

Environmental fate modelling of agrochemicals and their transformation products at catchment scale

Thesis submitted in partial fulfilment of the requirements
for the degree of Philosophiae Doctor of the
Faculty of Environment and Natural Resources,
Albert-Ludwigs-Universität
Freiburg im Breisgau, Germany

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December 2013

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Date of thesis' defence: 15. November 2013

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Summary

Although the usage of agrochemicals contributes to the well-being of mankind, by enhancing plant growth and increasing crop yield, the negative effects of residual export on water resources are undeniable. The incomplete degradation of pesticides may lead to the formation of equally or more toxic transformation products (TPs), which additionally tend to be more stable and more mobile in the environment. Process-based environmental fate models provide the possibility of assessing the impact of agrochemical application on river contamination considering degradation and sorption. Even though conceptualizations of transformation processes are available in the literature, the assessment of TP fate and export has not yet been incorporated in catchment scale models. Furthermore, experimental studies suggest a more detailed sorption assessment, by using non-linear isotherms and sorption kinetics for agrochemicals, which was only partially implemented in the past. In order to approach these issues, five studies were carried out in the course of this thesis, implementing and testing new environmental fate processes in agricultural non-point source models.

In the first study, the environmental fate processes of two insecticides and their TPs, leading to export by the first rainfall after a dry summer in the Mediterranean were investigated. For this purpose, rivers were sampled at four stations and a model was developed being able to assess concentration fractions between parent compounds (PCs) and TPs in the river, using instantaneous linear sorption and first-order transformation processes. Sampling results revealed that the TPs were exported in a higher fraction than their PCs at most stations. Two scenarios were defined for the model setup: soil transformation and surface transformation. The fact that only surface transformation was able to reproduce observed PC-TP fractions in the river confirmed experimental literature results about the formation of specific TPs. This study emphasized the importance of the knowledge of the transformation processes leading to the formation of a specific TP under given environmental conditions.

The modelling concept of study 1 was extended by a conceptual hydrological model and a substance mobilization module in the second study. The model was used to assess parameter sensitivity and model uncertainty in insecticide and TP river concentration modelling, based on Monte-Carlo sampling. Most parameters of both the hydrological and the fate model were found to be sensitive. Parameter correlation revealed that the linear isotherm and transformation parameters were correlated, leading to reduced parameter sensitivity. Furthermore, parameters for application timing and mass were correlated to the PC half-life. However, the modelling of a TP constrained the application mass parameter and thus increased its sensitivity. Comparing model results to observations showed that the

model reproduced the concentrations of the PC and one of the TPs adequately, but failed for the second TP, even though uncertainty ranges were wide. It was assumed that the predominating transformation process changed from the first to the second event in this study, which had consequences for the second TP but could not be considered by this conceptual model structure. Concluding, the additional modelling of TPs may increase the total model uncertainty, but the identifiability of some parameters may also be increased at the same time.

The aim of study 3 was the assessment of long-term phosphorus (P) export from a Mediterranean catchment towards a downstream reservoir under data scarce conditions. The model developed and applied exhibited an increased model complexity, including erosion and sediment transport modelling, a Langmuir isotherm and sorption kinetics for the modelling of P export, based on distributed hydrological modelling. The parameters of the newly implemented sorption approaches and the hydrological model parameters were equally sensitive regarding P export. Additionally, the initial soil P was highly sensitive, highlighting the importance of this initial condition. The assessed longterm P export of the study catchment was below the regional average, but further research is suggested regarding P cycling in the reservoir, using the model results as boundary condition.

For an investigation of the export pathways of PCs and TPs in hydrological catchments, the model of study 3 was extended by modules for the fate of soil-applied pesticides and TPs in study 4. The model was successfully calibrated to sampling data of discharge and three pesticides with one TP each at three sampling stations in a small headwater catchment. However, the assumption of spatially uniformly distributed soil residues of substances prior to application resulted in an overestimation of substance export during baseflow at one of the sampling stations. PC export pathways were found to be influenced by environmental fate processes in a similar way as reported in the literature. For TPs, however, the influencing factors were much more complex, since fate processes of both the PC and the TPs determined the behaviour of TPs in the environment. Especially the delayed formation and degradation of TPs as well as the possibly different places of formation were found to be responsible for a main export of TPs under different hydrological conditions than their PCs. It was concluded that PCs and TPs generally take different export pathways in hydrological catchments, due to their different environmental fate characteristics.

In study 5, the model developed in study 4 was applied in order to delineate critical source areas (CSAs) for PCs and TPs as influenced by sorption and transformation properties in twelve environmental fate parameter scenarios. Results suggested that environmental fate characteristics have a large influence on the export strength and the spatial distribution of CSAs. The spatial coefficient of variation was higher for PCs than for TPs, which shows that

the export of TPs was assessed to be more ubiquitous in the catchment. Averaging the results of all scenarios resulted in the conclusion that the CSAs were generally different for PCs and TPs.

The simulation of agrochemical export was performed with a high temporal resolution in this thesis, which enabled the models to catch the high dynamics of pollutant export events but also supported the assessment of longterm agrochemical export masses from catchments. It was found that this high temporal resolution required the consideration of sorption kinetics, especially for the desorption process. Considering all studies of this thesis, the following conclusions could be drawn:

- (i) It is possible to simulate the dynamic formation and fate of TPs at catchment scale, using current conceptualizations from the literature. A thorough investigation of contributing fate processes should precede the choice of a certain model structure for each considered substance.
- (ii) Sensitivity analysis revealed that it is essential to consider the interaction of transport, transfer and transformation processes for the modelling of agrochemical export from catchments. The modelling of TPs may increase model uncertainty, but may also constrain some parameters and therefore increase their identifiability.
- (iii) Uncertainty in the knowledge of agrochemical application may propagate through the model since application parameters were correlated to the PC half-life. The assumption of a uniformly spatial distribution of initial agrochemical residues in the soil may lead to a wrong spatial prediction of background substance export in the river, stressing the need for better methods to derive this initial condition.
- (iv) Export processes and critical source areas for substance export differ between PCs and their TPs, due to the impact of PC fate on TP fate and the generally different environmental fate parameters.

A field-scale model and a surface water body model are currently used for pesticide and TP exposure assessment of water resources in the pesticide registration procedure of the E.U. Transferring experiences made in this thesis to the registration procedure would allow for a more comprehensive risk assessment of pesticide exposure by considering the formation and fate of TPs at catchment scale.

Zusammenfassung

Auch wenn die Nutzung von Agrochemikalien durch Steigerung des Pflanzenwachstums und ihres Ertrags zum Wohlergehen der Menschheit beiträgt, sind die negativen Auswirkungen des Eintrags ihrer Rückstände in unsere Wasserressourcen unbestreitbar. Der unvollständige Abbau von Pestiziden kann zur Bildung von ähnlich oder höher toxischen Transformationsprodukten (TP) führen, welche die Tendenz dazu haben mobiler und schlechter abbaubar als die Muttersubstanz (MS) zu sein. Unter Berücksichtigung von Abbau und Sorption können die Auswirkungen der Applikation von Agrochemikalien durch prozessbasierte Stofftransportmodelle abgeschätzt werden. Obwohl Modellkonzepte für Transformationsprozesse in der Literatur existieren wurden die Entstehung und das Verhalten von TP bisher nicht in Modellen auf Einzugsgebietsebene berücksichtigt. Darüber hinaus legen Ergebnisse aus experimentellen Studien die Nutzung von nicht-linearen Isothermen und Sorptionskinetik zur Berechnung der Sorption nahe, was bisher nur teilweise in Modellen umgesetzt wurde. Um zum Fortschritt in dieser Thematik beizutragen, wurden in dieser Dissertation fünf Studien durchgeführt, in denen neue Prozesse zur Beschreibung des Umweltverhaltens von Agrochemikalien in Modelle zur Abschätzung von diffusen Stoffeinträgen in Flüsse implementiert und angewandt wurden.

In der ersten Studie wurden Prozesse, die zum Austrag von zwei Insektiziden und deren TP während der ersten Niederschläge nach einem trockenen mediterranen Sommer führten, untersucht. Dafür wurden Flüsse an vier Messstationen beprobt und ein Modell zur Abschätzung der relativen Substanzkonzentrationen zwischen MS und TP in Flüssen entwickelt. Die Ergebnisse der Messungen ergaben, dass TP an den meisten Stationen in höheren Konzentrationen vorhanden waren als die MS. Zwei verschiedene Modellszenarien wurden definiert: Transformationsprozesse im Boden und Transformationsprozesse an der Oberfläche. Die Tatsache, dass ausschließlich die oberflächlichen Transformationsprozesse in der Lage waren die gemessenen Daten nachzubilden bestätigte Ergebnisse aus der Literatur über die Bildungsprozesse bestimmter TP. Diese Ergebnisse unterstreichen die Bedeutung der Kenntnis von Prozessen, die zur Bildung bestimmter TP führen, für die Modellierung von TP unter gegebenen Umweltbedingungen.

Das Modellierungskonzept aus Studie 1 wurde in der zweiten Studie durch ein konzeptionelles hydrologisches Modell und ein Modul zur Mobilisierung von Substanzen erweitert. Das Modell wurde angewandt um die Parametersensitivität und Modellunsicherheiten bei der Abschätzung von MS- und TP-Konzentrationen, basierend auf einer Monte-Carlo Simulation, zu untersuchen. Die meisten Parameter des Modells waren sensitiv, aber eine Korrelation zwischen Parametern der linearen Isotherme und des Transformationsmoduls verringerte

deren Sensitivität. Weiterhin waren die Parameter für die Ausbringung der MS mit der Halbwertszeit der MS korreliert. Durch die Modellierung eines TP konnte jedoch die Sensitivität des Parameters für die Applikationsmasse erhöht werden. Ein Vergleich der Modellierungsergebnisse mit den Messungen zeigte, dass das Modell in der Lage war die Konzentrationen der MS und eines TP hinreichend nachzubilden, aber trotz großer Unsicherheitsbereiche erfolglos beim zweiten TP war. Es wurde vermutet, dass sich der vorherrschende Transformationsprozess zwischen dem ersten und zweiten Ereignis verändert hatte, was bedeutende Auswirkungen auf das zweite TP hatte, aber in dieser konzeptionellen Modellstruktur nicht berücksichtigt werden konnte. Letztendlich wurde geschlossen, dass die zusätzliche Modellierung eines TP die Gesamtmodellunsicherheit erhöhen kann, aber gleichzeitig auch Parameter dadurch besser konditioniert werden können.

Das Ziel der dritten Studie war die Abschätzung des langjährigen Phosphor- (P) Austrags aus einem mediterranen Einzugsgebiet in Richtung eines stromabwärts gelegenen Reservoirs bei verringerter Messdatenverfügbarkeit. Das dafür entwickelte Modell basiert auf einem flächenverteilten hydrologischen Modell und beinhaltet Erosion und Sedimenttransport, eine Langmuir-Isotherme und Sorptionskinetik für die Modellierung des P-Austrags. Die Parameter der neu implementierten Sorptionsprozesse waren ähnlich sensitiv hinsichtlich des P-Austrags wie die hydrologischen Parameter. Zusätzlich war der anfängliche P-Gehalt des Bodens sehr sensitiv, was die Bedeutung dieser Anfangsbedingung hervorhob. Die erfolgreiche Modellierung für das Studiengebiet ergab, dass der langjährige P-Austrags unter dem regionalen Durchschnitt lag, aber weitere Forschung bezüglich des P-Kreislaufs im Reservoir notwendig ist, welche die Ergebnisse dieser Studie als Randbedingung nutzt.

Um die Eintragspfade von MS und TP in hydrologischen Einzugsgebieten abzuschätzen, wurde das Modell aus Studie 3 in Studie 4 um ein Modul für das Umweltverhalten von Pestiziden und TP erweitert. Das erweiterte Modell wurde erfolgreich für die Simulation von Abfluss und drei Herbiziden mit jeweils einem TP an drei Messstationen in einem kleinen Einzugsgebiet angewandt. Die Annahme von räumlich gleichverteilten Rückständen der Substanzen im Boden vor der aktuellen Ausbringung führte teilweise zu einer Überschätzung der Substanzflüsse während des Basisabflusses. Während die Eintragspfade der MS in dieser Studie wie in der Literatur beschrieben direkt von den Umwelteigenschaften abhingen, war die Situation bei den TP komplexer: TP wurden verzögert gebildet und abgebaut und ihr Umweltverhalten wurde sowohl von ihren eigenen als auch von den physikochemischen Eigenschaften der MS beeinflusst. So wurden TP in höherem Maß durch Drainagen ausgetragen als ihre MS. Schlussendlich konnte mit dieser Studie gezeigt werden, dass MS und TP durch ihre unterschiedlichen Substanzeigenschaften generell unterschiedliche Eintragspfade in Oberflächengewässer haben.

In Studie 5 wurde das für Studie 4 entwickelte Modell angewandt um kritische Austragsflächen für MS und TP unter dem Einfluss 12 verschiedener Kombinationen von Sorptions- und Transformationsparameter in einem kleinen Einzugsgebiet abzuschätzen. Die Resultate zeigten, dass die Substanzeigenschaften einen großen Einfluss auf die Stärke des Austrags und dessen räumliche Verteilung hatten. Der Variationskoeffizient der räumlichen Verteilungen deutete an, dass TP flächenverteilter in die Gerinne eingetragen wurden als ihre MS. Unter Einbeziehung aller Szenarios konnte gezeigt werden, dass die kritischen Austragsflächen zwischen Pestiziden und TP generell unterschiedlich waren.

Die Simulation des Austrags von Agrochemikalien wurde in dieser Arbeit mit einer hohen zeitlichen Auflösung durchgeführt um die hohe Dynamik von Schadstoffereignissen zu erfassen, aber auch um die Abschätzung des langjährigen Austrags von Agrochemikalien zu unterstützen. Ein Effekt der Wahl kurzer Zeitschritte war die hohe Bedeutung der Sorptionskinetik für die Austragsmodellierung. Unter Berücksichtigung aller Studien dieser Arbeit konnten folgende Schlüsse gezogen werden:

- (i) Es ist möglich anhand von aktuellen Modellkonzepten die Entstehung und das Umweltverhalten von TP auf Einzugsgebietsebene dynamisch zu simulieren. Die Auswahl einer bestimmten Modellstruktur sollte anhand einer gründlichen Analyse der beitragenden Umweltprozesse für jede betrachtete Substanz der vonstattengehen.
- (ii) Sensitivitätsanalysen zeigten, dass es notwendig ist, das Zusammenspiel zwischen Transport-, Transfer- und Transformationsprozessen bei der Modellierung des Austrags von Agrochemikalien zu berücksichtigen. Die Modellierung von TP kann die Modellunsicherheit erhöhen, aber kann auch zur Identifizierbarkeit von Modellparametern beitragen.
- (iii) Die Unsicherheit bei der Ausbringung von Agrochemikalien kann sich im Modell ausbreiten da Parameter für die Ausbringung mit der Halbwertszeit der MS korreliert waren. Die Annahme einer gleichverteilten Anfangskonzentration im Boden kann zu Fehlern in der räumlich verteilten Austragsmodellierung führen, was zeigt, dass verbesserte Methoden benötigt werden, diese Anfangsbedingung abzuschätzen.
- (iv) Exportprozesse und kritische Beitragsflächen für den Austrag von Substanzen unterscheiden sich zwischen MS und TP aufgrund des Einflusses des Umweltverhaltens der MS auf das TP und aufgrund des unterschiedlichen Umweltverhaltes beider.

Momentan werden ein Modell auf Feld-Skala und ein Oberflächengewässersmodell für die Abschätzung der Belastung von Wasserressourcen durch Pestizid- und TP-Rückstände im Zulassungsverfahren der E.U. verwendet. Eine Berücksichtigung der Ergebnisse dieser Arbeit würde im Zulassungsverfahren eine umfassendere Risikoanalyse der Pestizidbelastung durch die Einbeziehung des Verhaltens von TP auf Einzugsgebietsebene ermöglichen.

1 Introduction

1.1 Motivation

Agrochemicals such as fertilizers and pesticides have been applied for a long time in agricultural areas in order to enhance plant growth and increase crop yields. Thus, these substances contribute to the well-being of mankind by enhancing food-production for a rising population (Carvalho, 2006). However, once in the environment, agrochemicals may be transported from their application point towards groundwater resources, rivers and receiving waters such as lakes, lagoons and reservoirs. They may contribute to eutrophication (e.g. Conley et al., 2009) or may be toxic for non-target organisms by acute (Cold and Forbes, 2004) or chronic (Silva et al., 2006) exposure. In case of pesticides, incomplete degradation and thus transformation into other substances is rather the rule than exception. The emerging transformation products (TPs) may be similar or even more toxic than their parent compounds (Figure 1). While the appearance of nutrients and pesticides in surface water bodies was well documented during previous decades (Schulz, 2004, Alvarez-Cobelas et al., 2009), evidence for TPs in rivers is only recently being accumulated (Rebich et al., 2004, Huntscha et al., 2008). Therefore, TPs of pesticides may be referred to as relevant emerging contaminants in the environment (Kümmerer, 2010).

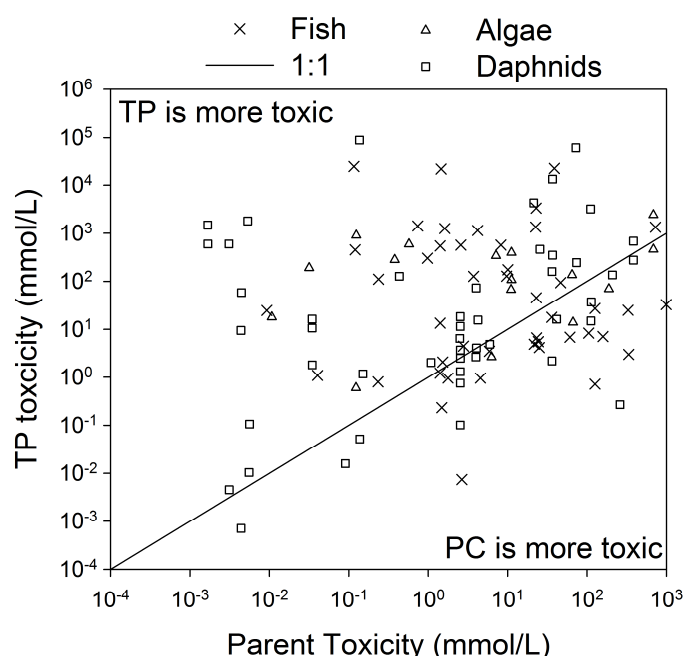


Figure 1: Quotients between acute toxicities (LD50 and EC50) of transformation products (TP) and parent compounds (PC) for various pesticides and toxicity end points (modified from Boxall et al., 2004).

The main focus of the management of water resources under pollution risk by agrochemicals is on the protection of aquatic ecosystems and on the sustainable use of water resources (Carter, 2000). However, the management of non-point source agrochemical pollution is more difficult than the management of water quantity since the number of required sampling parameters is much higher and the estimation of substance fluxes is more complex (Biswas and Tortajada, 2010). Still, the assessment of the impact of distinct agrochemical usage and land management practices on water resources prior to application is crucial for water resources management (Reichenberger et al., 2007). A method to assess the quantity of agrochemical contamination in hydrological catchments is the application of non-point source export models, based on hydrological modelling (Borah and Bera, 2003). Since process knowledge from experimental studies constantly increases, current environmental models need to be refined and further developed (Schwarzenbach, 2006), including both environmental fate processes (EFPs) of agrochemicals as well as hydrological processes (Radcliffe et al., 2009). Consequently, in order to contribute to an adaptation of water resources management to relevant emerging contaminants in the water cycle, the environmental fate of these substances should also be included in non-point source models.

1.2 Environmental fate processes of agrochemicals

Being anthropogenic substances, the environmental fate of agrochemicals starts from application onto agricultural fields. Substance fate in the environment is affected by chemical, physical, biological and hydro-meteorological processes in soil, water and air (Gavrilescu, 2005). These processes can be separated into transport processes, transformation processes and transfer processes (Figure 2).

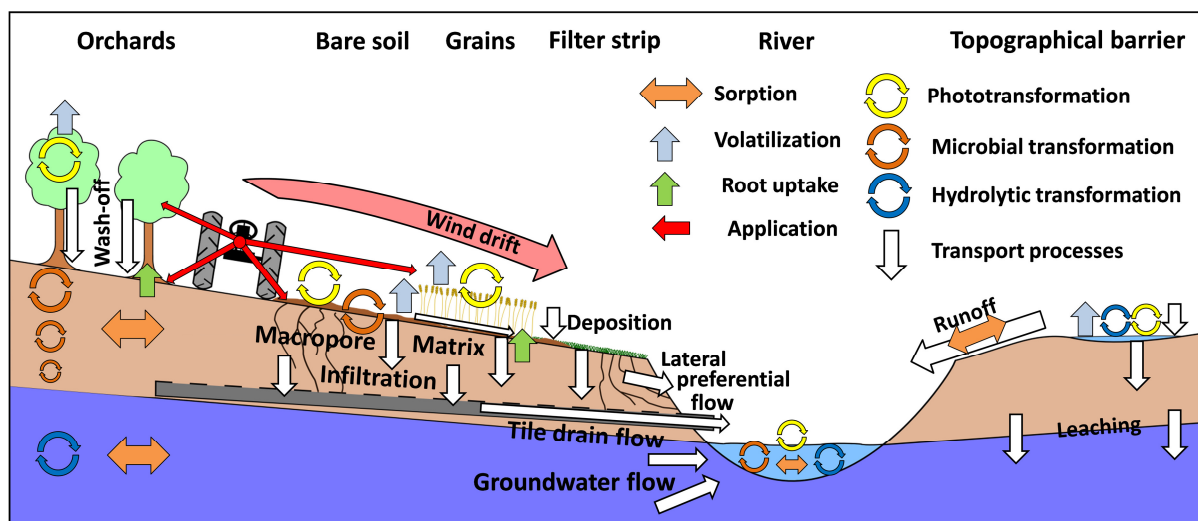


Figure 2: Transport, transfer and transformation processes of agrochemicals in the environment.

Transport processes refer to the translocation of substances away from their application point. In the environment, the main transport media are air and water. At the field and catchment scale, wind drift of pollutants was found to contaminate non-target areas during pesticide application (Lefrancq et al., 2013). Atmospheric transport processes in the gaseous phase or attached to aerosols are especially important at the global scale for long-range transport to remote areas such as the Arctic (Scheringer, 2009). In water, agrochemicals can be transported in dissolved form or attached to soil particles (Hladik et al., 2009). They may enter rivers via point or diffuse sources. Diffuse sources are the most important input pathways in agricultural areas. Point sources are less important but may also occur e.g. by farmyard runoff or rainwater sewer inflow (Neumann et al., 2002). Among diffuse sources, a variety of hydrological processes are able to mobilize agrochemicals. After application, agrochemicals may be washed off of plants to the soil surface by rainfall (Wauchope et al., 2004). Surface runoff was shown to be a major pathway for river contamination by agrochemicals (Schulz, 2001) and especially the first rainfall-runoff events after pesticide application are able to mobilize large amounts (Shipitalo and Owens, 2003). Leaching of pollutants may contaminate groundwater (Djodjic et al., 2004, Fava et al., 2005). In baseflow, the concentrations of pesticides were found to be lower than the concentrations of their TPs (Kalkhoff et al., 2003). Preferential transport of agrochemicals in soils may also be an important source of freshwater contamination, especially in combination with tile drains (Stamm et al., 1998, Zehe and Flühler, 2001, Kahl et al., 2008), which may act as short-cuts for the transport of agrochemicals towards surface waters (Doppler et al., 2012).

Transfer processes control the distribution of pesticides and TP between environmental compartments like plant, water, soil and air. Volatilization is the direct evaporation of an organic compound, which is only seen important if its rate is faster than water evaporation (Mackay and Yuen, 1980). Plant uptake via roots is the primary goal of applying nutrients at agricultural fields. However, pesticides can also be uptaken via leaves, which results in potentially harmful food concentrations (Conacher and Mes, 1993). Sorption is the process by which agrochemicals are bound to or released from soil particles. It is influenced by soil texture, soil particle size distribution, soil moisture, soil organic carbon, pH and temperature (Wauchope et al., 2002) and can be responsible for a delayed and lowered substance peak concentration in water (retardation). Sorption can be characterized by a relationship between soil organic carbon and sorption strength for many substances (Gerstl, 1990). For some substances, such as the herbicide Glyphosate, sorption to clay minerals plays an important role (Vereecken, 2005). Sorption is a kinetic process, meaning that the sorption equilibrium is not reached instantly. It consists of two stages: a fast kinetic reaction is followed by a slow reaction, resulting from diffusion into soil aggregates (Boesten and van der Pas, 1988). Especially desorption kinetics was identified as limiting factor for the export

of agrochemicals by overland flow (Gouy et al., 1999). Additionally, the hysteresis between the adsorption and desorption isotherm may be partially explained by sorption kinetics (Limousin et al., 2007).

Transformation processes change the molecule of an agrochemical. Usually, the term 'transformation' is applied to organic chemicals such as pesticides. The resulting transformation products may be more mobile in the environment and more persistent to degradation (Boxall et al., 2004). If an organic molecule is degraded in a way that only CO₂, water and minerals are left, the complete process is called mineralization. The most common transformation processes in the environment are photolysis, microbial degradation and hydrolysis. Microbial degradation is the breakdown of molecules to smaller products by bacteria (Aislabie and Lloyd-Jones, 1995). The highest amount of bacteria in soil can be found near the surface, decreasing non-linearly with depth (Susyan et al., 2006, Tate III, 1979), resulting in slower degradation in the subsoil (Rodríguez-Cruz et al., 2006). If a substance is exposed to sunlight at the soil or plant surface, photodegradation may break molecule bonds. The amount of photodegradation is dependent on the intensity and the spectrum of the sunlight (Katagi, 2004). Thus, photodegradation in the environment varies throughout the year and with latitude (Zepp and Cline, 1977). During hydrolysis, a molecule reacts with water. Besides molecular characteristics, pH is the main driver for hydrolysis (Gavrilescu, 2005). Generally, each transformation process results in the formation of distinct transformation products (Racke, 1993, Roberts et al., 1999).

In the environment, above mentioned transport, transfer and transformation processes determine the fate and behaviour of agrochemicals by interaction with each other. Transfer and transformation processes are dependent on intrinsic physico-chemical characteristics of the substances and affect transport processes (Tang et al., 2012). Higher sorption reduces the leaching of chemicals to deeper soil layers, groundwater or tile drains (Brown and van Beinum, 2009). It is supposed to reduce removal by overland flow but increases the fluxes of chemicals adsorbed to eroded sediment. The transport of agrochemicals in preferential flow pathways reduces the influence of sorption by bypassing the soil matrix (Singh et al., 2002). Still, sorption even occurs during fast transport in macropores or in preferential flow pathways, especially in small macropores (Jarvis, 2007). Faster transformation reduces the amount of pesticides available for export towards rivers but favours the fast formation of transformation products. High persistence may lead to accumulation of pesticides and their TPs, even in remote areas of the world such as the Arctic (e.g. Weber et al., 2010).

1.3 Conceptualizations of environmental fate processes

Since environmental processes are complex, not fully understood or too comprehensive to be mathematically described, model conceptualizations are always simplifications. They result from the modellers' choice of the representing equations and the importance of single processes for the purpose of the model (Petit et al., 1995, Arhonditsis et al., 2008). Due to the importance of overland flow for agrochemical mobilization, the interaction between overland flow and the surface soil gained much attention for model development of the environmental fate of agrochemicals in the past. The main concept is that applied agrochemicals reach a thin upper soil layer where they can interact with surface runoff by sorption processes (McGrath et al., 2010) or erosion. This soil layer was often called mixing layer and was found to be in the range of mm to cm (Ahuja et al., 1981). Interactions between soil-bound residues and the dissolved phase are expressed by sorption kinetics and three main types of sorption isotherms in the literature (Figure 3a): a linear isotherm, a non-linear Freundlich isotherm and a Langmuir isotherm, which considers a maximum adsorbed concentration (Appelo and Postma, 2005). From experimental studies, a Langmuir isotherm was found to be applicable to phosphorus (P) sorption (House et al., 1995) and the Freundlich isotherm for many pesticides (Baskaran and Kennedy, 1999). However, due to its simplicity, the linear isotherm is often used in environmental modelling (Wauchope et al., 2002). Conceptualizations of sorption kinetics include non-linear relationships with time such as a first-order rate equation (Azizian, 2004) or Elovich equation (House et al., 1995). Generally, it can be assumed that adsorbed and dissolved agrochemicals are not in equilibrium in the environment due to e.g. mixing processes or sediment settling/erosion and sorption kinetics. Thus, from the sum of the given adsorbed and dissolved concentration and the suspended sediment concentration, the equilibrium concentration has to be determined. While this is possible for a linear and a Langmuir isotherm, the Freundlich isotherm cannot be solved analytically (Frolkovič and Kačur, 2006). Hence, for the solution of the Freundlich isotherm, numerical methods have to be applied.

In the literature, degradation of agrochemicals in the environment is solely calculated by first-order kinetics. It is assumed that there is a predominant transformation process in each environmental compartment. Thus, model parameterization lumps different degradation processes (microbial degradation, photolysis, hydrolysis) into environmental compartments such as plant or soil degradation (e.g. Knisel, 1980, Neitsch et al., 2010). For the formation of TPs, a formation fraction (Fenner et al., 2009) of the degraded mass of the PC is considered to build the mass of the TP. This formation fraction includes the change of the molecular mass of the TP compared to the PC, the possibility of the formation of multiple TPs and the fraction of complete mineralization of the PC (Kern et al., 2011).

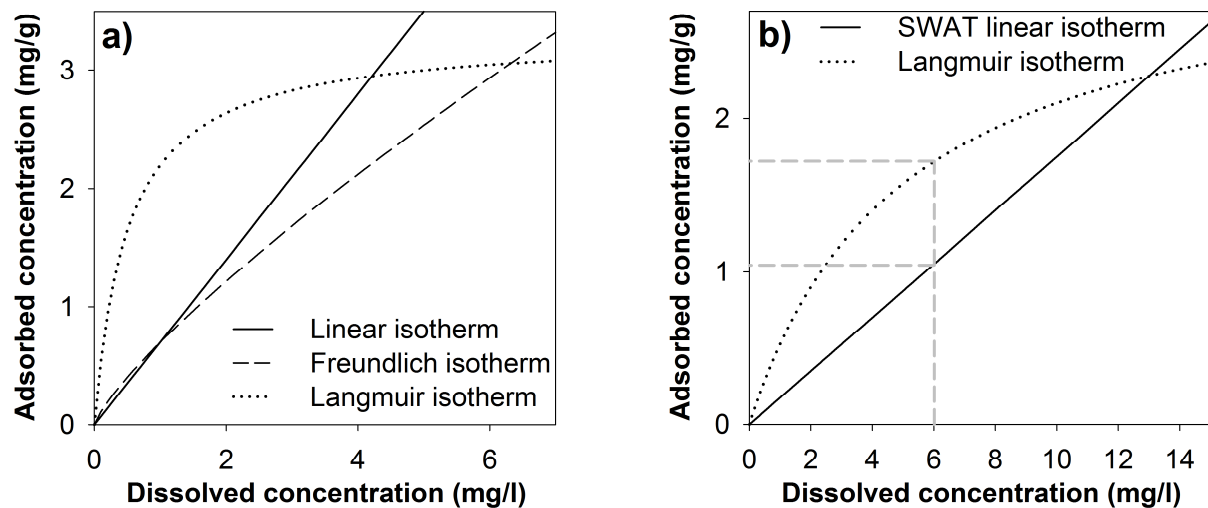


Figure 3: a) Comparison of typical conceptualizations of sorption equilibrium. b) SWAT model standard linear isotherm and site-specific Langmuir isotherm for phosphorus sorption (data from Rossi et al., 2012).

1.4 Existing models for agrochemical fate assessment at catchment scale

For the quantitative modelling of agrochemical fate and export from hydrological catchments, a variety of process-based deterministic models have been applied in the past, depending on physico-chemical properties of substances and based on water fluxes including HSPF (Laroche et al., 1996), SWAT (Kannan et al., 2006, Fohrer et al., 2013), AnnAGNPS (Flanagan et al., 2008), CATFLOW (Zehe et al., 2001) or the OECD method (Dabrowski et al., 2002). Empirical models such as export coefficient models (Johnes, 1996) and models relating catchment properties (e.g. slope, catchment size or fraction of agricultural fields) to sampled concentrations were additionally applied for nutrients, mainly nitrogen and phosphorus (Ekholm et al., 2000). Due to neglecting fate processes such as sorption and transformation, empirical models are useful for the assessment of total substance export for long periods of time rather than studying environmental fate. Process-based models can be differentiated by their spatial representation: Conceptual models neglect spatial variability but consider fate and transport processes. They are able to estimate concentrations of substances with different environmental fate characteristics at the outlet of small catchments (Berenzen et al., 2005). Spatially distributed models consider the variability of contributing areas in catchments. By using gravity-driven overland flow routing, they may reproduce catchment connectivity realistically and thus are useful for the delineation of critical source areas for agrochemical export (Frey et al., 2009).

1.5 Uncertainty in agrochemical fate modelling

One of the main challenges during the application of environmental fate models is the determination of fate parameter values. The more detailed an approach, the more parameters are left for calibration (Dean et al., 2009). Especially for pesticide fate modelling the sampled ranges of half-lives and sorption coefficients are wide, since different studies were carried out under different environmental conditions (Wauchope et al., 2002). The other extreme also frequently occurs. Since there are thousands of pesticides on the market, for some substances, and especially for TPs, there is often no experimental data available (PPDB, 2009). Therefore, estimation methods for fate parameters, based on the molecule structure, gain importance (Meylan et al., 1992, US-EPA, 2009). However, the reliability of the predictions of these approaches has been criticised (Gouin, 2004). Overall, the choice of fate parameters is highly uncertain in agrochemical fate modelling. Furthermore, model structural uncertainty may result from a wrong choice of mathematical process representations or the choice of processes implemented in the model (Dubus et al., 2003b). An example would be the choice of a wrong sorption isotherm, resulting in over- or underestimation of the sorption equilibrium (Figure 3 b).

2 Research gaps

The rapid growth of knowledge about EFPs of agrochemicals makes it difficult to keep current models up-to-date. This is why there have been occasional attempts to extend the computer code of models for special purposes (e.g. Holvoet et al., 2008, Gevaert et al., 2008). One still unaddressed issue is related to the modelling of sorption at catchment scale: most models use a linear isotherm for all agrochemicals, whereas experimental studies suggest the use of non-linear approaches. Additionally, the calculation of sorption kinetics is often neglected, especially for pesticide fate modelling. A major unresolved issue concerns transformation processes: field and laboratory study results induce the need for assessment tools of TP formation, fate and behaviour in the environment. Up until now, the modelling of the formation and fate of TPs has solely been addressed in pesticide leaching models at the field scale (Fox et al., 2007, Rosenbom et al., 2009) and in global scale box models (Schenker et al., 2007, Fenner et al., 2000). Although hydrological catchments influence the water quality of receiving waters largely (Schindler, 2006) and conceptualizations of transformation processes are available (Fenner et al., 2009), the assessment of TP fate and export has not yet been incorporated in catchment scale models.

The information about the total agrochemical river export may be most important for water quality management in river basins. However, the knowledge about the distinct EFPs contributing to diffuse substance export might help to improve the management of agrochemical residues in the environment (Tang et al., 2012). Using process-based models provides a possibility to estimate the quantity of each contributing transport process as influenced by physico-chemical substance characteristics. Still, most modelling studies have only focused on the total export of agrochemicals at the catchment outlet in the past (e.g. Brown et al., 2002, Ficklin et al., 2012). Especially the potential differences of physico-chemical characteristics between PCs and TPs imply that the transport processes contributing to their export may be different, which has not yet been investigated, either by experimental or by modelling methods.

Environmental fate modelling of agrochemicals is burdened by uncertainties associated with the choice of model parameters, the model structure and the input data such as agrochemical application and initial soil concentrations (Dubus et al., 2003b, Dean et al., 2009, Fohrer et al., 2013). Nevertheless, although uncertainty estimates might result in more reasonable environmental model predictions (Hartmann et al., 2012), the number of studies considering uncertainty in agrochemical modelling is still low. Especially the uncertainty of TP modelling, which may be affected by uncertainties of the modelling of its PC and of the underlying transport model, has not been addressed at all.

3 Research questions and thesis structure

Experimental evidence of agrochemical TPs in rivers and the knowledge about the toxicity of a variety of TPs lead to the necessity for new modelling tools, which are able to assess the fate and behaviour of pesticides and TPs at catchment scale. Thus, the main topic of this thesis is the implementation of the formation and environmental fate of TPs of pesticides into catchment scale hydrological models, using process conceptualizations from the literature. Besides transformation processes, more detailed approaches for the estimation of sorption equilibrium and sorption kinetics are implemented and tested for their relevance at catchment scale. Newly developed models will be evaluated regarding their ability to reproduce river sampling data and to give information about export processes contributing to agrochemical release from catchments. Thus, in contrast to current models, the new developments may help water managers to assess the hazard for receiving waters resulting from the transformation of agrochemicals in agricultural catchments. Furthermore, the assessment of transport processes contributing to agrochemical export in this thesis may be used to identify best agricultural management practices for specific catchments. Related to the overall aim, the following research questions are asked in the course of this thesis:

- (i) Is it possible to implement the dynamic formation and fate of pesticide TPs in catchment scale agrochemical export models using current conceptualizations from the literature? Which model complexity is needed?
- (ii) What is the role of environmental fate parameters for agrochemical export modelling? What are the consequences of TP modelling for model uncertainty?
- (iii) Which are the most important boundary and initial conditions for modelling of agrochemical fate and what uncertainties may be associated with their parameterization?
- (iv) Is it possible to estimate the influence of physico-chemical substance characteristics on the export pathways of agrochemicals from catchments? Are there differences in the export pathways of pesticides and their TPs from hydrological catchments?

Chapter 4 introduces the model structures and EFPs implemented in the models of the different studies of this thesis. In chapters 5-8, achieved research is presented by short descriptions of manuscripts, which are published or accepted for publication in peer-reviewed journals. In chapter 9, a further study is presented, which is not intended for publication in a scientific journal. The contributions of the presented studies to the research questions of this thesis are discussed in chapter 10 and an outlook is given pointing to future research directions (chapter 11). For the most detailed and complex model (ZIN-AgriTra), developed and used in studies 3-5, a manual can be found in Appendix A1.

4 Implemented environmental fate conceptualizations and model structures

In chapters 5-9 modelling tools with different model structures and implementations of transport, transfer and transformation processes and their interplay are developed and applied to answer specific research questions. An overview of the specific implementations (Table 1) is given in the following.

Transfer: Among transfer processes sorption was implemented in the models of this thesis with different complexity. In studies 1 and 2 the linear sorption was not calculated based on concentrations but based on interplay between the fraction of effective rainfall and insecticide mass in the field. Strictly speaking, the approach is not an isotherm but rather an immobilization coefficient, parameterized by the organic carbon sorption coefficient. For phosphorus fate a Langmuir isotherm was used in study 3, since it was repeatedly shown that it could be fitted better to experimental phosphorus sorption data than the often used linear type. It would also have been preferable to implement a non-linear Freundlich isotherm for pesticide sorption instead of the linear type in studies 4 and 5, but the missing analytical solution of the Freundlich isotherm would have led to a computationally intensive numerical solution; therefore, a linear isotherm was used instead. Sorption kinetics was implemented in the process-based models of studies 3-5 by a pseudo first-order equation in order to take the effect of possibly short contact times between water and soil particles into account. In studies 1-2 instantaneous sorption equilibrium was assumed.

Transformation: Transformation was conceptualized by first-order decay in combination with formation fractions in all pesticide modelling studies. In studies 1 and 2 one transformation process was considered for each substance, neglecting differences of transformation processes in different environmental compartments such as plant surface or soil. In studies 4 and 5 a non-linear decrease of the first-order transformation rate with soil depth was considered, taking a decreasing microbial activity into account. Transformation in the mixing layer of the latter studies is supposed to include both phototransformation and microbial transformation in the first centimetres of the soil. In study 3 transition between phosphorus fractions may also be seen as transformation and is restricted to the soil.

Transport: Except in the first study, where transport was not considered, water was the only transport medium for agrochemicals in this thesis. A conceptual hydrological model with linear storages for overland flow, interflow and baseflow was used in the second study, but it was assumed that substances were mobilized by overland flow only. In the process-based model of study 3 transport in the soil matrix was considered besides export by overland flow

in order to simulate baseflow concentrations of dissolved phosphorus. Additionally, erosion and sediment transport were included to allow for particulate phosphorus export from the catchment. In the last two studies the subsurface transport of substances was realized by a dual-porosity model of macropores and soil matrix. This enabled the fast export of substances towards tile drains, transport by water in the soil matrix and in overland flow. While surface runoff was implemented by linear storage outflow in study 2, the process-based models used a distributed kinematic or diffusive wave approach based on surface elevation. Therefore, these models were able to consider catchment connectivity and thus a more realistic simulation of contributing areas.

Spatio-temporal resolution: The choice of timesteps and the spatial representation were adapted to the size of the considered catchment, the data availability and the research question in each study. Few samples were available at four sampling stations for the first flush event in the large-scale catchment of study 1. A lumped approach was chosen and event mean values were considered sufficient to give information about the processes leading to the emergence of specific TPs in the region. A different way was chosen to deal with data scarcity in study 3. A process-based model was supposed to result in relatively stable predictions of phosphorus export fluxes and the short timestep (1h) was chosen in order to enable a comparison of model results to discontinuous sampling data. Methods for the estimation of uncertainty in the modelling of timeseries often require a large amount of model runs. Thus, a lumped, conceptual model structure with short computations times was used in study 2. The determination of agrochemical and TP export pathways and their temporal change in a headwater catchment (study 4) required a high temporal resolution and a process-based model. The importance of catchment connectivity and an additional assessment of critical source areas were the reasons for the chosen high spatial resolution of the models in studies 4 and 5.

Table 1: Overview of implemented environmental fate conceptualizations, data availability and model structures in the five studies of this thesis (A_{catch} - catchment area).

Study	A_{catch} (km ²)	Spatial resolution	Time step	Transport model	Sorption isotherm	Sorption kinetics	Trans- formation	Data availability
1	613	Lumped	Event	none	Linear ¹	No	First-order	Medium
2	64	Lumped	1 h	Conceptual	Linear ¹	No	First-order	Medium
3	37	80m x 80m	1 h	Process-based	Langmuir	First-order	First-order ²	Low
4	2	10m x 10m	10 min	Process-based	Linear	First-order	First-order	High
5	2	10m x 10m	10 min	Process-based	Linear	First-order	First-order	High

¹based on substance mass and effective rainfall; ²between phosphorus fractions

5 Summary of study 1: Fate of pesticides and their transformation products during a First Flush event

Olsson, O., Khodorkovsky, M., Gassmann, M., Friedler, E., Schneider, M., Dubowski, Y. (2013). Fate of pesticides and their transformation products: First Flush effects in a semi-arid catchment. Clean-Soil Air Water 41 (2), 134–142.

5.1 Introduction

Following application, pesticides are usually not fully degraded but rather transformed into TPs. The TPs may be more stable, more mobile and even more toxic than their parent compounds. There is increasing evidence that TPs are transported to rivers in high concentrations. The formation of each single TP depends on the transformation processes working on the parent compound (e.g. microbial degradation or photodegradation). In semi-arid regions, agricultural chemicals may accumulate on the field in the long, dry summer time and are washed off during the first rainfall events in autumn. This effect is commonly called the first flush effect. Since the dry time spreads over several months, the time for the formation of TPs is long and thus the first flush may be under risk of delivering a large quantity of TPs in river water. The aim of this study was to assess the possible thread of insecticides and TPs for surface water resources during the first flush in a Mediterranean catchment and to assess the processes contributing to the formation of TPs prior to the first flush.

5.2 Methods

The catchment under investigation of this study was the Hula basin, which is a part of the Upper Jordan River basin in Northern Israel. Due to relatively high amounts of rainfall and fertile soils, the Hula Valley is under heavy agricultural use. A sampling campaign was set up in order to catch the response of the catchment to the first significant rainfall. Four sampling points were investigated: the inlet and the outlet of the valley, one artificial channel collecting drainage water from the agricultural fields and one tributary collecting water from the Golan Heights and from fields in the Hula Valley (Kalil River). The substances under investigation were the insecticide Chlorpyrifos (CP) with its TPs Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP) and the insecticide Endosulfan with TP Endosulfan Sulfate (ES). Under environmental conditions, CP may be transformed into TCP and CPO while CPO can also be transformed into TCP. Endosulfan consists of the two isomers α -Endosulfan (aE) and β -Endosulfan (bE), which may both be transformed into ES.

In order to assess the predominating transformation process before the event, a parsimonious modelling tool was developed to estimate relative substance concentrations of CP residues in the river. It consisted of relative mass storages of substances connected by their transformation scheme. Transformation kinetics of the substances was calculated by a first-order approach. Sorption was included in the model in the same way as it was used in the pesticide release equation of the OECD (Organisation for Economic Co-operation and Development), assuming a linear sorption isotherm and instantaneous equilibrium. The model was set up using environmental fate parameter values from the literature. The predominating transformation process was investigated by comparing model runs with different parameter sets (soil or surface transformation) to the sampling results. Although the model was independent of the actual pesticide application mass, it required the time of application as input. Since knowledge about this point in time was limited, it was used as the only calibration parameter.

5.3 Results and Discussion

During the first flush event, all investigated CP residues could be detected in river water of the Hula basin. CPO and CP were found in similar high concentrations at the catchment outlet whereas TCP was significantly lower. In the Kalil River, CPO was the dominating substance and TCP the lowest. At the inlet and in the drainage channel, no CP could be detected but > 80% CPO. Of the Endosulfan residues, aE was the major compound and bE was not detected at all. ES was detected only in the Kalil River but in high concentrations. Only aE could be found at the inlet to the Hula Basin in the drainage channel. No Endosulfan residues were identified at the catchment outlet. The flushing nature of the event could be seen by the fact that discharge only increased about 20-30% but was accompanied by a huge rise in pollutant concentrations.

The results of the model investigation suggested predominantly TCP and CP in river water for the soil transformation scheme and CPO and CP for the surface transformation scheme. Comparing these results to sampling data showed that surface transformation processes were able to reproduce the general distribution of CP and its TPs in river water. This is in accordance with experimental studies, showing that CPO can be formed via photo-oxidation of CP on the soil surface. Since only TPs of CP were found at the catchment inlet but also the parent compound at the outlet, CP was applied much closer to the event in the Hula basin than in the catchment above. This assumption was supported by the fact that the approximate time of application was calibrated to have a mean of 10 days before the event in the basin using the surface model.

5.4 Conclusions

The Hula Basin is both, an agricultural area and an important source of freshwater for Israel. In this study we could show that the first rainfall event after the long dry time was able to flush large amounts of insecticides and TPs to the rivers of the Hula Basin. Modelling and sampling results suggested that surface transformation processes prevailed prior to the event and formed a huge amount of TPs. Since investigated substances have adverse effects on human and environmental health, awareness of the capability of the first flush events to mobilize substances is important for pesticide monitoring campaigns. Further sampling is suggested to get more representative information about the impact of the first flush event and surface transformation processes on the export of substances in river water of Mediterranean regions.

6 Summary of study 2: Uncertainty during the export modelling of pesticides and transformation products

Gassmann, M., Khodorkovsky M., Friedler, E., Dubowski, Y., Olsson, O. (2014). *Uncertainty in the river export modelling of pesticides and transformation products. Environmental Modelling and Software* 51, 35-44.

6.1 Introduction

Current catchment scale models for environmental fate assessment of pesticides consider pesticides to be completely degraded and thus neglect the formation and fate of TPs. The main concepts implemented in such models consider reversible adsorption of pesticides to soil particles and degradation in different environmental compartments such as soil, plant or water. Implementing TPs in modelling would result in an increased data demand and higher complexity of the model structure. A major difficulty in modelling pesticides and TPs in the environment is the determination of model parameters, since either experimental ranges are wide or no data is available at all. Therefore, the uncertainty in the choice of model parameters results in uncertain model predictions. Additionally, the setup of boundary conditions for pesticide fate modelling at catchment scale may raise model uncertainty by uncertain pesticide application data or incorrect hydrological modelling. In this study, we investigated above mentioned uncertainty in a parsimonious conceptual model for the assessment of discharge and river concentrations of an insecticide and two of its TPs by Global Sensitivity Analysis (GSA) and the Generalized Likelihood Uncertainty Estimation (GLUE) method in an agricultural catchment located in Northern Israel.

6.2 Methods

The organic chemicals in focus of this study were the insecticide Chlorpyrifos (CP) and two of its TPs, Chlorpyrifos Oxon (CPO) and 3,5,6-trichloro-2-pyridinol (TCP). CP can be transformed into TCP in soil and CPO at the surface and CPO can further be transformed into TCP. While information could be gathered for half-lives and sorption parameters, the formation fractions – the fraction of the degraded pesticides appearing to be the TP – were largely unknown. The hydrological model formulated in this study followed local hydrological process understanding and was implemented as a combination of linear reservoirs. For the chemical modelling, it was differentiated between a module for pesticide transformation and a module for substance mobilization. Transformation was implemented according to the transformation scheme explained above. Mobilization was calculated by an equation using the runoff coefficient, the fraction of agricultural area contributing to export, a rainfall

threshold value for mobilization and a linear sorption isotherm. Since information about pesticide application was uncertain, we introduced two parameters regulating the application timing and amount. The model was run in a warm-up phase of about one year and was evaluated in a timespan of about six weeks with two significant rainfall events.

Both, GSA and GLUE need the specification of parameter ranges, a strategy for sampling the parameter space, an informal likelihood measure (ILM) and a behavioural model threshold. Parameter ranges were derived by literature review or prior analysis. Parameters values were uniformly distributed within these ranges, in order to derive prior parameter distributions, which were sampled by the Monte-Carlo sampling method. As an ILM, we chose the Nash-Sutcliffe efficiency for single time series or in a multi-objective way, including discharge and substance concentration time series with equal weights. The behavioural model threshold was not chosen a priori but by analysing parameter sensitivity for different thresholds. The sensitivity of parameters in the GSA is expressed by differences between prior and posterior parameter distributions for behavioural models. The GLUE method is based upon the equifinality assumption, and results in time series of prediction bounds, which can be interpreted as a representation of model uncertainty.

6.3 Results and Discussion

Parameter sensitivity revealed that the majority of parameters were sensitive with increasing sensitivity for increasing threshold values of some parameters. The threshold value with the first considerable rise in sensitivity was taken as behavioural model threshold for further analysis. Sorption parameters gained sensitivity only for the best models, which could be related to the relatively narrow ranges of these parameters. Among transformation parameters, TCP had the most sensitive formation fraction and half-life. For the behavioural models a correlation matrix of environmental fate parameters revealed that transformation and sorption parameters were correlated, showing the dependence of the modelling concepts of both fate processes. Within the transformation conceptualization, formation fractions, introduced by the modelling of environmental fate of TPs, and degradation parameters were correlated. Sequentially adding time series for model evaluation showed that the pesticide application mass parameter became more sensitive by adding the TCP time series to the calculation of the ILM. Additionally, the temporal shift and the application mass parameter were both negatively correlated to the degradation half-life of CP, indicating that erroneous application assumptions may be compensated by the choice of the CP half-life to some extent.

Model results were evaluated for the ability of the model to simulate each time series separately and by consecutively adding constraining time series. The number of behavioural

models decreased markedly by addition of TPs to the model evaluation. TCP had the lowest efficiency in single calibration. Considering the high sensitivity of TCP transformation parameters and the TCP-caused increased identifiability of pesticide application, this shows that the well-defined TCP model had the largest share in constraining the model parameters.

Model uncertainty expressed by the GLUE prediction ranges showed that the model was largely able to reproduce sampled values during the first event but experienced problems in the second event, especially for CPO calculations. The overall uncertainty was largest for CPO and lowest for TCP. Additionally, CPO export was largely overestimated in the second event, which pointed towards a structural deficit of the model. It is likely that the predominating transformation process changed during the first event from surface to soil transformation, which would explain the low sampled CPO concentrations after the first event. This conceptual model structure only allowed for the parameterization of one transformation process and was thus not able to consider this change. The lower uncertainty in combination with the lowest ILM of TCP showed that the poorer predictions of TCP were less uncertain than the predictions of the other substances with higher ILM. Combining load and concentration uncertainties showed that the uncertainty of the hydrological model had an effect on substance uncertainty in the second event.

6.4 Conclusions

By applying sensitivity analysis and uncertainty estimation to a conceptual model for pesticide and TP export, we could show that the parameters of current environmental fate conceptualizations for sorption and transformation estimation were correlated to each other, resulting in parameters which were only sensitive for the best models. The timing and mass of pesticide application was correlated to the half-life of the pesticide in this study, indicating that a wrong application setup may be compensated by the parameterization of pesticide degradation. However, the modelling of the TP TCP increased the identifiability of the pesticide application mass. Due to a structural error, the modelling of the second TP, CPO, failed. Still, the successful modelling of TCP showed that a specific model structure may be applicable for specific TPs only. We recommend using a parsimonious conceptual model like this only in cases where the same transformation process dominates the whole timespan.

7 Summary of study 3: Estimation of phosphorus export from a Mediterranean catchment with scarce data

Gassmann, M., Brito, D., Olsson, O., (accepted). Estimation of phosphorus export from a Mediterranean agricultural catchment with scarce data. Accepted for publication in 'Hydrological Sciences Journal'.

7.1 Introduction

The solution to water quality problems of receiving waters like lakes, reservoirs or lagoons is often to be found in their catchments. Diffuse contaminant sources from agricultural areas may account for a major proportion of nutrient input such as phosphorus (P), which is a minimum-factor for primary production and thus a catalyst for algae bloom in the aquatic environment. If only short and discontinuous sampling data is available in a catchment, process-based models, along with methods for prediction in ungauged basins and soft data, may help to gain knowledge about the longterm export of nutrients. Currently applied models for P export from catchments run at a daily time step, which may result in problems in small catchments with runoff response to rainfall in the order of a few hours. Since P is a highly sorptive substance, the representation of sorption is a central question in P export modelling. Former approaches all followed a linear sorption isotherm, although a Langmuir isotherm was fitted repeatedly in experimental studies, considering a maximum sorption capacity of soil particles. In this study, we present a method for estimating longterm phosphorus export under data scarce conditions. For this purpose, we applied a physically-based model in combination with scarce sampling data in the small Mediterranean Enxoe catchment, feeding a reservoir, which suffered from Cyanobacteria bloom in the past.

7.2 Methods

The river water of the Enxoe catchment was not sampled for nutrients in the past. Thus, in addition to weekly grab samples in two tributaries forming the main Enxoe River, we installed an automatic sampler during eight rainfall-runoff events in 2010-2011. Samples were analysed for suspended sediment concentration (SSC), dissolved phosphorus (DP) and particulate phosphorus (PP) concentrations. However, discharge measurements could not be taken. Hence, for hydrological model calibration, we used discharge data from neighbouring catchments and freely available hourly rainfall data.

The model applied in this study (Zin-Sed 2D) is a process-based deterministic model, running at an hourly time step, which is able to simulate hydrology, erosion/sediment transport and phosphorus export at the catchment scale. Hydrological components include Green and

Ampt infiltration, Richards equation for unsaturated flow, the Mualem - van Genuchten equation for unsaturated hydraulic conductivity and a diffusive wave two-dimensional overland flow routing. Potential evapotranspiration was calculated by the FAO crop evapotranspiration method and lowered by a relationship with relative soil moisture. Erosion was calculated as rainfall erosion and erosion by flowing water, using a shear stress approach. P cycling in the soil was taken from the SWAT model. Initial soil P content was supposed to decrease non-linearly with soil depth. In contrast to existing models, sorption was calculated using a Langmuir isotherm instead of the linear approach. Additionally, we included sorption kinetics by a first-order approach and different rate constants for adsorption and desorption.

For the longterm export estimation of P towards the Enxoe reservoir, we performed a model run from the year 2001 to 2011. In order to get information about the influence of single model parameters on model outputs, a regional sensitivity analysis was performed. For the calibration of the hydrological model we applied a method for regionalisation of flow duration curves (FDCs), using discharge data of neighbouring catchments in order to derive a FDC for the Enxoe catchment. Since FDCs contain no information about temporal distributions, we additionally compared our results to seasonal Pardé coefficients of the available catchments. A further hydrological model evaluation was done by comparison of the modelled longterm water balance to surrounding catchments. The performance of water quality modules was examined by comparing sampled and modelled event mean concentrations of DP, PP and SSC. Additionally, we compared DP estimations with baseflow samples in the two tributaries. A discussion of our results regarding soft data from the literature was done in order to confirm the plausibility of the model setup.

7.3 Results

The sensitivity analysis revealed that the initial soil P content and the Langmuir parameters were the most influencing factors for DP modelling. PP export was controlled by soil depth, erosion parameters and the initial soil P content. All water quality model results were highly sensitive to changes in hydrological model parameters. The modelled and the regionalized FDCs were close, expressed by a high Nash-Sutcliffe efficiency. The general temporal trend, expressed by seasonal Pardé coefficients, could be reproduced and the modelled water balance was within sampled ranges of surrounding catchments. The model performance of water quality endpoints was in a medium but significant range for coefficients of determination with low Root Mean Square Errors. Baseflow concentrations of DP from weekly grab samples in the main tributary of the Enxoe River were found significantly correlated to model results at the outlet, but no correlation was found to a second tributary. Especially high concentrations at the beginning of the dry Mediterranean summer could not

be reproduced. The longterm estimation (10 years) of P export from the Enxoe catchment resulted in highly variable annual loads of all variables. An annual average export of 0.27 kg/ha/year was calculated in this decade for DP, 0.31 kg/ha/year for PP export, 0.27 t/ha/year of sediment yield and 4.08 hm³/year of discharge. 90% of the annual TP was released in all years during 8-17 (not subsequent) days, with the exception of a dry year (90% TP during two days).

7.4 Discussion

The successful application of the ZIN-Sed 2D model for DP and PP modelling confirmed, in combination with the high sensitivity of the Langmuir parameters, that the Langmuir isotherm can successfully be used at catchment scale. The high sensitivity of hydrological parameters on water quality estimations underlines the importance of the hydrological model as boundary condition for export modelling of agricultural chemicals. The topsoil P content was found highly sensitive, which was also reported by other studies. Former studies reported on the importance of single events for P export modelling in the Mediterranean. This could be confirmed here since 90% of annual TP was exported in all years in less than 17 not subsequent days, which exhibits a document of the conceptual correctness of the P module parameterization of our model setup. Several studies reported average annual TP export of around 0.7 kg/ha/year from catchments in the Mediterranean region and the variability of exports worldwide reached values as high as 50 kg/ha/year. Thus, the estimated long-term TP release of this study (0.58 kg/ha/year) can be classified as below average for this region and far below highest values worldwide.

7.5 Conclusions

This study examined a combination of methods for prediction in ungauged basins, sampling data and soft-data for the calibration of the model ZIN-Sed 2D, applied for the estimation of P export from a Mediterranean catchment with scarce data. It may help water managers to tackle the problem of data availability, if the knowledge of nutrient inputs from a catchment is mandatory but sampling data is scarce. We consider the short modelling time step of this approach especially appropriate, if only short and discontinuous sampling data is available. Additionally, the implemented Langmuir isotherm is an alternative to the linear isotherm for the calculation of P sorption in process-based models. Although our results suggest a below-average P export from the Enxoe catchment towards the downstream reservoir, we suggest further investigations regarding P cycling processes in the reservoir, using our results as boundary condition.

8 Summary of study 4: Estimation of pesticide and transformation product export pathways

Gassmann, M., Stamm, C., Olsson, O., Lange, J., Kümmerer, K., Weiler, M. (accepted). Model-based estimation of pesticides and transformation products and their export pathways in a headwater catchment. Accepted for publication in 'Hydrology and Earth System Sciences'.

8.1 Introduction

Pesticides applied in the field are usually only partially degraded and form potentially hazardous TPs, which tend to be more mobile and more persistent than their PCs. A small proportion of both, pesticides and TPs, may be transported to adjacent rivers, which can be enough to be harmful for aquatic organisms. A variety of hydrological processes are able to transport substances towards rivers, including surface runoff, soil water flow in the soil matrix and in preferential pathways and export via tile drains. Besides hydrological processes, EFPs such as sorption and transformation were found to influence export pathways. In addition to transformation processes, current conceptualizations of EFPs include a mixing layer in the surface soil, interacting with runoff by sorption, sorption isotherms and sorption kinetics. Process-based models have the capabilities to distinguish between different export pathways as influenced by EFPs. Still, current non-point source models concentrated mainly on total export at the catchment outlet. Additionally, those models only incorporated PCs but neglected TPs. Considering that TPs have generally different environmental fate characteristics, we hypothesize that TPs and PCs also have different export pathways. This hypothesis is tested in this study, by introducing and applying a process-based hydrological and environmental fate model for pesticides and TPs in a headwater catchment.

8.2 Methods

The Ror catchment (2 km²) is located in the Swiss Plateau and was the subject of various hydrological and pesticide fate investigations in the past. During one of the former studies, three pesticides were applied on certain fields under controlled conditions and the rivers were subsequently sampled at three stations. Resulting river sampling data was used in this study for model evaluation and included the herbicides Dimethenamid with the TP Dimethenamid OXA (D-OXA), Atrazine with the TP Desethylatrazine (DEA) and Metolachlor with the TP Metolachlor ESA (M-ESA). All TPs were more mobile and more persistent than their PCs.

The model used in this study (ZIN-AgriTra) is spatially distributed and is able to simulate small timesteps. Hydrological processes implemented in ZIN-AgriTra include surface infiltration calculated by the Green and Ampt approach, water flow in the soil matrix by the Richards equation, preferential flow in macropores based on the law of Hagen-Poiseuille, diffusive wave overland flow and kinematic wave channel routing. Soil water may reach the river channel by lateral flow and via tile drains. For evapotranspiration calculation soil and interception storage evaporation and plant transpiration as affected by soil moisture were considered. EFPs of pesticides considered in the model were first-order transformation, using formation fractions, sorption by a linear isotherm based on a relationship with organic carbon in soil, sorption kinetics and a mixing layer for exchange of substances between runoff and soil. Considering above processes, it can be distinguished between substance export by overland flow, lateral soil water flow and soil matrix or preferential flow to tile drains in the model.

The model was set up in 10x10 m spatial and a 10 min temporal resolution in order to reproduce discharge and substance fluxes at the three river sampling stations. The modelling timespan included three months, following pesticide application with a preceding warm-up period of 7 months. The hydrological and the environmental fate parameters were fixed or calibrated, using literature values or observations from former studies. Initial soil concentrations of substances were calibrated to baseflow river concentrations sampled before pesticide application, assuming a spatially equally distributed soil concentration in the catchment. In order to discuss the influence of fate characteristics on substance export, a conservative solute (CS) was modelled in addition to pesticide residues.

8.3 Results and Discussion

Overall, the model performed reasonably well for river fluxes of pesticides, TPs and discharge at all three sampling stations but had some problems for smaller events. This may have been an effect of an underrepresentation of impervious surfaces such as roads in the model, which react fast to rainfall and may have collected pesticides due to spray drift during application. Additionally, the uniform distribution of soil residues resulted in an over-estimation of baseflow concentrations at the southern subbasin, showing that the real initial soil mass was rather non-uniformly distributed in the catchment. Thus, the usage of a more comprehensive method to determine initial soil residues is suggested.

Considering the whole modelling period, the estimated recovery rates were about 30% of the applied amount for the CS but below 1% for all pesticide residues showing the effect of intrinsic substance fate characteristics of the substances. Export via overland flow prevailed in sampling at the catchment outlet and in the southern subbasin for most substances

except M-ESA, which additionally had a remarkable fraction of subsurface export. This could be attributed to the high mobility of this TP and the initial soil residues. In agreement with the literature, a higher mobility of PCs was related to higher export by overland flow at the outlet and the southern subbasin. However, the temporally delayed formation and a potentially altered place of formation compared to PCs inhibited the inclusion of TPs in this relationship. Macropore and matrix flow to tile drains were estimated to be the only export processes for all pesticide residues at the eastern subbasin, but the fractions of matrix flow to tile drains were always higher for TPs than for their PCs, again a result of lower sorptivity of TPs. This could additionally be confirmed by the overall relatively low amount of CS in the third soil layer even towards the end of the study, since the catchment was assumed to be free of CS before application. Fractions of preferential flow to tile drains were in the same order of magnitude for all substances, regardless of the widely varying environmental fate characteristics. Thus, as suggested by other studies, a reduced importance of fate characteristics could be confirmed. Still, the contribution of preferential flow to total tile drain export was higher for stronger sorbing substances.

Comparing modelled peak fluxes of substances in the main export event (23 days after application) to later events (60-71 days after application) showed that TPs tended to be exported to a higher degree in the later season than their PCs, which can be explained by their delayed formation and higher persistence. Further, the later events had a higher fraction of matrix flow to tile drains, which resulted in an equally higher fraction of substance export via soil matrix flow to tile drains. This is a document of the importance of the hydrological model for substance export and shows that the main export of PCs and TPs may occur under different hydrological conditions.

8.4 Conclusions

In the past, the modelling of pesticide residue export from agricultural catchments was focused on PCs. In this study, we introduced a catchment scale model including the dynamic formation and environmental fate of TPs. The successful simulation of three pesticides with one TP each and three sampling sites showed that current conceptualizations of transformation processes can be applied at catchment scale. The model results confirmed dependencies of PC export processes on physico-chemical properties as given in the literature. However, the environmental fate of TPs was determined by both the EFPs of PC and TP. Thus, it could be concluded that PCs and TPs generally have different export pathways in a catchment, due to their different environmental fate characteristics. This fact should be considered in risk assessment for the export of agricultural chemicals to adjacent rivers and catchment scale models should be extended to include both PCs and TPs.

9 Study 5: Spatial variability of critical source areas for pesticides and transformation products

9.1 Introduction

In the literature, two types of agrochemical sources for river pollution are differentiated: point sources and diffuse sources. While point sources are spatially restricted to small areas, diffuse sources enter the stream constantly along a river network. Although the export of agrochemicals from agricultural fields represents a diffuse source, there are areas in catchments which are more prone to substance export than others. These areas are called critical source areas (CSA). In the past, approaches for the delineation of CSA concentrated mainly on phosphorus and nitrate, by considering their specific environmental behaviour (Pionke et al., 2000, McDowell et al., 2002). CSA assessment for pesticide export was based on the assumption that hydrological and topographical characteristics of a catchment are more important than fate characteristics (Heathwaite et al., 2005, Frey et al., 2009). According to this concept, changing hydrological processes in a catchment (e.g. tile drains, buffer strips) also alters the extent and spatial distribution of CSA (Thompson et al., 2012). For delineating CSA it may not only be important to differentiate between fast and slow runoff generation processes but also between the specific types of runoff generation (Lyon et al., 2006). Furthermore, the delineation of CSA may be influenced by tile drains (Doppler et al., 2012) or small agricultural ditches (Buchanan et al., 2013). However, the export of agrochemicals is not solely governed by hydrological processes but sorption and transformation characteristics of substances have also a large influence on export amounts and pathways (Tang et al., 2012). Additionally, emerging TPs of pesticides generally have different export pathways compared to the PCs, which is a result of their different physico-chemical properties, especially their delayed formation and degradation (Chapter 8). Therefore, the hypothesis of this study was that changing substance characteristics alter the spatial extent and distribution of CSA and are generally different for pesticides and their TPs. In contrast to previous studies, full reactive transport modelling, based on distributed hydrological modelling, was used for the delineation of CSAs in a small headwater catchment.

9.2 Methods

This study was performed using data from the Ror catchment (2 km²), which is located in the Swiss Plateau (Figure 4). It has been the subject of many pesticide export and hydrological studies in the past and thus the hydrological functioning is well known (Chapter 8). Most of the catchment is under agriculture and only a smaller part is covered by forest. Settlements

are restricted to loosely located farms and many small roads cross the catchment. Large parts are underlain by tile drains, which were assumed to be active in delivering pesticide residues to the river (Leu et al., 2004b).

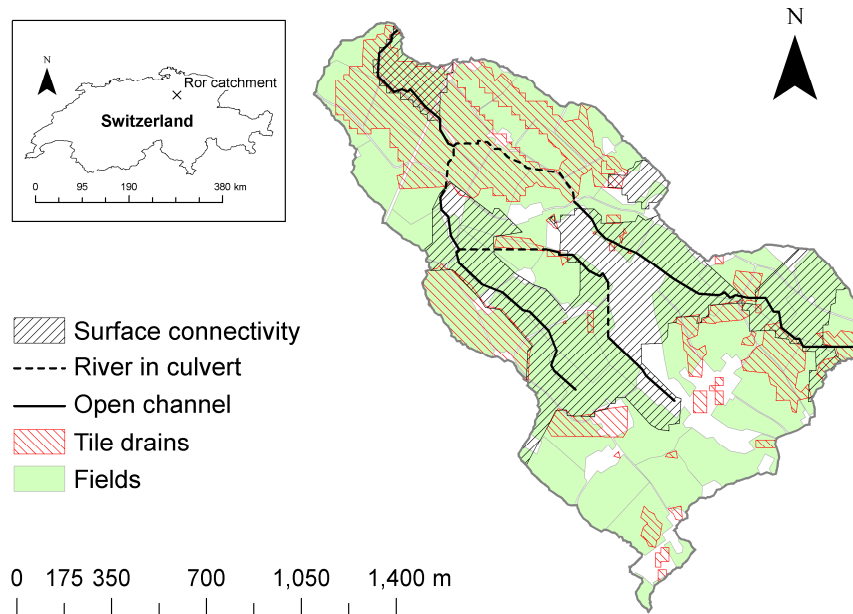


Figure 4: The Ror catchment with its delineated fields, the tile drained areas (swisstopo (Art. 30 GeolV): 5704 000 000 / DHM@2003, reproduced with permission of swisstopo / JA100119) and surface connectivity (Frey et al., 2009).

In this study, the model ZIN-AgriTra was used, which is able to simulate agrochemical and transformation product export from agricultural catchments (a manual can be found in Appendix A1). The model runs in short timesteps and is spatially distributed, which makes it suitable for the delineation of CSA maps. In chapter 8, the model was set up and calibrated to three sampling stations in the Ror catchment, showing its ability to reproduce spatially distributed pesticide and TP export. For the assessment of CSA, agricultural fields were delineated in the catchment, using an aerial photo (Figure 4). Since these fields were used as potential pesticide application fields, non-agricultural areas such as residential areas, roads and forest were excluded. Although there were more agricultural fields visible in the catchment, the delineated 55 fields were considered to be an applicable trade-off between spatial representation and computation time.

The physico-chemical characteristics used for model setup of ZIN-AgriTra were the linear sorption coefficient, normalized by organic carbon K_{OC} , the mixing layer first-order half-life DT_{50} and the formation fraction representing the mass fraction of degraded agrochemical forming the TP. Half-lives for the deeper soil were calculated in the same way as in chapter

8: the mixing layer half-life was multiplied by 1.25 for the first soil layer, by 2 for the 2nd soil layer and by 10 for the 3rd soil layer, which was similar to the distribution suggested by Jury et al. (1987). In contrast to the former model setup, the catchment was assessed to be free of PC and TP residues prior to application.

In order to investigate the influence of physico-chemical substance characteristics on the delineation of CSA pairs of PC and TP were defined. Although the relationship of the fate characteristics between PCs and TPs can be manifold, it was found that relevant TPs are often more mobile and more persistent than their PC (Boxall et al., 2004). Since these facts are also most hazardous for the environment (assuming an existing toxicity), the choice of parameter values was restricted to TPs being more or equally mobile and persistent than the PC. This assessment was further restricted to moderately mobile PCs, since the model was not adapted to the needs of highly sorptive substances. Four PCs (1-4) and four TPs (a-d) were defined as given in table 2. Applying above restrictions resulted in 12 PC-TP pairs, named by the number of the PC, followed by the letter of the TP. The formation fractions of TPs were always considered to be 0.1.

Table 2: Parent compound (PC) and transformation product (TP) mixing layer half-lives (DT50) and organic carbon sorption coefficients (K_{oc}) used to determine scenarios.

Parameter	unit	PC				TP			
		1	2	3	4	a)	b)	c)	d)
DT50	days	15	30	15	30	30	60	30	60
K_{oc}	ml/g	10	10	100	100	10	10	100	100

The model was run from 08.05.2000 - 18.07.2000, starting with PC application at the same rate as metolachlor in the previous study (chapter 8). For the delineation of CSAs, export fractions of PC and TP were calculated in relation to the applied PC amount for each field. Drawing maps, using field export fractions for all PC-TP combinations, allowed for exploring differences between scenarios and relating the differences to physico-chemical characteristics. A final CSA map for mobile soil-applied agrochemicals and their TPs was calculated by normalized average export fractions of all scenarios. The variation of export fractions of a single field, due to the variation of physico-chemical properties CV_{field} , was explored by calculating the coefficient of variation of export masses from the 12 scenarios by

$$CV_{field} = \frac{\sigma_{field}}{\bar{f}_{field}} \quad (1)$$

σ_{field} is the standard deviation of export fractions for all scenarios and \bar{f}_{field} is the arithmetic average of the export fractions for all scenarios. The spatial variability of export

fractions in the catchment, due to changing fate parameters, was investigated by calculating the spatial coefficient of variation $CV_{spatial}$, using the standard deviation $\sigma_{spatial}$ and the arithmetic average of export fractions $\bar{f}_{spatial}$, including all fields for a single scenario:

$$CV_{spatial} = \frac{\sigma_{spatial}}{\bar{f}_{spatial}} \quad (2)$$

Thus, low values of $CV_{spatial}$ suggest a spatially uniformly distributed substance export and high values a spatially concentrated export. Statistical tests for the difference of two populations (t-test and Mann-Whitney Rank Sum Test) were performed using the software SigmaPlot Version 12.5.

9.3 Results and Discussion

Export fractions of different scenarios were highly variable for both PC and TPs (Figure 5). The largest area with PC export fractions > 5 % was found for PC 2, whereas maximum export fractions of single fields were always below 5 % for PC 3. The highest TP export was calculated for scenario 3b) and the lowest export for 4c). Only in scenarios 3a) and 3b) the export fractions of TPs were higher than their PCs (Table 3). However, this may be an effect of the short modelling timespan, since TPs are often exported in higher fractions in the late season (Kalkhoff et al., 2003). Generally, the lowest export fractions for PCs and TPs were found in the northern part of the catchment and in some fields west of the southern tributary. The PCs with highest export were also those with the lowest K_{OC} values of 10 ml/g. Among currently soil-applied agrochemicals on the market, only few have such a low sorption and are additionally transformed into substances with similar low sorption. Examples would be the herbicides Metribuzin (CAS: 21087-64-9), being transformed to Desamino-diketo-metribuzin (CAS: 52236-30-3), or Sulcotrione (CAS: 99105-77-8), being transformed into 2-chloro-4-methylsulfonyl-benzoic acid (CAS: 53250-83-2) (PPDB, 2009). The PC with the lowest export fraction (PC 3) can be assigned to herbicides that were previously applied in this catchment such as Dimethenamide (CAS: 87674-68-8) or Metolachlor (CAS: 51218-45-2). The TP of Scenario 3a) is comparable to the common TPs Dimethenamide Oxa (CAS: 380412-59-9) and Metolachlor ESA (CAS: 171118-09-5) (PPDB, 2009) of these herbicides. Thus, among the investigated scenarios, the formerly in the catchment applied pesticides contained the least hazardous PCs, but their TPs were assessed to have the highest export fractions.

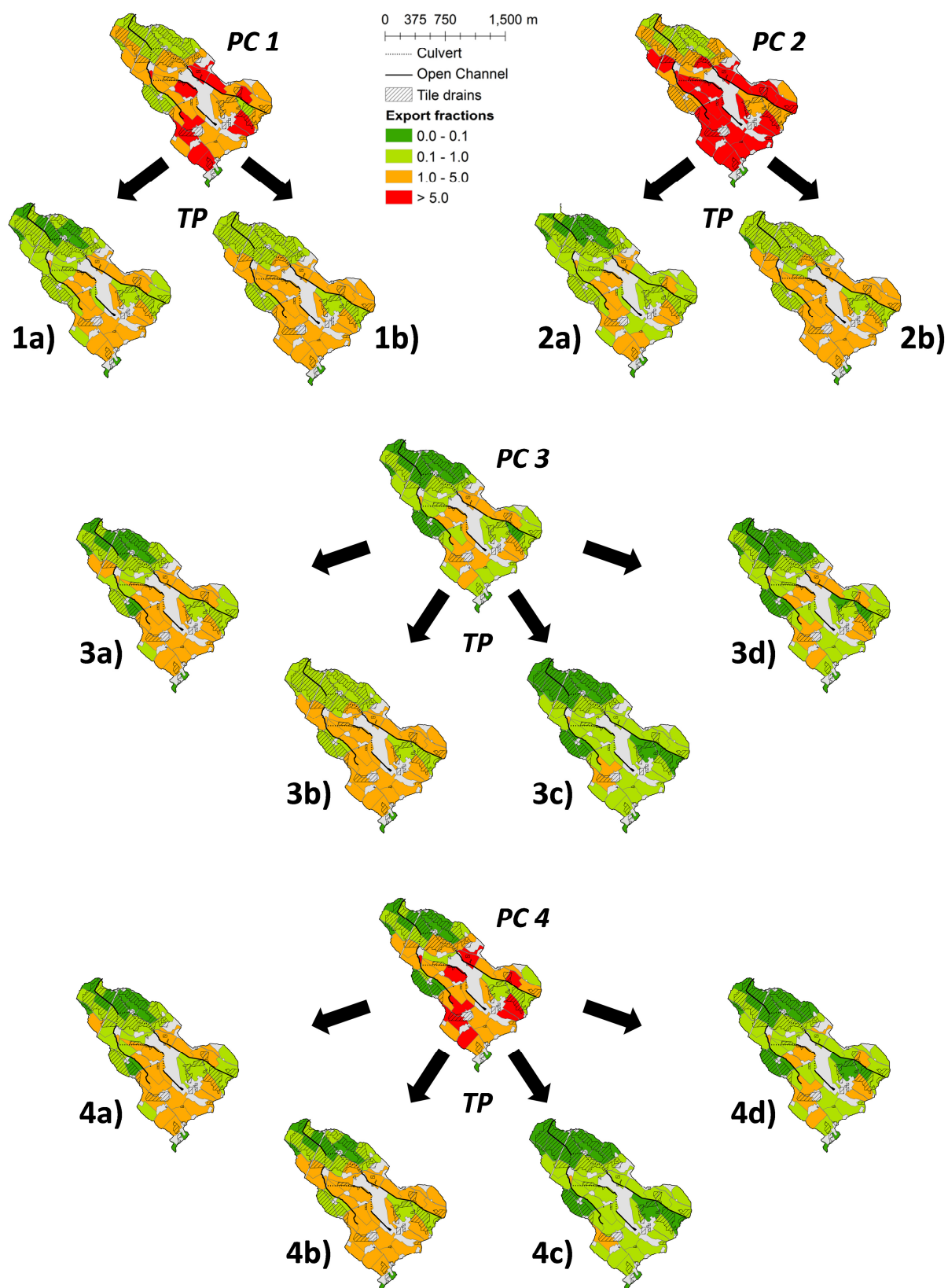


Figure 5: Export fractions (%) of fields in the Ror catchment for all scenarios. PC - parent compound, TP - transformation product.

The spatial variability $CV_{spatial}$ of all scenarios (Table 3) was found to be significantly greater for PCs than for TPs (two-tailed $p < 0.01$, t-test). Even scenarios with the same PC and TP substance properties (2a and 4c) had a lower spatial variability for TPs. Thus, TPs were assessed to be more ubiquitous in the catchment. The reason for this may be that PCs, which were transported away from their application point without reaching the river, may have been transformed and exported to the river as TPs later. Changes in physico-chemical properties may even have facilitated further transport. Comparing $CV_{spatial}$ with the environmental fate characteristics of the scenarios suggests that higher values of spatial variability may be related to higher values of K_{OC} .

Table 3: $CV_{spatial}$ and export fraction of the whole catchment for PCs and TPs for all scenarios.

Scenario	$CV_{spatial}$		Export fraction (%)	
	PC	TP	PC	TP
1a)	1.0	0.8	3.5	0.9
1b)		0.8		1.7
2a)	0.9	0.8	7.9	0.7
2b)		0.7		1.3
3a)	1.3	0.9	0.9	1.0
3b)		0.8		1.9
3c)		1.1		0.3
3d)		1.1		0.7
4a)	1.2	0.9	2.5	0.9
4b)		0.8		1.5
4c)		1.1		0.3
4d)		1.1		0.5

PC and TP export variability of each single field due to changes in fate characteristics CV_{field} is shown in Figure 6. The values of CV_{field} are significantly greater for PCs than for TPs ($p < 0.001$, Mann-Whitney Rank Sum Test). Hence, the export from single fields reacts stronger to changes in PC fate characteristics than TP fate characteristics. The fields with highest variability are located in the north and west of the catchment, which coincides with the areas of lowest export but also with the largest tile drain areas (Figure 4). The areas with the lowest export variability were located at places where the largest export was found in most scenarios. Thus, for the spatial export, variability of substance fate characteristics was more important for areas with lower export than for areas with higher export. Especially tiled drained areas appear to be susceptible to changes in fate characteristics for substance

export, which is probably an effect of substance sorption (Brown and van Beinum, 2009). Additionally, since PC fate characteristics influence TP behaviour, parts of the TP export variability may also be explained by the variability of PC characteristics.

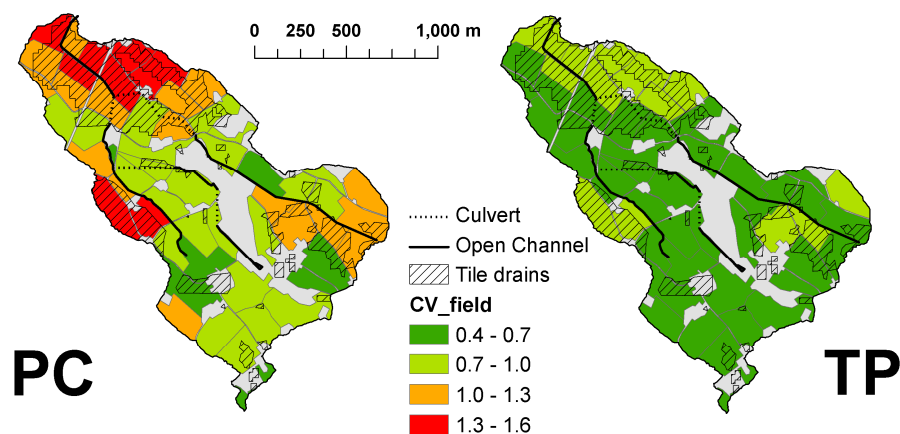


Figure 6: Map of CV_{field} for parent compound (PC) and transformation product (TP) export.

Average critical source areas for the export of mobile PCs and their more or equally mobile TPs are shown in Figure 7. A larger area contributed to the highest export class (0.75-1.0) and medium export classes (0.25-0.75) for TPs than for PCs. The highest PC export areas were all located next to streams and were connected to the river by overland flow, whereas the highest TP export areas also included more remote places, which were only connected to the river by subsurface flow processes, most likely by export via tile drains. The highest export areas were mainly located in areas where saturation excess overland flow was predicted to be the main runoff generation process (Schmocker-Fackel et al., 2007). Additionally, the spatial distribution was in good agreement with the connected overland flow areas of Frey et al. (2009). However, medium critical source areas, which accounted for about 60% of the average total substance export from the catchment for both PCs and TPs, could not be totally assigned to connected areas. Only by additionally considering the disconnected areas with generated runoff in Frey et al. (2009), a good agreement with CSA of this study could be found. This may again be an effect of fast tile drain export of overland flow, using preferential flow pathways from disconnected areas. Thus, without the consideration of export from topographically disconnected areas on substance export, the actual extent of CSA would have been underestimated.

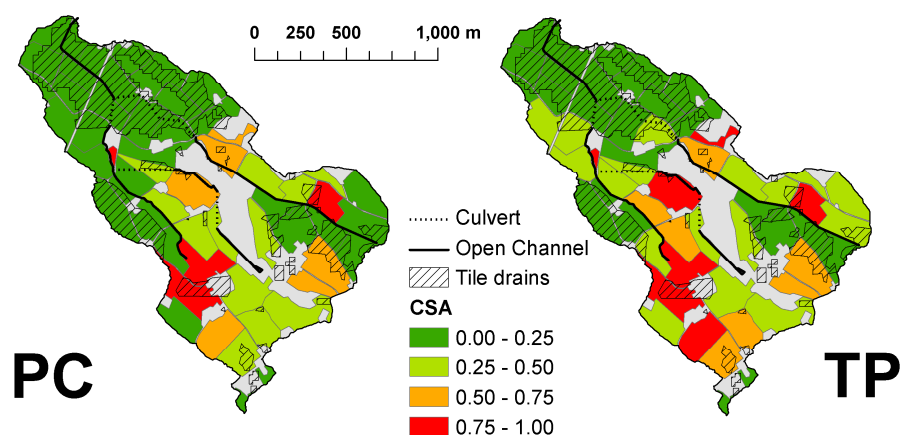


Figure 7: Normalized average export fractions including all scenarios.

Compared to former approaches, the method of this study is mainly limited by computational power. For each agricultural field and each fate parameter combination, a model run took about 1.25 hours at a spatial resolution of 10x10 meters and 10 min time step. Thus, the creation of one export fraction map on an Intel Core i5-3320M CPU with two processors required about 1.5 days. However, reducing the temporal and spatial resolution may still give sufficient spatial details and would reduce the computation time. Similar to the approach of Frey et al. (2009), a further bottleneck is the fact that the model should be calibrated before used for delineation of CSA, at least to hydrological sampling data. Still, due to the calibration, the reliability of this method may be superior to former uncalibrated approaches.

9.4 Conclusions

In contrast to former approaches, this study used full reactive transport modelling for the delineation of CSAs for pesticide export and considered the formation of TPs. It was revealed that physico-chemical properties influenced the extent and location of CSAs. Furthermore, the CSAs for TPs in the catchment were spatially more equally distributed, even if the physico-chemical properties of PCs and TPs were the same. Thus, these results add a new dimension to the delineation of CSAs for pesticide export. While, in the past, mainly hydrological modelling was used for this purpose, it now seems to be mandatory to include substance fate characteristics into the delineation of CSAs. In contrast to former studies, the method used in this study is not restricted to specific substances but can be used for a wide range of environmental characteristics, making it a generic approach.

10 Overall discussion

In the course of this thesis, several agrochemical fate process conceptualizations were implemented in catchment scale models, which were subsequently applied in agricultural catchments. The progress and limitations of the approaches, their implementations and the impact on agrochemical modelling are discussed, regarding the research questions in this chapter.

10.1 Model structure

The complexity of modelling tools in this thesis has a large variety. Basically, three different model structures (MS1 - MS3) can be differentiated:

(MS1) In study 1, river fractions between dissolved PC and TPs were estimated, considering first-order transformation and instantaneous linear sorption equilibrium but neglecting hydrological transport modelling. Model structure MS1 was chosen since the actual concentrations were not of interest in study 1 but only the relationships between PC and TPs as affected by two different transformation processes. Similar structural assumptions were made by Kern et al. (2011), searching for TPs with a high potential to be present in surface waters. In study 1, it could be shown that MS1 was sufficient to assign sampled PC-TP relationships to one of two investigated transformation processes. However, the lack of a transport model and spatial distribution may lead to an over- or underrepresentation of specific catchment areas or environmental compartments. It can be expected that there is heterogeneity in the importance of specific transformation processes in the catchment due to different ways of pesticide application and different hydro-meteorological conditions. Thus, the results of study 1 may be interpreted rather as a large-scale average of TP formation and mobilization than actual river pollutant fractions.

(MS2) In study 2 a conceptual hydrological model and a substance mobilization module were added to the fate processes considered in MS1. Thus, dissolved river concentrations of pesticides and TPs could be assessed at the catchment outlet. The basic structure of MS2 - the mobilization by overland flow and degradation of PCs - was shown to be applicable for an assessment of PC concentrations in headwater catchments before (Reus et al., 1999, Dabrowski and Schulz, 2003, Berenzen et al., 2005). However, uncertainty assessment in study 2 showed that it may be problematic to additionally simulate two TPs with the extended approach of this thesis, if the TPs originate from different transformation processes or if the predominant transformation process changes during the model run. The latter, however, would also be true for the original model structure, since degradation half-lives of PCs also change with changing transformation processes (PPDB, 2009). Thus, the

usage of MS2 should be preceded by a thorough analysis of the temporal evolution of transformation processes working on target substances.

(MS3) In studies 3-5, the distributed and process-based model structure was supposed to answer multiple questions: In study 3, a small amount of sampling data was extended in a way that a long-term estimate about the catchment export of total P could be made. Since P is highly sorptive, a differentiation between adsorbed and dissolved P was essential. The focus of study 4 was on the reproduction of pesticide and TP river fluxes at three sampling stations in a small catchment and on an estimation of export pathways. In study 5, the distributed nature of MS3 was used to answer the question about the potential spatial distribution of PC and TP export from a catchment as affected by fate characteristics. Thus, MS3 may be seen as the most flexible model structure, including key features for substance export in agricultural catchments such as subsurface export to tile drains (Stamm et al., 1998, Zehe and Flüher, 2001) and surface connectivity (Frey et al., 2009, Payraudeau et al., 2009). But it was also the most data demanding model structure, with the highest demand for computational power.

The choice of an appropriate modelling time step is part of the choice of a certain model structure (Smith et al., 2008). Concentrations of agrochemicals in rivers are highly variable and event peaks are often short (Leu et al., 2004a, Berenzen et al., 2005), highlighting the importance of single events for total agrochemical export from catchments (Torrent et al., 2007). Thus, for the modelling of water quality parameters, short timesteps are required, especially at the smaller catchment scale (Gassmann et al., 2012). In contrast to well-established models such as SWAT (Arnold et al., 1998) or AnnAGNPS (Bingner et al., 2011), studies 2-5 all used timesteps of one hour or below (Table 1). Even though the aim of study 3 was the longterm P export, it was shown that the short time step could assist model calibration and, thus, predictions in poorly gauged basins, since short and discontinuous sampling data often do not allow for the calculation of a sufficient daily mean. In studies 2 and 4, event peaks would have been underestimated by using a daily time step, which could have resulted in a wrong prediction of threshold concentration exceedances (Schulz, 2004).

Overall, choosing between model structures for a specific purpose is a critical issue not only for hydrological modelling (Clark et al., 2008) but also for environmental fate modelling. The results of this thesis showed that a careless choice may result in a model structure not being able to represent all important EFPs. Furthermore, the choice of a model structure may also be influenced by the quantity of available sampling data, which is often limited for agrochemicals.

10.2 Uncertainty in environmental fate modelling

Experimental parameter values of agrochemical fate conceptualizations often contain wide ranges in the literature (PPDB, 2009), which may be an effect of insufficient conceptualizations, due to neglecting the dependence of processes on certain environmental conditions such as soil pH or soil moisture (Wauchope et al., 2002). The impact of wide parameter ranges on the modelling of agrochemical export was investigated in this thesis by sensitivity analysis and uncertainty estimation. Sensitivity analysis provides information on the importance of single parameters to alter the model output (Hamby, 1994). In former studies, sensitivity of agrochemical environmental fate parameters resulted in highly sensitive sorption or degradation parameters (Dubus et al., 2003a, Holvoet et al., 2005, Fohrer et al., 2013). The results of study 3 confirmed a high sensitivity of both Langmuir sorption isotherm parameters for dissolved P transport at catchment scale. In agreement with study 4, it further confirmed the sensitivity and thus the importance of desorption kinetics, which was hypothesized by Gouy et al. (1999). This effect may have been increased by the choice of short modelling timesteps in this thesis. Since pesticide sorption is fast, the importance of sorption kinetics may be reduced at a daily time step or longer. In study 2 all half-lives were more sensitive than corresponding linear sorption coefficients and TP sorption coefficients were hardly sensitive at all. This is a hint that the amount of TP export is rather limited by TP formation than by its transport (adsorption). Moreover, formation fractions were sensitive, pointing to the influence of these newly introduced parameters for river export modelling of TPs. However, similar to Larsbo and Jarvis (2005), parameter correlation analysis showed a strong relationship between sorption and transformation parameters, which raised the probability for equifinality of different model parameterizations (Beven, 1993). Thus, the model predictions of study 2 were supported by uncertainty estimation. At some periods of the time series uncertainty was high and did not cover all of the samples, which often occurred for agrochemical modelling (Larsbo and Jarvis, 2005, Rankinen et al., 2006, Dean et al., 2009). Overall, the sensitivity analysis confirmed the importance of the EFPs for export modelling. Additionally considering uncertainty estimation revealed that the introduction of TPs into agrochemical export modelling increased total model uncertainty, but that TP modelling also may help to constrain model parameters.

All agrochemical transport processes considered in the studies of this thesis were hydrological processes. Thus, the hydrological model was supposed to have a large influence on agrochemical export (Borah and Bera, 2003). In study 2, most of the hydrological parameters were sensitive in multi-objective calibration. It could further be shown that the hydrological model contributed to higher uncertainty of load estimations in the second event. In study 3, parameters of the hydrological model were highly sensitive for changes in

sediment, dissolved and adsorbed P amounts. Therefore, only in years with high discharge amounts high amounts of P were exported. Moreover, underestimations of small PC and TP export events in study 4 could be assigned to underestimations of the hydrological model. Hence, similar to former studies (Cryer and Havens, 1999, Fohrer et al., 2013), the hydrological model had a large share in conditioning the export of agrochemicals in this thesis. Therefore, uncertainty analysis of agrochemical fate models should include both the uncertainty of the hydrological model and the environmental fate model.

10.3 Export pathways of transformation products

There are numerous processes and pathways contributing to the export of agrochemicals towards a river (Tang et al., 2012). However, there was no special consideration of the pathways of TPs in the past. Study 4 showed that the relationships between sorption and export by overland flow or sorption and leaching (Brown and van Beinum, 2009), which were assumed for pesticides, are not automatically applicable to TPs. Reasons for this were the processes determining the formation and fate of TPs: since TPs originate from degradation of PCs, they reach their mass peak in the catchment later than the PCs. The time point they reach their peak is dependent on the half-life of the PC and the TP (Fenner et al., 2009). Thus, although the environmental fate parameters of TPs may be the same, their mass peak may still be different, due to different PC half-lives. Therefore, a TP may reach its mass peak under different hydrological conditions than the PC or other TPs, which may result in different mobilization processes. Additionally, the often determined higher mobility of TPs results in higher leaching towards tile drains. Furthermore, TPs may be formed after initial pesticide transport and subsequent deposition, due to infiltration and adsorption. Hence, their place of formation may be different to the place of pesticide application, which may again result in different environmental conditions for mobilization compared to the PC. An effect of the different export processes and pathways of PCs and TPs was elaborated during the delineation of critical source areas in study 5: the main export areas in a catchment are not necessarily the same for TPs and PCs and the TPs may be exported to the river from a larger area.

10.4 Initial and boundary conditions

Initial and boundary conditions may have a large influence on hydrological and nutrient export modelling (Zehe and Blöschl, 2004, Weiler and McDonnell, 2006). In this respect, two questions were frequently raised during model parameterization in the different studies of this thesis: (i) What was the amount and the temporal course of agrochemical applications? (ii) What was the amount of agrochemical residuals of former applications?

(i) The application of the commercial product onto agricultural fields is one of the most important boundary conditions for agrochemical fate modelling at the catchment scale (Bach et al., 2001). The ways how this data was derived in former modelling studies vary widely from ready availability from agricultural authorities (Ficklin et al., 2012, Flanagan et al., 2008) to different assessment methods (Huber et al., 1998, Gevaert et al., 2008, Parker et al., 2007). The same holds true for the studies of this thesis: In studies 1 and 2, application mass and timing had to be assessed, using local information, whereas in studies 3 and 4, agrochemical application was known. The effect of erroneous pesticide application information may be a large over- or underestimation of total export masses and failures in predicting large peak concentrations (Kannan et al., 2006, Fohrer et al., 2013). Changing the application timing in study 1 could not alter the ability of the modelling tool to differentiate between the two transformation processes. In study 2, this uncertainty was tackled by varying both timing and mass of application, during Monte-Carlo sampling. It could be shown that both parameters were relatively insensitive, due to correlations to the pesticide half-life. Therefore, erroneous pesticide application data may result in the modellers' choice of an erroneous PC half-life. Since the half-lives of PCs influence the formation of TPs, application uncertainties not only affect PC modelling but also the reliability of TP modelling.

(ii) The importance of initial soil residues of agrochemicals for modelling (Dubus et al., 2003b) could be seen in two studies in this thesis: In study 3, the initial soil P content was among the most sensitive parameters for dissolved and adsorbed P export. Further, in study 4, pesticides and TPs were found in river water before the application, which required the definition of initial soil concentrations. The assumed spatially uniformly distributed soil concentration resulted in an overestimation of baseflow river export in one of the tributaries for PCs and TPs. This behaviour was most probably caused by spatially heterogeneous soil residues (Walker and Brown, 1983). Thus, a more sophisticated method to derive initial residues such as a relationship to soil texture (Farlin et al., 2013) is suggested. An underestimation of P baseflow concentrations in one of the tributaries of study 3, however, could rather be assigned to anthropogenic influences of an upstream settlement. Although the influence of this point source boundary condition was low, it confirms that non-agricultural sources of agrochemicals should additionally be considered during catchment scale model setup (Caille et al., 2012).

11 Conclusions and Outlook

The aim of this thesis was to investigate the implementation of new agrochemical EFPs in catchment scale hydrological models with a focus on the formation and fate of TPs. This was done during five studies modelling the environmental fate of phosphorus, insecticides or herbicides in small to medium-sized catchments. The fate processes newly implemented in this thesis included a Langmuir isotherm for the modelling of P sorption, sorption kinetics considering the temporal delay of sorption processes and the formation and environmental fate of pesticide TPs. Modelling tools were developed in three different complexities and were evaluated for their ability to reproduce substance export in river water. Regarding the four research questions (chapter 3), the following conclusions can be drawn:

(i) The studies showed that it is possible to simulate the dynamic formation and fate of TPs at catchment scale, using current transformation conceptualizations from the literature. The degree of the required model complexity depends on the specific question of a study. A thorough investigation of contributing EFPs for each considered substance should precede the choice of a distinct model structure.

(ii) Most parameters of the investigated transport, transformation and transfer processes were sensitive. Thus, environmental fate parameters had a large impact on agrochemical export modelling, but the effects of hydrological processes were equally important. Therefore, it is essential to consider the interaction of transport, transfer and transformation processes during the modelling of agrochemical export from catchments. The modelling of TPs may increase model uncertainty but may also constrain some parameters and thereby increase their identifiability.

(iii) Pesticide application is one of the most important boundary conditions, but application timing and mass were found to be correlated to the PC half-life. This may increase the uncertainty associated with the choice of a transformation half-life, which may propagate through the model. Therefore, the knowledge of pesticide application is crucial for agrochemical modelling in order to reduce model uncertainty. Soil residues of former agrochemical applications have to be considered in model parametrization, but the assumption of a uniform spatial distribution may lead to a wrong spatial prediction of substance export. Thus, more sophisticated methods to determine initial soil residues are needed in order to reduce uncertainty associated with the setup of initial residues.

(iv) The influence of pesticide fate characteristics on their export pathways was confirmed by the models of this thesis. TPs and PCs had different export pathways towards the river, which could be explained by the generally different environmental fate characteristics and

the impact of PC fate on TP fate. Furthermore, the main source areas for PC and TP export were found to be different, which should be considered during the determination of agricultural management practices.

The simulation of agrochemical export was performed with a high temporal resolution in this thesis, which enabled the models to catch the high dynamics of pollutant export events but also supported the assessment of longterm export masses from catchments. This high temporal resolution required the consideration of sorption kinetics, especially for the desorption process.

Future research directions may result from unresolved issues identified in this thesis. The parameter correlation between sorption and transformation parameters increased model uncertainty in one study, which is especially problematic since the ranges of fate parameters are often wide in the literature. Hence, there is a need for better defined fate parameter values. These may result from further experimental studies on the factors influencing sorption and transformation or from advances in the determination of Quantitative Structure Property Relationships (QSPR). Furthermore, the estimated change of the predominating transformation process from surface transformation (phototransformation) to soil transformation (microbial transformation) in one of the studies suggests further work for the implementation of EFPs of plant-applied pesticides in agrochemical fate models. Especially the differentiation between TPs built at the surface, the wash-off process by rainfall and the subsequent soil transformation, resulting in different TPs, might give new insights into the fate of pesticide residues in the environment.

Although TPs of plant protection products are increasingly considered in the registration procedure of the European Union (E.U. Directive 1107/2009), the environmental fate models used for this purpose currently assess the dynamic formation and fate of TPs at field scale only. The results of this thesis show that TPs can be modelled at catchment scale by means of current conceptualizations and that the difference of the export behaviour between TPs and PCs can be large. Thus, transferring experiences made in this thesis to the chemical registration procedure would allow for a more comprehensive risk assessment of pesticide exposure by considering the formation and fate of TPs at catchment scale.

12 Acknowledgements

I'd like to thank my first supervisor Markus Weiler for his support and ideas and for accepting me as PhD student although I was living and working several hundred kilometres away. I'm grateful to my second supervisor Klaus Kümmerer for the chance to work in his research group in the last years of my thesis, providing a more chemical point of view towards my work. I want to thank Erwin Zehe for the second review of this thesis.

I'm much obliged to my 'secret' supervisor Oliver Olsson for the precious discussions and his persistent encouragement during the whole thesis. I very much appreciate his constant efforts to gain funding for my work. Thus, I had the chance to work in and was funded by three research projects: DYKE, funded by the 'Niedersachsen - Israel Research Cooperation Program' of the Ministry of Science and Culture of Lower Saxony, the project MIRAGE, funded by the European Union (ref: FP7 ENV 2007-1) and PhytoRET, funded by the European Union INTERREG program (Project No. C21).

A person in the background during my thesis was Jens Lange who put me in touch with my first supervisor and is responsible for the contact to my second supervisor. We always had constructive and fruitful discussions. Thank you very much, Jens!

I'd like to thank my former and current colleagues for their support, discussions and comradeship: Lutz Brödl, Nina Manig and Melanie Bauer from my time at the University of Hanover; the group around Yael Dubowski and Eran Friedler at the Technion - Israel Institute of Technology, where I had the chance to work for five weeks; the group around Christian Stamm who supported me during my one-week stay at the EAWAG in Dübendorf; the whole group of the Chair for Sustainable Chemistry and Material Resources at Leuphana University of Lüneburg, which absorbed me immediately once I started working there; Sylvain Payraudeau, Marie Lefrancq, Elodie Maillard and Gwenael Imfeld who supported me during my week at the University of Strasbourg; all PhD students and employees of the Chair of Hydrology at University of Freiburg, which I met regularly at the "Hüttenworkshop".

I'm in debt to Andreas Hartmann, who always provided a roof over my head when I was staying in Freiburg, regardless whether he was at home or not. I also want to thank his varying flatmates for enduring me.

Most of all, I want to thank my wife Sarah not only for her constant moral support and her love but also for proof-reading manuscripts and the thesis. I'm very grateful to and for my family and friends.

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14 List of publications and declaration of authorship

Four manuscripts, which were published or accepted for publication in international peer-reviewed journals, are part of this thesis:

Manuscript 1 (published):

Olsson, O., Khodorkovsky, M., Gassmann, M., Friedler, E., Schneider, M., Dubowski, Y. (2013). Fate of pesticides and their transformation products: First Flush effects in a semi-arid catchment. Clean-Soil Air Water 41 (2), 134–142.

Oliver Olsson was the leading author of this study and put the contributions and the document together. Miriam Khodorkovsky did the river sampling and laboratory analysis. Matthias Gassmann formulated the model, did the modelling analysis, wrote the text about modelling and supported the first author. Eran Friedler and Yael Dubowski reviewed the data analysis and the manuscript. Mandy Schneider wrote the part about toxicity of the substances.

Manuscript 2 (published):

Gassmann, M., Khodorkovsky M., Friedler, E., Dubowski, Y., Olsson, O. (2014). Uncertainty in the river export modelling of pesticides and transformation products. Environmental Modelling and Software 51, 35-44.

Matthias Gassmann was leading author, formulated the model, did all modelling analysis and wrote the text. Miriam Khodorkovsky did the river sampling and laboratory analysis. Eran Friedler and Yael Dubowski reviewed the model formulation and the manuscript and provided local information. Oliver Olsson contributed by discussions about the model structure and the uncertainty analysis and reviewed the manuscript.

Manuscript 3 (accepted):

Gassmann, M., Brito, D., Olsson, O., (accepted). Estimation of phosphorus export from a Mediterranean agricultural catchment with scarce data. Accepted for publication in 'Hydrological Sciences Journal'.

Matthias Gassmann developed the model and performed the simulations of this study. He also analysed the majority of the sampling data. David Brito provided the sampling data,

wrote the part about river sampling and helped with local information. Oliver Olsson reviewed the study design and the structure of the document.

Manuscript 4 (accepted):

Gassmann, M., Stamm, C., Olsson, O., Lange, J., Kümmerer, K., Weiler, M. (accepted). Model-based estimation of pesticides and transformation products and their export pathways in a headwater catchment. Accepted for publication in 'Hydrology and Earth System Sciences'.

Matthias Gassmann developed the model, performed the simulations and the analysis of results and wrote the text. Christian Stamm provided sampling data and local information, contributed to the design of the model and reviewed the manuscript. Oliver Olsson helped during model development by discussions and reviewed the manuscript. Klaus Kümmerer reviewed the manuscript from a chemical point of view. Jens Lange helped during model development by discussions and reviewed the manuscript. Markus Weiler provided his ideas during model development and the design of the study and reviewed the manuscript.

15 Appendix

A1 Manual of ZIN-AgriTra

Manual of ZIN-AgriTra

A model for the environmental fate of
Agricultural contaminants and **T**ransformation products
in agricultural catchments

Preface

In 1999 the model ZIN was introduced as non-calibrated single-event hydrological model for large arid catchments by Lange et al. (1999). It consisted of a fully distributed infiltration excess runoff generation module, a unit hydrograph based runoff concentration and a Muskingum-Cunge channel routing, being able to simulate transmission losses with constant infiltration rates. The first application was in the catchment of Nahal Zin, Israel, providing the name for the model. In the following years, the model was used for hydrological modelling under different climatic and land use conditions in students' thesis only (Wagner, 2002, Thormaehlen, 2003, Guwang, 2004, Leistert, 2005, Hartmann, 2006).

The ZIN model experienced significant changes within the GLOWA Jordan project. It was coupled with the evapotranspiration model TRAIN (Menzel, 1999) and adapted to the needs of semi-arid conditions (e.g. introducing a soil storage) in further students' thesis (Schuetz, 2006, Fischer, 2007, Hagenlocher, 2008, Kohn, 2008). Consequently, the name was changed to TRAIN-ZIN. It was not until 2008 that an application of the model was published as peer-reviewed work in a dissertation (Shadeed, 2008) and 2010 in peer-reviewed journals (Shadeed and Lange, 2010, Gunkel and Lange, 2011).

A second branch of the ZIN model family started to develop with a thesis implementing erosion and sediment transport (Gassmann, 2007), still based on former hydrological developments. The model was called ZIN-Sed in the peer-reviewed article by Gassmann et al. (2012). Subsequently, the hydrological and erosion model was largely changed, including 2D diffusive wave overland flow, vertical and lateral soil water flow in three soil layers and a replacement of TRAIN by the FAO crop evapotranspiration method. Further, the fate of phosphorus was implemented and the name was changed once more to ZIN-Sed 2D (Gassmann et al., accepted,a).

This manual basically describes the implementations of the model ZIN-Sed 2D and the further developments regarding the fate and behaviour of pesticides and transformation products leading to its current name ZIN-AgriTra (Agricultural contaminants and Transformation products). An application of the model was published in Gassmann et al. (accepted,b). In this version of ZIN-AgriTra, only some very basic technical developments of the former TRAIN-ZIN model are left in the source code. Hence, the development of the model explained in this manual is a major part of the PhD work of Matthias Gassmann, done at the universities of Lüneburg, Hannover and Freiburg i. Br., Germany.

The manual consists of two parts. The first part (Part I) describes the theoretical background of the processes implemented in ZIN-AgriTra. In the second part (Part II), the style and keywords of the input and output files is given in combination with instructions on how to set up the model.

Matthias Gassmann, July 2013

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Part I: Model Theory

ZIN-AgriTra is a fully distributed catchment model, considering a raster of cells with lateral flows from cell to cell and vertical flow within three soil layers. Although it may be classified as physically-based, some empirical and conceptual equations are additionally implemented. Transport equations are solved by an explicit numerical finite differences scheme. The spatial discretisation can be cells with a few meters to cells with a few hundred meters, depending on the heterogeneity of soil and landuse properties. The model is designed for short modelling time steps of one hour or less.

1 Hydrological processes

The hydrological modules of the ZIN-AgriTra catchment scale model cover the whole water balance. Thus, in addition to single events, the model may be run continuously. Water storages include an interception storage, soil water storage in the matrix or in macropores and water storage in overland flow and the river channel. Hydrological fluxes considered by the model are evapotranspiration, soil matrix flow, preferential flow in soil macropores, overland flow and channel routing (Figure 1). Further, tile drain flow may be simulated if necessary.

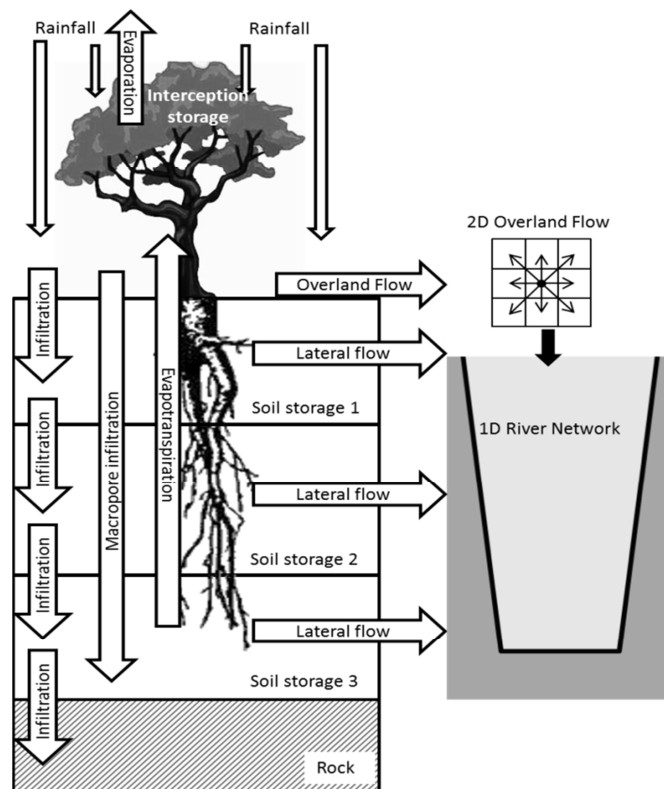


Figure 1: Scheme of the hydrological fluxes in ZIN-AgriTra.

1.1 Interception storage and evapotranspiration

Once rain is falling it reaches an interception storage and the soil surface simultaneously, depending on the fraction of the surface covered by plants f_{canopy} . The interception storage can be interpreted as the loss of rainwater to plant interception and depressions at the surface where water doesn't infiltrate. This storage is emptied by evaporation.

Actual evapotranspiration ET_a is calculated as the sum of interception storage evaporation ET_{int} , soil evaporation ET_{soil} and plant transpiration ET_{plant} :

$$ET_a = ET_{int} + ET_{soil} + ET_{plant} \quad (1)$$

The calculation of ET_{int} starts from a value of potential evapotranspiration ET_p and considers the actual water volume in the interception storage I_{act} :

$$ET_{int} = \begin{cases} f_{canopy} \cdot ET_p & \forall f_{canopy} \cdot ET_p \leq I_{act} \\ I_{act} & otherwise \end{cases} \quad (2)$$

Soil evaporation decreases with soil depth z using the SWAT approach (Neitsch et al., 2011):

$$ET_{soil} = ((1 - f_{canopy}) \cdot ET_p) \cdot \frac{z}{z + \exp(2.374 - 0.00713 \cdot z)} \quad (3)$$

The fraction of ET_p which was not evaporated from the interception storage or the soil is used for ET_{plant} calculations. For this purpose, the root depth z_{root} and the actual soil moisture θ_{act} are considered:

$$ET_{plant} = C_{crop} \cdot (ET_p - ET_{int} - ET_{soil}) \cdot \frac{z_{root}}{z} \cdot \frac{\theta_{act} - \theta_{PWP}}{\theta_{FK} - \theta_{PWP}} \quad \forall \theta_{PWP} \leq \theta_{act} \leq \theta_{FK} \quad (4)$$

ET_{plant} is zero below permanent wilting point θ_{PWP} and has its maximum between field capacity θ_{FK} and saturation. C_{crop} is the crop coefficient, considering variations in the water demand of different land use types (Allen et al., 1998).

1.2 Soil water

1.2.1 Matrix infiltration

Two different matrix infiltration approaches are implemented: the Green and Ampt infiltration approach and a constant infiltration rate. If a constant infiltration is chosen, it is assumed that matrix infiltration velocity is constant over time. Otherwise, the Green and Ampt infiltration approach calculates the infiltration rate $K_{s(matrix)}$, depending on soil moisture and the cumulative infiltration F . Thus, the infiltration rate decreases with infiltration time towards the final infiltration rate K :

$$K_{s(matrix)} = K \cdot \left(1 + \frac{(\Phi - \theta_i) \cdot S_f}{F}\right) \quad (5)$$

Φ is the effective porosity, θ_i the initial water content and S_f the effective suction head at the wetting front. K and S_f can be taken from the literature (e.g. Rawls et al., 1983) or K can be estimated as half the saturated hydraulic conductivity K_s (Maidment, 1993). F is set back to 0.0 if there is no water column at the surface. Optionally, Green and Ampt factors for crust formation and macropore infiltration can be specified. Infiltration is then calculated according to equations developed in Rawls et al. (1989) and Rawls et al. (1990).

1.2.2 Macropore infiltration

As soon as the matrix infiltration rate is exceeded, water starts infiltrating into macropores. The maximum infiltration velocity $K_{s(ma)}$ of vertical macropores per m² is calculated by an approach delineated from pipe flow using the law of Hagen-Poiseuille (Wang et al., 1994):

$$K_{s(ma)} = n_{ma} \cdot \frac{\pi \cdot g \cdot \left(\frac{d_{ma}}{2}\right)^4}{8 \cdot \nu} \quad (6)$$

g is the acceleration due to gravity, d_{ma} is the diameter of the macropore and ν is the viscosity of water, which is assumed to be constant over time. n_{ma} is the number of macropores per m².

1.2.3 Transfer of water in the soil matrix

Water movement within the unsaturated soil matrix is calculated by the Richards equation. The unsaturated hydraulic conductivity is estimated according to Mualem-Van Genuchten equation (van Genuchten, 1980) for each cell and each soil layer in each time step:

$$K_{unsat} = A_{lat} \cdot K_s \cdot \Theta^L \left(1 - \left(1 - \Theta^{1/m}\right)^m\right)^2 \quad (7)$$

with

$$\Theta = \frac{\theta_{act} - \theta_{FK}}{\Phi - \theta_{FK}} \quad (8)$$

A_{lat} is the anisotropy factor, which can be specified to distinguish lateral and vertical hydraulic conductivity. L is an empirical factor often taken as 0.5. The parameter m of the van Genuchten equation is calculated in the model from the given parameter n by

$$m = 1 - \frac{1}{n} \quad (9)$$

The soil moisture of the permanent wilting point (θ_{PWP}) and the field capacity (θ_{FK}) are calculated by the Van Genuchten equation, using given values of the constants n and α as well as the hydraulic heads $h = 333$ cm for field capacity and $h = 15000$ cm for the permanent wilting point:

$$\theta = \left(\frac{1}{1 + (\alpha \cdot h)^n}\right)^m \quad (10)$$

Lateral matrix flow K_{lat} is calculated simultaneously to the Darcy-equation, using unsaturated hydraulic conductivity:

$$K_{lat} = K_{unsat} \cdot \frac{\partial H}{\partial d_{cell}} \quad (11)$$

The slope $\frac{\partial H}{\partial d_{cell}}$ is either only gravity driven (∂H is elevation difference) or additionally by the hydraulic potential (∂H is elevation difference + hydraulic head difference). Although lateral flow is only calculated if the target cell is less saturated than 99.9%, there is the possibility for fast matrix flow to 'over-saturate' a cell. In order to keep the water balance, soil water is vertically transported

to the upper cell in case of oversaturation. If the top layer is oversaturated soil water exfiltrates and generates overland flow.

1.2.4 Transfer of water in the soil in macropores

The outflow velocity of water from vertical macropores is calculated by a power law depending on the relative filling of the macropores θ_{ma} , following the MACRO model (Larsbo et al., 2005):

$$K_{ma} = K_{s(ma)} \cdot \theta_{ma}^{n^*} \quad (12)$$

where n^* is an exponent representing macropore size distribution and tortuosity. Once water is present in a macropore, it is in interaction with the soil matrix. The infiltration of macropore water into the soil matrix is calculated in the model by a radial Green and Ampt approach, following Weiler (2005). Lateral transfer of water in macropores is calculated as slope-corrected flow by

$$K_{ma,lat} = f_{ma,lat} \cdot K_{ma} \cdot \sin(\arctan(s_{DEM})) \quad (13)$$

Where s_{DEM} is the surface slope and $f_{ma,lat}$ the fraction of macropores laterally connected. If s_{DEM} is going towards infinity (vertical flow) $K_{ma,lat} \rightarrow f_{ma,lat} \cdot K_{ma}$.

1.2.5 Virtual water table

The vertical resolution in the model is relatively rough (3 soil layers) and thus the formation of a water table would not be represented well if soil moisture was assumed to be uniformly distributed in a layer. Additionally, lateral water velocity in the soil matrix would be underestimated. Thus, a virtual water table was introduced considering that soil moisture within a layer increases from field capacity θ_{FK} to saturation θ_{Sat} with depth z using a power law function:

$$\theta(z) = z^c \cdot (\theta_{Sat} - \theta_{FK}) \quad (14)$$

The exponent c is an empirical parameter representing drainage properties of a soil and thus the ability to form a capillary fringe. Integrating equation (14) between $z = 0$ and $z = WT$ (water table) and considering the upper boundary condition $\theta(0) = \theta_{FK}$ results in

$$WT = \frac{Q_{sat} - Q_{act}}{\theta_{Sat} \cdot \frac{1}{c+1} \cdot (\theta_{FK} - 1) - \theta_{FK} + 1} \quad (15)$$

Q_{act} is the actual water content (mm) and Q_{sat} the saturated water content (mm). A water table is only calculated for a soil water content above θ_{FK} . In the model the soil layer establishes a water table successively from bottom layer to top layer. The exponent c can be estimated from the water retention curves of each soil starting from the assumption of a linear decreasing soil water potential with depth in the unsaturated zone. By normalizing the unsaturated soil depth in equation (14), the exponent c can be estimated as illustrated in Figure 2 a). Figure 2 b) shows an example of the estimation of the water table from equation (15) for different values of c .

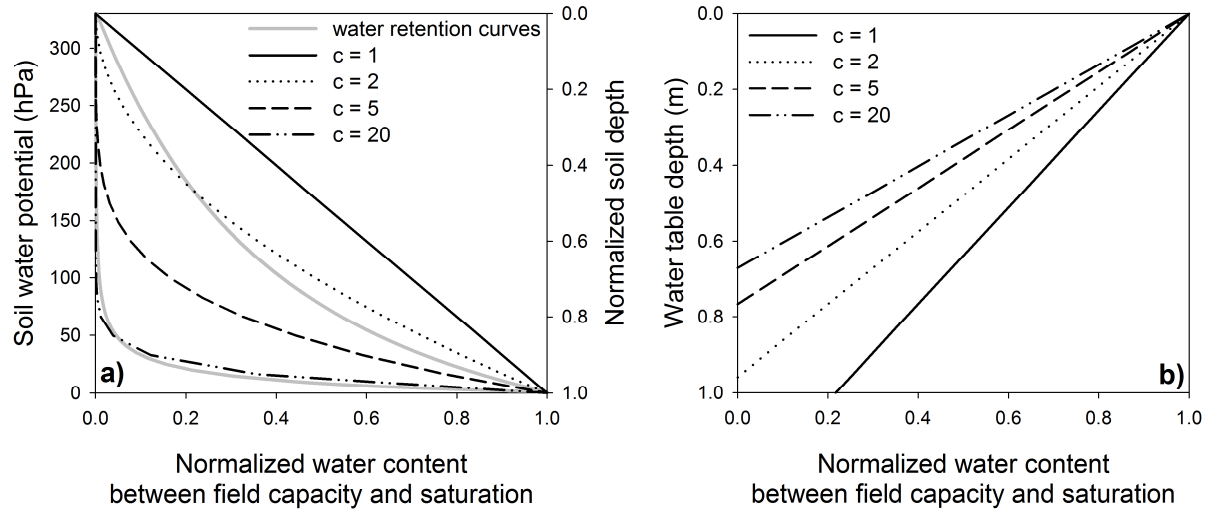


Figure 2: a) Equation (14) for different values of the exponent c with examples of soil water retention curves. b) Example of the impact of the exponent c on the formation and depth of a groundwater table (equation 15).

1.3 Overland flow routing

Overland flow is calculated in two dimensions by a diffusive wave approach. The implementation was done in a similar way as presented for the CASC-2D model by Johnson et al. (2000), with the difference that flow is calculated in ZIN-AgriTra in eight possible flow directions (Figure 1). Overland flow velocity v_{OF} is derived by Mannings' flow equation:

$$v_{OF} = \frac{1}{n_{Man}} \cdot R_h^{\frac{2}{3}} \cdot s^{\frac{1}{2}}, \quad (16)$$

where R_h is the hydraulic radius, n_{Man} Mannings' roughness coefficient and s the friction slope:

$$s = s_{DEM} + \frac{\Delta WT_{surface}}{d_{cell}}. \quad (17)$$

s_{DEM} is the surface slope, $\Delta WT_{surface}$ the surface water table difference between two neighbouring cells and d_{cell} the cell length. Although realistic catchment connectivity should be possible with this setup, inadequacies in the digital elevation model (DEM) may hamper a correct assessment of connectivity. Thus, a forcing grid can be specified differentiating areas where overland flow is connected to the river from areas not connected.

Stability of overland flow calculation is reached by the Courant criterion. Thus, the flow velocity must not exceed the cell length l divided by the time step dt :

$$v_{OF} \leq \frac{l}{dt} \quad (18)$$

Additionally, the calculated possible flow per time step q_{OF} must not exceed the available water volume V_{OF} by more than a predefined percentage:

$$q_{OF} \cdot dt \leq V_{OF} \cdot (1 + OF_{stab}) \quad (19)$$

Water flows are limited by the available water volume in a cell in order to keep the water balance closed. If one of above criterions is not fulfilled, the calculation stops, all values are set to their initial state; the time step is divided by two and calculation re-starts.

1.4 Flow to river

1.4.1 Flow to tile drains

Tile drains are short-cuts for soil water to reach the river and are conceptualized as follows: all vertical subsurface flow (matrix and macropore flow) in an area affected by tile drains is directly routed to the adjacent river segment (Frey et al., 2009). Lateral matrix flow is considered to reach the tile drain from two sides, driven by water table elevation above the drain pipe WT_{drain} :

$$q_{drain} = K_s \cdot \frac{WT_{drain}}{d_{drain}/2} \cdot 2, \quad (20)$$

where K_{drain} is the lateral matrix flow to the tile drain and d_{drain} the distance between drain pipes. All vertical macropore flow in the drainage soil layer is supposed to reach tile drains in drained areas.

1.4.2 Flow to the river channel

Lateral matrix flow to the river channel only occurs if the water table calculated by equation (15) is above the riverbed. The flow is calculated as saturated flow according to Darcy's law considering the seepage area from WT to the riverbed for the whole cell (Figure 3):

$$q_{in,matrix} = K_s \cdot d_{cell} \cdot (z - WT - z_{river}) \cdot \frac{\partial H}{\partial d_{cell}} \quad (21)$$

Lateral flow of preferential flow by macropores to the river depends on the lateral macropore flow and the depth of the river bed:

$$q_{in,ma} = K_{ma,lat} \cdot \frac{z_{river}}{z} \quad (22)$$

Overland flow discharge to the river channel is calculated slightly different to subsurface flow. The fraction of the actual water column WC in a cell underlain by the river channel is taken as overland flow input per time step dt (Figure 3):

$$q_{in,OF} = \frac{WC \cdot \frac{A_{river}}{A_{cell}}}{dt} \quad (23)$$

with A_{river} the area covered by the river and A_{cell} the area of the cell.

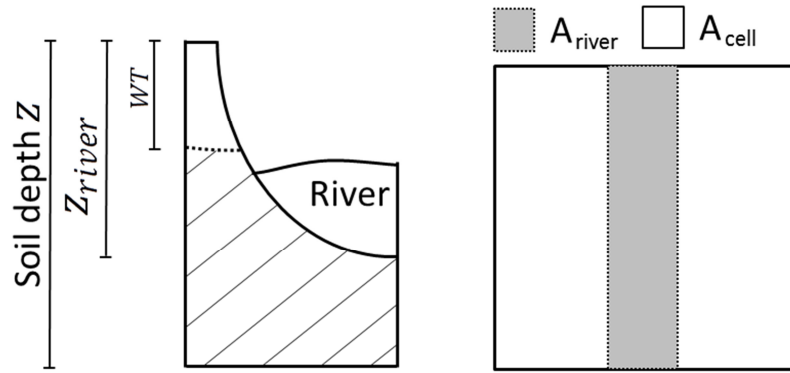


Figure 3: Illustration of measures used for calculation of flow to river. **Left:** cross section through soil (equations 21-22), **right:** surface areas of the river compared to the cell (equation 23).

1.5 Channel Routing

The channel routing uses a one-dimensional explicit kinematic or diffusive wave routing scheme, as it is used in CASC2D (Rojas et al., 2003). In each river segment, the water balance can be written as:

$$\frac{dQ}{dt} = Q_{upper} - Q_{lower} + Q_{inflow} \quad (24)$$

Q_{lower} is the water volume flowing out of the river segment and is calculated by Mannings' equation:

$$Q_{lower} = \frac{1}{n_{Man}} \cdot (R_h)^{2/3} \cdot s^{0.5} \cdot A \quad (25)$$

Q_{upper} is the amount of inflowing water from the upper segment, i.e. it is equal to Q_{lower} of the upper segment. Q_{inflow} consists of all possible inflows to a river segment and is calculated as

$$Q_{inflow} = q_{in,matrix} + q_{in,ma} + q_{in,OF} + q_{drain} \quad (26)$$

2 Erosion and sediment transport

Erosion processes can roughly be divided into sheet erosion processes, driven by the impact of raindrop splash and rill erosion by flowing water. While sheet erosion is only calculated at the land surface, rill erosion and transport capacity equations are used in both land surface and river routing module.

2.1 Sheet erosion

Sheet erosion E_{sheet} per area and time step is calculated by a relationship between erosion and rainfall intensity PI (Hairsine and Rose, 1991):

$$E_{sheet} = a \cdot C_e \cdot PI^b \quad (27)$$

where C_e is the fraction of soil that is not protected by vegetation, a is the detachability and b is an empirical parameter. C_e is equivalent to the C-factor of the Universal Soil Loss Equation (USLE, Wischmeier and Smith, 1978), which is well reported in the literature for various surface types. It includes vegetation coverage as well as soil management (e.g. crop rotation) for applications in shorter time periods. Sheet erosion is only calculated for raster cells and time steps in which the hydrological modules report overland flow generation.

2.2 Rill erosion

Rill erosion follows a critical shear stress approach. The actual shear stress is calculated by one of two available methods. The first method determines shear stress τ by surface slope including water density ρ , gravity acceleration g , slope s and water column WC as

$$\tau = \rho \cdot g \cdot WC \cdot s \quad (28)$$

The second method uses water velocity v_{OF} and the drag coefficient C_d (Schlichting, 1979):

$$\tau = \rho \cdot C_d \cdot v_{OF}^2 \quad (29)$$

C_d can be related to Mannings' roughness coefficient n_{Man} and the water column WC (DHI, 2011):

$$C_d = \frac{g}{n_{Man}^2 \cdot WC^{\frac{1}{3}}} \quad (30)$$

As soon as the critical shear stress $\tau_{c,erosion}$ is exceeded erosion E_{rill} starts with (Partheniades, 1962):

$$E_{rill} = C_e \cdot \alpha_{ero} \cdot \left(\frac{\tau}{\tau_{c,erosion}} - 1 \right) \quad (31)$$

The amount of erosion amount can be calibrated by the erosion coefficient $\alpha_{ero} \left[\frac{g}{m^2s} \right]$.

Deposition D of suspended sediments occurs if the actual shear stress is below the critical value for deposition $\tau_{c,depo}$, influenced by suspended sediment concentration SSC and particle fall velocity v_{sed} (Krone, 1962):

$$D = v_{sed} \cdot SSC \cdot \left(1 - \frac{\tau}{\tau_{c,depo}} \right) \quad (32)$$

2.3 Transport capacity

Depending on the kinetic energy of flowing water, a certain amount of soil particles can be held in suspension. The maximum transport capacity for overland flow is calculated by (Govers, 1990):

$$SSC_{max} = k \cdot q^\beta \cdot s^\gamma \quad (33)$$

where SSC_{max} is the sediment transport capacity, q the runoff rate ($m^3/(sec \ km^2)$), s the mean slope of a cell, k the transport capacity coefficient and β and γ are empirical coefficients. In a review of sediment transport capacity, Prosser and Rustomji (2000) concluded a median value of $\beta = \gamma = 1.4$. To ease the model setup, γ and β were set to 1.4, while k can be used for calibration.

3 Contaminant sorption

The sorption process describes the attachment of pollutants to soil particles. It distributes available substance mass between the dissolved and adsorbed phase. Sorption is calculated between soil matrix and soil water, between overland flow and the mixing layer, in overland flow to suspended sediments and in the river between suspended sediment and river water in the model. Although the movement of substances in preferential flow pathways greatly reduces sorption due to a small contact area with soil and short contact time (Singh et al., 2002), sorption even occurs during fast macropore transport and especially in small macropores (Jarvis, 2007). Thus, dissolved solutes in macropores are considered to be in contact with and sorbed to soil particles around the macropores in ZIN-AgriTra.

3.1 Sorption equilibrium

The equilibrium partitioning between dissolved pollutant $c_{e,solved}$ and adsorbed pollutant $c_{e,sorbed}$ is governed by an isotherm, i.e. the relationship between both (Figure 4). The quotient between adsorbed and dissolved material is called partitioning coefficient K_d . Since isotherms are generally non-linear, the actual partitioning coefficient is calculated as the first derivation of the isotherm equation or the slope of the isotherm in a specific point. In ZIN-AgriTra, different types of isotherms can be chosen in order to adapt the sorption process to specific substances.

The simplest isotherm considers a linear relationship, using K_d :

$$c_{e,sorbed} = K_d \cdot c_{e,solved} \quad (34)$$

The Langmuir isotherm non-linearly considers a maximum sorption capacity c_{max} and the sorption strength K_L (Langmuir constant):

$$c_{e,sorbed} = \frac{K_L \cdot c_{max} \cdot c_{e,solved}}{1 + K_L \cdot c_{e,solved}} \quad (35)$$

A generalized form of the linear isotherm is the Freundlich isotherm with the Freundlich sorption coefficient K_F and an exponent n :

$$c_{e,sorbed} = K_F \cdot c_{e,solved}^n \quad (36)$$

Generally, it can be assumed that adsorbed and dissolved agrochemicals are not in equilibrium in the environment due to e.g. mixing processes or sediment settling/erosion and sorption kinetics. Thus, from the sum c_{total} of the given adsorbed c_{sorbed} and dissolved concentration c_{solved} and the suspended sediment concentration SSC , the equilibrium dissolved $c_{e,solved}$ and adsorbed $c_{e,sorbed}$ concentrations are determined by:

$$c_{e,sorbed} = \frac{c_{total} - c_{e,solved}}{SSC} \quad (37)$$

For the linear isotherm, $c_{e,solved}$ is calculated by

$$c_{e,solved} = \frac{c_{total}}{1 + K_d \cdot SSC} \quad (38)$$

For the Langmuir isotherm $c_{e,solved}$ is the solution of a quadratic equation:

$$c_{e,solved} = \frac{K_L \cdot c_{total} - 1 - K_L \cdot c_{max} \cdot SSC}{2K_L} + \sqrt{\mu^2 + \frac{c_{total}}{K_L}} \quad (39)$$

The Freundlich isotherm cannot be solved analytically (Frolkovič and Kačur, 2006). Thus, for the solution of the Freundlich isotherm, the numerical bisection method is applied to:

$$c_{e,sorbed} = K_F \cdot (c_{total} - c_{e,sorbed} \cdot SSC)^n \quad (40)$$

Due to the inefficiency of the numerical method, long runtimes are expected. Thus, this solution may only be seen as a preliminary approach.

K_d and K_F are calculated in the model according to a relationship with the fraction of organic carbon f_{OC} as $K_d = K_{OC} \cdot f_{OC}$ and $K_F = K_{FOC} \cdot f_{OC}$. Thus, an organic carbon normalized sorption coefficient K_{OC} or K_{FOC} is used as substance specific model parameter and the variability of sorption is calculated due to variability of f_{OC} in the different soil types and soil layers.

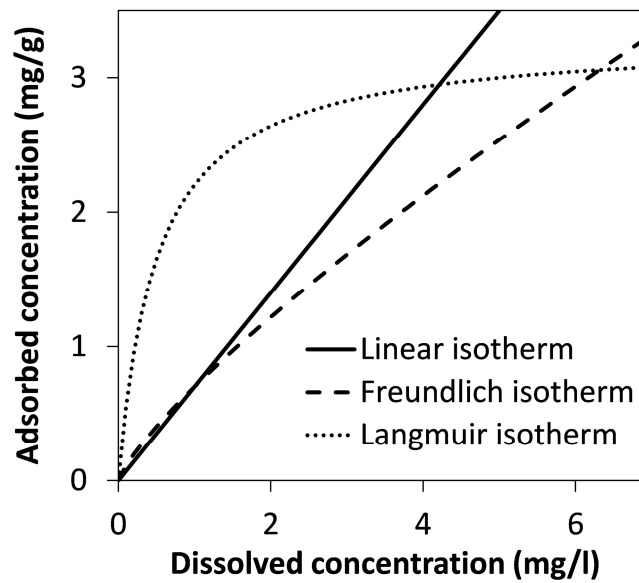


Figure 4: Sorption isotherm types in ZIN-AgriTra.

3.2 Sorption kinetics

In order to describe the temporal delay of the sorption/desorption process (retardation), a pseudo first-order rate equation is implemented (Azizian, 2004):

$$\frac{dc_{sorbed}}{dt} = r(c_{e,sorbed} - c_{sorbed}) \quad (41)$$

r is the rate constant and dt the time step. Adsorption and desorption velocity are usually different. Thus, the rate constant r has generally a different value for adsorption (r_{ad}) and desorption (r_{de}).

3.3 Mobilization by overland flow

Agrochemicals applied in the field reach a rather thin upper soil layer. This soil layer interacts with runoff by sorption processes and is often called mixing layer. The depth of the mixing layer was found before to be in the range of mm to cm (Ahuja et al., 1981). In the ZIN-AgriTra model the mixing layer is incorporated as a soil layer, which is in interaction with surface runoff.

Compared to the bulk soil, eroded sediment in overland flow is enriched with adsorbed pollutants (Sharpley, 1995). This effect can be explained by the fact that fine sediments are more readily eroded than coarse sediments and contain a larger pollutant transport capacity due to a larger surface area. With increasing erosion, fine and coarse particles are eroded in same amounts and thus the ratio between substance content in eroded sediment and substance content in bulk, the enrichment ratio (PER), decreases. This process is implemented using a relationship between PER and the erosion amount SSY (CREAMS model; Menzel, 1980):

$$PER = \exp(2.0 - 0.16 \cdot \ln(SSY)) \quad (42)$$

4 Phosphorus fate processes

4.1 Input function

Phosphorus (P) enters the modelling system in two possible ways: as initial soil concentration and with fertilizer. The initial soil concentration is calculated as non-linear distribution with depth. An initial concentration for the mixing layer P_{ini} has to be specified as input parameter from which the concentrations of subsequent layers P_{layer} is calculated by:

$$P_{layer} = P_{ini} \cdot \left(\frac{z_{layer}}{z_{mixing}} \right)^{c_P} \quad (43)$$

z_{layer} is the mean soil depth of a layer and z_{mixing} the mean depth of the mixing layer. c_P is an empirical coefficient describing the strength of soil P concentration decrease with soil depth.

4.2 P cycling

The following agricultural P cycling processes (Figure 5) are considered in the model (Neitsch et al., 2011):

- 10 % of the biomass P is added to particulate organic P (POP) during harvest
- POP decays at a rate of 5%/day. 80% of the degradate is mineralized to mineral particulate P (PP), 20% ends up as dissolved organic P (DOP)
- DOP is mineralized at a rate of 0.03%/day towards PP.
- DP and PP interact by sorption processes as described above.
- The uptake of P by plants is controlled by biomass growth

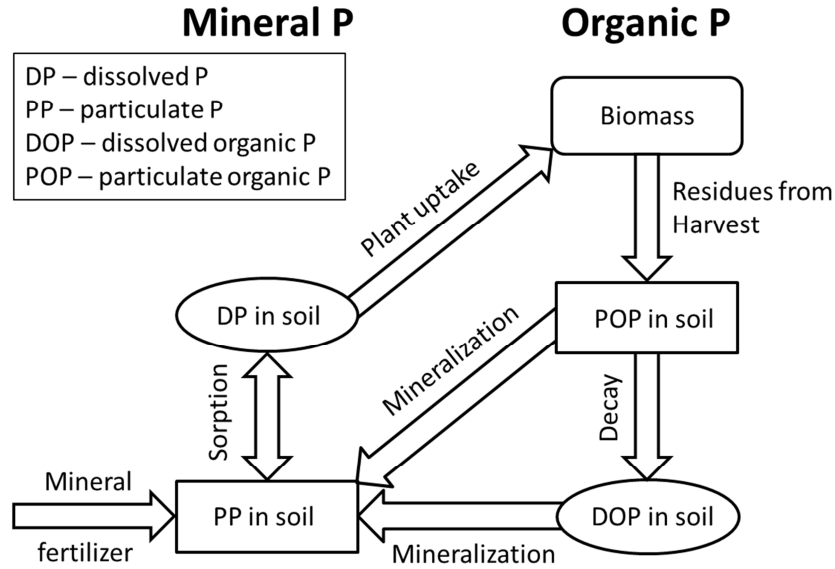


Figure 5: Phosphorus (P) pools and cycling in ZIN-AgriTra.

4.3 Biomass growth

Biomass growth equations were taken from the SWAT model (Neitsch et al., 2011), using heat units HU derived by the air temperature T_a and the base temperature T_{base} , which is a threshold temperature for the begin of plant growth:

$$HU = T_a - T_{base} \quad (44)$$

For each plant there is a heat unit sum PHU required for maturity.

The actual biomass growing at a specific day is calculated as

$$\Delta bio = RUE \cdot 0.5 \cdot H_{day} \cdot (1 - \exp(-k_l \cdot LAI)) \quad (45)$$

RUE is the radiation-use efficiency of the plant, $0.5 \cdot H_{day}$ the incident photosynthetically active radiation (MJ/m^2), $k_l = 0.65$ is the light extinction coefficient and LAI the leaf area index. The total biomass available at a given day is calculated as the sum of Δbio . Equations for P and water uptake by plants as well as growth stress due to missing P or water can be found in Neitsch et al. (2011), sections 5:2.2, 5:2.3 and 5:3.1.

4.4 Crop rotation

In order to calculate the temporal change of plant growth in ZIN-AgriTra, crop rotation is implemented using an

- (i) Intra-annual scheme: sowing and harvesting of different crops change within a year and is the same for each year.
- (ii) Inter-annual scheme: sowing and harvesting of different crops appear once a year. Three years can be specified until the rotation cycle restarts.

5 Pesticide fate processes

5.1 Application

Pesticides are applied at the soil surface or at the plant. Pesticides applied at the soil surface reach the mixing layer. Plant applied pesticides can only be washed off to a certain fraction $f_{wash-off}$. In Knisel (1980), a value of $f_{wash-off} = 0.6$ was found to be applicable to a wide range of substances. Even during application of plant-applied pesticides, a fraction of the substance is deposited at the soil surface, which can be specified in the model by the plant-application fraction $f_{plant-soil}$.

5.2 Transformation

The transformation of a pesticide in direction to the transformation product (TP) is calculated in the model by a first order degradation approach. The formation of a TP is ruled by the formation fraction ff_{PC-TP} as suggested by Kern et al. (2011). Thus, the mass balances of parent compound (PC) mass m_{PC} and TP mass m_{TP} in the soil can be written as:

$$\frac{dm_{PC}}{dt} = m_{app} - \left(\frac{\ln(2)}{DT50_{PC}} \cdot m_{PC} \right) - m_{PC,Runoff} - m_{PC,inf} \quad (46)$$

and

$$\frac{dm_{TP}}{dt} = \left(ff_{PC-TP} \cdot \frac{\ln(2)}{DT50_{PC}} \cdot m_{PC} \right) - \left(\frac{\ln(2)}{DT50_{TP}} \cdot m_{TP} \right) - m_{TP,Runoff} - m_{TP,inf} \quad (47)$$

m_{app} is the pesticide mass applied in the field and $DT50_{PC}$ and $DT50_{TP}$ the transformation half-lives of PC and TP respectively. The mass exported towards the river ($m_{PC,Runoff}$ and $m_{TP,Runoff}$) and the mass infiltrating ($m_{PC,inf}$ and $m_{TP,inf}$) into deeper soil are also considered in these equations. In the model, a transformation half-live can be specified at the plant surface, in the mixing layer, in each of the three soil layers and in overland flow/channel flow.

5.3 Wash-off

Especially for plant-applied pesticides (e.g. insecticides and fungicides), the wash-off process is important during the first rainfall event after application (Wauchope et al., 2004). Additionally, pesticides and TPs may be washed off from roads where they were deposited from spray drift during application. The wash-off of pesticides from plants and roads is implemented as outflow of water with mean concentrations from the interception storage due to storage overflow, induced by ongoing rainfall. Thus, the mass of substance leaving the interception storage M_{wash} is:

$$M_{wash} = P_{out} \cdot \frac{M_{int}}{P_{int}} \quad (48)$$

with

$$P_{out} = \begin{cases} P_{int} + P_{in} - I_{max} & \forall P_{int} + P_{in} > I_{max} \\ 0.0 & otherwise \end{cases} \quad (49)$$

M_{int} is the current mass of pesticide in the interception storage as influenced by transformation processes, $f_{wash-off}$ and $f_{plant-soil}$. P_{int} is the volume of precipitation water currently stored in the interception storage, P_{out} is the amount of water flowing out of the interception storage, P_{in} is the rainfall falling to the interception storage and I_{max} is the interception storage capacity.

6 Pollutant transport

Pollutant transport is calculated as mass transport from cell to cell or soil layer to soil layer. The fraction of pollutant being transported to an adjacent cell is equal to the fraction of transported water. In overland flow and in the river, pollutants may be transported attached to suspended sediment and thus are subject to erosion/deposition processes. Pollutants may enter the soil matrix and soil macropores in dissolved form by infiltration. Generally, substances can be exported to the river via macropore flow, matrix flow, tile drain flow and surface runoff.

7 Boundary conditions

7.1 Flow boundaries

The surface catchment delineates itself due to the 2D overland flow calculation for a given DEM. The border of the DEM is treated as no-flow boundary condition. Water can leave the catchment by reaching the river channel, by evapotranspiration or by vertical subsurface flow from the third soil layer. The latter provides the possibility to deal with vertical infiltration into deeper aquifers or unknown soil layers. Therefore, a saturated hydraulic conductivity can be specified in the geology input file. It is recommended to delineate the catchment prior to modelling since the model calculates all cells of the DEM. Hence, water outside of the catchment boundaries may accumulate at the DEM grid boundaries. Thus, calculation time can be reduced by a prior delineation.

7.2 Initial conditions

Initial values for soil moisture can be specified per soil layer by (i) input grids with relative soil moisture, (ii) uniformly distributed values in the catchment or (iii) by field capacity. Similarly, pesticide initial concentrations in soil can either be given as grids or as spatially uniformly distributed concentrations per layer. Initial mixing layer soil P can be specified per land use type as explained above.

7.3 Precipitation

There are three ways of generating spatially distributed rainfall from point data in the model:

- (i) A single timeseries input is taken as spatially constant value for the whole catchment.
- (ii) Thiessen-Polygons delineate areas of same rainfall values for multiple rainfall stations.
- (iii) Inverse-Distance-Weighting (IDW) calculates spatially distributed rainfall between multiple rainfall stations.

If IDW is chosen, it is possible to specify an elevation correction, using linear dependence of rainfall increase to elevation. Rainfall input timeseries have to be provided in the basis time step of the model. If the time step is lowered for model stability, rainfall is equally distributed between the new, smaller time steps.

7.4 Evapotranspiration

There are several options how values of evapotranspiration can be derived in the model:

- (i) Timeseries input of ET_a .
- (ii) Timeseries input of ET_p .
- (iii) Calculation of ET_p using the FAO method (Allen et al., 1998).

Option (i) skips calculations regarding the relationship between soil moisture and evapotranspiration as explained above. By choosing option (iii) meteorological timeseries of air temperature (°C), wind velocity (m/s), global radiation (W/m²) and air humidity (-) have to be provided. If several meteorological stations are specified, ET_p is calculated at each station and is spatially distributed by an IDW approach. Either an automatically derived factor, using the station with the highest and the lowest value, is used to correct ET_p according to elevation or the factor can be specified in the input files.

Daily values of ET_p are distributed to values of the rainfall time steps $ET_{p,step}$ by means of solar radiation and precipitation. The pre-conditions for evapotranspiration in the model are: there is no rainfall in the corresponding time step and the (hourly) value of radiation has to be > 0:

$$ET_{p,step} = ET_p \cdot \frac{R_{hour}}{\sum(R_{hour}) \cdot no_{\Delta t}} \quad (50)$$

where R_{hour} is the radiation of the actual hour, $\sum(R_{hour})$ is the daily sum of radiation and $no_{\Delta t}$ the number of time steps per hour.

7.5 Irrigation, agrochemical application and point sources

Irrigation, pesticide and phosphorus application can be specified for each rainfall time step. Agrochemicals are applied to the mixing layer and irrigation reaches the first soil layer or the interception storage, depending on the specification of the irrigation type. It is mandatory to specify a grid containing the agricultural fields which are given by the same number per field.

In the river network point sources of discharge, PP and DP can be specified at each river segment. The point source mass appears as source term in the transport equation.

Part II: Input and output files

1 Controller file and model run

The model is provided as 64-bit windows executable file and can be run from the command line. It is essential to provide the complete path and name of a *.ctr file, containing keywords for the model setup and run, as an argument to the ZIN model executable. The model run can be started by:

```
ZIN-AgriTra.exe [Drive letter]:\[folder]\[controller_filename].ctr
```

At the beginning of the controller file, the keyword

```
startcoding
```

tells the model that keywords are provided afterwards. In the following the essential or optional keywords which are called from the controller file are explained. Keywords are generally followed by arguments, which consist of plain text, integers or floating-point numbers. The arguments provided in the following sections are examples, not default values.

1.1 Input/Output folders

Keyword	Argument	Explanation
Proj_Fold	c:\model-project\	Root folder of the Project
Input folders		
iniGrids	c:\model-project\ini\	Folder for initial grids. Optional
appFolder	Input\application \	Folder containing agrochemical application files.
Output folders		
Output	Output\	Basic output folder, relative to 'Proj_Fold'.
ET_fold	Output\ETout\	Folder for evapotranspiration grids.
Outfold_Q	Output\Qout\	Folder for river timeseries output.
Outfold_sums	Output\PCPout\	Folder for precipitation output files.
Outfold_erosion	Output\Erosion\	Folder for erosion output files.

1.2 Input file locations

Keyword	Argument	Explanation
RainPos	Input\RainPos.txt	Location of the Rainfall Stations. Locations are obsolete if 'stationGrid' is used.
stationGrid	Input\grids\stationGrid.asc	ASC-Grid with the locations of the rainfall stations. Single integers are stations, rest is NODATA.
MeteoPos	Input\MeteoPos.txt	Location of the Meteorological Stations. Locations are

		obsolete if 'stationGrid' is used.
Zin_soils	Input\grids\soils.asc	Grid with integers of the soil numbers.
Zin_land use	Input\grids\land use.asc	Grid with integers of the land use numbers.
fieldGrid	Input\grids\fields.asc	Grid with integers of the field numbers for agrochemical application and crop rotation.
Zin_geology	Input\grids\geology.asc	Grid with integers of the geological unit numbers as vertical boundary condition.
DEM	Input\grids\dem.asc	Digital elevation model (float).
Soildepth_grid	Input\grids\soildepth.asc	Soildepth grid (float).
outGrid	Input\grids\outGrid.asc	Grid specifying the locations and the numbers where the model writes timeseries output files – only if this option is chosen (integer).
drainageGrid	Input\grids\outGrid.asc	Grid delineating drained areas. Different drainage areas have different integers.
DrainSeg	Input\drainseg.txt	File allocating drainage areas to river segments.
connectivityGrid	Input\grids\outGrid.asc	Grid separating overland flow areas connected to the river (integer = 1) from unconnected (integer = -9999).
Zin_soilPrp_1	Input\soilprops_1.txt	File containing soil properties of the first layer.
Zin_soilPrp_2	Input\soilprops_1.txt	File containing soil properties of the 2nd layer.
Zin_soilPrp_3	Input\soilprops_1.txt	File containing soil properties of the 3rd layer.
Zin_landusePrp	Input\landuseprops.txt	File containing land use properties.
Zin_geologyPrp	Input\geologyprops.txt	File containing conductivity of the underlying bedrock.
CropRotationPrp	Input\croprotation.txt	File defining crop rotation.
ZIN_DischProps	Input\disch_props.txt	File defining point sources.
Streamgrid	Input\grids\streamgrid.asc	Grid delineating the cells with open channel (integer = 1), culverts (integer = 0) and no channels (integer = -9999).
RiverNet	Input\segments.txt	File defining the river network by connections of river segments.
ChanSegGrid	Input\grids\chanseg.asc	Grid defining the channel segments. Same location of the river as 'Streamgrid' but with continuing integers for channels segment defined in 'RiverNet'.
typeProps	Input\ChanProps.txt	File defining the Channel properties.
EvapDay	Input\Evap\evap.txt	File containing daily values of actual or potential evapotranspiration values.
Radiation	Input\Radiation.txt	Hourly Radiation time series for sub-daily evapotranspiration distribution.
pestController	Input\pesticide.ctr	Controller file containing pesticide physico-chemical properties.

1.3 Keywords

1.3.1 Basic Setup

Keyword	Argument	Unit	Explanation
startDate	7.5.2000		Starting date of the model runs.
endDate	31.7.2000		Ending date of the model run.
RouteStep	1.0	min	Constant routing time step (float)
RainStep	10.0	min	Time step of rainfall input (float)
ZinStep	10.0	min	Maximum time step of model run, is lowered if necessary (float)
SF_stab	5.0	%	Max percent soilmoisture change per iteration (float).
OF_stab	5.0	%	Max percent water column change per iteration (float).
Macro_stab	10.0	%	Max percent macropore saturation change per iteration (float).
max_iter	20		Maximum number of iterations, after max number, stabilizer is doubled (float).
sqmPerCell	100	m ²	Square meters per cell in input grids.
xSize	200		Number of cells in x-direction.
ySize	220		Number of cells in y-direction.

For the calculation of soil depth, a relationship with either the digital elevation model or the surface slope can be specified. '1' means 'on' and '0' mean 'off'.

Keyword	Argument	Explanation
useDepthGrid	1	Switch ON/OFF: Read soil depth from a grid.
soildepthEQDEM	1	Switch ON/OFF the calculation of soil depth by an elevation or slope dependent function. Overrides 'useDepthGrid'.
RelationGrid	2	To which grid do you want to relate soil depth? 1: DEM-Grid, 2: slopeGrid;
EQtype	2	Choose the type of relationship. 1: $a + b \cdot \text{DEM}$; 2: $a \cdot \text{DEM}^b$
EQ_a	0.34	Constant 'a' in 'EQtype' (float)
EQ_b	4.23	Constant 'b' in 'EQtype' (float)

1.3.2 Continue model run

A model run can be continued from a former finalized run using output grids of the former run as input for the actual run.

Keyword	Argument	Explanation
Cont_date	000506	Date of the end of the former model run in format YYMMDD.
iniGridHydro	1	Switch ON/OFF: Continue run for hydrology modelling.
iniGridPest	0	Switch ON/OFF: Continue run for pesticide / TP modelling.
iniGridErosion	0	Switch ON/OFF: Continue run for erosion modelling.

For example, a continuous model run at the 06.05.2000 would require the following grids, located in the folder 'iniGrids' for hydrology:

- ZIN_000506_soilmoisture_1.asc
- ZIN_000506_soilmoisture_2.asc
- ZIN_000506_soilmoisture_3.asc
- ZIN_000506_macrostorage_1.asc
- ZIN_000506_macrostorage_2.asc
- ZIN_000506_macrostorage_3.asc
- ZIN_000506_initialLoss.asc
- WaterColumn_ZIN_000506.asc

For erosion sediment transport it would be:

- SSY_ZIN_000506.asc

For pesticide run, it would be (same applies to corresponding grids for TP modelling):

- ZIN_000506_PestMixingLayer.asc
- ZIN_000506_DPestSoil_1.asc
- ZIN_000506_DPestSoil_2.asc
- ZIN_000506_DPestSoil_3.asc
- ZIN_000506_PPestSoil_1.asc
- ZIN_000506_PPestSoil_2.asc
- ZIN_000506_PPestSoil_3.asc
- ZIN_000506_DPestMacro_1.asc
- ZIN_000506_DPestMacro_2.asc
- ZIN_000506_DPestMacro_3.asc

Initial loss and overland flow pesticide residues are currently neglected.

1.3.3 Modules

The argument provided with the modules are all of type Boolean. '1' means 'on' and '0' mean 'off'.

Keyword	Argument	Explanation
doPhosphorus	1	Switch ON/OFF Phosphorus fate module.
doPesticide	1	Switch ON/OFF Pesticide fate module.
doTP1	1	Switch ON/OFF Transformation product 1 fate module.
doTP2	1	Switch ON/OFF Transformation product 2 fate module.
doRouting	1	Switch ON/OFF river routing module.
doErosion	1	Switch ON/OFF erosion and sediment transport.
doCropRotation	1	Switch ON/OFF crop rotation module.
doPlantGrowth	1	Switch ON/OFF plant growth model.
doIrrigation	1	Switch ON/OFF irrigation.
do_P_Application	1	Switch ON/OFF phosphorus application.
useMacropores	1	Switch ON/OFF macropore flow.

doDischarges	1	Switch ON/OFF point sources.
useDrainages	1	Switch ON/OFF tile drain flow module.
doSubFlow	1	Switch ON/OFF lateral subsurface flow in soil matrix.

1.3.4 Approaches

Keyword	Argument	Explanation
Hydrology		
OF_method	2	Method for overland flow routing: 1: kinematic wave, 2: diffusive wave (integer)
use_green_ampt	1	Switch ON/OFF Green and Ampt infiltration calculation (Boolean)
GreenAmptFactors	0	Switch ON/OFF calculation of Green and Ampt factors for extended infiltration estimation.
RoutingMethod	2	Channel Routing method: 2 - Kinematic Wave, 3 - Diffusive wave.
correctSeg	0	Switch ON/OFF Try to correct slopes in channel routing from DEM
RouteAutoSetup	0	Switch ON/OFF: Automatic setup of channel network - only to ease the setup. Manual corrections are still required!
useStationGrid	1	Switch ON/OFF: Use a grid to define the location of rainfall and meteorological stations as defined in keyword 'stationGrid'
RainMethod	3	Definition of spatial distribution of rainfall data. 0: homogenous; 2: Thiessen-Polygons; 3: inverse distance weighting
CalcHydrHead	1	Switch ON/OFF calculation of the hydraulic potential in lateral subsurface flow (time demanding).
ET_Method	2	Define method to derive evapotranspiration (ET) data: 1: timeseries of ET, 2: calculation with FAO crop ET method (requires meteorological data)
useE_pot	1	Switch ON/OFF: If input timeseries are used, are the timeseries of potential (ON) or actual (OFF) evapotranspiration.
useConnectivityMap	1	Switch ON/OFF the usage of 'connectivityGrid' to determined overland connectivity
UnconnectRouting		Switch ON/OFF the routing in areas not connected to the river as defined in 'connectivityGrid'.
useChanSeg	1	Switch ON/OFF: the use of a predefined river segment grid 'ChanSegGrid'.
CropRotType	1	Define the type of crop rotation. 1: intra-annual (in 1 year), 2: inter-annual (1 crop each year)
irrigationPractice	1	Define the type of irrigation: 1: irrigation below canopy. 2: irrigation above canopy.
Erosion/Sediment transport		
Tau_method	2	Method to calculate Shear Stress. 1:slope-related (equation 28) 2: Schlichting (equation 29)
RiseDropDEM	0	Switch ON/OFF landscape evolution: calculate the rise or drop of the DEM due to erosion/deposition.
Phosphorus fate		
P_isotherm_type	3	Define the type of isotherm for phosphorus sorption calculation. 1: linear, 2: Freundlich, 3: Langmuir isotherm

doP_latFlow	0	Switch ON/OFF the calculation of lateral subsurface flow of phosphorus flow in soil (time demanding).
<i>Pesticide and transformation product (TP) fate</i>		
doPest_latFlow		Switch ON/OFF the calculation of lateral subsurface flow of pesticide and TP flow in soil (time demanding).
<i>All agrochemicals fate</i>		
enrichment_type	1	Define agrochemical enrichment in eroded sediment. 0:constant enrichment ratio, 1: variable enrichment ration during event (equation 42)

1.3.5 Parameters

Keyword	Argument	Explanation
<i>Hydrology</i>		
IniFK1	1	Initialize soil moisture with field capacity in layer 1.
IniFK2	0	Initialize soil moisture with field capacity in layer 2.
IniFK3	0	Initialize soil moisture with field capacity in layer 3.
initMoist_1	55	If 'IniFK1' = 0, initial soil moisture for layer 1 (0-100%).
initMoist_2	75	If 'IniFK2' = 0, initial soil moisture for layer 2 (0-100%).
initMoist_3	85	If 'IniFK3' = 0, initial soil moisture for layer 3 (0-100%).
min_water_col	0.1	Minimum water column initiation of overland flow (mm).
Soildepth_multi	1.0	Multiplier for soil depth - useful for calibration.
drainLayer	3	Layer in which the tile drains are located.
drainDistance	14	Distance between tile drains pipes (m).
EtaGrad	0.1	Elevation correction of evapotranspiration (mm/100m); -9999: gradient is automatically derived from multiple input stations.
lat_Kf_multi_1	5	Anisotropy factor for layer 1 (equation 7).
lat_Kf_multi_2	5	Anisotropy factor for layer 2 (equation 7).
lat_Kf_multi_3	5	Anisotropy factor for layer 3 (equation 7).
macroDistr	4	Parameter for macropore distribution (n^* in equation 12).
<i>Erosion/Sediment transport in Overland Flow</i>		
TransCapCoef	1.3	Transport capacity calibration coefficient (equation 33).
TauEros	1.0	Critical shear stress above which erosion occurs (N/m^2).
TauDepo	0.1	Critical shear stress below which deposition occurs (N/m^2).
SettlVelo	0.1	Settling velocity of suspended sediment (mm/s).
EroCoeff	0.5	Erosion coefficient ($g/m^2/s$).
<i>Phosphorus fate</i>		
P_isotherm_K	1.8	Sorption strength parameter for all isotherm types (l/g).
P_isotherm_parm	0.9	Freundlich isotherm: exponent. Langmuir: maximum sorption capacity (mg/g);
PAdsorption_rate	4.0	Adsorption rate coefficient from equation 41 (1/day).

PDesorption_rate	0.4	Desorption rate coefficient from equation 41(1/day).
IniPconcChannel	0.3	Initial concentration of P in channel sediments (g/kg).
P_depth_factor	-0.5	Factor describing the initial P distribution in soil as given in equation 43.
All agrochemicals fate		
mixingLayerDepth	1	(cm). Depth of the mixing layer.
sorptionMacro_depth	1	(mm) depth of soil around macropores in interaction with dissolved agrochemicals in macropores by sorption (float).
enrichment_const	30	Define the constant enrichment ratio. If variable enrichment was chosen, this defines the maximum enrichment ratio.
OF_OC_frac	0.02	Fraction of organic carbon in overland flow. Used for linear and Freundlich isotherm.
Channel Routing		
streamDir	8	StreamGrid only in 4 directions (horizontal and vertical) or in 8 directions (also diagonal). Only needed for 'RouteAutoSetup = 1'
channel_x	1	Steepness of river banks, 1= 45°, increase = less steep
TransCapCoef_river	1.2	Transport capacity calibration coefficient (eq. 33)
TauEros_river	50	Critical shear stress above which erosion occurs (N/m ²).
TauDepo_river	1	Critical shear stress below which deposition occurs (N/m ²).
SettlVelo_river	0.1	Settling velocity of suspended sediment (mm/s).
EroCoeff_river	0.1	Erosion coefficient (g/m ² /s).
Precipitation pre-processing		
rainGrad	0.01	Gradient of precipitation increase with elevation (%/100m).
refHeight	500	Reference elevation for precipitation correction (m.a.s.l.)
Max_Stats	99	Maximum number of neighbouring rainfall stations to be used for inverse distance weighting.
pcpUnit	1	Unit in which precipitation is given as input. 0-mm/h, 1- mm/time step
NoData_zero		Switch ON/OFF: interpret '9999' in rainfall input file as 0.0.

1.3.6 Output options

Keyword	Argument	Explanation
doOutGrid	1	Switch ON/OFF. Use grid given in 'outGrid' to define timeseries outputs.
TimeseriesX	204	If doOutGrid=0, give cell number in X-direction of single timeseries output. 0/0 is upper left corner of grid.
TimeseriesY	134	If doOutGrid=0, give cell number in Y-direction of single timeseries output. 0/0 is upper left corner of grid.
PCP_output	1	Switch ON/OFF: write precipitation grid per time step (idw only) (mm)
WriteSums	1	Switch ON/OFF: write daily rain sum grids (idw only)
reWriteSums	1	0: no (use an existing rain sum grid), 1: yes (overwrite or file doesn't exist)
soilMois	1	Switch ON/OFF: write output gridfile of soil moisture at the end of a day (fraction 0-1)
writeWC	1	Switch ON/OFF: write output gridfile of water column at the end of a day

		(mm)
writeWCstep	1	Switch ON/OFF: write output gridfile of water column every rainfall step (mm)
writeErosion	1	Switch ON/OFF: write daily grid of net erosion(<0) and deposition(>0) (kg/m ²)
writeInitialLoss	1	Switch ON/OFF: write output gridfile of initial loss storage at the end of a day (mm)
writeExfiltration	1	Switch ON/OFF: write output gridfile of exfiltration at the end of a day (mm)
writePestSoil	1	Switch ON/OFF: write output gridfile of pesticide and TPs from the mixing layer, the three soil matrix and three macropore layers at the end of a day (kg/cell).
writePestOF	1	Switch ON/OFF: write pesticide and TPs in overland flow for each rainfall time step (g/cell).
writeETGrids	1	Switch ON/OFF: write daily grid of calculated FAO crop evapotranspiration after inverse distance weighting (mm).
mergeQ	1	Switch ON/OFF: Merge all daily river timeseries output files at the end of the model run into one large file.

1.3.7 Pathway analysis

In order to evaluate contributions of distinct pathways to total water and substance export, it is possible to switch on/off the river transport of each pathway. The process switched off appears to be an error in the water/substance balance. In this version, only water, pesticide and TP fluxes can be analysed.

Keyword	Argument	Explanation
UseSwitches	1	Switch ON/OFF the usage of below switches for process testing.
MatrixSwitch	1	Switch ON/OFF lateral matrix water flow to the river
PestMatrixSwitch	1	Switch ON/OFF lateral matrix pesticide flow to the river
TP1MatrixSwitch	1	Switch ON/OFF lateral matrix TP1 flow to the river
TP2MatrixSwitch	1	Switch ON/OFF lateral matrix TP2 flow to the river
MacroSwitch	1	Switch ON/OFF lateral macropore water flow to the river
PestMacroSwitch	1	Switch ON/OFF lateral macropore pesticide flow to the river
TP1MacroSwitch	1	Switch ON/OFF lateral macropore TP1 flow to the river
TP2MacroSwitch	1	Switch ON/OFF lateral macropore TP2 flow to the river
OFSwitch	1	Switch ON/OFF overland flow to the river
PestOFSwitch	1	Switch ON/OFF pesticide overland flow to the river
TP1OFSwitch	1	Switch ON/OFF TP1 overland flow to the river
TP2OFSwitch	1	Switch ON/OFF TP2 overland flow to the river
DrainMatrixSwitch	1	Switch ON/OFF matrix water flow to tile drains
PestDrainMatrixSwitch	1	Switch ON/OFF matrix pesticide flow to tile drains
TP1DrainMatrixSwitch	1	Switch ON/OFF matrix TP1 flow to tile drains
TP2DrainMatrixSwitch	1	Switch ON/OFF matrix TP2 flow to tile drains
DrainMacroSwitch	1	Switch ON/OFF macropore water flow to tile drains

PestDrainMacroSwitch	1	Switch ON/OFF macropore pesticide flow to tile drains
TP1DrainMacroSwitch	1	Switch ON/OFF macropore TP1 flow to tile drains
TP2DrainMacroSwitch	1	Switch ON/OFF macropore TP2 flow to tile drains

2 Pesticide controller file

The pesticide controller file contains environmental fate parameters pesticide and both transformation products (TP1 and TP2). Its location is specified in the Controller File by the keyword 'pestController'. It also has to start with 'startcoding'.

Keyword	Argument	Explanation
ff_pest_TP1	0.1	Formation fraction of pesticide to TP1. (equation 47)
ff_pest_TP2	0.1	Formation fraction of pesticide to TP2. (equation 47)
ff_TP1_TP2	0.01	Formation fraction of TP1 to TP2. (equation 47)
ff_TP2_TP1	0.0	Formation fraction of TP1 to TP1. (equation 47)
Pesticide		
Pest_isotherm_type	1	Define the isotherm used for the pesticide. 1: linear, 2: Freundlich, 3: Langmuir isotherm
Pest_isotherm_K	0.05	Sorption strength parameter (l/g). Normalized to organic carbon content for linear and Freundlich isotherm. Not normalized for Langmuir isotherm.
Pest_isotherm_parm	0.9	Freundlich isotherm: exponent. Langmuir: maximum sorption capacity (mg/g).
PestAdsorption_rate	10	Adsorption rate coefficient from equation 40 (1/day).
PestDesorption_rate	5	Desorption rate coefficient from equation 40 (1/day).
wash_frac_Pest	0.6	Fraction of intercepted pesticide that can be washed off.
plant_frac_Pest	0.1	Fraction of pesticide intercepted by plants.
DT50_plant_Pest	5	Plant half-life (days).
DT50_surface_Pest	15	Mixing layer half-life (days).
DT50_soil_Pest_1	20	Soil layer 1 half-life (days).
DT50_soil_Pest_2	30	Soil layer 2 half-life (days).
DT50_soil_Pest_3	150	Soil layer 3 half-life (days).
DT50_hydro_Pest	300	Hydrolysis half-life (days)
Pest_Solubility	5.3	Solubility in mg/l.
iniPest_1	0.1	Initial pesticide concentration in soil layer 1 (µg/l).
iniPest_2	0.2	Initial pesticide concentration in soil layer 2 (µg/l).
iniPest_3	0.3	Initial pesticide concentration in soil layer 3 (µg/l).
Transformation product 1 (TP1)		
TP1_isotherm_type	1	Define the isotherm used for TP1. 1: linear, 2: Freundlich, 3: Langmuir isotherm

TP1_isotherm_K	0.05	Sorption strength parameter (l/g). Normalized to organic carbon content for linear and Freundlich isotherm. Not normalized for Langmuir isotherm.
TP1_isotherm_parm	0.9	Freundlich isotherm: exponent. Langmuir: maximum sorption capacity (mg/g);
TP1Adsorption_rate	10	Adsorption rate coefficient from equation 40 (1/day).
TP1Desorption_rate	5	Desorption rate coefficient from equation 40 (1/day).
DT50_plant_TP1	5	Plant half-life (days).
DT50_surface_TP1	15	Mixing layer half-life (days).
DT50_soil_TP1_1	20	Soil layer 1 half-life (days).
DT50_soil_TP1_2	30	Soil layer 2 half-life (days).
DT50_soil_TP1_3	150	Soil layer 3 half-life (days).
DT50_hydro_TP1	300	Hydrolysis half-life (days)
TP1_Solubility	5.3	Solubility in mg/l.
iniTP1_1	0.1	Initial TP1 concentration in soil layer 1 (µg/l).
iniTP1_2	0.2	Initial TP1 concentration in soil layer 2 (µg/l).
iniTP1_3	0.3	Initial TP1 concentration in soil layer 3 (µg/l).
Transformation product 2 (TP2)		
TP2_isotherm_type	1	Define the isotherm used for TP2. 1: linear, 2: Freundlich, 3: Langmuir isotherm
TP2_isotherm_K	0.05	Sorption strength parameter (l/g). Normalized to organic carbon content for linear and Freundlich isotherm. Not normalized for Langmuir isotherm.
TP2_isotherm_parm	0.9	Freundlich isotherm: exponent. Langmuir: maximum sorption capacity (mg/g);
TP2Adsorption_rate	10	Adsorption rate coefficient from equation 41 (1/day).
TP2Desorption_rate	5	Desorption rate coefficient from equation 41 (1/day).
DT50_plant_TP2	5	Plant half-life (days).
DT50_surface_TP2	15	Mixing layer half-life (days).
DT50_soil_TP2_1	20	Soil layer 1 half-life (days).
DT50_soil_TP2_2	30	Soil layer 2 half-life (days).
DT50_soil_TP2_3	150	Soil layer 3 half-life (days).
DT50_hydro_TP2	300	Hydrolysis half-life (days)
TP2_Solubility	5.3	Solubility in mg/l.
iniTP2_1	0.1	Initial TP2 concentration in soil layer 1 (µg/l).
iniTP2_2	0.2	Initial TP2 concentration in soil layer 2 (µg/l).
iniTP2_3	0.3	Initial TP2 concentration in soil layer 3 (µg/l).

3 Spatial input parameters

The spatial distribution of parameters is generally determined by ASCII-grids as provided by ESRI ArcGIS software. The grids define zones with same parameter values. The parameter values are provided in property files (plain text: *.txt). The structure of the property files and the meaning of parameters are explained in this section. The first row of the property files is always a description of the corresponding properties (descriptions can be chosen freely, order of values is important) and the first column consists of the type-number followed by columns of the properties.

3.1 Land use properties

In the land use properties file the following properties are defined for each land use in subsequent columns:

1. No: Type number of land use.
2. I_{max} : Interception storage capacity (mm).
3. z_{root} : Root depth (m).
4. f_{imp} : Fraction of a cell being impervious.
5. C_{crop} : Single crop coefficient.
6. f_{can} : fraction of soil covered by canopy
7. C_e : Crop and management factor of USLE.
8. n_{Man} : Mannings roughness coefficient
9. d_{ma} : Macropore diameter (mm)
10. n_{ma} : number of macropores per square meter
11. $f_{ma,lat}$: fraction of macropores laterally connected
12. P_{ini} : initial soil P content of mixing layer (mg/kg).
13. HU_m : Heat units at maturity
14. HU_{frac} : Fraction of HU_m at simulation beginning
15. T_{base} : Threshold temperature for plant growth (°C)
16. LAI : Leaf areas index
17. RUE: Radiation-use efficiency of the plant (Neitsch et al., 2011)
18. fr_{P1} : Normal fraction of P in the plant biomass at emergence (Neitsch et al., 2011)
19. fr_{P2} : Normal fraction of P in the plant biomass at 50% maturity (Neitsch et al., 2011)
20. fr_{P3} : Normal fraction of P in the plant biomass maturity (Neitsch et al., 2011)

Table 1: Example of a land use property file

No	I_{max}	z_{root}	f_{imp}	C_{crop}	f_{can}	C_e	n_{Man}	d_{ma}	n_{ma}	$f_{ma,lat}$	P_{ini}	HU_m	HU_{frac}	T_{base}	LAI	RUE	fr_{P1}	fr_{P2}	fr_{P3}
1	2.2	1.5	0.00	1.1	0.95	0.10	0.40	4.0	200	0.05	200	15000	1.0	2.50	4.50	22.5	0.0030	0.0012	0.0008
2	2.0	0.1	0.50	0.3	1.00	0.01	0.10	4.0	0	0.05	100	20000	0.0	5.00	5.00	15.0	0.0007	0.0004	0.0003
3	2.0	0.1	0.50	0.5	1.00	0.10	0.05	4.0	0	0.05	300	1500	0.4	6.00	3.00	46.0	0.0063	0.0029	0.0023
4	0.0	0.1	0.00	0.0	1.00	0.80	0.15	4.0	200	0.05	50	0	0.0	-9999	0.00	0.00	0.0000	0.0000	0.0000

3.2 Soil properties 1st layer

The soil properties file of the 1st layer is different to the two following layers since parameters for the Green and Ampt infiltration approach and two erosion equation parameters are additionally included. The following properties are defined for each soil in subsequent columns:

1. No: Type number of soil
2. K : Infiltration parameter, depending on chosen approach:
 - a. Soil hydraulic conductivity for the Green and Ampt approach in cm/h.
 - b. Constant infiltration rate (cm/h)
3. S_f : Effective suction head at the wetting front for the Green and Ampt approach (cm).
4. G_{cr} : Green and Ampt crust factor (Rawls et al., 1990).
5. G_{ma} : Green and Ampt macropore factor (Rawls et al., 1989).
6. z_{layer} : Soil depth depending on approach
 - a. If no soil depth grid is used: soil depth in m.
 - b. If soil depth grid is used: fraction of total soil depth.
7. Φ : Effective soil matrix porosity.
8. K_s : Soil hydraulic conductivity in cm/h.
9. n : Parameter of Mualem-van Genuchten equation.
10. α : Parameter of Mualem-van Genuchten equation.
11. L : Parameter of Mualem-van Genuchten equation.
12. a : Detachability for sheet erosion calculation.
13. b : Empirical parameter for sheet erosion calculation.
14. c : Exponent determining the dynamics of the virtual GW table.
15. f_{ma} : Factor for variation of macropore number (specified in land use file) due to soil properties.
16. ρ_{soil} : Soil density (g/cm³).
17. f_{oc} : Fraction of organic carbon in soil (-).

Table 2: Example of soil properties file for the 1st layer

No	K	S_f	G_{cr}	G_{ma}	z_{layer}	Φ	K_s	n	α	L	a	b	c	f_{ma}	ρ_{soil}	f_{oc}
1	0.77	14.32	0.5	1.2	0.20	0.52	1.55	1.466	0.014	0.50	0.00	2.00	2.5	1.0	1.20	0.03
2	0.92	8.89	0.2	1.2	0.20	0.54	1.85	1.498	0.012	0.50	0.00	2.00	5.0	1.0	1.20	0.02
3	0.66	19.40	0.7	1.5	0.20	0.52	1.31	1.457	0.013	0.50	0.00	2.00	1.0	1.0	1.20	0.01
4	1.20	13.72	0.8	0.9	0.20	0.53	2.41	1.457	0.015	0.50	0.00	2.00	10	1.0	1.20	0.07

3.3 Soil properties 2nd and 3rd layer

The parameters for each soil in the 2nd and 3rd soil layer are the same. The parameters values can be specified in the soil property files of both layers. The parameters are:

1. No: Type number of soil.
2. z_{layer} : Soil depth depending on approach.
 - If no soil depth grid is used: soil depth in m.
 - If soil depth grid is used: fraction of total soil depth.
3. Φ : Effective soil porosity.
4. K_s : Soil hydraulic conductivity in cm/h.
5. n : Parameter of Mualem-van Genuchten equation.
6. α : Parameter of Mualem-van Genuchten equation.
7. L : Parameter of Mualem-van Genuchten equation.
8. c : Exponent determining the dynamics of the virtual GW table.

9. f_{ma} : Factor for variation of macropore number (specified in land use file) due to soil properties.
10. ρ_{soil} : Soil density (g/cm³).
11. f_{OC} : Fraction of organic carbon in soil (-).

Table 3: Example of soil properties file for the 2nd and 3rd layer

No	z_{layer}	Φ	K_s	n	α	L	c	f_{ma}	ρ_{soil}	f_{OC}
1	0.51	0.47	0.89	1.439	0.016	0.5	2.5	1	1.4	0.03
2	0.77	0.47	0.59	1.439	0.014	0.5	2.0	1	1.4	0.02
3	0.28	0.47	0.84	1.428	0.016	0.5	2.5	1	1.4	0.01
4	0.12	0.50	3.54	1.480	0.026	0.5	3.0	1	1.4	0.07

3.4 Geology properties

In the geology properties file, only the saturated hydraulic conductivity of the underlying bedrock is defined as:

1. Type number of rock.
2. K_s : Saturated hydraulic conductivity of bedrock (mm/d).

Table 4: Example of geology properties file

type	K_s
1	86.40
2	864.00
3	0.86

3.5 Channel properties

In the channel properties file the following properties are defined for each channel type:

1. No: Type number of channel.
2. n_{Man} : Mannings' roughness coefficient.
3. z_{chan} : Depth of river channel (m).
4. C_e : Erodible fraction of river bed.
5. Sed_{ini} : Initial sediment mass in the channel (kg/m²).

Table 5: Example of channel properties file.

No	n_{Man}	z_{chan}	C_e	Sed_{ini}
1	0.035	3.0	1.00	500
2	0.03	4.0	0.50	1000

3.6 Definition of river network

The river network is defined in a text file by connections and properties of river segments. The meaning of the columns in the input file is:

1. No_{seg} : Number of the river segment.
2. upper: Number of the upper stream segment; '0' indicates a headwater segment.
3. lower: Number of the lower steam segment; 0 indicates the outlet of the catchment.
4. trib_1: Number of the first tributary; 0 indicates no tributary;
5. trib_2: Number of the second tributary; 0 indicates no tributary;
6. s_{DEM} : Slope of the segment (-).
7. l_{seg} : Length of the segment (m).
8. b_{seg} : Width of the segment (m).
9. $type_c$: Channel type as defined in the channel properties file.
10. out_c : '1': write output timeseries at this segment, '0' don't write output timeseries.

Table 6: Example of river network definition file.

No_{seg}	upper	lower	trib_1	trib_2	s_{DEM}	l_{seg}	b_{seg}	$type_c$	out_c
1	0	2	0	0	0.02	50.50	0.5	1	0
2	1	4	0	0	0.02	56.40	1.0	2	0
3	0	4	0	0	0.01	22.12	0.5	1	0
4	3	0	3	0	0.005	62.34	1.5	2	1

3.7 Definition of tile drain flow network

Outputs of tile drained areas are associated with certain river segments. This association is defined in a file containing:

1. No_{drain} : Number of the tile drained area.
2. No_{seg} : Number of the river segment the tile drained areas is discharge to.

Table 7: Example of tile drain definition file

No_{drain}	No_{seg}
1	4
2	3
3	2
4	2

4 Boundary conditions

4.1 Point sources

Point sources can be defined for discharge, suspended sediment, dissolved and adsorbed phosphorus. Currently, only constantly discharging point sources are implemented.

1. No : Number of the point source.
2. Name: Name of the point source (text). Only for user convenience.
3. No_{seg} : Number of the river segment the point source discharges into.
4. type: 'constant': constantly discharging point source, 'timeseries': timeseries file providing variable point sources input (not yet working).

5. Q_{const} : Discharge value of constant point source (m^3/s).
6. DP_{const} : Dissolved phosphorus value of constant point source. Unit defined in *unit*.
7. PP_{const} : Adsorbed phosphorus value of constant point source. Unit defined in *unit*.
8. SSC_{const} : Suspended sediment value of constant point source. Unit defined in *unit*.
9. *unit*: Unit of constant point source. 'mg/l' or 'kg/d'.
10. file: Filename of timeseries point source (not yet working).

Table 8: Example of point source definition file.

<i>No</i>	Name	<i>No_{seg}</i>	type	Q_{const}	DP_{const}	PP_{const}	SSC_{const}	<i>unit</i>	file
1	WWTP_1	2	constant	0.025	0.78	0.00	0	mg/l	none
2	WWTP_2	1	constant	0.038	8.42	0.00	0	mg/l	none
3	WWTP_3	3	constant	0.002	0.72	0.00	0	mg/l	none
4	Animal_1	4	constant	0.005	2.74	0.00	21.6	kg/d	none

4.2 Crop rotation

Crop rotation is defined by planting and harvesting days. Up to three crops can be defined in the rotation. '-9999' defines the end of the rotation cycle.

1. No_{field} : Field number.
2. $Luse_1$: Land use number of the
3. $SowD_1$: Sowing day of the 1st crop (Julian Day of the year).
4. $HarvD_1$: Harvesting day of the 1st crop (Julian Day of the year).
5. $SowD_2$: Sowing day of the 2nd crop (Julian Day of the year).
6. $HarvD_2$: Harvesting day of the 2nd crop (Julian Day of the year).
7. $SowD_3$: Sowing day of the first 3rd (Julian Day of the year).
8. $HarvD_3$: Harvesting day of the 3rd crop (Julian Day of the year).

Table 9: Example of crop rotation input file.

No_{field}	$Luse_1$	$SowD_1$	$HarvD_1$	$Luse_2$	$SowD_2$	$HarvD_2$	$Luse_3$	$SowD_3$	$HarvD_3$
1	1	-9999	-9999	-9999	-9999	-9999	-9999	-9999	-9999
2	4	105	242	4	243	104	-9999	-9999	-9999
3	2	32	244	4	245	31	-9999	-9999	-9999

4.3 Irrigation

Irrigation is defined as input of water (mm) per field and time step. For each field an input file of irrigation in the same time step of rainfall has to be defined. The files are located in 'appFolder' and are named by *irrigation_<Field number>.txt* (i.e. irrigation_2.txt for irrigation at field 2). Several days can be defined in the input file, but only whole days.

The input files contain the following columns:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. *min*: Minute of the actual day.
3. *amount*: Quantity of irrigation water in the time step (mm).

Table 10: Example of irrigation input file for a 30 min time step.

<i>date</i>	<i>min</i>	<i>amount</i>
01.07.2010	0	0.0
01.07.2010	30	10.0
01.07.2010	60	20.0
01.07.2010	90	0.0
...
01.07.2010	1410	0.0

4.4 Agrochemical application

Agrochemical application is similarly defined as irrigation. The input files are located in ‘appFolder’ and are named by *P_<Field number>.txt* for phosphorus application and *Pest_<Field number>.txt* for pesticide application. Several days can be defined in the input file, but only whole days.

The input files contain the following columns:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. *min*: Minute of the actual day.
3. *amount*: Quantity of agrochemical application in the time step (kg/ha).

Table 11: Example of irrigation input file for a 30 min time step.

<i>date</i>	<i>min</i>	<i>amount</i>
01.07.2010	0	0.0
01.07.2010	30	0.50
01.07.2010	60	0.50
01.07.2010	90	0.0
...
01.07.2010	1410	0.0

5 Meteorological input files

5.1 Rainfall input files

Rainfall input is defined by a file relating the rainfall stations to input files and the actual rainfall input files. The rainfall station definition file contains the following columns:

1. Station: Station number.
2. xPos: x-position of station if no grid is used (Keyword: ‘useStationGrid’). The origin (0/0) is the upper left corner of a grid.
3. yPos: y-position of station if no grid is used (Keyword: ‘useStationGrid’). The origin (0/0) is the upper left corner of a grid.
4. elevation: elevation of rainfall station.
5. file: location of rainfall file.

Table 12: Example of rainfall station definition file.

Station	xPos	yPos	elevation	file
1	5	110	79	C:\ZIN\Input\rainfall\station_1.txt
2	56	39	303	C:\ZIN\Input\rainfall\station_2.txt

The actual rainfall data file may have gaps, but whole days have to be provided with data:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. *min*: Minute of the actual day.
3. *amount*: Quantity of rainfall. The unit is defined in Keyword 'pcpUnit'.

Table 13: Example of rainfall station file for a 30 min time step.

<i>date</i>	<i>min</i>	<i>amount</i>
01.07.2010	0	0.0
01.07.2010	30	3.2
01.07.2010	60	7.1
01.07.2010	90	2.8
...
01.07.2010	1410	0.0

5.2 Input files for evapotranspiration

A meteorological file has to be defined if evapotranspiration is calculated by the FAO method in the model. The location of rainfall and meteorological files are the same and either defined in the station-grid or in the rainfall station position file. The file defining the meteorological input timeseries only contains:

1. Station: Station number.
2. file: location of rainfall file.

Table 14: Example of meteorological station definition file.

Station	file
1	C:\ZIN\Input\meteo\station_1.txt
2	C:\ZIN\Input\meteo\station_2.txt

Since evapotranspiration is calculated as daily value, the meteorological data has to be provided as daily values as well. The files with meteorological station data contain:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. T_a : Average daily air temperature (°C)
3. v_{wind} : Average daily wind velocity (m/s)
4. *rad*: Average daily global radiation (W/m²)
5. R_h : Average daily relative humidity (-)

Table 15: Example of meteorological data file.

<i>date</i>	T_a	v_{wind}	<i>rad</i>	R_h
12.01.2001	9.5	1.2	64	0.92
13.01.2001	8.1	1.0	60	0.91

14.01.2001	9.2	0.4	105	0.91
15.01.2001	6.4	0.1	59	0.98

If evapotranspiration is not calculated in the model but given as input timeseries, the evapotranspiration timeseries file contains:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. *evap*: Daily evapotranspiration (mm).

Table 16: Example of evapotranspiration input file.

<i>date</i>	<i>evap</i>
12.01.2001	1.5
13.01.2001	0.1
14.01.2001	2.2
15.01.2001	1.4

For the distribution of the daily evapotranspiration to hourly values, a global radiation file has to be provided as input in a hourly resolution. Since this data is not readily available in many regions and it is only used for a temporal distribution, artificial data of a cloudless day as affected by latitude and longitude may be provided. A complete timeseries has to be provided (no gaps). The input file contains:

1. *date*: Date of the actual day in format dd.mm.yyyy
2. *min*: Minute of the actual day.
3. *rad*: Average hourly global radiation (W/m²)

Table 17: Example of hourly radiation input file.

<i>date</i>	<i>min</i>	<i>rad</i>
01.07.2010	0	0.0
01.04.2010	60	0.0
...
01.04.2010	720	757
01.04.2010	780	789
...
01.04.2010	1380	0.0

6 Output files

6.1 River output

Daily output timeseries of the channel routing are located in the folder given by the keyword 'Outfold_Q'. The folder always contains discharge and water level timeseries for the river segments where outputs were specified. If agrochemicals are modelled, the river concentrations are also provided in this folder. The files are named by "ZIN_ "<date>"_ "<substance>".txt". <substance> can be "Q" for discharge, "level" for water level, "P" for phosphorus, "Pest" for pesticide and "TP1"/"TP2" for the two transformation products. In the upper left corner of the discharge file, the substance and the unit are given.

Table 18: Example of river discharge output timeseries for segments 2, 7 and 12.

Q(m3/s)	'2	'7	'12
"2.1.2000 0:0:0"	0.0125166	0.0342932	0.0104278
"2.1.2000 0:10:0"	0.0125155	0.0342521	0.0104156
"2.1.2000 0:20:0"	0.0125103	0.0342176	0.0104052
...

6.2 Soil timeseries

Soil output timeseries files are written for specified points in the catchment. The files are located in the main output folder. The hydrological output file (e.g. timeseries_1.txt) contains columns with the following headers:

1. "Date/Time"
2. "Rainfall": Amount of rainfall in the time step(mm)
3. "Evap(mm)": Amount of evapotranspiration in the time step
4. "Soilmoisture_1": Soil moisture of layer 1.
5. "Soilmoisture_2": Soil moisture of layer 2.
6. "Soilmoisture_3": Soil moisture of layer 3.
7. "MacroMoisture_1": Relative filling of the macroporosity of layer 1.
8. "MacroMoisture_2": Relative filling of the macroporosity of layer 2.
9. "MacroMoisture_3": Relative filling of the macroporosity of layer 3.
10. "Water_Column": Depth of the water column (mm).
11. "SSY(kg)": Amount of suspended sediment in the water column.
12. "DP_soil(mg/l)": Dissolved phosphorus concentration in soil layer 1 (mg/l).
13. "PP_soil(g/kg)": Particulate phosphorus concentration in soil layer 1 (g/kg).
14. "PinBiomass(kg/ha)": Amount of phosphorus in biomass (kg/ha).
15. "Biomass(kg/ha)": Amount of biomass in cell (kg/ha).

The meaning of the columns of the pesticide soil (e.g. timeseries_Pest_1.txt) time series are:

1. "Date/Time"
2. "DPest_plant(g/m²)": Dissolved substance at the plant surface (g/m²).
3. "Pest_mixing_layer(mg)": Amount in the mixing layer (mg/cell).
4. "DPest_soil_1(μg/l)": Dissolved substance concentration in soil layer 1 (μg/l).
5. "DPest_soil_2(μg/l)": Dissolved substance concentration in soil layer 2 (μg/l).
6. "DPest_soil_3(μg/l)": Dissolved substance concentration in soil layer 3 (μg/l).
7. "PPest_soil_1(mg/kg)": Adsorbed substance concentration in soil layer 1 (mg/kg).
8. "PPest_soil_2(mg/kg)": Adsorbed substance concentration in soil layer 2 (mg/kg).
9. "PPest_soil_3(mg/kg)": Adsorbed substance concentration in soil layer 3 (mg/kg).
10. "DPest_OF(μg/l)": Dissolved substance concentration in overland flow (μg/l).
11. "PPest_OF(mg/kg)": Adsorbed substance concentration in overland flow (mg/kg).

The meaning of the transformation product soil output time series columns (e.g. timeseries_TP1_1.txt) are accordingly.

6.3 Balance files

Balance files contain daily values of different variables and are located in the main output folder. The water balance (waterBalance.txt) contains columns with the following headers:

1. ModelRun:Date/Time: Date and time when the model run took place.
2. sim-Day Rain(mm): Date simulated by the model.
3. Evap(mm): Actual evapotranspiration sum (mm).
4. GW_recharge(mm): Sum of water leaving the third soil layer towards the bedrock (mm).
5. storage_change(mm): Storage change in soil and interception storage (mm).
6. WaterColChange(mm): Amount of water storage change in overland flow (mm).
7. exfiltration(mm): Amount of water leaving the first soil layer towards overland flow (mm).
8. OFlowToRiver(mm): Amount of overland flow reaching the river (mm).
9. MatrixflowToRiver(mm): Amount of soil matrix flow reaching the river (mm).
10. MacroporeflowToRiver(mm): Amount of soil macropore flow reaching the river (mm).
11. DrainageflowToRiver_Matrix(mm): Amount of soil matrix flow reaching tile drains (mm).
12. DrainageflowToRiver_Macro(mm): Amount of soil macropore flow reaching tile drains (mm).
13. Q_Outlet(mm): Amount of water leaving the catchment (mm).
14. Sed_Outlet(t/ha): Amount of suspended sediment leaving the catchment (t/ha).
15. PP_Outlet(kg/ha): Amount of adsorbed phosphorus leaving the catchment (t/ha).
16. DP_Outlet(kg/ha): Amount of dissolved phosphorus leaving the catchment (t/ha).
17. Balance-Error: Water balance error due to rounding or numerical errors (mm).

In the pesticide balance file (pesticideBalance.txt) the daily fate of pesticide and the two transformation products are given in (g/ha). The following columns are included (Pest-pesticide, TP1-first transformation product, TP2-second transformation product):

1. ModelRun:Date/Time: Date and time when the model run took place.
2. sim-Day: Date simulated by the model.
3. Pest_Outlet(g/ha): Mass of Pest leaving the catchment.
4. TP1_Outlet(g/ha): Mass of TP1 leaving the catchment.
5. TP2_Outlet(g/ha): Mass of TP2 leaving the catchment.
6. Pest_ChانRest(g/ha): Mass of Pest currently in the river channel.
7. TP1_ChانRest(g/ha): Mass of TP1 currently in the river channel.
8. TP2_ChانRest(g/ha): Mass of TP2 currently in the river channel.
9. Pest_MixingLayer(g/ha): Mass of Pest in the mixing layer.
10. TP1_MixingLayer(g/ha): Mass of TP1 in the mixing layer.
11. TP2_MixingLayer(g/ha): Mass of TP2 in the mixing layer.
12. Pest_Soil(g/ha): Sum of Pest in all three soil layers.
13. TP1_Soil(g/ha): Sum of TP1 in all three soil layers.
14. TP2_Soil(g/ha): Sum of TP2 in all three soil layers.
15. Pest_Plant(g/ha): Mass of Pest at the plant surface.
16. TP1_Plant(g/ha): Mass of TP1 at the plant surface.
17. TP2_Plant(g/ha): Mass of TP2 at the plant surface.
18. Pest_OF(g/ha): Mass of Pest in overland flow.
19. TP1_OF(g/ha): Mass of TP1 in overland flow.
20. TP2_OF(g/ha): Mass of TP2 in overland flow.
21. Pest_inf(g/ha): Mass of Pest infiltrated into the soil.

- 22.TP1_inf(g/ha): Mass of TP1 infiltrated into the soil.
- 23.TP2_inf(g/ha): Mass of TP2 infiltrated into the soil.
- 24.Pest_degraded(g/ha): Mass of Pest transformed/degraded.
- 25.TP1_degraded(g/ha): Mass of TP1 transformed/degraded.
- 26.TP2_degraded(g/ha): Mass of TP2 transformed/degraded.
- 27.Mineralization(g/ha): Mass of substance mineralized.
- 28.Pest_rock_inf(g/ha): Mass of Pest leaving the 3rd soil layer towards the bedrock.
- 29.TP1_rock_inf(g/ha): Mass of TP1 leaving the 3rd soil layer towards the bedrock.
- 30.TP2_rock_inf(g/ha): Mass of TP2 leaving the 3rd soil layer towards the bedrock.
- 31.Pest_MacroRiver(g/ha): Mass of Pest reaching the river via macropores.
- 32.TP1_MacroRiver(g/ha): Mass of TP1 reaching the river via macropores.
- 33.TP2_MacroRiver(g/ha): Mass of TP2 reaching the river via macropores.
- 34.Pest_MatrixRiver(g/ha): Mass of Pest reaching the river via soil matrix.
- 35.TP1_MatrixRiver(g/ha): Mass of TP1 reaching the river via soil matrix.
- 36.TP2_MatrixRiver(g/ha): Mass of TP2 reaching the river via soil matrix.
- 37.DPest_OFRiver(g/ha): Mass of dissolved Pest reaching the river via overland flow.
- 38.DTP1_OFRiver(g/ha): Mass of dissolved TP1 reaching the river via overland flow.
- 39.DTP2_OFRiver(g/ha): Mass of dissolved TP2 reaching the river via overland flow.
- 40.PPest_OFRiver(g/ha): Mass of adsorbed Pest reaching the river via overland flow.
- 41.PTP1_OFRiver(g/ha): Mass of adsorbed TP1 reaching the river via overland flow.
- 42.PTP2_OFRiver(g/ha): Mass of adsorbed TP2 reaching the river via overland flow.
- 43.PestDrainage_Matrix(g/ha): Mass of Pest reaching the river by soil matrix flow to tile drains.
- 44.TP1Drainage_Matrix(g/ha): Mass of TP1 reaching the river by soil matrix flow to tile drains.
- 45.TP2Drainage_Matrix(g/ha): Mass of TP2 reaching the river by soil matrix flow to tile drains.
- 46.PestDrainage_Macropore(g/ha): Mass of Pest export to the river by macropore flow to tile drains.
- 47.TP1Drainage_Macropore(g/ha): Mass of TP1 reaching the river by macropore flow to tile drains.
- 48.TP2Drainage_Macropore(g/ha): Mass of TP2 reaching the river by macropore flow to tile drains.
- 49.PestApplication(g/ha): Mass of Pest applied in the catchment.

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