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DYNAMIC INTEGRATED MODELLING OF BASIC WATER QUALITY AND FATE AND EFFECT OF ORGANIC CONTAMINANTS IN RIVERS

GEINTEGREERDE DYNAMISCHE MODELLERING VAN ALGEMENE WATERKWALITEITSPARAMETERS EN GEDRAG EN EFFECT VAN ORGANISCHE CONTAMINANTEN IN RIVIEREN

door

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Dedicated to Tigist and Iddoosa

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List of symbols and abbreviations

7Q10	Lowest continuous flow for a 7 days period expected to occur every 10 years	$[L^3T^{-1}]$
A	Surface area of the river tank	$[L^2]$
α	Hydraulic parameters estimated from stage flow relations	
A_{cross}	Cross-sectional area of the river tank	$[L^2]$
ASM	Activated Sludge Model	
$A_{surface}$	Surface area of the river tank	$[L^2]$
BBM	South African Building Block Methodology	
BCF	Biological Concentration Factor	$[L^3\ M^{-1}]$
BOD	Biological Oxygen Demand	$[M\ L^{-3}]$
C	Concentration in the outflow rate	$[M\ L^{-3}]$
$C_{c,b}$	Concentration of toxicant in the biota	$[M\ M^{-1}]$
$C_{c,f}$	Sorbed contaminant concentration	$[M\ M^{-1}]$
$C_{c,w}$	Toxicant concentration in the water	$[M\ L^{-3}]$
C_d	Concentration in the side stream or effluent discharge	$[M\ L^{-3}]$
C_{in}	Concentration in the inflow rate	$[M\ L^{-3}]$
COD	Chemical Oxygen Demand	$[M\ L^{-3}]$
CSOs	Combined Sewer Overflows	
CSTRS	Continuously Stirred Tank Reactors in Series	
CWA	Clean Water Act	
D	Dispersion coefficient	$[L^2\ T^{-1}]$
d_{bed}	Active sediment depth	$[L]$
DO	Dissolved Oxygen	$[M\ L^{-3}]$
DOC	Dissolved Organic Carbon	$[M\ L^{-3}]$
DWAF	Department of Water Affair and Forestry	
EQO	Environmental Quality Objective	

EQS	Environmental Quality Standards	
ET	Evapotranspiration	[L T^{-1}]
Φ	Porosity of benthic sediment	
FAII	Fish Assemblage Integrity Index	
f_d	Truly dissolved fraction in the bulk water	[-]
$f_{d,bed}$	Truly dissolved fraction in the pore water	[-]
f_{DOC}	Sorbed fraction in the bulk water	[-]
$f_{DOC,be}d$	Sorbed fraction in the pore water	[-]
f_{POC}	Sorbed fraction in the bulk water	[-]
$f_{POC,bed}$	Sorbed fraction in the pore water	[-]
F_T	Temperature correction factor	[-]
F_w	Water uptake rate efficiency	[-]
h	Water level	[L]
H	Henry's law constant	[-]
HC_5	Hazardous Concentration for 5% of species	
HRT	Hydraulic Residence Time	
IWA	International Water Association	
k_1	Toxicant uptake rate from the aqueous phase	[L^3 M^{-1} T^{-1}]
k_2	Toxicant elimination/detoxification rate	[T^{-1}]
k_{b1}	Second order biodegradation rate constant in the bulk water	[L^3 M^{-1} T^{-1}]
k_{b2}	Second order biodegradation rate constant in the biofilm	[L^3 M^{-1} T^{-1}]
k_{biodeg}	Overall pseudo first order biodegradation rate constant	[T^{-1}]
$k_{biofilm}$	Pseudo first order biodegradation rate constant in the biofilm	[T^{-1}]
k_{bulk}	Pseudo first order biodegradation rate constant in the bulk water	[T^{-1}]
K_{doc}	Truly dissolve organic carbon normalized partition coefficient	[L^3 M^{-1}]
k_f	Ingestion rate of the organism	[M M-1]
K_L	External mass transfer coefficient	[L T^{-1}]
K_{LC}	Mass transfer coefficient for the organic contaminant;	[L T^{-1}]
Koc	Carbon normalized partition coefficient	[L^3 M^{-1}]
Kow	Octanol-water partition coefficient	[L^3 M^{-1}]
K_T	Total mass-transfer coefficient	[L T^{-1}]
LAS	Linear Alkylbenzene Sulphonate	
LBR	Lethal Body Residue	[M M^{-1}]
LC_{50}	Median lethal concentration	[M L^{-3}]
L_f	Biofilm thickness	[L]
PEC	Predicted Environmental Concentration	[M L^{-3}]

PNEC	Predicted No-observed Effect Concentration	[M L^{-3}]
POC	Particulate Organic Carbon	[M L^{-3}]
Q_{in}	Inflow rate	[L^3 T^{-1}]
Q_{max}	Maximum outflow rate	[L^3 T^{-1}]
q_{max}	Maximum rate of substrate utilization	[$MM^{-1}T^{-1}$]
Q_{min}	Minimum outflow rate	[L^3 T^{-1}]
Q_{out}	Outflow rate	[L^3 T^{-1}]
QSAR	Quantitative Structure-Activity Relationships	
QWASI	Quantitative Water Air Sediment Interaction	
r	Overall reaction rate	[$ML^{-3}T^{-1}$]
RCC	River Continuum Concept	
RMS	Root Mean Square	
RWM1	River Water Quality Model No.1	
S_{GC}	Generic compound concentration (e.g. inorganic nitrogen)	[M L^{-3}]
S_{NH}	Ammonia nitrogen concentration	[M L^{-3}]
S_{O2}	Dissolved oxygen concentration	[M L^{-3}]
S_R	Relative sensitivity function	[-]
SSD	Species Sensitivity Distribution	
t	Simulation time step	[T]
TD	Truly Dissolved phase	
TDS	Total Dissolved Solids	[M L^{-3}]
TMD	Total Maximum Daily Load	[M T^{-1}]
TSS	Total Suspended Solids	[M L^{-3}]
u	Average flow velocity	[L T^{-1}]
U	Factor used to validate the model	[-]
UES	Uniform Emission Standard	
V	Volume of the tank	[L^3]
v	Water flow velocity	[L T^{-1}]
W	River water width	[L]
WFD	Water Framework Directive	[
WWTP	Wastewater Treatment Plant	
X_f	Biofilm density	[M L^{-3}]
β	Hydraulic parameters estimated from stage flow relations	
Θ	Temperature correction factor	[T^{-1}]

Part 1

Introduction

Chapter 1

Introduction

Rivers and streams are an important component of the natural environment, and need to be protected from all sources of pollution because man's own survival depends on their sustainable use. Rivers, however, are increasingly under threat from different pollutants, which include conventional pollutants (organic matter and inorganic nutrients) and hazardous substances (organic contaminants and heavy metals). Despite the fact that the river water quality can be influenced by natural phenomena such as climate and geology (DWAF, 1995; Boorman, 2003), the main sources of pollution are related to anthropogenic activities: mining, agriculture, forestry, cattle farming and urbanization. As a result, river water quality is affected by both point and diffuse sources of pollution. Point sources of pollution include domestic or industrial discharges via pipe connections to the river system, whereas diffuse sources of pollution include runoff from the agricultural land and mining sites. Currently, both point and diffuse sources of pollution have resulted in two important water quality problems in surface waters: eutrophication (nutrient enrichment) and contamination by hazardous organic compounds.

To tackle these typical water quality problems, and for the sake of both ecological and human welfare, rivers (all water resources in general) must be protected, restored and sustained. This needs appropriate nationwide environmental regulations and assessment tools. The most widely applied environmental regulations are the Environmental Quality Objectives/Standards (EQO/EQS) and the Uniform Emission Standard (UES) (Tyson *et al.*, 1993). The former is based on the pursuit of a certain immission level, i.e. the receiving water quality, whereas the latter is based on the selection of an allowed emission level, e.g. effluent water quality. In the most recent developments, the combined approach of EQO and UES - a holistic approach - is the best approach towards the protection of all waters from all types of pollutants, including both conventional pollutants and hazardous substances (Blöch, 2001).

In the assessment tools, both monitoring and modelling provide important tools for water quality evaluation. However, when one wants to predict the response of the receiving water (quality) to external stimuli (pollutant loads) only mathematical models can be used. For their predictive capabilities and cost-effectiveness, mathematical models are becoming increasingly important in water quality management, particularly in the countries where EQO is used as a regulatory framework. Hence, river water quality models are an integral part of environmental assessment tools, as they assist the environmental regulators to reach water quality objectives.
River water quality models are also applied as a tool in environmental risk assessment. There are millions of xenobiotic organic chemicals and approximately one thousand new organic chemicals are synthesized and used commercially every year (Schnoor, 1996). Some of these are carcinogenic/mutagenic (e.g. polycyclic aromatic hydrocarbons; Grimmer *et al.*, 1981), have an estrogenic effect or other adverse effects (Kime, 2001). An environmental risk assessment is therefore required to evaluate the fate and transport of these chemicals and their ultimate adverse effect to the environment. According to the principle adopted by the European Union (EU), an environmental risk assessment is based on the comparison of the Predicted Environmental Concentration (PEC) and the Predicted No-observed Effect Concentration (PNEC) (EEC, 1993). When the PEC to PNEC ratio - often called risk quotient - is less than one, the chemical of concern may not pose a risk. But when the ratio is larger or equal to one, the chemical may pose a risk and further consideration is needed. As determination of PEC (exposure assessment) or PNEC (effect assessment) requires mathematical models, a river water quality model is an integral part of environmental risk assessment too.

In this work, dynamic integrated modelling of basic water quality and organic contaminant fate and effect in rivers is explored. In this framework, a basic river water quality model and an organic contaminant fate submodel were developed and then linked. The former submodel describes the in-stream fate of conventional pollutants, i.e. nutrients, whereas the later describes the in-stream fate of hazardous organic compounds. In this integrated model, a simple effect/toxicity submodel of organic contaminant for fish is also included in order to demonstrate the application of the proposed modelling approach.

Such integrated approach is suitable to investigate the combined effects (toxicity) of both conventional pollutants and hazardous organic compounds on the aquatic organisms. This approach is different from the traditional river water quality modelling approach, which is based on studying the separate issues. However, to achieve a given water quality objective, e.g. a “good” biological quality, which is the case in the new European water policy - the Water Framework Directive (WFD) - these two water quality problems and their interaction must be considered at the same time. This is due to the fact that the biological quality of rivers depends on both conventional pollutants and contamination of organic compounds, and interaction between the two. As such, the proposed modelling approach addressed an important issue in water resource management.

In this work, a dynamic exposure modelling approach is explored. Such modelling approach is very useful for time-varying effect assessment. Time-varying effect assessment is a realistic approach because in the real world the exposure concentrations of environmental pollutants are time-varying can be variable due to different circumstances: varying rates of input, dilution, changes in chemical form, solubility, degradation, runoff events and sewer overflows. Furthermore, toxicity depends on the duration and frequency of exposure (Reinert *et al.*, 2002), and only such a dynamic exposure model can describe the compliance with the duration and frequency of the exposure concentration (Arbor, 1985).

The *problem definition* and *goal* of this Ph.D. thesis is presented in detail in the last subsection of the literature review (Chapter 2), whereas the scientific contribution and thesis outline are described below.

Thesis outline

The content of this thesis can be broadly divided into three parts. The *first part* (Chapters 4.1 and 4.2) deals with conventional river water quality modelling, where model selection, simplification and applications are discussed. The *second part* of the thesis (Chapters 5.1, 5.2 and 5.3) describes a dynamic in-stream fate model of xenobiotic organic compounds. The *third part* of the thesis (Chapter 6) deals with the integrated modelling of basic water quality (eutrophication) and fate and effect of organic contaminants. The scientific contribution and thesis outline are described below.

In Chapter 2, first the general water quality problems and sources of pollution in rivers are reviewed. Secondly, the water quality regulations applied to prevent water quality problems under consideration are discussed. Third, the general water quality modelling concepts in relation to both conventional pollutants and organic contaminant fate and effect are presented. Finally, the state-of-the-art mechanistic river water quality modelling approaches are revised and their limitations are highlighted: eutrophication, organic contaminant fate, bioaccumulation, effect assessment, and coupling of all these models towards integrated ecological effect assessment.

Chapter 3 describes the WEST® simulator in which different river water quality models were developed and implemented within the framework of this research: the simplified dynamic basic river water quality, the dynamic exposure model, and the integrated model of basic water quality (eutrophication) and organic contaminant fate and effect in rivers. Besides, problems encountered during model implementation and their solutions are discussed.

Chapter 4.1 discusses a simplified dynamic basic river water quality model, which is conceptual and suitable to apply in data-limited situations. Such a model simplification is also needed for integrated modelling of basic water quality and organic contaminant fate and effect (Chapter 6).

Chapter 4.2 describes the application of the simple dynamic river water quality model developed in Chapter 4.1 as a tool to analyse different water quality management options that can be applied to prevent the deterioration of river water quality in the downstream section of a river. It addresses essential issues of water resource management in arid and semi-arid regions.

Chapter 5.1 describes a conceptual, one-dimensional dynamic organic contaminant fate model in rivers. The effect of nutrient and dissolved oxygen dynamics on the fate of organic contaminants is taken into account.

Chapter 5.2 describes a microcosm study. The effect of nutrient dynamics on the fate of organic contaminants was investigated experimentally. This chapter provides experimental findings that give insight into the complex interaction of conventional pollutants and organic contaminants.

Chapter 5.3 describes a refinement of the integrated modelling of basic water quality and organic contaminant fate in rivers using the above microcosm study. Experimental data collected in Chapter 5.2 were used to refine the integrated model.

Chapter 6 describes the integrated modelling of eutrophication and organic contaminant fate and effect in rivers. This chapter also gives insight into the interaction of eutrophication and organic contaminant fate and effect in rivers. The toxicity under time-varying exposure concentrations is also included in the model.

Chapter 7 gives a general discussion on the results obtained during this thesis work in relation to literature studies. Furthermore, this chapter also draws some general conclusions and suggestions for future research.

Part 2

Literature review

Chapter 2

Literature review

2.1. River water quality problems and sources of pollution

Rivers and streams are an important component of the natural environment. They have many values such as aesthetic (recreation), economic (fishing, electricity generation, transport and irrigation) and ecological (biodiversity), water for consumption (water supply for domestic and industrial uses), and conveying wastewater discharges (treated or untreated). To maintain these values and their sustainable use, a given water quality standard must be met. Table 2.1 shows the typical water quality standard required for fish in the European Union (EU) member countries (CEC, 1978). This standard includes both conventional pollutants and toxic/hazardous substances. For the conventional pollutants, dissolved oxygen (DO), Biological Oxygen Demand (BOD) as a measure of carbonaceous organic matter, inorganic nitrogen (ammonia and nitrite), phosphorus and suspended solids are included. For the hazardous substances, organic pollutants, e.g. petroleum and hydrocarbons, and heavy metals (e.g. mercury and cadmium) are also considered.

However, it becomes more and more difficult to meet such water quality standards because of continuous economic expansion, urban development and growing population pressure. As a result, without appropriate water quality management or regulations the surface or ground water quality continues to deteriorate. Two water quality problems are well known in surface waters (rivers and lakes): (1) eutrophication (algal bloom due to nutrient enrichment) and (2) contamination by hazardous substances. These two problems are the main causes for deterioration of aquatic ecosystems. The contamination by hazardous substance can in particular pose risk to human health via the food chain. Subsequently, both conventional pollutants and hazardous substances remain the main focus of both basic and applied research.

Table 2.1: EU water quality standards for freshwater fishes (CEC, 1978)

Parameters	Annual average dissolved concentration	
	Salmonid fish	Coarse fish
• Total ammonia (mg L^{-1} NH_4)	<0.031	<0.16
• Non-ionized ammonia (mg L^{-1} NH_3)	<0.004	<0.004
• Nitrite (mg L^{-1} NO_2)	<0.003	<0.003
• Biochemical Oxygen Demand (BOD_5 at 20°C) (mg L^{-1})	<3	<6
• Suspended solids (mg L^{-1})	<25	<25
• pH	6-9	6-9
• Dissolved oxygen (mg L^{-1} O_2)	>5	>5
• Impacted temperature change (°C)	Must not exceed 1.5	Must not exceed 3
• Phosphate (mg L^{-1} H_3PO4)	<65	<131
• Poly Aromatic Hydrocarbons	Must not be detected	Must not be detected
• Dissolved Mercury (mg L^{-1} Hg)	<0.001	<0.001
• Dissolved Cadmium (mg L^{-1} Cd)	<0.004	<0.004

2.1.1. Eutrophication

Eutrophication is the result of nutrient enrichment in surface waters like rivers and lakes. Although it is a natural process, eutrophication can often be accelerated by anthropogenic activities, and thus it is sometimes called cultural eutrophication (Laws, 1993). The anthropogenic acceleration is due to a direct discharge of organic wastes or nutrients into the rivers and/or indirect nutrient loads via runoff from the agricultural sites. The degree of eutrophication or nutrient enrichment is a continuum, and has been attempted to classify it according to the relative extent of nutrient enrichment (Laws, 1993): oligotrophic, mesotrophic and eutrophic. Oligotrophic systems are undernourished, i.e. biological production is limited by nutrient additions. Eutrophic systems on the other hand are over-fertilized, whereas mesotrophic waters lie somewhere in between the two.

Nutrient enrichment in rivers (particularly in slow flowing ones) has a number of deleterious effects. It encourages excessive algal blooms, which can result in large fluctuations of the dissolved oxygen concentration. In some extreme cases, the rapid drop in oxygen concentration during the night due to algal respiration can kill fish. During day on the other hand, pH elevation can occur; and carbon dioxide levels may be depleted during peak photosynthetic activity (usually in the early afternoon), and thereby results in a shift in the carbonate balance. The shift in carbon balance causes the pH to increase, and this can result in unionized ammonia toxicity (when pH becomes more than 9).

Furthermore, excessive amounts of algae and macrophytes in rivers create aesthetic problems, and reduce the value of water as a recreational resource. The death and decomposition of large amounts of plant biomass can create noxious taste and odour, which is undesirable from the standpoint of recreational use. Besides, excessive biomass growth in the eutrophic systems results in competition for limited resources. A high degree of competition combined with severe chemical and physical stresses can result in the loss of species diversity. So, species diversity is much lower in eutrophic than oligotrophic systems (Laws, 1993). In other words, due to high competition a smaller number of species are able to survive in eutrophic systems.

2.1.2. Contamination by xenobiotic organic substances

In addition to eutrophication, contamination by xenobiotic organic contaminants is also an important issue in-streams or rivers. As the word ‘contamination’ reveals, the concentrations of xenobiotic organic compounds in the environment are relatively very low (in the order of $\mu g\ l^{-1}$) compared to the conventional organic or nutrient concentration (usually in the order of $mg\ L^{-1}$). Despite this low concentration, they can be toxic to the aquatic life via bioaccumulation/biomagnification in the food chain when the concentration reaches toxic level in the target site. This biomagnification property of organic contaminants, particularly for persistent organic substances, e.g. methyl mercury, DDT and PCB, is dangerous for higher trophic levels in the food chain, including humans (Olssson and Jenssen, 1975; Bro-Rasmussen, 1996; Burreau *et al.,* 2004).

It is also indicated in Chapter 1 of this work that in addition to millions of xenoboitic organic chemicals, approximately thousands of new organic chemicals are synthesized and used commercially every year (Schnoor, 1996). Some of these chemicals are carcinogenic/mutagenic (e.g. polycyclic aromatic hydrocarbons; Grimmer *et al.*, 1981), have an estrogenic effect (Kime, 2001) or other advers effects. Although the majority of them are degraded in the environment, it needs to be checked that they do not pose any adverse effect on the environment. In an attempt to assure that a chemical-of-concern does not pose any adverse effect or risk to the environment, environmental risk assessments need to be carried out (Schnoor, 1996). More details are given in section 2.4.

2.1.3. General sources of pollution

Although natural processes, e.g. rock weathering and climate changes can affect water quality (DWAF, 1995), the main sources of water pollution are caused by anthropogenic activities that can affect surface water quality. The sources of water pollution are mainly divided into two categories: *point* and *non-point* (diffuse) sources.

Point sources are typically piped discharges from municipal wastewater treatment plants, industrial facilities, small packaged treatment plants, large urban and industrial stormwater systems and residential straight piping. Non-point sources on the other hand include stormwater runoff from timber harvesting, agricultural lands, rural residential development, failing septic systems and mining. Nutrient enrichment of surface water, as the result of runoff from agricultural land in particular, is the most challenging problem in environmental management (Duda, 1993; Carpenter *et al.*, 1998). Whilst the impacts of point source pollution can be minimized with proper management of wastes and land use activities, it is difficult and resource intensive to reduce the contributions of non-point pollution sources to water quality degradation in a given watershed.

2.2. Water quality regulations

Water is limited both in quantity and quality. As available fresh water is limited (only 1% of the total water reserve), its good quality must be maintained and polluted water must be restored. Thus pollution and scarcity of water resources are the most important challenges in some countries, especially in arid and semi-arid regions (Al-Kharabsheh and Ta'any, 2003). The problem of water scarcity can be addressed by efficient water use, whereas the problem of water pollution requires the implementation of an appropriate water quality regulation. In order to protect all water bodies from all sources of pollution, every nation therefore needs to have appropriate water quality regulations.

In the early stages, water quality regulation was based on physical and chemical water quality criteria. However, this is not reliable unless it is supplemented by biological criteria. Currently, the physicochemical method is thus supplemented by biological and ecological criteria for the purpose of restoring and maintaining the ecological integrity of water resources. Among such water quality criteria, the new EU Water Framework Directive (WFD) (CEC, 1999) and the Clean Water Act (CWA) of the USA (Chen *et al.*, 1993) are the most important water quality regulations.

2.2.1. EU Water Framework Directive

The historical development of the European Union (EU) water legislation is presented elsewhere (Tyson *et al.*, 1993; Blöch, 2001; Kallis and Butler, 2001; Zabel *et al.*, 2001), and can be summarized into three "waves". In the "first wave" of EU water regulations, before 1980 (after the Treaty of Rome was signed in 1972), the main concern was directed to at the protection of "public health" and harmonization of environmental rules to avoid market distortion. This first legislation can be broadly characterized into two types (Somsen, 1990): water use directives and water pollutant directives. The water use directives include drinking water directives (CEC, 1975 and 1980a), the water for bathing directive (CEC, 1976a), fish and shellfish harvesting directives (CEC, 1978; CEC, 1979). Water pollutant directives include the dangerous substance directives for surface waters (CEC, 1976b) and for groundwater (CEC, 1980b). This legislation addressed only a limited number of waters such as those rivers and lakes used for drinking water abstraction. As the ecological degradation was not addressed in this early water legislation, the nutrient load from urban systems and agricultural sites resulted in considerable deterioration of the ecosystems mainly due to eutrophication, disappearance of wetlands and salination of coastal groundwater.

This ecological problem resulted in the "second wave" of EU water legislation in which two important water legislations were adopted: the Urban Wastewater Directive (CEC, 1991a), which addresses the water pollution from all settlements; and the Nitrates Directive (CEC, 1991b), which addresses the water pollution by nitrates from agriculture; whereas the Urban Wastewater Directive has already achieved considerable progress in getting the surface water cleaner, the nitrate level still remains high in rivers, and the implementation of the nitrate directive is indicated to be unsatisfactory because the EU water policy was fragmented in terms of objectives and means to control water pollution.

Consequently, a new single piece of framework legislation was proposed, which involves a range of instruments, scientific and technical cooperation at regional and European level. This brings about the "third wave" or the current period of EU water legislation, the so-called new European water policy or the Water Framework Directive (WFD).

This new directive is established with the following key objectives (Blöch, 2001):

- protection of all waters such as surface water and groundwater;
- achieving "good" ecological and chemical status for all water by a set deadline of 15 years;
- water management based on a river basins approach;

- emissions and discharges control by a “combined approach” of emission limit values and quality standards;
- getting the price right: mandatory pricing policy for water, contributing to the wise use of water and thus to resource protection, and
- getting the citizen involved more closely: strengthen public participation.

Summarizing, the ultimate goal of the directive is to achieve a “good” ecological and chemical status in the surface waters and “good” chemical status in groundwater. Surface water is defined as of good ecological quality if there is only slight departure from the biological community that would be expected in conditions of minimal anthropogenic impact. This indicates that the standard process is provided in the WFD for defining local standards accordingly. To achieve the ultimate objective, the directive introduced other mandatory approaches as indicated above: river basin approach, combined approach, setting water price and strengthen public participation. The river basin approach is the main innovation of the directive in the sense that rivers and lakes will need to be managed by the natural geological and hydrological unit instead of according to only administrative or political boundaries. This approach is generally agreed as the most effective way to address water pollution by all possible sources.

2.2.2. USA: the Clean Water Act of 1972

Increasing environmental concerns resulting from water quality degradation in the United States led to the passage of the Federal Water Pollution Control Act Amendments of 1972 (PL 92 92-500) and amendments passed in 1977 (PL 95-217) and in 1987 (PL 100-4), collectively referred to as the CWA (Chen *et al.*, 1993). The objectives of the Clean Water Act (CWA) include:

- restoring and maintaining the chemical, physical, and biological integrity of the nation’s waters;
- achieving water quality suitable for protection and propagation of aquatic life and to provide for water recreation, and
- achieving the ultimate goal of eliminating the discharge of pollutants (zero discharge).

The Total Maximum Daily Load (TMDL) is used as a guiding principle to restore the polluted waters. It accounts for all sources of pollution: since 1999 both point and non-point source pollution are considered. Before that time TMDL only considered point source pollution. The TMDL is the amount of specific pollutants that a river, stream or lake can assimilate and still meet the water quality standards. The Clean Water Act requires that regulatory agencies determine total maximum daily loads for every water body that does not meet water quality standards. The TMDL is calculated for water bodies and the control measures are implemented to ensure that this level is never exceeded. It is developed in two steps: calculation of the maximum amount of a pollutant that a water body can take in and still meet the water quality standards, and a distribution of that amount to the pollutant's sources. To implement the TMDL, the regulations agency works with local governments and the public to determine how to reduce pollutant loads to bring the impaired water into compliance. The implementation of TMDL most often involves putting Best Management Practices (BMPs) in place or upgrading the wastewater treatment plants.

Being based on the river basin approach, the water legislation in the EU and the USA share the same approach in addressing the protection of all waters from all sources of pollution. Indirectly, the water legislation in both EU and USA may influence wider international developments in water policy, as they will provide a major reference to other countries in reforming their water policies and institutions.

2.2.3. Developing countries

Here, it is important to note the difference between developing and poor developing countries, as these two groups of countries differ in setting their priorities. In developing countries like in Malaysia, South Africa and Thailand numerous efforts haven been initiated to overcome environmental degradation (Ujang and Buckley, 2002), e.g. setting new regulations and policies, and initiating university-industry collaboration on pollution prevention and cleaner production. It is also indicated that the water quality policy development in developing countries is progressing in a similar way to the developed countries (EU, USA and Japan), i.e. they are moving towards the river basin approach.

In poor developing countries on the other hand, the situation is different in the sense that economic activities are declining, leading to political instability and environmental degradation. In many situations, water resources are limited and water quality is deteriorating, particularly in the case of Africa and South Asia (Ujang and Buckley, 2002). In these countries, water pollution issues are therefore not the main concern because other issues such as national security, food availability and epidemic control are more pressing. The general problems in these countries are also outlined in Ujang and Buckley (2002) and summarised as follows:

- lack of environmental awareness among the majority of policy makers and the general public create a situation where water and wastewater management sectors are

perceived to be less important than other sectors such as military empowerment, food security, road improvement, electricity, mass education and health care facilities;
- insufficient expertise, leading to gaps between ideal policies and implementation;
- inappropriate policies on the conservation of water resources, e.g. no legislation for deforestation activities in water catchment areas;
- insufficient funding for water supply and sanitation programmes because of competing public expenditure due to rapid urbanization and population growth;
- insufficient water resources, especially in arid and urban areas, and
- inappropriate management systems and institutional support for providing water supply and sanitation facilities.

It should be noted that water quality management needs to be developed in line with economic development otherwise the environmental issues may limit the progress of the economy. Many examples can be given. Developing artificial ponds or lakes for water supply and irrigation service in arid and semi arid regions is particularly an important one. If the artificial pond or lake is not protected from pollution due to agricultural runoff, the water quality of the lake or pond will deteriorate with time due to high salinity or contamination by pesticides/herbicides. Such water quality deterioration will in turn affect the economic activities such as irrigation and drinking water supplies.

2.2.4. Regulatory frameworks: Comparison of approaches

Two most widely applied water pollution prevention approaches are briefly discussed elsewhere (Tyson *et al*., 1993): the Environmental Quality Objective (EQO) or Environmental Quality Standards (EQS) and the Uniform Emission Standard (UES) approach. In the EQO, the principle is to establish the use requirement, which can be a single use or multiple uses (e.g. conveying treated effluents, fisheries, abstraction for agricultural and drinking water supply, industrial uses, etc). The EQS is then derived for a given water body as a numerical standard to achieve the EQO. Using appropriate mathematical modelling, the discharge standards in terms of quality, load and frequency of occurrence, which will satisfy the EQS, can be derived. In this approach, the assimilative capacity of the receiving water is taken into account. It therefore takes into account not only point source but also non-point or diffuse source pollution.

In the UES approach (some times called emission level), the objective of achieving a particular water quality in the receiving water is not of direct concern. Rather it is focused on effluent quality, which is controlled with the same standard irrespective of the local discharge circumstances. It is a technology-based approach that follows principles of Best Practicable

Control Technology Currently Available (BPT), Best Conventional Pollutant Control Technology (BCT), Best Available Technology (BAT), and Best Available Technology Not Entailing Excessive Cost (BATNEEC). In this approach, the compliance is based on the technology rather than the assimilative capacity of the receiving water.

For those pollutants associated with discharges from urban drainage that degrade receiving water quality by imposing an oxygen demand and increased nutrient levels, the EQO/EQS is appropriate. However, the EQO/EQS is not applicable for the hazardous substances that originate from industrial sources like heavy metals and persistent organic contaminants. In that case, the UES should be applied.

It may be argued that EQO might be applied to protect for hazardous substances. In a sense dilution by the receiving water may reduce the persistent toxic substance to levels where they will not result in an adverse effect. Although their concentration can be low due to dilution in the receiving water, persistent pollutants can be potentially toxic to the ecosystem via bioaccumulation in the food chain. In this case, EQO is not a favoured approach. Instead, the UES approach has been extended to the anticipatory or precautionary principle, which seeks to reduce and eliminate such toxic, persistent and bioaccumulative substance in the environment irrespective of any proven environmental harm being demonstrated.

The combination of both EQO and UES approaches is termed the combined approach. The combined approach appears to be the best approach towards the protection of all waters from all types of pollutants (both conventional pollutants and hazardous substances). This approach is hence becoming more and more applied than a single approach (EQO or UES) in both developed and developing countries where the environmental protection programmes are well developed, e.g. in Europe, USA, South Africa, Malaysia, Japan, etc.

2.2.5. Link to water quality modelling

When setting water quality objectives (EQO), a number of important steps should be followed: (1) the establishment of water quality standards required to protect the defined water quality objectives (e.g. the EU WFD objective, good ecological status), (2) collecting monitoring data, and (3) a scenario analysis to evaluate alternative management options by utilizing a suitable mathematical model (water quality simulator) for the whole wastewater/receiving water system. The second and third steps indicate that water quality monitoring and modelling are an integral part of environmental impact assessment or water quality regulation. While both monitoring and modeling provide important tools for different needs, water quality modelling is becoming increasingly important due to its unique predictive capabilities and its cost-effectiveness.

2.3. General concept of river water quality modelling

This subsection gives an insight about the general concepts of water quality modelling. First, the River Continuum Concept is presented, and then the general water quality modelling methods including types, terminologies and comparison of different modelling approaches are highlighted.

2.3.1. River Continuum Concept (RCC)

Understanding the theoretical framework of the river as an ecological continuum provides a fundamental basis for understanding ecosystem dynamics and water quality modelling strategies in rivers. The River Continuum Concept (RCC) was first introduced by Vannote *et al.* (1980) (see Figure 2.1). It provides an insight in the way biological communities may change from the headwater stream to larger rivers in the absence of human influence. Since then, the concept is widely used in river water quality assessment and modelling (e.g. Shanahan *et al.*, 2001; Carpenter, 2001). The physical basis of the RCC is the size of the river or stream (stream order) and location along the stream. According to the RCC concept, the biotic and abiotic structure and function of the running water is characterized by longitudinal, vertical and lateral gradients.

According to the RCC, longitudinally, the river system can be subdivided into three zones: the headwater stream (1st – 3rd order stream), mid-reach (4th – 6th order stream) and downstream regions (> 6th order stream). The headwater streams depend on the surrounding forest for energy and nutrients sources, where leaf-shredding macroinvertebrates constitute a large portion of the macroinvertebrate population. As this part of the river is shaded by riparian vegetation, there is almost no algal growth and the main source of organic carbon is from allochthonous primary production, and heteroterophs dominate the microbial community. Consequently, the ratio of gross primary productivity (P) to community respiration (R), P/R, is less than one. The important compartments in this river section are the bulk water, the riverbed and the hyporheic compartment (the transition zone between surface water and groundwater).

In the mid-reach, the influence of riparian vegetation becomes less important. The amount of grazers that scrape algae from rock surfaces and that are nearly absent in head streams

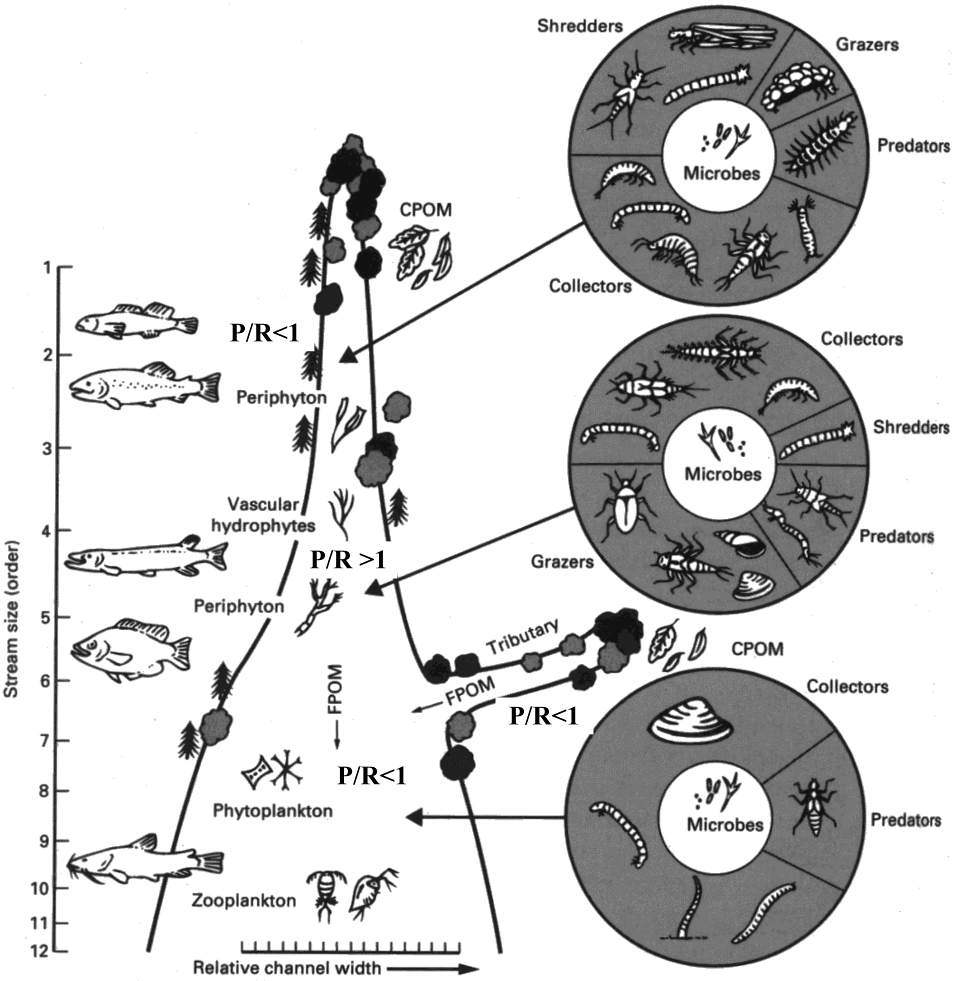


Figure 2.1: River Continuum Concept (RCC): relationship between the stream size and the progressive shift of structure and function of lotic communities (after Vannote *et al.*, 1980)

becomes larger. The absence of the shading effect enhances the stream shift from heterotrophic to authotrophic, and the growth of attached algae or periphyton. Thus, P/R is larger than 1, and the main source of nutrient is from authochthonous (internal source) and allochthonous (external source) detritus. The important compartments are bulk water, riverbed and hyporheic compartment.

The downstream regions receive fine particulate organic matters that are washed downstream from the upstream sections of the river. The collectors that filter or gather fine particles from the stream become dominant. As the effect of riparian vegetation is insignificant, the main source of nutrients is authochthonous detritus. The primary production is often limited by depth and turbidity, and hence P/R is less than 1. In this river section therefore, the important compartments are bulk water and flood plain.

In the presence of human influence, the structure and function of river ecosystems become unpredictable with the RCC (Stout, 1994; Carpenter, 2001). The presence of disturbances such as nutrient enrichment, organic pollution, alteration of riparian vegetation through grazing, clear-cutting or impoundment may cause the overall continuum response to be shifted. The shift in structure and function of the river continuum indicates strong human influence and pollution of the river system, and thus the river needs restoration. In order to restore the polluted river, identification of the water quality problems and the sources of pollution are required, and this must be supported by water quality regulations.

RCC provides the characteristics of the river ecosystem that should be considered in the river water quality modelling. The modelling approaches must address the ecological characteristics of the river by appropriate consideration of compartments (bulk water and benthic sediment) and processes description in representative spatial and temporal scales (Shanahan *et al.*, 2001). For example, in the headwater and middle stream with coarse substrates, it is necessary to consider both suspended and benthic compartments and their processes. This means the model should include the activities of microbial biomass both in suspension and attached to the benthic sediment. The activities of attached bacteria and algae predominate the activities of suspended microbial biomass, especially in small rivers where the wetted surface area to volume ration is large. In large rivers or in the downstream region of a river on the other hand, the suspended bacteria and algae in the water column dominate the conversion rates.

2.3.2. Water quality models: types and terminologies

Types of water quality models and related terminologies are well documented in Carstensen *et al.* (1997). Basically, there are two types of water quality models called stochastic and deterministic. If the model contains elements of randomness it is called stochastic. Including randomness in a model can be considered in order to account for the uncertainty associated with the model input variables and parameter values and model structure. Thus, a stochastic model will generate a range of values (rather than a single one) as model output in the form of a frequency distribution of e.g. pollutant concentration.

If the model contains no elements of randomness or does not comprise uncertainty, the model output is a single value. This type of model is termed deterministic. A deterministic model can be further described as mechanistic (white-box), grey-box and black-box model. Mechanistic (white-box) models are based on physical, biological and chemical laws, whereas the black-box models are those models that are not based on any physical or biological laws; instead they are based on a data driven transfer function, e.g. a neural network (Lek *et al.*, 1999). If a model contains elements of both the white-box (mechanistic submodel) and the black-box model, the model is called grey-box.

Mechanistic models may vary in their level of representation, model components, and temporal representation. On the basis of the level of representation, the mechanistic models vary from very simple (lumped models) to very complex (distributed models). In the lumped models, several processes may be combined and expressed as one, whereas in the distributed model, the model attempts to represent every significant process.

The other important concepts that must be considered in water quality modelling are related to the model components. There are three basic components: variables, constants and parameters. The model inputs (components that influence the system), outputs (the one that one wants to predict) and states (the components that are required to be known to calculate the output) are all variables, and therefore called input variables, output variables and state variables. The state variables can be all variables that must be calculated based on the other variables. Model components that do not change their values throughout all possible applications are termed constants, e.g. the gravity constant and unit conversion constants (day to seconds; mg to kg, etc). Model components that change their value according to the application are called parameters. The value of the parameter can be related to time, location or input variables, e.g. bacterial maximum growth rate, temperature correction factors, etc.

Concerning the temporal representation of the model, the distinction should be made between steady-state and dynamic (unsteady-state) models. In steady-state models, all inputs and state variables are constant in time. In dynamic models however, inputs variables and state variables may vary with time, and thus result in a time variable output.

2.4. Dynamic mechanistic river water quality modelling

Mechanistic river water quality models are based on the conservation of mass, i.e. within a finite volume of water, mass is neither created nor destroyed. In quantitative terms, the principle is expressed as mass-balance equations that account for all transfers of matter across the system's boundaries and all transformations occurring within the system.

The pollutant loading into the river and the water quality variables (e.g. the concentration of dissolved oxygen) may vary due to various factors such as storm events and sewer overflows. A dynamic mechanistic river water quality model therefore takes into account such temporal variability of pollutant loading and water quality variables in rivers.

In the following subsection dynamic mechanistic river water quality modelling approaches that are applied in both basic water quality and organic contaminant fate and effect modelling are discussed under seven subsections: (1) complex hydraulics routing, (2) complex pollutant transport, (3) conceptual hydraulic routing, (4) conceptual pollutant routing, (5) segmentation and model resolution, (6) basic water quality modelling (biochemical reactions), and (7) environmental risk assessment.

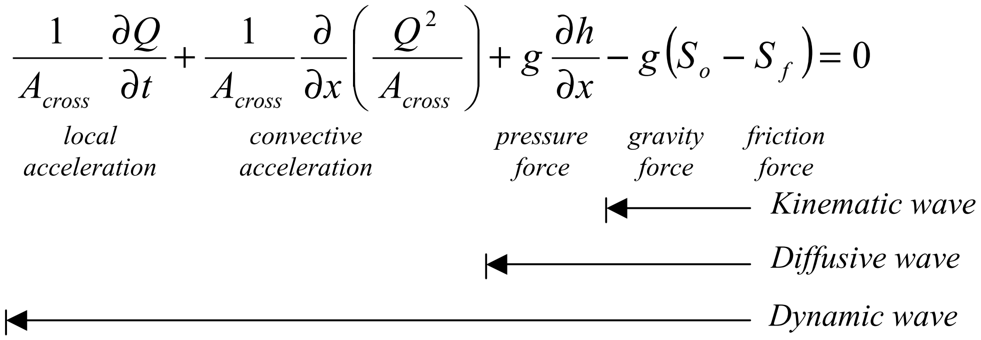
2.4.1. Complex hydraulic routing

Various models available to simulate dynamic water movement (flood propagation) in rivers are based on the usage of the St. Venant equations (de St. Venant, 1971), which comprise the mass and momentum balances on a one-dimensional channel. When the wind shear and eddy losses are omitted, the model is as follows:

Continuity equation including lateral inflow (mass balance):

$$\frac{\partial Q}{\partial x} + \frac{\partial A_{cross}}{\partial t} = q \qquad (2.1)$$

Momentum equation (momentum balance):



$$\frac{1}{A_{cross}}\frac{\partial Q}{\partial t} + \frac{1}{A_{cross}}\frac{\partial}{\partial x}\left(\frac{Q^2}{A_{cross}}\right) + g\frac{\partial h}{\partial x} - g\left(S_o - S_f\right) = 0$$

Figure 2.2: Simplification of momentum equation by dropping terms (after Chow, 1988)

where Q	flow rate [$m^3\ s^{-1}$]
A_{cross}	cross-sectional area [m^2]
h	absolute elevation of water level from the datum [m]
g	gravitational acceleration constant [$m^2\ s^{-1}$]
q	lateral inflow per unit length [$m^2\ s^{-1}$]
S_o	river channel side slope [-]
S_f	friction slope [-]
x	longitudinal distance of the river [m]

The momentum balance in Figure 2.2 can be simplified by dropping terms (Chow, 1981). When the pressure and acceleration terms are dropped or only the friction term and gravity force are considered, the equation describes the kinematic wave only, which is limited to the monotonically decreasing of the riverbed. When one ignores the variation of flow, the equation is simplified to the diffusive wave approximation, which allows describing backwater effects of weirs or other hydraulic controls like tidal effects. It can be applied when the river is not monotonically decreasing. If no term is ignored, the dynamic wave equations are able to describe the full dynamic wave.

By considering constant water width and rearranging equation 2.1 and equation indicated in Figure 2.2, one can get the St. Venant equations as follows:

$$\frac{\partial h}{\partial t} = -\frac{1}{b}\frac{\partial Q}{\partial x} + \frac{1}{b}q \tag{2.2}$$

$$\frac{\partial Q}{dt} = -\frac{\partial}{\partial x}\left(\frac{Q^2}{A_{cross}}\right) - gA_{cross}\frac{\partial h}{\partial x} + gA_{cross}(S_0 - S_f) \tag{2.3}$$

where *b* is the river water width [m].

2.4.2. Complex pollutant transport (advection-dispersion) modelling

Pollutant routing in a river is often described by the advection-dispersion (mass balance) equation, which is based on the principle of conservation of mass and Fick's law. The mass balance for non-conservative (non-reactive) pollutants in three directions (longitudinal *x*, vertical *y* and lateral *z*) is written as:

$$\frac{\partial C}{\partial t} = \underbrace{-u_x\frac{\partial C}{\partial x} - u_y\frac{\partial C}{\partial y} - u_z\frac{\partial C}{\partial z}}_{advection} + \underbrace{E_x\frac{\partial^2 C}{\partial x^2} + E_y\frac{\partial^2 C}{\partial y^2} + E_z\frac{\partial^2 C}{\partial z^2}}_{dispersion} - \underbrace{R}_{reaction} \tag{2.4}$$

where		
	C	concentration [g m^{-3}]
	t	time [s]
	$u_{x,y,z}$	average velocity in the ith direction [m s^{-1}]
	x, y, z	distances in x, y and z directions [m]
	$E_{x,y,z}$	the dispersion coefficients in the x, y and z directions [m^2 s^{-1}]
	R	reaction transformation rate [g m^{-3} s^{-1}]

Equation 2.4 is also called the basic water quality equation. It assumes both the flow velocity and dispersion coefficient to be constant over all the three directions. It cannot be solved alone in itself but requires the application of a hydraulic model as an input.

The full-form of equation 2.4 is rarely applied in river water quality studies, as it requires a lot of data for the three-dimensional velocity fields. It is hence often applied in a simplified form. Assuming the absence of temporal velocity gradient in both vertical and lateral direction, pollution routing for one-dimensional river water quality can be expressed as follows:

$$\frac{\partial(A_{cross}C)}{dt} = -\frac{\partial(QC)}{\partial x} + EA_{cross}\frac{\partial^2 C}{\partial x^2} - A_{cross}R \tag{2.5}$$

To solve equation 2.5 numerically, it is coupled to the numerical solution of open channel flow such as provided for the St. Venant equations (equations 2.2 and 2.3).

One-dimensional dynamic river water quality models that are based on the St Venant equations include *CE-QUAL-ICM* (Cerco and Cole, 1995), *DUFLO-EUTROF1* (Alderink *et al.*, 1995), *MIKE11* (DHI, 1992), *ISIS* (Wallingford Software, 1994), *SALMON-Q* (Wallingford Software, 1996), etc. The St. Venant equations require numerical methods (typically finite difference and finite element method) to solve them. These methods require small time steps to overcome the numerical problem of instability. As the application of the full St. Venant equations already requires long computation times, further extension of this model towards integrated water quality modelling will result in even more computation time. Consequently, a conceptual mechanistic surrogate model was proposed for the sake of faster simulation and easy implementation of water quality models (e.g. Meirlaen *et al.*, 2001).

2.4.3. Conceptual hydraulic routing

The conceptual model consisting of a cascade of Continuously Stirred Tank Reactor in Series (CSTRS) can be applied for dynamic hydraulic modelling in rivers. The schematic representation of this modelling approach is indicated in Figure 2.3. It is based on the mass balance of water that can be expressed around a control volume, an incremental element (slice) of stream volume, as follows:

$$\frac{dV}{dt} = Q_{in} - Q_{out} \tag{2.6}$$

where V control volume [m^3]

Q_{in} inflow rate [$m^3\ d^{-1}$]
Q_{out} outflow rate [$m^3\ d^{-1}$]

Around a control volume, box or river tank, a side stream or effluent discharge can be connected. In that case, equation 2.6 can be extended as follows:

$$\frac{dV}{dt} = Q_{in} + Q_d - Q_{out} \tag{2.7}$$

where Q_d is the flow rate of the side stream or effluent discharge [$m^3\ d^{-1}$].

Equations 2.6 and 2.7 are based on simple mass balance where the change in volume over time is the difference between the overall inflow rates and outflow rates. It respects the continuity equation, equation 2.1. The outflow rate Q_{out} can be calculated in different ways, e.g. Shaw (1996), but the simplest way is as indicated in equation 2.8. The parameters of the power function α and β can be calculated on the basis of stage-flow data on available relationships, as follows:

$$Q_{out} = \alpha h^{\beta} \tag{2.8}$$

Equation 2.8 is conceptually equivalent to the momentum conservation.

The underlying concept of the conceptual hydraulic model is that the river must be discretised (segmented) into a series of tanks (control volume). The only limitation of this formulation, however, is that it does not simulate backwater-effects due to dams, weirs or tidal effects. The conceptual hydraulic model can, however, be applied for dynamic flow propagation in non-tidal influenced rivers.

2.4.4. Conceptual pollutant routing

A cascade of CSTRS (see Figure 2.3) is among the simplest systems that can be used to model a natural water body (Chapra, 1997). This conceptual approach is also called moving segment model, box model or cells in series model, and has been successfully applied in river water quality modelling (Beck and Reda, 1994; Park and Lee, 1996; Lewis *et al.*, 1997; Park and Lee, 2002; Sincock and Lees, 2002).

On the basis of equation 2.6, a pollutant mass balance for unsteady flow conditions in every CSTRS can be expressed as follows:

$$\frac{d(VC)}{dt} = Q_{in} C_{in} - Q_{out} C + rV \tag{2.9}$$

where C_{in} concentration in the inflow [g m^{-3}]
C concentration in the outflow [g m^{-3}]
r the overall reaction rate [g m^{-3} d^{-1}]

If the side stream and wastewater effluent discharge is connected as indicated in Figure 2.3, equation 2.9 can be extended as follows:

$$\frac{d(VC)}{dt} = Q_{in} C_{in} + Q_d C_d - Q_{out} C + rV \tag{2.10}$$

where C_d is the concentration in the side stream or effluent discharge [g m^{-3}].

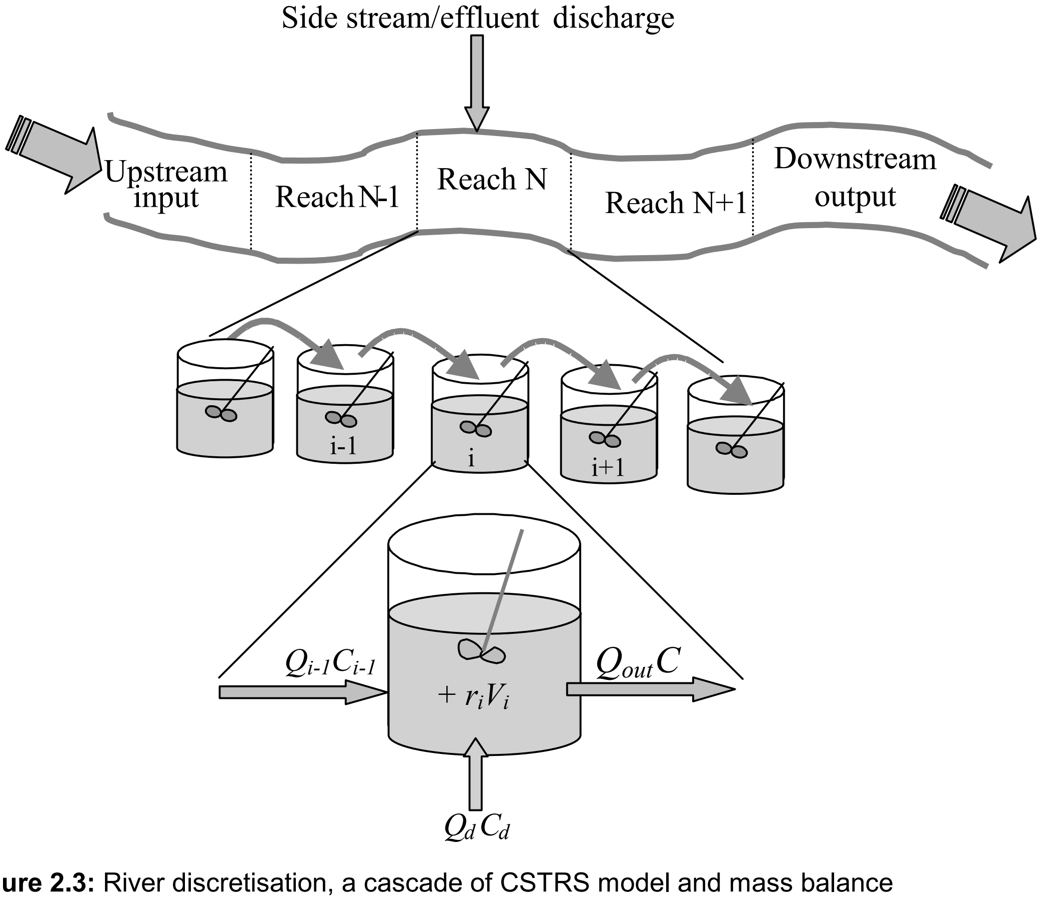


Figure 2.3: River discretisation, a cascade of CSTRS model and mass balance

Equations 2.9 and 2.10 are based on a simple mass balance and relatively easy to apply. They can be used for both steady-state and dynamic flow conditions, where for the dynamic flow conditions, the derivative term must be solved numerically.

2.4.5. Segmentation and model resolution

In developing mechanistic water quality models, the first aspect that must be explored is the necessary river segmentation and model resolution (Chapra, 1997). Segmentation is related to the division of space and matter into compartments, which is fundamental to the application of mass conservation to water quality problems. For example, a one-dimensional river water quality model is based on the longitudinal variation of river water quality and physical characteristics of the river. Division of space therefore refers to the river discretization like the one indicated in Figure 2.3, whereas dividing, for example, phytoplankton into algae and microbial biomass refers to dividing the matter into compartments to perform appropriate mass balances. If a model takes into account the temporal variability, the time segmentation can be a short (daily) or a long time step (yearly) to compute the mass balances.

The degree to which space, time and matter are segmented is called model resolution. The selection of spatial and temporal resolution of a water quality model may depend on two main factors: physicochemical properties of the pollutant, and the physical characteristics of the receiving water. In relation to physicochemical properties of the pollutant, modelling a readily biodegradable substance requires a fine temporal resolution and spatial resolution near the source. In the contrary case, i.e. a conservative substance or a slowly reacting (persistent) pollutant, coarse resolution can be applied.

The physical characteristics of the receiving water also determine the required level of segmentation. For example, modelling eutrophication in a deep river where there is significant vertical flow velocity variation, multiple segments are required because it is strongly influenced by thermal stratification.

The level of process resolution is also another important factor that needs to be considered in river water quality modelling. The level of process resolution refers to the theoretical detail of the equations used to describe the various processes affecting the pollutant's fate and transport such as biodegradation, settling, resuspension, volatilization, partitioning, etc. Under low-process resolution, for example for biodegradation, a constant value is used as the overall biodegradation constant. Under high-level process resolution, a complex mathematical description of the process is used, for example the nutrient limited microbial growth.

To select the model resolution, different methods might be used. Reichert *et al*. (2001) introduced an important concept, the so-called time constant, which can be used to select the model resolution. The time constant refers to the time frame within which changes are expected to occur. A reference time constant in rivers is:

$$\tau = \frac{L}{\bar{u}} \tag{2.11}$$

where τ is the time constant, L is the length scale and $\bar{u}$ is the average velocity.

The time constant concept can then be applied to determine the temporal and process representation of the model. In stagnant waters like lakes, the average velocity is very small and the time constant can be very large, and the lake eutrophication is the response to annual nutrient load. In flowing waters like rivers, however, the upper bound (τ_1) and lower bound (τ_2) of characteristic time constants must be defined on the basis of the corresponding length scale (L_1 and L_2) respectively, e.g. L_1 is the mixing length, whereas L_2 is the river length (Vanrollegem, 2001). These bounds depend on the problem being modelled and the process that dominates the problem, e.g. travel time for pollutant advection, rain storm duration and watershed time of concentration for non-point source pollution, a day for photosynthesis, etc.

If τ_1 and τ_2 are known, the representation of processes over time-either dynamic or steady-state-can be selected. When the processes of interest proceed at some rate constant k (in units of inverse of time), then the processes time constant τ_c can be defined as $\tau_c=1/k$. If $\tau_1<\tau_c<\tau_2$ then a dynamic model is required. If $\tau_c>>\tau_2$ then the process may be omitted. If $\tau_c<<\tau_1$ then a steady-state model will suffice.

The influence of sediment processes is also another important factor to be considered. If the reference time constant of the sediment process is defined as τ_s (the time between the floods that lead to sediment resuspension), processes in the sediment can be neglected only if $\tau_c>>\tau_s$. If $\tau_1<\tau_s<\tau_c$, processes in the sediment should be described dynamically. In the typical case where sediment processes occur slowly, $\tau_s>>\tau_c$, the sediment processes can be captured as a time invariant parameter, such as the Sediment Oxygen Demand (SOD) in traditional stream dissolved oxygen models, e.g. *QUAL2E* (Brown and Barnwell, 1987).

2.4.6. Basic water quality modelling (eutrophication)

The eutrophication model is concerned with the fate of algae (phytoplankton) and green plants and with their implications for the dissolved oxygen concentration and the nutrient cycle. The complexity and number of state variables of these models increase from the simplest Streeter-Phelps model (Oxygen sag curve; Streeter and Phelps, 1925) to extended models such as *QUAL1* (Masch and Associates, 1970), *QUAL2* (Water Resource Engineering, 1973), *QUAL2E* (Brown and Barnwell, 1987) and *QUAL2K* (Park and Lee, 2002). The latest version, *QUAL2E,* is the most widespread in-stream water quality model that has been adapted in various water quality simulators like *ISIS* (Wallingford Software, 1994), *DUFLOW-EUTRO* (Aalderink *et al.*, 1995) and *MIKE11* (DHI, 1992). Recently, an International Water Association (IWA) task group proposed the more complex eutrophication model River Water Quality Model No. 1 (*RWQM1*) (Reichert *et al*., 2001), which is different in the state variable and process description from *QUAL2E* type models.

In the following subsection two distinct modelling approaches will be discussed: *QUAL2E* and *RWQM1*.

2.4.6.1. QUAL2E

The *QUAL2E* model is the most widely known model for river water quality. It had a significant impact on river water quality modelling because a large number of eutrophication models are based on its processes description, e.g. *QUAL2K, WASP5* (Ambrose and Martin, 1993)*, SWAT* (Neitsch *et al*., 2000)*; ISS, DUFLOW-EUTRO, MIK11,* etc. The state variables and processes of this model are given in Tables 2.2 and 2.3 respectively.

Table 2.2: State variables in QUAL2E (after Brown and Barnwell, 1987)

	State variables	Description
1	DO	Dissolved oxygen [M L^{-3}]
2	BOD	Biochemical oxygen demand (BOD) [M L^{-3}]
3	Ch-a	Algae as chlorophyll a [M L^{-3}]
4	ON	Organic nitrogen as N [M L^{-3}]
5	NH_3+NH_4^+	Ammonia as N [M L^{-3}]
6	NO_2	Nitrite as N [M L^{-3}]
7	NO_3	Nitrate as N [M L^{-3}]
8	OP	Organic phosphorus as P [M L^{-3}]
9	DP	Dissolved phosphorus as P [M L^{-3}]

Table 2.3: Biochemical conversion processes in *QUAL2E* (after Brown and Barnwell, 1987)

	Process
1	Reaeration
2	Biodegradation
3	BOD sedimentation
4	Sediment oxygen demand
5	Photosynthesis
6	Respiration
7	Algal sedimentation
8	Organic nitrogen hydrolysis
9	1^{st} stage nitrification
10	2^{nd} stage nitrification
11	Nitrogen sedimentation
12	Nitrogen sediment release
13	Phosphorous hydrolysis
14	Phosphorous sedimentation
15	Phosphorous sediment release

which cannot be fractionated into different forms of organic carbon. The decay of algal biomass (authochthonous source) is not included in the BOD either. All these limitations indicate that the mass balance is not complete in *QUAL2E*.

Furthermore, for integrated water quality studies, another means of quantification of carbonaceous organic matter, chemical oxygen demand (COD), is considered in order to make the river water quality model compatible with the existing typical activated sludge wastewater treatment plant models (Henze *et al.*, 2000). As it is not based on COD and the mass balance also is not closed, *QUAL2E* is not suitable for the integrated water quality studies unless an appropriate modification is made (Fronteau, 1999; van Griensven and Bauwens, 2002).

It is also important to note that whereas *QUAL2E* is designed for steady-state conditions, it has been coupled to complex hydrodynamic models (see section 2.4.1) to be applicable for unsteady-state conditions, e.g. *CE-QUAL-RIV1* (U.S. Army Corp of engineers, 1995), *CE-QUAL-W2*, *CE-QUAL-ICM* (Cerco and Cole, 1995) and *WASP5*.

2.4.6.2. RWQM1

Due to the limitations in *QUAL2E*, the IWA Task Group on River Water Quality Modelling proposed the River Water Quality Model No.1 (*RWQM1*) (Reichert *et al.*, 2001). The procedure applied to formulate the *RWQM1* is based on a typical activated sludge wastewater treatment modelling approach, the so-called Activated Sludge Models (ASMs): *ASM1*, *ASM2* and *ASM3* (Henze *et al.*, 2000) in which additional important state variables were considered and a complete mass balance was pursued from the beginning. Among some, bacterial biomass is an important state variable. Substrate utilization during bacterial growth thus depends on the amount of bacterial biomass. Unlike *QUAL2E,* which considers only dissolved oxygen as electron acceptor, the *RWQM1* model considers both dissolved oxygen and nitrate nitrogen as electron acceptor for aerobic and anoxic conditions, respectively.

For the consistency in mass and elemental balance, *RWQM1* uses COD as a measure of carbonaceous organic matter, and assumes constant elemental composition of compounds and organisms in the system. Such assumption allows using mass fractions of elements (C, N, O, H, P) as model parameters (see Reichert *et al.*, 2001 for details). The stoichiometric coefficients of conversion processes are therefore formulated as a function of these parameters. Because different units are used to characterise organic material, conversion formulae are given between mass of organic substances and chemical oxygen demand. The composition of organic matter is approximated by mass fractions of the elements C, H, O, N, and P. The mass fractions of the other elements are neglected. For this reason, the composition of organic material can uniquely be described by the mass fractions, which are assumed to be constant. In reality, algae can accumulate P in their tissue for further use in case the concentration of P in the river system is very low. In such a “luxury” uptake, the assumption of constant mass fraction does not apply, and in that case the model needs to be modified.

The state variables and biochemical conversion processes in the *RWQM1* are given in Table 2.4 and Table 2.5 respectively. As one notes from these tables, the model has a relatively large number of state variables and biochemical processes, which are required for realistic characterization of river water quality. The processes indicated in Table 2.5 are all for the bulk water compartment only. If a similar number of state variables are considered in the benthic sediment compartment, the number of state variable becomes considerable, resulting in a larger computation times. More importantly, it incurs more cost to obtain the required data. As the availability of data is often the main limitation for the practical applicability of such a complex model, simplification of the model is indispensable. The simplification of the model can be done on the basis of an appropriate selection of biochemical processes.

Table 2.4: State variables in RWQM1 (after Reichert *et al.*, 2001)

	State variables	Description
1	S_S	Rapidly biodegradable soluble organic substrate as COD [M L^{-3}]
2	S_I	Inert dissolved organic material as COD [M L^{-3}]
3	S_{NH4}	Ammonium nitrogen as N [M L^{-3}]
4	S_{NH3}	Ammonia nitrogen as N [M L^{-3}]
5	S_{NO2}	Nitrite nitrogen as N [M L^{-3}]
6	S_{NO3}	Nitrate nitrogen as N [M L^{-3}]
7	S_{HPO4}	Part of inorganic dissolved phosphorus as P [M L^{-3}]
8	S_{H2PO4}	Part of inorganic dissolved phosphorus as P [M L^{-3}]
9	S_{O2}	Dissolved oxygen as O [M L^{-3}]
10	S_{CO2}	Dissolved carbon dioxide as C [M L^{-3}]
11	S_{HCO3}	Dissolved bicarbonate as C [M L^{-3}]
12	S_{CO3}	Dissolved carbonate as C [M L^{-3}]
13	S_H	Hydrogen ions as H [M L^{-3}]
14	S_{OH}	Hydroxyl ions as H [M L^{-3}]
15	S_{Ca}	Dissolved calcium ions as Ca [M L^{-3}]
16	X_H	Heterotrophic organism as COD [M L^{-3}]
17	X_{N1}	Bacteria oxidising ammonia to nitrite as COD [M L^{-3}]
18	X_{N2}	Bacteria oxidising nitrite to nitrate as COD [M L^{-3}]
19	X_{ALG}	Algae as COD [M L^{-3}]
20	X_{CON}	Consumers as COD [M L^{-3}]
21	X_S	Particulate organic material as COD [M L^{-3}]
22	X_I	Inert particulate organic material as COD [M L^{-3}]
23	X_P	Inorganic phosphorus adsorbed to particles as COD [M L^{-3}]
24	X_{II}	Particulate inorganic material as COD [M L^{-3}]

The steps or criteria required for the selection of the biochemical submodels are documented elsewhere (Vanrolleghem *et al.*, 2001) and are summarized below. As nitrite is usually short-lived and stays low in concentration in rivers, it can often be omitted, and nitrite and nitrate nitrogen can be lumped as one state variable. Then, two nitrification processes can also be considered together as a single-step process. Based on the field data, e.g. in well-aerated streams with a small load of organic matter, the anoxic condition can be omitted and the anoxic bacterial growth (process 3) and anoxic respiration (process 4) in Table 2.5 can be eliminated. When the contribution of algal activity for the dissolved oxygen budget is insignificant as it is the case in fast flowing rivers (hydraulic residence time less than 4 to 7

Table 2.5: The biochemical processes in *RWQM1* (after Reichert *et al.*, 2001)

	Processes
1	Aerobic growth of heterotrophs
2	Aerobic endogenous respiration of heterotrophs
3	Anoxic growth of heterotrophs
4	Anoxic endogenous respiration of heterotrophs
5	Growth of 1st-stage nitrifiers
6	Aerobic respiration of 1st-stage nitrifiers
7	Growth of 2nd-stage nitrifiers
8	Aerobic respiration of 2nd-stage nitrifiers
9	Growth of algae
10	Aerobic respiration of algae
11	Death of algae
12	Growth of consumers
13	Aerobic respiration of consumers
14	Death of consumers
15	Hydrolysis
16	Equilibrium CO_2 <-> HCO_3^-
17	Equilibrium HCO_3^- <-> CO_3^{2-}
18	Equilibrium H_2O <-> $H^+ + OH^-$
19	Equilibrium NH_4^+ <-> NH_3
20	Equilibrium H_2PO_4 <-> HPO_4^-
21	Equilibrium Ca^{2+}<-> CO_3^{2-}
22	Adsorption of Phosphate
23	Desorption of Phosphate

days, Kimmel *et al.*, 1990), the state variable and related processes can be eliminated. If the pH is not varying in the system significantly it can be assumed constant during the process, and the pH-dependent processes such as chemical equilibria (processes 16 to 21) in Table 2.5 can be eliminated.

2.4.7. Environmental risk assessment

As indicated earlier (section 2.1.2), an environmental risk assessment is required to investigate whether a chemical (existing or new) will pose adverse effects on the ecosystem structure and function. The procedure of such assessment is also called risk characterization, and is based on the comparison of the Predicted Environmental Concentration (PEC) and the Predicted No-Observed Effect Concentration (PNEC) introduced by the EEC (1993) (see Figure 2.4). When the ratio of PEC to PNEC (some-times called risk quotient) is less than one the chemical of concern is safe. Otherwise, it may pose a risk and further consideration or refinement of the assessment is required.

As illustrated in Figure 2.4, the PEC values can be measured or predicted from emission rates and fate and transport modelling, whereas the PNEC values are usually extrapolated from standard laboratory toxicity test, which is often based on results of data set composed of a single or limited species test. In the following subsections, different techniques applied for the assessment and modelling of exposure and effect are reviewed.

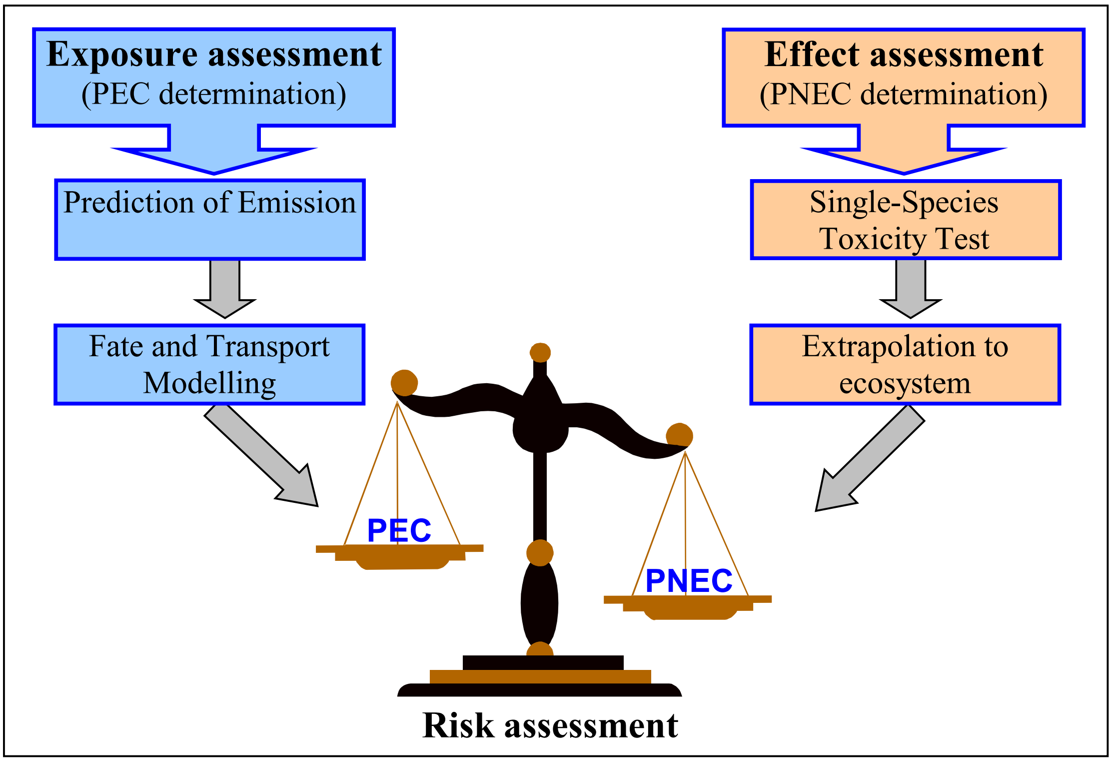


Figure 2.4: Traditional risk assessment process in the EU (modified from EEC, 1993)

2.4.7.1. Exposure assessment: organic contaminant fate modelling

As indicated in Figure 2.4, exposure assessment includes to the procedure of identifying the source and quantifying the level of emission and immission, i.e. PEC determination. For example, exposure assessment for xenobiotic organic compounds can be carried out based on the organic contaminant fate modelling. Organic contaminant fate models describe the fate and distribution of contaminants in the environment. Based on the spatial scale, a distinction can be made between local-scale (near-field), regional-scale and continental-scale models. The local-scale models describe the fate of contaminants in the river water (e.g. GREAT-ER, Schowanek *et al.*, 2001), in soil (e.g. SoilFug, Di Guardo *et al.*, 1994) or in wastewater treatment plants (e.g. WW-TREAT, Cowan et al., 1993). The regional-scale models describe the fate of contaminants in user-defined regions (e.g. ChemCAN 4, Mackay *et al.*, 1996b). Finally, the continental-scale models are generic models that describe the fate and distribution of chemicals at the continental scale (e.g. SimpleBox 2.0, Brandes *et al.*, 1996).

Although there are many types of organic contaminant fate models available in literature, two distinctions can be made: the generic multimedia fugacity approach and the non-fugacity approach. The fugacity approach is using fugacity (the escaping tendency of the compound from the system) as a surrogate measure of concentration, whereas the non-fugacity approaches directly use concentration for the quantification of all contaminants of concern in the system (e.g. *EXAMS*, Burns and Cline, 1985).

Multimedia fugacity models have four levels: level I, II, III and IV (Mackay, 2001). They are also sometimes called Mackay models of level I, II, III and IV. In the fugacity model level I, steady-state and equilibrium conditions are assumed between environmental compartments (air, water, soil, sediment and biota). The chemical transformation (reaction term), however, is not considered. Level II assumes steady-state and equilibrium conditions, but adveection and the chemical transformation is considered. Level III assumes steady-state and considers transformation, but assumes non-equilibrium conditions between the environmental compartments (e.g. between water and sediments). Level III is relatively more realistic than the other levels, and is hence widely applied in exposure assessment. Examples of regional scale contaminant fate models that are based on fugacity model level III include EQC model (Mackay *et al.*, 1996a), *ChemCAN* (Mackay *et al.*, 1996b), *CalTOX* (McKone, 1993), *Fug3ONT* (Maddalena *et al.*, 1995), *EUSES* (RIVM, 1996) and *SimpleBOX* (Brandes *et al.*, 1996). *EUSES* and *SimpleBOX* models are regional multimedia models used by the European Union to describe the fate of new or existing chemicals in environment. Level IV is formulated for non-equilibrium between compartments under non-steady-state conditions. Due to the complexity of the model and data requirements, it is rarely used as a tool in risk management (Mackay, 2001).

The use of fugacity (defined with the unit of pressure Pa) as an equilibrium criterion is only suitable for chemicals that can establish measurable concentrations in the vapor phase. It is not applicable to chemicals that have a negligible or zero vapor pressure, e.g. metals, organometals (Grüter *et al.*, 2001) or inorganics. For such chemicals, the concept of "aquivalent concentration" or "aquivalence" was also introduced (Mackay *et al.*, 1989). Aquivalence is expressed in the same way as concentration [$M\ L^{-3}$].

Although both the fugacity and the non-fugacity modelling approach can be applied for exposure assessment, the choice is made depending on the ultimate goal of modelling. If the model is intended to simulate the organic contaminant fate over long-time and regional scales, a fugacity approach is suitable. However, for a local scale and short-term simulation, and for integrated modelling of basic water quality (e.g. *RWQM1* and *QUAL2E;* both are not fugacity-based) and organic contaminant fate, a non-fugacity approach is appropriate.

In relation to the temporal aspect of the model, a distinction can be made between steady-state and dynamic exposure modelling. In a steady-state model, the temporal variation of the contaminant in the environmental compartment is neglected. A dynamic exposure model takes into account temporal variations of toxicants in rivers. As toxicity depends on the duration and frequency of exposure (Reinert *et al.*, 2002), it is only by a dynamic exposure model that the violation of the duration and frequency of exposure in the receiving water can be described. Furthermore, the dynamic exposure model can be used to describe the recovery time of the environment after emission reduction or cease.

The most widely used steady-state multimedia fate model, in regulation, is the Mackay level III model. It is widely used in the screening phase of exposure assessments (*RIVM*, *VROM* and *WVC*, 1994; *HAZCHEM (ECETOC*, 1994); *EUSES*, 1997). The current exposure assessment in the European Union is also based on such a generic model that estimates only the average or generic local and regional PEC value (RIVM, 1996). This model does not take into account both temporal and spatial variability, where the PEC value varies in time and space.

Recently a new model that can take into account variability due to factors such as landscape characteristics, river flows and/or chemical emissions was introduced (*GREAT-ER*; Schowanek *et al.*, 2001). In *GREAT-ER*, the spatial variability is taken into account by geo-referencing the exposure concentration or data set instead of only providing generic or average values. This model was also developed for steady-state conditions. The temporal variability, however, was incorporated by using the Monte Carlo simulation technique. Such a method also does not give time series of Predicted Environmental Concentration (PEC) values that would be used for further analysis, e.g. duration and frequency analysis. Rather it provides a frequency distribution of PEC at a particular location.

In order to take into account the temporal variation, the Mackay level III model was extended to a more complex dynamic model, the Mackay level IV (Mackay, 2001). The fugacity level IV model is particularly suitable for describing the long-term (multiyear or multi-decade) behaviour of existing persistent chemicals that have accumulated in soils and sediments, e.g. Polychlorinated Biphenyls (PCBs), Polycyclic Aromatic Hydrocarbons (PAHs), dioxins, furans, and metals that are inherently non-degradable (Sweetman *et al*., 2002). The model can identify new chemicals that may accumulate in soils and sediments over long periods of time and thus experience unacceptably long recovery times.

Although a dynamic multimedia fugacity model (level IV) can describe the time course of pollutant fate and transport in the environment, it treats the environment as a single well-mixed box. This is rarely applicable for lakes, rivers or estuaries in which the contaminant concentration can vary longitudinally, vertically or laterally. To take into account this spatial variation in addition to the temporal variation in lakes and rivers, another modelling approach, the so-called Quantitative Water Air Sediment Interaction (QWASI), was proposed (Mackay *et al*., 1989). In the QWASI modelling approach, the river is treated as a series of connected lakes or reaches, each of which is assumed well mixed, with unique water and sediment concentrations. The larger the number of reaches, the more closely simulated is the "plug flow" behaviour of the river. There can be varying discharges into the reach, and tributaries can be introduced as desired. The practical difficulty in applying this model is also indicated in Mackay (2001): changes in flow volume, velocity or depth cannot be easily included. Therefore, the equation necessary applies only to idealized conditions.

For short-term emission management in non steady-state conditions, we still need an appropriate dynamic exposure model that takes into account both spatial and temporal variability. Despite the fact that the same hydraulic or transport model can be applied as in basic water quality modelling, the (physicochemical and biochemical) processes that determine the fate of organic contaminants can be different (see Figure 2.5). Since not all these processes are important for in-stream removal, an appropriate processes-rate selection is an important task.

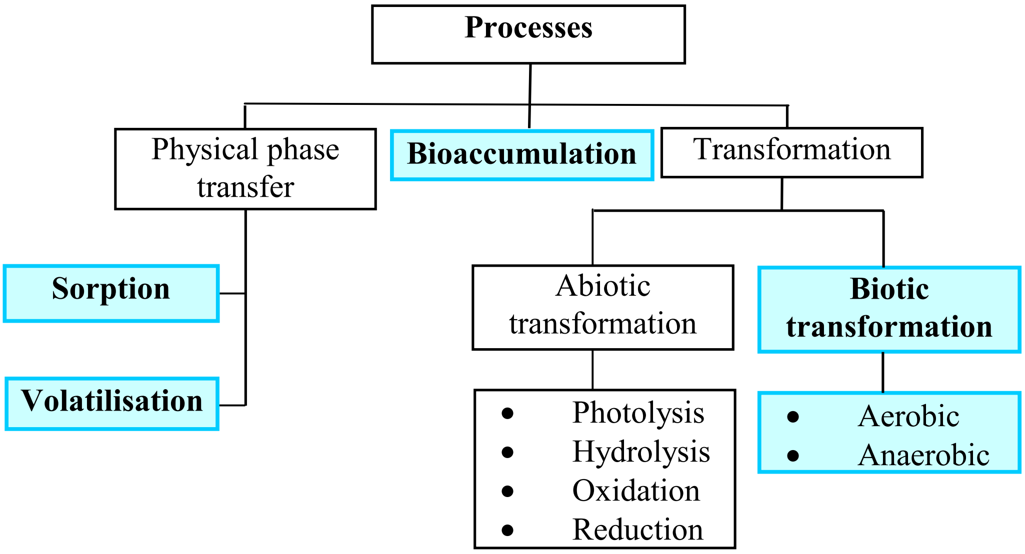


Figure 2.5: Schematic representation of in-stream removal processes: highlighted processes are those often considered in the in-stream fate modelling

In-stream reaction processes

In this subsection an attempt is made to provide background information on the relevant processes (see Figure 2.6) determining the fate of organic contaminants in-streams or rivers, and mathematical equations that can be used to predict the rates at which these processes proceed. Figure 2.6 shows possible processes/reactions of organic contaminants that can take place in-streams. Biological transformations, chemical hydrolysis, oxidation/reduction, photodegradation, volitilisation, sorption and bioaccumulation are among the important reactions that organic chemicals undergo in natural waters. Of these processes, sorption, volatilisation and biodegradation will be the main focus of this review. Abiotic transformations: photolysis, hydrolysis, oxidation and reduction will not be further considered because, for most compounds, they are of minor importance as compared to biochemical oxidation (EEC, 1993).

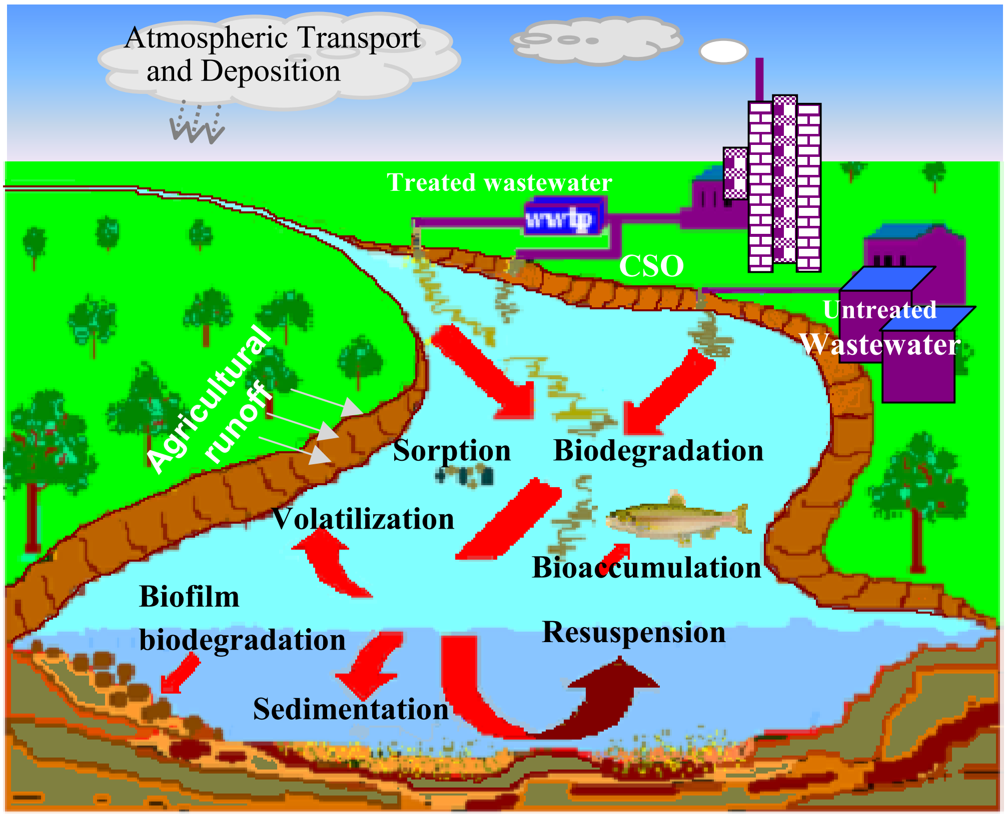


Figure 2.6: Schematic representation of sources and fate of organic contaminants in rivers

Sorption

Sorption has been an important aspect of risk assessment in the context of both groundwater and surface water resources because it governs the bioavailability of the xenobiotic organic contaminant in the environment. Sorption is a process by which a dissolved substance is transferred to and becomes associated with solid material. It includes both accumulation of dissolved substances on the surface of solids (adsorption) and the interpenetration or intermingling of substances with solids (absorption). The opposite process whereby a sorbed substance is released from a particle is called desorption. For neutral organic substances, several mechanisms determine the sorption process. These includes (Schnoor, 1996):

- physical adsorption due to van der Waals forces;
- chemisorption due to chemical bonding or surface coordination reaction, and
- partitioning of organic chemicals into the organic carbon phase of the particulates.

It must also be noted that neutral organic chemicals can also be sorbed to inorganic solids that contain clay minerals. However, such inorganic solid sorption is usually significant only when the organic carbon content of the solids is quite low (Schwarzenbach and Westall, 1981). On the other hand, for charged toxins, the additional mechanism of ion exchange can occur.

Understanding the mechanism of adsorption/desorption or partitioning of chemicals between particulate matter and the dissolved phase plays three important roles in in-stream removal processes: (i) sorption of the chemical into the suspended or sediment Particulate Organic Carbon (POC) reduces the aqueous phase concentration, and thereby reduces the bioavailabilty for microbial biodegradation, particularly in case of a slow sorption/desorption rate (Stuijfzand, 2000), (ii) the sorbed phase can be removed from the bulk water due to sedimentation of POC, and thereby reduces the concentration of toxicant in the overlying water, and (iii) the sorbed phase the of toxicant is not bioavailable for gill uptake, and thus sorption can reduce toxicity (Neely *et al.*, 1974; Landrum *et al.*, 1992).

Application of equilibrium partitioning

The most common method of modelling the sorption of hydrophobic compounds to natural materials such as soils, sediments, and aquifer materials is based on a partitioning process derived by hydrophobic interactions (Karickhoff *et al.*, 1979). The sorption isotherm indicates that the sorbed phase concentration increases with dissolved concentration until the available sorption sites begin to become saturated (see Figure 2.7). Several mathematical models are proposed to represent such isotherm. Among such models, the Langmuir (1918) and Freundlich (1906) isotherms are widely used (among some, Schnoor, 1996; Chiou and Li, 2002; Abburi 2003; Kim, 2003; Wu *et al.*, 2003). Generally, a sorption isotherm has two parts: a linear and a non-linear part (see Figure 2.7 as example). A linear isotherm implies that the sorbed phase concentration increases when the dissolved phase is increased and vice versa. It is equivalent to a partition coefficient.

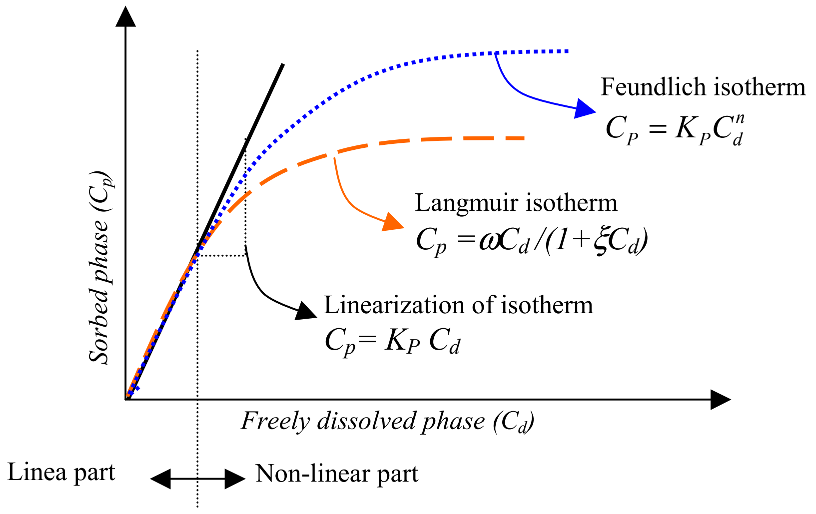


Figure 2.7: Sorption isotherm: K_p partition coefficient, ω,ξ and n are parameters

Linear isotherms have been indicated to be adequate to represent the sorption of neutral organic contaminants onto the sediments up to half of their water solubility (Karickhoff, 1981). This author found that sorption isotherms were linear, reversible, and characterized by a partition coefficient, K_P. The following relation was proposed:

$$K_P = f_{OC} K_{OC} \tag{2.12}$$

where f_{OC} is the fraction of organic carbon and K_{OC} is the carbon normalized partition coefficient (l mg^{-1}).

K_{OC} can be estimated by using Quantitative Structure-Activity Relationships (QSAR): water solubility, octanol-water partition coefficient (K_{OW}) or melting point (see Schnoor, 1996 for details). An excellent review for K_{OC} is also given in Wauchope *et al.* (2002).

On the basis of the local equilibrium assumption, both the aqueous (f_d) and sorbed (f_p) fractions of organic contaminants in the bulk water can be determined based on the following relations:

$$f_d = \frac{1}{1 + K_P SS} \tag{2.13}$$

$$f_p = \frac{K_P SS}{1 + K_P SS} \tag{2.14}$$

where SS is the suspended solids concentration (mg L^{-1}).

It is generally accepted that for hydrophobic organic contaminants K_P is a function of the particle's organic carbon content rather than the whole suspended particles mass. Therefore, rather than modelling suspended solids concentration, a more direct approach is to model Particulate Organic Carbon (POC) (Chapra, 1997). Furthermore, organic contaminants tend to associate to both POC and Dissolved Organic Carbon (DOC). DOC therefore represents the third phase (see Figure 2.8). Thomann and Mueller (1987) defined "dissolved" as all material, which is not particulate (passing a 0.45 micron filter).

Several studies have shown the significance of third phase partitioning (sorption of organic contaminant onto DOC) in the sense that it reduces gill uptake (bioavailability), and hence reduces toxicity (McCarthy and Jimenze, 1985; Traina *et al.*, 1996; Burkhard, 1998; Mott, 2002). The equlibrium partition coefficient for DOC is:

$$K_{doc} = 1.0 K_{OC} \tag{2.15}$$

where 1.0 is the fraction of organic carbon content of DOC.

To include the effect of the third phase, the fraction of toxicant in all three phases can be determined by the following relations (modified from Chapra, 1997):

$$f_d = \frac{1}{1 + K_{OC}(POC + DOC)} \tag{2.16}$$

$$f_{POC} = \frac{K_{OC} POC}{1 + K_{OC}(POC + DOC)} \tag{2.17}$$

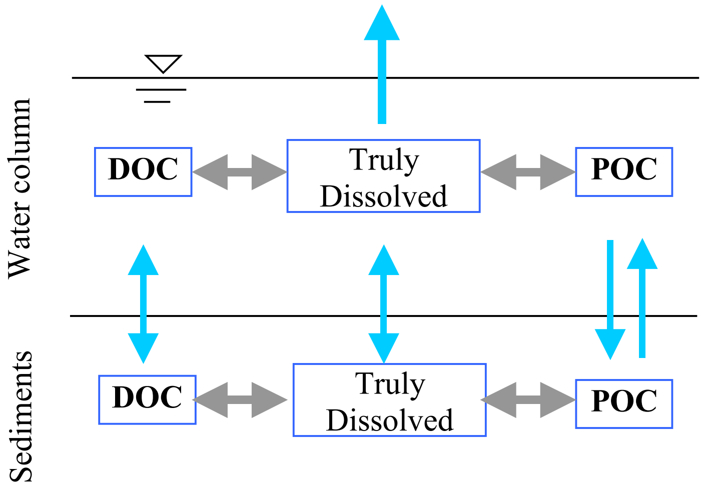


Figure 2.8: Schematic representation of how a DOC "third phase" competes with POC for dissolved toxicant in both water and the underlying sediment (modified from Chapra, 1997)

$$f_{DOC} = \frac{K_{OC}DOC}{1 + K_{OC}(POC + DOC)} \tag{2.18}$$

It is also important to note that the above relations (equations 2.12 to 2.18) are based on the hydrophobic property, i.e. K_{OC} is determined based on K_{OW} and organic carbon content of the system. Such an approach must be applied carefully. For instance, the principle of K_{ow} does not hold for LAS (Hand and William, 1987). For this chemical, the partition coefficient does not increase with the organic carbon content of the sediments. Hand and his co-worker found that the sorption of LAS to the river sediment increases with the chain length and phenyl position. Furthermore, the K_{ow} is applied mainly for neutral compounds. For ionic compounds, other governing factors such as pH and particle size distribution need to be considered (Karickhoff *et al.*, 1979).

Volatilisation

Volatilization refers to the movement of chemicals across the air-water interface. It is a transfer process in which a toxicant moves from the liquid phase to the gas phase, or vice versa, as the dissolved neutral concentration attempts to equilibrate with the gas phase. This process is one of the important processes that must be considered when modelling organic chemicals in the environment. It doesn't result in the breakdown of a substance, but the chemical moves from one compartment (e.g. water) to another (air).

Volatilisation is commonly modelled based on the well-known two-film theory of a gas-liquid transfer velocity. The two-film theory was originally developed for the process industry (Whitman, 1923), and has later been adapted to environment systems (Liss and Slater, 1974). The two-resistances approach assumes the two "stagnant films" are bound on either side of the film by well-mixed compartments. In such a two-film theory, volatilisation is a function of Henry's constant (H), the gas-film resistance (k_{gas}) and the liquid-film resistance (k_{liq}). The well-known equation for this theory can be expressed as follows:

$$\frac{1}{K_T} = \frac{1}{k_{Liq}} + \frac{1}{Hk_{Gas}} \tag{2.19}$$

The total resistance ($R_T = 1/K_T$) is the sum of the series of resistances in the liquid ($R_{Liq}=1/k_{Liq}$) and gas ($R_{Gas} = 1/k_{Gas}$) interface. The overall mass transfer can be expressed in terms of a saturation concentration in equilibrium with the gas phase and interfacial surface area as:

$$\frac{d(C_d)}{dt} = \frac{K_T}{h}\left(C_{sat} - C_d\right) \tag{2.20}$$

where C_d is the truly dissolved phase concentration (mg L^{-1}) K_T is the total mass-transfer coefficient through both stage boundary layers (m d^{-1}), h is the average water depth (m), and C_{sat} is the substance saturation in the gas phase (g m^{-3}).

Equation 2.20 describes a reversible process, and applies for both gas absorption or gas striping from the water body. When C_{sat} is not available or is assumed negligible (Mackay and Leinonen 1975) and only the unionized fraction α_{vol} is volatilized, equation 2.20 can be reduced to a gas striping from the water body as follows:

$$\frac{d(C_d)}{dt} = -\frac{K_T}{h}\alpha_{vol}\,C_d \tag{2.21}$$

where $K_T\alpha_{vol} \,/\, h$ is a pseudo first-order-rate constant (d^{-1}).

Several methods are available to compute the mass transfer coefficients k_{Liq} and k_{Gas}, and most of them are summarised in Ambros and Martin (1993) and Schnoor (1996). These methods take into account the influence of both chemical properties (molecular weight, Henry's law constant) and environmental conditions at the air-water interface (turbulence-controlled by wind speed, current velocity, and water depth). For more details, see Ambros and Martin (1993) and Schnoor (1996).

Bioaccumulation

The term bioaccumulation refers to the absorption/uptake and concentration of toxic chemicals (e.g. heavy metals and certain pesticides) in plants and animals over time. The term bioaccumulation must not be confused with the other similar terms bioconcentration and biomagnification. Bioaccumulation involves the net accumulation of a chemical by an aquatic organism as a result of uptake from all environmental sources through gill membranes and dietary uptake. Bioconcentration includes the net accumulation of a chemical by an aquatic organism as a result of uptake directly from the ambient water through gill membranes or other external body surfaces. Biomagnification involves the increase in concentration of a chemical in the tissue of organisms along a series of predator-prey associations or trophic levels. As biomagnification was not studied in this Ph.D. thesis, it will not be considered further.

In modelling bioaccumulation or bioconcentration, two modelling approaches are known: one-compartment and multi-compartment modelling. In the former approach, the organism under consideration is assumed to consist of only one compartment in which the chemical is assumed uniformly distributed. In the latter approach, on the other hand, the organism of interest is divided into two or more compartments (e.g. gill and gut).

The most widely used method of modelling the accumulation of a chemical in an organism is a first-order one-compartment model for its two important advantages: (i) it is relatively simple, and (ii) it requires a small number of parameters to determine or measure, whereas the multi-compartment models require a lot of parameters to be measured or estimated (Clason *et al.*, 2003; Lindholst *et al.*, 2003). Subsequently, the one-compartment model has been used with different complexities as summarized below.

The simplest one-compartment model is a model with toxicant uptake via a single route (Branson *et al.*, 1975; Spacie and Hamelink, 1982; Mancini, 1983) written as follows:

$$\frac{dC_{c,b}}{dt} = k_1 F_w C_{c,w} - k_2 C_{c,b} \tag{2.22}$$

where $C_{c,b}$ is the concentration of toxicant in the biota (g g^{-1}), k_1 is the toxicant uptake rate from the aqueous phase (m^3 (g.d)$^{-1}$), $C_{c,w}$ is the toxicant concentration in the water (g m^{-3}), $C_{c,b}$ is the toxicant concentration in the biota (g g^{-1}), and k_2 is the elimination/detoxification rate (d^{-1}); F_w is the water uptake rate efficiency (-).

When toxicant uptake via two exposure routes is considered, the following model was proposed (Mackay *et al.*, 1992):

$$\frac{dC_{c,b}}{dt} = k_1 F_w C_{c,w} + k_f F_f C_{c,f} - k_2 C_{c,b} \tag{2.23}$$

$C_{c,f}$ is the sorbed contaminant concentration in the feed of organism (suspended particulate) (g g^{-1}); k_f is the ingestion rate of the organism (g particulates (g biota d)$^{-1}$); and F_f is the food uptake rate efficiency (-).

Equation 2.23 can further be extended to a more complex model, called the bioenergetics-based toxicokinetic bioaccumulation model (Hickie *et al.*, 1999). Such complex models allow uptake to occur via multiple routes including overlying water, interstitial water, and ingested sediment, as well as elimination via multiple routes. Uptake from each route is assumed to be independent and additive. In such model, the toxicant uptake via multiple routes can be modelled as follows (Hickie *et al.*, 1999):

$$\frac{dC_{c,b}}{dt} = \underbrace{k_1 F_w C_{c,w} + \sum_{j=1}^{n} k_{f,j} F_{f,j} k_2 C_{c,f,j}}_{uptake\ \ term} - \underbrace{k_2 \left(m + g\right) C_{c,b}}_{elimination\ \ term} \qquad (2.24)$$

where $F_{f,j}$ is the assimilation efficiency from food j (-), $k_{f,i}$ is the toxicant assimilation efficiency from food j (g g^{-1}), n is the total number of food types, m and g are dilution rates due to metabolism and growth, respectively.

The elimination rate k_2 is sometimes expressed as k_D, as the overall elimination rate constant (Loonen *et al.*, 1997) including three parameters: the true elimination rate, the first-order growth dilution rate and the biotransformation rate. When the growth dilution rate and biotransformation rate are negligible, it is reduced to one parameter as expressed in equation 2.22 and 2.23. Microbial biomass (both bacteria and algae) is also considered as a carrier or food (Ashley, 1998).

Biotic transformation

Biological transformation refers to the microbially mediated transformation of organic chemicals. Microorganisms decompose not only the conventional organic material, but also the xenobiotic organic compounds such as fuels, solvents, and pesticides to obtain carbon, energy or nitrogen (Higgins and Burns, 1975). In natural waters, biotransformation is often considered as the predominant removal process for the biodegradable organic contaminants. Bacteria or fungi can transform organic compounds by an array of mechanisms (Schnoor, 1996) like dealkylation (e.g. $ROCH_3 \rightarrow ROH + CH_3$), ring cleavage (e.g. $Ar \rightarrow ArOH$), dehalogination (e.g. $RCHClCH_3 \rightarrow RCHOHCH_3 + Cl^-$), etc. These biological transformation processes can occur either under aerobic conditions (e.g. benzene biodegradation; ring cleavage) and anaerobic conditions (polychlorinated biphenyls degradation; dehalogenation) (e.g. Kuo, 1999). The term “biodegradation” is used synonymously with “biotransformation”, but the former refers to the oxidation reactions that break down the chemical. The process in which the organic chemical is broken down into H_2O and CO_2 is referred to as “mineralisation”. Biodegradation provides energy and carbon for bacterial growth and maintenance, whereas biotransformation does not have to yield carbon nor energy for microbial growth or maintenance. Although it may not lead to a complete breakdown of the organic compound, biotransformation is still an important process when it changes the original toxic chemical into a non-toxic form. It should also be noted that biotransformation may also result in more toxic forms as well (e.g. epoxidation).

The other important processes include secondary substrate utilization and co-metabolism (Rittmann, 1992). The term secondary utilization refers to the utilization of organic chemicals at low concentrations (less than the concentration required for growth) in the presence of one or more primary substrates that are used as carbon and energy sources. The term co-metabolism refers to the transformation of a substrate that cannot be used as a sole carbon or energy source but can be degraded in the presence of other substrates. For example, no microbial species has been found which can grow on DDT as a sole carbon and energy source, but microbial consortia (a group of microbial species) are known to degrade DDT in the presence of other substrates (Schnoor, 1996).

Biodegradation/biotransformation may be modelled using Monod limitation or Michaelis Menten enzyme kinetics, first-order or zero-order kinetics. The actual biodegradation/biotransformation rate following the Monod limitation or Michaelis Menten enzyme kinetics is expressed as follows:

$$\frac{dS_{GC}}{dt} = \frac{-\mu_m}{Y} X \left[\frac{S_{GC}}{K_{GC} + S_{GC}} \right] \quad \Rightarrow \textit{substrate utilization} \qquad (2.25)$$

$$\frac{dX}{dt} = \mu_m X \left[\frac{S_{GC}}{K_{GC} + S_{GC}} \right] \quad \Rightarrow \textit{microbial growth} \qquad (2.26)$$

where S_{GC} is the generic organic contaminants (mg L^{-1}); μ_m is the maximum microbial growth rate (d^{-1}); X is the active microbial biomass concentration (mg L^{-1}); Y is the microbial biomass yield coefficient (mg of X produced/ mg S_{GC} removed), and K_{GC} is the Michaelis or Monod half saturation constant (mg L^{-1}).

If $S_{GC} << K_{GC}$, equation 2.25 is reduced to second-order biotransformation kinetics in S_{GC} as:

$$\frac{dS_{GC}}{dt} = -\frac{\mu_m}{YK_M} XS_{GC} = -k_{b1} XS_{GC} \qquad (2.27)$$

where k_{b1} is the second-order rate constant (l (mg d)$^{-1}$).

When X is assumed constant, equation 2.27 becomes first-order biotransformation kinetics in S_{GC} as:

$$\frac{dS_{GC}}{dt} = -kS_{GC} \qquad (2.28)$$

where k is the pseudo-first-order biotransformation rate constant (d^{-1}).

When $\mu_m X / Y$ are grouped together as one constant (q_m), called maximum substrate utilization rate, equation 2.25 can be expressed as follows:

$$\frac{dS_{GC}}{dt} = -q_m \left[\frac{S_{GC}}{K_{GC} + S_{GC}} \right] \quad \Rightarrow \textit{substrate utilization}$$

If the substrate concentration $S_{GC} >> K_M$ (not after the case in a natural environment) the microorganisms are growing exponentially. In that case equation 2.25 can further be reduced to zero-order kinetics in S_{GC} , but first-order in X as :

$$\frac{dC}{dt} = -\frac{\mu_m}{Y} X \tag{2.29}$$

Equation 2.29 assumes that S_{GC} is not limiting the microbial growth, and it is present sufficiently. Since, the concentration of organic contaminant in the aquatic system, however, is often very low (in the order of $\mu g\ l^{-1}$), the first order biotransformation kinetics is recommended as default (Schnoor, 1996; Chapra, 1997).

Incorporation of a biofilm model

Attached biofilms in the benthic sediment of the river play an important role in removing organic pollutants and oxygen from the river. Several studies have shown that biofilm activities dominate the biodegradation process in shallow streams (see among others, Boyle and Scott, 1984; Pignatelo *et al.*, 1985; Rutherford *et al.*, 1991a,b; Takada *et al.*, 1994). Srinanthakumar and Amirtharaja (1983) also showed that attached biofilms were much more effective in removing organic carbon than the suspended biomass in a swift, shallow stream. Recently, Boeije *et al.* (2000) showed that biofilms have the highest relative importance in rivers with higher surface area to volume ratio. In shallow streams therefore, disregarding the sessile bacterial activities in water quality modelling may result in unrealistically overestimating the biodegradation rate coefficient of suspended bacteria, while an attempt is made to fit the simulated set with the measured data.

The concept of biofim modelling can be briefly summarised below using the scheme of the idealised biofilm model illustrated in Figure 2.9. In the idealised biofilm model, a uniform biofilm thickness (L_f), uniform density (X_f) and uniform diffusion layer (also called liquid boundary layer) (L) are considered. Substrates like soluble organic carbon (S_S) and dissolved oxygen (S_{O2}) are transferred from the bulk water to the biofilm through such uniform diffusion layer (L) by molecular diffusion (D) according to Fick's first law of diffusion. The substrate concentrations at the surface of the biofilm ($S_{S,0,}$ and $S_{O2,0}$) can be less or equal to the bulk water concentration (S_S and S_{O2}) depending on the rate of external mass transfer relative to the substrate utilization rate. On the other hand, the transfer of substrate within the biofilm by molecular diffusion follows Fick's second law of diffusion (Rittmann and McCarty, 1980), and the substrate can fully or partly penetrate the biofilm and gives raise to the biofilm concentrations $S_{S,f}$ and $S_{O2,f}$. The biofilm activity can be limited by one of the limiting substrates, which is the one that does not fully penetrate the biofilm and tends to become zero prior to the other substrates, for example $S_{O2,f}$ in Figure 2.9. The fraction of biofilm that is penetrated by all substrates is considered as an active fraction, whereas the rest is called inactive. The active fraction of the biomass Φ is equal to the dimensionless penetration depth. The maximum penetration depth as is the case for S_S is equal to L_f.

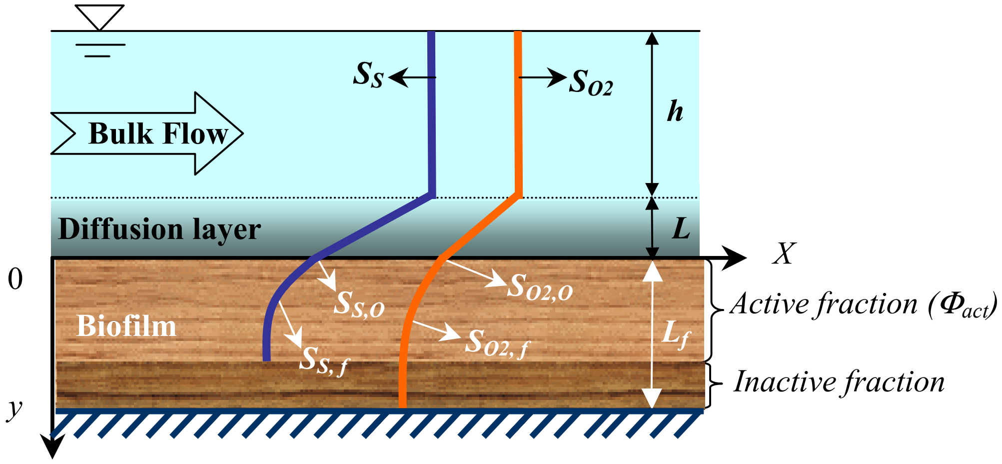


Figure 2.9: Concept of biofilm-channel flow system (modified from Li and Chen, 1994); *h* is the water level

Based on the concept delineated above, several biofilm kinetic models have been formulated. The complexity of these types of models varies from the simple steady-state model of a single species and single growth-rate limiting substrate developed by Rittmann and McCarty (1980) to the very complex dynamic biofilm model, the so-called multi growth-rate limiting substrate, mixed culture model (Gujer and Wanner, 1990; Wanner and Reichert, 1996). Most of these models, however, were developed for wastewater treatment systems.

By taking into account the biofilm attached on the riverbed, a few river water quality models have been developed. Lau (1990) proposed an analytical model of biofilm consumption of dissolved substrate in open-channel flows based on the assumption of a single rate-limiting substrate and zero or first-order kinetics. The analytical model is not applicable when there are multiple rate-limiting substrates. Besides, dissolved oxygen was not considered in the model. Rutherford (1991a,b) then proposed a model to predict the organic contaminant and dissolved oxygen concentration in a mobile-bed river. There is a restriction, however, on the application of this model because it is an empirical model. The effect of attached biofilm was not modelled explicitly, but taken into account in the overall deoxygenation rate coefficient that was obtained from a correlation analysis.

Subsequently, Li and Chen (1994) proposed a mechanistic steady-state model assuming that the diffusion and reaction within the biofilm are steady-state and follow Monod kinetics. This model predicts organic contaminant degradation and oxygen consumption by biofilm in an open-channel flow. It is more realistic than Lau's model because it considers a dual rate-limiting substrate (organic carbon and oxygen). Furthermore, it takes into account the effect of hydraulic characteristics like flow velocity on the removal rate of organic contaminant. Li and his co-worker demonstrated that flow velocity influences the removal rate in two ways. The decrease in flow velocity prolongs the contact time and thus increases the removal rate. On the other hand, it results in the increase in diffusion layer thickness, which decreases the removal rate. It was also concluded that under specified conditions of simulation, the effect of contact time is more significant than that of the diffusion layer thickness.

Melcer and co-authors (1995) also proposed a simple steady-state model for Volatile Organic Contaminants (VOCs) using first-order kinetics assuming a single rate-limiting substrate and a single microbial species. This model was proposed for wastewater treatment systems (trickling filter), but was also applied to describe the fate of organic contaminants in small rivers (Boeije *et al.*, 2000). It is also relatively easy to incorporate in other basic water quality models.

Summarizing, all biofilm models described above have several limitations: (1) they assume constant biofilm thickness, and (2) they do not take into account the effect of a mixed culture or the presence of multiple species of bacteria and the interaction between the activities of different species is missing.

Rauch and Vanrolleghem (1998) thus proposed a conceptual dynamic model that describes the dynamics of a benthic biofilm and the influence of the conversion processes to the water quality in shallow eutrophic rivers. This model is based on an analytical solution that predicts the exchange of converted material between the bulk liquid and the biofilm known as the half-order kinetic biofilm model. The model describes the simultaneous or sequential conversion of multiple substrates such as readily biodegradable organic matter, ammonia, nitrate and dissolved oxygen by multiple bacterial species such as heterotrophic, nitrifying and denitrifying organisms. In this approach, the biofilm thickness is a function of growth, decay, attachment and detachment assuming constant biofilm density (see for details Rauch and Vanrolleghem, 1998; Rauch *et al.*, 1999). Subsequently, the author proposed the following equation for the biofilm thickness:

$$L_f = \frac{\sum M_{bi}}{\rho . A_f} \tag{2.30}$$

where L_f is the biofilm thickness (m), M_{bi} is the mass of particulate component i in the biofilm (g), ρ is the constant biofilm density (g m^{-3}) and A_f is the surface of biofilm (m^2).

Assuming zero order kinetics in substrate, the volumetric reaction rate (substrate utilisation rate) r_{vi} with respect to the substrate in the bulk liquid can also be expressed as follows (Rauch and Vanrolleghem, 1998):

$$r_{vi} = \sum - \mu_j v_{ij} \phi_{act,j} \frac{M_{bj}}{V} \tag{2.31}$$

where V is the volume of the bulk liquid compartment (m^{-3}), M_{bi} /V is the concentration of particulate matter j in the biofilm per unit of volume of the bulk liquid compartment (g m^{-3}), μ_j is the maximum specific growth rate of species X_j (d^{-1}), v_{ij} is the stochiometric coefficient, i and j are suffixes denoting the substrates and the microbial species respectively, and $\Phi_{act,}$ is the active fraction of biofilm.

Being an analytical solution, the Rauch and Vanrolleghem modelling approach provides substantial gain in computational efficiency. The model is described according to the background given in the IWA activated sludge model No. 1 (*ASM1*; Henze *et al.*, 1987). It can be applied easily in a water quality model that has a lower number of processes than *ASM1*, but it is complicated to apply as part of the River water Quality Model No. 1 (*RWQM1*; Reichert *et al.*, 2001). So, much effort needs to be done to develop a more simplified conceptual biofilm model that can be incorporated easily in existing river water quality models like *RWQM1*.

2.4.7.2. Effect assessment

Static approach

In standard/traditional laboratory toxicity tests, the test organisms are continuously exposed to several different test compound concentrations for a period of time (e.g. 48 h or 96 h) and then monitored to relate the specified responses to the contaminant concentration (e.g. 48 h LC50 or 96 h LC50). Such laboratory toxicity tests utilize a fixed or static initial concentration and have the following limitations: (1) they do not consider the response of organisms after the time of observation (Naddy and Klaine, 2001), and (2) they do not investigate the toxicity of short-term pulsed exposure or intermittent exposures of substances to aquatic organisms (Hickie *et al.*, 1995; Petersons *et al.*, 2001) (3) they do not consider the seasonal variation of organism sensitivity. As they assume steady-state conditions, static approaches may produce data that inaccurately predict the safety of toxicants in a real environment. Their inaccuracy is related to the fact that (1) constant exposure for the initial concentration may overestimate the toxicity of toxicants, as the concentration may change over time due to rapid biodegradation, hydrolysis or photolysis, and (2) the levels of exposure in the real environment is time variable due to different circumstances, e.g. runoff events and sewer overflows.

Dynamic approach

In a real environment, the exposure concentration varies with time (see Figure 2.10), and effect or toxicity should hence vary with time. Such time-dependent effect assessment is termed dynamic-effect assessment. In the dynamic-effect assessment a time-varying exposure concentration is used for a time-varying (dynamic) toxicity test. Such advanced method of toxicity assessment is a realistic exposure assessment, especially in agrochemical exposure assessment (Petersons *et al.*, 2001; Reinert *et al.*, 2002; Wadianarko *et al.*, 2001). In studies examining toxic responses to time-varying exposures, various terms have been used to describe the exposure patterns, including pulse, plug, spike, episodic, fluctuating, and intermittent/batch exposures. These patterns can be generalized and classified into two types of variable exposures: pulse exposures, which involve one or more isolated and brief exposure periods; and fluctuating exposures, which involve continuously varying concentrations during a prolonged period. In both pulse and fluctuating exposures, the exposure concentration, duration and frequency are the controlling factors for toxicity.

Pulsed exposure and related terminology are indicated in Figure 2.10. In fluctuating exposure, toxicity depends on the pulse height, width, frequency and recovery time. The higher the frequency of the pulsed exposure with a shorter recovery time, the more it will be potentially toxic to the exposed organism (Reinert *et al.*, 2002; Naddy and Klaine, 2001, Naddy *et al.*, 2000). It is also indicated that for a longer recovery time, organisms get more time to repair damage by eliminating the accumulated toxicant in their tissue.

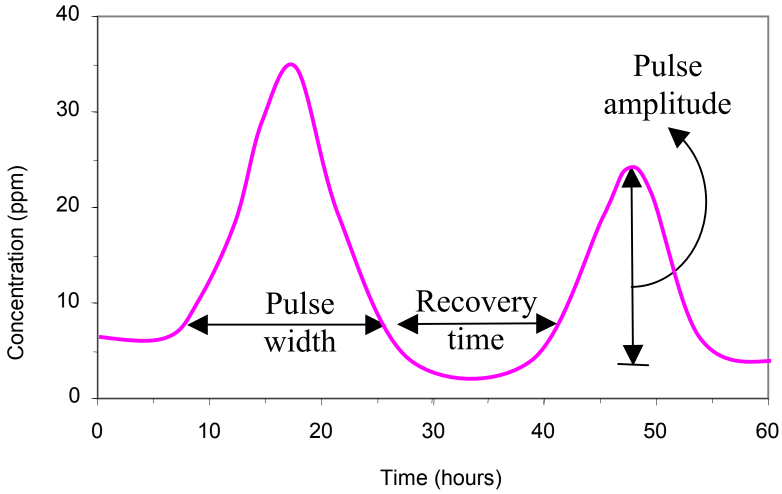


Figure 2.10: Schematic representation of pulse, time-varying, or repeated-exposure relationships and terminology (modified from Reinert *et al.*, 2002)

Determination of PNEC

Predicted No-Observed Effect Concentration (PNEC) refers to the maximum concentrations of chemical of concern that pose No-Observed adverse effects to all organisms in an ecosystem (EEC, 1993). In principle, the toxicity test needs to be conducted for all species in an ecosystem under consideration. Performing toxicity tests for all species, however, is practically impossible. Therefore, PNEC is extrapolated usually from a limited toxicity database. In such extrapolation procedure, some allowance for uncertainty must be made. There are basically three general approaches: empirical extrapolation factors, statistical models, and probabilistic approach.

In empirical approaches, an empirical extrapolation factor or assessment factor is used. First, the Organisation for Economic Co-operation and Development (OECD) introduced assessment factors of 10, 100, and 1000 for the derivation of PNEC (OECD, 1992). Later, the commission of European Communities (CEC) recommended more stringent assessment factors (1-10, 10, 50, 100 and 1000) that, however, require a relatively more extensive data set (CEC, 1994).

In a statistical approach on the other hand, the substance concentration that will protect 95% of species or the hazardous concentration for 5% of species (HC_5) is used. HC_5 is commonly described by plotting a cumulative distribution curve using available single-species test of chronic data or No-Observed Effect Concentration (NOEC) data (see Figure 2.11). Such curves are termed Species Sensitivity Distribution (SSD) (Posthuma, 2001). Typical examples of such methods are the USEPA model, which is based on a minimum data set of eight

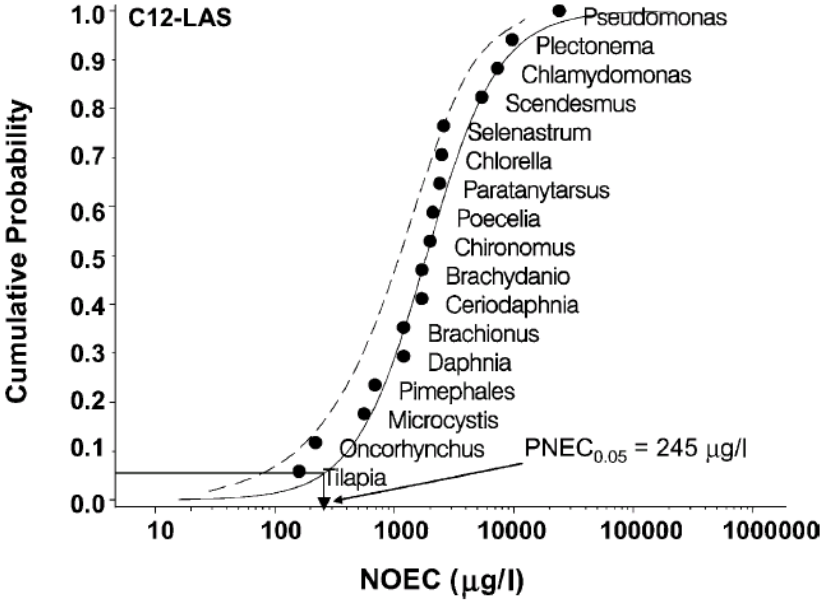
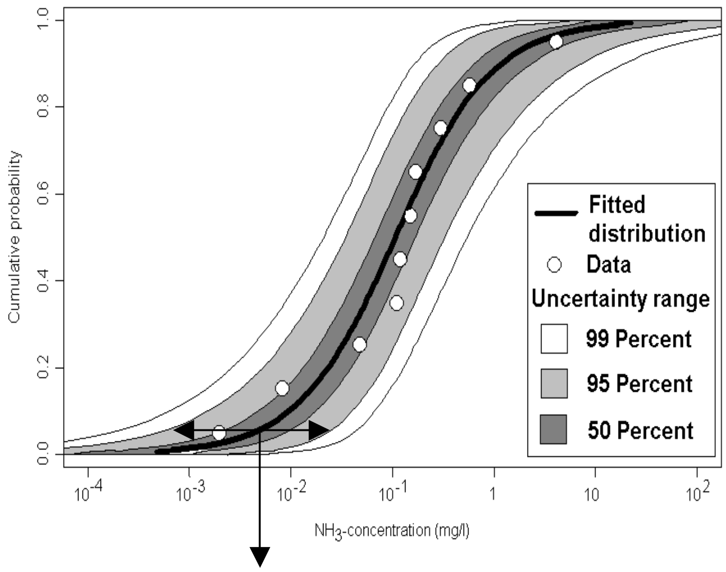


Figure 2.11: Deriving PNEC or HC_5 from SSD based on log-logistic cumulative probability distributions of NOEC (solid line), with lower 95% confidence limit (dashed), for C12-LAS (Dyer *et al.*, 2003)

families from both acute and chronic toxicity tests (Stephan *et al.*, 1985), and the Dutch National Institute for Public Health and the Environment (RIVM), system for derivation of water quality standards (Aldenberg and Slob, 1993).

Although both empirical and statistical methods provide PNECs that appear to be protective for the ecosystem, they are strongly influenced by the available data and hence have limitations (Selck *et al.,* 2002). In the empirical approach, the assessment factor 10 is applied when chronic data (NOEC values) is available. When chronic data are not available, and minimum acute data (LC50s or EC_{50}s, the concentration that leads to mortality of 50% of the test species) is not is not available either, a larger assessment factor, e.g. 1000, is applied. The statistical approach on the other hand, requires a large data set; they assume that protecting 95% of species will protect the ecosystem as a whole, whereas the most sensitive 5% of species may be ecologically important species. The resulting value depends upon the statistical distribution of data rather than on data for the most sensitive species.

In both the empirical and statistical approaches, toxicity data that are obtained in a static approach are employed, whereas in reality the NOEC value varies in time and space. These approaches also assume steady-state exposure concentrations. Subsequently, more advanced methods such as probabilistic and dynamic mechanistic modelling approaches are required. The probabilistic modelling approach can deal with the uncertainty of NOEC values due to temporal and spatial variability, species sensitivity, measurement error, etc (Verdonck *et al.*, 2002). The analysis of this approach is generally based on distributions of NOEC and species sensitivity (SSD). This type of model can predict the 5th percentile of the Hazard Concentration (HC_5) with e.g. 95% of uncertainty band/range (see Figure 2.12). However, it assumes that both NOEC and species sensitivity are a random variable. Both spatial and temporal variability are also considered as a random noise. Spatial variably of effect can be taken into account by geo-referencing the NOEC value (Verdonck, 2003). In geo-referencing approach, e.g. in GREAT-ER, the river network is divided into the river stretches to each of which the corresponding NOEC value is determined. These NOEC values of river stretches are then used to calculate the NOEC value of the whole catchment. To take into account the temporal variability of effect on the other hand, a dynamic model needs to be applied. Time-varying effect/toxicity is the result of time-varying exposure concentration.



95% uncertainty interval on
5th- percentile = HC_5

Figure 2.12: Deriving PNEC or HC_5 with uncertainty band-probabilistic approach (after Verdonck *et al.*, 2002)

Dynamic mechanistic effect modelling

A toxic effect refers to any adverse effect of a toxic chemical on aquatic organisms. It is important to note the concept in toxicology that in general no chemical is completely safe and no chemical is completely harmful (Rand and Petrocelli, 1985). The factors that determine a chemical agent is potentially harmful or safe is the relationship between the concentration (quantity) of the chemical to which an organism is exposed and the duration of the exposure.

There are two different concentrations relevant to the toxicity assessment: the concentration of toxicant in the environment (external) and the concentration in the target receptor, tissue or organ. In standard regulatory patterns such as water quality criteria, the environmental/external concentration is used as a surrogate for the concentration at the receptor site. Under steady-state conditions, the three-dimensional analysis of toxicity (effect, exposure concentration and exposure duration) is illustrated in Figure 2.13. A high lethal concentration will kill an exposed organism at a faster rate than a low concentration and vice versa.

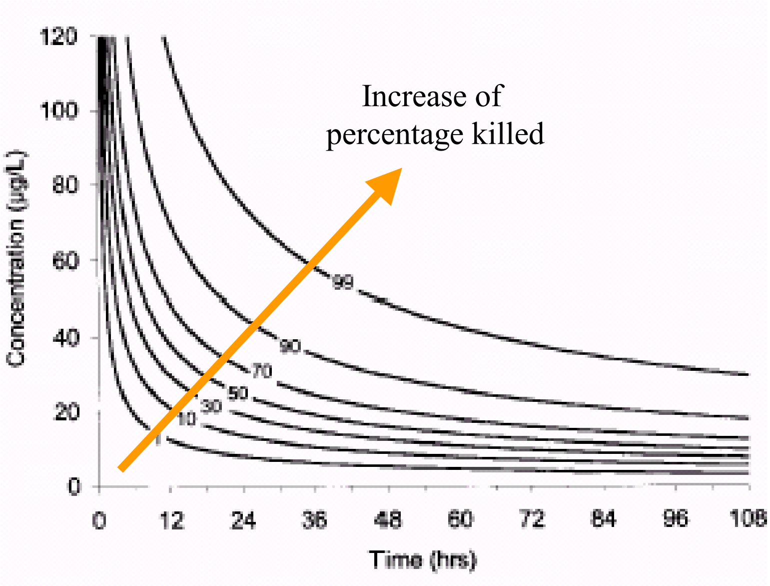


Figure 2.13: Interaction of concentration (mg/L) and time of exposure (hours) on percent mortality as predicted from the model $y = -10.86 + 4.83\ln(C_{c,w}) + 3.0\ln(t)$; lines represent percent mortality *y* for various combinations of concentration *C* and time (*t*) (after Peterson *et al.*, 2001)

The limitation of using the external concentration as a surrogate for the tissue/target site concentration is that it is not species specific, and it is therefore difficult to determine the ultimate effect of pulsed doses or time-varying exposure concentrations (Hickie *et al.*, 1995). Under time-varying exposure concentrations, toxicity depends on the bioaccumulated internal concentration, rather than on the external concentration.

Toxicity/effect models that deal with time-varying exposures are utilizing the concept of Critical Body Residues (CBR) or Critical Body Burden (CBB), or Critical Body Concentration (CBC), which all refer to the internal concentration above which toxicity manifests itself in the organism of concern (Mancini, 1983). The CBR concentration can be based on the whole body or on a particular target organ, and can provide a more direct measure of a predicted adverse effect than can external exposure concentrations (Reinert *et al.,* 2002). The CBR concept includes not only concentration but also exposure duration and frequency. It is also the result of multiple exposure routes including dietary uptake.

Acute effects

Based on the one-compartment toxicokinetic model similar to equation 2.22, assuming negligible growth dilution or volume, the internal body concentration $C_{c,b}$ at any time t can be derived as follows:

$$\frac{dC_{c,b}}{dt} = k_1 C_{c,w} - k_2 C_{c,b} \tag{2.32}$$

Integrating equation 2.32, replacing $C_{c,w}$ by $LC50$, $C_{c,b}$ by the Lethal Body Residue (LBR) , and rearranging it, the median lethal concentration ($LC50_t$) at any time t becomes (Mancini, 1983; Crommentuijn *et al.*, 1994):

$$LC50_t = LBC / \{(k_1 / k_2) \cdot (1 - e^{-k_2 t})\} \tag{2.33}$$

When the organism is exposed long enough one can rearrange 2.33, resulting in the widely applied relation to determine the value of LBR for narcotic type class chemicals, as follows:

$$LBR = (k_1 / k_2) \cdot LC50 = BCF \cdot LC50 \tag{2.34}$$

where LBR is the lethal body residue that causes mortality (μg kg^{-1}), and $k_1/k_2=BCF$.

The $LC50$ of the compound under consideration can be obtained from experimental results if available; otherwise it can be estimated from a Quantitative Structure-Activity Relationships (QSAR) approach. The following correlation based on the QSAR approach is sometimes used (Kooijman, 1981):

$$Log(1/LC50) = 0.87 \log K_{OW} - 4.87 \tag{2.35}$$

This correlation expresses two processes: partitioning and toxicity. Such correlation is uncertain due to chemical variation and partitioning differences. Therefore, such relations need to be established for every sensitive organism considered.

Once LBR is known, the cumulative fraction of organisms killed or surviving is estimated on the basis of the Weibull distribution (Christensen, 1984; Mackay *et al.*, 1992), as follows:

$$P = 1 - e^{-(C_{c,b} / LBR) \cdot 1 / S} \tag{2.36}$$

where P is the cumulative fraction killed; and S is a parameter expressing the variability in the toxic response (0.1–0.33 show best fits, Mackay *et al.*, 1992).

Chronic effects

To predict chronic effects, ratios of chronic to acute toxicity have been used (Kooijman, 1981, EPA, 2001). For example, the effect of growth inhibition is given as follows:

$$AFGrowth = EC50_{growth}/LC50 \tag{2.37}$$

$$AFReprod = EC50_{reprod}/LC50 \tag{2.38}$$

$$RedGrowth = 1 - e^{-(Cc,b/(LBR*AFGrowth))\wedge 1/S} \tag{2.39}$$

$$RedReprod = 1 - e^{-(Cc,b/(LBR*AFReprod))\wedge 1/S} \tag{2.40}$$

AFGrowth is the chronic to acute ratio for growth inhibition; *EC50growth* is an external concentration of toxicant at which a 50% reduction in growth is observed (mg/l); *AFReprod* is the chronic to acute ratio of reproduction failure; *RedGrowth* is the factor for reduced growth in organisms (unitless), and *RedReprod* is the factor for reduced reproduction (unitless).

2.4.8. Integrated modelling of eutrophication and fate and effect of organic contaminants

When separate eutrophication and organic contaminant fate models are used, the interaction between nutrient dynamics and organic contaminant fate and effect is missed because they are single-issue models or they are concerned with a single problem. For example, an eutrophication model is concerned with only nutrient sources and sinks and algae blooms whereas an organic contaminant fate-and-effect model is only dealing with the fate and transport of organic contaminants. As both eutrophication and contamination by organic contaminants interact in various ways (Gunnarsson *et al.*, 1995; Hylland *et al.*, 1996; Skei *et al.*, 1996), linking these two models is essential.

Furthermore, there is a great demand for knowledge about the interaction of eutrophication and organic contaminants in order to make decisions about how to handle contaminated sediments (dredging, capping, i.e. depositing of clean material, usually coarse sand over contaminated sediments, etc). So, integrated modelling of eutrophication and organic contaminant fate and effect gives insight into mechanisms and interactions that are of value to environmental decision makers.

There are a few integrated models of eutrophication and organic contaminant fate proposed for lakes: *GBMB* (US-EPA, 1989), *AQUATOX* (Park *et al*., 1995), modified *QWASI* model (Wania, 1996), and Ashley (1998). Of these models, only the *AQUATOX* model was applied in-streams and small rivers. The *AQUATOX* model is a general ecological risk assessment model that represents the combined environmental fate and effects of conventional pollutants, such as nutrients and sediments, and toxic chemicals in aquatic ecosystems. It considers several trophic levels, including attached and planktonic algae and submerged aquatic vegetation, invertebrates …; it also represents associated organic toxicants. It can be implemented as a simple model or as a truly complex food-web model. The model is intended to evaluate the likelihood of past, present, and future adverse effects from various stressors including potentially xenobiotic organic chemicals, nutrients, organic wastes, sediments, and temperature. The stressors may be considered individually or together.

Though the *AQUATOX* model is the most complete integrated eutrophication and organic contaminant fate-and-effect model, it has some limitations: (1) it does not explicitly simulate the bacterial biomass; (2) the elemental balance is not considered and hence mass balance are not consistent; (3) it uses BOD as measure of carbonaceous organic matter; and (4) the dissolved mass flux (except dissolved organic carbon) between the pore water and the overlying bulk water is not considered.

As bacterial biomass is not simulated in *AQUATOX*, microbial activities such as nitrification, denitrification and microbial decomposion are modelled in such a way that the maximum rate of the processes under consideration is reduced by limitation factors for sub-optimal dissolved oxygen pH and temperature. Such modelling approach is relatively simple, but does not handle the variation of bacterial biomass.

General limitations of integrated modelling

In the state-of-the-art, integrated modelling of conventional pollutants and xenobiotic organic contaminant fate and effect is often done by coupling the existing submodels, but these lack some important process descriptions because they were developed for different purposes. In most of the eutrophication models, organic matter is included, but an appropriate description of DOC and POC dynamics is lacking (Koelman *et al*., 1999). They assume “carbon as carbon” while different types of organic matter have different affinities for organic contaminants. In modelling bioconcentration/bioaccumulation, describing organic carbon in both DOC and POC forms is crucial because they determine the bioavailability of the contaminant. Therefore, DOC is proposed as an extra state variable in integrated modelling (Koelman *et al.,* 1999). Furthermore, bacteria are important not only for the carbon cycling in aquatic food webs but also for sorbing organic contaminants. Ashley (1998) also showed that bacteria and protozoa should be included as carriers of organic contaminants in bioaccumulation models. In spite of this report, the incorporation of bacteria as state variable in an eutrophication model, as well as in an organic contaminant fate model, is not common in traditional surface water quality modelling (Reichert *et al*., 2001; Koelman *et al*., 1999).

2.5. Problem definition and goal of the Ph.D. thesis

In developing an integrated river water quality model that can be used as a tool in water quality regulations, four important problems can be outlined. The *first problem* is the use of a complex hydrodynamic model. In the state-of-the-art, St Venant equations are typically used for all types of rivers, although a conceptual model can be used for non-tidal-influenced rivers (Whithead *et al*., 1997). The St Venant equations are too complex to be used in higher tier water quality modelling. In order to refine the river water quality models, conceptual hydraulic routing needs to be used.

The *second problem* is related to the lack of appropriate process descriptions. In traditional basic water quality modelling (eutrophication), both carbon forms DOC and POC are not considered explicitly as state variables, and their dynamics are not simulated. However, the distribution or partitioning of organic contaminants is determined by the DOC and POC dynamics in the system. Thus, to take into account the effect of bioavailablity on bioaccumulation and toxicity, three-phase partitioning into a truly dissolved phase, a phase sorbed to DOC and a phase sorbed to POC, should be taken into account. Besides, bacteria mediate the biotransformation of contaminants or carbon cycle, but they are not considered explicitly as state variables in the traditional models of eutrophication and organic contaminant fate and effect.

The *third problem* concerns the prediction of the effect or toxicity using a static approach. Traditional effects assessment is based on a static approach in which the organism is exposed to a constant concentration for a given time. In reality, however, the organism is exposed to a time-varying concentration. To take into account such temporal variability, toxicokinetic models need to be applied.

The *fourth problem* is due to the lack of attention given to the interaction between eutrophication and contamination by organic contaminants in traditional river water quality modelling. Eutrophication and organic contaminants may interact by many mechanisms (Gunnarsson *et al*., 1995; Bondavalli, 2003). For example, eutrophication may cause dilution of contaminants by increasing the amounts of suspended Particulate Organic Carbon (POC), and thereby reduces toxicity. Organic contaminants on the other hand, may have a direct effect (toxic effect) or indirect effect (decrease or increase of grazing or predator pressure) on aquatic organisms. Such effect in turn will affect the organic contaminant fate and nutrient cycles (Legovic, 1997). As separate models do not address these interactions, an integrated model of eutrophication and organic contaminant fate and effect is essential.

The objective of this thesis is therefore *threefold*. The *first goal* is to give insight in conceptual dynamic basic-water-quality modelling with appropriate process descriptions. The model should be relatively simple and applicable to data limited situations, for instance in developing countries. Using such a simplified model, water quality control options in semi-arid regions were investigated. The intention of model simplification is not only valid for the applicability of the model in data-limited conditions but also for suitability of the model in integrated water quality studies.

The *second goal* is to develop a dynamic organic contaminant fate model that can be used as a tool in time-varying exposure assessment. Besides, the effect of time-varying exposure concentration on the bioaccumulation and toxicity of an organic contaminant is investigated.

The *third goal* is to develop a dynamic integrated river water quality model that gives insight into the complex interaction of conventional pollutants (nutrient enrichment or eutrophication) and contamination by xenobiotic organic compounds. Such knowledge of interaction can then be explored to analyse the effect/toxicity of multiple-stressors like nutrients, conventional organic matter and xenobiotic organic substances in aquatic ecosystems.

Part 3

WEST: Modelling integrated river water quality

Chapter 3

WEST: Integrated river water quality modelling

In this chapter, the water quality simulation software used in this work, the World Wide Engine for Simulation, Training and Automation (WEST$^{®}$) is briefly discussed towards its application for integrated river water quality modelling. The WEST$^{®}$ simulator is mainly used to model wastewater systems, despite the fact that it is potentially applicable to model river systems too. During this study, different river water quality models, varying from simple single issue river water quality model to the complex integrated river water quality model, were developed and implemented in the WEST$^{®}$ simulator. The hierarchical procedures by which these models were built in the simulator are also presented. Before this, however, the importance of integrated modelling of basic water quality (eutrophication) and organic contaminant fate in rivers is highlighted. Also, a brief summary of other river water quality simulators in relation to the WEST$^{®}$ simulator is given.

3.1. Why modelling integrated river water quality?

The use of mathematical models as a tool in water quality management is largely driven by legislation, and their practices also vary from country to country (Cox, 2003). In a country where the water quality is based on the water quality objectives (see Chapter 2), the mathematical models are required to assist the water quality regulator to achieve the water quality objective. For instance, the basic river water quality models, which simulate the transport and fate of conventional pollutants (e.g., RWQM1, Reichert *et al.*, 2001; QUAL2E, Brown and Barnwell, 1987) assist water quality managers to evaluate the impact of conventional pollutant loads on the receiving water, e.g. to determine the maximum pollutant load that does not exceed the assimilative capacity of the river, and to estimate the wastewater treatment efficiency required to meet the receiving water quality standards. The exposure models, which simulate the transport and fate of toxic substances, assist the environmental risk manager to determine the Predicted Environmental Concentration (PEC) of xenobiotic organic substance under consideration.

Despite the fact that both problems can co-exist in rivers, both conventional pollutants and organic contaminants are considered separately as single-issue models in traditional river water quality modelling.

Rivers can be polluted by conventional pollutants, and at the same time can be contaminated by xenobiotic organic compounds. Aquatic organisms in rivers can then be subjected to multiple adverse impacts that result from both conventional pollutants and xenobiotic organic contaminants. Such multiple adverse impacts and their interaction cannot be addressed using single-issue models. Integrated modelling of basic water quality/eutrophication and organic contaminant fate in rivers are therefore required to take into account both water quality problems (eutrophication and contamination by xenobiotic organic compounds) and their interaction. Such modelling approach provides a better understanding of the interaction between the fate of the basic water quality components and xenobiotic organic compounds, and thereby appropriate prediction of their possible ecological effect or toxicity is possible. It also allows making scenario analyses to drive an appropriate remediation action. Such work needs appropriate simulation software.

In the next subsection, first the available computer packages applied for river water quality modelling are briefly discussed. Then, the general steps that must be followed hierarchically while developing new river water quality model in the WEST® simulator is described. Besides, general steps in building the modelbase for the integrated river water quality model (RIVEUTOX1), the basic futures, the limitations and proposed solutions for the current versions of the WEST® simulator were presented.

3.2. Simulation software

Except for a simplest approach, all mathematical models for the prediction of the water quality in rivers require the use of a computer (Rauch *et al.*, 1998). The best-known river water quality simulator in literature is the *QUAL2E* model developed by the US Environmental Protection Agency (EPA) (Brown and Barnwell, 1987), which is applied only for steady state conditions. For the time variable conditions, a dynamic river water quality simulator is needed. The dynamic river water quality simulators include *WASP5* (Ambrose and Martin, 1993), *CE-QUAL-RIV1* (Environmental Laboratory, 1995), *ISIS* (Wallingford Software, 1994), *SALMON-Q* (Wallingford Software, 1996) and *MIKE-11* (DHI, 1992).

There are generally two categories of computer programmes that can be used for the integrated river water quality modelling: closed model structure programmes and open model structure programmes. Being open or closed in model structure has both advantages and disadvantages for the users. In a closed model structure, the user does not have to formulate his model because the program has already included the relevant model components for a given environmental system. Thus, the user can change only some parameters, but he cannot change the model structure. Examples of such closed model structures include *QUAL2E* (Brown and Barnwell, 1987), *WASP5* (Ambrose *et al.*, 1988), *CE-QUAL-ICM* (Cerco and Cole, 1995), *MIKE11* (DHI, 1992), *SALMON-Q* (Wallingford Software, 1996) …

In open model structure programmes, the user can change the model structure. They give the users a large freedom in model definition so that state variables, parameters, transfer functions and differential equations can be chosen freely. The programmes provide the mathematical routines for solving the resulting set of Ordinary Differential Equations (ODE) and, if available, Partial Differential Equations (PDE). The disadvantage of an open model structure programme is that the user must develop the model that suits the intended condition, and this requires detailed knowledge of model formulation. Such types of open structure programmes are also called general-purpose simulation software, and are mainly applied as research tools.

The available open model structure programmes that can be used for river water quality modelling include AQUASIM (Reichert, 1995) and DUFLOW-EUTRO (Aalderink *et al.*, 1995). These models are particularly suitable for situations where complex hydrodynamic modelling based on the St. Venant equations (de St. Venant, 1971) is needed.

Another open model structure programme is the so-called World Wide Engine for Simulation, Training and Automation (WEST®) (Vanhooren *et al.*, 2003) that can be applied as a tool for river water quality modelling. Despite the fact that WEST® is basically a modelling and simulation environment for any kind of processes that can be described as a structured collection of Differential and Algebraic Equations (DAE), it is mainly applied to the modelling and simulation of wastewater treatment plants. It can also used to work with river water quality models that are based on a conceptual hydraulic model (e.g. tank-in-series or box model). Due to the huge effort needed for the implementation of a model into a computational environment the use of existing computer programmes is recommended whenever possible (Rauch, 1998). Since it is simple and available in the research centre where this work was carried out, the WEST® simulator was used for this Ph.D. study. The important features of this simulator, and the procedure how the river water quality modelbase was built, are briefly presented in the following sections.

3.3. The WEST® modelling and simulation software

In order to formulate and run a new model for a specific application in the WEST® simulator, three main general steps must be followed hierarchically:

1. Writing a MSL-USER model
2. Use the modelling environment to make the particular configuration
3. Use the experimentation environment to perform model evaluations

In the first step, the user-defined model is described or written using the Model Specification Language (MSL code). Once the model is described and documented with the appropriate syntax, it will be loaded in the modelling environment, also called the configuration builder. In the second step, which occurs in the modelling environment, the user represents the set up of the system (e.g. wastewater treatment plant or river) graphically using annotated icons. Each icon is linked with an appropriate model implemented in the first step. The compiler of the modelling environment translates the MSL code into so called MSL-EXEC (C++ code), which is then used by a standard C++ compiler to create executable code. In the WEST® compiler, the MSL-EXEC is prepared for experimentation. In the third step within, the experimentation environment, the compiled model is used to simulate the system, plot the output, make sensitivity analysis and do parameter estimation or optimisation. More details for these three steps will be given in the following subsections.

3.3.1. Writing MSL-USER

The general description of writing MSL-USER is given in previous works (Vangheluwe, 2000; Vanhooren *et al*., 2003) and is summarized below. The MSL-USER language is the language used to represent models. It is used to specify the models in the model library. Using this language specification, it is possible to create a new model or modify existing ones. Since MSL-USER is a modelling language rather than a programming language, it is purely declarative, which means that the model is presented without specifying how to solve it.

One of the important features of MSL-USER is that it follows the major principle of object-oriented programming in that it uses TYPE, CLASS and OBJect to represent the hierarchy of the items in the model base. A TYPE declaration only specifies an abstract data type's signature. A CLASS attaches values (objects) to a TYPE. As a result of this definition, multiple classes can correspond to the same type. An OBJect is an instance of a class or type. An object binds the different parts of a type structure to concrete values. Examples are given later below.

The other two important characteristics of MSL-USER are (1) it allows the reuse of the existing model by extending it using the EXTENDS inheritance mechanism, and (2) it allows the classification of the model using the SPECIALISES mechanism, which is also used for rigorous type checking. EXTENDS can be used for both types and classes, while SPECIALISES is used for classes, see examples later below.

The basic TYPES found in MSL-USER are integer, real, string, char and boolean. Based on these basic types, a number of type structures (type signatures) can be built. Such type structures include Enumerated type, the Vector type and Record type.

The Enumerate type is a user-defined type consisting of a set of unique identifiers called enumerators, and declared as follows:

```
TYPE type_name = ENUM {id_1, id_2, ..., id_n};
TYPE Boolean "Logic type" = ENUM {True, False};
```

The vector type is used to specify vectors and matrices. A vectors is declared, respectively as follows:

```
TYPE type_name = type [dimension,] //for row vectors
TYPE type_name = type [dimension;] //for column vectors
```

A matrix can be specified as a vector of vectors as follows:

```
TYPE type_name = type [dimension;][dimension;];
```

For example, a matrix of 6 rows and 3 columns, each element of type Real is expressed as follows:

```
TYPE Matrix "example of matrix type" = Real[6;][3;];
```

The basic types can also be used to create user-defined types, such as UnitType, QuantityType and RealIntervalType. The UnitType and QuantityType are defined as strings. The RealIntervalType describes if the bounds are included in the interval, and is defined as a record of two real values and two booleans. In MSL-USER, the descriptions for names, types, classes or objects are expressed between double quotations. Examples are given below.

```
TYPE UnitType
```

```
"The type of physical units" = String;
TYPE QuantityType
"The different physical quantities"= String;
TYPE RealIntervalType
"Interval of real numbers" = RECORD
    {
     lowerBound: Real;
     upperBound: Real;
     lowerIncluded: Boolean;
     upperIncluded: Boolean;
    };
```

An existing type can be extended. For example, extra fields can extend the record type. If the BasicType is extended into the ExtendedType, the declaration should be as follows:

```
TYPE BasicType "Basic type"
= RECORD
{
 value: Real;
};
TYPE ExtendedType "Extended type"
EXTENDS BasicType WITH
RECORD
{
 quantity: QuantityType;
 unit: UnitType;
 interval: RealIntervalType;
};
CLASS Concentration "A class of concentration" SPECIALISES
ExtendedType:=
   {:
     quantity <- "Concentration";
     unit <- "g/m3";
     interval <- {:lowerBound <- 0; upperBound <-PLUS_INF:}
   :};
```

CLASSES are used to represent objects. It is a definition of an abstract data type, defining the representation of the data of all objects of that type. In MSL-USER, classes can be constructed in different ways: using a regular class declaration, through specialisation of an existing class and through extension of an existing class or type. A regular class declaration uses type-based signatures as follows:

```
CLASS class_name "description" [class_declaration];
CLASS RealVector = Real[4;];
```

A class representing a model that can be selected in the configuration editor of WEST® always has some class annotations, which are written within the class declaration statement as follows:

```
CLASS VariableVolume
(* class = "river"; category = "" *)
"River water quality model based on variable volume"
SPECIALISES
```

The `VariableVolume` is the model name to be linked or visible in the class id of the node "river" in the configuration interface.

An object (OBJ) is an instance of a type or a class. It binds the different parts of a type or class structure to concrete values. It is declared as follows:

```
OBJ   obj_name   "description":object_declaration:   =   {:value   <-
      value_number:};
```

Where `obj_name` is the name of the object; description is a string expression, `object_declaration` is the name of the type or class the object instantiated from (type or class object), `value_number` is the value assigned to the object. In MSL-USER, an object can be either a type object or a class object. A type object is an instance of a type e.g.

```
OBJ k "Biodegradation rate constant": Real:= {:value <- 0.05:};
```

While a class object is an instance of a class e.g. the river length L_distance can be declared as follows:

```
CLASS Length
"A class for river length"
SPECIALISES PhysicalQuantityType :=
{:
 quantity <- "Length";
 unit      <- "m";
 interval  <- {: lowerBound <- 0; upperBound <- PLUS_INF :};
:};

OBJ L_distance "Longitudinal distance of the river":Length: = {:value
    <- 1000:};
```

When the values of parameters or initial conditions of variables depend on the value of other parameters, it is possible to these parameters or variables appear fixed in the experimentation environment so that the user cannot change their values except via changing the parameters they depend on. This can be done by the fixed annotation, which can have the values "0" or "1". When the fixed annotation value is "1", the parameter value is fixed, and the user cannot change or adjust it in the experimentation environment; "0" means the value is not fixed and the user can adjust it. The default value is "0". For example, the parameter value of k can be fixed as follows:

```
OBJ k (*fixed = "1"*) "Biodegradation rate constant": Real:= {:value <-
     0.05:};
```

Another object annotation is “hidden”. When a parameter or variable object has the annotation hidden this object is not shown in the experimentation environment. This is useful when parameters are used as intermediate values for efficiency reasons. Like the fixed annotation, the hidden annotation can have the values of “0” or “1”, which means respectively show or hide in the experimentation environment. Note that the default annotation is “0”. This is specified as follows:

```
OBJ k (*hidden = "1"*) "Biodegradation rate constant": Real:= {:value
     <- 0.05:};
```

Many other built-in MSL statements are possible. The ordinary differential equation is declared using the DERIV statement. Other built-in MSL statements also include FOREACH, SUMOVER, and IF-THEN-ELSE. Other built-in MSL functions such as Cardinality and SelectByType are also used. Examples are given below:

```
DERIV(state.V,[independent.t]) = state.Q_In - state.Q_Out ;
{FOREACH Comp_Index IN {1 .. NrOfComponents}:
     state.FluxPerComponent[Comp_Index] =
(SUMOVER In_Terminal IN {SelectByType(interface,InWWTPTerminal)}:
In_Terminal[Comp_Index]) +
(SUMOVER Out_Terminal IN {SelectByType(interface,OutWWTPTerminal)}:
Out_Terminal[Comp_Index]);};
```

Some other built-in MSL statements will also be explained in the following sections.

3.3.2. Building a generic modelbase

In order to build model of a real physical system (e.g. rivers or wastewater treatment plants) and subsequently simulate the behaviour of this system, a modelbase must be constructed. The modelbase is simply a collection of models (MSL files) which are hierarchically connected to one another to efficiently construct the complex models describing the behaviour of the system of concern (e.g. river). The procedure of building the modelbase for any physical system follows the following steps (Vangheluwe, 2000):

- Choosing an appropriate level of abstraction.
- Identify relevant quantities.
- Define transferred input-output quantities: terminals.

- Build a model class hierarchy starting from general (conservation and constraint) laws and refining these for specific cases.

Level of abstraction

In the first step of modelling a real/physical system, idealised physical models are built representing behaviour of the real system at a certain level of abstraction. Abstract models of system behaviour can be described at different levels of abstraction or detail. Despite the fact that the real/physical system has a spatial distribution, which requires Partial Deferential Equations (PDEs), it is often described by lumped parameter models, so-called Ordinary Differential Equations (ODEs). This level of abstraction is when the homogeneity assumption is a reasonable approximation. Indeed, the levels of abstraction used depend on the goals of modelling as well as on the system modelled. The WEST® simulator is based on the ODE abstraction level, and so is the dynamic integrated river water quality modelling used in this work.

Relevant quantities

In the second step of modelling the physical system, the quantities of interest must be identified. These quantities can be subsequently used to describe the *types* of entities used in modelling: constants, parameters, interface variables, and state variables. Such types of quantities include basic quantities, typical quantities for the physical system under consideration and transferred input-output quantities. Details are given below. It must also be specified whether an entity is of Real, Integer, Boolean, or String type. Besides, information about the causality of a quantity (input or output) must be included when a causal model is developed. A causal model is a model that its output is the consequence of given input. Also, other information like the quantity's unit and constraints (e.g. interval) can be added. In the used modelbase, the Physical Quantities are encoded as PhysicalQuantityType. Examples are given below:

```
TYPE QuantityType
"The different physical quantities. For the time being, a string" =
   String;
TYPE UnitType
"The type of physical units. For the time being, a string" = String;
TYPE CausalityType
" Causality of entities: CIN: input (cause) only, COUT: output
   consequence)only"
= ENUM {CIN, COUT};
```

```
TYPE PhysicalQuantityType
"The type of any physical quantity" =
RECORD
{
 quantity : QuantityType;
 unit : UnitType;
 interval : RealIntervalType;
       value : Real;
 causality : CausalityType;
};
```

Basic quantities

The PhysicalQuantityType structure can be specialized for specific quantities. Here for example, the physical quantity *Area* is defined as follows:

```
CLASS Area
"A class for Area"
SPECIALISES PhysicalQuantityType :=
{:
 quantity <- "Area";
 unit <- "m2";
 interval <- {: lowerBound <- 0; upperBound <- PLUS_INF:};
:};
```

Definitions of physical quantity types are used to instantiate OBJects of those types. The ISO 1000 standard also defines physical constants such as the universal gravity constant whose MSL-USER description is given as an OBJect declaration below:

```
OBJ UniversalGravityConstant
"Universal gravity constant" : PhysicalQuantityType :=
{:
 quantity <- "G";
 unit <- "m/s2";
 value <- 9.8;
:};
```

In the WEST® environment, the unit as well as the parameter value and description of the model are used not only for dimensional checking during model compilation, but are also passed on to the experimentation environment where the user is presented with the default parameter value, its upper and lower boundary, unit and description.

Quantities typical for the biological processes of RWQM1

Simulation of biological processes in the river water quality models, for example in the RWQM1, consists of the major processes known to be responsible for carbon, nitrogen, phosphorus, oxygen and hydrogen cycles: carbon oxidation, nitrification, denitrification, chemical equlibria, algal growth and decay, and primary consumer's growth and death (Reichert *et al.*, 2001). The state variables (components) of the complete RWQM1 are described in MSL-USER as an enumerated type:

```
TYPE Components
“The biological components considered in the RWQM1 models”
= ENUM {H2O, S_S, S_I, S_NH4, S_NH3, S_NO2, S_NO3, S_HPO4, S_H2PO4,
S_O, S_CO2, S_HCO3, S_CO3, S_H, S_OH, S_Ca, S_N2, S_ALK, X_H, X_N1,
X_N2, X_ALG, X_CON, X_S, X_I, X_P, X_CaCO3, X_II, X_ND};
```

Reducing the above model components and introducing the fate of xenobiotic organic contaminants, when pH is not varying significantly in the system under consideration, the other model components can be described as follows:

```
TYPE Components
"The biological components considered in the RivEuTox models"
= ENUM {H2O, S_I, S_S, S_NO, S_O, S_PO, S_GC, S_NH, S_ALK, X_I, X_S,
X_P, X_H, X_N, X_ALG, X_CON, X_ND};
```

The description for each model component indicated above is given in Chapter 2, except for S_GC, which represents the total concentration (the sum of sorbed and dissolved phases) of a generic xenobiotic organic contaminant in the bulk water.

Other typical biological quantities for river water quality modelling include kinetic and stoichiometric parameters. The kinetic parameters characterise the rate of reaction of the conversions in the model (e.g. maximal specific growth rate, decay rate, …), stoichiometric parameters indicate the stoichiometric relations between the different components in the model (e.g. yield coefficient, …). In MSL, these parameters can easily be declared as object of a certain, more general, class specification:

```
CLASS YieldForHeterotrophicBiomass
"A class for Yield For Heterotrophic Biomass"
SPECIALISES PhysicalQuantityType :=
{:
quantity      <- "Y_H";
unit          <- "-";
interval      <- {: lowerBound <- 0; upperBound <- 1 :};
```

```
:};
CLASS MaxSpecifGrowthRateHetero
"Maximum specific growth rate for heterotrophic biomass"
SPECIALISES PhysicalQuantityType :=
{:
quantity     <- "Mu_H";
unit         <- "1/d";
interval     <- {: lowerBound <- 0; upperBound <- 20 :};
:};
CLASS HalfSatCoeffForHetero
"Half-saturation coefficient for heterotrophic biomass"
SPECIALISES PhysicalQuantityType :=
{:
quantity     <- "K_S";
unit         <- "gCOD/m3";
interval     <- {: lowerBound <- 0; upperBound <- 100 :};
:};

OBJ Y_H      "Yield for Heterotrophic Biomass"
  :YieldForHeterotrophicBiomass:= {:value <-0.67:};
OBJ mu  "Maximum specific growth rate for heterotrophic biomass"
  :MaxSpecifGrowthRateHetero:= {:value <- 4.00:};
OBJ K_S "Half-velocity constant for heterotrophic biomass"
  :HalfSatCoeffForHetero:= {:value <- 20.00:};
```

Transferred input-output quantities: terminals

As described above, the real physical system is represented by a combination of submodels that describe part of the system processes (behaviour). These submodels require connection *ports* or *terminals* through which the interactions between submodels occur. This means, all submodels interact through their terminals. These connection terminals are replaced by appropriate algebraic equalities when the coupled model is parsed.

In WEST® models, different terminal types are used, but the main terminal is the so-called WWTPTerminal. In the basic model base discussed here, only a flux of biochemical material is considered. Heat flow for example is not considered. This terminal is declared as follows:

```
CLASS WWTPTerminal
"
The variables which are passed between WWTP model building blocks
Currently, we only consider a flux of biochemical material"
= MassFlux[NrOfComponents;];

OBJ NrOfComponents
```

```
"The number of biological components considered in the WWTP models"
: Integer:= Cardinality(Components);
```

The WWTPTerminal is a vector of mass fluxes for each of the components taken into consideration in the model. The size of the vector is given by the cardinality of the Components enumerated type and hence depends entirely on how many components the user includes in this type. This way of WWTPTerminal definition assumes (1) the same terminals are used everywhere in a configuration for biochemical transport, (2) all WWTPTerminals of a model have the same cardinality, and (3) the number of components in WWTPTerminal is the same as the number of state variables. These assumptions indicate that the coupled model must have the same type and number of components; otherwise an explicit conversion block must be defined in order to make one terminal compatible with another terminal. For example the river model (RWQM1) cannot directly be connected to the Activated Sludge Model No. 1 (ASM1) because they have a different type (in some components, e.g. algae) and number of components. If one wants to connect ASM1 with the RWQM1, an additional MSL-USER model must be written for a connector, which must obey the conservation law (Meirlaen *et al.*, 2001).

At the two ends of the coupled model (input and output), a vector of concentrations rather than fluxes is often used, and with this in mind the concentration terminal (WWTPConcTerminal) is used. The combined usage of both flux and concentration-based terminals requires the conversion of WWTPConcTerminal into WWTPTerminal and vice versa using a convertor block (concentration to flux (C_to_F) convertor and flux to concentration (F_to_C) convertor). Linking the two terminals in the WEST® modelling environment looks as indicated in Figure 3.1.

In the modelling environment, the parser checks whether compatible terminals are connected. At the level of the graphical interface, the number of connected terminals is also checked. For example, a river submodel can have two (see Figure 3.1) or more possible terminals (see Figure 3.2) that should be defined in the river node. The number of terminals is determined by

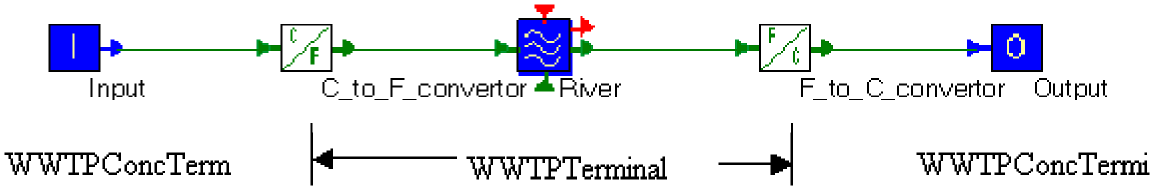


Figure 3.1: Configuration of model terminal connection in the absence of side stream

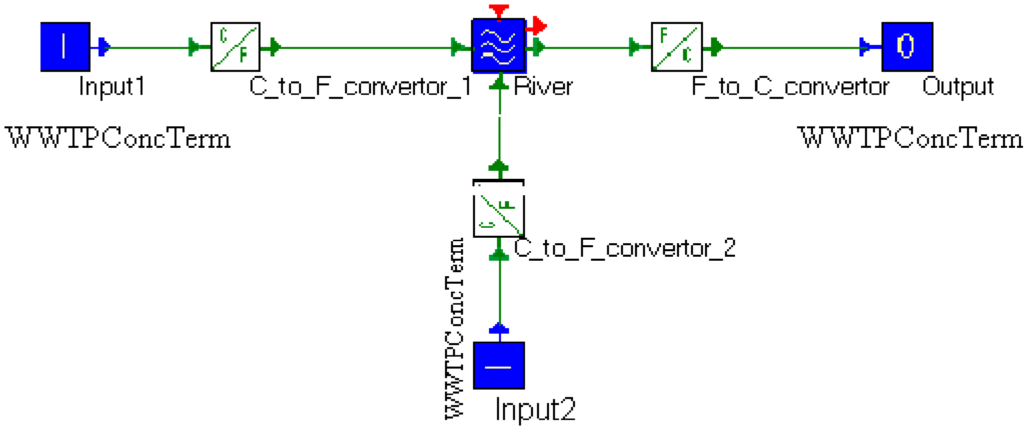


Figure 3.2: Configuration of model terminal connection with one side stream (Input2)

the number of tributaries or wastewater effluent discharges connected to the main river compartments under consideration. For example, if one side stream or wastewater effluent discharge is introduced to the one shown in Figure 3.1, the configuration becomes the one shown in Figure 3.2.

Building the model class hierarchy starting from general physical laws

Introduction to the general mass conservation laws

As indicated in the previous paragraph, the mass flux transfer is used rather than the directly measurable quantities such as concentration and flow rate. This comes from two main reasons. First, in the unit of concentration [$M\ L^{-3}$], the unit of volume [L^{-3}] only represents the water or the suspension volume and not the entire transferred volume (that may also include gas and carrier material). This can be a source of error during model development. Secondly, the mass conservation law can be easily formulated as dM/dt when mass flux [$M\ T^{-1}$] rather than concentration [$M\ L^{-3}$] or flow rate is used. This conservation of mass can be calculated for each of the components i of the WWTPTerminal, so that the elemental balances for carbon, nitrogen, phosphorus, hydrogen and oxygen are easily derived.

Modelling biochemical conversion: the Petersen matrix

Biochemical conversion (bioconversion) is a chemical reaction mediated by microorganisms. In the IWA publications, the Petersen matrix (see Table 3.1) introduced by Petersen (1965) is generally accepted as a standard notation for conversion modelling. This matrix notation has two advantages: it allows to understand the interaction of different processes and it allows for a quick continuity check or closed mass balance check.

Modelling biochemical reactions and construction of the Petersen matrix comprises three important considerations. First, the dominant biochemical processes must be defined or identified (e.g. carbon oxidation, nitrification and denitrification). Second, the type and number of components representing the process of interest are to be selected. Third, each process should be represented by process equations quantifying both kinetics and stoichiometry. Finally, the three considerations are summarised in a matrix notation, which then gives the Petersen matrix.

Such matrix notation, e.g. for the simplified IWA River Water Quality Model No. 1 (RWQM1), is as depicted in Table 3.1. The description of Table 3.1 is summarised here. The components which are considered in the model and the transformation processes are characterized with the indices *i* and *j* respectively. Stoichiometric coefficients are presented in the form of a stoichiometric matrix *vi,j*. The stoichiometeric coefficients set out the mass relationships between the components i in the individual processes *j*. For example, aerobic growth of heterotrophs (XH) with ammonia (SNH3 and SNH4) occurs at the expense of readily biodegradable substrate (SS), ammonia (SNH), phosphate (SPO) and dissolved oxygen (SO2). Some stoichiometeric coefficients may be dimensionless with unit value (+1 or –1). For all other stoichiometric coefficients that are neither unity nor zero, only the signs are given: "+" indicates a positive stoichiometric coefficient, "-" a negative coefficient, "?" indicates a coefficient the sign of which depends on the composition of the organic substances involved in the process and on the stoichiometric parameters, and "(+)" is the same as "?", but in this case, the composition of compounds and the stoichiometric parameters should be chosen in a way that it guarantees that this coefficient is nonnegative (because there is no limiting factor to the corresponding compound in the process rate). This indicates that for all non-unit and non-zero stoichiometric coefficients algebraic equations must be given on the basis of the conservation principle. The stoichiometric and kinetic equations as well as parameters related to RWQM1 are well documented in Reichert *et al*. (2001).

The stoichiometry matrices that are not given (empty) or zero columns indicate components which are transported but do not react. In MSL-USER, by default, when a variable is not given a value, the initial value is 0. Thus, if we don't assign anything to elements of the stoichiometry matrix, it is a matrix of zeroes, which means no biochemical reactions can take place.

Table 3.1. Qualitative matrix notation of the simplified RWQM1 (modified from *Reichert et al.*, 2001): NH is the ammonia plus ammonium nitrogen, NO is the nitrite plus nitrate nitrogen

Components $\rightarrow i$		1	2	3	4	5	6	7	8	9	10	11
j	Process $\downarrow$	S_S	S_I	S_{NH}	S_{NO}	S_{O2}	S_{PO}	X_H	X_N	X_S	X_I	X_P
(1a)	Aerobic growth of Heterotrophs with NH	-		?		-	?	1				
(1b)	Aerobic growth of Heterotrophs with NO	-			-	-	?	1				
(2)	Aerobic Respiration of Heterotrophs			+		-	+	-1			+	
(3)	Anoxic growth of Heterotrophs (Denitrification)	-			-		?	1				
(4)	Anoxic respiration of Heterotrophs			+	-		+	-1			+	
(5)	Growth of Nitrifiers (Nitrification)			-	+	-	-		1			
(6)	Aerobic respiration of Nitrifiers			+		-	+		-1		+	
(7)	Hydrolysis	+		(+)		(+)	(+)			-1		
(8)	Adsorption of phosphorus						-1					1
(9)	Desorption of phosphorus						1					-1
		Rapidly biodegradable soluble substrate	Inert dissolved organic matter	$NH_4^+ + NH_3$ nitrogen	NO_2^-+NO_3 nitrogen	Dissolved oxygen	HPO_4^-+$H_2PO_4^-$ phosphorus	Heterotrophic bacteria	Nitrifying bacteria	Slowly biodegradable particulate matter	Inert inorganic material	Adsorbed phosphorus

Mass balance

In a Continuously Stirred Tank Reactors in Series (CSTRS) with volume *V* and terminals α, the basic equation for a mass balance for the component *i* within each tank can be expressed as follows:

$$\frac{dM_i}{dt} = flux_i^{in} - flux_i^{out} + r_i V = \sum_{\alpha} flux_{i,\alpha} + r_i V \tag{3.1}$$
$$\Rightarrow mass\ accumulation = transport\ term\ + reaction\ \ term$$

The input ($flux_i^{in}$) and output ($flux_i^{out}$) are transport terms for the component *i*, they can also be denoted as FluxPerComponent. The *flux* stands for the product of flow rate and concentration [M T^{-1}]. The system reaction term for the component *i* (r_i), which can also be denoted as ConversionTermPerComponent, is obtained by summing the products of the stoichiometric coefficients v_{ij} and the process rate expression P_j as follows:

$$r_i = \sum_j v_{i,j} P_j \tag{3.2}$$

The biochemical components considered in the modelbase are declared as follows:

```
TYPE Components
"The biological components considered in the simplified RWQM1 model
(Table 3.1 including three additional components: water (H2O),
alkalinity (S_ALK) and organic nitrogen (X_ND)”

= ENUM {H2O, S_S, S_I, S_NH, S_NO, S_O2, S_PO, S_ALK, X_H, X_N, X_S,
X_I, X_P, X_ND};
```

Once the biochemical components are declared, the mass balances given above (equations 3.1 and 3.2) are declared as follows: The transport term (FluxPerComponent) (see equation 3.1) is the sum of all incoming (positive) and outgoing (negative) fluxes:

```
{FOREACH Comp_Index IN {1 .. NrOfComponents}:
   state.FluxPerComponent[Comp_Index] =
     //The FluxPerComponent is the sum of all incoming (positive) and
     //outgoing (negative) fluxes
   SUMOVER In_Terminal IN {SelectByType(interface,InWWTPTerminal)}:
   In_Terminal[Comp_Index])+
   (SUMOVER Out_Terminal IN {SelectByType(interface,OutWWTPTerminal)}:
   Out_Terminal[Comp_Index]);
};
```

The mass balance equation (equation 3.1) that is composed of transport terms and of reaction terms for each component are expressed in MSL-USER as follows:

```
{FOREACH Comp_Index IN {1 .. NrOfComponents}:
   DERIV(state.M[Comp_Index],[independent.t]) =
   state.FluxPerComponent[Comp_Index]
   + state.ConversionTermPerComponent[Comp_Index];
```

```
};
```

The reaction term (ConversionTermPerComponent) is the sum of all process reactions related to a given component (equation 3.2), and is expressed in MSL-USER as follows:

```
{FOREACH Comp_Index IN {1 .. NrOfComponents}:
   state.ConversionTermPerComponent[Comp_Index] =
   SUMOVER Reaction_Index IN {1 .. NrOfReactions}:
   (parameters.Stoichiometry[Reaction_Index][Comp_Index]
   *state.Kinetics[Reaction_Index])*state.V;
};
```

Inheritance hierarchy

In the WEST® modelbase, the model must be constructed for each type of building block. This is achieved in the form of a class inheritance hierarchy. Hereby, maximum re-use and clarity is achieved. Clarity is a direct result of the relationship between the inheritance hierarchy on the one hand and the different levels of specificity of the models on the other hand. The inheritance hierarchy starts with the generic model type (see Figure 3.3) declared as follows:

```
TYPE GenericModelType
"The signature of the generic part of any (whatever the formalism)
model"
=
RECORD
{
  comments : String;
  interface : SET_OF (InterfaceDeclarationType);
  //declared object must be interface
  parameters : SET_OF (ParameterDeclarationType);
  //declared object must be parameters
};
```

The generic model type allows defining the interfaces and the number of parameters. This type can be extended to describe the essence of the CoupledModelType and the DAEmodelType as follows:

```
TYPE CoupledModelType "The signature of a coupled (network) model"
EXTENDS GenericModelType WITH RECORD
{
    sub_models : SET_OF (ModelDeclarationType);
    coupling : SET_OF (CouplingStatementType);
 };
TYPE DAEModelType
```

```
"The signature of a Differential Algebraic Equation (DAE) model within
DAEModelType models, connect() has the following (flattening)
semantics: quantity and units are checked for equality, equations are
generated to equal (=) all algebraic state variables and all other
labels are ignored"
EXTENDS GenericModelType WITH
RECORD
{
independent : SET_OF (ObjectDeclarationType);
//independent variable (time)
   state: SET_OF (PhysicalQuantityType);
//variables those variables occurring in DERIV(v, [t]) statements are
derived state variables
   initia: SET_OF (EquationType);
   equations: SET_OF (EquationType);
   terminal: SET_OF (EquationType);
};
```

The synonym PhysicalDAEModelType is used for DAEModelType when we use it for modelling physical systems:

```
TYPE PhysicalDAEModelType
"within physicalDAEModelType models, connect() has the following
(flattening) semantics: quantity and unit are checked for equality,
equations are generated to equal (=), all across variables equations
are generated to sum all through variables to zero, all other labels
are ignored"
= DAEModelType;
```

Figure 3.3 shows the top-level inheritance hierarchy. Some of the model classes are derived directly from the PhysicalDAEModelType. Figure 3.4 shows the inheritance hierarchy representing the river water quality modelbase in WEST®. The shallowness of such inheritance hierarchy reflects the very diverse nature of the different model types, not allowing for much re-use unlike Figure 3.5. The difference between Figure 3.4 and Figure 3.5 is that the former inheritance hierarchy does not allow much re-use of the model, whereas the later allows much re-use of the model. The top-level model, e.g. WWTPAtomicModelWithVolume in Figure 3.5) can be re-used to build the models below it: WWTPAtomicModelWithVariableVolume and WWTPAtomicModelWithFixedVolume.

```
GenericModelType
|
|___CoupledModelType
|___DAEModelType = = PhysicalDAEModelType
```

Figure 3.3: Top-level inheritance hierarchy in the WEST® simulator modelbase

```
PhysicalDAEModelType
|
|__ BasicRiverWaterQualityModel
|               |
|               |__ RWQM1
|               |__ Bulk_Benthic_River
|               |__ BenthicRiver
|
|__CHETOX1
|__ RIVEUTOX1
```

Figure 3.4: Class hierarchy of models with volume derived from the PhysicalDAEModelType

```
PhysicalDAEModelType
|
|__WWTPAtomicModel
      |
      |__WWTPAtomicModelWithVolume
                |
                |__WWTPAtomicModelWithVariableVolume (Q_e = f(water volume in tank))
                |          |__ VarVolumeConversionModel
                |                    |__ VarVolumeASMConversionModel
                |                              |__ VarVolumeInOutIAWQ
                |                                        |__ VarVolumeRiver
                |                                                  |__ BasicRiverWaterQualityModel
                |                                                  |          |__ RWQM1
                |                                                  |          |__ Bulk_Benthic_River
                |                                                  |          |__ BenthicRiver
                |                                                  |__ CHETOX1
                |                                                  |__ RIVEUTOX1
                |
                |__ WWTPAtomicModelWithFixedVolume (Q_e = Q_i)
                           |__ FixVolumeConversionModel
                                     |__ FixVolumeASMConversionModel
                                               |__ FixVolumeInOutIAW
                                                         |__ FixVolumeRiver
                                                                   |__ BasicRiverWaterQualityModel
                                                                   |          |__ RWQM1
                                                                   |          |__ Bulk_Benthic_River
                                                                   |          |__ BenthicRiver
                                                                   |__ CHETOX1
                                                                   |__RIVEUTOX1
```

Figure 3.5: WEST® modelbase for rivers

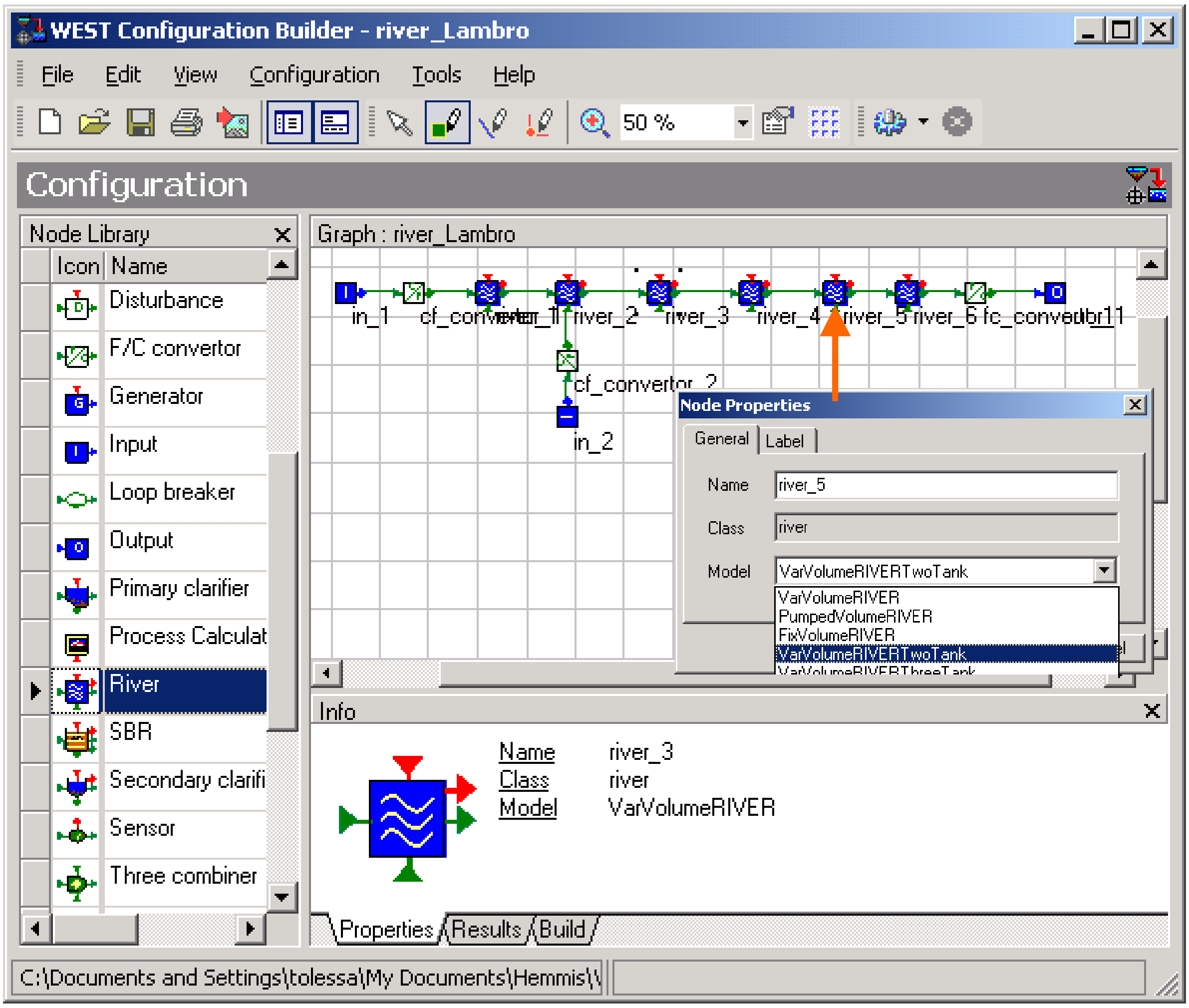
3.3.3. The modelling environment

The WEST® modelling environment currently allows for graphical representation of the system under study (e.g. a river), the translation of the MSL-USER model descriptions into

MSL-EXEC code and the creation of coupled models in a graphical way. These steps are discussed briefly in the following paragraphs.

The WEST® modelling environment contains a highly configurable interactive graphical tool for the construction of annotated graphs (nodes), which are data structures consisting of nodes and edges (see Figure 3.6). A node can be a physical component within the system, a physical input or output of a system, or any other process affecting the biological or data flow (e.g. transformers). This interactive graphical tool is called the Hierarchical Graphical Editor (HGE). The HGE can be tuned for a user-defined application by setting up a library with configurations for that specific application. Such libraries can be loaded from within the HGE, and the behaviour of the HGE then depends on the loaded library.

When the appropriate model library (user defined) is loaded, the user constructs the configuration of the system under consideration (e.g. a wastewater treatment or river) using the available nodes. For each node, except for nodes for input and output interfaces, an



Name river_5

Class river

Model VarVolumeRIVERTwoTank

Name river_3

Class river

Model VarVolumeRIVER

Figure 3.6: The configuration of river Lambro system as a series of connected CSTRS with one side stream (wastewater effluent discharge)

appropriate submodel must be selected, to characterize the behaviour of that node. The selection of the model can be automatic when there is only one model available for a given node (e.g. Concentration to Flux convertor, cf_convertor). When there is more than one model available for a node, an appropriate model must be selected by the user.

For example, the user can build the physical configuration of a river system by representing the river section under investigation as a series of CSTRS (see Figure 3.6). The nodes are then representing the interconnected CSTRS. The models are selected for each river node and then the interface variables of the models are automatically connected. The connections represent the biological or data flows between the nodes. Linking the model interface is then followed by generating the MSL model for the coupled model, which represents the combination of two or more submodels representing the combination of different system components, e.g. a series of connected CSTRS for river system. The generated MSL model declares the complete characteristics of the coupled model. This generated MSL model is then transformed to the executable form MSL-EXEC (C++ code) during parsing.

3.3.3.1. Parsing MSL-USER

During the parsing step, the parser (a stand-alone pre-compiler) or the transformer engine of the modelling environment transforms the generated MSL model of the coupled model into MSL-EXEC (C++ code). Furthermore, the MSL-USER code is automatically checked for its correct syntax and semantic representation as well as the compatibility of the nature of the variables passed on between the sub-models. If there is a syntax or compatibility error, parsing will not be completed, and the source of the error is generated. This will help the user to correct the written MSL-USER code.

3.3.3.2. Compilation

Once the parser generates the MSL-EXEC (C++ code), the compilation process transforms the parsed MSL model (C++ code) into a runtime model that can be loaded in the experimentation environment. In the compilation step, a library file with executable code is generated. This file will be loaded into the experimentation environment. During this step, standard C libraries are linked to the generated model. Besides, user defined external C code can also be included in the model library, and the compiling process generates the coupled C++ code or coupled MSL-EXEC models.

In some applications, the generated C++ code can be very large and the compilation step cannot be completed. In that case the user must reduce/simplify the model, which means the model must be revised. This cannot always be the solution, for instance in river models in which a considerable number of tanks in series is used. The larger the number of tanks in series is used, the larger the size of the MSL-EXEC code that is generated. When the parser generates too big file size of MSL-EXEC (C++ code), the compilation step cannot be completed. This then limits the application of the WEST® simulator to a small part of the river or a small number of state variables in the modelbase.

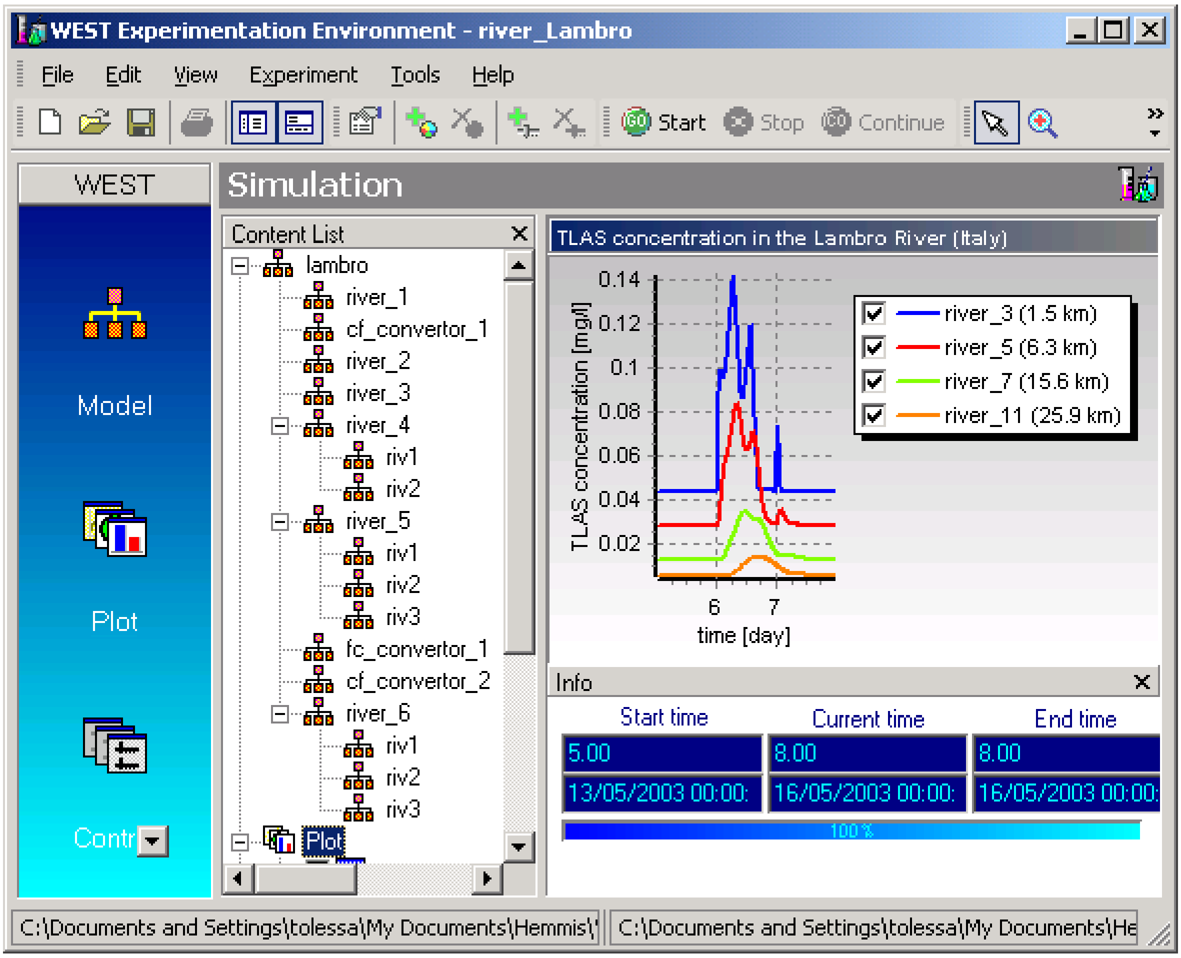
3.3.4. The experimentation environment

In the experimentation environment, the current version of WEST® (version 3.4.0 and more) allows for the simulation, optimisation and sensitivity analysis of models described by Differential and Algebraic Equations (DAE). The WEST® simulator has a simulation engine server, which is capable of simulating the model, encoded in MSL-EXEC generated by the model compiler. The simulation output data can be either sent to a file specified by the user or to the plot server. The plot server is able to open multiple windows and plot one or more graphs in each of these (see Figure 3.7). It does not have a data generator and is therefore totally dependent on the simulation engine servers for the generation of data.

3.3.4.1. Simulation environment

Figure 3.7 shows the simulation environment. During simulation, the ordinary differential equations are numerically integrated in time and the algebraic equations are simultaneously solved. In the simulation environment, a number of steps must be followed before running the simulation. First, the type of numerical solver, and the start and end time of the simulation must be selected. In order to solve the ordinary differential equations in the WEST® simulator, there are several solvers (integrators) available such as *Adams-Bashforth, Euler, RK4, RK4ASC* and *Rosenbrock*. The numerical solver is selected depending on the suitability of the solver for a given situation of the system. The choice is often related to two fundamental characteristics: accuracy and stability. Both issues are connected with the accumulation of the local truncation error of the procedure (i.e. the error that occurs during the computation of one time step) when the integration is proceeding. The total error that has accumulated at the end of the simulation period is denoted as global truncation error.

Accuracy is the problem of loss of precision in the numerical procedure as compared to the true (analytical) solution. When the loss of precision in the numerical method gets catastrophic (often indicated by negative simulation output for a strictly positive output), the



Start time	Current time	End time
5.00	8.00	8.00
13/05/2003 00:00:	16/05/2003 00:00:	16/05/2003 00:00:

C:\Documents and Settings\tolessa\My Documents\Hemmis\

C:\Documents and Settings\tolessa\My Documents\He

Figure 3.7: Experimentation or simulation environment for the river Lambro (Italy) case study

method is unstable. In order to overcome the problem of inaccuracy and instability, a small time step is required which, however, results in more calculation time. In the WEST® simulator the *RK4ASC* method is commonly used because it is relatively the most stable and calculation-efficient.

3.3.4.2. Trajectory optimisation

The WEST® trajectory optimisation experiment allows to perform a parameter estimation for model calibration and process design optimisation. The parameter estimation is based on the comparison of simulated data with the available measured data. In a trajectory optimisation experiment, a set of model parameters or derived state variables is tuned. A number of simulation runs with different parameter values are executed. The simulation results are compared to measured values by means of a cost function (as a measure of distance between the simulated and measured values). A best fit is obtained when the cost function is minimized with respect to the parameters. The optimisation algorithm, which chooses the different parameter values, attempts to minimize this cost function based on one of the following two criteria: the sum of the squared errors or the sum of the absolute errors. The error is the difference between the simulated result and the available (or measured) data point. The estimated parameters are then the parameters with which the simulation results fit best with the available data or the parameter value with which the cost function is minimal.

3.3.4.3. Sensitivity analysis

In the sensitivity analysis environment (see Figure 3.8), the sensitivity of the model output with respect to a small change of a model parameter or input is analysed based on two sensitivity functions: absolute and relative sensitivity. The difference between the two sensitivity functions is not only the mathematical expression (see equations 3.1 and 3.2) but also their dependency on the unit of the model variables and model parameters: the absolute sensitivity function depends on the unit of model parameters or variables, whereas the relative sensitivity function doesn't depend on either unit. For each sensitivity function, the sensitivity of the model output is calculated in two steps actor (De Pauw and Vanrolleghem, 2003). First, a reference simulation is run without changing the parameter value. Next, a new simulation is run (a perturbation simulation) in which the parameter value of the under consideration is perturbed by a certain factor (the perturbation factor, e.g. 0.01). Then, the absolute (S_A) and relative (S_R) sensitivity are calculated for each time step as follows:

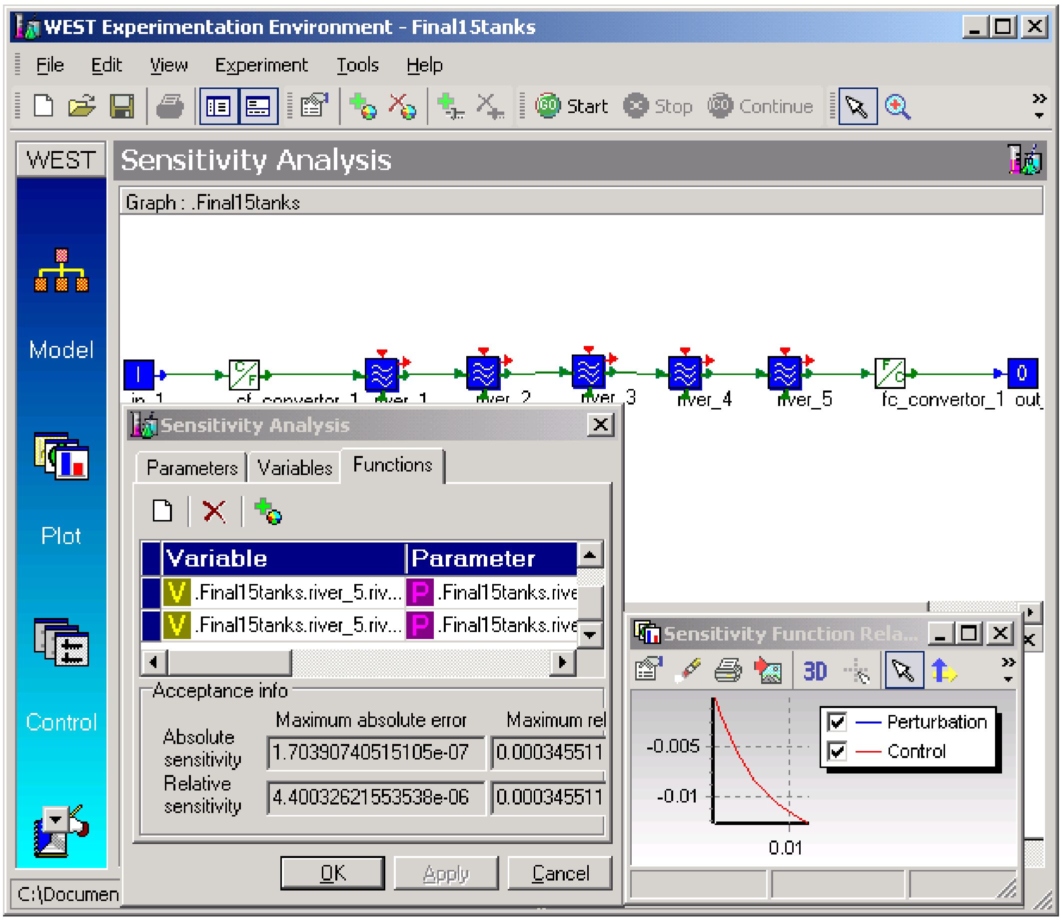
$$S_A(t) = \frac{\Delta Y}{\Delta P} \tag{3.3}$$

$$S_R(t) = \frac{\Delta Y / Y(t)}{\Delta P / P} = \frac{\Delta Y}{\Delta P} \cdot \frac{P}{Y(t)} \tag{3.4}$$

where Y is the model output, P is the model parameter, $\Delta P / P$ is the perturbation factor.

Both relative and absolute sensitivity can be used for the investigation of the model sensitivity to parameter changes.

The sensitivity functions are defined as partial derivatives, but are usually solved by their finite difference approximation. The finite difference method is applicable mainly for the linear models in which the variable should change linearly with respect to a change of the parameter. For non-linear models like RWQM1, a very small change in model parameter or input must be used in order to use the finite difference method. The acceptance or the



Variable	Parameter
.Final15tanks.river_5.riv...	.Final15tanks.rive
.Final15tanks.river_5.riv...	.Final15tanks.rive

Acceptance info

	Maximum absolute error	Maximum rel
Absolute sensitivity	1.70390740515105e-07	0.000345511
Relative sensitivity	4.40032621553538e-06	0.000345511

Figure 3.8: Sensitivity analysis environment

accuracy of a sensitivity analysis can be quantified by running two perturbation simulations, and calculate two sensitivities at each point. First, the simulation is run with a given change of the parameter (e.g. 1% increase) as a reference simulation, and then the absolute and relative sensitivity are calculated. Then, the second simulation is run as control simulation with another change of the parameter (e.g. 1% decrease), and the absolute and relative sensitivity are again calculated. The control sensitivity is compared with the reference sensitivity, and the difference is quantified using objective functions: maximum absolute error, maximum relative errors, sum of squared errors and sum of absolute errors. When the errors (differences) are very small the sensitivity analysis is acceptable, otherwise it is rejected.

3.4. Building the river water quality modelbase

The modelbase is structured as a collection of MSL files in which the hierarchy of model classes is built. In the modelbase, references are made to the other files using C preprocessor commands. The main file of the standard WEST® modelbase that contains only references to other models is *wwtp.msl* (WWTP_MSL). For the river water quality modelbase, the following modelbase structure was built:

```
#ifndef WWTP_MSL
#define WWTP_MSL

//reused model bases
#include "generic.msl"

#include "wwtp.quantity.msl"

#include "wwtp.general.msl"
#include "wwtp.base.convertors.msl"

//Level 1
//problem definitions
#include "river_definitions.msl"

//Level 2
//river model bases
#include "river.base.msl"
#include "river.FreshWaterLossesl.base.msl"
#include "river.bulk_benthic.base.msl"
#include "river.n_FixVarTanks.msl"
#endif
```

The C preprocessor directive or commands begin with a #. The main preprocessor statements included in the MSL code are ifdef, define, ifndef, endif, and include. The `#include` directive instructs WEST® to include, into the processed file, the file specified in the include statement. The `ifdef/ifndef` command the preprocessor to check whether a certain variable has been defined previously or not. If the condition is true, the code following the command is executed, other wise the code is skipped until a `#endif` statement is reached. The `ifndef` is used when the file is processed for the first time, and instructs the preprocessor to check whether the variable has already been defined before for example #ifndef `WWTP_MSL` as indicated in the above examples. If the variable `WWTP_MSL` has already been defined, the preprocessor skips all `includes` until it reaches the `#endif` command. If it is defined for the first time `#define WWTP_MSL` is used and all `#includes` are read.

Note that the use of such C preprocessor commands in building a new modelbase is very useful for the following reasons:

- it is easier to develop,
- it allows re-use of the existing model/code, and
- it is easier to modify.

These advantages allow one to overcome problems associated with constructing a new modelbase that is not compatible with the already existing models in the WEST® simulator. When one has to build a new modelbase without using the C preprocessor commands, the necessary codes might be copied from the existing modelbase and used in the new modelbase. This approach results in a very large modelbase written in one file, and subsequently can cause problems in correcting errors or modifying the model. This is not an efficient way of re-using the modelbase, and hence the C preprocessor commands become a very useful approach.

In the WEST® modelling environment, re-use of the already available generic modelbase as much as possible is very useful as it is already checked for free of syntax error (Vangheluwe, 2000). As indicated above the MSL-USER files that can be re-used for the river water quality modelbase include `generic.msl`, `generic.quantity.msl`, `wwtp.general.msl`, and `wwtp.convertor.base.msl.`

`generic.msl`

This file contains two files: `generic.base.msl` and `generic.quantity.si.msl.` The former contains generic declarations for the modelling of dynamic Differential Algebraic Equations (DAE) based physical systems: built-in atomic types, built-in composite types, type declarations for physical systems and formalism-independent declarations. The latter contains the class definition of SI quantities, units and constants defined on the basis of the ISO 1000 standard. The MSL code is as indicated below:

```
CLASS Mass
"A class for Mass"
 SPECIALISES PhysicalQuantityType :=
{:
 quantity <- "Mass";
 unit     <- "g";
 interval  <- {: lowerBound <- 0; upperBound <- PLUS_INF; :};
:};

CLASS Density
"A class for Density"
SPECIALISES PhysicalQuantityType :=
{:
 quantity  <- "Density";
 unit      <- "g/m3";
 interval  <- {: lowerBound <- 0; upperBound <- PLUS_INF; :};
:};
```

wwtp.quantity.msl

This file contains class definitions for the WWTP domain quantities. Rather than using concentrations, the generic models are expressed in terms of masses and fluxes:

```
CLASS MassFlux
"Mass per time unit"
SPECIALISES PhysicalQuantityType :=
{:
 quantity  <- "MassFlux";
 unit      <- "g/d";
 interval  <- {: lowerBound <- MIN_INF; upperBound <- PLUS_INF :};
:};
```

wwtp.general.msl

This file contains declarations to describe Waste Water Treatment Plants (WWTPs). As this declaration was built for general purpose, it can be applied to river water quality modelling too. In this modelbase, the following classes are declared:

- Components and reactions definition
- Class terminal for flux: WWTPTerminal(InWWTPTerminal and OutWWTPTerminal)
- Class terminal for concentration: WWTPConcTerminal (InWWTPConcTerminal and OutWWTPConcTerminal)
- Definitions to make the BOD to COD transformation
- Global variables: Comp_Index, Reaction_Index, Terminal, …
- Vector CLASSES: MassVector, MassFluxVector, ConcentrationVector, …

river.definitions1.msl

In this file the model components (state variables) are declared. These components are taken into account in order to describe the processes in the system and to act as interface (input/output) variables of the model. For example, in the Activated Sludge Model No. 1 (ASM1) (Henze, 1987) the following components are taken into account in order to describe the removal of carbon and nitrogen: water (*H2O*), inert soluble matter (*S_I*), readily biodegradable matter (*S_S*), dissolved oxygen (S_O), nitrate and nitrite (S_NO), soluble biodegradable organic nitrogen (*S_ND*), free and saline ammonia (*S_NH*), alkalinity (*S_ALK*), inert particulate matter (*X_I*), slowly biodegradable matter (*X_S*), heterotrophic biomass (*X_BH*), autotrophic biomass (*X_BA*), particulate products resulting from biomass decay (X_P) and particulate biodegradable organic nitrogen (*X_ND*).

In the `river.definitions1.msl,` the model components are defined as follows:

```
TYPE Components
"The biological components considered in the Activated sludge model No.
1 (ASM1) and different version of river water quality models (RM1,
PHRM1, PHRM2, RM1, CHETOX1 and RIVEUTOX1"

//Activated sludge model number 1, required for bulk-benthic
//(biofilm) model developed by Rauch and Vanrolleghem (1998).

#ifdef ASM1
= ENUM {H2O, S_I, S_S, S_O, S_NO, S_ND, S_NH, S_ALK,
X_I, X_S, X_BH, X_BA, X_P, X_ND};
#endif // ASM1

//The following components are given for original version of IWA
//river water quality model number 1 (RWQM1), for the description of
//each components, see Chapter 2.

#ifdef RWQM1
 = ENUM {H2O, S_I, S_S, S_O, S_N2, S_NO2, S_NO3, S_HPO4, S_H2PO4,
S_CO2, S_HCO3, S_CO3, S_H, S_OH, S_Ca, S_NH3, S_NH4, S_ALK, X_I, X_S,
X_H, X_N1, X_N2, X_ALG, X_CON, X_II, X_CaCO3, X_P, X_ND};
#endif //RWQM1

//RM1 is a simplified RWQM1, so that it can be applied for data
//limited situations.

#ifdef RM1
= ENUM {H2O, S_I, S_S, S_NO, S_O, S_PO, S_NH, S_ALK, X_I, X_S, X_P,
X_H, X_N, X_ND};
#endif //RM1

//RM1 is extended to include a simplified pH calculation, S_Z_Plus is
//for positive charges, S_Z_Min is for negative charges that are not
//considered in the measurement, they are added to keep the charge
//balance.

#ifdef PHRM1
= ENUM {H2O, S_I, S_S, S_O, S_NO, S_PO, S_IC, S_Z_Plus, S_Z_Min, S_NH,
S_ALK, X_I, X_S, X_H, X_N, X_ALG, X_P, X_ND};
#endif //PHRM1

  //PHRM1 is extended to calculate pH, EC and calcite precipitation
  #ifdef PHRM2
  = ENUM {H2O, S_I, S_S, S_O, S_NO, S_PO, S_IC, S_SO4, S_Mg, S_K, S_Na,
  S_Cl,
  S_Ca, S_Z_Plus, S_Z_Min, S_NH, S_ALK, X_I, X_S, X_H, X_N, X_ALG, X_P,
  X_ND};
  #endif // PHRM2
```

```
//RM1 is extended to include generic organic contaminant fate (S_GC)
#ifdef CHETOX1
= ENUM {H2O, S_I, S_S, S_NO, S_O, S_PO, S_GC, S_NH, S_ALK, X_I, X_S,
X_P, X_H, X_N, X_ND};

#endif //CHTOX1

//CHETOX1 is extended to include eutrophication (algal bloom) and
//bioaccumulation

#ifdef RIVEUTOX1
= ENUM {H2O, S_I, S_S, S_NO, S_O, S_PO, S_GC, S_NH, S_ALK, X_I, X_S,
X_P, X_H, X_N, X_ALG, X_CON, X_ND};
#endif //RIVEUTOX1
```

`river.base.msl`

In the `river.base.msl`, the atomic modelbase with all possible extensions are declared. The main submodelbases for every model category indicated in the `river.definitions1.msl:` ASM1 (Activated sludge model number 1, for the bulk benthic submodel), RWQM1, RM1 (simplified river RWQM1), CHETOX1 (organic contaminant fate model), and RIVEUTOX1 (for integrated eutrophication and organic contaminant fate model) are declared as follows:

```
CLASS VarVolumeASMConversionModel EXTENDS VarVolumeConversionModel WITH
{:
   #ifdef ASM1
     #include "wwtp.VolumeASM1ConversionModel.body.msl"
       // for the bulk benthic submodel
   #endif //ASM1

   #ifdef RWQM1
     #include "river.VolumeRWQM1ConversionModel.body.msl"
       //for the complete IWA task group RWQM1
   #endif //RWQM1

   #ifdef RM1
     #include "river.VolumeRM1ConversionModel.body.msl"
       //for the simplified RWQM1
   #endif //RM1

   #if (defined PHRM1 || defined PHRM2)
     #include "river.VolumePHRM1ConversionModel.body.msl"
       //extended RM1 for the simplified pH calculation
   #endif //PHRM1 || defined PHRM2

   #ifdef CHETOX1
     #include "river.VolumeCHTOX1ConversionModel.body.msl"
       //for the organic contaminant fate model
```

```
    #endif //CHETOX1

    #ifdef RIVEUTOX1
      #include "river.VolumeRIVEUTOX1ConversionModel.body.msl"
    //for the integrated modelling of eutrophication and organic
    //contaminant fate
    #endif //RIVEUTOX1
  :};
```

`river.FreshWaterLossesl.base.msl`

The *river.FreshWaterLossesl.base.msl* is a hydraulic submodel that describes the downstream flow on the basis of water loss due to evaporation and high upstream fresh water withdrawal for irrigation or drinking water supplies.

`river.bulk_benthic.base.msl`

The *river.bulk_benthic.base.msl* is the biofilm submodel developed by Rauch and Vanrolleghem (1998) for shallow eutrophic rivers. This model was developed based on the activated sludge model number 1 (ASM1) (Henze *et al.*, 1987) components.

`river.n_FixVarTanks.msl`

The *river.n_FixVarTanks.msl* is the model that can be assigned to the n tanks in series. This modelbase is built such that it can be used for both fixed and variable volume hydraulic models.

3.5. Model implementation: problems and solutions

The WEST® simulator was developed for modelling wastewater systems. In order to apply it for river water quality modelling, especially in integrated river water quality modelling, some modifications are indispensable During this research, two main important problems were encountered which are related to (1) the limitation of the compiler and (2) the stiffness of the model structure itself.

3.5.1. The limitation of the compiler

When selecting a conceptual hydraulic model (see Chapter 2, section 2.4.4), a series of CSTRS is used in order to accurately represent dispersion of pollutants in rivers. As indicated in Figure 3.6, this conceptual model is based on dividing the river section under consideration into a number of tanks in series. The higher the number of tanks applied, the closer it becomes a plug flow. The size of the MSL-EXEC generated by the parser is linearly proportional to the number of tanks in series. When the size of MSL-EXEC is too big (>10 MB in RIVEUTOX1 model), it exceeds the capacity of the C-compiler. This was indeed a bottleneck for the application of the current version of the WEST® simulator.

To tackle this problem, the following measures were taken stepwisely:

- splitting the generated C++ file (MSL-EXEC) manually or using 'split' program;
- modifying the batch file so that it includes all the C++ files, and then
- running the build compose runtime.

The disadvantage of this technique is that it has to be done manually, but it avoids the problem related to the compiler limitation.

3.5.2. Model stiffness

The stiffness of the model is related to the solver or the integrator of the simulator. This problem has become very important when one implements the chemical equilibrium equations and *pH* calculation in the form of differential equations, which is the case in RWQM1. The rate of chemical equilibrium reactions is much faster than the rate of the biological reactions. Such fast rates result in numerical errors, unless a very small time step is used. However, using a very small time step leads to very long calculation times. To overcome this problem, two solutions can be considered. The first solution is implement a stiff solver in the WEST® simulator. The second solution is related to simplifying the modelbase and using an external C++ function for algebraic pH calculation. For the pH calculation, the differential equations can be solved by considering a steady state conditions at every time step, and then solve the chemical equilibrium equations algebraically using an external C++ function (see Volcke *et al.*, 2003). Currently, both solutions are under consideration, and particularly the latter approach was implemented in the WEST® simulator during this study. The calculation speed of such implementation is indeed by far faster than the other approach implemented as differential equations.

3.6. Conclusions and recommendations

Different versions spanning from very simple to complex river water quality models were implemented in the WEST$^{®}$ simulator. The simplified versions of a river water quality model including pH calculation (from simple to complex) are currently available in the modelbase. Furthermore, new models such as the model of in-stream fate of organic contaminants (CHETOX1), integrated model of basic water quality (eutrophication) and organic contaminant fate and effect (RIVEUTOX1) are also implemented.

Since extended models have many state variables and processes, the use of a large number of tanks in series is limited by the capacity of the available compiler. This problem can be important when one tries to model a long river system. Therefore a new more efficient parser is needed, which is currently under development. Besides, the elimination of zero elements in the Petersen matrix (see Table 3.1) may also increase the efficiency of the compiler, and thus needs to be considered in a future version of WEST$^{®}$.

Furthermore, implementing a “stiff solver” can reduce the problem related to the numerical stiffness when solving slow (biological) and fast (physicochemical) processes in the WEST$^{®}$ simulator. In the meantime, simplifying the model and including an external C++ function for pH calculation is very useful.

Part 4

Basic water quality modelling

Chapter 4.1

Simplified dynamic river water quality modelling[1,2]

The important parts of this chapter were (will be) published as:

[1] Deksissa T., Meirlaen J., Ashton P. J and Vanrolleghem P. A. (2001). Simplifying dynamic river water Quality Modelling: A case study of inorganic nitrogen dynamics in the Crocodile River (South Africa). In: *Proceedings of the IWA conference on water and wastewater management for developing countries*, 29-31 October 2001, Kuala Lumpur, Malaysia, Vol. 2, 332-339.

[2] Deksissa T., Meirlaen J., Ashton P. J and Vanrolleghem P. A. (2004). Simplifying dynamic river water Quality Modelling: A case study of inorganic nitrogen dynamics in the Crocodile River (South Africa). *Water, Air and Soil Pollution*, 155, 303-319.

Chapter 4.1

Simplified dynamic river water quality modelling

In this chapter, a simplified dynamic river water quality model is discussed. It was derived from the already existing complex river water quality model, which was principally developed for data rich conditions. The simplified model is meant to be applied in data limited situations, as is the case in developing countries, as well as for integrated river water quality modelling. The model was applied on the Crocodile River case study (South Africa) in order to investigate the seasonal dynamics of nitrate and ammonia nitrogen concentrations. Its application was evaluated using monitoring data collected during the years 1987 to 1990. The relationship between river flow rates and inorganic nitrogen concentrations was analysed. The sensitivity of the model output to changes of model input parameters is discussed.

4.1.1. Introduction

The challenge of using mathematical models in developing countries as a support tool to evaluate water quality remediation options is well documented (Ongley and Booty, 1999). Modelling is expensive, requires substantial investment in reliable data, development of scientific capacity and a relatively sophisticated management culture that are often not found in developing countries. Nevertheless, new developments in water quality management policies and strategies require a mathematical model to predict the in-stream fate of pollutants as well as to estimate the likely effects that the resultant water quality may have on recognized water uses. Furthermore, the complex relationships between waste load inputs, and the resulting water quality responses in receiving water bodies are best described using mathematical models.

Several types of river water quality models for conventional pollutants (e.g. organic and inorganic nutrients) are available. These models simulate the major reactions of nutrient cycles and their effect on the dissolved oxygen balance. The complexity and number of state variables of these models increase from the simplest Streeter-Phelps (Oxygen sag curve) (Streeter and Phelps, 1925) to extended models such as *QUAL1* (Masch and Associates, 1970), *QUAL2* (Water Resource Engineering, 1973), and *QUAL2E* (Brown and Barnwell, 1987). Currently, *QUAL2E* is the most widely available stream water quality model that has been adapted for use on a personal computer. Many water quality simulators are following similar modelling approaches like *ISIS* (Wallingford Software, 1994), *DUFLOW* (Aalderink *et al.*, 1995) and *MIKE11* (DHI, 1992), *STREAM* (Park and Lee, 1996), *DYRESM* (Hamilton and Schladow, 1997), *QUAL2K* (Park and Lee, 2002).

However, the *QUAL2E* model types were indicated to have some limitations. One of the major limitations is the lack of provision for conversion of algal death to Biological Oxygen Demand (BOD) (autochtonous source of organic matter), denitrification, and Dissolved Oxygen (DO) change caused by fixed plants (Ambrose *et al.*, 1988; Park and Lee, 2002). Furthermore, these models take into account neither suspended nor attached microbial biomass as state variables despite the fact that microbial biomass are the main component in the biotransformation processes (Reichert *et al.*, 2001). They are also using Biological Oxygen Demand (BOD) as a measure of carbonaceous organic matter, which cannot be fractionated properly to different phases (dissolved and particulate) of organic carbon, and therefore not suitable to calculate mass balance.

An integrated water quality modelling approach requires a river water quality model that can be connected easily to, and is compatible with, a typical Activated Sludge wastewater treatment plant Models (ASM) (Reichert *et al.*, 2001). In contrast to QUAL2E type models, ASMs are based on Chemical Oxygen Demand (COD) as a measure of carbonaceous organic matter, and also consider microbial biomass as state variable. Accordingly, the IWA Task Group on River Water Quality Modelling recently proposed the River Water Quality Model number 1 (RWQM1) (Reichert *et al.*, 2001). This model considers microbial biomass as state variables, and it is also based on COD. It is thus compatible with the existing IWA Activated Sludge Models: *ASM1* (Henze *et al.*, 1987), *ASM2* (Henze *et al.*, 1995) and *ASM3* (Gujer *et al.*, 1999).

RWQM1, however, is considered to be too comprehensive and complex to be applied directly in many situations, as is the case in developing countries where the availability of data is very limiting. In data poor situations, one needs to focus on a simple river water quality model that describes components of the C, O, N and P cycles reasonably and which is still compatible with Activated Sludge Models.

In this study, a simple dynamic river water quality model was developed based on a simple conceptual hydraulic model and the simplification of the available complex RWQM1 model (Reichert *et al*., 2001). The model was evaluated based on the case study of the inorganic nitrogen (ammonia and nitrate) concentration in the Crocodile River, South Africa.

4.1.2. Crocodile River case study

The Crocodile River catchment is located in the Mpumalanga Province of South Africa (Figure 4.1.1), where it comprises 1.2% of the total area of the country and supports one of South Africa's largest and most important irrigation areas. The total irrigated area of approximately 132,000 ha comprises some 91,000 ha of vegetables and other crops, 21,000 ha of sugarcane and 20,000 ha of citrus orchards (van der Zel, 1977; DWAF, 1995). The total population residing in the catchment has been estimated to be 632,500 in the year 2005 (Ashton *et al*., 1995) with approximately 76% of these residents located in urban areas. This river catchment is well known for its scenic attractions, high tourist potential, and sensitivity to environmental degradation.

By South African standards, the Crocodile River is considered as a relatively large river. The river has a total length of some 320 km and drains a catchment area of about 10,450 km^2 before joining the Komati River and flowing into Mozambique. Annual rainfall varies from 1200 mm in the mountainous area at the head of the catchment to 600 mm in the eastern Lowveld. The mean annual precipitation is 880 mm, with 85% of all rainfall received as convective thunderstorms during the warm summer months of November to March.

The water quality of this river catchment is influenced by pollutants discharged from industrial and domestic wastewater treatment plants, as well as by runoff and return flows from extensive areas of irrigated agriculture, and mining sites. The middle reaches of the catchment contain a total of 30 conventional sewage treatment works whose effluent is directly discharged to the middle of the river and its tributaries (DWAF, 1995). As a result, downstream sections of the river often experience serious water quality problems, particularly the presence of toxic heavy metals, increased salinity and escalating eutrophication.

Since the river is relatively large, and very few measured data concerning pollution loads in the upper catchment are available, a section of some 70 km of the downstream reaches of the Crocodile River was selected for this study. The chosen section represents the most sensitive portion of the river, where nitrate and ammonia concentrations often exceed the recommended maximum limit of 0.5 mg L-1 (nitrate) and 0.03 mg L-1 (ammonia) for oligotrophic systems (DWAF, 1993; Ashton et al., 1995). High nitrate concentrations create

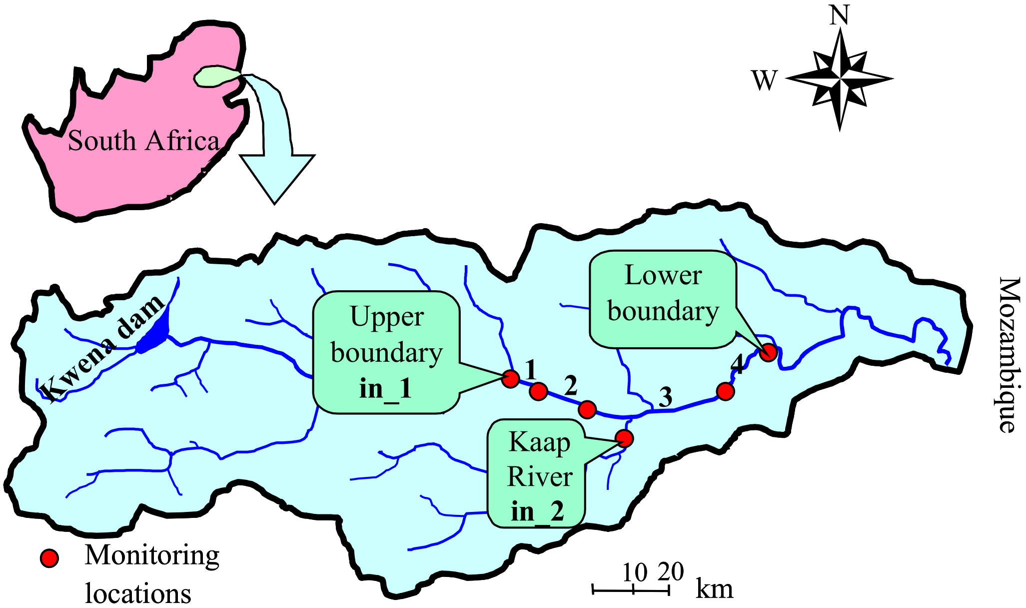


Figure 4.1.1: Crocodile River basin: the distance between the two arrows (about 70 km) is the sensitive river section included in the model; In_1 (upstream point) and In_2 (Kaap River) are model inputs; 1 to 4 are main river segments/reaches

an imbalance in the natural surface water system causing excessive growth of algae and other vegetation. In shallow areas, an over-abundance of algae can block the light needed by underwater vegetation and animals. Algae use dissolved oxygen during night for respiration and when they die and decompose. The resulting lack of oxygen affects fish and aquatic invertebrates. Note that the elevation of pH above 9 due to photosynthetic activity can result in a shift in the ammonia balance. At elevated pH, even acceptable concentrations of ammonia will be converted to the un-ionised form (NH_3), which is much more toxic to fish than the ionised form (NH_4^+) (Train, 1979).

Within the selected reach, the river forms meanders that are shallowly incised into a wide sandy riverbed (20 - 30 m). This slow flowing reach is prone to extensive infestations of water hyacinth, particularly in the slower-flowing portions near several flow-gauging weirs. These dense mats of water hyacinth occasionally cause fish kills by depleting the dissolved oxygen underneath the mats. The daily flows and monthly water quality data for NO_3-N + NO_2-N, NH_3-N + NH_4-N and PO_4-P collected for four years (1987 – 1990) are available. These data were used in order to evaluate the applicability of the proposed model.

4.1.3. Model formulation

The procedure of model formulation can be discussed under two main categories: hydraulics and water quality. First, the formulation of the hydraulic submodel is presented. The formulated hydraulic model is then extended to include the water quality submodel.

4.1.3.1. Hydraulics

The complex hydrodynamic river model, which is based on the St. Venant equations (de St. Venant, 1971), was simplified to a typical Continuously Stirred Tank Reactor in Series (CSTRS) modelling approach in which the river is represented as a series of river compartments (tanks), each of which is assumed completely mixed (Beck and Reda, 1994; Seok and Yong, 1996; Whitehead *et al*., 1997). Using CSTRs in series as a surrogate for the complex hydrodynamic model, the water balance equation in a single tank can be expressed as follows:

$$\frac{dV}{dt} = Q_{in} - Q_{out} - ET * A \qquad (4.1.1)$$

where V volume of the tank (m^3)
Q_{in} inflow rate ($m^3\ d^{-1}$)
Q_{out} outflow rate ($m^3\ d^{-1}$)
ET evapotranspiration ($m\ d^{-1}$)
A surface area of the river tank (m^2)

In this water balance equation, water loss due to ET is incorporated. This is very important in arid and semi-arid regions, particularly when dealing with long and wide rivers. In the Crocodile River, the mean annual potential evapotranspiration for the catchment (1800 – 2000 mm) exceeds the mean annual precipitation (< 800 mm) by a wide margin (DWAF, 1995). Such considerable water loss by evapotranspiration leads to an increase in the constituent concentrations in the river, and thus its impact on the river water quality should not be neglected. Excessive salinity, for example, is one of the adverse consequences in downstream reaches of the catchment. Obviously, such a problem also can be exacerbated by human activities such as mining, irrigation, and upstream freshwater abstraction for irrigation and industrial supply. Data collected in July 1990 indicate that the electric conductivity (as a measure of salinity) increases with river length (from about 13 mS m^{-1} at a distance of 14 km, to 40 mS/m at 270 km down from Kwena Dam. Given the minimum and maximum values, seasonality of the *ET* value was approximated for every river segment based on a sine function.

Calculating effluent flow rate and flow velocity

The effluent flow rate from each "tank" can be calculated using a power function approximation as follows:

$$Q_{out}(t) = \alpha h^{\beta}(t) \tag{4.1.2}$$

and the flow velocity can be calculated as:

$$v(t) = \frac{Q_{out}(t)}{A_{cross}(t)} \tag{4.1.3}$$

where	$h(t)$	the water level h at time t [m] = $V(t)/A_{surface}$
	α, β	parameters estimated from stage flow relations
	$v(t)$	flow velocity at time t [m d^{-1}]
	$A_{cross}(t)$	cross-sectional area at time t [m^2] = $V(t)/L$
	L	the river reach length (m)
	t	the time variable [d]

The hydraulic parameters (α and β) were determined based on the flow (Q) and water level (h) relationship. This was done easily by fitting the power function to the relationship of Q and h.

4.1.3.2. Water quality

The above relatively simple hydraulic model can be extended quite easily to include the water quality submodel. A conceptual one-dimensional river water quality model in a variable volume of river stretch is expressed by the mass balance:

$$\frac{d(VC)}{dt} = Q_{in}C_{in} - Q_{out}C + Vr \tag{4.1.4}$$

where C_{in} concentration in the inflow [mg L^{-1}]

C concentration in the outflow [mg L^{-1}]
r reaction rate [mg L^{-1} d^{-1}]

Based on equations 4.1.1 and 4.1.4 another interesting equation can also be derived as:

$$\frac{dC}{dt} = \frac{Q_{in}}{V} C_{in} - \frac{1}{V}(Q_{in} - ET * A)C + r \tag{4.1.5}$$

As illustrated in equation 4.1.5, the concentration dynamics in a tank with variable volume is not dependent on the effluent flow rate Q_{out} but rather depends on the influent flow rate Q_{in} and evapotranspiration *ET* that can be calculated by the Hargreaves method (Hargreaves and Samani, 1985). This means that the mass balance is calculated with the same equation as for a tank with constant volume, but now a time-dependent volume is used. This approach requires the hydraulics calculations to be performed separately and prior to the calculation of the water quality mass balance.

Biochemical conversions

The conversion process describes changes in constituent concentrations due to biological, chemical, biochemical, and physical processes. It is represented by *r* in equations 4.1.4 and 4.1.5. As it has already been introduced above, the RWQM1 (Reichert *et al.,* 2001) modelling approach is adopted in this study because it is compatible with the ASMs, consistent in mass balances and suitable for integrated water quality studies. For the consistence in mass and elemental balances, the RWQM1 modelling approach is based on COD as a measure of carbonaceous organic matter rather than BOD, and it assumes constant elemental composition of compounds and organisms in the system. This allows using the mass fraction of the considered elements as model parameters. The stoichiometric coefficients of the conversion processes are formulated as a function of these parameters. The conversion or processes rates are formulated with Monod-type limitation factors.

The RWQM1 model, however, is rather complex and requires large input data sets. It includes pH and zooplankton (primary consumer) calculation, which requires large sets of specific monitoring data and high computational power. By selecting and modifying the most important sub-model components, a simplified version of RWQM1 was derived during this study. The procedure for sub-model selection is presented elsewhere (Vanrolleghem *et al.,* 2001). The state variables and process descriptions in the simplified version of the model are given in Tables 4.1.1 and 4.1.2 respectively.

Table 4.1.1: State variables in the simplified river-quality model and relation to RWQM1 formulation (Reichert *et al*., 2001)

	State variables	Description
1	*S_I*	Inert soluble COD
2	*S_S*	Readily biodegradable COD
3	*S_O*	Dissolved oxygen
4	*S_NH* ($S_{NH4}+S_{NH3}$)	Ammonia nitrogen
5	*S_NO* ($S_{NO2}+S_{NO3}$)	Nitrite + Nitrate nitrogen
6	*S_PO* ($S_{HPO4}+S_{H2PO4}$)	Phosphate phosphorus
7	*X_H*	Heterotrophic biomass
8	*X_N* ($X_{N1}+X_{N2}$)	Nitrifying biomass
9	*X_P*	P adsorbed to particles
10	*X_I*	Particulate inert COD
11	*X_S*	Particulate organic matter

Table 4.1.2: Processes used in the simplified river quality model and relation to RWQM1 formulation (Reichert et al., 2001)

	Processes
1	Aerobic growth of Heterotrophs with ammonia
2	Aerobic growth of Heterotrophs with nitrate
3	Aerobic respiration of Heterotrophs
4	Anoxic growth of Heterotrophs with nitrate
5	Anoxic respiration of Hetrotrophs
6	Growth of Nitrifiers
7	Aerobic respiration of Nitrifiers
8	Hydrolysis of particulate organic materials
9	Adsorption of Phosphate
10	Desorption of Phosphate

The selection of state variables and processes given in Tables 4.1.1 and 4.1.2 are based on the following simplifying assumptions:

- Only microbial biomass suspended in the water column were considered to dominate the conversion rates. Algae, macrophytes and consumers were assumed not to be relevant.
- CO_2, N_2, and H^+ were used to determine stoichiometric coefficients but were not included in the model as limiting factors, because they were considered always to be present in sufficient quantity.

- Nitrification was modelled as a single step (first step nitrifires (X_{N1}) + second step nitrifires (X_{N2}) = nitrifying biomass (X_N); and nitrite nitrogen (S_{NO2}) + nitrate nitrogen (S_{NO3}) = S_{NO}).
- The pH was assumed not to change significantly during the process, thus the pH-dependent state variables and related processes such as chemical equilibria can be omitted.

4.1.4. Model implementation

The proposed model was implemented in the WEST® modelling and simulation software (Vanhooren *et al.*, 2002). For the Crocodile River case study, the complete tank-in-series model configuration in the WEST® simulator is shown in Figure 4.1.2.

As indicated in Figure 4.1.2, the main sources of inorganic nitrogen for the studied section of the Crocodile River are the upstream (In_1) and side stream (In_2) only. In these two inputs, the daily flow and monthly water quality variables are available. The contribution of other sources of pollution, e.g. from agricultural runoff, in the intermediate river section is negligible (DWAF, 1995). This simplifies the implementation of the model as the system can be implemented as a point source pollution model. The number of tanks in series determines the hydraulics and transport term of the model. The model must therefore be calibrated for the optimum number of tanks-in-series as will be detailed in the next section. The hydraulic characteristics of the river section under consideration are given in Table 4.1.3.

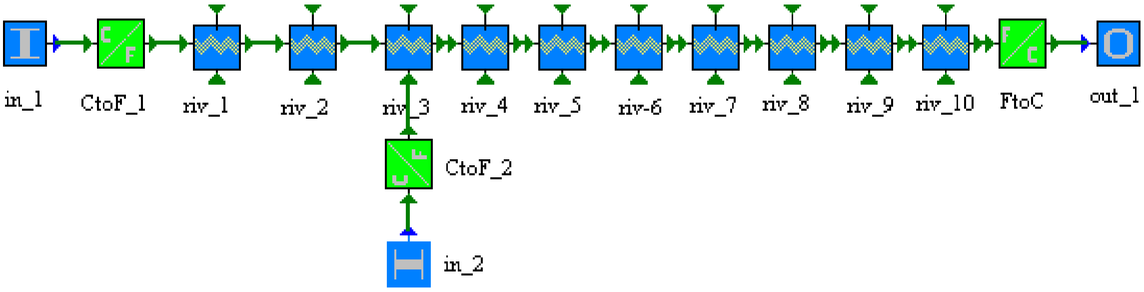


Figure 4.1.2: Diagram of the complete tank-in-series model, where: In_1 represents the upstream input; In_2 is the input from the side river (Kaap River); boxes riv_1 to riv_10 describe continuously stirred tanks-in-series, and CtoF and FtoC boxes indicate the concentration-to-flux and flux-to-concentration conversions sub-models respectively

Table 4.1.3 Characteristics of the studied section of river compartments

Segment No.	Length (km)	Number of tanks in series	Name of boxes included	Cumulative distance (km)
1	16	2	riv_1 - riv_2	16
2	9	1	riv_3	25
3	34	6	riv_4 - riv-9	59
4	11	1	riv_10	70

4.1.5. Model calibration and validation

The appropriate number of tanks-in-series was selected on the basis of the results obtained after several simulations with an increasing number of tanks. The higher the number of tanks, the greater is the tendency towards ideal plug-flow conditions. With progressively larger numbers of tanks, it can become difficult to compile the model and the calculation time also increase accordingly. Therefore, low number of tanks was considered to represent an acceptable compromise between calculation time and accurate representation of the river system.

After the appropriate number of tanks-in-series was obtained, the water quality submodel was calibrated by tuning the most sensitive parameters (based on the sensitivity analysis detailed below) in order to get the best curve fit with the measured data. The model was calibrated by tuning the values for X_N and X_H in the upstream (In_1) and tributary inflows (In_2), with the assumption that the microbial biomass density does not vary significantly. The stoichiometric coefficients were calculated based on the simplified processes rates, and the other parameters (yield coefficients and rate constants) were taken from literature (Reichert *et al*., 2001). The values of these parameters were selected on the basis of best curve fitting with the measured data.

Once the model is calibrated, all one knows is that the model fits with the one set of data that is used for calibration of the model. Prior to the application of the model as a tool for water quality managements, the model must be validated. In order to do that, the model should be run with independent data (ideally several independent data sets) without changing the calibrated parameters.

4.1.6. Results and discussion

4.1.6.1. Estimation of hydraulic parameters: α and β

Using data collected in 1987 and 1988, the hydraulic parameters (α and β) were determined based on the available flow (Q)-stage (h) relationships, by fitting the power function (equation 4.1.2) to the measured data set (see Figure 4.1.3). These parameters need to be determined for every river stretch. However, data are available only for four locations. The parameter values of these locations were then assigned to the corresponding river segment (see Table 4.1.4). This is based on the assumption that the river hydraulic characteristics are the same for the whole river segment under consideration.

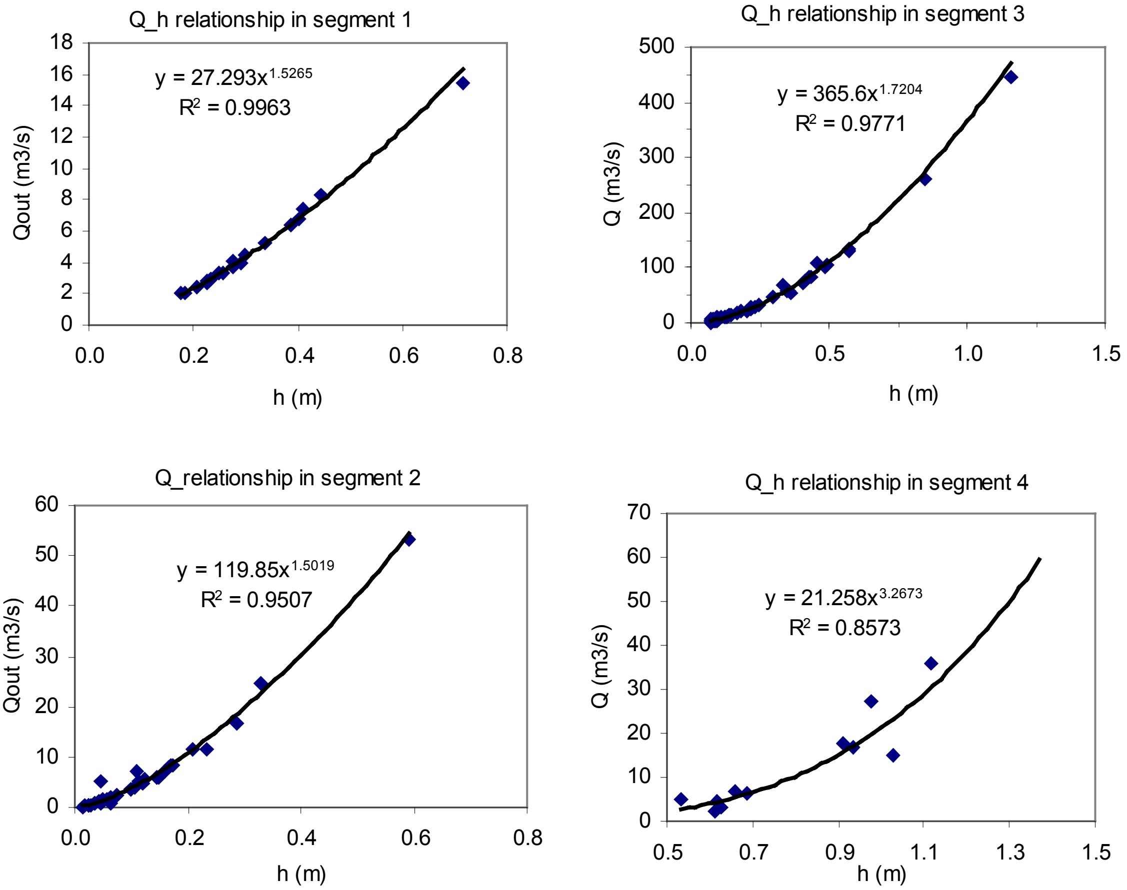


Figure 4.1.3: Q versus h relationships or estimation of α and β

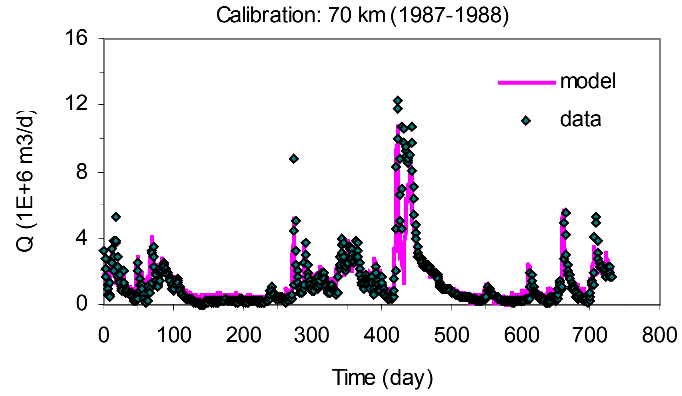
Table 4.1.4: Hydraulic parameters

Segment No.	River tanks	α	β	r^2
1	riv_1 - riv_2	27.293	1.5265	0.9963
2	riv_3	119.85	1.5019	0.9507
3	riv_4 - riv-9	365.6	1.7204	0.9771
4	riv_10	21.258	3.2673	0.8573

4.1.6.2. Model calibration and validation

Hydraulics

On the basis of the hydraulic parameters given in Table 4.1.4, the hydraulic submodel was calibrated and validated using independent data collected for four years (1987 to 1990) and 10 tanks-in-series. The results of both the model calibration and model validation revealed that the simulated data set agrees well with the measured data set (see Figure 4.1.4). This indicates that 10 tanks-in-series can adequately describe the hydraulic routing of the river.



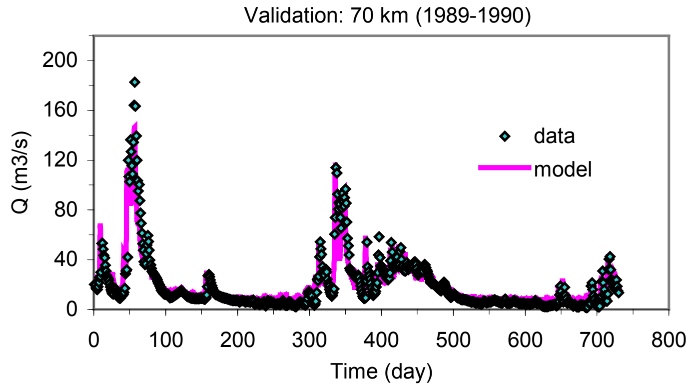


Figure 4.1.4: Calibration and validation of the hydraulic submodel: lines show the simulated data set, whereas symbols indicate the measured data set

Water quality

Using data collected in 1987 and 1988, the calibration results for the inorganic nitrogen concentrations in the downstream river sections (at 16 km and 70 km) are given in Figure 4.1.5. The results show that the general trend of the simulated nitrogen concentrations (for both nitrate and ammonia) agree well with measured data within 20% error. This result was obtained by setting the model input variables to 0.1 mg L^{-1} X_N and 2 mg L^{-1} X_H. In some points, there were indeed some differences between the two data sets. These differences could be due to the limited data available. Monthly water quality data were based on the collection of point measurements (once per month), which do not represent the average monthly water quality. However, the model requires daily measurements as inputs (In_1 and In_2). Thus, the daily water quality data were linearly interpolated from the point monthly water quality measurements.

To validate the model, the calibrated model was run with new independent data collected in 1989 and 1990, and the results are presented in Figure 4.1.6. The results show that the general trend of predicted data (-sim) agrees with the trend of measured data (-data) (within 20% error) for both ammonia and nitrate nitrogen concentrations at the two monitoring stations (16 km and 70 km). The need for a higher model accuracy would ask for more data such as daily water-quality data in every river section of the main river and in all its tributaries. Obviously, this is not economically feasible, especially in a developing country where only limited funds are available for the monitoring campaigns. Nevertheless, the simplified model adequately describes the general seasonal dynamics of the nitrogen concentrations.

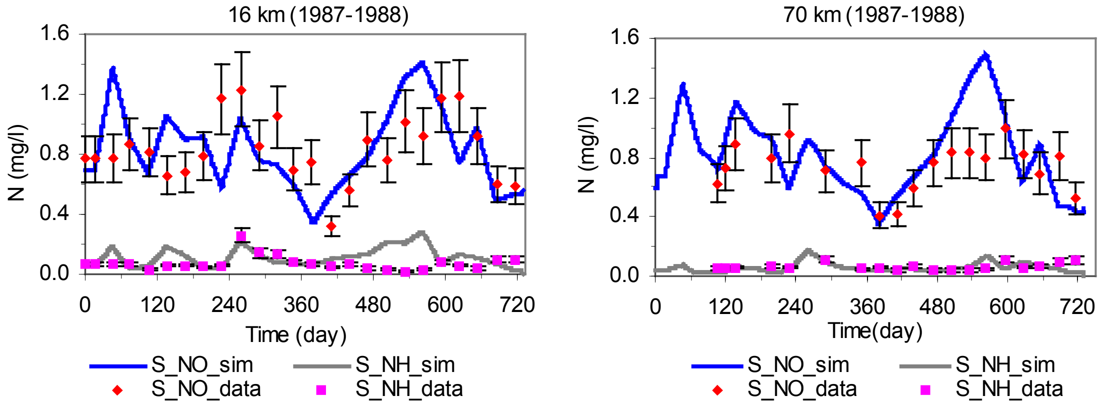


Figure 4.1.5: Model calibration: Comparison of measured nitrate (S_NO_data) and ammonia nitrogen (S_NH_data) with simulated nitrate (S_NO_sim) and ammonia nitrogen (S_NH_sim) concentrations in the downstream river sections (16 km and 70 km)

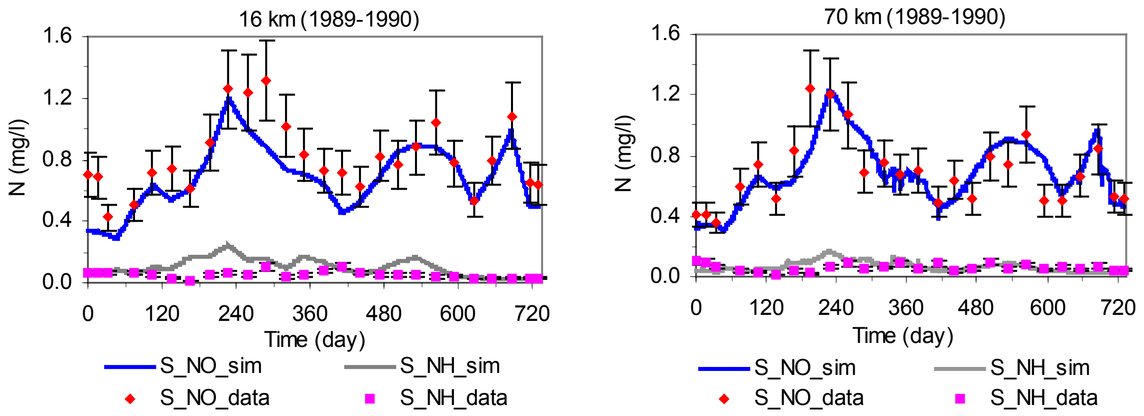


Figure 4.1.6: Model validation: nitrate (S_NO) and ammonia (S_NH) nitrogen concentration in the downstream section of the Crocodile River (16 km and 70 km) (1 Jan 1989 to 31 December 1990); where -sim and –data are for the simulated and measured data set respectively

4.1.6.3. Sensitivity analysis

A sensitivity analysis was made to get an understanding of the likely model response to a small change of input parameters, and to provide the relative importance of model parameters or variables.

In this study, relative sensitivities (S_R) were used. The relative sensitivity measures the relative change of the model output in relation to a relative change of parameters. This choice is advantageous over absolute sensitivities because it does not depend on the units of model parameters nor the model output variables. The relative sensitivity (S_R) was calculated numerically, based on the change in predicted nitrogen concentration (N) upon a 10% increase of each parameter (P) at every simulation time step as follows:

$$S_R = \frac{\Delta N / N}{\Delta P / P} = \frac{\Delta N / N}{0.1 . P / P} = 10 . \frac{\Delta N}{N} \tag{4.1.6}$$

Accordingly, the calculated concentrations of nitrate (S_{NO}) and ammonia (S_{NH}) nitrogen were subjected to a sensitivity analysis once the stoichiometric and kinetic parameters had been set using values obtained from literature. The model parameters indicated in Table 4.1.5 were each increased by 10%, and average values of the absolute relative sensitivity of the predicted concentration of nitrate and ammonia nitrogen were calculated (Table 4.1.5).

Table 4.1.5: Result of the sensitivity analysis of the simplified model: relative sensitivity (S_R)

Parameters	Descriptions	$\lvert \bar{S}_R \rvert$ (%)	
		Nitrate	Ammonia
X_N	Nitrifiers concentration	6.62	56.25
β	Hydraulic parameter	4.66	36.13
α	Hydraulic parameter	4.07	30.88
T_max	Maximum water temperature	3.16	22.94
ET_max	Maximum ET	0.31	2.73
X_H	Heterotrophs concentration	0.16	6.00
S_S	Readily biodegradable COD	0.09	0.35
S_O	Oxygen concentration	0.04	0.04
v	Flow velocity	0.04	0.01

As the value of the sensitivity function for a dynamic simulation is in the form of time series, the average absolute values of S_R ($\lvert \bar{S}_R \rvert$) are used to rank the relative importance of the parameters. The sensitivity of the predicted nitrate concentration to the parameters is as follows (ordered from most to least sensitive): concentration of X_N, β, α, T_max, ET_max, X_H, S_S, S_{O2} and v. The model sensitivity for ammonia is similar, except that the X_H concentration is placed fourth in the sequence of sensitive parameters. The sensitivity of both nitrate and ammonia to S_S, S_{O2} and v is negligible and the uncertainty related to these parameters will therefore have less importance than the concentration of X_N. Even though the sensitivity of nitrate to *ET* is negligible, it is not negligible for ammonia because it determines the dilution rate. A higher *ET* value can result in higher ammonia concentration predictions. The nitrogen concentration prediction also is relatively sensitive to the hydraulic parameters (α and β) because these parameters determine the flow rates. Nitrogen predictions are also sensitive to T_max as the latter determines the temperature dependent kinetic parameters (growth rate of nitrifiers and heterotrophs).

In general, the relative sensitivity is higher for ammonia nitrogen than for nitrate nitrogen. This can be mainly due to the fact that ammonia nitrogen concentrations are very low compared to nitrate nitrogen, which amplifies the relative sensitivity for ammonia.

4.1.6.4. River flow versus nitrogen concentration

Using data collected in 1986 to 1990, the relationship between river flow versus inorganic nitrogen concentration in the down stream section of the river (at 50 km) was analysed. The results show that the concentration of nitrogen is inversely related to the river flow (see Figure 4.1.7). The higher nitrogen concentrations occur during the dry season when the river

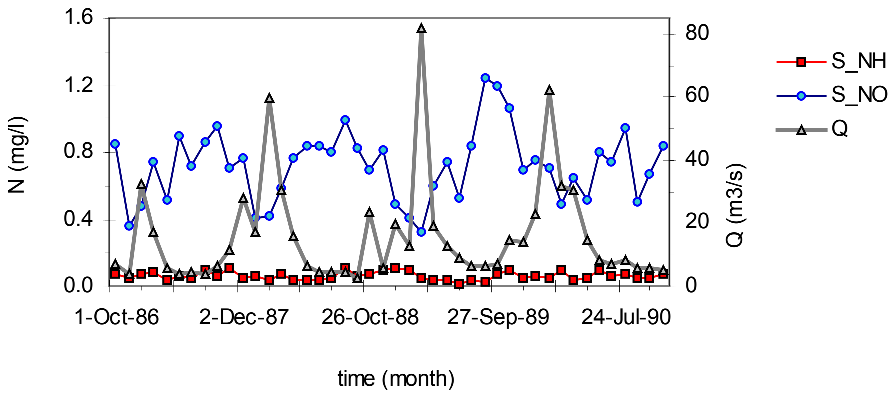


Figure 4.1. 7. River flows versus inorganic nitrogen-concentrations at 50 km, Q is the flow rate

is at its minimum flow. As the river flow increases the concentration of nitrogen decreases and vice versa. Therefore, low flow periods (dry season) are the worst case for nitrate and ammonia.

Furthermore, one may expect higher nitrogen concentrations during the wet season than during the dry season because of the higher nitrogen load washed from agricultural land or mining sites into the river system during the wet season. This is true when the contribution from non-point source (diffused source) is higher than from point sources or side streams (Behrendt, 1993). In the studied section of the Crocodile River however, the concentrations of inorganic nitrogen (or better, nitrate nitrogen) remain low during high flows because of the greater dilution, and vice versa. Such inverse relationship between the concentrations of inorganic nitrogen and river flows in a downstream point of the study section shows that the main sources of inorganic nitrogen are side streams (point sources). The main contribution is from the Kaap River (in_2), which drains an extensive area of active and abandoned gold mines. This has resulted in poor water quality of the river in the downstream sections from the Crocodile-Kaap River confluence (Kleynhans, 1999). In the water quality management of the Crocodile River, more attention should therefore be given to the low flow period when the main river flow might be too low to dilute the Kaap River and to flush possible wastewater effluent discharges.

4.1.6.5. Model application and data requirement

The data requirement of the proposed model is determined by the application of the model. If the seasonal dynamics of the water quality variables is of interest, monthly water quality data can be used like in this study. If the monthly water quality data are based on point measurements (measuring once a month), reliability may be doubted as this is influenced by inherent variation of runoff events or river flows. As the model is designed for short-term river water quality studies, the more frequent the monitoring data are collected (e.g. weekly to daily, depending on the available financial and material resources) the better will be the model accuracy in describing the dynamics of nutrients in the river. To apply this model on a daily basis the following minimum data are required: physical and hydraulics characteristic of the river, estimated dissolved and particulate organic matter, dissolved oxygen, inorganic nitrogen, (nitrate + nitrite) and (ammonia + ammonium), water temperature and phosphate phosphorus.

4.1.7. Conclusions and further research

In this study, a conceptual modelling approach is introduced to reduce the complex river water quality model (RWQM1) so that it can be applied in data-limited situations, especially in developing countries where it is difficult to find the necessary facilities to determine/measure all required water quality variables. Based on the result obtained during this study, one can draw the following general conclusions.

1. Use of the simplified model reduced the data requirements significantly, and the model could successfully be applied to the Crocodile River with limited available data. Besides, in its new configuration, the model is faster and requires less simulation time than the more complex original RWQM1. This study hence shows the usefulness of model reduction (model simplification).

2. The model still has sufficient complexity for the description of short-term dynamics of ammonia and nitrate (periods spanning a few days to a few weeks depending on the availability of data). The model complexity can therefore be increased step-wisely based on the available data and required accuracy.

3. The demonstrated sensitivity of the model output to hydraulic parameters requires accurate parameter estimation based on flow and stage relations in every river reach. In addition, the concentration of nitrifiers is the most sensitive parameter, and it should be estimated properly. Practically nitrifier activity measurement may be appropriate for this. The prediction of the ammonia nitrogen concentration is much more sensitive to the hydraulic related parameters, including *ET*, than the nitrate nitrogen because of the low ammonia nitrogen concentrations.

4. The relationship between the river flow rate and the inorganic nitrogen concentration in the Crocodile River indicates that both ammonia and nitrate nitrogen concentrations

> are more important during low flow periods than during high flow periods. During such a low flow period, the water quality of the river can further be deteriorated in the downstream section of the river due to a high upstream fresh water withdrawal, e.g. for irrigation.

Furthermore, high upstream fresh-water withdrawal is very important especially in the arid and semi-arid regions, and must be considered in the Crocodile River water quality modelling in future research, which is the driving force for the following research work presented in Chapter 4.2.

Chapter 4.2

Control options for downstream river water quality improvement[1,2]

The important parts of this chapter were published as:

[1] Deksissa T., Peter Ashton J. and Vanrolleghem P. A. (2002). Application of a simple dynamic model for river water quality management: A case study of inorganic nitrogen and TDS in the Crocodile River (South Africa). In: *Proceedings 6th international Conference on diffuse pollution*, Amsterdam, The Netherlands, September 30-4 October 2002.

[2] Deksissa T., Ashton P. J. and Vanrolleghem P. A. (2003). Control options for river water quality improvement: A case study of TDS and inorganic nitrogen in the Crocodile River (South Africa). *Water SA,* **29**, 209-217.

Chapter 4.2

Control options for downstream river water quality improvement

In this chapter, using the simple water quality model presented in Chapter 4.1 with some modifications in the hydraulic submodel, different basin-wide water quality management options were investigated in order to enhance the downstream river water quality. The modified version of the hydraulic submodel includes upstream fresh water withdrawal and low flow augmentation. When a river is impacted by high rates of freshwater withdrawal (in its upstream reaches), and also receives polluted side-stream inflows and wastewater effluent discharges (in the middle reaches), the downstream river water quality can deteriorate seriously over time, particularly in semi-arid regions, as is the case in the Crocodile River (South Africa). Such problem becomes important during dry seasons when the river flow is too low to dilute the polluted side streams or effluent discharges. This chapter therefore focuses on two main water quality problems: progressive increases in the concentrations of Total Dissolved Solids (TDS) as a measure of salinity, and the concentrations of inorganic nitrogen (nitrate-plus-nitrite and ammonia) as a measure of nutrient pollution/eutrophication. After thorough investigation, different management options that can improve water quality in the downstream section of the river are proposed.

4.2.1. Introduction

As the demand for water increases in line with human population pressure and economic development activities, river ecosystems will continue to deteriorate unless they are managed in a sustainable way. The main causes for deterioration, particularly in their downstream reaches, are related to not only water quality but also water quantity. The problem related to water quantity (e.g. the occurrence of extremely low flows) is governed by both natural events (drought) and human-induced factors (e.g. large upstream freshwater withdrawals). Because they reduce the dilution capacity of the river, high levels of water withdrawal or loss from upstream river sections or tributaries can considerably affect the water quality of downstream river reaches. High upstream water losses result in the reduction of dry weather flows. In turn, reduced flows can cause accelerated sedimentation and increase total dissolved solids (TDS) concentrations in downstream reaches of the river (Qader, 1998; Mokhlesur *et al.*, 2000). Many other studies have also shown that extremely low flows can have severe effects on river ecosystems, e.g. the failure of natural reproduction processes of many fish species, declining fish yields, and reduced biological productivity (Dubinina and Kozlitina, 2000). In addition, reduced flows also have adverse effects on benthic macro-invertebrate communities, either through direct changes in habitat and flow hydraulics, or through indirect changes in water quality (Caruso, 2002).

While methods for basin-wide water quantity controls are well established, though not yet fully implemented, similar considerations are less common for optimum water quality management. When an extreme low-flow event is combined with inflows from highly polluted tributaries or wastewater effluents, there will be a dramatic decline in the water quality status of downstream river reaches. To deal with problems of this nature, the setting of effluent quality standards and non-point source pollution regulations is usually ineffective. Hence, additional cost-effective control options must be considered.

The objective of this study is to investigate a range of possible management control strategies for the Crocodile River, which receives several inflows from polluted side-streams and also experiences high levels of water withdrawal. Salinity and eutrophication are the major water quality problems in this river. Using a conceptual dynamic hydraulic model, the seasonal dynamic of TDS (as a measure of salinity) and inorganic nitrogen concentrations (nitrate plus nitrite and ammonia, as measures of eutrophication), are simulated in the downstream reaches of the Crocodile River, and the results are compared with monitoring data.

4.2.2. Problem definition: the Crocodile River case study

To derive the best options for the downstream water quality of the Crocodile River (see Figure 4.2.1), relatively much more detailed information about the hydraulic characteristics and water quality related factors is needed. The general characteristics and climate of the catchment are already discussed briefly in Chapter 4.1. DWAF (1995) provides a summary of the Crocodile River catchment hydrology and water quality as is summarized here. The hydraulic characteristics of the river have been changed by the construction of dams and afforestation and water abstraction for irrigation. The Kwena Dam (capacity = 167×10^6 m^3)

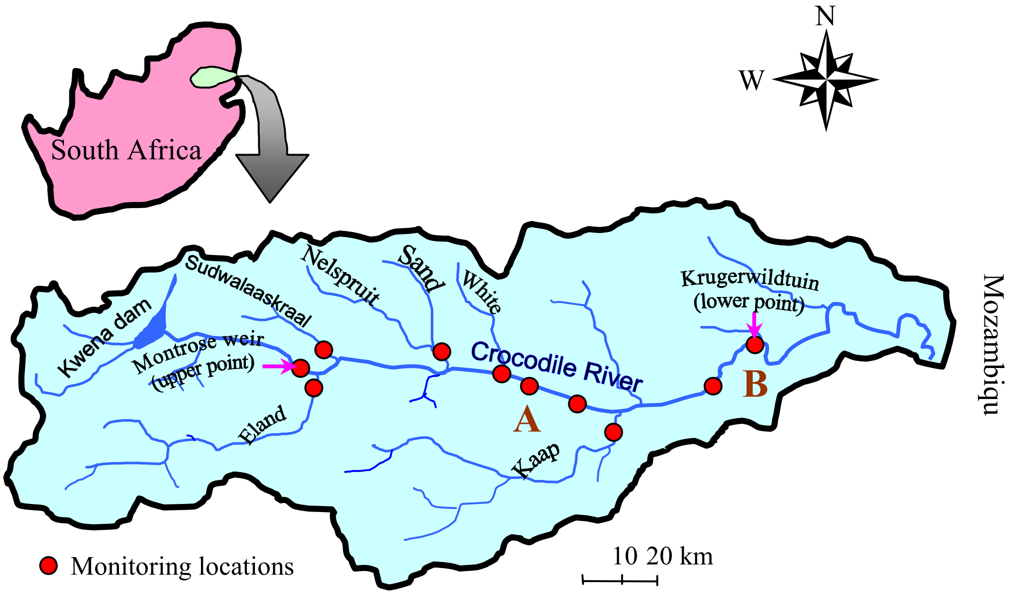


Figure 4.2.1: Crocodile River basin and water quality monitoring stations: The model considers only the distance between two arrows (about 153 km); marks A (82 km) and B (153 km) are the monitoring sites where the model was calibrated and validated

was constructed at a point some 40 km upstream of the upper point of the study site in order to regulate the river flows. Generally, water is released from this dam during the dry winter months to ensure that a minimum flow of 7 $m^3 \cdot s^{-1}$ reaches irrigation farmers along the middle and lower reaches of the Crocodile River in the Lowveld, and to help flush out wastewater effluent discharges from the towns of Nelspruit and Malelane in the middle reaches of the catchment. Apart from the Kwena Dam, seven more medium-sized dams exist in the catchment, as well as over 200 small farm dams. The quantities of water abstracted for irrigation, as well as the decreased inflows caused by increased afforestation, have resulted in a marked decline in winter flows from many tributaries and the main stem of the Crocodile River. Moreover, the mean annual potential evaporation losses for the catchment ranging between 1800 to 2000 mm, exceed the mean annual precipitation by a wide margin and considerable quantities of water are lost via evaporation. These high water losses have had a considerable impact on water quality in the downstream river reaches.

It is also indicated that water quality in the Crocodile River is influenced not only by direct human interventions, but also by natural phenomena such as climate and geology (DWAF, 1995). Geological processes such as chemical weathering contribute some chemical ions but there are indicated to be far less (<1%) than the contributions from soil erosion and land use. The primary effect of climate on water quality is expressed through the effects of rainfall seasonality on the timing and duration of high or low river flows. High summer rainfalls with discrete storm events result in sudden increases and decreases in runoff, causing rapid changes in river water levels and suspended sediment concentrations. In contrast, river flows decline gradually to very low levels during the dry winter months, and the lowest flow levels are usually less than 10% of the average flows recorded in the dry season. This decrease in flow, combined with relatively high rates of evaporation (>100 mm/month), causes a gradual increase in the concentration of dissolved salts present in the lower reaches of the river.

Such natural problems can be aggravated when a low flow is combined with a high load of point and/or non-point source pollution that can exceed the so-called “dilution capacity” of the river. TDS concentrations in the Crocodile River increase markedly after its confluence with the Kaap River, which drains an extensive area of active and abandoned gold mines. Subsequently, the lower reaches of the Crocodile River (downstream from the Kaap River confluence) have poor water quality due to agricultural runoff and return flows, as well as additional mining activities (Kleynhans, 1999). Any additional freshwater withdrawals in the upstream reaches during periods of extremely low flow can cause a further increase in salinity and deterioration of water quality.

Furthermore, the study of the Fish Assemblage Integrity Index (FAII) in the Crocodile River has indicated the potential impact of human activities in the downstream section of the catchment (Kleynhans, 1999). It has been indicated that the relative FAII score per fish habitat segment decreases longitudinally in the Crocodile River. The FAII calculation is based on rating the individual species in terms of intolerance, frequency of occurrence and health. Then the relative FAII score (the ratio of expected and observed FAII scores) is used to classify the integrity class of the fish habitat segment. The integrity class is called “unmodified” or “natural condition” if the relative FAII score is 90 to 100%, “largely modified” if it is 80 to 89%, “moderately modified” if it is 60 to 79%, “largely modified” if it is 40 to 59%, “seriously modified” if it is 20 to 39%, and “critically modified” if it is less than 19%. It is also indicated that the progressive and longitudinal decline of the relative FAII per fish habitat segment along the lower reaches of the catchment is related not only to altitude but also to agricultural and domestic runoff, industrial effluents (in the middle of the catchments, from Montrose to the Kaap River confluence) and mining activities (in the lower catchment downstream of the Kaap River confluence). The relation of TDS and relative FAII score per fish habitat segment (ASPT/Seg) is given in Figure 4.2.2. The data show that the longitudinal increase of TDS in the Crocodile River is inversely related to the biotic index.

The current flow-release pattern from the Kwena Dam also has a dramatic effect on attempts to improve water quality in downstream river reaches. Water is generally released from the dam to ensure that a minimum flow of 7 $m^3 s^{-1}$ reaches irrigation farmer along the river in the Lowveld but does not follow the natural flow pattern of the river.

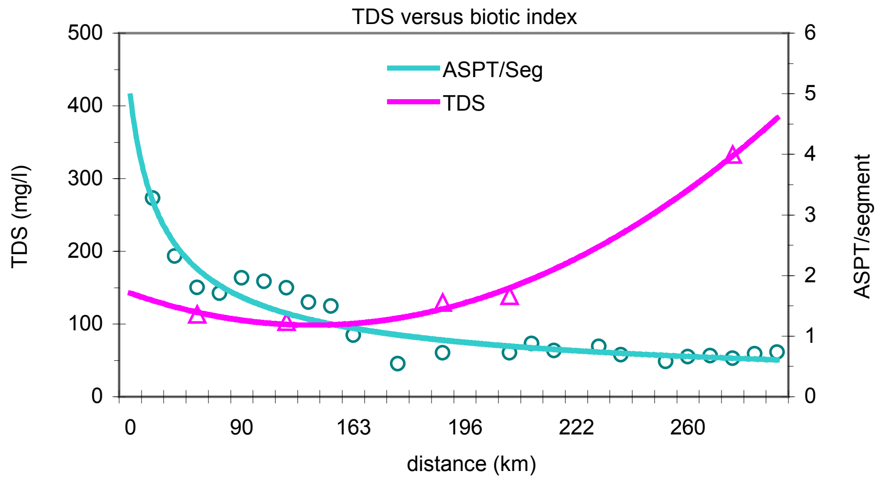


Figure 4.2.2: The relationship between TDS and biotic index (ASPT/Seg): Symbols are the measured data set, whereas the lines are predicted by powere functions

Besides, water quality criteria are not explicitly considered in the flow-release pattern. Such flow modifications imposed by the Kwena Dam have already been reported to decrease the biodiversity of fish in reaches downstream of the Kwena Dam (*State of the Crocodile River*, 2001).

In this study, attention was focused on the 153 km long central section of the Crocodile River (see Figure 4.2.1), between Montrose Weir (upper point) and Kruger National Park (lower point), as this is the section that is under the greatest human influence. This section represents the most sensitive portion of the river, where nitrate and ammonia concentrations often exceed the recommended maximum limits of 0.5 mg L^{-1} (nitrate) and 0.03 mg L^{-1} (ammonia) for oligotrophic systems (DWAF, 1993; Ashton *et al.,* 1995). In certain years, the TDS concentration is also shown to exceed the water quality objective for irrigation (>260 mg L^{-1}, for sensitive crops).

4.2.3. Methods

4.2.3.1. Model formulation

In order to control further deterioration of river water quality caused by high levels of upstream water abstraction and by downstream contributions of polluted inflows in the downstream reaches of the river, a simple model was developed based on the simple mass balance introduced in Chapter 4.1. In Chapter 4.1, the water loss due to upstream fresh water abstraction was not considered explicitly in the water balance.

Water is abstracted from the main river or its tributaries for irrigation, industry and domestic water supply. Most of this water will be lost through evaporation and very little may return to the river. High rates of water withdrawal at the upstream point or from tributaries in the upper reaches can cause an increase in TDS concentrations in the downstream reaches of the river. This is due to the fact that the volume of water reaching the downstream sections of the river is too low to dilute the inflows from polluted side streams and /or effluent discharges. In such cases, a relatively simple dynamic water quality model consisting of completely mixed tanks-in-series can be applied as indicated in the following general mass balance formulation of one such tank:

$$\frac{d(VC)}{dt} = Q_{in}C_{in} - \left(Q_{out} + Q_{wd} + ET \cdot A\right) \cdot C - rV \tag{4.2.1}$$

$$Q_{out} = \alpha h^{\beta} \tag{4.2.2}$$

where V	volume of the tank [m^3]
C_{in}	inflow concentration [$g \cdot m^{-3}$]
C	outflow concentration [$g \cdot m^{-3}$]
Q_{in}	inflow rate [$m^3 \cdot d^{-1}$]
Q_{out}	outflow rate [$m^3 \cdot d^{-1}$]
Q_{wd}	rate of water withdrawal from the tank [$m^3 \cdot d^{-1}$]
ET	water loss by evapotranspiration [$m \cdot d^{-1}$]
A	surface area of the river tank [m^2]
r	reaction rate [$g \cdot m^{-3} \cdot d^{-1}$]
h	hydraulic depth at a time t for rectangular cross-section [m] = V/A
β,α	parameters estimated from stage flow relations
t	simulation time step [d]

In equation 4.2.1, state variables such as V, C, Q_{in}, Q_{out}, Q_{wd}, ET and h vary with time, and the ordinary differential equation should be solved numerically. The overall reaction rate r is obtained from the simplified version of the River Water Quality Model number 1 (RWQM1) (Reichert *et al.,* 2001) introduced in Chapter 4.1 as summarized below. The biochemical processes included in this model are aerobic growth of heterotrophs with ammonia and nitrate, aerobic respiration of heterotrophs, anoxic growth of heterotrophs with nitrate, anoxic respiration of heterotrophs, growth of nitrifiers, aerobic respiration of nitrifiers, hydrolysis of particulate organic materials, adsorption and desorption of phosphate. Stoichiometric coefficients were determined using a simple standard mass composition for organic substances considering the elemental C, H, O, N and P, and charge balances. The conversion rates were all formulated with Monod-type limitation factors. The state variables include the concentrations of dissolved oxygen (S_{O2}), inorganic nitrogen such as total ammonia nitrogen (S_{NH}) and nitrite plus nitrate (S_{NO}), inorganic phosphorus (S_{PO}), soluble readily biodegradable Chemical Oxygen Demand (COD) (S_S) and microbial biomass heterotrophs (X_H) and nitrifiers (X_N). TDS is considered as a conservative substance and it is not involved in the biochemical reaction, and hence its *r*-value in the above general mass balance (equation 4.2.1) is zero. Therefore only transport of this substance is accounted for in the model.

4.2.3.2. Data requirements

The proposed model requires daily time steps of flow and chemical water quality variables indicated above. If only the seasonal dynamics of water quality are of interest, monthly time step data can also be applied. The river flow depth and width, minimum and maximum upstream fresh water withdrawal and temperature need to be known.

4.2.3.3. Model implementation

Using the WEST® modelling and simulation software (Hemmis NV, Kortrijk, Belgium) (Vanhooren *et al.*, 2002), the complete tank-in-series model is illustrated in Figure 4.2.3. The physical details of each river section are given in Table 4.2.1.

The proposed model is formulated on the basis of the following key assumptions:

- Only the pollution loads from the major tributaries and the upstream end of the main river were considered. As it was difficult to collect suitable water quality information for the tributary rivers, the contributions of minor tributaries were assumed to be negligible. This assumption, however, should be tested by future field studies.

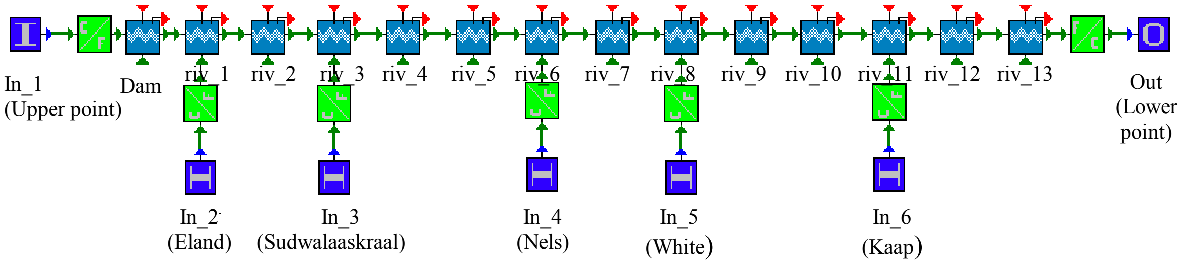


Figure 4.2.1: Completely mixed tanks-in-series model in the WEST® modelling and simulation software; riv_1 to riv_13 are river reaches that are further subdivided into 4 to 5 tanks; "Dam" is the hypothetical reservoir as a control volume; In_2 to In_6 are major tributaries

- The rate of water withdrawal in the upstream river reaches is time-varying (high during the dry season and low during the wet season) because the high water abstraction for irrigation mainly occurs during the dry season.

Table 4.2.1: River segmentation into completely mixed tank-in-series (CSTR)

Name	Monitoring station	Reach length (km)	Cumulative length (km)	Tank length (km)	Number of tanks
riv_1	Montrose Weir – Section 1	4	4	4	1
riv_2	Section 1 - Sudwalaaskraal River	8	12	4	2
riv_3	Sudwalaaskraal River – Section 1	5	17	5	1
riv_4	Section 1 – Section 2	20	37	5	4
riv_5	Section 2 - Boschrand	20	57	5	4
riv_6	Boschrand – Section 1	4	61	4	1
riv_7	Section 1– Goede Hoop	16	77	4	4
riv-8	Goede Hoop – Karino Weir	5	82	5	1
riv_9	Karino Weir – Weltevrede	16	98	4	4
riv_10	Weltevrede – Kaap River	10	108	5	2
riv_11	Kaap River – Section 1	5	113	5	1
riv_12	Section 1 – Malelane Bridge	20	133	5	4
riv_13	Malelane Bridge–KrugerNat Park	20	153	5	4
	Sum				33

4.2.3.4. Model calibration and validation

On the basis of data provided by the South African Department of Water Affairs and Forestry (DWAF), the model was calibrated and validated for the river section between the Montrose weir and Kruger national park. The measured data collected in 1987 and 1988 were used for calibration. For the hydraulic submodel, the minimum and maximum water withdrawal were used to calibrate the hydraulic submodel, where as the microbial biomass used to calibrate the water quality submodels (assuming they do not vary significantly). The model was validated with independent data collected in 1989 and 1990. The only data available in the main stem of the Crocodile River and its tributaries include daily flow rate and monthly water quality variables such as ammonia nitrogen, nitrate plus nitrite nitrogen inorganic phosphorus and TDS. Subsequently, a trial and error procedure was used to calibrate the hydraulic component of the model (by ‘tuning’ the amount of water lost per length of each river reach until the best agreement was obtained between the simulated and measured data sets).

4.2.4. Model application and management options

4.2.4.1. Setting maximum water withdrawal

During low flow periods, setting a maximum water withdrawal can prevent further water quality deterioration caused by high upstream fresh water withdrawal. Low-flow periods in rivers are widely used for traditional water quality modelling as the design condition (the likely worst-case scenario) for waste load allocation studies (Chapra, 1997). The lowest continuous flow for a 7 days period that would be expected to occur every 10 years (also called the “7Q10” flow) is generally accepted as the standard design flow for waste load allocation studies, as it incorporates a high level of assurance against risk. The typical set of procedures used to analyse 7Q10 has been described in Chapra (1997). Based on such a low-flow analysis for the Crocodile River, we can estimate the in-stream flow requirements (ecological reserve) and overall maximum water withdrawal that includes water supply for irrigation, industries or domestic supplies. The in-stream flow requirement or ecological reserve is the minimum flow required for the normal function of aquatic ecosystem (e.g. for fish reproduction). The maximum water withdrawal can be defined as the difference between the discharge in a low water base year (90% probability of exceedence) and the discharge critical for river ecosystem e.g. fish reproduction (95% probability of exceedence) (Dubinina and Kozlitina, 2000). The in-stream flow requirement varies from river to river and region to region. Hence, the South African Building Block Methodology (BBM) (King and Louw, 1998; Rowntree and Wadeson, 1998) is considered to be appropriate for the determination of the in-stream flow requirements in river ecosystems located in semi-arid and arid regions. As it is not the intention of this study to determine the critical in-stream flow requirements, the rate of water withdrawn was obtained after model calibration. The rate at which water is withdrawn per unit length of each river reach ($m^3 \cdot m^{-1} \cdot d^{-1}$) is one of the model parameters whose real values should be obtained by calibrating the model with real monitoring data.

4.2.4.2. Low-flow augmentation and water release patterns from the reservoir

Low-flow augmentation is generally required when dry season river flows are lower than those required in the downstream segments of a catchment. During the dry season, most South African rivers are characterized by low flows, or zero flows in the case of highly seasonal rivers. As a consequence, river water quality in the reaches downstream of many wastewater treatment works is usually very poor due to the lack of dilution (Dickens and Graham, 1998).

Thus, reservoir releases, one of the most important traditional forms of low-flow augmentation, must be considered.

Because reservoirs always modify river flow patterns and alter or interrupt the river continuum, they are frequently viewed as imposing strongly negative impacts on the aquatic environment (Ward and Stanford, 1983; Avakyan and Iakovleva, 1998). Despite these negative views, some studies have also indicated that reservoirs or impoundments can improve downstream water quality conditions; for example, impoundments that receive agricultural runoff and urban effluents generally cause an improvement in water quality downstream for most of the year (Palmer and O'Keeffe, 1990). Therefore, reservoirs can have both positive and negative impacts depending on their mode of operation and the prevailing downstream river water quality conditions. Indeed, reservoirs offer potentially important management tool if the relationships between modes of reservoir operation and the resulting influence on water quality can be understood (Straskraba, 1994).

Deriving and using appropriate reservoir operation rules therefore offers an important opportunity to improve water quality in downstream river reaches. If the flow release from a dam does not follow the natural flow seasonality patterns, it can and does result in dramatic ecological changes. However, using dynamic storage and release patterns, at least some resemblance of natural seasonality can be simulated. This can be formulated in such a way that the flow pattern should follow the general trend of natural flow patterns in the catchment. The algorithm for the governing equation of the general water balance in the control volume (dam) can be formulated as follows:

$$\frac{dV}{dt} = Q_{in} - Q_{out} \tag{4.2.3}$$

$$\begin{aligned} Q_{out} &= Q_{max} \text{ if } Q_{in} \geq Q_{max} && \text{to store some water during the wet season} \\ &= Q_{min} \text{ if } Q_{in} \leq Q_{min} && \text{to supplement the low flow during dry season} \\ &= Q_{in} \text{ if } V \leq V_{min} && \text{to avoid negative output (specific for the model)} \\ &= Q_{min} + \phi(Q_{in} - Q_{min}) \text{ if } Q_{min} \leq Q_{in} \leq Q_{max} && \text{for seasonal trends} \end{aligned}$$

where Q_{min} and Q_{max} are, respectively, the minimum and the maximum outflow rate required to release from the reservoir; V_{min} is the minimum velocity ϕ is the fraction ranging from 0 to 1 depending on the volume of water required to be released.

As indicated by the last expression in equation 4.2.3 for Q_{out}, changes in the outflow rate (Q_{out}) will depend on changes in the inflow rate (Q_{in}). In this way the general natural flow pattern can be maintained, albeit at a lower level than normal during high (wet season) flows because some water must be stored for low-flow augmentation. The value for Q_{max} must overlap, or coincide with, the timing of the natural maximum flows (see Figure 4.2.9). The magnitude of the maximum and minimum flow released from the reservoir depends on the storage capacity of the reservoir, the design capacity of the outflow control structure(s) and stream-flow requirements for sediment transport. The following conditions are considered:

- the maximum flow released should be set so that the flow is large enough to restore the natural size of the river channel by removing fine sediments and any other detritus deposited during low flows, and
- the remaining stored water volume should be sufficient to maintain the minimum flow required for fish passage and water quality targets during low-flow periods of the year.

Despite the fact that there is insufficient information for the calculation of exact values of the above flows, the usefulness of this approach can be demonstrated by choosing Q_{min} on the basis of the water quality target of TDS and inorganic nitrogen, and setting Q_{max} during high flow such that the remaining stored water volume is sufficient to maintain the minimum flow required during low flows. The influence of the above proposed new flow pattern on downstream water quality (i.e. downstream of the Kaap River confluence) was also evaluated.

4.2.5. Results and discussion

4.2.5.1. Model calibration

The model was calibrated on the basis of data collected in 1987 and 1988. The hydraulic model parameters the minimum and maximum water withdrawal were estimated, and the results for the hydraulics and transport of TDS are presented in Figure 4.2.4. The best fit was obtained with the minimum and maximum water withdrawal set at 2 and 4 $m^3 \cdot m^{-1} \cdot d^{-1}$, respectively. The results indicate that trends of the predicted data sets show good agreement with the measured data sets for both river flow rate and the concentrations of TDS. The estimated water use in 1997 was 580 × 10^6 $m^3 \cdot a^{-1}$ (*State of the Crocodile River*, 2001). By normalising this against the total length of the main-stem Crocodile River (320 km) the amount of water lost is approximately equivalent to 5 $m^3 \cdot m^{-1} \cdot d^{-1}$. This is comparable with the calibrated values (ranges between 2 and 4 $m^3 \cdot m^{-1} \cdot d^{-1}$).

The model was also calibrated for inorganic nitrogen using, using nitrate plus nitrite nitrogen (S_{NO}) and ammonia nitrogen (S_{NH}). The concentration of microbial biomass in the model inputs are estimated based on the model fit with the measurement. The best results were obtained with the concentrations of 1.4 mg L^{-1} and 0.34 mg L^{-1} for heterotrophs and nitrifiers

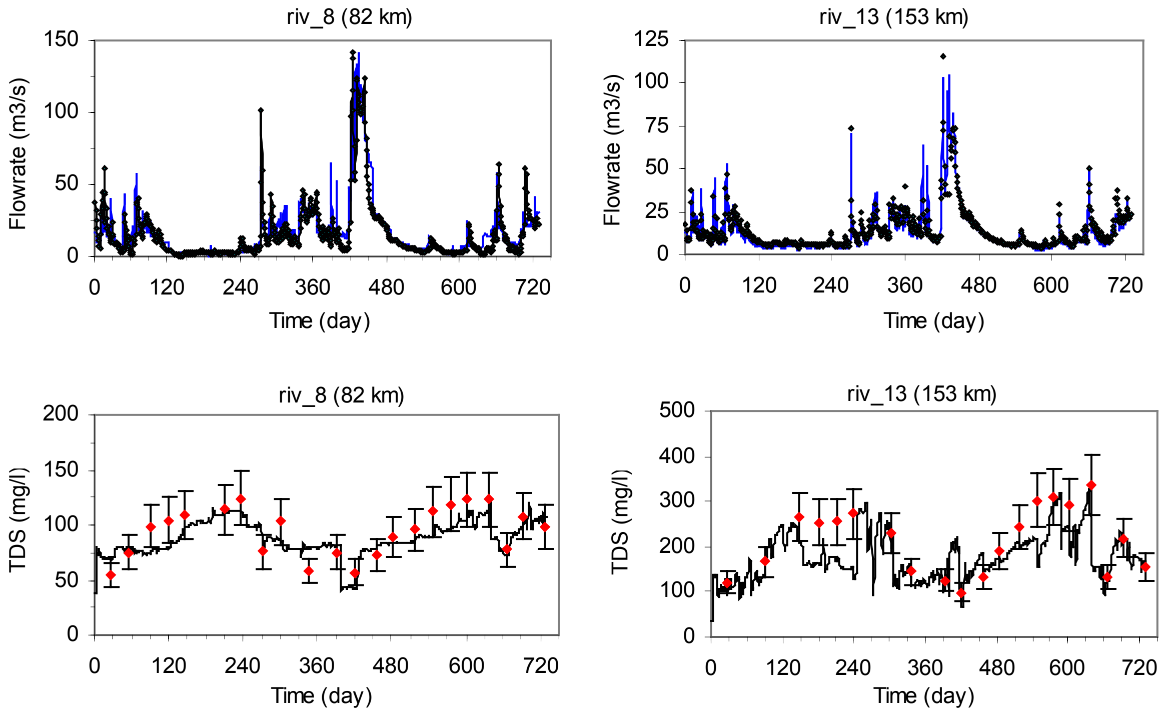


Figure 4.2.2: Model calibration: comparison of measured (symbols) and simulated (lines) data sets of TDS concentrations and river flow rate (using data of 1987-1988) at 82 and 153 km

respectively. The general trend of the model predictions agrees well with the measured data sets within 20 % error (see Figure 4.2.5). Though there are only limited data available (few monthly water quality data), the calibration result for nitrogen is quite satisfactory.

4.2.5.2. Model validation

The model was validated using data from 1989 to 1990, and the results for both TDS and inorganic nitrogen are indicated in Figure 4.2.6. Once again, the results show that predicted data sets agree well with the measured data sets. Like the calibration result, the model agrees well with the measured data set within 20 % error. Note that the nutrient load due to possible point effluent discharge and other small tributaries is not included in the model input. Thus, a higher accuracy of the model prediction will require the availability of many more detailed data, a feature that is seldom possible in practice.

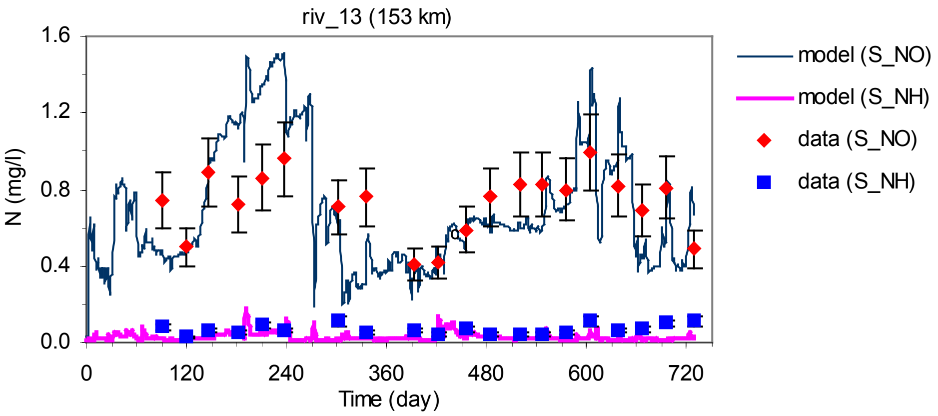


Figure 4.2.3: Model calibration for inorganic nitrogen: ammonia (NH) and nitrate plus nitrite (NO) at the lower end (153 km)

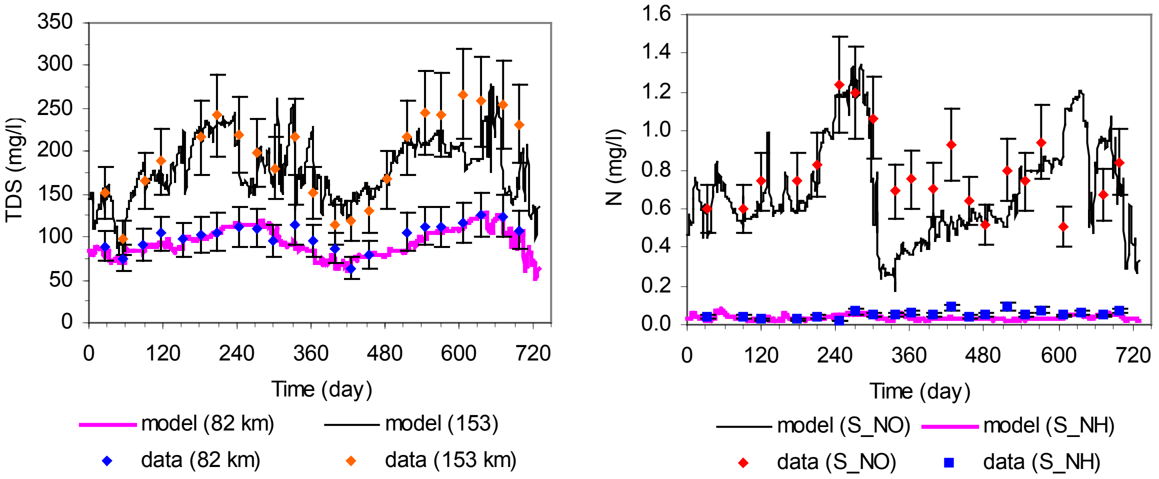


Figure 4.2.4: Model validation: comparison of measured and simulated data sets for TDS concentrations at 82 and 153 km (left), and nitrogen concentration at 153 km (right): NO and NH stand for nitrate and ammonia nitrogen concentration respectively

4.2.5.3. Low-flow analysis: in-stream flow requirement

Using 20 years of flow data prior to dam construction (1960 to 1979), the low-flow analysis (7Q10) results are indicated in Figure 4.2.7. The 7Q10 flows of the Crocodile River were calculated, and its value at the upper point (0.47 $m^3 \cdot s^{-1}$) is higher than that of the lower point (0.21 $m^3 \cdot s^{-1}$). This indicates considerable water losses along the river length. Dubinina and Kozlitina (2000) have indicated that the 90% and 95% probability of exceeding the

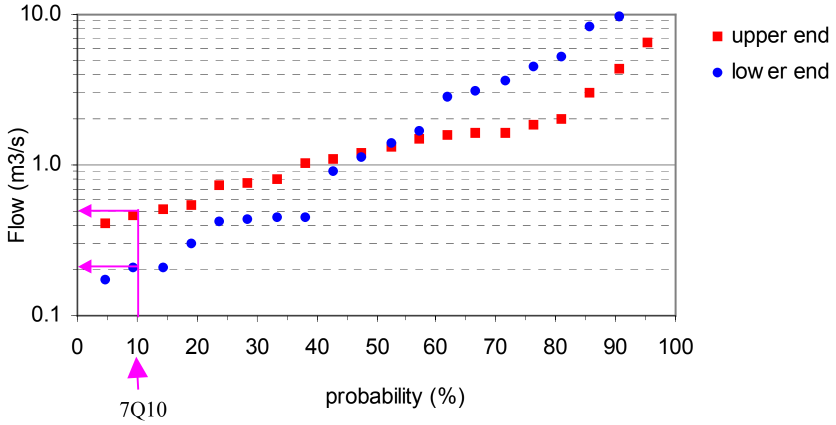


Figure 4.2.5: Low-flow analysis (1960-1979) for the two sites of the Crocodile River: upper end (0 km) and lower end (153 km); Arrows indicate the value of 7Q10, the minimum flow that occurs every 10 years; probability is the cumulative probability of occurrence of the corresponding low-flow rate

corresponding river flow can be used as the critical low base flow and the critical ecological flows, respectively. In Figure 4.2.7, these values correspond to 10% and 5% probability of occurrence, respectively. Based on this method, the value of the critical base flow and critical ecological flows at the lower end of the study site (as it reads from Figure 4.2.6) are 0.21 and 0.17 $m^3 \cdot s^{-1}$, respectively. It should be noted that these critical low flows are clearly far too low to dilute the wastewater effluent discharges and Kaap River inflows nor can they be enough for the ecological reserve in the lower reaches of the Crocodile River. Thus, the above statistical approach is not applicable for rivers in arid and semi-arid regions, where the 95% probability may indicate the likely low flow during drought periods. Furthermore, any additional water abstraction during such critical low flows can accentuate and accelerate further river water quality deterioration.

4.2.5.4. Maximum water withdrawal

The impact of the maximum rates of water withdrawal from the upstream section of the main river on water quality in the downstream section of the Crocodile River was investigated. Using the "pre-dam" flow data from 1989-90, an increase or decrease in the maximum rate of water withdrawal by approximately 30% (1 $m^3 \cdot m^{-1} \cdot d^{-1}$) caused an average increase or decrease in TDS concentrations of some 4% during low-flow periods at the lower point (153 km), but no significant change was observed in nitrogen concentrations (see Figure 4.2.8). This depicts that decreasing the water withdrawal by 1 m^3 m^{-1} d^{-1} can reduce the TDS concentration but it is not significant as compared to the 20% error of the model calibration for TDS concentration (see Figure 4.2.8). However, it still indicates a trend.

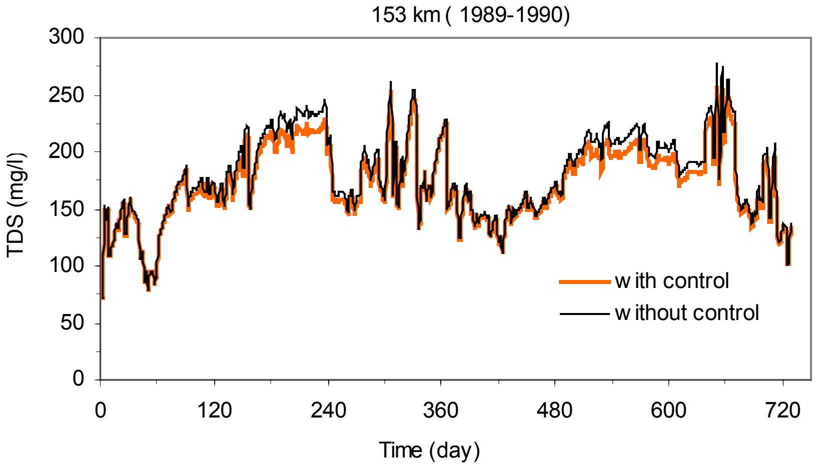


Figure 4.2.6: The effect of 30% reduction of water withdrawal on the TDS concentration at 157 km: with reduction of water withdrawal (with control) and without the reduction of water withdrawal (without control)

Setting an overall limit on the maximum permissible volume of water that can be withdrawn from the river basin during critical low flows can at least help to further reduce water quality deterioration caused by increased quantities of total dissolved salts. Efficient water use can reduce the necessary rate of water withdrawal. For example, using a covered irrigation canal instead of an open canal can reduce water loss by evaporation. Similarly, surface (flood) irrigation systems waste nearly two-thirds of the water used because of evaporation and seepage. Given that almost 50 % of the water used in the Crocodile River basin is used for irrigation, this offers an opportunity to achieve considerable reductions in water losses. A similar consideration is applied in the waste load allocation in the US, where > 1% of the river flow is considered as a significant water withdrawal (DYNATOX, 1985).

Besides, in order to meet the requirements of the European Water Framework Directive (2000/060/EC), the new legislation to control water abstraction in Scotland was also recommended (Dunn *et al.*, 2003). Mechanisms that are proposed to control such abstraction include a license system based on a maximum rate of abstraction combined with abstraction bans when the river flow is exceeded 95% of the time. This again indicates that water abstraction for irrigation becomes an important issue in reducing stream flow not only in arid regions (water poor countries) but also in humid regions (water rich countries).

4.2.5.5. Low-flow augmentation and water release from the reservoir

In addition to its use in setting the maximum limits for water withdrawal, low-flow augmentation was found to be an important management option. The concept of low-flow augmentation used in this study implies the storage of enough water during the wet season (high flow) and then releasing the stored water during the dry season in order to regulate or supplement low flow. The low flow is now supplemented not only on the basis of water quantity required for different uses (e.g. irrigation, domestic and industrial supplies) but also to meet the desired water quality target. With the minimum and maximum outflow rate set at about 5 $m^3{\cdot}s^{-1}$ and 7 $m^3{\cdot}s^{-1}$ respectively, the dynamics of water stored in the control dam (a hypothetical dam at Montrose Weir) are illustrated in Figure 4.2.9. The proposed minimum outflow is maintained as long as the reservoir storage volume is larger than zero. If the storage volume is equal to or less than zero, it indicates the so-called “alarm level” at which there is no longer enough water available for low-flow augmentation.

The minimum flow (at Montrose Weir) that maintains the target water quality (< 260 mg L^{-1} for TDS in irrigation water for sensitive crops; < 0.5 mg L^{-1} for nitrate nitrogen, and < 0.03 mg L^{-1} for ammonia nitrogen) at the lower point of the study area (153 km) was investigated in this study. The result (see Figure 4.2.9) shows that, with a minimum flow of 5 $m^3{\cdot}s^{-1}$ at the upper point of the study site, low-flow augmentation can improve the general downstream water quality (with the exception of nitrite plus nitrate nitrogen concentrations, which are higher in the outflow of the control reservoir than in its inflow (see Figure 4.2.10) due to nitrification. During low-flow periods, the controlled flow releases can reduce salinity (TDS concentration) by 20%, and ammonia nitrogen by 60% at the lower point. However, in the middle of the river section (at about 82 km from the upper point), the concentrations of ammonia nitrogen were reduced by 80%, whereas there was no significant difference in TDS concentrations. Such a large reduction of ammonia concentrations in the middle of the river section is due to dilution and nitrification processes. Besides, relatively low ammonium concentration accentuates the sensitivity of model output.

This method (low-flow augmentation or controlled flow release) can thus improve downstream water quality in TDS and ammonia nitrogen concentrations in the downstream section of Crocodile-Kaap confluence. According to an earlier study, water released from an impoundment that received agricultural runoff and urban effluents could generally improve the water quality of downstream reaches, with the exception of nitrate concentrations (Palmer and Keeffe, 1990). Whilst at least a minimum concentration of phosphorus is required for the growth of nitrifiers, the nitrification process in the reservoir is governed mainly by the

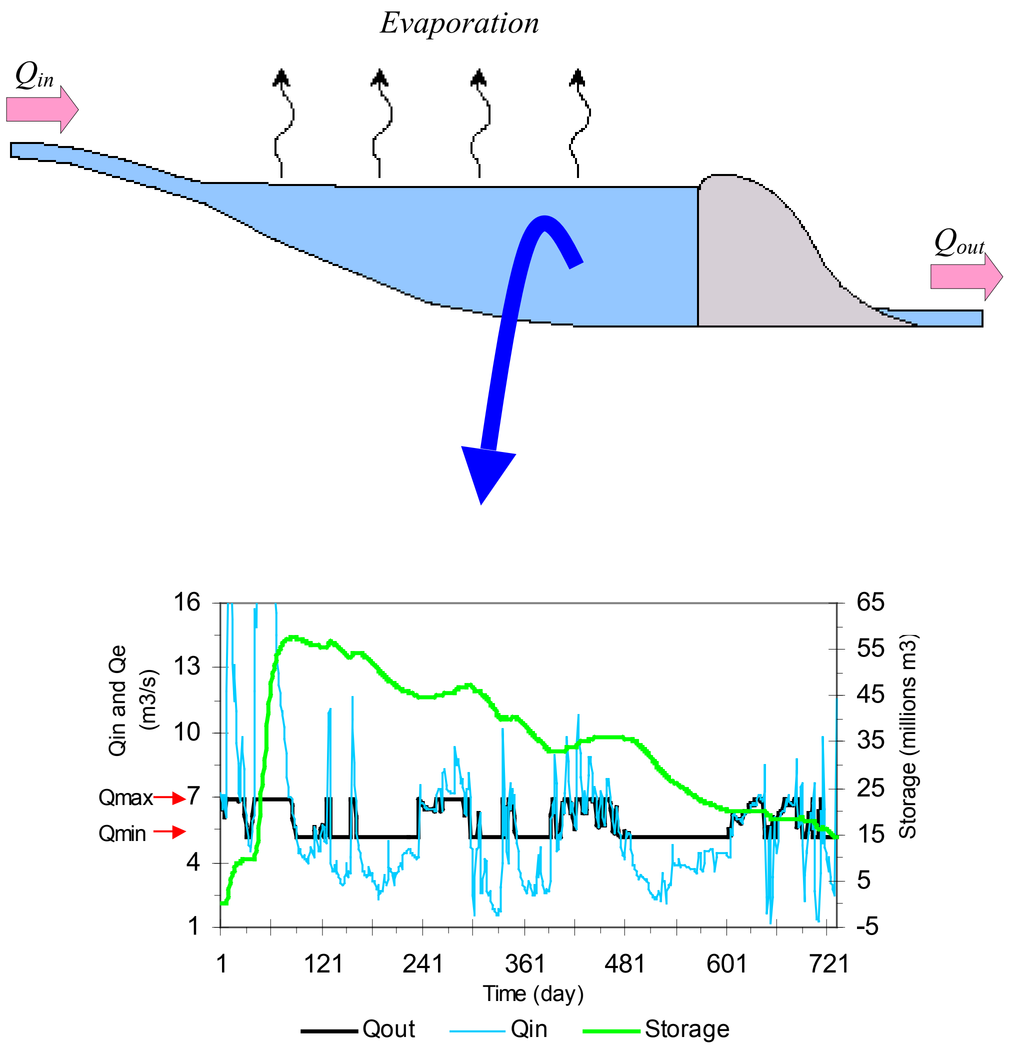


Figure 4.2.7: Controlling water release from the dam (hypothetical) at the Montrose Weir (upper point)

available concentration of ammonia and dissolved oxygen, as well as water temperature. The Palmer and O'Keeffe study shows that as long as these three conditions are satisfied, an increase in the hydraulic residence time of water stored in the reservoir can increase the concentration of nitrate nitrogen in the reservoir. It is therefore up to the water resource manager to decide which water quality parameters should be considered first (e.g. nitrate or ammonia). Ammonia (un-ionized) is however known to be more toxic to aquatic life than nitrate, and therefore, the proposed control option is very useful.

Low-flow augmentation seems to be a useful and cost-effective management option for the Crocodile River because the existing reservoir (Kwena Dam) can be used to regulate the downstream flow. The only change would be the water-release pattern from the dam, which as to be adjusted according to the required target water quality in the downstream reaches of the river. With this control strategy, the highly polluted tributary stream (the Kaap River),

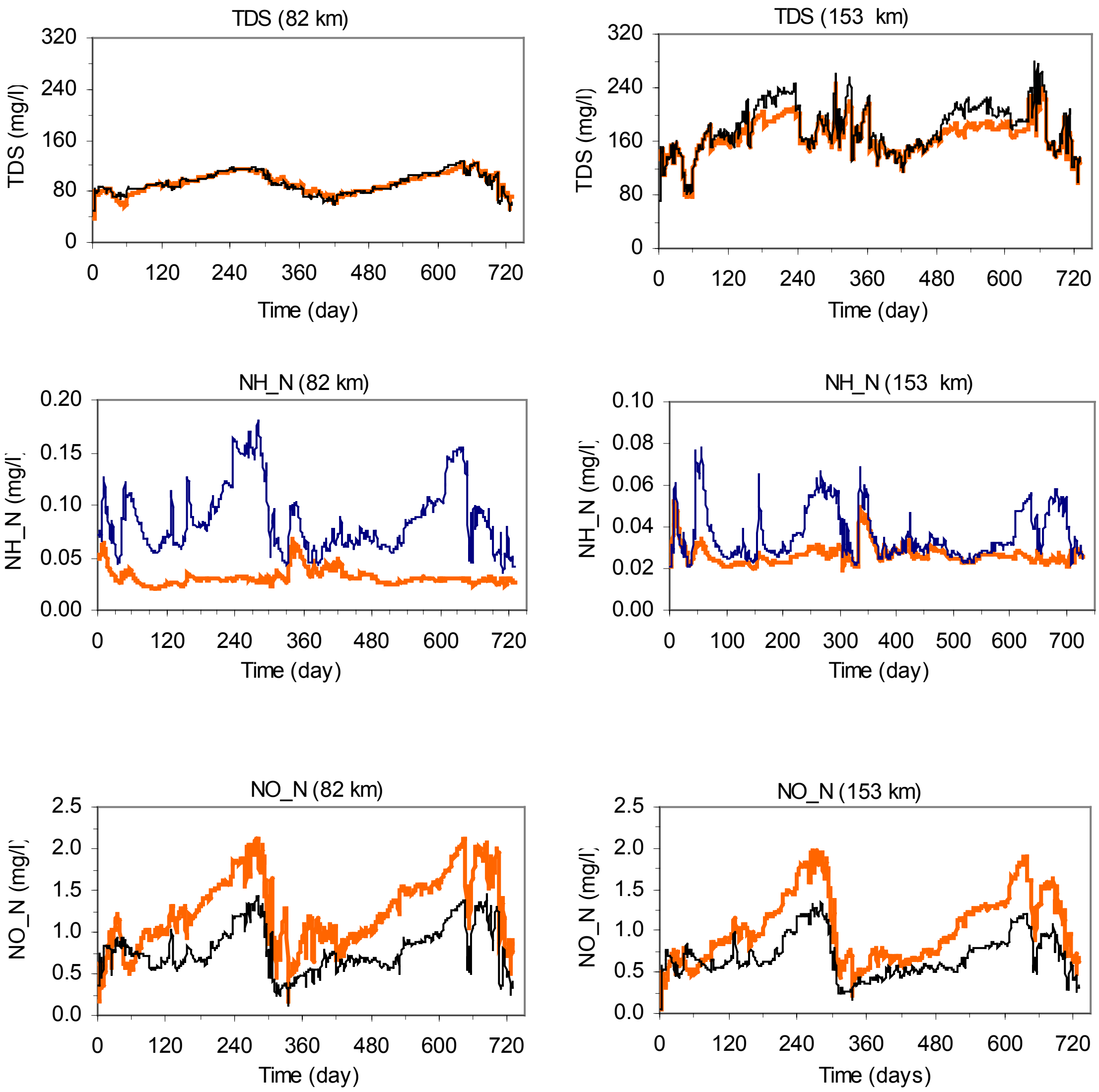


Figure 4.2.8: The effect of low-flow augmentation on the concentrations of TDS, nitrate plus nitrite nitrogen (NO_N), and ammonia nitrogen (NH_N) in the downstream sections of the river at 82 and 153 km (1989-1990): thick light lines stand for augmented, whereas thin dark lines stand for non augmented low-flows

with water quality that has been adversely affected by mining activities and agricultural runoff, can be diluted to improve water quality in the downstream section of the Crocodile River. In the Kaap River, on the basis of data collected in 1989/90, ammonia nitrogen is greater than 0.03 mg L^{-1} in most of the time, whereas the nitrate nitrogen concentration is greater than 0.6 mg L^{-1}, and the TDS concentration can reach about 700 mg L^{-1} during low flow). The adverse impacts of the Kaap River and the Nelspruit and Malelane wastewater effluents can be controlled by strict adherence to effluent-discharge standards and by controlling water releases at the upstream point. Importantly, the general water balance should be conserved, so enough water should be stored during the rainy season so that it can be used for later low-flow augmentation during the dry season. If insufficient rain falls during the preceding rainy season and insufficient water is stored in the control volume or reservoir, another alternative must be considered. In such a case, the second approach, namely that of setting a strict limit on the quantity of water that can be withdrawn could reduce the adverse effects associated with extremely low flows.

4.2.6. Conclusions and recommendations

In this study, different water quality management alternatives were evaluated by using the proposed model. Based on the results obtained, two catchment-based water quality control strategies can be proposed for further testing and possible use on a routine basis.

The first proposed control strategy focuses on setting strict maximum limits for water withdrawal during periods of low flow, and ensuring that there is always a minimum river flow available to maintain the target water quality during the dry season. This method is applicable when rivers do not normally experience frequent extremely low flows.

The second control strategy, low-flow augmentation by an upstream reservoir is proposed when rivers experience frequent low flows, for example in arid and semi-arid regions. In this control strategy, the relationships between reservoir operation and the resultant river water quality in downstream reaches should be well understood. As shown, regulating the flow pattern of water released from the Kwena Dam can achieve a remarkable reduction in the TDS and ammonia nitrogen concentration in the lower reaches of the Crocodile River. Ideally, the augmented flow pattern should follow or mimic the seasonal pattern of unregulated river flows. Based on flow data for 1987 to 1990, the minimum flow at the upper point of the Crocodile River study site should be at least 5 $m^3 \cdot s^{-1}$ so that the salinity (TDS) and ammonia concentrations in downstream reaches can be improved.

Importantly, one should also note that the proposed management options are not a standalone solution to guarantee the defined water quality objectives. There should be an integrated water quality control strategy, and thus, in addition to the proposed management options, effluent quality standards and diffuse pollution regulation should always be considered.

This study has shown that the proposed model has great potential for use as a basin-wide water quality management tool. The model used in this study is relatively simple and can be used for short-term (monthly) predictions of TDS and inorganic nitrogen concentrations.

Part 5

In-stream fate modelling of Organic contaminants

Chapter 5.1

Dynamic in-stream fate modelling of organic contaminants[1]

The important parts of this chapter were published as:

[1] Deksissa T., De Pauw D. and Vanrolleghem P. A. (2003). Dynamic in-stream fate modelling of Xenobiotic organic compounds: A case study of LAS in the river Lambro. *Environ. Toxicol. Chem.,* Vol. 23, No. 9, in press.

Chapter 5.1

Dynamic in-stream fate modelling of organic contaminants (CHETOX1)

In this Chapter, a conceptual, one-dimensional dynamic organic contaminant fate model (CHETOX1) is presented. The usefulness of the model was tested on the basis of Linear Alkylbenzene Sulfonates (LAS), an active ingredient of detergents, in the river Lambro (Italy), as a case study. The model is coupled with a basic water quality model in order to allow one to investigate the interaction of nutrient dynamics and organic contaminant fate. The model output sensitivity to the model input parameters was also analysed. Besides, scenario analysis in relation to the comparison of steady-state with dynamic simulation, and the effect of nutrient dynamics on the fate of LAS are presented. The results show the usefulness of the proposed model for the short-term simulation of organic contaminant fate in rivers, particularly in non-steady environmental conditions.

5.1.1. Introduction

The current exposure assessment in the European Union is based on the generic multimedia ‘unit world’ approach fate model, a steady-state level III fugacity model (Mackay, 2001). Such models have been indicated to have the following limitations (Sweetman *et al.*, 2002). It cannot be readily validated because environmental conditions are not at steady-state. It does not describe the time course of recovery, which is related to the environmental persistence, after emission reduction. The exposure concentrations of environmental pollutants can be variable due to varying rates of input and dilution, changes in chemical form and solubility, and degradation. Furthermore, different circumstances such as runoff events or sewer overflows can also result in time-varying exposure concentration.

Such time-varying exposure concentration can result in a time-varying toxic response (effect). With such time-varying exposure concentration, toxicity depends not only on exposure concentration (exposure amplitude) but also on the exposure duration and exposure frequency (Reinert *et al.*, 2002). For example, a lower exposure concentration requires either a longer period or a more frequent exposure to result in the same adverse effect or toxicity as for a higher concentration. A dynamic simulation provides a time series output of exposure concentrations based on which exposure frequency and duration can be derived.

Consequently, a dynamic in-stream fate model is proposed for the investigation of a time dependent exposure concentration: to simulate the time profile of pollutant concentrations in different environmental compartments, to investigate a short-term (high temporal resolution e.g. daily and sub-daily) and long term variation of exposure concentration.

Despite the fact that there might already exist dynamic in-stream fate models for basic water quality and organic contaminant fate, there are still some practical problems to apply such models in integrated water quality studies. Three major problems can be considered. First, the flow propagation in rivers is often described by a complex hydrodynamic model using the St. Venant equations (De St. Venant, 1971). The application of full St. Venant equations in integrated water quality studies results in long computation times, and detailed information about the system is needed, which is not often the case. As an alternative, a conceptual hydraulic model, a series of Completely Stirred Tanks Reactor in Series (CSTRS), was proposed (Meirlaen *et al.*, 2001).

The second problem is that the traditional organic contaminant fate models are treated separately as a single-issue model (considering either conventional pollutants or fate of organic contaminants) despite the fact that the effect of both conventional pollutants (nutrients enrichment or eutrophication) and contamination by xenobiotic organic pollutants may interact in many direct or indirect ways (Koelman *et al.*, 2001). Eutrophication may reduce the concentration of organic contaminants by increasing amounts of microbial biomass, enhancing biodegradation in the presence of oxygen, organic contaminant scavenging by suspended particulate organic matter (POC), sedimentation of contaminants and contaminant uptake in the food chain. Besides, organic contaminants may have a direct or an indirect toxic effect on aquatic organisms, which in turn affects the organic contaminant fate and nutrient cycles (Legovic, 1997). As single-issue models do not address these interactions, coupling of basic water quality to organic contaminant fate is very essential.

The third problem is selecting an appropriate single-issue basic water quality (eutrophication) and organic contaminant fate submodels. The most widespread eutrophication model for rivers is the QUAL2 (Brown and Barnwell, 1985) type model. But, it has many limitations (see Chapter 2 of this work in sub section 2.4.6.1) that are also important for exposure modelling. The sediment is not considered as state variable, and thus the mass balance is not complete. Furthermore, despite the fact that bacteria determine and control the rates of biotransformation processes, this model does not consider bacteria as state variable, and cannot therefore handle an increase or decrease of biomass concentration. A suitable basic water quality model must thus be coupled to an appropriate organic contaminant fate model, with sufficient complexity, in order to make scenario analyses.

Concerning the background information of the existing organic contaminant fate submodels including their limitations, details are given in Chapter 2 subsection 2.4.7.1. Based on extensive literature studies, it is found that the state-of-the-art fugacity based organic contaminant fate submodels are not suitable for the short time simulation of integrated basic water quality and fate of organic contaminants in rivers. For example, a dynamic multimedia fugacity model level IV (Mackay, 2001 applies only for a long simulation time (yearly basis) (Sweetman *et al.*, 2002).

Hence, for short-term emission management in non-steady-state conditions, we still need an alternative dynamic exposure model that takes into account both spatial and temporal variability, and is suitable for integrated modelling of basic water quality and organic contaminant fate.

In this Chapter, to tackle the three main problems explained above, attempts have been made to develop a relatively simple dynamic in-stream fate model that takes into account the interaction of nutrient dynamics and organic contaminant fate, and can be applied for short term simulation. A simple completely mixed tank-in-series model (CSTRS) was applied as a surrogate model for the complex hydrodynamic model (the St. Venant equations) (de St. Venant, 1971).

In addition to transport, the biochemical conversion submodels that contain both basic water quality and organic contaminants are set so that the model can simultaneously simulate the basic water quality (nutrient dynamics) and organic contaminant fate in rivers. This allows one to investigate the effect of nutrient dynamics on organic contaminant fate in rivers. Subsequently, the IWA River Water Quality Model No.1 (*RWQM1*) (Reichert *et al.*, 2001) was extended to include the organic contaminant fate model.

Furthermore, the proposed model considers both the bulk water and benthic sediment compartments as state variables in which, in addition to many physicochemical processes, detailed processes descriptions for biodegradation processes are presented. The usefulness of the proposed model is presented by using Linear Alkylbenzene Sulfonates (LAS), which are widely used anionic surfactants in synthetic detergents for household and industrial use, as a case study in the river Lambro. A comparison of the proposed model predictions and monitoring data is presented. Furthermore, a sensitivity analysis, the comparison of dynamic and steady-state simulations, and a scenario analysis are given.

5.1.2. Case study

The study was conducted at the river Lambro in Italy (see Figure 5.1.1). The Lambro river catchment is located to the North of Milan with a total drainage area of about 1950 km^2. The river Lambro flows Southwards from the Pre-Alps (1450 m asl) to the confluence with the river Po (50 m asl), and has an approximate length of 130 km. The average annual rainfall varies between 900 mm and 1500 mm. The site under consideration is limited to the part of the river Lambro between Mulino de Baggero (as upstream end), and Biassono (as downstream end) (Figure 5.1.1). The area drained by this river section at Biassono covers 400 km^2. Just downstream Mulino de Baggero, the most relevant pollutant discharge in this

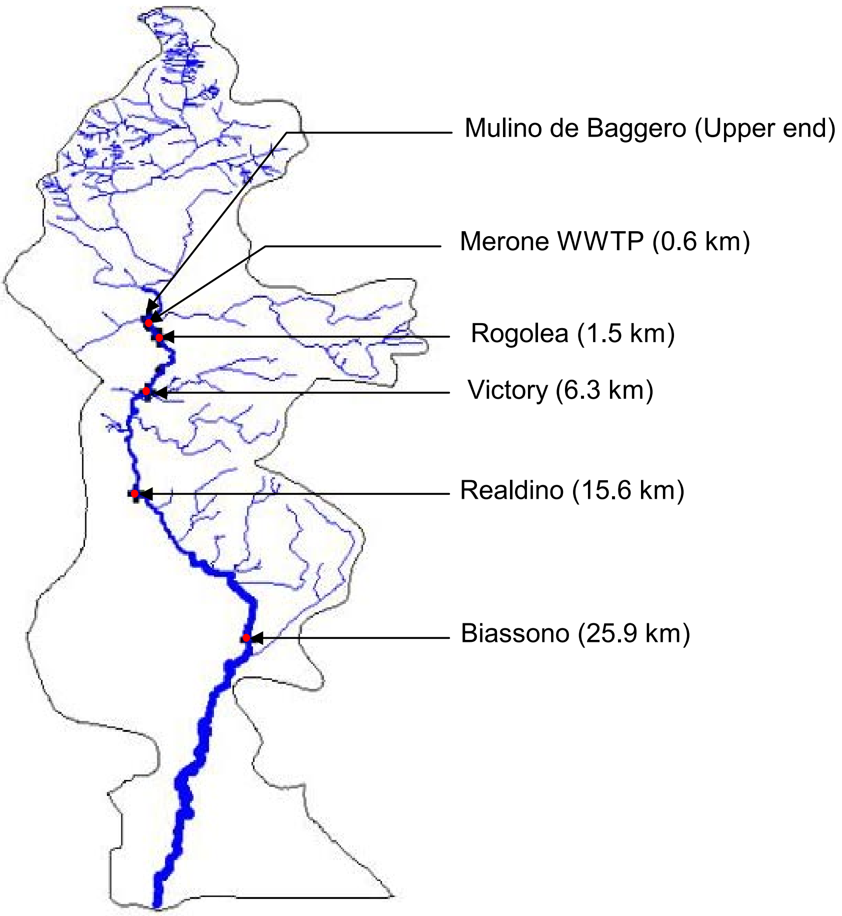


Figure 5.1.1: The Lambro River catchment with water quality measurement stations

section is from the wastewater treatment plant (WWTP) in Merone. The river receives a variable WWTP effluent and Combined Sewer Overflows (CSOs) from a pollution equivalent of 118,200 inhabitants, which produce in total 1400 m^3 d^{-1}. The holding capacity of the WWTP is only 1000 m^3. There is 400 m^3 d^{-1} sewer overflow, and thus the river is contaminated every day by sewer overflows. For this study site, two-hourly measured data sets of two days in February and May 1998, and ten days of daily flow and water quality data are available (Whelan *et al.*, 1999), on which the water quality modelling and evaluation was done. Note that the capacity of the wastewater treatment plant is upgraded, and currently treating at full capacity.

5.1.3. Methods

Model development activities conducted in this study can be divided into 9 component steps: (1) hydraulics, (2) biochemical conversion, (3) general mass balances, (4) generic organic contaminant mass balances, (5) DOC and POC mass balances, (6) parameter calculation, (7) model implementation, (8) model calibration and validation and (9) sensitivity analysis.

5.1.3.1. Hydraulics

For easy application of biochemical conversion mass balances and fast computation, a conceptual hydraulic modelling approach such as the completely mixed tank-in-series modelling (Beck and Reda, 1994) is applied as a surrogate model to typically used complex hydrodynamic model. Like the hydrodynamic model, the tank-in- series model can be applied to time-variable or non-steady flow conditions. The principle is that each tank (river stretch) has a time-variable volume with the outflow rate being increasing with the water level in the tank. A time-variable volume approach requires minimum hydraulic information such as stage and discharge measurement in time, stage/discharge relations or cross-sectional area/stage relation ships. Based on such minimum hydraulic information, the main hydraulic equations that are required to formulate a water quality submodel are given below.

In a mixed tank-in-series model, the hydraulics of every river tank-in-series can be expressed as follows:

$$\frac{dV}{dt} = Q_{in}(t) - Q_{out}(t) \tag{5.1.1}$$

$$Q_{out} = \alpha h^2(t) - \beta h(t) + \gamma \tag{5.1.2}$$

where V is the volume of the tank at time t [m^3], $Q_{in}(t)$ and $Q_{out}(t)$ are the inflow rate and the outflow rate at time t [m^{3}d^{-1}], respectively; h is the hydraulic depth [m]; α, β and γ are river specific hydraulic parameters, which are typically estimated on the basis of stage-flow relation ships.

In equations 5.1.1 and 5.1.2, V, Q_{in}, Q_{out} and h are time-variable. Equation 5.1.1 can be used to approximate both steady-state and dynamic hydraulics. Under dynamic conditions, the ordinary differential equation must be solved numerically.

Equation 5.1.2 can be easily formulated based on the analysis of field stage-flow relationships. Assuming river reaches have a trapezoidal cross-section (see Figure 5.1.2), the cross sectional area A_{cross} and the flow depth h can be calculated as follows (Neitsch *et al.*, 2000):

$$h(t) = \sqrt{\frac{A_{cross}(t)}{Z} + \left(\frac{W}{2Z}\right)^2} - \frac{W}{2Z} \tag{5.1.3}$$

$$A_{cross}(t) = \frac{V(t)}{L} \tag{5.1.4}$$

where $A_{cross}(t)$ is the cross sectional area at time t [m^2]; L is the length of river tank (m); Z is the inverse of the river channel slope [-], and W is the bottom width [m].

If the flow rate is constant, equation 5.1.1 becomes steady-state. One may use a constant or average flow with time-variable concentration as model input in order to simulate the temporal variation of concentrations. In this study, both the constant flow (average flow) and time-variable flow conditions are considered and a comparison of the results is presented.

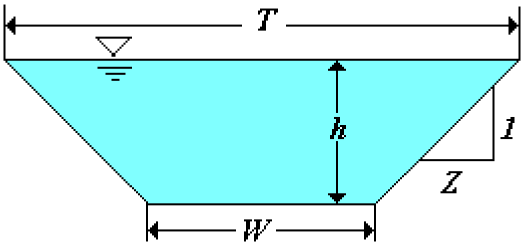


Figure 5.1.2: Trapezoidal river cross-section with top width T, bottom width W, water depth h, and channel slope 1/Z in cross section

5.1.3.2. Biochemical conversion

The biochemical conversion term involves all relevant governing equations that determine the fate of pollutants. It refers to the water quality submodel that includes physicochemical and biochemical processes taking place in the system. The biochemical conversion term is differentiated into two categories: the basic water quality (nutrient dynamics and microbial biomass growth) and organic contaminant fate.

Basic water quality

On the basis of the advantages described in the introduction part of this Chapter, the IWA River Water Quality Model number 1 (*RWQM1*) (Reichert *et al.*, 2001) was selected for the basic water quality submodel. The *RWQM1* is a set of equations that can be implemented in any suitable modelling and simulation software. It was developed to be a standard river water quality model in terms of conventional pollutants such as nutrients, suspended solids and algal blooms. The kinetics of the transformation processes are formulated on the basis of Monod kinetics, and the stochiometric coefficients are calculated by taking into account both elemental and mass balances. In contrast to *QUAL2E* (Brown and Barnwell, 1987), *RWQM1* takes into account both suspended and benthic microbial biomass as state variables, and therefore the model can handle the variation of microbial biomass and associated processes.

As the *RWQM1* was developed as a comprehensive river water quality model, and it is a relatively complex eutrophication model with many model parameters and state variables (Reichert *et al.*, 2001), its simplification is highly recommended for practical applications. The procedure for model simplification or sub-model selection is documented in Vanrolleghem *et al.* (2001). Subsequently, the simplified model presented in Chapter 4.1 was applied.

Organic contaminant fate

The simplified *RWQM1* model was extended again with an in-stream fate model of xenobiotic organic pollutants so that the model can be used to study the effect of conventional-pollutant dynamics (nutrients, carbonaceous organic matter as Biological Oxygen Demand (BOD), and suspended solids) on the fate of xenobiotic organic contaminants. For instance, consider the aerobic biodegradation of xenobiotic organic chemicals. The concentration of dissolved oxygen (DO) and heterotrophic biomass will determine the biodegradation rate. However, both dissolved oxygen and heterotrophic biomass concentration are also affected by the concentration of BOD in the water. A high concentration of BOD, on one hand, can result in low dissolved oxygen concentrations that will consequently decrease the aerobic degradation rate of the xenobiotic organic chemical under consideration. On the other hand, a BOD load can stimulate the growth of biomass, which can increase the degradation rate of the organic contaminant. Thus, integrated modelling of basic water quality and organic contaminant fate can provide valuable information related to the interaction of nutrient dynamics and xenobiotic organic contaminants fate.

The organic contaminant fate submodel was formulated based on a simple mass balance. The biochemical conversion processes that are included in this submodel are biodegradation, volatilization, sedimentation, resuspension and mass transfer between bulk water and benthic sediment. In the biodegradation processes, the distinction was made between bulk water and biofilm biodegradation, and their detailed mathematical expressions are presented below.

Figure 5.1.3 indicates the scheme of the overall model structure for the fate of xenobiotic organic chemicals in the river system (CHETOX1). Three environmental compartments: air, water and benthic sediment (the active sediment layer) are considered. If one ignores atmospheric deposition in the river under consideration, the air compartment can be considered as a sink for volatile compounds. The water compartment is further subdivided into three sub-compartments: the truly dissolved phase (TD_w), the sorbed phase to the suspended particulate organic carbon (POC_w) and the sorbed phase to the dissolved organic carbon (DOC_w). The benthic sediment also is subdivided into POC in the bulk volume of the benthic sediment (POC_{bed}), the truly dissolved phase in the pore water (TD_{bed}) and the fraction sorbed to the dissolved organic carbon in the pore water (DOC_{bed}). The air compartment and volatilisation processes are included in the model for a generic compound but will not be considered for the LAS case study as it is not volatile.

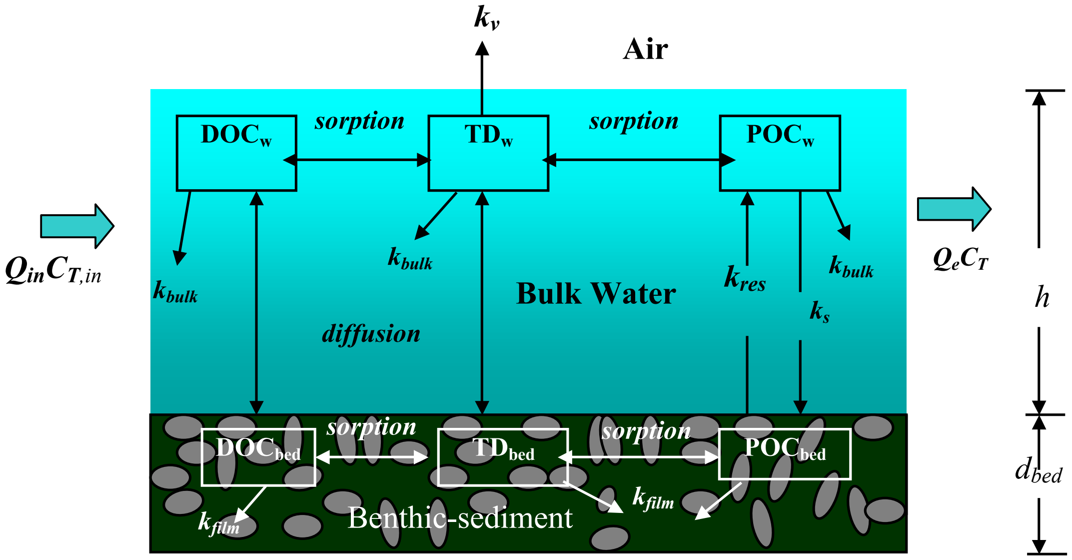


Figure 5.1.3: Schematic representation of the in-stream fate mode (CHETOX1)

5.1.3.3. Mass balances

General

Combining transport/hydraulics (equation 5.1.1) and biochemical conversion submodels, the general mass balances of a substance in a completely mixed tank-in-series can be described as follows:

$$\frac{d(VC)}{dt} = Q_{in}(t)C_{in}(t) - Q_{out}(t)C(t) + rV(t) \qquad (5.1.5)$$

where *dVC/dt* is the change of mass of the substance over time (accumulation); C_{in} and C are inflow and outflow concentrations respectively; r is the net conversion rate of the substance (mg L^{-1} d^{-1}).

In equation 5.1.5, r is given as the sum of the products of process rates and the stoichiometric coefficients of the substance as documented in (Reichert *et al.*, 2001) for the basic water quality submodels. The basic water quality submodel refers to the biochemical reaction equations for nutrients (both inorganic substrates and organic substrates), total suspended solids, and microbial biomass. In the process equations, Monod limitation kinetics is used. The basic water quality model was extended to link the organic contaminant fate model, in which r can be replaced by $kC(t)$, where k is the overall pseudo first-order rate constant even though the actual biotransformation follows Monod or Michaelis Menten enzyme kinetics (Schnoor, 1996). Selection of this first-order kinetics is based on the fact that the concentrations of organic contaminants in the environment are very low, in the order of microgram per liter, which is considerably lower than the half-saturation constants. Assuming negligible atmospheric deposition, the air compartment is considered as a source/sink, and the mass balances of the generic compound, POC and DOC are presented below for the other two compartments, i.e. water and benthic sediment.

Generic organic contaminant mass balance

On the basis of the hydraulic model (equations 5.1.1 to 5.1.4) and general mass balance (equation 5.1.5), instantaneous local equilibrium assumption and pseudo first-order kinetics, the general mass balances for the total organic contaminant concentration in the bulk water and benthic sediment respectively can be expressed as follows:

Bulk water

$$\frac{d(VC_T)}{dt} = Q_{in}C_{Tin} - Q_{out}C_T - k_{film}\left(f_d + f_{DOC}\right)C_T V - k_{bulk}C_T V - k_V C_T V - k_{sed} f_{POC} C_T V \\ + k_{res} f_{POC,bed} C_{T,bed} V_{bed} + K_{LC}\left(\left(1 - f_{POC,bed}\right)^{C_{T,bed}}\!\big/_{\Phi} - \left(1 - f_{POC}\right)C_T\right)A \qquad (5.1.6)$$

Benthic sediment

$$\frac{d(V_{bed}C_{T,bed})}{dt} = k_{sed} f_{POC} C_T V - k_{film} C_{T,bed} V_{bed} - k_{res} f_{POC,bed} C_{T,bed} V_{bed} \\ - K_{LC}\left(\left(1 - f_{POC,bed}\right)^{C_{T,bed}}\!\big/_{\Phi} - \left(1 - f_{POC}\right)C_T\right)A \qquad (5.1.7)$$

where C_T is the unfiltered/total whole water chemical concentration [g m^{-3}]; $C_{T,bed}$ is the volumetric total chemical concentration in the benthic sediment [g m^{-3}]; k_{sed}, k_v, k_{res}, k_{bulk} and k_{film} are pseudo first-order rate constants for sedimentation, volatilization, re-suspension, biodegradation only in the bulk water, and biodegradation in the benthic sediment or biofilm [d^{-1}], respectively; f_d and $f_{d,bed}$ are the truly dissolved fraction in the bulk water and in the pore water, respectively; f_{POC} and $f_{POC,bed}$ are the fraction sorbed to suspended and benthic sediment POC, respectively; f_{DOC} and $f_{DOC,bed}$ are the fractions sorbed to DOC in the bulk water and pore water, respectively; K_{LC} is the mass transfer coefficient for the organic contaminant; $S_{DOC,bed}$ is the concentration of DOC in the benthic sediment; $S_{POC,bed}$ is the concentration of POC in the benthic sediment; V_{bed} and A are the volume of benthic sediment (m^3) and surface area of the river tank [m^2], respectively; and Φ is the porosity of benthic sediment.

The formulation of equations 5.1.6 and 5.1.7 is based on the following assumptions. The truly dissolved fraction of organic contaminant (f_d) and the fraction sorbed to dissolved organic carbon (f_{DOC}) in the bulk water can be (a) degraded both by suspended microbial biomass (k_{bulk}) and by benthic biofilm (k_{film}), (b) removed by volatilization (k_v) for volatile organic compounds, and (c) removed or gained by mass transfer (diffusion) between benthic sediment and bulk water (K_{LC}). The sorbed fraction in the bulk water is (a) degraded by suspended microbial biomass (k_{bulk}), (b) removed by sedimentation of POC (k_{sed}), or (c) gained by resuspension of POC (k_{res}). Furthermore, the generic compound concentration in the benthic sediment is described in terms of mass of the substance per bulk volume of benthic sediment. In order to get the concentrations of the contaminant in the pore water, the concentrations of substances in the benthic sediment must be divided by the porosity (Φ) as indicated in equations 5.1.6 and 5.1.7.

DOC and POC

In equations 5.1.5 and 5.1.6, DOC and POC are state variables and their mass balances can be formulated using a similar approach in both river compartments. The general mass balance including transport for both organic carbon forms in the bulk water can be formulated as follows:

$$\frac{d(S_{DOC}V)}{dt} = Q_{in}S_{DOC,in} - Q_{out}S_{DOC} + K_{L,doc}\left({}^{S_{doc,bed}}\!/\!_{\Phi} - S_{DOC}\right)A - rV \quad (5.1.8)$$

$$\frac{d(S_{POC}V)}{dt} = Q_{in}S_{POC,in} - Q_{out}S_{POC} - k_{sed}S_{POC} + k_{res}S_{POC} - rV \quad (5.1.9)$$

The general mass balances for the POC and DOC in the benthic sediment can be expressed as follows:

$$\frac{d(S_{DOC,bed}V_{bed})}{dt} = K_{L,DOC}\left({}^{S_{DOC,bed}}\!/\!_{\Phi} - S_{DOC}\right)A \quad (5.1.10)$$

$$\frac{d(S_{POC,bed}V_{bed})}{dt} = k_{sed}S_{POC}V - k_{res}S_{POC,bed}V_{bed} \quad (5.1.11)$$

where S_{DOC} and S_{POC} are the concentrations of DOC and POC respectively, in the bulk water (g m^{-3}); and $S_{POC,bed}$ and $S_{DOC,bed}$ are the concentrations of POC and DOC in the bulk volume of the benthic sediment (g m^{-3}); $K_{L,DOC}$ is the mass transfer coefficient for the DOC between bulk water and benthic sediment [m d^{-1}].

The formulation of the above general mass balances (equations 5.1.6 to 5.1.11) is based on the following general simplifying assumptions:

- Only biodegradation, sorption, sedimentation and resuspension are considered in the decay and transport pathways of the specific chemical.
- As the apparent desorption equilibrium occurs rapidly (Larson, 1990; Hand and Williams, 1987), an instantaneous local sorption equilibrium can be assumed, and an equilibrium partition coefficient can be used. The literature also suggests that when the sorption and desorption processes are faster than the other transformation processes, this assumption holds (Chapra, 1997).
- A constant depth of the active sediment layer is considered, but the sediment solids concentration/density within this depth varies with time.

- The specific compound and sediment-solids loss due to sediment burial is assumed to be negligible. This can be supported considering the suggested value given in literature (Schnoor, 1996) 0.889 mm/yr. This is very low as compared to the sedimentation and resuspension velocity.
- The transport processes for the benthic sediment are assumed to be only sedimentation, resuspension and diffusion. The advection from downstream to upstream and between benthic sediment and the overlaying water is neglected.

Note that the above mass balances (equations 5.1.5 to 5.1.11) can be applied for steady-state conditions by assuming the accumulation term (*d(VC)/dt*) equal to zero. In the dynamic simulation, the ordinary differential equations must be solved numerically.

The total chemical concentration (C_T) given in equation 5.1.6 (in the bulk water) and equation 5.1.7 (in the benthic sediment) is the sum of the truly dissolved phase, C [g m^{-3}], the phase sorbed to the POC, C_{POC} [g g^{-1}], and to the DOC, C_{DOC} [g g^{-1}]. This can be expressed in a general form as follows:

$$C_{T,i} = C_i + C_{POC,i}S_{POC,i} + C_{DOC,i}S_{DOC,i} \tag{5.1.12}$$

Assuming instantaneous sorption equilibrium and that the toxicant associates similarly with both POC and DOC, equation 5.1.12 can be rewritten as follows:

$$C_{T,i} = C_i(1 + K_{OC}(S_{POC,i} + S_{DOC,i})) \tag{5.1.13}$$

where K_{OC} is equilibrium partition coefficient [m^3 g^{-1}]; *i* is the compartment: bulk water or benthic sediment.

5.1.3.4. Model parameter calculation

Partition coefficients

One of important parameters in the contaminant mass balances is the partitioning coefficient K_{OC}, which can be estimated based on either a sorption experiment or QSAR approaches. K_{OC} is often estimated based on the octanol-water partition coefficient (K_{ow}) and the organic carbon content of the environmental compartments (Karickhoff *et al.*, 1979). This approach assumes K_{OC} to be a function of the organic carbon content. It is also called the hydrophobic mechanism, which is indicated not to be a reliable approach to calculate K_{OC} for the chemical under study, LAS (Hand and Williams, 1987). The main reason is that the LAS sorption doesn't correlate well with the organic carbon content, as would be expected for a simple hydrophobic mechanism. As the fraction of organic carbon increases, the cation exchange capacity increases and the surface becomes more negative which consequently diminishes hydrophobic bonding by increasing repulsion. Consequently, the experimentally determined literature value was applied.

When the partition coefficient K_{OC} and the concentration of POC and DOC are known in compartment i, the model parameters f_d, f_{DOC} and f_{POC} in each compartment can be calculated as follows:

$$\begin{aligned} f_{DOC,i} &= \frac{K_{OC} S_{DOC,i}}{1 + K_{OC}(S_{POC,i} + S_{DOC,i})} \\ f_{POC,i} &= \frac{K_{OC} S_{POC,i}}{1 + K_{OC}(S_{POC,i} + S_{DOC,i})} \\ f_{d,i} &= 1 - f_{DOC,i} - f_{POC,i} \end{aligned} \qquad (5.1.14)$$

Note that in a dynamic simulation, both $S_{DOC,i}$ and $S_{POC,i}$ are varying in time (see equations 5.1.8-5.1.11), and hence $f_{DOC,i}$, $f_{POC,,i}$ and $f_{d,i}$ as well.

Equation 5.1.14 is very important for the mass balance of generic organic contaminants and their partitioning in the environmental compartments, and also has a very crucial role in exposure assessment. The sorption of xenobiotic organic compounds to DOC was shown to be the driving force in determining the bioavailability (Chin and Weber, 1998; Traina *et al.*, 1995). The dissolved but sorbed LAS to the DOC (mainly humic substance) is not available for gill uptake. As the sorbed LAS to the DOC is not available for gill uptake, considering the overall dissolved phase in the exposure concentration can overestimate the exposure concentration on the one hand and underestimate the risk on the other hand. Thus, incorporating the third phase partitioning can enable one to take into account the effect of DOC so that a better characterization of the exposure concentration can be obtained.

Pseudo first-order reaction rate constants

As indicated above, only four main processes are considered in the generic organic contaminant fate model: biodegradation, volatilization, sedimentation, and resuspension. For every process, the pseudo first-order reaction coefficient must be calculated. The pseudo first-order reaction rate constants included in the general mass balances (see equations 5.1.6 to 5.1.11) are k_{bulk}, k_{film}, k_v, k_{sed}, and k_{res}. Except k_{bulk} and part of k_{film}, these pseudo first-order reaction rate constants were estimated based on existing relations given in literature as described below.

Biodegradation

The degradation kinetics of organic contaminant is typically described as a first-order kinetics without coupling to the limiting substrate (Schnoor, 1996). Chemicals like LAS do not degrade in the absence of oxygen. Hence, coupling dissolved oxygen to the degradation of organic contaminant for such type of chemicals is essential. Therefore, assuming that the same rate constant holds for the sorbed and the dissolved phases (Larson, 1990), because of rapid sorption/desorption (Hand and Williams, 1987), the pseudo first-order biodegradation rate constant for total LAS in the bulk water, $\boldsymbol{k_{bulk}}$ [d^{-1}] can be calculated with the following relation:

$$k_{bulk}(t) = k_{b,bulk}\left(\frac{S_{O2}(t)}{K_{O2}+S_{O2}(t)}\right)X_H(t) \tag{5.1.15}$$

For slow sorption and desorption, as it is possibly the case for other organic contaminants, assuming the same degradation rate constant (equation 5.1.15) cannot be applied. In that case, k_{bulk} can be calculated as follows by introducing a biodegradable fraction for the sorbed phases:

$$k_{bulk}(t) = k_{b1}\left(f_d + f_{POC}\varepsilon + f_{DOC}\theta\right)\cdot\left(\frac{S_{O2}(t)}{K_{O2}+S_{O2}(t)}\right)X_H(t) \tag{5.1.16}$$

where k_{b1} is the second-order biodegradation rate constant [$m^3\ g^{-1}\ d^{-1}$]; S_{O2} is the dissolved oxygen concentration [gm^{-3}]; X_H is the heterotrophic biomass concentration [$g\ m^{-3}$]; ε and θ are the biodegradable fractions for LAS sorbed to suspended particulates and DOC respectively. Note that both S_{O2} and X_H are time-variable.

The heterotrophic biomass, X_H, is assumed to be the concentration of 'all rounder' heterotrophic organisms that can grow aerobically and many of them also anoxically (denitrification). Such assumption is typical in activated sludge models and is also used in *RWQM1*. It was followed here for the sake of model simplicity. These organisms are therefore responsible for metabolizing or degrading all degradable organic substances. Since LAS does not degrade under anoxic conditions, only aerobic growth of X_H is considered.

In addition to bulk water biodegradation, biofilm biodegradation is included in the model because the activities of a biofilm attached to the riverbed of shallow streams may be predominant in the biodegradation process (Takada, 1994; Boeije *et al.*, 2000). With the assumption that the rate of diffusion is balanced by the rate of substrate biodegradation in the biofilm (steady-state), the biofilm pseudo first-order biodegradation rate constant can be approximated by the method presented elsewhere (Melcer *et al.*, 1995).

$$\begin{aligned} k_{film}(t) &= a_f(t)\,K_L\,\frac{D_f r \tanh(rL_f)}{D_f r \tanh(rL_f)+K_L} \\ r &= \sqrt{\frac{X_f k_{b2}}{D_f}} \qquad (5.1.17) \\ K_L &= \frac{D}{L} \qquad\qquad D_f = 0.8D \end{aligned}$$

where a_f is the specific interfacial area at a time t [m^2m^{-3}], K_L is the external mass transfer coefficient [md^{-1}], D is the molecular diffusion rate constant in the bulk water [m^2d^{-1}], D_f is the molecular diffusion rate constant in the biofilm [m^2d^{-1}], L_f is the biofilm thickness [m], and X_f is the biofilm density [gm^{-3}]; where k_{b2} is the second-order biodegradation rate coefficient [$m^3\ g^{-1}\ d^{-1}$]. For simplification, a single biofilm species with constant biofilm density X_H is assumed; otherwise it leads to a more complicated biofilm model like the one presented elsewhere (Wanner and Reichert, 1996).

The a_f can be roughly estimated from river geometry when assuming a trapezoidal cross-section (see Figure 5.1.4) modified from Melcer and co-workers (1995):

$$a_f(t) = \xi \cdot \frac{2\,\left(h(t)-d_{bed}\right)\sqrt{1+Z}\ +\left(W+Z\,d_{bed}\right)d_{bed}\ a_{bed}}{\left(W+Z\,h(t)\right)\ h(t)} \qquad if\ d_{bed} > 0 \qquad (5.1.18)$$

$$= \xi \cdot \frac{W+2h(t)\sqrt{1+Z^2}}{\left(W+Z\cdot h(t)\right)h(t)} \qquad if\ d_{bed} = 0$$

where ξ is a correction factor for non-plane biofilm surface area (2 m^2m^{-2}), d_{bed} is the active sediment depth (m), and a_{bed} is the bed material specific surface area (100 m^2m^{-3}) (Boeije *et al.*, 2000).

As one notices from equation 5.1.18, k_{film} depends on the river cross-section, which allows k_{film} to vary with the flow depth. As the depth of water increases a_f decreases, which in turn reduces the k_{film}. This reveals that rivers with a high surface area to volume ratio (shallow

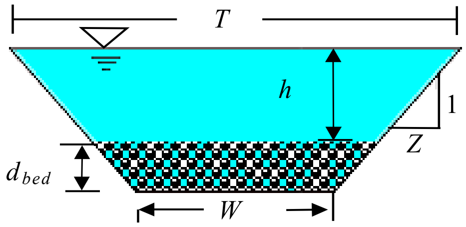


Figure 5.1.4 Schematic representation of active sediment layer (benthic sediment)

rivers) are expected to have higher biofilm activity than deep rivers.

Besides, the pseudo first-order biodegradation rate constants (k_{bulk} and k_{film}) are temperature dependent. The estimated values at water temperature T_w can be calculated based on the temperature correction factor Θ as:

$$k_{i,T_w} = k_{i,T_{ref}} \cdot \Theta^{(T_w - T_{ref})} \tag{5.1.19}$$

Thomann and Mueller (1987) have recommended the following value of Θ:

$$\begin{aligned} \Theta &= 1.047 && \text{if } T_w \geq 19°\text{C} \\ &= 1.187 - 0.00729T_w && \text{if } T_w < 19°\text{C} \end{aligned}$$

where $k_{i,Tw}$ is the pseudo first-order biodegradation rate constant k_{bulk} or k_{film} at water temperature T_w; T_{ref} is the reference temperature; $k_{i,}$ is the rate constant at the reference temperature; Θ is a constant temperature coefficient greater than 1.0 and usually within the range of 1.0 to 1.10 (Schnoor, 1996).

Volatilization

Despite the fact that LAS is a non-volatile compound, volatilization is included in the model because the proposed model is intended also for other xenobiotic organic compounds. For such molecules, a good estimation of the pseudo first-order volatilization rate constant is required. A chemical may be ionized, unionized or sorbed, in which only the unionized and unsorbed fraction α can volatilize. The pseudo first-order rate constant k_v can then be estimated as follows:

$$k_V(t) = -K_V \cdot \frac{A}{V(t)} \cdot \alpha \tag{5.1.20}$$

$$\alpha = \frac{1}{1+10^{(pH-pKa)}} \qquad \text{if it is an acid} \tag{5.1.21}$$

$$= \frac{1}{1+10^{(pKa-pH)}} \qquad \text{if it is a base}$$

where K_v is the overall air-water transfer velocity at time t, which can be estimated based on the well known two-film model of a gas-liquid transfer velocity given elsewhere (Liss and Slater, 1974).

Dissociation of an organic acid or base in water can affect not only volatilization but also solubility, photolysis, sorption and bioconcentration processes of an ionized compound. Although in principle the correction factor (equation 5.1.21) needs to be applied for the sorption process, it is not included in the sorption process assuming its impact is negligible for the chemical under consideration.

Sedimentation and resuspension

In sediment-water interactions, sedimentation and resuspension must be considered. The pseudo first-order sedimentation (k_{sed}) and re-suspension (k_{res}) rate constants can be approximated based on the particle settling velocity U_{sed} and the re-suspension/scouring velocity U_{res} as follows (Schnoor, 1996):

$$k_{sed} = \frac{U_{sed}}{h_m} \tag{5.1.22}$$

$$k_{res} = \frac{U_{res}}{h_m} \tag{5.1.23}$$

where U_{sed} is the settling velocity [m d^{-1}], U_{res} is the re-suspension velocity [m d^{-1}], and h_m is the mean water depth [m].

Note that according to the state of the art, the settling velocity is estimated using Stoke's law (Schnoor, 1996) in which the settling velocity is linearly dependent on the particle density and quadratically dependent on the particle diameter. It also depends on the shape of the particles (e.g. spherical particles settle faster than non-spherical particles of the same equivalent diameter). As particles in natural waters have a range of diameters and have complex shapes, it is practically difficult to calculate the U_{sed} with Stoke's law. Similarly, the resuspension velocity U_{res} depends on a number of factors: the magnitude of shear stress exerted at the bottom, the horizontal flow velocity, and the type of bottom sediment. This implies that both U_{sed} and U_{res} depend on many factors, which require more unknown parameters to be estimated. Subsequently, we decided to use literature values as an initial guess and obtain the real value by calibration (see Table 5.1.2). Chapra (1997) indicated that the sedimentation velocity ranges between 0.1 and 1 m d^{-1} for natural organic matter. The resuspension velocity is also indicated to be in the range of 0 and 0.008 m d^{-1} (Schnoor, 1996; Ambrose *et al.*, 1988).

5.1.3.5. Model implementation

The proposed model was implemented in the WEST® modelling and simulation software (Vanhooren *et al.*, 2002). Figure 5.1.5 shows the configuration of the complete tank-in-series model in WEST® simulator for the river Lambro case study. The WEST® simulator has been applied mainly to wastewater treatment plant systems. However, this simulator can also be applied readily to river water quality systems by extending the open “modelbase”. This simulation software is materially not different from other simulation software packages but has some important advantages: it does not require prior knowledge of any programming language; the tank-in-series model and the integrated water quality study that considers the interaction between a wastewater treatment and the receiving water can be easily implemented; and a large “modelbase”, sensitivity and optimization tools are already available.

5.1.3.6. Model calibration and validation

The calibration procedure includes two steps. First, the optimum number of tanks-in-series (see Figure 5.1.5) for the pollution transport is determined, and second the model is calibrated for its reaction parameters. In the tank-in-series model, the number of tanks determines the dispersion of the substance in the system. The higher the number of tanks one uses the less the dispersion of the substance will be. The optimum number of tanks-in-series can be determined on the basis of a tracer study in which a pulse of an inert substance is followed as it proceeds

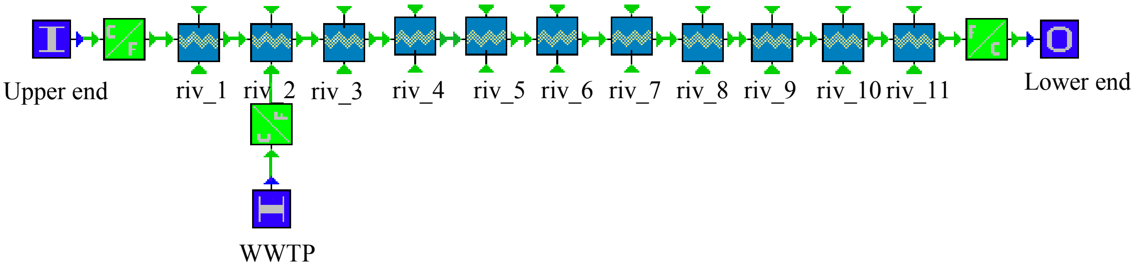


Figure 5.1.5: Tank-in-series model for the river Lambro: Upper end is the upstream input, WWTP is the side stream wastewater discharge, riv_1 to riv_11 are river reaches that are internally subdivided in a total of 47 tanks-in-series

downstream. For this case study, the optimum number of tanks-in-series has already been determined in a previous study that includes river water quality modelling using boron as a tracer (Meirlaen *et al.*, 2001). In this study, 47 tanks were considered to represent an acceptable compromise between calculation time and accurate representation of the river system under consideration.

As indicated in Figure 5.1.5, the river was divided into 11 different river stretches and each of these is internally further subdivided into a number of equal size tanks-in-series (see Table 5.1.1).

Table 5.1.1: Description of river tanks in the river Lambro

River- reach	Number of tanks	Tank Length (m)	Monitoring sites
riv_1	1	600	Mulino-Merone
riv_2	1	477	Merone-Sect_Rogo
riv_3	1	477	Merone-Rogolea
riv_4	4	602.75	Rogolea-Section_1
riv_5	4	602.75	Section_1-Victory
riv_6	6	514.17	Victory-Section_2
riv_7	6	514.17	Section_2-Section_3
riv_8	6	514.17	Section_3-Realdino
riv_9	6	570.33	Realdino-Section_4
riv_10	6	570.33	Section_4-Section_5
riv_11	6	570.33	Section_5-Biassono
Sum	47	26000	

Subsequently, the reaction (process) rates were calibrated on the basis of data collected in February 1998 (Whelan *et al.*, 1999) by varying some key parameters given in Table 5.1.2. Such key parameters were selected based on a sensitivity analysis results as indicated in the following sections. The key parameter values were tuned until the best fit between model prediction and measured data sets were obtained. The minimum sum of squared errors is applied to evaluate the fit.

To validate the model, the calibrated model was run for a new data set collected in May 1998 (Whelan *et al.*, 1999), with the physical parameters (e.g. water temperature) and the forcing functions changed to reflect the new conditions. Then, the model performance is evaluated on the basis of qualitative method or looking at the curve fit of simulated data set with the measured data set. As a quantitative method, different statistical methods can be used for model validation, e.g. Mayer and Butler (1993) and Bird *et al.* (2001). In this study,

Table 5.1.2: Parameter values used in the model

	Parameter	Average value	References	Calibration value
1	L_f	0.0001	[23, 30,]	0.0001
2	X_f	30500-60000	[22, 23, 30, 32]	40000
3	d_{bed}	0.001 - 0.1	[31]	0.085
4	a_{bed}	100	[22]	100
5	k_{b2}	0.0048 - 0.035	[23]	0.028
6	U_{sed}	0.1 - 1	[23]	0.25
7	K_{OC}	0.0048 - 0.085	[20]	0.0057
8	U_{res}	0.0-0.005	[30]	0.0008

however, equation 5.1.24 was selected due to the limited available data, as suggested in Garratt (1975) and Zhang *et al.* (2003):

$$U = \sqrt{\frac{1}{n}\sum_{i=1}^{n}\left(y_{i,simul} - y_{i,measrd}\right)^2} \Bigg/ \left(\sqrt{\frac{1}{n}\sum_{i=1}^{n} y_{i,simul}^2} + \sqrt{\frac{1}{n}\sum_{i=1}^{n} y_{i,measrd}^2}\right) \qquad 5.1.24$$

where U is the coefficient that can be used as a quantitative criterion to express the model validity, $y_{i,simul}$ is the simulated value at time i, $y_{i,\ measrd}$ is the measured value at time i, n is the number of data points. The value of U ranges from 0 (when the simulated data overlap perfectly with the measured data, complete fit) to 1 (when the fit is the worst). When the value is below 0.5, it is assumed that the model gives an acceptable fit.

5.1.3.7. Sensitivity analysis

A sensitivity analysis was performed in order to examine the effect of the model parameters and their relative importance to the model predictions. This was done using the WEST® simulation and modelling software (De Pauw and Vanrolleghem, 2003; Vanhooren *et al.*, 2002). Two types of sensitivity can be distinguished. The relative sensitivity S_R and the absolute sensitivity S_A, which can be calculated numerically based on the change in predicted concentration C upon a very small change of each parameter P. To obtain the sensitivity of the model output to the model parameters, first a reference simulation is run without changing the parameter value. Then the parameter value is changed with a very small perturbation factor $\left(\Delta P / P\right)$ (De Pauw and Vanrolleghem, 2003). By evaluating the difference in simulation results (ΔC), both S_A and S_R can be calculated in every time step as follows:

$$S_A(t) = \frac{\Delta C}{\Delta P} \tag{5.1.25}$$

$$S_R(t) = \frac{\Delta C / C(t)}{\Delta P / P} = \frac{\Delta C}{\Delta P} \cdot \frac{P}{C(t)} \tag{5.1.26}$$

Either of the above two equations can be used, but using relative sensitivities is more meaningful than absolute sensitivities, particularly if one is interested to compare the sensitivity of the model to different parameters. In contrast to S_A, the relative sensitivity S_R is indeed unitless, i.e. it does not depend on the unit of C and P.

As the values of the sensitivity for a dynamic simulation are expressed as a time series of sensitivities, i.e. a sensitivity function, the average of the absolute values of S_R is used to rank the relative importance of the parameters as follows:

$$\overline{S_R} = \frac{\sum_{i=1}^{n} \left| S_{R,i} \right|}{N} \tag{5.1.27}$$

where $\overline{S_R}$ is the average relative sensitivity, $\left| S_{R,i} \right|$ is the relative sensitivity at time i, and N is the number of points where the sensitivity is evaluated.

5.1.4. Results and discussion

5.1.4.1. Sensitivity analysis

The model sensitivity to different categories of model parameters such as biodegradation, porosity, sedimentation and resuspension velocity, and partition coefficients was examined. On the basis of relative sensitivity functions (equation 5.1.25), the parameters were ranked on the basis of the average of the absolute values of S_R (equation 5.1.26) (Table 5.1.3). Also, the maximum and minimum absolute values of S_R are given.

The results show that the model is most sensitive to the biofilm biodegradation parameters: d_{bed}, a_{bed}, X_f, and L_{film}, and to the bulk water biodegradation parameters k_{b1}. The model is moderately sensitive to k_{b2} and K_{CL}. The higher sensitivity of the model mainly to biofilm rather than bulk water biodegradation parameters is due to the difference in the microbial biomass density, which is higher in the benthic sediment than in the bulk water. The model is also considerably sensitive to the sedimentation velocity U_{sed} and the partition coefficient K_{OC}. The model is also reasonably sensitive to small changes of the biodegradable fraction of sorbed organic contaminants to the POC and DOC (ε and θ). This indicates that the parameter values of ε and θ need a proper estimation for a chemical with slow sorption/desorption. However, in the LAS case study, previous experimental studies (Hand and Williams, 1987) indicated fast sorption and desorption of LAS and for this situation the equal degradation rate holds, and introduction of ε and θ is not important. The model sensitivity to porosity and resuspension velocity is very low. Thus, exact estimation of their values is not necessary.

Table 5.1.3: Sensitivity analysis with 0.01% perturbation factor

Rank	Parameters	Average $\lvert S_R \rvert$ (%)	maximum $\lvert S_R \rvert$ (%)	minimum $\lvert S_R \rvert$ (%)
1	d_{bed}	2.316	4.772	0.918
2	a_{bed}	2.304	4.748	0.914
3	X_f	2.293	4.726	0.909
4	k_{b1}	2.273	4.448	1.007
5	L_f	0.377	14.103	0.052
6	Y_H	0.359	14.969	0.0004
7	k_{b2}	0.081	0.260	0.061
8	K_{CL}	0.012	0.023	0.005
9	μ_H	0.0036	0.0739	0.0008
10	U_{sed}	0.0027	0.1079	0.00005
11	K_{OC}	0.0019	0.0054	0.0008
12	Φ	0.0004	0.0008	0.000185
13	ε	0.00021	0.0007	0.0002
14	ϕ	0.00017	0.0010	0.00011
15	U_{res}	2.1E-05	0.00094	1.2E-06

5.1.4.2. Model calibration and validation

Based on the above sensitivity analysis result, the key model parameters were selected for calibration. On the basis of the monitoring data collected in February 1998 (Whelan *et al.*, 1999), the calibration result is indicated in Figure 5.1.6. Table 5.1.2 depicts the values of model parameters given in literature and the parameters values obtained after calibration. The sum of squared errors at four river stations, starting from Rogolea is 0.002, 0.013, 0.01 and 0.024 respectively. The results depict that the predicted data sets generally agree well with the measured data sets, within 20% error.

To validate the model, the calibrated model was run for a new data set collected in May 1998 (Whelan *et al.*, 1999), and the result is given in Figure 5.1.7. The general trend of the model predictions, in most of the cases agrees well with the measured data set, again within 20% error. Despite the fact that the measurement data sets do not fit well with the simulated data sets at the downstream reaches (15.6 and 26 km), due to a malfunctioning of the used auto-

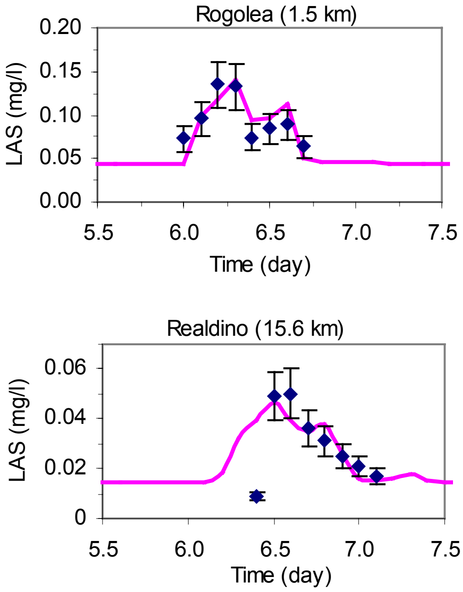


Figure 5.1.6: Model calibration results for 5.5 to 7.5 days: simulated (lines) and measured (symbols) total LAS concentration in the bulk water; the simulated data set mostly agrees with the measured data set within 20% error

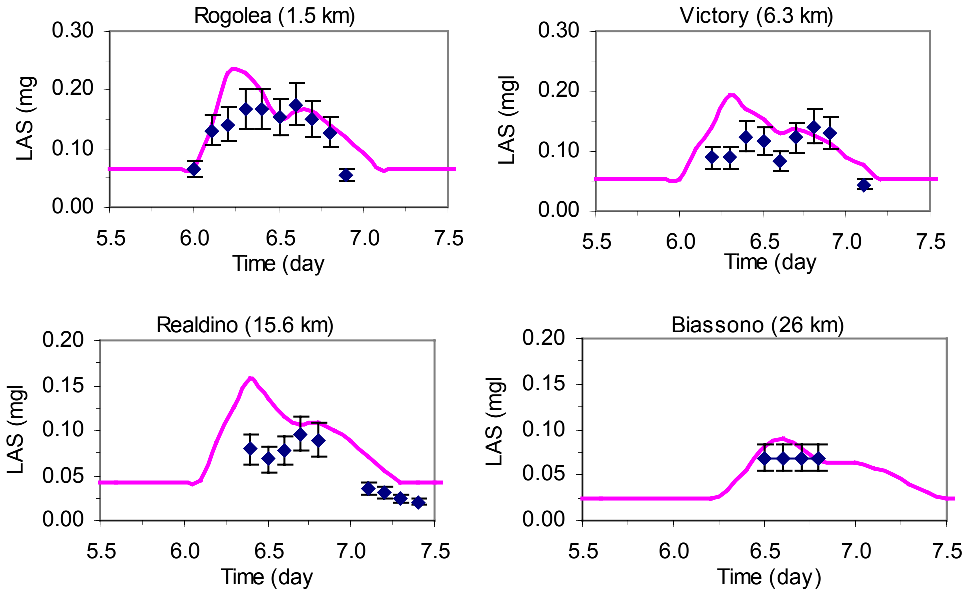


Figure 5.1.7: Model validation results for 5.5 to 7.5 days: simulated (lines) and measured (symbols) total LAS concentration in the bulk water; the simulated data set in most of the cases follows the same trend as the measured data set

samplers, the result is still reasonable. Further more, the *U* values at the four monitoring locations are 0.14, 0.19, 0.29 and 0.09 at Rogolea, Victory, Realdino and Biassono respectively. Furthermore, the *U* values (see equation at all four monitoring locations are less than 0.3, i.e. it is by far less than 0.5, and hence the model fit with the measurements can be assumed acceptable.

The concentration of LAS in the benthic sediment is simulated and found to be generally very low (see Figure 5.1.8). The concentrations of sorbed LAS in the benthic sediment, at 1.5 km and 26 km are less than 15 µg/g and less than 1 µg/g, respectively. Unfortunately, there are no monitoring data available to validate these values in the benthic sediment. However, the sorbed LAS concentration in the benthic sediment downstream of a normally operating WWTP effluent discharge was reported to be very low (<1 µg/g) (McAvoy *et al.*, 1993; Holt *et al.*, 1995; Feijtel *et al.*, 1999). This indicates that LAS will not accumulate in the aerobic river sediment because it degrades rapidly in the benthic sediment. Takada *et al.* (1994) also indicated that LAS does not accumulate in the benthic sediment because of its fast desorption and biofilm degradation. It is also important to note that the concentration profile of sorbed LAS in the benthic sediment (Figure 5.1.8 right) follows the same trends as the total LAS concentration profile in the bulk water (Figure 5.1.8 left).

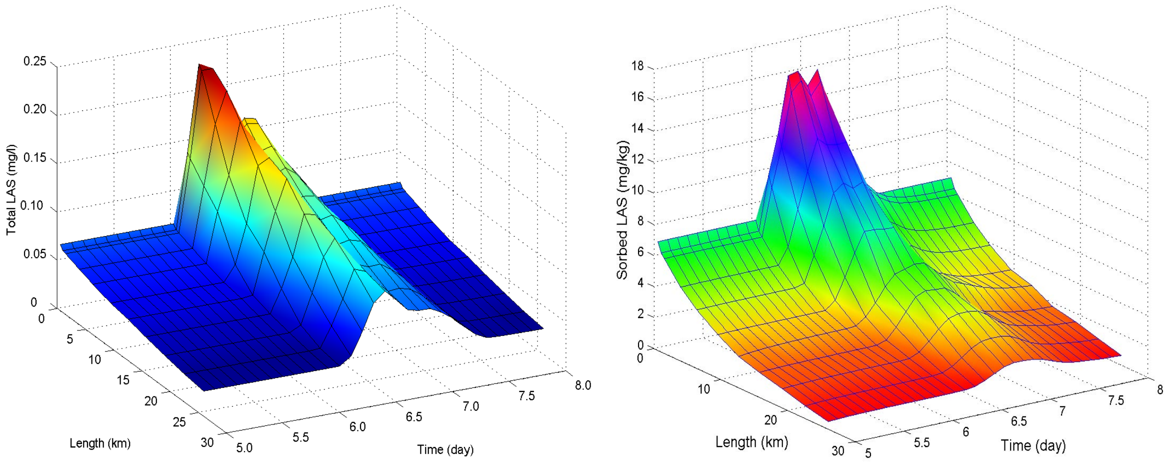


Figure 5.1.8: Simulated Total LAS concentration in the bulk water (left) sorbed LAS concentration in the benthic sediment (right) for 5 to 8 days in a three-dimensional graph of time, river distance and LAS concentration using data collected in May 1998

5.1.4.3. Scenario analysis

Comparison of steady and variable flow simulation

Note that the flow rate of the river Lambro upstream of the Merone wastewater treatment plant is almost constant. However, the downstream river flow varies with time due to the treated and untreated wastewater flows. Based on the simulation results obtained in the last river section (Biassono), the simulation results of four different approaches for input description were examined: (1) variable flow, (2) constant, i.e. average flow with time-variable inflow concentration, (3) daily averaged flow with daily averaged inflow concentration (daily average), and (4) average flow with overall averaged inflow concentration (steady-state). The comparison of simulation results is given in Figure 5.1.9. The results show that all information about the peak can be simulated by the first approach (variable flow). In the second approach, the time profile of the concentration can be simulated with a slight underestimation of the peak values. If one follows the third approach (constant flow with daily averaged concentration), most information related to the peak is lost. In the fourth approach (using overall the averaged flow and concentration), all information related to the peak is lost.

The results suggest that although the steady-state simulation may describe the long-term averaged exposure concentration adequately, dynamic simulation is still needed to obtain details or a higher temporal resolution of exposure assessment e.g. for pulse exposure. In pulse exposures, toxicity depends not only on the concentration but also on the frequency and the time interval between consecutive pulses (Reinert *et al.*, 2002). A higher frequency of the pulsed exposure with a shorter time interval between the pulses can result in more toxicity than a less frequent exposure with longer pulse interval. This is due to the fact that in a longer pulse interval, the exposed organism can get enough time to recover.

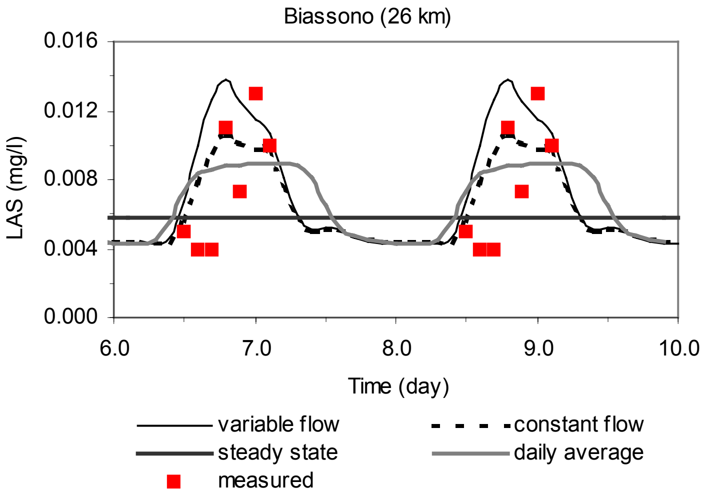


Figure 5.1.9: Comparison of the steady-state and dynamic simulations for LAS concentration at about 26 km; steady-state simulation describes the time averaged concentration profile of LAS in the river, and hence, information about the peak or concentration dynamics is lost

Effect of nutrient dynamics: simulation

To investigate the effect of nutrient dynamics on the fate of LAS, two important substrates such as ammonia nitrogen and soluble readily biodegradable organic substrates expressed as chemical oxygen demand (COD) were considered. Using a 10 mg L^{-1} heterothrophs concentration (X_H) in the inflow, the simulation results are presented in Figure 5.1.10. The trend shows that in the low ammonia loaded waters, increasing the ammonia nitrogen concentration up to 5 mg/l in the upstream end of river section can enhance the removal of LAS by biodegradation. However, a further increase of ammonia concentration does not considerably improve the LAS removal rate because then the biodegradable soluble COD becomes limiting. By a slight increase of COD input in the upstream end, the LAS removal can further increase due to heteroterophic biomass growth. However, further increases of the biodegradable soluble COD concentration, e.g. up to 92 mg L^{-1}, decreases the removal rate due to oxygen depletion. This suggests that the interaction of nutrient dynamics and organic contaminant fate can be either positive or negative depending on which substrate is limiting. At higher concentrations of ammonia nitrogen and biodegradable soluble COD, the dissolved oxygen (S_{O2}) is depleted and hence the removal rate of LAS decreases. If S_{O2} is not limiting, a small increase of nutrients (ammonia or biodegradable soluble COD) can enhance the removal rate of LAS in rivers by stimulating microbial growth.

Furthermore, consider the above scenario analysis in oligotrophic and eutrophic systems. It is obvious that a particular nutrient is limiting in an oligotrophic system, and therefore a little increase of nutrient can enhance LAS removal. In contrast, in a eutrophic system S_{O2} may be

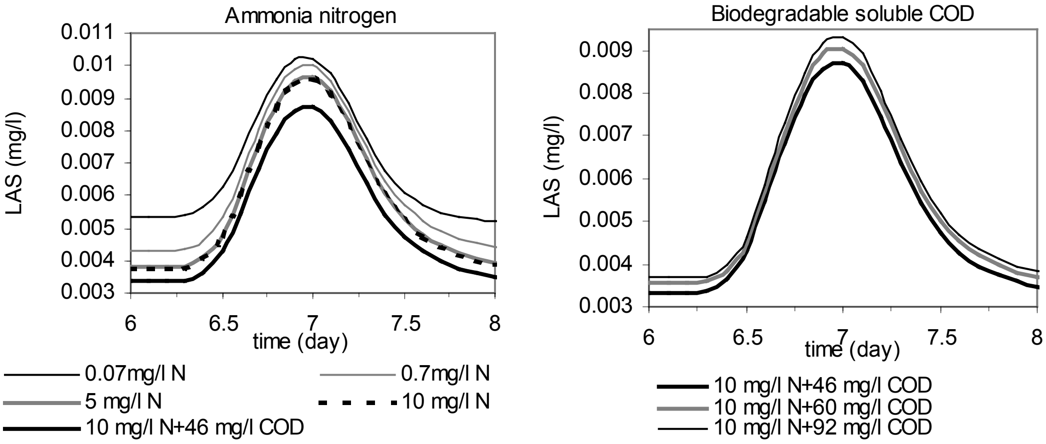


Figure 5.1.10: The interaction of nutrient dynamics and LAS fate in the last river section (26 km): As ammonia concentration increases, in the left hand side, the LAS concentration decreases until the readily biodegradable soluble COD is limiting; the degradation of LAS can be enhanced by farther increase of COD (up to 46 mg/l); in the right hand side, further increase of COD (e.g. 60 mg/l or more) decreased LAS biodegradation

limiting higher nutrient load to the system can result in further depletion of S_{O2}, which in turn can lead to a decrease of LAS degradation. Note that sorption to the high concentration of suspended solids in the eutrophic system can also cause a decrease of the free dissolved contaminant concentration.

5.1.5. Conclusions and further researches

A dynamic fate model of xenobiotic organic chemicals in a river system was presented using a conceptual hydrological simplification and local sorption equilibrium. The model was evaluated based on a LAS case study in the river Lambro (Italy). Model predictions and measured data were compared, and a parameter sensitivity analysis of the model was presented to identify the key parameters to be estimated from the available data. Subsequently the following general conclusions were drown:

1. The model validation and scenario analysis results indicate the applicability of the proposed model;
2. The high sensitivity of the model predictions to biodegradation parameters, particularly to the biofilm biodegradation parameters, indicates the importance of these parameters, and therefore their accurate estimation is required;
3. The dynamic simulation gives invaluable information for the time-varying exposure assessment such as exposure concentration and duration, and it is a realistic approach for short-term exposure assessment, particularly in non-steady-state conditions;
4. Integrated modelling of basic water quality and organic contaminant is very useful to assess the effect of nutrient dynamics on the organic contaminant fate;
5. Coupling of dissolved oxygen and organic contaminant to biodegradation, and allowing variation of biodegradation with the sorbed fraction are important considerations in the short-term analysis of organic contaminant fate in rivers.

Further research is required in order to experimentally investigate the effect of nutrient dynamics on the fate of organic contaminants (see Chapter 5.2). Besides, the importance of including nutrient limitation in the in-stream fate modelling of organic contaminant needs to be evaluated (see Chapter 5.3). It is also interesting to note that the relative importance of nutrient components can be further examined by analyzing the sensitivity of the model output (organic contaminant concentration) not only to the model parameters but also to the model state variables of the basic water quality submodels. This is briefly discussed in Chapter 5.3.

Chapter 5.2

The effect of nutrient dynamics on fate of organic contaminants in rivers [1,2]

The important parts of this chapter were (will be) published as:

[1] Deksissa T. and Vanrolleghem P. A. (2003). Effect of nutrient dynamics on organic contaminant fate in rivers: a microcosm study. *Med. Fac. Landbouww. Univ. Gent,* 68 (3), 111-114.

[2] Deksissa T. and Vanrolleghem P. A. (2004). Effect of nutrient dynamics on organic contaminant fate in rivers: A microcosm study. In: *Proceedings of the 2nd IWA young Researchers conference*, Wagingen, The Netherlands, May 2004, April 23-24 2004.

Chapter 5.2

The effect of nutrient dynamics on the fate of organic contaminants in rivers: A microcosm study

5.2.1. Introduction

Despite the fact that conventional pollutants (nutrient and suspended solids) can have considerable effects on the fate of organic contaminants in rivers, little attention has been given to link these two water quality problems in traditional river water quality modelling. Nutrient enrichment in the aquatic system can result in high suspended Particulate Organic Carbon (POC) concentrations, which has two possible effects depending on the physicochemical characteristics of the organic contaminant under study. The first effect is that a large amount of xenobiotic organic contaminant may be sorbed to the POC and Dissolved Organic Carbon (DOC) and thereby reduces the truly dissolved phase of the compound, which is readily bioavailable for gill uptake and toxicity (McCarthy, 1985). The second effect is related to the fact that nutrients regulate microbial growth, which enhances the degradation of organic contaminants in the environment (e.g. Strynar *et al.*, 1999; Granger *et al.*, 1999; Venosa *et al.*, 2002). While the first effect is commonly considered in organic contaminant fate modelling, the second effect is not quantitatively studied well, and hence not included explicitly in the model.

Furthermore, although some organic contaminants are indicated as readily biodegradable substances, e.g. Linear Alkylbenzene Sulphonate (LAS), considerable concentrations of such compounds can still be found in the downstream section of the river far from the outfall, e.g. in estuaries (Takada and Ogura, 1992). It is also unclear how LAS is degraded, and hence more research is proposed despite the fact that it can be completely mineralised (Cook, 1998).

Factors that may determine the fate of organic contaminants in-streams or rivers can be experimentally investigated by using artificial rivers (microcosm or mesocosm study). Artificial rivers have already been successfully applied for biodegradation experiments and toxicity tests (Schröder, 1995; Guckert *et al.*, 1996; Belanger *et al.* 1995). They have the advantage that hydraulic variables, which are difficult to monitor in the field, can be monitored easily. For example, flow rate, velocity and hydraulic residence time can be measured straightforwardly. Moreover, studying organic contaminant fate and effect in a real environment is difficult and harmful to the environment.

Thus the goal of this study was to investigate the effect of nutrient dynamics on the fate of organic contaminants in rivers by using an artificial river. Using LAS, an active ingredient of detergents as an example, the effect of different factors such as extra nutrient load, the aeration of the river and development of attached microbial biomass (biofilm) on the degradation of LAS was investigated.

5.2.2. Materials and methods

5.2.2.1. River system selection and design

As an artificial river should represent the real environment, an attempt was made to design an appropriate river system in view of a predefined goal. Figures 5.2.1 and 5.2.2 show the artificial river set-up of this study. The river was constructed as a cascade of 5 U-shaped gutters, each 2 m long. The total river length and volume are 10 m and 36.84 l respectively (see Table 5.2.1).

The design Hydraulic Residence Time (HRT) was chosen to correspond to the half-life of the chemical under consideration. In this study, LAS was selected which has a half-life of approximately 3 h, as calculated from the reported first-order degradation rate constant in both small natural streams (Schröder, 1996; Fox *et al.*, 2000) and mesocosm studies (Schröder, 1995; Steber, 1996) though it may vary from 0.4 to 116 h (Boeije *et al.*, 2000). HERA (2002) also reported 1-3 h for the primary degradation. The large variation is also indicated to be due to temperature and river size. Subsequently, for the chosen river size, the average flow rate was set to 0.2 l min^{-1} in all LAS degradation experiments so as to achieve the average hydraulic residence time of 3 h. Two air diffusers were placed in each gutter to provide oxygen and to counteract sedimentation.

The synthetic river water was prepared from the effluent of lab scale Sequential Batch Reactor (SBR) wastewater treatment plant which has a daily effluent discharge of 128 l and

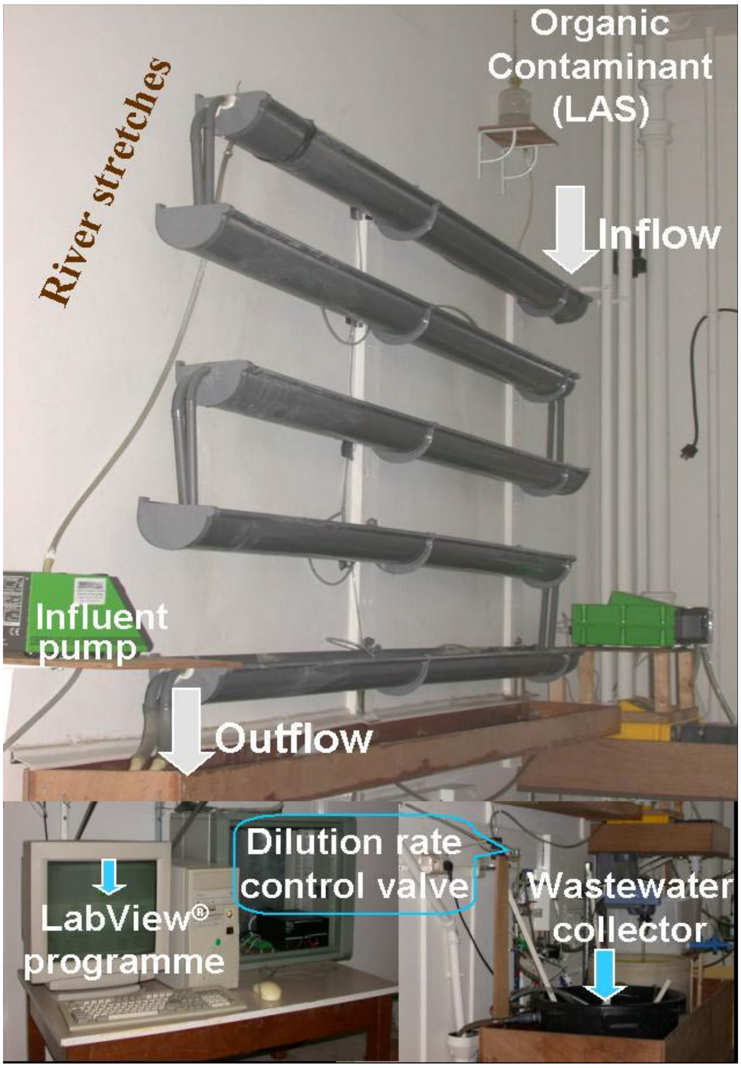


Figure 5.2.1: Artificial river (microcosm) set-up

has a known influent composition indicated elsewhere (Boeije *et al*., 1998) without LAS. The SBR effluent was collected in a collector tank with a capacity of 80 litres. The collector tank was aerated continuously with an air diffuser to provide complete mixing. Before it was pumped to the artificial river, the SBR effluent was diluted 4 times with softened tap water using a two-way valve. The inflow and dilution rate were controlled by creating a specific standalone application LabView® programme (www.ni.com). The inflow can vary to simulate a dynamic system. For simplicity a constant flow but variable LAS concentration was applied.

As attached microbial biomass plays a significant role in organic contaminant degradation, this experiment also includes a benthic sediment/biofilm compartment. The development of benthic biofilm on the surface of the gutters was achieved by allowing the river to run continuously for about 3 months without adding any carrier material. The addition of extra carrier material was not needed because in a previous study, with almost the same approach, it was found that about 60% of LAS could be removed at 10 m distance without adding carrier

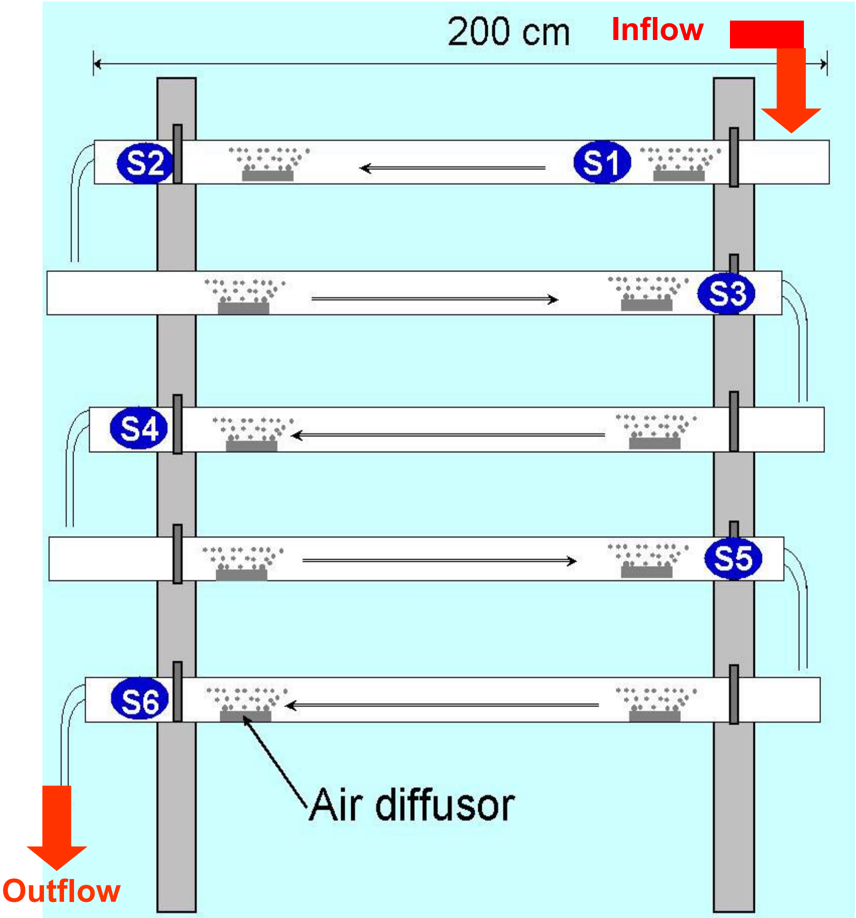


Figure 5.2.2: Schematic illustration of the artificial river set-up: S1 to S6 are monitoring locations

material, which provide extra surface for the growth of attached microbial biomass (Boeije *et al.*, 2000).

5.2.2.2. Hydraulic characteristics

Filling-up test

The volume and average HRT of each stretch of the microcosm were determined by filling each gutter with water until their overflow became operational. The average HRT was then estimated by recording the time required to fill the gutter under a constant flow rate (0.2 l min^{-1}). The volume of the stretch was hence straightforwardly determined by multiplying the average HRT by the flow rate. Table 5.2.1 shows the result. The variation in volume or HRT is due to imperfections of the construction (e.g. different height of the overflow).

Table 5.2.1: Filling test (Q = 0.2 l min^{-1})

Stretch	Length(m)	Volume(l)	Average HRT(h)
1	2	5.64	0.47
2	4	7.80	0.65
3	6	8.76	0.73
4	8	7.44	0.62
5	10	8.40	0.70
	sum	36.84	3.17

Tracer test

A hydraulic tracer test was performed using NaCl as conservative substance. The upper end of the river was injected with 50 ml of NaCl solution (20 mg L^{-1}). Conductivity (as a measure of the NaCl concentration with background correction) was measured at approximately 10 cm before the end of each stretch. The NaCl concentration at each sampling location was estimated using the corresponding calibration curves. On the basis of the E-curve, which refers to the surface area below the concentration curve normalized to 1, the dispersion coefficient *D* and the flow velocity *u* were calculated by applying the open vessel dispersion model (Levenspiel, 1999) as follows:

$$E(t) = \frac{u}{\sqrt{4Dt}} \exp\left(-\left(\frac{L - ut}{4Dt} \right)^2 \right) \tag{5.2.1}$$

The theoretical number of tanks in series for plug flow was estimated based on the calculated *D* and *u* values suggested by Levenspiel (1999) as follows:

$$N = \frac{uL}{2D} \tag{5.2.2}$$

where *N* is the number of tanks in series, and *L* is the length of the microcosm stretch, *t* is time, *E(t)* is the value of *E* at a time *t*.

In equations 5.2.1 and 5.2.2, *L* is known or can be measured, whereas *D* and *u* are estimated by fitting the open vessel dispersion model (equation 5.2.1) to the monitoring data.

Based on the monitoring data of the NaCl concentration in every river section, the average hydraulic residence time $\bar{t}$ in each river section can be calculated as given in Levenspeil (1999):

$$\bar{t} = \frac{\int_0^\infty tCdt}{\int_0^\infty Cdt} = \frac{\sum t_i C_i \Delta t_i}{\sum C_i \Delta t_i} = \frac{\sum t_i C_i}{\sum C_i} \qquad \text{with constant } \Delta t \tag{5.2.3}$$

where $\bar{t}$ is the average HRT [min]

t_i is the time step [min]

C_i is the concentration of a trace substance at time t [mg L^{-1}]

Δt_i the difference of time step between two data points at time t_i [min]

5.2.2.3. Water quality analysis

Analytical methods

The river set-up was run continuously and the required water quality variables were monitored. Samples were taken at distances of 0.5, 2, 4, 6, 8 and 10 m. The total (unfiltered) LAS concentration in the bulk water was measured on the basis of the Azure A analytical method (de Tonkelaar and Bergshoeff, 1969). This analytical method measures the total anionic surfactants and is not specific to LAS. However, since there is no anionic surfactant in the studied artificial river other than LAS, this method could be applied. Samples of the same locations were also analysed for the other water quality variables (Dissolved Oxygen (DO), carbonaceous soluble organic matter as Chemical Oxygen Demand (COD), NH_4-N, NO_3-N, temperature and pH). DO, pH, and temperature were measured with probes. The soluble COD and NH_4-N and NO_3-N were measured with Dr. Lange kits.

Furthermore, the suspended microbial biomass concentrations in the bulk water and the active sediment depth in each river reach were determined. The suspended biomass concentration was determined by conventional Total Suspended Solids (TSS) analysis, i.e. measuring the dry weight (24 hours at 105 °C) of a known volume of a filtered sample. The active sediment depth was estimated based on the dry weight of a sample, the biofilm density, and the surface area of the gutter that was sampled (e.g. 3.14 cm^2) as follows:

$$d_{bed} = \frac{M_{dwt}}{\rho_{bfilm} A_{surf}} \tag{5.2.4}$$

where d_{bed} is the active sediment depth [m], M_{dwt} is the dry weight of the sample [mg], ρ_{film} is the biofilm density [mg L^{-1}], and A_{surf} is the surface area of gutter wall that was sampled (3.14 cm^2).

In this experiment, the biofilm density and the biofilm thickness were not monitored/calculated but their typical literature values: 40 g l^{-1} and 100 µm respectively, were applied (Melcer *et al.*, 1996; Vanhooren, 2002).

Sorption experiment

The sorption experiment was conducted to estimate the time at which the sorption equilibrium is reached. Indeed, prior to detailed LAS monitoring it is important to know how long it will take to reach sorption equilibrium so that an appropriate monitoring campaign can be designed. Subsequently, a batch sorption experiment was conducted at room temperature (21 °C) using a low LAS concentration (15 mg L^{-1}) in one litre demineralised water. The type of LAS used in this study is a mixture of LAS homologues. To avoid aerobic biodegradation, nitrogen gas was supplied continuously in the test, and the dissolved oxygen concentration was also checked (using DO electrode) to be zero during the entire experiment. After adding about 4 g dry weight of sludge (dried for 24 hours at 105 °C) in one litre demineralised water, the LAS concentrations in the dissolved phase (filtered) were analysed after 2.5, 5, 10, 20, 30, 40, 50 and 60 minutes. The sorbed phase was calculated from the total (initial) concentration in water. The time of sorption equilibrium was then estimated from the graph of LAS concentration versus time. As the sorbed phase is not measured, this experiment cannot be used to determine the sorption rate coefficient or partition coefficient.

5. Experimental case studies

A series of batch experiments were conducted to investigate four cases. In the first case, the LAS degradation by only suspended biomass was investigated prior to observable biofilm development in the gutter. In the second case, the LAS degradation by both suspended and attached microbial biomass was examined after the biofilm had developed in the gutter. In the third case, the effect of aeration on LAS degradation was investigated by conducting two series of experiments namely one with aeration and the other without aeration. In the fourth case, the effect of nutrients on the LAS degradation was investigated by conducting a series of experiments with and without external nutrient additions: a readily biodegradable soluble COD (acetate) and inorganic nitrogen (ammonium chloride).

In all four cases an appropriate selection of LAS load is required to mimic the real environmental concentration. Previous studies (Larson and Payne, 1981) showed that the ultimate degradation of LAS by the indigenous microorganisms of the river waters is hampered at concentrations between 10 and 20 mg L^{-1} and totally inhibited at LAS concentration higher than 20 mg L^{-1}. Consequently, a prepared LAS solution was added in the river such that the concentration of LAS in the artificial river remain below 5 mg L^{-1}. Most of the experiments were, however, conducted at concentration of about 1 mg L^{-1}.

Statistical analysis

Data were analysed with the S-PLUS 6 statistical software, and statistical significance difference between mean values was determined by use of an unpaired t-test, one-way ANOVA or Kruskal-Wallis rank sum test at a 95% level of confidence.

5.2.3. Results and discussion

5.2.3.1. Hydraulic characteristics: Tracer test

In the tracer test different flow rates were applied and the corresponding hydraulic parameters were determined. For two flow rates (0.2 and 0.5 l min^{-1}), the model fit (E curve) is presented in Figure 5.2.3. The parameter values for u and D for every stretch were estimated on the basis of the model fit (Table 5.2.2). The influence of the flow rate on these parameter values was examined. Obviously, the results show that at the higher flow rate (0.5 l min^{-1}), the E curve is narrower and the average HRT ($\bar{t}$) is shorter as compared to the low flow rate (0.2 l min^{-1}). Also, D and u increase with flow rate. Using the same flow rate (0.2 l min^{-1}), the average HRT ($\bar{t}$) obtained on the basis of the tracer test is comparable with the result of the filling test.

On the basis of D and u, the ideal total number of tanks in series N was calculated by equation 5.2.2. The value of N for 0.2 and 0.5 l min^{-1} was found to be 17 and 39 respectively. Even though dispersion is higher for the higher flow rates, the number of tanks indicates a more plug flow character. This result is useful to determine the optimum number of tanks in series required for the water quality modelling.

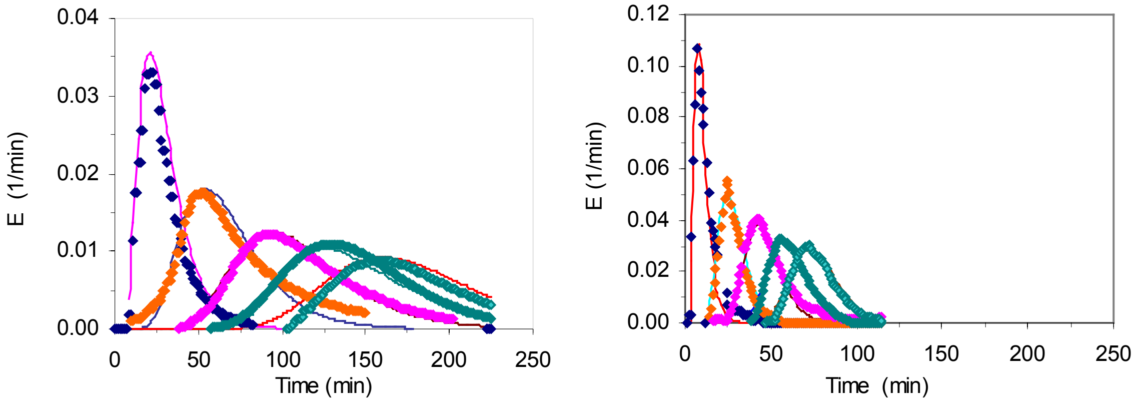


Figure 5.2.3: Effect of flow rate on the simulated (line) and measured (symbols) E curve: low flow rate (Q = 0.2 l min^{-1}) (left), and high flow rate (Q = 0.5 l min^{-1}) (right)

Table 5.2.2: Parameter values of *u*, *D* and $\bar{t}$ for two different flow rates along the microcosm stretches

Distance	$\bar{t}$ (min)		*D* (m^2/min)		*u* (m/min)	
	0.2 l/min	0.5 l/min	0.2 l/min	0.45l/min	0.2 l/min	0.45l/min
2	26.67	8.18	0.014	0.038	0.075	0.22
4	61.54	24.52	0.018	0.024	0.065	0.155
6	102.56	42.96	0.0182	0.0218	0.0585	0.135
8	136.05	58.21	0.016	0.0224	0.0588	0.134
10	170.07	72.06	0.018	0.0224	0.0588	0.136

5.2.3.2. Water quality

Sorption kinetics

Sorption kinetics refers to the time required for sorption and desorption. The results are indicated in Figure 5.2.4. The results show that the sorption equilibrium was reached within 5 minutes. This result is comparable with a previous study using activated sludge, which also indicated that equilibrium is reached in 5 to 10 min (Temmink, 2001). Hence, it can be concluded that LAS is rapidly sorbed and desorped (Hand and Williams, 1987). Such a physicochemical characteristic influences the fate of LAS in an aquatic ecosystem. If, for example, the benthic sediment is anoxic and LAS accumulates in the sediment (note that LAS degrades only in the presence of oxygen), its rapid desorption enhances its release from the sediment to the overlying water where it can degrade or be washed off once the emission ceases (see also step-down test in sub section 5.2.3.5.9 of this Chapter). Consequently, the previous studies also show that the presence and absence of a high level of suspended

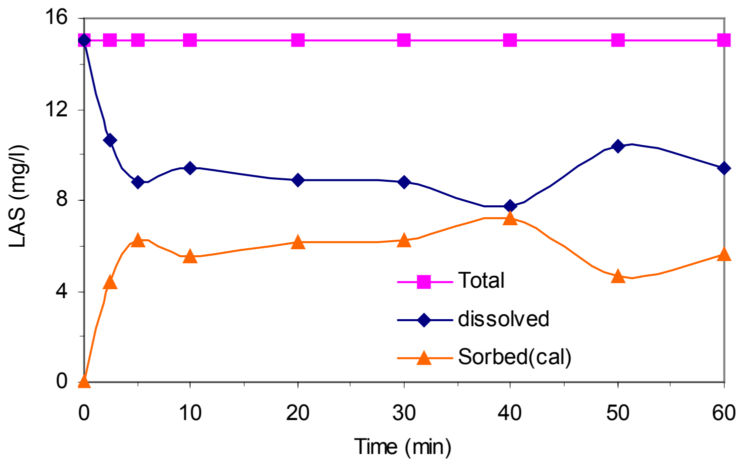


Figure 5.2.4: LAS sorption kinetics: sorbed phase is calculated (cal) based on the concentration of total and dissolved phase

solids (without significant difference in active microbial biomass) does not affect the degradation rate of LAS (Hand and Williams, 1987; Larson, 1990). This led to the conclusion that both the sorbed and desorbed phases can be assumed to degrade at an equal rate (Larson, 1990).

Bulk water degradation

Prior to the biofilm development, the bulk water degradation was examined. Samples were taken from every microcosm stretch and analysed for the water quality variables: water temperature, pH, microbial biomass concentration, dissolved oxygen and the organic contaminant concentration (LAS). The water temperature was 18-19 °C during winter and 20-23°C during summer, which indicates the temperature gradient along the microcosm stretch was small ($\leq$ 1°C). Similarly, the pH ranges from 8 to 9.

Figure 5.2.5 shows the monitoring results of DO, LAS and TSS. The DO concentration was about 7 mg L^{-1} in the upstream (2 - 4 m) and 8 mg L^{-1} in the downstream section (6-10 m). This shows that the DO concentration increased in the downstream section of the river because of the higher oxygen supply than consumption by aerobic degradation. The concentration of suspended microbial biomass (measured as TSS) decreased in the downstream section due to sedimentation and attachment to the gutter wall. Although there was no limitation of DO (> 6 mg L^{-1}), temperature (18 - 20 °C), pH ($\pm$ 8) and suspended biomass in the artificial river during the experiment, the results show that there is no significant LAS removal with suspended biomass alone (in the absence of biofilm). This

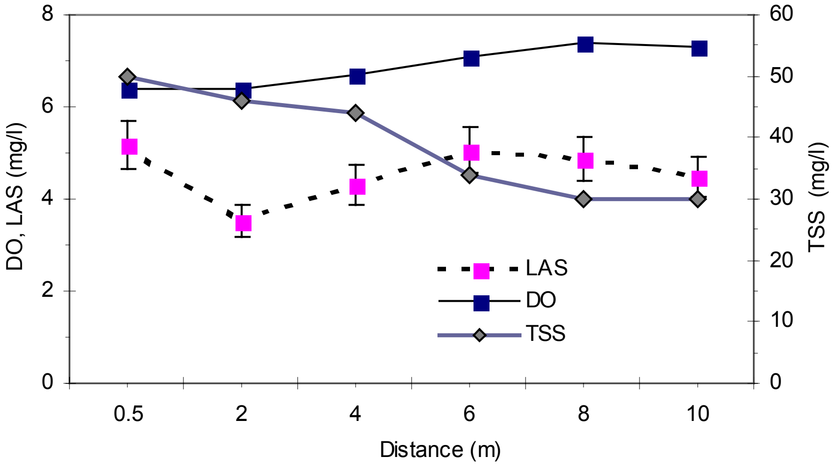


Figure 5.2.5: Concentration profile of LAS, DO and TSS in the absence of biofilm

might be due to the fact that 3 hours of average HRT does not provide sufficient contact time for the bacteria to degrade LAS.

Benthic biofilm degradation

To investigate the effect of benthic biofilm or attached microbial biomass on LAS degradation, the benthic sediment depth was determined on the basis of equation 5.2.4 (see Figure 5.2.6. A constant amount of LAS was added continuously between 6 to 24 hours depending on the experiment. The TSS, LAS and DO concentration, and water temperature were measured.

Figure 5.2.6 indicates the benthic sediment depth profile. The active sediment depth was higher in the middle of the microcosm stretches (6 to 8 m) than in the upper and lower stretches. This is due to the fact that part of the benthic sediment had been removed seriously in the upper river reaches (2 and 4 m) during maintenance, and because only slow biofilm growth (due to nutrient limitation) and relatively very low suspended solid concentrations in the lower reaches (10 m).

On the basis of the benthic sediment depth indicated in Figure 5.2.6, the concentration profiles of DO and LAS were monitored, and the results are depicted in Figure 5.2.7. The result depicts that in the presence of biofilm, the DO concentration gradient along the microcosm stretch is more pronounced (about 2 mg L^{-1}) than when the biofilm is not present (see Figure 5.2.7 left), which indicates the presence of more aerobic degradation or oxygen consumption when biofilm is present. The DO concentration profile in the bulk water indicates a low DO concentration at the discharge point (beginning of the river) and

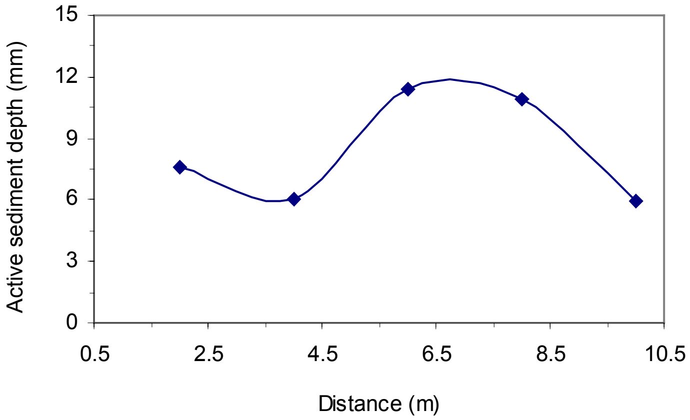


Figure 5.2.6: Benthic sediment depth

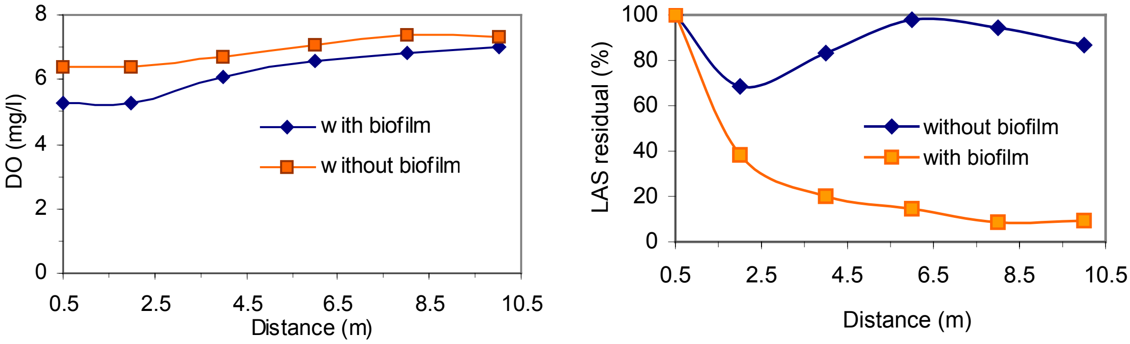


Figure 5.2.7: Effect of the presence/absence of biofilm on the DO profile (left) and LAS degradation (right)

progressively increases in the downstream section of the river due to reaeration.

The LAS removal rate in the presence of biofilm was compared with that in the absence of biofilm. The result shows that LAS degrades faster when biofilm is present than when it is not present (see Figure 5.2.7 right). In the absence of biofilm, there is no significant LAS degradation. There is, however a trend that shows an accumulation (increase again) in the downstream section of the river. Such increase in a steady-state concentration profile is not common for the conventional pollutants. However, it may occur for LAS due to its fast sorption and desorption. Further discussion is given in the subsection below.

Based on the benthic sediment depth profile indicated in Figure 5.2.6, the LAS degradation was extensively studied. Four series of experiments were conducted (see Figure 5.2.8). In all experiments, the LAS concentration profile shows a similar degradation curve, regardless of the initial concentration. The average LAS removal in the artificial river was estimated by

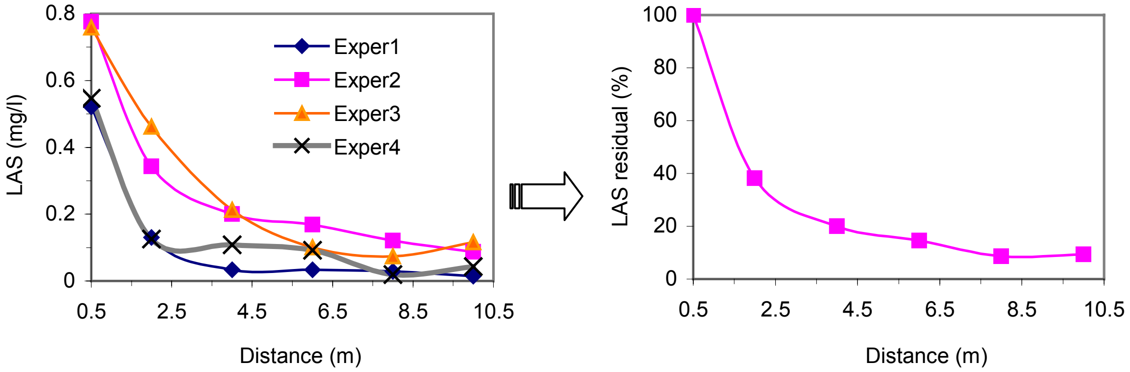


Figure 5.2.8: LAS degradation profile when biofilm is present: Monitoring result of four experiments (left), and the average removal (right)

taking the average percentage of the LAS residual during each experiment (Figure 5.2.8 right). It shows a typical first-order decay curve. The calculated overall pseudo first-order degradation coefficient varies between 6 and 10 d^{-1}, which is similar to the results of previous studies (Schröder, 1996; Fox *et al.*, 2000; Boeije *et al.*, 2000).

Effect of aeration and LAS accumulation

Despite the fact that LAS is indicated to be a readily biodegradable substance in aerobic conditions (Steber, 1996; EU Commission, 1997), it was not clear why, under some conditions, a considerable LAS concentration could be found in rivers, while the bulk water DO concentration was still not depleted (Quiroga *et al.*, 1989). This was further investigated in this work by looking into the effect of aeration/mixing on the biofilm activities and LAS accumulation.

To investigate the effect of aeration on the LAS degradation, the aeration through air diffusers was stopped and the concentrations of DO and LAS were monitored three times (Exp_1 to Exp_3, see Figure 5.2.9). The DO concentration in the bethic sediment is measured by inserting the DO electrode in the sediment. It was found that there was a considerable DO concentration in the bulk water while the benthic sediment became anoxic. Figure 5.2.10 shows a picture (made with an ordinary camera) of the benthic sediment/biofilm in the gutter in which anoxic and oxic zones are indicated. The fact whether a zone was anoxic or oxic was identified visually (also checked using DO electrode) in the sense that the black regions indicate an anoxic zone, whereas the brown regions indicate an oxic zone.

At section of the river downstream of stretch number 2 (4 m), a similar trend in LAS concentration profile was observed for all three experiments (see Figure 5.2.9 left). The

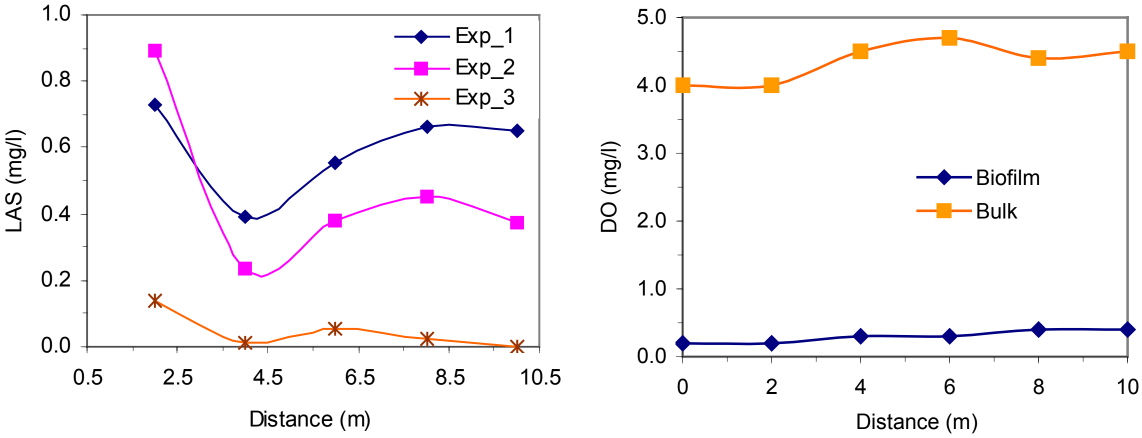


Figure 5.2. 9: LAS (in the bulk water) (left) and DO concentration profile without aeration (right): the difference among Exp_1, Exp_2 and Exp_3 is the initial concentration of LAS

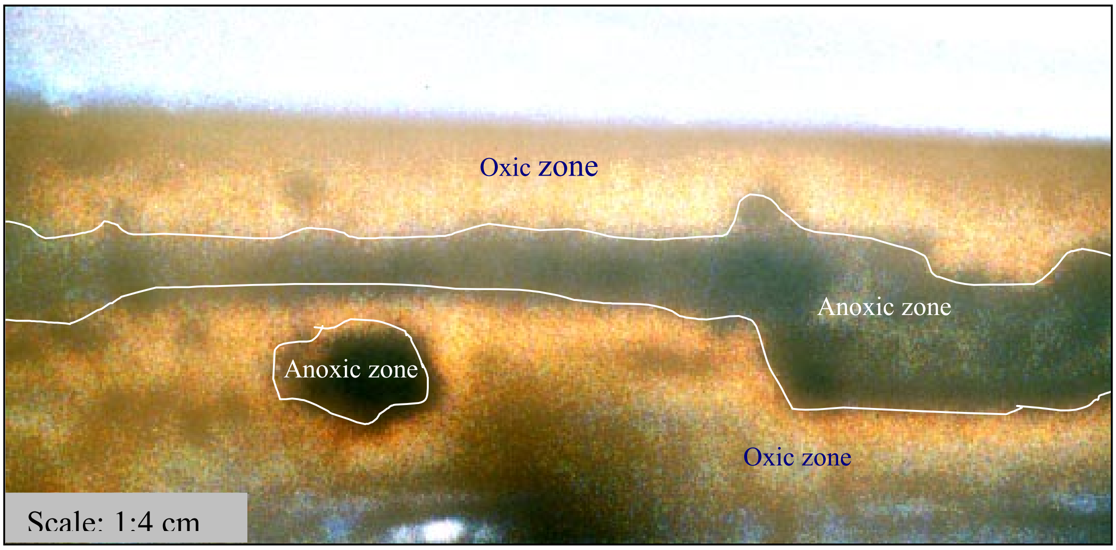


Figure 5.2.10: Picture of benthic biofilm with indicated oxic zone (brown color) and anoxic zone (dark color)

concentration profile is even higher than expected despite the fact that dispersion alone can result in about 30% reduction (based on simulation) at 6 m river reach. The results indicate the slowdown of LAS degradation and its accumulation if DO is limiting in the biofilm (< 0.5 mg L^{-1}), regardless of the DO concentration in the overlying water, which is still higher (> 4 mg L^{-1}) than the minimum oxygen required for aerobic degradation (0.2 mg/l) to occur. This suggests that diffusion is the determining factor for the oxygen concentration in the biofilm.

Aeration is not only providing oxygen for the aerobic biodegradation but may also induce turbulence/mixing, which breaks structured plug flow, induces fast oxygen transfer from the overlying water to the biofilm, provides uniform distribution of the contaminant and nutrients in the bulk water, prevents localized high levels of organic contaminants and nutrient concentrations, and thereby enhances organic contaminant degradation.

In the absence of biofilm, the accumulation of LAS in the downstream section of the microcosm stretch (i.e. at 6 and 8 m) can be explained in relation to the hydraulic characteristics of the river and benthic biomass, if steady-state is not yet reached. The HRT is relatively shorter in the upstream section (2 m) and longer in the downstream section (6 m) of the microcosm stretches (see Table. 5.2.1 and Figure 5.2.11). The longer HRT provides more time for the already sorbed phase of LAS to be released to the overlying water. The benthic biomass is also higher in the downstream than in the upstream sections (see Figure 5.2.12). The amount of LAS released to the overlying water is proportional to the amount of LAS sorbed to the benthic biomass, and therefore a higher amount of LAS is expected to be released in the downstream river section (e.g. at 6 m). Thus, when there is no significant degradation, the concentration of LAS in the overlying water follows the same trend as that of HRT (see Figure 5.2.11) and benthic biomass.

Furthermore, when biofilm is not present, a trend similar to the one in the absence of aeration was observed (see Figure 5.2.11) after 4 m because LAS can also be sorbed/desorbed to/from

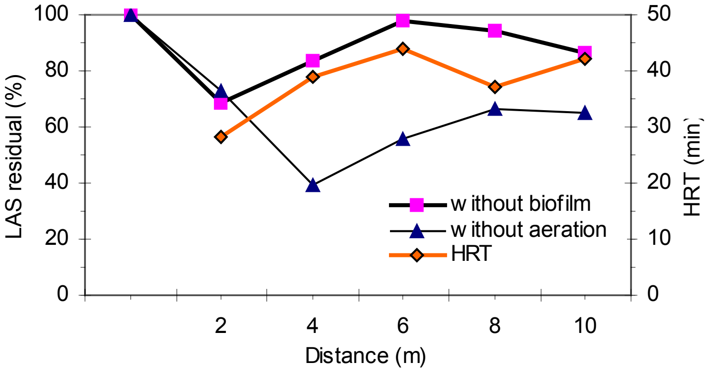


Figure 5.2.11: LAS residual versus HRT during the absence of aeration and biofilm

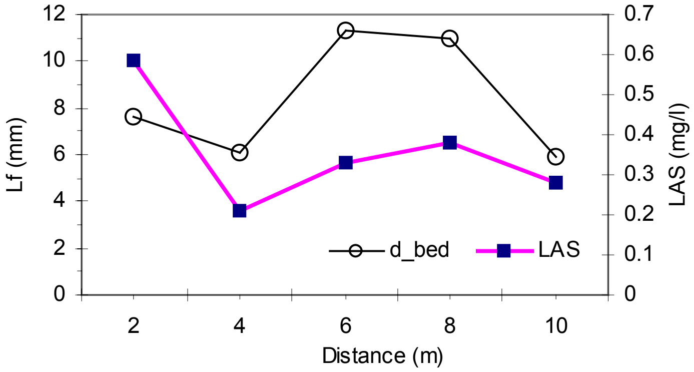


Figure 5.2.12: LAS concentration versus benthic biomass during the absence of aeration and biofilm

the wall of the gutter. As biodegradation was not significant due to the absence of biofilm, the concentration of LAS in the downstream section of 4 m is therefore influenced again by a physical process (sorption and desorption process). This result is consistent with the previous studies conducted in the real river (Takada *et al*., 1994).

Effect of nutrients

COD and ammonia nitrogen

To investigate the effect of nutrient limitation on the LAS degradation, two general sets of experiments were conducted as a preliminary test. First, an experiment was run for 20 hours without adding any extra nutrients. This was followed by adding 0.375 mg min^{-1} of readily biodegradable soluble COD for 6 hours. Subsequently, 0.5 mg min^{-1} NH_4-N was added, also for 6 hours. The concentration of LAS was measured in 6 locations (0.5, 2, 4, 6, 8, and 10 m), and the results are given in Figure 5.2.13 left. The experiment was repeated, without addition of external COD, and the results are given in Figure 5.2.13 right.

The effect of 0.375 mg min^{-1} readily biodegradable COD load on LAS-removal is statistically not significant ($p > 0.05$). Nevertheless, the trend shows that extra readily biodegradable COD load can slightly enhance the LAS degradation by stimulating the growth of microbial biomass. Measuring the concentration of total soluble COD in the artificial river, the above finding was further tested, and it was indeed very low (average concentration 0.05 mg L^{-1} COD) indicating it was converted to biomass. Hence, the presence of readily biodegradable COD can influence the LAS degradation because it provides energy and carbon for the microbial biomass to grow.

An extra load of ammonium nitrogen resulted in a significantly ($p < 0.05$) rapid degradation (immediate uptake) of LAS, which indicates that the concentration of ammonium nitrogen was limiting the LAS degradation in this system (see Figure 5.2.13). This finding was further examined by measuring the concentration of inorganic nitrogen (NO_2-N, NO_3-N and NH_4-N) in all microcosm stretches. It was found that the concentration of NH_4-N was very low (< 0.05 mg L^{-1} NH_4-N); however, the concentration of NO_3-N was high (> 5 mg L^{-1} NO_3-N). This again confirms that ammonium nitrogen is limiting the LAS degradation regardless of a high concentration of total inorganic nitrogen, which is an interesting finding that deserves further research.

For the sensitivity of LAS degradation to the presence of ammonia nitrogen, the following possible reason can be given. Heterotrophic bacteria can use nitrate as a nitrogen source in aerobic conditions, but it costs them more energy than in the case for ammonia (Varistratae, personal communication). Addition of extra ammonia nitrogen in aerobic conditions induces growth of ammonia oxidizers, whereas addition of extra nitrate nitrogen supports anoxic degradation (Rihn *et al.*, 1997; Vanhooren *et al.*, 2003). The latter is however not relevant to the LAS degradation, which only occurs aerobically. It is also indicated in the previous study that ammonia oxidizers are responsible for LAS degradation (Schleheck *et al.*, 2000)**.** This supports the finding that the concentration of ammonium nitrogen can limit the LAS degradation regardless of high concentrations of nitrate nitrogen, which can potentially be used as a nitrogen source.

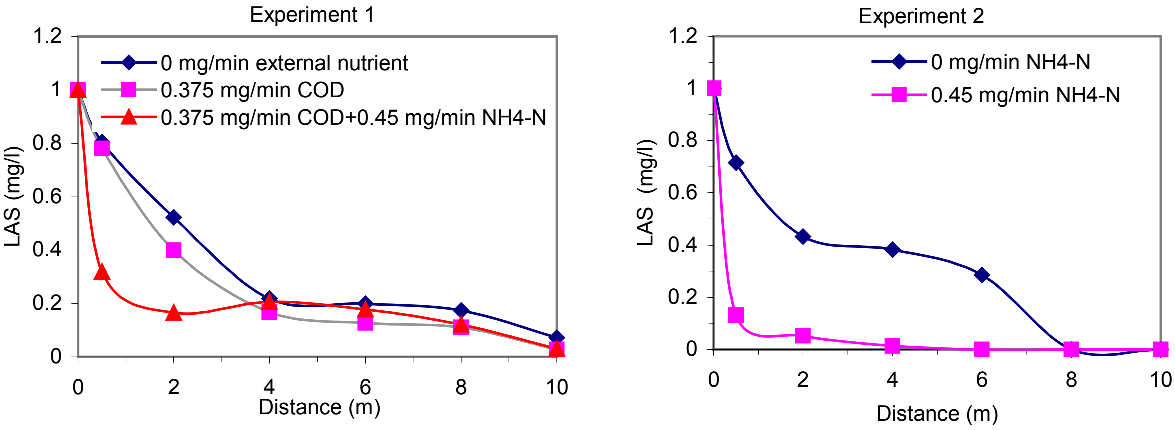


Figure 5.2.13: Effect of external ammonia nitrogen and COD load on LAS degradation

Effect of COD: A detailed study

In the above preliminary test (Figure 5.2.13), only one COD load was used, and it does not give any information about the extent to which the level of external COD load influences the LAS degradation. Therefore additional experiments were conducted with fixing NH$_4$-N load at 0.5 mg min^{-1}:

1. No extra COD addition
2. 0.0125 mg min^{-1} COD
3. 0.0375 mg min^{-1} COD
4. 0.375 mg min^{-1} COD
5. 0.375 mg min^{-1} COD plus absence of aeration

The results of the above five cases (Figure 5.2.14) are significantly different ($p < 0.05$). The results of case 1 to 4 are however not statistically significant ($p > 0.05$). The trend shows that the highest LAS degradation was achieved by loading the lowest external COD (0.0125 mg min^{-1} COD) with aeration. This indicates that the lowest COD load can already enhance the LAS degradation by stimulating microbial growth. A too high COD load has, however a negative impact on LAS degradation. Such a negative impact is of course due to the fact that a high COD load depletes the dissolved oxygen concentration in the system, particularly in the benthic sediment where the most dominant LAS degradation takes place. A combination of high COD load with the absence of aeration can further slowdown the LAS in-stream removal rate (see Figure 5.2.14, the upper curve). This also coincides with the fact that LAS degradation highly depends on the presence of sufficient DO in the system.

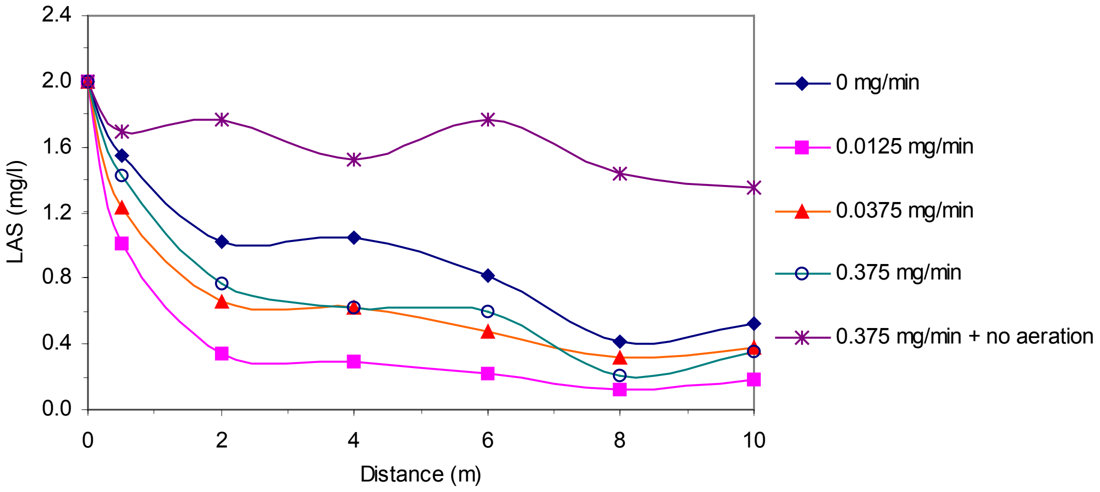


Figure 5.2.14: Effect of extra COD load level on the LAS degradation

Step-down test: Persistence test

To investigate how long LAS can stay in the river system, after the input ceases, two experiments were conducted. In the first experiment, an LAS solution was added continuously to the artificial river at steady-state (at a constant load) for 20 hours, without aerating the river to allow LAS accumulation in the river. After stopping the addition of LAS, the river was aerated and LAS concentrations in the river were monitored in 2, 6 and 10 m every 20 minutes. The second experiment was similar to the first experiment but this time the river was aerated while LAS was continued to being added (for about 20 hours). The result shows that there is no significant difference between the two experiments (see Figure 5.2.14). Regardless of the initial concentration (higher LAS concentration when the river was not aerated), the LAS concentrations at 6 and 10 m become below the detection limit within about 120 minutes (2 hours) and 160 min (2.7 hours) respectively, which is equal to the average hydraulic residence time of the corresponding locations.

This indicates that in aerobic water phase of real river system there will be a complete removal of LAS within a few hours (depending on the hydraulic residence time and river flow rate) from the system when the input ceases. This suggests that biodegradation, advection and fast sorption equilibrium are responsible for LAS in-stream removal. During aeration the LAS concentration in the pore water was found to be one order of magnitude lower than in the overlying water. Thus, adsorption and accumulation of LAS in the biofilm negligibly contributes to the fate of LAS in-streams or rivers (Takada, 1994).

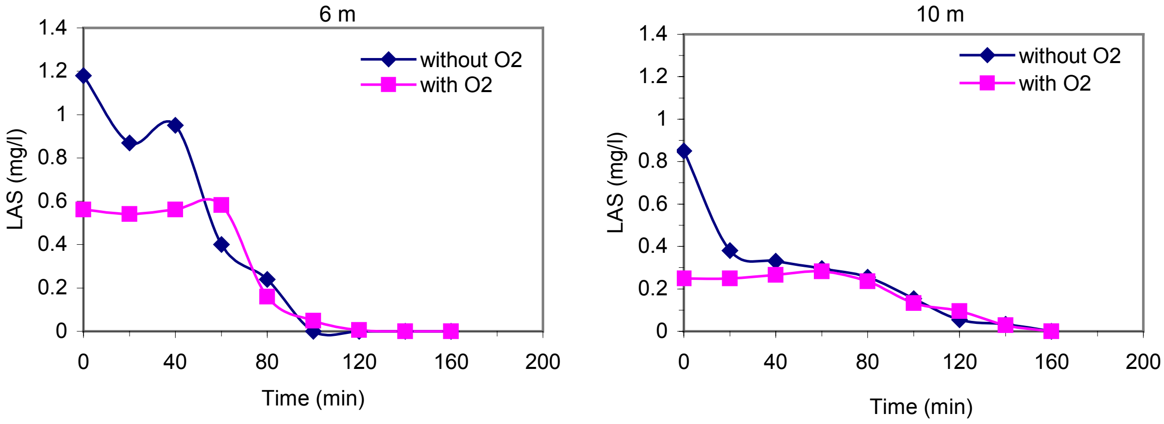


Figure 5.2.15: Step-down experiments at 6 and 10 m

5.2.4. Conclusions

The effect of different factors on the fate of LAS (extra nutrient load, aeration and presence of benthic biofilm) was investigated in an artificial river. The results show that the LAS sorption equilibrium is reached very rapidly (within 5 minutes). LAS degradation depends on the DO concentration in both biofilm and in the overlying water, and thereby any factor that influences the DO concentration in rivers (e.g. high COD) can influence LAS degradation. Furthermore, the presence of biofilm resulted in rapid LAS degradation.

Based on the results obtained during this study one can conclude that considering biofilm kinetics an organic contaminant fate model for rivers is very important, especially in shallow rivers. Besides, both in nutrient rich or nutrient poor rivers, the variation of the external nutrient load can affect the fate of an organic contaminant, and thus including limitations (oxygen and nitrogen) in the organic contaminant degradation models is necessary. The step-down test also confirms that biodegradation and advection, not sorption and accumulation, are most important for the fate of LAS in rivers. The sensitivity of LAS degradation to the ammonia nitrogen is an interesting finding and may induce further research to investigate the mechanism.

Chapter 5.3

Integrated modelling of basic water quality and fate of organic contaminants in rivers[1]

The important parts of this chapter will be published as:

[1] Deksissa T. and Vanrolleghem P. A. (2003). Integrated modelling of conventional pollutant and organic contaminant fate in rivers: a microcosm study. In: *Proceedings of the IWA World Congress and Exhibition*, Marrakech, Morocco, September 19–24 2004, in press.

Chapter 5.3

Integrated modelling of water quality and fate of organic contaminants in rivers: A microcosm study

5.3.1. Introduction

In traditional river water quality modelling, both water quality problems, basic water quality (nutrients, organic matter and suspended solids) and contamination by xenobiotic organic substances, have been considered as separate issues and their interaction is hardly studied. As discussed in Chapter 5.2, nutrients can influence the organic contaminant fate in many different ways. Readily biodegradable organic substrate, COD, can induce microbial growth and thereby enhance the biodegradation of organic contaminants. Besides, limiting inorganic substrates/nutrients such as ammonia, nitrate and phosphate can limit microbial growth, and thereby influence the biodegradation of organic contaminants (Perrin-Ganier *et al.*, 2001; Greer *et al.*, 2003).

In the previous chapter (Chapter 5.2) the effect of nutrients (DO, ammonium and COD) on the fate of LAS in rivers were extensively studied by using an artificial river. The results of this experimental study will be used in this chapter to refine and validate the integrated exposure model developed in Chapter 5.1.

Thus, the specific goal of this study is to refine the biodegradation submodel of the organic contaminant fate model for rivers. The biodegradation submodel is refined so that it includes not only the bulk water and benthic sediment/biofilm degradation but also the interaction with nutrients and DO limitation. The performance of the refined model is then compared with the traditional first-order decay model (as a lumped model) on the basis of data collected under steady-state conditions. Finally, the relative importance of model parameters and basic water quality variables is examined on the basis of a sensitivity analysis.

5.3.2. Materials and methods

5.3.2.1. Model formulation

In the experimental study (Chapter 5.2), it was found that biodegradation and dispersion/advection are the dominant removal mechanisms for LAS in-streams or rivers. This section will therefore mainly focus on the conceptual hydraulic model, the so-called cascade of Continuously Stirred Tank Reactors in Series (CSTRS), and the biodegradation submodels. In the conceptual hydraulic model, the number of tanks-in-series required to represent the dispersion of the river can be estimated on the basis of a tracer study, in this case using NaCl as a conservative substance (non-reacting or inert substance, which ideally should not be present in the system under consideration).

The organic contaminant fate submodel (based on a general mass balance) was discussed in detail in Chapter 5.1. So, only the general concept of the method will be summarised below. The integrated model has two main submodels: a basic water quality submodel (simulates nutrient fate) and an organic contaminant fate submodel. For the basic water quality submodel, the simplified River Water Quality Model Number 1 (Deksissa *et al.*, 2001; see Chapter 4.1) was applied. The organic contaminant fate submodel is a refinement of the biodegradation submodel developed by (see Chapter 5.1). Replacing the lumped parameter of the overall pseudo first-order biodegradation coefficient by terms corresponding to sedimentation, resuspension, and mass transfer (diffusion): $k_{biodeg,}$ r_{sed}, r_{resusp}, and r_{diffu} respectively, the general mass balance for the total organic contaminant in e.g. the bulk water (see Chapter 5.1, equation 5.1.6) can be rewritten as follows:

$$\frac{d(VC_T)}{dt} = Q_{in}C_{Tin} - Q_{out}C_T - k_{bio\deg}C_TV - r_{sed}\cdot V + r_{resusp}\cdot V_{bed} + r_{diffu}\cdot A \tag{5.3.1}$$

$$r_{sed} = f(U_{sed}, h_{depth}, f_{POC}, C_T) \tag{5.3.2}$$

$$r_{resusp} = f(U_{resus}, f_{POC}, C_{T,bed}) \tag{5.3.3}$$

$$r_{diffu} = f(K_L, f_d, f_{doc}, C_T, C_{T,bed}) \tag{5.3.4}$$

As the first aim of this chapter is to refine the biodegradation submodel, the other processes such as sedimentation, resuspension, and mass transfer (diffusion) between the river bed and the overlying water will not be discussed further in this chapter except in the model calibration and sensitivity analysis, as this should consider all processes included in the model. The details of the model formulation for those processes other than the biodegradation model are given in Chapter 5.1.

5.3.2.2. Refining the biodegradation submodel: Incorporation of nutrient limitation

In Chapter 5.1, only oxygen was considered as the limiting factor for biodegradation of an organic contaminant. In this chapter, based on the results obtained in Chapter 5.2 that not only dissolved oxygen but also other substrates like inorganic nutrient sources can limit degradation of organic contaminants, the overall pseudo first-order degradation coefficient (k_{biodeg}) can be further detailed as follows:

$$k_{bio\deg} = k_{bulk} + k_{biofilm} \tag{5.3.5}$$

$$k_{bulk} = k_{b1} \cdot F_T \cdot F_{NH} \cdot F_{O2} \cdot X_H \tag{5.3.6}$$

$$F_{NH} = \frac{S_{NH}}{K_{NH} + S_{NH}} \tag{5.3.7}$$

$$F_{O2} = \frac{S_{O2}}{K_{O2} + S_{O2}} \tag{5.3.8}$$

$$k_{biofilm} = f(k_{b2}, S_{O2}, S_N, K_L, L_f, X_f, d_{bed}) \text{ (see Chapter 5.1)} \tag{5.3.9}$$

$$F_T = \theta^{(T-T_0)} \qquad \begin{array}{ll} \theta = 1.047 & \text{if } T \geq 19°\text{C} \\ \theta = 1.187 - 0.00729T & \text{if } T < 19\ °\text{C} \end{array} \tag{5.3.10}$$

where

k_{biodeg}	overall pseudo first-order biodegradation rate constant [d^{-1}]
k_{bulk}	pseudo first-order biodegradation rate constant in the bulk water [d^{-1}]
$k_{biofilm}$	pseudo first-order biodegradation rate constant in the biofilm [d^{-1}]
k_{b1}	second-order biodegradation rate constant in the bulk water [L $mg^{-1}.d^{-1}$]
k_{b2}	second-order biodegradation rate constant in the biofilm [L $mg^{-1}.d^{-1}$]
F_{NH}	Monod limitation factor for ammonia nitrogen [-]
F_{O2}	Monod limitation factor for oxygen [-]
F_T	temperature correction factor (Thomann and Mueller, 1987) [-]
S_{O2}	dissolved oxygen concentration [mg L^{-1}]
K_{O2}	half saturation constant for oxygen [mg L^{-1}]
S_{NH}	ammonia nitrogen concentration [mg L^{-1}]
K_{NH}	half saturation constant for ammonia [mg L^{-1}]
S_{GC}	generic organic compound concentration [mg L^{-1}]
X_H	suspended microbial biomass concentration [mg L^{-1}]

K_L	external mass transfer coefficient [m d^{-1}], determined based on empirically derived formula ($K_L = 0.19\Phi M^{-2/3}$; DiToro *et al.*, 1981); Φ and M are the porosity and the molecular weight of the compound under consideration respectively
L_f	biofilm thickness [m]
X_f	biofilm density [g m^{-3}]
d_{bed}	active sediment depth [m]

Other conventional pollutants can also affect the fate of organic contaminants. Apparently, the soluble COD variation affects the fate of organic contaminant in two ways: (1) it depletes the DO concentration during high COD load, and thereby inhibits aerobic degradation, (2) it enhances biodegradation by stimulating microbial growth in both aerobic degradation (in low loaded waters) and anaerobic degradation (in anoxic conditions). Note that whether a chemical degrades in aerobic or anoxic conditions depends on its biodegradation properties. For example, LAS degrades only in aerobic conditions (Federle and Schwab, 1992; Steber and Berger, 1995), whereas polychlorinated biphenyls can only degrade in anaerobic conditions (Brown *et al.*, 1987; Kuo *et al.*, 1999). Thus, the above effects of soluble COD can be included in the model only when one couples the basic water quality to the organic contaminant fate model.

Similarly, aerobic biofilm degradation (equation 5.3.9) too depends directly on the concentrations of DO and ammonia nitrogen, and indirectly on the soluble COD. Two biofilm modelling approaches were applied: the half-order kinetics approach of Raugh and Vanrolleghem (1998) and the second-order kinetics approach (Melcer *et. al.*, 1995). The former was applied for DO, whereas the latter was used for other substrates (nutrients and organic contaminants). Nitrogen and oxygen limitations are not explicitly included in the model of Melcer and his co-workers. Therefore, an attempt has been made to consider both oxygen and nitrogen limitation in the model using a logistic function, e.g. if $S_{NH} > S_{NH,minimum}$ and $S_{O2} > S_{O2,minimum}$ then, the biofilm degradation for organic contaminant will take place. Of course, this method will result in a discontinuous function, but at least the effect of nutrient and dissolved oxygen is included.

5.3.2.3. Determination of second-order biodegradation rate constant: k_{b1}

The second-order biodegradation rate constant, k_{b1}, can be approximated on the basis of the Monod kinetics as follows:

$$\frac{dS_{GC}}{dt} = \frac{q_{\max}.S_{GC}}{K_{GS}+S_{GC}} \cdot X_H \approx \frac{q_{\max}S_{GC}}{K_{GC}} \cdot X_H = k_{b1}S_{GC}X_H \qquad \text{if } S_{GC} << K_{GC} \tag{5.3.11}$$

$$\Rightarrow k_{b1} = \frac{q_{\max}}{K_{GC}} \tag{5.3.12}$$

where q_{max} is the maximum rate of substrate utilization (mg S_{GC} (mg X_H)$^{-1}$ d^{-1}), and K_{GC} is the half saturation constant for the generic organic contaminants [mg L^{-1}].

The second-order kinetics (equation 5.3.11) is more advantageous than the first-order kinetics ($dS_{GC}/dt = -kS_{GC}$) because the removal rate of a generic compound S_{GC} depends on the heterotrophic biomass concentration (X_H), and the second-order kinetics can therefore handle the time variable biomass concentration. In contrast, first-order kinetics assumes constant biomass concentration. The values of q_{max}/K_{GC} for many organic contaminants are summarized in Schonnor (1996), ranging from 2.5 (for 1, 2 Dichorobenzene) to 50 L mg^{-1} d^{-1} (for Styrene). For the primary substrate, for example acetate, the value is 3.8 L mg^{-1} d^{-1}. These values can be used as initial guess for LAS, but site-specific values must be determined by calibration.

5.3.2.4. Sensitivity analysis

As indicated in previous sections of this thesis (Chapter 4.1 and 5.1), the sensitivity analysis is simply an investigation of the influence of changes in model parameters on simulated results. Like in the previous chapters, the relative sensitivity function (see equation 4.1.6 in Chapter 4.1 and equatins 5.1.25 and 5.1.26 in Chapter 5.1) is applied.

Here, sensitivity analysis is performed on model parameters and model inputs based on data collected on the 26th of January 2003. For the model parameters, the parameters were changed one at a time and the effects were ranked to show which parameters have most or least influence. In the dynamic simulation, ranking was done on the basis of the mean absolute value of the relative sensitivity function (equation 5.1.26 in Chapter 5.1). Such rank can be used to determine which parameters should be estimated for the particular case and which can be assumed. For example, if the model is very sensitive to the active sediment depth, this should be estimated from data rather than being assumed a default value from literature. If other parameters like the resuspension velocity and partition coefficients have little influence on the biodegradation submodel, very little effort should be spent in estimating their exact value.

In integrated modelling of the basic water quality and organic contaminant fate, it is also very important to consider sensitivity analysis not only for the model parameters but also for the model input in order to examine the relative importance of the basic water quality input variables for the organic contaminant fate prediction. In this work, the sensitivity for the model inputs is also analysed.

The sensitivity analysis for the model parameters was carried out using the WEST® simulator, which has a sensitivity analysis module for model parameters. For the model input, the original input file was modified by introducing a small change of the model inputs (e.g. by 1% increase). Subsequently, the simulation was run for both the original and modified input variables. Then, the output files of both input files were exported to a spreadsheet programme where the relative sensitivity function was calculated, and the mode inputs were ranked.

5.3.2.5. Model calibration and validation

Before a mathematical model is applied as a tool for water quality management, it has to be calibrated and validated for both hydraulic and water quality submodels. The important parameters that need to be calibrated are first selected using on the results of the sensitivity analysis as discussed above. The hydraulic submodel must be calibrated prior to the water quality model. In the conceptual hydraulic model (a cascade of tank-in-sires), first the number of tanks needs to be determined from a tracer study.

A cascade of tank-in-series was calibrated for the hydraulic submodel using NaCl as a conservative substance. The graphical representation (configuration) of the tank-in-series model for the artificial river implemented in the WEST® simulator is presented in Figure 5.3.1. First, the river was divided into 5 main microcosm stretches (river_1 to river_5). Then, each river stretch was further subdivided into a number of tanks (1 to 5) in order to obtain the corresponding total number of tanks-in-series 5, 10, 15, 20 and 25, respectively.

The simulation results of these different systems in terms of the number of tanks-in-series were examined, and the number of tanks was selected on the basis of the best fit. The best fit (agreement) between measured and simulated data set was evaluated based on the well known objective function Root Mean Square error (RMS) as follows:

$$RMS = \left[\frac{\sum (C_{measured} - C_{simulated})^2}{N} \right]^{0.5} \qquad (5.3.13)$$

where N is the number of measured data points, $C_{measured}$ and $C_{simulated}$ are the measured and simulated concentration of NaCl respectively.

Once the hydraulic submodel is calibrated, the calibration of the water quality submodel is initiated. Prior to this step, the most important parameters are selected on the basis of a sensitivity analysis and prior knowledge. Then the model is calibrated for both a dynamic and a steady-state simulation using equation 5.3.13 and data collected in January and June 2003.

Before the model is applied in the field as a tool for water quality management, it has to be validated with an independent data set. The predictions of the proposed, calibrated model are then compared with these data on the basis of both dynamic and steady-state conditions. Here again, equation 5.3.13 and data collected in January and June 2003 (but different from data used for calibration) are used to validate the model.

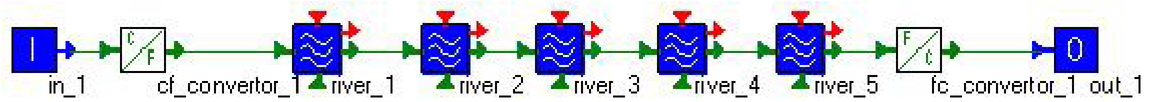


Figure 5.3.1: River (microcosm) setup in the WEST® simulator

5.3.2.6. Statistical analysis

Data were analysed with the S-PLUS statistical software, and statistical significance (t test and one-way analysis of variance) was considered at a $p < 0.05$.

5.3.3. Results and discussion

5.3.3.1. Determination of optimum number of tanks

Using a different number of tanks, the simulated NaCl data set was compared with the measured data set. The results are indicated in Figure 5.3.2 for the microcosm stretch number 3 (6 m).

The optimum number of tanks-in-series was determined on the basis of the RMS error (see Figure 5.3.3 left). This shows that the optimum number of tanks required for the artificial river with an average flow rate of 0.2 l min^{-1} is 15. Using 15 tanks-in-series, the comparison of simulated and measured data set for all measurement location along the river is indicated in Figure 5.3.3 right. The results show that 15 tanks-in-series can adequately describe the

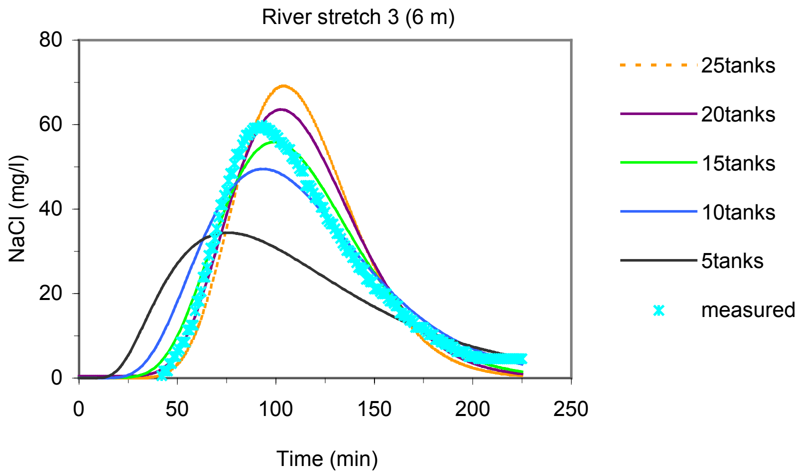


Figure 5.3.2: CSTRS model calibration: the best fit with 15 CSTRS

pollution propagation (dispersion) of the river under consideration for the average flow rate of 0.2 l min^{-1}.

This configuration with 15 tanks was also checked for a higher river flow rate (e.g. 0.5 l min^{-1}) and the result is indicated in Figure 5.3.4. The results show that 15 CSTRS, which gave the best fit for 0.2 l min^{-1} flow rate, is not enough to represent the pollution propagation at a higher flow rate of 0.5 l min^{-1} which leads to higher dispersion (see Figure 5.3.4 left).

Therefore, a larger number of tanks-in-series is required (see Figure 5.3.4 right). Subsequently, 25 tanks-in-series (CSTRS) were found to be the best number of tanks to represent the pollution propagation (dispersion) when the average flow rate is 0.5 l min^{-1}. Indeed, the number of CSTRS depends on the river flow rate.

Rivers are typically approximated as plug flow assuming negligible dispersion. This requires a large number of tanks (ideally infinite) in order to approach the plug flow (Levenspiel,

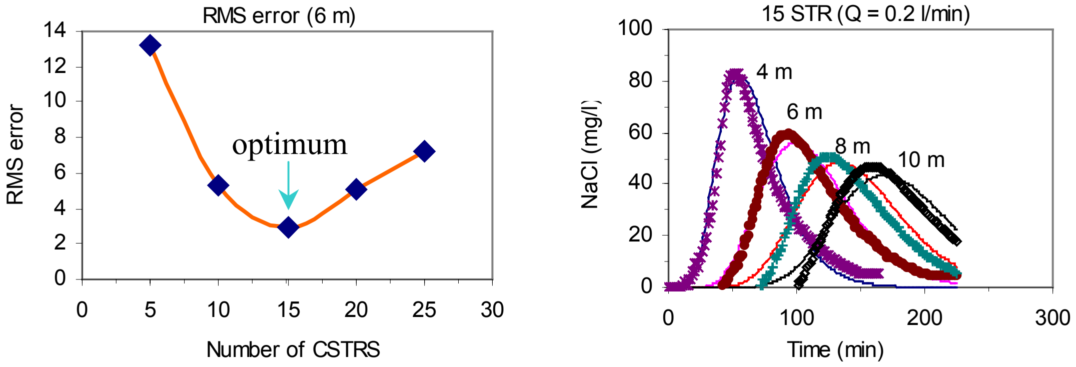


Figure 5.3.3: Optimum number of tanks (left) and model fit with the optimum number of tanks (right)

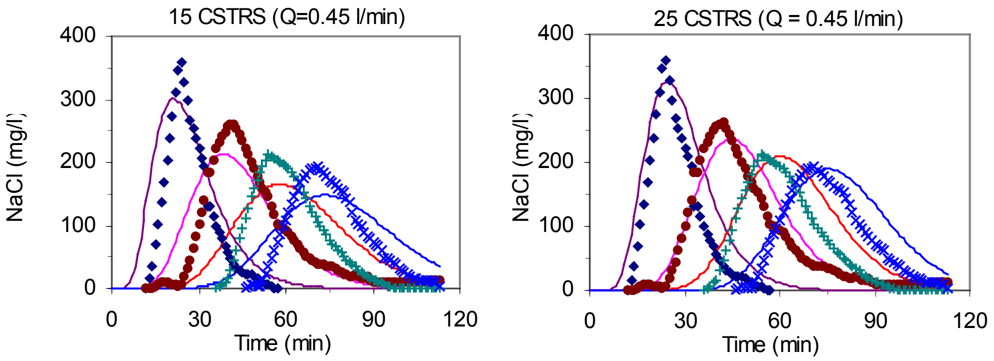


Figure 5.3.4: The number of CSTRS required for higher flow rate (0.5 l min^{-1}): symbols are for the measured data set, whereas lines are for the simulated data set

1999). In this study we found that there is indeed a minimal number of tanks that can adequately represent the pollution propagation in rivers. This means there is a significant contribution of dispersion.

5.3.3.2. Sensitivity analysis

Model parameters

The model output sensitivity to the model parameters was examined on the basis of a dynamic simulation (pulse input) and a relative sensitivity function (equations 5.1.25 and 5.1.26, in Chapter 5.1). The results are summarised in Table 5.3.1. After ranking, the biodegradation parameters turnout to be more influential than the physical parameters (u_{sed} and u_{resus}). The most sensitive parameters must normally be determined accurately. As the determination of

Table 5.3.1: Sensitivity analysis for the model parameters

Rank	Parameters	Average $\|S_R\|$ (%)	minimum $\|S_R\|$ (%)	maximum $\|S_R\|$ (%)
1	k_{b1}	0.08219	0.01175	0.12885
2	K_L	0.02099	0.00226	0.03224
3	K_{NH}	0.01926	0.00275	0.03021
4	K_{O2}	0.01167	0.00009	0.01908
5	k_{b2}	0.01128	0.00154	0.01871
6	X_f	0.01125	0.00154	0.01867
7	L_f	0.01125	0.00154	0.01864
8	d_{bed}	0.00657	0.00010	0.01486
9	u_{sed}	0.00093	0.00001	0.00173
10	u_{resus}	0.00002	0.00000	0.00007

all these parameters is beyond the scope of this study, literature values were applied for most of the above parameters but few were measured (e.g. d_{bed}) or calibrated (see Table 5.3.3).

Model input

In addition to model parameters, the sensitivity to the model input were analysed too. The results of this analysis provide information concerning the relative importance of the basic water quality input variables, and which nutrient is influencing the degradation of the contaminant. Four model input variables were considered, i.e. readily biodegradable COD, NH_4-N, dissolved oxygen and suspended heterotrophic biomass concentrations. The relative importance of these input variables was then evaluated. Running the model for a small (e.g. 1%) increase in one input variable at a time, the results of the relative sensitivity analysis are given in Table 5.3.2.

The sensitivity of the model output (LAS prediction) to the state variables of the basic water quality model show that S_{NH} ranks first followed by X_H, S_{O2} and S_S. The LAS degradation is very sensitive to small changes in ammonia nitrogen, suspended microbial biomass, dissolved oxygen, and relatively less sensitive to a small change of soluble readily biodegradable COD (S_S). This is due to the fact that S_{NH}, X_H and S_{O2} are explicitly incorporated in the organic contaminant fate submodel, while S_S only indirectly influences the fate of LAS degradation through X_H and S_{O2} by regulating the growth of X_H and increasing S_{O2} consumption.

The sensitivity of the LAS degradation to the soluble COD variation can be examined under two possible conditions. Under the first condition, an adequate COD concentration, but low concentrations of other inorganic nutrients such as dissolved oxygen, phosphorous, and nitrogen were considered. As the bacterial growth depends on such multiple substrates, the limitation of one of the substrate reduces aerobic microbial activities. If there is adequate oxygen, phosphorous and nitrogen concentrations, an increase of the COD concentration will

Table 5.3.2: Sensitivity analysis for model inputs (dynamic simulation)

Model inputs	Descriptions	Average $\lvert S_R \rvert$ (%)	Minimum $\lvert S_R \rvert$ (%)	Maximum $\lvert S_R \rvert$ (%)
S_{NH}	Ammonia nitrogen (NH_4-N+NH3-N) (mg L^{-1})	110.58	15.26	163.16
X_H	Active heterotrophic microbial biomass concentration (mg L^{-1})	16.06	2.23	24.24
S_{O2}	Dissolved oxygen concentration (mg L^{-1})	13.85	1.02	21.15
S_S	Readily biodegradable soluble COD (mg L^{-1})	0.11	0.01	0.17

determine the growth of heterotrophic bacteria, which will thereby enhance the LASdegradation. In contrast, for high COD and ammonia loaded waters, oxygen can be depleted and the LAS degradation can be retarded by development of anoxic conditions in the river bed.

5.3.3.3. Calibration and validation of water quality submodel

Calibration

The model was calibrated for two experimental conditions: dynamic simulation (during winter, in the beginning of the experiment) and steady-state simulation (during summer). Using the optimum number of tanks obtained above (15 tanks) and the parameter values indicated in Table 5.3.3, the model calibration results for both dynamic and steady-state simulations are presented in Figure 5.3.5. In the dynamic simulation, the biofilm thickness and active sediment were still relatively small. For both the dynamic and steady-state simulations, the calibration results show that the simulated data sets agree well with the measured data sets within 10 – 20 % error.

Table 5.3.3: Model parameter values applied in the model

	Parameter	Literature values	Calibrated/Fixed
1	L_f [m]	0.0001^{*}	0.0001
2	X_f [g m^{-3}]	40000^{*}	40000
3	k_{b1} [m^{3} g^{-1} d^{-1}]	3.8^{**}	3
4	k_{b2} [g m^{-3}]	$0.024^{\clubsuit}$	0.028
5	K_L [m d^{-1}]	0.00365^{+}	0.00365
6	K_{NH} [g m^{-3}]	$0.012^{\blacklozenge}$	0.012
7	K_{O2} [g m^{-3}]	$0.011^{\blacklozenge}$	0.011
8	d_{bed} [m]	measured	measured
9	u_{sed} [m]	$0\text{-}0.25^{\blacklozenge}$	0.25
10	u_{resus} [m]	$0.0\text{-}0.0008^{\spadesuit}$	0.0005

*Melcer *et al.* (1996); **Schnoor (1996); $^{\clubsuit}$Boejie, 2001; $^{\blacklozenge}$Giri (2001); $^{\spadesuit}$DiToro (1982); $^{+}$calculated based on the empirical formula given in DiToro *et al.* (1981); $^{\blacklozenge}$Reichert *et al.* (2001).

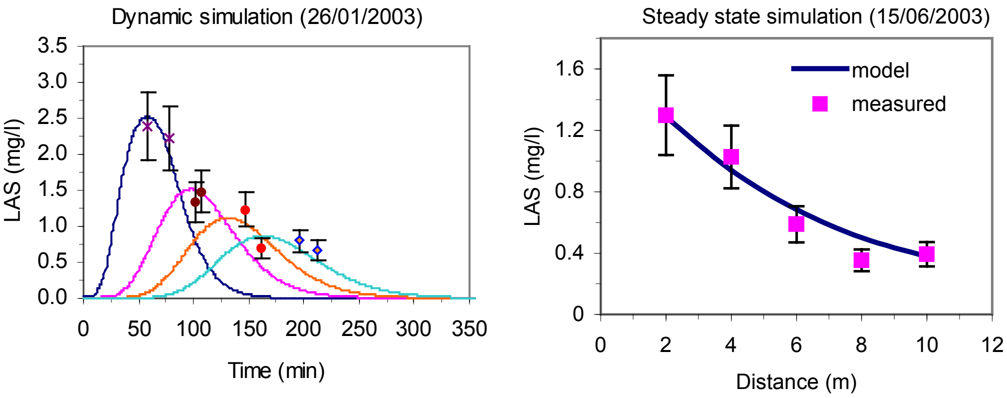


Figure 5.3.5: Model calibration: Dynamic simulation (left) and steady-state simulation (right); lines are the model predictions, the symbols with error bar represent the measured data sets

Validation

Dynamic simulation

In the validation study, the model was run on the basis of an independent data set without changing the calibrated values except for the forcing functions, e.g. temperature and the active sediment layer. Using data collected on January 27, 2003, the dynamic simulation result shows that the model can reasonably express the time profile of the contaminant concentration in the artificial river (see Figure 5.3.6).

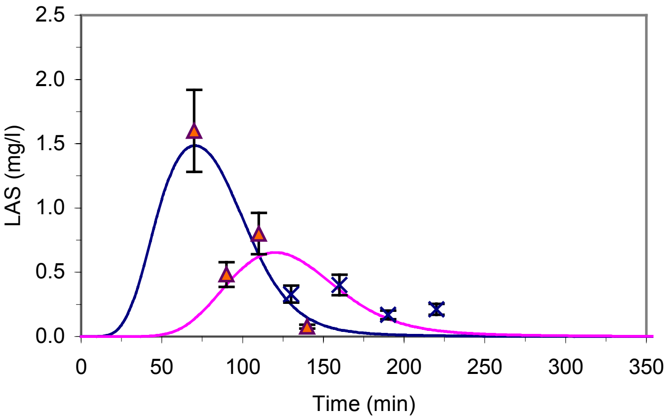


Figure 5.3.6: Model validation with a dynamic simulation

Steady-state simulation

The model was further run on the basis of several steady-state monitoring data sets in order to validate the model. The simulation results for two experimented conditions, i.e. with and without aeration, are presented in Figure 5.3.7. Under both conditions, the simulated data sets agree well with the measured ones.

Furthermore, adding a constant flux of ammonia nitrogen (0.54 mg min^{-1}), the model output for two conditions (with and without aeration) were compared with measured data sets (see Figure 5.3.8). Again, the simulated data set agrees well with the measured data set within 20% error. This suggests that the model can adequately predict the concentration of LAS. In the absence of aeration, LAS accumulates more in the system, which confirms that LAS does not degrade under anoxic condition (Steber and Berger, 1995). Oxygen limitation results in high LAS concentrations, which can be predicted adequately by the proposed model as depicted in Figure 5.3.8.

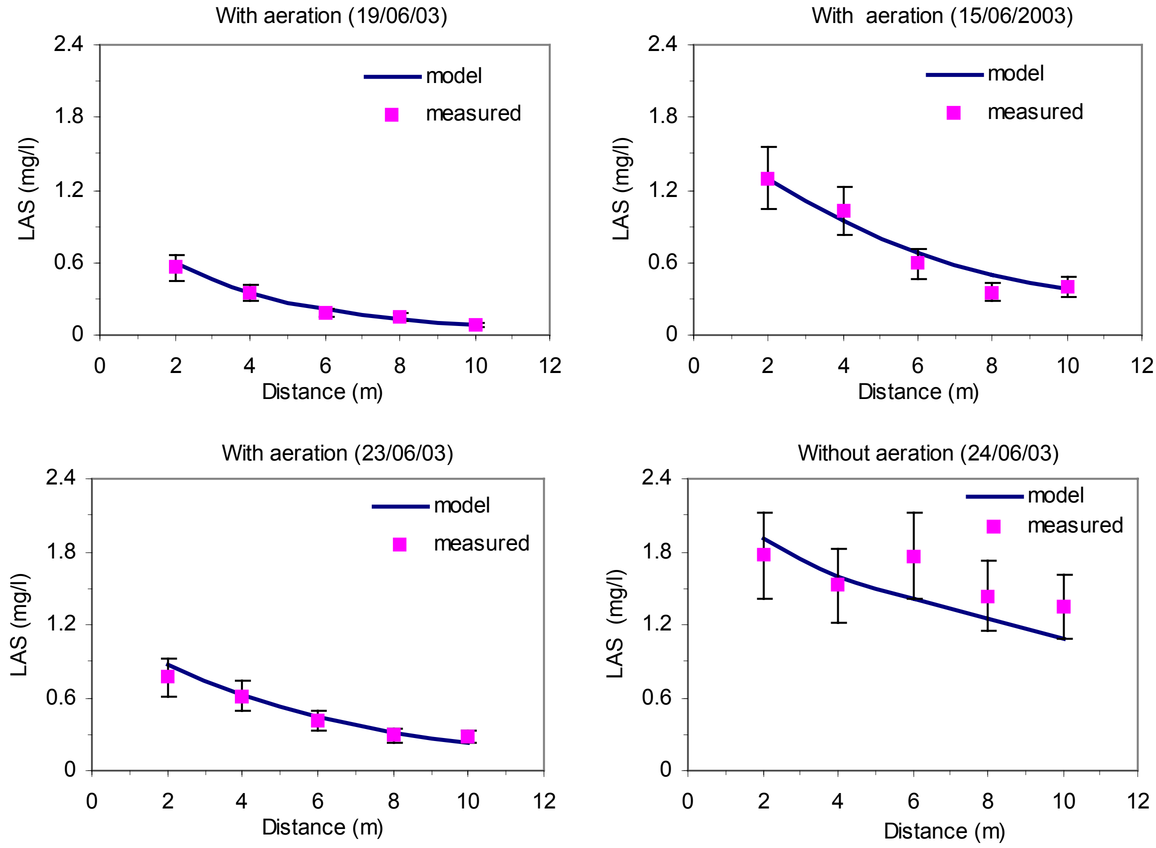


Figure 5.3.7: Model validation under steady-state conditions

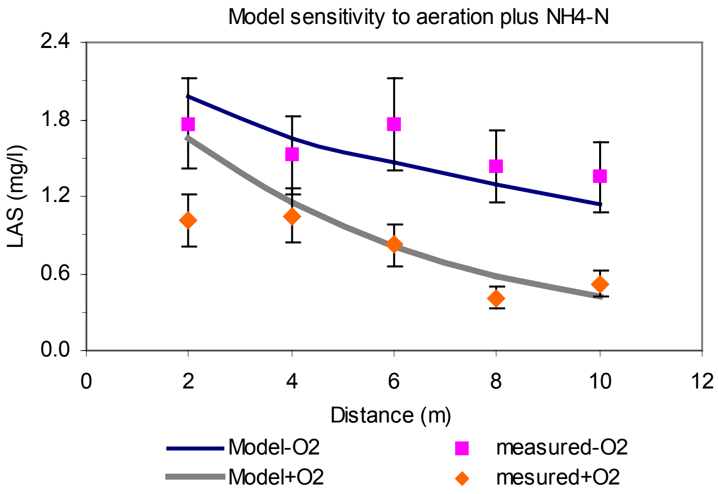


Figure 5.3.8: Comparison of model prediction with the measured data set: +O2 with aeration and -O2 without aeration

5.3.3.4. Comparisons of modelling approaches: Steady-state conditions

Under steady-state conditions, one may consider to use a simple in-stream fate model that is based on lumped parameters, which require less monitoring data to estimate. The simplest water quality models used in practice are based on the principle of first-order kinetics, and thereby decay/decomposition of a pollutant is proportional to the initial concentration of the pollutant and the factor of proportionality, the decay rate coefficient k [T^{-1}]. Assuming steady-state emissions, the chemical fate and advective transport can be described as follows:

$$\frac{dC}{dt} = -k \cdot C \Rightarrow C_x = C_0 e^{-k\frac{x}{u}} \qquad (5.3.16)$$

where C_x is the concentration of organic contaminant at river distance x [M L^{-3}], C_0 is the initial concentration of the pollutant [M L^{-3}], x is the river distance [m], u is the average flow velocity [L T^{-1}].

In the higher-tier approach (e.g. this study), the overall first-order decay coefficient k is typically determined based on separate sub-models: biodegradation, volatilisation (for volatile compounds), photolysis, sedimentation, etc. Subsequently, the overall first-order decay coefficient is obtained by summing these individual rate coefficients.

In the lower-tier approach (equation 5.3.16), it might be of interest to determine *k* by calibration (fitting the model output to the measured data set) rather than using individual sub-models. In this case *k* is considered as a lumped parameter, i.e. the overall removal rate constant, which does not take into account nutrient dynamics, variations of microbial biomass concentration, and sorbed or dissolved fractions of organic contaminants.

Here, the results of such simple modelling approach were compared with that of the proposed higher-tier approach. First, both models were calibrated once on the basis of the same monitoring data collected on 15th June 2003. Then, using monitoring data collected on 19th, 23rd and 24th June 2003, the simulation results of the two models were examined based on the mean of sum of square errors. The results are presented in Figure 5.3.9.

The results show that the refined model (higher-tier approach) has a superior prediction performance (low mean of sum of square error) to the simplest fate model when *k* is considered as a lumped parameter. This suggests that considering a single issue model including the biofilm kinetics, results in better model predictions. Note that this comparison is

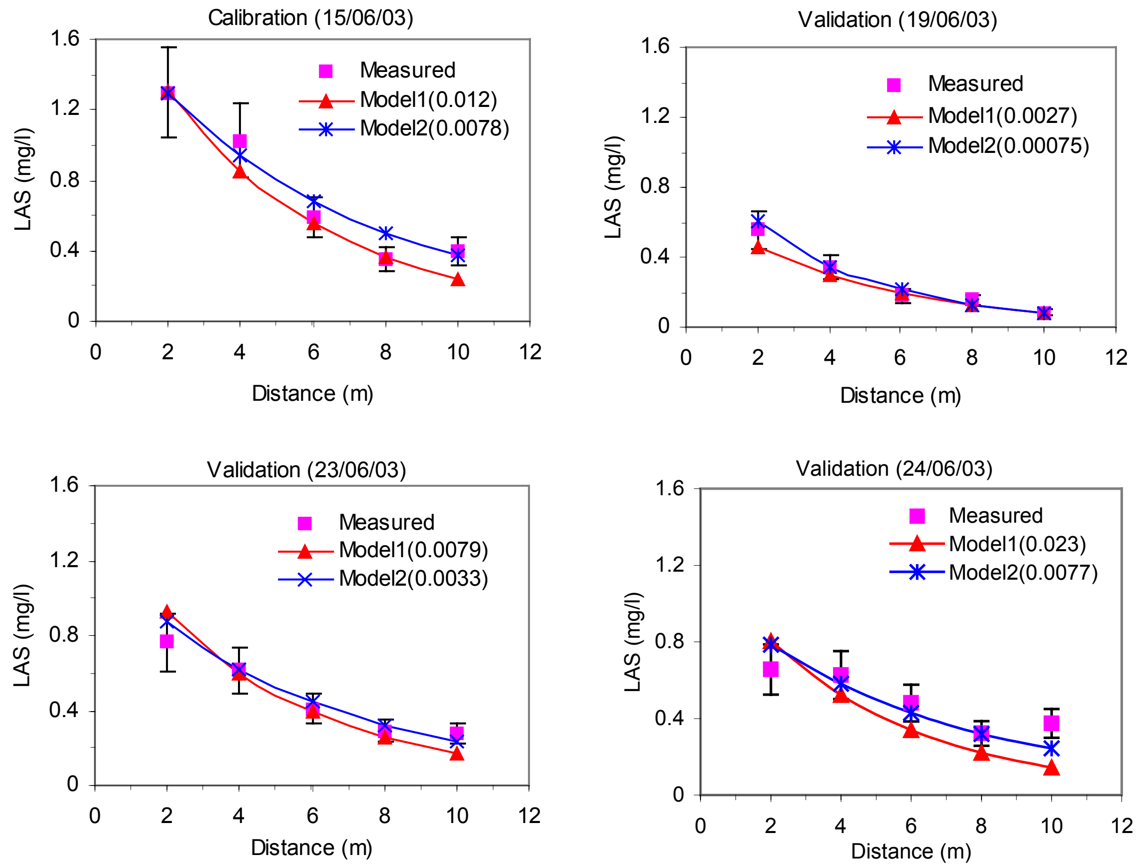


Figure 5.3.9: Comparison of simplest model (Model1) with the refined model (Model2), the mean of sum of square error is given in the legends within the parenthesis

under steady-state conditions, whereas under dynamic conditions, only the higher-tier approach is applicable as it considers individual sub-models and their temporal variations. Most important is that the lower-tire model does not allow any extrapolation, as k must be estimated for each case.

5.3.4. Conclusions and recommendations

The biodegradation submodel of the organic contaminant fate model was refined. A nitrogen limitation term was incorporated in the organic contaminant fate model. The relative importance of model parameters and inputs was analysed on the basis of a relative sensitivity analysis. The refined model output was compared with a simple or lumped model output (first-order decay).

Based on the results obtained, one can draw the following conclusions:

- the model can adequately describe the fate of organic contaminants (LAS) in the artificial river;
- coupling not only DO but also nutrient limitation to the organic contaminants is appropriate and necessary;
- including biofilm kinetics in the organic contaminant fate models is important, especially in shallow rivers;
- the refined model predicts the LAS concentration in rivers more accurately than a lumped pseudo first-order instream fate model, and
- the sensitivity analysis results show that the model is most sensitive to biodegradation parameters. Therefore these parameters need proper estimation.

For a further research, the proposed model needs to be tested on the basis of field data and other organic contaminants.

Part 6

Integrated modelling of eutrophication and organic contaminant fate and effect in rivers[1,2]

The important parts of this part were (will be) published as:

[1] Deksissa T. and Vanrolleghem P. A. (2004). Integrated modelling of eutrophication and organic contaminant fate in rivers. *Water and Environmental Management Series*, in press.

[2] Deksissa T. and Vanrolleghem P. A. (2003). Integrated modelling of eutrophication and organic contaminant fate in rivers. In: *Proceedings of the IWA conference on environmental biotechnology advancement on water and wastewater applications in the tropics*, Johor Bahru, Malaysia, August 7–8 2003.

Chapter 6

Integrated modelling of eutrophication and fate and effect of organic contaminants in rivers (RIVEUTOX1)

6.1. Introduction

Eutrophication/nutrient enrichment and contamination by xenobiotic organic pollutants are the main problems in surface water quality management. Although both problems have been subject to several studies, they have been treated as separate issues in traditional water quality modelling. In this study, the model that deals with such separate issues is defined as a single-issue model. The traditional modelling approach is based on the assumptions that the change in the trophic status has a negligible feedback on toxicant fate, and that the toxicity of toxic compounds produces a negligible feedback on processes that determine the fate of organic contaminants and the nutrient cycle. Therefore, their interaction is not considered.

The interaction between eutrophication and organic contaminants may occur via many mechanisms (Gunnarsson *et al.*, 1995; Bondavalli, 2003). Eutrophication may cause dilution of contaminants by increasing the amounts of microbial biomass, enhancing of biodegradation in the presence of oxygen, organic contaminant scavenging by suspended Particulate Organic Carbon (POC), sedimentation of contaminants and contaminant uptake in the food chain. Also, organic contaminants may have a direct or indirect toxic effect on aquatic organisms. Such toxic effect in turn affects the organic contaminant fate and nutrient cycles (Legovic, 1997). As the individual models for the separate issues do not address these interactions, an integrated model of eutrophication and organic contaminant fate and effect is required.

Few models, which take into account the interactions indicated above are available: *WASP5* (Ambrose and Martin, 1993), modified *QWASI* (Wania, 1996) and *AQUATOX* (Park *et al.*, 1995). Their limitations are highlighted below. *WASP5* is a combination of the eutrophication model *EUTRO5* and the fate of toxic compounds *TOXI5* including heavy metals and organic compounds. The limitation of *TOXI5* model is that Dissolved Organic Carbon (DOC) is not simulated as a state variable, and is assumed not to vary in time. This assumption affects the sorption kinetics. The limitation of dissolved oxygen and necessity of nutrient for biodegradation is also not explicitly considered. Besides, *WASP5* does not include toxicity.

Wania (1996) has presented an adapted version of the *QWASI* model (Mackay *et al.,* 1989) in order to study the interaction of nutrients and contaminants. This model includes POC settling, resuspension, sorption and burial. But the partitioning of organic contaminants to the non-particulate organic carbon, DOC is not taken into account. Like *WASP5*, this model does not include toxicity.

AQUATOX was built by combining three main submodels: an ecological model (*CLEAN*, Park *et al.*, 1974), toxic fate models (e.g. *PEST*, Park *et al.*, 1982), and an ecotoxicological model (*FGET,* Suárez and Barber, 1992). The *AQUATOX* model is reported to be the most complete integrated ecological model available in literature (Koelmans *et al.*, 2001). However, the most important limitation of this model is that it does not take into account microbial biomass as state variable, and thereby cannot handle the variation of microbial biomass in a system.

Furthermore, the general limitation of the available integrated models is that different models are linked without including all required linking processes and variables, as their specific purposes differ. For example, taking into account nutrient limitation, microbial biomass and dissolved oxygen as state variables in the organic contaminant fate (see Chapter 5.2) is of paramount importance.

In this part of the thesis, an integrated model is presented that takes into account the interaction of nutrient dynamics, eutrophication and organic contaminant fate and effect. The procedure of appropriate submodel (single-issue model) selection is described. The usefulness of the proposed modelling approach was evaluated based on the monitoring data of Linear Alkylbenzene Sulfonates (LAS) in the river Lambro (Italy). The acute and chronic effect of frequent contamination of this river by combined sewer overflows (CSOs) was also analysed.

6.2. Materials and Methods

6.2.1. Model formulation

6.2.1.1. Eutrophication

As a single-issue model (see subsection 6.1), an eutrophication model is concerned with the fate of algae (phytoplankton) and green plants and applied to simulate the Dissolved Oxygen (DO) concentration and the nutrient cycle in surface waters. The most widespread eutrophication models in rivers are the *QUAL2* (Brown and Barnwell, 1987) type models (Shanahan *et al.*, 1998; Drolc and Koncan, 1999; McAvoy *et al.*, 1993). This modelling approach however has several limitations as presented in Reichert *et al.* (2001). The fate of algal biomass is subjected to only three different processes: growth (photosynthesis), respiration and settling. Loss due to grazing and non-predatory mortality is not explicitly considered but lumped together with either the settling or the respiration process. Besides, autochtonous source of carbon (due to death of algae), dinitrification process, both suspended and attached microbial biomass (as state variables) are not considered.

Thus, the IWA Task group on River Water Quality Modelling proposed River Water Quality Model No.1, *RWQM1* (Reichert *et al.*, 2001). This model has an extended eutrophication model that includes the nutrient cycle and the simplified food chain model. It can be extended further towards an integrated eutrophication and organic contaminant fate and effect model, because of its advantages that both mass and elemental balances are the basis of the model. The current version of the model describes a simple food chain in which only one group of algae (as producer) and one group of primary consumers (as herbivores) are considered. This can however be extended to a more complex food chain model by describing the main subgroups of producers and consumers. Once an appropriate food chain model is formulated, bioaccumulation in the food chain model and toxicity can also be integrated. In this study, the interaction of nutrient dynamics and the simple food chain up to primary consumers are taken into account, in order to demonstrate the usefulness of the integrated modelling approach rather than pursuing completeness of the model.

As described in Chapter 4.1, the *RWQM1* modelling approach is relatively complex, and requires large input data sets. Thus, simplification of some process descriptions with an appropriate submodel selection is indispensable. The procedure for sub-model selection for this model is given elsewhere (Vanrolleghem *et al.*, 2001). Subsequently, in this study nitrification was modeled as a single-step process; pH was assumed not to change significantly during the process; and stoichiometric coefficients were determined using a fixed elemental composition for organic substances considering the elements C, H, O, N and P. The conversion rates for the bulk water compartment were formulated with Monod-type limitation factors (Reichert *et al.*, 2001). To reduce the complexity of the model in the integrated model, the anoxic process is not included because it is not relevant for LAS degradation. Such model simplification is assumed to have negligible impact on the nutrient submodel.

Furthermore, benthic sediment is considered as state variable, and a single layer of the biofilm model was applied to describe its behavior. As discussed in Chapter 5.1, two kinetic relations of the biofilm model were used: half-order kinetics with multi-substrate limitation (Rauch *et al.*, 1999) for dissolved oxygen, and first-order kinetics with mono-substrate limitation (Melcer *et al.*, 1995) for the other substrates. This choice was made based on the simplicity of the model implementation for integrated modelling. The interaction of the two compartments, the bulk water and the benthic sediment, is described by the governing process equations: diffusion, sedimentation and resuspension.

6.2.1.2. Organic contaminant fate

As a single-issue model (, organic contaminant fate models describe the fate and distribution of contaminants in the aquatic system. *EXAMS* (Burns and Cline, 1985) is a well-known example of such type of model. Distinction should be made between steady-state and dynamic organic contaminant fate models. Steady-state models do not take into account temporal variability, e.g. *SLSA* (Hydroqual, 1981); *EXAMS* (Burns and Cline, 1985); *TOXIC* (Schnoor and McAvoy, 1981); *SYMPTOX4* (US-EPA, 1989); *GREAT-ER* (Schowanek *et al.*, 2001). These can for instance only be applied during dry weather when temporal variability of the river flow is negligible. On the other hand, dynamic exposure models take temporal variations of the toxicant's fate into account. As toxicity depends on the duration and frequency of exposure (Reinert *et al.*, 2002), and the violation of such duration and frequency of exposure in the receiving water can only be described by a dynamic exposure model (Arbor, 1985), a dynamic organic contaminant fate model is proposed.

The details of the dynamic organic contaminant fate model applied for the integrated modelling, i.e. CHETOX1 are presented in Chapter 5.1. Consequently, only the main important features will be summarized below. The model is formulated on the basis of a simple dynamic mass balance approach. In this model, the "three phases partitioning" is incorporated in both bulk water and benthic sediment compartments, i.e. the partitioning of the contaminant between Particulate Organic Carbon (POC), Dissolved Organic Carbon (DOC) and Truly Dissolved (TD) material (see Figure 6.1). The model assumes local sorption equilibrium within the compartments, but no equilibrium is assumed between the compartments (water, sediment, air, and biota). Other dominant processes included in the model are volatilization, biodegradation (both in bulk water and in benthic sediment),

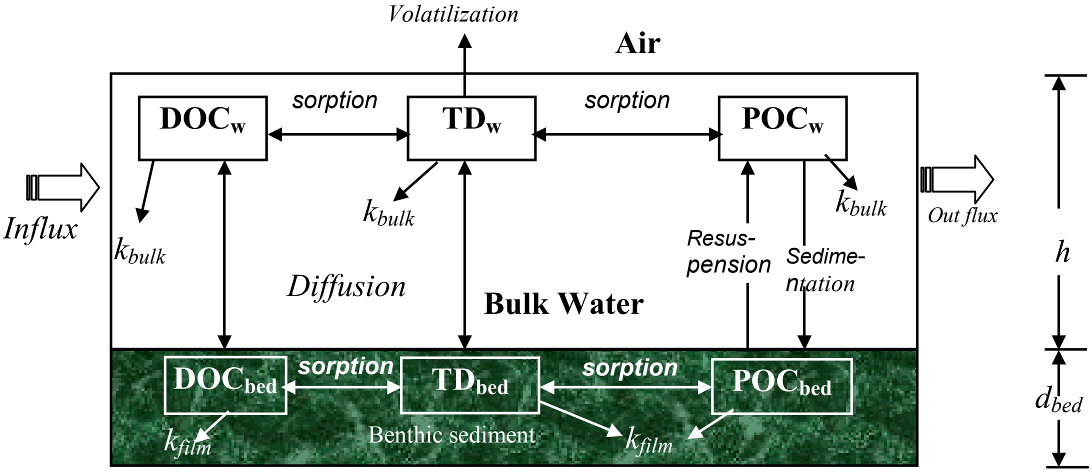


Figure 6.1: Schematic representation of organic contaminant fate in rivers (CHETOX1): h and d_{bed} are the depth of bulk water and active sediment layer (benthic sediment), respectively; k_{bulk} and k_{film} are the pseudo 1st order biodegradation coefficients in the bulk water and benthic sediment respectively (see Chapter 5.1, equations 5.1.16 and 5.1.17); the subscripts *w* and *bed* indicate the bulk water and the benthic sediment compartment, respectively

sedimentation, resuspension and diffusion. Some organic contaminants like LAS can degrade by heterotrophic biomass when dissolved oxygen is sufficiently present in the system. Besides, the presence of the limiting substrates/nutrients can also influence the biodegradation of organic contaminants. Thus, both dissolved oxygen and nutrient limitations are considered in the biodegradation submodel. Details of mathematical formulation have already been described in Chapter 5.1.

6.2.1.3. Bioaccumulation

Despite the fact that the contaminantion of organic contaminants in the aquatic environment is usually very low (in the order of ppm), bioaccumulted chemicals (e.g. DDT, poly chlorinated biphenyls, carbon tetra chloride, …) can result in adverse effects when their concentration in the target site reaches a toxic level. Bioaccumulation is therefore an important process through which chemicals can affect living organisms. As mensioned in a previous section of this thesis (Chapter 2, subsection 2.4.7.1), similar terms are also used to describe the accumulation of contaminants in living organisms: bioconcentration, bioaccumulation and biomagnification. Although these three terms are sometimes used synonymously to describe the concentration of a particular substance in a living organism, the meaning of the three terms is quite different. Bioconcentration refers to concentration of a particular substance in an organism after direct uptake via gill or skin, and is related only to the exposure concentration of the truly dissolved phase in water. The bioaccumulation process not only involves direct uptake via gill or skin but also indirectly via food. Organic contaminants that are both in truly dissolved phase and sorbed phase (sorbed to particulate organic matter or food) is relevant to bioaccumulation processes. Biomagnification occurs when a chemical becomes more and more concentrated as it moves up through a food chain. A typical food chain includes algae eaten by a water flea eaten by a minnow eaten by a trout and finally consumed by an osprey (or human being). If each step results in increased bioaccumulation, i.e. biomagnification, then an animal at the top of the food chain, through its regular diet, may accumulate a much greater concentration of chemical than was present in organisms lower in the food chain. Fortunately, bioaccumulation does not always result in biomagnification. As it requires a very complex food chain model, the biomagnification process will not be considered further in this study.

In this study, both bioaccumulation and bioconcentration processes are included. A bioaccumulation model describes the process of contaminant uptake, excretion, and transformation in aquatic organisms. Microbial biomass (bacteria and algae) is considered as a carrier for the organic contaminant in bioaccumulation. In the proposed integrated model, a widely applied one-compartment bioaccumulation model for fish is used (Branson *et al.*, 1975; Spacie and Hamelink, 1982; Mancini, 1983; Mackay *et al.*, 1992).

Different bioaccumulations model may exist, but this study only focuses on the dynamic model type. The model that can be applied for non-steady-state or dynamic exposure concentration is a toxicokinetic model. Such model has been used successfully in pharmacology and allows to predict the toxicant accumulation, distribution, and ultimate effects (Landrum *et al.*, 1992; Andersen, 2003). In such a model, distinction can be made between a simple one-compartment model and a multi-compartment model (Mackay *et al.*, 1992; Mancini, 1983). The one-compartment model is widely applied (Clason *et al.*, 2003; Lindholst *et al.*, 2003) because multi-compartment models require a lot of parameters to be measured or estimated. A schematic representation of the bioaccumulation model for pelagic fish is given in Figure 6.2.

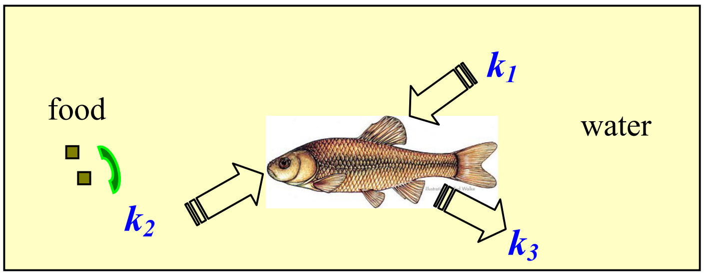


Figure 6.2: Schematic representation of simple bioaccumulation model for the pelagic fish

Two different one-compartment models in the bulk water can be given as follows:

$$\frac{dM_{c,b}}{dt} = k_1 \rho_b M_{c,w} - k_3 M_{c,b} \tag{6.1}$$

$$\frac{dM_{c,b}}{dt} = \left[k_1 M_{c,w} + k_2 C_{C,POC} V\right]\rho_b - k_3 M_{c,b} \tag{6.2}$$

where $M_{c,b}$ is the mass of toxicant in the biota (g); k_1 is the contaminant uptake rate from the truly dissolved phase ($m^3.g^{-1}.d^{-1}$), ρ_b is the density of biota ($g\ m^{-3}$); $M_{c,w}$ is the mass of contaminant in water (g); C_{POC} is the sorbed contaminant concentration in the suspended POC (g (g POC)$^{-1}$); k_2 is the ingestion rate of the organism (g POC (g biota d)$^{-1}$); k_3 is the elimination rate (d^{-1}), and V is the volume of water (m^3).

Note that equations 6.1 and 6.2 are the simplified forms of equations 2.22 and 2.23 in Chapter 2 when the parameter value of the water uptake rate efficiency and contaminant assimilation efficiency are taken into account in k_1 and k_2 respectively.

The concentration of organic contaminant in the organism ($C_{c,b}$) is then calculated as follows:

$$C_{c,b}(t) = \frac{M_{c,b}(t)}{\rho_b(t).V(t)}.1E6 \tag{6.3}$$

where $C_{c,b}$ is the concentration of toxicant in the organism (ppm), and $1E6$ is the unit conversion coefficient (10^6) from $g\ g^{-1}$ to ppm.

The difference between equation 6.1 and Equation 6.2 is that in Equation 6.1 only bioconcentration via gill uptake is considered, although dietary uptake can be important too (Carbonell *et al.*, 2000). In Equation 6.2, however, the accumulation of contaminants not only through gill uptake but also dietary uptake is considered. In this study, both equations were applied to simulate the contaminant concentration in the biota (herbivorous fish, a primary consumer).

6.2.1.4. Effect

Effect refers to an adverse response (toxicity) posed by a toxic substance. A distinction can be made between acute and chronic effects. Acute effects involve those effects that occur rapidly as a result of short-term exposure to a chemical, e.g. mortality to aquatic organisms. Chronic effects involve those effects that do not occur rapidly as a consequence of repeated or long-term exposures, e.g. growth inhibition and reproduction failure. Summarizing, effect is a function of different factors, and can be expressed conceptually as follows:

$$Effect = f\left(C_{c,b}, t, toxicant, biota\right) \tag{6.4}$$

where *Effect* is the response or toxicity (e.g. mortality, growth inhibition or reproduction failure …); $C_{c,b}$ is the concentration of toxic substance in the organism; *t* is the duration of exposure; *toxicant* is the type of chemical to which an organism is exposed; and *biota* is the exposed organism.

The concentration of organic contaminant in the organism, C_b, can be determined based on equations 6.1 to 6.3. These Equations can be used to simulate the effect of a time variable exposure concentration as described below.

Acute effect

As in *AQUATOX* (Park *et al.*, 1995), the cumulative fraction of organisms killed or surviving can be estimated for the narcotic chemical on the basis of the Weibull distribution (Mackay *et al.*, 1992; Christensen, 1984):

$$P = 1 - e^{-\left(C_{c,b}/LBR\right)^{1/s}} \tag{6.5}$$

where *P* is the cumulative fraction killed; $C_{c,b}$ is the internal concentration (mg kg^{-1}); *LBR* is the lethal body residue (mg kg^{-1}), and *s* is a parameter expressing the variability in the toxic response (Mackay *et al.,* 1992).

For narcotic chemicals, *LBR* can be calculated as follows (Suárez and Barber, 1992):

$$LBR = BCF \cdot LC50 \tag{6.6}$$

where *BCF* is the quasi equilibrium bioconcentration factor (L/kg) = k_1/k_3, and *LC50* is the concentration of toxicant in water that causes 50% mortality (mg L^{-1}).

Chronic effect

To predict chronic effects, the ratio of chronic to acute toxicity is used (Kooijman, 1981). For example, the effect of growth inhibition for narcotic chemicals is given as follows:

$$AFGrowth = {EC50_{growth}}\Big/{LC50} \qquad (6.7)$$

$$RedGrowth = 1 - e^{-\left(C_{c,b}\big/BCF\cdot AFGrowth\right)^{1/S}} \qquad (6.8)$$

AFGrowth is the chronic to acute ratio for the growth inhibition, and $EC50_{growth}$ is an external toxicant concentration at which a 50% growth reduction is observed (mg L^{-1}). *RedGrowth* is the factor for reduced growth in animals (unitless).

As indicated in the previous chapter of this thesis (Chapter 2, subsection 2.4.7.2), similar model formulation is applied for reproduction failure (see equations 2.38 and 2.40, in Chapter 2).

6.2.1.5. Integrated modelling

An integrated model is formulated by combining the three submodels: eutrophication, contaminant fate and bioaccumulation and toxicity/effect (see Figure 6.3). The linking processes in the three main submodels can be illustrated by general scheme of Figure 6.3.

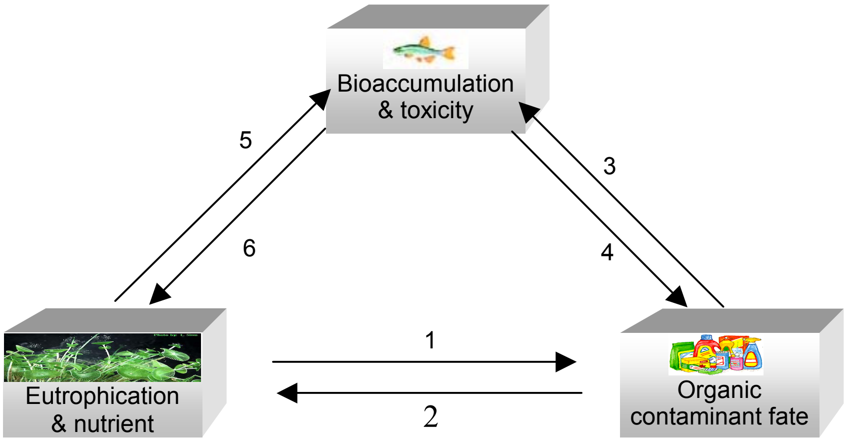


Figure 6.3: Schematic representation of the interaction of eutrophication, organic contaminant fate bioaccumulation and toxicity submodels; descriptions of the links/lines are given in the text

The linking processes description for the corresponding number of arrow in Figure 6.3 is given as follows:

1. Growth of microbial biomass and biodegradation
2. Association of organic contaminants with POC and DOC.
3. Transport and bioaccumulation of toxic substance (Connolly, 1991).
4. Toxicity of contaminants and its impact on the contaminant uptake (Legovic, 1997).

5. "Bottom up" control of the food chain structure by nutrient levels and fluxes (van der Molen *et al.*, 1998).
6. 'Top down' control of the food chain structure by grazing pressure exerted by zooplankton on algae (Krivtsov *et al.*, 2001).

The interactions illustrated above can be addressed by combining eutrophication, contaminant fate, bioaccumulation and toxicity submodels (see Figures 6.4). The linking variables between eutrophication (RWQM1) and organic contaminant fate model (CHETOX1) include Dissolved Oxygen (DO) for aerobic degradation, POC and DOC (mainly humic substance) for sorption, and inorganic nutrients (mainly nitrogen and phosphorus) for microbial growth to degrade the organic contaminant under consideration. All factors that directly or indirectly affect the fate of organic contaminants can determine fate and effect of organic contaminants. For example, readily biodegradable organic substrates regulate the microbial growth and can thereby enhance the biodegradation of organic contaminants. Also, if the organic contaminant is not readily biodegradable (e.g. DDT), eutrophication can still affect bioavailability of a contaminant. In eutrophic waters, most of the contaminant may be in the sorbed phase, and therefore will be removed (from the bulk water) by sedimentation. Such mechanism also reduces toxicity by reducing the bioavailable form of the toxic compounds.

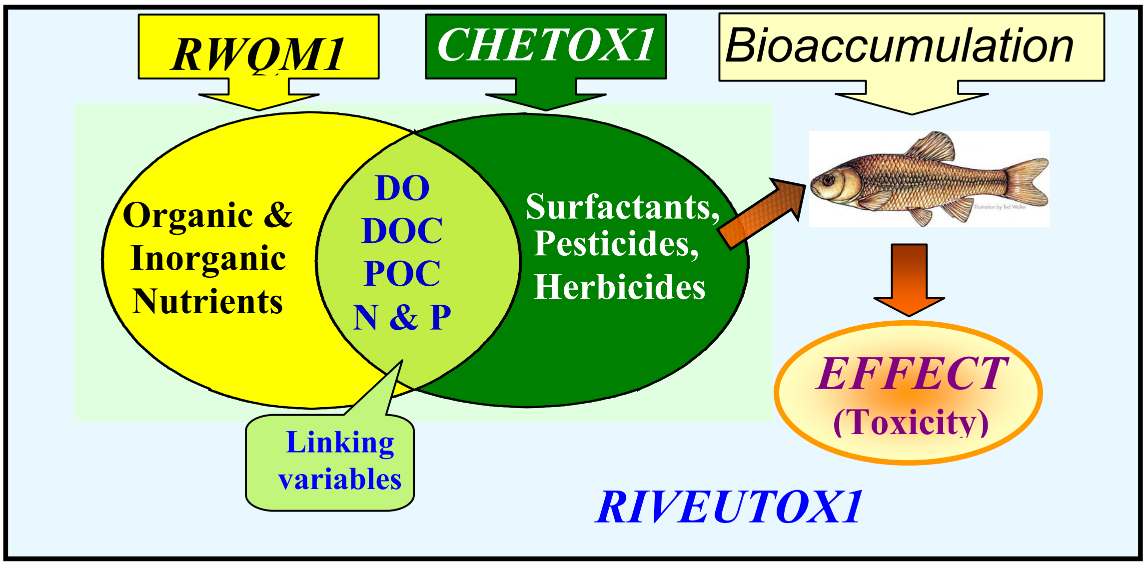


Figure 6.4: Conceptual design of the proposed integrated model (*RIVEUTOX1*) by linking submodels of eutrophication (*RWQM1*), in-stream fate of organic contaminants (*CHETOX1*) and effect (toxicokinetic); Dissolved Oxygen (DO), Dissolved Organic Carbon (DOC), Particulate Organic Carbon (POC) and inorganic nitrogen (N) and inorganic phosphorous (P) are the linking variables; the linking process is the carbon cycle

6.2.2. River Lambro case study

For this study, the river Lambro case study (see Figure 5.1.1, in Chapter 5.1) is considered because the monitoring data for an organic contaminant (LAS) and nutrients are available (Whelan *et al.*, 1999). Since the description for this river was already given in the previous chapter (Chapter 5.1), only the main points are summarized below. The study section is between Mulino de Baggero (as upstream point), and Biassono (as downstream point) with a total length of about 26 km. The most relevant pollutant discharge comes from the wastewater treatment plant (WWTP) effluent in Merone, and Combined Sewer Overflows (CSOs) with a pollution equivalent of 118,200 inhabitants. The river may be contaminated every day by CSOs. Such contamination frequency may have a considerable impact on the water quality of the downstream section of the river. Investigating the cumulative impact of such contamination frequency on the aquatic life is of great importance.

6.2.3. Model implementation

Using the Lambro river as a case study, *RIVEUTOX1* was implemented in the WEST® simulator (Vanhooren *et al.*, 2003) such that the state variables of all four submodels can be simulated simultaneously. As the number of state variables and model parameters is large, using a lot of tanks-in-series resulted in difficulties of compiling the model (see Chapter 3 sub secession 3.2.4).

In order to eliminate the problem encountered while compiling the model, 27 tanks-in-series were selected. This selection is supported by the previous study that a minimum of 24 tanks in series was shown to be appropriate, but 47 tanks in series can provide the least mean of sum of square error between measured and simulated tracer test data (Meirlaen, 2001). The configuration of 27 tank-in-series for the studied site is the same as given in Figure 5.1.5 in Chapter 5.1. The river was divided into 11 main river reaches (riv_1 to riv_11), which may vary in length. These river reaches were further subdivided into 27 river tanks-in-series as given in Table 6.1. The difference between Table 6.1 and Table 5.1.3 of Chapter 5.1 is that the length of each tank-in-series is longer in Table 6.1 than in Table 5.1.3. In another words, due to the reason indicated at the beginning of this paragraph a lower number of tanks-in-series was applied in the integrated model (*RIVEUTOX1*) than in the organic contaminant fate submodel (*CHETOX1*).

Table 6.1: Segmentation of the river Lambro for the integrated river water quality (*RIVEUTOX1*)

River- reach	Number of tanks	Tank Length (m)	Monitoring sites
riv_1	1	600	Mulino-Merone
riv_2	1	477	Merone-Sect_Rogo
riv_3	1	477	Merone-Rogolea
riv_4	2	1205.5	Rogolea-Section_1
riv_5	2	1205.5	Section_1-Victory
riv_6	4	771.3	Victory-Section_2
riv_7	4	771.3	Section_2-Section_3
riv_8	4	771.3	Section_3-Realdino
riv_9	4	855.5	Realdino-Section_4
riv_10	4	855.5	Section_4-Section_5
riv_11	4	855.5	Section_5-Biassono
Sum	27	26000	

6.2.4. Model calibration and validation

The calibration and validation of the hydraulic submodel (tank-in-series model) for the river Lambro case study was done in a previous study (Meirlaen, 2001). Therefore, this calibration will only focus on the water quality part. The model was calibrated and validated separately for both basic water quality and organic contaminant submodels in the previous chapters (Chapters 5.1 to 5.3). However, it needs to be recalibrated for the new integrated model, *RIVEUTOX1*.

The *RIVEUTOX1* model was calibrated using data collected in February 1998 (Whelan *et al.*, 1999). There is no available data other than the concentration of LAS and inorganic nutrients to check the model output for all state variables of *RIVEUTOX1*. Consequently, the model was calibrated and validated based on the monitoring data of LAS and ammonium. To validate the model, an independent set of data collected in May 1998 was applied. The model validation study was made for LAS only because the measured data set in May 1998 contains only LAS.

6.2.5. Scenario analysis

To obtain a better understanding of the complexity of the proposed model and what this model can do, some scenario analyses were made. The scenario analysis includes: the effect of nutrient dynamics, total suspended solids and partition coefficient on the fate of LAS; the effect of load and frequency of CSOs contamination on the bioaccumulation and effect of LAS in fish. For the sake of simulation, the toxicokinetic and toxicity parameters given in Table 6.2 for fish are applied, although these parameter values vary with fish type and the carbon chain length of LAS (Tolls, 2000).

Table 6.2: Bioaccumulation and toxicity submodel parameters for fish exposed to LAS: parameter values used in the simulation

Parameters	Literature values	References	Applied
Bioaccumulation			
k_1 [L g^{-1} d^{-1}]	0.1-0.2	(Tolls *et al.*, 2000a)	0.15
k_2 [g g^{-1} d^{-1}]	$1.25\text{x}10^{-3}$–$25\text{x}10^{-3}$	(Wootton, 1992)	0.0125
k_3 [d^{-1}]	0.31-0.72	(Tolls *et al.*, 2000b)	0.7
Effect			
s [-]	0.33	(Mackay et al., 1992)	0.33
LC50 [mg L^{-1}]	3.5	(HERA, 2000)	3.5
BCF [L kg^{-1}]	47-212	(Tolls *et al.*, 2000b)	100
$EC50_{growth}$ [mg L^{-1}]	0.25	(HERA, 2000)	0.25

6.3. Results and discussion

6.3.1. Model calibration and validation

Based on data collected in February 1998 (Whelan *et al.*, 1998), the *RIVEUTOX1* model was calibrated. Figures 6.5 and 6.6 show the calibration results for LAS and ammonia nitrogen respectively. Despite the fact that there are some differences in some monitoring stations (e.g. Victory (6.3 km)), the results show that the trend of simulated concentrations of LAS and total ammonia nitrogen generally agrees with the monitoring data within 20% error.

On the basis of independent data collected in May 1999 (Whelan *et al.*, 1999), the results of the model validation are illustrated in Figure 6.9. Except for the monitoring station of Realdino (15.6 km), which may be due to a sampling error, the results indicate that the trends of simulated data set generally agrees with the measured data set within 20% error.

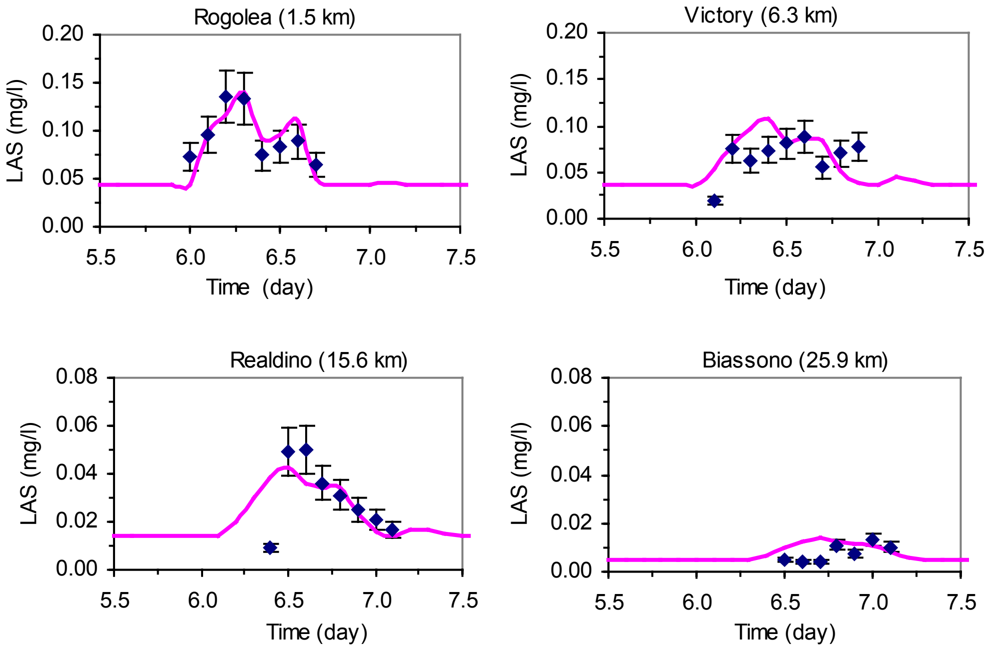


Figure 6.5: Calibration result for LAS

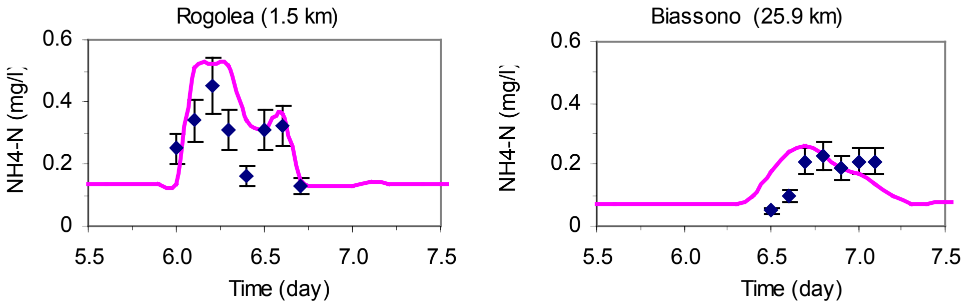


Figure 6.6: Calibration results for ammonia nitrogen: lines are the model predictions; the dot marks with error bar are the measured data set

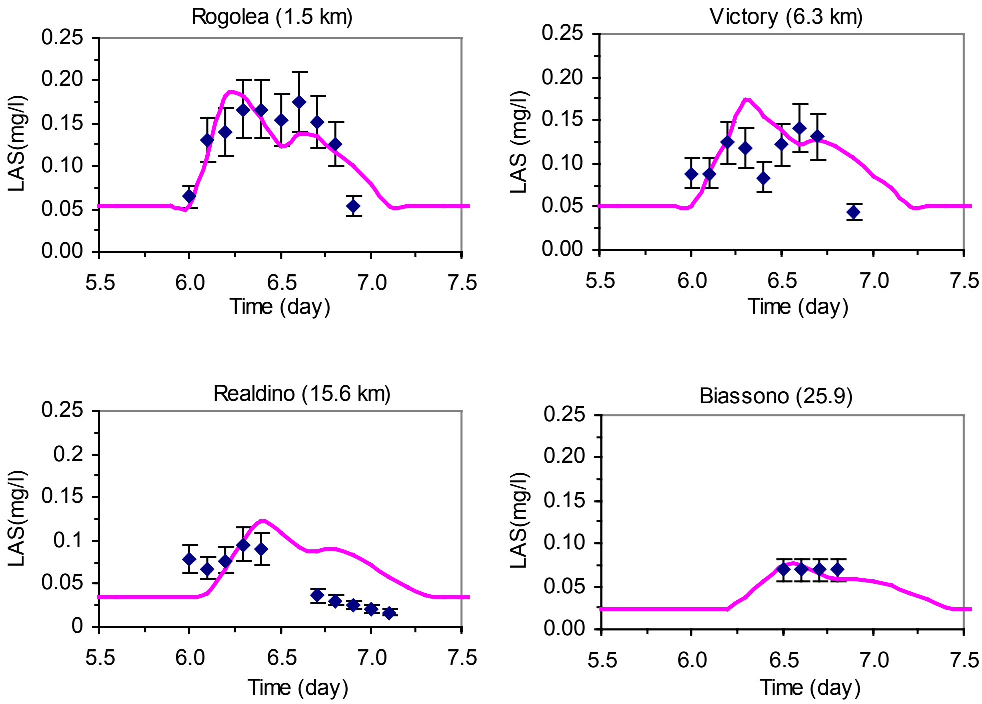


Figure 6.7: Model validation for LAS: lines are the model predictions; the symbols with error bar (20%) are the measured data set

6.3.2. Scenario analysis

6.3.2.1. Effect of nutrient dynamics and total suspended solids

The first scenario analysis focused on the effect of limiting nutrients (e.g. ammonia nitrogen) on the bioaccumulation of LAS in a primary consumer (small fish). Using single pulse, the model was run for three different data sets with concentrations in the upper end (see Figure 6.6) of 0.05, 1 and 5 mg L^{-1} NH_4-N. The trend shows that the increase of ammonia nitrogen concentration in an oligotrophic river system from 0.05 to 5 mg L^{-1} decreases the predicted LAS tissue concentration (see Figure 6.10 left). This depicts that the supply of limiting nutrients stimulates microbial growth, and thereby enhances biodegradation.

In the second scenario, a high ammonia nitrogen concentration (5 mg L^{-1}) and an increased Total Suspended Solid (TSS) concentration from 20 to 60 mg L^{-1} in inlet were considered. The results show that the increase of TSS (algal and bacterial biomass) increases LAS removal by sorption to POC, which is subsequently followed by sedimentation (see Figure 6.8 right). Thus increasing TSS by the increase of microbial biomass leads to an increase of POC in the system. An increase of TSS from 20 to 60 mg L^{-1} results in a significant difference in the tissue concentration. The model thus confirms the “biomass dilution” hypothesis, which states that increased primary production may result in a dilution of contaminants (Gunnarsson *et al.*, 1995).

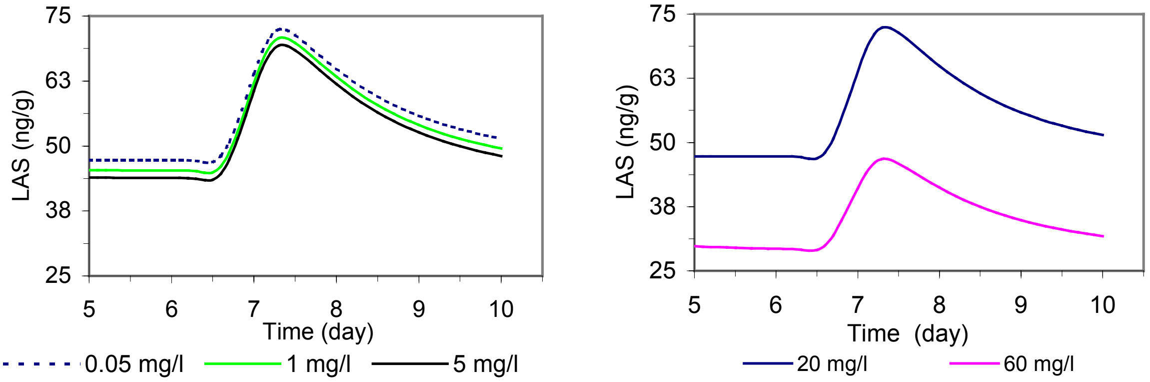


Figure 6.8: Effect of ammonia nitrogen (NH_N, left) and total suspended solid (TSS, right) dynamics on the tissue concentration of LAS in the river Lambro (25.9 km)

6.3.2.2. Partition coefficient

In the third scenario, the effect of physicochemical characteristics of the contaminant *Kp*, i.e. the organic carbon-water partition coefficient was investigated. The *Kp* values of different LAS homologues vary from 220 to 9000 L kg^{-1} and this range is used for this scenario analysis. The results show that there is no difference in the tissue concentration for *Kp* values of 220-1000 L kg^{-1} (see Figure 6.9). However, the *Kp* value of 9000 L kg^{-1} can substantially decrease the LAS concentration in the organism. Indeed, a higher *Kp* means that a higher contaminant mass is sorbed to POC and hence less contaminant is available for bioconcentration. Note that the organism can also get the sorbed contaminant via feeding on

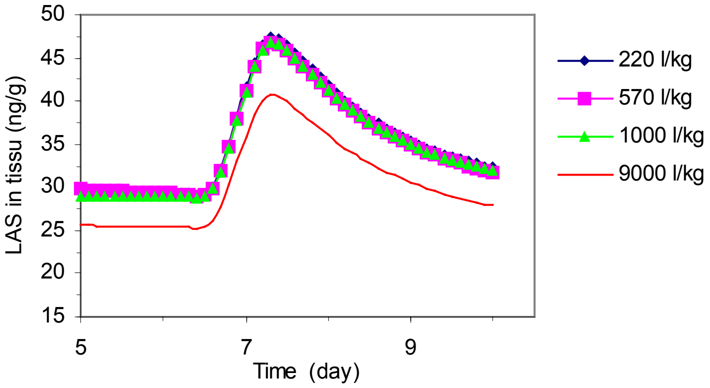


Figure 6.9: The effect of the partition coefficient *Kp* at the sampling location 25.9 km downstream of the WWTP when only gill uptake is considered

POC but then the assimilation efficiency governs the rate of bioaccumulation. The assimilation efficiency for toxic contaminants is generally very low (Mackay, 2001).

6.3.2.3. Effect of CSO contamination: Concentration and frequency

The fourth scenario is related to the frequency of a higher contaminant load, which is often associated with Combined Sewer Overflows (CSOs). As the LAS concentration in the treated wastewater treatment plant effluent is very low, the main cause for a high contaminant concentration in the river is usually CSOs. In many high rainfall regions, the contamination events due to CSOs are frequent. Alike in the river Lambro, Diaz-Fierros *et al.* (2002) reported daily CSO contamination of the receiving water in Spain. Analysing the effect of such frequent CSO contamination on aquatic life (in this case fish) can give useful information.

In this subsection, CSO frequencies of a two and four day interval were considered. Furthermore, the effect of low concentration (maximum concentration < 0.2 mg L^{-1}) and higher LAS concentration up to 10 mg L^{-1} (Moreno *et al.*, 1989) were analysed. Note that such high concentration should be considered as a worst-case situation, which might occur when untreated wastewater is discharged to the river.

Bioaccumulation

In the first case, consider contamination of the river by a CSO every 2 and 4 days with a small load, but with a fixed overall mass/load for the whole contamination period. The result shows that the peak and minimum concentrations in the tissue are reduced significantly for more frequent and less extreme events (see Figure 6.10 left).

In the second case, the same amount of mass/load per repeated pulse is considered - knowing that the total mass loaded within the given time is higher in the higher frequency than the lower frequency case (see Figure 6.10 right). The results show that the higher frequency CSO contamination results in a significantly higher LAS concentration ($p < 0.05$) in the organism in both peak and minimum concentrations (see Figure 6.10 right). This is due to the fact that there is less recovery time for the organism to reduce the tissue concentration by excretion or biotransformation.

Furthermore, the effect of more than one exposure route, e.g. gill and food uptake (equation 6.2), on the LAS concentration profile in fish was investigated. Here, the simulated LAS concentration profile in fish via bioconcentration (only gill uptake) and bioaccumulation (via

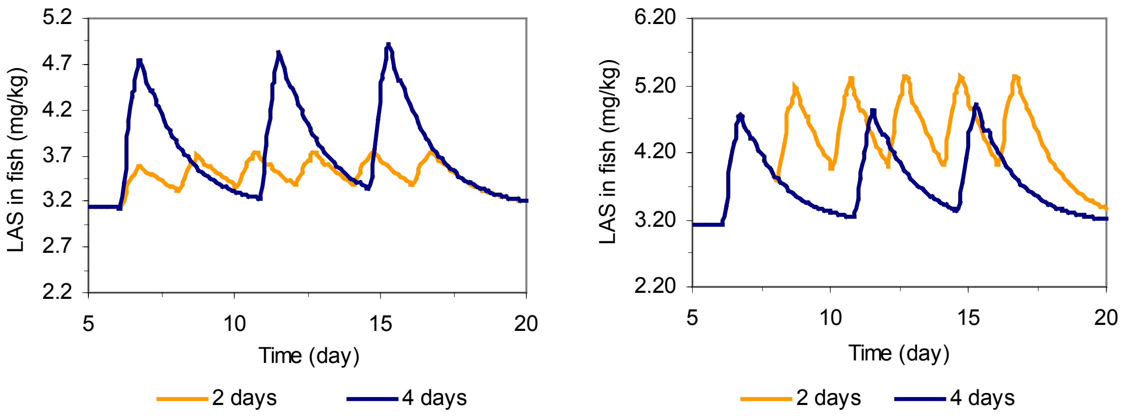


Figure 6.10: Comparison of effect of high (every 2 days) and low (every 4 days) frequency of CSO contamination on the fish tissue concentration in the river Lambro at 6.3 km: the left hand graph is when fixed overall load is distributed over the whole contamination period, whereas the right hand side graph is when every time the same load is considered at extreme conditions; in the right hand side graph more frequent contamination (every 2 days) results in higher LAS concentration in tissue than less frequent contamination (every 4 days)

gill and dietary uptake) were compared at both high (up to 4 mg L^{-1}, as a worst case) and low (< 0.2 mg L^{-1}, as an actual case) exposure concentrations (see Figure 6.11). The effect of a higher concentration for the worst case was obtained by increasing the actual concentration in the input data by a factor of twenty. In both high and low exposure concentrations, the results show that consideration of both gill uptake and dietary uptake results in more tissue concentration than considering only gill uptake. The contribution of dietary uptake depends on the concentration of the contaminant in the sorbed phase and the assimilation efficiency. If both sorbed phase concentration and the assimilation efficiency are large, the contribution of dietary uptake may be larger.

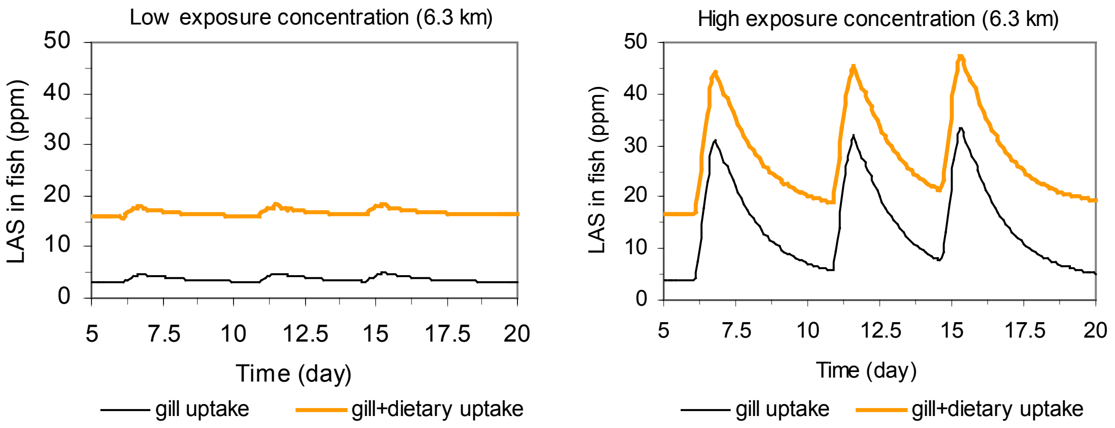


Figure 6.11: Comparison of routes of exposure in both low (left) and high (right) exposure concentration: gill plus dietary uptake resulted in more LAS concentration in tissue in both actual (low) and worst (high) exposure concentration cases

Acute and chronic toxicity

The effect of CSO frequency on the acute (mortality) and chronic effect (growth reduction) of fishes (primary consumer) was analysed based on the parameters indicated in Table 6.2. Two types of frequencies, every two and four days of actual CSO contamination, were examined based on the trend of the acute and chronic toxicity profile at a location 6.3 km downstream effluent discharge (see Figure 6.12).

The results show that the acute effect is negligible at the actual exposure concentration (<0.2 mg L^{-1}) (see Figure 6.12 left), whereas the simulation result of the chronic effect is considerable. Furthermore, the results show that the highly frequent CSO contamination (e.g. every two days) results in significantly higher toxicity ($p < 0.05$) than the less frequent contamination in terms of both chronic and acute effects.

Comparison was also made between the effect of high (< 4 mg L^{-1}, worst case) and low (< 0.2 mg L^{-1}, actual case) exposure concentration (see Figure 6.13). In this comparison, a CSO contamination frequency of every 4 days is used. The results evidently show that the higher concentration results in more toxicity. In high exposure concentration, complete growth reduction (100%) is also observed during peak periods (see Figure 6.13 right). The acute effect is, however, still negligible due to the high overall fish elimination rate constant (0.7 d^{-1}).

Using again every 4 days of CSO contamination for the actual (low) exposure concentration, the effect of the elimination rate constant and BCF on the chronic effect was investigated (see Figure 6.14). In the case of the elimination rate constant, four values of the elimination rate

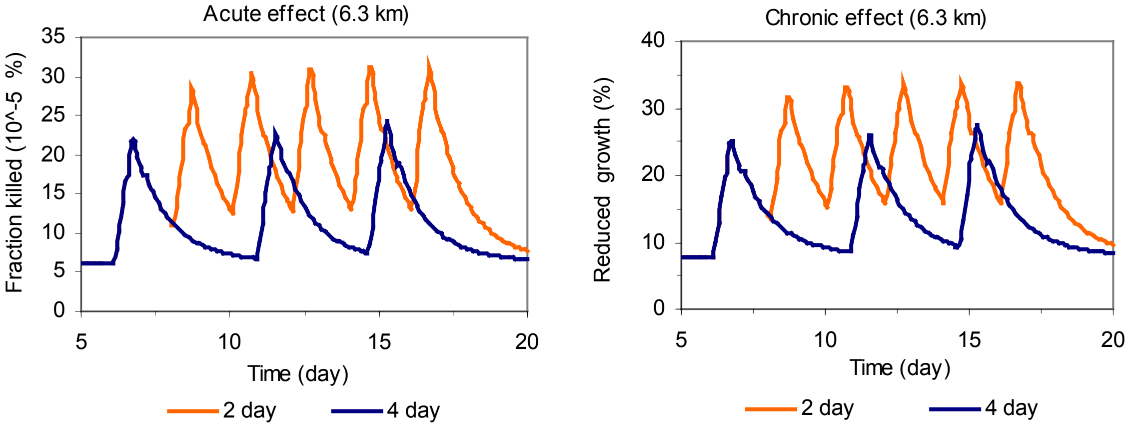


Figure 6.12: Comparison of simulated chronic effect (growth reduction) at 6.3 km downstream of SOC contamination: effect of multiple pulses every 2 and 4 days; negligible acute effect (left), but considerable chronic effect. A more frequent contamination (every 2 days) resulted in higher toxicity

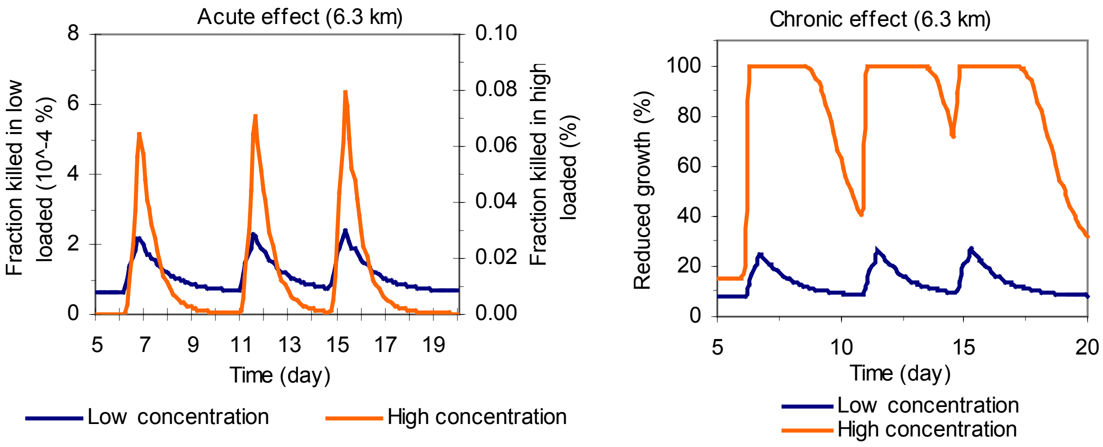


Figure 6.13: Comparison of chronic effect of a 4 daily pulse in the 6.3 km downstream section of the river: negligible acute effect in both high (< 4 mg L^{-1}, worst case) and low (0.2 mg L^{-1} actual case) exposure concentrations; complete reduced growth (100%) in high exposure concentration

constant (see Figure 6.14 left) were applied. The results obviously show that the higher elimination rate results in lower toxicity (chronic effect) and vice versa. The concentration profile of LAS in the organism indeed depends on the elimination rate. Figure 6.14 left also shows how the model predictions are sensitive to the elimination rate. Note that the elimination rate varies (see Table 6.2 for LAS), depending on the type of fish and physicochemical properties of the contaminant. For polychlorinated hydrocarbons, for instance, the elimination rate constant ranges between 0.005 and 0.12 d^{-1} (Mackay *et al.*, 1992; Opperuizen and Sijm, 1990). Hence, proper estimation of this parameter is essential.

Figure 6.14 right shows the influence of BCF on the chronic effect. The results show that a

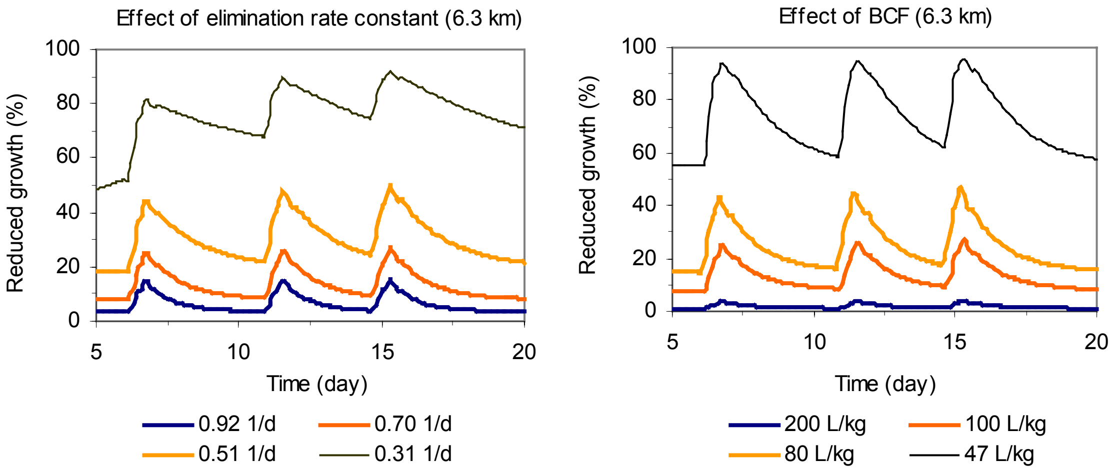


Figure 6.14: Effect of elimination rate constants (k_3) (left) and BCF (right) on the chronic effect (fraction of reduced growth) at low LAS concentration: increase of elimination rate constant (k_3) and BCF results in decrease of chronic effect significantly ($p < 0.05$)

higher BCF resulted in a lower chronic effect (reduced growth) and vice versa. In other words, BCF and toxicity show an inverse relationship (see equation 6.8), i.e. when BCF increases the LBR increases too.

6.3.3. Sensitivity analysis

In order to investigate the relative importance of the toxicokinetic parameters given in Table 6.2, a sensitivity analysis was carried out using equations 5.1.25 and 5.1.26 given in Chapter 5.1. Figure 6.15 shows the relative sensitivity analysis results. The results show that all five parameters (chemic to acute ratio (EC50growth/LC50), BCF, k1, k3 and s) are very influential. The sensitivity of EC50growth/LC50 and BCF are the same. A summary of the sensitivity analysis results and the relative importance of the parameters is given in Table 6.3.

As shown in Table 6.3, the relative sensitivity of the toxicity results (model output) to the toxicokinetic and toxicity parameters looks similar for both acute and chronic effects except

Table 6.3: Sensitivity analysis: the parameters of toxicokinetic/toxicity submodel are ranked based on average absolute sensitivity function for both chronic and acute effects

	Chronic effect				Acute effect		
Parameters	Minimum	Maximum	Average	Parameters	Minimum	Maximum	Average
k_3	1.93	3.17	2.83	s	12.93	14.30	13.80
BCF	2.91	2.57	2.82	k_3	2.24	3.34	3.03
$EC50_{growth}/LC50$	2.91	2.57	2.82	BCF	3.03	3.03	3.03
k_1	2.57	2.90	2.81	$LC50$	3.03	3.03	3.03
s	0.96	2.41	1.87	k_1	2.94	3.03	3.02

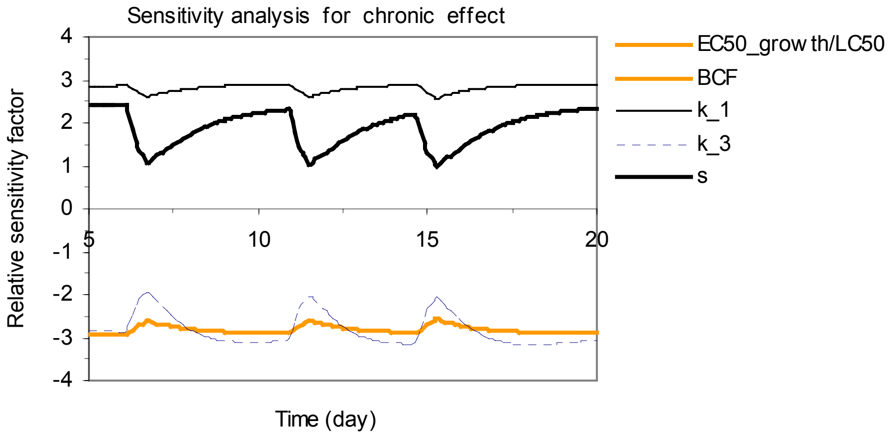


Figure 6.15: Sensitivity of the predicted chronic effect (% reduced growth) to toxicokinetic parameters using every 4 days CSO contamination as a case study; the line for BCF overlaps with the line for EC50_growth/LC50

for the parameter value *s*. In both types of effects, the elimination rate constant k_3 is the most sensitive parameter. The initial value of contaminant concentration/mass in the organism is found to be relatively the least sensitive. The model output is generally very sensitive to k_3, *BCF*, *LC50* (for acute effect), $EC50_{growth}/LC50$ (for chronic effect) and k_1 (gill uptake).

Summarizing, such high sensitivity of model outputs (toxicity) to the toxicokinetic parameters indicates the importance of these parameters for the reliability of the model. Thus, for the realistic prediction of toxicity, these parameters must be measured or estimated accurately for every type of chemical and organism under consideration.

6.4. Conclusions and recommendations

Simple dynamic bioaccumulation and toxicokinetic models were incorporated in the integrated model of eutrophication and organic contaminant fate and effect. The effect of eutrophication (nutrient enrichment and TSS) on the tissue concentration was examined. The proposed integrated model is based on simple mass balances. The model assumes completely mixed tank-in-series and local sorption equilibrium within the compartments. However, it assumes no equilibrium between the compartments (water, sediment, air, and biota). Besides, the model takes both spatial and temporal variability into account. Based on the scenario analysis, the following general conclusions can be drawn:

1. The proposed model comprises a dynamic exposure model and a relatively complex eutrophication model, and hence can be very useful for various scenario analyses.
2. Linking a bioaccumulation submodel with eutrophication and organic contaminant fate submodels gives more valuable information to understand the interaction of multiple stressors: nutrient pollution, eutrophication and contamination by xenobiotic organic substances in rivers.
3. The results of the scenario analysis show the usefulness of the model in integrated river water quality management. Integrating a dynamic exposure and toxicokinetic models allows one to investigate the cumulative effect of frequent organic contamination on aquatic life, e.g. frequent contamination by CSOs.
4. The proposed model can simulate the time dependent exposure concentration in three phases of environmental compartments (water and benthic sediment): truly dissolved, sorbed to dissolved organic carbon and suspended solids in the bulk water; truly dissolved and sorbed to dissolved organic carbon in the pore water, and sorbed to benthic sediment, and is therefore useful to link the exposure model with the bioaccumulation and toxicokinetic models.

As further research, the model should be extended to include more toxicokinetic models that can be able to predict the potential effect of a given contaminant on the aquatic macro invertebrates. The eutrophication submodel should be refined in such a way that the primary or secondary consumer must be subdivided into major subgroups. In general, an appropriate ecological model is needed to build a reliable ecotoxicological model.

Part 7

General discussion, conclusions and perspectives

Chapter 7

General discussion, conclusions and perspectives

Eutrophication and contamination by organic contaminants are the main water quality problems in surface waters (lakes and rivers). These problems are the result of both point and non-point sources of pollutions. To protect surface waters from all sources of pollution or contamination by hazardous substances, a holistic water quality regulation is required, such as the one adopted recently in the new European Union (EU) water policy, i.e. the Water Framework Directive (WFD). It is a combination of Environmental Quality Objective/Standards (EQO/EQS) and Uniform Emission Standards (UES). EQO/EQS is mainly applied for the conventional pollutants, whereas UES is applied for the hazardous substances (Tyson *et al.*, 1993).

The EQO/EQS approach is based on the receiving water quality (immisssion) rather than the effluent water quality (emission). In an immission-based approach, mathematical models are required in order to predict the possible river water quality in response to various pollutant loads (stimuli). An integrated river water quality model therefore assists the water quality regulator to achieve a predefined water quality objective. In this Ph.D. study, a dynamic integrated river water quality model was developed and used to investigate the combined effect of conventional pollutants and xenobiotic organic contaminants in rivers. This mechanistic model is conceptual in that it is based on a simple mass balance. It has a unique advantage: its output has a clear physical meaning, i.e. it can be interpreted on the basis of physical and chemical laws, and hence it is suitable for various scenario analyses and for the evaluation of remediation actions.

Here, the importance of such integrated modelling approach is highlighted. In the framework of water quality objectives, e.g. a “good” biological quality, which is the case in the EU WFD, there are at least three important points that need to be considered while developing tools for water quality management. First, the biological quality is a function of conventional pollutants (organic matter and inorganic nutrients) whose sources need to be identified and quantified: point sources (point discharges of treated or untreated wastewater effluent) and non-point or diffused sources, e.g. runoff from agricultural lands and mining sites. The effect of conventional pollutants, eutrophication, can result in a wide range of diurnal fluctuations of dissolved oxygen concentration in the system, and thereby cause fish kill. Eutrophication also reduces biodiversity due to interspecies competition combined with severe chemical and physical stresses (Law, 1993). In order to tackle such problems, mathematical tools that include a basic water quality submodel to assist in identifying and evaluating alternative water quality management options and remediation actions are needed.

Second, the biological quality also depends on the loads of xenobiotic organic contaminant into water systems. To evaluate the potential risk of the toxic chemicals of concern, it is necessary to conduct an environmental risk assessment that includes two main aspects, i.e. exposure and effect assessment. In the exposure assessment, exposure or fate models assist an environmental risk manager in identifying and quantifying the Predicted Environmental Concentration (PEC). The PEC value is then compared with the Predicted No-observed Effect Concentration (PNEC) that is safe for the whole ecosystem in order to characterize ecological risk. In a traditional risk characterization, a ratio of PEC to PNEC larger than 1 indicates risk to the ecosystem. It is therefore important for the water quality modeler or manager to consider the impacts of toxic compounds while analysing the biological quality of an ecosystem.

Third, the biological quality is also a function of the interaction between conventional pollutants and xenobiotic organic contaminants. Eutrophication and organic contaminants interact in various ways (Gunnarsson *et al.*, 1995; Hylland *et al.*, 1996; Skei *et al.*, 1996): eutrophication may cause dilution of contaminants by increasing amounts of microbial biomass, enhancing biodegradation in the presence of oxygen, organic contaminant scavenging with suspended Particulate Organic Carbon (POC), sedimentation of contaminants and contaminant uptake in the food chain. Organic contaminants may have a direct or an indirect toxic effect on aquatic organisms, which in turn affects the organic contaminant fate and nutrient cycles (Legovic, 1997). In traditional river water quality modelling, these two problems are modeled separately, and their interaction is missed. In order to take into account such interactions, however, integrated modelling of basic water quality (eutrophication) and organic contaminant fate and effect is essential.

In this concluding chapter, a general discussion of the obtained results in relation to literature is given under three main subsections: basic water quality, environmental risk assessment and modelling, and integrated modelling. Also the general conclusion and the perspectives are presented.

7.1. Basic water quality: model simplification

In the sense that mathematical models are simplifications of reality, a realistic river water quality model needs to be relatively complex. However, the more the model is complex, the larger the amount of data that is required and the more cost it incurs to calibrate and validate the model. Thus, there should be a compromise between the accuracy and data requirements of the model. To simplify river water quality models, different methods may be used. In this work, two methods were applied: (1) simplification of the hydraulic submodel, and (2) reducing the biochemical reaction submodels. These two methods will be discussed further in the following subsections.

7.1.1. Simplification of the hydraulic submodel

In the state-of-the-art, typical St.Venant equations (De St. Venant, 1971) are used for modelling hydraulic and pollution routing in unsteady state conditions. The application of full St. Venant Equations, however, requires long computation times, and further extension of such a complex hydraulic model towards integrated water quality modelling is difficult. Consequently, a conceptual mechanistic surrogate model was proposed for the sake of faster simulation and easy implementation of water quality models (Meirlaen, 2001).

In rivers, which are not highly regulated, a conceptual hydraulic model (Continuous Stirred Tank Reactor in Series, CSTRS) can be applied. Such a conceptual modelling approach is very popular because the Ordinary Differential Equation (ODE) form allows for an easier implementation, and numerical solution in comparison to the Partial Differential Equation (PDE) model structure (Rauch and Harremoes, 1996; Rauch *et al.*, 1998). Subsequently, this modelling approach was selected for this Ph.D. thesis because of its three main advantages: it is simple and can be solved relatively easily, it requires less simulation time than the full hydrodynamic model, and it has good numerical stability.

The number of ODE equations to be solved however, is proportional to the number of CSTRS used. The larger the number of tanks in series applied, the longer the simulation time will be. Thus, selection of the optimum number of tanks should be done such that the introduced implicit or numerical dispersion is roughly equal to that of the actual system (Shanahan and Harleman, 1984). The optimum number of CSTRS was determined in this work on the basis of a tracer study, except for the Crocodile River case study where selection of the number of tanks-in-series was made on the basis of a comparison between simulation results and measured data.

A simple hydraulic model (CSTRS) was applied to simulate the in-stream flow and water quality variables in the Crocodile River (South Africa). The model was implemented in the WEST® simulator (Vanhooren *et al.*, 2002), in which multiple side stream or effluent discharges can be incorporated. The results show that the model can adequately describe the hydraulics and pollutant transport in rivers. This work also confirms that the CSTRS model can adequately describe the hydraulics and water quality of a river that is not highly regulated or influenced by tidal effects. In the latter case when the river is influenced by tidal or backwater effects, a 1-D hydrodynamic model needs to be applied.

7.1.2. Water quality submodel selection

The historical development of basic water quality models shows step-by-step extensions of increasing complexity from the pioneering Streeter-Phelps model (Streeter and Phelps, 1925) to the more complex comprehensive eutrophication model *QUAL2E* (Brown and Barnwell, 1987), which was specifically designed to determine the allowable maximum effluent loads under steady low stream-flow to satisfy needs of legislation in the US (wasteload allocations). Although the *QUAL* type models are adequate for the specific regulatory situations for which they were developed, there is a need for a more comprehensive modelling framework for those water quality management problems not addressed by *QUAL2E* such as storm flow events, non-point sources, and transient stream flows (Reichert *et al.*, 2001).

Although the choice of modelling approach and level of complexity depends strongly on the purpose of the study for which the model is built, there are generally two criteria that a basic river water quality or eutrophication model needs to fulfil: (1) consistence in mass and elemental balance, and (2) appropriate description of processes and state variables. These two criteria are very crucial in the integrated modelling of eutrophication and organic contaminant fate and effect. As it fulfils the two criteria, the RWQM1 (Reichert *et al.*, 2001) proposed by the IWA task group on River water quality modelling was selected in this work.

As far as the first criterion, in contrast to activated sludge models in which only on overall mass balance is considered, both mass and elemental balances are crucial for river water quality models. The elemental ratio controls the structure and function of the aquatic ecosystem (Yamamoto, 2003). Yamamoto also indicated that there is an optimum elemental ratio for each species of phytoplankton to grow, but the average value can be used for water quality management. In RWQM1 therefore, the general law of conservation of mass is respected for both mass and elements of water quality components such that mass is neither created nor destroyed, but transformed from one form into the other.

As for the second criterion, the river water quality should include at least all important processes and components. For example, in QUAL type models, bacteria, which are determining the microbial biotransformation, are not considered as state variables. This affects the predictability of the model to such a degree that the model cannot handle the temporal variation of the microbial biomass concentration. Besides, describing organic carbon in both dissolved and particulate forms is important, particularly for organic contaminant fate modelling. These issues are considered in the RWQM1.

Although RWQM1 fulfils the criteria indicated above, the complexity of the model expressed in the number of processes and state variables included in the model, limits its wide application. In order to make use of the advantages of the RWQM1 modelling approach, model reduction often needs to be done.

7.1.3. Reducing the model complexity

In this thesis work, an attempt was made to reduce the complexity of *RWQM1* so that this model can be used for two important applications. First, the reduced model can be used in data limited situations, which is the case in South Africa where part of this study was carried out. Second, the reduced model can be used for the integrated modelling of organic contaminant fate and effect in rivers.

To reduce the *RWQM1* complexity, four important simplifying assumptions proposed in Varolleghem *et al.* (2001) were applied (see also chapter 4.1). First, the suspended microbial biomass dominates the conversion rates in large rivers or in the downstream sections of rivers (see also river continuum concept, chapter 2). As depth and turbidity limit the primary productivity of benthic sediment, the bulk water compartment can therefore be sufficient to describe the nutrient dynamics. For in-stream fate modelling of organic contaminants on the other hand, the benthic sediment compartment needs to be included.

Second, the contribution of algae to the oxygen budget can be assumed negligible when the hydraulic retention time is less than 4 to 7 days or if the concentration of chlorophyll is less than 10 mg l^{-1}, which is the case in the downstream section of the Crocodile River (South Africa).

Third, as the nitrite concentration in the Crocodile River is very low, nitrification was modelled as a single step so that nitrite plus nitrate can be considered as one state variable; consequently the first-stage and second-stage nitrifiers were therefore lumped to one state variable.

Fourth, the pH was assumed not to change significantly in time during the process, thus the pH-dependent state variables and related processes such as chemical equilibria could be omitted; as a result ammonia plus ammonium was considered as one state variable.

The applicability of such a reduced model was tested on the basis of an inorganic nitrogen (nitrate and ammonia) case study in the Crocodile River, South Africa (see also chapters 4.1 and 4.2). In this river, there was daily flow rate, but limited water quality data (monthly) in the main stem of the river and its main tributaries. The contribution of other sources of pollution, e.g. runoff from agricultural lands in the intermediate river section, was assumed negligible (DWAF, 1995). This assumption was also checked based on the analysis of monitoring data (see Chapter 4.1, subsection 4.1.6.4). The information about wastewater effluent discharge and water quality composition was not given. Despite such limited available information, the results show that the model can be applied to describe the seasonal dynamics of nitrate and ammonia in the Crocodile River.

7.1.4. Application of the simplified model

The simplified model was applied on the Crocodile River to evaluate different basin-wide water quality management options that can enhance the river water quality in the downstream section of the river (see also chapter 4.2). When the river is subjected to high rates of freshwater withdrawal (in its upstream reaches), and also receives polluted side-stream inflows or wastewater effluent discharges (in the middle reaches), the downstream river water quality can deteriorate seriously over time, particularly in semi-arid regions, as is the case for the Crocodile River (South Africa) due to, for example, high salinity. Therefore two management options were evaluated: setting maximum rates of upstream freshwater withdrawal and low flow rate augmentation.

7.1.4.1. Setting maximum upstream freshwater withdrawal

In some regions, water is abstracted or withdrawn from the main stem of the river or in its tributaries at a high rate in order to satisfy water needs mainly for irrigation or drinking water supply. Such high rate of upstream freshwater withdrawal can have a serious impact on the water quality in the downstream section of the river (Qader, 1998; Mokhlesur *et al.*, 2000), particularly during low flows. In the worst case, it can result in extremely low flows that can have adverse ecological consequences: change in habitat for micro-invertebrates and reproduction failure for fish (Caruso, 2002; Dubinina and Kozlitina, 2000). Besides, it reduces the dilution capacity of the main stem of the river that may receive highly polluted side streams or effluent discharges in the middle reach. Consequently, the water quality of the river in the downstream section can deteriorate due to high salinity or Total Dissolved Solids (TDS) and nutrient enrichment.

In this work, the influence of setting a maximum allowable freshwater withdrawal on the downstream river water quality of the Crocodile River was investigated. The results show that a decrease of 1 $m^3\ m^{-1}d^{-1}$ (30%) in maximum allowable upstream freshwater withdrawal can reduce TDS with about 15 mg l^{-1} (4%) during low flow periods. Such improvement looks not significant as compared to the 20% error of the model calibration. The trend however depicts that limiting maximum allowable water withdrawal can increase the water quality in the downstream. It should also be noted that the problem of over-abstraction of the river water in the upstream section of the river is common not only in water poor regions but also in water rich regions like in Scotland (Fox and Walker, 2002; Dunn *et al.*, 2003). There is a minimum river flow required for the ecosystem to function without deleterious effects. This is also called the ecological reserve or in-stream flow requirements. Thus, the “ecological reserve” must be taken into account while setting a maximum water withdrawal. In Chapter 4.2, two methods of determining the “ecological reserve” were highlighted: low flow analysis using a statistical method (Chapra, 1997), and the South African Building Block Methodology (King and Louw, 1998; Rowntree and Wadeson, 1998). In the former approach, the maximum water withdrawal can be defined as the difference between the discharge in a low water base year (90% probability of exceedence) and the discharge critical for river ecosystem, e.g. fish reproduction (95% probability of exceedence) (Dubinina and Kozlitina, 2000). The limitation of such a statistical method is that it also includes the draught period when the river flow is extremely low or zero, and hence it is not applicable for arid and semi-arid regions. The BBM is relatively complex and realistic, as the problem related to draught conditions is taken into account. It quantifies monthly value for four components of the in-stream flow requirement (ecological reserve). These are the maintenance and drought low flow requirements and the maintenance and drought high flow requirements. It can therefore be concluded that In South African cases, the BBM need to be applied.

7.1.4.2. Low flow augmentation

Low flow augmentation refers to supplementing the river flow during minimum flows that otherwise might have insufficient capacity to dilute polluted side streams. In this work, low-flow augmentation was investigated as an important water quality management option in the Crocodile River. Traditionally, low flow augmentation is used to satisfy water needs for irrigation and domestic water supply in the downstream section of the river. In this dissertation however, low flow augmentation is applied not only to satisfy the need for water quantity but also as a means to reach the water quality target in the downstream section of the river.

This water quality management option requires water storage during wet season and water usage during dry season in order to supplement low flows. To store water during the wet season, construction of reservoirs or impoundments in the upstream sections of the river is needed. Constructing dams or reservoirs, however, is often viewed as having a negative impact on the aquatic environment (Ward and Stanford, 1983; Avakyan and Iakovleva, 1998). Impoundment changes the river flow velocity, interrupts the river continuum, interferes with the fish passage, changes the water quality in the downstream, etc.

Some studies, however, have shown that impoundments improve water quality in the downstream sections. Palmer and O'Keeffe (1990) showed that impoundments could generally improve the downstream water quality in the impoundment that receives agricultural runoff and urban wastewater. Straskraba (1994) also indicated that reservoirs offer an important potential management tool if the relationships between modes of reservoir operation and the resulting influence on water quality can be understood. Recently, Campolo *et al.*, (2002) illustrated the improvement of Dissolved Oxygen (DO) in the downstream section of the river Arno (Italy) by appropriate selection of water release from the Levane dam. Yamamoto (2003) also illustrated that dams trap nutrients as particulate forms as the result of sedimentation of bloomed phytoplankton in the water column. This resulted in a low nutrient level in the river at the downstream of the reservoir.

Subsequently, since an existing reservoir (Kwena Dam) can be used to regulate the Crocodile River in the downstream section, the significance of controlling the water release pattern from the Kwena Dam for the downstream river water quality was investigated (see also Chapter 4.2). A procedure to control the water release from the dam was also introduced. The control is based on the concept that the augmented flow pattern should follow or mimic the seasonal pattern of unregulated river flows.

The results show that regulating the flow pattern of water released from the Kwena Dam can achieve a remarkable reduction in the TDS and ammonia nitrogen concentration in the lower reaches of the Crocodile River. These management options, however, increase the nitrate concentration in the downstream as a result of the high nitrate content of the reservoir water, because of nitrification. This result is consistent with the results obtained in literature (Palmer and O'Keeffe, 1990; Yamamoto, 2003). Since nitrate is less toxic to fish than ammonia, this management option can be selected providing that nitrate is not the limiting factor for algal bloom in the downstream section of the river. It is therefore up to the water quality manager to decide.

7.2. Environmental risk assessment and modelling

In the environmental risk assessment process, the Predicted Environmental Concentration (PEC) and Predicted No-observed Effect Concentration (PNEC) need to be determined or measured (EEC, 1993). The procedures used to determine PEC and PNEC are therefore termed exposure assessment and effect assessment respectively. The PEC to PNEC ratio, also called the risk quotient, is used to decide whether the chemical of concern poses an adverse effect on an ecosystem. In determining both PEC and PNEC, mathematical models play a significant role because of their cost effectiveness and predictive capabilities (Verdonck, 2003).

There are several modelling approaches that vary from a generic or static approach to case specific and dynamic approaches (see also Chapter 2, section 2.4.9.5). While selection of the model type strongly depends on the application of the model (purpose), generally two important model characteristics must be considered: (1) spatial and temporal representation, and (2) appropriate process descriptions and state variables.

7.2.1. Spatial and temporal representation

The spatial and temporal representation of the model is an important consideration in both exposure and effect modelling, and thus addressed in this work.

In relation to exposure modelling, the current exposure assessment in the EU member countries is based on the generic multimedia 'unit world' fate model, a steady state fugacity level III model (Mackay, 2001). Although this model is relatively simple and requires less monitoring data for regulatory purposes, it does not take into account both spatial and temporal variability. Recently, a new model was introduced (*GREAT-ER*; Schowanek *et al.*,

2001) which takes into account the spatial variability due to for instance river characteristics, discharge points and/or chemical emission. In *GREAT-ER*, the spatial variability is taken into account by geo-referencing the exposure concentration or data set instead of generic or average values. This model was also developed for steady-state conditions, although it can take temporal variability into account by using Monte Carlo simulation. This method also doesn't give a time series output as required for effect analysis such as duration and frequency. Indeed, chemical toxicity or effect is a function of not only concentration but also exposure duration and frequency. To refine this model, a new exposure model (*CHETOX1*) that takes into account such spatial and temporal variability in rivers was developed during this work (see Chapter 5.1). *CHETOX1* is a one-dimensional dynamic exposure model or in-stream fate model designed to describe the fate and transport of organic contaminants in rivers. The model is relatively simple because its hydraulic submodel is based on a conceptual approximation (a series of CSTRS) as a surrogate to the complex hydrodynamic model.

With respect to effects modelling, the traditional method used to determine PNEC is based on empirical extrapolation factors (OECD, 1992) and statistical approaches (Species Sensitivity Distribution, SSD approach). In both empirical and statistical approaches, the toxicity data is based on a static approach (assuming steady-state exposure concentration), where in reality the exposure concentration varies in time and space. These approaches do not take into account the exposure frequency and recovery time, while an organism in the real environment may be exposed to multiple pulses (e.g. Hosmer *et al.*, 1998; Reinert *et al.*, 2002). In this work, a time dependent toxicity prediction was investigated using toxicokinetic models that describe bioconcentration and toxicity (Meador, 1997).

Using the one-compartment first order kinetics model given in Landrum *et al.* (1992), the LAS accumulation in fish and its toxicity were investigated for the river Lambro (Italy). The results from the toxicokinetic model were not used directly in risk characterization but are useful in understanding the dynamics of toxic compound in environmental receptors. Subsequently, a statistical approach was employed to estimate the cumulative effect of multiple pulse exposures (Opperhuizen and Sijm, 1990; Mackay *et al.*, 1992). The results show that a higher exposure frequency with shorter recovery time may lead to higher acute and chronic effects. This is due to the fact that in the higher frequency situation there is a lower recovery period for the organism. An organism needs a long recovery time when the elimination rate of the chemical of concern is very low. This dynamic modelling approach is very useful because toxicity resulting from multiple pulse exposures can be predicted by uptake and elimination data combined with the critical body residues of the exposed organisms (Hickie *et al.*, 1995).

7.2.2. Appropriate description of processes and state variables

Although the level of process description and the number of state variables depend on the ultimate goal of the modelling exercise, some processes and state variables need to be considered in an exposure model. In this work, three important points are considered: (1) three-phase chemical partitioning: truly dissolved, sorbed onto Dissolved Organic Carbon (DOC) and sorbed onto Particulate Organic Carbon (POC), (2) incorporation of biofilm activities, and (3) microbial biomass as state variable.

In traditional exposure modelling, two important limitations are acknowledged. The first limitation is that only two-phase chemical partitioning (dissolved and sorbed to particulates; Karichoff *et al.*, 1979) is used in the organic contaminant fate modelling (e.g. Schnoor, 1996; Mackay, 2001). It assumes that organic contaminants associate identically with all types of organic forms. In two-phase chemical partitioning, the carbon normalized partition coefficient (K_{OC}) varies by as much as a factor of 10 mainly due to the presence of DOC (Mitra and Dickhut, 1999). Thus, several studies showed the importance of the third phase (sorption to DOC) because it enhances the solubility of highly hydrophobic organic substances and sorption to DOC reduces bioaccumulation (e.g. McCarthy and Jimenez, 1985; Day, 1990). Chemicals sorbed to DOC are not bioavailable for gill uptake, and hence DOC reduces toxicity.

The second limitation is that the microbial biomass is not often considered as state variable despite the fact that they predominates the biotransformation process. In some models, the maximum microbial degradation coefficient is used as a parameter, and is then corrected for temperature and dissolved oxygen limitations, e.g. *AQUATOX*. This assumes, however, that there is no nutrient limitation for bacterial growth. Biofilm activity in the benthic sediment is also not often considered explicitly as state variable.

In this work, the two limitations described above are included in the exposure modelling (*CHETOX1*). In *CHETOX1*, three-phase partitioning was considered: truly dissolved, sorbed to DOC and sorbed to POC. All three phases are considered as state variables. This approach has the advantage that the effect of inherent variations of POC and DOC on the fate and distribution of organic contaminants can be analysed.

Furthermore, bacteria are explicitly considered as state variables, and thereby the changes due to microbial mass dynamics can be taken into account. This consideration influences all processes related to bacterial activities such as biodegradation and chemical sorption to POC that includes (particulate) bacterial biomass. The contribution of biofilm biodegradation in the benthic sediment was also quantified using biofilm models (see also chapter 5.1). Nutrient limitation on the biodegradation of organic contaminants was also explicitly considered in the model after it was experimentally found that some substrates can limit the degradation of organic contaminants, e.g. LAS degradation limited by ammonia nitrogen (see also chapter 5.2).

To illustrate the effect of time-varying exposure concentrations on the bioaccumulated concentration in fish, a simple bioaccumulation (toxicokinetic) submodel was also included to demonstrate the application of the proposed modelling approach in the integrated modelling. Toxicokinetic models provide information about the dynamics of chemicals in the organism or the internal body residue. On the basis of the internal body residue, the cumulative effect of chemical toxicity (both chronic and acute) was simulated using a Weibull distribution (Christensen, 1984; Mackay *et al.*, 1992). This approach is advantageous in the sense that the internal body residue takes into account factors such as exposure concentration, exposure duration, exposure frequency and recovery time.

The influence of the exposure route on the bioaccumulation of LAS in fish and ultimate toxicity was also investigated on the basis of a scenario analysis. The results show that considering dietary uptake for fish resulted in higher toxicity than only considering the truly dissolved phase (see chapter 6).

7.3. Integrated modelling (RIVEUTOX1)

The individual models such as eutrophication and organic contaminant fate models are concerned with a single issue, and they do not take into account the possible interaction between the two. As eutrophication and organic contaminant fate may interact in various ways, linking these two models is therefore useful. There are only few models in literature known to link both models, e.g. *AQUATOX* (Park *et al.*, 1995). However, these integrated models have limitations because they are based on the individual models that lack appropriate linking processes or variables because these individual models were designed for different purposes.

In this work, a dynamic integrated model (*RIVEUTOX1*) was developed which takes into account the interaction of nutrient dynamics and organic contaminant fate and effect. This was done in two steps. In the first step, the individual submodels were formulated such that they include appropriate linking processes or variables in view of an integrated model. The individual models include a simplified *RWQM1* for the modelling of basic water quality or conventional pollutants, *CHETOX1* for the organic contaminants, a simple fish bioaccumulation model, and an effect model (see also chapter 6). In the second step, these individual models were linked using linking variables and processes under consideration. The linking processes are processes that are parts of the carbon cycle including biodegradation. The linking variables include DOC, POC, Dissolved Oxygen (DO) and ammonia nitrogen. The dynamics of DOC and POC influences the sorption kinetics of organic contaminants and their bioavailability, e.g. the fraction sorbed to DOC is not bioavailable for gill uptake. The fraction sorbed to POC can be removed from the bulk water by sedimentation, and thereby it reduces the truly dissolved fraction of organic contaminants in the bulk water. DO is required for the aerobic degradation of organic contaminants, whereas ammonia is required as a nitrogen source for the growth of microbial biomass on the organic contaminant.

The interaction of conventional pollutants and organic contaminant was experimentally investigated using a microcosm study. The effect of nutrients on the fate of LAS was evaluated using an artificial river (see Chapter 5.2). The results show that LAS degradation can be limited by the concentration of dissolved oxygen and the nitrogen source (ammonia). Furthermore, data obtained from the artificial river study was used to refine and validate the integrated model (see Chapter 5.3). The results indicate that the simulated data set agrees well with the measured data set.

The usefulness of the proposed model was then illustrated in Chapter 6 using a case study of the fate of LAS in the river Lambro (Italy). The model was applied to analyse various scenarios such as the effect of POC and nutrient dynamics on the fate and bioaccumulation in fish (Chapter 6). The results show that higher POC and ammonia nitrogen concentrations resulted in lower LAS concentrations in fish and, consequently, reduced toxicity. Particularly, a higher POC can significantly reduce the LAS concentration in fish. The frequency of contamination of the rive Lambro by Combined Sewer Overflows (CSO) influences bioaccumulation as well as toxicity of LAS in the river. When a small load is discharged to the river with more frequent CSO, the peak bioaccumulated concentration is reduced significantly, but the minimum bioaccumulated concentrations rise a little bit (see Chapter 6, section 6.6.2.3). The significance of such difference is thus depends on the PNEC value. When the same load of CSOs is considered in every discharge, the maximum as well as the minimum bioaccumulated concentrations increase. It was also found that considering two exposure routes, i.e. exposure via gill uptake and dietary uptake has resulted in different trend of bioaccumulated concentration. If the exposure concentration is variable, the bioaccumulated concentration continues to rise, and it also depends on the elimination rate coefficient of the compound under consideration. Indeed, a higher elimination rate coefficient resulted in a lower accumulation.

In view of the fact that this toxicity model can be further extended to include other species, it appears to be a promising approach in determining not only a direct effect (toxic effect to the sensitive species) but also indirect effects such as “bottom-up” and “top-bottom” control. The bottom-up control refers to the effects that are due to changes in nutrient/food concentration, whereas the top-bottom control refers to effects that are due to changes in grazing pressure and predatory-prey relationships. The output of the integrated model can then further be analysed using a statistical approach to determine the PNEC, and ultimately to characterise the ecological risk from the time-varying PEC. Such an approach is consistent with recent developments in integrated modelling of ecological risk assessment (Naito *et al.*, 2002, 2003; Bartell *et al.*, 1999).

7.4. General conclusions

Based on the general discussion given in this chapter, the following summarizing conclusions can be drown:

Model simplification and applications

- By using a simplified hydraulic and river water quality model (*RWQM1*) data requirements are reduced, as well as monitoring cost and simulation time. Model reduction also simplifies the integrated modelling of basic water quality and organic contaminant fate and effect in rivers. Such model reduction, however, requires a good understanding of the system under consideration because it is case specific, i.e. it depends on the river characteristics. Therefore, care must be taken not to exclude important linking processes or state variables that need to be considered in the integrated modelling of basic water quality and organic contaminants. So, any assumption made needs to be justified.
- The study of the water quality control option in the Crocodile River (South Africa) shows that setting maximum upstream freshwater withdrawal and controlling water release patterns from the reservoir can help to improve the river water quality in the downstream river stretches. To reduce the high rate of upstream freshwater withdrawal, efficient water use and water reuse policies need to be encouraged. In addition to the proposed water quality management options, a stringent effluent quality regulation is also required to guarantee the water quality targets.

Dynamic modelling

- In-stream flow and water quality variables are (for both conventional pollutants and xenobiotic organic contaminants) time as well as spatially variable due to storm events, combined sewer overflows, runoff from agricultural lands or mining sites.

Consequently, the aquatic organisms are exposed to time-varying exposure concentrations, and the resulting toxicity thus depends not only on the exposure concentration but also on duration, frequency and recovery time. The proposed dynamic mechanistic model can adequately describe the time evolution of water quality variables and exposure concentration in rivers. This approach is highly recommended for highly variable conditions. The resulting time-series output can also be used for further analysis such as exposure duration and frequency. Such analysis can then be explored for better prediction of effect (toxicity) on the aquatic system under consideration.

Integrated modelling

- Biological quality is the result of multiple stressors among which two are important: conventional pollutants (nutrient limitation, dissolved oxygen deficit, etc) and xenobiotic organic contaminants. The individual based modelling of basic water quality (single issue) and organic contaminant fate however only addresses a single issue, and the interaction between the two factors is not considered. To achieve the water quality objective, i.e. a "good biological quality", it requires the water quality modeler to address both conventional pollutants and organic contaminants at the same time.
- *RIVEUTOX1,* the proposed dynamic integrated model of eutrophication and organic contaminant fate with three-phase partition and toxicokinetic submodel, also takes into account the effect of bioavailability on chemical toxicity.

7.5. Perspectives

This work has discussed a number of concepts related to basic river water quality management and ecological risk assessment. For instance, setting the maximum water withdrawal and low flow augmentation, including nutrient limitation in the biodegradation of organic contaminant, incorporating a biofilm model, considering three-phase chemical partitioning and dynamic effect modelling. As such it addresses important issues that assist the water quality regulator to achieve water quality objectives. Much work, however, still needs to be done in the framework of integrated ecological risk assessment and integrated water quality management in river basins.

Among these, four important points are outlined. First, in the proposed model, only one sort of xenobiotic organic chemicals (LAS) is considered, whereas in reality the organism may also be exposed to heavy metals and other xenobiotic organic compounds: agricultural products (herbicides and pesticides), pharmaceutical products, etc. Therefore, it is important to extend the proposed concepts for at least the most important hazardous substances for which there is sufficient information in literature.

Second, in reality an organism may be exposed not only to a single chemical but to a cocktail of several chemicals. The mixture toxicity can be additive, synergetic or antagonistic. Although the mixture toxicity of several chemicals is not well understood, it is also important to consider the mixture toxicity by focusing on the most widely used chemicals, e.g. pesticides, herbicides and cleaning products. The application of a quantitative activity relationship approach and microcosm studies is certainly one way to go.

Third, the submodel included in *RIVEUTOX1* describes the direct effect/toxicity of LAS for fish and does not take into account the indirect effect on fish due to, for example biomass reduction in benthic invertebrates, which serve as food/prey for fish. To predict such an indirect effect an appropriate ecological model is needed (Naito *et al.*, 2002 and 2003).

Fourth, from a management perspective, knowledge of uncertainty in predictions is as important as the predictions themselves (Verdonck, 2003). It is therefore important to clearly communicate the uncertainty associated with the model results. This can be done in three steps: (1) the relative importance of the model inputs must be identified using a sensitivity analysis, (2) the value of the most sensitive inputs needs to be determined or measured accurately, and (3) the uncertainty associated with those most sensitive inputs should be quantified using e.g. a Monte Carlo analysis. The third step is not studied in this work, and needs to be considered in a future study. Furthermore, the propagation of uncertainty from the basic water quality model to the exposure and effect model needs to be studied.

Part 8

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Summary

Both conventional pollutants and organic contaminants in rivers are of concern to the water quality managers and environmental risk regulators to achieve water quality objectives. After an extensive literature study made in Chapter 2 it becomes clear that the complexity of ecological problems (particularly the interaction between conventional pollutants and organic contaminants) requires a different approach than traditional river water quality models can provide. The traditional models are focusing on the two issues separately, and hence, do not consider the interaction between the two main water quality problems. They also lack appropriate linking processes and state variables, and, thus, they cannot be coupled without modification.

The ultimate goal of this work is to develop a dynamic integrated model of conventional pollutants and organic contaminant fate and effect in rivers. This integrated modelling approach is a holistic approach that assists the water quality managers and environmental risk regulators to achieve a “good” biological water quality.

In this work, three key problems are addressed in order to achieve this goal (dynamic integrated river water quality modelling). The first problem is related to the complexity of the hydrodynamic model (the St. Venant equations) and the basic water quality model that is typically used to describe river water quality under unsteady state conditions. As the St. Venant equations require a long computation time, extending these equations for dynamic integrated modelling of basic water quality and organic contaminant fate and effect is not practically feasible. For instance, the River Water Quality Model No. 1 (RWQM1) is the most comprehensive basic river water quality model available in literature. It is, however, too complex to be applied in data limited situations, especially in developing countries.

The second problem is related to the development of a realistic organic contaminant fate (exposure) model. The current methods of risk assessment or regulation are based on steady state models (fugacity level III), e.g. in the EU member countries. However, as environmental conditions are never at steady state, this steady state model cannot be readily validated.

Besides, such a modelling approach lacks appropriate process descriptions and state variables, and, hence, cannot describe observed short-term dynamics of organic contaminants in rivers. The third problem is that traditional river water quality modelling describes both conventional pollutants and organic contaminants as separate issues. The effect of nutrient dynamics on the fate of organic contaminants and vice versa is not taken into account.

In this Ph.D. thesis, an attempt was made to tackle these three problems in four steps. First, a conceptual hydraulic model (Continuously Stirred Tank Reactors in Series) was applied as a surrogate to a complex hydrodynamic model. This conceptual approach applies only to rivers where tidal (or backwater) effects are absent. The optimum number of tanks-in-series required for this concept is best determined on the basis of a tracer study.

Second, the RWQM1 was simplified so that the model can be applied in data limited situations. The application of the simplified model was evaluated using a case study of inorganic nitrogen and total dissolved solids in the Crocodile River (South Africa). The results of model calibration and validation indicate that the proposed model can adequately describe the seasonal dynamics of inorganic nitrogen in that river. Two water quality management options were also investigated in order to improve the downstream water quality of the Crocodile River: (1) setting a maximum upstream freshwater withdrawal and (2) applying low flow augmentation. The results show that despite the fact that both methods can improve the downstream river water quality, a stringent urban water pollution prevention plan is also needed.

Third, a dynamic in-stream fate (exposure) model was developed on the basis of the conceptual hydraulic model and the simplified RWQM1. The simplified RWQM1 was extended in order to include a xenobiotic organic contaminant fate submodel. The usefulness of the proposed organic contaminant fate model was investigated using a Linear Alkylbenzene Sulphonate (LAS) case study in the River Lambro (Italy). The results indicate that the proposed model can adequately describe the short-term dynamics of LAS in the River Lambro. The effect of conventional pollutants (nutrients) on the in-stream fate of LAS was also investigated using an artificial river, and the in-stream fate model was further refined based on the results of the artificial river study. The proposed dynamic exposure model can simulate the time evolution of the exposure concentration in three phases of environmental compartments (water and benthic sediment): truly dissolved, sorbed to dissolved organic carbon and suspended solids in the bulk water; truly dissolved and sorbed to dissolved organic carbon in the pore water, and sorbed to benthic sediment. These different concentrations of contaminants in the three phases are needed to allow the proposed exposure model to be linked to the bioaccumulation and toxicokinetic submodels. Subsequently, dynamic effect/toxicity can be simulated, with the latter submodels.

Fourth, by linking the basic water quality submodel (for conventional pollutants) to the proposed organic contaminant fate and effect submodels, a dynamic integrated river water quality model was developed. Linking individual submodels was done by selecting appropriate linking processes or linking variables. The linking processes are part of the carbon cycle, whereas the linking variables are microbial biomass, particulate organic carbon, dissolved organic carbon, dissolved oxygen and mineral nutrients. The proposed model describes not only the time evolution of conventional pollutants and organic contaminants in rivers, but also the interaction between eutrophication and contamination by xenobiotic organic compounds. The model can, hence, simulate the effect of conventional pollutants on the fate and effect/toxicity of organic contaminants in rivers. The usefulness of the model was evaluated using a case study of LAS in the river Lambro with some scenario analyses such as the effect of nutrients and total suspended solids, the partition coefficient and the contamination frequency of the river by Combined Sewer Overflows (CSOs). The results of model validation and scenario analyses show that the model can adequately describe fate and effect of LAS in the river Lambro. A higher exposure frequency can increase toxicity, which depends on the critical body burden. The trends show that on increase of ammonia nitrogen concentration in an oligotrophic river system can decrease the predicted LAS tissue concentration.

Summarizing, this work has introduced some important new concepts, e.g. modelling dynamic exposure and the interaction of conventional pollutants and organic contaminants in rivers. It as such addresses important issues for water resource management. Much work, however, still needs to be done in the framework of integrated ecological risk assessment and integrated water quality management: extending the proposed concepts for other important hazardous substances; considering mixture toxicity and multiple stressors; appropriate ecological modelling for dynamic effect assessment; and considering the uncertainty associated with those most sensitive model inputs.

Samenvatting

Om waterkwaliteitdoelstellingen te bereiken dienen waterkwaliteitmanagers en milieurisicobeleidsbeslissers zich zowel over conventionele als organische polluenten te bekommeren. Een uitgebreide literatuurstudie in hoofdstuk 2 toont aan dat de complexiteit van ecologische problemen (voornamelijk door de interactie tussen conventionele en organische polluenten) een andere aanpak vergt dan de traditionele waterkwaliteitsmodellen kunnen verschaffen. De traditionele modellen focusseren immers op de twee polluenten apart, en beschouwen daardoor geen interacties. De modellen kunnen ook niet direct worden gekoppeld aangezien de processen en toestandsvariabelen op elkaar afgestemd dienen te worden.

De uiteindelijke doelstelling van dit werk is het ontwikkelen van een dynamisch, geïntegreerd model voor conventionele polluenten en het gedrag en effecten van organische polluenten in rivieren te beschrijven en te voorspellen. Deze modelintegratie is een holistische aanpak die waterkwaliteitsmanagers en milieurisicobeleidsbeslissers moeten ondersteunen om een “goede” biologische waterkwaliteit in rivieren te bereiken.

Om deze doelstelling te bereiken, werden drie belangrijke problemen in dit werk behandeld. Het eerste probleem is gerelateerd tot de complexiteit van het hydrodynamische model (gebaseerd op de St. Venant vergelijkingen) en het basiswaterkwaliteitsmodel dat typisch wordt gebruikt om rivierwaterkwaliteit te beschrijven onder onevenwichttoestands–voorwaarden. Aangezien de St. Venant vergelijkingen een lange rekentijd vergen, is het praktisch niet haalbaar om deze vergelijkingen uit te breiden voor dynamische geïntegreerde modellering van basiswaterkwaliteit en gedrag en effecten van organische polluenten. Zo bijvoorbeeld is het rivierwaterkwaliteitsmodel N° 1 (RWQM1) het meest alomvattende basisrivierkwaliteitsmodel beschikbaar in de literatuur. Het is echter te complex om toegepast te worden in gegevensarme situaties, zoals voornamelijk in ontwikkelingslanden.

Het tweede probleem is gerelateerd aan de ontwikkeling van een realistisch, organisch blootstellingsmodel. De huidige methoden van de risicoanalyse in bvb. de EU-wetgeving zijn gebaseerd op evenwichttoestandsmodellen. Zo’n model kan niet gemakkelijk gevalideerd worden aangezien milieucondities nooit in evenwichtstoestand zijn. Trouwens, dergelijke aanpak ontbreekt aan geschikte procesbeschrijvingen en toestandsvariabelen, en kan daardoor waargenomen korte termijn dynamica van organische polluenten niet beschrijven.

Het derde probleem is dat traditionele rivierwaterkwaliteitsmodellering aparte processen beschrijft voor conventionele en organische polluenten. Cruciale interacties zoals het effect van nutriëntendynamica op het gedrag van organische contaminanten en vice versa worden niet in beschouwing genomen.

In deze doctoraatsthesis werd een poging ondernomen om deze drie problemen aan te pakken in vier stappen. Vooreerst werd een conceptueel hydraulisch model (continu gemengde tankreactors in serie) toegepast als surrogaat voor een complex hydrodynamisch model. Deze conceptuele aanpak is alleen geldig voor rivieren zonder getijdenwerking. Het optimale aantal tanks-in-serie nodig voor dit concept wordt best bepaald op basis van een tracerstudie.

Ten tweede, RWQM1 werd vereenvoudigd zodat het model kan toegepast worden in gegevensarme situaties. De toepassing van het vereenvoudigd model werd geëvalueerd aan de hand van een gevallenstudie over anorganische stikstof en totale opgeloste stoffen in de “Crocodile River” (Zuid-Afrika). De resultaten van de modelcalibratie en –validatie tonen aan dat het voorgestelde model de seizoenale dynamica van de anorganische stikstof in de rivier adequaat kan beschrijven. Hierbij werden twee waterkwaliteitsmanagementopties onderzocht om de stroomafwaartse waterkwaliteit van de “Crocodile River” te verbeteren: (1) vastleggen van een maximale stroomopwaartse waterontrekking en (2) toepassen van een debietsverhoging. De resultaten tonen dat ondanks het feit dat beide methodes de stroomafwaartse rivierwaterkwaliteit kunnen verbeteren, ook een strikt stedelijk watervervuilingpreventieplan nodig is.

Ten derde werd een dynamisch rivierblootstellingsmodel ontwikkeld op basis van het conceptuele hydraulische model en het vereenvoudigde RWQM1. Het vereenvoudigde RWQM1 werd uitgebreid met een blootstellingsmodel voor organisch polluenten. De bruikbaarheid van het voorgestelde blootstellingsmodel werd onderzocht in een gevallenstudie voor Lineair Alkylbenzeensulfonaat (LAS) in de “Lambro” rivier (Italië). De resultaten duiden aan dat het voorgestelde model de korte termijn dynamica van LAS in de “Lambro”-rivier adequaat kan beschrijven. Het effect van conventionele polluenten (nutriënten) op het gedrag van LAS werd ook onderzocht in een artificiële rivier. De resultaten hiervan werden gebruikt om het rivierblootstellingsmodel verder te verbeteren. Het voorgestelde dynamische blootstellingsmodel kan de tijdsevolutie van de milieuconcentratie simuleren in drie fasen van de milieucompartimenten (water en bentisch sediment): werkelijk opgelost en gesorbeerd op opgeloste organische koolstof en opgeloste stoffen in het bulk water en in het poriënwater, en gesorbeerd op het benthische sediment. De verschillende concentraties in deze drie fases zijn nodig om het voorgestelde blootstellingsmodel te koppelen met bioaccumulatie- and toxicokinetische submodellen. Met deze laatste kunnen dynamische effecten/toxiciteit worden gesimuleerd.

Ten vierde, een dynamisch geïntegreerd rivierwaterkwaliteitsmodel werd ontwikkeld door het koppelen van het basiswaterkwaliteitsmodel (voor conventionele polluenten) met de voorgestelde organische blootstellings- en effectsubmodellen. Het koppelen van individuele submodellen werd gedaan door het selecteren van de nodige, gekoppelde processen van gekoppelde variabelen. De gekoppelde processen maken deel uit van de koolstofcyclus. De gekoppelde variabelen zijn microbiële biomassa, particulier organische koolstof, opgeloste organische koolstof, opgeloste zuurstof en minerale nutriënten. Het voorgestelde model beschrijft niet alleen de tijdsevolutie van conventionele en organische polluenten in rivieren, maar ook de interactie tussen eutroficatie en contaminatie door toxische organische stoffen. Het model kan bijgevolg het effect van conventionele polluenten op het gedrag en de effecten/toxiciteit van organische polluenten in rivieren simuleren. De bruikbaarheid van het model werd geëvalueerd in een gevallenstudie van LAS in de “Lambro” rivier aan de hand van enkele scenarios zoals het effect van nutriënten en totale opgeloste stoffen, de verdelingscoëfficiënt en de contaminatiefrequentie van de rivier door overstorten. De resultaten van de modelvalidatie en de scenarios tonen aan dat het model het gedrag en de effecten van LAS in de “Lambro” rivier adequaat kan beschrijven. Een grotere blootstellingsfrequentie kan de toxiciteit verhogen. De trends tonen dat een stijging in ammoniakstikstofconcentratie, in een oligotroof riviersysteem, de voorspelde LAS weefselconcentratie kan doen dalen.

Samengevat, dit werk heeft een aantal belangrijke nieuwe concepten geïntroduceerd zoals het modelleren van dynamische blootstelling en de interactie tussen conventionele en organische polluenten in rivieren. Deze adresseren belangrijke problemen in waterbeheer. Verder onderzoek is echter nodig in het kader van geïntegreerde, ecologische risicoanalyse en geïntegreerde waterkwaliteitsmanagement: uitbreiding van de voorgestelde concepten voor andere, belangrijke gevaarlijke stoffen; het beschouwen van toxiciteit door chemicaliënmengels; geschikte ecologische modellering van dynamische effecten; en het bepalen van de onzekerheid van de meest gevoelige modelinputs.

Curriculum Vitae

Personal

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1987-1991	B.Sc. (Grade Point Average 3.5/4) at Alemaya University of Agricultural Science, Faculty of Arid Zone Agriculture, Department of Arid Land Crop Production, Alemaya, Ethiopia.

Additional Courses

2002	Water quality modelling: Free University of Brussels, Belgium
2001	Numerical methods: Surface water quality modelling (SWAT): Free University of Brussels, Belgium.
2000	Bioinformatics: Ghent University, Belgium
2000	Modelling biosystem dynamics: Ghent University, Belgium
2000	Easy PC logging and instrument control: Ghent University, Belgium
2000	Land information systems (GIS): Ghent University, Belgium

1999-2000	1st year courses for the Master of Science Programme in Water Resource Engineering. IUPWARE, Catholic University of Leuven, Belgium

Study visits

Feb – March 2000	The Council of Scientific & Industrial Research (CSIR), Pretoria, South Africa. Collecting water quality data, assessing water quality problems and evaluating the applicaton of river water quality models in South Africa.

Employment

2000-present	Department of Applied Mathematics, Biometrics and Process Control (BIOMATH), Faculty of Agricultural and Applied Biological Sciences, Ghent University, Belgium. Research assistant. Research project: Dynamic integrated modelling of basic water quality and fate and effect of organic contaminant in rivers.
1995-1996	Ministry of Water Resource Development, West Shoa zone, Ethiopia. Senior expert in irrigation agronomy.
1992-1994	Ministry of Natural Resource Development and Environmental Protection, Kefficho and West Shoa Zones, Ethiopia. Department head.
1992	Ministry of Agricultural Development and Environmental Protection, Kefficho zone, Ethiopia. Junior expert in agroforestry, soil and water conservation.

Prizes

2003	First prize for the best poster presentation on the 9th Ph.D. symposium in Leuven, Belgium.
1991	First prize for the best student in the faculty of arid zone agriculture and department of arid land crop production, Alemaya University, Ethiopia.

Membership of professional organizations

2002-Present	International Water Assosciation (IWA)
2002-Present	Socity of Environmental Toxicology and Chemistry (SETAC)

Publications

Verdonck F. A. M., **Deksissa** T., Matamoros D. and Vanrolleghem P. A. (2004). Dealing with variability in chemical exposure modelling in rivers. *Environmental pollution,* submitted.

Deksissa T. and Vanrolleghem P. A. (2004). Integrated modelling of conventional pollutant and organic contaminant fate in rivers: A microcosm study. In: *IWA World Congress and Exhibition*, September 19–24 2004, Marrakech, Morocco, in press.

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Verdonck F. A. M., van Griensven A., **Deksissa** T., Holvoet, Seuntjes K. P. and P. A. Vanrolleghem. (2004). Harmonising chemical fate and basic water quality modelling at the catchment scale. In: the *14th annual meeting of SETAC Europe*, Prug, Czch Republic, 18-22 April 2004, in press.

Deksissa T., Meirlaen J., Ashton P.J and Vanrolleghem P.A. (2004). Simplifying dynamic river water Quality Modelling: A case study of inorganic nitrogen dynamics in the Crocodile River (South Africa). *Water, Air & Soil Pollution*, 155, 303-319.

Deksissa T. and Vanrolleghem P. A. (2003). Effect of nutrient dynamics on organic contaminant fate in rivers: A microcosm study. *Med. Fac. Landbouww. Univ. Gent,* 68 (3), 111–114.

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Verdonck F. A. M., **Deksissa** T., Matamoros D., Vandenberghe V. and Vanrolleghem P.A. (2002). Spatio-temporal probabilistic environmental modelling. *Med. Fac. Landbouww. Univ. Gent, 67 (4), 205-208.*

Deksissa T., Meirlaen J., Ashton P.J and Vanrolleghem P.A. (2001). Simplifying dynamic river water Quality Modelling: A case study of inorganic nitrogen dynamics in the Crocodile River (South Africa). In: *Proceedings of the IWA* *conference on water and wastewater management for developing countries*, 29 – 31 October, Kuala Lumpur, Malaysia, Vol. 2, 332-339.

Deksissa T. and Peter A. Vanrolleghem (2001). Dynamic exposure modelling. *Med. Fac. Landbouww. Univ. Gent, 66 (4), 239–244.*

Deksissa T., Ashton P. J and Vanrolleghem P. A. (2000). *Water quality assessment in South Africa: Progress report*, February 2000, Pretoria, South Afria.

International conferences and symposiums

2nd IWA young researcher conference, Wagingen, The Netherlands, April 23-24 2004. (Poster presentation)

9th Ph.D syposium on Applied Biological Sciences, Leuven, Belgium, 17 October 2003. (Poster presentation)

13th annual meeting of SETAC Europe, Hamburg, Germany, 27 April-1 May 2003**.** (Oral presentation)

6th international Conference on diffuse pollution, September 30-4 October 2002, Amsterdam, The Netherlands. (Poster presentation)

Joint international seminar on exposure and effects modelling in environmenta toxicology: A first dialogue between nuclear and non-neauclear environmental scientists and managers. 4-7 February 2002, Antwerp, Belgium. (Oral presentation)

8th Ph.D syposium on Applied Biological Sciences, Gent, Belgium, 9 October, 2002. (Poster presentation)

International symposium: Ecological Informatics Applications in water management, 6-7 November 2002, Ghent, Belgium. (Poster presentation)

SETAC Europe 12th meeting on challenges in environmental risk assessment and modelling: linking basic and applied research. 12-16 May 2002, Vienna, Austria. (Poster presentation)

7th FLTBW Ph.D symposium, Ghent, Belgium, 10 October 2001. (Poster presentation)

15th Forum for Applied Biological Technology, FAB 2001, 24-25 September 2001, Gent, Belgium.

5th international symposium, Systems analysis and computing in water quality management, WATERMATEX 2000, 18-20 September 2000, Gent, Belgium.