5/26. On 2008/8/4, lower concentration of PFCs were detected, <LOQ – 5.93 ng/L. PFOA was the most dominant PFCs, while PFPA and PFOS were also highly detected in most samples. Comparing with concentration in 2006 and 2007, PFCs concentration was relatively higher in 2008. In this study, the solid phase of PFCs was also analyzed. The ratio of solid:liquid PFPA (0.1:1.0) was lower than PFOA (0.7:1.0) and PFOS (0.96:1.0) indicating that the shorter chain (more hydrophilic) PFCs were better to dissolve in water rather than adsorbing onto suspended solids. To compare between PFOS and PFOA, PFOS had more potential to attach the suspended solids rather than PFOA.

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Potential of Amendments in Reducing Leaching of Chlorpyrifos to Groundwater

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Abstract

The efficacy of different applied soil amendments namely, gypsum (5 t ha^{-1}), pyrite (5

t ha^{-1}), farmyard manure (FYM, 5 t ha^{-1}), fresh cow-dung slurry (FCD, 0.5 t ha^{-1}) to reduce the leaching losses of chlorpyrifos (O,O-diethyl o-3,5,6 – trichloro-2-pyridinyl phosphorothioate), an organophosphate insecticide was studied in mollisols by column method. The desorption data of chlorpyrifos conformed well to a two step by two component (1+1) first order kinetics (R2=0.83 to 0.99, significant at p=0.05). Irrespective of the treatments, the leaching of applied chlorpyrifos occurred at faster rate up to 10 h and thereafter at slower rate upto 48 h. The leaching of chlorpyrifos was 39.5, 43.7, 37.6, 33.3 and 27.1 percent of total applied amount under control, gypsum, pyrite, FYM and FCD treatments, respectively. Among different treatments, organic amendments like FCD @ 0.5 t ha^{-1} and FYM @ 5 t ha^{-1} were most effective in reducing the leaching losses of chlorpyrifos.

Keywords

Amendments, chlorpyrifos, leaching, mollisols

INTRODUCTION

Chlorpyrifos (O,O-diethyl o-3,5,6 – trichloro-2-pyridinyl phosphorothioate) is used worldwide as an agricultural organophosphate insecticide. Its environmental fate has been extensively studied and the reported half life in soil varies from 10 to 120 d (Singh, 2003). It is widely used for insect pest control on grain, cotton, fruit, nut and vegetable crops as well as in lawns and ornamental plants, which has caused a wide range of soil contamination (EPA, 1997).

Insecticides are applied on either plant itself or soil to control various agricultural losses. Their residues are washed down from the soil and reach to aquatic bodies and groundwater through leaching. Though chlorpyrifos has greater sorption potential than other pesticides (Bondarenko and Gan, 2004) yet it's leaching may lead to ground water contamination as it has been reported to be present above MRL (maximum residue limit) values in soft drinks which are prepared using ground water as sole source of water (Down to earth, Aug.'2003). Contamination of surface water and groundwater by pesticides has been recognized as a major problem in many

countries and India too because of the persistence of some of these pesticides in the aquatic environments. The phenomenon of aging or sequestration has been widely observed in with many hydrophobic compounds including pesticides in aquifers and soils, due to which the half-life of the chemical increases drastically (Nam and Kim, 2002). The persistence of these insecticides in soil often lead to contamination of the agricultural produce. Sorption of pesticides to soil may exert a pronounced influence on physical, chemical and the biological fate of pesticides in soil (Thorstence et al. 2001; Liu et al.

2003). It has been recognized that the recommendation for pesticide use cannot be made until the information on persistence of residues are known for a variety of soil management practices (Ghodrati and Jury 1992).

Common organic manures like farmyard manure and organic sludges influence the sorption of pesticides to restrict their downward movement and promote their biodegradation in soil by accelerating the microbial activity in soils (Perrin –Ganier et al., 2001) The present study was therefore, undertaken to assess the potential of using amendments, namely gypsum, pyrite, farmyard manure (FYM), fresh cow dung (FCD) to reduce the leaching of chlorpyrifos from soil.

MATERIALS AND METHODS

Soil samples

Surface (0 –15 cm) soil sample was collected from Practical Crop production (PCP) Block located in G. B. Pant University of Agriculture and Technology, Pantnagar, India. The soil sample was air-dried in shade and passed through a sieve having openings of 2 mm. The experimental soil had silty clay loam texture, 46 percent water holding capacity, 8.16 pH and 0.130 dS m^{-1} electrical conductivity in 1:2 soil water suspension, 14.5 g organic C and 25.2 g CaCO3 kg-1 soil.

Treatment application

One hundred g soil was filled in each of five plastic bags. Gypsum, pyrite and FYM was added @ 5 t ha^{-1} and FCD @ 0.5 t ha^{-1} separately in different bags. The requisite amount of distilled water was added to the soil to maintain the moisture content near 50 percent of water holding capacity of soil. The bags were incubated for 15 d. After soil incubation, the soil was air-dried, crushed by a wooden roller, mixed thoroughly and estimated for soil pH, E.C and organic C content following standard analytical procedures (Jackson 1973) as shown in Table 1.

Table 1. Effect of different soil amendments on soil properties.

Treatments	Soil Properties		
	pH (1:2, soil water suspension)	E.C(dS m^{-1}, 1:2 soil water suspension)	Organic C (g kg^{-1} soil)
Control	8.16^a	0.125^a	14.5^a
FYM @ 5 t ha^{-1}	7.97^c	0.390^c	18.9^c
FCD @ 0.5 t ha^{-1}	8.01^c	0.280^b	17.4^b
Pyrite @ 5 t ha^{-1}	8.10^b	0.275^b	14.8^a
Gypsum @ 5 t ha^{-1}	8.17^a	0.817^d	14.6^a

The values with a similar letter in the superscript in a column are statistically not different.

Desorption experiment

Twenty five g soil treated with different amendments was taken in separate plastic bags and spiked with 5 ml aliquot of 10 µg ml-1 solution of the insecticide. The contents were mixed thoroughly and filled in 30 cm long glass columns having an internal diameter of 1.8 cm and a sinctered disc at the base with regular tapping with a rubber stopper attached to a glass rod. A solution of 0.01 M $CaCl_2$ was passed through the column maintaining a constant solution head over the soil column. The leachates collected between different time intervals i.e. 0.5, 1, 2, 3, 4, 5, 6, 10, 24, 36, 48 h were measured for volume.

Extraction and Analysis

A known volume of the leachate collected at different time intervals were partitioned twice with 20 ml of n-hexane and a pinch of sodium sulphate in separating funnel by shaking the mixture vigorously and keeping for 15 min for phase separation. The pooled organic phase of two extractions was evaporated in a rotatory flash evaporator and the residue was dissolved in 1 ml of n-hexane for estimation by G C. The gas chromatograph was equipped with packed column 10% SE 30 (8' length and 1.8' i.d) for chromatographic separation and Electron Capture Detector for quantitative analysis of the samples. The flow rate of carrier gas (nitrogen, UHP grade) was maintained at 30 ml min^{-1}. The column, injector and detector temperatures were maintained at

180^o C, 230^o C and 300^o C respectively. One µl of sample was injected every time for detection in G.C. The standard retention time of chlorpyrifos under these conditions was 8.7 minutes. The concentration of chlorpyrifos in the eluates was computed with the help of a calibration curve drawn between peak area and the concentrations of chlorpyrifos in the range of 0 to 5 µg $ml^{-1.}$

RESULTS AND DISCUSSION

The column desorption data of chlorpyrifos under different soil amendments at different time intervals revealed a curvilinear pattern when plotted and therefore, the data were fitted to a two component (1+1) first order kinetic equation (Equation 1).

$(C_t/C_0) = a.e^{-k1\,t} + b.e^{-k2\,t}$ ---- Equation 1

where, C_t = amount of chlorpyrifos remaining on soil (mg chlorpyrifos kg^{-1} soil) at time (t)

C_0 = amount of chlorpyrifos initially present on soil (mg chlorpyrifos kg^{-1}soil) at time t_0

a = fraction of chlorpyrifos associated with fast desorption

b = fast desorption rate coefficient

c = fraction of chlorpyrifos associated with slow desorption

d = slow desorption rate coefficient

t = time in h.

The computed values of model parameters and coefficient of determination (R2) for all the treatments are represented in Table 2. Highly significant values of R2 (significant at p =0.01) in case of all soil treatments indicated that the two component (1+1) first order kinetics could adequately describe the leaching of chlorpyrifos. The faster desorption of chlorpyrifos could be attributed to the content of chlorpyrifos present in soil solution while slower desorption could be related to diffusion controlled desorption of chlorpyrifos bound to soil particles. A comparison of fraction of chlorpyrifos associated with fast desorption (a) showed that it was the highest under treatment receiving gypsum @ 5 t ha^{-1} (0.6378) followed by control, application of pyrite @ 5 t ha^{-1}, FCD @ 0.5 t ha^{-1} and the lowest under FYM applied @ 5 t ha-1. Further, the comparison of fast desorption rate coefficients (k1) among the treatments revealed that it was the highest for application of FYM @ 5 t ha-1 followed by the treatment receiving FCD @ 0.5 t ha^{-1} and pyrite @ 5 t $ha^{-1.}$ Relatively significantly lower values of k1 were recorded under gypsum @ 5 t ha^{-1} and control in comparison to other treatments.

A comparison of fraction of chlorpyrifos associated with slow desorption (b) showed that it was the highest under treatment receiving FYM @ 5 t ha-1 followed by FCD @ 0.5 t ha^{-1}, application of pyrite @ 5 t ha-1, control and the lowest under gypsum @ 5 t ha-1. A comparison of slow desorption rate coefficients (k2) among the treatments revealed that it was the highest for control, followed by application of pyrite @ 5 t ha-1, FYM @ 5 t ha^{-1}, gypsum @ 5 t ha^{-1}, and the lowest for the treatment for FCD @ 0.5 t ha^{-1}.

CONCLUSIONS

Thus, the desorption of chlorpyrifos in soils occurs through a simultaneous two compo- nents first order reaction kinetics. The soils amended with organic manures may retain applied chlorpyrifos to reduce its percolation to the lower soils depths. Higher effectiveness of organic amendments like FYM or FCD in reducing the leaching losses of chlorpyrifos could be ascribed to an increase in the organic C content of the soil upon their application. This study revealed that application of 5.0 t FYM ha-1 can be a feasible method to reduce the leaching of chlorpyrifos and ultimately the risk of groundwater contamination.

Table 2. Effect of different soil amendments on two component first order kinetic desorption model parameters.

Treatments	a	k1	b	k2	R^2-value
Control	0.5235^{ab}	0.0452^{d}	0.4964^{c}	0.0454^{a}	0.996**
FYM @ 5 t ha^{-1}	0.2217^{d}	0.219^{a}	0.8257^{a}	0.0084^{c}	0.994**
FCD @ 0.5 t ha^{-1}	0.4063^{c}	0.1537^{b}	0.6102^{b}	0.0027^{e}	0.992**
Pyrite @ 5 t ha^{-1}	0.4886^{b}	0.1116^{c}	0.5101^{bc}	0.0132^{b}	0.994**
Gypsum @ 5 t ha^{-1}	0.6378^{a}	0.0502^{d}	0.3480^{d}	0.0038^{d}	0.993**

The values with a similar letter in the superscript in a column are statistically not different.
** Significant at p = 0.01.

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Substances that threaten the drinking water function of the river Meuse

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Abstract

The river Meuse is a source of drinking water for 6 million people in The Netherlands, Belgium and France. Drinking water companies monitor the water quality in the river Meuse, in close cooperation with the government. A comprehensive monitoring program is set up for the network of sampling stations and intake points along the river basin. The monitoring program currently includes many physicochemical, inorganic and microbiological parameters, but also a wide variety of organic compounds such as polyaromatic hydrocarbons and organohalogen compounds, pesticides and pharmaceuticals. Today, most water quality problems affecting the production of drinking water from the river Meuse are caused by pesticides and pharmaceuticals, including x-ray contrast media. Emerging substances, including many substances that threaten the drinking water function are present throughout the Meuse river basin and are often not (yet) monitored on a regular basis by the various water authorities. Sources of emerging substances are diverse and often diffuse. This requires implementation of measures at regional, national and river basin scale.

Keywords

Monitoring; diffuse pollution; emerging substances; pesticides; pharmaceuticals; x-ray contrast media; drinking water

INTRODUCTION

Water management authorities have monitored the quality of the surface water for decades. Monitoring results are necessary to take effective measures to protect and improve the ecological functioning of the aquatic environment and to assess the effectiveness of measures taken. However, ecological monitoring often does not take all relevant substances for drinking water into account and measures taken do not always improve the water quality with respect to those substances relevant to safe drinking water production. As an example, the installation and improvement of waste water treatment plants (WWTPs) in recent decennia have quantitatively decreased emissions of certain substances from urban sources as well as industry by-products like heavy metals and organic micro pollutants. In The Netherlands emissions of many contaminants to the main rivers have decreased significantly after the introduction and implementation specific national legislation setting rules for the discharge of waste water in the early 1970s. In addition, national and international measures have tackled nutrient emissions from agriculture to a certain extent and the effects of air pollution reduction schemes have had positive effects, improving the water quality in the river Meuse. Still, specific issues remain. Today, most drinking water related problems are caused by pesticides and pharmaceuticals, including x-ray contrast media (Bannink, 2009).

The impact of such pollutants on drinking water can be reduced to some extent through sophisticated but expensive treatment methods, such as advanced oxidation, activated carbon or membrane filtration, but all treatment methods have their limits. No treatment can eliminate 100% of these pollutants and its effectiveness does not remain constant over time. Also the treatment method itself can produce new unwanted chemical compounds, for instance the formation of carcinogenic N-Nitrosodimethylamine (NDMA) from the pesticide metabolite N,N-dimethylsulfamide during ozonation (Schmidt and Brauch, 2008). The precautionary principle and the ideal of pure and wholesome drinking water require that river water entering the treatment process is clean enough to allow the exclusive use of natural purification methods, such as bank or sand filtration, for the production of drinking water.

Goal of this study is to deduce a comprehensive list of substances that threaten the production of drinking water from water abstracted from the river Meuse. Starting point for our study was the monitoring database of RIWA-Meuse, the association of water companies that extract water from the Meuse river basin for their production of drinking water. As part of this study, additional measurements have been undertaken to fill up the gaps in data availability in the regular monitoring programs of the water companies. Finally, as an example, we have specifically focused on the presence of glyphosate and AMPA in the Meuse river basin.

MATERIALS AND METHODS

The river Meuse is over 900 kilometres long and flows from its source in France through Belgium to the Netherlands, where it discharges into the North Sea. Small parts of the river basin are situated in Luxemburg and Germany (see Figure 1). The river basin covers an area of 35 000 km^2 with a population of 9 million. The average flow through the river Meuse is 350 m^3/s at its mouth, but since the main source is rain water, flow rates fluctuate between 20 m^3/s and 3 000 m^3/s (De Wit, 2008). The river Meuse has many uses, such as navigation (commercial and recreational), industrial uses (including cooling water and hydroelectric power stations), agricultural uses, recreation, ecosystem, landscape and source for drinking water. The river Meuse is an important source for the production of drinking water. About 6 million people in the Netherlands, Belgium and France depend on the river Meuse as a source for their drinking water. Drinking water companies in Belgium and the Netherlands extract water for their production process. Table 1 shows the intake points as well as the abstracted volumes of water (in 2009). Since the average annual flow of the river Meuse in 2009 at Megen, representative for the Keizersveer sampling station, was around 300 m3/s the average abstracted volume for drinking water production was approximately 20%. However, the flow of the river Meuse is very variable, as described before, so this percentage is also very variable over the year. Table 1 shows the volumes which are abstracted.

Table 1. Abstraction of water from the river Meuse basin for drinking water production in 2009.

Intake point	Country	River/tributary	Total abstracted volume [Mm3]
Eupen	Belgium	Vesdre (reservoir)	
Nisramont	Belgium	Ourthe (reservoir)	
Verviers	Belgium	Gileppe (reservoir)	
		Subtotal	45.3
Tailfer	Belgium	Meuse	44.1
Broechem	Belgium	Albert Canal	83.9
Lier	Belgium	Nete Canal	48.2
Heel	The Netherlands	Lateral Canal	11.9
		Boschmolen Lake	1.1
Brakel	The Netherlands	Dammed Meuse	76.4
Keizersveer	The Netherlands	Bergse Meuse	187.1
Scheelhoek	The Netherlands	Haringvliet	6.2
		Total	**504.2**

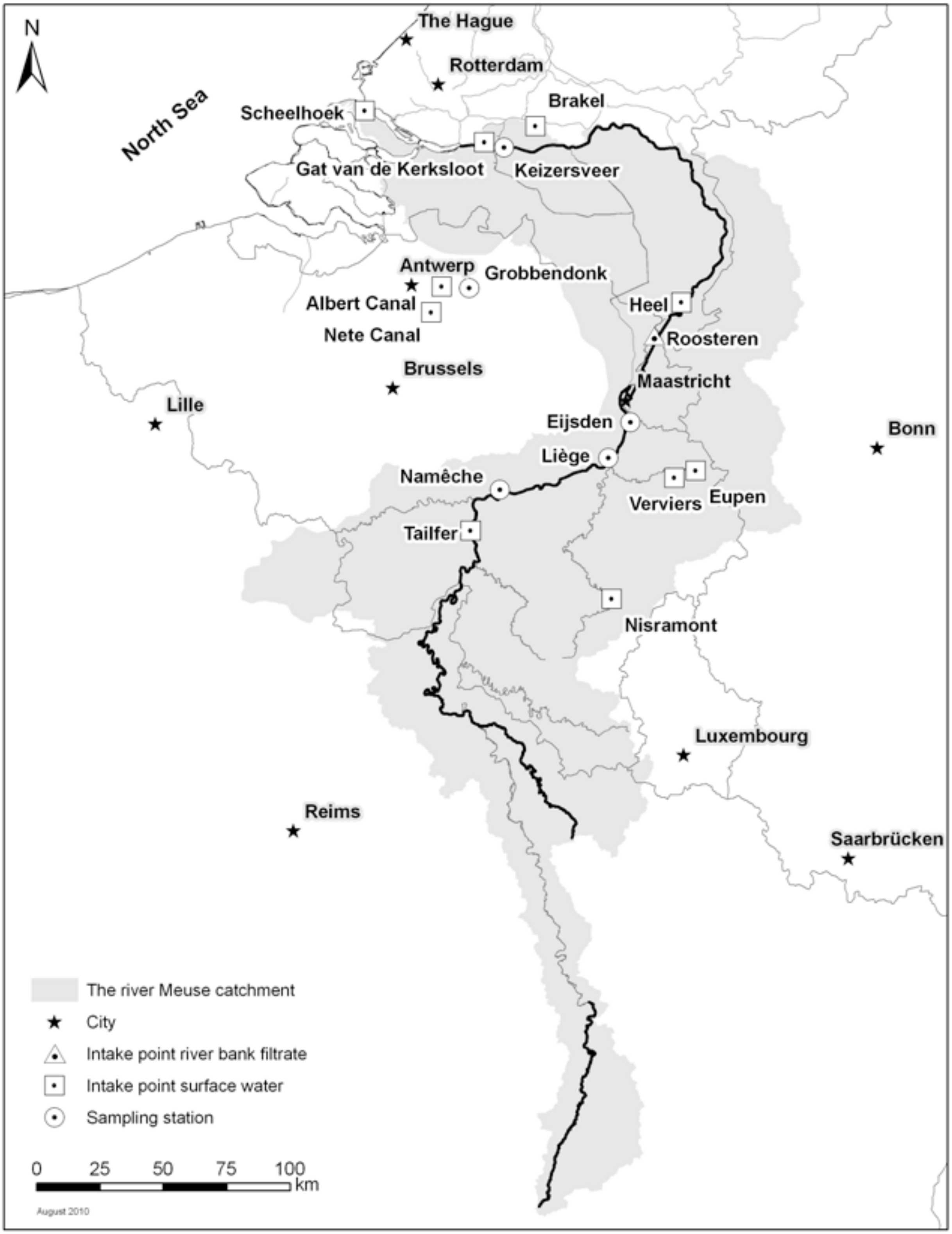

Figure 1. The Meuse river basin, intake points and sampling stations

Water quality monitoring database for the Meuse river basin

One of the activities of RIWA-Meuse and its members is to monitor the water quality in the river Meuse, in close cooperation with *Rijkswaterstaat*, the implementing body of the Dutch Ministry of Transport, Public Works and Water Management. A comprehensive monitoring program is set up for the network of sampling stations and intake points along the river (see Figure 1). The monitoring program currently includes many physicochemical, inorganic and microbiological parameters, but also a wide variety of organic compounds such as polyaromatic hydrocarbons and organohalogen compounds, pesticides and pharmaceuticals. Most substances have a minimum monitoring frequency of 13 times per year. The water quality database now consists of over 1 million measurements divided over 13 monitoring points and 865 parameters. Monitoring results are made available to the public through the RIWA-Meuse website (http://www.riwa-maas.org).

Data selection

Data from eight sampling stations and intake points, located throughout the Meuse river basin (see Figure 1) were used to determine which substances pose a threat to the drinking water function of the river (Van den Berg, 2009). These sampling locations are listed in Table 2.

Table 2. List of main sampling locations

Sampling location	Country	Type of location
Tailfer	Belgium	Intake point
Namêche	Belgium	Sampling point
Liège	Belgium	Sampling point, representative for the intake points *Broechem* and *Lier*
Eijsden	The Netherlands	Governmental border monitoring station
Heel	The Netherlands	Intake point
Brakel	The Netherlands	Intake point
Keizersveer	The Netherlands	Sampling point, representative for the intake point *Gat van de Kerksloot*
Scheelhoek	The Netherlands	Intake point

RESULTS AND DISCUSSION

Substances that threaten the production of drinking water from the river Meuse

A first analysis of the river Meuse monitoring database revealed that many substances fail to comply with the quality targets for surface water from which drinking water has to be produced (Van den Berg et al., 2007). Relevant substances fall into three main categories:

1. plant protection products (mainly herbicides);
2. pharmaceuticals (including x-ray contrast media), and;
3. industrial chemicals.

To make a list of substances threatening the drinking water we have defined the following four testable criteria:

1. the substance is insufficiently (< 40%) removed by simple treatment, for instance physical treatment (aeration, coagulation and rapid or slow sand filtration) and disinfection (with chlorine, ozone, peroxide and/or UV);
2. the substance was observed on at least two sampling locations in the period 2003 – 2008 (for a minimum of three years);
3. the substance was found to exceed the quality standard in the Dutch Drinking Water Ordinance (Dutch government, 2001) or the target value from the Danube, Meuse and Rhine memorandum 2008 (IAWR, IAWD and RIWA-Meuse, 2008) on at least two sampling locations at least once in the period 2003 – 2008 (taking into account possible removal by simple treatment), and;
4. the substance was found to exceed the drinking water standard or the target value from the Danube, Meuse and Rhine memorandum 2008, at least once in the period 2006-2008.

If all criteria are met, a substance is considered to pose a threat to the drinking water function of the river Meuse. Not all substances which fail to comply with quality targets are routinely monitored by drinking water companies and water management agencies. Based on the analysis of Van den Berg et al. (2007) a list of substances which fail the quality criteria and which are not routinely monitored, was composed. These substances were then included in an additional monitoring campaign in 2008. Goal of this survey was to get more quantitative data and show the relevance of these substances for the production of drinking water. Table 3 contains an up-to-date list of substances that threaten the drinking water function of the river Meuse. We recommend that these substances are frequently monitored and measures are taken to reduce their load.

Table 3: Substances that pose a threat to the drinking water function of the river Meuse and their target values from the Danube, Meuse and Rhine Memorandum 2008 (IAWR, IAWD and RIWA-Meuse, 2008)

Substance	Application	Target value
Diuron	Herbicide	0.1 µg/L
Isoproturon	Herbicide	0.1 µg/L
Chloridazon	Herbicide	0.1 µg/L
2,4-Dichlorophenoxyacetic acid (2,4-D)	Herbicide	0.1 µg/L
Aminomethylphosphonic acid (AMPA)	(metabolite of glyphosate and phosphonates)	0.1 µg/L
Carbendazim	Fungicide	0.1 µg/L
Chlorotoluron	Herbicide	0.1 µg/L
Glyphosate	Herbicide	0.1 µg/L
2-Methyl-4-chlorophenoxyacetic acid (MCPA)	Herbicide	0.1 µg/L
Methylchlorophenoxypropionic acid (MCPP)	Herbicide	0.1 µg/L
s-Metolachlor	Herbicide	0.1 µg/L
Metazachlor	Herbicide	0.1 µg/L
Nicosulfuron	Herbicide	0.1 µg/L
Carbamazepine	Anticonvulsant	0.1 µg/L
Diclofenac	Analgesic	0.1 µg/L
Iohexol	X-ray contrast medium	0.1 µg/L
Benzo[a]pyrene	(combustion by-product)	1 µg/L
Methyl *tert*-butyl ether (MTBE)	Fuel additive	1 µg/L
Diisopropyl ether	Solvent	1 µg/L
p,p'-Sulfonyldiphenol	Bulk chemical	1 µg/L
Fluoride	(fertilizer industry by-product)	1 mg/L

In addition to the substances in Table 3, we have also defined substances which may potentially threaten drinking water production. A substance is considered potentially threatening to the drinking water function of the river Meuse if:

- the lack of data excludes the testing of all criteria, but the substance is present in the river Meuse at concentrations well above the threshold value;
- the substance does not meet all criteria, but the concentration is expected to increase due to increased use in the catchment area in the near future (for instance due to a change in usage of pesticides);
- the substance has undesirable properties for the production of drinking water and is expected to be present in the river Meuse (based on research).

Among these substances are various pesticides and their metabolites, x-ray contrast media, painkillers and other pharmaceuticals, endocrine disrupting chemicals (EDCs), industrial compounds, household chemicals and others.

The results from this study are used to make additions to the regular surface water monitoring program. The drinking water companies in the Meuse river basin have now focussed their monitoring activities on the basis of these results. The substances in Table 3 are being measured every four weeks at the relevant sampling locations throughout the river basin. The substances that can potentially threaten the drinking water function of the river Meuse are being measured four times per year at selected sampling stations. These specific measurements are performed on top of the mandatory monitoring programs and the individual companies' own measurements.

Presence of glyphosate and AMPA in the Meuse river basin

One of the substances in the Meuse river basin that frustrates the production of drinking water is the herbicide glyphosate. Weed control on pavements is the largest contributor to high herbicide levels and most of the used products are based on the active ingredient glyphosate (Bannink, 2004). The herbicides are applied by both professional contractors and non-professional users. Figure 2 shows the development of glyphosate levels in the River Meuse at the Keizersveer sampling station in The Netherlands over the past 16 years, based on data from the RIWA Meuse database. This station is located at the end of the River (see Figure 1) and is influenced by almost the entire river basin.

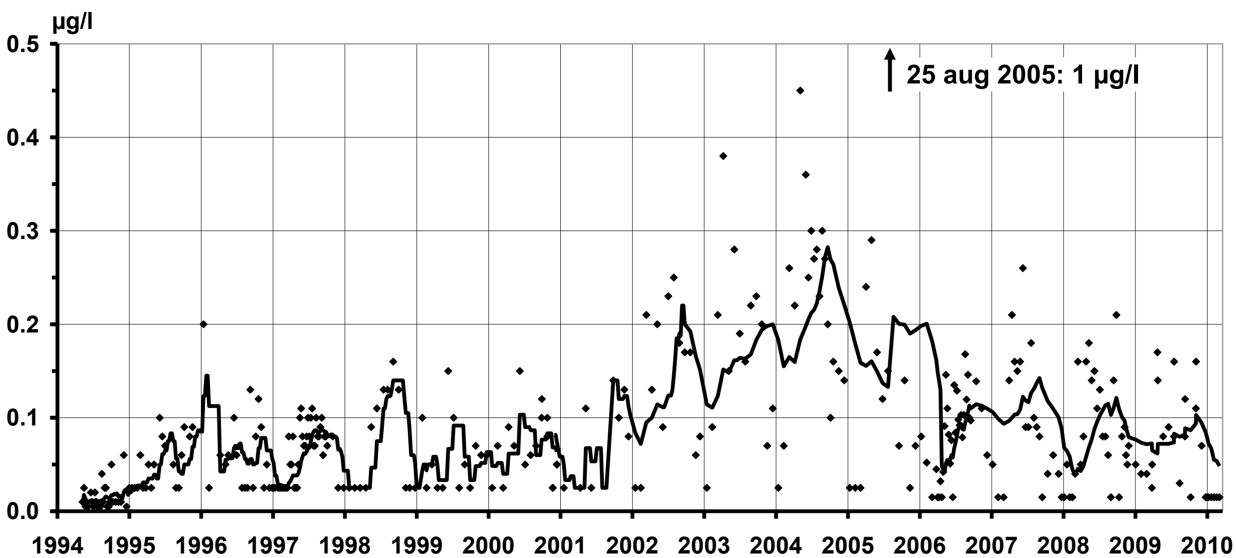

Figure 2: Glyphosate levels [µg/L] in the River Meuse at the Keizersveer sampling station in The Netherlands 1994-2010. The points are the individual measurements and the line represents the floating 12 month average

Two extensive monitoring campaigns were carried out in 2006 and 2008, focussing specifically on the presence of glyphosate and its metabolite AMPA (Volz, 2009). The campaign is being repeated in 2010. The monitoring campaigns of 2006 and 2008 revealed the presence of glyphosate and AMPA throughout the Meuse river basin in levels well above 0.1 µg/L, hindering drinking water production almost continuously.

The monitoring campaigns showed an increase of glyphosate load from tributaries of 87% between 2006 and 2008. WWTPs which discharge to the river Meuse showed an increase of glyphosate loads of 55% between 2006 and 2008. Also it became clear that WWTPs in areas with sustainable weed control projects have a substantially lower load. From the Waalwijk municipal WWTP, where non-chemical weed control on pavements is standard, the load was 0.04 grams of glyphosate per inhabitant per year (g/inh./a). The highest load found at a WWTP was 1.2 g/inh./a, whereas the average load was 0.48 g/inh./a (Volz, 2009).

The monitoring campaigns have also shown that the loads of glyphosate and its metabolite AMPA in the river Meuse originate almost exclusively from urban run-off. The contribution of agricultural sources is minimal even though the use of glyphosate for crop protection exceeds that of urban use many times. After application of the herbicide on paved areas rainfall events cause significant run-off to the sewer system. Since most of WWTPs do not remove glyphosate, the major part of the herbicide that runs off ends up in the effluent of the WWTPs. The monitoring campaigns showed that the contribution from the urban areas in France is the highest when corrected for the number of inhabitants. Also the contributions from the Netherlands, Wallonia and Flanders are considerable, whereas the contribution from Germany is the lowest. Germany has the toughest legislation to control herbicide run-off from paved areas (Kristoffersen et al., 2008), which may explain its low contribution to River Meuse loads.

Relevancy for water management

Based on the results of this study, we suggest the following actions to improve the water quality in the river Meuse basin.

Suggested measures to be taken at the source are:

- Introduce a registration procedure for new (emerging) substances (much like the assessment methodology for plant protection products (including post registration monitoring));
- Reduce the use of (emerging) substances;
- Promote development of less harmful substances and their sustainable use;
  - Regulations on the restricted use of substances;
  - Spray free zones along waterways (reduction of drift);
  - Sustainable weed management of pavements.

Suggested measures to be taken in the water system are:

- Introduce water quality standards for emerging substances that protect the (ecological) environment and functions of the river Meuse (bathing water, drinking water);
  - Pharmaceuticals and many other emerging substances such as MTBE do not have (ecological) quality standards for aquatic environments;
- Decrease the number of sewer overflows and frequency of overflow;
- Improvement of WWTPs;
- Renewal of effluent discharge permits;
  - Decrease number of untreated discharges and sewage overflows;
  - Relate permits for waste water discharge and discharge of industrial effluents to low river flows.

In general, we conclude that it is necessary to increase the capacity of the water system to cope with the autonomous effects of climate change, including:

- Direct effects of climate change on water quality (related to higher temperatures and lower flows);
- Indirect effects of climate change on water quality, interaction with existing human pressures (changing their impacts);
- Risks for non realisation of ecological goals and loss of opportunities for (commercial) use of water from the river Meuse.

With respect to glyphosate and AMPA some specific suggestions are made. The results of the glyphosate and AMPA monitoring campaigns are used by RIWA-Meuse to address this issue with national and regional water authorities in the river basin. Also, projects that stimulate sustainable working methods areas are supported, such as the European sustainable weed management system for pavements (SWEEP). Extensive field tests have shown that weed control under SWEEP guidelines is effective and that when herbicides are used runoff to surface water is reduced. This means that the risks regarding drinking water production from surface water are reduced as well. Key of the system is a number of practical guidelines that enable those responsible for weed control organisation and realisation to define and agree clear arrangements as regards boundary conditions, prevention, use of methods and products, and registration of herbicide use. In 2010 some of the SWEEP guidelines have become mandatory for the use of chemical weed control in the Netherlands.

CONCLUSIONS

We conclude that emerging substances, including many substances that threaten the drinking water function are present throughout the Meuse river basin and should be monitored on a regular basis by water authorities. Sources of emerging substances are diverse (household, agriculture, industry, WWTPs, etcetera) and often diffuse. This requires implementation of measures at regional, national and river basin scale.

ACKNOWLEDGEMENTS

We would like to express our gratitude to the water companies *Vivaqua* (Brussels), *Antwerpse Waterwerken* (Antwerp), *Waterleidingmaatschappij Limburg* (Maastricht), *Dunea* (The Hague) and *Evides* (Rotterdam) and to *Rijkswaterstaat* for making their monitoring data available.

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Emissions Emerging Substances To Surface Water. Source Identification, Loads, Emission Factors and Validation

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Abstract

In the Netherlands, emissions from point sources and diffuse sources to water, soil and air are quantified each year and the data (calculated loads) is made available on multiple geographical levels in the Dutch Emission Inventory system. Research is done in 2009 to expend the inventory by several prior hazardous and emergency substances: 4-nonyl phenols, Polybromic Diphenylether (PBDE, a broom flame retardant), non agricultural use of pesticides, used in urban or paved areas (glyfosaat, 2,4-D and MCPA) and 3 pharmaceuticals (carbamazepine, diclofenac and bezafibrate). For each 4 groups, the sources, emission pathways and emission factors are identified and quantified based on data (f.i. sales figures), literature and measurements. Especially recent measurements at public waste water treatment plants (wwtp) turned out to be very useful. Using those measurements, sound emission factors could be derived for the runoff of pesticides that are used on paved surfaces. Also excretion factors of the studied pharmaceuticals could be validated well, because the average intake could be derived from reliable sales figures. The sources and emission pathways of Nonyl Phenol and PDBE are relatively uncertain, but the diffuse emissions through sewer systems could be related to the available measurements at wwtp. It is recommended that water managers put more effort on measurements of emerging substances, especially in urban waste water. For pharmaceuticals, several pilot studies have started in 2010 in order to identify hot spots and to determine the effect of several measures.

Keywords

emissions diffuse and point sources, emerging substances, pesticides, pharmaceuticals, nonyl phenol, Polybromic Diphenylether (PDBE), mass flow analysis, emission factors, runoff..

INTRODUCTION

In the Netherlands, there's a long history in a nationwide Emission Inventory system. Emissions from point sources and diffuse sources to water, soil and air are quantified each year and the data (calculated loads) is made available on multiple geographical levels, e.g. country, province, river (sub)basins and even smaller regional catchments. The point sources are mostly quantified from annual (obligated) reports and measurements. Diffuse sources are calculated, based on the general principle: Emission = Activity level × Emission factor (E=A*EF). Data on Activities are based on national statistics. Emission factors are based on measurements, modelling results or derived from scientific publications. Information and results are available via http://www.emissieregistratie.nl.

The inventory system was widely used in the Netherlands to make up the river basin management plans for the Water Framework Directive in 2009. To support the follow up of these reports, the Waterdienst (a national service of the Directorate General of Public Works and Water Management (Rijkswaterstaat)) wanted to extend the inventory system with prior hazardous and emerging substances. In cooperation with Deltares and the Waterdienst, Grontmij selected 5 groups of those substances, identified the sources and important emission pathways and calculated the emissions to surface waters in the Netherlands over the last 10 years. In this paper, we explain the methodology of the performed mass flow analysis and present the results.

METHODOLOGY

Although the Emission Inventory System already contained many pollutants (nutrients, heavy metals, PAH, PCB's, pesticides), there's always a demand to expand the data set with new pollutants and new sources. For this study, 5 groups of substances (pollutants) are selected using the following criteria:

- The substance is not included in the Emission Inventory system or important sources are missing
- substances listed on the actual European guideline of priority and hazardous substances, annex II and candidate substances annex III (EU, 2008)
- Substances recently measured in the river basin districts (Meuse, Rhine, Schelde, Eems) above risk values (at a significant number of WFD monitoring sites)
- National and regional water boards and public drinking water companies drew much attention to the substances nowadays (year reports and information obtained by an inquiry)
- There's probably enough information available to estimate the source and validate emission factors.

To select the substances, a extensive database in Excel has been built with up to 235 substances, with for each substance information about the mentioned criteria, including concentration levels in surface and waste water. Following these criteria, 5 groups of substances have been selected. For each of the substances, a desk study was performed, gathering relevant literature, data to assess the amount of usage or production and measuring data. This inventory was supported by interviews with Dutch experts at the Waterdienst, Deltares, Wageningen UR and researchers from the European project Socopse (Socopse, 2009). Based on the results of this desk study, a mass flow analysis was set up. An example of such a mass flow analysis is given in figure 1.

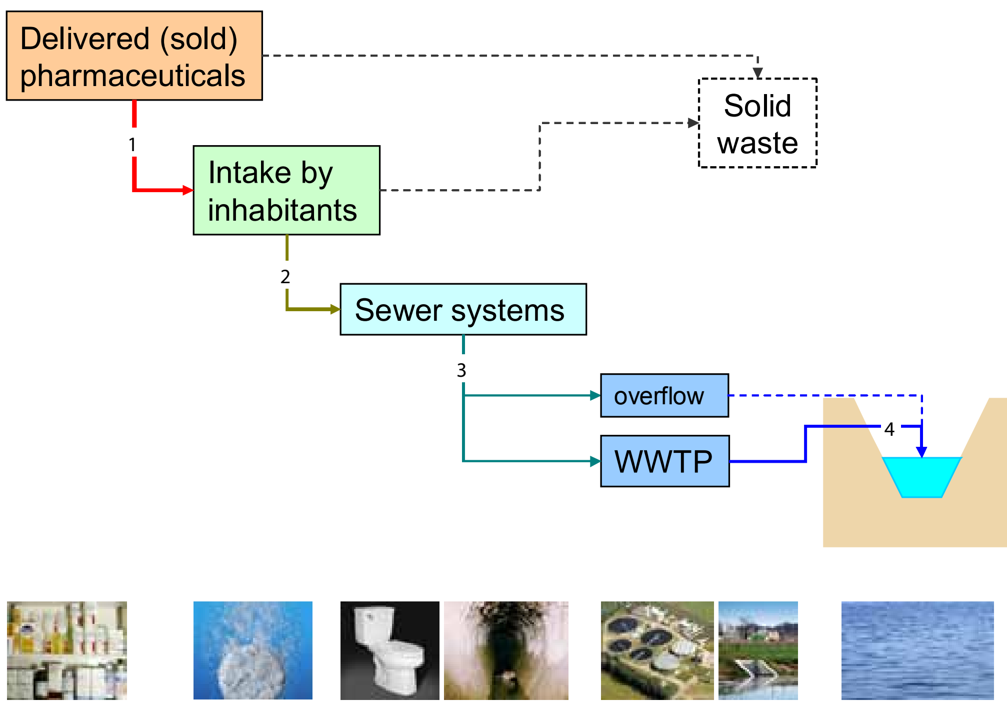

Figure 1. Mass flow of pharmaceutics (carbamazepine, diclofenac, bezafibrate). 1: usage of pharmaceuticals within urban households, health care institutes and hospitals (obtained from the Dutch Foundation for Pharmaceutical Statistics), 2: excrement's (factor for excretion by urine and faces), 3: waste water, 4: loads (emissions) to surface water

First, the amount of product, usage or sales figure are derived from national data and additional recent regional or thematic research. In the case of pharmaceuticals (see figure 1), this information is obtained by the Dutch Foundation for Pharmaceutical Statistics (www.sfk.nl). Subsequent, emission factors from national or international research are applied to calculate loads to waste water and surface waters. We used recent measurements from the inlet of several Waste Water Treatment Plants (wwtp) to validate the emission factors for excretion. For pharmaceuticals, we assumed that spills off not used tablets will end up mostly in solid waste and that subsequent emissions from landfills to surface waters (via leakage to groundwater) can be ignored. If measurements at the inlet and outlet of wwtp are available, an average removal efficiency by wwtp's (for the given substance) is calculated.

The total loads (for all surface waters in the Netherlands) are then calculated for the last 10 years. For each substance, the uncertainties of the calculated loads are classified in line with the methodology of the Dutch Emission Inventory database (in one of the following categories:

a) a value based on a large number of measurements from representative sources;
b) a value based on a number of measurements from some of the sources that are representative of the sector;
c) a value based on a limited number of measurements, together with estimates based on technical knowledge of the process;
d) a value based on a small number of measurements, together with estimates based on assumptions;
e) a value based on a technical calculation on the basis of a number of assumptions.

In order to recalculate the emissions each year, the inventory and calculations are summarized in factsheets which are adopted in the national Emission Inventory System.

RESULTS AND DISCUSSION

The selected substances to calculate the emissions to surface water are:

1. pharmaceuticals: carbamazepine, diclofenac and bezafibrate
2. medical radiographic contrast agents like jomeprol, jopromide and amidotrizoate acid
3. not agricultural use of the pesticides glyphosate (cas no. 1071-83-6), mcpa (2-Methyl-4-chlorophenoxyacetic acid, cas 94-74-6) and 2,4-D (2,4-dichlorophenoxy)acetic acid, cas 94-75-7)
4. nonlyphenol (cas no. 104-40-5 and 25154-52-3)
5. pentabromodiphenyl ether (PDBE, cas no. 32534-81-9 a brominated flame retardant)

Pharmaceuticals. The amount of usage (intake by inhabitants) was derived from quite reliable statistics from the Dutch Foundation of pharmaceutical statistics. These amounts include an estimated 0,5 % prescription by hospital pharmacies. Excretion factors (the percentage of the intake by a humans that leaves the body via urine and faces) can be found in several scientific literature. We used the excretion factors mentioned in Lienert (2008), because these factors are statistically derived from a extensive database with samples, selected from many pharmaceutical literature. The results of the mass flow analysis for the year 2008 are summarized in table 1. The loads are calculated per person using the formula: Emission = EVV * EF, with EVV is the number of inhabitants (around 16,4 million) and EF is the emission factor per inhabitant, calculated as the average intake per inhabitant multiplied by the excretion factor. In this way, the loads can be easily calculated and spatially distributed within the national emission inventory system like the emissions using spatial information about inhabitants per ha. The emission factors are more or less in line with the measurements from wwtp, however, it must be noticed that the available number of samples used to validate the emission factors was limited (4 wwtp, 3 to 4 samples of the inlet and outlet per wwtp) and concentrations are sometimes below detection limits (especially for bezafibrate). So, this validation only gives an impression of the magnitude of the emission factors. Since several pilot studies on pharmaceuticals in water have started in 2009 and 2010, soon (much) more measurements will become available and the validation of emission factors and calculation of removal efficiencies can be refined.

Table 1. Results of the mass flow analysis for pharmaceuticals for the year 2008

	Unit	Carbama-zepine	Bezafibrate	diclonenac
Prescribed amount pharmaceutics	$kg.year^{-1}$	8897	300	5278
Average intake inhabitants*	$mg.person^{-1}.year^{-1}$	542	18,3	322
Excretion factor (Lienert 2007)	-	0,12	0,51	0,16
Loads per person	$mg.person^{-1}.year^{-1}$	65,1	9,3	51,5
Average removal efficiency wwtp	%	0 %	? / 0%	0 %
Total emission to surface water	$kg.year^{-1}$	1068	153	844
Classification uncertainties	classification a–e (see methode)	C	D	C

* based on the total population in the Netherlands, in 2008 16,4 million inhabitants

Medical radiographic contrast agents: The idea was to analyze the mass flow in the same way as the pharmaceuticals. But, the SFK doesn't gather sales figures of pharmacies in hospitals, and the usage in hospitals is far more important then the use outside hospitals. Pharmacies in hospitals don't have a central registration of the use of pharmaceutical and contrast agents. It could be possible to obtain these statistics from wholesales (only 3 in the Netherlands), but this was not possible within this study. If available, it must be taken into account that the prescribed amounts should be specified per hospital preferably, because each different hospital has it's own preference in their use of different kinds of medical radiographic contrast agents. Another important aspect is the delay between intake and excretion. This can easily be days and many patients leave the hospital within this period after the radiographic tests.

Pesticides: the amount of not agricultural usage on paved and public areas was investigated by the Wageningen UR (Kempenaar et al, 2009). This estimation resulted in an estimated usage of glyphosate of 0,25 $kg.ha^{-1}$ in 1998 and 0,38 $kg.ha^{-1}$ in 2008, with an estimated uncertainty of ± 20 %. The percentage of the used pesticides that will disperse to surface waters by surface runoff was yet unknown, although source identification studies pointed out that the route via sewer systems is most important (Beltman, 2006, Volz 2009). Using actual measurements at he inlet of up to 11 wwtp and the estimated usage within the connected paved area, an actual emission factor for runoff is derived. And in addition, also the removal efficiency of waste water treatment plants are derived from measurements on the in- and outflow of those plants (measured on the same event / day). Figure 2a (left) shows the used measurements on glyphosate and ampa. Figure 2b (right) shows the loads at the inlet of the 11 wwtp, calculated from measurements (x-axis) compared to loads calculated using the estimated usage on paved urban areas (kg.ha paved area), the paved surface that is connected to the wwtp (ha) and the emission factor for runoff. This emission factor is set upon 0,086 (8,6 % of the used pesticide is emitted by runoff to the sewer system), which is in line with the expectations of experts at the WUR and RIVM who are involved in the authorisation and evaluation of pesticides and the development of specific policy on sustainable weed control on pavements. It must be noticed, that the amount of usage varies through the years significantly because of (inter)national legislation. For instance, till 2008 Dichlobenil was used for weed control widely in the Netherlands but is banned in 2008, which will probably the use of a (new) alternative pesticide. And since January 2008 professional application of glyphosate is restricted in the Netherlands in such way, that application is only permitted following the guidelines of Sustainable Weed Control (www.dob-verhardingen.nl). If implemented, this would theoretically result in much less emissions to sewer systems and surface waters. So the emission factor for runoff of pesticides must be interpreted as a snapshot.

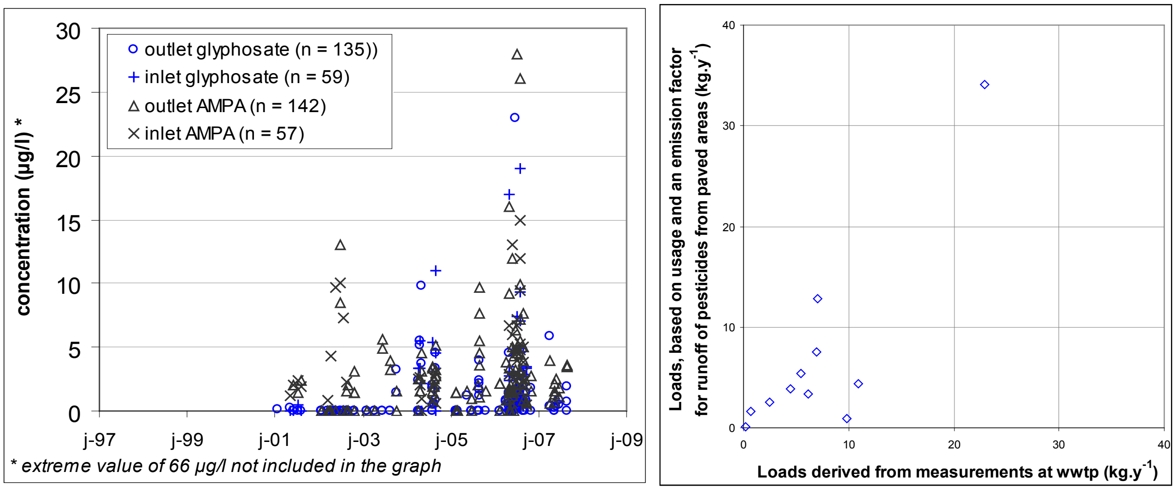

Figure 2. measurements at the influent of urban wastewater treatment plants (left) and paired measurements (influent on the x-axis and effluent on the y-axis, both measured at the day)

Nonyl phenol and PDBE: For these prior substances, much information from the European project Socopse was adopted. Point source emissions from industry have been important, because nonyl phenol is widely used for the production of the half fabricate nonyl phenol etoxylate. Important diffuse sources for nonyl phenols are households (application in many cleaning products), road runoff (wear of tires) and shipping (especially by the use of detergents). The emissions from households could be derived from many measurements at the inlet and outlet of wwtp. The calculated emissions from households in the Netherlands is about 475 kg.year^{-1}. The reliability of the emissions of nonyl phenols from households is classified in category D. Since 2004 the application of nonyl phenol and nonylethoxylaten in products is strongly restricted by the EU-guideline 2003/53/EC; application in many products like paint, pesticides and industrial degreasers is only allowed in concentrations below 0,1 %. Therefore, emissions have been diminished in time and will diminish further more.. For PDBE, the estimated loads remain quite uncertain, because emission pathways outside households are significant and there are hardly adequate measurements to quantify those. But like nonyl phenol, the emissions will diminish in time because application of this substance is nowadays totally banned. Much of the Nonylphenols and PDBE is removed at wwtp, especially by adsorption on the purification sludge (de Boer 2003, STOWA 2003); an average removal efficiency of 78 % and 90 % is calculated for respectively nonyl phenol and PDBE.

CONCLUSIONS

Emerging substances are measured in many surface waters. Effective measures can only be identified if sources, emission pathways and loads are well known. The study has resulted in a first quantification of emissions of pharmaceuticals to surface waters in the Netherlands and an important improvement of former estimations of diffuse emissions from (not-agricultural) application of pesticides on paved areas. Recent measurements at wwtp and especially samples of the inlet of wwtp turned out to be very useful to quantify these diffuse emissions. We recommend to continue these kind of measurements, not only at inlet of public wwtp, by preferably also at specific monitoring points in the urban sewer system that represent different types urban waste water (old town centres, suburban / new urban areas, business parks, industrial areas etc). We also recommend to build up national and international databases with these kind of (expensive) measurements, in order to support diffuse emission inventories and subsequent the evaluation of policy measures.

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6 MODELLING, MONITORING AND ANALYTICAL METHODS

Analysis of Non-point Source Pollution for Land Use Change at Kyoungan Watershed, Korea

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Abstract

Long-Term Hydrologic Impact Assessment (L-THIA) was applied at Kyungan watershed to analyze temperal and spatial change of surface runoff and nonpoint source pollution loads resulting from urbanization with regionalized L-THIA parameters, such as CN and EMCs values. Two simulation exercises were carried out to evaluate modelling performances associated with two different land use conditions. Although respectively, both simulations for 1981-1990 and for 1995-2005 with 1985 and 2000 land use condition showed high Nash-Sutcliff coefficient over modelling periods (0.93 for 1981-1990 simulation and 0.92 for 1995-2000 simulation), other hydrological behaviours differ. The average surface runoff was increased by 26.7 percent (163.4 mm/yr) for 1995-2005 as opposed to 119.7 mm/yr for 1981-1990). Also, significant amount of Non-point source pollutant loading were increased between two simulation periods. The average loadings were 12.4 BOD kg/ha, 2.8 TN kg/ha, and 0.43 TP kg/ha for 1981-1990 and 29.4 BOD kg/ha, 6.4 TN kg/ha, and 0.95 TP kg/ha for 1995-2005.. It appears that the rapid urbanization results in increasing surface runoff and non-point source pollution loadings over simulation periods.

Keywords

L-THIA, Non-point source, surface runoff, distributed model

INTRODUCTION

South Korea is currently in state of much urbanization due to rapid economic development and population increase since 1960s. In 2005, South Korea's urbanization rate is 89.5% with the highest level in the Organisation for Economic Co-operation and Development (OECD) countries and it has been continuously increasing trend of urbanization rate ever year (Lee, 2006). Rapid urbanization affects local hydrology such asbaseflow reduction due to increased impermeable land segments and more frequent environment perturbation (e.g. flood, soil erosion, and water quality (Lee et al., 2008). Also, the urbanization may accompany land use changes, hydrologic impact changes, and non-point source increases. In recently, non-point source pollution has been recognized as major source of water pollutants in South Korea. Non-point source pollution is released into the watershed so that it causes water quality problems, leading to a variety of pollution, degradation of water functions driven by eutrophication. However, it is challenging to estimating and managing non-point source pollutant loadings not only because it depends on characteristics of rainfall, but also it is the large seasonal and regional variation (Ministry of Environment, 2004). Non-point source pollution management measures have been established to reduce non-point source loadings and improve water quality for four major rivers, including Han River, Nakdong River, Youngsan River, and Gum River, in Korea (Ministry of Environment, 2003).

Since evaluating non-point source pollution in spatial and temporal domain is critical exercise in non-point source management, various watershed models have been developed and applied in watershed scale, especially for the United States(US

EPA, 1997). Long-Term Hydrologic Impact Assessment (L-THIA), in particular, is one of the distributed watershed models based on Arc-View GIS environment and it's applicapability has been evaluated to estimate surface runoff and non-point source pollutant loadings in many watersheds around world. Jeon et al. (2009) and Kim et al. (2009), for example, regionalized CN and EMCs values as the L-THIA parameters, respectively, and evaluated applicapability of L-THIA to Korea.

In this study, L-THIA with identified parameters, was applied to the Kyungan watershed which has been urbanized rapidly in Korea. The results of different two simulation periods, which were 1981-1990 with 1985 land use and 1996-2005 with 1990 land use were compared to analyze the effect of urbanization on the change of temporal and spatial distribution of non-point source pollution.

MATERIAL AND METHODS

L-THIA

L-THIA was developed by Purdue University to evaluate the long term effects of land use change such as urbanization on surface runoff and non-point source pollutant loading (Engel, 2005). L-THIA is based on different two environments: ArcView and Web version. L-THIA employing the event mean concentrations (EMCs) coefficient and curve number (CN) methods to estimate pollutant loads and surface runoff, respectively.

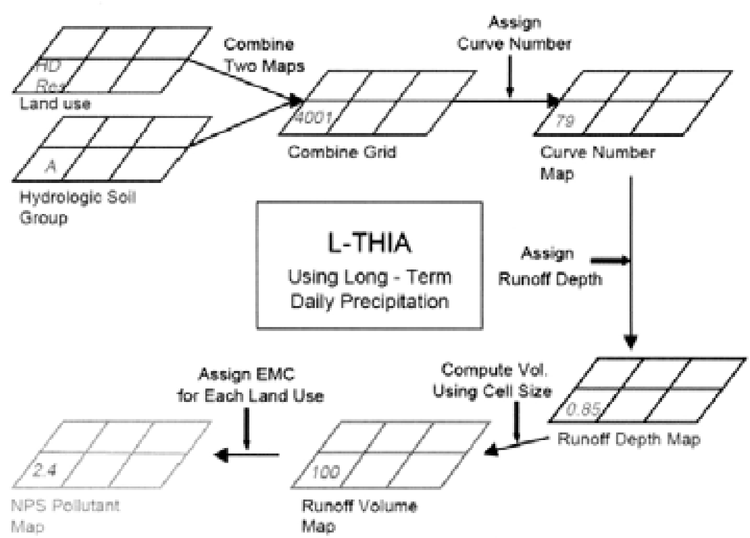


Figure 1. Procedure of L-THIA (Lim et al., 2006)

Study area

Kyungan watershed is located at Gyeonggi-do Youngin-si and Gwangju-si and Kyungan stream is first tributary of Han River formed (Fig. 2). Watershed area, average width, channel length, and average stream slope are 557.85 km^2, 170 m, 49.5 km, 1/720, respectively. Kyungan watershed has been urbanized resulting from economic growth and residential development. Furthermore total-nitrogen (T-N) or total-phosphorous (T-P) overflow from non-point source is affecting eutrophication in Paldang lake which is major source of water supplies to Seoul, Korea. In addition, disposed suspended solids on the bottom of Kyungan stream are flowing into the Paldang lake during the rainy season (Kim et al., 2002).

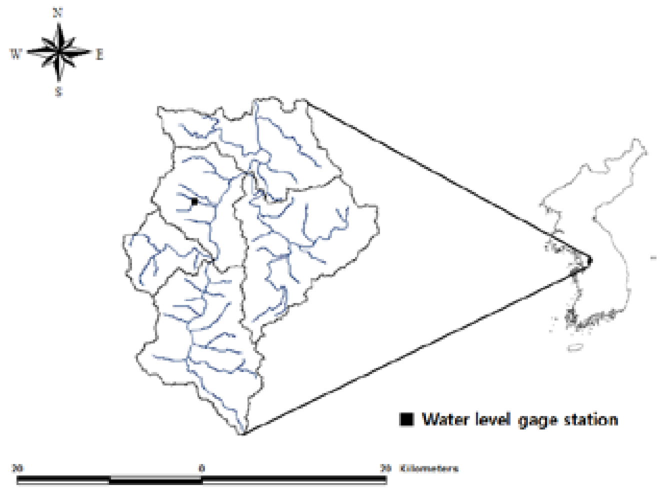


Figure 2. Location of Kyungan stream.

L-THIA model input data

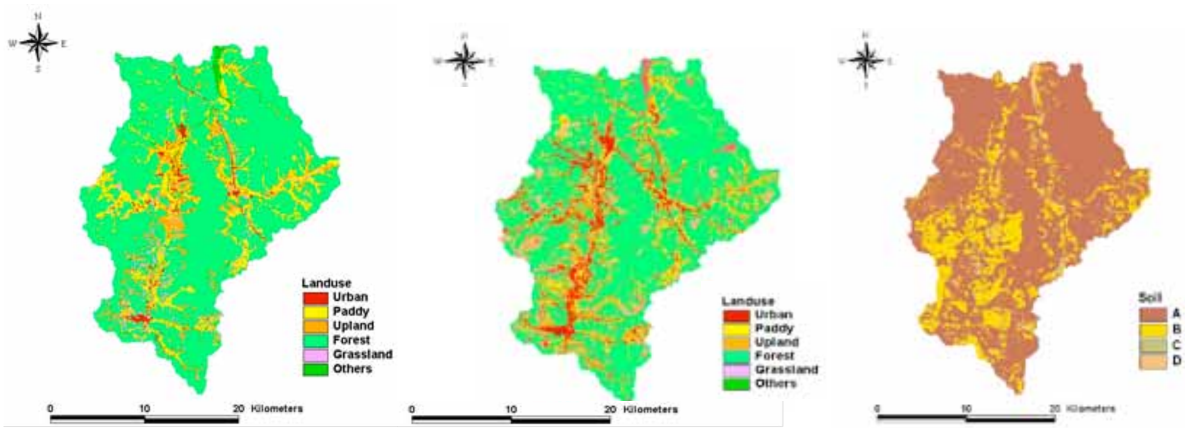
Daily rainfall and observed stream flow data were obtained from Korea Meteorological Administration (KMA) and Water Management Information System (WAMIS), respectively, during 1981-2005. Daily stream flow was separated to obtain the direct surface runoff by Web-based Hydrograph Analysis Tool called WHAT (Lim et al., 2005) because L-THIA simulates direct surface runoff. The WHAT is now available at http://pasture.ecn.purdue.edu/~what/. Spatial distributions of land cover for 1985 and 2005 as GIS grid format were downloaded from WAMIS website at http://www.wamis…(Fig. 3-a and 3-b). Kyungan watershed was used be a traditional non-urban area based on land use type data of 1985 and major land use type was forest area showing 72.2% of total area. Urban area of 2000 is about four times higher than that of 1985. Hydrologic soil group layer divided into four categories was provided by National Academy of Agricultural Science (Fig. 3-c). The characteristics of hydrologic soil allows the watershed to drain well, more infiltrate rainfall into soil, and less runoff.

Table 1. Land use change from 1985 to 2000 (unit: km^2)

	Urban	Paddy	Upland	Forest	Grassland	Others
1985	9.86	72.50	47.71	405.21	18.37	7.43
2000	39.28	51.71	42.70	361.60	46.10	19.71

Table 2. Classification of hydrologic soil group (HSG) (unit: km^2)

	HSG-A	HSG-B	HSG-C	HSG-D
Area	425.72	117.94	6.67	10.79



(a) Land use (1985) (b) Land use (2000) (c) Hydrologic soil group

Figure 3. Kyungan stream watershed.

Modeling method

Different two 10-year-simulation results were compared to analyze the effect of urbanization to runoff and non-point source loading from Kyungan watershed. A simulation for 1981-1990 was first carried out with 1985 land use condition and the second simulation for 1996-2005 was then conducted based on 2000 land use profile. Next, regionalized L-THIA parameters shown in Table 3 were employed to evaluate model performance between simulated and observed monthly runoff using Nash-Sutcliff (NS) coefficient and a 1:1 scatter plot to validate regionalized CN values.

Table 3. Regionalized L-THIA parameters

	Hydrologic soil group*				EMCs**		
	A	B	C	D	BOD	TN	TP
Residential	89.1	92.5	94.4	95.4	53.00	11.42	1.62
Industrial					13.34	4.01	0.31
Commercial					68.54	11.29	1.69
Leisure	92.8	94.9	95.9	96.5	14.00	1.26	0.28
Transportation					54.81	5.07	0.58
Public building					10.15	4.19	0.63
Paddy	69.1	78.5	85.8	88.9	8.39	3.93	0.28
Upland	69.1	83.1	90.6	93.9	19.21	2.21	0.82
Greenhouse					4.60	2.70	4.00
Orchard	69.0	83.1	90.6	93.9	3.55	4.78	0.59
Other crop					4.24	4.58	0.42
Deciduous forest	36.9	58.5	67.5	72.9	2.70	0.68	0.03
Coniferous forest	45.1	71.4	82.4	89.0	2.90	0.23	0.07
Mixed forest	41.3	65.4	75.5	81.5	1.11	0.23	0.04
Pasture					0.50	0.70	0.01
Golf course	51.7	72.8	83.3	88.6	9.00	1.29	1.33
Other grass					0.50	0.70	0.01
Wetland					4.00	1.38	0.08
Mining area	48.3	65.0	74.3	78.0	6.66	1.53	0.21
Other barren					1.50	1.25	0.05

* Source: Jeon et al. (2009)
** Source: Kim et al. (2009)

The Nash-Sutcliff coefficient is defined below (Nash and Sutcliff, 1970).

$$\mathrm{NS} = 1 - \frac{\sum_{i=1}^{n} (Q_{obs,i} - Q_{sim,i})^2}{\sum_{i=1}^{n} (Q_{obs,i} - \bar{Q}_{obs,i})^2}$$

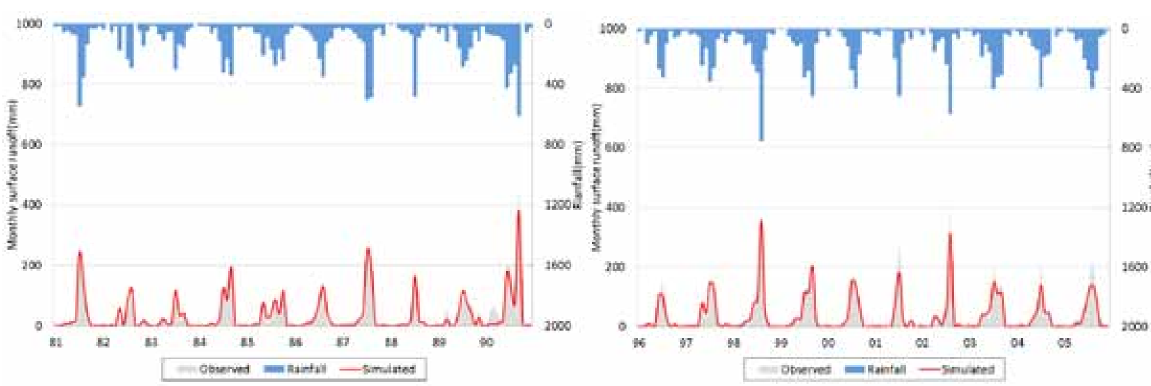
where, Q_{obs} is the observed direct monthly runoff, Q_{sim} is the simulated direct monthly runoff, and $\bar{Q}_{obs}$ is average observed direct monthly runoff. If the simulated and observed values are same, NS is 1.0.

RESULTS AND DISCUSSION

The performance of the regionalized L-THIA parameters is statistically and graphically shown in Table 3 and Figure 4 and 5, respectively. The simulated monthly surface runoff is well matched with observed data with showing high model efficiency.

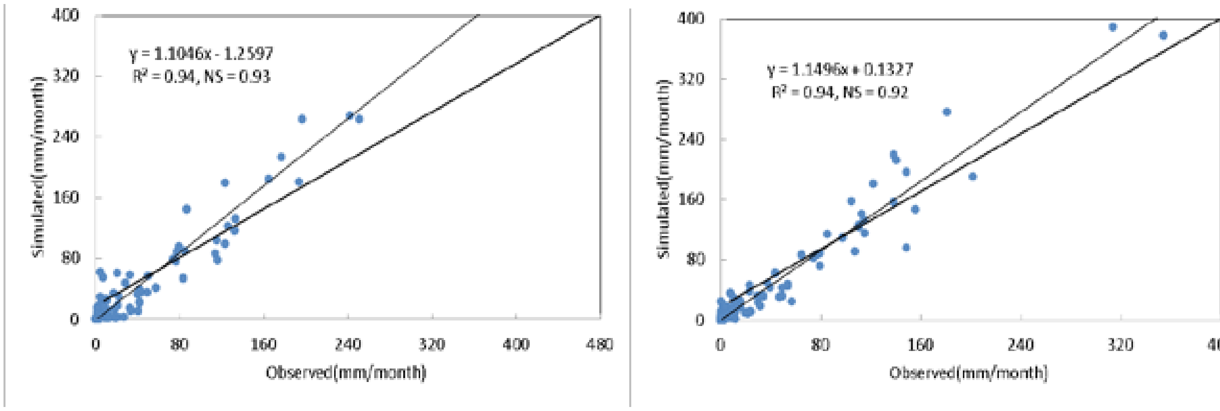
Table 3. Nash-Sutcliff coefficients for two different simulations

	1981~1990	1996~2005
NS	0.93	0.92
R^2	0.94	0.94



(a) (b)

Figure 4. 1985 (a) and 2000 (b) results for monthly surface runoff.



(a) (b)

Figure 5. Scatter plots of monthly runoff between observation and simulation during 1981-1990 (a) and 1996- 2005 (b)

The temporal changes of annual surface runoff and non-point source pollutant loading between 1981-1990 and 1996-2005 are shown in Table 2 and Figure 6. The urbanization could increase surface runoff and non-point source pollutant loading and increased level of pollutant loadings was much higher than that of surface runoff. Annual surface runoff from Kyungan watershed is about 119.69 mm during 1981~1990 and about 163.40mm during 1996~2005. Significant amounts of non-point source pollutions were loaded from Kyungan watershed resulting from rapid urbanization. Non-point source pollutant loadings were 12.44 BOD kg/ha, 2.76 T-N kg/ha, and 0.43 T-P kg/ha for simulation of 1981~1990 and 29.41 BOD kg/ha, 6.36 T-N kg/ha, and 0.95 T-P kg/ha for simulation of 1996-2005. Nonpoint source pollutant loading during 1996-2005 was two times higher than that during 1981-1990.

Table 4. Simulation results of non-point source load by L-THIA.

	1981-1990	1996-2005	Increasing rate
Runoff (mm/yr)	119.69	163.40	37%
BOD (kg/hr/yr)	697,206	1,616,349	132%
T-N (kg)	154,466	349,590	126%
T-P (kg)	24,039	51,988	116%

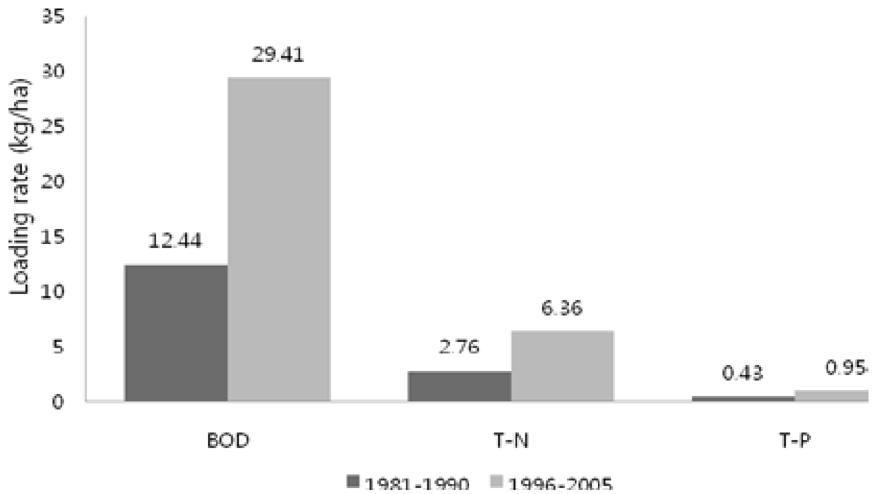
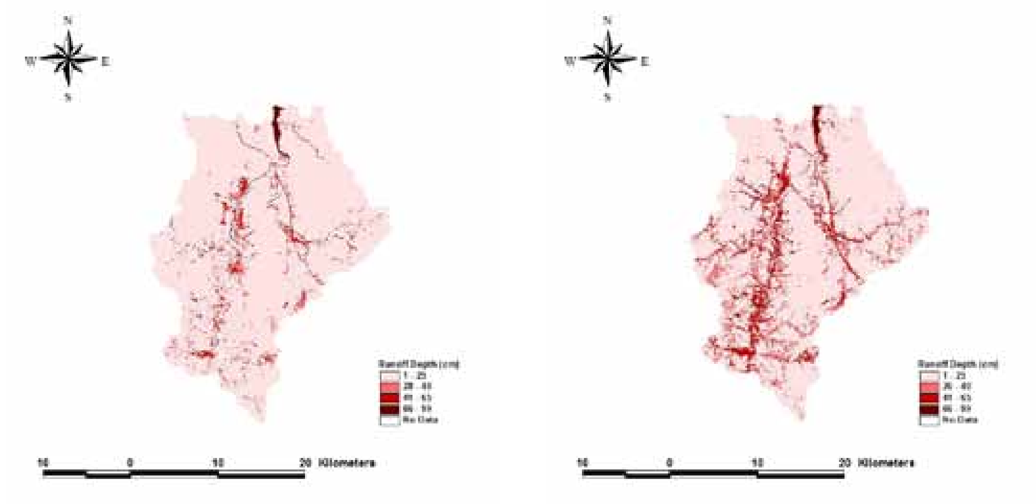


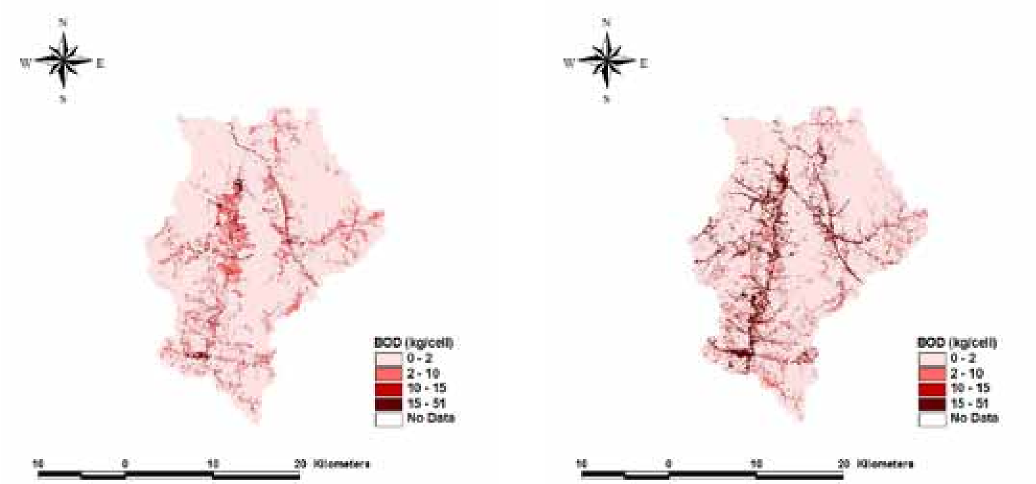
Figure 6. Temporal change of non-point source pollution loading from study area.

Comparison of spatial distribution of annual surface runoff and non-point source pollutant loading was shown in Figure 7. Compared with land cover of 2005 (Figure 2-b), it is clearly showed that urban area was dominated by increased surface runoff and pollutant loading. Note that the study area drains well into soil because most of soil were hydrologic soil A group as shown in Table 2, therefore urbanization of study area more influenced on increasing surface runoff due to the increased impervious area. It appears that increased rates of non-point source loadings can be accelerated by increased runoff driven by much higher increased EMC of pollutant.

1981-1990 **1996-2005**



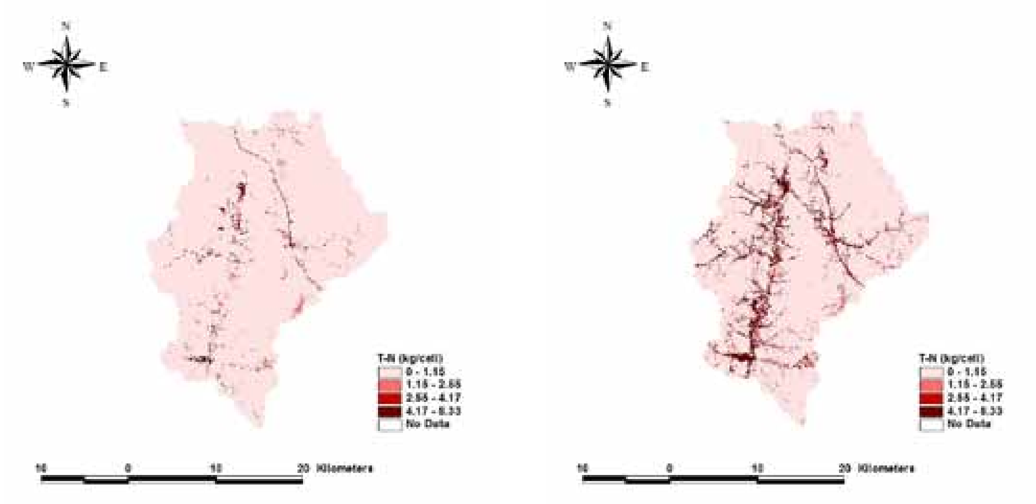
(a) Surface runoff



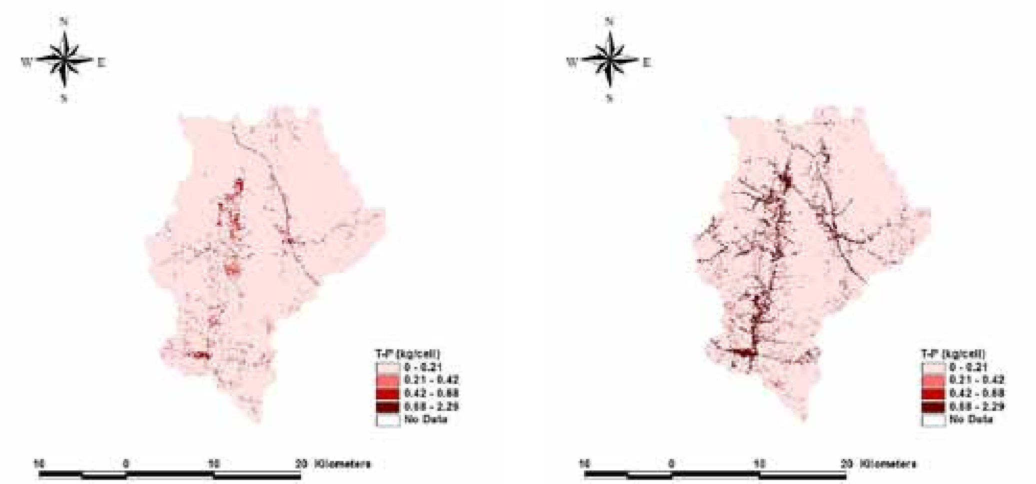
(b) BOD

Figure. 7. Comparison of spatial distribution of non-point source pollution loading between during 1981-1990 and 1995-2005.

1981-1990 **1996-2005**



(c) T-N



(d) T-P

Figure. 7. Comparison of spatial distribution of non-point source pollution loading between during 1981-1990 and 1995-2005. (suite)

Conclusion.

The temporal and spatial chances of surface runoff and non-point point source pollutant loadings from Kyungan watershed, Korea, were analyzed using L-THIA by comparison of different two 10-year simulations which were 1981-1990 with land use of 1985 and 1996-2005 with land use of 2000. Regionalized L-THIA parameters in Korea were used in this study. The simulated monthly surface runoff showed good agreement with observed surface runoff with showing 0.93of NS coefficient for the simulation period of 1981~1990 and 0.92 for 1996~2005. The regionalized CN value was well applicapable to Kyungan watershed. Surface runoff was increased from 119.69 mm/yr for 1981~990 to 163.40 mm/yr for 1996-2005. The non-point source pollutant loadings were 12.4 BOD kg/ha/yr, 2.8 TN kg/ha/yr, and 0.43 TP kg/ha/yr for 1981-1990 and 29.4 BOD kg/ha/yr, 6.4 TN kg/ha/yr, and 0.95 TP kg/ha/yr for 1995-2005. Pollutant loadings during 1996-2005 were about four times higher than those during 1981-1990. The magnitude of increased nonpoint source pollutant loading was much higher than that of increased surface runoff. The result shows that the regionalized L-THIA parameters improve simulation performance of L-THIA in the study area so that it can be also widely applicapable into other watersheds. Advantage of L-THIA is identify critical areas of non-point source pollutant loading, where such area is in the urbanization progress

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Modelling catchment scale recovery from diffuse pollution

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Abstract

A modelling study has been undertaken in an agricultural catchment in the east of Scotland to identify key processes determining nitrate pollution and to evaluate how the nitrate signal in the catchment might respond to changes in land use over time. The model has been constructed based on a range of hydrometric, tracer and hydrochemical monitoring data. Model simulations indicate that full recovery of nitrate concentrations in the groundwater could take many years following changes in land use or management. Scenarios of land use change reveal the scale of management changes required to achieve suitable reductions in nitrate leaching.

Keywords

Groundwater; land use; model; nitrate; recovery; tracer;

INTRODUCTION

Significant areas of agricultural land in eastern Scotland have been designated as Nitrate Vulnerable Zones (NVZ) under the requirements of the EU Nitrates Directive. Agricultural sources have been identified as the single most important cause of diffuse pollution by nitrates in Scotland (Scottish Environment Protection Agency, 2007) and agricultural activities in NVZs are subject to an Action Programme of Measures (Scottish Statutory Instrument, 2003), based on implementation of good agricultural practice. The effectiveness of these measures depends partly on catchment hydrology and groundwater dynamics. Because of the wide ranging activities that take place in catchments, the natural temporal variability inherent in hydrological processes, and the fact that responses to changes may not be instantaneous, it can be very difficult to evaluate the success of specific measures in terms of catchment recovery (Novotny, 2005). Modelling tools can be used to assist with this evaluation providing they are capable of representing the relevant catchment processes. This includes consideration of the time-scales that may be required for changes to be observed in surface and groundwater, a factor that is often poorly represented in catchment models (McGuire and McDonnell, 2006), yet which can be significant for underpinning expectations of changes (Jiang and Somers, 2009).

OBJECTIVES

The objective of this research was to develop a conceptual model of hydrology and nitrate transport through surface and groundwater pathways in an agricultural catchment in eastern Scotland using a learning framework approach. The purpose of the model was to provide a tool for simulating future catchment recovery from diffuse pollution taking into account potential lags in the system response. This approach involved developing hypotheses of behaviour through an iterative process of data interpretation, model development and application (Dunn et al., 2008). In particular, the method utilised data from a field monitoring programme to underpin the model conceptualisation. The development and application of the model are presented in this paper and its practical utility is demonstrated through an analysis of simple land use change scenarios.

STUDY AREA

The study was undertaken in the catchment of the Lunan Water, which drains an area of 134 km^2 from its source near the town of Forfar to the North Sea at Lunan Bay (Figure 1). The Lunan is a lowland agricultural catchment with a maximum elevation of 250 m, but with most of the area lying along a flat broad valley. Typically, 77 % of the area is used for arable agriculture with crops such as spring barley, winter wheat, and winter barley covering the largest areas. The remainder of the land use is mainly forestry and grassland with only a few small settlements. Average annual rainfall for 2000-2008 was 820mm, quite uniformly distributed throughout the year and annual evapotranspiration is around 400mm. The main stream of the Lunan Water is gauged at Kirkton Mill (122 km^2), where the average annual runoff for 2000-2008 was equivalent to 467 mm.

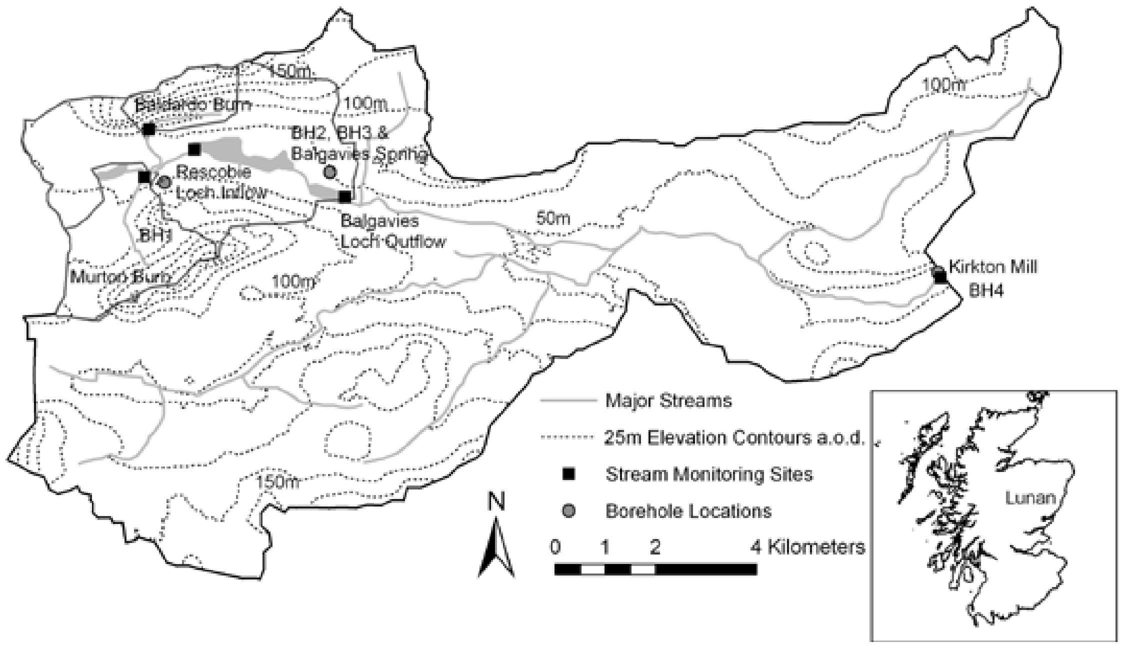

Figure 1. Map of the Lunan catchment showing major streams, topography and locations of monitoring sites

The catchment is underlain by Lower Devonian Sandstone with two principal formations present. The Dundee Formation has been classed as a highly productive aquifer and supports a combination of intergranular and fracture flow (Browne et al., 2001, Ó Dochartaigh et al., 2006). The Montrose Volcanic Formation has been classed as an aquifer of low productivity where fracture flow dominates (Browne et al., 2001). Relatively freely draining podzols and brown forest soils have developed on glacial till over much of the catchment and these facilitate groundwater recharge. However around 30% of the soils are gleyed with impeded drainage. Many soils have been under-drained to improve their agricultural potential.

Hydrology and Nitrate Processes

A conceptualisation of hydrological processes in the Lunan catchment has been presented by Birkel et al. (2010 a and b). This highlighted three important characteristics of the hydrology: occurrence of groundwater recharge leading to a water balance deficit in the upper catchment (Figure 2a); rapid transfer of a fraction of incoming rainfall during high flow events as evidenced by isotope time-series (note sharp fluctuations in stream isotope content that correspond with fluctuations in incoming precipitation during high flow events, Figure 2a and b); and mixing of runoff in the upper catchment loch system as evidenced by isotope (not shown) and hydrochemical data (Figure 2d).

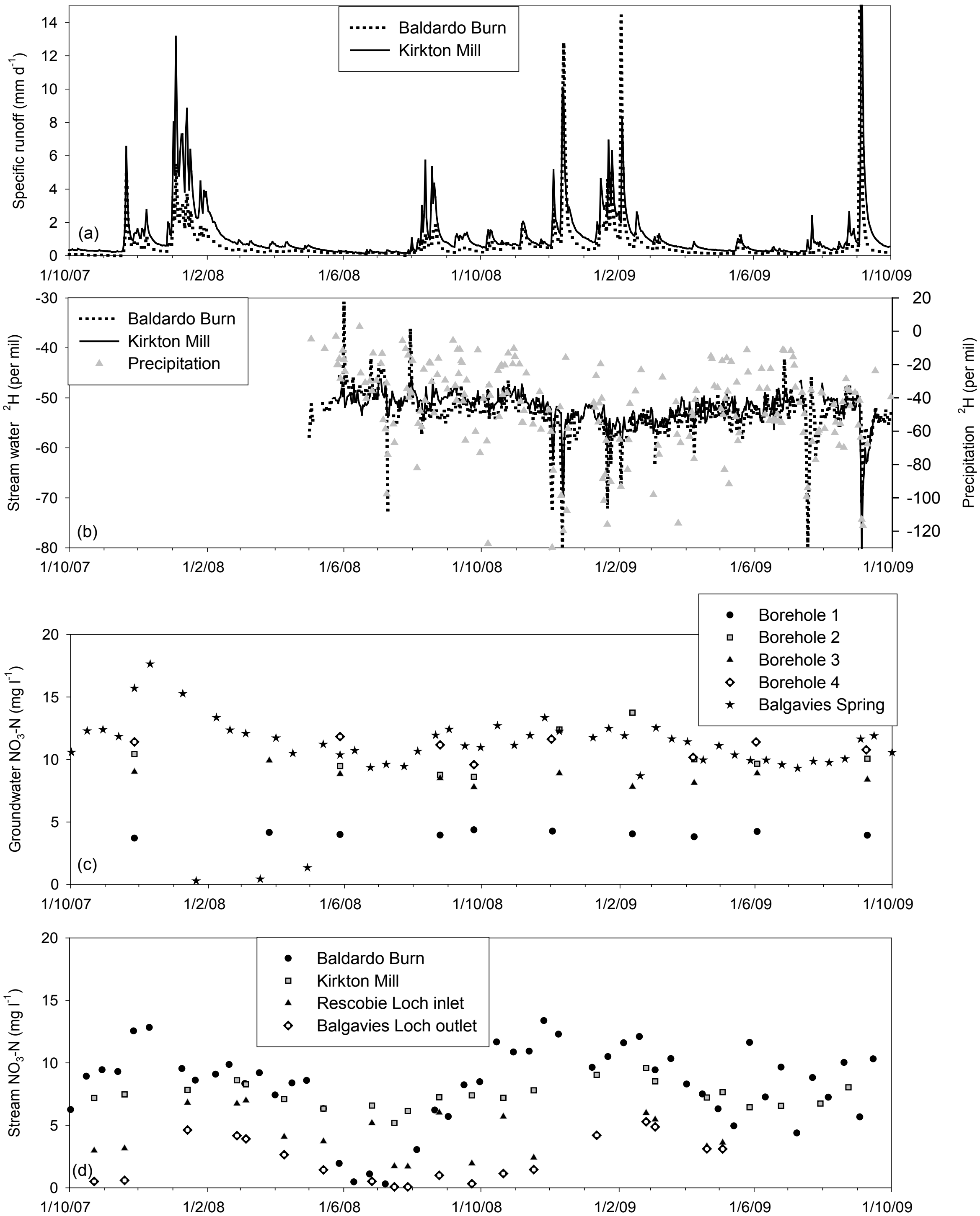

Figure 2. Monitoring data from the Lunan catchment including (a) specific discharge, (b) daily δ ^{2}H measurements from precipitation and stream water, (c) groundwater nitrate concentrations and (d) stream nitrate concentrations

The Lunan catchment was designated as a Nitrate Vulnerable Zone (NVZ) in 2002 because of high concentrations of nitrate in groundwater (Figure 2c). An investigation of characteristic groundwater ages has been undertaken using measurement of dissolved atmospheric trace gases, chloroflurocarbons (CFC) and sulphur hexafluoride (SF_6) in five boreholes and one groundwater spring (Dunn et al., 2010, Dunn et al., submitted). The boreholes have all been drilled in the Dundee Formation; two previous boreholes drilled in the Montrose Volcanic formation were abandoned due to insufficient yield. The data from the dating study were interpreted by applying a lumped dispersion model to simulate groundwater transport and showed that mean tracer transit times varied from recent to greater than 100 years. The site with the longest mean tracer transit time was Borehole 1, where low groundwater nitrate concentrations were also measured (Figure 2c). An increase in nitrate concentrations might be expected at this location in the future as greater proportions of water recharged during the 1970s and 80s arrive. No relationship was found between the depth of groundwater sampled (between 12 and 37m for the various boreholes) and either nitrate concentration or estimated mean transit time.

Surface water monitoring highlights heterogeneity in nitrate concentrations (Figure 2d) and in-stream processes, such as uptake and de-nitrification, occur within the loch system resulting in lower concentrations at the outflow of Balgavies Loch compared with the loch inlet. Downstream, nitrate concentrations at Kirkton Mill are much higher.

MODELLING

The final conceptualisation of the key catchment processes represented in the model is illustrated in Figure 3 and described below.

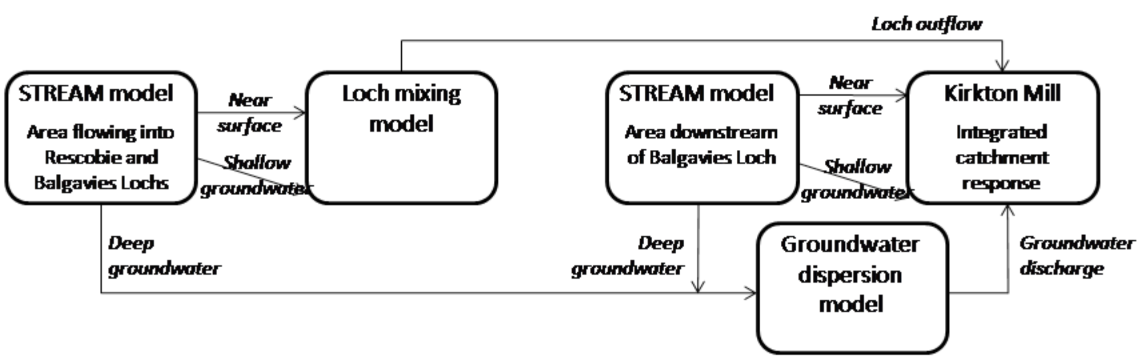

Figure 3. Model components linked to form integrated model of the Lunan catchment

Hydrology Model

A catchment model has been constructed from a combination of the STREAM model (Dunn et al., 2007) to represent key runoff generation processes, a simple loch mixing model, and a lumped dispersion model for groundwater transport. The STREAM model is semi-distributed, with topographic and other physical data allocated on a grid cell basis (50 m resolution) and applied using a daily time-step. It includes three separate flow paths: near surface storm response, sub-surface / shallow groundwater flow and deep groundwater recharge. Water transported by the near surface flow pathway is routed rapidly to surface streams via macropore and drain flow, whilst sub-surface / shallow groundwater flow represents a "hillslope" runoff, with flow routed to streams according to the local topographic gradient and directions. Equations describing these runoff mechanisms are presented in Dunn et al. (2007). The combined groundwater recharge simulated by the STREAM model is applied to a lumped dispersion groundwater model (Dunn et al., 2010) to calculate time-series of discharge of deep groundwater to the lower Lunan. The parameterisation of flows within this transport model is based on the results of the groundwater dating study (using dissolved atmospheric trace gases) to provide suitable characterisation of groundwater residence times. The model representation of the catchment is completed by a loch mixing model, deemed essential as a result of the monitored changes in water quality within the loch system. The loch model assumes a steady-state between inflow and outflow, but carries out mixing of the inflows within a storage reservoir representative of the volume of loch water.

Nitrate Model

A model of nitrate processes is linked with the hydrological representation, based on a daily balance of inputs and outputs of nitrate, according to land use and crop types assigned to each grid cell within the STREAM model. The daily balance calculates the amount of nitrate available for leaching at any time:

$$AvailN_t = AvailN_{t-1} + FertN_t - CropN_t + DepN_t + MinerN_t - DenitN_t + OrgN_t \quad (1)$$

Where $AvailN_t$ is nitrate available for leaching at time-step t, *FertN* is input of nitrate as inorganic fertiliser, *CropN* is uptake of nitrate by crops, *DepN* is input of nitrate from atmospheric deposition, *MinerN* is release of nitrate by mineralisation, *DenitN* is loss of nitrate by de-nitrification, *OrgN* is input of nitrate from organic material. Values for *FertN* and *CropN* are estimated according to crop type and take seasonally varying values. Application of fertiliser is assumed to be spread across two periods; from the beginning of September to end of October and from the middle of February to end of March. The soils in the catchment are mostly very fertile and high in organic content. Organic wastes are applied to the land but, in accordance with guidelines for agricultural practice, it is assumed that the amount of organic material used is compensated for by reductions in inorganic fertiliser applications. Spreading of fertilisers is not permitted between the middle of November and middle of February when the catchment is vulnerable to direct losses from the land to surface waters. Crops start uptake of nitrate in the middle of March with the rate increasing until the end of June, after which it declines until harvest. For grassland, a simplified version of the N balance assumes that an estimated annual excess of nitrate is available for leaching throughout the year, except during the growing season. Mineralisation and de-nitrification rates are both temperature and moisture dependent. In common with other similar models (e.g. Wade et al., 2002) the following rate functions are defined for temperature:

$$fn(temp) = 1.047^{tSoil_t - 20} \; fn(temp) = 1.047^{tSoil_t - 20} \quad (2)$$

$$tSoil_t = 0.57 * \left(\frac{tMax_t + tMin_t}{2}\right) + 3.3 \; tSoil_t = 0.57 * \left(\frac{tMax_t + tMin_t}{2}\right) + 3.3 \quad (3)$$

Where $tSoil_t$ is mean daily soil temperature, $tMax_t$ is mean daily atmospheric temperature and $tMin_t$ is mean daily atmospheric temperature.

And for soil moisture:

$$fn\,(moisture) = \mathbf{1} \;\; fn\,(moisture) = \mathbf{1} \quad \text{for} \quad \frac{store_t}{fc} \geq 0.95 \;\; \frac{store_t}{fc} \geq \mathbf{0.95}$$

$$fn\,(moisture) = \frac{\left(\frac{store_t}{fc} - 0.3\right)}{0.65} \quad \text{for} \quad \frac{store_t}{fc} \geq 0.3\mathbf{0} \;\; \frac{store_t}{fc} \geq 0.3\mathbf{0}$$

$$fn\,(moisture) = \mathbf{0} \quad \text{for} \quad \frac{store_t}{fc} < 0.30 \;\; \frac{store_t}{fc} < 0.3\mathbf{0} \qquad (4)$$

Where $store_t$ is the modelled soil water content at time t and *fc* is field capacity of the soil.
Mineralisation and de-nitrification are then calculated as:

$$Mineral_t = K_{min} \times fn(temp) \times fn(moisture) \qquad (5)$$

$$Denit_t = K_{denit} \times fn(temp) \times fn(moisture) \times \frac{NS_t}{store_t} \qquad (6)$$

Where K_{min} and K_{denit} are rate constants and NS_t is the mass of stored nitrate. It is assumed that the amount of soil organic N available for mineralization is unlimited.

The nitrate model is coupled with the hydrology model for each of the three flow pathways. Runoff generated during storm events by the near surface pathway is assumed to cause dilution of nitrate as a result of minimal mixing with sub-surface storage. Sub-surface flows and groundwater recharge leach nitrate from the sub-surface storage at a rate proportional to $AvailN_t$ and dependent on moisture conditions.

Nitrate fluxes that reach the stream by near surface or sub-surface runoff are also subject to modification by in-stream processes. De-nitrification in streams has been shown to depend on a wide variety of factors, including NH_4^+ concentration and ecosystem respiration rate, and to range from very low levels to 100% removal in different situations (Mulholland et al., 2009). A term to account for in-stream processing of nitrate is included here using a sinusoidal function that removes nitrate from the stream between the start of April and end of September, peaking in magnitude at the end of June.

Model Application

Application of the full catchment model first involved calibration to historic hydrological and stream nitrate data for the period from October 2007-October 2009, followed by validation using data from October 2000-October 2004.

Hydrological Model Calibration Measurements of daily stream flows were available for the Baldardo Burn, and the Lunan Water at Kirkton Mill for the calibration period. The following calibration procedure was adopted:

1. Hydrological parameters were first calibrated by applying the STREAM model to the Baldardo Burn.
2. These parameter values were transferred to simulate flow for the whole of the Upper Lunan catchment, into Rescobie and Balgavies Lochs.
3. Near surface and sub-surface flow for the lower catchment below Balgavies Loch was simulated using the same model parameterisation.
4. Deep groundwater flows into the Lower Lunan were calculated from the combined recharge for the whole catchment.
5. Flows at Kirkton Mill were calculated by summing the flow from the Upper Lunan, Lower Lunan and deep groundwater and compared with the observed flows for Kirkton Mill.

6. Steps 3-5 were repeated to refine the deep groundwater contributions and other parameter values for the lower catchment.

In calibrating the parameters, several observations from monitoring data were used to constrain values to ensure that key processes affecting nitrate transport were suitably represented. Firstly, from the time-series of stream isotope content (Birkel et al., 2010a) it was observed that a fraction of precipitation is transferred very rapidly to streams whenever the daily precipitation exceeds 15-24 mm per day. These values were therefore used to define lower and upper calibration limits for an infiltration excess threshold parameter. Secondly, deep groundwater recharge was constrained in the upper catchment such that 100-200 mm per year is lost from the water balance. The remaining (four) hydrological parameters were calibrated to achieve the best possible flow simulation, using the Nash Sutcliffe efficiency measure (Nash and Sutcliffe, 1970). For the lower catchment, groundwater inflows were also included.

Nitrate Model Calibration Weekly stream nitrate data from five different locations were used to calibrate the nitrate model. The calibration was largely undertaken in the upper catchment where measurements from the Baldardo Burn, Murton Burn and the integrated signal into Rescobie Loch indicated quite differing nitrate behaviour. This was believed to be related to land use with a significantly higher proportion of arable land in the Baldardo Burn sub-catchment and greater areas of less intensively managed land in the Murton Burn and Rescobie sub-catchments. This provided an opportunity to help calibrate the land management component of the nitrate model. Measurements at the outflow from Balgavies Loch were used to calibrate the loch mixing model. Measurements from Kirkton Mill at the outlet of the catchment were largely used to validate the integrated model, without further adjustment of parameter values. Components of the nitrate model were parameterised as follows:

1. Fertiliser inputs and crop uptakes were based on recommended levels and previous estimates for different crop types (Dunn et al., 2004).
2. Timing of inputs and uptake were based on known management with some calibration of relative amounts of autumn versus spring fertilisation to fit the observed nitrate signal.
3. Atmospheric deposition was assumed constant throughout the year with a total annual input of 8 kg ha^{-1}
4. Parameters for soil mineralisation and de-nitrification rates, K_{min} and K_{denit}, were calibrated to give an approximate balance of the N cycle and to give cumulative totals comparable with those estimated for other areas (e.g. Wade et al., 2002).
5. The parameter determining in-stream processing of nitrate was calibrated to fit the observed data, whilst retaining a level of consistency across the whole catchment.
6. The deep groundwater dispersion model was applied using parameter values for the apparent dispersion parameter, $P^*_D = 0.5$ and the solute mean transit time, $T^* = 30$ years. These values were based on the results of the groundwater dating analysis presented in Dunn et al (2010). The dispersion model was run to steady state to estimate the concentration of nitrate discharging to the surface water in the lower catchment.

Land use scenarios Land use scenarios were derived using real land parcels and their broad land use definitions (e.g. forestry, roads, built-up) based on Ordnance Survey Mastermap polygon data. The crop types, proportions and potential locations of broad agricultural categories (intensive arable and continuous grass) were derived from spatially explicit agricultural census data (Integrated Administration and Control System (IACS)). Over the period from 2000-2009, the proportion of intensive arable land ranged from 65% to 83%, and continuous grass from 14% to 24%. For calibration and validation of the model it was therefore assumed that the ratio of arable crops to grassland was 80:20 %. A set of hypothetical future land use scenarios was developed to explore the scale of long-term changes in agricultural practice that would be required to reduce nitrate pollution in the Lunan catchment. The first two scenarios involved changing 20 % of arable land first to grassland and then removing it completely from agricultural management. A third scenario explored the potential importance of soil organic matter, through modifying the K_{min} parameter to achieve a reduction in soil mineralisation. The scenarios were applied using data from the six year period from 2000-2006, cycling the meteorological data to generate long time-series and permit the long term change in nitrate response (i.e. over time-scales up to 100 years) to be examined.

Consideration of Uncertainty Application of a model of this nature incorporates significant uncertainty arising from errors in measured data inputs, estimation of parameter values, limitations of the model structure and errors in measured calibration and validation data. By using a broad suite of data and process understanding to set this model up, it is expected that some of the issues regarding equifinality of model predictions are overcome. A full uncertainty analysis is beyond the scope of this paper. However, iterative development of the model permitted identification of the most sensitive variables for simulation of nitrate concentrations. These were found principally to relate to the timing of inputs, uptakes and losses of nitrate as represented by the temporal variability in e.g. *FertN* and *CropN*. These variables have an important control on the excess N available for leaching at any time (*AvailN*), being significantly greater in magnitude than other components of the balance. In addition, the in-stream de-nitrification function was found to play a significant role in determining the nitrate response in this catchment.

RESULTS AND DISCUSSION

The results of the model calibration for the period Oct 2007 – Oct 2009 are presented in Figure 4 (a-f). The figure shows simulated and measured stream nitrate concentrations at each of the five calibration sites and simulated nitrate in deep groundwater recharge. Simulated stream flows are also shown for Baldardo Burn and Kirkton Mill. Simulations were evaluated using a combination of statistical (R^2, RMSE, volumetric) and graphical evaluation. Although statistical measures are an appealing method of providing quantitative comparison between model simulations they tend to be narrowly focussed on particular aspects of the relationship between the model and the data (NIST, 2003). Additional graphical evaluation also helps to illustrate a broad range of complex aspects of the relationship between the model and the data. The statistical measures for simulation of stream nitrate concentrations, quoted for each site on Figure 4, are generally poor although the visual representation appears acceptable. The total simulated nitrate loads were also compared with loads estimated from the measured data (using a flow weighted algorithm). According to this method, the simulated loads were underestimated by the model by around 20%. However extrapolation of the sporadic point data to continuous time-series may lead to errors in this figure, especially during high flow events when dilution of nitrate concentrations are simulated by the model.

Baldardo Burn displays the greatest variability in nitrate concentrations with the main characteristics of this variability quite successfully simulated. Stream flow simulation is satisfactory with a Nash Sutcliffe efficiency of 0.6. The nitrate dynamics in Murton Burn are much less temporally variable, with an average of ~6 mg l^{-1} throughout the year. The main difference between the two sub-catchments is the land use, which includes 76% arable and 21% grassland in Baldardo Burn and 60% arable, 8% grassland and 32% other land in Murton. The higher temporal variability in nitrate can be explained by the seasonality in arable fertiliser applications, with a clear peak following flushing of autumn fertiliser inputs.

Nitrate concentrations at the inflow to Rescobie Loch are less well simulated, perhaps because of the effect of additional smaller lochs upstream of Rescobie Loch, not accounted for here. The calibration at the outlet of Balgavies Loch demonstrates the importance of mixing within the loch system in terms of modifying the nitrate response. Simulations of nitrate at Kirkton Mill combine the outflow signal from the loch with nitrate losses from the lower catchment and the nitrate from groundwater recharge. The groundwater plays an important role in raising the mean streamwater nitrate concentration throughout the year. Comparison of the simulations at Kirkton Mill with the measured data indicate a good fit of the nitrate model and flow simulations achieved a Nash Sutcliffe efficiency of 0.73. Estimates of the nitrate concentration in groundwater were extracted from the modelled characteristics of recharge water. These were found to be broadly similar across the catchment, varying between 9.7 and 10.4 mg l^{-1}, with the highest concentrations in recharge from the Baldardo Burn sub-catchment. These are comparable with the spot measurements from 3 of the boreholes (Figure 4f). Borehole 1, where low groundwater nitrate concentrations were measured, corresponded to the site with the greatest mean tracer transit time of over 100 years.

Measured data for validation from Oct 2000 – Oct 2006 were only available for Balgavies Loch outlet and Kirkton Mill (Figure 4g,h). The results show similar patterns to the calibration runs and flows at Kirkton Mill achieved a Nash Sutcliffe efficiency of 0.60.

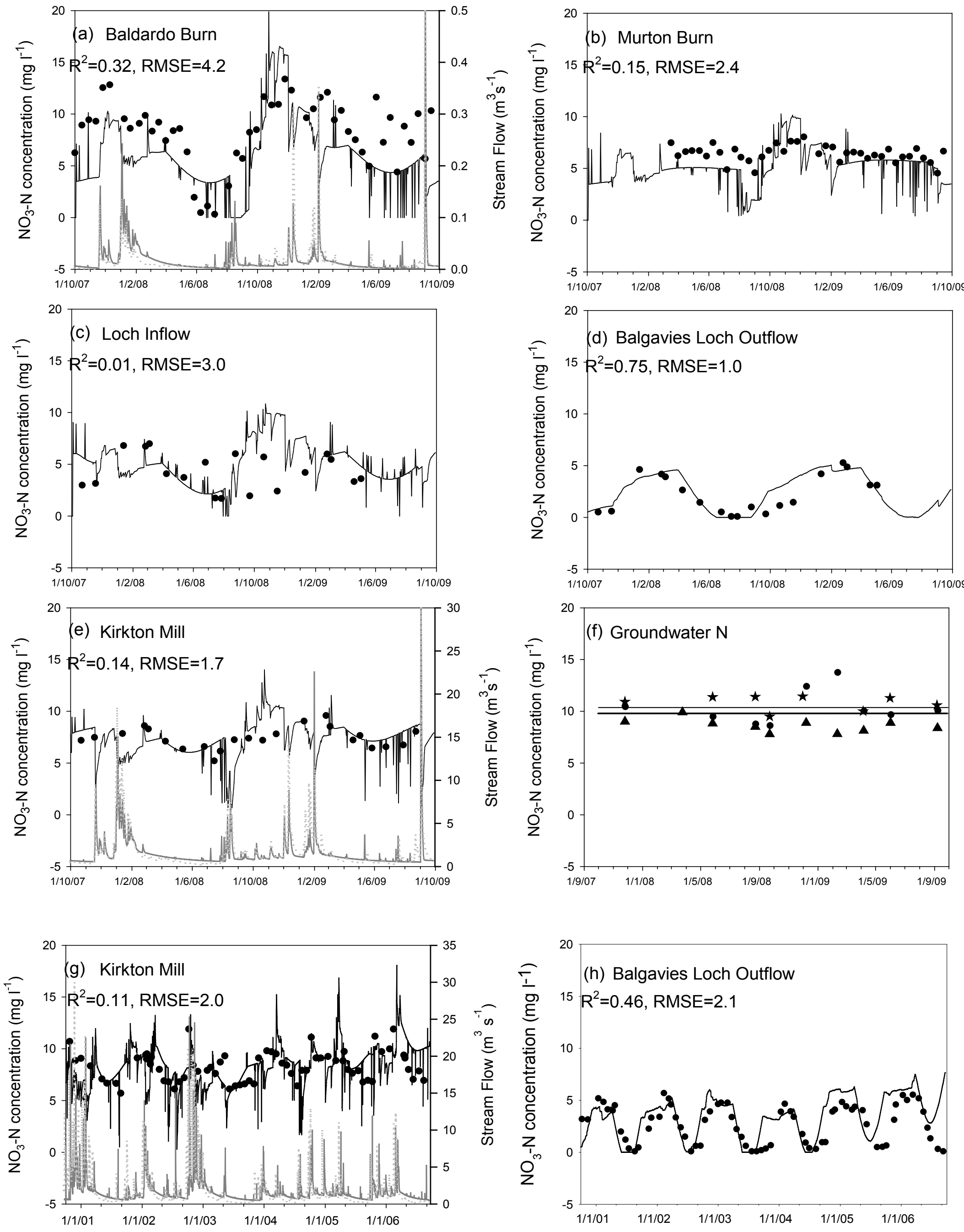

Figure 4. Results of model calibration simulations for Oct 2007 – Oct 2009 and validation for Oct 2000 – Oct 2006

Based on the model results, the proportions of runoff associated with the three different flow pathways were estimated to be approximately equal in magnitude with 32% of runoff generated by a near surface storm response, 34% generated by sub-surface flow and 36% by deep groundwater flow. However, the amount of nitrate lost by each of these flow paths differed, with only 14% associated with the near surface storm response, 41% with the sub-surface flow and 45% with the deep groundwater flow. Furthermore, the relative contribution of nitrate from deep groundwater was greater than this at the bottom of the catchment because of the in-stream de-nitrification losses that reduced the net level of nitrate contributions from near surface and sub-surface flow. This emphasises the importance of the deep groundwater flow pathway and the issue of expected lag times in recovery of the system following diffuse pollution mitigation.

The calibration and validation simulations do not test the reliability of the groundwater transport representation in terms of the recovery characteristics of the catchment. This was the reason that the age dating study, using dissolved atmospheric trace gases, was undertaken and used to parameterise the groundwater component of the model. The importance of this part of the model is demonstrated in the scenario simulations of land use change described below. However, the data underpinning the groundwater transport model were felt to be limited by the number of sites from which measurements were made. Large differences in estimated mean tracer transit times were observed between these sites and therefore interpretation of the data at a catchment scale is problematic. Whilst it is always easy to suggest that more data should be monitored and collected to enhance understanding of catchment processes, in practice, time and resources are rarely available to support such activities. The data already collected within this study give a significantly better overview and depth of understanding than is likely to be the case for most practical situations of catchment management. It is therefore important that as much understanding as possible is gleaned from the data to ensure that robust models are constructed. The tracer data, in particular, were felt to be beneficial in this respect.

Following calibration and validation, the model was applied to explore the effects of land use change on nitrate concentrations in groundwater and stream water. Table 1 presents the results from these scenarios, detailing both the magnitude and time-scales of recovery of the water bodies.

Table 1 Mean flow weighted nitrate concentrations (NO_3-N mg l^{-1}) in groundwater (Dgw N) and streamwater at Kirkton Mill (Stream N) at various times following land use change scenarios, and total N export (kg ha^{-1} y^{-1}). Baseline land use gave Dgw N = 9.62 mg l^{-1}; Stream N = 7.70 mg l^{-1}; N Export Dgw =9.8 kg ha^{-1} y^{-1}; N Export Stream = 34.0 kg ha^{-1} y^{-1}.

	20% arable to grass		20% arable to non agric		50% reduction in K_{min}	
	Dgw N	**Stream N**	**Dgw N**	**Stream N**	**Dgw N**	**Stream N**
10 y	9.19	6.99	9.06	6.77	9.23	7.31
20 y	8.95	6.93	8.74	6.69	9.00	7.25
30 y	8.88	6.91	8.64	6.67	8.93	7.24
40 y	8.86	6.91	8.61	6.66	8.91	7.23
100 y	8.82	6.90	8.56	6.65	8.88	7.22
N Export	9.0	30.4	8.7	29.3	9.0	31.8

Groundwater concentrations would reduce steadily during the 20 years following implementation of each scenario. Within the first 10 years the concentrations would drop by 52% of their final decrease, and by 20 years would drop by 83% of their final decrease. The stream water would be expected to achieve 89% of its final drop in concentration by 10 years. In terms of the effectiveness of the scenarios in reducing nitrate losses, 20% change in land use from arable to grassland could be expected ultimately to lead to an approximate 10% reduction in nitrate concentrations. Complete removal of this area of land from arable agriculture would give a slightly greater reduction. The third scenario, where the soil mineralization rate was reduced, simulated a greater effect in reducing long term groundwater concentrations compared with the overall stream response. This reflects a relationship between groundwater recharge and mineralization through soil moisture, as higher rates of both processes occur under wetter conditions. The overall stream nitrate concentrations are proportionately less affected by the reduction in mineralization rates, since runoff generation by the shallower flow paths continues under drier conditions. In all cases, simulated concentrations of nitrate in groundwater were higher than the stream water average, because the timing of groundwater recharge coincides with the timing of highest nitrate losses and no de-nitrification losses are associated with the groundwater. The level of reductions achieved by the different scenarios helps to give an indication of the length of time and scale of management changes that would be required before nitrate concentrations can be consistently lowered by a suitable amount.

CONCLUSIONS

A conceptual model has been developed and applied to simulate nitrate behaviour in an agricultural catchment in the east of Scotland. The model is based on a conceptualisation of key processes in the catchment derived from a range of different types of spatial and temporal hydrometric, isotopic and chemical data. Statistical measures of fit for the model simulations were reasonable for flow simulation but relatively poor for simulation of nitrate concentrations. However the nitrate simulations were capable of graphically reproducing key time-varying characteristics of the nitrate response at five different surface water locations, as well as being consistent with measurements of nitrate in the groundwater. Simple scenarios for changes in management gave an indication of the scale of reduction in nitrate leaching that might be expected according to the scale of the management changes. Groundwater nitrate concentrations are likely to recover quite slowly from reductions in leaching and this could cause a notable delay in recovery of the stream nitrate, since around 25% of the streamflow was estimated to be generated from deep groundwater discharge.

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Single-Objective vs. Multi-objective Autocalibration in Modelling Total Suspended Solids and Phosphorus in a Small Agricultural Watershed with SWAT

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Abstract

To obtain greater precision in modelling small agricultural watersheds, a shorter simulation time step is beneficial. A daily time step better represents the dynamics of pollutants in the river and provides more realistic simulation results. However, with a daily evaluation performance, good fits are rarely obtained. With the Shuffled Complex Evolution (SCE) embedded in the Soil and Water Assessment Tool (SWAT), two calibration approaches are available, single-objective or multi-objective optimization. The goal of the present study is to find which approach can improve the daily performance with SWAT, in modelling flow (Q), total suspended solids (TSS) and total phosphorus (TP). The influence of weights assigned to the different variables included in the objective function has also been tested. The results showed that (i) the model performance depends not only on the choice of calibration approach, but essentially on the influential parameters; (ii) the multi-objective calibration estimating at once all parameters related to all measured variables is the best approach to model Q, TSS and TP; (iii) changing weights does not improve model performance; and (iv) with a single-objective optimization, an excellent water quality modelling performance may hide a loss of performance of predicting flows and unbalanced internal model components.

Keywords

Calibration; water quality modelling; sensitivity analysis; parameter estimation.

INTRODUCTION

Small agricultural watersheds need to be modelled for better management of water resources, although usually only little data is available. Here, the model used for simulating the fate of pollutants and identifying the best management practices is the Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998). To achieve better precision in modelling small watersheds, a shorter simulation time step is useful. A daily time step better represents the dynamics of pollutants in the river and provides more realistic simulation results. However, case studies on small agricultural watersheds using daily time step are rare, given that SWAT was originally developed for large watersheds with lots of data. In addition, river water quality modelling performance is generally carried out on a monthly or yearly time step and rarely on a daily time step. Among the literature reviewed (Gassman et al., 2007; Moriasi et al., 2007), only a few case studies show a good daily performance on water quality. Given this context, the goal of the present study is to find how to improve water quality modelling performance with SWAT on a daily time step. There are two calibration approaches for modelling flow (Q), total suspended solids (TSS) and total phosphorus (TP): single-objective and multi-objective optimization. The present study compares these two approaches in terms of their performance in modelling TSS and TP at a daily time step in small rural watersheds. Given that there are too many parameters due to the complexity of the model in comparison to the amount of data, a sensitivity analysis is necessary to identify the most important parameters. Each variable is sensitive to different parameters and in case of many variables some parameters appear in multiple subsets. So, two types of parameters will be considered, (i) those only related to the variable of interest and (ii) all those influencing all variables. In addition, the influence of weights assigned to the different objective functions in the case of multi-objective optimization has been tested. Indeed, the calibration algorithm prioritizes fitting the most numerous data and the higher valued data that can induce large global errors. In that sense, the phosphorus data are the most disadvantaged, as they are small in number and magnitude, explaining the difficulty of the model to fit phosphorus data. In the study, the weights will be chosen according to the typical measurement errors and the model fitting errors.

MATERIALS AND METHODS

Study area description

The study was conducted on the Ruisseau du Portage watershed, a 21.41 km^2 small agricultural watershed located in the Boyer river basin in Québec, Canada. Based on the bacteriological and physico-chemical index, the water quality in the watershed is described as "bad" to "very poor" due to high turbidity and excessive enrichment of its water by nutrients (nitrogen and phosphorus) (Ministère du Développement Durable, Environnement et Parcs, Québec or MDDEP). The major sources that can affect its water quality originate from agricultural activities taking place in the lower reaches of the basin. The territory is composed of 48% forest, 44% of agriculture (6.88% cereals, 0.13% corn, 36.97% grassland and pasture) and 8% wetlands.

This study focuses on data collected between October 1999 and December 2002 for Q, TSS and TP. Precipitation and temperature of the site average on a year respectively 1300 mm and 5.25°C. The climate is temperate continental. The topography is relatively flat, the altitude ranging from 46-117 m, with an average of 86 m. The slopes range from 1.6 to 3.1%, those closest to the outlet being most pronounced. The soil characteristics vary according to the area occupied, the major ones being stony sandy loam, gravelly sandy loam and gravelly loam (Baril and Rochefort, 1957; Ouellet et al., 1995; Marcoux, 1966; Pageau, 1976).

Input data

The data used for modelling are the following:

1. Digital Elevation Model (DEM): produced by Geobase (www.GeoBase.ca), 1 :50000, grid 23.17m
2. Soil map: from IRDA (Institut de Recherche et de Développement en Agroenvironnement, Québec, Canada), 1:20000
3. Streamflow data: produced by BDTQ (Base de Données Topographiques du Québec), 1:20000
4. Land use: provided by Canards Illimités, grid 25m
5. Hydrometeorological data : from the MDDEP and Service Météorologique Canada (SMC)
6. Observed data: Flow data were collected by the Centre d'Expertise Hydrique du Québec (CEHQ) while water quality data were obtained from the Centre d Expertise en Analyse Environnementale du Québec (CEAEQ). Flow data were measured daily while water quality data were discontinuous, grab samples, that are therefore not representative of the whole day, especially when agricultural activities like manure spreading, or rainfall occur. The flow data show an interannual average of 0.35m^3/s. The flow variations closely follow the variations of precipitation, showing that the basin responds quickly to rainfall due to its small size. The peak flows occur during snowmelt (April-May), causing 46% of the runoff of the entire study period (October 1999 to December 2002), while the flows are lowest in winter (January to March) and July to September. As for TSS, the median value of 7 mg/l is slightly less than the magnitude of the median measured in 16 small agricultural catchments (9.25 mg/l), but 3-4 times higher than those measured in 30 forested catchments in Québec (2 mg/l) (Gangbazo and Babin, 2000). A concentration of 4 to 5 mg/l of TSS persists throughout the year, which is harmful to aquatic life because a standard of 5mg/l has been set for chronic toxicity (Gangbazo and Le Page, 2005). The median

TP, 0.05 mg/l, is slightly above the criterion for the prevention of eutrophication set at 0.03 mg/l in Quebec (Menviq, 1990, rév. 1992). The daily concentrations of TP fluctuate much during the year, with peaks occurring in April-May and August-September. Around 55% of the TP is soluble. During rain events, given the various land use types, the level of phosphorus in the river is not necessarily high.

The Watershed Model

The watershed model used in this study is the 2005 version of the Soil and Water Assessment Tool (SWAT) (Arnold et al., 1998), which is one of the most widely used watershed models in the world.

For the simulations, the study site is divided into 5 subbasins and 33 Hydrologic Response Units (HRU) (64 ha on average). A sensitivity analysis of all parameters related to the 3 variables (flow, TSS, TP) was done. Each variable is sensitive to different parameters and in case multiple variables are considered, some parameters appear in multiple subsets: flow and TSS, flow and TP, flow and TSS and TP. The parameters used for calibration are presented in the appendix (tables A-1 to A-4). Calibrations were performed by using these different sets of parameters (see Results section).

After implementation of the model, simulations were carried out from January 1st, 1998 to December 9, 2002, including:

- January 1st, 1998 to October 3, 1999: warm-up
- October 4, 1999 to July 31, 2001: calibration period
- and August 1st, 2001 to December 9, 2002: validation period

The simulations were conducted throughout the year but the calibration focused on summer (June-October 2000) because of the water use requirements during this period (e.g: bathing, swimming, fishing, canoeing,…).The parameter intervals were defined based on the recommendations in Neitsch et al. (2005), except for the parameters related to the sediment reentrained during channel sediment routing (SPCON, SPEXP), the sediment concentration in lateral and groundwater flow (LAT_SED) and the depth to the subsurface drain (DDRAIN), which all needed adjustments. The predefined SPCON and SPEXP parameter range were not adequate for small watersheds and low flows, the LAT_SED parameter interval was too large causing excess export of sediment and the DDRAIN parameter range was narrowed based on drainage data.

Optimization in SWAT 2005: Shuffled Complex Evolution algorithm-Uncertainty Analysis (SCE-UA)

SWAT2005 includes an automatic multi-objective calibration and uncertainty analysis in a single run, called Parasol (Parameter Solutions method), developed by van Griensven and Bauwens (2003). The calibration procedure, based on the "Shuffled Complex Evolution" algorithm or SCE, is a global search algorithm for the minimization of a single function (Duan et al., 1993).

The optimization can be single-objective or multi-objective. For single-objective optimization, there is only one objective function (OF) that needs to be optimized. For multi-objective optimization problems, a series of OF need to be taken into account simultaneously. The most commonly OF used is the Sum of the Squares of the Residuals (SSQ):

$$SSQ = \sum_{i=1}^{n} (O_i - S_i)^2$$

where n is the number of pairs of observed (O_i) and simulated (S_i) variables.

For multi-objective calibration, a single global optimization criterion (GOC), defined as an aggregation of several objective functions, is computed as follows:

$$GOC = \sum_{j} \frac{SSQ_j * n_{obs,j}}{SSQ_{\min,j}}$$

with j the number of objective functions. OF get thus weights that are equal to the number of observations ($n_{obs,j}$) divided by the minimum of the objective function ($SSQ_{min,j}$) (van Griensven, 2006).

The methodology used for the two calibration approaches is described as follows.

Calibration approaches

The most common single-objective approach is to successively calibrate flow, TSS and TP, while the second, the multi-objective approach is to calibrate several components in a single optimization run. A general calibration procedure chart for both single and multi-objective optimization for flow, sediment and total phosphorus is presented in figure 1. The single-objective calibration techniques are summarized on the SWAT website[1]. The multi-objective optimization procedure differs after flow calibration. The flow is re-calibrated with the TSS and TP and the performance criteria are readjusted.

The daily model evaluation limits, that are less strict than the monthly ones because of the lack of averaging over multiple data (Engel et al., 2007), have been adjusted from the monthly evaluation guidelines proposed by Moriasi et al. (2007). Each step is evaluated using two criteria, the Nash Sutcliffe Efficiency (NSE) (Nash and Sutcliffe, 1970) and the Percent of Bias (PBIAS) (Moriasi et al., 2007).

$$NSE = 1 - \frac{\sum_{i=1}^{n} (O_i - S_i)^2}{\sum_{i=1}^{n} (O_i - \overline{O})^2}$$

$$PBIAS = \frac{\sum_{i=1}^{n} (O_i - S_i) * 100}{\sum_{i=1}^{n} O_i}$$

where n is the number of pairs of observed (O_i) and simulated (S_i) variables.

The NSE values range from $-\infty$ to 1, with 1 being the optimal value. Negative values indicate that the average of the observed values is a better model than the model fitted to the data, leading to rejection of the model. As for PBIAS, it measures the average trend of the simulated data to be above or below the observed data. The optimum value of PBIAS is zero, indicating a perfect model simulation. A positive PBIAS indicates an underestimation of the model while a negative PBIAS represents an overestimation of the model. This test is recommended because of its ability to clearly demonstrate the poor performance of the model (Gupta et al., 1999).

1. http://www.brc.tamus.edu/swat/publications/swat-calibration-techniques_slides.pdf

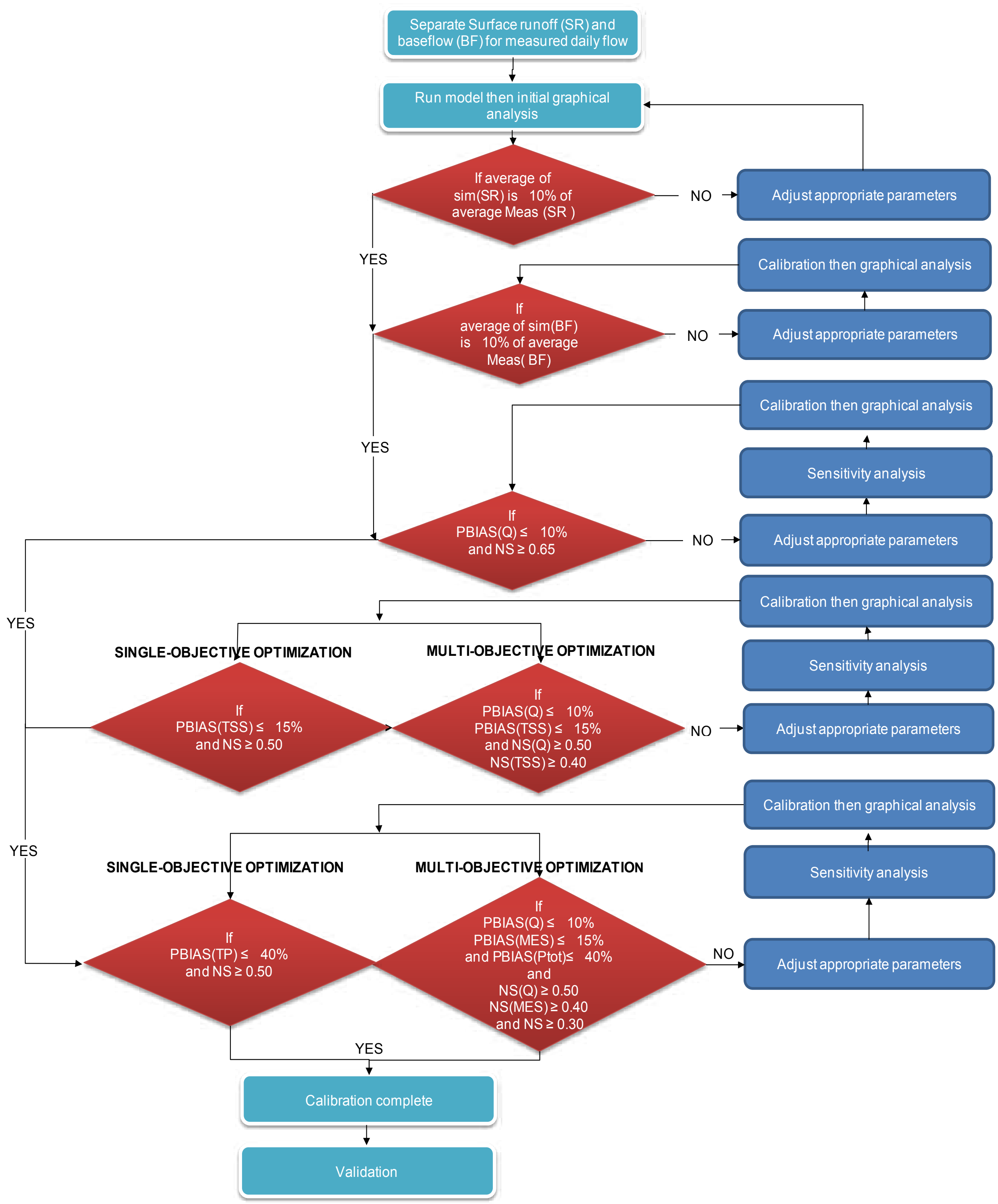

Figure 1. General single and multi-objective calibration procedure for flow, sediment and total phosphorus in the watershed model

RESULTS AND DISCUSSION

Tables 1 and 2 compare some of the results obtained after either the single-objective and the multi-objective calibration. The Q, TSS and TP results presented illustrate the differences between the two calibration approaches with SWAT2005.

Four types of parameters were considered:

- parameters only influencing TSS
- parameters only influencing TP
- parameters influencing Q-TSS
- and parameters influencing Q-TSS-TP

Please note that the parameters influencing the flow have been set to the values obtained by fitting to the flow data, unless specified otherwise.

The results in Table 1 were obtained with modified data, given that the data above four times the standard deviation were considered as outliers. They present excellent performance, especially for TP, and a good mass balance for Q, TSS and TP for the whole watershed. However, verification showed that the internal mass balances for Q, TSS and TP inside each HRU were not correct.

To get a more realistic model, manual adjustments of certain parameters were undertaken, all data were considered and only realistic changes of the parameters were allowed during calibration (e.g: little change by percentage for the parameters related to the geomorphology of the basin). The new worse results, are shown in Table 2. The number of influencing parameters is not the same, because the value of the parameters has changed.

In both calibrations, the same advantages and drawbacks of each calibration approach were noted.

On the one hand, given that the flow parameters are no longer touched when trying to calibrate TSS data, the single-objective calibration with only parameters relating to TSS leads to less unbalanced internal hydrologic components. Internal hydrological components are unbalanced when the distribution of fluxes between rainfall and river flow is not realistic. However, the performances obtained are capped at a certain threshold. Indeed, the NSE didn't exceed 18% for TSS and -36% for TP (see Table 1) and 13% for TSS and -1671% for TP (see Table 2). Subsequently, by reconsidering the parameters influencing flow in the calibration of TSS, the performance could be improved significantly for TSS (NSE 49% and 24% respectively for Tables 1 and 2, PBIAS less than 1%) at the expense of the flow's performance: NSE 15%, PBIAS 53% (Table 1) and NSE 33%, PBIAS 18% (Table 2). Unfortunately, this excellent TSS-performance can only be obtained by unbalancing internal components: high surface runoff, low groundwater flow, a huge export of sediments and no tile flow may occur (e.g: in single-objective calibration with 21 Q-TSS parameters in Table 1). For TP, the performance was just a little bit enhanced by considering all influencing parameters.

On the other hand, these calibrations were also conducted in the multi-objective way using the same sets of influential parameters. With only TSS-influencing parameters, the performance of Q is a little bit improved but the fit to TSS is worse than in the single-objective optimization. With Q-TSS-influencing parameters, the opposite to the results of the single-objective calibration happened: the Q performance was kept at the expense of the TSS performance. The runoff was decreased while the groundwater flow was increased. Less export of sediments could be obtained by manual adjustment of some critical parameters affecting this process. For TP, the multi-objective approach leads to better results with TP-influencing parameters, especially the TP performance was enhanced very much (see Table 1) (from NSE -29% in single-objective to +29% in multi-objective optimization) with all influencing parameters. Unfortunately, such good results couldn't be obtained with the more realistic parameters. This big improvement is due to the better simulation of the baseline TP concentration. In multi-objective calibration, the Q performance is worse than the performances obtained in single-objective calibration, given the compromises that had to be made to optimize both variables simultaneously.

In addition, to improve the multi-objective calibration performance, the influence of the weights assigned to the individual objective functions has been tested. Indeed, the algorithm prioritizes the most numerous data and the higher valued data that can induce large global errors. The phosphorus data are the most disadvantaged, as they are small in number and magnitude, explaining the difficulty of the model to fit phosphorus data. Given that the user-defined choice of weights with SCE in SWAT2005 is not operational, we have manually tried to add weights calculated according to the measurement errors. Smaller weights were given to variables that were accepted to be less important in the strategy of optimum search (van Griensven and Bauwens, 2003). The measurement errors taken into account were 5% for Q, 15% for TSS and 10% for TP. The estimation methodology adopted is as follows: *m* influential parameters were selected after sensitivity analysis among all parameters related to Q, TSS ad TP. *n* initial parameter estimates were produced with these *m* influential parameters by using latin hypercube sampling (van Griensven, 2006). Thereafter, multi-objective calibrations were carried out, each with a maximum of 20 000 tries. The *GOC* was computed by trying various weights and evaluating the objective functions for each of the large number of simulations (in total 400 000 simulations were carried out, n=20, 20 000 tries each), with their corresponding parameter values. After ranking, the minimal *GOC* was identified and the corresponding parameters were the optimal ones for a particular set of weights.

Through this weighted multi-objective optimization:

- the flow was very well simulated, with NSE between 62 and 75% ;
- TSS-performance was good (NSE 11 to 35%) ;
- The best TP-performance was a NSE of 6% ;
- The internal hydrologic components were very unrealistic: the surface runoff was too high or inexistant, tile flow was too low or inexistant, sediment loads were uncontrolled and TP loads very low.

Table 1. Comparison of results obtained after single-objective and multi-objective calibration, with modified data and wrong mass balance of Q, TSS and TP inside each HRU

	Single-objective optimization				**Multi-objective optimization**			
OF	**TSS**	**TSS**	**TP**	**TP**	**Q-TSS**	**Q-TSS**	**Q-TSS-TP**	**Q-TSS-TP**
Parameters influencing	TSS	Q-TSS	TP	Q-TSS-TP	TSS	Q-TSS	TP	Q-TSS-TP
Number of parameters	10	21	13	19	10	21	13	19
NSE*(Q)(%)	64.6	15.19	53.09	56.22	69.28	66.51	53.18	58.67
NSE*(TSS)(%)	18.02	48.66	38.23	30.99	20.46	11.51	38.85	34.11
NSE*(TP)(%)			-35.7	-28.65			-38.03	28.57
PBIAS*(Q)(%)	6.72	53.19	3.8	15.53	-10.57	11.94	15.16	11.71
PBIAS*(TSS)(%)	6.36	0.74	7.81	10.48	16.25	7.27	7.95	11.12
PBIAS*(TP)(%)			13.77	10.05			3.58	3.29
Runoff (mm)	165.02	234.62	203.92	191.04	428.35	159.41	203.94	205.5
Lateral flow (mm)	9.39	9.66	50.81	4.63	3.72	20.55	54.86	42.07
Tile flow (mm)	113.23	0	100.06	122.86	51.87	36.39	99.9	104.03
Groundwater flow (mm)	157.24	14.21	128.05	121.53	69.48	292.72	125.8	148.02
Sediment export (t/ha)	5.359	69.169	0.765	0.400	0.912	2.791	0.764	0.445
Soluble P export (kg/ha)	0.016	0.023	0.078	0.129	0.039	0.02	0.083	0.133
TP export (t/ha)	0.131	0.155	0.253	0.515	0.118	0.244	0.346	0.424

*NSE: Nash Sutcliffe Efficiency; PBIAS: Percent of Bias.

Table 2. Comparison of results obtained after single-objective and multi-objective calibration, with no modified data and right mass balance of Q, TSS and TP inside each HRU

	Single-objective optimization				Multi-objective optimization			
OF	**TSS**	**TSS**	**TP**	**TP**	**Q-TSS**	**Q-TSS**	**Q-TSS-TP**	**Q-TSS-TP**
Parameters influencing	TSS	Q-TSS	TP	Q-TSS-TP	TSS	Q-TSS	TP	Q-TSS-TP
Number of parameters	8	20	9	14	8	20	9	14
NSE(Q)(%)	62.98	32.57	70.47	63.11	65.26	71.7	72.05	74.87
NSE(TSS)(%)	12.96	23.59	4.73	12.62	7.83	17.45	12.05	14.58
NSE(TP)(%)			-1671	-934			-1404	-681
PBIAS(Q)(%)	14.37	17.75	12.02	2.16	16.15	10.79	11.22	6.29
PBIAS(TSS)(%)	22.63	0.53	35.36	3.10	40.75	9.24	32.16	10.2
PBIAS(TP)(%)			-186.7	-151.9			-169.7	-165.5
Runoff (mm)	268.49	317.96	254.23	282	251.23	270.37	265.9	262.86
Lateral flow (mm)	35.6	26.35	54.74	168.7	35.66	47.59	53.9	116.25
Tile flow (mm)	104.86	105.6	104.33	38.8	100.47	102.1	102.2	57.33
Groundwater flow (mm)	145.38	126.74	142.97	100.9	146.58	138.31	138.5	138.67
Sediment export (t/ha)	1.876	5.21	0.181	0.354	1.837	6.7	0.213	0.455
Soluble P export (kg/ha)	0.181	0.202	0.102	0.114	0.149	0.165	0.111	0.096
TP export (t/ha)	1.633	1.629	1.622	2.296	2.549	1.627	1.623	1.528

Therefore, we can conclude that the two multi-objective optimization approaches tested, one with weights based on measurement errors and the other one with the number of observations divided by the minimum objective function (weights imposed by SWAT2005), lead to a calibrated model with the same performance for Q and TSS. However, for TP, with which it was so difficult to get good performance with a simultaneous good model fit of Q and TSS, the multi-objective optimization gives worse performance when using the search strategy with weights based on measurement errors. Other optimization algorithms such as SUFI2, NSGA-II, coupled with SWAT, may lead to better performance (Abbaspour et al., 2007; Zhang et al., 2010). Moreover, subjectivity in the choice of weights is one of the main challenges in multi-objective optimization. In addition, a good fit of the hydrograph and good values of the performance criteria of the model do not guarantee a correct distribution of the internal components of the model, namely surface runoff, groundwater flow, tile drainage, export of sediment and nutrients. The optimizer does not care about the realism of the parameters and internal components of the model. More data may be also needed on these internal components. That is the reason why manual adjustments of parameters or routines in the source code play a crucial role before, during and after calibration.

CONCLUSION

A multi-objective optimization using a modified SCE-UA algorithm, is incorporated in SWAT2005. Two calibration approaches are possible: single-objective and multi-objective optimization. The obtained model performance depends on the choice of calibration approach, but essentially on the selected influencing parameters. Indeed, each variable is sensitive to different parameters and in case of many variables, some parameters appear in multiple subsets: flow and TSS, flow and TP, flow and TSS and TP. Considering them all for calibration improved the obtained water quality fitting performance very much. Based on the results obtained in this study, even if the user-defined choice of weights with SCE in SWAT2005 is not operational, the multi-objective calibration remains the best approach to model TSS and TP, with a daily evaluation performance in the small agricultural Ruisseau du Portage watershed. The following conclusions can be drawn:

1. The multi-objective optimization considering all parameters related to the variables is the best approach to enhance the daily water quality simulation with SWAT2005. The performance of describing flow data is maintained and the water quality prediction performance, especially that of TP, is very much improved.
2. Excellent results on the whole watershed may hide unrealistic mass balance for Q, TSS and TP for each HRU. Forcing a correct mass balance for each HRU leads to a worse daily performance, and the combination of the realistic parameters may not facilitate the search of the optimum.
3. Despite the normalization of the objective functions, the SCE algorithm incorporated in SWAT2005 prioritizes the most numerous data among the variables considered. To overcome this problem, the choice of other weights assigned to objective functions can be a solution but this is not operational in SWAT2005. The attempt to change the weights manually did not improve the performance to describe TP data.
4. With single objective optimization, the excellent water quality performance that can be achieved may hide a loss of flow performance and unbalanced internal hydrological components.
5. For both calibration approaches, manual adjustments based on good insight in the SWAT model remain crucial.

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APPENDIX: INFLUENTIAL PARAMETERS FOR CALIBRATION

Table A-1. Influential parameters for the calibration of flow, TSS and TP

Variable	Influential parameter	Min	Max	Default values	Description	Files
Flow,TSS,TP	GWQMN	0.001	5000		Threshold depth of water in the shallow aquifer required for return flow to occur	HRU(.gw)
	ALPHA_BF	0.001	1	slow: 0.1-0.3 ; rapid : 0.9-1	Baseflow alpha factor	HRU(.gw)
	HRU_SLP	0.00001	0.6	Average slope of the subbasin(m/m)	Average slope steepness	HRU(.hru)
	GDRAIN	0	100	0	Drain tile lag time	HRU(.mgt)
	SOL_K	0.001	500	Variable	Saturated hydraulic conductivity	HRU(.sol)

Table A-2. Influential parameters for the calibration of flow and TSS

Variable	Influential parameter	Min	Max	Default values	Description	Files
Flow and TSS	TIMP	0.01	1	1	Snow pack temperature lag factor	basin (.bsn)
	SURLAG	0	4000	4	Surface runoff lag time	basin (.bsn)
	SMFMX	0	10	4.5	Maximum melt rate for snow during the year (occurs on summer solstice)	basin (.bsn)
	SMFMN	0	10	4.5	Maximum melt rate for snow during the year (occurs on summer solstice)	basin (.bsn)
	SNO50COV	0	1	0.5	Minimum melt rate for snow during the year (occurs on winter solstice)	basin (.bsn)
	RCHRG_DP	0.001	1	0 à 1	Deep aquifer percolation fraction	HRU(.gw)
	GW_REVAP	0.02	0.2	variable	Groundwater ``revap``coefficient	HRU(.gw)
	GW_DELAY	0.001	365	variable	Groundwater delay	HRU(.gw)
	SLSUBBSN	10	150	90	Average slope length	HRU(.hru)
	LAT_TTIME	0	180	0	Lateral flow travel time	HRU(.hru)
	DDRAIN	900	1100	0	Depth to subsurface drain	HRU(.mgt)
	TDRAIN	0	72	0	Time to drain soil to field capacity	HRU(.mgt)
	CN2	30	98	SCS	SCS runoff curve number for moisture condition II	HRU(.mgt)
	SOL_Z	1	5000	variable	Depth from soil surface to soil layer	HRU(.sol)
	SOL_AWC	0.001	1	variable	Available water capacity of the soil layer	HRU(.sol)
	CH_K2	-0,01	150	variable	Effective hydraulic conductivity in main channel alluvium	subbasin(.rte)
	CH_S2	0	1	variable	Average slope of main channel	subbasin(.rte)
	CH_N2	0.001	0.5	variable	Manning's ``n`` value for the main channel	subbasin(.rte)
	CH_K1	0	150	variable	Effective hydraulic conductivity in tributary channel alluvium	subbasin(.sub)
	CH_S1	0.0001	10	variable	Average slope of tributary channels	subbasin(.sub)
	CH_N1	0.01	30	variable	Manning's ``n`` value for the tributary channels	subbasin(.sub)

Table A-3. Influential parameters for the calibration of flow and TP, flow only and TSS only

Variable	Influential parameter	Min	Max	Default values	Description	Files
Flow and TP	BIOMIX	0	1	0.2	Biological mixing efficiency	HRU(.mgt)
Flow only	SHALLST	0	1000		Initial depth of water in the shallow aquifer	HRU(.gw)
TSS only	SPCON	0.000005	0.01	0.0001	Linear parameter for calculating the maximum amount of sediment that can be reentrained during channel sediment routing	basin (.bsn)
	PRF	0	2	1	Peak rate adjustement factor for sediment routing in the main channel	basin (.bsn)
	SPEXP	0	1.5	1	Exponent parameter for calculating sediment reentrained in channel sediment routing	basin (.bsn)
	CANMX	0.001	10	variable	Maximum canopy storage	HRU(.hru)
	LAT_SED	0	10	0	Sediment concentration in lateral flow and groundwater flow	HRU(.hru)
	USLE_K	0	0.65	variable	USLE equation soil erodibility (K) factor	HRU(.sol)
	CH_EROD	-0.05	1	0	Channel erodibility factor	subbasin(.rte)
	CH_COV	-0.001	1	0	Channel cover factor	subbasin(.rte)

Table A-4. Influential parameters for the calibration of TP only

Variable	Influential parameter	Min	Max	Default values	Description	Files
TP only	PSP	0.4	0.01	0.7	Phosphorus sorption coefficient	basin (.bsn)
	CMN	0.001	0.003		Rate factor for humus mineralization of active organic nitrogen	basin (.bsn)
	PPERCO	10	10	17.5	Phosphorus percolation coefficient	basin (.bsn)
	PHOSKD	175	100	200	Phosphorus soil partitioning coefficient	basin (.bsn)
	P_UPDIS (UBP)	20	0	100	Phosphorus uptake distribution parameter	basin (.bsn)
	SOL_ORGN	0	10000	0	Initial organic N concentration in the soil layer	HRU(.chm)
	SOL_SOLP	0	100	0	Initial labile (soluble) P concentration in surface soil layer	HRU(.chm)
	SOL_ORGP	0	4000	0	Initial organic P concentration in the soil surface layer	HRU(.chm)
	ERORGP	0	5	0	Organic P enrichment ratio	HRU(.hru)
	SOL_BD	1.1	2.5	variable	Moist bulk density	HRU(.sol)
	RS2	0.001	0.1	0.05	Benthic (sediment) source rate for dissolved phosphorus in the reach at 20°C	HRU(.swq)
	RS5	0.001	0.1	0.05	Organic phosphorus settling rate in the reach at 20°C	HRU(.swq)
	BC4	0.01	0.7	0.35	Rate constant for mineralization of organic P to dissolved P in the reach at 20°C	HRU(.swq)

Eutrophic Waters: Cyanobacteria and Toxin Occurrence and Modelling

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Abstract

The sudden appearance of toxic cyanobacteria blooms is still largely unpredictable in meso- and eutrophic waters in Quebec and worldwide. Literature results suggest that the ratio of nitrogen (N) to phosphorus (P) concentration in the water column can explain cyanobacterial bloom occurrence. However, a consensus has not been reached with regards to the quantitative value of this ratio. The objectives of this study were to determine the predominant physical and chemical factors, such as meteorological and nutrient conditions, that were related to toxic cyanobacteria occurrence, with the goal of developing a modelling tool for Missisquoi Bay (Quebec, Canada) to aid with the prediction of blooms and the development of water management plans. Results showed that the nitrogen to phosphorus ratio did not explain cyanobacteria bloom occurrence in this lake. It appears that blooms are better related to weather events. A factor representing weather conditions, including temperature, wind speed and direction and relative humidity, had an effect on cyanobacteria occurrence in 2008. The weather conditions demonstrated significant covariation with the growth of cyanobacteria over 2 to 3 day periods in 2008, although the relationship was not strong. Thus weather conditions, such as wind speed and direction, temperature, relative humidity and precipitation must be integrated into the coupled hydrodynamic cyanobacteria model.

Keywords

Cyanobacteria; toxins; modelling

INTRODUCTION

Harmful cyanobacterial bloom occurrences have been noted in Quebec and worldwide. Blooms may be accompanied by toxin production, which can be harmful for aquatic communities and constitutes a threat to sources of drinking water. For this reason, bloom occurrences limit recreational and economic activities in water bodies. In the case of the Missisquoi Bay, a large bay of Lake Champlain which straddles the U.S.-Canada border where this research was performed, public health authroities have restricted recreational access to the lake repeatedly over the last decade. The eutrophic character of the bay has been the target for the reduction of the phosphorus concentration by a bilateral agreement between the province of Quebec (Canada) and the state of Vermont (United States).

Given the economic problems that accompany bloom occurrence, considerable efforts have been applied worldwide in order to understand the environmental factors related to these phenomena. For their growth, cyanobacteria need mainly phosphorus, nitrogen and other micro-nutrients such as iron (Sevilla et al, 2008). The stoichiometric ratio of nitrogen to phosphorus concentration in water and in biomass has been identified as potentially important in many studies. Many cyanobacteria are able to fix atmospheric nitrogen for their growth. Schindler (1977) concluded that when the nutrient ratio decreases below 15, the cyanobacterial community responds by an increase of nitrogen-fixing biomass. Based on this mechanism, cyanobacterial biomass in lakes was shown to be greatest where the N/P ratio was lower than 29 (Smith, 1986). In order to investigate the role of nitrogen-fixing cyanobacteria, Lilover and Stips (2008) studied the effect of excess of dissolved inorganic phosphorus (eDIP) on community structure. This variable represents the quantity of phosphorus which remains in the water following a period of strong cyanobacteria proliferation in the spring. It assumes that all the nitrogen was used for the development of the phytoplankton and that DIP (dissolved inorganic phosphorus) and DIN (dissolved inorganic nitrogen) are consumed in a ratio of 16 to1, respectively:

$$\text{eDIP (excess dissolved inorganic phosphorus)} = \text{DIPtotal} - \text{DIPconsumed}$$

with DIPconsumed = DIN/16, thus eDIP = DIPtotal – DIN/16. They concluded that there is a relation of causality between the excess of dissolved inorganic phosphorus and the probability of a cyanobacteria bloom.

In the study of Steinberg and Hartmann (1988), reported by El Herry et al. (2008), it was suggested that eutrophication caused by phosphorus is the main cause which leads to cyanobacteria blooms. According to the studies of Chellapa et al. (2008), cyanobacteria blooms do not coincide with periods during which the N/P ratio is below 10, which is considered as being weak. In many freshwater bodies of Sri Lanka, Jayatissa et al. (2006) found that an N/P ratio lower than 15 sometimes lead to abundant proliferation of cyanobacteria, while in other cases it did not. Thus, the N/P ratio is not the only indicator to predict cyanobacteria blooms and a consensus does not exist with regards to the quantitative value of this ratio. Other parameters are required in order to complete the explanatory effect of nitrogen and/or phosphorus on cyanobacteria blooms.

Hu et al. (2009) demonstrated that weather parameters such as relative humidity, the minimum temperature of the day and the amount of solar radiation give a good description of cyanobacteria density by time series analysis using a generalized linear model and a classification and regression tree (CART). Wind speed and relative humidity were negatively correlated with cyanobacteria biovolume, in contrast to the minimum temperature and the rain. Thus, as mentioned by these authors, consideration of weather parameters may be useful when implementing a warning system for possible proliferation of cyanobacteria.

For the present study site, McQuaid et al. (2009) showed that there is a good correlation between cyanobacterial biovolume and toxin concentration, which might be used to empirically determine toxin occurrence in a coupled cyanobacterial growth/hydrodynamic model. The objectives of this study were to determine whether the predominant factors identified previously, such as weather conditions, nutrient load, etc., can be usefully related to toxic cyanobacteria occurrence, for the development of a modelling tool to aid with the development of water management plans.

METHODOLOGY

On-line 6600V2-4 multi-probe systems (MPS) from YSI (YSI, Yellow Springs, Ohio) measuring phycocyanin (590 nm for the excitation and 660 nm for the emission), chlorophyll (470 nm for the excitation and 680 nm for the emission), pH, temperature, dissolved oxygen, turbidity have been installed at the study site (at the east of Missisquoi Bay) since 2007. A time-series analysis was performed to determine the effects of weather conditions on cyanobacteria biovolume in the source water of the treatment plant.

The weather data was obtained from Burlington's weather station (National Climatic Data Center, U.S. Department of commerce, 2009). The data was available for the period between 2007 and 2008. Wind data was kindly provided by the

Quebec Ministry of the environment (MDDEP 2009). Data were analyzed using Statistica 9.0 (StatSoft.Inc, Tulsa, OK USA). The nutrient data were provided by the Division of Water Quality, State of Vermont.

Algal biovolumes were calculated using the data of the probe and the correlation between RFU (ratio fluorescence units) of the probe and the biovolume found in environmental conditions following the work of McQuaid (2009). The relation found from two study sites including the Missisquoi Bay was linear over the range we encountered:

$$Log\ (biovolume) = -0.4768 + 1.089 \times Log\ (RFU)$$

For the influence of the weather parameters on growth rate (Yu et al., 2002), a combination of factors was developed into an index of cyanobacteria growth. It is considered as a correction function for the growth rate. According to these authors, growth rate, taking into account the influence of the weather parameters, is written as:

$$\mu = \mu_0 \times f(p)$$

where μ_0 is the external growth rate without influence, p is the weather parameters and $f(p)$ the representative function of the influence of the parameters p on the growth rate. Taking into account the aquatic environment in which cyanobacteria live, we supposed that water temperature would also influence growth rate. Thus, a function f(Temp) is also taken into account. Thus, growth rate μ is written as:

$$\mu = \mu_0 \times f(p) \times f(Temp).$$

Considering weather parameters X1, X2, X3….XN, for a given period of several days, the function f(p) during one day would be written in the form:

$$f(p_j) = (K(j)/Kmax)$$

with

$$K(j)=\sum[F(X1)\times F(X2)\times F(X3)\dots F(XN)]$$

And $Kmax=max(K(j))$

$f(p_j)$ has a value between 0 and 1. Within this study, simple functions of the type F (X) = X were considered. Concerning the effect of the temperature of the water, the function f(temp) represented by the model described in the studies of in Lehman et al. (1975) and reported by Bouarab et al. (2002) was considered. It is written as:

$$f(Temp)=exp(2.3\times[(T-Topt)^2/b^2])$$

With $b=T_{max}-T$ if $T<T_{opt}$ and $b=T-T_{min}$ if $T>T_{opt}$

T_{min}= minimal temperature; T_{max}: maximal temperature; T_{opt}= optimal temperature.

In their work, which was centered on the predominance of the cyanobacteria in fresh water in polar environments, Tang et al. (1997) showed that growth was undetectable when the temperature of the aquatic environment in which the cyanobacteria live was less than or equal to 5 °C. In their experiments made on 27 isolated species from several water bodies, when the temperature reaches 35°C growth was also undetectable. This work supported the results of Seaburg et al. (1982) who found that the majority of cyanobacteria have an optimal temperature of 25 °C. Thus, it was assumed in this work, that minimum and maximum temperatures are respectively of 0 °C and 35 °C and that the optimal temperature is of 25 °C.

RESULTS AND DISCUSSION

The ratio of total nitrogen to total phosphorus showed little relation to cyanobacterial bloom occurrence (Fig. 1); the increase of cyanobacterial biovolume does not correspond to the same dynamic of the nitrogen to phosphorus ratio. Thus, the relationship between nitrogen and total phosphorus or dissolved phosphorus cannot be considered as an indicator of cyanobacterial abundance in this lake.

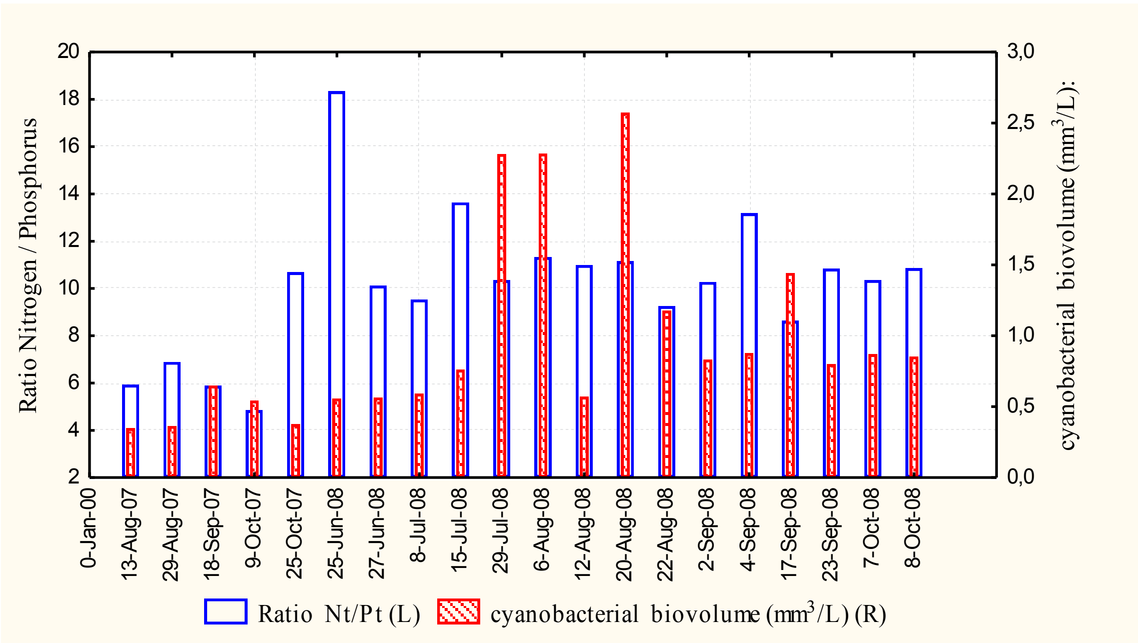

Figure 1. Changes in the ratio of total nitrogen to total phosphorus concentration, and cyanobacteria biovolume in the epilimnion of Missisquoi Bay for different dates in 2007 and 2008

It appears that the increase of biovolume did not follow changees in the N:P ratio. However, the Missisquoi Bay is a eutrophic water body, and nutrient levels are high throughout the year. Therefore, it seemed likely that physical factors might hold more importance. An analysis based on matrix correlations for several meteorological parameters is shown in tables 1 and 2.

Table 1. Matrix of correlation between meteorological and probe parameters (2008)

Meteorological parameter	Daily average dissolved oxygen	Daily average Chlorophyll	Cyanobacterial biovolume
AWND	-0.05	-0.08	0.23*
MNRH	-0.13	0.10	-0.26*
MNTP	0.35	0.28	-0.22*
MXRH	-0.03	0.11	-0.10
RDIR	-0.18	-0.22	0.27*
RWND	0.01	-0.07	0.25*

* Significant correlation values in 2008 ($p<0.050$, N=105)

AWND (TL): wind speed (in miles/hour)

MNRH (P): minimal relative humidity

MNTP (F): average temperature (max tem+Min Tem)/2

MXRH (P): maximum relative humidity

RDIR (DW): resultant of the direction of the wind

RWND (TL): wind speed (miles/hour)

Table 2. Matrix of correlation between meteorological and probe parameters (2007)

Meteorological parameter	Daily average dissolved Oxygen	Daily average Chlorophyll	Cyanobacterial biovolume
AWND	-0.12	-0.15	-0.02
MNRH	-0.24*	0.25*	0.00
MNTP	0.30*	-0.56*	-0.24*
MXRH	0.16	0.06	0.02
RDIR	-0.01	-0.01	-0.04
RWND	-0.12	-0.13	-0.03

* Significant correlation values in 2007 ($p<0.050$, N=105)

Based on the work of Hu et al. (2009) and taking into account the matrix of correlations for 2008, the parameters such as AWND, MNTP, MXRH and RWND were considered. Maximum relative humidity MXRH was included in the analysis because it is a good indicator of the lowest temperature even if it is not correlated with cyanobacterial biovolume.

Thus it appears from the results presented in Figures 2 and 3 that the variations of the calculated meteorological factor would have a more or less intense effect on the changes in biovolume of cyanobacteria in 2008 in contrast to 2007.

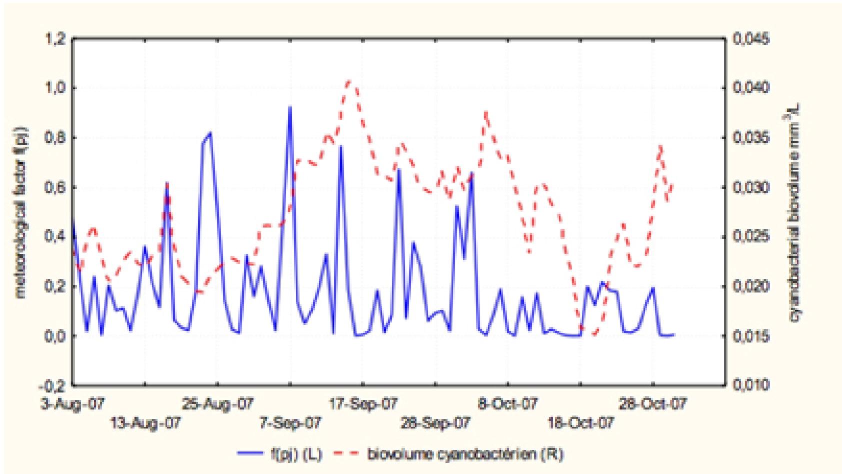

Figure 2. Meteorological factor f(pj) and cyanobacterial biovolume versus time for 2007

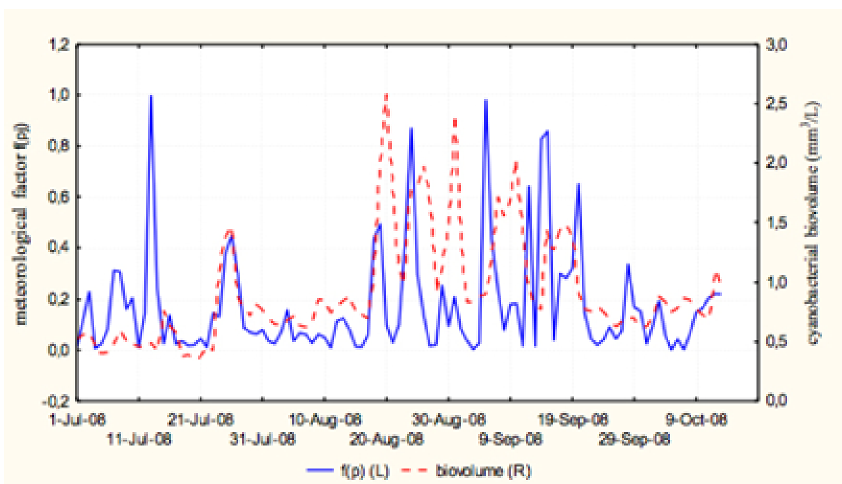

Figure 3. Meteorological factor f(pj) and cyanobacterial biovolume versus time for 2008

The covariation (Cox, 2004), of the reduced centered values of the time series (cyanobacteria biovolume and the meteorological factor f(pj) daily) were calculated. A significant value of this covariation confirms the existence of a relationship between the two time series.

The results of this statistical analysis are given in Table 3. Thus, for 2008, the linear coefficient of covariation with a lag of one or two days appeared to be more important than the condition without a lag.

Table 3. Covariation test with or without offset of phase of f(P) versus cyanobacteria biovolume

Offset	2008	2007
0 day (without offset)	0.2292*	-0.0025
1 day	0.3497*	0.0748
2 days	0.3483*	0.1634
3 days	0.2312*	0.1574

* Significant values ($p<0.050$, N=105 and N=84 respectively for 2008 and 2007)

The computed values for 2008 are significant but do not show a very strong relationship (when the coefficient is equal to 1 in absolute value terms). For 2007 data, the coefficients of linear covariation were out of phase or did not have a clear relationship. The explanation is supported by Figures 4 and 5 between 2007 and 2008.

Wind frequency during August, July, September and October 2007 and 2008 is represented in these figures 5 and 6. The probe was installed at the western region of the study site. Thus, the results suggest that wind effects from the south were dominant in 2008 and not in 2007.

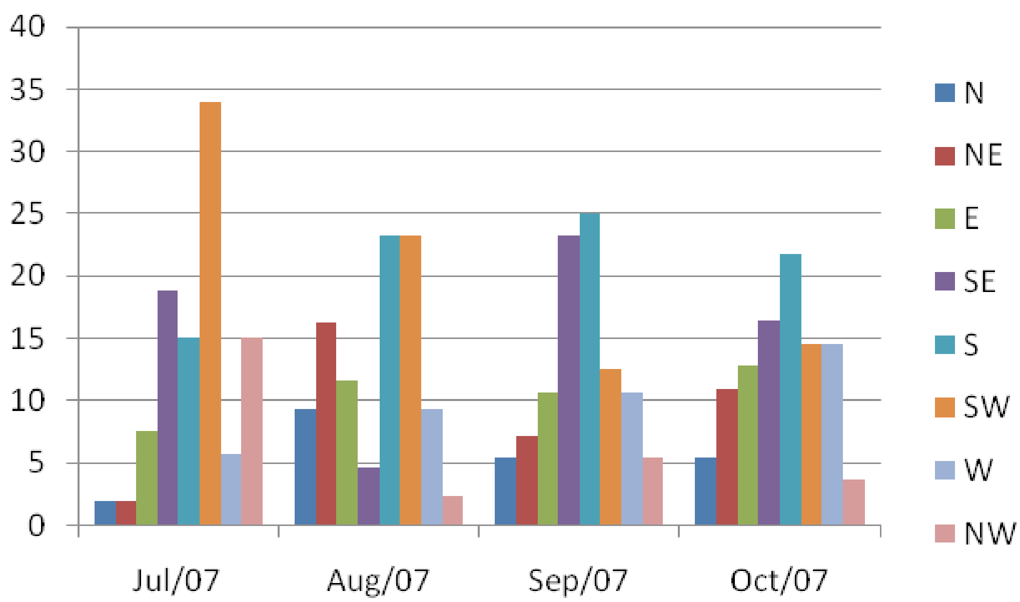

Figure 4. Wind frequency by direction (from July to October 2007)

N: North; NE: North East; E: East; SE: South East; S: South; SE: South East; West; North West

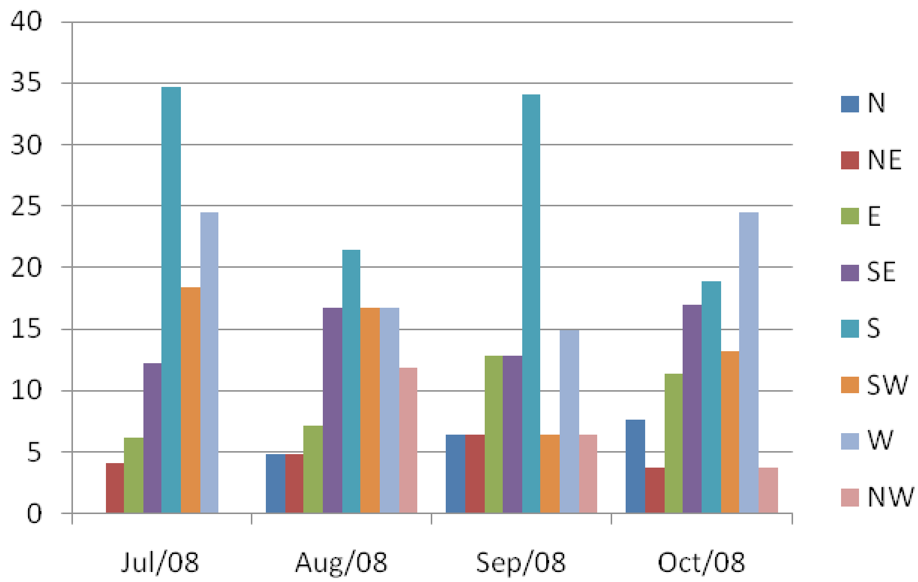

Figure 5. Wind frequency by direction (from July to October 2008)

The results of this investigation demonstrated that the wind effect cannot be ignored for explaning the occurrence of cyanobacteria blooms at any given point in the water body. This is also proposed in the study by Izydorczyk et al. (2005) although they did not quantitatively demonstrate an effect from the wind.

The correlation matrix presented in Tables 1 and 2 along with the contribution of Hu et al. (2009) reinforces the choice made of further consideration of the weather parameters Meteorological factors will be included when developing a coupled hydrodynamic-cyanobacterial growth model.

Thus, the continuation of this work will be directed towards a better approach to prevent negative consequences of cyanobacteria bloom occurrence in a water body (such as impairment of drinking water quality and recreational uses).

CONCLUSION

This study shows that there is an existing relationship between the weather parameters included in the meteorological factor that was calculated. Cyanobacteria growth modelling in aquatic environments must take into account this factor.

A coupled hydrodynamic-cyanobacterial growth model will be developed. The SIMPLE algorithm developed by Patankar (1980) will be used to simulate the hydrodynamics of the bay to further elucidate the effects of a multitude of factors on cyanobacterial occurrence and their effect on a variety of water uses such as recreation and drinking water quality.

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Pollutants Runoff Characteristics on Various Stormwater vents in Industrial Complex

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Keywords

First flush; Industrial complex; Nonpoint source; Stormwater runoff; Water quality

Abstract

This paper assesses the impact and quantifies the relative contribution of stormwater runoff (diffuse pollution sources) on the quality of receiving water in the industrial complex catchment of Korea. The selected qualitative parameters were biochemical oxygen demand, chemical oxygen demand, suspended solids, total phosphorus, total nitrogen and heavy metals. Total of 13 stormwater events were monitored to investigate the first flush phenomenon. The first flush phenomenon may be defined as the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than during later stages. The catchment presented a strong first flush for almost all storms and most constituents. The analysis shows that treating the maximum amount of the early part of the runoff is a better strategy than treating a constant flow rate. First flush criteria was between pollutant mass 41.2 to 63.4% (Ind-A) and 28.8 to 56.8% (Ind-B) in the first 20% of runoff volume.

INTRODUCTION

Urban stormwater discharge during wet weather flow is a major contributor to the pollution of many receiving waters [1, 2, 3, 4]. Climatic conditions such as the existence of long dry or wet periods may greatly impact pollutant emissions from urban stormwater discharges. Nonpoint sources (NPSs) occurs when precipitation from rain or snowmelt flows over the ground. Impervious surfaces like paved storage yards, driveways, parking lots, roof tops, sidewalks and streets prevent stormwater from naturally soaking into the ground. NPSs pollution, unlike pollution from industrial and sewage treatment plants, comes from a large variety of sources and is so widespread because of its possible occurrence at any type of land use [5, 6, 7]. Introducing urban developments, with paved and impervious surfaces, to rural catchments increases surface runoff that is discharged more quickly to the receiving water. Specialised land uses such as storage and trade centres in commercial and industrial areas, agricultural property and airports may contribute additional pollutant loading such as nutrients from agricultural property or deicer from airports. These special-use properties must be studied individually to determine specific pollutant loading. Storm water falling on partly sealed surfaces generally partly infiltrates directly in the subsurface. Paved areas such as industrial areas and commercial areas are stormwater intensive land uses since they are highly impervious, and have high pollutant mass emission from vehicular activities [8].

The early runoff in a storm event is often more contaminated than the later part of runoff, which may be due to several factors, including the mobilization of material accumulated during antecedent dry periods, a lack of dilution flow and a disproportionate runoff volume from the impervious surfaces, where pollutants may accumulate. Strong first flushes are usually associated with small impervious catchments such as highways and parking lots [9], and specific rainfall patterns [10]. Stormwater runoff has been identified as one of the leading causes of deterioration in the quality of receiving waters, especially during the first-flush. Very restrictive criteria were proposed by French researchers [11], who pointed out that the phenomenon occurs when at least 80% of the pollution load is carried by the first 30% of the runoff volume. Following this definition, rainfall events characterized by such an intense pollutant wash-off are so rare that it almost means to renounce to the first flush concept itself. Less restrictive criteria, based just on the condition that the pollutant mass cumulative curve exceeds the curve of runoff volume, were assumed in other studies [12, 13]. Deletic [14] defined the first flush as the percentage of total event pollution load transported by the first 20% of the storm runoff volume. Best management practice (BMP) focusing on treating first flush runoff is being considered as a more economical approach for reducing contaminates from stormwater [15,16].

This paper describes the results of a monitoring program for stormwater runoff in a 1.2 and 2.1 km^2 watershed located in Kimhae (Ind-A) and Busan (Ind-B) cities, Korea. which were located to national industrial complex. This study documents the existence of strong first flush for almost all storms and most water quality parameters.

METHODOLOGIES

Catchment description

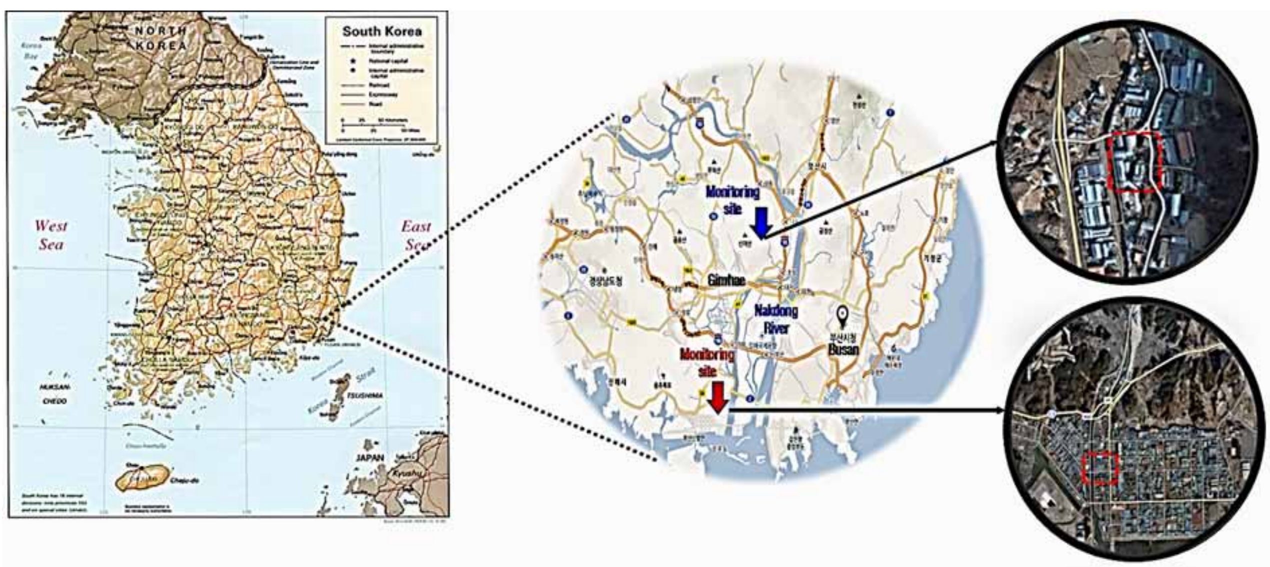


Figure 1. Location of sampling sites of industrial complexes in the Kimhae (Ind-A) and Busan (Ind-B).

Two industrial complexes watershed in Kimhae (Ind-A) and Busan (Ind-B), South Korea, were selected for monitoring during the period of January-November 2009 (Fig. 1). The industrial watershed, Ind-A and Ind-B, have an open channel separated sewer system. Ind-A receives on average 1200 mm of rainfall per year, and most of the stormwaters are concentrated during summer. The watershed area of Ind-A is 1.2 km^2, and was recently developed as an industrial complex area. The stormwater runoff from the Ind-A watershed was the Sachon stream by outlet of manhole. Ind-B receives on average 1491 mm of rainfall per year, and most of the rainfall is concentrated during summer. The watershed area of Ind-B is 2.1 km^2, and was recently developed as an industrial complex area and the stormwater runoff from the Ind-B watershed was located seaside by outlet of manhole. The Industrial complex watershed is divided into two sub-basins by factory type. Table 1 summarizes the watershed physical characteristics of these monitored sites.

Table 1. Description of catchments used in this study

Experiment catchments	Drainage area (km^2)	General characteristics	Impervious area (%)	Land slope (%)
Sub-basin Ind-A	1.2	Metal, paper, food	85	0.8
Sub-basin Ind-B	2.1	Machine, commercial	95	1.0

Sampling and analysis

In order to measure stormwater runoff flow rate from the industrial area, a manhole was opened and the velocity and depth of water runoff was measured by using a flow velocity sensor (PLO-tote3, Marsh-mcmir). Flow rate was calculated from the velocity and the water depth. At the same time, manual samples were collected from the outfall of the manhole. The sampling was started at the initiation of a rain event and ended at the time when the flow receded down to the dry weather water level. The sampling interval was approximately 3–5 min till the flow reached at the peak flow rate, and 15–120 min after the peak flow rate. The samples were transported to the laboratory for analysis according to APHA standard methods (APHA, 2004). Water quality parameters including pH, bio chemical oxygen demand (BOD), chemical oxygen demand (COD), total organic carbon (TOC), total suspended solid (TSS), total nitrogen (TN) and total phosphorus (TP). Heavy metal was measured using atomic absorption spectrophotometry (Perkin Elmer AAS300) with microwave digestion assisted. Table 2 shows the mean and median values, standard deviation and range of the water quality parameters for the samples collected during the 13 storms.

Table 2. Basic statistics of all storm events

Catchments	Parameters(μg/L)					Parameters(mg/L)				
	pH	Cu	Cd	Cr	As	TSS	COD	TOC	TN	TP
Ind-A										
Mean	8.26	33.96	0.07	0.51	0.09	20.53	44.03	9.44	24.71	4.12
SD	0.24	29.72	0.10	0.41	0.09	14.17	18.81	3.32	14.88	2.98
Ind-B										
Mean	5.53	49.69	0.15	0.71	0.19	54.04	49.2	7.82	6.27	0.32
SD	0.12	45.71	0.13	0.61	0.11	28.09	70.96	2.15	3.30	0.17

Data collection

Water quality and flow measurement data have been collected for 13 stormwater events. In Table 3 the main characteristics of the monitored stormwater events are summarized. It can be noted that such events, collected mainly during the spring and summer periods, present wide spread characteristics. The storms had rainfall depths ranging from 7 to 191 mm and the duration ranged from 0.5 to 16 hr. The dataset includes a wide range of storms with different intensities and depths. The antecedent dry days (ADD) ranged from less than 2 to 21 day. Thirteen of the storms were successfully sampled with 10 or more grab samples. Equipment failures or insufficient rainfall limited sampling from five storms. A subset of representative storms was selected for first flush analysis.

Table 3. Characteristics of each stormwater events

Event no.	Area (km^2)	ADD (day)	Total rainfall (mm)	Runoff Duration (hr)	Runoff rate
Event 1	1.2	3	12	7:15	0.41
Event 2		2	7	5:34	0.54
Event 3		21	24	8:18	0.66
Event 4		3	40	13:00	0.71
Event 5		4	191.5	13:00	0.79
Event 6		9	15.5	7:21	0.64
Event 7		2	19	4:59	0.67
Event 1	2.1	21	20.5	9:01	0.64
Event 2		3	44.5	12:50	0.71
Event 3		9	7.5	0:28	0.51
Event 4		4	191	16:03	0.81
Event 5		9	21	6:16	0.62
Event 6		2	18.5	4:59	0.63

Table 4 shows event mean concentration (EMC) of SS, BOD and COD for the selected storms. The EMC was calculated as a flow weighted average of the individual grab samples. This result is probably due to urban surfaces generating runoff constituted mainly by streets, parking lots and other paved surfaces that may contain the same pollutants as runoff from industrial area Taking into account the existing relationship between suspended solids and heavy metals in aggregated form, in the present study a greater attention has been paid to the monitoring of heavy metals in dissolved form. In fact, the presence of pollutants in dissolved form plays a primary role in the design of suitable first flush treatment processes since high concentrations of dissolved pollutants could make settling or filtration alone scarcely efficient [17,18,19].

Table 4. EMC of runoff pollutants for the selected storms

Parameter		Unit	Ind-A				Ind-B			
			Ave.	SD.	Min.	Max.	Ave.	SD.	Min.	Max.
Physico-Chemical parameters										
1	EC	μS/cm	44.5	24.8	5.7	159.4	353.0	164.5	145.0	743.0
2	pH	-	7.1	1.0	4.3	8.6	5.5	0.6	4.5	6.6
Sum parameters										
3	BOD_5	mg/l	7.9	3.9	7.9	13.9	11.7	6.6	3.1	19.0
4	COD	mg/l	10.8	5.7	10.8	23.2	21.9	13.2	4.7	38.1
5	TOC	mg/l	3.7	1.4	3.6	6.2	5.3	3.1	1.4	9.3
6	TSS	mg/l	15.3	4.9	15.3	24.9	20.9	11.4	9.7	38.3
Nutrients										
7	TN	mg/l	2.9	2.9	2.8	7.8	2.5	1.4	1.6	5.4
8	TP	mg/l	0.22	0.18	0.05	0.6	0.61	0.5	0.09	1.2
Heavy metals										
9	As	μg/l	1.1	0.9	0.4	1.6	1.5	0.8	0.1	2.1
10	Cd	μg/l	1.2	0.7	0.2	3.5	2.7	1.5	0.1	3.5
11	Cr	μg/l	4.6	3.7	1.8	8.5	6.3	2.9	0.5	8.3
12	Cu	μg/l	29.5	19.7	1.2	47.2	36.4	24.3	1.2	45.1

First flush effect

A definition of the first flush is the initial period of stormwater runoff during which the concentration of pollutants is substantially higher than those observed during the latter stages of the storm event [20]

$$[Pi/\ Pi]/[Qi/\ Qi] \tag{1}$$

where *Pi*, dimensionless cumulative pollutant mass; *Qi*, dimensionless cumulative runoff volume. A first flush exists at time t if the dimensionless cumulative pollutant mass *Pi* exceeds the dimensionless cumulative runoff volume *Qi* at all instances during the storm events. 1 :1 line, when plotting *Pi* vs. *Qi*, indicates that pollutants are uniformly distributed throughout the storm events. If the data for a particular storm falls above the 1 :1 line, a first flush is suggested. The existence of a first flush depends on the type of pollutant, size of the catchment as well as the surfaces.

Mass first flush ratio

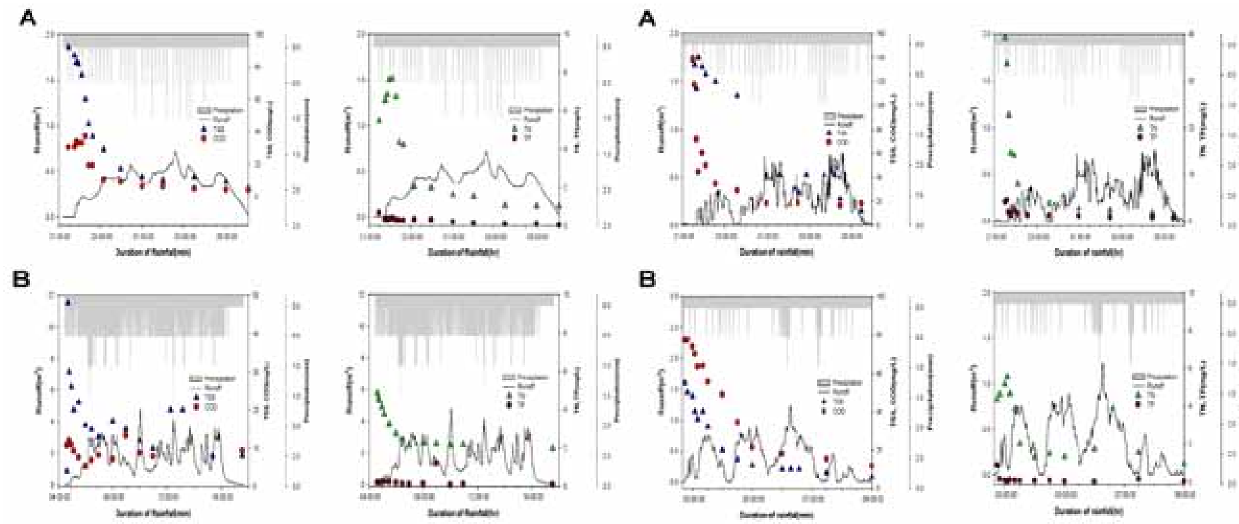
The MFF describes the fractional mass of pollutants emitted as a function of the storm progress. It can be calculated for any point in a storm and defined as follows:

$$MFF_n = \frac{\dfrac{\int_0^{T_1} c(t)q(t)dt}{M}}{\dfrac{\int_0^{T_1} q(t)dt}{V}} \tag{2}$$

where n is the index or point in the storm, and corresponds to the percentage of the runoff, ranging from 0% to 100%. M is the total mass of emitted pollutant, V is the total runoff volume c(t) and q(t) are the pollutant concentration and runoff volume as functions of time. By the definition, MFF is equal to zero at the storm beginning and always equals to 1.0 at the end of the storm. Values greater than 1 indicate first flush. The MFF ratio is a useful tool for quantifying first flush and can be statistically characterized or used in regressions or other investigations to understand the magnitude of a first flush and storm or catchment characteristics.

RESULT AND DISCUSSION

Pollutographs analysis of surface runoff



Kimhae (Ind-A) Busan (Ind-B)

Figure 2. Pollutographs for (A) 2009/04/13 and (B) 2009/07/07 stormwater events in Ind-A and Ind-B catchment.

Combining runoff quality and flow data at Ind-A and Ind-B catchments produces pollutographs. The pollutographs of major pollutants from two stormwater events are showed in Fig. 2. The peak concentration of TN precedes the peak runoff flow rate in all stormwater events. TN concentration shows higher level at the early stage of surface runoff. It tends to be decreased with the runoff flow, no matter whether another flow peak exits or not. Especially for the rainfall event of A and B, the highest concentration of TN appears at the first sample and then gradually decreases, showing strong flushing effects. This suggests that TN source might be exhausted and subjected to dilution at the initial phase of surface runoff.

The tendency of the concentration of TSS and COD changing with runoff flow varies between rainfall events. For the stormwater events on 13 April and 7 July, the peak runoff flow rate precedes the peak concentrations of TSS and COD. The stormwater characteristic, ADD condition and land cover in catchment influences the profile of pollutographs. Lower stormwater intensity (stormwater event on 13 April) made rainfall slowly infiltrate, generate the surface runoff, and wash off the pollutants on the surface of the catchment. As mentioned before, a park located in the upstream of Ind-A and Ind-B catchments may cause short time processes. Comparably, the stormwater event on 7 July with more depth (190 mm) and runoff rate (0.79 and 0.81) enabled the buildup mass on the surface to wash off quickly and continuous runoff of pollutants.

First flush effect of

The first flush was observed when the data ascended above the 1:1 line. The 1:1 line represented the case when the concentration of pollutants remained constant throughout the storm runoff. Conversely, dilution was assumed to have occurred when the data fell below the 1:1 line. The first flush is greatest for events 13 and 20 but fall short of fitting either that Buffleben [21] or He [22] definitions of first flush (only 73% of the mass, as opposed to 80% of the mass is discharged in the first 30% of the runoff volume). The lack of consensus is motivation to use quantitative, continuous first flush definition such as the MFF ratio. Fig. 3A and B shows the first flush for TSS, COD, BOD, TOC, TN and TP for event on 21 July. TSS, COD and TOC had a larger first flush than the other pollutants. Again, there is an obvious first flush, but it falls short of the most stringent definitions of first flush.

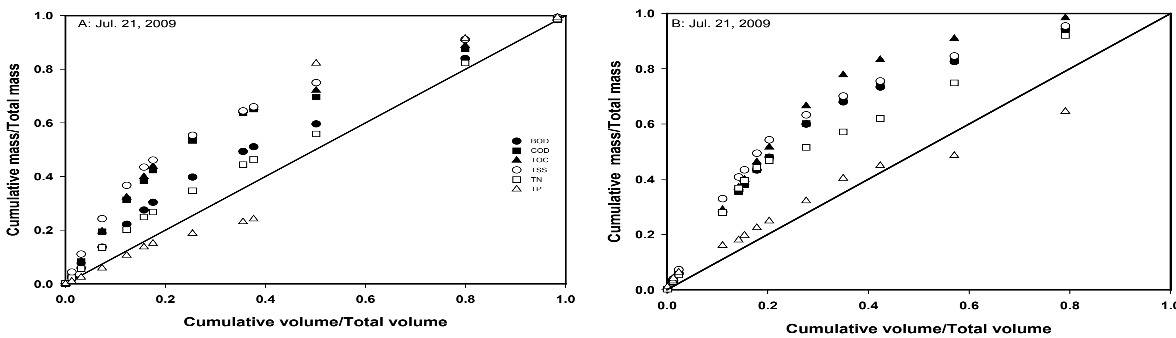


Figure 3. Cumulative mass and volume curves for runoff pollutants in stormwater event (Date: 21 July).

Quantification of first flush using MFF ratios

Table 5 shows the MFF_{20} for all events and parameters. For example, an MFF_{20} equal to 2.5 means that 50% of the pollutant mass is contained in the first 20% of the runoff volume. The ranges of Ind- A and B MFF_{20} are from 0.7 to 6.5 and 0.5 to 5.8, respectively. Event 2 (Ind-A) has the lowest values of MFF_{20} for all the pollutants observed. Small intensity rainfall such as event seven typically shows weak first flush because the runoff flow does not have time to develop sufficient energy to scour and mobilize the pollutants, and short rainfall events may not have sufficient time to wash out the pollutants so that a decline in concentration can be observed near the end of the stormwater. The MFF for COD varied for different storm events resulting from different stormwater-runoff characteristics, and generally has similar trend with the MFF for TSS. This is likely because of the affinity of COD for particulate matter, resulting in similar washoff behavior with that of TSS.

In contrast, the TP MFF_{20} changes only slightly for different events. Event 4 (Ind-A and B) had the largest MFF_{20} for TSS (MFF_{20} = 4.2 and 3.7) and COD (MFF_{20} = 3.5 and 2.8).

Table 5. MFF_{20} for Ind-A and Ind-B stormwater events at various quality parameters

Event No.	Total rainfall (mm)	BOD	COD	TOC	SS	TN	TP	Elapsed Time (min)	Cumulative Rainfall Depth (mm)
Ind-A									
Event 1	12	2.06	2.06	1.58	1.21	4.03	4.71	65	4.5
Event 2	7	1.38	1.12	1.13	1.39	1.21	1.52	85	6.5
Event 3	24	3.03	2.76	2.75	2.66	2.66	1.67	50	2.5
Event 4	40	3.02	3.46	2.64	4.17	4.32	4.99	60	2.0
Event 6	15.5	1.6	2.65	2.62	2.64	1.41	0.74	50	2.5
Event 7	19	1.87	1.86	2.11	1.92	2.22	2.37	75	8.0
Mean	19.58	2.16	2.32	2.14	2.33	3.02	2.67	64	4.3
Maximum	40.00	3.03	3.46	2.75	4.17	4.32	4.99	85	8.0
Minimum	7.00	1.38	1.12	1.13	1.21	1.21	0.74	50	2.0
Standard Deviation	11.57	0.71	0.82	0.66	1.09	2.01	1.77	14	2.5
Ind-B									
Event 3	20.5	1.38	1.12	1.13	1.39	1.21	1.52	120	8.5
Event 4	44.5	3.03	2.76	2.75	3.66	2.66	1.67	120	5.0
Event 6	21.0	1.60	2.15	2.12	1.44	1.02	0.74	40	1.5
Event 7	18.5	2.49	2.44	2.87	2.88	2.85	1.62	105	3.0
Mean	26.1	2.13	2.12	2.22	2.34	1.94	1.39	96	4.5
Maximum	44.5	3.03	2.76	2.87	3.66	2.85	1.67	120	8.5
Minimum	18.5	1.38	1.12	1.13	1.39	1.02	0.74	40	1.5
Standard Deviation	12.3	0.77	0.71	0.80	1.12	0.95	0.44	38	3.0

In order to treat surface runoff pollution, the values of MFF_{20} (mass first flush ratio) and FF_{20} (first 20% of runoff volume) can be considered as split-flow control criteria to obtain more effective and economical design of structural BMPs (best management practices) facilities.

Table 6 shows MFF_n for storm no. 5 with n ranging from 10% to 50%. Using the MFF_{20} ratio definition, all events except storm 13 showed a mass first flush.

Table 6. MFF_n for stormwater event (Date: 7 July)

Parameter	MFF10	MFF20	MFF30	MFF40	MFF50
Ind-A					
BOD	1.73	1.61	1.29	1.12	1.09
COD	2.42	2.65	1.78	1.32	1.25
TOC	2.57	2.62	1.89	1.21	1.13
SS	2.52	2.64	1.17	1.15	1.12
TN	1.35	1.41	1.39	1.25	1.19
TP	1.35	1.39	1.69	1.51	1.5
Average	2.09	2.16	1.54	1.26	1.21
Elapsed Time (min)	30	50	85	125	185
Cumulative Rainfall Depth (mm)	1.5	2.5	3.5	6	8
Ind-B					
BOD	2.39	2.49	2.11	1.23	1.12
COD	2.42	2.44	2.12	1.31	1.25
TOC	2.76	2.87	2.45	1.71	1.68
SS	2.59	2.88	2.31	1.75	1.69
TN	2.72	2.85	1.18	1.15	1.14
TP	1.35	1.61	1.43	1.51	1.11
Average	2.37	2.52	1.93	1.38	1.33
Elapsed Time (min)	30	40	50	110	140
Cumulative Rainfall Depth (mm)	1.5	1.5	2	5	6

CONCLUSION

The monitoring of stormwater runoff pollutants, which was performed separately for 13 stormwater events, allowed to characteristics the pollutants load in stormwater runoff from two industrial complexes. The following conclusions can be made:

1. TN source might be exhausted and subjected to dilution at the initial phase of surface runoff. The tendency of the concentration of TSS and COD changing with runoff flow varies between rainfall events.
2. TSS, COD and TOC had a larger first flush than the other pollutants. Again, there is an obvious first flush, but it falls short of the most stringent definitions of first flush.
3. First flush criteria was between pollutant mass 41.2 to 63.4% (Ind-A) and 28.8 to 56.8% (Ind-B) in the first 20% of runoff volume. Thus, the first flush management was important for NPS of industrial complex. Mass first flush ratio was obtained in this study that expected to provide the basic information for the design and operation of NPS treatment facility.

The net result of selecting BMPs to take advantage of the first flush will be cost savings, since more treatment can be affected with the same investment in BMPs. Industrial site may be every effort should be made to treat as much as possible of the first flush.

ACKNOWLEDGEMENTS

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Mitigation of Nitrate Contamination of Groundwater: Stable Isotopes and insights into the Importance of Soil Processes

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Abstract

Much of the focus on the impact of intensive fertilizer use on groundwater (GW)-nitrate levels has been on N inputs, rather than the role cropping practices play in the overall N cycling. Stable isotope studies in eastern North America, suggest nitrification of soil organic material (SOM) dominates non-growing season N fluxes to GW in both row crop and livestock settings. Here we examine the isotopic composition of tile drain effluents from experimental potato plots during the non-growing season after harvest. Isotopic characteristics nitrate are nearly identical for fertilized and non-fertilized plots, and point to nitrification of crop residues (SOM) as the dominant mediating process in the transfer of N to GW during this period. Factors affecting these losses may be as closely related to cropping practices as initial N application rates. With non-growing season fluxes representing the largest portion of annual N transfer to GW, increased winter-soil temperatures as a result of climate change raise the importance of these processes with respect to overall N losses to GW. Accordingly, attention should be given to overall cropping practices and the management of these non-growing season N losses in addition to regular nutrient management planning.

Keywords

Nitrate; agriculture; groundwater; stable isotopes, potato

INTRODUCTION

Global efforts to provide a sufficient food supply to meet the needs of a rapidly growing population have depended on the expansion and intensification of agricultural production. These efforts have been accompanied by increases in the wide-spread and intensive use of fertilizers (inorganic and organic) and in many areas, by a progressive degradation of GW and surface water (SW) quality; Galloway *et al.*, 2004, Townsend and Howarth, 2010). Furthermore, our reliance on inorganic fertilizers is not likely to change in the short term. Galloway *et al.* (2004) project that global production of reactive N by the Haber-Bosch process to reach 165 Tg Nyr-1, compared to the 100 Tg Nyr-1 produced in the early 1990's. With this heavy reliance on fertilizers, it is not surprising that much of the emphasis on reducing agricultural impacts on water quality have focused on manipulation of N inputs, and less attention has been devoted to the complex role that agricultural soils and cropping practices employed on these lands play in the overall cycling of nutrients and their release to GW and SW resources. Previously we have documented the importance of nitrification of crop residues in mediating the transfer of N from agricultural lands to GW on a watershed scale (Savard *et al.* 2007, 2009, Somers and Savard, 2009). Here we use nitrate stable isotopes to examine the sources of non growing season N-fluxes in tile drain effluents from a suite of experimental potato plots under typical crop rotation practices at the Harrington Experimental Farm. Our aim is to provide insights into the processes controlling N losses to GW that will support the on-going development of effective remediation strategies within the Province and for similar settings under temperate climate conditions.

BACKGROUND

The current study area is situated in Prince Edward Island, a small eastern Canadian province in the Gulf of St. Lawrence, which relies entirely on GW supplied from a series of un-confined, fractured sandstone aquifers as a source of potable water. The Province has gently rolling topography, a humid-continental climate, and 46% of its overall land mass of 5,656 km^2 is devoted to agriculture. Elevated GW nitrate levels have become a growing concern for drinking water, and the discharge of nitrate-rich GW to SW is believed to be the dominant factor in N loading of small but ecologically and economically important estuaries where the frequency and severity of eutrophication and anoxic events has been increasing. In spite of over two decades of study, the situation continues to worsen in many parts of the Province, and a drop in N losses by as much as 50% may be required to reduce groundwater nitrate concentrations to acceptable levels in some areas (Jiang and Somers, 2008, Paradis *et al.*, 2007).

METHODS

Stable isotope characteristics ($\delta^{15}N$ in soils and soil-water nitrate, $\delta^{18}O$ in soil-water nitrate, $\delta^{2}H$ and $\delta^{18}O$ in soil water) and nitrate concentrations were determined for samples of agricultural tile drain effluents collected from selected experimental plots following a potato crop at the Harrington Experimental Farm of Agriculture Canada, located 11 km north of Charlottetown (PEI). Plots selected included one treated with chemical fertilizers, one with liquid hog manure and a third one with no fertilizer.

Sampling

A suite of tile drain effluent samples were collected from an established tile drain facility comprised in total of twelve 0.5 ha sub-surface tile drain plots under a single field in the northern portion of the Harrington Experimental Farm. The design and set-up of these experimental tile-drain plots have been described in detail by Milburn and MacLeod (1991) and are not discussed further here. Samples were obtained on five occasions from 3 of the 12 plots during the period of November 2007 to June 2008, when sufficient discharge from the tile lines made sampling possible. All samples were collected directly from the outlets from individual tile lines under a field in a traditional three-year potato rotation (potato-grain-hay) with clover being grown in 2006, potatoes in 2007 and grain in 2008. The treatments (e.g. plots) selected for sampling included 300 kg/ha N in fertilizer as ammonium nitrate, 200 kg/ha N from liquid hog manure and a check plot with no added N. Samples were collected during periods when active flow was evident, and kept cool until delivery to the laboratory, where they were filtered, and aliquots for nitrate $\delta^{15}N$ and $\delta^{18}O$ analyses immediately frozen. In addition to water samples, to more specifically characterize the isotopic composition N in soils for the three test plots, soil samples from each plot were collected in January of 2008, and analyzed for $\delta^{15}N$ ratios. Sampling was conducted by auger, with collection mid-way and at the bottom of the ploughing depth, at three points in each selected plot (total of 18 samples). Samples were collected directly from auger flights and placed in zip-lock bags, and immediately frozen prior to transport to the laboratory for analysis.

Analyses

Water samples were analyzed for nitrate concentrations and isotopic characteristics of water ($\delta^{2}H$ and $\delta^{18}O$ values) and nitrate ($\delta^{15}N$ and $\delta^{18}O$). Nitrate concentrations were determined at the PEI Analytic Laboratories by quantitatively reducing nitrate to nitrite by passage of the sample through a copper cadmium column. The nitrite (reduced nitrate plus original nitrite) is then determined by diazotizing with sulfanilamide followed by coupling with N-(1-naphthyl) ethylenediamine dihydrochloride (NED). The resulting water soluble dye is measured by colorimetry at 520 nm, using a Quickchem 8000 Flow Injection Analyzer. Precision for nitrate analysis is 7%. All isotopic analyses were performed by the Delta-Lab of the Geological Survey of Canada (Québec). The preparation for $\delta^{15}N$ and $\delta^{18}O$ analyses of NO_3^- is performed following ion-exchange resin extraction and silver-nitrate precipitation as described in Savard *et al.* (2007). Silver nitrate sub-samples are placed in silver capsules then processed using an Elemental Analyzer on-line with an gas-source Isotope Ratio Mass Spectrometer (GS-IRMS) for the analyses of $\delta^{15}N$ values, and a pyrolysis system connected to an GS-IRMS for the ^{18}O analysis. Average precisions obtained on sample replicates are 0.1‰ for $\delta^{15}N$, and 0.2‰ for $\delta^{18}O$ values.

RESULTS AND INTERPRETATION

Nitrate concentrations in tile-drain effluent samples collected at Harrington Farm in mid November 2007, after harvest of the potato crop, were 17.6, 50.5 and 20.0 mg/L NO_3-N for the fertilizer, manure and check plots, respectively (Figure 1a). Over the following 6 months, nitrate concentrations in effluents from all test plots gradually declined, ranging from 11mg/L (fertilizer plot) to 13.2 mg/L (manure plot) by June of the following year.

Initial $\delta^{15}N$ values for dissolved nitrate in soil water from the fertilizer plot are essentially the same as those from the check plot (Fig. 1b), and remain so throughout subsequent sampling periods, while the initial manure plot results are significantly higher but converge somewhat with results for the other two plots over the sampling period (Figure 1). The $\delta^{18}O$ values in nitrate from the same samples initially show significant differences for all plots but again gradually converge to nearly identical results by early summer (Figure 1c).

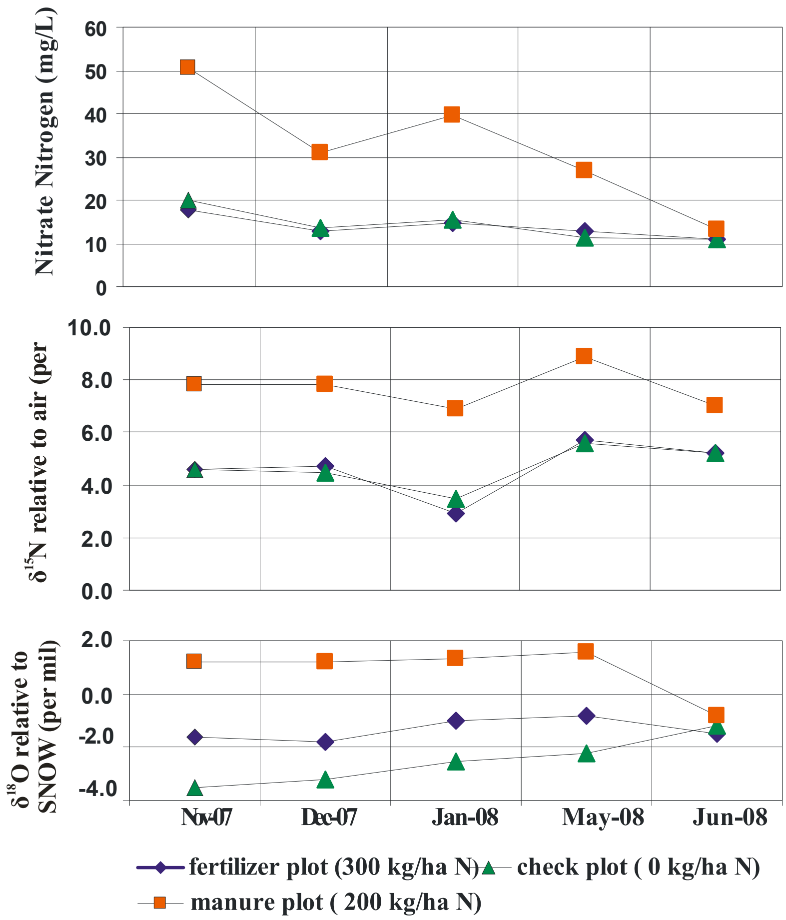

Figure 1. Nitrate nitrogen (a), nitrate $\delta^{15}N$ (b), and $\delta^{18}O$ values (c) for tile drain effluents (soil water)following potato harvest from the Harrington Experimental Farm

The 18 soil samples for the three test plots have a mean $\delta^{15}N$ value of +4.0‰. Values for the check and manure plots were very similar (+4.5 and +4.1‰, respectively), while mean values for the fertilizer plot were slightly lower (+3.5‰).

We note that $\delta^{15}N$ values are essentially identical for both the fertilizer and check plots (initial values of +4.6‰,) and fall in the same general range as values from solid soil samples collected from the same plots (+4.1 to +4.5‰). The similarity of $\delta^{15}N$ values in tile drain effluents and soils suggests that by harvest, much of the applied N not incorporated into the crop has been incorporated into the broader soil organic matter pool, and is subsequently released during the non growing season by nitrification of SOM. We emphasize, that for the purpose of the discussion here, we take the term 'SOM' to include the combined constituents of residues from the current and preceding crops, as well as the associated microbial biomass involved in the nitrification of this organic material. Given the importance of crop residues both as a source of N and as a substrate for microbial activity, we use the terms 'crop residues" and SOM interchangeably throughout the following discussion. Oxygen isotopes in nitrate of effluents from the fertilizer and check plots remain somewhat distinctive over time until early summer of the following year (Figure 2b). For the fertilizer plot $\delta^{18}O$ ratios are initially 1.6‰ compared with 3.5‰ for the check plot, suggesting some remnants of unmodified inorganic fertilizer are still present in the soil. For the manure plot, the higher initial nitrate concentrations and $\delta^{15}N$ and $\delta^{18}O$ ratios suggest some influence by organic sources, consistent with a slower release of N from manures relative to inorganic fertilizer. Nonetheless, over the course of the following 6 months, both nitrate concentrations and nitrate isotopes gradually converge toward those of the other two plots suggesting a progressive increase of the influence of nitrification of soil organic matter over time.

To shed further light on the relative contribution of different sources to the non-growing season flux of nitrate observed for each of the test plots, we use the same source apportionment model described in detail by Savard *et al.*(2009). Briefly, we use the isotopic characteristics of key N sources (inorganic fertilizer, manure and SOM), and observed isotopic values for nitrate from tile drain effluents in a system of 3 unknown variables and 3 equations (1 to 3), to estimate the proportions of nitrate derived from these discrete N sources. A constant contribution of 5% from atmospheric deposition of N is assumed, based on Environment Canada data and mass balance calculations, thus N proportions from the three main sources are calculated to total 95%.

$$1 = F_{pr} + F_m + F_{cf} \qquad \text{(eq. 1),}$$

$$\delta^{18}O_{mea} = F_{som} \times \delta^{18}O_{pr} + F_m \times \delta^{18}O_m + F_{cf} \times \delta^{18}O_{cf} \qquad \text{(eq. 2),}$$

$$\delta^{15}N_{mea} = F_{som} \times \delta^{15}N_{pr} + F_m \times \delta^{15}N_m + F_{cf} \times \delta^{15}N_{cf} \qquad \text{(eq. 3),}$$

where, F stands for fractions of nitrate from the 3 sources identified with the subscripts som, m and cf for soil organic matter, manures and chemical fertilizers, respectively. We use observed $\delta^{18}O$ and $\delta^{15}N$ values in nitrate of effluents from each plot from the period immediately following harvest, and in assigning isotopic characteristics to the three source end-members, we have used available measured values supplemented by literature data where necessary (sources $\delta^{15}N$ and $\delta^{18}O$ values used in the calculations are shown on Fig. 2). The proportions of N sources estimated by these calculations (excluding a 5% atmospheric contribution) suggest that for the fertilizer plot, 85% of N is derived from nitrification of SOM, 7% from unmodified leaching of fertilizer N and 3% from organic sources. For the check plot, 93% is attributed to nitrification of SOM, 1%, to organic sources, and there is no influence from chemical fertilizers. For the manure plot, 69% of N is inferred to be derived from SOM, 25%, to organic sources, and 1%, to inorganic fertilizers.

DISCUSSION

The results of the current study suggest that the principle contribution of nitrate leaching to GW under a setting typical of row crop production in PEI, during the non growing season, can be attributed to the nitrification of crop residues regardless of the initial N sources. This interpretation is consistent with previous observations from watershed-scale stable isotope studies conducted in the Wilmot intensive row-crop setting with extensive inorganic fertilizer application (Savard *et al.* 2007, 2009), and in the Earnscliffe Peninsula intensive livestock and associated forage crop production (Somers and Savard, 2009). The $\delta^{15}N$ and $\delta^{18}O$ results for non-growing season samples from each watershed, and for the Harrington

Farm tile drain effluents show similar average values (Fig. 2). In the Wilmot row-crop setting, while growing season N fluxes (not shown) are marginally dominated by direct leaching of inorganic fertilizers (41%), on average, non growing seasons fluxes are dominated by nitrate derived from the nitrification of SOM (76%) with direct leaching of inorganic fertilizers accounting for only 13% of the observed N load (Fig. 2).

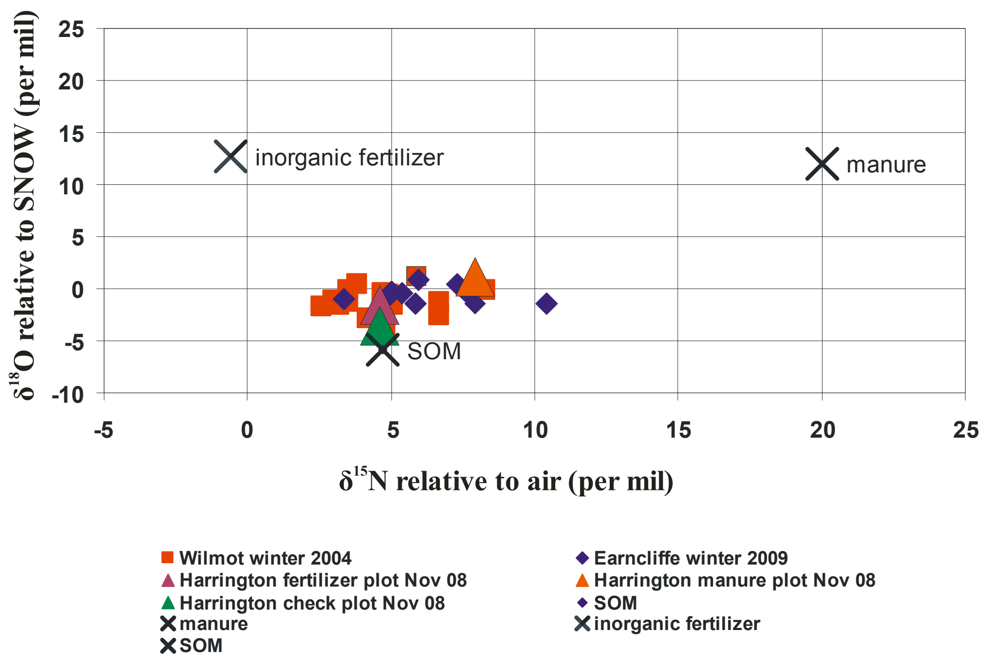

Figure 2. Non growing season nitrate isotopes for Wilmot and Earnscliffe GW samples and Harrington Farm soil water (tile drain effluent). Shown for reference are the δ15N and δ180 values used in the source apportionment calculations for the tile drain effluents

In the current work in an experimental row-crop setting, we again observe small remnant portions of nitrate attributable to leaching of unmodified inorganic fertilizer during the non-growing season for the fertilizer plot, but the majority of N losses appear to reflect the process of nitrification of SOM. In the Earnscliffe-livestock setting with extensive manure use, only slight seasonal variations in isotopic values of nitrate are observed, and on average N fluxes were dominated year round by the products of nitrification of SOM (74 to 76%), with only 15% attributed to the direct influence of organic sources. Comparison between the experimental tile drain manure plot and the Earnscliffe livestock setting is difficult because the crops and cropping practices are somewhat distinct, but nonetheless, we infer that in either case, the magnitude of leaching of unmodified manures is limited, and the dominant process responsible for the loss of N to the water table is nitrification of SOM.

Collectively, these observations support the premise that regardless of the initial source, the majority of N not taken up by crops during the growing season is incorporated into the broader SOM pool, to be subsequently released during the non-growing season by mineralization and nitrification of N temporarily "stored" in this reservoir either as crop residual material or the associated microbial biomass. It is important to note that while it can be assumed that under conditions of over fertilization, the magnitude of direct leaching of N may be related primarily to the application rate, for N released by nitrification of SOM, additional factors must be considered. The importance of tillage in stimulation of mineralization and nitrification is noted by Martens (2001) and other researchers. They have suggested that, except immediately after the fertilization period, N mineralization may be influenced by the accumulation of easily mineralized substrates (i.e. crop residual material) as a result of successive years of cultivation, rather than by instantaneous input of N fertilizers. Maly *et al.* (2002), attribute increased N mineralization rates in spring and late summer and fall (relative to main growing season) to root development (spring) and availability of post-harvest residues (fall), and suggest only a short-term response of mineralization to N application rates after fertilization.

From the data presented here little difference is apparent in non-growing season N losses from fertilized and non-fertilized plots. It is noted that however, that unpublished daily data from the full suite of 12 plots, while variable (both temporally and between replicates of the same treatment), does suggest a systematic positive correlation between initial N input rates and non-growing season nitrate concentrations in tile drain effluents (Yefang Jiang, personal communication 2011). Given the isotopic evidence implying that most of the non-growing season N flux is derived from nitrification of SOM, it is suggested that the response in non-growing season nitrate leaching concentrations to initial N application rates is largely a function of increased plant bio-mass and the resulting increased availability of plant residues in the post harvest soil profile.

Another important consideration is the timing of N transport from these soils to GW. Here we estimate the non-growing season N-flux derived from discrete N sources for each of the three study areas, by combining total non-growing season recharge with the proportionate contribution of specific N sources from our apportionment models (Fig. 3). Estimates of seasonal recharge are made following the approach of Healy and Cook, (2002) and we have used mean GW nitrate concentrations for the Wilmot and Earnscilffe data and mean tile-drain effluent concentrations for Harrington Farm experimental plots. We note that the use of average GW nitrate concentrations for the Wilmot and Earnscliffe situations underestimates the actual N flux, as these values represent averages for GW of the watershed as a whole, not just agricultural lands, and by the fact that GW sampled from domestic wells represents a mixture of seasonally recharged waters and deeper, multi-season water (Savard *et al.*, 2007). For the Harrington Farm N-flux estimates, observed concentrations from tile field effluents are believed to be a reasonable representation of seasonal leaching losses. To put these values in context, independent estimates of N loading for the full year for the Wilmot setting range from 30.2 kg/ha (van Bochove, 2007) to 34.6 kg/ha (Jiang and Somers, 2007), and for the Earnscliffe region estimated annual loasing is 36.5 kg/ha (Somers and Savard, 2009). Somers and Savard (2009) have estimated that non growing season losses in these regions may represent as much as two thirds to three quarters of overall annual N losses.

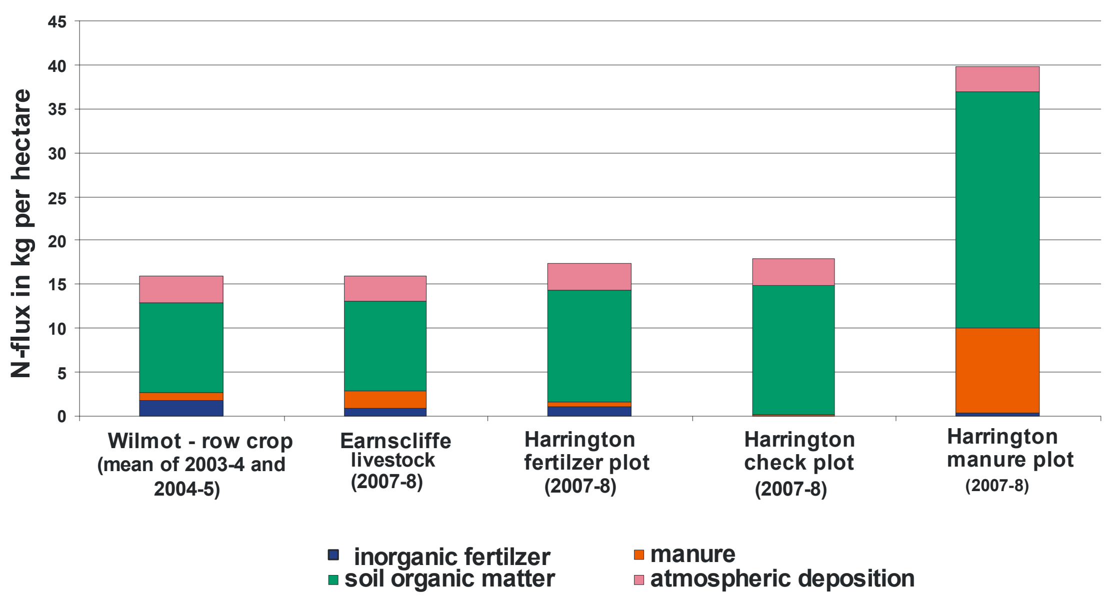

Figure 3. Estimated contribution of principle N sources to GW during the non-growing season for the Wilmot Watershed, Earnscliffe Peninsula and Harrington Farm various plots

The dominant controls on the rate of nitrification of SOM relate to a significant extent on factors other than N application rate, and as well, non-growing season fluxes are likely to be at least as important as growing-season N losses (Somers and Savard, 2009). It follows that we need to expand the scope of modification of current agricultural practices beyond traditional nutrient management and contemplate what measures can be taken to minimize non-growing season N losses to GW. Furthermore, climate change is expected to result in warmer winter-soil temperatures and potentially more frequent winter recharge events, thus these processes might play an increasingly critical role in the mitigation of N losses to GW.

Assessing the quantitative impact of possible changes to current agricultural practices on a reduction of N losses holds significant uncertainties. Nonetheless, from a qualitative perspective, it is clear that both the timing of N inputs and the agricultural practices which influence N releases are worth examination. With respect to non-growing season N losses, we suggested that delaying ploughing from fall until spring could leave more N from crop residues immobilized in the winter SOM pool, allowing its release in association with spring ploughing closer to the period of crop needs during the subsequent growing season, and reducing pre-planting fertilizer requirements. Similarly, the application of manures early enough in the fall to allow for uptake by cover crops, or delaying application until spring when N can be used by subsequent crops could also be expected to reduce non-growing season losses.

CONCLUSIONS

Our stable isotope data suggest that regardless of initial N sources, the nitrification of crop residues plays a critical role in the cycling of N in various agricultural settings. While nitrogen applied in excess of crop requirements may result in undesirable leaching of nitrate to GW during the growing season, a significant proportion of this excess nitrogen appears to be rapidly incorporated into plant residual material or other components of SOM, where its subsequent rate of release during the non-growing season is controlled by a variety of factors including cropping practices and seasonal weather and hydrologic conditions. Accordingly, effective strategies to mitigate N losses from agricultural lands must consider the impact of nitrification of crop residues, and such cropping practices as the timing of tillage or application of manure. While it is difficult at this point to quantify the benefits of such modifications, ongoing work in another region dominated by potato production is being conducted with the intent of comparing differences in N releases between spring and traditional fall ploughing of forage fields preceding planting of potato crops.

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Evaluation of an applicable extraction method for the determination of bioavailable phosphorus

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Abstract

The P_i-test is a simple chemical extraction technique to estimate bioavailable phosphorus (BAP). The test was initially developed for soil samples and has recently been used for water quality studies. In the course of this study, the reliability of the P_i-test was evaluated for phosphonates. They are used in an increasing variety of industrial and household applications such as cooling water systems, oil production, textile industry and detergents. Since most of the phosphonates are of anthropogenic origin, they may be subject to mitigation measures with regard to eutrophication. However, only little is known about their ecological relevance. The bioavailability of the phosphonates was evaluated with the P_i-test and in an algal assay with Phaeodactylum *tricornutum*, a marine diatom. While the P_i-test showed satisfactory results in comparison to the algal assay for the reference substances K_2HPO_4 and an inorganic polyphosphate, the results for the phosphonates were not adequate. All phosphonates were found to be at least partly bioavailable according to the P_i-test. However, all phosphonates showed an inhibitory effect to a greater or lesser extent on biomass growth in the algal assay. Thus, the P_i-test may lead to an overestimation of BAP in presence of significant concentrations of dissolved organic phosphorus.

Keywords

Bioavailable phosphorus; iron oxide-impregnated filter paper (P_i-test); algal assay; phosphonates

INTRODUCTION

The Water Framework Directive (WFD) targets include biological, hydromorphological and physical/chemical criteria in attaining good chemical and ecological status of surface waters by 2015. The key focus of the WFD is placed on the role of nutrients in eutrophication (Hilton et al., 2006). The term “eutrophication” is synonymous with increased growth of the biota in water ecosystems. The rate of increasing productivity is accelerated over that rate that would have occurred in the absence of perturbations to the system (Wetzel, 2001). Severe reductions in water quality and fish population may occur depending on the severity of eutrophication. The transport of nutrients, phosphorus and nitrogen, from diffuse sources (e.g. agricultural runoffs) and point sources (e.g. wastewater treatment plants) can accelerate surface water eutrophication (Sharpley, 1993b). However, the term “nutrients” is not specified precisely in the WFD. Whitney and Rolfes (2005) define a nutrient as “a chemical that an organism needs to live and grow or a substance used in an organism’s metabolism which must be taken in from its environment”.

Generally, phosphorus is often considered the most important nutrient in reference to eutrophication. However, not all phosphorus species are available for algal uptake. Boström et al. (1988) define bioavailable phosphorus (BAP) as “a component of total P which is available to biological uptake, including components of dissolved inorganic and organic P and well as bioavailable particulate P”. Dissolved reactive phosphorus (DRP) or soluble reactive phosphorus (SRP) is usually considered the most available form of phosphorus. Commonly, it is equated with orthophosphate; although there is strong evidence that an overestimation of orthophosphate is possible using the molybdenum method according to EN ISO 6878 (see e.g. Rigler, 1968; Jarvie et al., 2002; Denison et al., 1998). The bioavailability of dissolved unreactive phosphorus

(DUP) and particulate phosphorus (PP) seems to be fluctuating (see e.g. Ekholm and Krogerus, 1998). Some authors concluded a relationship between dissolved phosphorus (DP) and BAP (Young et al., 1982; Bradford and Peters, 1987). However, this correlation seems questionable, in regards to the partial availability of particulate phosphorus (see e.g. Boström et al., 1988).

Consequently, the objective of the WFD is not reducing total phosphorus, but reducing BAP. This statement is true for emissions from diffuse and point sources. However, political efforts to address BAP instead of TP are hardly to be found which can be attributed to the following: a) a lack of awareness of TP not necessarily being fully bioavailable and b) difficulties in determining BAP in routine analysis.

For the determination of BAP, algal assays and chemical extraction methods have been employed. Extraction methods are ion exchange resin-impregnated membranes (e.g. Abrams and Jarrell, 1992) as well as using NH_4F and NaOH (Sharpley, 2000). However, most of these methods are inapplicable for routine analysis, they are complex and protracted, e.g. due to long assay incubation, chemical extraction times or large solution volumes. The amount of extracted P depends on different boundary conditions, e.g. ionic strength, cationic species and pH of the extract (Sharpley et al., 1981). These limitations will be difficult to overcome.

The P_i-test is a rather simple chemical extraction technique to estimate BAP. The idea is to adsorb bioavailable phosphorus by a P-sink, in this case a strip of iron oxide-impregnated filter paper. Sharpley (1993b) states that the FeO strip method has a stronger theoretical justification for its use over chemical extractants to estimate BAP. The amount of P sorption by FeO is determined after dissolution of the FeO coating in acid (Chardon et al., 1996). Sharpley (1993c) observed that extraction from runoff sediment with FeO paper and the growth of algal cells show an excellent correlation ($R^2 = 0.92 - 0.96$). According to Sharpley (1993b), the strips can provide a highly reproducible estimate of BAP. The strips are advantageous in situations where laboratory facilities are minimal. Sharpley (1993a) attributes lower estimates of BAP from the P_i-test to a greater transport of dissolved acid-hydrolysable organic and condensed dissolved phosphorus. This implies that the mentioned P fractions do not respond to the test. The question arising here is whether these fractions are really not bioavailable or if the P_i-test fails. However, the reliability of the P_i-test must be evaluated in particular for these P fractions where bioavailability is unclear, since there is no doubt of DRP being bioavailable. The necessity for a simple reliable test for the determination of BAP is of striking evidence in order to identify the best mitigation options for eutrophication.

MATERIAL AND METHODS

The reliability of the P_i-test was evaluated with standard solutions of dissolved inorganic and organic P species that may be dominant in emissions from point sources. This is of utmost importance for the applicability of the P_i-test for the determination of BAP in real runoffs or effluents. The bioavailability of the dissolved inorganic and organic P species was tested in algal assays with *Phaeodactylum tricornutum*, a marine diatom.

Choice of P species

DUP is frequently equated with dissolved organic phosphorus (see e.g. Reichert and Wehrli, 2005; Monbet et al., 2009; Worsfold et al., 2008). This is inadequate for two reasons: a) the before mentioned evidence that a part of organic phosphorus is molybdenum reactive and thus detected as DRP and b) the presence of inorganic unreactive phosphorus in concentrations that may even exceed DRP concentrations (e.g. Sundareshwar et al., 2001). Inorganic dissolved phosphorus occurs as phosphates, which can be divided in the following groups: a) orthophosphates, b) polyphosphates, c) metaphosphates and d) ultraphosphates (Broberg and Persson, 1988). Dissolved organic phosphorus cannot be described that easily; it embraces nucleic acids, phospholipides, inositol phosphates, phosphoamides, phosphoproteins, sugar phosphates, phosphonic acids, organophosphate pesticides, humic-associated organic phosphorus compounds and organic condensed phosphates (McKelvie, 2005). Considering this variety of organic phosphorus compounds, it becomes evident that a description of the ecological significance of DUP can lead to case specific results only. A generalisation of results from e.g. the determination of bioavailable phosphorus, be it with algal assays or chemical extraction, is consequently not permissible. In contrast, for the determination of bioavailable phosphorus from the total sample, the generalisation of results may be possible if the DUP fraction is comparatively small.

In this study, the main focus is laid on the bioavailability of phosphonates. They are used in an increasing variety of industrial and household applications such as cooling water systems, oil production, textile industry and detergents (Nowack and Stone, 2000). Their use only as flame retardants accounted for about 200.000 tons worldwide in 2006 (European Flame Retardants Association, 2007). Turner et al. (2005) mention only one naturally occurring phosphonate (2-Aminoethyl phosphonic acid). For the mitigation of eutrophication, naturally occurring organic phosphorus compounds are of no relevance; they belong to the natural phosphorus cycle. Mitigation of eutrophication consequently has to address anthropogenic phosphorus inputs which are strongly the case for phosphonates.

Phosphonates are removed to a high degree by adsorption in wastewater treatment plants (Nowack, 2003); however, in case phosphonates play a significant role in the influent, the concentrations found in the effluent will still be significant and can even be dominant. From a case in Germany, temporary phosphonate effluent concentrations of more than 5 mg P/L are known (Neft et al., 2010).

There is little information available concerning the fate of phosphonates in surface waters. Nowack and Stone (2000) reported that phosphonates are substantially degraded in presence of manganese and molecular oxygen. Phosphonates may also be significantly degraded by UV radiation (Leseur et al., 2005). Presumably, the most important elimination pathway for phosphonates is adsorption or precipitation as described for calcium diethylenetriaminepentakis (methylenephosphonic acid) by Kan et al. (1994). This way, phosphonates are however not substantially degraded and may thus interfere when applying algal assays or chemical extraction procedures for the determination of bioavailable phosphorus.

The phosphonates investigated in this study were obtained from two sources: a) additives for textile finishing from a company employing them and therewith drastically increasing phosphorus effluent concentrations in the wastewater treatment plant receiving discharge from the company and b) from a company producing these additives for textile finishing. The initial P concentrations of the additives were in the range of 50 to 250 g P/L with little DRP only (< 7.5%). The additives are listed in Table 1. In addition, two other P substances were used to allow an appropriate assessment of the bioavailability of the additives: a) an inorganic polyphosphate that is used as dying additive and b) the phosphonate glyphosate, and herbicide.

Table 1. Characterisation of the additives investigated

Additive number			Characterisation	Use
	a)	1	(nitrilotris(methylene)) triphosphonic acid	Dying additive
		2	Pekoflam PES (nitrogenous phosphonate)	Flame retardant
		3	Flamentin MSG (blend of cyclic phosphonates)	Flame retardant
	b)	4	Heptol ESW (diethylenetriamine penta(methylene phosphonic acid))	Complexing agent
		5	Heptol ANO (amino tri(methylene phosphonic acid)-N-oxide)	Complexing agent
	c)	6	Polyphosphate	Dying additive
	d)	7	Glyphosate (carboxymethylamino)methylphosphonic acid)	Herbicide

Experimental design of P_i-test

The P_i-test was initially developed for soil chemical studies in the late 1970s (Chardon, 2000). Sharpley et al. (1995) described the use of the P_i-test for water quality studies. The method for the P_i-test as described in detail by Chardon et al. (1996) was slightly modified with some recommendations from the author, as given in van Rotterdam et al. (2009):

a) Take a disc of ash-free hard filter paper (e.g. Whatman No. 50);
b) Cut paper to rectangle (12·12.5 cm²) and wax 1.25 cm at two ends using paraffin; thus leaving an uncovered rectangle of 12·10 cm²;
c) Immerse the paper in 0.4 M $FeCl_3$ without any further acidification;
d) Let the paper drip dry at room temperature for 1 hr;
e) Pull the paper rapidly and uninterrupted through a bath containing 2.7 M NH_4OH (5% w:v) to neutralize the $FeCl_3$ and produce amorphous iron (hydr)oxide (ferrihydrite, denoted as FeO);
f) Rinse the paper with water to remove adhering particles of FeO;
g) After air drying, cut the paper into two 12.5 cm² strips, having a reactive surface of twice 10 cm² and two waxed ends of 1.25 cm each;
h) Shake 50 mL of P solution (as proposed by Sharpley et al. (1995) for run-off samples) end-over-end at 23 rpm (adjusted to maintain physical stability of filter papers) during 16 hrs, with one filter paper in a fixed position, mounted with the waxed ends on a holder attached to the cap of a 100 mL bottle;
i) Take out the filter paper, rinse with distilled water and let it dry at room temperature;
j) Dissolve the FeO with adsorbed P by shaking 1 hr in 40 mL 0.1 M H_2SO_4;
k) Determine P in the acidic extract.

The P_i-test experiments were performed at fairly constant room temperature of 25 ± 2°C. All P_i-tests were in triplicate.

The original calculation method of Chardon (2000) was modified to appropriately refer the amount of re-dissolved P to the dissolved P species:

$$P_i = \frac{C_P \cdot V_{H_2SO_4}}{V_{Sample}}$$

where:

P_i	FeO-extractable P content of the sample [mg/L]
C_P	P concentration in H_2SO_4 [mg/L]
$V_{H_2SO_4}$	Volume of H_2SO_4 [L]
V_{Sample}	Volume of initial sample [L]

The mean relative bioavailability of the P sample determined with the P_i-test (P_i-BAP) was calculated by referring mean P_i to the initial dissolved phosphorus concentration DP_0 by:

$$P_i\text{ - BAP} = \frac{P_i}{DP_0}$$

In addition to the determination of the P concentration in H_2SO_4, the P concentration in the sample after FeO extraction and in the rinsing water was determined for P mass balancing. All P analyses were done with the molybdenum blue method according to EN ISO 6878.

Experimental design of algal assay

The algae used for the determination of BAP, *Phaeodactylum tricornutum*, have a very strong phosphoesterase activity and can give greater estimates for BAP than the algae used in the past for the determination of BAP (Ekholm et al., 2009). Garcia Ruiz et al. (1997) found that *Phaeodactylum tricornutum* is capable of exploiting several sources of organic P for growth.

The algae were obtained from SAG Culture Collection of Algae and cultivated in sterile conditions in a brackish water medium as suggested by the supplier (SAG, 2007). For the preparation of the culture medium, a soil extract had to be produced. In total, three relevant P sources were identified in the assays: a) K_2HPO_4 as given in the medium recipe, b) P from the soil extract and c) from the inoculum. Consequently, even the blank samples where no K_2HPO_4 was added contained a small amount of P (approx 0.06 mg P/L).

The non-aerated algal assays were set up as batch assays in 250 mL flasks with 90 mL culture media without K_2HPO_4, 5 mL of P solution of interest and 5 mL of inoculum. The culture media was autoclaved before the set-up in order to avoid any contamination. The cultures were illuminated 12 hours a day with a halogen bulb giving "cool white" light which comes close to natural conditions. The pH of the assays was initially 8.0 and remained fairly constant throughout the experiment. The optimal pH range for *Phaeodactylum tricornutum* is between 5.5 and 9.0 (Bitaubé Pérez et al., 2008). The temperature was maintained constant at 25 ± 1°C in a climate chamber. *Phaeodactylum tricornutum* shows good tolerance to growth at temperatures between 15 and 25°C (op. cit.).

Phaeodactylum tricornutum growth was measured daily by extraction of 1 mL from each assay and subsequent determination of optical density at a wavelength of 600 nm. Optical density can be determined rapidly with a small amount of sample so that adverse effects to the assay could be minimised. The optical density showed adequate correlation with the dry mass of the algae that was determined at the end of the experiment.

The bioavailability of the DUP species was measured at comparatively high concentrations of 1.5 mg P/L in the assay against DRP standards of 0, 0.3 and 0.5 mg K_2HPO_4/L (as P) in the assay in addition to the P input from soil extract and inoculum. The chosen DUP concentrations exceed those found in natural waters by far. It was assumed before the experiment that the DUP species are not as available as K_2HPO_4 – choosing these high concentrations was motivated by the objective to see an effect that was beyond speculations about measurement uncertainty. All assays with K_2HPO_4 were in triplicate while the assays with DUP were in duplicate only.

Optical density remained fairly constant in all algal assays at day 30 after incubation. The relative bioavailability of the P sample as determined with the algal assay at day 30 (A-BAP_{30}) was calculated by referring the mean optical density of the individual samples at day 30 ($OD_{S,30}$) to the mean optical density of the blank samples at day 30 ($OD_{0,30}$).

$$\text{A-BAP}_{30} = \frac{OD_{S,30}}{OD_{0,30}}$$

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RESULTS AND DISCUSSION

The results from algal assays and P_i-test are given in Table 2.

Table 2: Comparison of results from algal assay and P_i-test

Additive / P source	Concentration [mg P/L]	$A\text{-}BAP_{30}$ [-]	P_i-BAP [-]
Blank sample	0	100%	n/a
1	1.5	90%	36%
2	1.5	44%	81%
3	1.5	69%	13%
4	1.5	86%	58%
5	1.5	93%	86%
6	1.5	171%	91%
7	1.5	47%	93%
K_2HPO_4	0.3	129%	n/a
K_2HPO_4	0.5	168%	93%

The results from the algal assay show that none of the phosphonates (additives 1-5) was available to *Phaeodactylum tricornutum* for the concentration given. In comparison to the blank sample, the increase in biomass was even less for the assays with the phosphonates as major P source so that an inhibitory effect on algal growth can be concluded here. Additive 2 showed an inhibition that was similar to the inhibition for the herbicide glyphosate (additive 7). From the additives, the only available was the inorganic polyphosphate (additive 6). The relative increase in biomass was similar to the increase found for 0.5 mg K_2HPO_4/L despite the three times higher concentration in P. However, the culture medium may have impeded further growth in the assay with the inorganic polyphosphate due to limitations by other nutrients.

The experiments with the P_i-test gave somewhat contrasting results. For the additives 2, 5, 6, 7 and K_2HPO_4 most of the P in the samples was found to be bioavailable. For the additives 1, 3 and 4 only a part of the initial P concentrations was found in the acidic solution. The numbers for the results given in table are to be interpreted with utmost caution. The P mass balances showed that a significant share of the initial P adsorbed on the paper strips, but was not re-dissolved with H_2SO_4. For example, the mass balance for the P_i-test for additive 1 showed a loss of P in the range of 62% which can only be attributed to P remaining on the strips after treatment with H_2SO_4. An increase of acidic strength from 0.1 M to 1.0 M increased P_i-BAP slightly.

The comparison of the results from algal assays and P_i-test shows that the results match only for the inorganic polyphosphate and K_2HPO_4. In both cases, the results from the tests showed that these P sources where bioavailable. For all phosphonates, including the herbicide glyphosate, the results from the tests lead to different conclusions. Due to methodical constraints, the P_i-test is not able to disclose inhibitory effects. Only for additive 3, the blend of cyclic phosphonates, the results of the P_i-test come satisfyingly close to the results from the algal assays. For all other phosphonates, the P_i-test did not yield acceptable results, as the amount of BAP was overestimated drastically.

CONCLUSIONS

The results from this study show that the P_i-test may overestimate bioavailable phosphorus in presence of phosphonates. The algal assays with *Phaeodactylum tricornutum* showed that all phosphonates investigated had an inhibitory effect on algal growth while the P_i-test classified all phosphonates to be available, however to a differing extent. For the inorganic P species investigated, i.e. K_2HPO_4 and a polyphosphate, the P_i-test showed that these P species were available as was also found in the algal assays.

It can be concluded that the P_i-test may fail to disclose the amount of BAP in case of significant DUP concentrations, as these DUP concentrations may contain significant levels of P species with no or even an inhibitory effect on algal growth as was discovered for phosphonates. However, the inhibitory effect of phosphonates may depend on their concentration. Further investigations on the role of phosphonates in the aquatic environment are needed.

The suitability of the P_i-test to estimate BAP should be evaluated for more organic and inorganic P species and for different experimental set-ups, as a simple and reliable test for BAP is doubtless needed in order to identify adequate mitigation measures for eutrophication. In addition, some methodical issues of the P_i-test should be addressed, as a significant P mass balance error was observed in the evaluation of measurement data. This mass balance error was attributed to P adsorbed on the paper strips but not re-dissolved by sulphuric acid. It can only be speculated about the ecological significance of this mass balance error.

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