available at www.sciencedirect.com
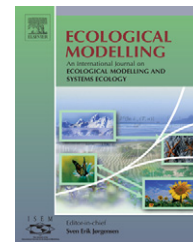
ScienceDirect

journal homepage: www.elsevier.com/locate/ecolmodel

ELSEVIER

Review

Monitoring and modeling pesticide fate in surface waters at the catchment scale

Katrijn M.A. Holvoet [a,b], **Piet Seuntjens** [b,*], **Peter A. Vanrolleghem** [a,c,1]

[a] BIOMATH, Department of Applied Mathematics, Biometrics and Process Control, Ghent University, Belgium
[b] VITO, Flemish Institute for Technological Research, Land and Water Management, Boeretang 200, B-2400 Mol, Belgium
[c] modelEAU, Département de génie civil, Pavillon Pouliot, Université Laval, Québec, QC G1K 7P4, Canada

ARTICLE INFO

Keywords:
Pesticides
Modeling
Surface water
Catchment
Monitoring

ABSTRACT

In this paper, a state-of-the-art is given of the current knowledge related to the occurrence and sources of pesticides in surface waters. An emphasis is put on sources and transport routes that contribute most to the pesticide loads found in river systems. Possible mitigation measures are described. Once pesticides have entered a river system, they are exposed to different physical, chemical and microbial processes which determine their fate. As mathematical models can describe the fate of pesticides in river systems and can be used for the control of environmental pollution and management of resources, an overview is given of available watershed and in-river water quality models able to predict pesticide concentrations in surface waters. Advantages and disadvantages of simple screening tools and complex watershed models are discussed. Finally, some recommendations are made concerning monitoring, modeling and their combined use in order to achieve the water quality goals set by the EU Water Framework Directive.

© 2007 Published by Elsevier B.V.

Contents

* *Corresponding author*. Fax: +32 14321185.
   E-mail address: piet.seuntjens@vito.be (P. Seuntjens).
[1] He holds the Canada Research Chair in Water Quality Modelling. Fax: +1 418 656 2928.

1.   Introduction

Pesticides are of concern to water quality managers and environmental risk regulators to maintain and achieve a good water quality status. Pesticides can enter river systems as point sources, i.e. at certain locations along the river, or as diffuse sources which are inputs along the whole water course. Examples of point sources of pesticides are sewage plants, sewer overflows and losses due to bad management practices of farmers. As diffuse input pathways runoff, drainflow, drift, deposition and a contribution through groundwater can be distinguished. We reviewed the state-of-the-art on monitoring and modeling pesticide fate in river systems at the catchment scale. The review consists of an overview of occurrence and sources of pesticides in rivers, mitigation measures, pesticide processes in rivers, model tools for calculating pesticide fate at the catchment scale and future prospects in monitoring and modeling of pesticides.

2.   Occurrence and sources of pesticides in rivers

From large-scale studies that monitored herbicide losses to surface water it can be concluded that, on average, less than 2% of the total mass applied within large catchments is ultimately lost to surface waters and that losses occur primarily during and right after the application period (Capel et al., 2001). Furthermore, such studies show that weather conditions, soil type, land use, intrinsic properties of the compound, as well as point sources are crucial factors influencing the overall herbicide loss from a watershed (Kreuger, 1998; Capel et al., 2001). Kreuger and Törnqvist (1998), Neumann et al. (2002) and Tesfamichael and Kaluarachchi (2006) found that the amount applied in the catchment region is more important than the octanol–water partition coefficient K_{ow}, in influencing the load of pesticides occurring in the river for all pesticide classes considered.

2.1.   Point sources

The contribution of point sources to pesticide pollution in river systems was demonstrated to be very important in several catchments in Europe. In different catchments in Germany (Seel et al., 1994; Fischer et al., 1996, 1998a; Bach et al., 2001; Neumann et al., 2003) with varying catchments sizes between 7 and 1940 km^2, in Switzerland (Gerecke et al., 2002; Leu et al., 2004a), in Sweden (Kreuger, 1998), in the UK (Hankinson and Welland, 2001; Mason, 2003) and in Belgium (Beernaerts et al., 2002; Holvoet et al., 2005), it was shown that the load of pesticides in rivers could be attributed for 20–80% to point sources. Fig. 1 shows an example of the occurrence and hourly dynamics of two pesticides in a typical rural Belgian 32 km^2

catchment. The catchment is a typical example of pesticide occurrence in rivers at scales close to the worst-case edge-of-field scenarios for surface water, as used in the EU FOCUS guidelines for the registration of pesticides. Elevated pesticide concentrations during dry periods indicate point sources.

The spill during filling of the spraying equipment, cleaning of the equipment and processing of spray waste on paved surfaces are examples for bad management practices (Fischer et al., 1998a; Kreuger, 1998; Beernaerts et al., 2002; Neumann et al., 2002). Pesticide concentrations tend to be higher in small catchments with intensive agriculture and when older spraying equipment is used (Fischer et al., 1998a).

2.2.   Diffuse sources

Pesticides enter river systems via diffuse sources. As diffuse input pathways, runoff, drainflow, drift, atmospheric deposition and groundwater flow can be distinguished. Based on modeling, Bach et al. (2001) showed that surface runoff is expected to be a major source of diffuse pesticide input in Germany. Non-point source input via preferential flow through macropores in soil is important in tile-drained structured soils (Leu et al., 2004a) and spray-drift may be dominant in orchard
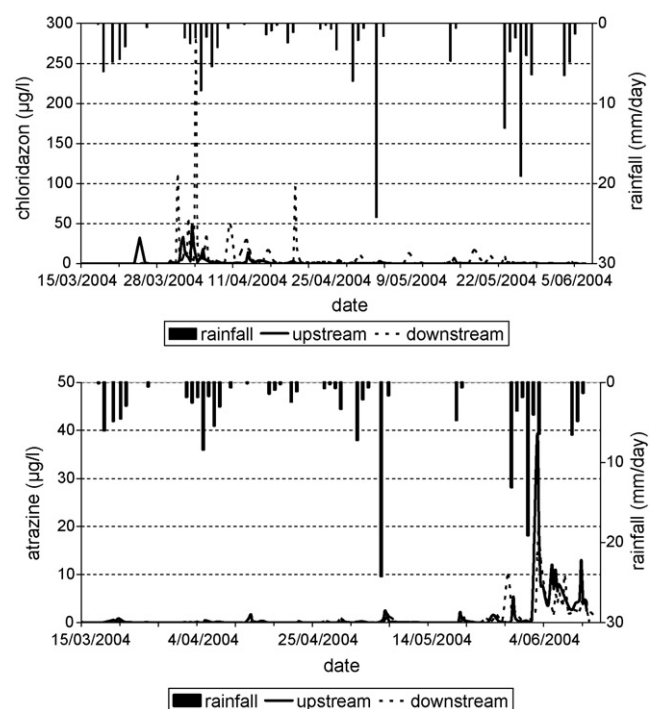

Fig. 1 – Measured rainfall (bars), concentrations of chloridazon (top) and atrazine (bottom) at the mouth (downstream) and 8 km upstream in the river Nil in Belgium during spring 2004.

regions (Bach et al., 2001; Ritter, 2001) or flat areas with a dense network of ditches (Meli et al., 2007). From field measurements, Kreuger (1998) found that inputs by drift or direct spraying were less important, as did Majewski et al. (2000) and De Rossi et al. (2003) for the contribution from precipitation and Foreman et al. (2000) for dry deposition.

Surface runoff occurs whenever the rate of water application to the ground surface exceeds the rate of infiltration and the surface storage capacity is exceeded. The amount and rate of runoff depend on rainfall and watershed characteristics. Important rainfall characteristics include duration, intensity and areal distribution. Watershed characteristics that influence runoff include soil properties, land use, vegetation cover, soil moisture condition, size, shape, topography, orientation, geology, cultural practices and channel characteristics (Wolfe, 2001). The abrasive power of surface runoff and the impact of raindrops will detach soil particles and cause soil erosion. Some soils erode more easily than others even when all other factors are the same. For example, Wischmeier and Smith (1978), Bielders et al. (2003) and Knapen et al. (2007) noted that a soil type usually becomes less erodible with decrease in silt fraction, regardless of whether the corresponding increase is in the sand fraction or clay fraction. Runoff susceptibility and soil erodibility are enhanced by silting and crusting of the soil surface due to raindrop impact and splash during high-intensity rainfalls (Le Bissonais et al., 1995). The sediment delivery towards surface waters depends on the size and shape of the contributing area; the steepness, length and shape of contributing surfaces; sediment characteristics; buffer zones; storm characteristics; and land use (Nearing et al., 2001).

Both pesticides in solution and pesticides sorbed to sediment particles can be transported during a runoff event. The partitioning of a pesticide between the solution and soil solid phases is influenced by factors like the organic carbon and clay content of the soil. For soluble pesticides losses via surface runoff are considered far more important than losses via soil erosion, because the amount of eroded soil lost from a field is usually small compared with the runoff volume (Leonard, 1990). Only for strongly sorbing substances with a K_{OC} greater than ca. $1000 \, L \, kg^{-1}$, erosion is considered to be the main loss pathway (Kenaga, 1980; Dabrowski et al., 2002; Wu et al., 2004). The amount of pesticides lost towards the river through runoff depends on the amount of pesticide in the active zone at the soil surface at the time of runoff and is mainly determined by the period of time between application and the first rainfall event and by the application dose (Müller et al., 2003). Martin and Owens (2003) came to the conclusion that the timing of rainfall and runoff relative to atrazine application can have a much greater effect on the yearly losses of the parent compound and its metabolites than the agronomic management practices investigated. Also the slope (Leu et al., 2004b), the width of buffer strips and the presence of erosion rills are important catchment variables determining runoff (Dabrowski et al., 2002).

Consistent research findings have demonstrated that preferential flow phenomena are key contributors to the rapid transfer of pesticides to *drainage* systems (Kladivko et al., 1991; Novak et al., 2001; Neumann et al., 2002; Gardenas et al., 2006). Pesticide transport by preferential flow in soil macropores to drains can cause high transient concentrations in agricultural ditches and small rivers (Williams et al., 1996; Fenelon and Moore, 1998; Brown et al., 2004; Leu et al., 2004b).

Spraydrift can occur during pesticide application by spraying. During the application, a part of the spray liquid may be carried out of the treated area by wind or the air stream of the sprayer and reach a nearby river system (Bach et al., 2001). Drifting spray is a complex problem in which equipment design and application parameters, spray physical properties and formulation, and meteorological conditions interact and influence pesticide loss (Gil and Sinfort, 2005). Although its contribution to surface water pollution in European countries is thought to be rather small (Kreuger, 1998; Huber et al., 2000; Neumann et al., 2002; Röpke et al., 2004), few studies found contributions from spray drift in ditches (Meli et al., 2007).

Leaching of pesticides into deep groundwater and a possible input of pesticides into surface waters by outflowing groundwater is assumed to be negligible as pesticides in groundwater resources occur locally or in low concentrations (Groenboek, 2002). Moreover, slow groundwater movement and pesticide attenuation in the groundwater due to sorption and degradation further diminishes the pesticide concentrations (Röpke et al., 2004).

Further diffuse input pathways for pesticides into surface waters are atmospheric deposition after volatilization, and aeolian deposition of pesticide-loaded soil particles previously eroded by wind. For volatile pesticides downwind short-range transport can become important under certain weather conditions (Bedos et al., 2002; Siebers et al., 2003).

3. Mitigation

3.1. Point sources

The pesticide contamination of surface waters through point sources can be significantly reduced without relevant financial consequences for the agricultural sector, by only minimizing improper operations. Careful pesticide handling (Neumann et al., 2002) and the execution of as many operations as possible directly on the treated field (e.g. rinsing of spray tank with fresh water) are already highly effective strategies (Gerecke et al., 2002; Campbell et al., 2004). This can be supported by intense information campaigns (Fischer et al., 1996, 1998b; Kreuger and Nilsson, 2001; Beernaerts et al., 2002), action programmes (Saethre et al., 1999; Kreuger and Nilsson, 2001) or sending a letter containing the most important points of 'good agricultural practice' for pesticide application (Gerecke et al., 2002). This sensitization of farmers should be repeated frequently and maintained in order to preserve low pesticide loads towards the river (Fischer et al., 1998b; Beernaerts et al., 2002). Kreuger and Nilsson (2001) found that farmers are more willing to accept information when given personally and adjusted to site specific conditions than when received through general letters and pamphlets. The different initiatives have proven their usefulness: pesticide load reductions from 20 up to more than 80% were achieved (Fischer et al., 1996; Kreuger and Nilsson, 2001; Beernaerts et al., 2002; Gerecke et al., 2002). Besides, biobeds can be installed on the farm yard to collect and treat spillage during filling of the agricultural spraying equipment and during rinsing afterwards

(Torstensson, 2000; Mason, 2003; Fogg, 2004; Vischetti et al., 2004; Spliid et al., 2006). A phytobac is a similar system, but it has an impervious bottom (Phytofar, 2006). A biofilter exists of different biobeds in series with drainage systems at their bottom. Especially for mobile pesticides, the efficiency of the biobed technique will be improved by having several passages (Phytofar, 2006, http://www.phytofar.be/).

3.2. Diffuse sources

The contamination of surface waters through diffuse pesticide sources can be significantly reduced by (i) a reduction in pesticide use, (ii) the implementation of runoff and erosion control practices and (iii) drift-reducing measures. A *reduction in pesticide use* is possible through guided pest control with a warning system that informs farmers when to use, for example, insecticides (targeted pest control) (Campbell et al., 2004; Baets et al., 2005), through biological control (van Lenteren, 2000; Corrales and Campos, 2004) or by means of an integrated approach (van Lenteren, 2000; Tantau and Lange, 2003; Mansingh et al., 2007).

Different *runoff and erosion control* practices exist which will reduce pesticide loads towards the river. Their effectiveness depends upon the amount of infiltration, the adsorption characteristics of the pesticide and the degree of fine-sediment transport reduction. Through conservation tillage practices, minimal cultivation systems leave crop residues near the surface. These crop residues protect soils from erosion by increasing the organic matter content and structural stability in the top few centimetres. This reduces runoff by increasing the infiltration capacity of the soil and reduces the detachment effect of raindrop impact (Ritter, 2001). Other erosion control practices that will reduce pesticide loads are to grow green manure crops after harvest, to sow crops such as grass and cereals that protect vulnerable soils, to use crop residue mulches (Rice et al., 2006), to perform contour ploughing or contour strip cropping, to construct diversion terraces and to implement vegetated buffer strips (Campbell et al., 2004). Several studies investigated the benefits of vegetated buffer strips. They function through infiltration, which reduces the volume of runoff, and through adsorption/sedimentation, which reduces the concentration of pollutants in runoff (Doskey, 2001; Connolly et al., 2002). The results of these studies show high removal efficiencies for pesticides and sediments (Klöppel et al., 1997; Syversen and Bechmann, 2004; Kronvang et al., 2005; Syversen, 2005; Syversen and Haarstad, 2005; Vianello et al., 2005), which are variable in time (Viaud et al., 2004). For example, in a study of Popov et al. (2006) the total load of atrazine could be reduced by 40–85%. In buffer strips, a relatively larger amount of the coarser fractions will be trapped compared to the clay fraction (Syversen and Bechmann, 2004). In order to capture more clay particles and as such more sorbed pesticides, the buffer width should be extended (Syversen, 2002). Several models were developed in order to derive an optimal buffer width, adapted to variable regional geographic factors (Lin et al., 2002, 2004; Watanabe and Grismer, 2003). Nevertheless, questions remain concerning the subsequent leaching of trapped pesticides (e.g. Delphin and Chapot, 2001). Pesticides in runoff can also be retained through wetlands (Kohler et al., 2004; Blankenberg et al., 2005) and grassed depressions or waterways (Campbell et al., 2004).

Pesticide inputs into surface waters by *spraydrift can be mitigated* by the use of drift-reducing nozzles or anti-drift agents (Campbell et al., 2004), by vegetated buffer strips along field edges and water bodies (i.e. hedges and bank vegetation) (de Snoo and de Wit, 1998), or by simply keeping a sufficient distance to the nearest water body when spraying. In the current regulatory practice in Belgium, for each plant protection product there is a legally prescribed minimum spraying distance between 2 and 200 m that must be kept by the farmer. These and other best management practices (BMP) have been published and summarized (Carter, 2000; Ritter and Shirmohammadi, 2001; Campbell et al., 2004).

4. Pesticide processes in rivers

When pesticides enter an aquatic environment, they are exposed to different physical, chemical and microbial processes. Fig. 2 schematically illustrates the pertinent processes: photolysis, volatilization, sedimentation, resuspension, sorption/desorption, biodegradation, bio-accumulation and bio-transformation. Two processes which have a major impact on the fate of pesticides are the sorption–desorption processes and biodegradation. Both are strongly influenced by the presence of a sediment layer (Warren et al., 2003).

The final destination of pesticides in rivers is strongly determined by their sorption behaviour. Besides the effect that sorption has on the physical transport, it can also influence directly or indirectly the degradation of the pesticide. The chemical reactivity of a sorbed pesticide is significantly different from that in solution (Warren et al., 2003). Natural sorbents, like sediments, can indirectly control processes in the water phase by release or uptake of pesticides. Hence, natural sorbents form buffers that influence the reactivity of pesticides in a considerable way. For hydrophobic organic substances and for soils and sediments with a total organic carbon content higher than 0.1%, it is proven that the content of natural organic carbon is the dominant sorbent (Karickhoff, 1984; Ying and Williams, 2000; Chefetz et al., 2004; Chen et al., 2004; Cooke et al., 2004). Sorption is then often described by a constant normalized for the organic carbon content K_{OC} (Karickhoff, 1984; Warren et al., 2003). For sediments with a low organic carbon content, the sorption of polar compounds (acids/bases) is proportional to the cation exchange capacity, to the sediment specific surface and to pH (Rae et al., 1998; Madsen et al., 2000; Ertli et al., 2004; Weber et al., 2004). The process of desorption of pesticides from sediment is commonly observed to be biphasic, involving a relatively fast initial release of sorbed pesticides followed by a prolonged and increasingly slower release as desorption proceeds (Gao et al., 1998). This suggests that the soil organic matter comprises two principal reactive domains: a highly amorphous, swollen domain and a condensed, tightly cross-linked domain (Chefetz et al., 2004; Chen et al., 2004; Cooke et al., 2004). It was shown that lipid content was the main factor to affect hysteresis phenomena (Chen et al., 2004). As the sorbent matrix is so important, it is practically impossible to find
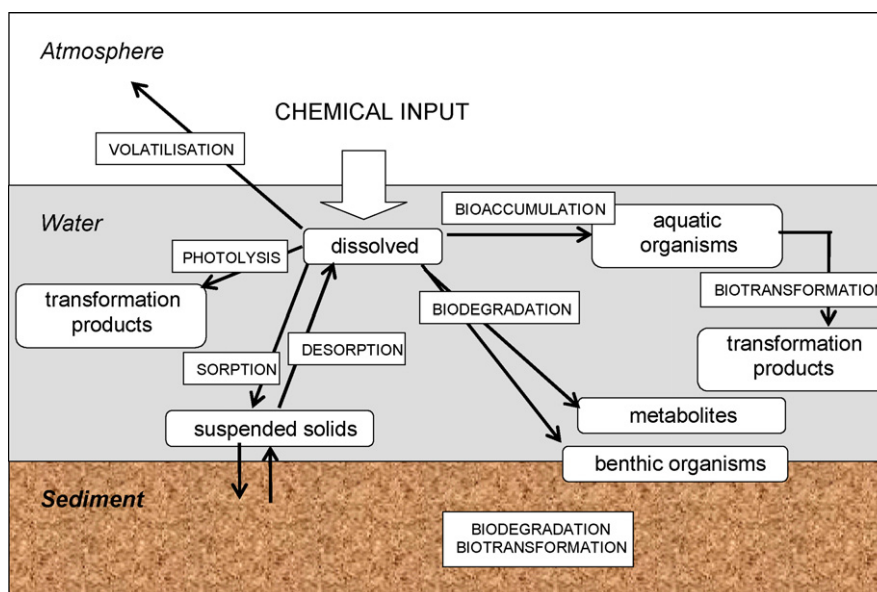
Fig. 2 – Processes of pesticides in surface water (after Petit et al., 1995).

some generally applicable and accurate K_{OC} value (Chen et al., 2004; Cooke et al., 2004).

Biodegradation is a continuous process in aquatic environments (Pagga, 1997). Surface waters are good environments for pesticide breakdown, especially when micro-organisms are able to attach on surfaces, such as the sediment–water interface, rocks and plants. Several scientists (Ying and Williams, 2000; Smalling and Aelion, 2004) believe that the sorption of pesticides to suspended solids and to sediment organic carbon reduce the decay rates of pesticides in water systems. Many studies (Warren et al., 2003) have indeed demonstrated an inverse relationship between decay rates and the amount of organic matter. However, in some cases the opposite is observed, i.e. sorption accelerates degradation which is mainly the consequence of abiotic pathways (Ying and Williams, 2000). It should be realised that measured degradation rates are system dependent as they may be influenced by the dilution rate in the chemostat, the composition of the population of micro-organisms, the test chemical and the composition of the medium (Rönnefahrt et al., 1997; Schrap et al., 2000). In natural systems, the pathways and rates of microbial degradation will depend on type of substrate, temperature, O_2 availability, nutrient supply, similarity of the compound to other food sources, previous exposure to the compound or similar ones and previous environmental conditions which will control the current population make-up (Warren et al., 2003). In the sediment, many types of compound will degrade more slowly below the oxic zone of bed-sediment and may therefore be persistent once buried (Warren et al., 2003).

5. Modeling pesticide fate at the catchment scale

To model pesticide fate at the catchment scale, spatially variable land management and landscape characteristics, temporally variable meteorology and hydrology as well as dissipation processes in the river need to be taken into account. Therefore, the combination of watershed models and river water quality models is needed to calculate pesticide fluxes to the river and transformation processes in the river, respectively.

5.1. Watershed models

A number of computer codes has been developed in recent years to model pesticide fluxes from land to surface water at the catchment scale. In Belgium, the SEPTWA model was developed (Beernaerts et al., 2005), taking into account both diffuse and point sources. It calculates average fortnight pesticide concentrations at the mouth of a river, based on detailed application data of the catchment and emission factors for the different input pathways of pesticides into surface waters. The model allows to make predictions of average pesticide loads leaving the system during a fortnight. In Germany, the DRIPS model was developed (Röpke et al., 2004), which is a GIS-based model that simulates on a daily basis pesticide inputs via surface runoff, drainflow and spraydrift for pixels of $1\,\text{km} \times 1\,\text{km}$ size, based on spatially distributed input variables. Dispersion of the pesticide peak during transport in the river is accounted for in DRIPS by a convection–dispersion approach as proposed by Gustafson et al. (2004).

Some of the models have single-event capabilities such as AGNPS (Young et al., 1987; Merritt et al., 2003) and DWSM (Borah et al., 2002). Others are useful for analyzing long-term effects of hydrological changes and water management practices such as AnnAGNPS (Bingner and Theurer, 2001), HSPF (Donigian et al., 1995) and the Soil and Water Assessment Tool SWAT (Neitsch et al., 2002). According to a software review by Borah and Bera (2003), SWAT is a promising model for continuous simulations in predominantly agricultural watersheds and HSPF is promising for mixed agricultural and urban watersheds. Different studies comparing both models for flow reveal that they are equally well predicting hydrology (Im et al., 2003; Nasr et al., 2004; Singh et al., 2004). SWAT gives better predic-

tions for pesticides and is better documented and user friendly as compared to HSPF (Im et al., 2003). MIKE SHE (Refsgaard and Storm, 1995) is both a single-event and long-term continuous simulation model. It is a physically based model using multi-dimensional flow-governing equations with numerical solution schemes, which makes the model computationally intensive. MIKE SHE is suitable for small areas or watersheds for detailed studies of hydrology and non-point source pollution (Borah and Bera, 2003). The new generation of models includes fully coupled watershed models. The main distinguishing feature of these models is that they fully couple the surface and subsurface hydrologic domains by simultaneously solving one system of non-linear discrete equations describing flow and transport in both flow regimes. This is in contrast to the previous generation of watershed models, which solve separate equations for the different subsystems, followed by iteration (or not) between the two solutions. Three fully coupled numerical models are currently available, namely InHM (VanderKwaak, 1999; VanderKwaak and Loague, 2001; Loague and VanderKwaak, 2002; Loague et al., 2004, 2006), MOD-HMS (Panday and Huyakorn, 2004) and HydroGeoSphere (Sudicky et al., 2005; Colautti et al., 2005).

To our knowledge, the listed models were occasionally validated against measured concentrations in surface water. HSPF was applied and verified against pesticide concentrations in a Canadian watershed (Laroche et al., 1996). MIKE–SHE has been used for calculating macropore leaching to groundwater of pesticides at the catchment scale (Christiansen et al., 2004) and was used as the basis of an alternative tool for pesticide fluxes to Danish rivers (Styczen, 2002). SWAT is increasingly being used for predicting pesticide fluxes to rivers (Holvoet et al., 2005; Kannan et al., 2006, 2007) and is put forward in reviews from Borah and Bera (2003) and Quilbe et al. (2006) who looked at 36 watershed models. The SEPTWA model (Beernaerts et al., 2005) was validated with a data set based on daily grab samples. Pesticide concentrations predicted with the DRIPS model at the closing section of the river underestimated measured concentrations due to the lack of point sources (Röpke et al., 2004).

5.2. *In-river water quality models*

There exists a whole range of models predicting fate of pesticides in rivers. They range from rather simple screening tools to complex models. A brief overview is given here. The simple screening tools predicting pesticide concentrations in the different compartments of a river system assume steady state conditions, e.g. EXAMS (Burns, 2000), EUSES (2004), the Mackay Level III Model (Mackay, 2001), QUAL2E (Brown and Barnwell, 1987) and principal component analysis (Gramatica and Di Guardo, 2002). They are based on the partitioning tendency of a certain pesticide. The advantage of such tools is that they require relatively few input data, but they can never reflect the dynamics – both in space and time – observed for pesticides in real river systems (Kreuger, 1998; Neumann et al., 2002; Leu et al., 2004a,b). As the occurrence of pesticides is highly dynamic and can pose acute toxicity to ecosystems, dynamic models are necessary to perform reliable risk assessments.

There exist various dynamic in-stream water quality models that predict fate of generic chemicals such as MIKE11 (DHI, 1995), ISIS (HR Wallingford and Halcrow UK, 1998) and RWQM1 (Reichert et al., 2001). All models need the addition of several differential equations describing the fate of pesticides in order to predict pesticide concentrations along the river and in its different compartments. The disadvantage of ISIS lies in the fact that parameters are fixed throughout the model and as such no spatial variability in the parameters is possible (Cox, 2003). Another complex model is WASP (Wool et al., 2001). It is a dynamic compartment-modeling programme for aquatic systems, including both the water column and the underlying benthos. WASP allows the user to investigate 1D and quasi-2D systems, and a variety of pollutant types. Since WASP focusses on local scale processes in the river and is not easy to be built for watershed applications, its use is limited to short-term continuous simulations in river stretches.

Specifically for pesticide fate modeling in surface water, the European Surface Water FOCUS workgroup (FOrum for the Coordination of pesticide fate models and their USe) which is an initiative of the European Commission with the objective to harmonise the calculation of predicted environmental concentrations (PEC), advises to use the model TOXSWA (FOCUS, 2001; ter Horst et al., 2002). TOXSWA needs pesticide inputs calculated by other models via runoff and erosion (PRZM, Carsel et al., 1984, 2003), drainage (MACRO, Jarvis, 1991, 2003) and spraydrift. The model is used for edge-of-field calculations, which means that it predicts the fate of a single pesticide over a certain distance when released at the origin of the flow domain. Additional inputs from tributaries or fields along the river are not taken into account. The model neglects sedimentation, resuspension and biomass growth. It was tested against field measurements in ditches (Adriaanse et al., 2006).

To predict pesticide fate in surface water, the RWQM1 model was extended with a sediment compartment and with the fate of pesticides, while the activity of algae and protozoa is neglected. The model is based upon the earlier developed model CHETOX1 (Deksissa et al., 2004). Fig. 3 shows predictions of concentrations of two pesticide concentrations at the outlet of the river Nil in Belgium, based on measured concentrations in the upstream part of the catchment and input from agricultural fields calculated with the SWAT model.

The results show the ability of the model to reproduce the extensive dynamics of the pesticide without extensive calibration for the pesticide parameters. Calibration in SWAT by adjusting curve numbers was needed to reproduce flow. To our knowledge, this is the first time the combination of a watershed model and a river water quality model is used to calculate daily pesticide dynamics in surface water at the catchment scale.

6. Monitoring and modeling pesticides in surface water: the way ahead

6.1. *Monitoring pesticides*

Measurements of pesticides in European surface waters during application periods have shown that the concentration patterns are highly dynamic and influenced to a significant extent by point sources. The few continuous monitoring studies showed that dramatic hourly variations in concentrations
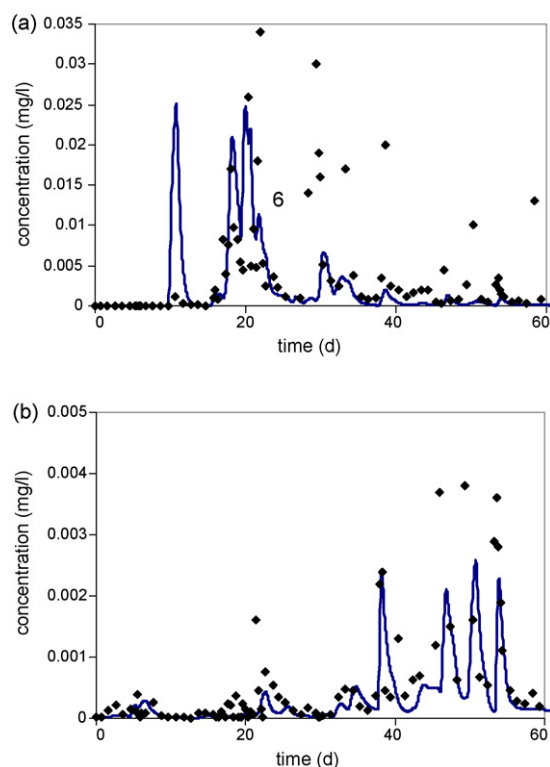
Fig. 3 – Simulated (full lines) and measured (dots) concentrations of chloridazon (a) and diuron (b) at the closing section of the river Nil.

Fig. 4 – Schematic representation for the optimal experimental design procedure (adapted from Dochain and Vanrolleghem, 2001).

can be expected, especially in small catchments driven by runoff processes. These observations have important consequences for monitoring requirements for pesticides, i.e. by the Environmental Agencies in the EU in view of the EU Water Framework Directive. To this time, most agencies take grab samples at regular time intervals during application periods. This monitoring strategy is driven by practical constraints, and to a lesser extent by financial limitations. It results in non-representative sampling and a higher probability of misinterpretation of the water quality status. To assist in the optimization of sampling strategies, the combined use of monitoring data and models is advised (Vanrolleghem et al., 1999; Dochain and Vanrolleghem, 2001; De Pauw, 2006; De Pauw and Vanrolleghem, 2006). By iterating between model runs and experiments cost-optimized sampling schemes for the next experimental stages can be designed (Fig. 4). A first and essential requirement of the experimental design procedure is the availability of a preliminary model. This model may have been calibrated on the basis of data of an initial experiment or default or literature parameter values can be assumed. Another important assumption in order for the design procedure to produce useful results is the validity of the model structure. Once the experimental degrees of freedom, constraints and objective have been defined, the iterative search for the optimal experiment can start. This is done by simulating different experiments by varying the degrees of freedom within the applicable constraints and calculating the design criterion. The optimal experiment is found when the selected design criterion is maximized or minimized, depend-
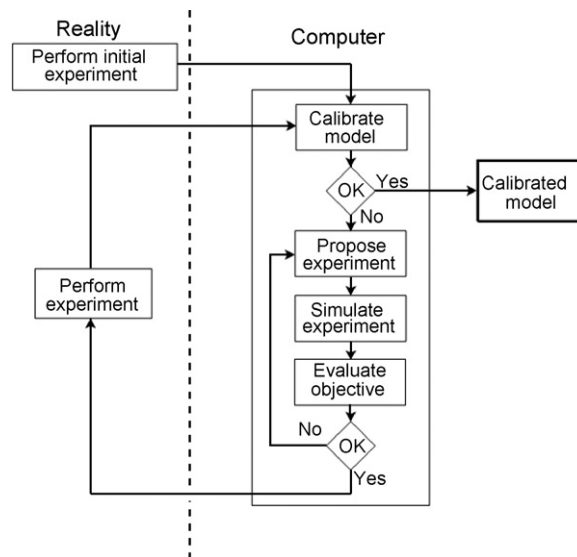
ing on the chosen objective. Once the optimal experiment is found, it can be performed in reality resulting in new data. Based on these data the model can be recalibrated and the quality of the parameter estimates evaluated. If required, another iteration of the design loop can be performed potentially leading to an even better experiment.

Recent developments in sampling and analytical tools allow for a more representative and cost-effective assessment of pesticides in surface water (Allan et al., 2006). Biological monitoring techniques include biomarkers, biosensors, biological early warning systems and whole-organism bioassays. Sampling and analytical tools developed for chemical assessment comprise biosensors, immunoassays, passive samplers and sensors. Diffusive samplers, such as solid phase microextraction (SPME), semipermeable membrane device (SPMD), polar organic chemical integrative sampler (POCIS) allow for a time-integrated measurement. Additional advantage of this kind of samplers is that they directly provide an estimate of the bioavailable fraction of the pesticide in the surface water.

To monitor the ecological quality of the surface water and to perform realistic risk assessments, ecotoxicological testing and risk assessment needs to be further tuned to the specific dynamics of the pesticides in surface water. Conventional ecotoxicological tests impose a constant dose to the organism and do not impose multiple pulses of a certain contaminant.

6.2. Modeling pesticide fate in surface water

To this stage, relatively few examples exist of catchment scale modeling of pesticides in surface water. Most of the modeling efforts are restricted to edge-of-field type calculations that reduce the catchment to a single field and tend to overestimate pesticide concentrations for the larger catchments. However, there is a need for more realistic predictions of pesticide concentrations in surface water, taking spatial and temporal variations into account. Consensus on the neces-

sity of catchment surface water models is growing, also in the field of pesticide modeling. More and more users worldwide are applying and verifying SWAT for various applications (Arnold and Fohrer, 2005). Although the simplifying process description in SWAT allows the model to be used in practical problems and for decision making, improvements for pesticide modeling were needed. These include the incorporation of (adjusted) submodels for drift and point sources, and implementation of mitigation. Since the model description for river water processes is oversimplified in SWAT, the coupling to a surface water quality model such as RWQM1 results in a better in-river process description. The process description in SWAT further needs to be verified against process-based models and ameliorated where needed. Some parameters, e.g. reduction percentages of certain mitigation measures, need to be confirmed by new experiments.

Conventional ecotoxicological thresholds such as predicted no effect concentrations (PNEC) or hazard concentrations (HC5s) are not suitable for highly dynamic pollutants such as pesticides. As such, the approach does not take into account the frequency of exceedance of concentrations. This could be done by means of a concentration–duration–frequency curve (Dixon, 2002; Verdonck, 2003; Verdonck et al., 2003). As there are no analogue effect–duration–frequency data available, this approach cannot be applied in risk assessment yet. Furthermore, also the synergetic or antagonistic action of certain active ingredients is currently not taken into account. Finally, several models look promising for ecological risk calculations. The DREAM model (Karman, 2002) is an example of the application of mechanistic time-to-event models and is expected to generate a more realistic estimation of the environmental impact of produced water discharges coming from oil companies. Analogue work in the pesticide field would be helpful for realistic risk assessment. The PERPEST model (Van den Brink et al., 2006) predicts the effects of a given concentration of a pesticide based on the outcome of already performed experiments using experimental ecosystems. It quantifies uncertainty by taking a probabilistic approach and it provides uncertainty limits to the predicted values. For the moment, PERPEST cannot handle mixtures of pesticides (Van den Brink et al., 2006). Analyses of standard data sets are required to validate such models and to identify the advantages and disadvantages of time-to-event analysis in risk assessment (Karman, 2002).

7. Conclusions

In this article, an overview is given of issues relevant to the occurrence, mitigation, monitoring and modeling of pesticides in surface waters. The main conclusions are:

- point losses form an important contribution to pesticide loads in rivers which can be easily reduced by simple measures without relevant financial consequences for the agricultural sector;
- best management practices can diminish diffuse pesticide inputs to a large extent, but more field experiments should be performed in combination with modeling exercises in order to gain insight in which measures are most effective;

- to optimize sampling strategies, a combined use of monitoring data and models is advised;
- integrated sampling techniques such as diffusive samplers or online techniques result in more reliable monitoring results than grab samples;
- a lot of development work still has to be done at the effects side of pesticide risk assessment, more specifically on the effects of pesticides on ecosystems rather than single species, on the effect of pulse exposures of pesticides, on synergetic or antagonistic action of active ingredients, etc.

The fate of pesticides is a complex process and still a lot of it and of its effects is currently unknown. Monitoring and modeling the fate of pesticide and its effects will be supporting the development of an environmentally friendly use of pesticides. Improvements in monitoring of pesticides in surface water based on better understanding of the underlying processes will improve monitoring strategies that need to be developed in the EU as part of the implementation of monitoring programmes in the Water Framework Directive. Advances in catchment scale modeling of pesticides fate and effects in surface water will allow to accurately build river basin management plans and reduce pesticide loads to surface water.

REFERENCES

Adriaanse, P.I., ter Horst, M.M.S., Crum, S.J.H., 2006. Fate of prosulfocarb in an outdoor ditch: measured concentrations compared to calculations with the TOXSWA model. In: Abstracts of the Conference on Pesticide Behaviour in Soils, Water and Air, Warwick, UK, 27–29 March 2006.
Allan, I.J., Vrana, B., Greenwood, R., Mills, G.A., Roig, B., Gonzales, C., 2006. A "toolbox" for biological and chemical monitoring requirements for the European Union's Water Framework Directive. Talanta 69, 302–322.
Arnold, J.G., Fohrer, N., 2005. SWAT2000: current capabilities and research opportunities in applied watershed modeling. Hydrol. Process 19, 563–572.
Bach, M., Huber, A., Frede, H.-G., 2001. Input pathways and river load of pesticides in Germany—a national scale modeling assessment. Water Sci. Technol. 43 (5), 261–268.
Baets, W., Bollen, B., Debussche, B., D'Hont, D., Maes, I., Neven, H., Tyvaert, D., Uyt-dewilligen, L., Verstrynge, J., Wellemans, K., 2005. Code van goede landbouwpraktijk bestrijdingsmiddelen. ALT, Leuven, Belgium, 90 pp.
Bedos, C., Rousseau-Djabri, M.-F., Flura, D., Masson, S., Barriuso, E., Cellier, P., 2002. Rate of pesticide volatilization from soil: an experimental approach with a wind tunnel system applied to trifluralin. Atmos. Environ. 36, 5917–5925.
Beernaerts, S., Debongnie, P., De Vleeschouwer, C., Pussemier, L., 2002. Het pilootproject voor het Nil bekken. Groenboek Belgaqua-Phytophar 2002, Belgium, pp. 33–38 (in Dutch).
Beernaerts, S., Debongnie, P., Gérard, M., Barthelemy, J.-P., Copin, A., Guns, M., Pussemier, L., 2005. Evaluation of crop-protection-product losses into surface waters with the SEPTWA system. Int. J. Anal. Chem. 85 (1), 41–50.
Bielders, C.L., Ramelot, C., Persoons, E., 2003. Farmer perception of runoff and erosion and extent of flooding in the silt-loam belt of the Belgian Walloon Region. Environ. Sci. Policy 6 (1), 85–93.
Bingner, R.L., Theurer, F.D., 2001. AnnAGNPS Technical Processes: Documentation Version 2. Available at

http://www.ars.usda.gov/Research/docs.htm?docid=5222 (17/01/2007).

Blankenberg, A.-G.B., Haarstad, K., Braskerud, B.C., 2005. Pesticide retention in an experimental wetland treating non-point source pollution from agriculture runoff. In: Abstracts of the IWA Specialist Conference on Diffuse Pollution, Johannesburgh, South Africa, 9–12 August 2005.

Borah, D.K., Xia, R., Bera, M., 2002. DWSM—a dynamic watershed simulation model. In: Singh, V.P., Frevert, D.K. (Eds.), Mathematical Models of Small Watershed Hydrology and Applications. Water Resources Publications, Colorado, USA, pp. 113–116.

Borah, D.K., Bera, M., 2003. Watershed-scale hydrologic and nonpoint-source pollution models: review of mathematical bases. Trans. ASAE 46 (6), 1553–1566.

Brown, L.C., Barnwell, T.O., 1987. The Enhanced Stream Water Quality Models QUAL2E and QUAL2E-UNCAS: Documentation and User Manual. EPA/6003-87/007. Athens, GA, USA.

Brown, C.D., Dubus, I.G., Fogg, P., Spirlet, M., Gustin, C., 2004. Exposure to sulfosulfuron in agricultural drainage ditches: field monitoring and scenario-based modelling. Pest Manag. Sci. 60, 765–776.

Burns, L.A., 2000. Exposure Analysis Modeling System (EXAMS): User Manual and System Documentation. EPA/600/R-00/081. U.S. Environmental Protection Agency, North Carolina, 206 pp.

Campbell, N., D'Arcy, B., Frost, A., Novotny, V., Sansom, A. (Eds.), 2004. Diffuse Pollution: An Introduction to the Problems and Solutions. IWA Publishing, Cornwall, UK, p. 322.

Capel, P.D., Larson, S.J., Winterstein, T.A., 2001. The behavior of thirty-nine pesticides in surface waters as a function of scale. Hydrol. Process 15, 1251–1269.

Carsel, R.F., Smith, C.N., Mulkey, L.A., Dean, J.D., Jowise, P., 1984. User's Manual for the Pesticide Root Zone Model (PRZM). Technical Report Release 1. EPA-600/3-84-109. U.S. Environmental Protection Agency (USEPA), Athens, GA, USA.

Carsel, R.F., Imhoff, J.C., Hummel, P.R., Cheplick, J.M., Donigian Jr., A.S., 2003. PRZM-3, A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 3.12. Center for Exposure Assessment Modeling (CEAM), U.S. Environmental Protection Agency (USEPA), Athens, GA, USA.

Carter, A., August 2000. How pesticides get into water – and proposed reduction measures. Pesticide Outlook, pp. 149–156.

Chefetz, B., Bilkis, Y., Polubesova, T., 2004. Sorption–desorption behaviour of triazine and phenylurea herbicides in Kishon river sediments. Water Res. 38, 4383–4394.

Chen, Y.-X., Chen, H.-L., Xu, Y.-T., Shen, M.-W., 2004. Irreversible sorption of pentachlorophenol to sediments: experimental observations. Environ Pollut. 30, 31–37.

Christiansen, J.S., Thorsen, M., Clausen, T., Hansen, S., Refsgaard, J.C., 2004. Modelling of macropore flow and transport processes at catchment scale. J. Hydrol. 299 (1–2), 136–158.

Colautti, D., Sudicky, E.A., Sykes, J.F., Fall 2005. Impacts of climate change on the surface and subsurface hydrology of the Grand River Watershed, American Geophysical Union, Meeting 2005.

Connolly, R.D., Silburn, D.M., Freebairn, D.M., 2002. Transport of sediment and pesticides in surface waters. In: Kookana, S., et al. (Eds.), Environmental Protection and Risk Assessment or Organic Contaminants. Science Publishers Inc., Enfield, USA, pp. 143–167.

Cooke, C.M., Shaw, G., Collins, C.D., 2004. Determination of solid–liquid partition coefficients (K_d) for the herbicides isoproturon and trifluralin in five UK agricultural soils. Environ. Pollut. 132, 541–552.

Corrales, N., Campos, M., 2004. Populations, longevity, mortality and fecundity of *Chrysoperla carnea* (Neuroptera, Chrysopidae) from olive-orchards with different agricultural management systems. Chemosphere 57, 1613–1619.

Cox, B.A., 2003. A review of currently available in-stream water-quality models and their applicability for simulating dissolved oxygen in lowland. Sci. Total. Environ. 314–316, 335–377.

Dabrowski, J.M., Peall, S.K.C., Van Niekerk, Z., Reinecke, A.J., Day, J.A., Schulz, R., 2002. Predicting runoff-induced pesticide input in agricultural sub-catchment surface waters: linking catchment variables and contamination. Water Res. 36, 4975–4984.

Deksissa, T., De Pauw, D., Vanrolleghem, P.A., 2004. Dynamic in-stream fate modeling of xenobiotic organic compounds: a case study of linear alkylbenzene sulfonates in the Lambro river, Italy. Environ. Toxicol. Chem. 23, 2267–2278.

Delphin, J.E., Chapot, J.Y., 2001. Leaching of atrazine and deethylatrazine under a vegetative filter strip. Agronomie 21 (5), 461–470.

De Pauw, D., 2006. Optimal experimental design for calibration of bioprocess models: a validated software toolbox. Ph.D. Dissertation. Faculty of Applied Biological Sciences, Ghent University, Belgium, 246 pp.

De Pauw, D.J.W., Vanrolleghem, P.A., 2006. Designing and performing experiments for model calibration using an automated iterative procedure. Water Sci. Technol. 53 (1), 117–127.

De Rossi, C., Bierl, R., Riefstahl, J., 2003. Organic pollutants in precipitation: monitoring of pesticides and polycyclic aromatic hydrocarbons in the region of Trier (Germany). Phys. Chem. Earth 28, 307–314.

de Snoo, G.R., de Wit, P.J., 1998. Buffer zones for reducing pesticide drift to ditches and risks to aquatic organisms. Ecotox. Environ. Safe. 41 (1), 112–118.

DHI, 1995. MIKE 11 User and Reference Manual.

Dixon, P.M., 2002. Just how much better is a time to event analysis? In: Crane, M., Newman, C., Chapman, P.F., Fenlon, J. (Eds.), Risk Assessment with Time to Event Models. Lewis Publishers, London, p. 175.

Dochain, D., Vanrolleghem, P.A., 2001. Dynamical Modelling and Estimation in Wastewater Treatment Processes. IWA Publishing, London, UK.

Donigian Jr., A.S., Bicknell, B.R., Imhoff, J.C., 1995. Hydrological simulation program—Fortran (HSPF). In: Singh, V.P. (Ed.), Computer Models of Watershed Hydrology. Water Resources Publications, Colorado, USA, pp. 395–442.

Doskey, M., 2001. Toward quantifying water pollution abatement in response to installing buffers on crop-land. Environ. Manage. 30 (5), 641–650.

Ertli, T., Marton, A., Fôldényi, R., 2004. Effect of pH and the role of organic matter in the adsorption of isoproturon on soils. Chemosphere 57, 771–779.

EUSES, 2004. European Union System for the Evaluation of Substances (EUSES 2.0). Prepared for the European Chemicals Bureau by the National Institute of Public Health and the Environment (RIVM). Bilthoven, The Netherlands. Available via the European Chemicals Bureau, http://ecb.jrc.it, 16/01/2007).

Fenelon, J.M., Moore, R.C., 1998. Transport of agrichemicals to ground and surface water in a small central Indiana watershed. J. Environ. Qual. 27, 884–894.

Fischer, P., Bach, M., Burhenn, J., Spiteller, M., Frede, H.G., 1996. Pflanzenschutzmittel in Fließgewässer: Teil 3: Anteil diffuser und punktueller Einträge in einem kleinen Vorfluter. DGM 40 (4), 168–173 (in German).

Fischer, P., Hartmann, H., Bach, M., Burhenne, J., Frede, H.G., Spiteller, M., 1998a. Gewässerbelastung durch Pflanzenschutzmittel in drei Einzugsgebieten. Gesunde Pflanzen 50 (5), 142–147.

Fischer, P., Hartmann, H., Bach, M., Burhenne, J., Frede, H.G., Spiteller, M., 1998b. Reduktion des Gewässereintrags von

Pflanzenschutzmitteln aus Punktquellen durch Beratung. Gesunde Pflanzen 50 (5), 148–152.

FOCUS, 2001. FOCUS Surface Water Scenarios in the EU Evaluation Process under 91/414/EEC. Report of the FOCUS Working Group on Surface Water Scenarios, EC Document Reference SANCO/4802/2001-rev.2, p. 245.

Fogg, P., 2004. Fate and behaviour of pesticides in biobeds. Ph.D. Dissertation. Cranfield University, Cranfield, UK, 166 pp.

Foreman, W.T., Majewski, M.S., Goolsby, D.A., Wiebe, F.W., Coupe, R.H., 2000. Pesticides in the atmosphere of the Mississippi River Valley, part II—air. Sci. Total Environ. 248, 213–226.

Gao, J.P., Maguhn, J., Spitzauer, P., Kettrup, A., 1998. Sorption of pesticides in the sediment of the Teufesweiher pond (southern Germany). II: competitive adsorption, desorption of aged residues and effect of dissolved organic carbon. Water Res. 32, 2089–2094.

Gardenas, A.I., Simunek, J., Jarvis, N., van Genuchten, M.T., 2006. Two-dimensional modelling of preferential water flow and pesticide transport from a tile-drained field. J. Hydrol. 329 (3–4), 647–660.

Gramatica, P., Di Guardo, A., 2002. Screening of pesticides for environmental partitioning tendency. Chemosphere 47, 947–956.

Gerecke, A.C., Schärer, M., Singer, H.P., Müller, S.R., Schwarzenbach, R.P., Sägesser, M., Ochsenbein, U., Popow, G., 2002. Sources of pesticides in surface waters in Switzerland: pesticide load through waste water treatment plants—current situation and reduction potential. Chemosphere 48, 307–315.

Gil, Y., Sinfort, C., 2005. Emission of pesticides to the air during sprayer application: a bibliographic review. Atmos. Environ. 39, 5183–5193.

Groenboek, 2002. Available at http://www.phytofar.be/nl/pdf/livrvert.pdf, 16/01/2007.

Gustafson, D.I., Carr, K.H., Green, T.R., Gustin, C., Jones, R.L., Richards, R.P., 2004. Fractal-based scaling and scale-invariant dispersion of peak concentrations of crop protection chemicals in rivers. Environ. Sci. Technol. 38 (11), 2995–3003.

Hankinson, G., Welland, G., 2001. The effectiveness of a stewardship campaign in Severn Trent Water. In: Proceedings of the BCPC Symposium No. 78: Pesticide Behaviour in Soils and Water, pp. 325–333.

Holvoet, K., van Griensven, A., Seuntjens, P., Vanrolleghem, P.A., 2005. Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. Phys. Chem. Earth 30, 518–526.

HR Wallingford and Halcrow UK, 1998. http://www.wallingfordsoftware.com/products/isis/ (17/01/2007).

Huber, A., Bach, M., Frede, H.-G., 2000. Pollution of surface waters with pesticides in Germany: modeling non-point source inputs. Agric. Ecosyst. Environ. 80, 191–204.

Im, S., Brannan, K., Mostaghimi, S., Cho, J., 2003. A comparison of SWAT and HSPF models for simulating hydrologic and water quality responses from an urbanizing watershed. In: 2003 ASAE Annual International Meeting, American Society of Agricultural Engineers, Las Vegas, Nevada (ASAE Paper No. OS2175).

Jarvis, N.J., 1991. MACRO—a model of water movement and solute transport in macroporous soils. Reports and Dissertations 9, Dept. Soil Sci., Swedish Univ. Agric. Sci., Uppsala, 58 pp.

Jarvis, N.J., 2003. The MACRO model (version 5.0). Technical Description. http://bgf.mv.slu.se/ShowPage.cfm?OrgenhetSida_ID=5658 (16/1/2007).

Kannan, N., White, S.M., Worrall, F., Whelan, M.J., 2006. Pesticide modelling for a small catchment using SWAT-2000. J. Environ. Sci. Health Part B-Pesticides Food Contam. Agric. Wastes 41, 1049–1070.

Kannan, N., White, S.M., Whelan, M.J., 2007. Predicting diffuse-source transfers of surfactants to surface waters using SWAT. Chemosphere 66 (7), 1336–1345.

Karickhoff, S.W., 1984. Organic pollutant sorption in aquatic systems. J. Hydraul. Eng.-ASCE 110, 707–735.

Karman, C.C., 2002. Using time to event modeling to assess the ecological risk of produced water discharges. In: Crane, M., Newman, C., Chapman, P.F., Fenlon, J. (Eds.), Risk Assessment with Time to Event Models. Lewis Publishers, London, p. 175.

Kenaga, E.E., 1980. Predicted bioconcentration factors and soil sorption coefficients of pesticides and other chemicals. Ecotox. Environ. Safe. 4, 26–38.

Kladivko, E.J., van Scoyoc, G.E., Monke, E.J., Oates, K.M., Pask, W., 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam soil in Indiana. J. Environ. Qual. 20, 264–270.

Klöppel, H., Kördel, W., Stein, B., 1997. Herbicide transport by surface runoff and herbicide retention in a filter strip—rainfall and runoff simulation studies. Chemosphere 35, 129–141.

Knapen, A., Poesen, J., Govers, G., Gyssels, G., Nachtergaele, J., 2007. Resistance of soils to concentrated flow erosion: a review. Earth-Sci. Rev. 80 (1–2), 75–109.

Kohler, E.A., Poole, V.L., Reicher, Z.J., Turco, R.F., 2004. Nutrient, metal, and pesticide removal during storm and non-storm events by a constructed wetland on an urban golf course. Ecol. Eng. 23 (4–5), 285–298.

Kreuger, J., 1998. Pesticides in stream water within an agricultural catchment in southern Sweden, 1990–1996. Sci. Total Environ. 216, 227–251.

Kreuger, J., Törnqvist, L., 1998. Multiple regression analysis of pesticide occurrence in streamflow related to pesticide properties and quantities applied. Chemosphere 37 (2), 189–207.

Kreuger, J., Nilsson, E., 2001. Catchment scale risk-mitigation experiences—key issues for reducing pesticide transport to surface waters. In: Proceedings of the BCPC Symposium Proceedings No. 78: Pesticide Behaviour in Soil and Water, pp. 319–324.

Kronvang, B., Laubel, A., Larsen, S.E., Andersen, H.E., Djurhuus, J., 2005. Buffer zones as a sink for sediment and phosphorus between the field and stream: Danish field experiences. Water Sci. Technol. 51 (3–4), 55–62.

Laroche, A.M., Gallichand, J., Lagace, R., Pesant, A., 1996. Simulating atrazine transport with HSPF in an agricultural watershed. J. Environ. Eng.-ASCE 122, 622–630.

Le Bissonais, Y., Renaux, B., Delouche, H., 1995. Interactions between soil properties and moisture content in crust formation, runoff and interrill erosion from tilled loess soils. Catena 25, 33–46.

Leonard, R.A., 1990. Movement of pesticides into surface waters. In: Cheng, H.H. (Ed.), Pesticides in the Soil Environment: Processes, Impacts, and Modeling; SSSA Book Series No. 2. Soil Science Society of America, Madison, WI, USA, pp. 303–349.

Leu, C., Singer, H., Stamm, C., Müller, S.R., Schwarzenbach, R.P., 2004a. Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment. Environ. Sci. Technol. 38, 3827–3834.

Leu, C., Singer, H., Stamm, C., Müller, S.R., Schwarzenbach, R.P., 2004b. Variability of herbicide losses from 13 fields to surface water within a small catchment after a controlled herbicide application. Environ. Sci. Technol. 38, 3835–3841.

Lin, C.Y., Chou, W.C., Lin, W.T., 2002. Modeling the width and placement of riparian vegetated buffer strips: a case study on the Chi-Jia-Wang stream, Taiwan. J. Environ. Mange. 66, 269–280.

Lin, Y.F., Lin, C.Y., Chou, W.C., Lin, W.T., Tsai, J.S., Wu, C.F., 2004. Modeling of riparian vegetated buffer strip width and placement: a case study in Shei Pa National Park, Taiwan. Ecol. Eng. 23, 327–339.

Loague, K., VanderKwaak, J.E., 2002. Simulating hydrologic response for the R-5 catchment: comparison of two models and the impact of the roads. Hydrol. Proc. 16, 1015–1032.

Loague, K., Heppner, C.S., Abrams, R.H., Carr, A.E., VanderKwaak, J.E., Ebel, B.A., 2004. Further testing of the Integrated Hydrology Model (InHM): event-based simulations for a small rangeland catchment located near Chickasha, Oklahoma. Hydrol. Proc. 19, 1373–1398.

Loague, K., Heppner, C.S., Mirus, B.B., Ebel, B.A., Ran, Q., Carr, A.E., BeVille, S.H., VanderKwaak, J.E., 2006. Physics-based hydrologic-response simulation: foundation for hydroecology and hydrogeomorphology. Hydrol. Proc. 20, 1231–1237.

Mackay, D., 2001. Multimedia Environmental Models: The Fugacity Approach, second ed. Lewis Publishers, Boca Raton, FL, 261 pp.

Madsen, L., Lindhardt, B., Rosenberg, P., 2000. Pesticide sorption by low organic carbon sediments: as screening for seven herbicides. J. Environ. Qual. 29, 1488–1500.

Majewski, M.S., Foreman, W.T., Goolsby, D.A., 2000. Pesticides in the atmosphere of the Mississippi River Valley, part I—rain. Sci. Total Environ. 248, 201–212.

Mansingh, G., Reichgelt, H., Bryson, K.-M.O., 2007. CPEST: an expert system for the management of pests and diseases in the Jamaican coffee industry. Expert Syst. Appl. 32 (1), 184–192.

Martin, J.S., Owens, L.B., 2003. Atrazine, deethylatrazine, and deisopropylatrazine in surface runoff form conservation tilled watersheds. Environ. Sci. Technol. 37, 944–950.

Mason, P., 2003. Point source contamination of surface water by pesticides. Ph.D. Dissertation. Coventry University in Collaboration with ADAS and Horticulture Research International, UK, 365 pp.

Meli, S.M., Capri, E., Gennari, M., 2007. Exposure of surface water bodies to chlorpyrifos and chlorpyrifos-methyl in the Mediterranean area. Fresenius Environ. Bull. 16 (1), 50–56.

Merritt, W.S., Letcher, R.A., Jakeman, A.J., 2003. A review of erosion and sediment transport models. Environ. Modell. Softw. 18, 761–799.

Müller, K., Deurer, M., Hartmann, H., Bach, M., Spiteller, M., Frede, H.-G., 2003. Hydrological characterisation of pesticide loads using hydrograph separation at different scales in a German catchment. J. Hydrol. 273, 1–17.

Nasr, A., Bruen, M., Jordan, P., Moles, R., Kiely, G., Byrne, P., O'Regan, B., 2004. Physically-based, distributed, catchment modelling for estimating sediment and phosphorus loads to rivers and lakes: issues of model complexity, spatial and temporal scales and data requirements. National Hydrology Seminar 2004, Ireland.

Nearing, M.A., Norton, L.D., Zhang, X., 2001. Soil erosion and sedimentation. In: Ritter, F., Shirmohammadi, A. (Eds.), Agricultural Nonpoint Source Pollution: Watershed Management and Hydrology. CRC Press LLC, Florida.

Neitsch, S.L., Arnold, J.G., Kiniry, J.R., Williams, J.R., King, K.W., 2002. Soil and Water Assessment Tool User's Manual: Version 2000. Texas Water Resources Institute, College Station, TX, 438 pp.

Neumann, M., Schulz, R., Schäfer, K., Müller, W., Mannheller, W., Liess, M., 2002. The significance of entry routes as point and non-point sources of pesticides in small streams. Water Res. 36, 835–842.

Neumann, M., Liess, M., Schulz, R., 2003. A qualitative sampling method for monitoring water quality in temporary channels or point sources and its application to pesticide contamination. Chemosphere 51, 509–513.

Novak, S.M., Portal, J.-M., Schiavon, M., 2001. Effects of soil type upon metolachlor losses in subsurface drainage. Chemosphere 42 (3), 235–244.

Pagga, U., 1997. Testing biodegradability with standardized methods. Chemosphere 35, 2953–2972.

Panday, S., Huyakorn, P.S., 2004. A fully coupled physically-based spatially-distributed model for evaluating surface/subsurface flow. Adv. Water Resour. 27, 361–382.

Petit, V., Cabridenc, R., Swannell, R.P.J., Sokhi, R.S., 1995. Review of strategies for modelling the environmental fate of pesticides discharged into riverine systems. Environ. Int. 21 (2), 167–176.

Phytofar, 2006. Belgian Association of the Pesticide Industry. Available at http://www.phytofar.be/ (16/1/2007).

Popov, V.H., Cornish, P.S., Sun, H., 2006. Vegetated biofilters: the relative importance of infiltration and adsorption in reducing loads of water-soluble herbicides in agricultural runoff. Agric. Ecosyst. Environ. 114, 351–359.

Quilbe, R., Rousseau, A.N., Lafrance, P., Leclerc, J., Amrani, M., 2006. Selecting a pesticide fate model at the watershed scale using a multi-criteria analysis. Water Qual. Res. J. Canada 41, 283–295.

Rae, J.E., Cooper, C.S., Parker, A., Peters, A., 1998. Pesticide sorption onto aquifer sediments. J. Geochem. Explor. 64, 263–276.

Refsgaard, J.C., Storm, B., 1995. MIKE SHE. In: Singh, V.P. (Ed.), Computer Models of Watershed Hydrology. Water Resources Publications, Colorado, USA, pp. 809–846.

Reichert, P., Brochardt, D., Henze, M., Rauch, W., Shanahan, P., Somlyody, L., Vanrolleghem, P.A., 2001. Scientific and Technical Report No. 12: River Water Quality Model No. 1. IWA Publishing, London, 136 pp.

Rice, P.J., Horgan, B.P., Hapeman, C.J., McConnell, L.L., Sadeghi, A.M., 2006. Reducing the environmental impact of agricultural and non-agricultural systems: mitigating off-site transport of pesticides and fertilizer with runoff. In: Abstracts of the SETAC Europe 16th Annual Meeting, The Hague, The Netherlands, 7–11 May 2006 (Abstract No. TU1/Y1/P13).

Ritter, W.F., 2001. Pesticides and water quality impacts. In: Ritter, F., Shirmohammadi, A. (Eds.), Agricultural Nonpoint Source Pollution: Watershed Management and Hydrology. CRC Press LLC, Florida.

Ritter, W., Shirmohammadi, A., 2001. Agricultural Nonpoint Source Pollution: Watershed Management and Hydrology. CRC Press LC, Florida, 341 pp.

Rönnefahrt, U.T.-E., Kördel, W., Stein, B., 1997. Comparison of the fate of isoproturon in small- and large-scale water/sediment systems. Chemosphere 35, 181–189.

Röpke, B., Bach, M., Frede, H.-G., 2004. DRIPS—a DSS for estimating the input quantity of pesticides for German river basins. Environ. Model. Softw. 19, 1021–1028.

Saethre, M.-G., Orpen, H.M., Hofsvang, T., 1999. Action programmes for pesticide risk reduction and pesticide use in different crops in Norway. Crop. Prot. 18, 207–215.

Schrap, S.M., van den Heuvel, H., van der Meulen, J., Ruiter, H., Parsons, J.R., 2000. A chemostat system for investigating pesticide biodegradation in continuous mixed bacteria cultures originating from surface water. Chemosphere 40, 1389–1397.

Seel, P., Knepper, T.P., Gabriel, S., Weber, A., Haberer, K., 1994. Einträge von Pflanzenschutzmitteln in ein Fliebgewässer-Versuch einer Bilanzierung. Vom Wasser 83, 357–372.

Siebers, J., Binner, R., Wittich, K.-P., 2003. Investigation of downwind short-range transport of pesticides after application in agricultural crops. Chemosphere 51, 397–407.

Singh, J., Knapp, H.V., Demissie, M., 2004. Hydrological modeling of the Iroquois river watershed using HSPF and SWAT. J. Am. Water Resour. Assoc. 41, 343–360.

Smalling, K.L., Aelion, C.M., 2004. Distribution of atrazine into three chemical fractions: impact of sediment depth and organic carbon content. Environ. Toxicol. Chem. 23, 1164–1171.

Spliid, N.H., Helweg, A., Heinrichson, K., 2006. Leaching and degradation of 21 pesticides in a full-scale model biobed. Chemosphere 65, 2223–2232.

Styczen, M., 2002. Development of a tool for estimation of pesticide occurrence in surface water under Danish conditions. Int. J. Environ. Anal. Chem. 82 (8–9), 611–630.

Sudicky, E.A., Therrien, R., Park, Y.-J., McLaren, R.G., Jones, J.P., Lemieux, J.-M., Brookfield, A.E., Colautti, D., Panday, S., Guvanasen, V., 2005. On the challenge of integrated surface-subsurface flow and transport modeling at multiple catchment scales. In: Geological Society of America Abstracts with Programs, Salt Lake City Annual Meeting, vol. 37, no. 7, October 2005, p. 28.

Syversen, N., 2002. Cold-climate vegetative buffer zones as filters for surface agricultural runoff. Ph.D. Dissertation. Agricultural University of Norway, As, Norway.

Syversen, N., 2005. Cold-climate vegetative buffer zones as pesticide-filters for surface runoff. Water Sci. Technol. 51 (3–4), 63–71.

Syversen, N., Bechmann, M., 2004. Vegetative buffer zones as pesticide filters for simulated surface runoff. Ecol. Eng. 22, 175–184.

Syversen, N., Haarstad, K., 2005. Retention of pesticides and nutrients in a vegetated buffer root zoned compared to soil with low biological activity. Int. J. Environ. Anal. Chem. 85 (15), 1175–1187.

Tantau, H.-J., Lange, D., 2003. Greenhouse climate control: an approach for integrated pest management. Comput. Electron. Agric. 40, 141–152.

ter Horst, M.M.S., Adriaanse, P.I., Beltman, W.H.J., van den Berg, F., September 2002. Manual of FOCUS_TOXSWA version 1.1.1β. Draft 27. Alterra, Wageningen, the Netherlands, 62 pp.

Tesfamichael, A.A., Kaluarachchi, J.J., 2006. A methodology to assess the risk of an exiting pesticide and potential future pesticides for regulatory decision-making. Environ. Sci. Policy 9, 275–290.

Torstensson, L., October 2000. Experiences of biobeds in practical use in Sweden. Pesticide Outlook, pp. 206–210.

Van den Brink, P.J., Brown, C.J., Dubus, I.G., 2006. Using the expert model PERPEST to translate measured and predicted pesticide exposure data into ecological risks. Ecol. Model. 191, 106–117.

VanderKwaak, J.E., 1999. Numerical simulation of flow and chemical transport in integrated surface-subsurface hydrologic systems. Ph.D. Dissertation. University of Waterloo, Waterloo, Ontario.

VanderKwaak, J.E., Loague, K., 2001. Hydrologic-response simulations for the R-5 catchment with a comprehensive physics-based model. Water Resour. Res. 37, 999–1013.

van Lenteren, J.C., 2000. A greenhouse without pesticides: fact or fantasy? Crop. Prot. 19, 375–384.

Vanrolleghem, P.A., Schilling, W., Rauch, W., Krebs, P., Aalderink, H., 1999. Setting up measuring campaigns for integrated wastewater modelling. Water Sci. Technol. 39 (4), 257–268.

Verdonck, F., 2003. Geo-referenced probabilistic ecological risk assessment. Ph.D. Dissertation. Faculty of Agricultural and Applied Biological Sciences, Ghent University, Belgium, 200 pp. Available at http://biomath.ugent.be/publications/download/verdonck frederik_phd.pdf.

Verdonck, F.A.M., Rousseau, D., Bixio, D., Thoeye, C., Vanrolleghem, P.A., 2003. Added value of concentration–duration–frequency curves of wastewater treatment effluent quality. In: Proceedings International Congress on Modelling Simulation (MODSIM2003), Townsville, Australia, 13–17 July 2003, pp. 338–343.

Viaud, V., Merot, P., Baudry, J., 2004. Hydrochemical buffer assessment in agricultural landscapes: from local to catchment scale. Environ. Manage. 34 (4), 559–573.

Vianello, M., Vischetti, C., Scarponi, L., Zanin, G., 2005. Herbicide losses in runoff events from a field with a low slope: role of a vegetative filter strip. Chemosphere 61, 717–725.

Vischetti, C., Capri, E., Trevisan, M., Casucci, C., Perucci, P., 2004. Biomassbed: a biological system to reduce pesticide point contamination at farm level. Chemosphere 55, 823–828.

Warren, N., Allan, I.J., Carter, J.E., House, W.A., Parker, A., 2003. Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. Appl. Geochem. 18, 159–194.

Watanabe, H., Grismer, M.E., 2003. Numerical modeling of idazinon transport through inter-row vegetative filter strips. J. Environ. Manage. 69, 157–168.

Weber, J.B., Wilkerson, G.G., Reinhardt, C.F., 2004. Calculating pesticide sorption coefficients (K_d) using selected soil properties. Chemosphere 55, 157–166.

Williams, R.J., Brooke, D.N., Clare, R.W., Matthiessen, P., Mitchell, R.D.J., 1996. Rosemaund Pesticide Transport Study 1987–1993. IH Report No. 129. Institute of Hydrology, Wallingford, UK, 68 pp.

Wischmeier, W.H., Smith, D.D., 1978. Predicting Rainfall Losses: A Guide to Conservation Planning. USDA Agricultural Handbook No. 537. U.S. Gov. Print. Office, Washington, DC.

Wolfe, M.L., 2001. Hydrology. In: Ritter, F., Shirmohammadi, A. (Eds.), Agricultural Nonpoint Source Pollution: Watershed Management and Hydrology. CRC Press LLC, Florida, pp. 1–27.

Wool, T.A., Ambrose, R.B., Martin, J.L., Comer, E.A., 2001. WASP6 Users Manual. US Environmental Protection Agency, Atlanta, GA, USA, 267 pp.

Wu, Q., Riise, G., Lundekvam, H., Mulder, J., Haugen, L.E., 2004. Influences of suspended particles on the run-off of pesticides from an agricultural field at Askim, SE-Norway. Environ. Geochem. Health 26, 295–302.

Ying, G.-G., Williams, B., 2000. Laboratory study on the interaction between herbicides and sediments in water systems. Environ. Pollut. 107, 399–405.

Young, R.A., Onstad, C.A., Bosch, D.D., Anderson, W.P., 1987. AGNPS, Agricultural Nonpoint-Source Pollution Model: A Watershed Analytical Tool. Conservation Research Report No. 35. Washington, DC, USA.