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Runoff of Pesticides: Achievements and Limitations of Modelling Agrochemical Dislocation from Non-Point Sources at Various Landscape Related Scales

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Abstract

In the absence of drainage systems, runoff is a major transport pathway of pesticides from agricultural areas to aquatic systems. We provide an overview of existing runoff models eligible to describe the transport and fate of pesticides in the terrestrial environment. We distinguish between leaching, erosion, and hydrological models. Recent developments in runoff modelling include the evolution of complex deterministic models, combinations of models and probabilistic approaches on a GIS-platform. The latter enable users to make geo-referenced predictions of diffuse pesticide emissions from small to large scales. Simulated loads mostly correlate well with measured pesticide loads and concentrations on a catchment scale, but often overestimate measured concentrations, because the edge-to-field approach applied does not consider any attenuation by degradation or sorption between the location of pesticide application and surface waters. Therefore, future developments of horizontal pesticide transport models should focus on detention and retention mechanisms during transport on highly resolved temporal and spatial scales. Additionally, for the simulation of realistic scenarios of pesticide emissions on a catchment scale, the evaluation and standardization of probabilistic approaches can be helpful.

Keywords: pesticides, runoff, hydrological models, leaching models, erosion models, probabilistic approach, upscaling

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1 Introduction

The development of numerical pesticide models started when negative consequences of agricultural pesticide applications for humans had been recognized in the 1960s and 1970s. The driving forces of continual improvements of pesticide models over 40 years have been the intention to describe the dispersal of pesticides in terrestrial and aquatic systems and to assess the risk of pesticide applications. For the same reason in the 1970s, the registration and partly the prohibition of pesticides were initiated in industrialized countries in the northern hemisphere. Since 1992, the requirement of sustainable use of natural resources, prone to agricultural practices, provided further motivation to increase the performance of pesticide models.

Since the 1970s, numerous models of pesticide transport in the agricultural environment have been developed. Early conceptual and deterministic approaches to model the fate of pesticides on soil surface and in above-soil canopy were limited to certain pesticides and environments and described the transport of the soluble phase as one-dimensional (1D) flow without using geo-referenced data (Goodman *et al.*, 1983; Vithayathil *et al.*, 1979). However, from the very beginning of pesticide modelling, sorption and degradation of pesticides were explicitly incorporated as attenuation and retention factors. Figure 1 provides an influence diagram of processes affecting pesticides loads via runoff.

In a next phase, the focus was on leaching of pesticides to groundwater and a variety of 1D leaching models for agricultural soils was generated, which predict pesticide concentrations in various soil depths in the vadose and phreatic zones (Bonazountas, 1987; Matthies and Behrendt, 1991; Crowe and Mutch, 1992; Persicani, 1996; Wauchope *et al.*, 2003). Few of these models include the transport mechanism runoff as loss term of pesticides and none distinguishes between surface and subsurface runoff.

As partly described in leaching models, preferential flow through soil macropores can significantly increase the risk of pollution of surface water bodies by pesticides. While many field studies have shown the importance of preferential flow on a field scale, few have included detailed numerical modelling of the processes involved (Gärdenäs *et al.*, 2006).

Contemporarily, modellers improved the universal soil loss equation (USLE) leading to a revised equation (RUSLE), and 1D or two-dimensional (2D) models of surface erosion and soil particle transport were created. Previous studies had recognized that surface erosion is a function of rainfall intensity rather than of total annual rainfall and therefore, event-oriented 1D and 2D approaches of surface erosion and particle transport were developed that are physically based or of hybrid nature with both, empirical and deterministic elements (Jetten *et al.*, 2003; Morgan *et al.*, 1998). These models neglect subsurface flow and are hardly applicable for the transport of the soluble pesticide phase.

Dynamic hydrological models deal with these deficits and are able to predict transport and fate of soluble pesticides for small watersheds with moderate temporal and spatial resolution (Borah and Bera, 2004; Tarboton *et al.*, 2002). As a prerequisite of such simulations, Geographical Information Systems (GIS) were developed, so that hydrological models could be implemented on a GIS-platform that in turn allows for using and producing geo-referenced data. Hydrological and leaching models partly originate from the same roots, as it is exemplified by the leaching model GLEAMS (Sabbagh *et al.*, 1993), which is based on the hydrological model CREAMS (Rudra *et al.*, 1985).

Recognizing the need for models that enable the prediction of soluble pesticide losses via surface and subsurface runoff recently, leaching models and transport or erosion models were combined to calculate pesticide transport to the aquatic environment with high temporal and moderate spatial resolutions. The combination of both, elaborate descriptions of horizontal and vertical transport, and retention and detention mechanism within or above soil, resulted in reliable simulations of pesticide transport and fate on a watershed or even river basin scale (Röpke *et al.*, 2004; Jackson *et al.*, 2005; Ramanarayanan *et al.*, 2005). Combinations of hydrological models with leaching models, which include the description of preferential flow, might augment the accuracy of predictions of pesticide concentrations in runoff even more.

All models mentioned above are capable to calculate realistic worst case scenarios, but are barely adequate tools for probabilistic approaches on a watershed scale. 2D and 3D erosion and hydrological models are supposed to be suitable tools for simulations at large scales, but these models demand extremely high computational effort for Monte Carlo simulations. In turn, leaching models scarcely incorporate horizontal flow and hence, they need to be combined with hydrological models if the aim is to simulate horizontal runoff. Therefore, another development of modelling pesticide transport via runoff started in the 1990s, which relies on simple empirical or hybrid approaches in order to make robust predictions of pesticide exposure by conducting Monte Carlo simulations (Franke and Teutsch, 1994; Kapo and Burton Jr, 2006).

In summary, models of pesticide transport became more elaborate as time went by, including mathematical and numerical complexity, as well as spatial resolution and extent. However, the progresses made in model development have been confined by the state of scientific knowledge of pesticide behaviour in and above soil. For example, there are still deficits in describing preferential flow in soils and the sorption behaviour of pesticides, owing to the fact that every soil patch seems to have a different partitioning coefficient K_D. The discrepancy between small-scale patchiness of soils and vegetation and the purpose to provide reliable predictions of pesticide transport and fate at large scales remains unsolved. However, various types of models and model combinations experienced an evolution that enables the prediction of geo-referenced pesticide exposure from small to large scales. In the following, we will provide an overview of existing runoff models eligible for pesticides. We will discuss their advantages and disadvantages and give a perspective for future developments.

2 Surface erosion models

Erosion models experienced a rapid evolution from the empirical USLE to event-oriented semi-deterministic models that work on a GIS-platform. However, recent models, such as KINEROS (Michaud and Sorooshian, 1994) and EUROSEM (Morgan *et al.*, 1994) deliver realistic results of soil erosion and particle load for small watersheds, but are less efficient on even larger scales, because a great variety of erosion and transport processes and phenomena that require high spatial resolution are considered in these models. Table 1 provides an overview of some modern surface erosion models.

Erosion model	**First description**
ANSWERS	Park *et al.* (1982)
KINEROS	Michaud and Sorooshian (1994)
EUROSEM	Morgan *et al.* (1994)
LISEM	DeRoo *et al.* (1996)
EROSION-3D	Schmidt *et al.* (1999)
EROSION-2D	Abel *et al.* (2000)
WEPP	Ascough II *et al.* (1997)

Table 1: *Surface erosion models and their first description in chronological order*

KINEROS is a single rainfall event model useful for the design of single-event storms and evaluating watershed management practices, especially structural measures. KINEROS is based on the SCS curve number method and divides the watershed into a cascade of elements of planes and channel segments, whereby flow and sediment are routed from one segment to another. The elements allow rainfall, infiltration, runoff and erosion to vary spatially. 1D Hortonian overland flow starts when rainfall exceeds infiltration capacity. The sediment transport is described by a mass balance equation and does not include any chemical and biological transformation. KINEROS provides reliable long-term simulations although it was developed to map single or repeated events (Kalin and Hantush, 2006).

EUROSEM is a single event process-based model with modular structure for predicting water erosion from fields and small catchments. Runoff is routed over the soil using the kinematic wave equation. Continuous exchange of particles between water flow and soil surface is balanced within the model. Soil loss is computed as sediment discharge by a dynamic mass balance equation. EUROSEM was tested for single catchments and showed good correlation between simulated and measured soil loss. However, EUROSEM significantly underestimates soil loss and runoff, because the model disregards the patchiness of vegetation (Mati *et al.*, 2006).

Contrary to KINEROS and EUROSEM, LISEM (DeRoo *et al.*, 1996) and EROSION-2D (Abel *et al.*, 2000) are raster-based models for single storm events. However, the latter two models describe the same processes as do EUROSEM and KINEROS, which account for rill and inter-rill erosion and transport. EROSION-2D was tested in a small German catchment and overestimated runoff at dump slope, but worked well at hill slope (Abel *et al.*, 2000). LISEM revealed bad performance for low raster point densities, but worked better when the density was increased (Jetten *et al.*, 2003).

Contrary to the erosion models mentioned above, WEPP (Ascough II *et al.*, 1997) was designed to calculate continuous simulations of particle-bound substances. The model is based on fundamentals of erosion theory, soil and plant science, channel flow hydraulics, and rainfall-runoff relationships, and contains hill slopes, channels, and impoundments as primary components. The hill slope and channel components can be further divided into hydrology and erosion components.

WEPP partly incorporates equations from CREAMS (Rudra *et al.*, 1985) and includes gully erosion and channel transport. Small-scale morphological structures are additionally considered. In a Norwegian study, WEPP simulated fewer runoff events than measured, and improvements in winter hydrology calculations were recommended (Grønsten and Lundekvam, 2006).

In most erosion models, runoff and sediment load are only computed for one point in the catchment: the outlet. Therefore, validations can be only carried out for the outlet and just a few tests compared simulated erosion with observed erosion patterns. Most models predicted total runoff better than peak runoff, which again was better predicted than sediment load (Jetten *et al.*, 2003). At any rate, calibration is desirable or necessary prior to any simulation runs. Correlations to measured runoff and loads were often good, but in most cases the models over- or underestimated empirical results especially for small erosion events.

In conclusion, modern erosion models combine high temporal resolution with the capability to simulate runoff on watershed scales. However, modelled results are often doubtful, because the spatial resolution of the models is insufficient to account for a small-scale heterogeneous environment. Furthermore, although erosion models may be capable to calculate the transport of soluble substances, these models do not consider any attenuation or partitioning during transport and therefore fail to predict loads of soluble pesticides to surface waters.

3 Leaching models

The description of vertical flow of water and pesticides in soils not only accounts for water percolation and downward flux, but also for chemical and biological pesticide attenuation processes, such as sorption and microbial degradation. Numerous 1D and 2D models describe pesticide leaching from soils to the phreatic zone, such as EXSOL (Matthies and Behrendt, 1991), LEACHP (Hutson and Wagenet, 1993), VARLEACH (Walker *et al.*, 1996), and MACRO (Jarvis *et al.*, 1994). Table 2 provides an overview of existing numerical leaching models.

Leaching model	**First description**
PRZM	Lorber and Offutt (1986)
EXSOL	Matthies and Behrendt (1991)
GLEAMS	Sabbagh *et al.* (1993)
LEACHP	Hutson and Wagenet (1993)
MOUSE	Persicani (1993)
TETRANS	Persicani (1993)
PESTLA	Brouwer (1994)
HYDRUS	Persicani (1993)
MACRO	Jarvis *et al.* (1994)
PELMO	Klein (1994)
PLM	Hall (1994)
VARLEACH	Walker *et al.* (1996)
PEARL	Boesten and van der Linden (2001)
VADOFT	Miao *et al.* (2003)

Table 2: *Pesticide leaching models and their first description in chronological order.*

Differences between these models arise from diverse approaches to describe water flow. PRZM (Lorber and Offutt, 1986; Donigian and Carsel, 1987), PELMO (Klein, 1994), PLM (Hall, 1994), and VARLEACH use a capacity approach to describe water flow, whereby water in excess of field capacity in any layer moves down to the next layer within the same time step. Capacity based approaches generally have a low computational demand, but they reveal some significant deficiencies. For example, the upward movement of water due to evaporation cannot be simulated. PESTLA (Brouwer, 1994), LEACHP, and MACRO use the Richards equation, whereby water flow is determined by differences in water potential and soil hydraulic conductivity. All leaching models describe plant uptake of water, and convective transport is described equally, whereas diffusive and dispersive fluxes are handled differently: PRZM, VARLEACH, EXSOL, and PLM adopt numerical procedures based on soil layer thickness; MACRO, PESTLA, and LEACHP calculate these fluxes based on user-specified diffusivity and dispersivity parameters, and PELMO uses a combination of both approaches. Most of the models are able to simulate time-dependent changes in sorption: LEACHP, PESTLA, PELMO, and MACRO are able to describe non-linear sorption according to the Freundlich-isotherm. PELMO can also simulate higher order degradation pathways. Except for PRZM, all models consider temperature and moisture on microbial degradation rates. Most models can simulate pesticide uptake by plants. In addition, PRZM, PELMO, EXSOL, and LEACHP consider volatization of pesticides.

Compared to LEACHP, HYDRUS (Persicani, 1993) represents the modern type of leaching models, which use Richards equation to calculate water flow and which describe solute transport by a convective-dispersive equation. HYDRUS was found to be sensitive to the K_D value employed to describe partitioning, but delivered robust results in a comparative study (Persicani, 1996). Gärdenäs *et al.* (2006) used HYDRUS-2D to account for preferential flow. A dual-permeability approach was found to accurately simulate preferential drainage flow, while equilibrium and mobile-immobile approaches largely failed to capture the preferential flow process.

Leaching models are deterministic or hybrid and describe the same processes of attenuation. However, only few of them consider horizontal runoff as a loss term. GLEAMS (Sabbagh *et al.*, 1993), PRZM and PELMO can calculate water and pesticide runoff and thus may provide simulated pesticide loads to a 2D transport model to simulate diffuse emissions on larger scales. GLEAMS uses a curve number approach driven by daily rainfall and relates the runoff curve number to daily soil water content in the root zone, while PRZM uses the same (SCS) approach relating curve number to soil moisture limits in the surface zone. PELMO uses the same approach as does PRZM. In these three models, loads in runoff are calculated from edge-to-field water runoff volumes, empirical extraction coefficients and sediment concentrations, assuming linear sorption isotherms and a constant mixing depth at the surface.

Ma *et al.* (1999) compared the runoff components of PRZM and GLEAMS and found good correlations of simulated loads to empirical results measured on a field scale, but both models failed to calculate pesticide concentrations in runoff water and underestimated pesticide loads. It remains doubtful, if both models would exhibit a reasonable performance on even larger scales, because PRZM and GLEAMS do not consider any retention above soil surface during horizontal transport and thus may overestimate actual pesticide loads.

Gottesbüren *et al.* (2000) compared MACRO, LEACHP, GLEAMS, PELMO, and further leaching models by simulating the leaching of the herbicide isoproturon and the water tracer bromide in a profile of a silty loam soil. The blind test employing eight persons who applied the models exhibited an overwhelming influence of the individual users on the simulation results. Herbst *et al.* (2005a) executed a test of the models MARTHE (Thiéry and Amraoui, 2001), TRACE (Herbst *et al.*, 2005b), ANSWERS (Park *et al.*, 1982), and MACRO. These authors found that the Richards equation-based models MARTHE, TRACE, and MACRO performed better for water flow predictions than the capacity-based model ANSWERS. Preferential flow implemented in the models MARTHE, TRACE, and ANSWERS did not influence the simulation of water flow significantly, but had great influence on the simulated pesticide concentrations. In another study, Vanclooster *et al.* (2000) not only tested several leaching models, but also gave recommendations how to improve them.

Generally, leaching models were made to predict pesticide concentrations in groundwater and therefore, horizontal transport was not implemented or was described only in a rudimentary way. Hence, these models need to be combined with surface transport models, if runoff to surface waters shall be predicted accurately.

4 Hydrological models

Table 3 provides an overview of existing hydrological models. These models exhibit a great diversity ranging from purely empirical approaches created to predict long-term loads to surface waters (MONERIS: Behrendt and Opitz, 2000) to hybrid dynamic three-dimensional (3D) models working on a GIS-platform, such as MIKE SHE (Bøggild *et al.*, 1999).

Hydrological model	**First description**
CREAMS	Rudra *et al.* (1985)
AGNPS	Young *et al.* (1989)
HBV	Harlin (1991)
HSPF	Chew *et al.* (1991)
PRMS	Yan and Haan (1991)
ACRU	Kienzle and Schulze (1992)
CASC2D	Julien *et al.* (1995)
SWAT	Rosenthal *et al.* (1995)
WASMOD	Schimming *et al.* (1995)
DHSVM	Nijssen *et al.* (1997)
SWIM	Krysanova *et al.* (1998)
MIKE SHE	Bøggild *et al.* (1999)
HMS	Yarnal *et al.* (2000)
MONERIS	Behrendt and Opitz (2000)
WASIM	Rode and Lindenschmidt (2001)
ARCEGMO	Klöcking and Haberlandt (2002)
J2000	Krause (2002)
DRIPS	Röpke *et al.* (2004)
DWSM	Borah *et al.* (2004)
MARTHE	Thiéry and Amraoui (2001)
TRACE	Herbst *et al.* (2005b)
MIKE BASIN	Ireson *et al.* (2006)

Table 3: *Hydrological models and their first description in chronological order.*

MONERIS predicts diffuse emissions of nutrients for mid-sized to large catchments and includes a module that describes the emission path runoff. The temporal resolution of MONERIS is low amounting to one year and until present, the model fails to provide good estimates of nutrient emissions for catchments smaller than 50 km^2. Correlations between modelled and measured loads were significantly well, but total nitrogen loads are generally overestimated (Behrendt and Opitz, 2000).

CREAMS (Rudra *et al.*, 1985) is composed of three modules: hydrology, erosion, and chemistry and was created to predict diffuse emissions via runoff. CREAMS is a precursor of the leaching model GLEAMS. Hence, runoff is similarly modelled in both models and is based on the Soil Conservation Society (SCS) curve number approach. Results of a simulation on a field scale generally matched the observed order of magnitude (Yoon *et al.*, 1992).

The GIS-based hydrological model SWAT (Rosenthal *et al.*, 1995) has a modular structure and consists of hydrological, sedimentological, and chemical subroutines applicable to watershed-scales. The hybrid model spatially based on hydrological response units includes both, conceptual and physical approaches. A central part of SWAT is the general water balance equation. Surface runoff is determined by the SCS Curve Number approach. Frede *et al.* (2002) found that physical soil properties affect total runoff moderately, but highly influence surface runoff in SWAT. The model was found to be less efficient in predicting runoff in relation to land cover in a semi-arid watershed, therefore calibration was strongly recommended (Hernandez *et al.*, 2000). Nonetheless, SWAT (Borah and Bera, 2004) was found suitable for predicting annual flow volumes, sediment, and nutrient loads. Monthly predictions were generally good, except for months with extreme storm events and hydrologic conditions (Borah and Bera, 2004).

Similar to SWAT, MIKE SHE (Bøggild *et al.*, 1999) has a modular structure and calculates 3D surface, sub-surface, and stream flow involving distributed grid points. In a case study in an arctic environment, the model was found to overestimate measured runoff, because modelled surface retention of melting water was too low. However, there has been little information on how well MIKE SHE works simulating the transport of pesticides.

MIKE BASIN (Ireson *et al.*, 2006) is another product within the MIKE family and functions as an extension of *ArcView*. The water resources management tool is raster-based and works on a basin scale. In a case study, the main flaw of MIKE BASIN was that it failed to simulate high water flow, but otherwise satisfactory results were achieved (Ireson *et al.*, 2006).

Further watershed-scale models, such as AGNPS (Young *et al.*, 1989), CASC2D (Julien *et al.*, 1995), and PRMS (Yan and Haan, 1991) were found to be eligible to simulate diffuse pollutant loads to surface waters (Borah and Bera, 2004). Muleta *et al.* (2006) tested AGNPS simulating soil erosion and nutrient transport in an Ethiopian catchment and succeeded in identifying hot spots of sediment and nutrient release.

The 2D raster-based model MARTHE (Thiéry and Amraoui, 2001) has successfully been tested to predict salinity in groundwater (Weinthal *et al.*, 2005) and may be applied to simulate transport and fate of pesticides, as well. However until present, there are scarce published results of such simulations using MARTHE as platform.

In the model SWIM (Krysanova *et al.*, 1998), a three-level scheme of spatial disaggregation from basins to sub-basins and to hydrotopes is used. The processes of transpiration, evaporation, and percolation within soils are implemented in SWIM. Retention of water and solutes is described by means of a dimensionless retention coefficient. SWIM was successfully validated for the Elbe catchment (Hattermann *et al.*, 2005), but these authors recommend to accompany macroscale simulations of runoff with empirical investigations in small catchments, in order to identify the dominant hydrological processes.

TRACE is a recent development in hydrological modelling documented by Herbst *et al.* (2005b). The Richards equation based numerical model calculates the three-dimensional saturated/unsaturated water flow. For the modeling of regional scale pesticide transport TRACE was combined with the plant module SUCROS and with 3DLEWASTE, a hybrid Lagrangian/Eulerian approach to solve the convection/dispersion equation (Herbst *et al.*, 2005b). A first-step application of TRACE/3DLEWASTE to a 20 km^2 test area for a ten-year period was used to identify hot spots of isoproturon in groundwater. In general, the model results were consistent and reasonable.

Röpke *et al.* (2004) developed a simple model (DRIPS) on horizontal pesticide transport. In this model, surface runoff is described as a function of rainfall and water infiltration. In contrast to the majority of hydrological models, other parameters such as slope and surface roughness are disregarded in this model. Horizontal attenuation is considered by implementing partitioning between the soluble and solid phases (K_D) and degradation of pesticides. The authors found a good correlation between measured and modelled pesticide concentrations, but in an uncertainty analysis, the confidence interval spanned several orders of magnitude. Therefore, the results of DRIPS have to be evaluated cautiously, although this model seems to be an efficient alternative to more elaborate hydrological approaches.

All hydrological models explicitly describe water runoff, but they were seldom created to model exclusively transport of pesticides. Although hydrological models often use the same SCS curve number approach to relate land use to runoff as do leaching models including a runoff component, the former provide more realistic results because of their larger horizontal resolution. In addition, hydrological models differentiate between surface and subsurface runoff and thereby their performance is improved again. However, surface and subsurface attenuation processes of pesticides are often insufficiently described and for peak flow modelled water runoff did not always match measured results. Therefore, in order to calculate more realistic results, hydrological models need to be augmented in temporal resolution.

Most hydrological models can account for changes in land use. For example, Wang *et al.* (2005) reported a successful test of AnnAGNPS combined with a lake model, when several scenarios of sediment and nutrient loadings were calculated for different land use scenarios. In contrary, Klöcking and Haberlandt (2002) tested the model ArcEGMO for changes in land use and found that problems of impact studies in large river basins resulted mainly from a huge spatial heterogeneity of land use and a rough input database. These authors stated that simple approaches are needed to setup possible land use changes on the basis of easily available spatial data.

The role of crops for the fate of pesticides has been described in leaching models, but hydrological models only consider the effect of vegetation on surface roughness, rather than of pesticide export by harvesting. This deficit is easy to remove. In contrary, it remains doubtful if a more detailed description of retention and detention by nonlinear sorption and desorption would improve the performance of hydrological models. At least, an elaboration of sorption processes would also increase the number of input parameter required, which in turn would be barely available in high resolution at large scales.

5 Combinations of leaching models and hydrological models

As outlined above, leaching models include the description of attenuation processes within soils, while hydrological models partly describe attenuation processes during horizontal transport. Therefore, combinations of both model genera could improve the predictions of pesticide emissions via runoff, but to date only few studies successfully tested such combinations to calculate pesticide loads to or concentrations in surface waters.

Ramanarayanan *et al.* (2005) applied a combination of GLEAMS, elements of PRZM, and SWAT to provide an estimate of pesticide concentrations within surface waters on a watershed scale. PRZM's edge-to-field prediction was transformed to a watershed scale using a convection-dispersion equation. GLEAMS was integrated into SWAT to describe the fate of pesticides in the terrestrial environment. This combination differentiates between the soluble and the sorbed phase, and pesticide leaching is calculated for each soil layer. Transformation processes are described by first-order-relationships. Four factors were found to determine residues of pesticides in surface waters: watershed morphology, magnitude of timing of runoff or drainage events, management practices, and degradation rate within the water body. The validation with monitoring data showed good and significant correlation.

Miao *et al.* (2003) tested a combination of RICEWQ (Capri and Miao, 2002) and VADOFT to simulate pesticide fate and transport in rice paddies and underlying soils. RICEWQ is a multiple dimension flow model that describes precipitation, irrigation, evapotranspiration, runoff, and seepage. Miao *et al.* (2003) found a high sensitivity of soil permeability and management practices. The combination was successfully validated by means of a two-year field study.

A combination of LEACHP with AS, an attenuation factor model was tested by Chatupote and Panapitukkul (2005). LEACHP was used to simulate downward fluxes of pesticides in soils, and AS working on a GIS-platform served to extrapolate simulation results to a catchment in Thailand. The extrapolation showed that efficient measures to reduce pesticide concentrations in surface waters are the reduction of application rates and the optimization of irrigation measures. However, Chatupote and Panapitukkul (2005) did not verify their results.

Tournebize *et al.* (2006) combined PCPF-1 (Watanabe and Takagi, 2000), a lumped model simulating pesticide behaviour in paddy water and soil with SWMS-2D (Wu *et al.*, 1995), a finite element numerical model that solves the Richards and the advection-dispersion equation for solute transport in soil. The coupling involves interactions of water flow and concentrations of the soil interface. Monitoring data were used to parameterize and calibrate soil hydrodynamics. The coupling of both models was conducted by linking percolation flux and pesticide concentration at the soil interface. A sensitivity analyses highlighted the impact of daily fluctuating water levels on pesticide concentrations, but again a validation was missing in the study of Tournebize *et al.* (2006).

Tiktak *et al.* (2002) used a model combination which is based on an analytical expression that describes the mass fraction of pesticide leached. To have the seepage and drainage fluxes correctly described, PEARL was loosely coupled with a regional groundwater model. Comparison with a standard scenario showed that the latter was not applicable to the full range of registered pesticides. The metamodel EuroPEARL (Tiktak *et al.*, 2006), which is a probabilistic application of a model combination further developed, could explain over 90% of the variation of the original model with only four independent spatial attributes, but until present, validation results of EuroPEARL have not been available.

The combination of leaching models with other models that describe runoff seems to be a promising development that started during the last decade. However in some studies, validation is missing, and some combinations are useful only for special land use. Further combinations have to be tested in order to find more general solutions applicable to a wide range of landscapes.

6 Probabilistic approaches

Probabilistic approaches of modelling pesticide runoff are mainly based on existing models, which can be deterministic, hybrid, or empirical. Insofar, these approaches are not based on fundamentally new algorithms, but progress should be achieved by a higher certainty of model predictions compared to the common realistic worst case scenarios delivered by deterministic models. Apparently, probabilistic approaches represent a great progress compared to the calculation of single scenarios and might dominate future developments in modelling transport of pesticides via runoff. However in the following passages, we will also reveal some deficits of existing probabilistic methods.

Tiktak *et al.* (2006) applied the metamodel EuroPearl, which is based on an analytical expression that describes the mass fraction of pesticide leached. The metamodel ignores vertical parameter variations and assumes transient flow and solute transport, Freundlich adsorption, first-order degradation, and passive plant uptake of pesticides. The calibration was carried out by calculating approximately 60,000 simulations done for 56 pesticides with different half-lives and partitioning coefficients. Thus, EuroPEARL was evidenced to be a suitable tool for probabilistic simulations, but its validation is still missing.

Shaaban and Elprince (1989) presented a hybrid pesticide leaching model that partly is of probabilistic nature: downward flow velocity and the diffusion coefficient D are selected with a Monte Carlo method from probability distributions given by mode, median and mean values. Contaminated depth is predicted as random variable and is highly sensitive to surface rates of recharge.

The latter study was performed on a small scale, but probabilistic approaches are supposed to be eligible for predictions of pesticide emissions on large scales, as it was evidenced by Franke and Teutsch (1994). These authors applied a combination of LEACHM (Eckhardt and Wagenet, 1996) and a 3D-groundwater flow model to account for the spatial heterogeneity of an aquifer and found that hydraulic conductivity has only little effect on pesticide concentrations. However, this approach was created to estimate subsurface flow within the phreatic zone rather than to predict surface runoff of pesticides.

Surface runoff was modelled using a probabilistic approach by Huber *et al.* (1998). Runoff losses of pesticides were calculated by incorporating various spatial data sets on climate, soil, land use and other topics that have significant effects on pesticide runoff from fields. The lack of reliable information on the behaviour of pesticides under site-specific conditions constitutes the most important limitation of this approach.

Probabilistic approaches have been possible, since the recent development of computer hardware has allowed for calculating Monte Carlo simulations of elaborate numerical models within reasonable time spans. There have been two directions in the evolution of probabilistic approaches. The first relies on existing deterministic or hybrid models (Franke and Teutsch, 1994), while the second includes the development of new simple runoff models with less computational demands (Röpke *et al.*, 2004). The former approaches deliver geo-referenced pesticide concentrations or loads, but until present, these approaches are scarcely applicable to entire watersheds, because the computer hardware is still insufficient for such purposes. However, the newly developed condensed runoff models seem to fill the need of reliable predictions at large scales, yet the simplicity of these models neglects the complexity of partly interacting processes influencing pesticide loads in runoff (Figure 1). Probably, future developments of computer hardware will enable the user to run Monte Carlo simulations of deterministic runoff models at large scales and thus, the condensed empirical and hybrid models will become redundant.

In general until present, the hypothesis remains unproven that probabilistic approaches deliver more reliable results than calculations of single runoff scenarios. Beulke *et al.* (2006) investigated the reliability of results from probabilistic procedures in the leaching model PELMO. Different

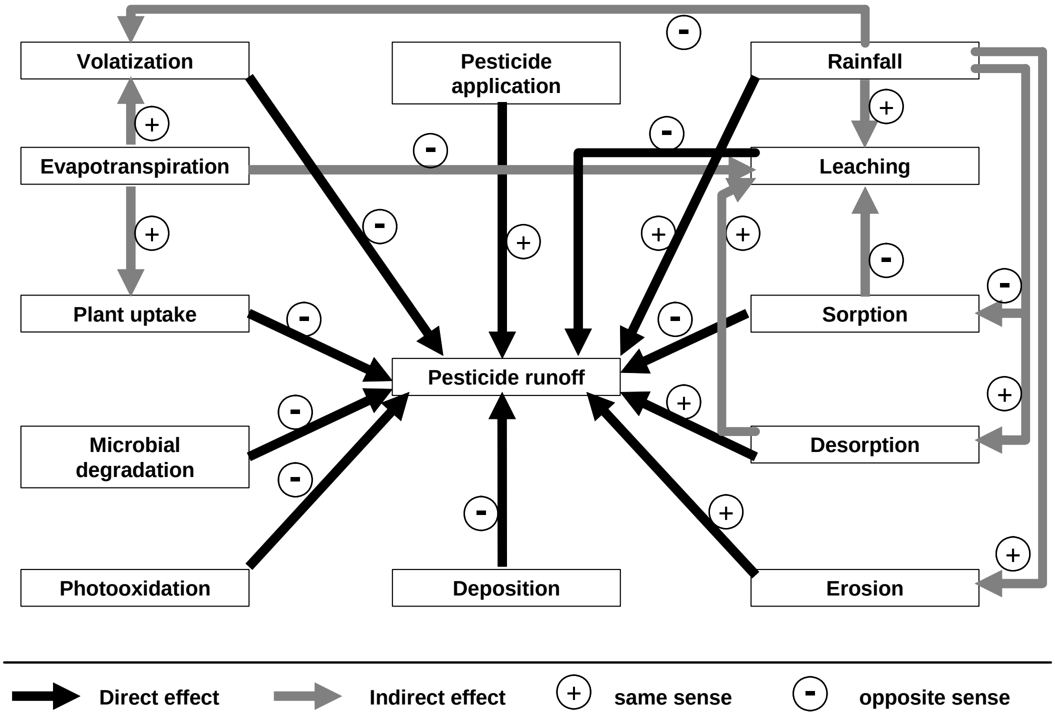

Figure 1: *Influence diagram of processes which affect pesticide loads to surface waters via runoff; +/- indicate influence in the same or opposite sense, respectively.*

distributions of input parameters resulted in high variability of agreement between modelled and measured data. Beulke *et al.* (2006) concluded that subjective choices in Monte Carlo simulations may introduce large variability into probabilistic modelling. Therefore, results of probabilistic approaches have to be evaluated cautiously, also because stochastic approaches favour simple models with small predictive accuracy, in order to diminish computational effort of Monte Carlo simulations.

7 Diverse mathematical models at various scales

We presented an overview of models that predict pesticide loads via runoff in significantly different ways. Empirical models are opposed to mechanistic approaches, but some elements of the former are often incorporated into the latter. In general, leaching models are mainly of deterministic or hybrid nature and describe processes, such as microbial degradation, percolation, and plant uptake. Leaching models are mostly one-dimensional and therefore, the computational effort to calculate downward fluxes of pesticides is moderate, although the processes affecting pesticide concentrations in soils are described elaborately. The results of leaching models may feed into horizontal transport models, but the applicability of leaching models is confined to a field scale.

Mechanistic or hybrid erosion and hydrological models use the SCS curve number approach to describe the horizontal transport of pesticides. In some models, the retention of pesticides during runoff is only considered by applying a simple attenuation factor. These linear approaches seem to be poor compared to the complex nature of 2D- or 3D-hydrological and erosion models, but still progressive compared to the edge-to-field approach, which disregards any retention between application areas and surface waters. Therefore, complex hydrological and erosion models, such as MIKE SHE and EUROSEM, still have problems to predict pesticide loads during rainfall events on catchment scales. Furthermore, their spatial resolution is mostly insufficient to account for small-scale retention structures, and thus, these models often overestimate actual pesticide loads.

Above, we demonstrated a deficit of erosion model validation, which in the past was mainly performed for the outlets of catchments. Validation of hydrological models have the same problem, because contrary to leaching models, they are created to work at scales larger than field scale. However, validation procedures which regard locations within the simulation areas are confined by the great logistic demand of pesticide monitoring. For the same reason, the validation based on long-term monitoring has seldom been performed (but see: Herbst *et al.*, 2005b).

Empirical models such as USLE and MONERIS use very simple equations often derived by simple linear regression analyses and provide relatively low spatial and temporal resolutions. Therefore, these empirical models are suitable tools to deliver robust predictions of long-term developments in pesticide loadings to surface waters on river basin scales, but fail to calculate short-term pulses of pesticide loads on field and catchment scales.

Recent developments of probabilistic approaches consider vegetation patches and small geomorphological structures as retention sites for pesticides during horizontal transport (Röpke *et al.*, 2004; Bach *et al.*, 2001). The major advantage of the mathematical simplicity of these approaches is their small computational effort, which permits to conduct Monte Carlo-simulations for large river basins. Despite reliable results on a catchment scale, Bach *et al.* (2001) state that the results should be addressed mainly to comparative interpretations with the focus on the proportions between different active ingredients, soil regions, climates and application periods. In addition, the empirical equations implemented are in contrast to the high spatial resolution of these probabilistic approaches, and they still need to be validated on river basin scales.

Qualitative progress in modelling fate and transport of pesticides is also necessary concerning substance classes. Leaching models have been used for a variety of pesticides different in chemical properties and behaviour (Tiktak *et al.*, 2002), but hydrological models working at regional scales were mainly used for one or two substances in one study. Therefore, there is still a lack of a comparative study in which the dispersal of the most important pesticide classes is simulated at river basin scale.

Future developments in computer hardware will enable to use probabilistic approaches on a GIS-platform to predict pesticide loads via runoff for river basins, applying reliable deterministic models and model combinations. In addition, it is desirable to increase spatial resolutions of hydrological models, so that small-scale geomorphological and canopy structures can be considered as potential retention sites of pesticides. In contrary, the commonly used edge-to-field approach leads to large overestimations of pesticide loads to surface waters and therefore should be avoided. Overall, the evolution of pesticide transport models probably will go into two major directions, which not necessarily are contradictive to each other: increase in spatial resolution and extension to large scales, both of which will be performed on GIS-platforms.

8 Conclusions

The description and implementation of pesticide runoff varies significantly between models and model types. Leaching models neglect horizontal transport and therefore are barely useful tools to predict pesticide surface runoff. In contrary, erosion models elaborate surface transport, but do not consider any degradation or transformation between soluble and particle-bound phases. Hydrological models apparently provide the most robust estimates of pesticide runoff and work from medium to large scales. However, hydrological models reveal deficits in temporal resolution and often need to be improved considering pesticide attenuation during transport. Their combination with leaching models delivers realistic results from small to large scales, but there is still a need for a model combination applicable to a wide range of landforms. In order to calculate pesticide emissions on large scales with high certainty, probabilistic approaches could be useful if they were based on deterministic models rather than on simple empirical models.

Future modelling should therefore find standard procedures to apply probabilistic approaches. Generally, deterministic models have to incorporate newly gained knowledge by empirical investigations continually, in order to improve the model performances with regard to sorption behaviour, effects of diversely structured vegetation patches, and small-scale geomorphological structures on pesticide transport. For the same reasons, pesticide models not only have to be improved qualitatively, but they also have to gain higher temporal and spatial resolutions, as we demonstrated that some hydrological models overestimated pesticide loads due to low temporal resolution. However, the resolution of pesticide models is additionally limited by the resolution of available input data and by computer hardware, the latter of which is supposed to experience further rapid improvements.

In summary, the modelling of pesticide runoff has experienced great progress since the early stages in the 1970s, but until now there is no ultima ratio that enables to predict pesticide emissions accurately from small to large scales.

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