Pesticide transport during erosive rainfall-runoff events

Meindert Commelin

Propositions

1. Assessments of pesticide transport on temporal scales larger than rainfall events causes underestimation of environmental pollution by pesticides. (this thesis)

2. More accurate pesticide uptake simulations require developing a process-based description rather than increasing the details of the current conceptualization. (this thesis)

3. In code-rich publications, the code needs to be peer-reviewed as well as the manuscript.

4. In modelling, meaningful simplicity is only reached through a thorough understanding of the systems complexity.

5. Pesticide use is an essential part of a sustainable agricultural system.

6. Individual digital sovereignty is a key element of a free society.

Propositions belonging to the thesis, entitled:

Pesticide transport during erosive rainfall-runoff events

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Pesticide transport during erosive rainfall-runoff events

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Pesticide transport during erosive rainfall-runoff events

Meindert C. Commelin

Thesis

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"Ponder Stibbons was one of those unfortunate people cursed with the belief that if only he found out enough things about the universe it would all, somehow, make sense. The goal is the Theory of Everything, but Ponder would settle for the Theory of Something and, late at night, when Hex appeared to be sulking, he despaired of even a Theory of Anything." [1]

[1] Terry Pratchett, The Last Continent. Corgi Books 1999. p. 28

Contents

List of symbols and abbreviations

AMPA	amino-methyl phosphonic acid	
AS	active substances	
B	constant in transformation reduction equation by soil moisture	(-)
C	concentration	
C_0	initial pesticide concentration in soil	mg kg^{-1}
DEM	digital elevation model	
DP	dissolved phase (of pesticide)	
Δt	timestep	sec
DT_{50}	degradation half-life time	days
DU	discrete uniform distribution	(-)
Δx	cell size	m
e	single rainfall runoff event as simulated with OLP	(-)
EES	Earth and environmental sciences	
EFSA	European Food Safety Authority	
EVI	event index	(-)
FOCUS	FOrum for Co-ordination of pesticides fate models and their USe	
GOF	goodness-of-fit (statistic for model performance)	
GSA	global sensitivity analysis	
Δh	water depth in Parshall flume	m
h_0	surface storage depth before runoff	cm
HRU	hydrologic response unit	
k	number of parameters the sampled parameter space	(-)
k_d	soil - water partition coefficient	ml g^{-1}
k_{film}	mass transfer rate of dissolved uptake of pesticides	mm sec^{-1}
KGE	Kling-Gupta efficiency	(-)
KNMI	Dutch meteorological institute	
k_{oc}	organic carbon - water partition coefficient	ml g^{-1}
k_{sat}	saturated hydraulic conductivity	mm h^{-1}
LOQ	limit of quantification	
M	mass of pesticide flux between control volumes	mg
M_e	mean transported mass for a specific event	mg
ME	mean error	
M_r	relative transported mass	(-)
n	Mannings' coefficient	
n	sample size	(-)
N	total number of simulations in Sobol' GSA	(-)
n	soil porosity	m^3 m^{-3}
n_m	n parameter in the Mualem-Van Genuchten equations	(-)
NSE	Nash-Sutcliff efficiency	(-)

OAT	one-at-a-time sensitivity analysis	
OLP	OpenLISEM-pesticide	
OM	soil organic matter percentage	%
P	precipitation	mm h^{-1}
PP	particulate phase (of pesticide)	
PPDB	Public pesticide database	
Q	flux of water, sediment or pesticide	kg sec^{-1}
q_{inf}	infiltration rate	m sec-1
QRN	quasi random sample	
RMSE	root mean squared error	
ROI	RMSE and Overlap Index	
RSE	residual standard errors	
S_c	soil cohesion	kPa
sd	standard deviation	
SE	standard error	
S_i	Sobol' single order sensitivity index	
SOBOL	Sobol' variance based GSA	
S_w	solubility in water	mg L^{-1}
SWAP	Soil Water Atmosphere Plant	
T_i	Sobol' total order sensitivity index	
TSS	total suspended solids	g L^{-1}
U	uniform distribution	
y	model output used to calculate Sobol' sensitivity indices	
z_m	mixing layer depth	mm
α	coefficient in the enrichment ratio equation	(-)
β	exponent in the enrichment ratio equation	(-)
γ_r	surface runoff resistance	days
γ_T	factor in transformation reduction by temperature	$^{o}C^{-1}$
θ	volumetric water content of the soil	m^3 m^{-3}
θ_{sat}	porosity of the soil	m^3 m^{-3}
Ψ	wetting front capillary pressure	cm

Chapter 1

Introduction

1.1 Effects and impact of pesticide use in agriculture

Since the start of the Green Revolution, global agricultural production has increased substantially (Godfray et al., 2010). One of the major contributors to this increase is the use of plant protection products, also known as pesticides (European Environment Agency, 2023; Liu et al., 2015; Oerke, 2006; Sabzevari and Hofman, 2022). By using pesticides the quantity and the quality of yields increased (Aktar et al., 2009) and some studies state that pesticides are required to sustain food production for the growing world population (Oerke, 2006; Sabzevari and Hofman, 2022). In agriculture there are three main types of pesticides: herbicides, insecticides and fungicides (Eurostat, 2023). Herbicides are used to suppress weeds and prevent competition for resources with the cultivated crop, insecticides and fungicides have various applications to prevent pests and improve crop quality (Aktar et al., 2009).

Because pesticides are abundantly used it is important that they are effective and safe. In a scientific guide to pesticide use (Bennett et al., 2021) the following definition is given:

"Ideally any pesticide will act rapidly on pests, yet be completely harmless to people, domestic animals, wildlife, and other aspects of the environment. Its residues would only last as long as was necessary to create the desired effect, usually for very short periods. It would also be inexpensive and readily available in necessary quantities, chemically stable (before application), non-flammable, and otherwise safe to use around homes or industrial sites. It would be easily prepared and applied, non-corrosive and non-staining, and it would have no undesirable odour."

The authors directly add: *"Unfortunately, no such (synthetic) pesticide exists."* Pesticides stay in the environment for longer than necessary, they can be transported to other domains in the environment and affect off-target organisms (European Environment Agency, 2023; Rittenburg et al., 2015; Sabzevari and Hofman, 2022).

A recent study, investigating the occurrence of pesticide in many domains of our environment (houses, food and human bodies), concludes that pesticides are omnipresent and residues are detected everywhere (Silva et al., 2023). Pesticide residues are detected in humans (Huber et al., 2022) and various health effects, including increased cancer risks, reduced reproductivity and hormone disruptions, are related to pesticides (Kortenkamp et al., 2021; Leemans et al., 2019; Rizzati et al., 2016). Beside the many effects on human health pesticides also affect different ecosystems in direct and indirect ways (Mamy et al., 2022). Insect populations decrease, and especially bees are affected by the use of insecticides (Murcia-Morales et al., 2021; Zioga et al., 2020). Recently also more attention is raised for the synergistic effect of pesticide mixtures, where combinations of pesticide residues have more impact on an ecosystem than the individual pesticides have (Cedergreen, 2014; Siviter et al., 2021). Indirect effects include changing interactions in the food-web (Russo et al., 2020). In addition, pesticide pollution decreases natural pest control and increases resistance to pesticides by target species (Bonato et al., 2023), which creates a vicious cycle of increased pesticide pressure.

Also for the Netherlands several studies show the spread of pesticides in the environment. Emerging pesticides are detected in drinking water (Sjerps et al., 2019), nature areas (Buijs and Mantingh, 2022) and pesticide levels are exceeding water quality thresholds in rivers (Kool et al., 2023). The pollution risks of pesticides has led to a prohibition of pesticide use in lily cultivation close to built-up areas in Drenthe in 2023 (Berg, 2023). While pesticides have their benefits and are required for our global food production, safe and sustainable use for humans and the environment must be guaranteed.

In Europe regulations are implemented aiming to guarantee this safety. Before a pesticide is allowed on the market, extensive testing and assessment is required. This also includes assessment of the environmental fate of pesticides (FOCUS, 2015). Only if it is demonstrated that the pesticide is safe for humans and has no unacceptable environmental impacts, a pesticide is approved (EFSA, 2018). However, there is much debate about the accuracy and robustness of the current implementation for approvals (Brühl and Zaller, 2019). For example, mixture effects are currently not taken into account (Sybertz et al., 2020) and new insights for an approved pesticide are not always included in the reassessments (Mie and Rudén, 2022). Despite the fact that the required assessments were applied to all currently approved pesticides, the environmental impact as previously described still occurs. In the European Union, the only hard limit of pesticide occurrence is 0.1 $\mu g\ L^{-1}$ for surface and ground water resources (EC, 2000; Weisner et al., 2022), and this limit is still frequently exceeded (EEA, 2024). For other domains of our environment, including soils, no regulatory limits are currently in place.

1.2 Fate of pesticides in the environment

Pesticides are detected in many soils (Silva et al., 2019) and, though applied on specific fields, they are transported to off-target environments. Since pesticides are not harmless, and since they are abundantly used, a clear understanding of their fate in the environment is important. Pesticide residues in the environment originate from point sources or diffuse sources (Bach et al., 2001; Rittenburg et al., 2015). Point source pollution, e.g. spillage during preparation and washdown of pesticide applications on farms, can cause high pollution rates (Rose et al., 2004). However, technical measures, like protected pesticide handling areas, are effective to reduce this pollution (Reichenberger et al., 2007; Rose et al., 2004). Diffuse pollution occurs by transport of pesticide after application on the field (Figure 1.1), with two major transport modes: through air or with water (Reichenberger et al., 2007). Transport through air includes volatilization, spray drift and wind erosion (Boonupara et al., 2023; Cessna et al., 2013; Gil and Sinfort, 2005). These transport modes can dislocate the pesticides over long distances and cause pollution of all domains of our environment (Boonupara et al., 2023).

Transport with water includes leaching, sub-surface flow and overland flow. Depending on the topography, soil type and land use, different transport pathways might be dominant (Rittenburg et al., 2015). For example, flat peat soils have a higher leaching risk compared to a Mediterranean vineyard on a steep slope, where overland transport might be the main transport route. Pesticide transport with runoff can be a major transport route, especially on sloping lands (Tang et al., 2012). In case overland flow on sloping lands causes erosion, besides transport in the dissolved phase (DP) with runoff, the pesticides can also be transported in the particulate phase (PP), sorbed to the eroded soil particles (Rittenburg et al., 2015).

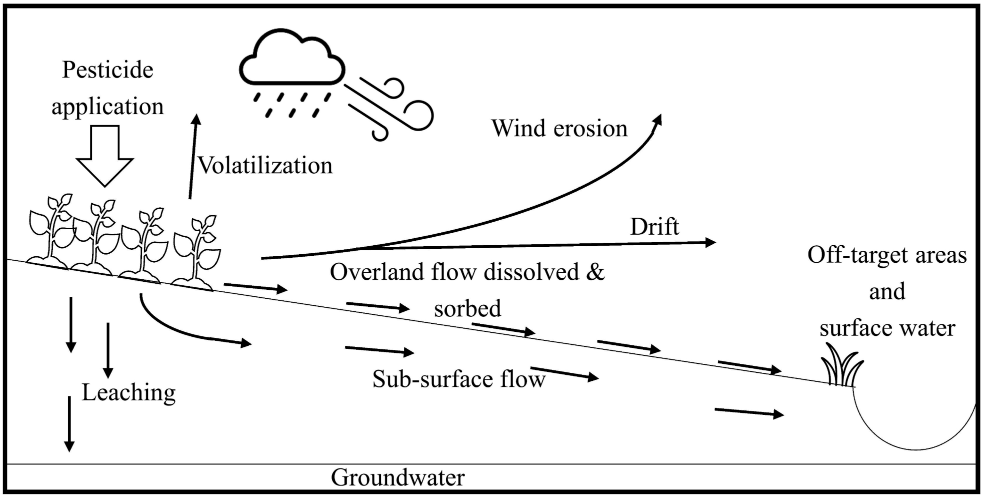

Figure 1.1 *Pathways of diffuse pesticide transport into the environment.*

Estimates of pesticide transport with runoff compared to the total applied mass vary around 0.5% with extremes up to 5% (Wauchope, 1978). The amount of transport with runoff depends on various factors. The topography, the soil type and land management influence the possibility for runoff and erosion (Bento et al., 2018; Elias et al., 2018; Yadav and Watanabe, 2018). The possibility for transport is also affected by the application method of the pesticide: on the foliage, at the soil surface or incorporated into the soil. The soil chemical characteristics in combination with the chemical properties of the pesticide influence sorption to soil particles as well as the degradation rate of the pesticide (Gassmann et al., 2015; Tang et al., 2012; Yang et al., 2015a). The sorption and solubility characteristics influence the availability of a pesticide for transport dissolved in the runoff (Jarvis, 2016; Vagi and Petsas, 2021; Wauchope, 1978). Finally, the timing of the runoff event compared to the date of pesticide application has a strong influence on the availability of pesticides for transport, with events close to the date of application causing the most transport (Imfeld et al., 2020; Louchart and Voltz, 2007; Meite et al., 2018; Sandin et al., 2018).

In several previous studies from the 1980s and 1990s, transport in the PP was estimated to be very small compared to transport in the DP (Leonard, 1990; McCall et al., 1980; Wauchope, 1978). Strongly sorbing pesticides were categorized as 'non-mobile' (McCall et al., 1980), however, when erosion occurs, strongly sorbing pesticides can be transported attached to the soil particles. Based on recent studies, the contribution of PP versus DP is unclear and various studies show contradictory results. Several studies on field scale conclude that PP transport is of minor importance (often <5% of the total transported load) (Maillard et al., 2011; Napoli et al., 2016; Oliver et al., 2012; Todorovic et al., 2014). However, other plot scale and flume experiments show potentially high transport of pesticides in PP (Bento et al., 2018; Melland et al., 2016; Yang et al., 2015b). Yang et al. (2015) observed a natural rainfall event 2 days after pesticide application and detected DP concentrations of 0.7–1.3 $\mu g\ L^{-1}$ and PP content of 40–60 $\mu g\ L^{-1}$. The contribution of PP to total observed pesticide transport was 71%. At larger scales, concentrations of pesticides in total suspended solids (TSS) in rivers, and in river or stream sediments, are often much higher than in water (Climent et al., 2019; Cruzeiro et al., 2016; Masiá et al., 2013) which points to significant transport of pesticides in the particulate phase.

Headwater streams and their catchments are the smallest parts of the river and stream network (Baattrup-Pedersen et al., 2018), but they represent a major part of the landscape. In Europe more than half of the land area is part of headwater catchments (Globevnik, 2007) and these streams account for more than 80% of the river network (Kristensen and Globevnik, 2014). Due to their wide diversity these areas are important habitats for microbial, plant and animal life (Biggs et al., 2017; Ferreira et al., 2023). Agriculture, including pesticide applications, is a major land use in headwater catchments (Ferreira et al., 2023). Off-site transport of pesticides will first impact the diverse terrestrial and aquatic habitats in the headwater catchments. In addition, when pesticides enter the stream network, transport downstream will cause further pollution through the river network.

In recent years, many studies show increased concentrations of pesticides and other pollutants in small streams in Europe (Casado et al., 2019; Cor et al., 2021; Halbach et al., 2021; Lefrancq et al., 2017a; Vormeier et al., 2023) and globally (Andrade et al., 2021; Mayora et al., 2024). Often these studies identify rainfall runoff processes as a major contributor to the high concentrations in the streams (Halbach et al., 2021; Lefrancq et al., 2017a) and close correlation between precipitation and peak concentration has been shown (Vormeier et al., 2023).

1.3 Modelling pesticide transport

Model simulations can provide a better understanding of pesticide transport processes and mechanisms, across diverse landscapes, climates and pesticide types. Therefore, many models have been developed since the start of pesticide use in agriculture that describe one or multiple transport pathways of pesticides in the environment (Centanni et al., 2023; Mottes et al., 2014; Payraudeau and Gregoire, 2012). These models are used to estimate and predict the risks pesticide use poses on the surrounding environment (Dowling et al., 2019; Iturburu et al., 2019; Sybertz et al., 2020). Models like FOCUSPEARL and PRIZM5 (Adriaanse et al., 2017; Dowling et al., 2019; FOCUS, 1997) are used in the European Union to predict pesticide transport form fields to groundwater and surface water bodies. Other modelling studies include simulations with SWAT on larger catchment scales to analyse river pollution (Cambien et al., 2020), smaller catchment scale simulations with PESHMELBA on the influence of different landscape elements on pesticide transport (Rouzies et al., 2019) and simulations of particulate phase transport from plots with RZWQM (DeMars et al., 2018).

Within the European Union the FOCUS (FOrum for Co-ordination of pesticide fate models and their USe) modelling framework is used to assess the fate of pesticides into the environment and the associated toxicological risk (Adriaanse et al., 1997; FOCUS, 2015). One of the evaluated pathways is transport with runoff. The assessment is done in a tiered approach, where first very simple extreme cases are evaluated, and the assessment becomes more and more complex when on lower tiers the evaluated pesticide is not safe. For runoff the first level tier consists of a direct application of the annual load of a pesticide into a stream, when this does not cause exceedances of toxicological limits, the compound is regarded as safe. The higher-level tiers (three and four) include modelling pesticide transport with runoff and erosion. The default model for tier three is PRZM, and for tier four also GLEAMS or PELMO can be used. Four different runoff scenarios throughout Europe are defined to simulate different pedoclimatic zones and agricultural systems. One of the identified potential weaknesses of the selected models is the temporal resolution: the standard timestep is one day, and runoff processes typically occur on shorter timespans (Adriaanse et al., 1997, p. 49).

When using a model, the spatial and temporal representation of the simulated processes should fit the aim for which the model is applied. The temporal representation can be either static or dynamic: most pesticide transfer models are dynamic models since the transfer and degradation of pesticides over time are being simulated. Three types of spatial representation can be distinguished: lumped, semi-distributed and distributed (Sitterson et al., 2017). A lumped model simulates the catchment or field as one homogeneous unit (e.g. SWAP and PEARL). Semi-distributed models combine different homogeneous units to describe different sections of the landscape, these can be connected with a stream network (e.g. SWAT and PESHMELBA). Lastly a fully-distributed model applies a grid with a specific resolution over the catchment area, processes within and interactions between the cells are simulated (e.g. ZinAgriTra).

Pesticide transport at the headwater catchment scale is highly influenced by catchment heterogeneity (Payraudeau and Gregoire, 2012), including hydrologic connectivity and spatiotemporal variability depending on rainfall characteristics, soil properties and landscape elements such as tillage roughness (Takken et al., 2001b) or hedges and roads (Favis-Mortlock et al., 2022). Although this heterogeneity cannot be fully known or described, physical-based fully distributed models could be helpful to take into account the complexity of interacting processes during a rainfall-runoff event. Moreover, they can describe alterations in land use, management or climate change and assess their impact on pesticide transport (Mottes et al., 2015; Payraudeau and Gregoire, 2012). A fully distributed dynamic model might be valuable in further understanding the transport processes of pesticides during erosive rainfall-runoff events.

In Figure 1.2 some commonly used pesticide fate models are compared on properties relevant for the simulation of pesticide transport during rainfall-runoff events. Several well-known models have been thoroughly tested and evaluated on pesticide leaching, degradation in the soil and transport with runoff, including PRZM, FOCUSPEARL, RZWQM and SWAT (DeMars et al., 2018; Purnell et al., 2020; Van den Berg et al., 2016; Young and Fry, 2019). However, the spatial representation (homogenous or hydrologic response units) and temporal scale (minimal timesteps of hours or days) of these models is not targeted at event scale dynamics. Besides these, other models have been developed, aiming at specific topics of pesticide fate. For example, ZinAgriTra analyses the transport of transformation products of pesticides (Gassmann, 2013) and VFSMOD was specifically designed to predict the effect of vegetative filter strips to trap pesticides (Muñoz-Carpena et al., 2018). The GSSHA model does have a promising combination of properties (Pradhan et al., 2014), however very little prior research or information on applications for pesticide transport was found.

In a recent review 17 different models were identified that were used in the past decade to simulate the fate and transport of pesticides (Centanni et al., 2023). In most of these modelling studies particulate transport of pesticides is not taken into account due to lack of data or model limitations (e.g. Gassmann, 2013; Purnell et al., 2020; Young and Fry, 2019). When particulate transport was included, the model performance in terms of sediment transport is reported as not adequate (e.g. Chen et al., 2017; DeMars et al., 2018). Dynamics within the runoff event and different contributing areas could not be simulated with these lumped edge-of-field models.

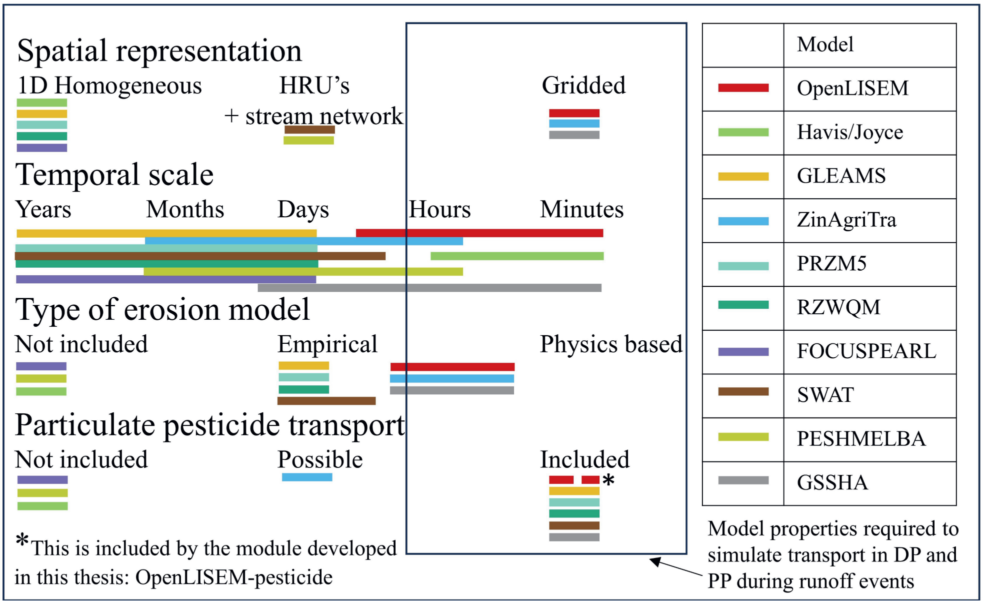

Figure 1.2 *Overview of model properties of some commonly used pesticide fate models.*

A more complex model, although including more details, often also has more uncertainties and less predictive capacity than simpler models (Wainwright and Mulligan, 2012). Often the predictive performance and robustness of a model to simulate a wide variety of different cases correctly, decreases with increasing model complexity (De Vente and Poesen, 2005). Describing more processes requires more input data and knowledge of the simulated system. Environmental modelling is often done in data scarce situations, which increases the challenge to correctly parameterize a complex model (Cambien et al., 2020). However, by considering spatial and temporal heterogeneity (Meinen and Robinson, 2021) and by aiming to simulate the physical or chemical processes, rather than describing these empirically, these models are tools to increase our understanding of dynamic processes, like runoff or pesticide transport, in the environment. Knowing the uncertainties related to the simulations of distributed models, and knowing which parameters influence the model output the most, is of major importance for using the model outputs for policy and decision making (Rouzies et al., 2023). A sensitivity analysis contributes to the understanding of these uncertainties by investigating how variations in the model output are caused by variations in the input and by identifying non-influential parameters (Pianosi et al., 2016). Based on the sensitivity analysis, uncertainty can be reduced by better targeting data collection and prioritizing the parameters which most influence the model output.

1.4 Objectives and research questions

This thesis research aimed to better understand the transport of pesticides from agricultural fields during rainfall-runoff events. The typical spatial scale of pesticide transport due to runoff or erosion is between 1 - 1000 ha with a corresponding temporal scale ranging from minutes to several hours. In this thesis, I indicate these spatiotemporal scales with the terms "field-scale" or "event-scale". This transport pathway can cause high transport rates and many recent studies show increased concentrations in headwater streams in relation to rainfall events (Casado et al., 2019; Halbach et al., 2021; Mayora et al., 2024; Vormeier et al., 2023). These studies report high concentrations dissolved in water, however, on sloping lands particulate transport with erosion might also be a substantial pathway. In a laboratory rainfall simulation study, we found high transport of glyphosate sorbed to soil particles from a loess soil (Bento et al., 2018). A better quantification of overall transport by runoff, and PP transport specifically, will provide insights to prevent further pollution of our environment. The quantification of PP transport should first be done by upscaling of the observations to field and small catchment scale. In addition, simulating the transport process can further improve our understanding of the transport dynamics and source areas and provide a means to test scenarios of mitigation measures of changing land use or climatic conditions. At the start of the thesis research, no suitable model to simulate event-based DP and PP transport of pesticides was known to us.

Therefore, this thesis had the following three objectives:

1. Quantify the contribution of particulate phase transport to total overland transport of pesticides for a small agricultural headwater catchment.
2. Develop a model for event-based overland transport of pesticides that includes both dissolved and particulate phase transport of pesticides.
3. Determine the input parameter influence on the output of the new model and investigate its suitability to simulate and predict pesticide transport for a small agricultural headwater catchment.

These three objectives were achieved through five research steps (see Figure 1.3). In order to quantify the transport of pesticides in DP and PP from a small catchment, we first developed a sampling device to accurately collect suspended sediment samples from a small stream. Secondly, we performed a two-year field observation campaign where we monitored land use, land management, pesticide applications and rainfall-runoff events and related erosion processes. The third research step was the development and proof-of-concept testing of a pesticide transport extension for the OpenLISEM model. OpenLISEM is a process based, distributed model for runoff and erosion processes on event timescales. The sensitivity of the newly developed model extension, OpenLISEM-pesticide (OLP), was then tested with a global sensitivity analysis in the fourth step. Finally, in step five, the predictive performance for a well-studied event was tested with ensemble simulations.

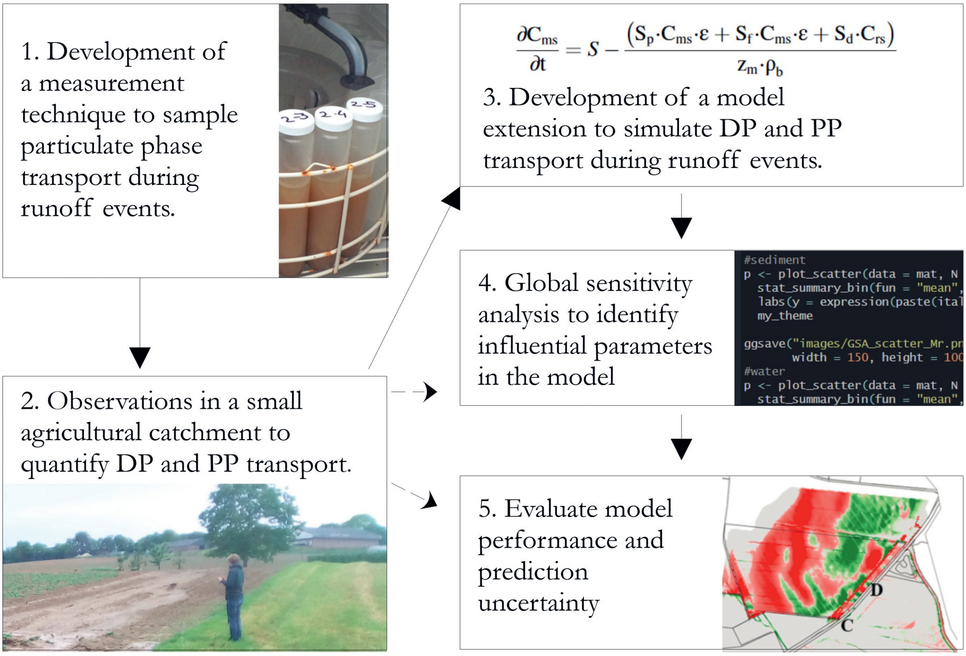

Figure 1.3 *Research steps in this thesis.*

1.5 Study area

Sampling and field observations were done in a small agricultural headwater catchment (38.6 ha) in the hilly area of South-Limburg, The Netherlands (Figure 1.4). This region is part of the loess belt covering parts of Belgium and the south of Limburg in the Netherlands. Loess soil is erosion prone, and runoff and erosion cause flooding and mudflows in this region (WiB, 2020; Winteraeken and Spaan, 2010). The study area was selected for multiple reasons: it is relatively close to Wageningen University so an intensive measurement campaign was possible, a flume was already installed and maintained by the waterboard and lastly the catchment contains diverse types of agricultural land use (grass lands, orchard and arable agriculture) which gave the opportunity to compare pesticide transport from different sources.

The catchment had a typical land use pattern for the loess belt. Arable agriculture was the main land use covering 25.2 ha, consisting of a crop rotation of winter cereals and intensive crops like potatoes, sugar beet and chicory. An apple orchard covered 5.3 ha and 5.0 ha was extensively managed grassland. The remaining area consisted of roads, urban area, and a small tree nursery. All agricultural fields were under conventional crop management, including pesticide applications, with apple and potato cultivation having the highest annual application rates. The catchment has an elevation difference of 30 m (80–110 m.a.s.l.) and an average slope of 6.3% (sd ± 4.0%, range 0.1–30%). The catchment borders were calculated with QGIS 3.16 (QGIS 2021), based on the AHN3 DTM with a 0.5 m resolution (AHN 2019). The borders were adjusted if field observations showed different flow lines. The soil type is a Luvisol, a homogenous, fertile, but erosion sensitive loess soil with a silt loam texture. Soil characteristics are (mean ± SE): sand 45.6 ± 2.2%, silt 51.0 ± 2.1%, clay 3.5 ± 0.2%, OM 3.6 ± 0.3%, pH 6.5 ± 0.10. The catchment is located in a temperate climate (Cfb) with a mean annual temperature of 10.7 ± 0.7°C (KNMI, 2021a) and mean annual precipitation of 757 ± 108 mm (KNMI, 2021b), based on measurements from 1991–2020 at a weather station 2.5 km from the catchment. A dry ditch connects the fields to the catchment outlet, in which only for short periods after intensive rainfall events discharge occurs.

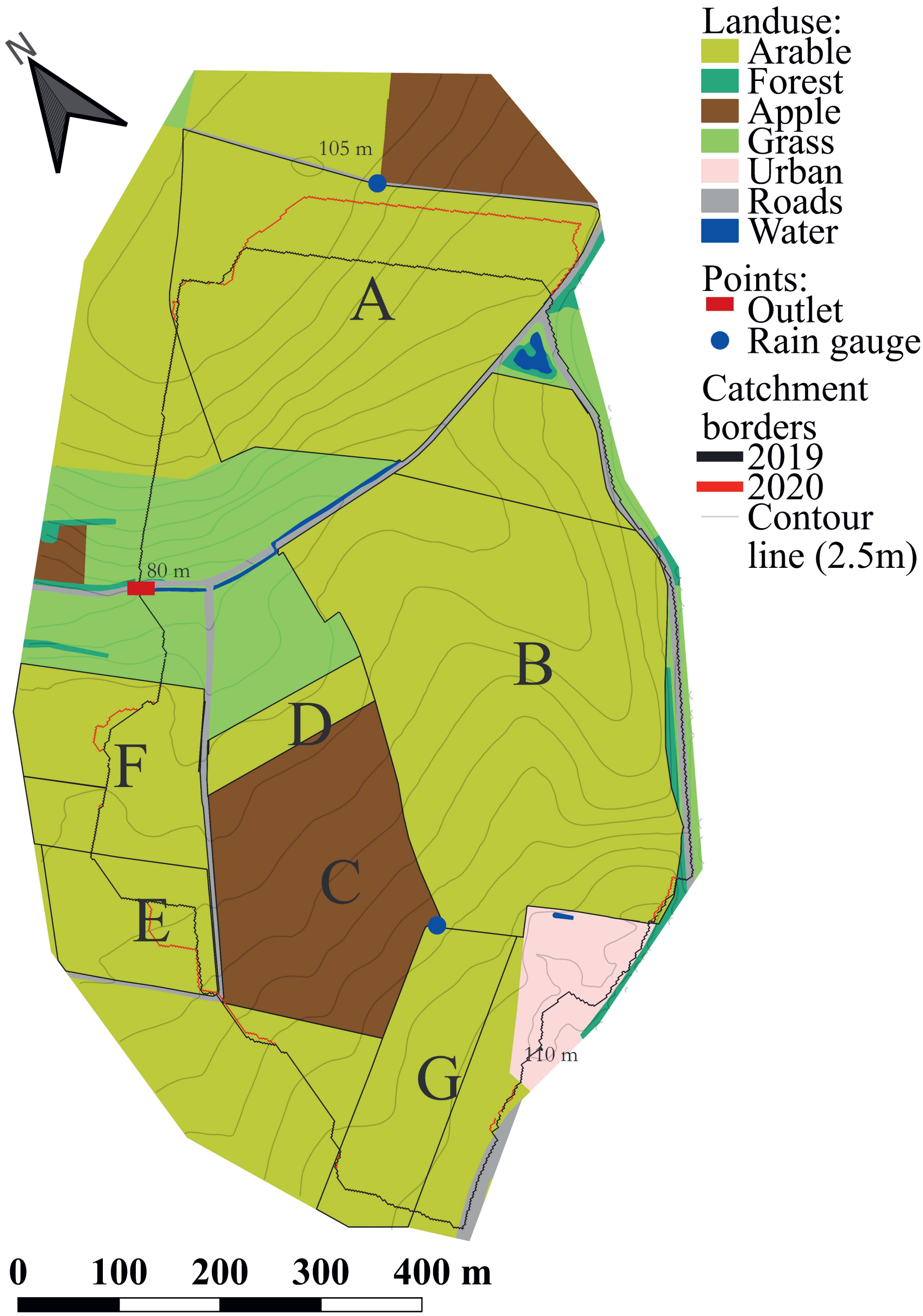

Figure 1.4 *Map of the study area. The catchment borders for the two seasons varied due to variations in tillage patterns. On the labelled fields pesticide samples were collected for the two events.*

1.6 This thesis

The next chapters of this thesis are built up as follows. The observation study including research step one and two are described in chapter 2. Chapter 3 describes the development and a proof-of-concept of the pesticide extension for OpenLISEM. Chapter 4 presents the sensitivity analysis of the model extension and the results of the ensemble simulations. The final chapter of this thesis, chapter 5, combines the new insights with a synthesis of the results and reflects on the implications these have for modelling pesticide transport and pesticide use in general.

Chapter 2

Quantifying transport of pesticides with runoff and erosion in a small agricultural catchment[2]

Abstract

Agriculture on sloping lands is prone to processes of overland flow and associated soil detachment, transportation, and deposition. The transport of pesticides to off-target areas related to runoff processes and soil erosion poses a threat of pollution to the downstream environment. This study aimed to quantify transport of pesticides both dissolved in water and in the particulate phase in transported sediments. Particulate phase transport of pesticides on short temporal time scales from agricultural fields is scarcely studied. During two growing seasons (2019 and 2020) rainfall—runoff events were monitored in a catchment of 38.5 ha. We selected 30 different pesticides and one metabolite based on interviews with the farmers on the application pattern. Concentrations for these 31 residues were analysed in runoff water (dissolved phase–DP) and sediment (particulate phase–PP) and in soil samples taken in the agricultural fields. In all runoff events active substances (AS) were detected. There was a clear difference between DP and PP with 0–5 and 8–18 different AS detected in the events, respectively. Concentrations in PP were higher than in DP, with factors ranging from 12 to 3,700 times. DP transport mainly occurs in the first days after application (69% within 10 days), and PP transport occurs over the long term with 90% of transported mass within 100 days after application. Potato cultivation was the main source of runoff, erosion, and pesticide transport. Cereals and apples with grassed inter-rows both have a very low risk of pesticide transport during overland flow. We conclude that for arable farming on sloping lands overland transport of pesticide in the particulate phase is a substantial transport pathway, which can contribute to pollution over longer time periods compared to transport in water. This process needs to be considered in future assessments for pesticide fate and environmental risk.

[2] Based on: Commelin, M.C., Baartman, J.E.M., Zomer, P., Riksen, M., Geissen, V., 2022. Pesticides are substantially transported in particulate phase, driven by land use, rainfall event and pesticide characteristics—a runoff and erosion study in a small agricultural catchment. Frontiers in Environmental Science 10, 830589. DOI: 10.3389/fenvs.2022.830589

2.1 Introduction

The use of pesticides in agriculture is one of the key components in the rapid increase of food production in the past decades. In the coming decades, sustaining food security for the growing world population is one of the main global challenges (FAO et al., 2020). Aktar et al. (2009) stated that without pesticide use, the current quantity and quality of global food production cannot be sustained. However, the downside of the extensive use of pesticides is that it poses threats to human health and the environment (Bevan et al., 2017; Casado et al., 2019; Silva et al., 2019), including significant biodiversity loss (Geiger et al., 2010; Lanz et al., 2018). On average 3.14 kg ha^{-1} of pesticides was applied on cropland in the EU-28 in 2018 (FAO, 2020). Beside reaching the target pest, these pesticides can be pollutants to other parts of on- and offsite ecosystems (Boivin and Poulsen, 2017; Topping et al., 2020). Although many improvements in pesticide type, application efficiency and mitigation are made, still uncertainties and threats exist on off-target effects of pesticide use (Lechenet et al., 2017; Sattler et al., 2007), especially in cases of farming on sloping land.

Agriculture on sloping lands is prone to processes of overland flow and associated soil detachment, transportation, and deposition. For the EU the average soil loss on arable land, which covers 28% of the surface area, has been estimated at 2.46 t ha^{-1} per year (Panagos et al., 2015), but locally it can exceed 50 t/ha depending on rainfall erosivity, slope, erodibility of the soil, land use and land management. Soil erosion itself is a threat due to the loss of fertile topsoil which is needed for crop cultivation. However, the transport of pesticides to off-target areas related to runoff processes and soil erosion poses another threat of pollution to the downstream environment (Tang et al., 2012). Runoff and erosion events are often characterized by short high intensity peaks (Lefrancq et al., 2017a) which can contain high concentrations of pesticides in both runoff water and transported sediment (Climent et al., 2019; Peruzzo et al., 2008). Multiple studies investigating the pesticide pollution of headwaters and rivers show increased concentrations of pesticides in water after runoff events (Casado et al., 2019; Climent et al., 2019; Halbach et al., 2021; Lefrancq et al., 2017a; Peruzzo et al., 2008), often exceeding the regulatory limits. In the current legal framework in the EU, the limits in water are 0.1 μg l^{-1} for single substances and 0.5 μg l^{-1} for combined mixtures (European directive 2013/39/EC). However, threshold values for soils and eroding sediments as well as sediment in surface water bodies are not set and are complex to derive due to the wide diversity in active substances, toxicity and possible degradation (Geissen et al., 2021; Silva et al., 2019).

In sloping areas, soil erosion occurs alongside runoff, and beside the dissolved phase (DP) the particulate phase (PP) is a transport pathway for pesticides. The contribution of particulate phase transport to total transport of pesticides, and the potential risk this could pose for off-site locations, is currently not well understood. Payraudeau and Gregoire (2012) concluded that dissolved and particulate transport of pesticides in rapid flow processes, mainly via overland flow, can function as a main transport pathway for pesticides to open water. Enrichment processes during rainfall events and erosion cause the transported sediment to contain higher amounts of pollutants than the surrounding soils (H. Ghadiri and Rose, 1991) which increases off-site pollution risk (H Ghadiri and Rose, 1991). In a review of the transport characteristics of pesticides (Wauchope, 1978), erosion related transport of pesticides was stated to be relevant only for strongly sorbing pesticides and main transport risk was by water. Less water-soluble pesticides with a higher sorption coefficient were introduced into the market to avoid leaching to groundwater and overland transport. Several widely used pesticides adsorb strongly to sediment and organic materials (Tang et al., 2012) and are thus classified as slightly mobile or non-mobile substances (McCall et al., 1980).

Synthesizing the results presented in multiple studies in the past decade, reveals that the contribution of pesticide transport in PP versus DP is unclear and various studies are contradicting. On the one hand, several studies on field scale conclude that PP transport is of minor importance (often <5% of the total load) (Maillard et al., 2011; Napoli et al., 2016; Oliver et al., 2012; Todorovic et al., 2014). However, other plot scale and flume experiments show potentially high transport of pesticides in PP (Bento et al., 2018; Melland et al., 2016; Yang et al., 2015b). Yang et al. (2015) observed a natural rainfall event 2 days after pesticide application and detected DP concentrations of 0.7 – 1.3 $\mu g\ l^{-1}$ and PP content of 40 – 60 $\mu g\ l^{-1}$. The contribution of PP to total observed pesticide transport was 71%. At larger scales, concentrations of pesticides in total suspended solids (TSS) in rivers, and in river or stream sediments are often much higher than in water (Climent et al., 2019; Cruzeiro et al., 2016; Masiá et al., 2013), which is related to significant transport in the particulate phase.

Within the mentioned studies there is variation in design how the process of overland transport of pesticides is studied. On small plot scale, experiments are usually done within several days after pesticide applications. These experiments are on arable soils comparing tillage (Todorovic et al., 2014) or residue cover effects on transport (Bento et al., 2018; Melland et al., 2016). Field scale studies include vineyard or fruit tree orchards (Maillard and Imfeld, 2014; Napoli et al., 2016; Oliver et al., 2012), but no results for arable land on field scale are known to the authors. Lastly several studies investigated pesticide transport dissolved in water and in TSS of river systems throughout the growing season (Climent et al., 2019; Cruzeiro et al., 2016; Masiá et al., 2013). However, runoff, erosion and related pesticide transport processes occur on short temporal scale and evaluation on annual basis is not sufficient to understand the exact scope of this transport (Lefrancq et al., 2017a; Tang et al., 2012). On the other hand, the spatial scale of erosion processes demands to be analysed on field and small catchment scale (Cerdan et al., 2004). Plot experiments can indicate effects but cannot include larger scale connectivity, heterogeneity and topography effects (Boardman and Evans, 2020). To gain a further understanding of PP and DP transport of pesticides, field observations that include different land use types are needed.

In this study multiple season field scale observations were done to quantify the contribution of PP transport of pesticides in a small agricultural catchment. Observations were done for multiple land uses and active substances (AS). We hypothesize that PP pesticide transport will contribute substantially to total overland transport of pesticides from small agricultural catchments in sloping areas during erosive rainstorm events. To verify this hypothesis, this study quantified the contribution of particulate phase transport to the total off-site transport of pesticides during and after rainfall events. For this purpose, a measurement campaign was set up in which we sampled rainfall-runoff events at high temporal resolution at the catchment outlet and performed multiple field sampling surveys within the catchment during 2019 and 2020.

2.2 Methods

2.2.1 Study area

Sampling and field observations were done in a small agricultural catchment (38.6 ha) in the hilly area of South-Limburg, The Netherlands (Figure 2.1). The catchment has a typical land use pattern for the loess belt covering parts of Belgium and the south of Limburg in the Netherlands. Arable agriculture was the main land use covering 25.2 ha, consisting of a crop rotation of winter cereals and intensive crops like potatoes, sugar beet and chicory. An apple orchard covered 5.3 ha and 5.0 ha was extensively managed grassland. The remaining area consisted of roads, urban area, and a small tree nursery. All agricultural fields were under conventional crop management, including pesticide applications, with apple and potato cultivation having the highest annual application rates.

The catchment has an elevation difference of 30 meter (80 – 110 m.a.s.l.) and an average slope of 6.3% (sd ± 4.0%, range 0.1 – 30 %). The catchment borders were calculated with QGIS 3.16 (QGIS, 2021), based on the AHN3 DTM with a 0.5m resolution (AHN, 2019). The borders were adjusted if field observations showed different flow lines. The soil type is loess soil, a homogenous, fertile, but erosion sensitive Luvisol with a silt loam texture. Soil characteristics are (mean ± SE): sand 45.6 ± 2.2%, silt 51.0 ± 2.1%, clay 3.5 ± 0.2%, OM 3.6 ± 0.3%, pH 6.5 ± 0.10. The catchment is located in a temperate climate (Cfb) with a mean annual temperature of 10.7 °C (± 0.7 °C) (KNMI, 2021c) and mean annual precipitation of 757 mm (± 108mm) (KNMI, 2021b), based on measurements from 1991 – 2020 at a weather station 2.5 km from the catchment. A dry ditch connects the fields to the catchment outlet, in which only for short periods after intensive rainfall events discharge occurs.

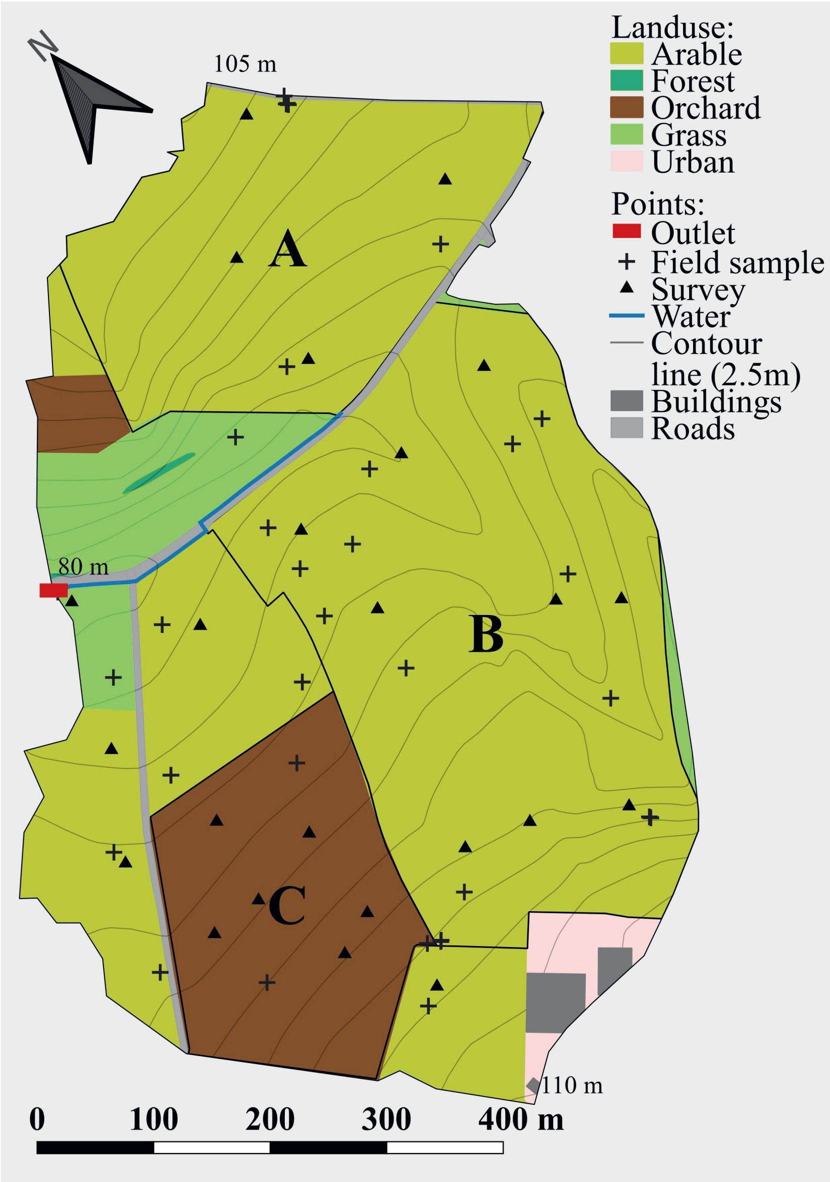

Figure 2.1 *Map of the study area in South-Limburg, the Netherlands indicating sampling points. The letters (A, B and C) indicate the three fields of main interest in this study.*

2.2.2 Measurement design

To relate measured pesticide concentrations at the outlet to application and management on the fields, samples were collected throughout the catchment after five runoff events (**+** in Figure 2.1).

A baseline soil survey (04 March 2020), consisting of 30 samples covering the whole catchment through a structured random design, was done before the growing season of 2020 (▲ in Figure 2.1). A total of 68 samples from the top 1 cm of the soil was collected. These samples were stored in a freezer and used for analysis of pesticides, texture, organic matter content, and pH. The concentrations of different pesticides in the upper layer of the fields indicates potential transport risk by runoff and erosion. In addition, pesticide application data (date, pesticide type, application concentration) were obtained from the landowners of the three main agricultural fields in the catchment (A, B and C in Figure 2.1).

Other data on climate, land use and soil conditions were monitored to investigate the dynamics and processes driving the pesticide transport during the rainfall events. Data was collected for rainfall, crop type, crop cover and soil moisture content of fields. Rainfall was measured at the outlet with a 0.2 mm tipping bucket (ARG100, Campbell Sci.) on a 1 minute resolution. Crop height and cover was measured during surveys, soil moisture content was measured using a Time Domain Reflectometer during surveys after events. Finally, radar precipitation data (5 minute, 1 km^2) from KNMI was used (KNMI, 2021d) to obtain a spatial coverage of rainfall in the catchment and to fill gaps in the timeseries of the tipping bucket.

At the outlet of the catchment the water and sediment discharge was measured by a two feet Parshall flume, with an accurate measurement range between 12 and 650 L sec^{-1} (see Figure 2.7). Data was collected during runoff events and independent of pesticide application pattern. When free flow conditions in the channel were met, the accuracy of the Parshall flume is ± 3% (Bos, 1989; Parshall, 1926). Water level readings were collected every minute at two locations in the flume. Automated sampling at the outlet, with an ISCO 3700 (Teledyne Isco, Inc. USA), was activated when the discharge would exceed 12 L sec^{-1}. Then, a runoff sample was pumped from the stream every six minutes. This was done using an inlet device, optimized for sampling of sediment and water samples, adapted from (Eads and Thomas, 1983; Gettel et al., 2011), see section 2.2.3 for a detailed description of this device. All details on the flume measurement set-up are given in the supplementary materials (section 2.5.1). A maximum of 12 samples could be taken by the sampler, resulting in 72 minutes of sampled event duration, which covered 80% of the runoff peaks occurring in this catchment in 2019 and 2020.

During the measurement years 2019 and 2020, based on the discharge data from the flume, 39 runoff events occurred. Due to temporarily malfunctioning of the equipment or because of insufficient sample coverage during some events, the analysis in this study is based on 14 events. The analysed events do not show significant ($p < 0.05$) differences with the not analysed events, when comparing runoff and erosion characteristics. However, due to limitations in event duration for sample collection and minimal erosion for pesticide analysis, the analysed subset shows a tendency for shorter events with higher runoff and erosion rates (see Figure 2.8).

2.2.3 Measurements of (PP) pesticide transport

To obtain detailed observations of the transport dynamics in DP and PP from agricultural fields during rainfall-runoff events, we identified two requirements. Firstly, the collected samples should capture the temporal dynamics of the transport process, which can be done by high-frequency sampling with an automated sampler (Lefrancq et al., 2017a). Multiple samples throughout one event can contribute to the identification of source areas within the catchment. Secondly, the PP transport should be measured separately from the DP transport. As first step in our research we developed a sampling device to collected multiple accurate runoff and suspended sediment samples during a rainfall runoff event. These samples were used for the quantification of DP and PP transport.

Multiple methods exist to collect suspended sediment samples from streams, including grab samples (Li et al., 2005), composite samples with a hydrodynamic separator (Kim and Sansalone, 2008) or pumping samples from the stream with an automatic sampler (Gettel et al., 2011). Using automatic samplers has two benefits: multiple samples can be collected over time during an event, and the collection can be done without being present at location during the event. In a study regarding urban storm water sampling, Gettel et al (2011) showed that the design of the sampling device has major implications for the accuracy of the collected suspended sediment samples. Using one inlet which is fixed to the bottom or side of the channel can overestimate suspended sediment concentrations up to 6600%. This study proposes a depth integrated sampling device with a winged arm, which fits sewer systems. This design improved the sampling error of suspended sediment samples to < 10% for particles sizes up to 250 μm (Gettel et al., 2011).

To adapt the depth integrated sampling design by Gettel et al., (2011) to fit the conditions in our study area, we combined it with the intake rod and floater as proposed by Eads and Thomas, (1983). In Figure 2.2 the design of the sampling device is shown. A rod of 145 cm was connected to the bottom of the stream at one end, while a float at the upper side was always at maximum water level (Δh). Along the rod inlet tubes were connected at 2/8 and 6/8 of the rod length, which corresponds with the same ratio of the water depth. The two inlet tubes were combined into one sample before reaching the automatic sampler. Since pressure differences between inlet tubes can influence the equal collection of material, these dimensions were standardized. The inlet tubes on the boom were pvc tubes with 4 mm internal diameter, each 230 cm meter long. These were connected with an Y division to an 710 cm long vinyl tube with 9.5 mm internal diameter, which was connected to the automatic sampler.

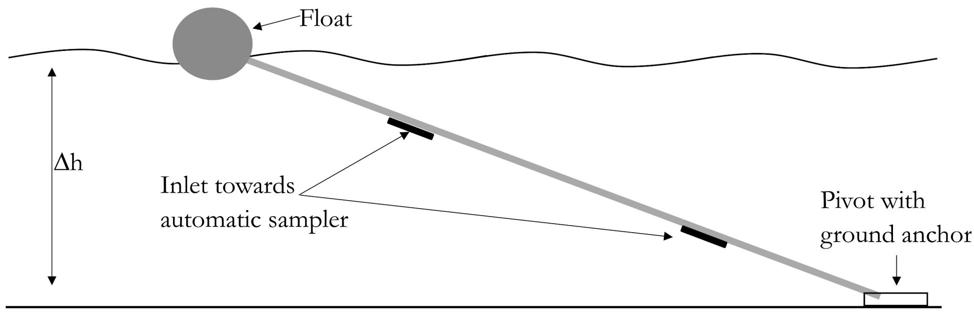

Figure 2.2 *Design of depth integrating sampling device. With inlet points at 2/8 and 6/8 of total water depth (Δh).*

In the design by Gettel et al., (2011) the sample was integrated over four depths and a wing was used to keep the upper end of the rod at maximum water level. In our design we used a float, which would be at maximum water level independent of the velocity of the flowing water. Integrated samples over two depths were selected because of technical limitations in the combination of the tubes towards the automatic samplers, in the initial setup in the field the sampling was split over two automated samplers however the two samplers where needed to collect separate samples for chemical and physical analysis. The first sampler collected samples from the lower half (inlets at 1/8 and 3/8 of the water depth) and the second the upper half (inlets at 5/8 and 7/8) of the water depth. The suspended sediment concentration in the upper half of the water depth is consistently lower than in the lower half (see Figure 2.3-A), which is expected due to the settling of larger sediment particles. When the suspended sediment concentration increased, the difference between the two halves increased as well. Based on laboratory test we did not find substantial differences between both setups.

The accuracy of the collected suspended sediment samples was tested for three known concentrations (20, 50 and 100 g L^{-1}) prior to the installation in the field. The sediment material used for this test was loess soil, with a silt loam texture, which corresponds with the soils in the study area. During the collection of the samples, the water was kept in high turbulent state to simulate turbulent flow in a ditch. The collected samples slightly underestimate the source concentration, and the mean absolute error was 7% (see Figure 2.3-B). Based on these samples a linear model was fitted and applied as correction factor to the TSS samples collected during the field observations:

$$TSS = \frac{S}{0.951} \qquad Eq\ 2.1$$

were *TSS* is the suspended solids concentration in g L^{-1} and *S* is the sample concentration in g L^{-1}. The correlation coefficient of the fitted equation is 0.99.

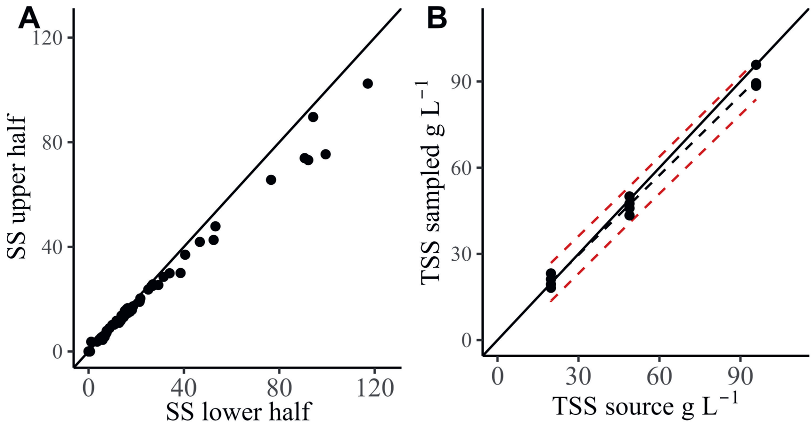

Figure 2.3 *A. Comparison of sampled suspended sediment concentration in the upper and lower half of the water depth during the field sampling. B. Relation between source and sampled concentration with the adapted depth integrated sampling device during initial testing in the lab, dotted red lines show the 95% confidence interval from the fitted linear model.*

These results of the initial testing and field observations, although not very extensive, are in accordance with the results of the study by Gettel et al., (2011). For smaller particle sizes this design is very accurate, when the soil particle size increases the TSS tends to be underestimated. An advantage for this specific study was that the majority of the soil particles in loess soils are smaller than 88 µm, which is the most accurate region of this design (Gettel et al., 2011).

2.2.4 Analysis of soil, runoff water and TSS samples

Each sample during a runoff event consisted of two bottles with identical content. One was used for analysis of pesticides in sediment and water, the other was used to derive total suspended solids (TSS) in water and other parameters of interest (OM, pH, and texture).

The soil and sediment analysis was done at the Soil Hydro Physics laboratory at Wageningen University. For TSS determination the samples were weighed and dried at 105 °C for 24 hours. For runoff TSS samples and soil samples in the catchment, dried sediment was collected and used to determine pH (suspension in 0.01M CaCl), OM (loss on ignition) (Roper et al., 2019) and texture. For the determination of texture, 1 gram of dried sediment was sieved on 500µm, and analysed with laser diffraction (Mastersizer S, Malvern Panalytical) in triplicate on wet samples by the department of Earth and Environmental Sciences, KU Leuven, Belgium.

To investigate pesticide concentrations for both components of the runoff (water and TSS), the samples were separated using a centrifuge (30 min at 3600 rpm). The water part was transferred to a new tube and both samples were stored in a freezer until further analysis. During this stage samples were combined when the sediment content was too low for individual analysis; sediments from the 6 minute timesteps were combined until a minimum of 7 grams dry material was obtained for analysis.

2.2.5 Pesticide applications, selection, and analysis

The selection of pesticides for analysis was based on the application of pesticides in the growing season of 2019. The applications by the two landowners managing the 3 largest fields (A, B and C in Figure 2.1) of the area, where used as initial pesticide list. A selection of these compounds was analysed, based on analysis possibilities within the limited mass of TSS samples (often <10 gr) and financial budget. Compounds were selected that could be analysed with a multi-residue method (LC- MS/MS positive). Prior studies (Bento et al., 2018; Yang et al., 2015b) indicated particulate phase (PP) transport for glyphosate and AMPA to be important, so these compounds were also selected for this research, and a single residue method was used for determination. These two analyses covered 31 compounds: 20 fungicides, five herbicides and five insecticides, and amino-methyl phosphonic acid (AMPA) as metabolite of glyphosate. The chemical characteristics of the selected AS range for adsorption (k_{oc}) from 1.6 – 4.2 10^6 ml g^{-1} and for degradation (DT_{50}) from 0.8 – 419 days, according to data retrieved from the Public Pesticide Database (PPDB) (Lewis et al., 2016).

Chemical determinations and response analysis

The list of chemicals and reagents used for the analysis is identical to Silva et. al (2019). The glyphosate and AMPA analysis was done several weeks earlier than the multi-residue analysis. To minimize sample disturbances, aliquots for both analyses were prepared at the same moment and stored in a freezer until further analysis. Because TSS sediment samples did not always provide enough material for the standard analysis, adapted masses (1/4 or 1/2 of the standard weight) were used if needed. Analysis for glyphosate and AMPA was done following the procedure described by (Bento et al., 2018, 2016).The multi residue analysis was done according the QuEChERS approach for soil and sediment samples (Anastassiades et al., 2003; Mol et al., 2008).

The quality control and chemical determination of the samples was done according to the guidance document for pesticide residues in food and feed (European Commission, 2019). Calibration standards were prepared and injected at the start and end of each sampling sequence. The standards consisted of 1.25, 3.125, 6.25, 12.5 and 50 ng mL^{-1}; 0.625 and 25 ng mL^{-1} were added during analyses of diluted samples. The glyphosate/AMPA standards were 5, 10, 20, 50, 100, 200, 500, 1000 and ng mL^{-1}. See the supplementary material S 2.1 in Commelin et al. (2022) for further details.

Since all analysed soil and sediment samples contained soil moisture, and in varying amounts, the measured concentrations had to be adjusted for the volumetric water content (θ). This was done by drying the sample material after the extraction to derive the dry weight of the soil or sediment. The concentration was corrected for θ and the concentration of the compound in the relating water sample. All final concentrations were adjusted for the recovery of the compound. The recovery was detected based on 9 quality control samples, with a known concentration for each compound.

2.2.6 Data analysis and accuracy

All data analysis, calculations and statistics were done using R software (R Core Team, 2023), including the 'drc' package for first order decay analysis (Ritz et al., 2015). To compare rainfall events with each other the event index (EVI) was calculated (Baartman et al., 2013).

The discharge was calculated based on the water height measured in the Parshall flume. Discharge was calculated based on the empirical formulas given by Parshall (1926). When submergence exceeded 50%, free flow conditions were not met and the discharge was corrected (Parshall, 1926), for more details see 2.5.1.

The calculations of the total pesticide loads in particulate (PP) and dissolved phase (DP) were based on variables that each introduce uncertainty towards the final quantification. Propagation of uncertainty was calculated with the standard deviation expressed as relative error for each variable (Taylor and Thompson, 1998). The uncertainty for each variable is presented in more detail in supplementary materials 2.5.3. While uncertainty of primary measurements (e.g., rainfall or water discharge) is still low, the propagation of the error during calculations results in uncertainty of 18% for pesticide loads in TSS.

The datasets presented in this chapter are available in a 4TU repository: https://doi.org/10.4121/19690684. The code for analysis is available at 4TU: https://doi.org/10.4121/19690840 or GitHub: https://github.com/mcommelin/pesticide_transport_runoff_erosion

2.3 Results and discussion

Synthesizing the results obtained in this study, we found that transport of pesticides during erosive runoff events is determined by three main aspects. Both the quantity as well as the main mode of transport are influenced by (1) the precipitation events and related runoff, (2) the chemical characteristics of the transported active substances as well as by (3) the land use and managements on the fields. The findings and dynamics of each of these processes in relation to pesticide transport are discussed in detail below.

2.3.1 Runoff and erosion as transport modes for pesticides

Rainfall events, runoff and erosion

The 14 events included in this study cover a wide range in terms of rainfall intensity, total precipitation and related runoff and erosion (Figure 2.4). Two events (28 May 2019 and 16 August 2020) had high erosion rates, with mean TSS concentrations of 44 and 21 g L^{-1} respectively, while the mean TSS concentration for all events was 7.5 g L^{-1}. The total water discharged from the catchment during the selected events was 5800 (± 290) m^3 and the total soil loss was 79 (± 5) ton dry soil, resulting in a ratio Q_{sed} : Q_{wat} of 1 to 73. This sediment loss equals 3.1 t ha^{-1} for the arable fields in the catchment. Although not all events that occurred in these two seasons (39) are included, the observed erosion rates are in line with the estimated average of 2.46 t ha^{-1} y^{-1} for arable lands in Europe (Panagos et al., 2015).

There is no significant relation between rainfall characteristics and runoff or erosion. Linear regression was applied on the total discharge of water and sediment, with total rainfall and event duration as explanatory variables. This results in an r^2 of 0.68 for total amount of runoff. No direct relationship between the event characteristics and the amount of erosion could be found. This can be related to other variables like crop cover and soil moisture which varied between events and influence erosion rates and runoff (Morgan et al., 1984; Zambon et al., 2021). Because of the event-based nature of overland flow, longer term monitoring is needed to understand the variability between rainfall events, cultivated crops and seasons within the year (Borrelli et al., 2021). The events included in this study, show the different mechanisms that affect transport and partitioning between phases of AS during overland flow. However, the high variability does not allow for generalizations, because adding or subtracting several events can influence general findings to a large extent.

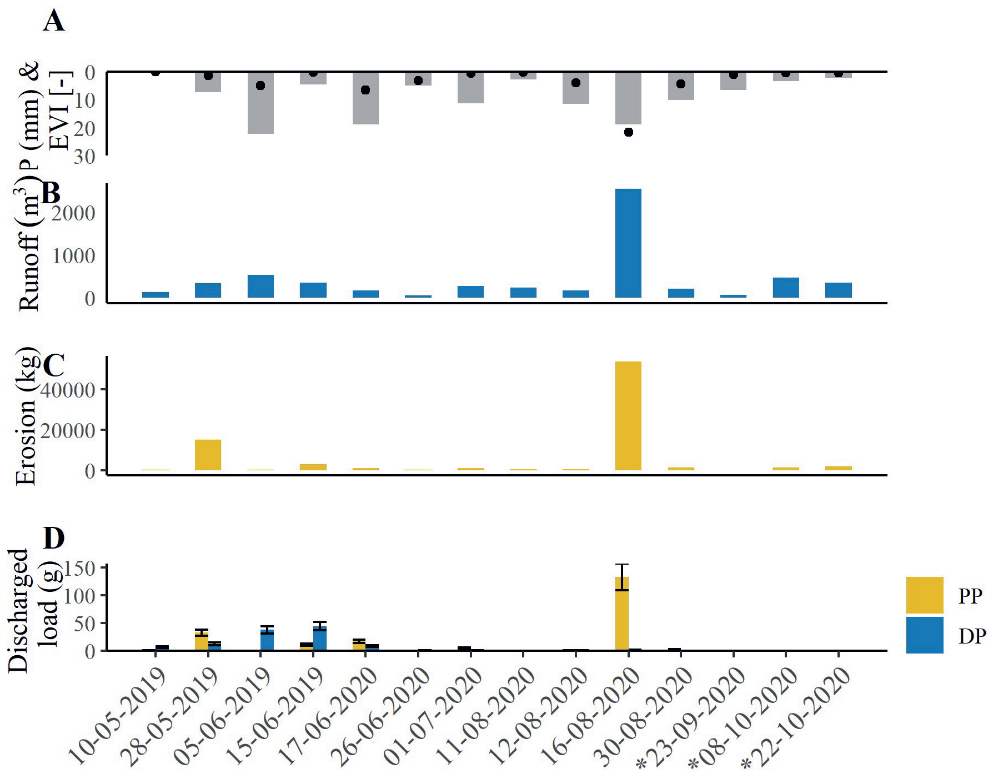

Figure 2.4 *Overview of rainfall (A), runoff (B), related erosion (C) and total pesticides transported (g) by particulate (PP) and dissolved phase (DP) (D) for the 14 events measured in 2019 and 2020. Error bars indicate uncertainty of total value (± 18% PP and ± 17% DP, see section 2.2.5).*

Pesticides transported during rainfall – runoff events

The Glyphosate and AMPA results for the three events from 23-09-2020 are excluded from further analysis, due to occurrence of point source pollution. The glyphosate concentration on 23-09-2020, which is a small event in terms of runoff and erosion, is 550 mg kg^{-1} in PP and 2.2 mg L^{-1} in DP. These values are a factor 20 – 50 higher than all other detected levels in the discharge as well as on the fields in the catchment. Point source pollution which reaches the outlet at the first rainfall event can explain these extreme peaks (Reichenberger et al., 2007; Syafrudin et al., 2021). Because this study aims to investigate diffuse source transport, these results are not taken into account. A detailed description and further discussion is given in the supplementary materials (section 2.5.2).

Within the analysed events, six events occurred with substantial transport (> 5 gram) of pesticides in DP and PP combined, in the other events the transported load was small (see Figure 2.4-D). The pesticide concentrations (PP and PD combined) during the 14 events ranged from 0.2 (± 0.04) to 160 (± 30) μg L^{-1}. The contribution of PP transport to total overland transport shows high variability between events, ranging from 0.1% to 99%. When comparing the transport for each event with the characteristics of rainfall, runoff and erosion, the concentrations of pesticides were not related to the intensity of rainfall or runoff. Both the quantity of runoff as well as the concentrations of active substances transported could result in high total mass transported from the catchment. The event of 16-08-2020 had a high discharge of water and sediment (Figure 2.4-B and C), but the concentrations of AS were not high (Figure 2.5). Opposingly, the event of 17-06-2020 was relatively small in terms of runoff, but had high concentrations, resulting in substantial amounts of transported pesticides.

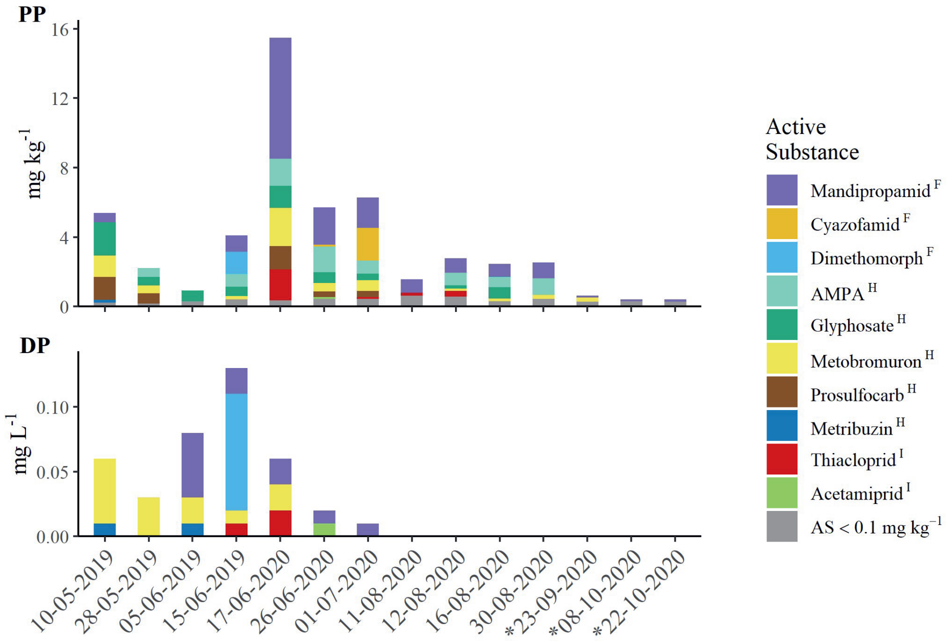

Figure 2.5 *Concentrations of active substances (AS) detected in runoff during each event in (A) the particulate and (B) the dissolved phase. Superscript in legend denotes: ^{F} Fungicides, ^{H} Herbicides, and ^{I} Insecticides. All AS in a specific event with a content in the PP below 0.1 mg kg^{-1} are grouped for visualization. * For the events after 23-09-2020, Glyphosate and AMPA are excluded due to point source pollution.*

The high concentrations of pesticides detected in the PP of runoff, caused increased transport of pesticides in PP when total erosion during a runoff event increased ($r^2 = 0.60$). The two events with TSS above 10 g L^{-1} had most transport in PP. In events with TSS concentrations between 3 and 10 g L^{-1} the dominant transport mode can vary, and with lower concentrations the PP share drops towards zero. The partitioning between DP and PP in terms of concentration varied through the events. In all events the PP concentration was higher than DP, with factors ranging from 12 to 3700 for the 9 events in which DP was detected, for six events no DP concentration was measured. Other studies taking both PP and DP into account report factors ranging from 10 – 1000 times higher PP concentrations compared to DP (Cruzeiro et al., 2016; Maillard and Imfeld, 2014; Todorovic et al., 2014; Yang et al., 2015a).

The mean concentrations were always cocktails of multiple active substances (AS). Figure 2.5 shows the composition of AS for each event in both phases of the runoff. The number of detected AS in PP ranged from 8 – 18, compared to 0 – 5 different AS in the DP. During the whole observation period 8 different AS were measured in DP against 24 (including AMPA) in the PP. However the LOQ for water samples in this study was 2.5 μg L^{-1}, which corresponds with analysis in other studies (Melland et al., 2016; Peruzzo et al., 2008). This limits the detection of lower concentrations of AS in water.

The difference in measured concentrations, and related evaluation of environmental risks, between short term local events and larger temporal scales was emphasized by Lefrancq et al. (2017a). During peaks in runoff, pesticide concentrations up to 387 μg L^{-1} were detected in runoff water by Lefrancq et al. (2017a); in the present study the maximal concentration during an event was 128 μg L^{-1}. Concentrations, in both PP and DP, increased a lot during the main application period when rainfall events occurred shortly after pesticide applications (see Figure 2.5). In 9 of the 14 events observed during our study the single substance as well as combined concentrations exceeded the regulatory limits, 0.1 and 0.5 μg L^{-1} respectively, set by the EU (European directive 2013/39/EC). When the pesticides enter the headwater streams they are also easily transported over longer distances, and pesticides are detected in many smaller streams throughout Europe (Casado et al., 2019).

Increased PP transport related to higher erosion rates corresponds with other studies investigating the PP and DP transport of pesticides. Melland et al. (2016), found that the PP could be significant (up to 47% of total load) with TSS concentrations ranging from 1.4 – 10.3 g L^{-1}. Yang et al. (2015) also reports high (70 – 80%) PP transport in a study with erosion rates of 7 – 10 tons ha^{-1}. Several studies that conclude PP transport is not substantial (Maillard et al., 2011; Napoli et al., 2016; Oliver et al., 2012) all observed low TSS concentrations. The erosion rates in the region of the catchment of this study were assessed to be between 1 – 2 t ha^{-1} y^{-1} (Panagos et al., 2015), while observed erosion rates during the seasons 2019 and 2020 were slightly higher in this study. However the estimated mean of 2.46 t ha^{-1} y^{-1} for erosion prone lands in Europe (Panagos et al., 2015), stresses the need to take particulate phase transport of pesticides into account in further assessments for pesticide fate and environmental risk.

2.3.2 Influence of pesticide characteristics on transport

Whether pesticides are transported to off-site areas also depends on the behaviour of the specific active substance after application on the field. Biodegradability (DT_{50}), adsorption (k_{oc}) to soil particles and solubility in water (S_w) are the main characteristics that prescribe this behaviour (Leonard, 1990). During the observations in this study, dissolved phase (DP) transport occurred mainly shortly after the applications of AS to the field: 62% of total DP transport occurred within 5 days after field application, 69% within 10 days and 98% within 50 days. In contrast, PP transport occurred over a much longer period, with 9% of the total transported mass within 5 days, 10% within 10 days, 31% in 50 days and 90% within 100 days after application. All AS which were transported in high loads in DP shortly after applications, were transported for longer periods in PP afterwards. The field plot studies on differences in DP and PP transport from arable fields (Melland et al., 2016; Todorovic et al., 2014), have analysed transport rates for events occurring shortly (<3 days) after pesticide application, concluding that DP transport is dominant. The data from the current study also shows that shortly after application DP transport occurs in substantial amounts. However, for rainfall events longer after application, pesticides are still detected in PP and can be transported during events with runoff and erosion.

Adsorption and water solubility

Table 2.1 compares the amount of applied AS for each chemical characteristic with the amount of transported AS. Statistical analysis, including regression, correlation and multivariate analysis did not show a relation between k_{oc} or S_w of AS and transport in either DP or PP. The transport in 'high' as well as 'low' solubility classes occurs more in PP than in DP, and no relation with transport can be found in this study. However, the mass transported for each class of adsorption does show a trend. The ratio of transport in DP to PP shifts from mainly DP for 'mobile' AS to mainly PP for AS classified as 'mobile'. This result corresponds with the expected behaviour of pesticides, in relation to this adsorption coefficient (Leonard, 1990; Wauchope et al., 2002). However, not all individual AS follow this pattern. The AS which were detected in DP have k_{oc} values ranging from 48 up to 1.6 10^4 ml g^{-1}, according to the PPDB, which covers the classes 'mobile' up to 'non-mobile'. Moreover, nine AS were detected in PP but not in DP, which were applied within 10 days before an occurring rainfall event. k_{oc} values for these AS range from 1.6 up to 1.6 10^4 ml g^{-1} (Lewis et al., 2016a). Based on the chemical classification at least Flonicamid (very mobile) and Cymoxanil (mobile) would be expected to be detected in DP.

Table 2.1 *Overview of application and transport of AS in relation to chemical characteristics.*

Class	Range of class	Application in catchment			Transport at outlet			
		AS applied (n)	Mass applied (kg)	% of applied mass	AS detected (n)	PP mass (g)	DP mass (g)	% of transported mass
Solubility in water (S_w, mg L^{-1})								
Low	< 50	20	111	46%	16	89	70	57%
Moderate	50 – 500	3	29	12%	2	26	39	23%
High	> 500	7	104	42%	5	47	8	20%
Soil adsorption (k_{oc}, mL g^{-1})								
very mobile	< 15	1	3	1%	1	0	0	0%
Mobile	15 – 75	2	8	3%	2	1	7	3%
moderately mobile	75 – 500	7	35	14%	5	25	65	32%
slightly mobile	500 – 4000	15	131	54%	12	90	45	48%
non-mobile	> 4000	5	67	28%	3	46	1	17%
Biodegradability (DT_{50}, days)								
non-persistent	< 30	14	121	50%	8	24	12	13%
moderately persistent	30 – 100	9	52	21%	8	85	104	68%
persistent	100 - 365	7	70	29%	7	53	1	19%
Note: the biodegradability class 'very persistent' (> 365 days) did not occur in this study. AMPA as metabolite is excluded from this overview. Characteristics of chemicals (class and range) are obtained from the PPDB (Lewis et al., 2016).								

These findings correspond with analysis in other studies, where some AS were found to follow the theoretical classification well, but other AS were transported more in an unexpected phase. Oliver et al. (2012) reported that the AS with highest solubility was transported proportionally less in DP compared to AS with lower solubility properties. In a field experiment with runoff two days after the application of pesticides, the AS with higher adsorption to soil particles were also transported most in PP (Melland et al., 2016). On larger scales, also no significant correlation was found between adsorption characteristics of AS and partitioning between DP and PP (Climent et al., 2019), although more different AS and in higher frequency where detected in PP (Cruzeiro et al., 2016). These results from other studies as well as the observations in the present study indicate that solubility and adsorption characteristics may not suffice to predict the dominant transport mode and related environmental fate of pesticides.

Mandipropamid, glyphosate, metobromuron and prosulfocarb were the main transported AS in PP. Prosulfocarb has a high k_{oc} and low solubility, and it is only detected in PP. Glyphosate is detected in both phases although the majority of transport occurred in PP (97%). The other two AS have more affinity for dissolved transport and were also transported in DP, mandipropamid for 41% and metobromuron for 63% of total mass. During the growing seasons a total of 52 different AS were applied. Due to limitations in the analysis, several AS that might be interesting for analysis, had to be excluded. This were mancozeb, diquat and captan among others, of which some were applied in high frequency or had chemical characteristics that suggested high potential for PP transport (Chiovarou and Siewicki, 2008). Therefor the transported loads in this study cannot be used as a mass balance, because including or excluding several AS from the analysis can influence the quantities that are reported.

Transport in relation to persistence and application frequency

The persistence of an AS is of major influence for the transport by runoff. Of the 30 analysed AS, seven where not detected in any runoff event, these are characterized by a fast degradation (DT_{50} < 32 days). Two of these AS were applied during potato cultivation and 5 on the apple orchard. Table 2.1 shows that persistence influences the risk of transport. Of total applied AS mass, 50% is non-persistent, and 50% is moderately persistent or persistent. However, in the runoff, these ratios change, and only 13% of transported AS belong to the 'non-persistent' class, compared to 87% of transported mass belonging to the moderately-persistent and persistent class.

In Figure 2.6, a comparison of the decrease of transported concentration over time since application is shown for six AS that were detected on a regular basis. Three of these were transported in both phases. The data shows that after 60 days no transport in DP is detected, while transport in PP lasts much longer. In addition, the concentrations transported in DP drop faster over time; even for metribuzin where the fitted 1st order decay curves have nearly the same slope for

DP and PP. After 150 days significant concentrations were still detected in PP. The fitted curves show a reasonably good fit for DP with residual standard errors (RSE) between 0.06 and 0.12. This confirms the overall observation that in the 14 events of this dataset, 69% of all DP transport occurs within 10 days after application on the field. This finding corresponds with other studies, which report DP transport mainly close to application (Boithias et al., 2014; Cruzeiro et al., 2016; Melland et al., 2016). PP concentrations have a higher RSE, meaning that the time between application and event alone cannot explain concentration or transported load in PP. Differences in reported degradation rates (e.g. PPDB) with observed degradation in the field can be caused by the high variability in environmental degradation of AS (Arias-Estévez et al., 2008; Bento et al., 2016).

The three AS shown in Figure 2.6, that were transported in both phases, were all applied frequently, which increases the chance for a runoff event to occur close to the application date. Epoxiconazole and Bixafen both show low or no decrease in transported concentration over time: both compounds have slow biodegradation (98 and 203 days DT_{50} respectively) and originate from applications of the previous growing season. Bixafen was applied one time in 2019 and once in 2018 but was detected on stable levels around 50 $\mu g\ kg^{-1}$ on arable fields in this study.

The concentrations in which these AS were transported are low compared to e.g., prosulfocarb, however these AS were transported with every erosive runoff event and in this way formed a constant source of pollution. No studies were found that relate the transported load of different AS to the varying biodegradation rate in the environment. However studies on concentrations and detection of AS in rivers, clearly show increased levels and numbers of different AS during periods with intensive pesticide use, often spring and summer (Climent et al., 2019; Cruzeiro et al., 2016; Peruzzo et al., 2008).

The three chemical characteristics of interest; biodegradation, water solubility and adsorption coefficient alone cannot explain the transported concentrations or the partitioning between dissolved and particulate phase. The transported mass during an event, both in DP and PP, depends not only on concentration, but also on runoff and erosion quantity and related variables, which are strongly event specific. The transport dynamics on field scale are also influenced by runoff generation processes and sediment connectivity (Bracken and Croke, 2007; Heckmann et al., 2018), which takes into account factors like upstream area, spatial land use distribution and field specific land management (see section 2.3.3.), distance to the outlet (Borselli et al., 2008; Cavalli et al., 2013) and rainfall amounts and intensity (López-Vicente and Ben-Salem, 2019).

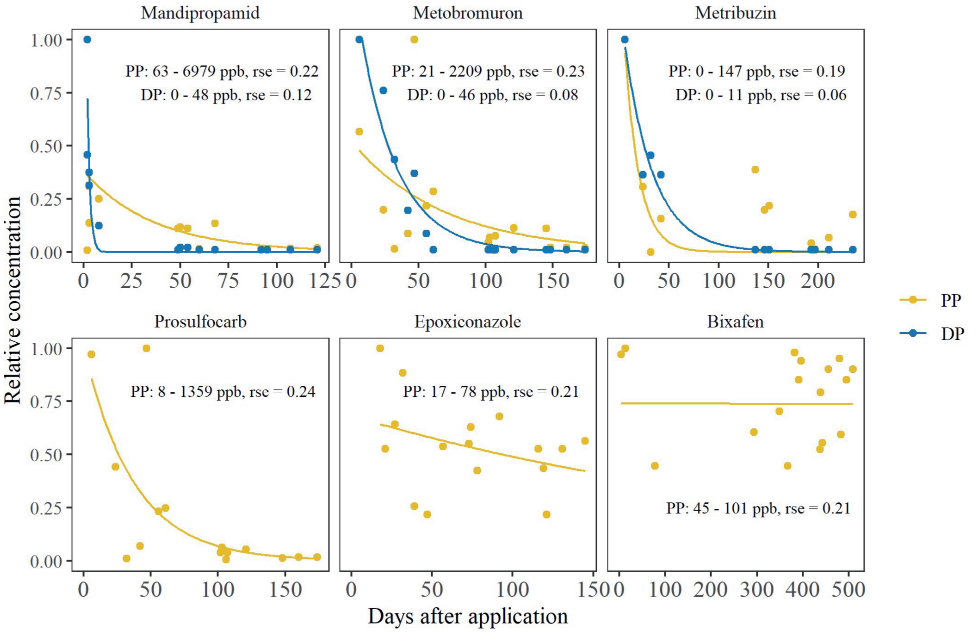

Figure 2.6 *Decrease of the relative concentrations in DP and PP for six AS. The concentration range (min – max) of the AS detected in runoff is given, ppb in PP is µg kg^{-1}, and in DP µg L^{-1}. rse is the residual standard error.*

2.3.3 Land use effect on transport in PP and DP

Based on the application data for each field and the concentrations of AS during field surveys in the soil, the source field and associated land use type can be derived for the AS detected at the catchment outlet during the events. Land use and management of agricultural fields affect runoff, erosion, and thus the potential transport of AS to off-site locations. The number of detected AS in runoff is the highest in the main cropping season (June – August), which corresponds with the frequency of applications on the fields.

Apples

On the apple orchard the highest total amount of pesticides was applied, with a mean of 21 kg ha^{-1} active ingredients (Table 2.2), and the frequency of applications throughout the growing season is high. This does however not result in high discharges of pesticides at the catchment outlet. Six AS were detected in the runoff, of which four were fungicides, one herbicide and one insecticide. Four of these (fluxapyroxad, pyraclostrobin, chlorantraniliprole and difenoconazole) were only applied on apples and were not transported in DP, only in PP and contributed 1% to total PP load. Besides that, boscalid and glyphosate were applied, which are also used in potato cultivation, the exact source field could not be derived based on this dataset. These compounds contribute 1% and 23% tot total DP and PP transport respectively. The borders and interrow area of the orchard were covered with grass, which has a reducing effect on soil erosion and a filtering and buffering effect on the transport of pesticides (Muñoz-Carpena et al., 2018; Reichenberger et al., 2019; Yu et al., 2019). During field observation, no signs of erosion were recorded from the apples. These findings correspond with studies on orchards and vineyards with grassed rows, also reporting low AS transport (Napoli et al., 2016; Oliver et al., 2012).

Cereals

None of the transported AS can be directly associated with the cereal cultivation. This corresponds with the low erosion risk associated with cereals in summer (Prasuhn, 2020) and the low total amount of applied pesticides (0.4 kg ha^{-1}, Table 2.2). However, during cereal cultivation persistent AS were applied (epoxiconazole, bixafen and isopyrazam), which were still detected in the soil in the next growing season, when a different crop was grown on the field (i.e. the next crop in the rotation). These three AS were detected in 100%, 100% and 93% of all runoff events respectively. They were transported from the field in the rotation after the cereals, when potatoes were cultivated, which caused the runoff and erosion. The transport of these AS one year after application contributes for 4% of the PP transported mass from the catchment. To the authors no other studies are known presenting results of delayed transport of pesticides in overland transport, however persistent AS were shown to be a risk for leaching to groundwater (Reichenberger et al., 2007; Schuhmann et al., 2019).

Potatoes

The main source of pesticide transport in this study was the field cultivated with potatoes. 21 of all detected AS (including AMPA) where related to this cultivation, this also included persistent AS which were applied in previous cropping seasons (see previous section). At least 72% of PP and 99% of DP transport originates from the potato cultivation. As discussed above, glyphosate and boscalid can originate from apples as well as potato cultivation. Based on the observations of major runoff and erosion the potato field is likely to also be the main source area for these AS. Potato cultivation on sloping lands is a combination of erosion prone land use (Olivier et al., 2014) with high amount of pesticide applications (11 kg ha^{-1}, Table 2.2). During field observations potato cultivation was identified as the main source of runoff and erosion (see photos S.3 – S.5), which corresponds with the detected AS in the runoff and TSS. These results show that erosion prone and pesticide intensive cultivations form the main risk for both DP and PP transport of pesticides during runoff events. In the currently available literature of PP transport of pesticide only plot scale simulations on arable fields are available, comparing either tillage practices or crop and mulch cover (Bento et al., 2018; Melland et al., 2016; Todorovic et al., 2014; Yang et al., 2015a). These studies show the effect of increased transport with erosion prone land management types.

However, the smaller scale and often short time between application and runoff event of these studies, did not suffice to understand the extent of potential PP transport from arable fields with an erosion prone cultivation.

The large difference in observed transport between the potato cultivation and the cereals or apple orchard, emphasize that preventing erosion and runoff will also reduce the overland transport of pesticide. Implementation of on-site measure like vegetated filter strips (Muñoz-Carpena et al., 2019) or micro-dams between the potato ridges (Olivier et al., 2014) can reduce runoff and erosion from the specific fields. Moreover off-site erosion measures like riparian buffers and wetlands are shown to mitigate further transport of pesticides in to the environment (Imfeld et al., 2021).

2.4 Conclusions and recommendations

This study confirmed our hypothesis that particulate phase transport contributes to total overland transport of pesticides on field scale on sloping land. Based on observations in two growing seasons (2019 and 2020) in which 14 rainfall-runoff events were sampled we can conclude that in a small agricultural catchment with intensive arable farming, PP transport contributed substantially to total overland transport of pesticides.

Event specific contributions of PP show high variability, which is the result of interacting factors, including hydrological and sediment dynamics during the event, chemical characteristics of the transported active substances and land management on the fields. This results in high variability in quantity, phase and type of the transported pesticides. Land use types which are pesticide intensive and erosion prone, pose a threat for high discharges of pesticides via runoff, both in dissolved and particulate phase.

Transport in DP occurred mainly shortly after application of the pesticide (69% within 10 days). Opposingly, the transport of pesticides in PP occurs over much longer time spans, where 90% of the total transport is reached within 100 days after application in this study.

Biodegradability (DT_{50}), adsorption to soil (k_{oc}) and solubility in water (S_w) of AS alone cannot explain the transport mode and related fate of individual pesticides after application. However, the biodegradability of an active substance determines how long it will be available for overland transport either in PP or DP. Most non-persistent AS were not transported or only shortly after application, where several persistent AS were transported year-round during erosive runoff events.

Considering the extent of erosion from arable land, significantly more transport occurs than is predicted when PP transport during runoff events is not taken into account. Our results imply that event-scale dynamics are important for pesticide transport and that interactions between management, event characteristics and applied active substances can cause events that contribute disproportionally high to total transport. Because most transport of pesticides occurred from erosion prone land use, this study emphasizes the need for on-site and off-site erosion mitigation to prevent off-site transport of pesticides in the environment.

For further generalization and understanding of the findings in the study, additional observational data will be valuable. Transport behaviour in different pedoclimatic and geomorphic environments as well as under different land management practices, will further increase our understanding of these dynamics. The current study is limited to three land use types, on erosion prone loess soils. Moreover the observation period of two years, results in a variety of rainfall events, but longer term observations are needed to be able to derive generalized conclusions. Other research methods, such as modelling studies that investigate the relevant variables and that can explicitly simulate the dynamics within the catchment, might add to our ability to assess the pollution risk of currently used pesticides.

2.5 Supplementary Materials

2.5.1 Field measurements

Rainfall and runoff analysis

To compare rainfall events with each other the event index (EVI) was calculated (Baartman et al., 2013). This combines rainfall intensity, duration, and total amount of precipitation to reflect the impact of the event:

$$EVI = \frac{PI_{max} \cdot P_{tot}}{D} \qquad Eq\ 2.2$$

With PI_{max} being the maximal 1 minute rainfall intensity (mm h^{-1}), P_{tot} the total rainfall in mm and D the duration of the event in minutes. A high EVI reflects a relatively short event with higher intensities and total amount of rainfall.

Measured discharge was calculated based on the water height measured in the Parshall flume. The water level was measured on 2 locations (h_a and h_b), the ratio between both is an indicator for the level of submergence. When the submergence relation is below 50%, free flow conditions were met and the discharge can be calculated with Eq 2.3 (Parshall, 1926), note that these formulae are in feet, while collected data is in metric units:

$$Q = 1.428 \cdot h_a^{1.550} \qquad Eq\ 2.3$$

When free flow conditions were not met the discharge was corrected for submergence. With the h_a/h_b approaching 100% the accuracy of the flume starts to decrease substantially. Correction of discharge is done with:

$$Q = Q_{free} - Q_{cor} \qquad Eq\ 2.4$$

With Q_{free} the discharge based on the free flow formula (Eq. 2.3) and Q_{cor}:

$$Q_{cor} = \left(\left(\frac{h_a}{\left(\frac{1.8}{K}\right)^{1.8} - 2.45} \right)^{4.57-3.14K} + 0.093 * K \right) * w^{0.815} \qquad Eq\ 2.5$$

where h_a is the upstream water head in feet, h_b is downstream water head in feet, w is the flume throat width in feet, K is h_b/h_a, Q is the discharge in $f^3\ s^{-1}$ when $K < 0.5$ and Q_{cor} the discharge correction when $K > 0.5$.

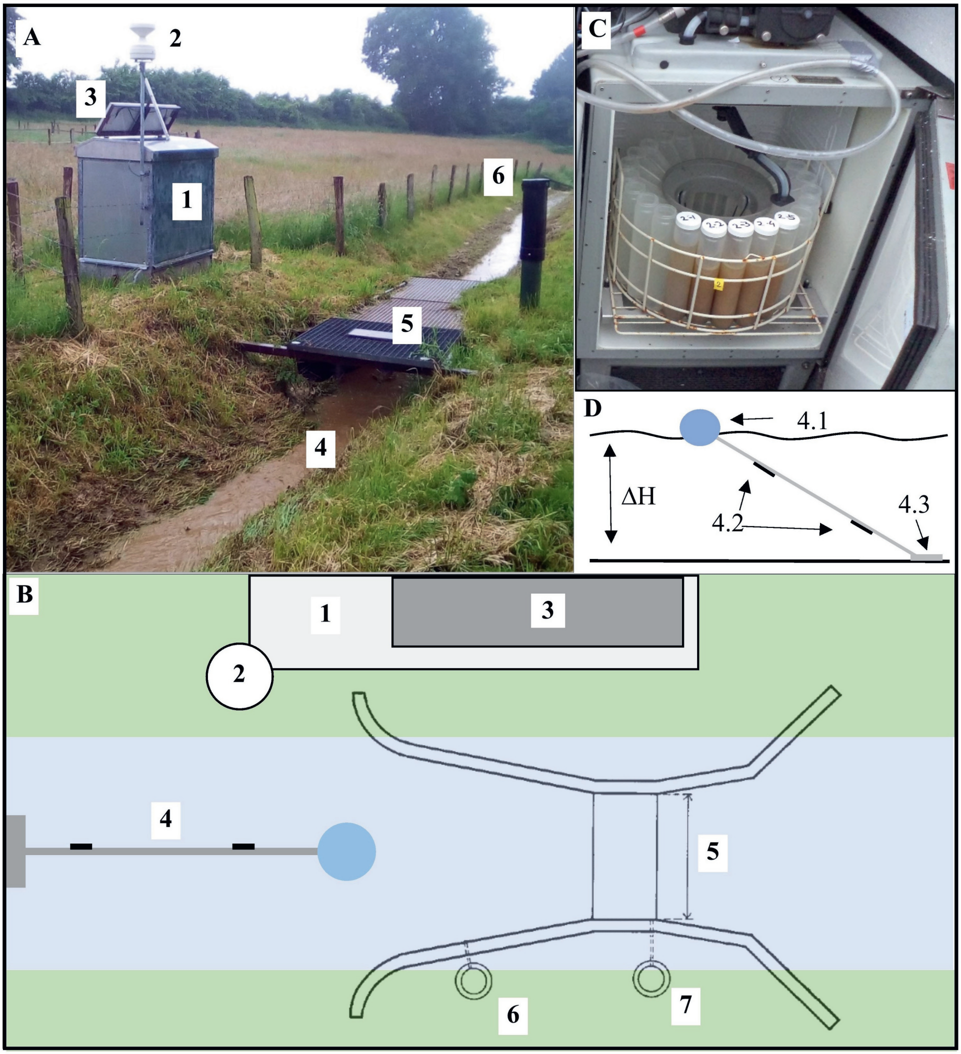

Figure 2.7 *Overview of the measurements at the catchment outlet. A. Photo with stream flow during event of 2019-05-28, B. Top view of outlet and installed equipment, C. ISCO automatic sampler with 5 samples collected, D. Side view of inlet device for runoff sampling with: 4.1 = Float, 4.2 = inlet tubes on 25 and 75% of water depth (Δh), 4.3 = ground anker with pivot on stream bed. The indicated equipment is: 1 = Equipment unit including ISCO automated samplers, batteries and datalogger, 2 = tipping bucket rain gauge, 3 = Solar panel, 4 = Runoff sampling inlet device, 5 = Parshall flume with 2 feet throat width, 6 = Water level sensor upstream (h_a), 7 = Water level sensor downstream (h_b).*

Events selected for further analysis

During the measurement years 2019 and 2020, based on the discharge data from the flume, 39 runoff events occurred. From these, 25 events were also sampled by the ISCO automatic sampler. The 14 missed events were not included due to temporary malfunctioning of the measurement setup. For 17 of the 25 events, pesticide analysis was done. Five events were not analysed because the samples were not stored cold enough until analysis, and for 3 events the total collected sediment by the samplers was too low (< 4 grams) to perform a pesticide analysis. Three other events were excluded from further analysis because event duration was much longer than 72 minutes, which is the maximal sampling time for the automatic samplers. Thus, eventually 14 events were considered for the analysis of this study.

The subsets of analysed and not-analysed events are compared on runoff and erosion characteristics. No significant differences ($p < 0.05$) were found between the groups. In Figure 2.8 a comparison for six characteristics is presented. The boxplots show a tendency for shorter, more intense events with higher median TSS and total erosion in the analysed subset. This can be explained by limitations in the observation and measurement design; the maximal duration of sampling was 72 minutes, events which lasted much longer had to be excluded from analysis. Besides that, the sediment for pesticide analysis was collected from 800 mL discharge samples. Events with low TSS values therefor could not be included in the analysis. This trend will influence the results by presenting an overestimation of erosion, and analysing events which caused more sediment and hydrologic dynamics in the catchment.

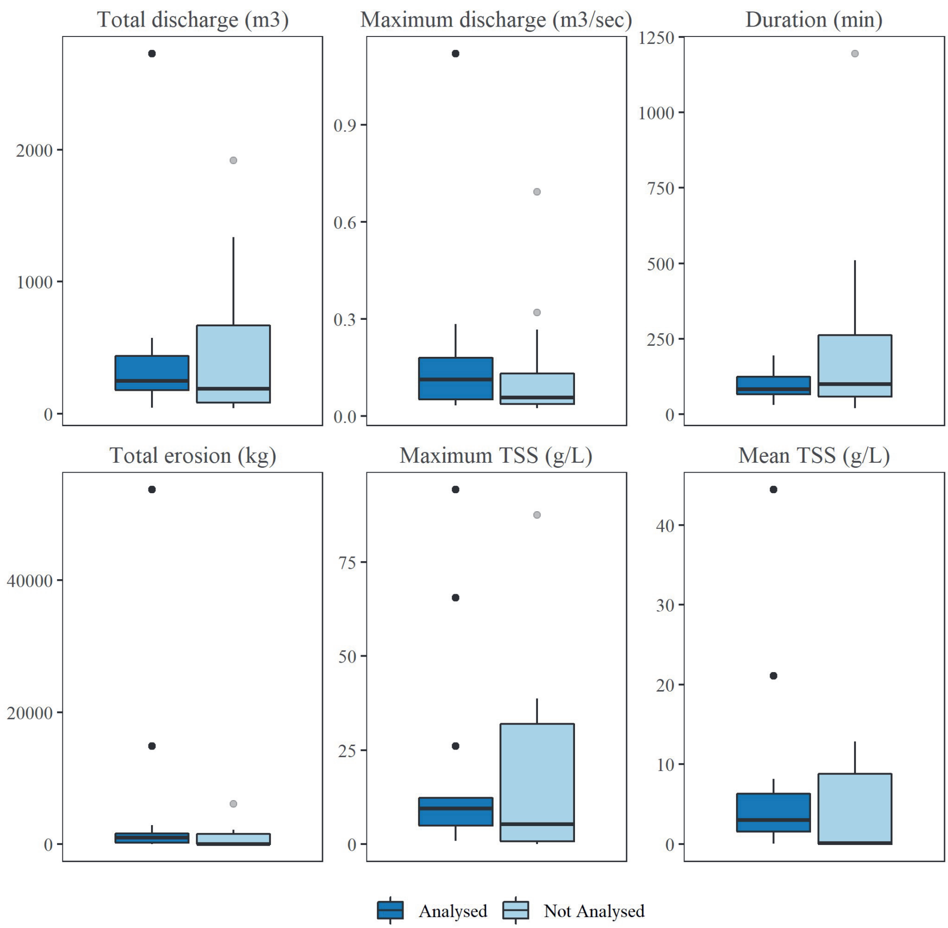

Figure 2.8 *comparison of runoff and erosion statistics between analysed and not-analysed events during the observation period. No significant differences are found (p = 0.05). Of 39 events, one (2019-08-18) is excluded due to errors in the sensor on water level readings. For discharge; analysed n = 14, not-analysed n = 24. For erosion and TSS; analysed n = 14, not-analysed n = 9. For 14 events no TSS data was collected.*

2.5.2 Pesticides applications and analysis

Land use and pesticide applications

From the landowners of the fields A, B and, C the pesticide application data was obtained. In total 58 different active substances (AS) were applied during the study period, of these 31 where analysed in this study.

Table 2.2 *Overview of pesticide applications, and detection for major crops in the catchment for the period 2018 - 2020.*

Field [1]	A			B			C		
Area (ha)	7.9			14.1			5.3		
Year	2018	2019	2020	2018	2019	2020	2018	2019	2020
Crop	Sugar beet	Wheat	Potato	Wheat	Potato	Wheat	Apples		
Number of application days	8	3	21	3	26	3	?[4]	26	20
kg ha^{-1} y^{-1} active substances (AS)	7.4	0.4	9.1	0.4	13.0	0.3	?	24.9	17.5
Number of different AS applied per growing season	10	7	14	8	22	7	?	20	13
Applied AS analyzed in this study	3	4	12	4	17	2	?	12	8
Residues detected in soil [2]	-[3]	7	13	-	25	15	-	16	13

[1] For field locations, see Figure 2.1. [2] Including AMPA, which is a degradation product of glyphosate, not applied, always detected. [3] Not measured. [4] No data obtained for this field/season. AS = active substances. A list with all applied and analysed AS is presented in Annex A of the original publication.

Response analysis

Linear response of each calibration standard was tested against the 3.125 ng mL^{-1} standards. If the response deviated more than 20% the standard was not included in the linear model. The linear range of each compound per sequence was limited to the minimal and maximal standards that had a linear response. The correlation coefficients for the fitted linear models were all above 0.98. Samples were evaluated on quality based on the ion ratio (±30% from mean of standards) and retention time (± 0.05 minutes from mean of standards). If the sample response was outside the linear range for a compound, a dilution was made and reanalysed. Dilutions had to be made for 97 out of 175 samples consisting of 8 runoff water samples, 47 TSS in runoff and 42 soil samples in the catchment. Dilution factors ranged from 4 times up to 1000 times. This indicates the high variety in concentrations found in the samples.

The limit of quantification (LOQ) for the different analysis and sample materials is shown in table 2.3. To derive total pesticide load in runoff water and TSS the pesticide measurements below LOQ were assumed to be zero (0). For sediment this does not introduce a significant error because the measured concentrations were much higher than LOQ, however for water the potential pesticide load that is not accounted for can be significant. To estimate this difference, the maximal undiscovered pesticide load in water ($P_w max$) was derived by calculating the total load with LOQ concentrations for each compound that was also detected in TSS during the same event. This statistic gives an added indication of uncertainty in the presented total loads of pesticides in runoff water.

Table 2.3 *Overview of limits of quantification for different analysis types and sample materials.*

Analysis	Sample material	LOQ (ppb*)
Glyphosate/AMPA	Runoff water	10
	Runoff TSS and soil	50
Multi-residue (individual compounds)	Runoff water	2.5
	Runoff TSS and soil	10
*ppb equals µg L^{-1} for water and µg kg^{-1} for soil and sediment		

Point source pollution by Glyphosate

The main pesticide source during the events in this study are the agricultural fields. For these diffuse pollution sources, relations can be found between field application, detected AS in the soil and measured concentrations in DP and PP at the outlet. However, the high concentrations of glyphosate detected in the runoff event of 2020-09-23 cannot be explained by the applications of glyphosate on the three main fields. A possible usage of glyphosate in the month September is related to the preparation of fields for the winter cover crop after cereals cultivation when using minimum tillage (Griffin and Dabney, 1990; Schappert et al., 2018). At the borders of the catchment, there were eight other fields cultivated with cereals in the growing season of 2020. Spillage and point source losses of pesticides at field borders can contribute to pollution (Moser et al., 2018; Reichenberger et al., 2007; Syafrudin et al., 2021; Wenneker et al., 2010) and in this case such a point source is the most likely explanation of the high concentrations detected. The point source pollution was suggested by one of the landowners during an interview. The point source would be located on the tarmac road bordering the apple orchard, and was a result of spilling the left-over of a field treatment on the road. These extreme concentration peaks due to point source pollution in runoff pose a threat to the environment which is not detected when long term averages are studied (Boxall et al., 2013; Hamer et al., 2019).

In Table 2.4 the concentrations and transported load of Glyphosate and its metabolite AMPA are presented. On 23-09-2020 the concentrations and resulting transported loads in PP and DP are extremely high compared to concentrations detected in other events and for other AS (see also Figure 2.5).

Date	Glyphosate				AMPA			
	PP		DP		PP		DP	
	mg kg^{-1}	load (g)	mg L^{-1}	load (g)	mg kg^{-1}	load (g)	mg L^{-1}	load (g)
23-09-2020	566	11	2.2	134.8	23.6	0.5	0	0
08-10-2020	2.9	3	0.003	12.5	2.4	2.8	0	0
22-10-2020	1.2	2	0.001	2.6	1.9	3.4	0.0001	0.6

Table 2.4 *concentrations and transported load of Glyphosate and AMPA in the three events influenced by the point source pollution.*

2.5.3 Propagation of uncertainty

The calculations of the total pesticide loads in particulate (PP) and dissolved phase (DP) were based on variables that each introduce uncertainty towards the final quantification. Propagation of uncertainty was calculated with the standard deviation expressed as relative error for each variable (Taylor and Thompson, 1998). The use of relative error was chosen because for most of the primary measurements (Q_w and TSS) the expected error will be relative to the absolute value and not fixed independently. Moreover, propagation of uncertainty in cases of multiplication is better performed on relative errors.

For precipitation and discharge measured in the Parshall flume the uncertainty was obtained from literature. The accuracy of the Parshall flume was improved by using a correction formula, see section 2.5.1 for more explanation. TSS was calibrated in the laboratory for this research. The prediction error of the fitted model was 6%.

For the pesticide analysis, the uncertainty was based on the variation detected in the quality control samples. The variation in recovery and detected concentration is used as indication for the uncertainty of the whole chemical analysis including extraction, matrix effect and random variation during analysis. To take a conservative uncertainty estimate, the largest standard deviation among the compounds was applied to the whole study. The correction for θ was based on a model fitted based on the relation between volumetric water content in the collected samples and estimated water content of the material used for LC-MS/MS analysis.

Propagation of uncertainty was calculated using:

$$\frac{\delta X}{|X|} = \sqrt{\left(\frac{\delta a}{a}\right)^2 + \left(\frac{\delta b}{b}\right)^2 + \cdots} \qquad Eq\ 2.6$$

where $\frac{\delta X}{|X|}$ is the relative error of the calculated variable and $\frac{\delta a}{a}$ etc. are the relative errors of the used variables.

The relative standard deviation was calculated with:

$$\frac{\delta X}{|X|} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}\left(\frac{\delta x_i}{|x_i|} - \frac{\delta \mu}{|\mu|}\right)^2} \qquad Eq\ 2.7$$

The resulting uncertainties are presented in Table 2.5.

Table 2.5 *Uncertainty and propagation of errors for major variables to derive total pesticide load in DP and PP.*

Variable	Unit	Estimated uncertainty	Calculations and propagation
Precipitation: P	mm h^{-1}	Tipping bucket: ± 4% at 25 mm h^{-1} (Parkin et al., 1982).	Calibration showed mean of 0.203 mm (This research)
Water discharge: Q	m^3 sec^{-1}	K < 0.7 ± 3%, K > 0.7 ± 5% (Bos, 1989; Parshall, 1926)	See Eq. 2.4 for Q corrections
TSS	g L^{-1}	± 3% (This research)	RMSE from model fit
Sediment discharge: Q_{sed}	kg sec^{-1}	± 6%	Eq. 2.6 with $a = Q$ and $b = TSS$
Pesticide concentration	ppb	± 16% (This research)	Max sd compound recovery
θ correction	%	± 6% (This research)	RMSE from model fit
Pesticide load water	mg	± 17%	Eq 2.6 with $a = Q$ and $b = Pest\_conc\_water$
Pesticide load sediment	mg	± 18%	Eq 2.6 with $a = Q_{sed}$, $b = Pest\_conc\_sed$ and $c = \theta\_cor$
Note: all uncertainties are given as the relative standard deviation of the given variable.			

Chapter 3

Simulating event-based pesticide transport with runoff and erosion; OpenLISEM-pesticide[3]

Abstract

This study presents a novel pesticide transport module for the OpenLISEM runoff and erosion model. During water erosion events, high amounts of pesticides can be transported alongside the runoff. Simulating this process helps to mitigate adverse effects of pesticides in the environment. We conceptualized pesticide uptake during runoff with a mixing-layer, including mass transfer of dissolved pesticides into the runoff water and detachment in combination with enrichment of sorbed pesticides. Lateral transport of pesticides is modelled with a kinematic wave based on the overland flow of water. The model simulations were in line with observations for two events in a small agricultural catchment in South-Limburg, the Netherlands. A sensitivity analysis showed that pesticide transport was mainly influenced by the mass transfer rate, the soil-water partitioning and the exponent for the enrichment ratio. The accurate simulation of runoff and erosion by OpenLISEM, enables OpenLISEM-pesticide to simulate transport and redistribution adequately.

[3]Based on: Commelin, M.C., Baartman, J.E.M., Wesseling, J.G., Jetten, V., 2024. Simulating event-based pesticide transport with runoff and erosion; OpenLISEM-pesticide v.1. Environmental Modelling & Software 174, 105960. DOI 10.1016/j.envsoft.2024.105960

3.1 Introduction

Understanding the fate of pesticides in the environment and their effect on off-site ecosystems is needed to prevent further pollution and to mitigate current adverse effects of pesticides in our environment (Lykogianni et al., 2021). The environmental fate of pesticides starts after their application on the crop and field, in which part of the pesticides can be transported to off-site areas through runoff (Kalyabina et al., 2021). In recent studies it was found that peak concentrations in streams can be directly related to rainfall events, based on evidence from a large number of agricultural headwater (<30 km^2) catchments in Germany (Halbach et al., 2021). Regulatory acceptable concentrations are often exceeded for samples collected during runoff events (Vormeier et al., 2023), posing significant risks to ecosystems (Liess et al., 2021). Peak concentration of pesticides related to rainfall-runoff events are also observed in many other studies (Casado et al., 2019; la Cecilia et al., 2021; Lefrancq et al., 2017a; Schönenberger et al., 2022).

These studies mainly focus on pesticides concentrations in runoff water. However, pesticides are also sorbed to soil particles and overland flow often results in surface erosion and transport of these soil particles with the runoff water. Estimated erosion rates on agricultural fields in EU are 2.5 t/ha/y on average (Panagos et al., 2015) and within the same order of magnitude for agricultural soils worldwide (Borrelli et al., 2021; Thaler et al., 2022). These rates can increase substantially depending on factors like vegetation cover, land management and local topography and climate (Panagos et al., 2015). Papers published in the past decade give an unclear picture of the contribution of sorbed pesticide transport to total pesticide transport and various studies present contradictory results (Commelin et al., 2022a). Some studies show that sorbed transport is a minor flux (Maillard et al., 2011; Napoli et al., 2016) other studies show potentially high transport of sorbed pesticides (Bento et al., 2018; Climent et al., 2019; Melland et al., 2016). In a previous field study in which we investigated sorbed and dissolved transport during rainfall-runoff events in a small agricultural catchment in South-Limburg, results showed that sorbed pesticide transport often contributes substantially to total pesticide transport, although variation between events is large (Commelin et al., 2022a). Considering both sorbed and dissolved pesticide transport during rainfall-runoff events is thus important.

Pesticide transport at the headwater catchment scale is highly influenced by catchment heterogeneity (Payraudeau and Gregoire, 2012), including hydrologic connectivity and spatiotemporal variability depending on rainfall characteristics, soil properties and landscape elements such as tillage roughness (Takken et al., 2001b), hedges and roads (Favis-Mortlock et al., 2022). Although this heterogeneity cannot be fully known or described, physical-based fully distributed models could be helpful to take into account the complexity of interacting processes during a rainfall-runoff event. Moreover they can describe alterations in land use, management or climate change and assess their impact on pesticide transport (Mottes et al., 2015; Payraudeau and Gregoire, 2012). Havis et al., (1992) developed a soil-runoff interaction model to simulate pesticide transport with dynamic runoff processes on a timescale ranging from a few seconds to minutes. The model was further implemented and tested by Joyce et al., (2010, 2008), and performed well for plot scale rainfall experiments. However, the model was not implemented in a fully distributed model on field or headwater catchment scale.

In Table 3.1 some commonly used pesticide fate models are compared on properties relevant for the simulation of pesticide transport during rainfall-runoff events. Several well-known models have been thoroughly tested and evaluated on pesticide leaching, degradation in the soil and transport with runoff, including for example PRZM, FOCUSPEARL, RZWQM and SWAT (DeMars et al., 2018; Purnell et al., 2020; Van den Berg et al., 2016; Young and Fry, 2019). However, the spatial representation (homogenous or hydrologic response units) and temporal scale (minimal timesteps of hours or days) of these models is not targeted at event scale dynamics. Besides these, other models have been developed, aiming at specific topics of pesticide fate. For example ZinAgriTra analyses the transport of transformation products of pesticides (Gassmann, 2013) and VFSMOD was specifically designed to predict the effect of vegetative filter strips to trap pesticides (Muñoz-Carpena et al., 2018). A fully distributed model including physical based runoff and erosion processes and related pesticide transport might contribute to a better understanding of the peak transport of pesticides during erosive rainfall-runoff events.

In a recent review 17 different models were identified that were used in the past decade to simulate the fate and transport of pesticides (Centanni et al., 2023). In most of these modelling studies particulate transport of pesticides is not taken into account due to lack of data or model limitations (e.g. Gassmann, 2013; Purnell et al., 2020; Young and Fry, 2019). When particulate transport is included, the model performance in terms of sediment transport is reported as not adequate (e.g. Chen et al., 2017; DeMars et al., 2018). Dynamics within the runoff event, and different contributing areas could not be simulated with these lumped edge-of-field models. A fully distributed dynamic model, although more complex, might be valuable in further understanding the transport processes of pesticides during erosive rainfall-runoff events. The GSSHA model does have a promising combination of properties (Pradhan et al., 2014), however very little prior research or information on applications for pesticide transport was found. A combination of the conceptual model of Havis et al. (1992) extended with particulate phase transport and the OpenLISEM model for hydrology and sediment dynamics would have the required properties.

Table 3.1 *Overview of model properties for some commonly used pesticide fate models.*

Model	Spatial scale[1]	Temporal scale[2]	Description of erosion	Particulate pesticide transport	Source
OpenLISEM	Gridded	m - D	Process	This study	De Roo et al. 1996, Bout and Jetten, 2018
Havis/Joyce	HRU	m - H	na	na	Havis et al., 1992, Joyce et al., 2008
GLEAMS	1D	D - Y	Empirical	Yes	Leonard et al. 1978
ZinAgriTra	Gridded	m - M	Process	na	Gassmann et al., 2013
PRZM5	1D	D - Y	Empirical	Yes	Young and Fry, 2014
RZWQM	1D	D - Y	Empirical	Yes	DeMars et al., 2018, Ma et al., 2012
FOCUSPEARL	1D	D - Y	na	na	Van den Berg et al., 2016
SWAT	HRU	H - Y	Empirical/ process	Yes	Neitsch 2011, Purnell et al., 2020
PESHMELBA	HRU	H - M	na	na	Rouzies et al., 2019
GSSHA	Gridded	m - D	Process	Yes	Pradhan et al., 2014

[1] Spatial scale: 1D: homogeneous representation of scale. HRU: Hydrologic Response Units with homogeneous properties. Gridded: a raster describes the spatial heterogeneity of parameters.

[2] Temporal scale: m = Minutes, H = Hours, D = Days, M = Months, Y = Years.

Therefor in this study we developed an extension for OpenLISEM to simulate pesticide transport during erosive rainfall-runoff events: OpenLISEM-pesticide (OLP). We selected the physically-based fully distributed hydrology and sediment dynamics model OpenLISEM (v6.91) to implement pesticide dynamics because it can simulate both runoff and sediment dynamics in high detail, both spatially and temporally, and was designed for catchments from 1 ha up to approximately 100 km^2 (De Roo and Jetten, 1999). Moreover this model is well tested and can simulate runoff and erosion processes during rainfall-runoff events adequately (Baartman et al., 2012; Jong and Jetten, 2007; Lefrancq et al., 2017b; Wu et al., 2021). The objectives of the study were to (1) include particulate pesticide transport in the models from Havis et al., (1992) and Joyce et al., (2008), and to implement this in the OpenLISEM model; (2) show a proof of concept of the model's capacity using two erosive rainfall events, for two different pesticides on small catchment scale; and (3) further explore the behaviour of the newly developed module with a sensitivity test of the pesticide-related model parameters.

3.2 Methods and model formulation

3.2.1 Concepts and equations describing pesticide dynamics during runoff

The movement of pesticides by runoff consists of two main processes, the uptake of the pesticide from the soil into the runoff water and the lateral transport with runoff over the soil surface. When pesticides are applied on a field a thin layer with high concentrations forms on the soil surface (Gassmann et al., 2015; Leonard, 1990). The uptake of the pesticides from the soil into runoff is often conceptualized with a 'mixing layer' (Ahuja and Lehman, 1983; Gao et al., 2004; Havis et al., 1992; Tong and Ye, 2020).

Different versions of the mixing layer model have been formulated, including complete mixing between the soil and the runoff (Ahuja et al., 1982) and non-uniform mixing decreasing with soil depth (Ahuja and Lehman, 1983; Young and Fry, 2019). These models assume complete mixing between runoff and the mixing zone, which is valid for timesteps of several hours or longer. When simulating soil-runoff interactions for runoff dynamics with timesteps of minutes or seconds, a mass transfer model can be used. The mass transfer coefficient describes the rate on which dissolved pesticides are taken up from the mixing layer into the runoff (Havis et al., 1992; Joyce et al., 2008). The exact physical and chemical processes in the mixing layer are highly complex and the mixing layer is simplified as a finite, steady and completely mixed reactor (Havis et al., 1992; Shao et al., 2021). The thickness of the mixing layer is defined as the depth of interaction between the soil and turbulent overland flow (Havis et al., 1992).

Sorption-desorption processes in the soil generally take several minutes to hours to reach equilibrium (Felsot and Dahm, 1979; Pignatello, 2015). At the start of a rainfall event sorption equilibrium can be assumed. With the soil-water partition coefficient (k_d) a linear, instantaneous, equilibrium concentration between dissolved and sorbed pesticides in the soil matrix can be described. This is valid if the sorption process is fast compared to the uptake of pesticides from the mixing layer (Havis et al., 1992). Because simulations for rainfall-runoff events are generally not longer than several hours, degradation of pesticides can be neglected.

In addition to dissolved uptake by the runoff, sorbed pesticides can be entrained with eroding sediments. This can be either through splash detachment by raindrops (De Roo et al., 1996), or flow detachment based on the transport capacity of the runoff water (Govers et al., 1990). When deposition occurs, sorbed pesticides are added to the mixing layer together with the sediment. The concentration of sorbed pesticides in runoff sediment can be higher than the concentration in the original soil. This enrichment occurs due to preferred transport of smaller soil particles and organic matter, which also tend to have a higher sorptivity for pesticides (Ghadiri and Rose, 1993; H. Ghadiri and Rose, 1991). In a study comparing the enrichment rates for different soils and rainfall events, a decreasing exponential relation with the erosion rate was found (Menzel, 1980). When comparing organic matter contents between the fields and suspended sediment at the outlet in our observation dataset (Commelin et al., 2022a), the OM increases substantially indicating enrichment processes. For more details on observed enrichment see section 3.6.2.

When the pesticides are taken up by the runoff, either dissolved in water (dissolved phase, DP) or sorbed to entrained soil particles (particulate phase, PP), lateral flow will transport the pesticides further downstream. The OpenLISEM model routes water over the soil surface with a kinematic wave based on the local drain direction (Chow, 1988). In OpenLISEM diffusion is assumed to be neglectable for the lateral transport of suspended sediment, because overland transport is an advection-dominated process. We also apply this assumption to the lateral transport of particulate and dissolved pesticides.

Combining the soil-runoff interactions and lateral transport of pesticides, at each raster cell in time and space, four concentrations in respective control volumes are relevant for the transport of pesticides:

1. The dissolved concentration in the runoff *(C_{rw}, mg m^{-3})*
2. The dissolved concentration in the soil water in the mixing layer *(C_{mw}, mg m^{-3})*
3. The sorbed concentration in the soil matrix in the mixing layer *(C_{ms}, mg kg^{-1})*
4. The sorbed concentration in the suspended sediment in the runoff *(C_{rs}, mg kg^{-1})*

These concentrations are influenced by transfer between the runoff and the mixing layer and lateral transport. The water related pesticide fluxes are (1) infiltration through the mixing layer to deeper soil layers, (2) dissolved phase overland runoff and (3) uptake of pesticides by diffusion, convection and turbulent mixing from the mixing layer into the runoff (Joyce et al., 2008). For sediments, the pesticide fluxes include (4) enriched uptake through splash or flow detachment into the runoff, (5) deposition onto the soil surface with deposited sediment and (6) suspended sediment flow which transports the pesticides sorbed to sediment particles downstream. Finally (7) within the soil matrix equilibrium sorption redistributes pesticides between the dissolved and particulate phase. Contrary to the conceptualization of Havis et al. (1992) we do not include dissolved pesticide concentrations in the precipitation but assume that this is negligible.

This conceptual model can be described with equations for the governing processes. The flux of pesticides in runoff is described as:

$$\frac{1}{\Delta x} \cdot \frac{\partial Q_{rw}}{\partial x} \cdot \frac{\partial C_{rw} A}{\partial t} = k_{film} \cdot (C_{mw} - C_{rw}) - q_{inf} \cdot C_{rw} \qquad Eq\ 3.1$$

where Δx is the cell size (m), C_{rw} the dissolved concentration of pesticides in the runoff ($mg\ m^{-3}$), Q_{rw} the discharge of runoff ($m^3\ sec^{-1}$), A the cross-sectional area of the flow (m^2), x is distance in the direction of runoff (m), t is time (sec), k_{film} the transfer rate of the mixing layer ($m\ sec^{-1}$), C_{mw} the dissolved concentration of pesticides in the mixing layer ($mg\ m^{-3}$), q_{inf} the infiltration rate ($m\ sec^{-1}$).

The flux of dissolved pesticides in the mixing layer is calculated as:

$$n \cdot z_m \frac{\partial C_{mw}}{\partial t} = k_{film} \cdot (C_{mw} - C_{rw}) - q_{inf} \cdot (C_{mw} - C_{rw}) - z_m \cdot S \qquad Eq\ 3.2$$

where n is the soil porosity ($m^3\ m^{-3}$), z_m the depth of the mixing layer (m) and S is a sorption source or sink ($mg\ kg^{-1}\ sec^{-1}$) either based on equilibrium sorption (Havis et al, 1992) or kinetic sorption (Joyce 2008). The equilibrium sorption source or sink is calculated as:

$$S = \left(C_{mw} - \frac{C_{mw} \cdot n + C_{ms}(1-n)\rho_s}{n + k_d(1-n)\rho_s}\right) \cdot \frac{n}{\Delta t} \qquad Eq\ 3.3$$

with Δt the discrete timestep in the model, k_d the soil-water partitioning coefficient ($ml\ g^{-1}$), ρ_s is the soil particle density ($g\ cm^{-3}$) and, C_{ms} the sorbed concentration of pesticides in the mixing layer ($mg\ m^{-3}$). The flux of sorbed pesticides in the mixing layer is described with:

$$\frac{\partial C_{ms}}{\partial t} = S - \frac{\left(S_p \cdot C_{ms} \cdot \varepsilon\ +\ S_f \cdot C_{ms} \cdot \varepsilon + S_d \cdot C_{rs}\right)}{z_m \cdot \rho_b} \qquad Eq\ 3.4$$

where S_p is the splash detachment rate ($kg\ sec^{-1}\ m^{-2}$), S_f is the flow detachment rate ($kg\ sec^{-1}\ m^{-2}$), S_d the deposition rate ($kg\ sec^{-1}\ m^{-2}$), ρ_b the soil bulk density ($kg\ m^{-3}$) and ε the enrichment ratio of the sorbed pesticide in the runoff compared to the mixing layer, calculated with:

$$\varepsilon = \alpha \cdot S_j^{\beta} \qquad Eq\ 3.5$$

where α is a coefficient for which 7.4 is proposed as a general value by Menzel (1980), S_j the specific detachment rate of either splash or flow detachment ($kg\ sec^{-1}\ m^{-2}$) and β the exponent, which was found to be -0.2 for many soil and management types (Menzel 1980). Finally, the sorbed flux in suspended sediment is calculated as:

$$\frac{1}{\Delta x} \cdot \frac{\partial Q_{rs}}{\partial x} \cdot S_c \frac{\partial C_{rs} A}{\partial t} = S_p \cdot C_{ms} \cdot \varepsilon\ +\ S_f \cdot C_{ms} \cdot \varepsilon + S_d \cdot C_{rs} \qquad Eq\ 3.6$$

With Q_{rs} the discharge of suspended sediment ($kg\ sec^{-1}$), S_c the suspended sediment concentration in the runoff ($kg\ m^{-3}$).

3.2.2 Numerical solution and implementation in OpenLISEM

The numerical solution for overland flow with a 1D kinematic wave in OpenLISEM solves the Manning's equation with a semi-implicit Newton-Raphson method (Bout and Jetten, 2018; Chow, 1988; De Roo et al., 1996). The routing of substances in the runoff water, including pesticides, is calculated with an explicit solution of the momentum equation. To optimize mass conservation all pesticide fluxes are expressed as mass transfers from one control volume to the other. The different mass transfer processes are simulated separately in the following order (see Figure 3.1): losses of pesticides by infiltration, equilibrium partitioning between sorbed and dissolved pesticides in the mixing layer, uptake of dissolved pesticides from the mixing layer to the runoff, uptake of sorbed pesticides by splash erosion, mass transfer of sorbed pesticides by flow detachment or deposition and finally the discharge of dissolved and particulate phase pesticides with runoff. This order of processes is in accordance with the calculation of both water and sediment fluxes by OpenLISEM. The extended OpenLISEM model with pesticide dynamics is named OpenLISEM-pesticide (OLP). Further details on the numerical implementation and the exact equations used in OLP can be found in the supplementary materials (section 3.6.1).

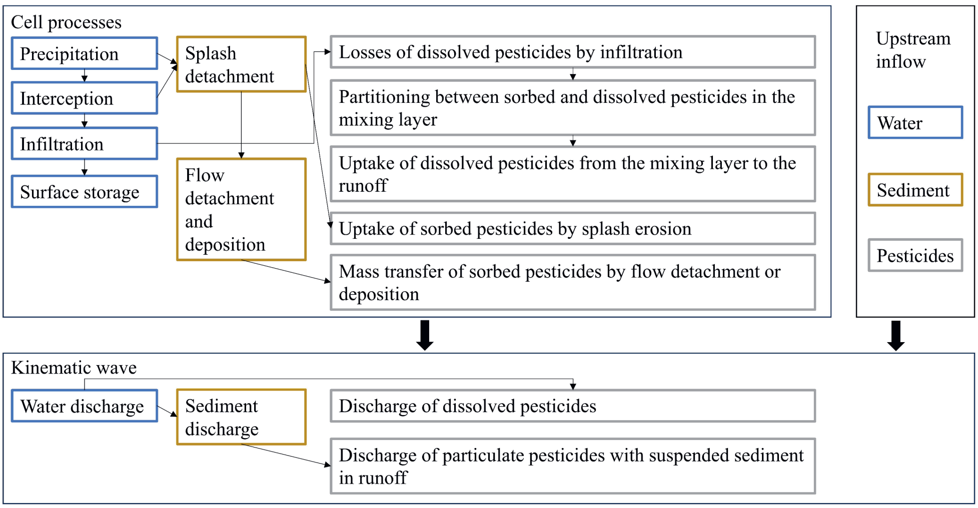

Figure 3.1 *Overview of the order of processes as calculated by OpenLISEM-pesticide (OLP).*

3.2.3 The OpenLISEM model

To simulate pesticide dynamics during a rainfall event in detail, the hydrological processes need to be simulated first, because the pesticide transport is a secondary process. OpenLISEM is a physically-based hydrological model, which is a further development and open source version of the original Limburg Soil Erosion Model (LISEM) (De Roo et al., 1996; De Roo and Jetten, 1999). Overland flow is calculated with Manning's equation. Infiltration is simulated with a multi-layered implementation of the Green & Ampt equation (Downer et al., 2003; Green and Ampt, 1911). For erosion both splash detachment by raindrops and flow detachment are included. The transport capacity for suspended sediment by runoff is calculated with the equations presented by Govers et al., (1990).

In the past decade upgrades have been added to the model, with most notable the addition of 2D dynamic wave solutions for overland flow and suspended sediment transport (Bout and Jetten, 2018). Originally, the model simulates overland flow by a 1D kinematic wave which uses a local drain direction (LDD) for flow routing. This latter option allows to define flow patterns not only based on topography, but also on tillage direction and landscape elements that are not captured in the DEM. This is of major importance for the correct simulation of overland flow patterns and identification of contributing areas within an agricultural catchment (Favis-Mortlock et al., 2022; Takken et al., 2001b). Therefore, in this study we used the 1D kinematic wave for flow routing.

3.2.4 The South-Limburg dataset

To test the performance of OLP we used two events (2019-05-28 and 2020-08-16) from an observational dataset collected in 2019 and 2020 (Commelin et al., 2022b). The study area is a small agricultural catchment (38.6 ha) in the hilly area of South-Limburg, the Netherlands (Figure 1.4). Arable agriculture with a crop rotation of potatoes and winter cereals was the main land use (27 ha). Other land uses were an apple orchard (5 ha) and extensively managed grasslands (5 ha). The remaining area consisted of roads, buildings and some forest. All agriculture was under conventional crop management including pesticide applications. The catchment has an elevation difference of 30 m (80 – 110 m.a.s.l.) and average slopes of 6% (range 0.1 – 30%). The soil type is a Luvisol with a silt loam texture. The catchment has a temperate climate (Cfb) with a mean annual precipitation of 757 mm and a mean annual temperature of 10.7 °C. A dry ditch connects the fields to the catchment outlet, and runoff only occurs for short periods after rainfall events. In the catchment, soil surface samples (0 – 10 mm depth) were taken in the agricultural fields (see Figure 1.4). At the outlet of the catchment runoff and sediment samples were collected automatically every 6 minutes during runoff events. Pesticide analysis for glyphosate was done following the procedure described by Bento et al., (2016) and metobromuron was analysed with the QuEChERS method (Anastassiades et al., 2003; Mol et al., 2008). The available samples for both events are presented in Table 3.2. Further details on the used dataset, data collection and analysis of pesticides are described in section 2.2.

Table 3.2 *Collected samples in the catchment and at the outlet for both events in this study.*

	Outlet		Catchment	
Event date	Suspended sediment samples	Pesticide samples	Total samples	Sampled fields
2019-05-28	12	8	7	A B C D E G
2020-08-16	12	5	6	A B C

The two events were selected because field samples were taken during or close to the occurrence of the rainfall events, and thus OLP could be initialized directly. Other events in this dataset will need additional long-term simulations to provide the concentrations in the mixing layer at the start of the rainfall event. During the two selected events the only compound detected in both dissolved phase (DP) and particulate phase (PP) transport was metobromuron; in addition, we also selected glyphosate for model evaluation, which was detected in PP. Glyphosate is often applied just before the start of the growing season in arable no-tillage management, to reduce weed pressure. In addition, in the apple orchard glyphosate was used to prevent vegetation growth under the trees. Metobromuron is also a pre-emergence herbicide used to control weeds and grasses. Both compounds were applied on the potato fields before emergence of the crop, and glyphosate was applied, at the start of the growing season, below the trees on the apple orchard.

3.2.5 Model initialization

OpenLISEM-pesticide is an event-based model that needs to be initialized with the conditions for water, sediment and pesticide dynamics at the start of the simulated rainfall-runoff event. The required data can be obtained by field measurements, the use of available datasets (e.g., topography, aerial imagery or satellite data) as well as by the use of models designed for larger temporal scales. The uncertainty in occurrence time of rainstorm events will make it difficult to obtain accurate field measurements of pesticide concentrations before an event.

Input data and initialization of the pesticide module

At the start of a rainfall event, the dissolved and sorbed concentrations of the simulated substance in the mixing layer in combination with the partition coefficient (k_d) are input for OLP. The initial concentrations of pesticides in the soil can be obtained either by observations through soil samples or from another model. In our two year dataset, we obtained field observation samples for two events, which we use in this study. The partitioning of a pesticide is uncertain for specific pedoclimatic conditions (Kumari and John, 2020; Sadegh-Zadeh, 2017), however best estimates are available from literature, where possible adjusted for soil type.

When soil partitioning was not provided, we estimated this from the organic carbon partitioning (k_{oc}) with:

$$k_d = k_{oc} \cdot \frac{OM}{2.0} \qquad Eq\ 3.7$$

With OM the organic matter fraction which we divide by 2.0 to convert to organic carbon. A conversion factor of 2.0 is shown to be generally more accurate that the conventional 1.724 conversion factor (Pribyl, 2010). For glyphosate the k_d is 48 mL g^{-1} for a silt loam (European Food Safety Authority (EFSA), 2015). In case of metobromuron a k_{oc} of 197 mL g^{-1} is given (Lewis et al., 2016). Using equation 7 with an organic matter content of 3.6% in the fields in our study area the k_d of metobromuron is 3.5 mL g^{-1}. The depth (z_m) and the mass transfer rate (k_{film}) of the mixing layer are also needed. Reported mass transfer rates in previous studies are in the range of 0.001 – 0.1 mm sec^{-1}, combined with mixing layer depths of 0.1 to 25 mm (Havis et al., 1992; Joyce et al., 2010; Watanabe and Grismer, 2003). In this study we used a fixed mixing layer depth of 6 mm as a best estimate in accordance with the mean mixing layer depths found for arable field plots by Havis et al., (1992). The mass transfer rate was used for calibration, an initial value of 0.007 mm sec^{-1} was used. A test over a large range of mass transfer rate values (1 10^{-6} to 100 mm sec^{-1}) showed that from 1 mm sec^{-1} upwards, equilibrium between the mixing layer and the runoff is simulated (see for more details supplementary materials section 3.6.2, Table 3.10).

Initialization of OpenLISEM

The OpenLISEM model requires input data on topography, land use and related crop cover, and soil characteristics for infiltration and erosion. All this data was obtained from available public data sets (AHN4 0.5 m DTM, Top10NL topography, open satellite images) and field measurements and observations (crop cover and crop height, infiltration speed, and images of spatial distribution of runoff and erosion patterns after rainfall events). To obtain realistic initialization for each event, and to differentiate between events throughout a growing season, the temporal constraint strategy as proposed by Lefrancq et al. (2017) was applied. This relates infiltration and erosion parameters to temporal variation throughout the season. The crop and soil characteristics were specified either homogeneously for the whole catchment, or specifically for each crop type within the catchment (homogeneous per field), the only exception for this was the addition of wheel track patterns in potato cultivation. Other studies relate wheel tracks with increased runoff (Prasuhn, 2020) and higher herbicide transport (Baker and Laflen, 1979). We therefore selected wheel tracks in the potato field based on aerial images and modelled these with a width of 50 cm. The crop cover, hydraulic conductivity, porosity, Manning’s n, random roughness and soil cohesion in the wheel tracks differ compared to the potato field due to the higher compaction of the soil caused by machines driving on the tracks regularly. On other fields no wheel track patterns were observed.

When simulating runoff and erosion during rainfall-runoff events, the correct representation of topography and stream patterns within a catchment is fundamental for meaningful model simulations (Favis-Mortlock et al., 2022). One important aspect in this case was the influence of tillage operations on streamflow (Couturier et al., 2013; Souchère et al., 1998; Takken et al., 2001b). Since our observational dataset includes fields with potato cultivation, a model was required that could incorporate tillage direction into flow patterns in the field, since these are not captured by the digital elevation model. The cultivation of potatoes was done on ridges of about 25 cm high. We applied the Tillage Controlled Runoff Pattern (TCRP) model (Takken et al., 2001a) to recalculate flow patterns for each growing season within the catchment. The spatial resolution used in the model simulations was two meter (2 m) and the timestep five (5) seconds. Details on all specific parameters, and the method of estimation is given in section 3.6.2, Table 3.8.

After initial initialization, adjustments were made to improve simulation within the catchment. Small discretization errors or mismatches between different map layers can have large impacts on simulation results at the outlet. Two examples of improvements are (1) the adjustment of the tarmac road cells, to coincide with the predicted streamline of the LDD. Observations showed clearly that water flowed over the road and not one meter besides it through the grassland. This changed the simulated timing of the peak at the outlet due to faster flow over roads. In addition (2), LDD flow perpendicular to the tillage direction through a thalweg or valley bottom should include the water buffering effect of the tilled ridges. OpenLISEM uses the random roughness to calculate the depression storage before overland flow occurs, for a cell in the thalweg the RR was increased with half the height of the tillage structures. On potato fields this resulted in buffering of runoff which would otherwise have been simulated, but which was not observed during the events and field inspections.

3.2.6 Model calibration and evaluation

To evaluate the performance of the model we did a qualitative assessment of the simulated spatial patterns of runoff and erosion based on observations in the catchment during the event and we calculated goodness-of-fit parameters for runoff, suspended sediment and transported pesticides at the outlet. We visited the study area during or shortly after the rainfall events to collect samples from the fields and the outlet. During these visits we observed the flow patterns on the different fields. The quantitative evaluation of the hydro- and sedigraph at the outlet was done by calculating the root mean square error (RMSE), the Nash-Sutcliff (NSE) (Nash and Sutcliffe, 1970) and Kling-Gupta (KGE) (Gupta et al., 2009) efficiency coefficients. Many studies have shown that using a single goodness-of-fit (GOF) parameter can lead to incorrect evaluation of model adequacy

(Clark et al., 2021; Knoben et al., 2019; Seibert et al., 2018). As benchmark we compared the RMSE with the uncertainty of the observations as calculated in section 2.5.3.

3.2.7 Sensitivity analysis

To explore the sensitivity of the model predictions to variations in input a one at a time (OAT) sensitivity analysis was done. By varying a specific parameter around a calibrated baseline more understanding of the model dynamics and interactions can be obtained (Joyce et al., 2008; Lefrancq et al., 2017b). The influence was evaluated based on the change in the total simulated transport for DP and PP. Besides pesticide related parameters, we also included runoff and erosion related parameters that are identified as sensitive in earlier studies for OpenLISEM (Lefrancq et al., 2017b; Wu et al., 2021). These consist of the saturated hydraulic conductivity, the capillary pressure at the wetting front, Mannings' n, soil cohesion and precipitation. Varying these parameters will show the relationship between model performance for runoff and erosion and pesticide simulations. All parameter values were varied these ±20% around the calibrated value. The sensitivity analysis was applied on the event of 2019-05-28 for metobromuron, since in this case transport in both DP and PP was observed.

3.2.8 Software used for data analysis and model development.

The OpenLISEM-pesticide model was written in C++ and compiled using QT and CMake. It is available under both Windows and Linux operating systems. The field scale simulations in this study have a runtime of 4 – 8 minutes on an Intel i7 3632QM CPU, depending on the selected model options. The main data analysis and workflow was done with R (R Core Team, 2023). All codes to perform the analysis and model runs for this study, including a windows executable of OpenLISEM-pesticide v.1 can be found on the code repository:
https://doi.org/10.4121/1838022f-05ee-4243-b599-097a777cde1c and
https://github.com/mcommelin/openlisem_pesticide_model_development. Input maps for OpenLISEM were produced in PCRaster 4.4.0 (Karssenberg et al., 2010) which we integrated with R. Spatial analysis and manipulation of maps was done using QGIS 3.28 (QGIS.org, 2023). For this study we used OpenLISEM version 6.91 with pesticide extension version 1.0. The code is available at github.com (https://github.com/vjetten/openlisem/tree/lisem_pest).

3.3 Results

3.3.1 Simulations of runoff and erosion

The model performance after manual calibration is shown in Table 3.3. At initialization the predicted amount of runoff was far below the observations, and too much infiltration was simulated. The main adjustments in both events were done for the saturated hydraulic conductivity (k_{sat}) and the wetted front capillary pressure (Ψ), these two parameters are of main importance in the Green & Ampt infiltration model (Downer et al., 2003). Further small adjustments were done for Manning's n and the initial soil moisture to improve runoff and erosion predictions, for initial and calibrated settings see Table 3.9 in the supplementary materials (Ch 3.6.2). After calibration, the second event (2020-08-16) had a lower performance for simulated runoff compared to the first event (2019-05-28). The falling limb of the hydrograph was too steep and simulated runoff decreased much faster than observed.

Table 3.3 *Performance statistics of OpenLISEM after the calibration procedure*

Rainfall event	Runoff				Erosion			
	NSE	KGE	RMSE (L sec^{-1})	Obs. Error[1] (L sec^{-1})	NSE	KGE	RMSE (kg sec^{-1})	Obs. Error (kg sec^{-1})
28-05-2019	0.93	0.75	21	2.3	0.98	0.81	1.0	0.23
16-08-2020	0.56	0.58	186	11.1	0.97	0.95	3.2	0.79

[1] Based on calculations from Commelin et. al. (2022); the mean observation error over all sample points during the event.

Figure 3.2 shows the observed and simulated discharge and suspended sediment loads for both events. The runoff and erosion for the first event are simulated adequately. The two consecutive rainfall peaks also result in two runoff peaks, where the second was substantially higher due to decreased infiltration rates. For the second event, less detailed rainfall data was available. OpenLISEM simulates a first main peak, which originates from the potato cultivation (field A in Figure 1.4), because of the high rainfall intensity also runoff occurs on other fields in the catchment. These fields have a higher soil cover, grass or cereal stubbles, which increases the flow resistance, leading to a later arrival of the water at the outlet. This is visible in both the simulated and the observed hydrograph.

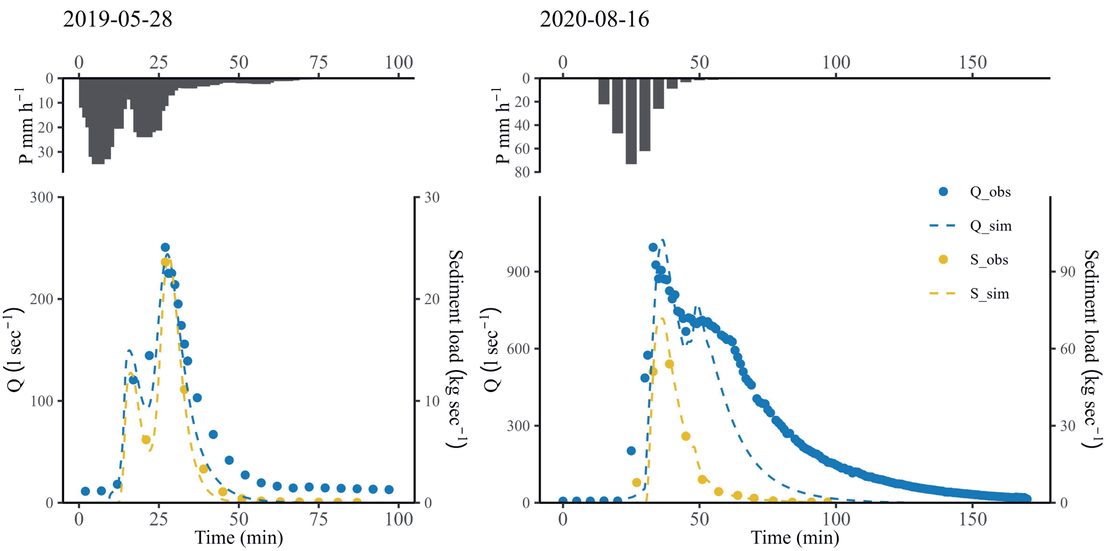

Figure 3.2 *Observed and simulated runoff and sediment transport for both events, after manual calibration of OpenLISEM.*

3.3.2 Pattern comparison of observed and simulated runoff and erosion in the catchment

The crops grown during each event varied per field due to crop rotations, with as main difference a switch from potatoes on field B and winter wheat on field A in 2019 and vice versa in 2020 (see Figure 1.4). Field observations showed that during both events the potato cultivation was the main source of runoff and erosion. During the event on 28 May 2019 we were in the catchment and could observe the runoff and erosion patterns. The cereal fields did not generate any runoff, which was also shown by the dry channel upstream from the potato field (A, C in Figure 3.3). On the field with potato cultivation runoff occurred and flow was directly connected to the channel discharge (B, D in Figure 3.3). The wheel tracks and potato ridges influence the flow direction, and mainly at the bottom of the slope where the flow was concentrated also erosion signs were visible (E, F in Figure 3.3). More uphill a section was visible where water and sediment stagnated, and sedimentation filled the whole height of the potato ridges (Figure 3.3-F). The soil loss map of this OpenLISEM simulation coincides with the field observations in showing the main wheel tracks from upslope downwards as main source of erosion, and there is a section with simulated increased deposition (dark green close to Figure 3.3-F).

For the event on 16 August 2020 the same patterns are visible. The discharge peak (~1000 l sec^{-1}) was much higher than the maximum capacity of the installed flume (650 l sec^{-1}) which correspond with the overflow signs at the outlet (Figure 3.4-A).

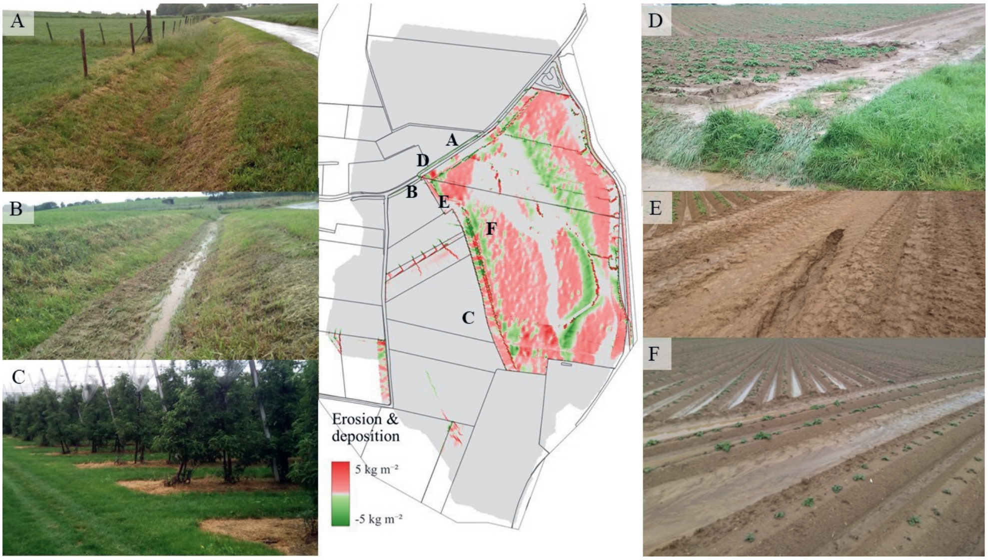

Figure 3.3 *Simulated erosion patterns compared with field observations on 28 May 2019. A: No flow visible in upper section of the channel. B: Water flow in the channel downstream of the potato field (B in Fig 1.4). C: No runoff signs in the apple orchard (C in Fig. 1.4). D: Runoff and erosion from the potato field. E: Erosion signs (small rills) on the wheel tracks in the potato field. F: The wheel tracks facilitate runoff.*

Again, the main runoff was observed from the potato field (Figure 3.4-D), however a second peak was visible at the outlet, and the model simulated this peak as coming from the arable fields in the south of the catchment. This water flowed through the apple orchard, which corresponds to observations where we found apples at the outlet after this event. Based on observations the main peak of water from the potato field flowed in two pathways to the outlet, firstly through the channel, but a large part of the water had crossed the road and flowed through the cereals field back to the road (Figure 3.4-C). Although the model performs well, also some patterns do not correspond with the observations. When inspecting the catchment, we did not observe any runoff or erosion signs on the cereals fields (Figure 3.4-E), however runoff as well as erosion were simulated here by OpenLISEM. Moreover, close to the outlet the channel crosses a road section, and a lot of sedimentation was observed at this location, however no sedimentation was simulated here.

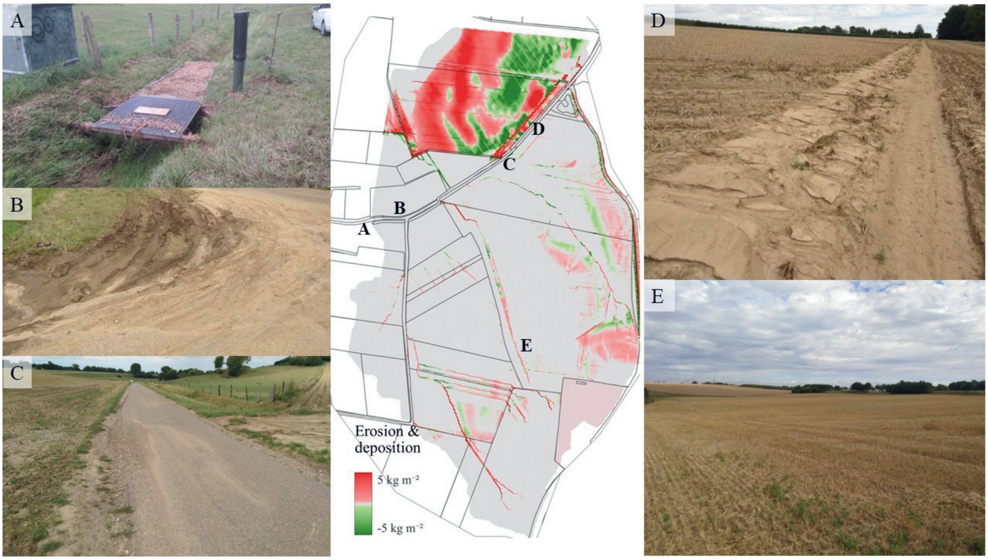

Figure 3.4 *Simulated erosion patterns compared with field observation for the event on 8 August 2020. A: The flume at the outlet is overflown indicating high discharge rates. B: Sedimentation layer of several centimetres thick at road crossing. C: The main flow from the potato field (A in Fig. 1.4), crosses the road. D: Signs of runoff and erosion on the wheel tracks in the potato field. E: No observed runoff on the cereals field (B in Fig. 1.4).*

3.3.3 Simulated load and spatial distribution of pesticides

The patterns of runoff and erosion within the catchment define the potential source areas for pesticide transport. In addition, the land use and management, including pesticide applications, will affect the availability of pesticides for transport. The model performance after manual calibrating OLP is shown in Table 3.4. Overall the simulations perform well, except for the PP transport of metobromuron on 2019-05-28, where the simulated concentrations are much higher than observed (see also Figure 3.4-A). For this event the DP simulation of metobromuron has a good total load simulation but does not perform well in simulating the high concentration peak at the start of the event. The PP transport of glyphosate simulated on 2020-08-16 has a low performance, partly because there is a delayed start of transport which also is visible in the suspended sediment simulations. Besides that, high concentrations were simulated from the apple orchard in the second phase of the runoff event, which are not measured in the observations.

The initial and calibrated values of specific parameters are presented in Table 3.5, the initial concentrations for each field are presented in the supplementary materials section 3.6.2, Table 3.10. We used two parameters for calibration, the mass transfer rate for DP transport and the exponent (β) in the enrichment ratio equation (Eq. 5) for PP transport. The initial value of 0.007 mm sec^{-1} used for k_{film} had to be decreased about a factor ten (0.0008 mm sec^{-1}) to improve the prediction of dissolved transport. For PP transport the β was adjusted for each event ranging from -0.11 to -0.5, which corresponds to the range reported by Menzel (1980).

Table 3.4 *Performance statistics of predicted load by OpenLISEM-pesticide compared to observations.*

	Rainfall event	Runoff				Erosion			
		NSE	KGE	RMSE [2]	Obs. Error	NSE	KGE	RMSE	Obs. Error
Meto-bromuron	28-05-2019	0.27	0.63	2.13	0.48	-1.82	-0.72	4.2	0.39
	16-08-2020	-[1]	-	-	-	0.15	0.40	3.4	0.92
Glyphosate	28-05-2019	-	-	-	-	0.90	0.70	1.0	0.45
	16-08-2020	-	-	-	-	-0.63	0.26	8.9	2.63

[1] No transport observed in dissolved phase, however concentrations below limit of quantification can occur. [2] The units of RMSE and the Observation Error are: mg sec^{-1}.

In Figure 3.5 the transported load and concentrations are presented for metobromuron and glyphosate during both events. The load predictions in PP for metobromuron for the event on 2019-05-28 are too high, which also is reflected by the simulated concentration. The observed concentrations in the fields for metobromuron during this event were higher than the concentrations in the runoff. During the event of 2020-06-16 the model also predicts DP transport for metobromuron. We did not detect metobromuron in our observations, however the limit of quantification of the analysis was higher than the predicted discharge (see Figure 3.4-C). The performance of the glyphosate simulations was lower for the event of 2020-08-16. In this event OLP did show a peak at the start of the runoff, but too low and not at the right time. Besides that, an increase in concentration occurs in the second half of the runoff event, which correspond to runoff from the apple orchard.

Besides loads and concentrations at the outlet, OLP also produces maps with the redistribution of the pesticides in the catchment during the event. The redistribution can show source and accumulation areas of pesticides and can for example be used to simulate the effects of best management practises (BMP's) for specific fields. Figure 3.6 shows the final concentration and mass change for glyphosate during the event of 2019-05-28. Glyphosate was detected in three fields (B, C and D, Figure 1.4), where the concentration in the apple orchard is about 10 times higher than in the two arable fields (Figure 3.6-A).

Table 3.5 *Initial and calibrated values of parameters in OLP.*

Fixed parameters	Compound	Initial		
k_d	Glyphosate	48		
	Metobromuron	3.5		
z_m		0.006		
α		7.4		
z_s		0.05		
Calibrated parameters			2019-05-28	2020-08-16
k_{film}		0.007	0.0008	0.0008
β	Glyphosate	-0.2	-0.28	-0.11
	Metobromuron	-0.2	-0.5	-0.12

The mass of PP transport follows the patterns of erosion: where slopes in the fields increase glyphosate is entrained in the runoff and where the flow velocity decreases due to reduction in slope or due to change in land use from arable land to grass land, deposition occurs and the glyphosate is deposited (Figure 3.6-B). This pattern is also reflected in the final concentration in field B. Dissolved uptake and transport of glyphosate depends on the availability of runoff water, and where infiltration is dominant the dissolved glyphosate can return to the soil matrix (Figure 3.6-C). In the valley section in field B a lot of ponding is simulated between the potato ridges, this results in increased uptake of glyphosate into the runoff water. The channel bottom and grassed field where runoff occurs, function as infiltration site. Here up to 0.05 $mg\ m^{-2}$ is added to the soil matrix.

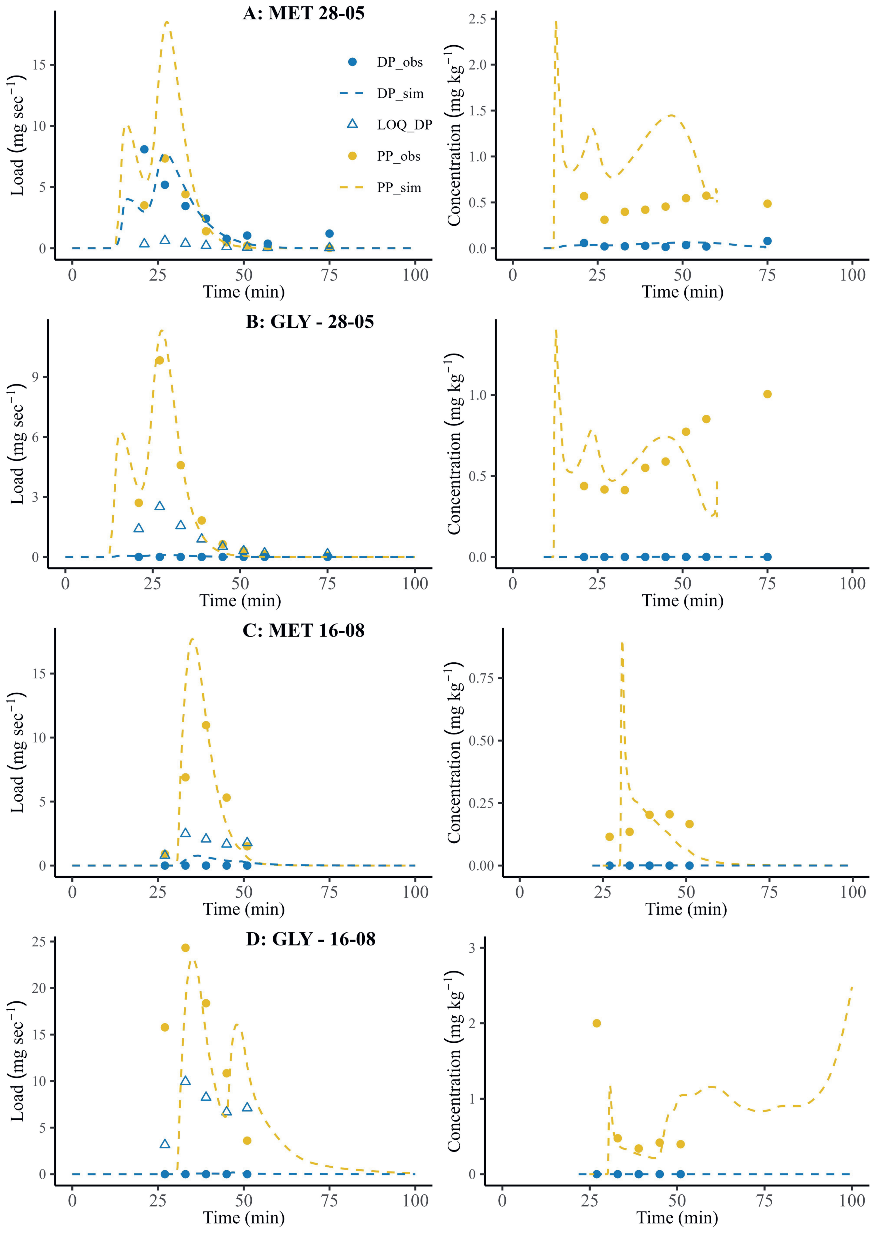

Figure 3.5 *Observed and simulated discharge in DP and PP of pesticides. MET = Metobromuron, GLY = Glyphosate. DP_obs = dissolved phase pesticides observed, DP_sim = dissolved phase pesticides simulated, LOQ_DP = limit of quantification dissolved phase load, PP_obs = particulate phase pesticides observed and PP_sim = particulate phase pesticides simulated.*

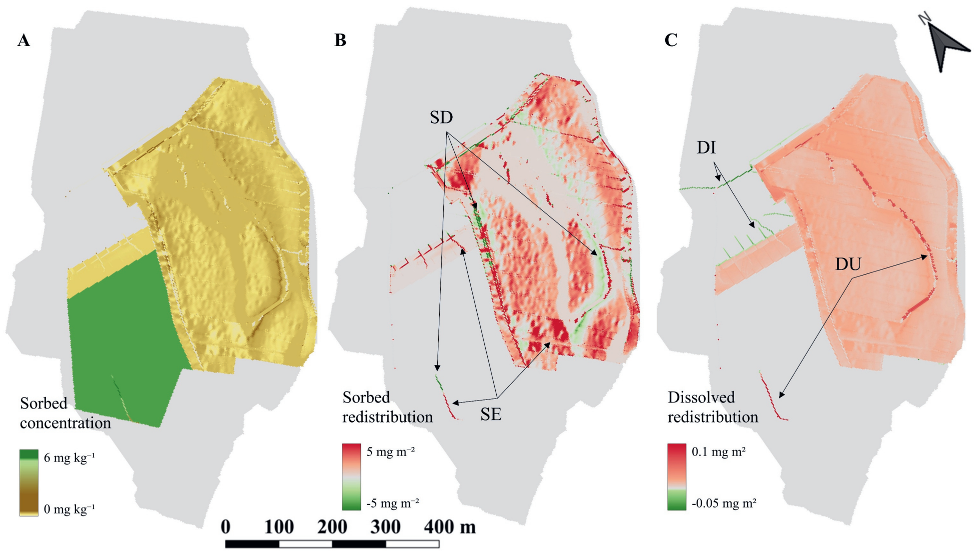

Figure 3.6 *Final soil concentration (A), and simulated redistribution of sorbed (B) and dissolved (C) glyphosate during the event on 2019-05-28. SD = sorbed deposition, SE = sorbed entrainment areas, DU = dissolved uptake, DI = infiltration of dissolved glyphosate.*

3.3.4 Sensitivity analysis results

Table 3.6 shows the results of the 'one-at-a-time' (OAT) sensitivity analysis in which we explored the behaviour of the pesticide module on transport of DP and PP pesticides. The mass transfer rate and the soil water partitioning both have a strong effect on the total load of dissolved pesticides, a 20% change in these parameters also results in about 20% change in transported mass. The mixing layer depth has less influence with a three to four percent change in discharge. Particulate phase transport is mainly influenced by the parameters in the equation for the enrichment ratio. A 20% change in the exponent results in more than 20% change in particulate phase discharge. The soil-water partitioning and mixing layer depth also influence the PP transport but only to a small extent. In several cases a change in one of the input parameters increased the KGE for PP transport, for example a higher exponent (β) for the enrichment ratio.

Table 3.6 *Variation of pesticide transport due to variation in input parameters*

Parameter	Value	Relative (%) DP total load	Relative (%) PP total load	KGE DP	KGE PP
Base run	base	100	100	0.62	0.23
Exponent enrichment (β)	20%	101	74	0.62	0.46
Base = -0.5	-20%	99	136	0.61	0.06
Coefficient enrichment (α)	20%	100	118	0.61	0.13
Base = 7.4	-20%	100	81	0.62	0.38
Initial concentration field	-20%	80	80	0.38	0.39
(mg kg^{-1})	20%	120	120	0.61	0.13
Mass transfer mixing layer to	-20%	83	100	0.43	0.23
runoff (k_{film}), (mm sec^{-1}) Base = 0.0008	20%	116	100	0.62	0.23
Soil-water partitioning (k_d),	-20%	122	98	0.6	0.25
(g ml^{-1}) Base = 3.5	20%	85	102	0.47	0.22
Mixing layer depth (z_m), (mm)	-20%	96	96	0.6	0.26
Base = 6.0	20%	103	103	0.62	0.21
Saturated hydraulic conductivity,	-20%	132	139	0.65	0.09
ksat (mm h^{-1})	20%	72	67	0.32	0.46
Precipitation (mm h^{-1})	-20%	38	23	-1.5	-0.21
	20%	144	190	0.63	-0.02
Soil cohesion (kPa)	-20%	100	94	0.61	0.28
	20%	100	104	0.62	0.2
Surface resistance to flow,	-20%	101	121	0.6	0.14
Mannings n (-)	20%	99	84	0.62	0.33
Wetting front capillary pressure,	-20%	122	129	0.68	0.12
Ψ (cm)	20%	80	76	0.44	0.38

Note: The mass balance error for water, sediment and pesticides in all above model runs is < 1 10^{-10} %. The total simulated loads of DP and PP in the base run were 7792 and 14740 mg respectively.

Besides the specific parameters included in the new pesticide module, we also varied several parameters related to runoff and erosion processes. For this we observe that infiltration and precipitation had a major influence and variations of ±20% resulted in very large changes in pesticide transport. For example, 20% more precipitation produced 190% PP transport and, vice versa, 20% less rainfall resulted in only 23% of transport in PP. We also varied the soil cohesion as the main parameter influencing erosion. As expected, this did not influence the transport of dissolved pesticides and only had a minor influence on PP transport. In general, the changes of runoff related parameters in the setup of OpenLISEM had a larger impact on the PP transport than on DP transport. In both cases the variations due to uncertainty in these parameters were larger than for the specific pesticide parameters.

3.4 Discussion

During rainfall-runoff events large amounts of pesticides can be transported either dissolved in water or sorbed to suspended sediment (Commelin et al., 2022a; Halbach et al., 2021). Potentially, physically-based models which are spatially fully distributed can increase our understanding of the transport process, the source areas and redistribution of pesticides in fields or in catchments (Payraudeau and Gregoire, 2012). With OLP we extended the OpenLISEM model to simulate the event-based dynamics of pesticides, which creates future options to further explore transport during rainfall-runoff events and test different best management practises (BMP's) for possible mitigation. OLP is a more complex model than many conventionally used pesticide models. These other models often aim for longer term load predictions, however event-specific simulations need a different approach to simulate the relevant processes on this time scale. The advantages and drawbacks of OLP are discussed in the following section, followed by a discussion of the accuracy of the runoff and erosion simulations underlining OLP. Finally we discuss of the main sensitive parameters and further perspectives for OLP use is given.

3.4.1 Advantages and drawbacks of OLP

Conceptualization in OLP

OLP is an implementation of the conceptual model initially developed by Havis et al (1992). This model was further developed and tested to include crop wash off and kinetic sorption (Joyce et al., 2008; Watanabe and Grismer, 2003), these studies showed that the model could reliably simulate dissolved pesticide transport with overland flow on plot scale. In OLP we added particulate phase transport, including enrichment of sorbed pesticides when transported with detached sediment, and applied this model on small catchment scale (38 ha). The enrichment was based on experimental relations reported by Menzel (1980), which is also included in the GLEAMS model (DeMars et al., 2018; Leonard et al., 1987). Conceptually the OLP module is suitable for transport simulations of all types of pesticides, including herbicides, fungicides and insecticides. If pesticides, like fungicides or insecticides, are applied on the crop shortly before a rainfall-runoff event, crop wash-off might contribute substantially to pesticide transport (Joyce et al., 2008; Morselli et al., 2018). Crop cover wash off was not included in OLP since the two events in this study had a low crop cover (< 20%) on the pesticide source fields. Other more complex process descriptions were currently not included in OLP. For example, the estimation of mixing layer depth dependent on rainfall intensity (Havis et al., 1992) or relating the mass transfer rate to flow speed and turbulence (Wallach et al., 1988).

OLP calibration and performance

To calibrate the pesticide simulations in OLP we used two parameters: the mass transfer rate (k_{film}) for the dissolved transport, and the exponent in the enrichment ratio (β) for particulate transport. The β we had to adjust to a different value for each event and pesticide to improve the simulations. Specific calibration for each event is a well-known issue for event-based models (Baartman et al., 2012; Vieira et al., 2022), and further simulations on a larger dataset including multi-event calibration and temporal constraining are needed to further understand the temporal variations of the simulated processes (Lefrancq et al., 2017b). However, even with an event specific simulation, the simulation provides insight in the dynamics in the catchment and a calibrated simulation can be used to test the effect of BMPs (Kabeja et al., 2021).

After calibration the main transport peaks and source areas of pesticides within the catchment were well simulated for the events and compounds in this study. However, hydrologic connection of different source areas with high concentrations at the start or end of the runoff event were not well captured. For example, the contribution of glyphosate transport from the apple orchard was not clarified by OLP simulations. The observations suggest transport from this field but in the OpenLISEM simulation no runoff and thus no pesticide transport was simulated. Another unexplained process entails the metobromuron transport during the event on 2019-05-28. Were in the other simulations the field concentrations was lower than the PP concentration at the outlet, in this simulation the concentration observed in the field was higher than in the runoff. Based on the concept of enrichment an increase would be expected (Ghadiri and Rose, 1993). In the calibration the β was increased to the lowest value reported by Menzel (1980) to improve the simulation.

OLP compared with other pesticide models

When comparing OLP to other available overland transport pesticide models, each model has its specific focus resulting in strengths and limitations (see also Table 3.1). The temporal scales on which the models are applied varies from multiple years to several days (e.g. SWAT, PRZM, RZWQM, ZinAgriTRA and DYNAPLUS) (Cambien et al., 2020; DeMars et al., 2018; Gassmann et al., 2015; Morselli et al., 2018; Young and Fry, 2014), to event-specific simulations (e.g. PESHMELBA and VFSMOD) (Reichenberger et al., 2023; Rouzies et al., 2019). The spatial representation of the catchment differs between hydrological units (SWAT, PESHMELBA, VFSMOD, PRZM and RZWQM) or fully distributed (ZinAgritra). However, none of these models simulate pesticide transport with the conceptual model by Havis et al (1992), which aims to describe the transport process on small time scales relevant for the dynamics in headwater catchments during runoff events.

The GSSHA model has promising properties to also simulate pesticide transport dynamic during erosive rainfall-runoff events, as identified in Table 3.1. We did not find an application of GSSHA for pesticide transport, but a study simulating nitrate discharge shows the potential of GSSHA (Pradhan et al., 2014). There are several differences in the process descriptions for infiltration, erosion processes and pesticide uptake and transport between OLP and GSSHA. For example the erosion is calculated with different a equation (OLP – Govers 1990, GSSHA – Kilinc & Richardson 1973) and GSSHA takes particles size distribution of the suspended sediment into account. A future comparison of both models might give more understanding of the implications of these differences.

Previous modelling studies investigating particulate phase transport of pesticides, identify low performance, and lack of spatial distribution of erosion predictions as limiting factors (Chen et al., 2017; DeMars et al., 2018). The mechanistic soil erosion simulations by OpenLISEM include specific source areas and redistribution within the catchment. In this study the performance of sediment load predictions was good (KGE > 0.85), which forms a basis for adequate PP pesticide transport simulations. By combining mechanistic erosion simulations and enrichment of sorbed pesticides compared to the concentration in the soil, the PP transport could be simulated. Other modelling studies on pesticide transport have identified this as a relevant addition (Cambien et al., 2020; Morselli et al., 2018; Rouzies et al., 2019). The fully distributed characteristics of OLP make it suitable to simulate effects of best management practises on field and catchment scale, a need that is identified in previous review articles (Centanni et al., 2023; Payraudeau and Gregoire, 2012).

OLP applicability

Modelling runoff, sediment, and pesticide dynamic processes with OLP is complex and reliable results need observation data for initialization and calibration as was also observed for other models (Gassmann et al., 2015; Morselli et al., 2018; Purnell et al., 2020; Rouzies et al., 2019). Several models on pesticide transport (e.g. VFSMOD and SWAT) have as one of the design goals, to be applicable by non-modellers (Carluer et al., 2017; Purnell et al., 2020). With OLP, this is less the case, and the demands for input data, system knowledge and model setup are high. Therefore, the current version of OLP has limited use for policy makers and stakeholders but is suitable for improved understanding and application on specific case studies. In this first study we used field observations to initialize OLP, however these might often not be available. Many models exist that are suitable to simulate pesticide fate over a growing season, for example FOCUSPEARL, PRZM or SWAT. OpenLISEM-pesticide can be coupled with one of these, and soil concentrations at the start of the rainfall event can be obtained from this model.

3.4.2 Accuracy of runoff and erosion simulations

Since the quality and accuracy of simulated pesticide transport depends on the correct prediction of water and sediment dynamics in a catchment (Reichenberger et al., 2023), adequate performance of OpenLISEM in terms of runoff and erosion predictions is a prerequisite for further pesticide simulations with OLP. However, when simulating dynamic spatio-temporal processes with complex models, two major risks are equifinality and modelling 'right-results-for-wrong-reasons' (Beven and Lane, 2022; Kelleher et al., 2017). Additional qualitative evaluation of the results can reduce these risks (Batista et al., 2019; Knoben et al., 2019; Schürz and Schulz, 2022). We limited these risks by combining detailed understanding of the catchment, adjustments for tillage directions (Takken et al., 2001a) and landscape elements influencing flow patterns (Favis-Mortlock et al., 2022; Sidle et al., 2017), with temporal variations throughout the growing season for the most influential parameters (Lefrancq et al., 2017b). The predictions of OpenLISEM were adequate for both runoff and erosion. This was not only tested in terms of discharge at the outlet, but also verified with spatial observations within the catchment (section 3.3.3).

Several specific processes, which might influence the quantity, as well as the source area of runoff and sediment remain hard to capture in the initialization of the model. Two examples are the connection or disconnection of potato ridges to the wheel tracks, which trapped water and sediment before flowing onto the wheel tracks, or the sub-resolution effects of tree lines in the apple orchard. Other processes that could not be simulated well within the current possibilities of the OpenLISEM model include for example, divergence of flow directions based on the amount of discharge. In our simulations all water flows through the main channel, while observations show that also some water flowed over the road along the channel. This could have been simulated by using 2D dynamic-wave flow routing, but this has as disadvantage that sub-resolution patterns like potato ridges cannot be included in the flow pattern. We decided that potato ridges were in this case more important for correct simulations.

3.4.3 Sensitive parameters and perspectives

The results of the sensitivity analysis in this study correspond to a large extent to the results presented by Joyce et al. (2008). The mass transfer rate influences the uptake of dissolved pesticides, although uptake also depends on the availability of water on the soil surface. The spatial distribution of pesticide uptake as shown in Figure 3.6-C shows that extended ponding will increase the amount of pesticides entering runoff water. The main processes influencing the transport of dissolved pesticides from agricultural fields are the uptake from the mixing layer and the infiltration rate. If high infiltration rates occur, either in the field, or in a vegetated buffer zone, the dissolved pesticides in runoff can re-enter the soil matrix. For PP pesticide transport the enrichment ratio parameters showed the most influence on simulated transport. Moreover, there is a very strong relation between soil detachment and pesticide transport: if the erosion rates in the field are reduced the transported load of PP pesticide will also decrease.

In this study we did not include a thorough evaluation of the model. However, multi-event and multiple compound calibration, evaluation and sensitivity analyses, including parameter correlations, might improve the robustness of the model, and our understanding of the scope and quantification of the pesticide-related parameters under field conditions. This was done in chapter 4 for this thesis.

3.5 Conclusions

In this study we present a novel model extension, OpenLISEM-pesticide (OLP), that is designed to simulate overland transport of pesticides in both dissolved and particulate phase, during rainfall-runoff events. In conclusion:

- We combined particulate pesticide transport, including enrichment, with the pesticide transport model by Havis et al. (1992) and integrated this with OpenLISEM.
- The simulations for two compounds and two events, which are in line with field observations, are a proof-of-concept that OLP can give more insight in transport dynamics, source areas and redistribution of pesticides during erosive rainfall-runoff events.
- The sensitivity analysis showed that for dissolved phase transport the mass transfer rate of the mixing layer was of main importance. Particulate phase transport is most sensitive to the parameters in the enrichment ratio equation. Besides that, the performance and accuracy of the pesticide transport predictions, depend strongly on the accuracy of runoff and erosion simulations.

This extension of OpenLISEM can be applied to further investigate and understand the contribution of rapid runoff and related erosion to the transport of pesticides into the environment. OLP has the potential to help mitigate environmental pollution by simulating redistribution within the field or catchment, as well as identifying main source areas, which can be used to target BMPs. Further research is needed to test the robustness of the model for different pesticides, agronomical systems and pedo-climatic zones.

3.6 Supplementary Materials

3.6.1 Numerical implementation of OpenLISEM-pesticide

Numerical implementation of equations

The four differential equations governing the transport of pesticides by overland runoff are implemented in OpenLISEM-pesticide using an explicit (Euler forward) numerical solution in time, and a semi-implicit backward solution in space (Chow, 1988). Because all secondary fluxes, suspended sediment, DP and PP transport are based on the solution of the water flow, which is solved with the Newton-Raphson method. The model is stable over a large range of $\Delta t\ /\ \Delta x$ (Chow, 1988). The different processes are solved in multiple intermediate steps, following the same procedure as the calculations for water and sediment in OpenLISEM. In the following section the exact implementation in the code for each process is described in detail.

Dissolved transport by infiltration

The first process calculated is the mass transfer by infiltration. This is done in two steps; from the mixing layer to the deeper soil and from the runoff to the mixing layer. From the mixing layer to deeper soil:

$$M_{inf} = q_{inf} \cdot C_{mw} \cdot 1000 \cdot \Delta x^2 \cdot \Delta t \qquad Eq\ 3.8$$

And from the runoff to the mixing layer:

$$M_{inf} = q_{inf} \cdot C_{rw} \cdot 1000 \cdot \Delta x^2 \cdot \Delta t \qquad Eq\ 3.9$$

with M_{inf}, the mass of pesticides transported by infiltration (mg), q_{inf} the infiltration rate $\left(m\ sec^{-1}\right)$ and C_{rw} the concentration of dissolved pesticide in the runoff water. When there is infiltration or runoff it is assumed that the mixing layer is saturated.

Soil – water partitioning in the mixing layer

After mass transported by infiltration the mass exchanged by soil-water partitioning to reach equilibrium in the mixing layer is calculated.

$$M_{da} = M_{mw} - \frac{M_{mw} + M_{ms}}{1 + k_d / M_{wat} \cdot M_{sed}} \qquad Eq\ 3.10$$

with M_{da} the mass exchanged withing the mixing layer per timestep (mg), k_d the soil water partition coefficient $\left(kg\ L^{-1}\right)$, M_{mw} the mass of dissolved pesticide in the mixing layer (mg), M_{ms} the mass of sorbed pesticide in the mixing layer (mg), M_{sed} the mass of sediment in the mixing layer (kg) and M_{wat} the mass of water in the mixing layer(kg). The sediment mass is calculated with:

$$M_{sed} = \rho_b \cdot z_m \cdot \Delta x^2 \qquad Eq\ 3.11$$

with z_m the thickness of the mixing layer (m), Δx the cell size (m) and ρ_b the soil bulk density ($kg m^{-3}$).

Dissolved uptake from the mixing layer into runoff

Next the dissolved mass uptake from the mixing layer into the runoff is calculated with:

$$M_{wrm} = k_{film} \cdot (C_{mw} - C_{rw}) \cdot A_{mix} \cdot \Delta t \cdot 1000 \qquad Eq\ 3.12$$

with M_{wrm} the dissolved mass exchange between runoff and the mixing layer (mg), A_{mix} the surface area over which the mixing layer interacts with the runoff water (m^2). When precipitation occurs $A_{mix} = \Delta x^2$, however when only overland flow occurs, for small flow depths we cannot assume that the whole surface area of a raster cell is active in dissolved mass transfer. When the water height of runoff water is lower than WH_{lim} the A_{mix} is reduced to keep the effective water height to WH_{lim}, this is set to 1.0 mm. Uptake of pesticide only occurs when the concentration in the mixing layer is higher than the concentration in the runoff water, no transfer in the other direction is simulated. However, dissolved pesticides can re-enter the soil matrix with infiltration.

Transport of dissolved pesticides with runoff water

The discharge of dissolved pesticides is calculated following the same approach as Lefrancq (2014) proposed for sediment, based on the solution for the kinematic wave given by Chow (1988):

$$\frac{\delta Qp}{\delta x} + \frac{\delta CpA}{\delta t} = 0 \qquad Eq\ 3.13$$

which we approach in space by:

$$\frac{\delta Q}{\delta x} \approx \frac{Q_{i+1}^{j+1} - Q_i^{j+1}}{\Delta x} \qquad Eq\ 3.14$$

with j denoting the position in time and i the position in space. The approximation in time is:

$$\frac{\delta Cp}{\delta t} \approx \frac{Cp_{i+1}^{j+1} - Cp_{i+1}^{j}}{\Delta t} \qquad Eq\ 3.15$$

and the area (A) is based on the combination of Manning's and the continuity equation:

$$A = \alpha Q^{\beta} \qquad Eq\ 3.16$$

were $\alpha = \frac{n}{\sqrt{S \cdot \Delta x^{2/3}}}^{0.6}$, with S the gradient and n the Manning's number and were $\beta = 0.6$. After rewriting this results in:

$$Qp_{i+1}^{j+1} = \frac{-\overline{Cp} \cdot \alpha\beta\overline{Q}^{\beta-1}\left(Q_{i+1}^{j+1} - Q_{i+1}^{j}\right) \cdot \Delta x + \alpha\overline{Q}^{\beta}\frac{Qp_{i+1}^{j}}{Q_{i+1}^{j}} \cdot \Delta x + Qp_{i}^{j+1} \cdot \Delta t}{\Delta t + \alpha\overline{Q}^{\beta}\frac{\Delta x}{Q_{i+1}^{j+1}}} \qquad Eq\ 3.17$$

with Qp_{i+1}^{j+1}, the new dissolved pesticide flux $\left(mg\ sec^{-1}\right)$, $Cp = C_{rw}$, Q the water flux at different positions in space and time $\left(m^3 sec^{-1}\right)$ and α and β factor from the solution of the Mannings equation (Chow, 1988). $\overline{Cp}$ and $\overline{Q}$ are spatial average concentrations as calculated by Chow (1988), the following equation is a general form that is applied for dissolved and adsorbed pesticides as well as in calculations of sediment fluxes:

$$\overline{C} = \frac{M_i^{j+1} + M_{i+1}^{j}}{V_i^{j+1} + V_{i+1}^{j}} \qquad Eq\ 3.18$$

with $\overline{C}$ the average concentration assuming linearity in space $\left(mg\ L^{-1}\right)$, M the mass of the pesticide (mg) or sediment and V the volume, mass or flux of the control volume.

Detachment and deposition of sorbed pesticides

Sorbed pesticides are influenced by soil-water partitioning and either detachment or deposition. Detachment processes moves sorbed pesticides from the mixing layer to the suspended sediment, deposition adds PP to the mixing layer. The mass of detachment and deposition are calculated in two steps in OpenLISEM based on the governing physical process. First splash detachment by raindrops is calculated, and after that the flow detachment in combination with the transport capacity of the runoff water results in flow detachment or deposition. The PP pesticide mass added to suspended sediment by splash erosion is calculated with:

$$M_{spl} = S_{spl} \cdot C_{ms} \cdot \varepsilon \qquad Eq\ 3.19$$

with M_{spl} the PP mass (mg) added to the suspended sediment control volume, S_{spl} the mass (kg) of eroded sediment, C_{ms} the adsorbed concentration in the mixing layer $\left(mg\ kg^{-1}\right)$ and ε the enrichment ratio of the suspended sorbed concentration compared to the concentration in the mixing layer. The enrichment ratio is calculated with Eq 3.5. In OLP we use the value of α also as maximal enrichment ratio to prevent extreme enrichment rates with very low erosion rates. Based on the suspended sediment concentration in the runoff water and the transport capacity, either flow detachment or deposition occurs. When flow detachment occurs the addition eroded PP mass is calculated with:

$$M_{fl} = S_{fl} \cdot C_{ms} \cdot \varepsilon \qquad Eq\ 3.20$$

with M_{fl} the PP mass (mg) added to the suspended sediment control volume, S_{fl} the mass (kg) of eroded sediment by flow detachment. In case of deposition the PP mass added to the mixing layer is calculated with:

$$M_{dp} = S_{dep} \cdot C_{rs} \qquad Eq\ 3.21$$

with M_{dp} the PP mass (mg) added to the mixing layer, S_{dep} the mass (kg) of deposited sediment. Based on this exchange masses, the masses in all involved control volumes are updated.

Sorbed transport with runoff

Adsorbed pesticides are passively transported with suspended sediment, and we assume there is no interaction between PP and DP pesticides in the runoff water. Therefor the adsorbed pesticide transport is proportional to the transport of suspended sediment. The PP flux is calculated using Eq 3.17, with $C_p = PM_{rs}/Vol_w$, were PM_{rs} is the PP pesticide mass (mg) in the suspended sediment and Vol_w the volume $\left(m^3\right)$ of water in the runoff.

Mass balance calculations

Three mass balances are calculated for pesticide in OLP. The first is a total mass balance, tracking the total mass of pesticides in the system and in sinks, e.g. at the outlet, and comparing it to the mass at initialization. The other two mass balances are more specific for PP and DP transport, inspired on the approach used by OpenLISEM for water and sediment. The mass balance is calculated for all mass the is 'activated' by exchange to the runoff from the mixing layer for DP or by erosion for PP pesticide. After each intermediate calculation as described above the mass balance is updated. The mass balance is calculated with:

$$M_{err} = \frac{M_{det} + M_{dep} - M_{act}}{M_{det}} \cdot 100 \qquad Eq\ 3.23$$

With M_{err} the mass balance error (%) of the checked substance, $M_{det}, M_{dep}, M_{act}$ the spatial and temporal totals of detached, deposited and active substance mass respectively. The detached mass is defined as all mass entering the runoff domain, and the active mass includes all substance in the runoff layer as well as all mass that left the model domain at the outlet.

3.6.2 Additional data on model setup and results

Comparison of texture distribution and organic matter content between soil and suspended sediment

In the study area the main soil texture is a silt loam. We analysed samples collected on the fields and suspended sediment samples in the stream on texture and organic matter content to see if substantial changes in particle size distribution occurred during runoff. In Table 3.7 the mean ± se for both groups are given. The data in Table 3.7 suggests that the particles distribution in the suspended sediment is slightly more course than on the fields in the catchment, this is contrary to the observations of Ghadiri and Rose (1991) who suggest an higher affinity for transport of smaller particles. On the other hand the organic matter content is two times higher in the suspended sediment, this supports enrichment during overland transport. We did not do a texture analysis for all samples collected in the dataset. Based on these results in combination with available literature we include enrichment processes in the OpenLISEM-pesticide model.

Table 3.7 *Texture distribution and organic matter content in soils and the suspended sediment.*

fraction / variable	Field soils n = 16	Suspended sediment n = 11
Clay (%)	3.5 ± 0.2	3.0 ± 0.5
Silt (%)	51.0 ± 2.1	43.1 ± 1.4
Sand (%)	45.6 ± 2.2	53.7 ± 1.6
D50 (μm)	46.8 ± 1.8	54.9 ± 3.1
D90 (μm)	124.4 ± 15.1	250.9 ± 18.0
OM (%)	3.5 ± 1.2	7.0 ±2.4

Initialization of OpenLISEM

To find initialization values for all variables related to hydrology and soil surface representation, we applied the temporal constraint strategy as proposed by Lefrancq et. al. (2017). In Table 3.8 all variables that are needed for OpenLISEM are described, and the method to obtain the initialization values is explained.

Table 3.8 *Initialization choices to setup OpenLISEM for runoff and erosion.*

		Units	Spatial variation	Temporal variation	Method/source
Catchment morphology					
Digital elevation model		(m)	Spatialised	fixed	AHN4 – 5 meter surface model – resampled with GDAL-warp: cubic spline
Slope		(m m^{-1})	Spatialised	Seasonal	Calculated based on DEM and tillage direction with TCRP
Local drain direction		(-)	Spatialised	Seasonal	Calculated based on DEM and tillage direction with TCRP
Soil surface					
RR (random roughness)		(cm)	Land unit		Field images and estimations and equation by Potter. (Potter, 1990)
	Non-fields			fixed	
	Grass + apples			fixed	
	potato, wheat, sugarbeet			Temporally	RR = RRi * exp(Pcum/b)^0.6 b = 63 + 62.7 * ln(OM) + 15.7 * clay – 0.25 * clay^2 OM = 3.6%, Clay = 3.5%, Pcum based on daily precipitation data (Commelin et al., 2022a). RRi = RR after tillage, estimate from Potter (1990).
	Wheel tracks potato			Temporally	0.5 * RR potato
Manning's n		(-)	Land unit	temporally	

Non-fields			Fixed	Estimates based on (Lefrancq et al., 2017b; Phillips, 1989)
Fields			Calibrated	Equation and residue and vegetation estimates by Philips (1989, table 1) n = RR/100 + n_residue + cover * n_vegetation
Wheel tracks potato			Calibrated	Same as fields
Vegetation				
Land use		Land unit	Seasonal	Satellite images, public maps and field observations.
Crop cover	(m^2 m^{-2})	Land unit	Temporally	Satellite images and field observations
Crop height	(m)	Land unit	Temporally	field observations
Canopy storage	(mm)	Land unit	Temporally	LAI based on SWAP simple crop models (J. G. Kroes et al., 2017) and field observations. Smax = 0.935 + 0.498 * LAI – 0.00575 LAI^2 (Von Hoyningen-Huene, 1981). Modelled with canopy openness of 0.1.
vegetated main channel			Temporally	same as grassland
Infiltration (Green and Ampt)				
Layer 1 (0-30 cm)				
Saturated hydraulic conductivity (*k_{sat}*)	(mm h^{-1})	Land unit		Estimations from the Soil Water Characteristics model (SWC) in combination with the observed compaction state

					on the fields (Saxton and Rawls, 2006).
	Non-fields			Fixed	Estimates based on soil texture (Lefrancq et al., 2017b; Saxton and Rawls, 2006)
	Fields			Calibrated	
	Wheel tracks potato			Calibrated	0.2 mm/h – based on high compaction
	vegetated main channel			Fixed	Same as grassland
Initial moisture content (θ_i)		(m^3 m^{-3})	Homo-geneous	Calibrated	Antecedent rainfall index adjusted for temperature for top 25 cm of soil (Zhao et al., 2019) +- 20% . The API is a rough estimate, from which further calibration is possible, in further research where focus is on multiple events a more sophisticated soil moisture model is (e.g. SWAP (J. G. Kroes et al., 2017)) is advisable. In the API calculations, alpha was estimated on 0.87 and the temperature effect is used as calibrated by Zhao et al (2019).
Soil porosity θ_s)		(m^3 m^{-3})	Homo-geneous	Fixed	Field measurement: 0.44
	Wheel tracks potato		Spatialised	Fixed	Field observation (Chamen et al., 1992; Vermeulen and Klooster, 1992): 0.9 * Porosity

Suction at the wetting front (Ψ)	(cm)	Land unit		Estimates based on soil texture and organic matter content, and the study by Rawls et al. 1983. This shows a very wide uncertainty range!
Non-field			Fixed : 11	
Fields			Calibrated	
Soil depth	(m)	Homo-geneous	Fixed: 0.25	Field observation (tillage depth)
Layer 2 (30 – 150 cm)				
Saturated hydraulic conductivity (k_{sat})	(mm h^{-1})	Homo-geneous	Fixed: 7.6	Soil measurements in 1994 ("Erosienormeringsonderzoek ZUID-LIMBURG," 1994) and the SWC model.
Initial moisture content (θ_i)	(-)	Homo-geneous	Temporal	Soil moisture 0.1 below estimated porosity.
Soil porosity (θ_s)	(-)	Homo-geneous	Fixed: 0.42	1994 ref + SWC
Suction at the wetting front (Ψ)	(cm)	Homo-geneous	Fixed: 11	Based on texture and table from Rawls (1983).
Soil depth	(m)	Homo-geneous	Fixed: 1.5	1994 ref + SWC
Erosion variables				
Cohesion (S_c)	(kPa)	Crop	Fixed	Based on measurements on similar loess fields in Belgium (Baets et al., 2008). To adjust for concentrated flow, which differs from sheet flow detachment, the detachment efficiency for the main concentrated flow paths is set to 0.001 (this corresponds to a cohesion value of 7.85 kPa).

Median grain size (D50)	(µm)	Homo-geneous	Calibrated	Field measurements: 50
Aggregate stability	(drops)	Homo-geneous	Fixed	(Jetten et al., 1998) : 14 in combination with a splash delivery ratio of 0.1 and the default rainfall kinetic energy (van Dijk et al., 2002).
Pesticide variables				
Soil water partitioning *(k_d)*	(kg L^{-1})	Homo-geneous	Fixed	Value from EFSA reports Metobromuron (European Food Safety Authority, 2014) and Glyphosate (European Food Safety Authority (EFSA), 2015). In combination with OM content of soils.
Enrichment ratio exponent *(β)*	(-)	Homo-geneous	Calibrated	Reported range between -0.1 and -0.5 (Menzel, 1980)
Enrichment ratio coefficient (α)	(-)	Homo-geneous	Fixed: 7.4	Reported as general default (Menzel, 1980)
Mixing layer transfer rate *(k_{film})*	(mm sec^{-1})	Homogeneous	Calibrated	Range of 0.0001 – 0.1 mm sec^{-1} based on previous modelling studies (Havis et al., 1992; Joyce et al., 2010; Watanabe and Grismer, 2003)
Pesticide soil depth		Homo-geneous	Fixed: 0.05 m	Estimate, used to accommodate for soil loss by erosion.
Mixing layer depth *(z_m)*	(mm)	Homo-geneous	Fixed: 6.0 mm	Estimate based on results for bare soil by Havis et. al., (1992).

PP concentration *(C_{PP})*	(mg kg^{-1})	Land unit	Temporal	Based on field measurements
DP concentration *(C_{DP})*	(mg L^{-1})	Land unit	Temporal	Assume equilibrium: $C_{DP} = C_{PP}/K_d$

Initial and calibrated input settings for OpenLISEM for runoff, erosion and pesticides

After initialization, to calibrate the model adjustments have been made to selected variables for specific fields. These variables were selected based on the sensitivity of OpenLISEM to this variables in combination with the estimated observation uncertainty. During calibration we only made small adjustments to erosion related variables. For infiltration the main adjustments were decreasing the infiltration speed by lowering the saturated hydraulic conductivity and the wetting front capillary pressure. Table 3.9 shows all specific values that were assigned as 'calibrated' during the setup.

Table 3.9 *Variable settings for OpenLISEM before and after calibration.*

		2019		**2020**	
Variable	**Crop type**	**initial**	**manual**	**initial**	**manual**
Soil cohesion (kPa)	apple	5.9	5.9	5.9	5.9
	cereals	5.1	5.1	4.58	5.62
	potato	2.67	2.67	2.84	2.84
	sugarbeet	2.84	2.84	4.2	4.2
	wheeltracks	7.85	7.85	7.85	7.85
Median texture, D50 (µm)	apple	50	50	50	50
	cereals	50	50	50	50
	potato	50	50	50	50
	sugarbeet	50	50	50	50
	wheeltracks	50	50	50	50
Saturated hydraulic conductivity,	apple	35	10.5	35	5.25
	cereals	15	4.5	15	2.55
	potato	4.7	0.7	4.7	1.27

k_{sat} (mm h^{-1})	sugarbeet	4.7	1.41	4.7	0.8
	wheeltracks	0.3	0.04	0.3	0.08
Surface resistance to flow, Mannings n (-)	apple	0.07	0.06	0.07	0.06
	cereals	0.42	0.33	0.11	0.14
	potato	0.01	0.01	0.02	0.01
	sugarbeet	0.03	0.02	0.2	0.17
	wheeltracks	0.01	0.01	0	0.01
Wetting front capillary pressure, Ψ (cm)	apple	11	5.5	11	4.4
	cereals	11	5.5	11	7.7
	potato	11	5.5	11	4.4
	sugarbeet	11	5.5	11	5.5
	wheeltracks	11	5.5	11	7.7
Initial soil moisture, θ (-)	apple	0.23	0.29	0.1	0.13
	cereals	0.23	0.29	0.1	0.13
	potato	0.23	0.29	0.1	0.13
	sugarbeet	0.23	0.29	0.1	0.13
	wheeltracks	0.23	0.29	0.1	0.13

With these calibrated settings also the predictions for pesticide transport were optimized. Table 3.4 in section 3.3.3 shows the initial and calibrated values for the pesticide simulations. Table 3.10 shows the pesticide concentrations per field and event.

Table 3.10 *Initial concentration for OpenLISEM-pesticide per field and event.*

Compound	Variable	Field	2019	2020
Metobromuron	Initial sorbed concentration in the mixing layer (mg kg^{-1})	A	0	0.12
		B	1.21	0.008
		C	0.011	0
		D	0.011	0
		E	2.3	0
		F	0	0
		G	0.01	0
Glyphosate	Initial sorbed concentration in the mixing layer (mg kg^{-1})	A	0	0.121
		B	0.26	0
		C	3.738	1.456
		D	0.174	0
		E	0	0
		F	0	0
		G	0	0

Sorption equilibrium and mass transfer assumptions

In addition to the sensitivity analysis, we tested the influence of assumptions concerning sorption-desorption and the mixing layer mass transfer rate. The mass transfer rate was measured in experiments by Havis et al. (1992), with values between 0.001 to 0.1 mm sec^{-1}. In models with longer typical timesteps (hours or days) complete mixing is assumed. We varied the mass transfer rate to test which values of k_{film} would correspond with the complete mixing assumption and how these relate to the used mass transfer rates in this study. In Table 3.11 we show that the equilibrium mixing assumption will result in about 600% more dissolved phase transport than modelled when using a k_{film} of 0.0008 mm sec^{-1}. The maximum value reported in literature (0.1 mm sec^{-1}) approaches the complete mixing assumption. When the mass transfer rate is reduced below the reported values in literature DP transport also decreases fast. These results show that when simulating the uptake of pesticide into runoff on timesteps of seconds, the assumptions of complete mixing cannot be made, as also stated by Havis et al (1992).

Table 3.11 *Influence of mass transfer rate (k_{film}) on dissolved phase transport for metobromuron in the event on 2019-05-28.*

k_{film} (mm sec^{-1})	Relative (%) DP total load	Relative (%) PP total load
0.000001	1	101
0.0001	14	101
0.0008	100	100
0.01	445	98
0.1	595	97
1	607	97
10	607	97
100	607	97

Instead of instantaneous sorption equilibrium in the soil matrix also a kinetic sorption model can be used (Joyce et al., 2008), which describes the sorption rate in the soil matrix. However, sorption rates are unknown and, the sorption-desorption process is fast compared to the mass transfer which reduces the impact of this parameter on model outcomes. A simulation with a kinetic sorption model with an equilibrium time of 20 minutes (k_r = 0.05 min^{-1}), reduces the total load in DP with 4%.

Chapter 4

Sensitivity analysis and performance evaluation of OpenLISEM-pesticide, simulating event-based transport of metobromuron from agricultural fields[4]

Abstract

Because pesticides are abundantly used in agriculture, it is important to know their environmental fate and transport to off-target ecosystems to prevent adverse effects. In chapter 3 we presented a proof-of-concept of the OpenLISEM-pesticide model (OLP). We designed OLP to better understand the high transport rates of pesticides observed in headwater catchments during rainfall-runoff events. When using a model, knowing the uncertainties related to the simulated processes and input data, and which parameters influence the model output the most, is of major importance for further applications of the model. In this study we determined the input parameter influence on the output of OLP and investigated its suitability to simulate and predict pesticide transport for a small agricultural catchment. We performed a Sobol' global sensitivity analysis for the parameters describing pesticide transport and evaluated OLP's predictive performance for one event for metobromuron transport in sorbed and dissolved phase. The global sensitivity analysis showed that the hydrology and erosion related parameters have a major influence on the simulated transport of pesticides. Of the parameters introduced in OLP, the mixing layer depth is the main influential parameter for both dissolved and particulate phase transport. In addition, the mass transfer rate and the parameters in the enrichment ratio equation are influential. The 90% prediction uncertainty of the ensemble simulation to evaluate OLP covered the observed concentrations well. However, in combination with the simulated runoff and erosion, errors in the load predictions occurred. The evaluation of OLP in this study shows that predictions without calibration based on observations have a large uncertainty. To improve pesticide transport simulations, further research is needed to improve the process-based descriptions of the mixing layer and the enrichment process, to reduce the uncertainty currently related to these parameters.

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[4] In prep for: Commelin, M.C., J.G. Wesseling, M. Riksen, J.E.M. Baartman and V. Geissen. (in prep) Sensitivity analysis of OpenLISEM-pesticide, simulating event-based transport of metobromuron from agricultural fields.

4.1 Introduction

Because pesticides are abundantly used in agriculture (FAO, 2020), it is important to know their environmental fate and transport to off-target ecosystems to prevent adverse effects (Lykogianni et al., 2021), including health risks for humans and biodiversity decline (Bevan et al., 2017; Geiger et al., 2010; Liess et al., 2021). Since the start of pesticide use in agriculture, studies have been performed to investigate, describe, and simulate the transport of pesticides through the environment. As a result, many models exist that describe one or multiple transport pathways of pesticides in the environment (Centanni et al., 2023; Mottes et al., 2014; Payraudeau and Gregoire, 2012), and these models are used to estimate and predict the risks posed by pesticide use on the surrounding environment (Dowling et al., 2019; Iturburu et al., 2019; Sybertz et al., 2020).

Models like FOCUSPEARL (Adriaanse et al., 2017; FOCUS, 1997) and PRIZM5 (Dowling et al., 2019) are used in the European Union to predict pesticide transport to groundwater and surface water bodies on timescales ranging from a few days to multiple years. Despite regulatory limits based on these models, multiple observation studies in the past decade have shown that in headwater catchments the concentration of pesticides often exceeds the regulatory limits (Casado et al., 2019; Mayora et al., 2024; Vormeier et al., 2023). Concentration peaks have been identified to closely relate to rainfall-runoff events (Commelin et al., 2022a; Halbach et al., 2021). However, the typical timescale (days) and spatial distribution (homogeneous fields) of the regulatory models are too coarse to simulate and understand the dynamics of pesticide transport and redistribution in such detail, i.e. during and shortly after rainfall-runoff events (Ippolito and Fait, 2019). An event-based distributed model could contribute to understanding and simulating pesticide transport in headwater catchments during rainfall-runoff events.

In general, models are a simplified representation of reality. A more complex model, although including more details, often also has more uncertainties and less predictive capacity than simpler models (Wainwright and Mulligan, 2012). Often the predictive performance and robustness of a model to simulate a wide variety of different cases correctly, decreases with increasing model complexity (De Vente and Poesen, 2005). Describing more processes requires more input data and knowledge of the simulated system. Environmental modelling is often done in data-scarce situations, which increases the challenge to correctly parameterize a complex model (Cambien et al., 2020). Nevertheless, depending on spatial and temporal scale, process-based models can describe more heterogeneity in the environment and improve our predictions of the simulated process (Meinen and Robinson, 2021). By considering spatial and temporal heterogeneity and by aiming to simulate the physical and chemical processes, rather than describing these empirically, these models are tools to increase our understanding of dynamic processes, like runoff and pesticide transport, in the environment. In case of the application of a distributed event-based model, we identify two steps required to obtain adequate simulations of pesticide transport.

Firstly, knowing the uncertainties related to the simulations, and which parameters influence the model output the most, is of major importance to use the model outputs for policy and decision making (Rouzies et al., 2023). The output of a model is based on a set of stated and unspoken assumptions which are a source of uncertainty (Saltelli et al., 2019). These assumptions range from data choices (e.g., which rainfall data is used) to how the system is conceptualized (e.g., the use of enrichment ratio to describe sorbed pesticide uptake) and numerically represented (Saltelli et al., 2019). A sensitivity analysis contributes to the understanding of these uncertainties by investigating how variations in the model output are caused by variations in the input (Pianosi et al., 2016). With a global sensitivity analysis (GSA) the variability of the model output can be quantified by simultaneously varying input parameters (Puy et al., 2022; Saltelli et al., 2019). A GSA can be applied for multiple purposes, including the attribution of model output uncertainty to various sources of uncertainty in the model input, quantifying the relative influence of a specific model parameter on the predictive accuracy of the model and supporting decision-making based on the model output (Wesseling et al., 2020). Applying a GSA for an event-based model can provide knowledge on the uncertainties related to a more complex model. Besides that, based on the GSA results, uncertainty can be reduced by better targeting data collection and prioritizing the parameters which most influence the model output and identifying non-influential parameters (Pianosi et al., 2016).

Secondly, an event-based model needs to be initialized with appropriate values for e.g. soil moisture, vegetation growth and pesticide concentrations (Beven, 2012). Because rainfall-runoff events within a headwater catchment often have a maximum duration of a few hours, the model must be initialized with the specific hydrology, land use and especially pesticide conditions at the start of each rainfall event. A solution for the initialization problem is to couple a longer-term model with the event-based model. The longer term model can simulate the dynamics on a coarser temporal scale but provide initialization data for the more detailed event-based simulations at a particular point in time (Brandmeyer and Karimi, 2000; Nunes et al., 2013), for example the soil moisture content on the day of the event.

In chapter 3 we presented a proof-of-concept of the OpenLISEM-pesticide model (OLP). We designed OLP to better understand the high transport rates of pesticides observed in headwater catchments during rainfall-runoff events. The two required steps also apply to OLP, and in this chapter we address both: we coupled the continuous, longer term, Soil-Water-Atmosphere-Plant model (SWAP) (J.G. Kroes et al., 2017), with OLP to provide the required initialization data for each event. Then, the influence of specific OLP parameters on the simulated pesticide transport was studied with a GSA.

Since OLP is a newly developed model, little is known about the sensitivity and interactions of the model parameters. In the previous chapter a simple 'one-at-a-time' (OAT) sensitivity analysis was done (Commelin et al., 2024). The mass transfer rate (k_{film}) and the soil-water partitioning coefficient (k_d) were identified to influence dissolved phase transport the most, and the coefficient (α) and exponent (β) in the enrichment ratio equation had most impact on the particulate phase transport (see Table 3.6, section 3.3.4). However, sensitivity to parameter variations might vary a lot within the feasible parameters space, and the results of an OAT analysis are only valid for the chosen starting point (Saltelli et al., 2019). In addition, an OAT analysis cannot identify parameter interactions, which might exist in OLP. A GSA is suitable to address these limitations. Variance based GSA are commonly applied in environmental modelling and are suitable for ranking and screening of model input parameters (Puy et al., 2022; Saltelli et al., 2019). Based on a GSA we can identify which parameters have the most influence on model output for both dissolved and particulate pesticide transport (ranking), as well as identify non-informative parameters (screening).

The aim of the present study was to determine the input parameter influence on the output of OpenLISEM-pesticide (OLP) and to investigate its suitability to simulate and predict pesticide transport for a small agricultural catchment. We did this by (1) coupling and calibrating the SWAP and OpenLISEM models to obtain adequate initial pesticide concentrations, and runoff and sediment dynamics simulations as a basis to apply OLP. Based on this (2) we performed a global sensitivity analysis (GSA) for the parameters describing pesticide transport in OLP to explore interactions and prioritize influential and identify non-influential parameters. Finally (3) we evaluated OLP's predictive performance for one event, considering parameter uncertainty, for metobromuron transport in sorbed and dissolved phase.

4.2. Methods

In this study we combine the SWAP and OpenLISEM-pesticide models with data from an observation dataset collected in South-Limburg, the Netherlands. In this section we describe (4.2.1) the dataset, the selection of rainfall events and explain the choice of simulating metobromuron. This is followed by a description of the used models and software (4.2.2) and a description of our modelling workflow (4.2.3) with a short description of each modelling step. Then, in the order of our three objectives, we describe (4.2.4) the coupling of SWAP and OpenLISEM including the model setup, (4.2.5) the setup of OLP for the GSA and lastly (4.2.6) the used approach to evaluate OLP performance with ensemble simulations.

4.2.1 The South-Limburg study area and dataset

An observation dataset was collected in 2019 and 2020 in a small agricultural catchment (38.6 ha) in South-Limburg, the Netherlands. A detailed description, and exploration of the observed runoff, erosion and related pesticide transport are given in chapter 2, the dataset is published in the 4TU repository (Commelin et al., 2022b). The study area has a typical land use for the loess belt covering parts of Belgium and Limburg in the Netherlands. Arable agriculture was the main land use covering 25.2 ha, consisting of a crop rotation of winter cereals and potatoes. An apple orchard covered 5.3 ha and 5.0 ha was extensively managed grassland. Roads, built up area and a small pond made up the remaining area in the catchment. All fields were managed under conventional practises including pesticide applications, see also Figure 1.4 for an overview of the catchment. Two hills form the borders of the catchment with an elevation difference of about 30 meters to the outlet (80–110 m.a.s.l.), the average slope is 6.3% (sd ± 4.0%, range 0.1–30%). A dry ditch and road system connect the main fields to the outlet. Measured soil characteristics at the surface are (mean ± SE): sand 45.6 ± 2.2%, silt 51.0 ± 2.1%, clay 3.5 ± 0.2%, OM 3.6 ± 0.3%, pH 6.5 ± 0.10. The catchment is located in a temperate climate (Cfb) with a mean annual temperature of 10.7°C (±0.7°C) (KNMI 2021b) and mean annual precipitation of 757 mm (±108 mm) (KNMI 2021a).

To quantify the transport of pesticides during rainfall-runoff events, data was collected both at the outlet and on the fields in the catchment. At the outlet a Parshall flume measured the discharge and an automatic sampler collected discharge samples every 6 minutes, when water was flowing through the ditch. The samples at the outlet were used to quantify suspended sediment, and pesticide concentrations in dissolved (DP) and particulate phase (PP). Details on the chemical analysis of the samples are given in chapter 2. At the outlet also a tipping bucket rain gauge was used to measure precipitation. During two growing seasons, five field sample campaigns (May and August 2019 and March, June and August 2020) were done to measure pesticide concentrations in the upper centimetre of the soil. Data on field management and pesticide applications was obtained from the landowners of the three main fields.

To represent the spatial variability in the catchment during model simulations in this study, we divided the catchment into hydrologic response units (HRUs) (Kouwen et al., 1993). The assumption was made that hydrologic and pesticide dynamics within a HRU are homogeneous on temporal scales larger than a rainfall-runoff event. The HRUs are based on the different forms of land use in combination with pesticide application patterns (Figure 4.1). The three main fields (A,B and C) that produce runoff, or function as source of pesticides during rainfall-runoff events (Commelin et al., 2022a) have a separate HRU assigned.

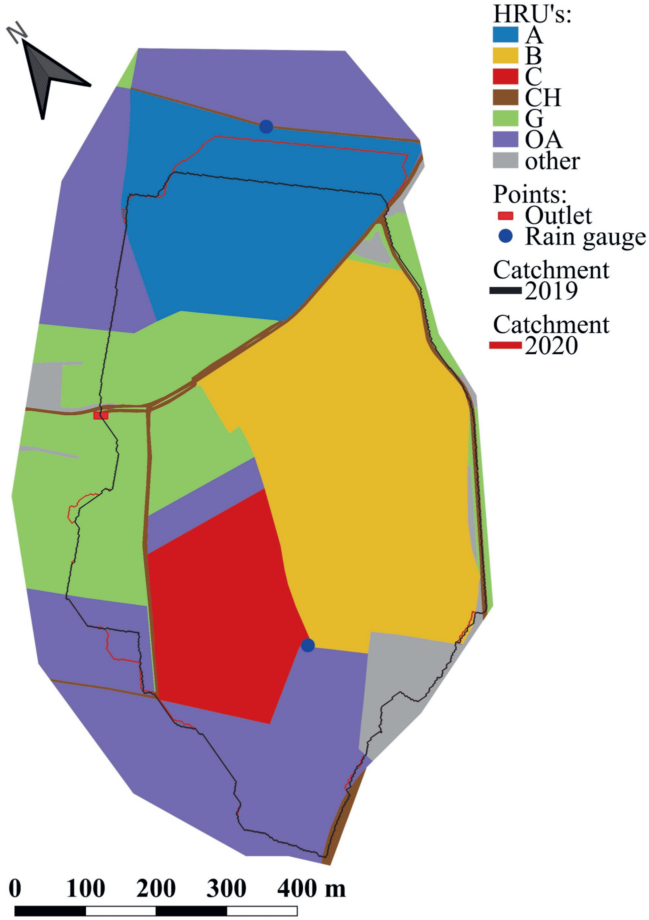

Figure 4.1 *The study area divided in Hydrologic Response Units (HRUs) same colours are lumped in SWAP simulations. The HRUs are: A, B and C the three main fields in the catchment. CH the road and channel area, G the extensive grasslands and OA all other arable fields in the catchment.*

The other HRUs consist of: all other arable agriculture (OA), the extensively managed grasslands (G) and the road and channel area (CH). Some small patches of land remained after selection of the HRUs, including build up area and a small pond (other). Based on field observations these were neglected, since they are not hydrologically connected to the outlet and will not contribute to the observed runoff.

Selection of metobromuron and rainfall events

29 different pesticides were analysed in the field samples, however, due to computational limitations we focussed on one pesticide for the sensitivity and uncertainty analysis. For this study

we selected metobromuron since this pesticide was regularly observed in both transport phases (particulate and dissolved). During the sampling period, metobromuron was applied at the start of potato cultivation of HRU B (2019-05-04) and A (2020-05-01) (Figure 4.1). An alternative compound could be glyphosate, a herbicide that is often involved in the public debate (e.g. on the renewed approval in the European Union (Reuters.com, 2023)). However, in our dataset we only measured glyphosate in the PP when transported and this would make an evaluation of DP transport simulations by OLP impossible.

During the sampling period we collected data for 25 events, 14 of these were suitable for pesticide analysis in DP and PP. Metobromuron was detected in all of these 14 events in PP and five times also in DP. When the collected mass of suspended sediment was lower than the minimal required mass for chemical analysis (2 grams) samples had to be lumped. Adjoining samples in time were lumped until the required sediment mass was reached, in Table 4.1 the collected and analysed samples for the selected events in this study are presented. The water samples were also lumped due to limitations in analysis capacity and to homogenize the dataset. For 8 of the 14 events all samples had to be lumped to obtain enough sediment material. The six (6) events that have multiple analysed samples within the event, enabled us to calculate time-based performance statistics for OLP compared to the observed transport. In all 6 events, and in all analysed samples, PP metobromuron was detected. Dissolved metobromuron was only detected in two events, but again in all samples analysed during these events (Table 4.1).

Table 4.1 *Number of samples and detection of metobromuron in the observation dataset.*

Event date	Samples outlet	Lumped samples[1]	Analysed samples	PP detected	DP detected
2019-05-28	12	5 → 1	8	8	8
2019-08-18	12	5 → 2	9	9	0
2020-06-17	12	9 → 3	6	6	6
2020-08-12	10	5 → 2	7	7	0
2020-08-16	5	0	5	5	0
2020-10-22	12	6 → 1	7	7	0

PP: particulate phase pesticides, DP: dissolved phase pesticides.

[1] Depending on the available sediment, samples were lumped to one or multiple analysed samples. This is denoted with: 'samples with < 2 grams of sediment' → 'number of lumped samples analysed'

4.2.2 Used models and software

The SWAP model

For the simulations of hydrology and pesticide fate over the full growing seasons (2019 – 2020) we used the Soil Water Atmosphere Plant (SWAP) model (version 4.2.0). SWAP is a dynamic model that simulates soil hydrology by solving the Richards equation (J.G. Kroes et al., 2017), and is applied in many studies (Faúndez Urbina et al., 2020; Kroes et al., 2019; Wesseling et al., 2020). SWAP also includes additional features including heat transport, crop growth, evapotranspiration and solute transport. The solute transport simulations are used in this study to simulate pesticide fate after application. The partitioning between dissolved and sorbed solutes is described with the Freundlich adsorption isotherms, assuming instantaneous equilibrium. Degradation of the solutes is simulated with a first order decay term combined with reduction factors for temperature, soil moisture and soil depth, analogous to Boesten and Van Der Linden, (1991).

The OpenLISEM model and pesticide module

OpenLISEM (version 6.91) is a process-based hydrological model to simulate runoff and sediment dynamics during rainfall-runoff events on catchment to small river scale (1 ha to 100 km^2) (Bout and Jetten, 2018; De Roo et al., 1996; De Roo and Jetten, 1999). The model has extensive options, including multiple equations for overland flow and infiltration. In this study, infiltration was simulated with a two-layer implementation of the Green & Ampt equation (Downer et al., 2003; Green and Ampt, 1911). Overland flow is calculated with the Manning's equation, and flow routing is done with a 1D kinematic wave, based on the local drain direction (Chow, 1988). Sediment detachment consists of both splash erosion by raindrops and flow detachment. The splash detachment depends on the kinetic energy of the raindrops (van Dijk et al., 2002) and for flow detachment an equation in relation to soil cohesion is used, as implemented in EUROSEM (Baets et al., 2008). The transport capacity for suspended sediment is calculated with the equation developed by Govers, (1990).

The pesticide extension for OpenLISEM (OLP version 1.0) was developed within this thesis project, and is presented and discussed in chapter 3. The conceptualization of pesticide uptake from the soil by runoff is based on the model presented by Havis et al., (1992) combined with enrichment of pesticide concentrations in particulate phase (Menzel, 1980). The interaction between the soil and the runoff takes place in the mixing layer, which is assumed to be a homogeneous completely mixed reactor. Due to the short timescale of the OLP simulations (up to multiple hours), pesticide degradation is not included. The soil-water partitioning is based on equilibrium sorption. The transfer of dissolved pesticides into the runoff is limited by the mass transfer rate and uptake of particulate phase pesticide is based on the splash and flow detachment of sediment in combination with an enrichment ratio.

Other used software and hardware

All data management, statistics and model output analysis was done using the R software (R Core Team, 2023). The main packages used were 'tidyverse' for general data manipulation and visualization (Wickham et al., 2019), 'sensobol' for parameter sampling and the global sensitivity analysis (Puy et al., 2022) and 'hydroGOF' for the calculation of performance statistics (Zambrano-Bigiarini, 2020). For OpenLISEM simulations the PCRaster GIS language was used to prepare and manipulate all input raster maps as described by Karssenberg et al., (2010). In addition, the local drain direction flow networks were adjusted for tillage patterns using the tillage controlled runoff pattern model (Takken et al., 2001a).

All simulations were performed on a personal computer with an i7 12700H CPU. Simulation times for SWAP (including all HRU's) were ~ 8 seconds, and time required for OpenLISEM-pesticide simulations ranged between 1 and 8 minutes depending on which processes were included.

4.2.3 Modelling workflow

To analyse parameter importance for OpenLISEM-pesticide simulations and to investigate the model's suitability to simulate and predict pesticide transport six sequential modelling steps were performed (Figure 4.2). The first four steps (A – D) are done to initialize OLP: here we coupled SWAP and OpenLISEM and calibrated the initialization for the OLP simulations. Modelling steps E and F consisted of the global sensitivity analysis (GSA) and ensemble simulations for OLP evaluation.

The first four modelling steps (A-D) all aimed to find a best parameter set to simulate the process of interest. This was done by varying influential parameters. To cover the resulting multidimensional parameter space efficiently, Quasi Random Number (QRN) samples were drawn from uniform distributions for each varying parameter. Because we do not have enough information to define a specific distribution (e.g. Gaussian or lognormal) for the varied parameters, best practise is to select a uniform distribution by default (Pianosi et al., 2016; Puy et al., 2022). QRN sampling was designed to reduce the number of samples needed to effectively cover the parameter space compared to full random sampling (Monte Carlo) (Kucherenko et al., 2015; Sobol, 1976).

We selected the best parameter sets for the modelling steps A to D based on two criteria. First the goodness-of-fit metric (GOF), the KGE or ROI was calculated for the simulated process. However, a simulation with the highest GOF is not always the best simulation, especially when only a limited amount of observations points is available, in this study in modelling steps B and D. The ROI is an adaptation of the RMSE, which includes the observation range per day, see for further details section 4.2.4. As a second verification we selected the best simulation based on expert judgement from the 10 parameter sets with the highest KGE. The qualitative criteria included for example the assessment of the source HRU's for SWAP hydrology (A) and number of simulated peaks compared to the precipitation pattern for OpenLISEM (C). An example of the selection procedure is given for modelling step C in the results (3.2.1).

Because we do not have data of pesticide concentrations in the soil or soil moisture content at the start of the events, we simulate these processes with SWAP. Since SWAP is a 1D model, we divided the catchment in HRU's with homogeneous characteristics (see Figure 4.1). We calibrated the hydrology (step A. Hydrology, Figure 4.2) by comparing simulated and observed daily runoff in the catchment. These simulations resulted in an estimate of the hydraulic conductivity (k_{sat}) and daily soil moisture content (θ) for each HRU.

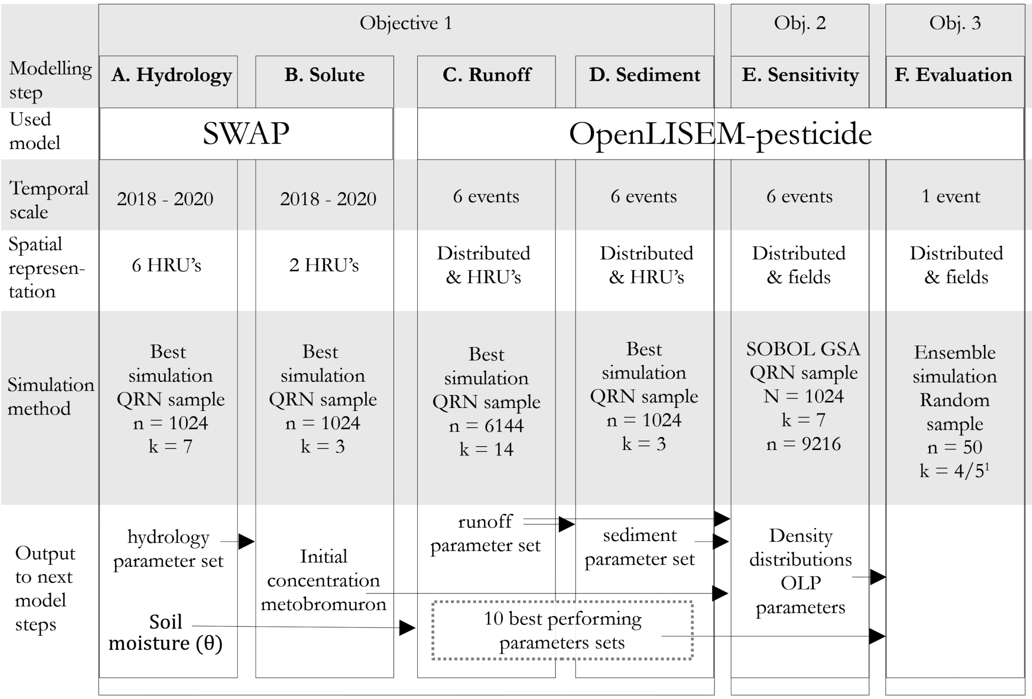

Figure 4.2 *modelling steps with main characteristics. Meaning of symbols, n: sample size, k: number of varied parameters, N: size of the initial sample matrix.*

[1] The evaluation is done with two cases: first varying only OLP parameters, secondly also varying the 10 best parameters sets from step 1C & 1D.

The solute simulations with SWAP (step B. Solute, Figure 4.2) were calibrated by comparing the simulated metobromuron concentration with the observations in the upper 1.0 centimetre of the soil available in the dataset.

Modelling step C and D aimed to find adequate parametrizations for runoff and sediment simulations with OpenLISEM for each of the six selected rainfall-runoff events. The runoff simulations were calibrated based on the observed discharge at the outlet, and for sediment simulations the observed suspended sediment load was used. Each modelling step also informed the next step by fixing parameters or providing input data, e.g., the SWAP solute simulations (B) provide the daily metobromuron concentration in the soil, which was used to initialize OLP simulations for each event.

The first four modelling steps (A – D) result in a best estimated initialization for each event to start OLP simulations. In modelling step E we applied a variance based global sensitivity analysis to OLP, following the methodology described by Sobol (2001), as built in the 'sensobol' R software (Puy et al., 2022). The GSA aims to test the sensitivity of the newly introduced parameters in OLP, so the runoff and sediment related parameters were all fixed to the best performing parameter sets based on the earlier modelling steps.

The first four modelling steps (A – D) result in a best estimated initialization for each event to start OLP simulations. In modelling step E we applied a variance based global sensitivity analysis to OLP, following the methodology described by Sobol (2001), as built in the 'sensobol' R software (Puy et al., 2022). The GSA aims to test the sensitivity of the newly introduced parameters in OLP, so the runoff and sediment related parameters were all fixed to the best performing parameter sets based on the earlier modelling steps.

Finally, in modelling step F, the predictive performance of OLP was evaluated. The sample matrix of the GSA can be used for uncertainty analysis and analysis on behavioural and non-behavioural parameter sets (Pianosi et al., 2016). We used the sample matrix of the GSA to inform random ensemble simulations (n = 50) for one event (2020-06-17), which also includes DP transport. This resulted in a prediction range of OLP, which we compared to the observed DP and PP concentrations at the outlet.

4.2.4 Model Coupling

Both the SWAP and OpenLISEM-pesticide models require initialization for many different processes to run a simulation. For both models, a subset of the parameters describing these processes is used for exploration of best performance. All other input was fixed. In this section we describe choices made for the fixed parameters, discretization of temporal and spatial processes and for the parameters that are varied during the modelling steps.

Setup of SWAP for hydrology

As described in section 4.2.1, we divided the catchment in South-Limburg in hydrologic response units (HRUs) for simulations with SWAP (see also Figure 4.1). The weather data and fixed soil parameters were equal for all HRUs, while crops and landuse related data was varied for each HRU.

Weather data

Weather data was obtained from a close-by meteorological station (KNMI, Maastricht Airport), and combined with precipitation data from our own observations. The KNMI data provided all required data on temperature, radiation and potential evapotranspiration. Since runoff is an important process in our study catchment, we used 5 minute precipitation data as input; temperature and reference evapotranspiration were provided with a daily basis. Actual precipitation amounts can vary substantially over short distances (Overeem et al., 2009), so as basic input our own tipping bucket measurements were used. The observation data has multiple gaps in the timeseries, which were filled with the precipitation data from the KNMI station.

Crops

For the main arable fields (field A, B C in Figure 4.1) the exact dates for tillage, sowing and harvest were available in the dataset, and this was used in SWAP. For the HRU 'other arable' (OA in Figure 4.1), this data was not available and estimated dates, based on the crop models provided with the SWAP model (J.G. Kroes et al., 2017) were used. Crop parameters for growth and leaf area index were also obtained from the SWAP crop data. In the winter season a cover crop (yellow mustard, *sinapis alba*) was grown on the arable fields, and this was simulated as a separate crop. This leads to the following crop types used in our simulations: apples, cereals, potatoes, arable general, grass and cover crop. The apple and grassland crops were perennial, covering the full year.

Infiltration and soil parameters

The soil characteristics in the catchment are homogeneous, and variations are only expected in the upper soil layer which is influenced by tillage. We simulated the soil with two layers/horizons, the first from 0 to 30 cm depth and the second from 30 to 120 cm. The actual loess soil layer in this area is even thicker, so free drainage at the bottom of the soil profile was assumed. Soil type and classifications were obtained from the Dutch soil map (BOFEK 2020, Heinen et al., 2021) and combined with the Staringreeks (Heinen et al., 2020) for soil physical characteristics for the different soil horizons. Soil texture was obtained in an extensive sampling campaign in 1994 ("Erosienormeringsonderzoek ZUID-LIMBURG," 1994) and combined with soil surface samples from our observational dataset.

Selection and range of calibration parameters

Since this study focusses on runoff processes, the performance of SWAP was evaluated by comparing predicted daily runoff with observed runoff at the catchment outlet. For the calibration we selected parameters that influence runoff and soil hydrology in SWAP. To limit the number of varied parameters, we fixed non-influential parameters based on initial testing, and on our understanding of the study area. Most runoff was observed from HRU's A and B as discussed in Ch 2.3 of this thesis. These fields have the same management, but a different crop rotation. For SWAP parameters which do not vary over time, we therefor give HRU A and B the same value, and they are calibrated together (denoted with 'hru2', in Table 4.2). Besides that, we included the other arable fields (OA) and the apple orchard (C) in the calibration of the surface storage depth.

During initial model testing we found that the surface storage depth before runoff (h_0) influenced daily runoff substantially. The soil roughness and related storage depth on arable fields changes depending on the season and the crop type. SWAP provides the option to vary the h_0 over time, we applied this by creating four different h_0 parameters: h_0_winter, h_0_arable, h_0_apple and h_0_potato (see Table 4.2). The h_0_apple was applied for HRU C, the apple orchard and did not vary over time. For the HRU's A, B, OA in the winter period h_0_winter was used, when potatoes were cultivated on a HRU h_0_potato was modelled and for all other arable crops h_0_arable was applied. In the QRN sample each of these four h_0 parameters was calibrated. The possible range for each h_0 parameter was estimated based on soil roughness values from literature (J.G. Kroes et al., 2017; Potter, 1990). In addition, the runoff resistance of the soil surface (γ_r) was varied for the combined HRU's A and B (hru2).

The soil hydrology in SWAP is sensitive for the parameters describing infiltration (Wesseling et al., 2020), mainly the saturated hydraulic conductivity (k_{sat}) and the n parameter in the Mualem van Genuchten equation (n_m). Both parameters were calibrated for the combined HRU A and B (hru2) but did not vary over time. The range of variation was based on the SWAP manual (J.G. Kroes et al., 2017) and field studies (Rawls et al., 1983). In total seven parameters were calibrated for the hydrology simulations with SWAP (Figure 4.2, modelling step A). All other parameters were fixed based on literature or field observations, more details and a table with all parameter values are given in the supplementary materials (Table 4.8).

Setup of SWAP for metobromuron

To simulate pesticide fate and degradation in SWAP both heat flow and solute calculations need to be included. For heat flow in the soil default values from the SWAP manual were used. Degradation of pesticides was simulated with a first order decay equation (Boesten and Van der Linden, 1991). In SWAP the reference degradation, or soil half-life time (DT_{50}) is influenced by soil moisture, temperature, and soil depth. After model testing we selected the constant (B) in the soil moisture reduction equation, the parameter (γ_T) in the temperature factor equation as described in the SWAP manual, in combination with the DT_{50}, for the calibration of the pesticide concentration in the upper 1.0 centimetre of the soil (Table 4.2). Variations for the DT_{50} are based on the reported values for silt loam soils in the EFSA assessment of metobromuron (European

Food Safety Authority, 2014). The parameters for pesticide fate simulations were homogeneous for all simulated HRUs.

Table 4.2 *Parameters and related distributions to optimize hydrology and metobromuron simulations in SWAP.*

parameter	HRU effected	Distribution[2]	model step	source
h_0_winter	hru2[1], C, OA	$U(1.0, 4.0)$	hydrology	Estimate, (J.G. Kroes et al., 2017; Potter, 1990)
h_0_arable	hru2, OA	$U(0.01, 1.5)$	hydrology	
h_0_potato	hru2	$U(0.01, 0.8)$	hydrology	
h_0_apple	C	$U(0.2, 2.0)$	hydrology	
γ_r	hru2	$U(0.01, 0.3)$	hydrology	
n_m	hru2	$U(1.001, 1.8)$	hydrology	
k_{sat}[3]	hru2	$U(0.1, 2.5)$	hydrology	(Heinen et al., 2020; Rawls et al., 1983)
DT_{50}	catchment	$U(5, 40)$	solute	Estimate, (EFSA, 2014)
γ_T	catchment	$U(0.0001, 0.025)$	solute	Estimate, (Kroes et al., 2017)
B	catchment	$U(0.5, 1.5)$	solute	

[1]hru2: the two main arable fields in this study, (A, B, figure 4.1) are grouped to find an optimal value for selected parameters in SWAP. [2]All distributions are uniform, denoted as *U*(lower, upper)

[3]In SWAP the unit of k_{sat} is $cm\ day^{-1}$ instead of $mm\ h^{-1}$ in OpenLISEM. The range in this table is given in $cm\ day^{-1}$.

Pesticides can be applied in SWAP by adding a solute concentration to irrigation events. From the observation dataset we knew the dates and applied concentrations of metobromuron in our study area. Since metobromuron is a pre-emergence herbicide we simulated the pesticide application directly on the soil.

Setup of OpenLISEM for runoff and erosion

Initialization of OpenLISEM

To simulate a rainfall-runoff event with OpenLISEM, data on topography, land use and related crop cover, soil characteristics and precipitation is required. We copied the setup of OpenLISEM as described in chapter 3. In summary, we simulated the infiltration with a two layer Green & Ampt model (Downer et al., 2003; Green and Ampt, 1911). The same soil layers were applied as for the SWAP hydrology simulations (0 – 30 and 30 – 120 cm). Parameters were spatially applied either homogeneously over the catchment (e.g. median soil texture) or specifically for each HRU (e.g. k_{sat} or crop cover). By applying the temporal constraint strategy, parameters like crop cover, soil roughness and surface flow resistance are varied over time (Lefrancq et al., 2017b), which improves the event specific initialization of OpenLISEM. In section 3.2.5 the general setup of OpenLISEM is described and Table 3.8 (section 3.6.2) details all parameter settings.

Contrary to chapter 3 of this thesis, the initial soil moisture content for this study was obtained from the SWAP simulation in modelling step A. For each HRU the mean soil moisture content for the two soil layers on the day before the rainfall event occurred, was used as initial soil moisture content for OpenLISEM, the differences between the OLP setup between chapter 3 and 4 are detailed in Table 4.9 (section 4.6.1).

Selection of parameters for calibration

For the calibration of OpenLISEM for runoff and erosion we selected the most influential parameters and forcings based on literature. Precipitation (P) data has a large uncertainty (Overeem et al., 2009), and variations in precipitation will influence runoff and infiltration. As default we used the tipping bucket precipitation data from our observation dataset as input for OpenLISEM. For two events (2020-08-12 and 2020-08-16) this was not available, and KNMI precipitation radar data was used instead. Based on the analysis of the KNMI radar data (Overeem et al., 2009) we applied an uncertainty of ± 20% homogeneously over the whole catchment (see Table 4.3).

Parallel to the calibration of hydrology in SWAP (step 1A) we varied parameters influencing overland flow and infiltration to calibrate runoff simulations with OpenLISEM. We calibrated each selected parameter for the HRU's A, B, OA, and C. HRU A and B were calibrated separately when potatoes were cultivated (in 2019 on A, in 2020 on B), for other crops they were joined with OA. This resulted in three classes for each parameter to be calibrated: arable, potato and apple. For the other HRU's (CH and G) all parameters were fixed.

The Manning's n (n) describes the surface resistance for overland flow, for each event an initial estimate is made by combining data on soil roughness, crop cover and litter (Phillips, 1989), however this calculation is very rough and we varied the n with ± 90%. Infiltration predictions in OpenLISEM, described with the Green and Ampt equations are sensitive to the initial soil moisture content (θ), the saturated hydraulic conductivity (k_{sat}) and the wetted front capillary pressure (Ψ) (Lefrancq et al., 2017b; Wu et al., 2021). The range of k_{sat} and Ψ was obtained from literature (Heinen et al., 2020; Rawls et al., 1983), and for the θ-value obtained from SWAP we estimate an uncertainty of ± 20%.

For erosion simulations the cohesion of the soil (S_c) influences the detachment of soil particles by raindrops or runoff. We selected initial values based on literature for arable agriculture on loess soils (Baets et al., 2008) and estimated an uncertainty of ± 70%. On the fields with potato cultivation, wheel tracks are a prominent feature, which influence runoff and erosion (Prasuhn, 2020). Since these are more compacted and have less roughness, we calibrated n and C separately for the wheel tracks.

Table 4.3 *Selected parameters for QRN simulations to optimize runoff and sediment input parameters for OpenLISEM.*

parameter	HRU effected[4]	Distribution[2]	Method[3]	model step	source
P	catchment	$U(0.8, 1.2)$	M	Runoff	(Overeem et al., 2009)
n	A, B, OA, C, wh[1]	$U(0.1, 1.9)$	M	Runoff	(Phillips, 1989), estimate
k_{sat}	A, B, OA, C	$U(0.2, 5)$	Abs	Runoff	(Heinen et al., 2020; Rawls et al., 1983)
Ψ	A, B, OA, C	$U(2, 17)$	Abs	Runoff	(Rawls et al., 1983)
θ	A, B, OA, C	$U(0.8, 1.2)$	M	Runoff	Estimate
S_c	A, B, OA, C, wh	$U(0.3, 1.7)$	M	Sediment	(Baets et al., 2008), estimate

[1]wh: wheel tracks, these are separately simulated for potato cultivation on HRU A and B

[2]All distributions are uniform, denoted as U(lower, upper)

[3]Two methods of applying the variation are used, depending on the parameter and best way of adjusting the input: multiplication (M) and absolute values (Abs).

[4]The number of varied parameters depends on the spatial representation. In total 14 parameters are varied for runoff and in the next model step four parameters for sediment optimization.

Performance statistics for model evaluation

The simulated model output, i.e. discharge at the outlet, suspended sediment and pesticide loads and concentrations, were compared to observations. To quantify model performance we used the Kling-Gupta Efficiency coefficient (KGE), which combines the linear correlation between the observations and simulations with a variability error and a bias term (Gupta et al., 2009).

For the metobromuron simulations with SWAP (modelling step 1B), we only have 5 survey days through time to evaluate the model performance. However, per survey day we obtained multiple samples per field, which resulted in a range of possible concentrations. We therefore calculated the performance of SWAP-solute with a combination of the root mean squared error (RMSE) and an overlap indicator, in this chapter abbreviated with ROI. The overlap indicator returns 1 if the simulated concentration is within the range of values observed on the field, and 0 if it does not fall within this range. Over the whole simulated period, the mean of the overlap values is taken. The ROI is calculated with:

$$ROI = \left(1 - \frac{RMSE}{10 \cdot \overline{C_{obs}}} + \frac{\sum_{i=1}^{n} I_{(C_{ol},C_{ou})}(C_{sim})}{n}\right)/2 \qquad Eq\ 4.1$$

With $\overline{C_{obs}}$, the mean observed concentration, C_{ol} the lowest observed concentration on the field, C_{ou} the highest observed concentration on the field and C_{sim} the simulated concentration on the field, all in $\mu g\ kg^{-1}$, n is the number of surveys and $I_{(C_{ol},C_{ou})}$ the overlap indicator calculated with:

$$I_{(C_{ol},C_{ou})}(C_{sim}) = \begin{cases} 1 & \text{if } C_{ol} < C_{sim} \text{ and } C_{sim} < C_{ou} \\ 0 & \text{otherwise} \end{cases} \qquad Eq\ 4.2$$

When the RMSE = 0 and the simulations overlap the range of observations during each survey the ROI = 1.0, the ROI will decrease with less overlap or larger RMSE values. In the supplementary materials (section 4.6.2, Figure 4.14) a comparison between the best runs for metobromuron simulations with SWAP, based on different GOF's (ROI, RMSE, NSE and KGE) shows that the ROI optimizes the model by including both high and low observed concentrations, where the other GOF's prioritize the high concentrations and do not simulate the slow degradation at lower concentrations correctly.

4.2.5 GSA for OLP

SOBOL variance based Global Sensitivity Analysis for OpenLISEM-pesticide

Setup of the GSA

Sobol' indices quantify the portion of the output variance of the model that can be attributed to the variance of one or multiple input parameters (Puy et al., 2022; Sobol′, 1993). The first-order indices, which quantify the variance apportioned to a single parameter without interactions, can be used to prioritize parameters (Pianosi et al., 2016). However, often parameters also interact with each other up to multiple orders. The total-order indices measures the first-order effect of a specific parameter in combination with its interactions with all other parameters included in the GSA (Puy et al., 2022). By including a dummy variable, which does not have any influence on the model output, the numerical approximation error of the indices can be estimated (Khorashadi Zadeh et al., 2017). If the total-order index of a parameter is lower than the total-order index of the dummy variable, it can be assumed to be non-influential on the model output. The choice of estimator equation to calculate the first and total-order indices, can influence the results of the GSA. In this study we used the first-order estimator by Saltelli (Saltelli et al., 2010) and the total order estimator by Jansen (Jansen, 1999) as these are reported to produce overall reliable results (Puy et al., 2022).

We did not include calculations of second or higher order indices since we were constrained by computational capacity. However, the results allow to qualitatively assess parameter interactions.

Besides the parameters in a model, also the model forcings influence the variance in the model output. For OLP these consist of the pesticide concentration at the start of the event (C_0) and the settings for the primary processes of each event (e) simulated by OpenLISEM. A strength of GSA is that model forcings can also be included in the analysis (Pianosi et al., 2016). Although 'event' is not a scalar, but a nominal value, it can be included in the calculation of first and total-order Sobol' indices because these do not use the input variability for calculation of the indices (Baroni and Tarantola, 2014), which is an additional reason to use this GSA methods.

Model output for Sobol' indices

The Sobol' indices are calculated based on the variance of the model output (y). For OLP multiple options exist to use for y, for example the total transported mass of pesticide, or a performance metric like the KGE or the mean error (ME). The choice of used y might influence the analysis results of the GSA. Besides that, if the distribution of y is highly-skewed, which can be the case for e.g. the KGE, this can break the required assumption that the output variance is a reasonable proxy for uncertainty (Khorashadi Zadeh et al., 2017; Pianosi et al., 2016). In this study we used KGE, and the relative total discharged mass (M_r), for both DP and PP transport as output measures. We selected KGE because we use it also in the other objectives of this study to evaluate the performance of OLP. Besides KGE, we also included M_r as a metric with a more homogeneous output distribution. The M_r is calculated with:

$$M_r = \frac{M_e^i}{\overline{M_e}} \qquad Eq\ 4.3$$

With M_e^i, the transported mass (either DP or PP) for a specific simulation of event number e and $\overline{M_e}$ the mean simulated transported mass for event e. This calculation was done to adjust for the difference in expected transported mass due to different initial conditions of the events (e.g initial pesticide concentration in the soil). Due to this property the Mr is a useful metric assess the influence of variation of an input parameter on the total transported mass. Besides that, M_r is more useful to investigate relations, trends and interactions between the other model parameters based on scatter plots due to its homogeneous distribution.

Setup of OpenLISEM-pesticide

In OLP five parameters describe the uptake and transport of pesticides: the mass transfer rate (k_{film}) for uptake of DP pesticides in the runoff, the mixing layer depth (z_m), the soil-water partitioning coefficient (k_d) and the coefficient (α) and exponent (β) in the enrichment ratio equation for PP uptake of pesticides. Besides these we selected two model forcings: event (e) and initial pesticide concentration (C_0) for the GSA. For a GSA the sampled range for the model parameters and forcings should cover the uncertainty in the input (Pianosi et al., 2016). In table 4.4 the selected ranges for all parameters are shown. Since six events are included in this study *e* varies between 1 and 6. In this analysis *e* represents the whole set of fixed settings for hydrology and sediment dynamics, as well as the rainfall characteristics and catchment situation (e.g., crop cultivation conditions on the day of the event, or number of days after the last pesticide application). The C_0 was obtained from the SWAP solute simulations in modelling step 1B, an uncertainty range of ± 20% was assumed. The range for z_m and k_{film} are based upon reported values from previous pesticide uptake modelling studies (Havis et al., 1992; Joyce et al., 2010; Watanabe and Grismer, 2003), the k_{film} upper value of 0.1 $mm\ sec^{-1}$ is close to the instant mixing assumption (see also Ch 3.6.2, Table 3.10).

Table 4.4 *Selected parameters and distribution used for the global sensitivity analysis in OLP.*

Parameter	Distribution[1]	Method[2]	source
e	$DU(1, 6)^2$	Abs	-
C_0	$U(0.8, 1.2)$	M	SWAP simulations, estimate
k_{film}	$U(0.0001, 0.1)$	Abs	(Havis et al., 1992; Joyce et al., 2010; Watanabe and Grismer, 2003)
z_m	$U(0.1, 25)$	Abs	
α	$U(3, 17)$	Abs	(Menzel, 1980), estimate
β	$U(-0.5, -0.04)$	Abs	
k_{oc}	$U(122, 199)$	Abs	(European Food Safety Authority, 2014; Lewis et al., 2016)

[1] Either uniform (U) or discrete uniform (DU) distributions are used, denoted as: *U*(lower, upper).

[2]Two methods of applying the variation are used, depending on the parameter and best way of adjusting the input: multiplication (M) and absolute values (Abs).

The organic carbon partition coefficients (k_{oc}) for pesticide are reported for regulatory purposes (European Food Safety Authority, 2014), k_d was calculated from the k_{oc} with:

$$k_d = k_{oc} \cdot \frac{OM}{2.0 \cdot 100} \qquad Eq\ 4.4$$

with OM the organic matter content of the soil which is divided by 2.0 to convert to organic carbon (Pribyl, 2010). The OM in our study area is 3.6 % resulting in k_d values between 2.2 – 3.6 $mL\ g^{-1}$. The enrichment of pesticide concentrations in detached sediment was studied and described by Menzel (1980) and we varied both parameters (α and β) in the enrichment ratio equation over the range observed in the field experiment performed in that study.

4.2.6 Evaluation of OpenLISEM-pesticide

The final modelling step in this chapter is an evaluation of the performance of OLP to simulate the transport processes of metobromuron in our study area. To evaluate OLP for both DP and PP transport we need an event in which also DP transport was observed. Since this only occurred in two events and one event of these was already extensively studied for chapter 3 (2019-05-28) we selected the other event (2020-06-17) for the evaluation of OLP. Due to the low number of events available for this study, we used all for the GSA. For the model evaluation we excluded the event on 2020-06-17 from our GSA simulations. Based on the parameter distributions found for the other five events, we evaluated the performance of OLP with a random ensemble simulation (n = 50).

We evaluated two different cases, first only the OLP parameters were sampled, and the best parameter set for runoff and sediment dynamics was fixed. In the second case also the runoff and sediment dynamics were sampled, and we varied these between the 10 best parameter sets selected during the calibration of OpenLISEM (modelling steps 1C and 1D).

The parameters for OLP that were identified as non-influential by the GSA were fixed to the mean of their range in the GSA. For the parameters identified as influential the probability density function of the behavioural simulations was used to sample the parameter sets for the 50 ensemble simulations. The threshold for behavioural simulation depends on the quality of the available simulations. For PP we selected a threshold of KGE = 0.5, which resulted in 2868 of 9216 available simulations to be included. In case of DP transport, one event was available with observed metobromuron transport (2019-05-28). And only a small number of simulations from the GSA had a good performance: when a KGE threshold of 0.0 was used seven (7) events were accepted, and when we decreased the threshold to -0.41, 14 events were accepted. The KGE value of -0.41 is the benchmark where the simulations have a predictive performance equal to the mean of the observations (Knoben et al., 2019). These numbers of accepted events are too small to calculate meaningful statistics, so we defined parameter ranges based on a qualitative assessment for DP transport. For both the DP and PP parameters we sampled from a uniform distribution since the used data did not allow for the selection of a more descriptive distribution.

4.3 Results

4.3.1 Hydrology and solute simulations with SWAP

The selected parameters for SWAP resulted in daily discharge simulations with a KGE value of 0.63. Although daily discharge peaks were sometimes over- or underestimated (Figure 4.3-A), the cumulative discharge for each growing season and over the whole period was simulated well (Figure 4.3-B). The main sources of discharge as simulated by SWAP were the arable agriculture fields (HRUs A, B and OA), the road and channel network (CH) also contributed a small portion. The land area covered with grass and the apple orchard did not produce substantial amounts of discharge in this simulation (Figure 4.3-B).

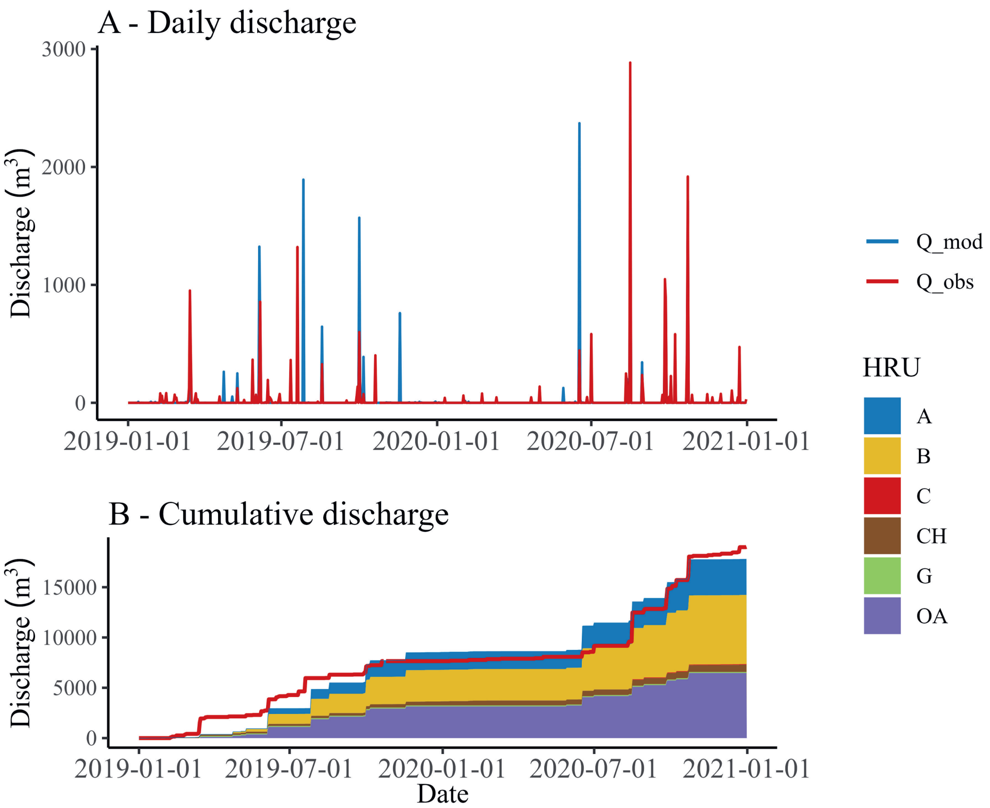

Figure 4.3 *Observed and simulated discharge in 2019 and 2020 in the study area. The daily discharge shows the discharge at the outlet, the cumulative discharge shows the development of the observed discharge at the outlet and the modelled contribution of each HRU.*

Compared to the observations, the early months in each year had lower simulated runoff, and in the autumn months more runoff was simulated. The calibrated parameter values for the hydrology simulation are presented in Table 4.5. The infiltration related parameters are selected close to the values found from literature. The n_m in the Mualem Van Genuchten equations is reported for this soils to be 1.302 in the Staringreeks (Heinen et al., 2020), we selected a value of 1.2881 for this. The k_{sat}, with a value of 1.48 $cm\ day^{-1}$, is a bit higher than reported in the Staringreeks (0.9 $cm\ day^{-1}$). The default value for γ_r is 0.5 day (J.G. Kroes et al., 2017), the selected value of 0.2592 day corresponds with the slopes and relatively fast runoff times in our study area. The different surface storage depths (h_0) selected, reflect the differences in surface roughness of different land use types. Roughness increases in the following order: potatoes, arable land, the apple orchard, and winter fields.

Figure 4.4 shows the calibrated SWAP-solute simulation compared to the observations. The ROI index is 0.18. Although the number of observations is low, and in 2020 no samples were taken during the simulated high peak concentrations of metobromuron, the simulated concentrations on both fields correspond to the available data points or ranges. In Table 4.5 the calibrated values are given. The DT_{50} selected is 14.2 days, compared to reported values in literature of 22.4 days (European Food Safety Authority, 2014). The effect of B (0.8809) and γ_T (0.0022) are both a bit higher in our simulations than the reported default values in the SWAP manual (J.G. Kroes et al., 2017).

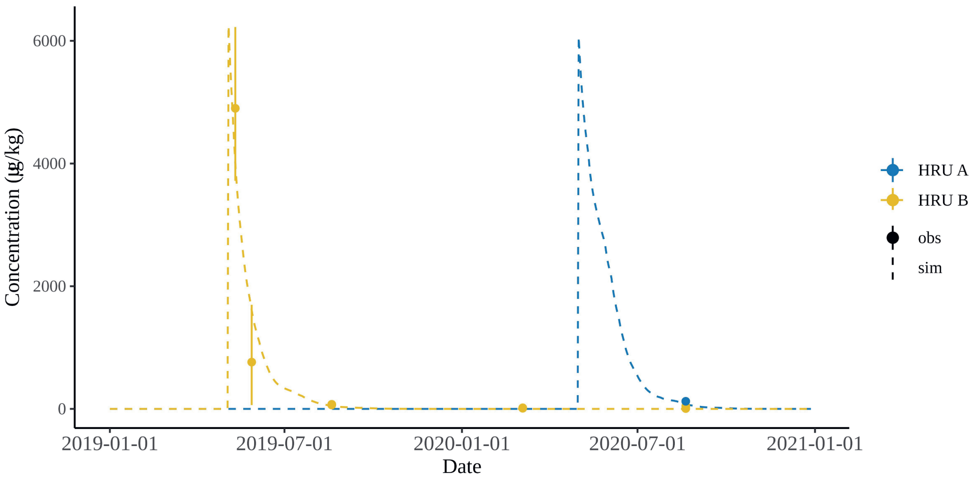

Figure 4.4 *Observed and simulated metobromuron concentration in the upper 1.0 centimetre of the soil. Simulations are done for the two fields were metobromuron was applied. The bars around the observation points denote the maximum and minimum measured concentration on a field ± the observation uncertainty.*

Table 4.5 *Selected values, after calibration, for SWAP hydrology and solute simulations.*

Hydrology	Selected value	Default value[1]	Solute	Selected value	Default value
h_0_winter	3.1094	0.2	DT_{50}	14.2285	22.4
h_0_arable	0.173		B	0.8809	0.7
h_0_apple	1.2969		γ_T	0.0022	0.0
h_0_potato	0.1211				
k_{sat}	1.4875	0.9			
n_m	1.2881	1.302			
γ_r	0.2592	0.5			

[1] The default values are the mean values from literature sources, or proposed by the SWAP manual (J.G. Kroes et al., 2017)

4.3.2 Runoff and erosion simulations with OpenLISEM

The selected best simulations for the 6 events result in KGE values between 0.61 and 0.95 for runoff and 0.22 and 0.93 for sediment load (Table 4.6). All selected simulations for runoff and sediment dynamics are shown in Figure 4.5. The simulations for the event on 2019-08-18 have the lowest performance. For this event, the pattern of the hydrograph does resemble the shape of the observations, but the timing of the simulation is too late. This also causes the sediment load to have a wrong timing. All simulations for the other events perform well, for both runoff and sediment discharge.

Table 4.6 *KGE values for simulated runoff and sediment discharge compared to observations at the outlet.*

Event	Runoff	Sediment
2019-05-28	0.89	0.62
2019-08-19	0.61	0.22
2020-06-17	0.95	0.77
2020-08-12	0.79	0.66
2020-08-16	0.80	0.93
2020-10-22	0.87	0.85

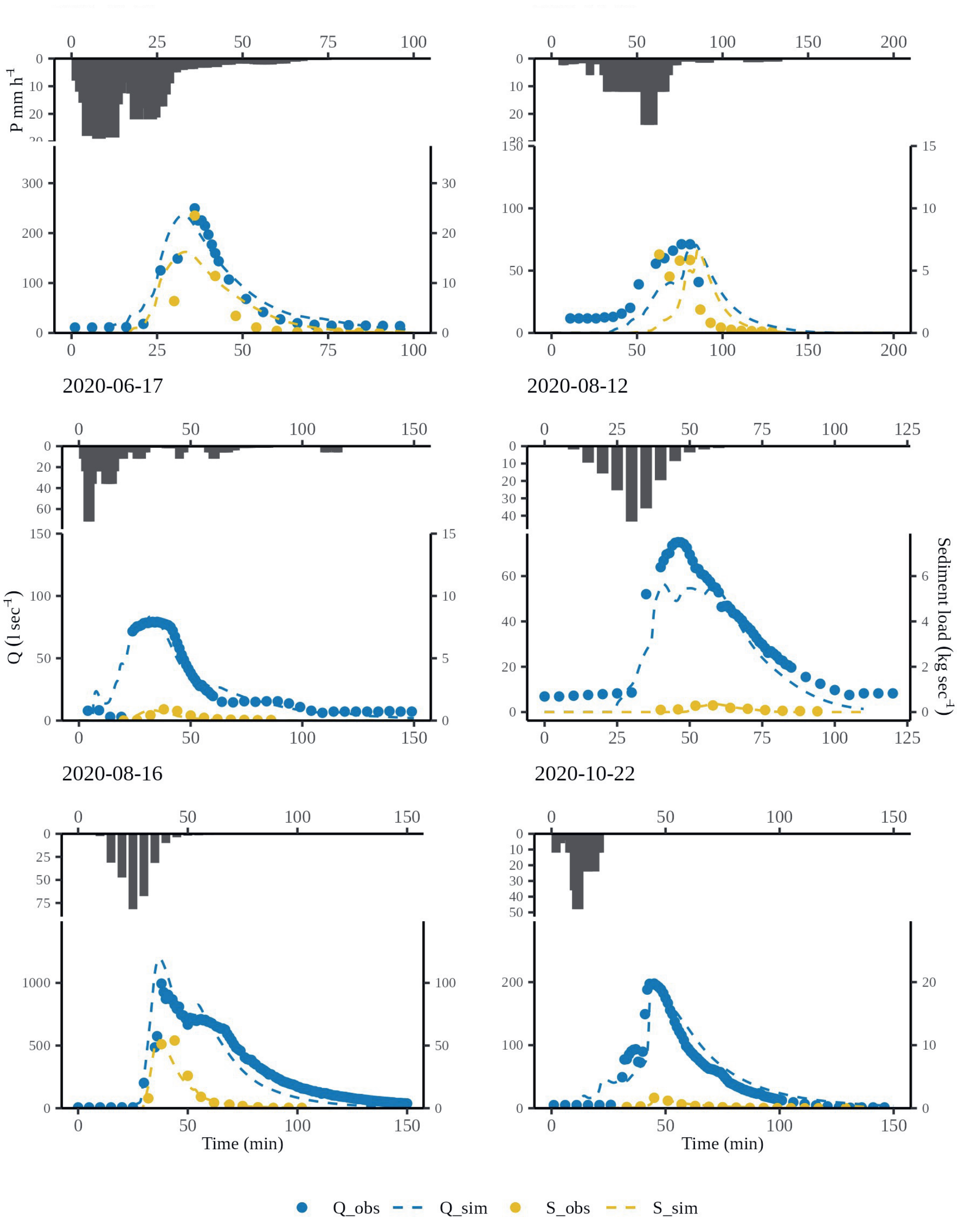

Figure 4.5 *Precipitation and observed and simulated runoff and sediment discharge for the six rainfall-runoff events.*

Selection of best simulation, an example

In figure 4.6, the 10 simulations with the highest KGE for runoff simulations (modelling step C) for the event on 2020-08-16 are shown. The KGE-values of these simulations range from 0.78 to 0.92, however not all the simulations show a pattern that corresponds to the observed runoff during the event. In the observations two peaks of runoff are distinguishable, a first fast response with the highest discharge, and then around 50 minutes a shoulder in the falling limb shows a second peak. In the simulations these two peaks are also visible, the first from the potato field (HRU A) and the second from the field with cereal stubbles (HRU B). However, most of the simulations with a high KGE predict a higher second peak from the cereal stubbles compared to the potato field, including the run with the highest KGE (red line in Figure 4.6). We qualitatively selected the final run, with a slightly lower KGE (0.80), because this simulation showed the higher peak from the potato field correctly. This pattern can be further checked when also simulating sediment dynamics (Figure 4.5-E). During the observations in the field, many signs of erosion were observed on the potato field, while on the contrary, no signs of erosion where visible on the field with cereals stubble (see also the comparison in section 3.3.3). The observed sediment load at the outlet also drops rapidly around 50 minutes, suggesting that the second discharge peak did not contain high sediment concentrations. With the calibrated parameter sets for both runoff and sediment dynamics, this is well simulated.

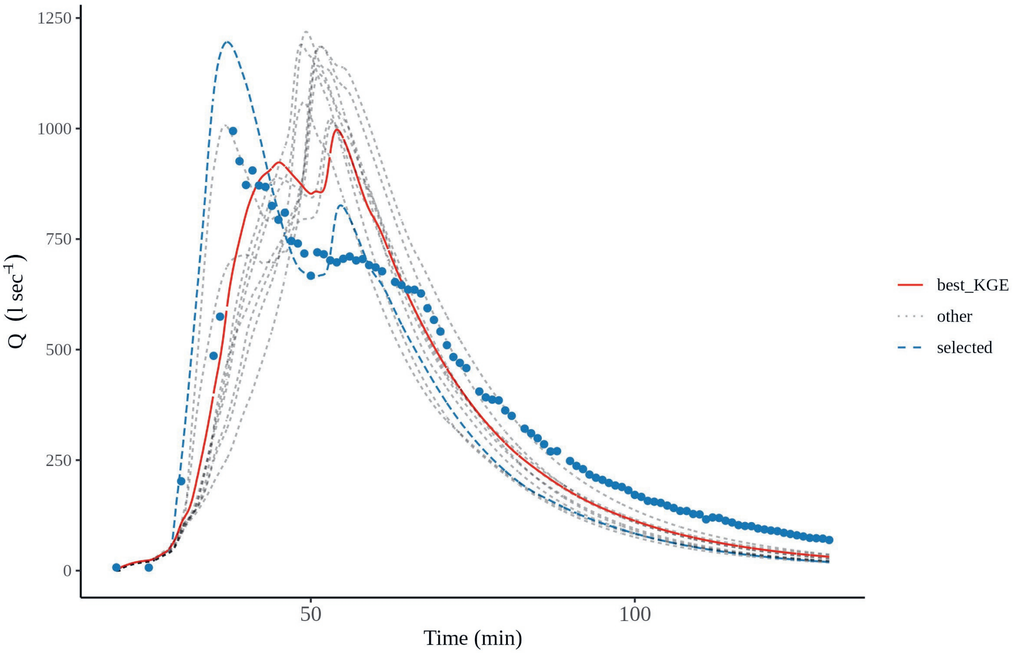

Figure 4.6 *Comparison of the 10 simulations with highest KGE for runoff for the event on 2020-08-16.*

4.3.3 Global sensitivity analysis for OpenLISEM-pesticide

OLP simulates transport of pesticides in dissolved (DP) and particulate phase (PP). These are two different model outputs, and in this study, we evaluate them separately. In the GSA we varied the five parameters introduced in OLP: soil-water partitioning (k_{oc}), the mass transfer rate (k_{film}), the mixing layer depth (z_m) and the coefficient (α) and exponent (β) in the enrichment ratio equation, in combination with two model forcings: event (e) and initial metobromuron concentration (C_0). As model output, we used both KGE and the relative transported mass (M_r). The output distribution of the KGE for both DP and PP transport was highly-skewed, for the M_r the output distribution was more homogeneous. The distributions are shown in section 4.6.3, Figure 4.15 for KGE and Figure 4.16 for M_r.

Sobol' indices for DP and PP transport in OLP

Figure 4.7 shows the Sobol' indices for PP and DP transport, calculated for both the M_r and KGE as model output. The most variance with KGE as model output (Figure 4.7, A and B) is attributed to e. The variations between events in runoff and sediment dynamics caused more variation of the KGE for both PP and DP than the specific parameters in OLP that describe pesticide uptake and transport. For PP transport e is the only model input with a significant first order index. In case of DP transport the most influential OLP specific parameter was found to be z_m, with a first order index of 0.28, which is substantially more than the other parameters involved in DP transport. The other parameter with a significant first order index is k_{film}, although its effect on the model output is about five times smaller than that of z_m.

When using M_r as model output (Figure 4.7, C and D) the effects of e on the variance in model output are reduced. As a result, the attributed variance on the model output for each parameter within one simulated event is now calculated. For PP transport we see a substantial change in the sum of the first order indices: less interaction occurs, and the sum of the first order indices increases from 0.22 to 0.77 for KGE or M_r as model output respectively. β, z_m and α are the influential parameters in order of their first order index. For DP transport there is no change in influential parameters with indices based on KGE or M_r, and z_m is clearly the most influential parameter for dissolved phase transport.

A clear difference between PP and DP transport is the occurrence of interaction: the sum of the first order indices is 0.22 and 0.80 for PP and DP respectively. A low sum of the first order indices indicates that higher order effects, or interactions, between parameters influence the model output substantially, which also shows in the much larger total order indices. For DP transport, some interaction occurs, but first order effects explain a large portion of the variance of KGE. In the case of PP transport, an example of interaction occurs between e and β: the effect of variation in β on the model output depends on the amount of simulated sediment transport in e. When little erosion is simulated within a specific event, the effect of variations in β on the resulting KGE will be much smaller compared to an event where much erosion is simulated.

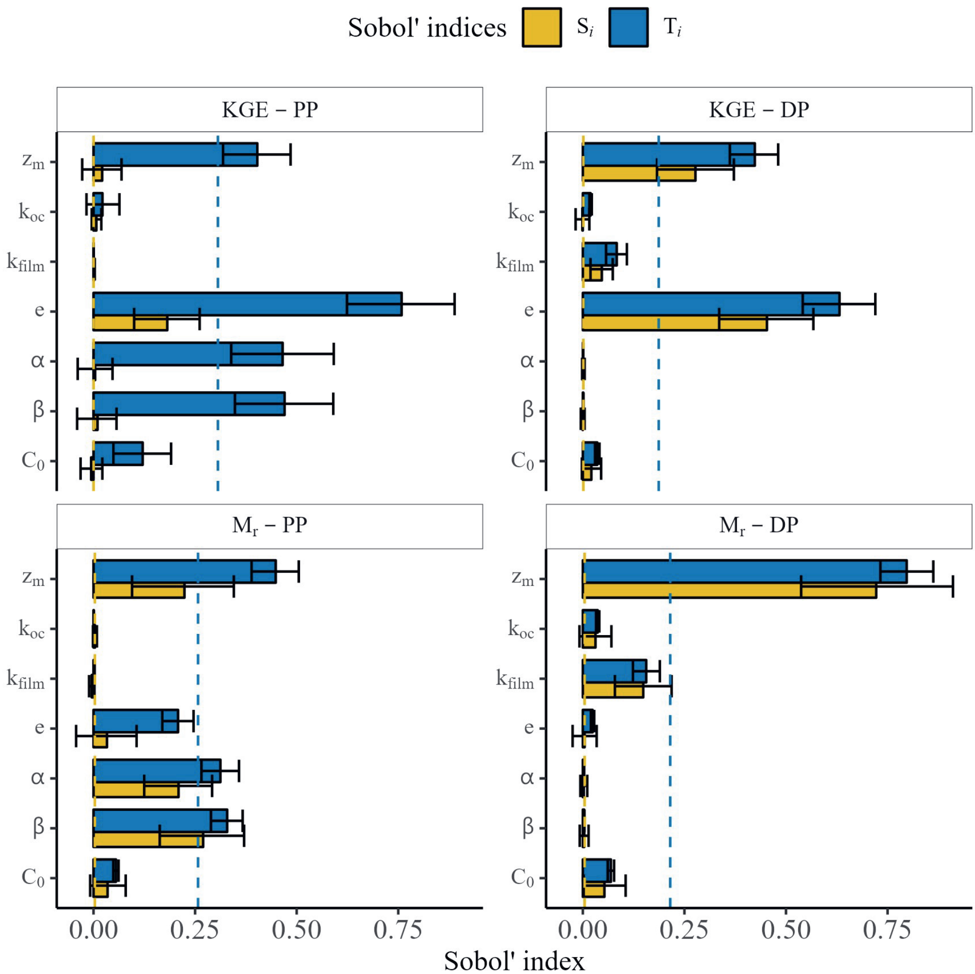

Figure 4.7 *Sobol' first (*S$_i$*) and total order (*T$_i$*) indices for dissolved transport in OLP, with the corresponding 95% confidence intervals. The vertical dotted lines show the numerical approximation error of the indices estimates.*

The purpose of this GSA was to determine influential parameters and screen for parameters which can be fixed because they do not influence the model output. Based on the presented analysis, the most important model input is e, which entails the whole setup of runoff and erosion simulations in OpenLISEM. When focussing specifically on the newly introduced parameters with OLP, z_m is influential for both PP and DP transport. For DP also k_{film} is influential and for PP the α and β in the enrichment ratio equation are influential. k_{oc} and C_0 are non-influential in both phases and can be fixed. Besides that, for both DP and PP transport, the parameters involved in the uptake of pesticide in the other phase are non-informative for the model output. In case of DP transport these are α and β, in case of PP the k_{film}.

Trends in first order effects

A scatter plot of the parameter values against the model output illustrates how each parameter influences the model output. Figure 4.8 shows the value of the influential parameters for PP and DP transport in OLP against the resulting M_r. The strongest trend is visible for z_m in DP, which also has the largest Sobol' index. For PP, z_m shows the same pattern as for DP transport, although the amplitude of the peak is smaller and there is a larger spread in the M_r for a specific value of z_m. In both phases increasing z_m from 0 to 5 mm also increases the M_r, while from 5 to 25 mm depth the M_r slowly decreases again. The peak around 5 mm depth of z_m, can be explained by the discretization of the pesticide concentration in the soil. The SWAP model output is given in 5 mm steps. When z_m is larger than 5 mm, the concentration is calculated as the mean over the depth, and in that way the concentration decreases with larger mixing layer depths. For the upper 5 mm in the soil, the total amount of available pesticides increases with increasing z_m, because the concentration remains the same.

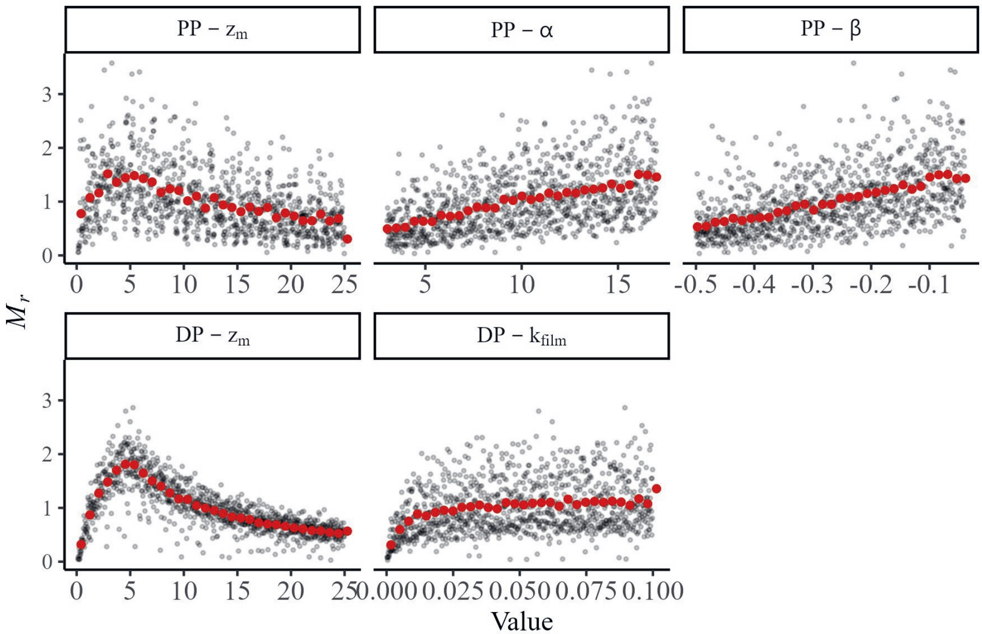

Figure 4.8 *Scatter plots for the variation of Mr depending on the input value. The red dots are bin averages to show the trend in the data.*

The other influential parameters for PP, α and β, both show an increasing trend of M_r with increasing parameter values. In case of DP transport, k_{film} has most influence on M_r when it approaches 0. Since k_{film} describes the uptake of pesticides into the runoff, close to 0 it limits the total transport, however when the k_{film} increases, other parameters will limit the pesticide transport (e.g., the available concentration) and the influence of k_{film} decreases.

Analysis of parameter interactions for PP

Since the total order indices for PP transport were much larger than the first order indices (see Figure 4.7), we expect interactions. To explore these in more detail we compare two input parameters on the x and y-axis with the M_r on a colour scale (Figure 4.9). Colour patterns in the plot are an indication for interaction (Puy et al., 2022). Because e is not a scalar value, we did not include it in this figure. The plots show the second order interactions for the other three influential parameters for PP transport in OLP. A combination of high α and β values results in a higher M_r. On the opposite, low values of z_m in combination with high values of either α or β result in a high M_r. One interesting observation here is that very low values of z_m again seem to result in lower M_r values indicated by the darker green colour over the full range of either α or β when z_m is close to zero.

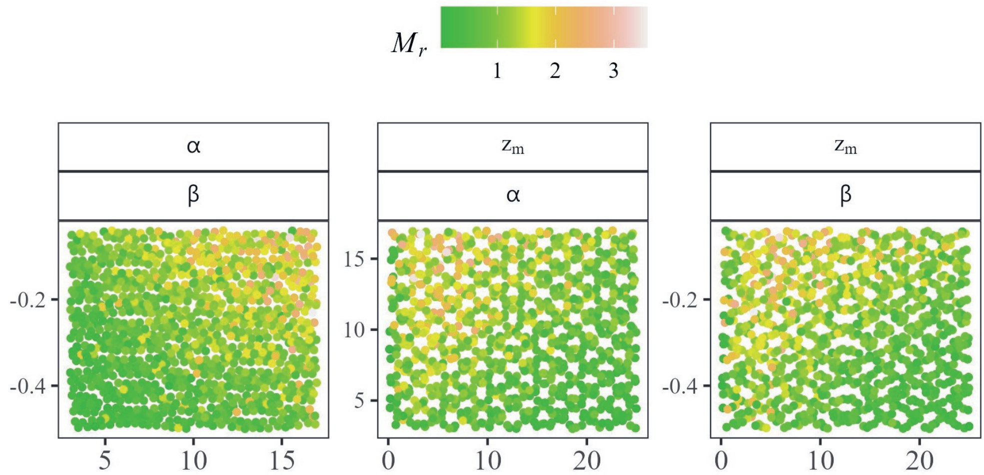

Figure 4.9 *Comparisons of pairs of model input for PP transport with OLP. The upper label refers to the x-axis and the lower to the y-axis. Note: spatial patterns in the scatter plots show the QRN sampling pattern.*

4.3.4 Evaluation of OLP performance

Selection of parameter ranges for the ensemble simulations

The simulations used for the GSA were also used to inform the parameter sampling for the ensemble simulations. The choice for the KGE threshold has a large influence on the derived density functions. For PP transport a KGE threshold > 0.25 results in the selection of three of the five events. However, if a lower KGE threshold is used the quality of the included simulations decreases a lot. In Figure 4.10 the density functions for the three influential parameters (z_m, α, β) for PP transport are shown in combination with the selected range for each parameter for the ensemble simulations. The density functions of the three events differ a lot, which corresponds with the high Sobol' index for *e* in the GSA. The black bars in Figure 4.10 show the range between the lowest and highest value for each parameter which is higher than the 3rd quantile of the mean density. Since the density functions do not have a clear distribution type and variations between events are large, we sampled with a uniform distribution from the selected ranges for the ensemble simulations.

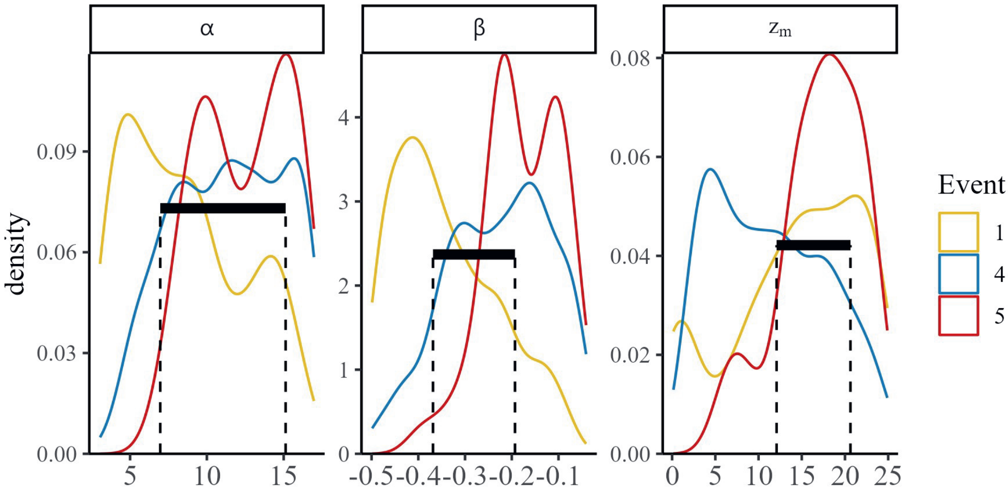

Figure 4.10 *Density functions for the three influential parameters for PP transport, a KGE threshold of 0.5 was used. The black bars show the selected parameter ranges for ensemble simulations to evaluate OLP, where the mean density is larger than the 3rd Quantile of the mean density.*

Figure 4.11 compares the parameter value of the two influential parameters for DP transport (k_{film} and z_m) with the resulting KGE value for the 14 simulations, which had a KGE value above -0.41. The dashed lines show the selected parameter ranges for the two parameters. For z_m we used the selected range from the PP analysis, since this parameter is influential for both phases. For k_{film} we observe a clustering of values at the low end of the range used in the GSA. The selected ranges for the four influential parameters are presented in Table 4.7.

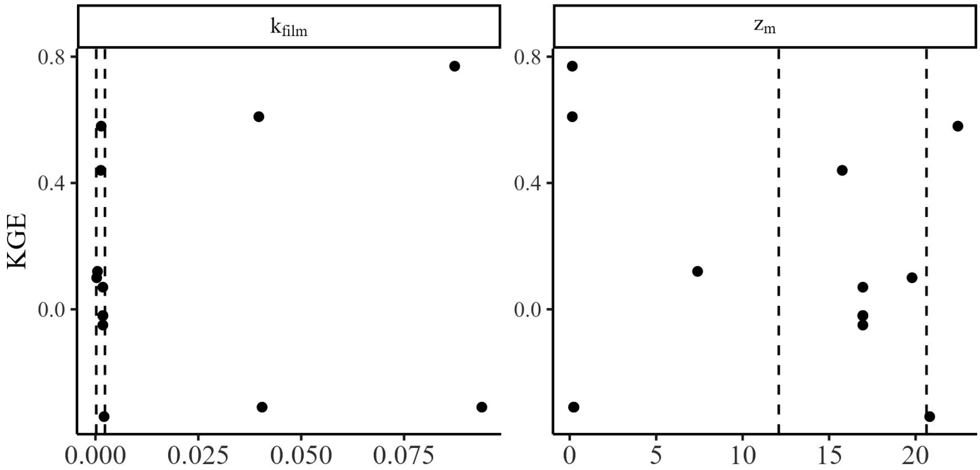

Figure 4.11 *values for k_{film} and z_m resulting in simulation with a KGE value above -0.41 for DP transport. The dashed lines denote the selected parameter range for the ensemble simulations.*

Table 4.7 *Selected parameter values for the ensemble simulations with OLP.*

parameter	value/range
β	*U*(-0.37, -0.19)[1]
α	*U*(6.9, 15.1)
z_m	*U*(12.1, 20.6)
k_{film}	*U*(0.0003, 0.0021)
k_{oc}	160.5
C_0	1.0
[1]Uniform distribution, denoted as *U*(lower, upper)	

Ensemble simulations

We evaluated OLP with two cases, the first case considers variation in the pesticide related parameters, while the runoff and sediment dynamics in OpenLISEM are set to the best simulation based on modelling steps C and D. For the second case, we also varied the runoff and sediment parameters, by varying between the 10 parameters sets with the highest KGE for runoff and sediment dynamics. An overview of the ensemble simulation for case 1 and case 2 is given in Figure 4.12 and Figure 4.13 respectively.

In Figure 4.12, A and B the predicted concentrations for PP and DP are shown. The simulated PP concentration increases instantly to a level between 1.5 and 3 $mg\ kg^{-1}$ and is relatively stable throughout the event. The 90% prediction uncertainty (90PPU) for PP concentration is largest at the start and decreases during the event. At about 90 minutes a large peak in concentration is simulated by OLP, this occurs at the moment the suspended sediment load approaches zero, and this concentration peak is not visible in the simulated pesticide load (Figure 4.12-E). Two PP concentration observations are higher than the 90PPU. The simulated DP concentration shows (Figure 4.12-B) a different pattern compared to the PP concentration: the 90PPU is largest at the peak of the event, both the concentration and the 90PPU decrease towards the start and end of the runoff event. Except for the four lumped samples at the start of the event, the DP observations fall within the 90PPU.

The simulated concentrations, in combination with the runoff or suspended sediment (Figure 4.12 C and D) give a load ($mg\ sec^{-1}$) of pesticide transport. For PP load (Figure 4.12-E), the timing is wrong and the transport peak is simulated too early, which corresponds to the timing error of the suspended sediment simulations. However, the time duration (width) of the peak and the maximum load are similar to the observations. This results in a KGE of 0.54 for the mean of the ensemble simulations. For DP transport visually the load corresponds well to the observations, however due to the error caused by the lumped samples at the start of the event, the KGE is -1.7.

When comparing the ensemble simulations for the two cases, we observe that the 90PPU for PP and DP concentration increases a lot for case two (Figure 4.13 A and B). For PP, the 90PPU range cover lower concentrations (close to 0 mg kg^{-1}) at the start of the event and stays wide during the whole event. From 90 minutes onwards the simulated PP concentration shows many peaks compared to the one high peak in the first ensemble. Similar to the first case, the peaks in the PP concentration are not visible in the discharged load, due to the already very low suspended sediment load simulated at that time. The timing error for the PP load also occurs in case 2, although the varying settings for sediment dynamics increase the 90PPU. Compared to case 1, the concentration in DP stays high after 50 minutes, and the 90PPU is wide until 150 minutes where the simulations end.

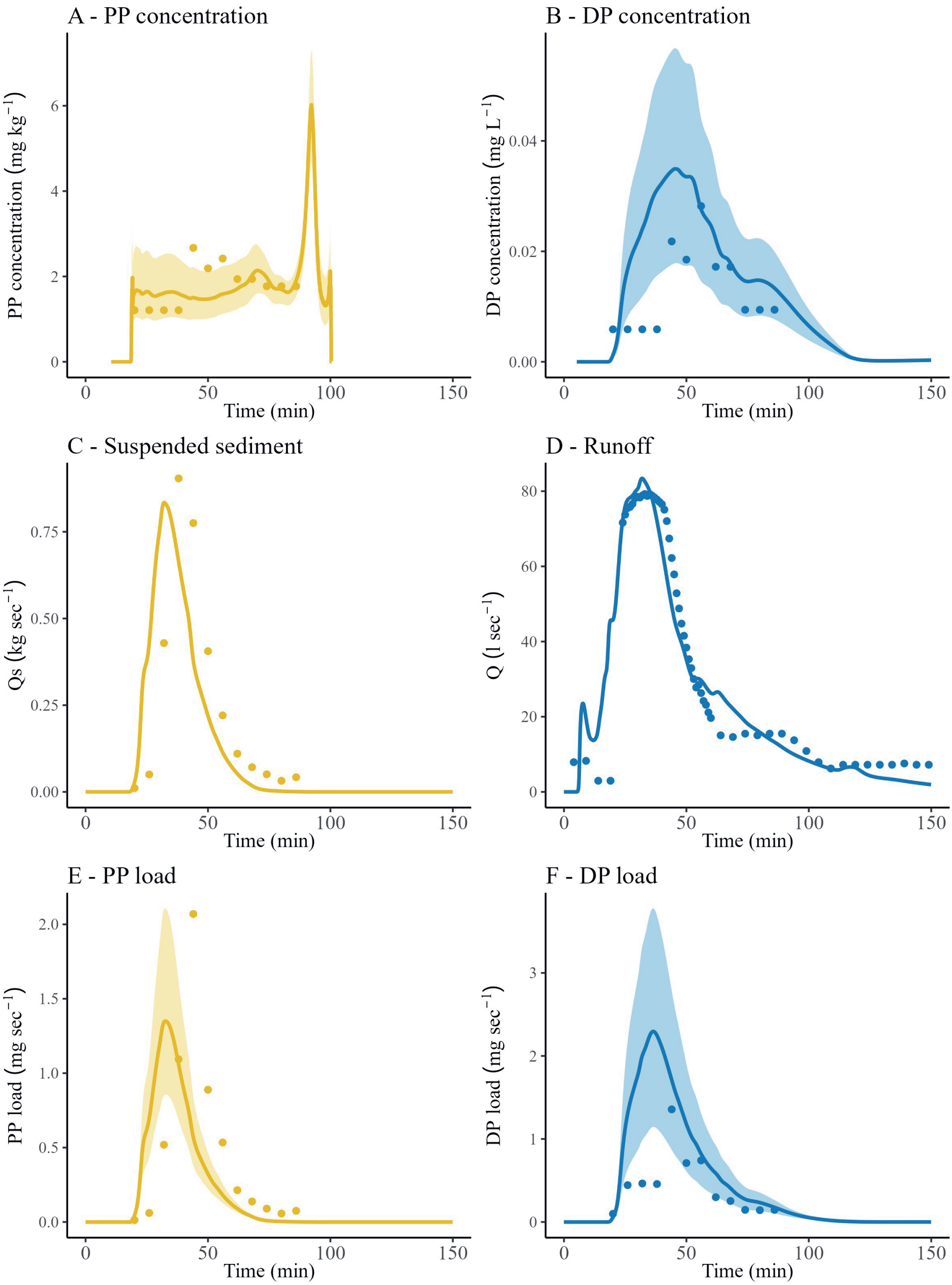

Figure 4.12 *Ensemble simulations of with fixed runoff and sediment parameters for PP and DP pesticide on 2020-06-17.*

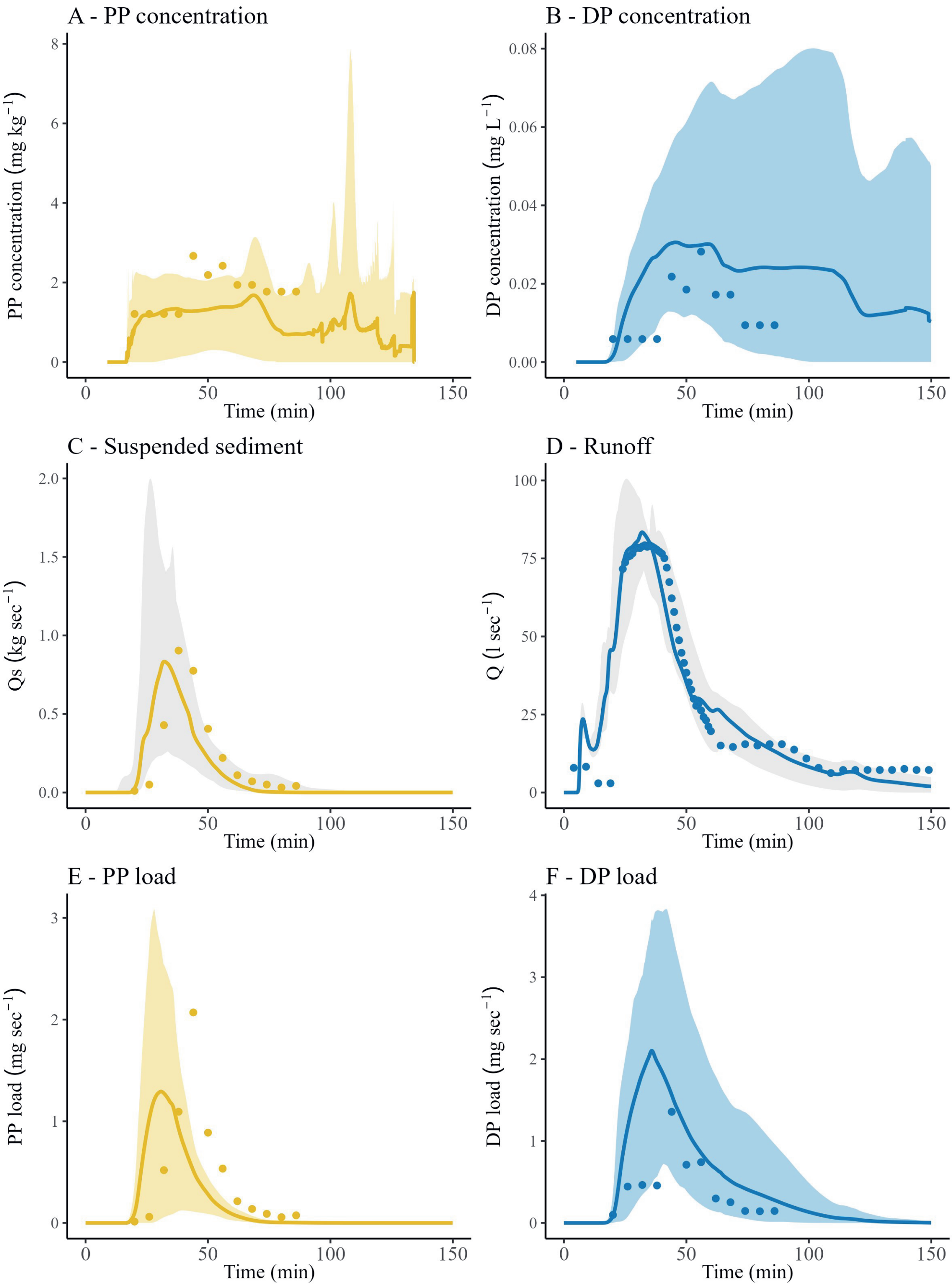

Figure 4.13 *Ensemble simulations of with variation in runoff and sediment parameters for PP and DP pesticide on 2020-06-17.*

4.4 Discussion

Model coupling

We calibrated SWAP for hydrology and pesticide concentrations for 2019 and 2020, to obtain initialization data for the event-based simulations with OpenLISEM. No other applications of SWAP calibrated for daily runoff were found in literature, however it is often applied for vertical flow in the soil (Faúndez Urbina et al., 2020; Wesseling et al., 2020). Several modelling studies on pesticide transfer that include hydrology simulations over full growing seasons use the SWAT model, which performs well compared to observed runoff (Dogan and Karpuzcu, 2023; Shi and Huang, 2021), and better than our SWAP simulations. In our simulations the used precipitation data might contain errors and does not always correspond to the observed runoff. For example, in July 2019 an observed rainfall-runoff event is not simulated and a few days later a high peak in our rainfall data causes runoff, but no discharge is observed (see Figure 4.3). Besides that, the SWAP model does not include the slope of a field when calculating runoff, but in our study area the average slope is 6% which influences runoff patterns substantially (A. Sharpley, 1985). In the next modelling step, the solute simulations with SWAP, we calibrated the pesticide concentration in the top 1.0 centimetre of the soil. Again, we did not find other studies with that specific objective. In SWAP applications that simulate pesticide fate and degradation in the soil, the half-life time (DT_{50}) of the pesticide is used for calibration (D'Andrea et al., 2020; Faúndez Urbina et al., 2020). We combined the DT_{50} with two parameters influencing the degradation based on temperature and soil moisture content. In the GSA by D'Andrea et al (2020) the temperature effect was found to be influential for the concentration of pesticides in the soil.

For small catchments, the event-based simulations with OpenLISEM need event per event calibration to improve performance (Baartman et al., 2012; Lefrancq et al., 2017b). One parameter set for all events cannot explain the variations in observed runoff or erosion between events (Vieira et al., 2022), and different approaches are used to vary parameter sets between events, including season based fitting (Vieira et al., 2022) or applying temporal constraints to parameters (Lefrancq et al., 2017b). We applied the temporal constraints for soil moisture, soil roughness and crop parameters, which lead to well performing simulations after further calibration. In contrast to other studies, we included uncertainty in the precipitation in the calibrations. We used precipitation radar data in combination with tipping bucket data from our own field observations, and both sources of rainfall data contain high spatiotemporal uncertainty (Molini et al., 2005; Overeem et al., 2009), excluding this uncertainty poses the risks of attributing variations in precipitation to other sensitive parameters, for example saturated hydraulic conductivity.

The SWAP and OpenLISEM modelling steps were calibrated by a quantitative and qualitative selection of the best simulation from a parameter space exploration with a limited number of simulations. Most other studies use optimization methods to find the best fit to the observations, including SUFI calibrations (Abbaspour, 2015) for SWAT optimization (Abbasi et al., 2019; Dogan and Karpuzcu, 2023; Shi and Huang, 2021), or parameters estimation methods for OpenLISEM (Lefrancq et al., 2017b; Vieira et al., 2022; Wu et al., 2021). With our approach we did not calibrate to find the best fit possible. However, the used approach has three advantages. First, we explored the whole selected parameters space, which prevents the risk of selecting a local minimum as optimal calibration as also indicated by Skahill and Doherty, (2006). Secondly, we combine the quantitative selecting of a best fit, with a qualitative assessment (see the example in section 3.2.1), which prevents selecting wrong simulations with high quantitative performance metrics (Clark et al., 2021; Knoben et al., 2019). Lastly, this approach limits the computational costs of the analysis, which can become large for OpenLISEM simulations, since it has simulation times ~5 minutes per event.

Sobol' global sensitivity analysis

In recent years, sensitivity analysis were done for models simulating pesticide transfer with runoff on field scale or larger, including SWAT (Shi and Huang, 2021), PESHMELBA (Rouzies et al., 2023), CATHY (Gatel et al., 2019) and VFSMOD (Lauvernet and Muñoz-Carpena, 2018) or for a 1D pesticide runoff model (Huang et al., 2021). Furthermore, some one-at-a-time (OAT) analyses are done for OLP or models with the same conceptualization (Commelin et al., 2024; Havis et al., 1992; Joyce et al., 2008). Our analysis corresponds to the two major conclusions found in these studies. Firstly, when hydrology parameters are included in the GSA, these parameters are the most influential, also for pesticide transport simulations (Gatel et al., 2019; Lauvernet and Muñoz-Carpena, 2018; Rouzies et al., 2023). This is in accordance with our findings, where the variation in event had most influence on the transported pesticides simulated with OLP. Secondly, from the parameters describing the specific processes of pesticide transport, the depth of the mixing layer (z_m) is often influential (Gatel et al., 2019; Havis et al., 1992; Huang et al., 2021; Joyce et al., 2008). In addition, the analysis by Joyce et al. (2008) shows the same trend for z_m as found in this study: pesticide transport decreases towards very small or large values of z_m. The trend in the relation of z_m to transported mass (Figure 4.8), showed the highest transport at 5 mm mixing layer depth. This corresponds with the discretization of pesticide concentrations in the SWAP simulations; SWAP is setup to calculate pesticide concentration for 5 mm layers. If the SWAP model is setup to discretize the pesticide concentration in the soil in smaller steps (e.g., 2 mm layers) this will influence the trend as shown in Figure 4.8. However, in field conditions the upper millimetres of the soil layer are often very heterogeneous, and simulating a detailed concentration gradient may be overfitting of the model, therefor the 5 mm discretization step was chosen in this study. A new aspect of this study and of OLP is the inclusion of PP transport. In a GSA including the particulate transport of phosphate in SWAT, the uptake parameter of particulate phosphate was found to be influential (Shi and Huang, 2021). This corresponds to our findings that the enrichment ratio equation is influential for PP transport. Another innovative aspect in this study is the inclusion of 6 different rainfall runoff events occurring at different moments throughout the growing season. In this way additional complexities and variations in catchment conditions like crop cover, hydrology and pesticide concentration were included in the analysis. A drawback of this approach is that we did not include all these parameter settings explicitly, but lumped them in the parameter e. This is computationally efficient, but including all primary parameters first in a screening (Mai, 2023), and selecting the influential parameters for the GSA will target the parameters with highest influence and result in more detailed understanding of model behaviour. This is for example applied in Rouzies et al. (2023).

Variance based sensitivity analysis, based on Sobol's methods are often applied for environmental models, and are suitable for ranking and screening of influential parameters (Pianosi et al., 2016; Saltelli et al., 2019). However, the full complexity of a distributed model and the simulated process, is never captured in an analysis. For example, the results of the GSA in this study show a large difference between the total and first order indices, especially for PP transport, which suggests higher order interactions. With a more extensive analysis, these interactions can be quantified (Huang et al., 2021; Puy et al., 2022). Due to limitations in the computational capacity available, we did not apply these methods. In section 4.3.3 (Figure 4.9) we explored the interactions qualitatively, these results emphasize the importance of the z_m and the enrichment ratio equation. Another aspect influencing the results of the applied GSA, is the choice in model output metric. A highly-skewed model output might result in wrong indices for a variance based GSA (Khorashadi Zadeh et al., 2017; Pianosi et al., 2016). In this study we used KGE as model output which has a highly-skewed distribution, therefore we also analysed the relative total mass (M_r) as model output which has a more homogeneous output distribution. Both metrics assign the same parameters as influential and non-influential in the same ranking order, which strengthens the findings of the GSA. As an alternative method, Pianosi et al (2016) suggest the use of density-based methods when a highly skewed model output is expected.

The predictive performance of OLP

We evaluated the predictive performance of OLP based on ensemble simulations for one rainfall event. The range of variation for the ensemble simulations was based on the well-performing simulations from the other five events in the GSA. However, the variations between these events are very large, also resulting in wide 90% prediction uncertainty ranges in the simulated DP and PP transport. When the uncertainties in runoff and erosion simulations are included in the ensemble, the prediction uncertainty increases more. We did not find other studies that compared event-based pesticide transport simulations with observations. Often an event-based model is analysed without comparisons to observations (Lauvernet and Muñoz-Carpena, 2018; Rouzies et al., 2023).

Longer term models, simulating transport over weeks to years include some observations (Abbasi et al., 2019; Dogan and Karpuzcu, 2023), however, the amount of observations is too small to evaluate the accuracy of the model. The results of this single event evaluation of OLP correspond to the findings of the GSA: for correct pesticide transport simulations, adequate simulations of runoff and erosion are required. Besides that, reducing the uncertainty of the influential parameters for pesticide transport (z_m, α and β) is required to improve the predictions with OLP.

Applicability and further research

OpenLISEM-pesticide is a detailed, fully distributed model, which can be applied to simulate pesticide transport during rainfall runoff events. Within a catchment, source areas of pesticides can be identified, and besides transport at the outlet also redistribution within the catchment is simulated. Therefore, OLP is suitable to increase our understanding of the processes causing the increased pesticide concentrations observed in many studies in headwater streams (Andrade et al., 2021; Commelin et al., 2022a; Halbach et al., 2021; Mayora et al., 2024). However, OLP is also complex, and requires extensive data and model preparation to perform the simulations. This makes OLP a research tool to further investigate pesticide fate in the environment rather than a tool for site specific decision making or to inform policy makers. The evaluation of OLP in this study shows that predictions without calibration based on observations have a large uncertainty.

To improve the applicability of OLP, improving the process-based description of z_m and the enrichment for PP transport is important. Currently there is no method, or measurement approach to estimate the z_m. In literature, the z_m is related to rainfall intensity (Ahuja, 1990; Havis et al., 1992) and the infiltration rate (Huang et al., 2021). Moreover, alternative conceptualizations are proposed including non-uniform mixing, because the mixing effect decreases with depth (Young and Fry, 2019), or an increasing mixing depth over time (Tong and Ye, 2020). These studies focus on the impact of rainfall and changing soil moisture during the event, but do not include the turbulence and detachment processes that occur with runoff. In addition, the compaction of the soil will also influence the interaction depth of runoff with the soil. Further research, for example by rainfall experiments based on the setup by Havis et al (1992) might provide more insight for a process-based description of the mixing layer depth. Besides improving processes descriptions, a comparison study with other models might provide valuable insight, also in the possibilities for integrated modelling of different spatiotemporal scale, interesting models to include in this comparison could be GSSHA, ZinAgriTra and RZWQM. Another aspect which will enhance the applicability of OLP is a further improvement of the software (e.g., full integration of OLP in the graphical user interface) and clear documentation.

4.5 Conclusions

In this study we aimed to identify the influential parameters for pesticide transport simulations with OpenLISEM-pesticide (OLP) and evaluate the predictive performance of OLP for one rainfall runoff event. We successfully coupled SWAP and OpenLISEM to obtain initial parameterization for OLP simulations of six rainfall-runoff events. The global sensitivity analysis (GSA) showed that the hydrology and erosion parameters have a major influence on the simulated transport of pesticides. The mixing layer depth (z_m) is the main influential parameter of the parameters introduced in OLP, for both dissolved (DP) and particulate phase (PP) transport. Besides that, for DP the mass transfer rate (k_{film}) and for PP the parameters (α and β) in the enrichment ratio equation are influential. The initial concentration and the soil-water partitioning are identified as non-influential parameters. We used this information to evaluate OLP by simulating pesticide transport for one event with an ensemble simulation. The 90% prediction uncertainty covered the observed concentrations well, however in combination with the simulated runoff and erosion errors in the load predictions occurred. The evaluation of OLP in this study shows that predictions without calibration based on observations have a large uncertainty. Further research is needed to improve the process-based descriptions of the mixing layer or the enrichment process, to reduce the uncertainty currently related to these parameters.

4.6 Supplementary Materials

4.6.1 Additional data on model setup

Initialization of SWAP

In Table 4.8 we present all parameter choices made for the hydrology and pesticide (solute) simulations with SWAP. All variables that are not described in the table have the default values as described in the SWAP manual (J.G. Kroes et al., 2017).

Table 4.8 *Initialization choices for SWAP hydrology and pesticide simulations*

		Unit	Spatial variation	Value	method/source
General settings					
HRU		One of the 6 defined hydrologic response units (Figure 4.1)			
simulation period		01-01-2018 - 31-12-2020			Observation period
precipitation		mm	Homogeneous	fixed	Tipping bucket and KNMI radar data
reference evapotranspiration		mm	Homogeneous	fixed	KNMI data
HRU specific settings					
Crop table					Observation dataset (Commelin et al., 2022b)
	cropstart	date	HRU	fixed	
	cropend	date	HRU	fixed	
	cropname		HRU	fixed	
	cropfile	naming convention: 'cropname.crp'			
	croptype		Homogeneous	fixed: 1	All crops use the simple crop model. SWAP manual
Pesticide application table					
application date		date	HRU	fixed	Observation dataset including application date, concentration and water volume per hectare
depth of applied water		mm	HRU	fixed	
concentration		mg cm^{-3}	HRU	fixed	

type of application		HRU	fixed: 1	all applications are directly on the soil
Hydrology				
Groundwater depth	cm	Homogeneous	fixed: -500	Dinoloket.nl, estimate
surface storage depth				Estimate, RR from OpenLISEM initialization
winter	cm	HRU	calibrated	
apples	cm	HRU	calibrated	
potatoes	cm	HRU	calibrated	
cereals	cm	HRU	calibrated	
grass	cm	HRU	fixed: 1.2	
channel	cm	HRU	fixed: 0.2	
runoff resistance	day-1	HRU		SWAP manual
hru2			calibrated	
other HRU			fixed: 0.03	
Exponent runoff resistance	[-]	Homogeneous	fixed: 0.15	
evaporation				
from ponding	[-]	Homogeneous	fixed: 1.25	
from bare soil	[-]	Homogeneous	fixed: 1.0	
Boesten coefficient	[-]	Homogeneous	fixed: 0.35	

Soil profile					
	layer	thickness (cm)	compartments		
	1.1	2	4		Observations, ("Erosienormeringsonderzoek ZUID-LIMBURG," 1994)
	1.2	8	4		
	2.1	20	4		
	2.2	90	9		
Mualem van Genuchten parameters					
Residual water content		L L^{-1}	Homogeneous	fixed: 0.01	Staring series (Heinen et al., 2020). Layer 1 = B14, Layer 2 = O15. Combined with data form the observations.
Saturated water content		L L^{-1}	Homogeneous		
	layer 1			fixed: 0.417	
	layer 2			fixed: 0.41	
Alfa parameter		cm	Homogeneous		
	layer 1			fixed: 0.005	
	layer 2			fixed: 0.008	
N parameter (n_m)		[-]			
	hru2		HRU	calibrated	
	other HRU		HRU	fixed: 1.302	
	layer 2		Homogeneous	fixed: 1.287	
Hydraulic conductivity		cm day^{-1}			
	hru2		HRU	calibrated	
	other HRU		HRU	fixed: 1.5	

	layer 2		Homogeneous	fixed: 2.8	
Exponent k_{sat}		[-]	Homogeneous		
	layer 1			fixed: -0.335	
	layer 2			fixed: 0	
Bulk density		g L^{-1}	Homogeneous		
	layer 1			fixed: 1500	
	layer 2			fixed: 1400	
Soil texture					
	sand	silt	clay	OM	Observations, ("Erosienormeringsonderzoek ZUID-LIMBURG," 1994)
layer 1	0.15	0.75	0.10	0.02	
layer 2	0.12	0.76	0.12	0.01	
Solutes					
Half-life time		day	Homogeneous	calibrated	EFSA report (European Food Safety Authority, 2014)
Factor temperature effect		[-]	Homogeneous	calibrated	SWAP manual
Constant moisture effect		[-]	Homogeneous	calibrated	
Dispersion length		cm	Homogeneous		
	layer 1			fixed: 5	
	layer 2			fixed: 10	
Freundlich coefficient		L kg^{-1}	Homogeneous	fixed: 3.5	EFSA report
Freundlich exponent		[-]	Homogeneous	fixed: 0.89	EFSA report
Crop specific settings					
Length crop growth		days	Crop	fixed	SWAP crop models and observations
Light extinction diffuse		[-]	Crop	fixed	

Light extinction direct	[-]	Crop	fixed	
Leaf area index	$m^2\ m^{-2}$	Crop	temporal	
Crop factor evaporation	[-]	Crop	temporal	
Root depth	cm	Crop	temporal	
Drought stress	cm	Crop		
hlim3h			fixed	
hlim3l			fixed	
hlim4			fixed	
Note: hru2 are the two main HRU's in the study (A and B) see figure 4.1 and the main text.				

Initialization of OpenLISEM

To find initialization values for all variables related to hydrology and soil surface representation, we applied the temporal constraint strategy as proposed by Lefrancq et. al. (2017). In section 3.6.2 Table 3.8 show the setup of OLP. For this study some parameters where initialized with a different approach, these values are presented in Table 4.9. The initial soil moisture content now is based on the simulations with SWAP instead of antecedent precipitation. Besides that, some of the parameters related to the pesticide transport are adjusted. The initial concentration is based on the SWAP solute simulations in this study and the Enrichment ratio coefficient, the pesticide soil depth and the mixing layer depth have a different range or value assigned to better reflect the variations or conditions on the field for OLP.

Table 4.9 *Changed initialization choices to setup OpenLISEM for runoff and erosion compared to chapter 3.*

	Units	Spatial variation	Temporal variation	Method/source
Initial moisture content (θ_i)	(m^3 m^{-3})	HRU	Calibrated	Assigned the soil moisture for each soil layer as calculated with the SWAP model.
Soil porosity θ_s)	(m^3 m^{-3})	Homogeneous	Fixed	Field measurements and Staring series: 0.417
Initial moisture content (θ_i)	(-)	Homogeneous	Temporal	Based on SWAP simulations
Pesticide variables				
Enrichment ratio coefficient (α)	(-)	Homogeneous	Calibrated	Reported as between 3 and 17 (Menzel, 1980)
Pesticide soil depth		Homogeneous	Fixed: 0.02 m	Estimate, used to accommodate for soil loss by erosion. Based on SWAP simulations
Mixing layer depth *(z_m)*	(mm)	Homogeneous	Calibrated	Range from 0.1 – 25 mm based on previous modelling studies.
PP concentration *(C_{PP})*	(mg kg^{-1})	Land unit	Temporal	Based on SWAP simulations

Calibrated settings for OpenLISEM for runoff, erosion.

We selected a best simulation for each of the 6 events in this study, see section 4.3.2 and Figure 4.5. The optimal values for each parameter and crop combination selected from the distributions as given in Table 4.3 are shown in Table 4.10.

Table 4.10 *Selected parameter values after QRN parameters space exploration and expert selection.*

Parameter		Event 1	2	3	4	5	6
P		1.15	1.16	0.99	1.04	0.9	1.15
n	arable	1.35	1.57	1.35	1.77	1.86	0.65
	apple	1.68	1.02	1.89	1.38	1.75	1.33
	potato	0.47	1.68	0.4	1.19	0.49	1.28
	wheel	1.04	0.21	0.68	1.11	0.69	0.16
k_{sat}	arable	2.51	2.57	2.79	4.3	3.63	0.85
	apple	2.96	4.6	2.34	4.13	4.11	1.36
	potato	2.63	2.12	1.06	2.11	2.12	3.4
Ψ	arable	8.8	10.15	7.27	12.83	13.99	9.33
	apple	2.61	14.98	2.12	12.46	3.7	3.14
	potato	2.94	5.7	15.71	16.29	2.62	7.8
θ	arable	1.15	1.15	0.86	0.99	0.95	1.1
	apple	1.02	1.04	1.03	0.97	0.87	1.05
	potato	0.9	1.01	1.02	1.16	1.13	0.95
S_c	arable	0.83	0.90	1.16	0.75	1.58	1.04
	apple	0.48	1.15	1.06	1.14	0.66	0.34
	potato	1.68	0.56	1.35	0.95	0.51	1.57
	wheel	0.34	0.31	1.62	1.62	0.48	1.31
Note: The values for P, n, θ and S_c, are multiplier values see Table 4.3 for more information.							

4.6.2 RMSE – Overlap Indicator (ROI) for SWAP-solute evaluation

In this study we used a special designed goodness-of-fit (GOF) metric to find the best simulation for metobromuron concentrations in our study area. In Figure 4.14 we compare the ROI with three other GOFs, RMSE, KGE and NSE. The shown simulations are all the best fit according to the specific GOF. Compared to the other GOFs the ROI selected a parameter set that also includes the lower concentrations observed later in the growing seasons both on field A and field B, the other GOFs optimize the higher concentration point, but do not take into account the lower range of observed concentrations.

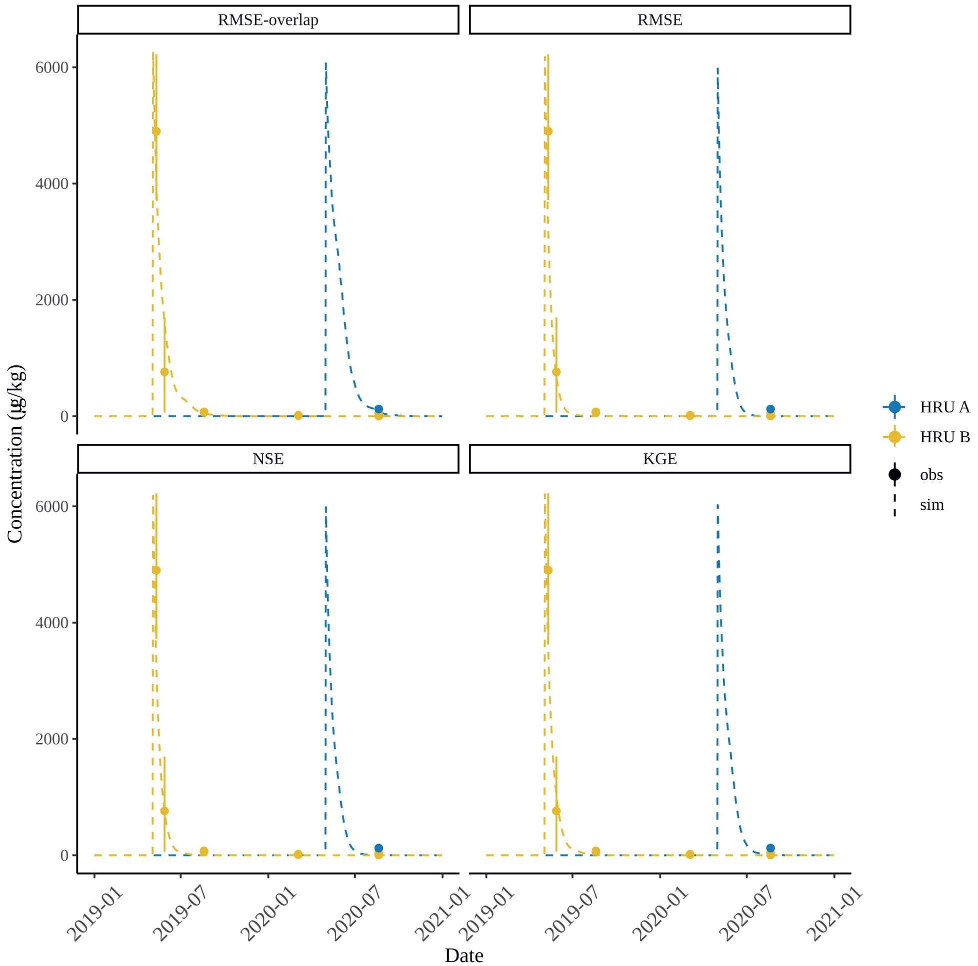

Figure 4.14 *Comparison of selected best simulations form 1024 parameter space explorations based on four different goodness-of-fit metrics.*

4.6.3 Additional data for the Global Sensitivity Analysis

The distribution of the model output should not be highly-skewed, when calculating variance based sensitivity indices, since the assumption is made that the variance fully captures the uncertainty (Khorashadi Zadeh et al., 2017; Pianosi et al., 2016). The Sobol' indices calculated for a highly-skewed distribution will be disproportionately influenced by the extreme model outputs. In Figure 4.15 the distributions for DP and PP transport with KGE as model output are shown. The KGE distributions are both highly-skewed. In case of KGE for DP transport in our study, the relatively small number of simulations resulting in KGE values < -30 describe about 40% of the variance in the model output.

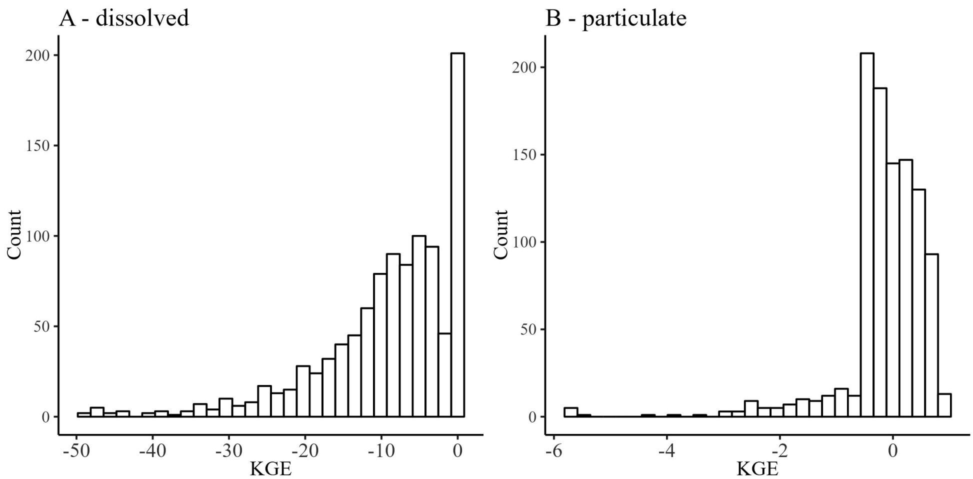

Figure 4.15 *Distribution of output KGE values for both dissolved (A) and particulate (B) transport by OLP in the first 1024 simulations of the GSA.*

As a verification of the analysis with KGE as model output, we also include the relative transported mass (M_r) as model output. In Figure 4.16 the distributions of the M_r for both DP and PP are given, which both are well distributed and not highly-skewed.

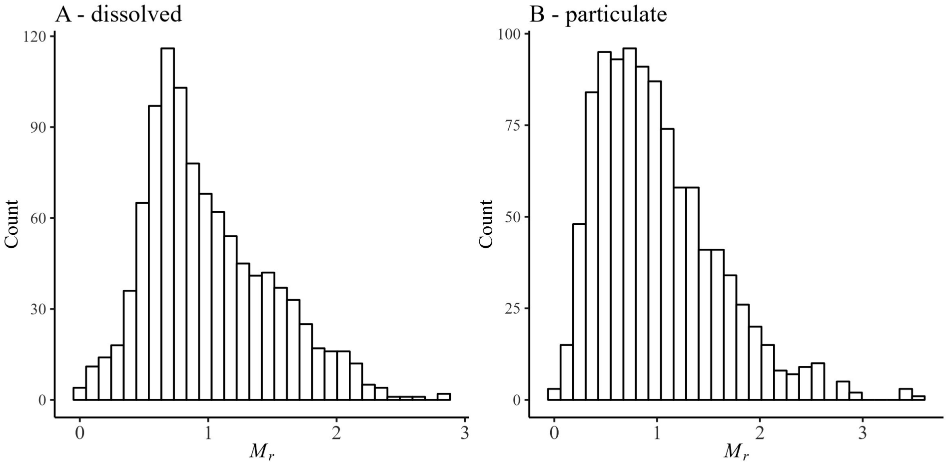

Figure 4.16 *Output distribution for M_r values of 1024 simulations with OLP for both DP and PP transport.*

Chapter 5

Synthesis

In this thesis research, I dived into the transport dynamics of pesticides with runoff and soil erosion during rainfall events. These processes were quantified and explored in more detail to increase our understanding of overland transport of pesticides. In the studies presented in the chapters 2, 3 and 4 the transport process of pesticide was observed, measured and modelled. The observations showed that particulate phase (PP) transport is a substantial contributor to overland transport of pesticides on sloping land, and drivers of transport like precipitation timing, land use and pesticide characteristics were identified. OpenLISEM-pesticide (OLP) implemented existing theories that describe the transport process of pesticides. The simulations with OLP work reasonably well to simulate pesticide transport in a small agricultural catchment. The implemented theories where developed 40 to 50 years ago and were in that time applied in many studies (Ahuja, 1990; Ahuja and Lehman, 1983; Havis et al., 1992; Leonard et al., 1987). Since then many models have been developed and used to assess the environmental fate of pesticides, but they often do not include PP transport, or do not focus on the event based transport dynamics and spatiotemporal scale of runoff events. In this synthesis I therefore first explore how knowledge and understanding are gained of earth and environmental processes, and why I think this research adds to our understanding of pesticide fate (5.1). After this the main findings of this thesis will be presented (5.2) and discussed (5.3) followed by the implications of these findings for observations, modelling, regulations and pesticide use in general (5.4). This chapter ends with an overall conclusion obtained from this thesis research (5.5).

5.1 Knowledge and understanding in earth and environmental sciences

In current day earth and environmental sciences (EES), and specifically in modelling, simplicity of the used theories and explanations is a goal, and often deemed a sign of quality (Wainwright and Mulligan, 2012). Adding complexity to process descriptions will add uncertainties that are related to additional parameters used to describe the process (Cambien et al., 2020; De Vente and Poesen, 2005). Besides that, EES aims to add to a sustainable environment, and increasing complexity will often reduce applicability, and increase costs and efforts required to apply the developed theory or model. Nonetheless, in this thesis research I collected many samples on the field, included PP transport data and added this to an already complex dynamic and distributed runoff and erosion model. This raises the question how this research adds to our understanding of pesticide fate, and how it fits in the broader aim of improving the sustainability of our food production. To answer this question, I take a step back and reflect on how knowledge and understanding are obtained in earth and environmental sciences.

According to Kleinhans et al., (2010) EES combine causal and historical scientific methods for explanation and for gaining knowledge and understanding. Causal explanations aim to formulate universal laws to explain processes or phenomena. The reductionist approach to EES, which uses causal explanation, is to deduce theories in EES from basic theories in physics or chemistry. On the other hand, historical sciences are typically associated with descriptions of past events. However, a problem in EES is that we encounter underdetermination or nonuniqueness when we aim for a causal explanation of observed processes or phenomena: the available evidence is too small to achieve a complete and unique causal explanation (Bethke, 1992; Kleinhans et al., 2010). One of the reasons is that many environmental processes and phenomena cannot (yet) be directly or even indirectly observed. For example in this thesis research, the surface resistance to overland flow is derived from multiple empirical relations that describe and predict the resistance, but accurately measuring it is (currently) not feasible (Parsons et al., 1994; Phillips, 1989). Related to that, many processes studied in EES are random, chaotic or have high spatiotemporal heterogeneity. In theory this can lead to an infinite number of possible initial states that lead to the observed outcome. This is also known as 'equifinality' (Beven and Lane, 2022; Kelleher et al., 2017).

An additional approach to explain processes and phenomena in EES is the use of narrative explanations (Kleinhans et al., 2010; Sterelny, 1996). Since the initial and boundary conditions of the studied system cannot be completely known, the causal evidence is combined with an inferred narrative, or in other words: a lens through which we study and explain the process or phenomenon. This lens combines our current understanding of the system with physical laws and the available evidence. Given the available evidence and our understanding of the system, different perspectives or lenses are possible to explain processes and phenomena. An example of explanation combining causal evidence and inference is the enrichment process of sorbed chemicals when transported with runoff. Here different lenses result in different explanations of the process, see Box 1.

However, a fitting explanation is never conclusive, and approaching the same processes with a different lens can result in new insights and another, potentially better fitting, explanation, as shown in the example about the enrichment process. Instead of approaching knowledge as a fixed state, i.e. we know exactly how a process works, or we don't know anything, we can approach it as a process. Modelling earth and environmental processes is 'knowledge in the making' and not just predicting a process or state in our environment based on our understanding and knowledge (Gramelsberger et al., 2020; Le Quéré, 2006). Models can be seen as lenses through which we study 'reality', and different lenses show different aspects. In a discussion on knowledge in earth system modelling, Le Quéré (2006) distinguishes three stages of understanding with different roles for modelling. First, based on hypotheses and our general understanding of how our environment works, a model can be developed for a process of which we lack observational data. In the second stage, the 'chaos phase', observations of the studied process are available and compared with our understanding and the current models. This is where the research in this thesis started, triggered by among others Bento et al. (2018). Often observations and model simulations contradict and challenge us to refine the models, in this way increasing our understanding of the process. The field observations in chapter 2 and the development of OLP in chapter 3 address this challenge. Finally in the last stage, our understanding of the process has improved so much, that the model and the observations often correspond well. In this stage the model can be used to make predictions, and these can be compared to observations to evaluate the performance of the model. In chapter 4 of this thesis the functioning of OLP is evaluated, however the correspondence between predictions and observations is still very small. Gramelsberger et al. (2020) conclude that not so much correspondence, but rather incoherence of our model with observations becomes fruitful for gaining knowledge, since this challenges us to rethink and refine our understanding of the studied process.

Box 1: Underdetermination, explanation and multiple lenses for the enrichment of sorbed chemicals transported with runoff

Many observations of the concentration of nutrients or pesticides in eroded sediment, show that the concentrations are higher compared to those in the original soil (H. Ghadiri and Rose, 1991; Menzel, 1980; Schiettecatte et al., 2008; A. N. Sharpley, 1985). This process is called enrichment. In 1980, Menzel (1980) combined available observation data to find correlations between erosion rates and the amount of enrichment. The observations show that the enrichment ratio increases with a decrease in the amount of soil eroded. This process can be described with a function, which is also used in OpenLISEM-pesticide, see equation 3.5. Menzel's explanation for this process is selective erosion of fine soil particles and organic matter. When less energy is available to detach and transport soil particles, the lighter particles will be transported relatively more than the heavy particles. Besides that, lighter particles e.g., clay, silt and organic matter, also have a higher specific surface area and thus chemicals sorb relatively more to these soil particles (Petersen et al., 1996). This results in higher concentrations of chemicals in eroded sediment, compared to those in the original soils. When the energy availability increases, for example due to a higher flow rate on the soil surface, larger soil particles are transported as well and the enrichment effect reduces. This also corresponds with the different transport rates for different soil texture classes as described by Engelund and Hansen (1967).

However, not all observations fit nicely to this explanation, and in 1991, Ghadiri and Rose (1991) set up controlled experiments to better understand the enrichment process. They used a different lens to assess the enrichment process and studied the effect of aggregate breakdown due to splash erosion by raindrops. The outer coat of aggregates contains higher chemical concentrations compared to the core. Since the raindrops detach the outer coat of the aggregates and make these particles available for transport, the concentration in eroded sediment is higher. The higher the erosion, the more the total aggregates will be transported and the lower the enrichment compared to the mean soil concentration.

This last study and explanation (Ghadiri and Rose, 1991) suggests that higher organic matter and pesticide concentrations will be found in eroded material compared to that in the original soil, but not necessarily higher concentrations of clay or silt fractions. Interestingly this corresponds with our observations, where OM and pesticide concentrations are higher in the runoff than in the original soil, but the clay and silt fractions did not increase, see Table 3.7 in section 3.62. However, both lenses, or explanatory theories, do not have complete causal evidence, and are underdetermined. For example, the study by Ghadiri and Rose (1991) analysed the enrichment process on plot scale, specifically designed to study rain drop impact on the enrichment process. Under these specific conditions the explanation fits, however many factors can differ in the field. A change in timing between chemical application and the rainfall event, or different chemical characteristics might allow the chemical to migrate deeper into the aggregate. Or a change in the dominant forces during the transport process from splash to flow detachment might affect this phenomenon. In the simulations with OpenLISEM used in this thesis flow detachment caused a factor 10 more sediment transport than splash detachment.

In this thesis research I tried to develop a different lens through which to study pesticide transport with runoff. I approached the overland transport of pesticides with a focus on the dynamics during rainfall-runoff events, including PP transport on field scale. This started because, as described in the introduction, observations of pesticides in the environment, the contribution of PP to transport and the effects these pesticides have on the environment, did not correspond with the expectations based on currently applied regulations and models (section 1.1). Referring to Gramelsberger et al (2020), this study can be positioned in the second stage or ‘chaos phase’ of gaining understanding. The used lens showed correspondence with the observations which triggered this study: the contribution of PP to overland transport (e.g., Bento et al., 2018; Napoli et al., 2016; Oliver et al., 2012; Yang et al., 2015) and high pesticide concentration in streams (e.g., Casado et al., 2019; Lefrancq et al., 2017). In addition, chapter 4 also identified parts of our current knowledge that requires further investigation and more evidence to improve the explanation of the process: the uptake of pesticides by interaction of runoff with the upper soil layer. Describing the soil-runoff interactions and pesticide uptake rate with measurable parameters would be a next step in understanding the uptake and transport of pesticides by erosive rainfall runoff events.

Although our overall efforts in science aim for such level of understanding that it becomes applicable and useful to impact society and ‘improve the quality of life’, the earth and environmental systems around us are of such complexity, that the ‘chaos phase’ cannot be skipped in the trajectory towards better understanding. On the disc world unfortunate Ponder Stibbons aims for a Theory of Everything, and often despairs a Theory of Anything[5], with this thesis research I hope to have contributed to knowledge in the making of Something: observing and modelling pesticide transport with runoff at the moment and place it occurs. In the following of this synthesis I will discuss the main findings of this research and explore future challenges, applications and research requirements.

5.2 Main findings

5.2.1 Quantifying the contribution of PP transport to total overland transport of pesticides for a small agricultural headwater catchment

For chapter 2 field observations were done to quantify the contribution of PP transport to total overland transport of pesticides, and to explore driving factors that influence the amount of pesticide transport from agricultural fields. Before reliable observations could be made, a depth-integrated sampling device was developed in the first research step (Figure 5.1). With this device accurate suspended sediment samples could be collected at the outlet of the catchment. This resulted in a detailed quantification of particulate phase transport during erosive runoff events (step 2, Figure 5.1), which was used in the following research steps in this thesis.

Based on the field observations, the hypothesis that particulate phase transport contributes substantially to total overland transport of pesticides was confirmed. Factors influencing the contribution include hydrological and sediment dynamics during the event, chemical characteristics of the transported active substances and land management on the fields (sections 2.3.2 and 2.3.3). These resulted in high variability in quantity, phase and type of the transported pesticides (Figure 2.5, section 2.3). Land use types which are pesticide intensive and erosion prone, pose a threat for high discharges of pesticides via runoff, both in DP and PP.

The observations showed that transport in DP mainly occurred shortly after application of the pesticide (69% mass within 10 days). Opposingly, the transport of pesticides in PP occurs over much longer time spans, where 90% of the total transported mass is reached within 100 days after application in this study. No clear statistical relations were found between biodegradability (DT_{50}), adsorption to soil carbon (k_{oc}) and solubility in water (S_w) of the pesticide to explain the transport mode and related fate of individual pesticides after application. However, the biodegradability of an active substance determines how long it will be available for overland transport either in PP or DP. Most non-persistent active substances were not transported or only shortly after application,

[5] See page 5.

where several persistent active substances were transported year-round during erosive runoff events (section 2.3.2).

Considering the extent of erosion from arable land, significantly more transport occurs than is predicted when PP transport during runoff events is not taken into account. The results presented in chapter 2 imply that event-scale dynamics are important for pesticide transport and that interactions between management, event characteristics and applied active substances can cause events that contribute disproportionally high to total transport. Because most transport of pesticides occurred from erosion prone land use, this study emphasizes the need for on-site and off-site erosion mitigation to prevent off-site transport of pesticides in the environment.

5.2.2 Development of OpenLISEM-pesticide: a model for event-based overland transport of pesticides that includes both dissolved and particulate phase transport of pesticides

To increase the understanding of the transport dynamics of pesticides during rainfall-runoff events, a dynamic, distributed model that simulates the transport process on the temporal resolution of the field-scale dynamics can provide new insights. This was the aim of chapter 3 in this thesis (step 3, Figure 5.1). The OpenLISEM runoff and erosion model was selected as base and an extension to simulate pesticide transport was developed: OpenLISEM-pesticide v1.0 (OLP).

The uptake of pesticides is simulated with a mixing layer: a thin (0.1 to 25 mm) layer of topsoil, that interacts with the runoff (section 3.2.1). From this layer pesticides in DP and PP can be taken up into the runoff to be transported downstream. Particulate pesticide transport is simulated with the enrichment process when soil particles are detached from the soil, see also Box 1. This is combined with a mass transfer rate for uptake of DP pesticides into the runoff, as described in the transport model by Havis et al. (1992).

With the newly developed model, simulations were done for glyphosate and metobromuron transport during two rainfall-runoff events from the collected observation dataset (section 3.3.3). The proof-of-concept simulations for the two compounds and two events were mostly in line with field observations. With its distributed simulations OLP can give insight in transport dynamics, source areas and redistribution of pesticides during erosive rainfall-runoff events. The local sensitivity analysis that was performed in this chapter showed that for DP transport the mass transfer rate of the mixing layer was most influential (section 3.3.4). PP transport was most sensitive to the parameters in the enrichment ratio equation. Besides that, the performance and accuracy of the pesticide transport predictions depended strongly on the accuracy of runoff and erosion simulations.

5.2.3 Determining the input parameter influence on the output of OpenLISEM-pesticide and investigate its suitability to simulate and predict pesticide transport for a small agricultural headwater catchment

Chapter 4 aimed to identify the influential parameters for pesticide transport simulations with OpenLISEM-pesticide (OLP) and evaluate the predictive performance of OLP for one rainfall runoff event (steps 4 and 5, Figure 5.1). SWAP and OpenLISEM were successfully coupled to obtain initial parameterization for OLP simulations of six rainfall-runoff events (section 4.3.1 and 4.3.2). For these six events a global sensitivity analysis (GSA) was done, to evaluate the newly introduced parameters in the pesticide model extension (section 4.3.3). The GSA showed that the hydrology and erosion parameters have a major influence on the simulated transport of pesticides. The mixing layer depth (z_m) is the most influential of the parameters introduced in OLP, for both dissolved (DP) and particulate phase (PP) transport. Besides that, for DP the mass transfer rate (k_{film}) and for PP the parameters (α and β) in the enrichment ratio equation are influential. The initial concentration and the soil-water partitioning are identified as non-influential parameters. The results of the GSA showed the weakness of the local sensitivity analysis performed in chapter 3. Different parameters were identified as influential, with as main difference that in the GSA the major importance of the mixing layer depth was shown, which corresponds to many other studies (Gatel et al., 2019; Havis et al., 1992; Huang et al., 2021; Joyce et al., 2008). In the local sensitivity analysis in chapter 3 the mixing layer was not identified as influential.

The information obtained from the global sensitivity analysis was used to evaluate OLP by simulating pesticide transport for one event with an ensemble simulation (section 4.3.4). The 90% prediction uncertainty covered the observed concentrations well, however in combination with the simulated runoff and erosion, errors in the load predictions occurred. The evaluation of OLP in this study shows that predictions without calibration based on observations have a large uncertainty. Further research is needed to improve the process-based descriptions of the mixing layer and the enrichment process, to reduce the uncertainty currently related to these parameters.

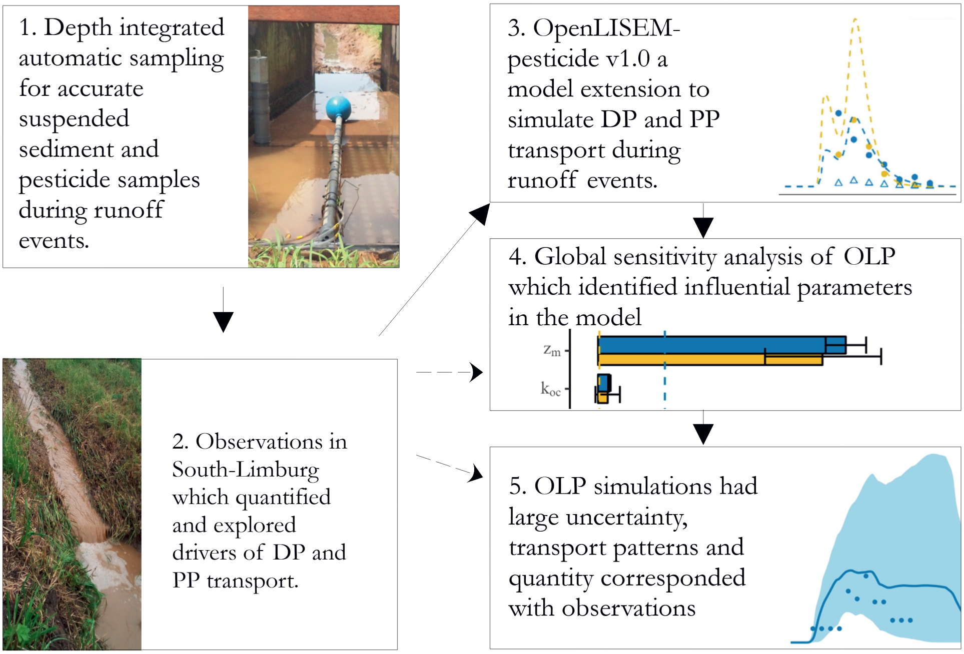

Figure 5.1 *Summary of findings for each research step in this thesis.*

5.3 Discussion

5.3.1 Observing pesticide transport during rainfall runoff events

The amount and accuracy of available evidence is closely related to the ability to understand processes in the environment, as discussed in section 5.1. With the field observations performed in this thesis research, the aim was to increase understanding on the transport of pesticides during rainfall-runoff events. However, several weaknesses in the collected evidence, or measurements and observations, limit the new understanding.

First, not all fields that discharge towards the outlet were covered with soil samples and pesticide application data. The three main fields, that cover about 90% of the area where pesticides were applied were covered, but the remaining fields could also be a source of pesticides detected at the outlet, and this cannot be checked with the current dataset. The main cause of limited data was that the owner of the land was unknown, or not willing to contribute data to this study. The analysis of pesticide fate is a sensitive topic to farmers, and confidentiality was very important to create willingness to share data.

Secondly, important variables like soil moisture and precipitation do not have full spatial or temporal coverage. Malfunctioning of the sensors or data loggers during the sampling period caused gaps in the data. Besides that, at the outlet about two thirds of the occurring events were not correctly captured; from the 39 occurring events, 25 were sampled and 14 were suitable for chemical analysis of pesticide concentrations and thus analysed in this thesis (section 2.2.1). There is a tendency for events with more runoff and erosion in the analysed events (see Figure 2.8 in section 2.5.1). The gaps in the collected data series limit the possibilities to calculate annual loads, and to asses differences in season or events characteristics in more detail. Precipitation and soil moisture data are crucial for accurate distributed model simulations (Lefrancq et al., 2017b; Wu et al., 2021), and due to limited observations the uncertainty in the simulations increases.

Lastly, the density and quality of the collected samples for pesticide concentrations in the soils was on the low side and limited the possibilities for statistical or model-assessment of the transport processes. A higher density of samples on each field would provide a better estimate of concentrations and more information on possible spatial patterns. The sample method was not standardized enough, so sample depths varied between 0.5 and 1.5 cm and sample locations were randomly chosen. By standardizing the sampling methods (e.g. an exact sampling depth in the soil) and by defining a better approach to sample location selection in the fields the reliability and interpretability of the pesticide concentration data could increase. The large influence of the mixing layer depth as analysed in chapter 4, also emphasizes the importance of an accurate sample depth.

In general when reflecting on these limitations, the initial aim of the field observations design was too broad. By trying to include as many different processes as possible, the observations lost target to answer some specific questions. An improvement could be to exclude some variables or shorten the observation period which would allow for better targeting of the data collection scheme. A higher density of tipping buckets for precipitation data collection and improved soil sampling strategies for pesticide analysis are the two aspects that would improve the observations, and the usability for detailed analysis of the pesticide transport process the most. The higher density of tipping buckets is needed due to the high spatial variability of precipitation (Dunkerley, 2020; Jaffrain and Berne, 2012). The high variability is also visible in data collected in this study: during the event on 2019-05-28 three tipping buckets recorded data and the rainfall intensity varied a factor two between tipping buckets located about 500 meter from each other.

By designing an accurate and detailed measurement setup, the dynamics of PP transport during a runoff event on field scale were quantified. The used approach was novel compared to the existing literature. Mainly plot experiments were available which showed corresponding results (Bento et al., 2018; Melland et al., 2016; Yang et al., 2015b). In addition, some larger scale studies showed high concentrations in PP, but due to the low suspended sediment mass this often did not contribute substantially to total load (Climent et al., 2019; Cruzeiro et al., 2016; Masiá et al., 2013). The results of this study contradict with studies that conclude that PP transport is of minor importance (Maillard and Imfeld, 2014; Napoli et al., 2016; Oliver et al., 2012; Wauchope, 1978).

The results of a study can often be attributed to the setup of the observations, including land use, spatiotemporal scale of the measurement and analysed pesticide types. This also applies to the results presented in this thesis, where high spatial and temporal variations in transport were observed. For example, high transport from potato cultivation is measured, but low transport from apples and cereals, although more pesticide mass was applied on the apple orchard. Chapter 2 concludes that the contribution of PP is highly variable, and depends on land use and pesticide characteristics. This study analysed multiple different land use types, including arable agriculture. In other field scale studies orchards or vineyards were studied (Napoli et al., 2016; Oliver et al., 2012). These have high pesticide application rates, but no high erosion rates were observed, which corresponds with our observations on the apple orchard. However, on arable agriculture on sloping lands erosion occurs (Panagos et al., 2015), and the findings in chapter 2 suggest that if erosion occurs on land where pesticides are applied, pesticide transport in PP will occur as well.

The findings in this thesis emphasize that transport dynamics in the environment depend on many different processes, and simple relationships or extrapolations often do not apply. For example, in the observations described in chapter 2, more pesticide mass was transported related to cereal cultivation than to the apple orchard, although the pesticide application rate was about 20 times higher on the apple orchard. The main explanation for this observation is that the apple orchard had very low vulnerability to runoff and erosion, and that the pesticides related to cereal cultivation were persistent in the soil and were transported a whole season later during the cultivation of a more runoff-prone crop.

Since this thesis is based on data collected in one specific study area, further research is needed to generalize these findings and understand the transport dynamics under different conditions. Assessment of the transport during rainfall runoff events in different pedoclimatic zones and for other (combinations of) land use and pesticide types, will contribute to a more robust understanding of the transport process with runoff and erosion. This thesis shows that a requirement of further assessments is to include both DP and PP transport, which also requires a suitable measurement setup. This research studied transport, however for the assessment of sustainability the environmental or ecotoxicological risk posed by the transport is important. Transported pesticides during runoff events cause pulses of high concentrations, which cause different effects than stable exposure rates (Hamer et al., 2019). PP transport contributes to the pollution of deposition sites (e.g. field borders), wetlands and riverbeds and can impact for example benthic organisms. A recent review indicates that ecotoxicological effects of pesticides on benthic organisms need more investigation (Li et al., 2017). During the runoff events, often multiple pesticides were transported; the effect of pesticide cocktails on the environment is often mentioned as an area we need to understand better to guarantee sustainable use of pesticides (Hasenbein et al., 2016; Siviter et al., 2021; Sybertz et al., 2020).

5.3.2 Modelling pesticide fate with runoff

The simulations performed with OLP in this research showed correspondence with the observations in terms of transported concentration and load of pesticides in both phases, DP and PP, during the rainfall-runoff events. This suggests that the used theories and conceptual descriptions of the uptake, enrichment and transport of pesticides with runoff describe the processes sufficiently, however there are some limitations in the conceptualization of OLP.

With OLP I aimed for process-based or even physics-based descriptions of the transport process of pesticides. However, the used equations and conceptualization of the soil runoff interactions in OLP include parameters that cannot be measured directly in the field, but are somewhat lumped or empirical. The lack of a measurable process-based description of the soil-runoff interaction limits the reliability of the OLP simulations. Other well-known models for pesticide transfer also use the mixing-layer concept, in different forms, to describe the interaction between the soil and runoff. For models on larger temporal scales, complete mixing per timestep can be assumed and uniform or non-uniform mixing are often applied (Young and Fry, 2019). In for example GLEAMS, this is combined with a fixed mixing layer depth of 1.0 cm (Leonard et al., 1987). Diffusion based interaction between runoff and the soil was suggested (Ahuja, 1990), but the used parameters are also hard to measure, and parameter fitting is still required. Most studies agree that the physical processes that affect the pesticide uptake from the soil are the turbulence of precipitation impact and overland flow, diffusion and dispersion (Ahuja, 1990; Havis et al., 1992; Shi et al., 2011; Wallach et al., 1988). Moreover, soil properties like cohesion, porosity and bulk density might add to the interaction dynamics.

The choices made in describing the interaction between the soil and runoff and the uptake of pesticides have a major influence on the resulting simulations. An example is the mixing layer (z_m) in OLP. The GSA in chapter 4 shows that z_m is the most influential parameter for both DP and PP transport in OLP. The influence of z_m is closely related to the simulated concentration in the mixing layer. The combination of both results in the available pesticide mass, in DP and PP, for uptake into the runoff. In OLP the pesticide concentration in the soil is simulated with (only) two layers: the mixing layer, and a two centimetre thick layer below this. The concentrations are obtained from longer term degradation simulations with the SWAP model, which discretised the soil concentrations in steps of 5 mm, which is a user setup choice. In chapter 4, the concentration in the upper 5 mm was homogeneous, which is visible in an increasing transport with increasing z_m between 0 and 5 mm. A more detailed discretization of the pesticide concentration profile might change this behaviour. However, a higher detailed simulation might not always be a better representation of the conditions in the field. In this specific case the soil roughness as observed on the fields is often around 5 mm, which makes simulating smaller soil depths mainly a theoretical exercise. Improvements in pesticide uptake simulations should be made by improving the process-based description rather than by increasing the details of the current conceptualization.

As discussed in section 3.4, many different pesticide transport models exist, all with their own strengths and limitations. OLP adds to these models by simulating both DP and PP with a distributed approach. In a previous model comparison from the 1980s, the strengths of both a lumped approach (simplicity) and a distributed approach (better prediction of timing, load and concentration) were already pointed out (Emmerich et al., 1989). This thesis aligns with these findings. For example, when comparing the results of OLP in this thesis to the PP transport simulations with RZWQM (Chen et al., 2017; DeMars et al., 2018), OLP results in higher detail, and additional insights in pesticide redistribution, source areas, timing and load during the events.

However, the complexity and related uncertainty in the simulations of OLP were shown in chapter 4, which indicated that OLP might not directly be suitable for applications in policy making or prediction (section 3.4.1). Nevertheless, OLP might contribute to a more detailed environmental risk assessments when different processes or ecotoxicological risks are taken into account.

Based on this thesis research (at least) two main topics require further investigation. Firstly, improving the process based descriptions of the uptake processes from the soil into the runoff is needed to reduce the uncertainty in the transport simulations of pesticides. The most desirable form of the descriptions would include well measurable parameters instead of the current parameters that need estimation (e.g. z_m and k_{film}) or are based on empirical data (the enrichment ratio). Secondly, a further evaluation of the performance of OLP, also in relation to other models, is needed. This will help to identify strengths and requirements for further improvements, which is a critical part in the development of further understanding (Gramelsberger et al., 2020). This model evaluation can be done by testing OLP on different datasets for other catchments and precipitation characteristics, however currently no other dataset with detailed PP transport observations is known. In addition, comparing the model simulations of OLP with simulations of models with different modelling approaches can give insights in how to optimally use the different models. For the collected dataset in South-Limburg, simulations with SWAT, PRZM and GSSHA would be interesting, since these models all include PP transport, but have different spatial and temporal scales.

5.3.3 Spatial temporal scale of pesticide transport assessment.

A leading aspect throughout this thesis regarding the questions about transport of pesticides during runoff events is the spatiotemporal scale on which the processes are assessed. Assessing pesticide fate on different spatial and temporal scales, whether this is with observations or by modelling, will influence the resulting findings. To obtain good understanding of pesticide fate, and to be able to assess the safety of pesticide use for our environment, assessment on different scales can be valuable. However, this thesis also shows that assessments on the field-scale, where the transport processes occur and the spatiotemporal dynamics are large, are needed to improve our qualitative and quantitative understanding of the transport process.

In the introduction I showed that headwater catchments are important for agriculture as well as nature and biodiversity (Biggs et al., 2017; Ferreira et al., 2023). Assessment on spatiotemporal scales that differ from the scales on which the dynamics in these areas occur, are not likely to provide full understanding. For example, when assessing transport on plot scale (e.g., Bento et al., 2018; Havis et al., 1992; Todorovic et al., 2014) specific processes or conditions are tested (tillage practises, slope, precipitation or soil type) but the interactions on field scale are not captured. A limitation for pesticide modelling caused by the smaller scales, is that all runoff-soil interaction studies focus on mixing due to raindrop impact. However, overland flow occurs a lot during a runoff event, and this might also cause interactions between runoff and the mixing layer. Within the simulations in this thesis, according to the OpenLISEM simulations, a factor 10 more sediment is detached by overland flow than by splash detachment. Another example of the influence of scale are larger scale assessments (e.g., Climent et al., 2019): the suspended sediment concentrations in the river water samples were very low compared to concentrations observed in this thesis. Often sediment transport is not directly connected from the hillslope to the river (Heckmann et al., 2018), and sediments are deposited lower in the landscape. However, the results of this research show that large amounts of transport can occur, which can cause pollution on different locations in the landscape. When assessing pesticide transport on a too large scale, spatial redistribution in a headwater catchment, or temporal peaks in relation to precipitation (Vormeier et al., 2023) might be missed.

In Figure 5.2 an overview is given of the observation and modelling studies referred to in this thesis. One observation study (Oliver et al., 2012) and one other modelling study (Chen et al., 2017) were found that include PP transport and assess the transport process on field scale and with a temporal resolution which captures the dynamics during an runoff event. However, in the modelling study the PRZM model was used, which is a lumped model and it did not perform adequately in terms of erosion simulations, which hampered detailed analysis of the dynamics during runoff events (Chen et al., 2017). Since there are many driving factors for pesticide transport during runoff events, as concluded in chapter 2 of this thesis, more observation studies within this spatiotemporal domain are required to improve our understanding of all interactions and processes. This is also observed for soil erosion research, which is one of the processes influencing pesticide transport. Here many studies on plot scale or larger catchment scale are available, but there is a high demand for more data on field scale (1 ha to 100 ha) where the runoff and erosion processes occur (Matthews, 2024; Poesen, 2018).

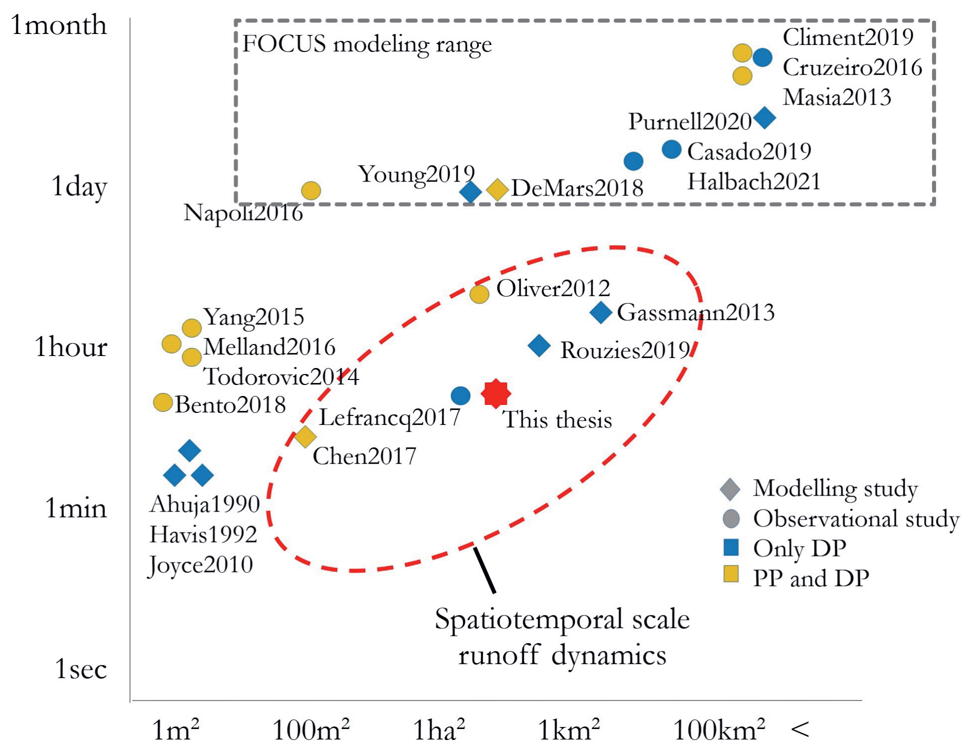

Figure 5.2 *Overview of the spatiotemporal scale of observation and modelling studies assessing the transport of pesticides with runoff.*

5.4 Implications of this thesis

The main findings of this thesis research emphasize that for the assessment of pesticide transport with runoff, the spatiotemporal scale of rainfall-runoff events needs specific attention. In addition, particulate phase transport of pesticides should be included in the environmental risk assessment. For observational studies this requires sampling strategies that capture the dynamics when they occur, for example automatic sampling and collecting suspended sediment in runoff, as shown in chapter 2 of this thesis. For modelling studies, the spatial representation of the modelled area and the temporal resolution should include the dynamics which occur during a rainfall-runoff event.

The main aim to study pesticide transport is to assess the environmental safety of the pesticide applications in agriculture. Regulations aim to guarantee sustainable use of pesticides, without major adverse effect to humans, biodiversity and our environment in general (EFSA, 2018). The current regulations and application of the FOCUS modelling framework does not succeed in this, according to studies showing adverse effects (Kortenkamp et al., 2021; Mamy et al., 2022; Murcia-Morales et al., 2021) and high concentrations in the environment (Silva et al., 2019; Vormeier et al., 2023) in Europe, as also discussed in the introduction of this thesis. The assessment of pesticide fate with runoff in the FOCUS modelling framework is a tiered approach based on 'worst-case' scenarios. In the higher level tiers, detailed modelling simulations are done to investigate the risk on high amounts of transport. Although OLP is still in its initial development stage, this modelling approach might contribute in the higher tiers (three and four) to an improved assessment of the environmental fate of pesticides on the spatiotemporal scales of rainfall-runoff events.

Despite the many reported adverse effects on humans and the environment (Huber et al., 2022; Mamy et al., 2022), pesticides are deemed an essential part for the global food production (Sabzevari and Hofman, 2022). However, when pesticides are used, increasing their sustainable use, and decreasing harmful effects on humans, biodiversity and the environment in general is of major importance. This research is one of the many recent studies that show increased transport (Casado et al., 2019; Cor et al., 2021; Halbach et al., 2021; Mayora et al., 2024) or link current pesticide use to impacts on biodiversity or human health (Kortenkamp et al., 2021; Mamy et al., 2022; Siviter et al., 2021). This thesis adds insights on the transport mechanisms which might contribute to targeting mitigation measures. Examples can be the reduced input of pesticides on land use types that are vulnerable for transport (e.g., potatoes in this research), or the implementation of erosion and runoff mitigation measures such as vegetated filter strips to reduce the transport to off-site environments.

Although the observations and simulations in this thesis show high amounts of transport during erosive runoff events, the implications for biodiversity and environmental safety or sustainability were not part of this research. Further research therefor is required to understand how dynamics on this scale impact our environment. For example: an exceedance of the water quality norm in the EU (0.1 $\mu g\ L^{-1}$) during a rainfall-runoff event on field scale has very different effects as compared to the same numeric exceedance for a time weighted annual concentration in a river. Another aspect of the findings in this thesis is that transport dynamics in the environment depend on many different systems, and simple relationships or extrapolations often do not apply. For example, in the observations described in chapter 2, more pesticide mass was transported in relation to cereal cultivation than to the apple orchard, although the pesticide application rate was about 20 times higher on apples. The main explanation for this observation is that the apple orchard had very low vulnerability to runoff and erosion, and that the pesticides related to cereal cultivation were persistent in the soil and were transported a whole season later during the cultivation of a more runoff prone crop!

5.5 General conclusions

This PhD research investigated pesticide transport during erosive rainfall-runoff events. This was done, because many studies found high transport rates with runoff, indicating a gap between current regulations and the field-scale processes. By approaching the processes with a different lens, a spatial scale of multiple fields and a temporal scale of minutes to hours, this study aimed to create new insights and increase our understanding of pesticide transport with runoff and erosion. Field observations showed that particulate phase (PP) transport is a substantial process that needs to be taken into account when assessing environmental fate of pesticides. The extent of PP contribution to total transport of pesticides depends on land use, pesticide type and pedoclimatic conditions. In this research the model extension OpenLISEM-pesticide was developed: a dynamic distributed model that simulates pesticide transport with runoff and erosion on event-scale. With OpenLISEM-pesticide the highly dynamic processes during rainfall-runoff events, like redistribution and transport in dissolved and particulate phase could be simulated. OpenLISEM-pesticide shows that available theories on pesticide uptake and transport, including mass transfer from a mixing layer and enrichment of sorbed pesticides, correspond with observations for field scale simulations. However, uncertainty in the simulations is large which hampers reliable predictions without observation data. To conclude; when assessing the transport of pesticides in dissolved and particulate phase during rainfall-runoff events on field and event scale, OpenLISEM-pesticide simulations corresponded with field observations, both showing high transport rates of pesticides.

This research is a first step in more detailed assessments of transport of pesticides on the headwater catchment scale, including PP transport. To further improve OpenLISEM-pesticide and extend our understanding of pesticide fate I identified three main research challenges:

- Pesticide transport processes under different conditions than studied in this thesis, including different land use, topography, climate and precipitation characteristics should be assessed. This can be done by reanalysis of existing datasets, or by new observational studies. Data with a spatiotemporal scale of rainfall runoff events, and the inclusion of particulate phase transport is needed to further test the findings in this thesis.
- To improve the predictions of pesticide transport with runoff the interactions between the soil and runoff should be better understood. A process based description of these interactions, with parameters that are measurable in the field, might be an improvement over the current conceptualization.
- A robust understanding of pesticide transport processes cannot be reached by one single model, or analysis of the process on one spatiotemporal scale. A model comparison study combining models with different conceptualizations and scales, and different case studies, will improve model applications and predictions, and further identify the contribution of dynamic distributed models like OpenLISEM-pesticide.

References

Abbasi, Y., Mannaerts, C.M., Makau, W., 2019. Modeling Pesticide and Sediment Transport in the Malewa River Basin (Kenya) Using SWAT. Water 11, 87. https://doi.org/10.3390/w11010087

Abbaspour, K.C., 2015. SWAT-CUP: SWAT calibration and uncertainty programs - a user manual.

Adriaanse, P., Allen, R., Gouy, V., Hollis, J., Hosang, J., Jarvis, N., Jarvis, T., Klein, M., Layton, R., Linders, J., Schäfer, H., Smeets, L., Yon, D., 1997. Surface water models and EU registration of plant protection products (No. 6476/VI/96), European Commision Document.

Adriaanse, P.I., Leerdam, R.C.V., Boesten, J.J.T.I., 2017. The effect of the runoff size on the pesticide concentration in runoff water and in FOCUS streams simulated by PRZM and TOXSWA. Science of the Total Environment 584–585, 268–281. https://doi.org/10.1016/j.scitotenv.2016.12.001

AHN, 2019. AHN3 DTM.

Ahuja, L., Sharpley, A., Lehman, O., 1982. Effect of soil slope and rainfall characteristics on phosphorus in runoff. Wiley Online Library.

Ahuja, L.R., 1990. Modeling soluble chemical transfer to runoff with rainfall impact as a diffusion process. Soil Science Society of America Journal 54, 312–321. https://doi.org/10.2136/sssaj1990.03615995005400020003x

Ahuja, L.R., Lehman, O.R., 1983. The Extent and Nature of Rainfall-soil Interaction in the Release of Soluble Chemicals to Runoff. Journal of Environmental Quality 12, 34–40. https://doi.org/10.2134/jeq1983.00472425001200010005x

Aktar, W., Sengupta, D., Chowdhury, A., 2009. Impact of pesticides use in agriculture: their benefits and hazards. Interdisciplinary Toxicology 2, 1–12. https://doi.org/10.2478/v10102-009-0001-7

Anastassiades, M., Lehotay, S.J., Štajnbaher, D., Schenck, F.J., 2003. Fast and easy multiresidue method employing acetonitrile extraction/partitioning and "dispersive solid-phase extraction" for the determination of pesticide residues in produce. Journal of AOAC International 86, 412–431. https://doi.org/10.1093/jaoac/86.2.412

Andrade, V.S., Gutierrez, M.F., Regaldo, L., Paira, A.R., Repetti, M.R., Gagneten, A.M., 2021. Influence of rainfall and seasonal crop practices on nutrient and pesticide runoff from soybean dominated agricultural areas in Pampean streams, Argentina. Science of The Total Environment 788, 147676. https://doi.org/10.1016/j.scitotenv.2021.147676

Arias-Estévez, M., López-Periago, E., Martínez-Carballo, E., Simal-Gándara, J., Mejuto, J.-C., García-Río, L., 2008. The mobility and degradation of pesticides in soils and the pollution of groundwater resources. Agriculture, Ecosystems & Environment 123, 247–260. https://doi.org/10.1016/j.agee.2007.07.011

Baartman, J.E.M., Jetten, V.G., Ritsema, C.J., de Vente, J., 2012. Exploring effects of rainfall intensity and duration on soil erosion at the catchment scale using openLISEM: Prado catchment, SE Spain. Hydrological Processes 26, 1034–1049. https://doi.org/10.1002/hyp.8196

Baartman, J.E.M., Temme, A.J.A.M., Veldkamp, T., Jetten, V.G., Schoorl, J.M., 2013. Exploring the role of rainfall variability and extreme events in long-term landscape development. Catena 109, 25–38. https://doi.org/10.1016/j.catena.2013.05.003

Baattrup-Pedersen, A., Larsen, S.E., Andersen, D.K., Jepsen, N., Nielsen, J., Rasmussen, J.J., 2018. Headwater streams in the EU Water Framework Directive: Evidence-based decision support to select streams for river basin management plans. Science of The Total Environment 613–614, 1048–1054. https://doi.org/10.1016/j.scitotenv.2017.09.199

Bach, M., Huber, A., Frede, H.G., 2001. Modeling pesticide losses from diffuse sources in Germany. Water Sci Technol 44, 189–196.

Baets, S.D., Torri, D., Poesen, J., Salvador, M., Meersmans, J., 2008. Modelling increased soil cohesion due to roots with EUROSEM. Earth Surface Processes and Landforms: The Journal of the British Geomorphological Research Group 33, 1948–1963.

Baker, J.L., Laflen, J.M., 1979. Runoff Losses of Surface-Applied Herbicides as Affected by Wheel Tracks and Incorporation. J. environ. qual. 8, 602–607. https://doi.org/10.2134/jeq1979.00472425000800040032x

Batista, P.V.G., Davies, J., Silva, M.L.N., Quinton, J.N., 2019. On the evaluation of soil erosion models: Are we doing enough? Earth-Science Reviews 197, 102898. https://doi.org/10.1016/j.earscirev.2019.102898

Bennett, G.W., Owens, J.M., Corrigan, R.M., Truman, L.C., 2021. Truman's scientific guide to pest management operations, Seventh edition. ed. North Coast Media, LLC, Cleveland, OH.

Bento, C.P.M., Commelin, M.C., Baartman, J.E.M., Yang, X., Peters, P., Mol, H.G., Ritsema, C.J., Geissen, V., 2018. Spatial glyphosate and AMPA redistribution on the soil surface driven by sediment transport processes–A flume experiment. Environmental pollution 234, 1011–1020. https://doi.org/10.1016/j.envpol.2017.12.003

Bento, C.P.M., Yang, X., Gort, G., Xue, S., van Dam, R., Zomer, P., Mol, H.G.J., Ritsema, C.J., Geissen, V., 2016. Persistence of glyphosate and aminomethylphosphonic acid in loess soil under different combinations of temperature, soil moisture and light/darkness. Science of the Total Environment 572, 301–311. https://doi.org/10.1016/j.scitotenv.2016.07.215

Berg, J. van de, 2023. Luidt Drentse zaak het einde van de bollenteelt in? "Die bollen gaan naar Azië, wij krijgen de troep." de Volkskrant.

Bethke, C.M., 1992. The question of uniqueness in geochemical modeling. Geochimica et Cosmochimica Acta 56, 4315–4320. https://doi.org/10.1016/0016-7037(92)90274-M

Bevan, R., Brown, T., Matthies, F., Sams, C., Jones, K., Hanlon, J., Vedrine, M.L., 2017. Human biomonitoring data collection from occupational exposure to pesticides. EFSA Supporting Publications 14, 1185E. https://doi.org/10.2903/SP.EFSA.2017.EN-1185

Beven, K., 2012. Rainfall-Runoff Modelling: The Primer, 1st ed. Wiley. https://doi.org/10.1002/9781119951001

Beven, K., Lane, S., 2022. On (in)validating environmental models. 1. Principles for formulating a Turing-like Test for determining when a model is fit-for purpose. Hydrological Processes 36. https://doi.org/10.1002/hyp.14704

Biggs, J., Von Fumetti, S., Kelly-Quinn, M., 2017. The importance of small waterbodies for biodiversity and ecosystem services: implications for policy makers. Hydrobiologia 793, 3–39. https://doi.org/10.1007/s10750-016-3007-0

Boardman, J., Evans, R., 2020. The measurement, estimation and monitoring of soil erosion by runoff at the field scale: Challenges and possibilities with particular reference to Britain. Progress in Physical Geography 44, 31–49. https://doi.org/10.1177/0309133319861833

Boesten, J.J.T.I., Van der Linden, A.M.A., 1991. Modeling the Influence of Sorption and Transformation on Pesticide Leaching and Persistence. J of Env Quality 20, 425–435. https://doi.org/10.2134/jeq1991.00472425002000020015x

Boithias, L., Sauvage, S., Srinivasan, R., Leccia, O., Sánchez-Pérez, J.M., 2014. Application date as a controlling factor of pesticide transfers to surface water during runoff events. Catena 119, 97–103. https://doi.org/10.1016/j.catena.2014.03.013

Boivin, A., Poulsen, V., 2017. Environmental risk assessment of pesticides: state of the art and prospective improvement from science. Environmental Science and Pollution Research 24, 6889–6894. https://doi.org/10.1007/s11356-016-8289-2

Bonato, M., Martin, E.A., Cord, A.F., Seppelt, R., Beckmann, M., Strauch, M., 2023. Applying generic landscape-scale models of natural pest control to real data: Associations between crops, pests and biocontrol agents make the difference. Agriculture, Ecosystems & Environment 342, 108215. https://doi.org/10.1016/j.agee.2022.108215

Boonupara, T., Udomkun, P., Khan, E., Kajitvichyanukul, P., 2023. Airborne Pesticides from Agricultural Practices: A Critical Review of Pathways, Influencing Factors, and Human Health Implications. Toxics 11, 858. https://doi.org/10.3390/toxics11100858

Borrelli, P., Alewell, C., Alvarez, P., Anache, J.A.A., Baartman, J., Ballabio, C., Bezak, N., Biddoccu, M., Cerdà, A., Chalise, D., Chen, S., Chen, W., De Girolamo, A.M., Gessesse, G.D., Deumlich, D., Diodato, N., Efthimiou, N., Erpul, G., Fiener, P., Freppaz, M., Gentile, F., Gericke, A., Haregeweyn, N., Hu, B., Jeanneau, A., Kaffas, K., Kiani-Harchegani, M., Villuendas, I.L., Li, C., Lombardo, L., López-Vicente, M., Lucas-Borja, M.E., Märker, M., Matthews, F., Miao, C., Mikoš, M., Modugno, S., Möller, M., Naipal, V., Nearing, M., Owusu, S., Panday, D., Patault, E., Patriche, C.V., Poggio, L., Portes, R., Quijano, L., Rahdari, M.R., Renima, M., Ricci, G.F., Rodrigo-Comino, J., Saia, S., Samani, A.N., Schillaci, C., Syrris, V., Kim, H.S., Spinola, D.N., Oliveira, P.T., Teng, H., Thapa, R., Vantas, K., Vieira, D., Yang, J.E., Yin, S., Zema, D.A., Zhao, G., Panagos, P., 2021. Soil erosion modelling: A global review and statistical analysis. Science of The Total Environment 780, 146494. https://doi.org/10.1016/j.scitotenv.2021.146494

Borselli, L., Cassi, P., Torri, D., 2008. Prolegomena to sediment and flow connectivity in the landscape: A GIS and field numerical assessment. CATENA 75, 268–277. https://doi.org/10.1016/J.CATENA.2008.07.006

Bos, M.G.G., 1989. Discharge measurement structures, 3rd ed, DELFT, THE NETHERLANDS, DELFT HYDRAUL. LAB., MAY 1976. ILRI. https://doi.org/10.1201/9781315141343-2

Bout, B., Jetten, V.G., 2018. The validity of flow approximations when simulating catchment-integrated flash floods. Journal of Hydrology 556, 674–688. https://doi.org/10.1016/j.jhydrol.2017.11.033

Boxall, A.B., Fogg, L.A., Ashauer, R., Bowles, T., Sinclair, C.J., Colyer, A., Brain, R.A., 2013. Effects of repeated pulsed herbicide exposures on the growth of aquatic macrophytes. Environmental Toxicology and Chemistry 32, 193–200. https://doi.org/10.1002/etc.2040

Bracken, L.J., Croke, J., 2007. The concept of hydrological connectivity and its contribution to understanding runoff-dominated geomorphic systems. Hydrological Processes 21, 1749–1763. https://doi.org/10.1002/HYP.6313

Brandmeyer, J.E., Karimi, H.A., 2000. Coupling methodologies for environmental models. Environmental Modelling & Software 15, 479–488. https://doi.org/10.1016/S1364-8152(00)00027-X

Brühl, C.A., Zaller, J.G., 2019. Biodiversity Decline as a Consequence of an Inappropriate Environmental Risk Assessment of Pesticides. Frontiers in Environmental Science 7, 177. https://doi.org/10.3389/fenvs.2019.00177

Buijs, J., Mantingh, M., 2022. Onderzoek verspreiding bestrijdingsmiddelen in Drenthe en omstreken. Meten = Weten.

Cambien, N., Gobeyn, S., Nolivos, I., Forio, M.A.E., Arias-Hidalgo, M., Dominguez-Granda, L., Witing, F., Volk, M., Goethals, P.L.M., 2020. Using the Soil and Water Assessment Tool to Simulate the Pesticide Dynamics in the Data Scarce Guayas River Basin, Ecuador. Water 12, 696. https://doi.org/10.3390/w12030696

Carluer, N., Lauvernet, C., Noll, D., Munoz-Carpena, R., 2017. Defining context-specific scenarios to design vegetated buffer zones that limit pesticide transfer via surface runoff. Science of The Total Environment 575, 701–712. https://doi.org/10.1016/j.scitotenv.2016.09.105

Casado, J., Brigden, K., Santillo, D., Johnston, P., 2019. Screening of pesticides and veterinary drugs in small streams in the European Union by liquid chromatography high resolution mass spectrometry. Science of the total environment 670, 1204–1225. https://doi.org/10.1016/j.scitotenv.2019.03.207

Cavalli, M., Trevisani, S., Comiti, F., Marchi, L., 2013. Geomorphometric assessment of spatial sediment connectivity in small Alpine catchments. Geomorphology 188, 31–41. https://doi.org/10.1016/J.GEOMORPH.2012.05.007

Cedergreen, N., 2014. Quantifying Synergy: A Systematic Review of Mixture Toxicity Studies within Environmental Toxicology. PLOS ONE 9, e96580. https://doi.org/10.1371/JOURNAL.PONE.0096580

Centanni, M., Ricci, G.F., De Girolamo, A.M., Romano, G., Gentile, F., 2023. A review of modeling pesticides in freshwaters: Current status, progress achieved and desirable improvements. Environmental Pollution 316, 120553. https://doi.org/10.1016/j.envpol.2022.120553

Cerdan, O., Le Bissonnais, Y., Govers, G., Lecomte, V., Van Oost, K., Couturier, A., King, C., Dubreuil, N., 2004. Scale effect on runoff from experimental plots to catchments in agricultural areas in Normandy. Journal of Hydrology 299, 4–14. https://doi.org/10.1016/j.jhydrol.2004.02.017

Cessna, A.J., McConkey, B.G., Elliott, J.A., 2013. Herbicide Transport in Surface Runoff from Conventional and Zero-Tillage Fields. Journal of Environment Quality 42, 782. https://doi.org/10.2134/jeq2012.0304

Chamen, W., Vermeulen, G.D., Campbell, D., Sommer, C., 1992. Reduction of traffic-induced soil compaction: a synthesis. Soil and Tillage Research 24, 303–318.

Chen, H., Zhang, X., Demars, C., Zhang, M., 2017. Numerical simulation of agricultural sediment and pesticide runoff: RZWQM and PRZM comparison. Hydrol. Process. 31, 2464–2476. https://doi.org/10.1002/hyp.11207

Chiovarou, E.D., Siewicki, T.C., 2008. Comparison of storm intensity and application timing on modeled transport and fate of six contaminants. Science of The Total Environment 389, 87–100. https://doi.org/10.1016/J.SCITOTENV.2007.08.029

Chow, W., Ven Te; Maidment, David R; Larry, 1988. Applied Hydrology. International edition, MacGraw-Hill, Inc 149.

Clark, M.P., Vogel, R.M., Lamontagne, J.R., Mizukami, N., Knoben, W.J.M., Tang, G., Gharari, S., Freer, J.E., Whitfield, P.H., Shook, K.R., Papalexiou, S.M., 2021. The Abuse of Popular Performance Metrics in Hydrologic Modeling. Water Resources Research 57, e2020WR029001. https://doi.org/10.1029/2020WR029001

Climent, M.J., Herrero-Hernández, E., Sánchez-Martín, M.J., Rodríguez-Cruz, M.S., Pedreros, P., Urrutia, R., 2019. Residues of pesticides and some metabolites in dissolved and particulate phase in surface stream water of Cachapoal River basin, central Chile. Environmental Pollution 251, 90–101. https://doi.org/10.1016/j.envpol.2019.04.117

Commelin, M., Baartman, J.E., Zomer, P., Riksen, M., Geissen, V., 2022a. Pesticides are Substantially Transported in Particulate Phase, Driven by Land use, Rainfall Event and Pesticide Characteristics—A Runoff and Erosion Study in a Small Agricultural Catchment. Front. Frontiers in Environmental Science 10, 830589.

Commelin, M., Baartman, J.E.M. (Jantiene), Peters, P., Zomer, P., Riksen, M.J.P.M. (Michel), Geissen, V., 2022b. Runoff, erosion and pesticide transport in a small catchment in Limburg - The Netherlands. https://doi.org/10.4121/19690684.v1

Commelin, M.C., Baartman, J.E.M., Wesseling, J.G., Jetten, V., 2024. Simulating event-based pesticide transport with runoff and erosion; OpenLISEM-pesticide v.1. Environmental Modelling & Software 174, 105960. https://doi.org/10.1016/j.envsoft.2024.105960

Cor, F.L., Slaby, S., Dufour, V., Iuretig, A., Feidt, C., Dauchy, X., Banas, D., 2021. Occurrence of pesticides and their transformation products in headwater streams: Contamination status and effect of ponds on contaminant concentrations. Science of The Total Environment 788, 147715. https://doi.org/10.1016/J.SCITOTENV.2021.147715

Couturier, A., Daroussin, J., Darboux, F., Souchère, V., Le Bissonnais, Y., Cerdan, O., King, D., 2013. Improvement of surface flow network prediction for the modeling of erosion processes in agricultural landscapes. Geomorphology 183, 120–129.

Cruzeiro, C., Pardal, M.Â., Rodrigues-Oliveira, N., Castro, L.F.C., Rocha, E., Rocha, M.J., 2016. Multi-matrix quantification and risk assessment of pesticides in the longest river of the Iberian peninsula. Science of the Total Environment 572, 263–272. https://doi.org/10.1016/j.scitotenv.2016.07.203

D'Andrea, M.F., Letourneau, G., Rousseau, A.N., Brodeur, J.C., 2020. Sensitivity analysis of the Pesticide in Water Calculator model for applications in the Pampa region of Argentina. Science of The Total Environment 698, 134232. https://doi.org/10.1016/j.scitotenv.2019.134232

De Roo, A., Jetten, V., 1999. Calibrating and validating the LISEM model for two data sets from the Netherlands and South Africa. Catena 37, 477–493.

De Roo, A., Wesseling, C., Ritsema, C., 1996. LISEM: a single-event physically based hydrological and soil erosion model for drainage basins. I: theory, input and output. Hydrological processes 10, 1107–1117.

De Vente, J., Poesen, J., 2005. Predicting soil erosion and sediment yield at the basin scale: Scale issues and semi-quantitative models. Earth-Science Reviews 71, 95–125. https://doi.org/10.1016/j.earscirev.2005.02.002

DeMars, C., Zhan, Y., Chen, H., Heilman, P., Zhang, X., Zhang, M., 2018. Integrating GLEAMS sedimentation into RZWQM for pesticide sorbed sediment runoff modeling. Environmental Modelling and Software 109, 390–401. https://doi.org/10.1016/j.envsoft.2018.08.016

Dogan, F.N., Karpuzcu, M.E., 2023. Modeling fate and transport of pesticides from dryland agriculture using SWAT model. Journal of Environmental Management 334, 117457. https://doi.org/10.1016/j.jenvman.2023.117457

Dowling, T.P.F., Beulke, S., Garratt, J., 2019. Spatial assessment of pesticide leaching risk to groundwater: sub-national decision making and model output aggregation. Pest Management Science 75, 2575–2591. https://doi.org/10.1002/ps.5419

Downer, C.W., Nelson, E.J., Byrd, A., 2003. Primer: Using Watershed Modeling System (Wms) for Gridded Surface Subsurface Hydrologic Analysis (GSSHA) Data Development-Wms 6.1 and GSSHA 1.43 C.

Dunkerley, D., 2020. Acquiring unbiased rainfall duration and intensity data from tipping-bucket rain gauges: A new approach using synchronised acoustic recordings. Atmospheric Research 244, 105055. https://doi.org/10.1016/j.atmosres.2020.105055

Eads, R.E., Thomas, R.B., 1983. Evaluation of a Depth Proportional Intake Device for Automatic Pumping Samplers. JAWRA Journal of the American Water Resources Association 19, 289–292. https://doi.org/10.1111/j.1752-1688.1983.tb05328.x

EC, 2000. Directive 200/60/EC, establishing a framework for Community action in the field of water policy.

EEA, 2024. Pesticides in rivers, lakes and groundwater in Europe. European Environmental Agency.

EFSA, 2018. HOW PESTICIDES ARE REGULATED IN THE EU: EFSA and the assessment of active substances. EFSA Supporting Publications.

Elias, D., Wang, L., Jacinthe, P.A., 2018. A meta-analysis of pesticide loss in runoff under conventional tillage and no-till management. Environmental Monitoring and Assessment 190, 79. https://doi.org/10.1007/s10661-017-6441-1

Emmerich, W.E., Woolhiser, D.A., Shirley, E.D., 1989. Comparison of Lumped and Distributed Models for Chemical Transport by Surface Runoff. J of Env Quality 18, 120–126. https://doi.org/10.2134/jeq1989.00472425001800010022x

Erosienormeringsonderzoek ZUID-LIMBURG, 1994.

European Commission, 2019. Analytical Quality Control and Method Validation for Pesticide Residues Analysis in Food and Feed (SANTE/12682/2019). Sante/12682/2019 1–48.

European Environment Agency, 2023. How pesticides impact human health and ecosystems in Europe, EEA Briefing. Publications Office, LU.

European Food Safety Authority, 2014. Conclusion on the peer review of the pesticide risk assessment of the active substance metobromuron. EFS2 12. https://doi.org/10.2903/j.efsa.2014.3541

European Food Safety Authority (EFSA), 2015. Conclusion on the peer review of the pesticide risk assessment of the active substance glyphosate. EFS2 13. https://doi.org/10.2903/j.efsa.2015.4302

Eurostat, 2023. Agri-environmental indicator - consumption of pesticides. URL https://ec.europa.eu/eurostat/statistics-explained/index.php?title=Agri-environmental_indicator_-_consumption_of_pesticides (accessed 2.12.24).

FAO, 2020. FaoStat: Pesticides indicators.

FAO, IFAD, UNICEF, WFP, WHO, 2020. The State of Food Security and Nutrition in the World 2020, The State of Food Security and Nutrition in the World 2020. https://doi.org/10.4060/ca9692en

Faúndez Urbina, C.A., Den Berg, F., Dam, J.C., Tang, D.W.S., Ritsema, C.J., 2020. Parameter sensitivity of SWAP–PEARL models for pesticide leaching in macroporous soils. Vadose zone j. 19. https://doi.org/10.1002/vzj2.20075

Favis-Mortlock, D., Boardman, J., Foster, I., Shepheard, M., 2022. Comparison of observed and DEM-driven field-to-river routing of flow from eroding fields in an arable lowland catchment. CATENA 208, 105737. https://doi.org/10.1016/j.catena.2021.105737

Felsot, A., Dahm, P.A., 1979. Sorption of organophosphorus and carbamate insecticides by soil. Journal of agricultural and food chemistry 27, 557–563.

Ferreira, V., Albariño, R., Larrañaga, A., LeRoy, C.J., Masese, F.O., Moretti, M.S., 2023. Ecosystem services provided by small streams: an overview. Hydrobiologia 850, 2501–2535. https://doi.org/10.1007/s10750-022-05095-1

FOCUS, 2015. Generic Guidance for Surface Water Scenarios (Version 1.4).

FOCUS, 1997. Soil persistence models and EU registration. Guidance Document 7617-VI-96. Soil Modelling WorkGroup. EU Commission, Directorate General for Agriculture VI B II-1 77 pp.

Gao, B., Walter, M.T., Steenhuis, T.S., Hogarth, W.L., Parlange, J.Y., 2004. Rainfall induced chemical transport from soil to runoff: Theory and experiments. Journal of Hydrology 295, 291–304. https://doi.org/10.1016/j.jhydrol.2004.03.026

Gassmann, M., 2013. Environmental fate modelling of agrochemicals and their transformation products at catchment scale.

Gassmann, M., Olsson, O., Stamm, C., Weiler, M., Kümmerer, K., 2015. Physico-chemical characteristics affect the spatial distribution of pesticide and transformation product loss to an agricultural brook. Science of The Total Environment 532, 733–743. https://doi.org/10.1016/J.SCITOTENV.2015.06.068

Gatel, L., Lauvernet, C., Carluer, N., Weill, S., Paniconi, C., 2019. Sobol Global Sensitivity Analysis of a Coupled Surface/Subsurface Water Flow and Reactive Solute Transfer Model on a Real Hillslope. Water 12, 121. https://doi.org/10.3390/w12010121

Geiger, F., Bengtsson, J., Berendse, F., Weisser, W.W., Emmerson, M., Morales, M.B., Ceryngier, P., Liira, J., Tscharntke, T., Winqvist, C., Eggers, S., Bommarco, R., Pärt, T., Bretagnolle, V., Plantegenest, M., Clement, L.W., Dennis, C., Palmer, C., Oñate, J.J., Guerrero, I., Hawro, V., Aavik, T., Thies, C., Flohre, A., Hänke, S., Fischer, C., Goedhart, P.W., Inchausti, P., 2010. Persistent negative effects of pesticides on biodiversity and biological control potential on European farmland. Basic and Applied Ecology 11, 97–105. https://doi.org/10.1016/j.baae.2009.12.001

Geissen, V., Silva, V., Lwanga, E.H., Beriot, N., Oostindie, K., Bin, Z., Pyne, E., Busink, S., Zomer, P., Mol, H., Ritsema, C.J., 2021. Cocktails of pesticide residues in conventional and organic farming systems in Europe – Legacy of the past and turning point for the future. Environmental Pollution 278, 116827. https://doi.org/10.1016/j.envpol.2021.116827

Gettel, M., Gulliver, J.S., Kayhanian, M., Degroot, G., Brand, J., Mohseni, O., Erickson, A.J., 2011. Improving suspended sediment measurements by automatic samplers. Journal of Environmental Monitoring 13, 2703–2709. https://doi.org/10.1039/c1em10258c

Ghadiri, H., Rose, C.W., 1993. Water Erosion Processes and the Enrichment of Sorbed Pesticides. Part 2. Enrichment Under Rainfall Dominated Erosion Process. Journal of Environmental Management 37, 37–50. https://doi.org/10.1006/jema.1993.1003

Ghadiri, H., Rose, C.W., 1991. Sorbed Chemical Transport in Overland Flow: I. A Nutrient and Pesticide Enrichment Mechanism. Journal of Environmental Quality 20, 628–633. https://doi.org/10.2134/jeq1991.00472425002000030020x

Ghadiri, H, Rose, C.W., 1991. Sorbed Chemical Transport in Overland Flow: II. Enrichment Ratio Variation with Erosion Processes. Journal of Environmental Quality 20, 634–641. https://doi.org/10.2134/jeq1991.00472425002000030021x

Gil, Y., Sinfort, C., 2005. Emission of pesticides to the air during sprayer application: A bibliographic review. Atmospheric Environment 39, 5183–5193. https://doi.org/10.1016/j.atmosenv.2005.05.019

Globevnik, L., 2007. Briefing Small water bodies (No. No. EEA/ADS/06/001-Water). European Environmental Agency.

Godfray, H.C.J., Beddington, J.R., Crute, I.R., Haddad, L., Lawrence, D., Muir, J.F., Pretty, J., Robinson, S., Thomas, S.M., Toulmin, C., 2010. Food Security: The Challenge of Feeding 9 Billion People. Science 327, 812–818. https://doi.org/10.1126/science.1185383

Govers, G., 1990. Empirical relationships for the transport capacity of overland flow. Erosion, Transport and Deposition Processes (Proceedings) IAHS Publ.

Govers, G., Everaert, W., Poesen, J., Rauws, G., De Ploey, J., Lautridou, J.P., 1990. A long flume study of the dynamic factors affecting the resistance of a loamy soil to concentrated flow erosion. Earth Surface Processes and Landforms 15, 313–328.

Gramelsberger, G., Lenhard, J., Parker, W.S., 2020. Philosophical Perspectives on Earth System Modeling: Truth, Adequacy, and Understanding. J Adv Model Earth Syst 12, e2019MS001720. https://doi.org/10.1029/2019MS001720

Green, W.H., Ampt, G.A., 1911. Studies on Soil Physics. The Journal of Agricultural Science 1, 1–24.

Griffin, J.L., Dabney, S.M., 1990. Preplant-Postemergence Herbicides for Legume Cover-Crop Control in Minimum Tillage Systems. Weed Technology 4, 332–336. https://doi.org/10.1017/s0890037x00025495

Gupta, H.V., Kling, H., Yilmaz, K.K., Martinez, G.F., 2009. Decomposition of the mean squared error and NSE performance criteria: Implications for improving hydrological modelling. Journal of Hydrology 377, 80–91. https://doi.org/10.1016/j.jhydrol.2009.08.003

Halbach, K., Möder, M., Schrader, S., Liebmann, L., Schäfer, R.B., Schneeweiss, A., Schreiner, V.C., Vormeier, P., Weisner, O., Liess, M., others, 2021. Small streams–large concentrations? Pesticide monitoring in small agricultural streams in Germany during dry weather and rainfall. Water research 203, 117535.

Hamer, M., Maynard, S.K., Schneider, S., 2019. A pulsed-dose study evaluating chronic toxicity of chlorothalonil to fish: A case study for environmental risk assessment. Environmental Toxicology and Chemistry 38, 1549–1559. https://doi.org/10.1002/etc.4421

Hasenbein, S., Lawler, S.P., Geist, J., Connon, R.E., 2016. A long-term assessment of pesticide mixture effects on aquatic invertebrate communities. Environmental Toxicology and Chemistry 35, 218–232. https://doi.org/10.1002/etc.3187

Havis, R.N., Smith, R.E., Adrian, D.D., 1992. Partitioning solute transport between infiltration and overland flow under rainfall. Water Resources Research 28, 2569–2580. https://doi.org/10.1029/92WR01366

Heckmann, T., Cavalli, M., Cerdan, O., Foerster, S., Javaux, M., Lode, E., Smetanová, A., Vericat, D., Brardinoni, F., 2018. Indices of sediment connectivity: opportunities, challenges and limitations. Earth-Science Reviews 187, 77–108. https://doi.org/10.1016/j.earscirev.2018.08.004

Heinen, M., Bakker, G., Wösten, J.H.M., 2020. Waterretentie- en doorlatendheidskarakteristieken van boven- en ondergronden in Nederland: de Staringreeks : Update 2018. Wageningen Environmental Research, Wageningen. https://doi.org/10.18174/512761

Heinen, M., Brouwer, F., Teuling, K., Walvoort, D., 2021. BOFEK2020 - Bodemfysische schematisatie van Nederland : update bodemfysische eenhedenkaart. Wageningen Environmental Research, Wageningen. https://doi.org/10.18174/541544

Huang, C., Tong, J., Ye, M., 2021. Global sensitivity analysis for a prediction model of soil solute transfer into surface runoff. Journal of Hydrology 599, 126342. https://doi.org/10.1016/j.jhydrol.2021.126342

Huber, C., Nijssen, R., Mol, H., Philippe Antignac, J., Krauss, M., Brack, W., Wagner, K., Debrauwer, L., Maria Vitale, C., James Price, E., Klanova, J., Garlito Molina, B., Leon, N., Pardo, O., Fernández, S.F., Szigeti, T., Középesy, S., Šulc, L., Čupr, P., Mārtiņsone, I., Akülova, L., Ottenbros, I., Vermeulen, R., Vlaanderen, J., Luijten, M., Lommen, A., 2022. A large scale multi-laboratory suspect screening of pesticide metabolites in human biomonitoring: From tentative annotations to verified occurrences. Environment International 168, 107452. https://doi.org/10.1016/j.envint.2022.107452

Imfeld, G., Meite, F., Wiegert, C., Guyot, B., Masbou, J., Payraudeau, S., 2020. Do rainfall characteristics affect the export of copper, zinc and synthetic pesticides in surface runoff from headwater catchments? Science of the Total Environment 741, 140437. https://doi.org/10.1016/j.scitotenv.2020.140437

Imfeld, G., Payraudeau, S., Tournebize, J., Sauvage, S., Macary, F., Chaumont, C., Probst, A., Sánchez-Pérez, J.M., Bahi, A., Chaumet, B., Gilevska, T., Alexandre, H., Probst, J.L., 2021. The role of ponds in pesticide dissipation at the agricultural catchment scale: A critical review. Water. https://doi.org/10.3390/w13091202

Ippolito, A., Fait, G., 2019. Pesticides in surface waters: from edge-of-field to global modelling. Current Opinion in Environmental Sustainability. https://doi.org/10.1016/j.cosust.2018.10.023

Iturburu, F.G., Calderon, G., Amé, M.V., Menone, M.L., 2019. Ecological Risk Assessment (ERA) of pesticides from freshwater ecosystems in the Pampas region of Argentina: Legacy and current use chemicals contribution. Science of the Total Environment 691, 476–482. https://doi.org/10.1016/j.scitotenv.2019.07.044

Jaffrain, J., Berne, A., 2012. Quantification of the Small-Scale Spatial Structure of the Raindrop Size Distribution from a Network of Disdrometers. Journal of Applied Meteorology and Climatology 51, 941–953. https://doi.org/10.1175/JAMC-D-11-0136.1

Jarvis, N., 2016. Extended sorption partitioning models for pesticide leaching risk assessments: Can we improve upon the koc concept? Science of the Total Environment 539, 294–303. https://doi.org/10.1016/j.scitotenv.2015.09.002

Jetten, V., Roo, A. de, Guérif, J., 1998. Sensitivity of the model LISEM to variables related to agriculture, in: Modelling Soil Erosion by Water. Springer, pp. 339–349.

Jong, S.M. de, Jetten, V.G., 2007. Estimating spatial patterns of rainfall interception from remotely sensed vegetation indices and spectral mixture analysis. International Journal of Geographical Information Science 21, 529–545. https://doi.org/10.1080/13658810601064884

Joyce, B.A., Wallender, W.W., Ginn, T.R., 2008. Modeling the Transport of Spray-Applied Pesticides from Fields with Vegetative Cover. Transactions of the ASABE 51, 1963–1976. https://doi.org/10.13031/2013.25401

Joyce, B.A., Wallender, W.W., Mailapalli, D.R., 2010. Application of pesticide transport model for simulating diazinon runoff in California's central valley. Journal of Hydrology 395, 79–90. https://doi.org/10.1016/j.jhydrol.2010.10.017

Kabeja, C., Li, R., Rwabuhungu, D.E., 2021. Quantifying the Effects of Simulated Changes in Land Use/Cover on Flood Reduction: an Insight From Kigali. Rwanda Journal of Engineering, Science, Technology and Environment 4.

Kalyabina, V.P., Esimbekova, E.N., Kopylova, K.V., Kratasyuk, V.A., 2021. Pesticides: formulants, distribution pathways and effects on human health – a review. Toxicology Reports 8, 1179–1192. https://doi.org/10.1016/j.toxrep.2021.06.004

Karssenberg, D., Schmitz, O., Salamon, P., De Jong, K., Bierkens, M.F.P., 2010. A software framework for construction of process-based stochastic spatio-temporal models and data assimilation. Environmental Modelling & Software 25, 489–502. https://doi.org/10.1016/j.envsoft.2009.10.004

Kelleher, C., McGlynn, B., Wagener, T., 2017. Characterizing and reducing equifinality by constraining a distributed catchment model with regional signatures, local observations, and process understanding. Hydrol. Earth Syst. Sci. 21, 3325–3352. https://doi.org/10.5194/hess-21-3325-2017

Khorashadi Zadeh, F., Nossent, J., Sarrazin, F., Pianosi, F., Van Griensven, A., Wagener, T., Bauwens, W., 2017. Comparison of variance-based and moment-independent global sensitivity analysis approaches by application to the SWAT model. Environmental Modelling & Software 91, 210–222. https://doi.org/10.1016/j.envsoft.2017.02.001

Kim, J.-Y., Sansalone, J.J., 2008. Event-based size distributions of particulate matter transported during urban rainfall-runoff events. Water Research 42, 2756–2768. https://doi.org/10.1016/j.watres.2008.02.005

Kleinhans, M.G., Buskes, C.J.J., De Regt, H.W., 2010. Philosophy of Earth Science, in: Allhoff, F. (Ed.), Philosophies of the Sciences. Wiley, pp. 213–236. https://doi.org/10.1002/9781444315578.ch9

KNMI, 2021a. Monthly and yearly mean temperatures.

KNMI, 2021b. Monthly and yearly amount of precipitation.

KNMI, 2021c. Monthly and Yearly Mean Temperatures.

KNMI, 2021d. Precipitation - Radar/Gauges 5 minute Final Reanalysis Accumulations over the Netherlands.

Knoben, W.J.M., Freer, J.E., Woods, R.A., 2019. Technical note: Inherent benchmark or not? Comparing Nash–Sutcliffe and Kling–Gupta efficiency scores. Hydrol. Earth Syst. Sci. 23, 4323–4331. https://doi.org/10.5194/hess-23-4323-2019

Kool, M., Kosters, H., Griffioen, J., Groothuijse, F., Buitenkamp, H., 2023. Wie Aa zegt, ... Aanbevelingen voor duurzame verbetering van de waterkwaliteit van de Drentsche Aa ten behoeve van de openbare drinkwatervoorziening. Gedeputeerde Staten provincie Utrecht.

Kortenkamp, A., Vinggaard, A.M., Mengelers, M., Slama, R., João Silva, M., Louro, H., Viegas, S., Tavares, A., Goen, T., Ermler, S., Martin, O., Brand, A. van den, Donkersgoed, G. van, Santonen, T., Tuovila, J., Ma, Y., Rosenmai, A.K., Rodríguez-Carrillo, A., Mustieles, V., Taxvig, C., Reiber, L., Kiesow, A., David, M., Löbl, N.M., Fernández, M.F., Chatterjee, M., Agier, L., Basagna, X., Luijten, M., 2021. D15.5 - Case study reports on mixture health effects. https://doi.org/10.5281/ZENODO.6602142

Kouwen, N., Soulis, E.D., Pietroniro, A., Donald, J., Harrington, R.A., 1993. Grouped Response Units for Distributed Hydrologic Modeling. J. Water Resour. Plann. Manage. 119, 289–305. https://doi.org/10.1061/(ASCE)0733-9496(1993)119:3(289)

Kristensen, P., Globevnik, L., 2014. European small water bodies. Biology and Environment 114B, 281–287. https://doi.org/10.1353/bae.2014.0025

Kroes, J., Van Dam, J., Supit, I., De Abelleyra, D., Verón, S., De Wit, A., Boogaard, H., Angelini, M., Damiano, F., Groenendijk, P., Wesseling, J., Veldhuizen, A., 2019. Agrohydrological analysis of groundwater recharge and land use changes in the Pampas of Argentina. Agricultural Water Management 213, 843–857. https://doi.org/10.1016/j.agwat.2018.12.008

Kroes, J. G., Van Dam, J.C., Bartholomeus, R.P., Groenendijk, P., Heinen, M., Hendriks, R.F.A., Mulder, H.M., Supit, I., Van Walsum, P.E.V., 2017. SWAP version 4. Wageningen Environmental Research.

Kroes, J.G., van Dam, J.C., Bartholomeus, R.P., Groenendijk, P., Heinen, M., Hendriks, R.F.A., Mulder, H.M., Supit, I., van Walsum, P.E.V., 2017. SWAP version 4 Theory description and user manual. Wageningen Universiy and Research, Wageningen. https://doi.org/10.18174/416321

Kucherenko, S., Albrecht, D., Saltelli, A., 2015. Exploring multi-dimensional spaces: a Comparison of Latin Hypercube and Quasi Monte Carlo Sampling Techniques. https://doi.org/10.48550/ARXIV.1505.02350

Kumari, D., John, S., 2020. Sorption Capacity of Pesticides on Soil in a Predominant Apple Cultivation Area. Soil and Sediment Contamination: An International Journal 29, 107–119. https://doi.org/10.1080/15320383.2019.1684876

la Cecilia, D., Dax, A., Ehmann, H., Koster, M., Singer, H., Stamm, C., 2021. Continuous high-frequency pesticide monitoring to observe the unexpected and the overlooked. Water Research X 13, 100125. https://doi.org/10.1016/j.wroa.2021.100125

Lanz, B., Dietz, S., Swanson, T., 2018. The Expansion of Modern Agriculture and Global Biodiversity Decline: An Integrated Assessment. Ecological Economics 144, 260–277. https://doi.org/10.1016/j.ecolecon.2017.07.018

Lauvernet, C., Muñoz-Carpena, R., 2018. Shallow water table effects on water, sediment, and pesticide transport in vegetative filter strips – Part 2: model coupling, application, factor importance, and uncertainty. Hydrol. Earth Syst. Sci. 22, 71–87. https://doi.org/10.5194/hess-22-71-2018

Le Quéré, C., 2006. The unknown and the uncertain in Earth system modeling. EoS Transactions 87, 496–496. https://doi.org/10.1029/2006EO450007

Lechenet, M., Dessaint, F., Py, G., Makowski, D., Munier-Jolain, N., 2017. Reducing pesticide use while preserving crop productivity and profitability on arable farms. Nature Plants 3. https://doi.org/10.1038/nplants.2017.8

Leemans, M., Couderq, S., Demeneix, B., Fini, J.-B., 2019. Pesticides With Potential Thyroid Hormone-Disrupting Effects: A Review of Recent Data. Front. Endocrinol. 10, 743. https://doi.org/10.3389/fendo.2019.00743

Lefrancq, M., Jadas-Hécart, A., La Jeunesse, I., Landry, D., Payraudeau, S., 2017a. High frequency monitoring of pesticides in runoff water to improve understanding of their transport and environmental impacts. Science of the Total Environment 587–588, 75–86. https://doi.org/10.1016/j.scitotenv.2017.02.022

Lefrancq, M., Van Dijk, P., Jetten, V., Schwob, M., Payraudeau, S., 2017b. Improving runoff prediction using agronomical information in a cropped, loess covered catchment. Hydrological Processes 31, 1408–1423. https://doi.org/10.1002/hyp.11115

Leonard, R.A., 1990. Movement of pesticides into surface waters, in: Pesticides in the Soil Environment: Processes, Impacts, and Modeling. John Wiley & Sons, Ltd, pp. 303–349. https://doi.org/10.2136/sssabookser2.c9

Leonard, R.A., Knisel, W.G., Still, D.A., 1987. GLEAMS: Groundwater Loading Effects of Agricultural Management Systems. Transactions of the ASAE 30, 1403–1418. https://doi.org/10.13031/2013.30578

Lewis, K.A., Tzilivakis, J., Warner, D.J., Green, A., 2016. An international database for pesticide risk assessments and management. Human and Ecological Risk Assessment: An International Journal 22, 1050–1064. https://doi.org/10.1080/10807039.2015.1133242

Li, H., Cheng, F., Wei, Y., Lydy, M.J., You, J., 2017. Global occurrence of pyrethroid insecticides in sediment and the associated toxicological effects on benthic invertebrates: An overview. Journal of Hazardous Materials 324, 258–271. https://doi.org/10.1016/j.jhazmat.2016.10.056

Li, Y., Lau, S.-L., Kayhanian, M., Stenstrom, M.K., 2005. Particle Size Distribution in Highway Runoff. J. Environ. Eng. 131, 1267–1276. https://doi.org/10.1061/(ASCE)0733-9372(2005)131:9(1267)

Liess, M., Liebmann, L., Vormeier, P., Weisner, O., Altenburger, R., Borchardt, D., Brack, W., Chatzinotas, A., Escher, B., Foit, K., Gunold, R., Henz, S., Hitzfeld, K.L., Schmitt-Jansen, M., Kamjunke, N., Kaske, O., Knillmann, S., Krauss, M., Küster, E., Link, M., Lück, M., Möder, M., Müller, A., Paschke, A., Schäfer, R.B., Schneeweiss, A., Schreiner, V.C., Schulze, T., Schüürmann, G., Von Tümpling, W., Weitere, M., Wogram, J., Reemtsma, T., 2021. Pesticides are the dominant stressors for vulnerable insects in lowland streams. Water Research 201, 117262. https://doi.org/10.1016/j.watres.2021.117262

Liu, Y., Pan, X., Li, J., 2015. A 1961–2010 record of fertilizer use, pesticide application and cereal yields: a review. Agron. Sustain. Dev. 35, 83–93. https://doi.org/10.1007/s13593-014-0259-9

López-Vicente, M., Ben-Salem, N., 2019. Computing structural and functional flow and sediment connectivity with a new aggregated index: A case study in a large Mediterranean catchment. Science of The Total Environment 651, 179–191. https://doi.org/10.1016/J.SCITOTENV.2018.09.170

Louchart, X., Voltz, M., 2007. Aging effects on the availability of herbicides to runoff transfer. Environmental Science and Technology 41, 1137–1144. https://doi.org/10.1021/es061186q

Lykogianni, M., Bempelou, E., Karamaouna, F., Aliferis, K.A., 2021. Do pesticides promote or hinder sustainability in agriculture? The challenge of sustainable use of pesticides in modern agriculture. Science of The Total Environment 795, 148625. https://doi.org/10.1016/j.scitotenv.2021.148625

Mai, J., 2023. Ten strategies towards successful calibration of environmental models. Journal of Hydrology 620, 129414. https://doi.org/10.1016/j.jhydrol.2023.129414

Maillard, E., Imfeld, G., 2014. Pesticide mass budget in a stormwater wetland. Environmental Science and Technology 48, 8603–8611. https://doi.org/10.1021/es500586x

Maillard, E., Payraudeau, S., Faivre, E., Grégoire, C., Gangloff, S., Imfeld, G., 2011. Removal of pesticide mixtures in a stormwater wetland collecting runoff from a vineyard catchment. Science of the Total Environment 409, 2317–2324. https://doi.org/10.1016/j.scitotenv.2011.01.057

Mamy, L., Leenhardt, S., Pesce, S., Sanchez, W., Achard, A.L., Amichot, M., Artigas, J., Aviron, S., Barthélémy, C., Beaudouin, R., Bedos, C., Bérard, A., Berny, P., Bertrand, Cédric, Bertrand, Colette, Betoulle, S., Bureau-Point, È., Charles, S., Chaumot, A., Chauvel, B., Coeurdassier, M., Corio-Costet, M.-F., Coutellec, M.-A., Crouzet, O., Doussan, I., Fabure, J., Fritsch, C., Gallai, N., Gonzalez, P., Gouy, V., Hedde, M., Langlais, A., Le Bellec, F., Leboulanger, C., Le Gall, M., Le Perchec, S., Margoum, C., Martin-Laurent, F., Mongruel, R., Morin, S., Mougin, C., Munaron, D., Nelieu, S., Pélosi, C., Rault, M., Sabater, S., Stachowski-Haberkorn, S., Sucré, E., Thomas, M., Tournebize, J., 2022. Impacts des produits phytopharmaceutiques sur la biodiversité et les services écosystémiques. Rapport de l'expertise scientifique collective. https://doi.org/10.17180/0GP2-CD65

Masiá, A., Campo, J., Vázquez-Roig, P., Blasco, C., Picó, Y., 2013. Screening of currently used pesticides in water, sediments and biota of the Guadalquivir River Basin (Spain). Journal of Hazardous Materials 263, 95–104. https://doi.org/10.1016/j.jhazmat.2013.09.035

Matthews, F., 2024. Dynamic modelling of soil erosion and sediment delivery in Europe.

Mayora, G., Sagardoy, M.E., Repetti, M.R., Paira, A., Frau, D., Gutierrez, M.F., 2024. Spatiotemporal patterns of multiple pesticide residues in central Argentina streams. Science of The Total Environment 906, 167014. https://doi.org/10.1016/j.scitotenv.2023.167014

McCall, P.J., Laskowski, D.A., Swann, R.L., Dishburger, H.J., 1980. Measurement of sorption coefficients of organic chemicals and their use in environmental fate analysis, in: Test Protocols for Environmental Fate and Movement of Toxicants. In: Proceedings of the 94th Annual Meeting of the American Association of Official Analytical Chemists (AOAC). Oct. pp. 21–22.

Meinen, B.U., Robinson, D.T., 2021. Agricultural erosion modelling: Evaluating USLE and WEPP field-scale erosion estimates using UAV time-series data. Environmental Modelling & Software 137, 104962. https://doi.org/10.1016/j.envsoft.2021.104962

Meite, F., Alvarez-Zaldívar, P., Crochet, A., Wiegert, C., Payraudeau, S., Imfeld, G., 2018. Impact of rainfall patterns and frequency on the export of pesticides and heavy-metals from agricultural soils. Science of the Total Environment 616–617, 500–509. https://doi.org/10.1016/j.scitotenv.2017.10.297

Melland, A.R., Silburn, D.M., McHugh, A.D., Fillols, E., Rojas-Ponce, S., Baillie, C., Lewis, S., 2016. Spot spraying reduces herbicide concentrations in runoff. Journal of Agricultural and Food Chemistry 64, 4009–4020. https://doi.org/10.1021/acs.jafc.5b03688

Menzel, R.G., 1980. Enrichment ratios for water quality modeling, in: CREAMS: A Field Scale Model for Chemicals, Runoff, and Erosion from Agricultural Management Systems. pp. 486–492.

Mie, A., Rudén, C., 2022. What you don’t know can still hurt you - underreporting in EU pesticide regulation. Environ Health 21, 79. https://doi.org/10.1186/s12940-022-00891-7

Mol, H.G.J., Plaza-Bolaños, P., Zomer, P., De Rijk, T.C., Stolker, A.A.M., Mulder, P.P.J., 2008. Toward a generic extraction method for simultaneous determination of pesticides, mycotoxins, plant toxins, and veterinary drugs in feed and food matrixes. Analytical Chemistry 80, 9450–9459. https://doi.org/10.1021/ac801557f

Molini, A., Lanza, L.G., La Barbera, P., 2005. The impact of tipping-bucket raingauge measurement errors on design rainfall for urban-scale applications. Hydrological Processes 19, 1073–1088. https://doi.org/10.1002/hyp.5646

Morgan, R.P.C., Morgan, D.D.V., Finney, H.J., 1984. A predictive model for the assessment of soil erosion risk. Journal of Agricultural Engineering Research 30, 245–253. https://doi.org/10.1016/S0021-8634(84)80025-6

Morselli, M., Vitale, C.M., Ippolito, A., Villa, S., Giacchini, R., Vighi, M., Di Guardo, A., 2018. Predicting pesticide fate in small cultivated mountain watersheds using the DynAPlus model: Toward improved assessment of peak exposure. Science of The Total Environment 615, 307–318. https://doi.org/10.1016/j.scitotenv.2017.09.287

Moser, A., Wemyss, D., Scheidegger, R., Fenicia, F., Honti, M., Stamm, C., 2018. Modelling biocide and herbicide concentrations in catchments of the Rhine basin. Hydrology and Earth System Sciences 22, 4229–4249. https://doi.org/10.5194/hess-22-4229-2018

Mottes, C., Lesueur-Jannoyer, M., Charlier, J.B., Carles, C., Guéné, M., Le Bail, M., Malézieux, E., 2015. Hydrological and pesticide transfer modeling in a tropical volcanic watershed with the WATPPASS model. Journal of Hydrology 529, 909–927. https://doi.org/10.1016/j.jhydrol.2015.09.007

Mottes, C., Lesueur-Jannoyer, M., Le Bail, M., Malézieux, E., 2014. Pesticide transfer models in crop and watershed systems: A review. Agronomy for Sustainable Development 34, 229–250. https://doi.org/10.1007/s13593-013-0176-3

Muñoz-Carpena, R., Fox, G.A., Ritter, A., Perez-Ovilla, O., Rodea-Palomares, I., 2018. Effect of vegetative filter strip pesticide residue degradation assumptions for environmental exposure assessments. Science of the Total Environment 619–620, 977–987. https://doi.org/10.1016/j.scitotenv.2017.11.093

Muñoz-Carpena, R., Ritter, A., Fox, G.A., 2019. Comparison of empirical and mechanistic equations for vegetative filter strip pesticide mitigation in long-term environmental exposure assessments. Water Research 165. https://doi.org/10.1016/j.watres.2019.114983

Murcia-Morales, M., Díaz-Galiano, F.J., Vejsnæs, F., Kilpinen, O., Van Der Steen, J.J.M., Fernández-Alba, A.R., 2021. Environmental monitoring study of pesticide contamination in Denmark through honey bee colonies using APIStrip-based sampling. Environmental Pollution 290, 117888. https://doi.org/10.1016/j.envpol.2021.117888

Napoli, M., Dalla Marta, A., Zanchi, C.A., Orlandini, S., Napoli, M., Marta, A.A.D.A., Zanchi, C.A., Orlandini, S., 2016. Transport of Glyphosate and Aminomethylphosphonic Acid under Two Soil Management Practices in an Italian Vineyard. J. Environ. Qual 45, 1713–1721. https://doi.org/10.2134/jeq2016.02.0061

Nash, J.E., Sutcliffe, J.V., 1970. River flow forecasting through conceptual models part I — A discussion of principles. Journal of Hydrology 10, 282–290. https://doi.org/10.1016/0022-1694(70)90255-6

Nunes, J.P., Seixas, J., Keizer, J.J., 2013. Modeling the response of within-storm runoff and erosion dynamics to climate change in two Mediterranean watersheds: A multi-model, multi-scale approach to scenario design and analysis. CATENA 102, 27–39. https://doi.org/10.1016/j.catena.2011.04.001

Oerke, E.-C., 2006. Crop losses to pests. J. Agric. Sci. 144, 31–43. https://doi.org/10.1017/S0021859605005708

Oliver, D.P., Kookana, R.S., Anderson, J.S., Cox, J.W., Waller, N., Smith, L.H., 2012. Off-site transport of pesticides in dissolved and particulate forms from two land uses in the Mt. Lofty Ranges, South Australia. Agricultural Water Management 106, 78–85. https://doi.org/10.1016/j.agwat.2011.11.001

Olivier, C., Goffart, J.P., Baets, D., Xanthoulis, D., Fonder, N., Lognay, G., Barthélemy, J.P., Lebrun, P., 2014. Use of mirco-dams in potato furrows to reduce erosion and runoff and minimise surface water contamination through pesticides. Communications in agricultural and applied biological sciences 79, 513–24.

Overeem, A., Holleman, I., Buishand, A., 2009. Derivation of a 10-year radar-based climatology of rainfall. Journal of Applied Meteorology and Climatology 48, 1448–1463. https://doi.org/10.1175/2009JAMC1954.1

Panagos, P., Borrelli, P., Poesen, J., Ballabio, C., Lugato, E., Meusburger, K., Montanarella, L., Alewell, C., 2015. The new assessment of soil loss by water erosion in Europe. Environmental Science and Policy 54, 438–447. https://doi.org/10.1016/j.envsci.2015.08.012

Parkin, D., King, W., Shaw, D., 1982. An automatic raingauge network for a cloud seeding experiment.

Parshall, R.L., 1926. The Improved Venturi Flume. Transactions of the American Society of Civil Engineers 89, 841–851. https://doi.org/10.1061/taceat.0003626

Parsons, A.J., Abrahams, A.D., Wainwright, J., 1994. On determining resistance to interrill overland flow. Water Resources Research 30, 3515–3521. https://doi.org/10.1029/94WR02176

Payraudeau, S., Gregoire, C., 2012. Modelling pesticides transfer to surface water at the catchment scale: A multi-criteria analysis. Agronomy for Sustainable Development 32, 479–500. https://doi.org/10.1007/s13593-011-0023-3

Peruzzo, P.J., Porta, A.A., Ronco, A.E., 2008. Levels of glyphosate in surface waters, sediments and soils associated with direct sowing soybean cultivation in north pampasic region of Argentina. Environmental Pollution 156, 61–66. https://doi.org/10.1016/j.envpol.2008.01.015

Petersen, L.W., Moldrup, P., Jacobsen, O., Rolston, D.E., 1996. Relations between specific surface area and soil physical and chemical properties. Soil Science 161, 9–21.

Phillips, J.D., 1989. Predicting minimum achievable soil loss in developing countries. Applied Geography 9, 219–236.

Pianosi, F., Beven, K., Freer, J., Hall, J.W., Rougier, J., Stephenson, D.B., Wagener, T., 2016. Sensitivity analysis of environmental models: A systematic review with practical workflow. Environmental Modelling & Software 79, 214–232. https://doi.org/10.1016/j.envsoft.2016.02.008

Pignatello, J.J., 2015. Sorption Dynamics of Organic Compounds in Soils and Sediments, in: Sawhney, B.L., Brown, K. (Eds.), SSSA Special Publications. Soil Science Society of America and American Society of Agronomy, Madison, WI, USA, pp. 45–80. https://doi.org/10.2136/sssaspecpub22.c3

Poesen, J., 2018. Soil erosion in the Anthropocene: Research needs. Earth Surf Processes Landf 43, 64–84. https://doi.org/10.1002/esp.4250

Potter, K., 1990. Soil properties effect on random roughness decay by rainfall. Transactions of the ASAE 33, 1889–1892.

Pradhan, N.R., Downer, C.W., Johnson, B.E., 2014. A Physics Based Hydrologic Modeling Approach to Simulate Non-point Source Pollution for the Purposes of Calculating TMDLs and Designing Abatement Measures, in: Leszczynski, J., Shukla, M.K. (Eds.), Practical Aspects of Computational Chemistry III. Springer US, Boston, MA, pp. 249–282. https://doi.org/10.1007/978-1-4899-7445-7_9

Prasuhn, V., 2020. Twenty years of soil erosion on-farm measurement: Annual variation, spatial distribution and the impact of conservation programmes for soil loss rates in Switzerland. Earth Surface Processes and Landforms 45, 1539–1554. https://doi.org/10.1002/ESP.4829

Pribyl, D.W., 2010. A critical review of the conventional SOC to SOM conversion factor. Geoderma 156, 75–83. https://doi.org/10.1016/j.geoderma.2010.02.003

Purnell, S., Kennedy, R., Williamson, E., Remesan, R., 2020. Metaldehyde prediction by integrating existing water industry datasets with the soil and water assessment tool. Water Research 183, 116053. https://doi.org/10.1016/j.watres.2020.116053

Puy, A., Piano, S.L., Saltelli, A., Levin, S.A., 2022. **sensobol** : An *R* Package to Compute Variance-Based Sensitivity Indices. J. Stat. Soft. 102. https://doi.org/10.18637/jss.v102.i05

QGIS, 2021. QGIS Geographic Information System. QGIS Assosaction.

QGIS.org, 2023. QGIS 3.28 Geographic Information System.

R Core Team, 2023. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria.

Rawls, W.J., Brakensiek, D.L., Miller, N., 1983. Green-ampt Infiltration Parameters from Soils Data. J. Hydraul. Eng. 109, 62–70. https://doi.org/10.1061/(ASCE)0733-9429(1983)109:1(62)

Reichenberger, S., Bach, M., Skitschak, A., Frede, H.G., 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; A review. Science of the Total Environment 384, 1–35. https://doi.org/10.1016/j.scitotenv.2007.04.046

Reichenberger, S., Sur, R., Kley, C., Sittig, S., Multsch, S., 2019. Recalibration and cross-validation of pesticide trapping equations for vegetative filter strips (VFS) using additional experimental data. Science of The Total Environment 647, 534–550. https://doi.org/10.1016/j.scitotenv.2018.07.429

Reichenberger, S., Sur, R., Sittig, S., Multsch, S., Carmona-Cabrero, Á., López, J.J., Muñoz-Carpena, R., 2023. Dynamic prediction of effective runoff sediment particle size for improved assessment of erosion mitigation efficiency with vegetative filter strips. Science of The Total Environment 857, 159572. https://doi.org/10.1016/j.scitotenv.2022.159572

Reuters.com, 2023. EU to renew herbicide glyphosate approval for 10 years. Reuters.

Rittenburg, R.A., Squires, A.L., Boll, J., Brooks, E.S., Easton, Z.M., Steenhuis, T.S., 2015. Agricultural BMP Effectiveness and Dominant Hydrological Flow Paths: Concepts and a Review. J Am Water Resour Assoc 51, 305–329. https://doi.org/10.1111/1752-1688.12293

Ritz, C., Baty, F., Streibig, J.C., Gerhard, D., 2015. Dose-response analysis using R. PLoS ONE 10, e0146021. https://doi.org/10.1371/journal.pone.0146021

Rizzati, V., Briand, O., Guillou, H., Gamet-Payrastre, L., 2016. Effects of pesticide mixtures in human and animal models: An update of the recent literature. Chemico-Biological Interactions 254, 231–246. https://doi.org/10.1016/j.cbi.2016.06.003

Roper, W.R., Robarge, W.P., Osmond, D.L., Heitman, J.L., 2019. Comparing Four Methods of Measuring Soil Organic Matter in North Carolina Soils. Soil Science Society of America Journal 83, 466–474. https://doi.org/10.2136/sssaj2018.03.0105

Rose, S., Basford, B., Carter, A., 2004. Development of a design manual for agricultural pesticide handling and washdown areas. Environment Agency, Bristol.

Rouzies, E., Lauvernet, C., Barachet, C., Morel, T., Branger, F., Braud, I., Carluer, N., 2019. From agricultural catchment to management scenarios: A modular tool to assess effects of landscape features on water and pesticide behavior. Science of The Total Environment 671, 1144–1160. https://doi.org/10.1016/J.SCITOTENV.2019.03.060

Rouzies, E., Lauvernet, C., Sudret, B., Vidard, A., 2023. How is a global sensitivity analysis of a catchment-scale, distributed pesticide transfer model performed? Application to the PESHMELBA model. Geosci. Model Dev. 16, 3137–3163. https://doi.org/10.5194/gmd-16-3137-2023

Russo, L., Buckley, Y.M., Hamilton, H., Kavanagh, M., Stout, J.C., 2020. Low concentrations of fertilizer and herbicide alter plant growth and interactions with flower-visiting insects. Agriculture, Ecosystems & Environment 304, 107141. https://doi.org/10.1016/j.agee.2020.107141

Sabzevari, S., Hofman, J., 2022. A worldwide review of currently used pesticides' monitoring in agricultural soils. Science of The Total Environment 812, 152344. https://doi.org/10.1016/j.scitotenv.2021.152344

Sadegh-Zadeh, F., 2017. Sorption, degradation and leaching of pesticides in soils amended with organic matter: A review. AET. https://doi.org/10.22104/aet.2017.1740.1100

Saltelli, A., Aleksankina, K., Becker, W., Fennell, P., Ferretti, F., Holst, N., Li, S., Wu, Q., 2019. Why so many published sensitivity analyses are false: A systematic review of sensitivity analysis practices. Environmental Modelling & Software 114, 29–39. https://doi.org/10.1016/j.envsoft.2019.01.012

Sandin, M., Piikki, K., Jarvis, N., Larsbo, M., Bishop, K., Kreuger, J., 2018. Spatial and temporal patterns of pesticide concentrations in streamflow, drainage and runoff in a small Swedish agricultural catchment. Science of the Total Environment 610–611, 623–634. https://doi.org/10.1016/j.scitotenv.2017.08.068

Sattler, C., Kächele, H., Verch, G., 2007. Assessing the intensity of pesticide use in agriculture. Agriculture, Ecosystems and Environment 119, 299–304. https://doi.org/10.1016/j.agee.2006.07.017

Saxton, K.E., Rawls, W.J., 2006. Soil Water Characteristic Estimates by Texture and Organic Matter for Hydrologic Solutions. Soil Science Society of America Journal 70, 1569–1578. https://doi.org/10.2136/sssaj2005.0117

Schappert, A., Messelhäuser, M.H., Saile, M., Peteinatos, G.G., Gerhards, R., 2018. Weed suppressive ability of cover crop mixtures compared to repeated stubble tillage and glyphosate treatments. Agriculture (Switzerland) 8. https://doi.org/10.3390/agriculture8090144

Schiettecatte, W., Gabriels, D., Cornelis, W.M., Hofman, G., 2008. Enrichment of Organic Carbon in Sediment Transport by Interrill and Rill Erosion Processes. Soil Science Soc of Amer J 72, 50–55. https://doi.org/10.2136/sssaj2007.0201

Schönenberger, U.T., Beck, B., Dax, A., Vogler, B., Stamm, C., 2022. Pesticide concentrations in agricultural storm drainage inlets of a small Swiss catchment. Environmental Science and Pollution Research 1, 1–18. https://doi.org/10.1007/s11356-022-18933-5

Schuhmann, A., Klammler, G., Weiss, S., Gans, O., Fank, J., Haberhauer, G., Gerzabek, M.H., 2019. Degradation and leaching of bentazone, terbuthylazine and S-metolachlor and some of their metabolites: A long-term lysimeter experiment. Plant, Soil and Environment 65 (2019), 273–281. https://doi.org/10.17221/803/2018-PSE

Schürz, C., Schulz, K., 2022. Reply to STOTEN 802 (2022) 149713: The fallacy in the use of the “best-fit” solution in hydrologic modeling. Science of The Total Environment 821, 153402. https://doi.org/10.1016/j.scitotenv.2022.153402

Seibert, J., Vis, M.J.P., Lewis, E., Van Meerveld, H.J., 2018. Upper and lower benchmarks in hydrological modelling. Hydrological Processes 32, 1120–1125. https://doi.org/10.1002/hyp.11476

Shao, F., Tao, W., Wang, Q., Wu, J., Su, L., Sun, Y., Zeng, S., 2021. A modified model for predicting nutrient loss in runoff using a time-varying mixing layer. Journal of Hydrology 603, 127091. https://doi.org/10.1016/j.jhydrol.2021.127091

Sharpley, A., 1985. Depth of surface soil-runoff interaction as affected by rainfall, soil slope, and management. Soil Science Society of America Journal 49, 1010–1015.

Sharpley, A.N., 1985. The Selection Erosion of Plant Nutrients in Runoff. Soil Science Soc of Amer J 49, 1527–1534. https://doi.org/10.2136/sssaj1985.03615995004900060039x

Shi, W., Huang, M., 2021. Predictions of soil and nutrient losses using a modified SWAT model in a large hilly-gully watershed of the Chinese Loess Plateau. International Soil and Water Conservation Research 9, 291–304. https://doi.org/10.1016/j.iswcr.2020.12.002

Shi, X., Wu, L., Chen, W., Wang, Q., 2011. Solute Transfer from the Soil Surface to Overland Flow: A Review. Soil Science Society of America Journal 75, 1214–1225. https://doi.org/10.2136/sssaj2010.0433

Sidle, R.C., Gomi, T., Loaiza Usuga, J.C., Jarihani, B., 2017. Hydrogeomorphic processes and scaling issues in the continuum from soil pedons to catchments. Earth-Science Reviews 175, 75–96. https://doi.org/10.1016/j.earscirev.2017.10.010

Silva, V., Gai, L., Harkes, P., Tan, G., Ritsema, C.J., Alcon, F., Contreras, J., Abrantes, N., Campos, I., Baldi, I., Bureau, M., Christ, F., Mandrioli, D., Sgargi, D., Pasković, I., Polić Pasković, M., Glavan, M., Hofman, J., Huerta Lwanga, E., Norgaard, T., Bílková, Z., Osman, R., Khurshid, C., Navarro, I., De La Torre, A., Sanz, P., Ángeles Martínez, M., Dias, J., Mol, H., Gort, G., Martins Figueiredo, D., Scheepers, P.T.J., Schlünssen, V., Vested, A., Alaoui, A., Geissen, V., 2023. Pesticide residues with hazard classifications relevant to non-target species including humans are omnipresent in the environment and farmer residences. Environment International 181, 108280. https://doi.org/10.1016/j.envint.2023.108280

Silva, V., Mol, H.G.J., Zomer, P., Tienstra, M., Ritsema, C.J., Geissen, V., 2019. Pesticide residues in European agricultural soils – A hidden reality unfolded. Science of the Total Environment 653, 1532–1545. https://doi.org/10.1016/j.scitotenv.2018.10.441

Sitterson, J., Knightes, C., Parmar, R., Wolfe, K., Muche, M., Avant, B., 2017. An Overview of Rainfall-Runoff Model Types (No. EPA/600?R-14/152). U.S. Environmental Protection Agency, Washington, DC.

Siviter, H., Bailes, E.J., Martin, C.D., Oliver, T.R., Koricheva, J., Leadbeater, E., Brown, M.J.F., 2021. Agrochemicals interact synergistically to increase bee mortality. Nature 2021 596:7872 596, 389–392. https://doi.org/10.1038/s41586-021-03787-7

Sjerps, R.M.A., Kooij, P.J.F., Van Loon, A., Van Wezel, A.P., 2019. Occurrence of pesticides in Dutch drinking water sources. Chemosphere 235, 510–518. https://doi.org/10.1016/j.chemosphere.2019.06.207

Skahill, B.E., Doherty, J., 2006. Efficient accommodation of local minima in watershed model calibration. Journal of Hydrology 329, 122–139. https://doi.org/10.1016/j.jhydrol.2006.02.005

Sobol′, I.M., 2001. Global sensitivity indices for nonlinear mathematical models and their Monte Carlo estimates. Mathematics and Computers in Simulation 55, 271–280. https://doi.org/10.1016/S0378-4754(00)00270-6

Sobol, I.M., 1976. Uniformly distributed sequences with an additional uniform property. USSR Computational Mathematics and Mathematical Physics 16, 236–242. https://doi.org/10.1016/0041-5553(76)90154-3

Souchère, V., King, D., Daroussin, J., Papy, F., Capillon, A., 1998. Effects of tillage on runoff directions: consequences on runoff contributing area within agricultural catchments. Journal of hydrology 206, 256–267.

Sterelny, K., 1996. Explanatory pluralism in evolutionary biology. Biol Philos 11, 193–214. https://doi.org/10.1007/BF00128919

Syafrudin, M., Kristanti, R.A., Yuniarto, A., Hadibarata, T., Rhee, J., Al-Onazi, W.A., Algarni, T.S., Almarri, A.H., Al-Mohaimeed, A.M., 2021. Pesticides in Drinking Water—A Review. International Journal of Environmental Research and Public Health 2021, Vol. 18, Page 468 18, 468. https://doi.org/10.3390/IJERPH18020468

Sybertz, A., Ottermanns, R., Schäffer, A., Scholz-Starke, B., Daniels, B., Frische, T., Bär, S., Ullrich, C., Roß-Nickoll, M., 2020. Simulating spray series of pesticides in agricultural practice reveals evidence for accumulation of environmental risk in soil. Science of the Total Environment 710, 135004. https://doi.org/10.1016/j.scitotenv.2019.135004

Takken, I., Govers, G., Steegen, A., Nachtergaele, J., Guérif, J., 2001a. The prediction of runoff flow directions on tilled fields. Journal of Hydrology 248, 1–13. https://doi.org/10.1016/S0022-1694(01)00360-2

Takken, I., Jetten, V., Govers, G., Nachtergaele, J., Steegen, A., 2001b. The effect of tillage-induced roughness on runoff and erosion patterns. Geomorphology 37, 1–14. https://doi.org/10.1016/S0169-555X(00)00059-3

Tang, X., Zhu, B., Katou, H., 2012. A review of rapid transport of pesticides from sloping farmland to surface waters: processes and mitigation strategies. Journal of Environmental Sciences 24, 351–361. https://doi.org/10.1016/S1001-0742(11)60753-5

Taylor, J.R., Thompson, W., 1998. An Introduction to Error Analysis: The Study of Uncertainties in Physical Measurements. Physics Today 51, 57–58. https://doi.org/10.1063/1.882103

Thaler, E.A., Kwang, J.S., Quirk, B.J., Quarrier, C.L., Larsen, I.J., 2022. Rates of Historical Anthropogenic Soil Erosion in the Midwestern United States. Earth's Future 10, e2021EF002396. https://doi.org/10.1029/2021EF002396

Todorovic, G.R., Rampazzo, N., Mentler, A., Blum, W.E.H., Eder, A., Strauss, P., 2014. Influence of soil tillage and erosion on the dispersion of glyphosate and aminomethylphosphonic acid in agricultural soils. International Agrophysics 28, 93–100. https://doi.org/10.2478/intag-2013-0031

Tong, J., Ye, M., 2020. A new soil mixing layer model for simulating conservative solute loss from initially saturated soil to surface runoff. Journal of Hydrology 590, 125514. https://doi.org/10.1016/j.jhydrol.2020.125514

Topping, C.J., Aldrich, A., Berny, P., 2020. Overhaul environmental risk assessment for pesticides. Science. https://doi.org/10.1126/science.aay1144

Vagi, M.C., Petsas, A.S., 2021. Sorption/Desorption, Leaching, and Transport Behavior of Pesticides in Soils: A Review on Recent Advances and Published Scientific Research. Springer, Cham, pp. 137–195. https://doi.org/10.1007/698_2021_803

Van den Berg, F., Tiktak, A., Boesten, J., Van der Linden, A., 2016. PEARL model for pesticide behaviour and emissions in soil-plant systems. Statutory Research Tasks Unit for Nature & the Environment.

van Dijk, A.I.J.M., Bruijnzeel, L.A., Rosewell, C.J., 2002. Rainfall intensity–kinetic energy relationships: a critical literature appraisal. Journal of Hydrology 261, 1–23. https://doi.org/10.1016/S0022-1694(02)00020-3

Vermeulen, G., Klooster, J., 1992. The potential of a low ground pressure traffic system to reduce soil compaction on a clayey loam soil. Soil and Tillage Research 24, 337–358.

Vieira, D.C.S., Basso, M., Nunes, J.P., Keizer, J.J., Baartman, J.E.M., 2022. Event-based quickflow simulation with OpenLISEM in a burned Mediterranean forest catchment. Int. J. Wildland Fire 31, 670–683. https://doi.org/10.1071/WF21005

Von Hoyningen-Huene, J., 1981. Die Interzeption des Niederschlags in Landwirtschaftlichen Pflanzenbeständen.". In Arbeitsbericht Deutscher Verband für Wasserwirtschaft und Kulturbau.

Vormeier, P., Schreiner, V.C., Liebmann, L., Link, M., Schäfer, R.B., Schneeweiss, A., Weisner, O., Liess, M., 2023. Temporal scales of pesticide exposure and risks in German small streams. Science of The Total Environment 871, 162105. https://doi.org/10.1016/j.scitotenv.2023.162105

Wainwright, J., Mulligan, M. (Eds.), 2012. Environmental modelling: finding simplicity in complexity, 2nd ed. ed. Wiley, Chichester, West Sussex ; Hoboken, NJ.

Wallach, R., Jury, W.A., Spencer, W.F., 1988. Transfer of Chemicals from Soil solution to Surface Runoff: A Diffusion-based Soil Model. Soil Science Society of America Journal 52, 612–618. https://doi.org/10.2136/sssaj1988.03615995005200030002x

Watanabe, H., Grismer, M.E., 2003. Numerical modeling of diazinon transport through inter-row vegetative filter strips. Journal of Environmental Management 69, 157–168. https://doi.org/10.1016/S0301-4797(03)00142-7

Wauchope, R.D., 1978. The pesticide content of surface water draining from agricultural fields—a review. J Environ Qual 7, 459–472. https://doi.org/10.2134/jeq1978.00472425000700040001x

Wauchope, R.D., Yeh, S., Linders, J.B.H.J., Kloskowski, R., Tanaka, K., Rubin, B., Katayama, A., Kördel, W., Gerstl, Z., Lane, M., Unsworth, J.B., 2002. Pesticide soil sorption parameters: Theory, measurement, uses, limitations and reliability. Pest Management Science. https://doi.org/10.1002/ps.489

Weisner, O., Arle, J., Liebmann, L., Link, M., Schäfer, R.B., Schneeweiss, A., Schreiner, V.C., Vormeier, P., Liess, M., 2022. Three reasons why the Water Framework Directive (WFD) fails to identify pesticide risks. Water Research 208, 117848. https://doi.org/10.1016/j.watres.2021.117848

Wenneker, M., Beltman, W.H.J., De Werd, H.A.E., Van Zeeland, M.G., Van Der Lans, A., Van Der Weide, R.Y., 2010. Quantifying point source entries of pesticides in surface waters. International Advances in Pesticide Application. library.wur.nl 99.

Wesseling, J., Kroes, J., Campos Oliveira, T., Damiano, F., 2020. The impact of sensitivity and uncertainty of soil physical parameters on the terms of the water balance: Some case studies with default R packages. Part II: Results and discussion. Computers and Electronics in Agriculture 170, 105072. https://doi.org/10.1016/j.compag.2019.105072

WiB, 2020. Water vasthouden op Landbouwpercelen in Zuid-Limburg. 15 maatregelen. Water in Balans.

Wickham, H., Averick, M., Bryan, J., Chang, W., McGowan, L., François, R., Grolemund, G., Hayes, A., Henry, L., Hester, J., Kuhn, M., Pedersen, T., Miller, E., Bache, S., Müller, K., Ooms, J., Robinson, D., Seidel, D., Spinu, V., Takahashi, K., Vaughan, D., Wilke, C., Woo, K., Yutani, H., 2019. Welcome to the Tidyverse. JOSS 4, 1686. https://doi.org/10.21105/joss.01686

Winteraeken, H.J., Spaan, W.P., 2010. A new approach to soil erosion and runoff in south Limburg—The Netherlands. Land Degrad Dev 21, 346–352. https://doi.org/10.1002/ldr.1009

Wu, J., Nunes, J.P., Baartman, J.E.M., Faúndez Urbina, C.A., 2021. Testing the impacts of wildfire on hydrological and sediment response using the OpenLISEM model. Part 1: Calibration and evaluation for a burned Mediterranean forest catchment. CATENA 207, 105658. https://doi.org/10.1016/j.catena.2021.105658

Yadav, I.C., Watanabe, H., 2018. Soil erosion and transport of Imidacloprid and Clothianidin in the upland field under simulated rainfall condition. Science of the Total Environment 640–641, 1354–1364. https://doi.org/10.1016/j.scitotenv.2018.06.008

Yang, X., Wang, F., Bento, C.P.M., Meng, L., van Dam, R., Mol, H., Liu, G., Ritsema, C.J., Geissen, V., 2015a. Decay characteristics and erosion-related transport of glyphosate in Chinese loess soil under field conditions. Science of the Total Environment 530–531, 87–95. https://doi.org/10.1016/j.scitotenv.2015.05.082

Yang, X., Wang, F., Bento, C.P.M., Xue, S., Gai, L., van Dam, R., Mol, H., Ritsema, C.J., Geissen, V., 2015b. Short-term transport of glyphosate with erosion in Chinese loess soil - A flume experiment. Science of the Total Environment 512–513, 406–414. https://doi.org/10.1016/j.scitotenv.2015.01.071

Young, D.F., Fry, M., 2014. PRZM5 A Model for Predicting Pesticide in Runoff, Erosion, and Leachate: User Manual. https://doi.org/10.13140/2.1.1828.6408.

Young, D.F., Fry, M.M., 2019. Field-scale evaluation of pesticide uptake into runoff using a mixing cell and a non-uniform uptake model. Environmental Modelling & Software 122, 104055. https://doi.org/10.1016/J.ENVSOFT.2017.09.007

Yu, C., Duan, P., Yu, Z., Gao, B., 2019. Experimental and model investigations of vegetative filter strips for contaminant removal: A review. Ecological Engineering 126, 25–36. https://doi.org/10.1016/j.ecoleng.2018.10.020

Zambon, N., Johannsen, L.L., Strauss, P., Dostal, T., Zumr, D., Cochrane, T.A., Klik, A., 2021. Splash erosion affected by initial soil moisture and surface conditions under simulated rainfall. Catena 196, 104827. https://doi.org/10.1016/j.catena.2020.104827

Zambrano-Bigiarini, M., 2020. hydroGOF v0.4-0. https://doi.org/10.5281/ZENODO.839854

Zhao, B., Dai, Q., Han, D., Dai, H., Mao, J., Zhuo, L., Rong, G., 2019. Estimation of soil moisture using modified antecedent precipitation index with application in landslide predictions. Landslides 16, 2381–2393. https://doi.org/10.1007/s10346-019-01255-y

Zioga, E., Kelly, R., White, B., Stout, J.C., 2020. Plant protection product residues in plant pollen and nectar: A review of current knowledge. Environmental Research 189, 109873. https://doi.org/10.1016/j.envres.2020.109873

Summary

In current day agriculture, plant protection products, also known as pesticides, play an important role in the production of food. Due to the use of pesticides the global food production has increased substantially and the diversity and quality of the produced crops has increased. However, pesticide use is not without risks, and the ubiquitous use of pesticides poses threats to humans, biodiversity and our environment in general. Pesticides are applied on a field to target a certain pest, for example weeds, insects or fungi that threaten the crop. However, these substances often also affect other organisms when the pesticides are transported to off-site locations. One of the transport pathways for pesticides is transport with runoff during and after rainfall events. Sloping lands are prone to processes of overland flow and associated soil detachment, transportation, and deposition. When water flows from and over agricultural fields during a rainfall event, it can cause soil erosion. Pesticide residues, both on the crops or in the top layer of the soil, can be picked up and transported by runoff as solute or attached to soil particles.

This thesis aimed to investigate the transport of pesticides from agricultural fields during rainfall-runoff events. The quantification of PP transport has first be done by observations on field and small catchment scale. In addition, simulating the transport process further improved our understanding of the transport dynamics and source areas and provided a means to test scenarios of mitigation measures of changing land use or climatic conditions. This thesis research had three objectives:

1. Quantify the contribution of PP transport to total overland transport of pesticides for a small agricultural headwater catchment.
2. Develop a model for event-based overland transport of pesticides that includes both dissolved and particulate phase transport of pesticides.
3. Determine the input parameter influence on the output of the new model and investigate its suitability to simulate and predict pesticide transport for a small agricultural headwater catchment.

The first chapter of this thesis gives the context of this research. More information is given about the benefits and adverse effects of pesticide use in agriculture, with special attention to recent studies that report high pesticide concentrations in the environment. Moreover, the pathways of pesticide transport into the environment are explained. The potential of modelling to add to our understanding of pesticide fate during rainfall-runoff events is discussed. The first chapter ends with a description of the research objectives and the study area where data for this research is

collected. In the next chapters the research answering each of the three objectives of this thesis is presented.

In chapter 2 the results of a two season (2019 and 2020) field study are presented. Based on the field observations, the hypothesis that particulate phase transport contributes substantially to total overland transport of pesticides was confirmed. Factors influencing the contribution of PP to total transport include hydrological and sediment dynamics during the event, chemical characteristics of the transported active substances and land management on the fields. The observations showed that transport in DP occurred mainly shortly after application of the pesticide (69% mass within 10 days). Opposingly, the transport of pesticides in PP occurs over much longer time spans, where 90% of the total transported mass is reached within 100 days after application in this study. Potato cultivation was the main source of runoff, erosion, and pesticide transport. Cereals and apples with grassed inter-rows both have a very low risk of pesticide transport during overland flow. Chapter 2 concludes that for arable farming on sloping lands overland transport of pesticide in the particulate phase is a substantial transport pathway, which can contribute to pollution over longer time periods compared to transport in water. This process needs to be considered in future assessments for pesticide fate and environmental risk.

Based on the results of the field observations the next objective was to develop a model to simulate pesticide transport during rainfall-runoff events. In chapter 3 a new model extension is presented: OpenLISEM-pesticide v1.0 (OLP). With the newly developed model, simulations were done for glyphosate and metobromuron transport during two rainfall-runoff events from the collected observation dataset. The proof-of-concept simulations for the two compounds and two events, were mostly in line with field observations. However, the functioning of a new model needs further investigation to understand which parameters are influential for the model output. In Chapter 4 further modelling and a sensitivity analysis are presented to test OLP. By optimizing a full season model (SWAP) and the event-based runoff and erosion simulations with OpenLISEM the initial conditions for the OLP simulations where obtained. Based on this a global sensitivity analysis was done to analyse the newly introduced parameters in OLP. Two main conclusions could be drawn from the results: firstly, the hydrology and erosion related parameters have a major influence on the simulated transport of pesticide, and secondly, the mixing layer depth is the main influential parameter for both dissolved and particulate phase transport. An analysis of the predictive performance of OLP showed that the uncertainty in the predictions is still large.

In chapter 5 the overall findings of this thesis research are presented. With this thesis research I focussed on the transport processes of pesticides on the temporal scale of rainfall runoff events and the spatial scale of fields to headwater catchments. The spatiotemporal scale on which a processes is studied has a large influence on the resulting findings. In the synthesis I argue that for the assessment of pesticide fate in the environment the field-scale transport, including PP transport with erosion, should be taken into account. Furthermore, limitations of the presented research are discussed. The two major limitations are the too broad setup of the field observations, and the uncertainty related to the conceptualization of soil-runoff interactions used in OLP. The synthesis ends with three main research challenges to further improve our understanding of pesticide transport. First, observing PP transport under different conditions is needed to further test the findings of this study. Secondly, a process-based description of the soil-runoff interactions for pesticide transport, with parameters that are measurable in the field, might be an improvement over the current conceptualization. And lastly, a model comparison study combining models with different conceptualizations and scales, will improve model applications and predictions.

Samenvatting

In de huidige landbouw spelen gewasbeschermingsmiddelen, ook wel pesticiden genoemd, een belangrijke rol in de productie van voedsel. Onder andere door het gebruik van pesticiden is de wereldwijde voedselproductie substantieel toegenomen, en de diversiteit en kwaliteit van de verbouwde gewassen is verbeterd. Het gebruik van pesticiden is niet zonder risico's; het wijdverspreide gebruik van pesticiden veroorzaakt risico's voor mensen, biodiversiteit en onze leefomgeving in het algemeen. Pesticiden worden toegediend op een akker om een specifieke ziekte of plaag te bestrijden, bijvoorbeeld onkruiden, insecten of schimmels die het gewas schade toebrengen. De gebruikte stoffen beïnvloeden vaak ook andere organismen, onder andere wanneer de pesticide *getransporteerd* wordt van de akker naar andere domeinen van onze omgeving. Een van de transportroutes voor pesticiden is transport met *oppervlakkige afstroming* tijdens en vlak na regenbuien. Hellingen in het landschap zijn gevoelig voor oppervlakkige afstroming en daaraan gerelateerde *erosie* van de bodem. Wanneer water over een akker stroomt tijdens een regenbui kunnen pesticiden uit de bovenste laag van de bodem meegenomen worden; dit kan zowel *opgelost* in het water als *gebonden* aan de bodemdeeltjes die door het erosieproces getransporteerd worden.

Dit onderzoek had als doel om het transport van pesticiden van akkers tijdens regenbuien en afstroming beter te begrijpen. In de eerste plaats is het transport van pesticiden gebonden aan bodemdeeltjes gekwantificeerd door middel van *observaties* in een klein stroomgebied in Zuid-Limburg. Vervolgens gaven *modelsimulaties* meer inzicht in de transportdynamieken en brongebieden van pesticiden op de akkers. Deze simulaties vormen een basis om verschillende scenario's van maatregelen of veranderend klimaat en landgebruik te testen. Dit onderzoek had de volgende drie doelen:

1. Het aandeel berekenen van aan bodemdeeltjes gebonden pesticiden ten opzichte van het totaal aan pesticidetransport via oppervlakkige afstroming in een klein stroomgebied met hoofdzakelijk landbouw.
2. Een model ontwikkelen om het transport van pesticiden, zowel opgelost als gebonden, te simuleren met oppervlakkige afstroming tijdens en na regenbuien.
3. De invloed van *invoerwaardes* op de uitkomst van het nieuwe model analyseren en de geschiktheid van het nieuwe model beoordelen om pesticidetransport te simuleren en voorspellen voor een klein stroomgebied met hoofdzakelijk landbouw.

Het eerste hoofdstuk van dit proefschrift schetst de context van dit onderzoek. Zowel de voordelen als negatieve effecten van pesticidegebruik in de landbouw worden belicht, met speciale aandacht voor recente onderzoeken die hoge concentraties in onze leefomgeving rapporteren. Vervolgens worden de verschillende transportroutes van pesticiden in het milieu beschreven. Modelsimulaties

bieden een mogelijkheid om meer inzicht te krijgen in de verplaatsing van pesticiden tijdens regenbuien, en verschillende modellen en modelstudies worden in dit hoofdstuk besproken. Het eerste hoofdstuk eindigt met een beschrijving van de onderzoeksdoelen en het studiegebied dat voor dit onderzoek gebruikt is.

In hoofdstuk 2 worden de resultaten van een veldonderzoek over twee seizoenen (2019 en 2020) gepresenteerd. Op basis van de observaties in het studiegebied werd de hypothese bevestigd dat pesticiden gebonden aan bodemdeeltjes substantieel bijdragen aan het totale oppervlakkig transport van pesticiden. Factoren die de bijdrage van gebonden pesticiden aan het totale transport beïnvloeden zijn onder meer de intensiteit van de afstroming en erosie, de chemische eigenschappen van de getransporteerde stoffen en het landbeheer op de akkers. Uit de waarnemingen bleek dat het transport van pesticiden opgelost in water vooral kort na toediening van de pesticide plaatsvond (69% van de totale massa binnen 10 dagen). Het transport van gebonden pesticiden daarentegen vond plaats over veel langere tijd, waarbij in dit onderzoek 90% van de totale getransporteerde massa binnen 100 dagen na toediening werd bereikt. De aardappelteelt was de belangrijkste bron van afstroming, erosie en transport van pesticiden. Akkers waarop granen verbouwd werden en een appelboomgaard hadden een zeer laag risico op transport van pesticiden tijdens oppervlakkige afstroming. Hoofdstuk 2 concludeert dat voor akkerbouw op hellingen het transport van pesticiden gebonden aan bodemdeeltjes een substantiële transportroute is, die over langere perioden kan bijdragen aan vervuiling vergeleken met transport in water. Met dit proces moet rekening worden gehouden bij toekomstige beoordelingen van de verspreiding van pesticiden en het daaraan gerelateerde risico voor het milieu.

Gebaseerd op de resultaten van de veldobservaties was het volgende doel het ontwikkelen van een model om het transport van pesticiden tijdens oppervlakkige afstroming te simuleren. In hoofdstuk 3 wordt een nieuwe modeluitbreiding gepresenteerd: *OpenLISEM-pesticide v1.0* (OLP). Met het nieuw ontwikkelde model werden simulaties uitgevoerd van het transport van glyfosaat en metobromuron tijdens twee regenbuien uit de verzamelde observaties. Deze eerste simulaties kwamen grotendeels overeen met de waarnemingen van de twee regenbuien. Het functioneren van een nieuw model vereist echter verder onderzoek om te begrijpen welke invoerparameters van invloed zijn op de modeluitvoer. In hoofdstuk 4 worden verdere simulaties en een gevoeligheidsanalyse gepresenteerd om OLP te testen. Door het optimaliseren van een model voor het volledige groeiseizoen (SWAP) en de afstromings- en erosiesimulaties met OpenLISEM werden de beginwaarden voor de OLP-simulaties verkregen. Op basis hiervan werd een gevoeligheidsanalyse uitgevoerd om de nieuw geïntroduceerde parameters in OLP te analyseren. Uit de resultaten kunnen twee belangrijke conclusies worden getrokken: ten eerste hebben de hydrologie- en erosie-gerelateerde parameters een grote invloed op het gesimuleerde transport van pesticiden, en ten tweede is de dikte van de 'mixing layer' (de dunne laag bodem die interacteert met het afstromende water) de meest invloedrijke parameter voor zowel het transport van opgeloste als gebonden pesticiden. Uit een analyse van de voorspellende kwaliteit van OLP bleek dat de onzekerheid in de voorspellingen nog steeds groot is.

In hoofdstuk 5 worden de overkoepelende bevindingen van dit onderzoek gepresenteerd. In dit onderzoek heb ik mij gericht op de transportprocessen van pesticiden op de *temporele schaal* van regenbuien en de *ruimtelijke schaal* van akkers en kleine stroomgebieden. De tijd- en ruimte-schaal waarop een proces wordt bestudeerd heeft een grote invloed op de resulterende bevindingen. In de synthese betoog ik dat voor de beoordeling van de verspreiding van pesticiden in het milieu rekening moet worden gehouden met transport op veldschaal, inclusief gebonden transport met erosie. Daarnaast worden de beperkingen van het gepresenteerde onderzoek besproken. De twee belangrijkste beperkingen zijn de te brede opzet van de veldobservaties en de onzekerheid in de beschrijving van de interacties tussen de bodem en het afstromende water die in OLP worden gebruikt om pesticidetransport te simuleren. De synthese eindigt met drie vervolgstappen die bij kunnen dragen aan ons begrip van het transport van pesticiden. Ten eerste is het observeren van gebonden transport onder verschillende omstandigheden (verschillende bodemsoorten, gewassen, gebruikte pesticiden etc.) nodig om de bevindingen van dit onderzoek verder te testen. Ten tweede zou een proces-specifieke beschrijving van de interacties tussen bodem en afstroming voor het transport van pesticiden, met parameters die in het veld meetbaar zijn, een verbetering kunnen zijn ten opzichte van de huidige conceptualisering. En ten slotte zal een modelvergelijkingsstudie, waarbij modellen met verschillende conceptualisaties en schalen worden gecombineerd, modeltoepassingen en voorspellingen verbeteren.

Acknowledgements

"What do you have, that you did not receive?"[6]

Writing acknowledgements scares me, and I am tempted to write 'Thank you all' and leave it with that. These acknowledgements describe a reality that exists between us; moments we shared and all the good things I received from you. In parallel with a model that does not correctly capture the reality it describes, these acknowledgements will not correctly describe the reality that exists between us. And contrary to a model, the code language between people is less specific than with a computer, and humans very rarely give error messages if there is a misunderstanding. However, again in parallel with a model, this does not withhold us from embarking on the journey to describe reality, because we believe that although reality cannot be captured, and misunderstanding might occur, making an effort to describe it is a good thing.

Reflecting back on the seven years I spent on this PhD project and the road that brought me to the point that I started the PhD, I think of many people that supported me and gave me opportunities, support, trust, confidence and love. Finishing a PhD was something that never crossed my mind before doing my MSc thesis, and achieving this now makes me proud. But it was only possible because of what I have received from all of you.

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[6] St. Paul, 1 Corithians 4:7

do the rainfall experiments, field studies and modelling helped me to actually do it, thank you for all the support you gave me. Violette, Michel and Jantiene, thank you for being my supervisors!

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The next phase in my PhD research was the development and evaluation of a model to simulate the transport of pesticides. When I started my PhD I was not very confident with writing code, and even less with mathematical equations. I want to thank George, for introducing me to Darcy and modelling in an Excel sheet in the Geohydrology course, here I discovered that I understood these equations and that I could even explain the use of them to other people. Jan, you were my tutor for modelling pesticide transport, and for writing code for a model. This started when we worked on a post processor for nanoparticle transport. I still remember (and have) the script in which you taught me how to use a loop in R to run OpenLISEM multiple times. Thank you for all your time, your ideas, support and never ending optimism when I sometimes struggled with code that didn't work. Victor, thank you for introducing me to the code of OpenLISEM and for your ideas and feedback on the development of the pesticide module.

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Meindert Cornelis Commelin

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has successfully fulfilled all requirements of the
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Wageningen, 3 September 2024

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The SENSE Research School declares that **Meinder Cornelis Commelin** as successfully fulfilled all requirements of the educational PhD programme of SENSE with a work load of 43.6 EC, including the following activities:

SENSE PhD Courses

- Environmental research in context (2018)
- Research in context activity: Workshop and wiki for OpenLISEM-pesticide: estimating pesticide transport during rainfall-runoff events (2023)

Other PhD and Advanced MSc Courses

- Statistical Uncertainty analysis of dynamic models, PE&RC (2017)
- Geostatistics, PE&RC (2021)
- Rmarkdown, PE&RC (2021)

Management and Didactic Skills Training

- Supervising 1 MSc student with thesis (2020): Using Sentinel-1 and field measurements to evaluate LISEM performance in Catsop, South Limburg.
- Supervising 1 BSc student with thesis (2021): The relationship between turbidity measurements and sediment samples from a small agricultural catchment in South-Limburg.
- Teaching in the BSc course ‘Hydrogeology’ (2017-2023)
- Teaching in the MSc course ‘Erosion processes and modelling’ (2017-2024)
- Teaching in the BSc course ‘Water and Air Numerical Theories’ (2018-2022)
- Teaching in the BSc course ‘Design in Land and water management 1 (2018-2022)
- Teaching in the BSc course ‘Water 1’ (2018-2022)

Oral Presentations

- *Reducing pesticide pollution by agriculture – a meta-analysis.* Land Use and Water Quality conference, 3-6 June 2019, Aarhus, Denmark
- *Particulate phase transport of pesticides is substantial for runoff and erosion in a small agricultural catchment.* European Geosciences Union, annual meeting, 23-27 May 2022, Vienna, Austria

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