Mitigation of aquatic nonpoint-source ncqrgagbc pollution with tcecr_rcb rreatment systems

Dissertation

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Earth is a water planet on which the quality of
water defines the quality of life.
Good water, good life.
Poor Water, poor life.
No water, no life.

Sir Peter Blake, Nairobi 2001

Danksagung

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List of abbreviations

ArtWET	EU-Life Project "Mitigation of agricultural nonpoint-source pesticides pollution and phytoremediation in artificial wetland ecosystems"
CLC	Corine land cover
Corine	Coordinated Information on the European Environment programme
CREAMS	Chemicals, Runoff and Erosion from Agricultural Management Systems
DP	detention pond
DRIPS	Drainage Spraydrift and Runoff Input of Pesticides in Surface Waters
DSS	decision support system
DT_{50}	Half life
EC_{50}	median effective concentration
EPIC	Erosion-Productivity Impact Calculator
EU	European Union
GIS	geographic information system
HLR	hydraulic loading rate (m^3/d)
HRT	hydraulic retention time (min)
K_{OC}	coefficient of sorption to organic carbon ml/g
LC_{50}	median lethal concentration
log K_{ow}	logP
logP	logarithm (base-10) of the partition coefficient of n-octanol and water
LOQ	limit of quantification
NaCl	sodium chloride - salt
OECD	Organisation for Economic Co-operation and Development
PEC	predicted environmental concentration (μ/L)
REXTOX	ratio of exposure to toxicity
SCS	Soil Conservation Service of the USDA
SPE	solid phase extraction
SRTM	shuttle radar topography mission
SWAT	Surface Water Attenuation
SWIM	Soil and Water Integrated Model
TOC	total organic carbon content
TU	toxic unit
USDA	United States (of America) Department of Agriculture
USLE	Universal Soil Loss Equation
VD	vegetated ditch
VTS	vegetated surface flow treatments systems

Content

Publications of the cumulative dissertation

Elsaesser, D., C. Stang, R. Schulz (2011), Influence of vegetation density on mitigation of a pesticide mixture in experimental stream mesocosms. Submitted to Water Science and Technology

Elsaesser, D., A.-G. B. Blankenberg, A. Geist, T. Mæhlum, R. Schulz (2011), Assessing the influence of vegetation on reduction of pesticide concentration in experimental surface flow constructed wetlands: Application of the toxic units approach, Ecological Engineering 37(6), 955 – 962.

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Elsaesser, D. (2011), Risk map of runoff-related pesticide pollution in small rivers of the European agricultural landscape. Submitted to Journal of Maps.

Elsaesser, D., R. Schulz (2011), A spatial decision support system for mitigation of runoff related pesticide pollution in surface waters across Europe. Submitted to International Journal of Geographical Information Science.

Other peer reviewed publications and conference contributions related to the study are listed in appendix IV.

Summary

Recent EU-frameworks enforce the implementation of risk mitigation measures for nonpoint-source pesticide pollution in surface waters. Vegetated surface flow treatments systems (VTS) can be a way to mitigate risk of adverse effects in the aquatic ecosystems following unavoidable pollution after rainfall-related runoff events. Studies in experimental wetland cells and vegetated ditch mesocosms with common fungicides, herbicides and insecticides were performed to assess efficiency of VTS. Comprehensive monitoring of fungicide exposure after rainfall-related runoff events and reduction of pesticide concentrations within partially optimised VTS was performed from 2006-2009 at five vegetated detention ponds and two vegetated ditches in the wine growing region of the Southern Palatinate (SW-Germany). Influence of plant density, size related parameters and pesticide properties in the performance of the experimental devices, and the monitored systems were the focus of the analysis.

A spatial tool for prediction of pesticide pollution of surface waters after rainfall-related runoff events was programmed in a geographic information system (GIS). A sophisticated and high resolution database on European scale was built for simulation. With the results of the experiments, the monitoring campaign and further results of the EU-Life Project ArtWET mitigation measures were implemented in a georeferenced spatial decision support system. The database for the GIS tools was built with open data. The REXTOX (ratio of exposure to toxicity) Risk Indicator, which was proposed by the OECD (Organisation for Economic Co-operation and Development), was extended, and used for modeling the risk of rainfall-related runoff exposure to pesticides, for all agricultural waterbodies on European scale.

Results show good performance of VTS. The vegetated ditches and wetland cells of the experimental systems showed a very high reduction of more than 90% of pesticide concentrations and potential adverse effects. Vegetated ditches and wetland cells performed significantly better than devices without vegetation. Plant density and sorptivity of the pesticide were the variables with the highest explanatory power regarding the response variable reduction of concentrations. In the experimental vegetated ditches 65% of the reduction of peak concentrations was explained with plant density and K_{OC}. The monitoring campaign showed that concentrations of the fungicides and potential adverse effects of the mixtures were reduced significantly within vegetated ditches (Median 56%) and detention ponds (Median 38%) systems. Regression analysis with data from the monitoring campaign identified plant density and size related

properties as explanatory variables for mitigation efficiency (DP: $R^2=0.57$, $p<0.001$; VD: $R^2=0.19$, $p<0.001$).

Results of risk model runs are the input for the second tool, simulating three risk mitigation measures. VTS as risk mitigation measures are implemented using the results for plant density and size related performance of the experimental and monitoring studies, supported by additional data from the ArtWET project. Based on the risk tool, simulations can be performed for single crops, selected regions, different pesticide compounds and rainfall events. Costs for implementation of the mitigation measures are estimated.

Experiments and monitoring, with focus on the whole range of pesticides, provide novel information on VTS for pesticide pollution. The monitoring campaign also shows that fungicide pollution may affect surface waters. Tools developed for this study are easy to use and are not only a good base for further spatial analysis but are also useful as decision support of the non-scientific community. On a large scale, the tools on the one hand can help to compute external costs of pesticide use with simulation of mitigation costs on three levels, on the other hand feasible measures mitigating or remediating the effects of nonpoint-source pollution can be identified for implementation. Further study of risk of adverse effects caused by fungicide pollution and long-time performance of optimised VTS is needed.

Zusammenfassung

Aktuelle Entwicklungen in der Europäischen Gesetzgebung fordern die Umsetzung von Risikominderungsmaßnahmen, die diffuse Einträge von Pestiziden in Oberflächengewässer und deren Schadwirkung mindern sollen. Bepflanzte Gräben und Feuchtgebiete (vegtated treatment systems: VTS) bieten die Möglichkeit potenzielle Schadwirkung von Pestizideinträgen infolge von Oberflächenabflussereignissen zu mindern, die mit anderen Maßnahmen unvermeidbar wären. Versuche in experimentellen Feuchtgebieten und bepflanzten Gräben wurden durchgeführt, um die Funktionstüchtigkeit möglicher Systeme zu untersuchen. In fünf Rückhaltebecken und zwei bepflanzten Gräben in der Weinbauregion Südpfalz (Südwestdeutschland) wurde von 2006 bis 2009 eine umfangreiche Beprobung von belastetem Wasser nach Starkregenereignissen vorgenommen und die Reduktionsleistung der Systeme bezüglich der eingetragenen Konzentrationen ermittelt. Der Einfluss von Pflanzendichte, Größe der Systeme und Eigenschaften der eingetragenen, bzw. experimentell eingespeisten Substanzen war Schwerpunkt bei der Auswertung der Ergebnisse.

Zur Vorhersage der Gewässerbelastung nach niederschlagsbezogenem Oberflächenabfluss wurde in einer Geoinformationsumgebung (GIS) ein Simulationswerkzeug entwickelt. Das Werkzeug arbeitet mit einer sehr exakten Datenbank von hoher räumlicher Auflösung auf Europäischer Ebene.

Basierend auf den Erkenntnissen der Experimente, den Ergebnissen der beprobten Gewässer und weiteren Daten von anderen Systemen, die im EU-Life Projekt ArtWET erhoben wurden, ist ein zweites räumliches Werkzeug entstanden, das zur Entscheidungsunterstützung dient und mit dem Risikominderungsmaßnahmen simuliert werden können.

Ergebnisse der Experimente und Feldstudien zeigen, dass in experimentellen Feuchtgebieten und bepflanzten Gräben Reduktionen von über 90% der eingetragenen Pestizidkonzentrationen möglich sind. Bepflanzte Gräben und Feuchtgebiete zeigten signifikant bessere Reduktion als unbepflanzte. Pflanzendichte und Sorptivität an organischen Kohlenstoff wurden als Variablen mit der größten Erklärungskraft für die Zielvariable Reduktion der Pestizidkonzentrationen identifiziert (im Gräben-Mesokosmos konnten 65% der Variabilität mit den Variablen Pflanzendichte und K_{OC} erklärt werden. In der Feldstudie wurde gezeigt, dass Fungizidkonzentrationen innerhalb der Rückhaltebecken (Median 38%) und bepflanzten Gräben (Median 56%) signifikant reduziert wurden. Die Regressionsanalyse mit diesen Daten zeigte, dass neben der

Pflanzendichte auch die Größe der Systeme Einfluss auf die Reduktion der Pestizidkonzentrationen hat (DP: R^2=0.57, p<0.001; VD: R^2=0.19, p<0.001).

Die Datenbank für die GIS Werkzeuge wurde mit frei verfügbaren Europäischen Daten aufgebaut. Der erweiterte, von der OECD empfohlene REXTOX Risikoindikator wurde modifiziert und für die Risikomodellierung für alle Agrargewässer auf Europäischer Ebene angewandt. Die Ergebnisse der Risikosimulationen bieten die Datenbasis für das zweite Werkzeug, in dem auch die VTS als Risikominderungsmaßnahme eingearbeitet sind. Die Berechnung der Risikominderungsmaßnahmen kann für die einzelnen Kulturen, ausgewählte Gebiete und unterschiedliche Pestizide durchgeführt werden. Kosten für die Risikominderungsmaßnahmen werden ermittelt.

Die Ergebnisse liefern wichtige neue Erkenntnisse zur Nutzung von bepflanzten Systemen als Risikominderungsmaßnahmen für diffuse Pestizideinträge in Agrargewässer. Die Proben der Weinbaugewässer zeigen, dass auch die bisher schlecht untersuchte Gruppe der Fungizide nachteilige Auswirkungen auf aquatische Ökosysteme haben kann. Die entwickelten GIS Werkzeuge sind leicht anwendbar und damit nicht nur als Basis für zukünftige Untersuchungen geeignet, sondern auch als Entscheidungsunterstützung in der praktischen Umsetzung außerhalb der Forschung hilfreich. Auf Europäischer Ebene können die GIS-Werkzeuge einerseits externe Kosten der Gewässerverschmutzung durch diffuse Pflanzenschutzmitteleinträge berechnen, indem die Kosten der unterschiedlichen Risikominderungsmaßnahmen abgeschätzt werden. Andererseits kann die Simulation der Maßnahmen bei der Entscheidungsfindung zur Umsetzung der Vorgaben der Wasserrahmenrichtlinie helfen. Zukünftige Studien sind insbesondere im Bereich der Fungizidbelastung von Oberflächengewässern und der langfristigen Funktionstüchtigkeit von bewachsenen Gräben und Feuchtgebieten als Risikominderungsmaßnahmen notwendig.

I. Introduction

1.1 Problem definition and Objectives

The aim of this study is the assessment of vegetated surface flow treatment systems (VTS) as a mitigation measure for aquatic nonpoint source pesticide pollution. Firstly, the lack of knowledge regarding the optimisation of VTS properties for risk mitigation is attended. Secondly, a comprehensive approach to georeferenced risk assessment on a large scale, was accomplished, combined with simulations, supporting decision making for implementation of mitigation measures.

The focus of the first part, with experiments and field monitoring, was set on performance in reducing concentrations and potential effects of pesticides within the VTS and central variables explaining this reduction. The second part was the implementation of the results in a GIS. One tool was built to model risk of runoff-related pesticide pollution on European scale. A second tool simulates required space and costs for VTS and other selected mitigation measures, to support decision making on landscape level.

The study is subdivided in five chapters:

- In chapter 1 the state of scientific knowledge on nonpoint-source pollution, mitigation measures and VTS is introduced.
- Studies in experimental vegetated ditches and experimental wetland cells, as well as tracer studies in vegetated ditches, are introduced in chapter 2.
- Field monitoring of aquatic fungicide exposure and mitigation performance of five vegetated detention ponds and two vegetated ditches in Southern Palatinate (SW-Germany), are introduced in chapter 3.
- In chapter 4 the development of the two georeferenced tools is introduced.
- Conclusion and outlook for further studies is given in chapter 5.

1.2 Scientific background

With the green revolution in the second half of the last century, agricultural regions throughout the world transformed into areas of monocultural mass production for food and energy resources (Evenson & Gollin, 2003). Intensification and mechanisation of agriculture raised the demand and use of agrochemicals. 230,000 tons of pesticides (active substance) were sold in EU15 in 2009 (ECPA, 2011). When pesticides are transferred from agricultural areas to adjacent ecosystems they may affect non-target organisms (Schäfer et al., 2011b). The three major types of pesticides are insecticides, herbicides and fungicides. Many studies monitoring exposure are focused on insecticides, most of them highly toxic to aquatic invertebrates (Schulz, 2004) and herbicides which are very often present in surface waters and may leach to the groundwater (Schmitt-Jansen et al., 2011; Hildebrandt et al., 2008; Borggaard & Gimsing, 2008). Only very few studies are reporting fungicide pollution (Bermúdez-Couso et al., 2007; Gregoire et al., 2010; Rabiet et al., 2010; Schäfer et al., 2011).

Nonpoint-source pollution

Contamination of aquatic ecosystems with agricultural insecticides, herbicides and fungicides through nonpoint-sources can pose a significant threat to aquatic communities (Schäfer et al., 2011) and drinking water resources (Vijver et al., 2008). Surface runoff, drainage and spray drift are the three major origins of nonpoint-source pesticide pollution of aquatic ecosystems (Gregoire et al., 2009).

Spray drift

To achieve regular deposition on the target surface, the spray liquid has to be finely atomised during spray. Near the field edges, up to 30% of the applied amounts are lost through spray drift. The distance to the field edge, the type of crop and the wind velocity are the main factors causing this loss (Rautmann et al., 2001).

Surface runoff

Surface runoff may occur after rainfall events. When rainfall exceeds the infiltration capacity of the soil and the topsoil is completely saturated, water starts to flow on the surface of the soil. Preferential flow pathways converge and the water is transported rapidly downhill (Kirkby & Chorley, 1967). Pesticide entries into surface waters through runoff are determined by many factors. Properties of the rainfall event (intensity and duration), soil properties (e.g. moisture, texture), pathway to the waterbody (length, paved road or densely vegetated buffer strip) and pesticide properties (e.g. K_{OC}, solubility in water and DT_{50}) are the most important variables for estimation of expected runoff entries (Probst et al., 2005). Focusing on pesticide concentrations in streams, and total masses transported to the waterbodies, several studies show the high relevance of surface runoff (Schulz, 2004; Liess et al., 1999)

Drainage

In artificially drained watersheds, subsurface flow is likely to be a major mechanism for the transport of soluble pesticides. Drainage systems are either perforated pipes or mole drainage systems above slowly permeable or impermeable subsoil. Leaching water is transported through the pipes or subsurface-channels directly to surface waters. Especially during wet winter months in central and northwestern Europe, the risk for pollution with mobile herbicides applied in drained areas is very high (Rose et al., 1991; Passeport et al., 2011).

Risk mitigation measures

With recent European regulatory frameworks like the Water Framework Directive (European Commission 2000), or the EU-framework for sustainable use of pesticides (European Commission 2009), risk mitigation of diffuse pesticide pollution is becoming increasingly important in the member states. Although pesticide risk management measures like limitations usage, and no spray on field buffers zones were implemented in national law, there are numerous studies reporting pesticide pollution of aquatic ecosystems. (Gregoire et al., 2010; Schulz, 2004; Thomas et al., 2001).

Possible actions can be classified as preventive, in-field measures, reducing measures at the edge of field, or remediating measures as “end of pipe” technologies.

Preventive measures are based on a reduction of emissions from the system. There are several methods of reducing the risk of pesticide loss. Low drift nozzles help to reduce spray drift. Reduction of amount applied or no-spray zones as a passive mitigation measure help to prevent mainly emissions through spray drift and runoff. The biological and mechanical treatment of pests and other measures of the integrated pest management are suitable for reduction of risk for all types of nonpoint sources.

Reducing measures are based on the reduction of immission into the subject of protection through edge of field measures. Filtering buffer zones are, for example, densely vegetated buffer strips for runoff pollution or high vegetation at the edge of field for spray drift (Reichenberger et al., 2007; Schulz, 2004; Lazzaro et al., 2008).

Remediating measures are end of pipe technologies treating the pollution directly before entering the subject of protection. Filter systems may be built at the inlet of the receiving ecosystem. They can be constructed with gravel or sand filters, organic material (e.g. straw), submerged or emergent vegetation as surface flow or subsurface flow systems. Filter systems were extensively studied in agricultural landscapes on their ability in mitigating nutrients and heavy metals. In literature from 1973 to 2007 devoted to vegetated mitigation systems, only 2% dealt with the fate of pesticides in the environment (Gregoire et al., 2009).

In the EU-Member states Germany, France and Portugal mitigation measures related to runoff as e.g. vegetated buffer strips are already part of the regulatory framework. Efficiency of vegetated buffer strips was intensively discussed in literature (Muscutt et al., 1993; Schulz, 2004; Reichenberger et al., 2007; Zhang et al., 2010). Efficiency of vegetated buffer strips for mitigation of runoff pollution is influenced by the width (Klöppel et al., 1997; ; Patty et al., 1997). However efficiency of buffer strips is very variable and can be lowered by soil and substance properties (Schulz, 2004; Reichenberger et al., 2007). In Germany reduction values of 50% for 5 m, 90% for 10 m and 97% for 20 m width of vegetated buffer is proposed as a base for calculation (Großmann, 2008). For mitigation of spray drift tall riparian vegetation was proposed to be taken into account for German regulations as effective edge of field measure (Schulz et al., 2009). For Drift reduction buffer strips are more efficient with increasing heights (Hewitt, 2007). In field measures for reducing risk arising from spray drift (drift-reduction technologies, no spray zones, applications are allowed only during low wind speeds) are developed and already implemented in some countries of the European Union (Reichenberger et al., 2007). Compared to runoff and spray drift, there are only a few possible mitigation measures for pollution through drainflow. If reduction of amounts applied and shift to application times with drier soil are not feasible VTS as “end of pipe” measures may be the only way to reduce risk of pollution (Reichenberger et al., 2007).

After rainfall events, pesticide concentrations in agricultural waterbodies may be in the range from values below 0.1 ng/L to more than 100 µg/L (Schulz et al., 1998; Elsaesser et al., 2011b). Large volumes of water during short periods of time due to heavy rainfall events cannot effectively be mitigated even by edge-of-field measures and lead to a “hydrological dilemma” (Ohliger & Schulz, 2010; Schulz, 2004). In this study the focus is set on vegetated surface flow treatments systems (VTS). VTS can be a way to treat these large amounts of potentially contaminated water after rainfall-runoff events.

To assess effectiveness of VTS, they need to have a defined inlet and outlet, and a densely vegetated area where the contaminated water interacts with plants and sediment. Possible VTS can be vegetated areas of agricultural ditches, detention ponds with dense vegetation which are only filled after rain events or shallow vegetated ponds. Despite the small number of publications dealing with VTS it can be stated that they have the ability to reduce agricultural pesticide pollution (Schulz, 2004; Reichenberger et al., 2007). VTS are particularly advantageous in areas with high quality crops where only a little space is available for mitigation measures.

A literature study was conducted to identify variables influencing the retention of pesticides in VTS for different types of pollution (nutrients, pesticides and wastewater). From the results of those studies and the reviews of Schulz (2004) and Reichenberger et al. (2007) it can be stated that vegetation has the most significant influence on efficiency of vegetated treatment systems (Budd et al., 2009; Cooper et al., 2004; Gill et al., 2008; Lizotte et al., 2011; Moore et al., 2002; Schulz et al., 2003; Rose et al., 2006; Mbuligwe, 2004; Tanner et al., 1995; Tanner et al., 1999; Schulz, 2004; Reichenberger et al., 2007). In several studies reduction efficiency was linked to size related system properties (Dierberg et al., 2002; Tanner et al., 1995; Bennett et al., 2005; Cooper et al., 2004). Hydraulic retention time, which is a function of volume and discharge and hydraulic loading rate, which is a function of inflow and surface size were observed in studies of Stearman et al. (2003) and Blankenberg et al. (2006, 2007). Nonetheless influence of the listed variables regarding efficiency in reducing pesticide concentrations was not sufficiently quantified.

Most of studies with pesticides in VTS focused on highly toxic and sorptive insecticides. For pesticide compounds with low sorptivity to organic material knowledge is marginal (Reichenberger et al., 2007).

Runoff models

There are several field-scale georeferenced approaches predicting rainfall-related runoff losses of pesticides from agricultural areas. Basic models for runoff approaches are the empirical "SCS runoff curve number model" (SCS, 1972) and soil erosion with sometimes modified Universal Soil Loss Equation (USLE). The SCS curve number model predicts the division of precipitation in surface runoff and infiltration (Mockus et al., 2004), whereas the USLE predicts soil loss from sheet and rill erosion (Wischmeier, 1976). CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems) was one of the first models predicting chemical losses through runoff (Knisel, 1980). Parts of this model are reused in several later approaches like SWAT (Arnold & Fohrer, 2005), SWIM (Soil and Water Integrated Model)(Krysanova et al., 1998) and EPIC (Erosion-Productivity Impact Calculator)(Williams, 1995).

On regional scale, pesticide inputs into surface waters can be simulated with georeferenced parameters and hydrological models such as Surface Water Attenuation (SWAT) (Arnold & Fohrer, 2005). SWAT is a continuous-time distributed simulation watershed model. Effects of alternative management decisions on water, sediment, and chemical yields for ungauged rural basins are to be predicted with this approach.

Another approach for calculating rainfall-runoff related pesticide concentrations in surface waters is the GIS-based model "Drainage Spraydrift and Runoff Input of Pesticides in Surface Waters" (DRIPS) (Röpke et al., 2004). Output is a 1km rasterised risk map, based on event, soil, land use and pesticide data. However, all of theese models are either very data demanding, and have a complex structure with a large number of parameters, which are not always available or deductible from available geodata, or have an output with no satisfying spatial accuracy or structure. For very complex approaches like SWAT the risk of overparametrisation and overfitting is given.

The OECD proposed several risk indicators for pollution after rainfall-related runoff events (OECD, 2000). The most sophisticated of those indicators is REXTOX (ratio of exposure to toxicity), which is based on a Dutch risk indicator but also includes features of German and Danish indicators (OECD, 1999; OECD, 2000). REXTOX uses a mechanistic approach for prediction of pesticide losses from field that may be transported to surface waters after rainfall-related runoff events. Central variables for runoff calculation are width of runoff buffer, log P, and half-life in soil (DT_{50}.soil). The model includes variables related to pesticide physico-chemical properties, pesticide-use and several environmental variables such as soil type and slope. Berenzen et al. (2005) extended REXTOX with a module for prediction of pesticide concentrations in stream. Probst et al. (2005) implemented the modified REXTOX for use in ArcGIS (Esri inc. Version 3.X).

Only very few applications of those models were performed on European scale, calculating with low spatial resolution (Schriever & Liess, 2007; FOOTPRINT, 2008). As input for a simulation of mitigation measures for agricultural headwaters, a georeferenced risk assessment on the one hand must have a relatively good spatial resolution, and on the other hand runoff risk needs to be calculated only for small buffers around the waterbodies.

Mitigation measures like widening of buffer zones, reducing amounts of pesticide applied on field and switching to compounds with different properties are partially integrated in the georeferenced models. End of pipe mitigation measures and estimation of costs related to the implementation of the measures are integrated in neither of the models.

1.3 Tasks of the study

Four major tasks were identified for research on the efficiency, optimisation and implementation of VTS as mitigation measures for agricultural nonpoint-source pesticide pollution.

- Assessment of the efficiency of VTS with experiments and field studies. Analysis with focus on the central properties plant density and size.
- Experiments with and monitoring of mobile and weakly sorptive compounds, especially fungicides
- Modeling of a simple but sophisticated, good resolution risk map on large scale for agricultural headwaters.
- Development of a tool for decision making with georeferenced simulation of mitigation measures (including VTS) and implementation costs.

2. Experiments

2.1 Studies at the experimental vegetated ditch mesocosm

Results of the experiments are submitted for publication in the Article “Influence of vegetation density on mitigation of a pesticide mixture in experimental stream mesocosms” (Elsaesser et al., 2011d)(Appendix I)

Experimental setup
Reduction of concentration of six common insecticides and fungicides was studied in a vegetated ditch mesocosm in Landau/Germany. Aim of the research was to determine the influence of pesticide properties and plant density within vegetated ditches on reduction of peak concentration during simulated contamination event.

Six concrete channels with a length of 45 m and a width of 0.4 m were built in Landau (south-western Germany) (Figures 2.1.1-2.1.3). The outdoor stream mesocosm system has an average water depth of 0.28 m on a sediment layer and is fed by spillways attached to a water reservoir. Sediment is a medium loamy sand with total organic carbon content (TOC) of 0.78%. Discharge can be controlled by manual water taps. The water in the 230 m³ reservoir derives from communal water supply and has drinking water quality. Three months prior to the experiment the ditches were planted with the submerged macrophyte Elodea nutallii (Planch). Plant density was manually adjusted to a regression design with a ditch without plants and ditches with 50%, 62.5%, 75%, 87.5% and 100% plant density. After the experimental season in each ditch plant samples of 0.8 m² were removed to quantify plant density.

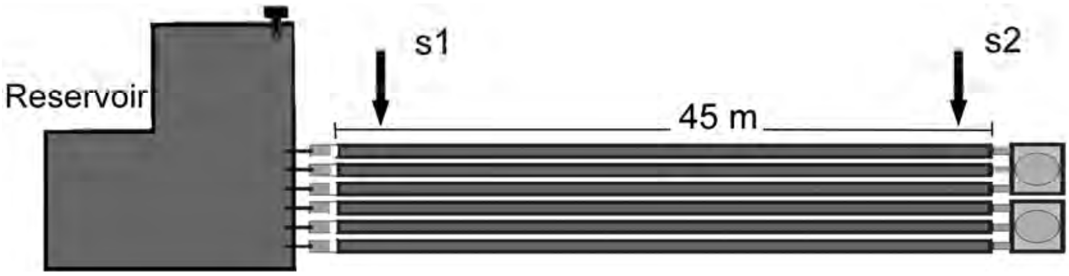

Figure 2.1.1: Layout of the experimental ditch prototype (Elsaesser et al., 2011d)

Figure 2.1.2: Overview of the mesocosm with outlet in the foreground (Stang et al., 2009)

Figure 2.1.3: First picture: Inlet of a ditch. The tap on the left is for circulation of the water through pumps within one ditch, the tap in the middle provides water supply through passive feeding from the reservoir and the tap on the right is connected to communal water supply. Center: *Elodea nuttallii*. Right: Water sampling (Stang et al., 2009)

Two sampling sites were established within each channel, one at 2 m downstream of the inlet (s1) and the second one at 1 m upstream of the outlet (s2) (Figure 1). Sampling times were determined with NaCl tracer tests prior to the experiment (Figure 2.1.4). In the present study, the focus was on the influence of plant density in small experimental ditches following a simulated runoff event with six commonly used insecticides and fungicides. The two main aims of the present study were (1) the effectiveness of vegetated ditches in mitigating potential risks and (2) the influence of variables explaining this effectiveness. We focused in the present study on the role of vegetation in optimising the potential of agricultural ditches and detention ponds for pesticide mitigation.

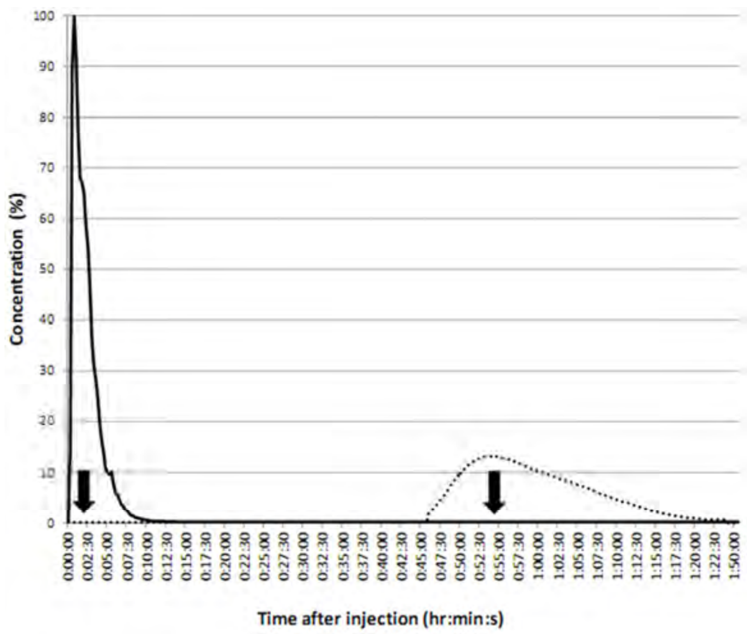

Figure 2.1.4: NaCl tracer run in the ditch with plant density of 72%. The solid line shows the normalized concentration values measured at the 2m sampling station, the dotted line shows the normalized concentration values measured at the 44 m sampling station. Peak sampling times are marked with arrows.

Results

Concentrations of a mixture of six common insecticides and fungicides were reduced to less than 10% within the 44 m of the ditch mesocosms. Vegetated ditches performed significantly better than the ditch without vegetation. Highly sorptive compounds are also significantly better retained. Linear regression analysis identified plant density and K_{OC} as variables with the highest explanatory power for the response variable reduction of peak concentration (Table 2.1.1).

Table 2.1.1: Multiple linear regression analysis results including most important factors predicting pesticide retention performance (n=30) in the first two metres of the experimental ditches (Model A) and over the full length of 44 m (Model B).

Model A: s1	Estimate	Std. Error	t value	Significance		Relative importance (%)
(Intercept)	25.0	6.9	3.6	<0.01	**	
Plant coverage (%)	0.3	0.1	3.7	<0.001	***	63
K_{OC} (ml/g)	0.004	0.001	2.8	<0.01	**	37
Model B: s2						
(Intercept)	91.5	0.7	129.6	<0.001	***	
Plant coverage (%)	0.1	0.01	5.8	<0.001	***	59
K_{OC} (ml/g)	0.001	0.0001	4.8	<0.001	***	41

Model A summary: R^2 = 0.45; adjusted R^2: 0.41; p<0.001. Excluded factors were: Log P, solubility in water (mg/L), water-sediment DT_{50} (d), water DT_{50} (d), photolytic DT50 (d). Model B summary: R^2 = 0.67; adjusted R^2: 0.65; p<0.001. Excluded factors were: Log P, solubility in water (mg L-1), water-sediment DT50 (d), water DT_{50} (d), photolytic DT_{50} (d).

2.2 Studies at the experimental vegetated wetlands in Lier/Norway

Results of the experiments are published in the Article "Assessing the influence of vegetation on reduction of pesticide concentration in experimental surface flow constructed wetlands: Application of the toxic units approach" (Elsaesser et al., 2011)(Appendix I)

Experimental setup

Reduction of concentrations and potential effects of five commonly used pesticides and retention of pesticide masses in an experimental system was assessed at the Lier experimental wetland site. The system is located 40 km south of Oslo (Blankenberg et al., 2006). Eight parallel wetland cells are approximately 40 m in length, 3 m in width, and depth varies from 0.05 to 0.5 m. The wetland system is gravity fed through pipelines with stream and drainage water (Braskerud & Haarstad, 2003; Blankenberg et al., 2006). Three of the eight surface flow wetland cells were used for the present experiment. Three sampling stations were located two m (SSt1) and 20 m downstream from the inlet (SSt2) and directly at the outlet (SSt3) (Figure 2.2.1)

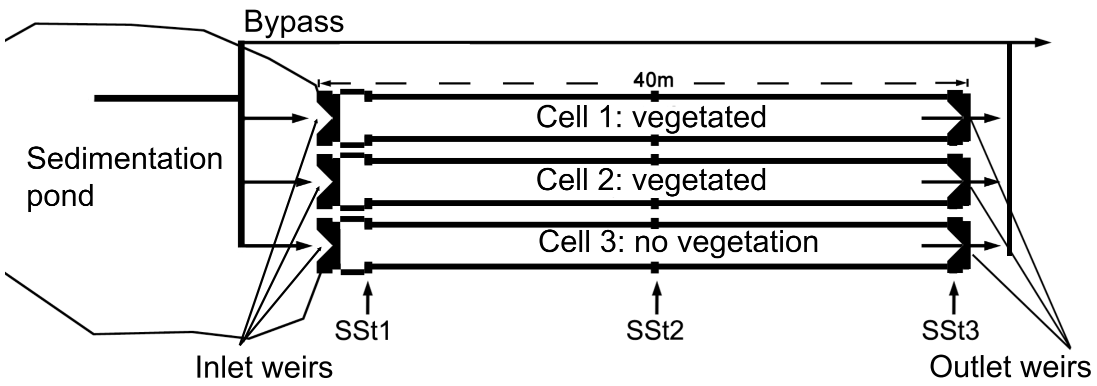

Figure 2.2.1:Layout of the Lier experimental wetland cells

Two of the cells were densely vegetated with submerged and emergent local aquatic plants (*Phalaris arundinacea* L., *Typha latifolia* L., *Phragmites australis* (Cav.) Trin. ex Steud., *Lemna* spec., *Solanum dulcamara* L., *Glyceria fluitans* L., *Sparganium erectum* L. emend Rchb. and *Ranunculus repens* L.). In cell 3 the plants and roots were completely removed. Sediment is a sandy silt covered by a sediment layer of fine silt. Mean water depth of the two vegetated cells (cell 1: 9.7 cm, cell 2: 13 cm) was larger than in cell 3 (6.5 cm).

Figure 2.2.2: Vegetation in the two vegetated wetland cells. Left picture: downstream view of cell 1. Right picture: upstream view of cell 2 (D. Elsaesser).

Sampling times and flow patterns were determined with NaCl tracer tests prior to the experiment (Figure 2.2.3).

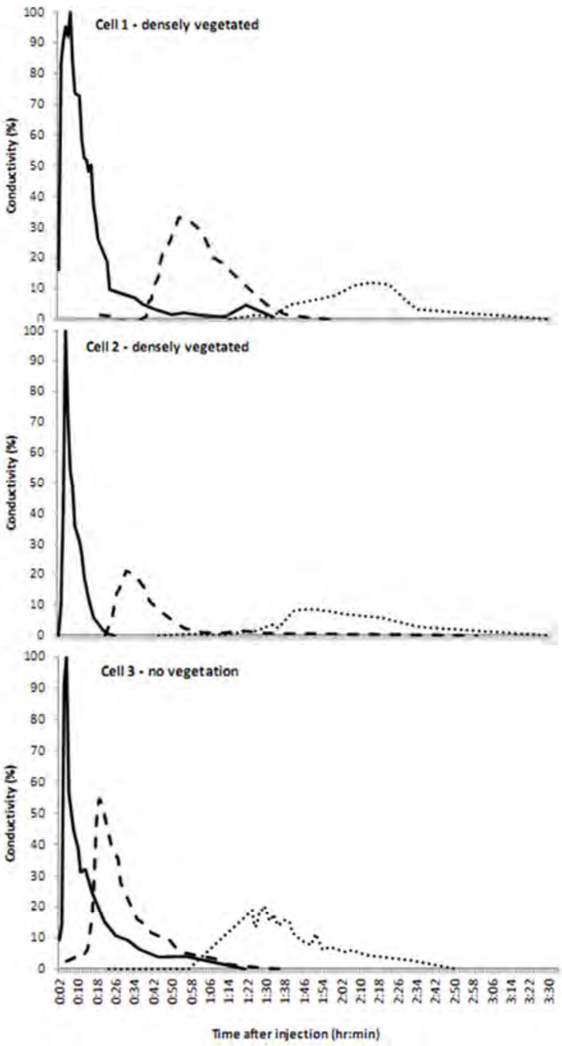

Figure 2.2.3: NaCl tracer runs in the three experimental wetland cells. Solid line: SS1 2m downstream of the inlet, dashed line: SS2 20m downstream of the inlet and dotted line: 40m downstream of the inlet.

Results

Mean peak retention was 72% in the non-vegetated cell and 89% (cell 1) and 91% (cell 2) in the vegetated cells. Less than 5% of the masses were retained within the wetlands. Uptake and sorption by plants was low (up to 4%), however higher for the vegetated cell dominated by Phalaris arundinacea L. (Figure 2.2.2, left picture) than for the one with Typha latifolia L. (Figure 2.2.2, right picture) as dominant plant. The toxic units (TU) approach was used to describe the potential toxicity retention within the wetland cells. Calculated toxicity of the substances decreased by 79% in the non-vegetated cell and by 95% in the two vegetated cells. Despite the low mass retention, the vegetated wetland system reduced the toxic effects, expressed as toxic units from values of 0.24 to 0.01, i.e. a concentration two orders of magnitude below the acute toxicity threshold, within a distance of 40 m while the non vegetated would need to be about 64 m long for the same efficiency.

2.3 Tracer studies in vegetated ditches

Results of the experiments are published in the article "Multi-tracer experiments to characterise contaminant mitigation capacities for different types of artificial wetlands" (Lange et al., 2011)(Supporting material on DVD). Work for this article was predominately done by the other authors. David Elsaesser did parts of the experimental work, analysis and interpretation for the two study sites near Landau/Germany (SFW5 and SFW6), as described in this chapter.

Experimental setup

Tracer experiments were performed in co-work with the University of Freiburg at two vegetated ditches located approximately 5 km north- and southwest of the city of Landau in the viticultural region of the southern palatinate, Germany (Lange et al., 2011). The aim of the experiments was the study of the fate of a highly soluble, a photosensitive and a stable and sorptive tracer in ditches with high vegetation density, and low vegetation density.

Salt tracer (sodium chloride) and the fluorescent tracers uranine (disodium 6-hydroxy-3-oxo-9-xanthene-o-benzoate) and SRB (sulforhodamine-B: 2-(3-diethylamino-6-diethylazaniumylidene-xanthen-9-yl)-5-sulfo-benzenesulfonate), were injected as a pulse into the inlet of two differently vegetated ditches. Highly soluble salt tracer documented wetland hydraulics. Uranine is easily photodegradable and has a KOC of 69-89 (Li et al., 1998) and shows very low sorption to negatively charged surfaces , whereas SRB is not photodegradable and highly sorptive (Morgenschweis, 2011; Passeport et al., 2010).

The first ditch (HB) was a 413 m segment of the Hainbach, a small river with a watershed of 455 ha. Vegetation (*Phragmites* australis) was removed above the water surface one day prior to tracer injection. Vegetated areas along the ditch were divided by several pool-riffle sequences. Water depth is highly variable with a mean value of about 0.2 m. During the tracer experiment flow was constant at 5.0 L/s (Table 2).

KB is a straight 80m ditch densely vegetated by *Phragmites australis*. During the experiment the water had a depth of 0.1 m and a low discharge of 0.9 L/s (Table 2.2.1, Figure 2.2.1).

Table 2: Size and discharge of the two vegetated ditches HB and KB

	outflow L/sec	**length** m	**depth** m	**area** m^2	**volume** m^3
HB_long	5	413	0.2	206	31
KB	0.9	80	0.1	40	4

Figure 2.2.1: upstream view on the HB-site (left) and downstream view of the KB-site (right) (Lange et al., 2011).

Concentrations of the salt tracer were measured as conductivity with portable conductivity meters (LF-92 sensors, WTW, Weilheim, Germany) at 0.5% accuracy (Lange et al., 2011). Breakthrough curves of the fluorescent tracers were measured directly in stream with portable flouorometers (GGUN-FL30) and in laboratory using a fluorescence spectrometer (LS-50B, Perkin-Elmer) (Lange et al., 2011).

Results

The tracers quickly passed the wetlands. Breakthrough curves showed single peaks for all three substances (Figure 2.2.2). Salt tracers were completely recovered at the outlet of the ditches. Uranine showed recovery of 100% in the shorter ditch (KB) and a loss of 17% in the HB. This loss is most likely caused by photolytic decay (Smart & Laidlaw, 1977). With removal of vegetation in HB the solar radiation was increased. The rhizomes and cut remnants of plants inside the ditch increased contact to sediments and vegetation which lead to SRB retention of 32% in the HB. SRB retention in the short KB site was even better with 35% (Table 2.2.2). In this ditch a shallow water depth and dense vegetation apparently caused the most favorable conditions for SRB sorption (Lange et al., 2011; Morgenschweis, 2011).

Table 3: injected masses and recovery of the tracer substances in the vegetated ditches HB and KB

	Injected mass			Sampling		Recovery		
	NaCl (g)	uranine (g)	SRB (g)	interval (min)	duration (d)	NaCl (%)	uranine (%)	SRB (%)
HB	2000	0.05	0.2	0.5–5	0.17	100	83	68
KB	1000	0.02	0.1	1–5	0.08	100	100	65

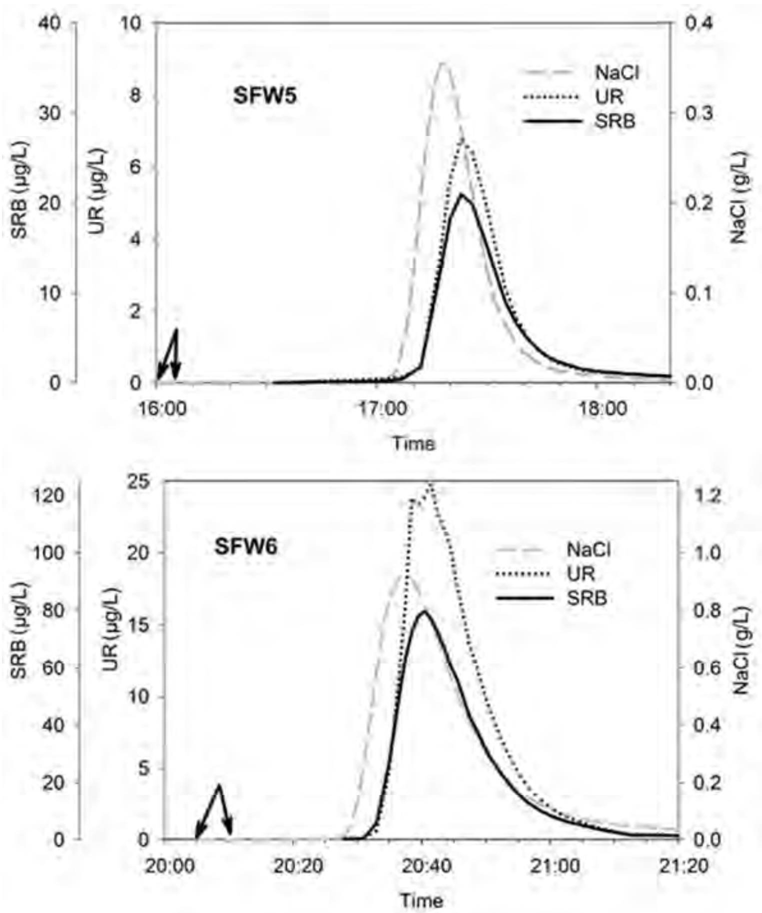

Figure 1: Breakthrough curves of NaCl, uranine and SRB at the Hainbach (upper graph) and KB (lower graph) (Lange et al., 2011)

Results of the tracer experiment show that substances with low sorptivity are not retained within vegetated ditches. For the sorptive substance SRB retention was 32% in the 413 m of ditch with low vegetation density and 35% in 80 m of the ditch with very high plant density. Photolytic decay of uranine was observed in the ditch with low vegetation density.

3. Field monitoring

Results of the monitoring are submitted for publication in the Article "Mitigation of agricultural nonpoint-source fungicide pollution in detention ponds and vegetated ditches" (Elsaesser et al., 2011b)(Appendix II).

Monitoring sites

In the present field study, vegetated systems in the winegrowing area of the Southern Palatinate in southwestern Germany (Figure 3.1.1) were monitored between 2006 and 2009.

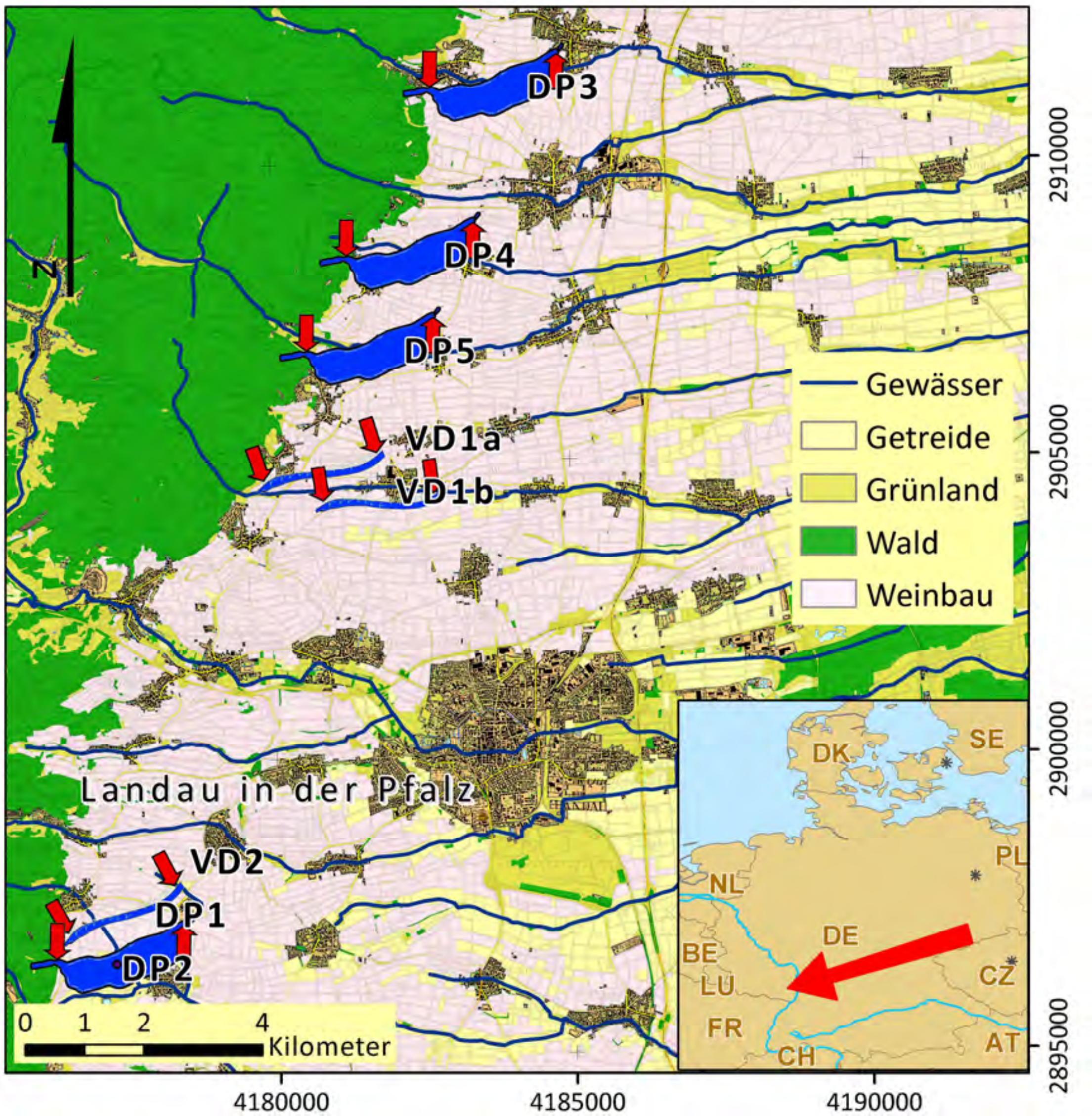

Figure 3.1.1: Study area in the southern Palatinate. Coordinate system: ETRS 1989 LAEA (Elsaesser et al., 2011b)

Sections of densely vegetated ditches (VD1 Figure 3.1.2 and VD2 Figure 2.2.1 right picture) and stormwater detention ponds (DP1-DP5 Figure 3.1.3-3.1.5) were selected as independent sampling sites. With approximately 23,000 ha the southern palatinate is the second-largest winegrowing region in Germany.

VD1 is a vegetated part of the Hainbach within consecutive detention ponds north of the village of Böchingen. Plant community is dominated by Phragmites australis. In 2006 and 2007 vegetation was mowed in early summer. In these two Years a section of 165 m (plant density 40%) was monitored. In 2008 and 2009 the vegetation in the downstream part was not removed prior to the monitoring season and the section was shortened to 105 m (plant density 90%) to exclude the upstream part without vegetation. Catchment area is 455 ha with 8% agricultural area (vineyards).

VD2 is a straight section of the Krottenbach between the villages of Eschbach and Göcklingen densely vegetated with *Phragmites australis* (Figure 2.2.1). The ditch has a length of 80 m and receives water from a catchment of 330 ha. 54% of the catchment is agricultural area (vineyards, orchards and cereals).

DP1 is a small basin of 26 m² within a large detention pond. The second half of this basin is densely vegetated with *Epilobium hirsutum* and *Phragmites australis*. DP1 receives water from the adjacent agricultural area (40 ha with vineyards and orchards). The water from the small basin discharges into the Krottenbach which flows into the dammed area of the detention pond (DP2)(Figure 3.1.2). This dammed area is densely vegetated with *Phragmites australis* and receives water from a total catchment of 370 ha (vineyards, orchards and cereals).

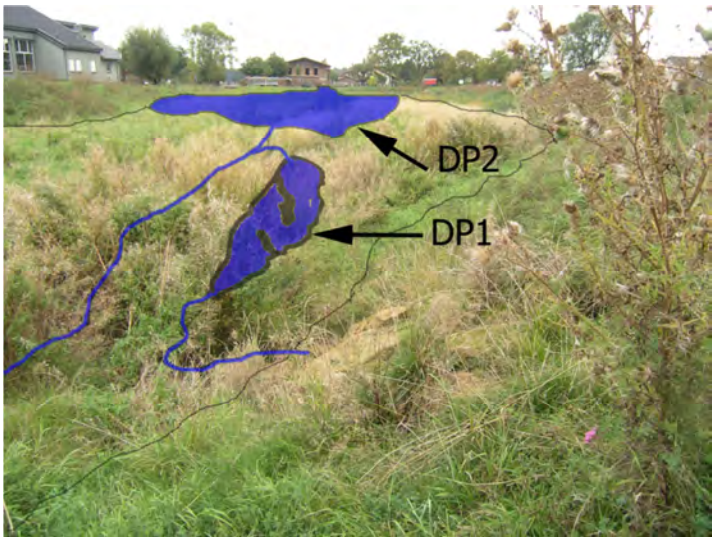

Figure 3.1.2: View from inlet of DP1 on DP1 an DP2

DP3 is located between the villages of St. Martin and Maikammer. It is a free water pond. The riparian area is densely vegetated with *Phragmites australis* and *Typha* spec.. The system receives water from a catchment of 864 ha (18% agriculture, predominantly viticulture).

VD5 is located near the village of Roth unter Rietburg. The detention pond is densely vegetated with Poaceae and herbaceous plants. It receives water from a catchment of 152 ha with 24% of agriculture (vineyards).

VD5 consist of an area densely vegetated with *Phragmites australis* and a freewater pond. The system is located west of Hainfeld at the Modenbach. It receives water from a catchment of 962 ha with 7.2% of agriculture (vineyards).

For each sampling site surface size, depth representative cross sections, plant density at water surface and flow length were recorded.

Discharge was calculated for each sampling site with NaCl tracer method (Equation 3.1.1, Figure 3.1.2 (LUBW, 2002) and with measurement of flow velocity and cross section of the ditch (Equation 3.1.2 (Schneider, 1996)).

Equation 3.1.1

$$Q = \frac{m_{NaCl}}{\int_{t1}^{t2} (Lf_i - Lf_0)\, dt * f}$$

Q is the discharge, m_{NaCl} is the mass of tracer injected, Lf_i is the conductivity of the single measurement, Lf_0 is the background conductivity of the ditch, t1 is the begin of the tracer peak, t2 is the end of the tracer peak, dt is the interval of measurement and f is the factor 0.00051 (g/L)/(µS/cm) for conversion of conductivity into concentration.

Equation 3.1.2

$$Q = V*A$$

Q is the discharge, v is the measured flow velocity and A is the cross section of the ditch which is filled with water.

To-the-minute rain intensity data was obtained for two weather stations in the area from the German weather service (DWD Offenbach/Germany).

At each site a sampling station was installed at the inlet and outlet of the wetland or the respective vegetated stretch of the ditch. Water levels for calculation of the discharge were recorded at the sampling stations. In 2006 and 2007 composite water samples representing the contamination levels during runoff were accomplished using bottles stored in the stream or river. The opening was fixed at a water level typically reached after heavy rainfall events (Schulz et al., 2001). During rainfall-induced surface runoff, the rising water level fills the bottles passively. In 2008 and 2009 the samples were taken manually 5 cm below water surface in the center of the stream when the peak level at the sampling site was reached after heavy rain events. Between 2007 and 2009, a total of 22 inlet-outlet pairs of samples were collected during 17 rainfall-related runoff events. Additional samples (in total 14 inlet-outlet pairs) were taken during normal discharge at least four days after the last rainfall. In 2008 and 2009 an additional total of nine samples of the runoff water were collected on paved waysides directly before entering the waterbody.

Exposure and retention

A total of 22 pairs of water samples from runoff events, 11 pairs of water samples at normal discharge and 9 samples of wayside runoff water were collected and analysed. Samples of runoff events showed maximum concentrations up to 11.49 μg/L (tebuconazole). At normal discharge maximum concentration was at 0.73 μg/L (boscalid) and maximum concentration from samples of wayside runoff was 13.9 μg/L (cyprodinil). Median values of total concentration of fungicides within the samples were 0.65 μg/L during runoff events, 0.49 μg/L at normal discharge and 5.86 μg/L in wayside runoff (Figure 3.1.8).

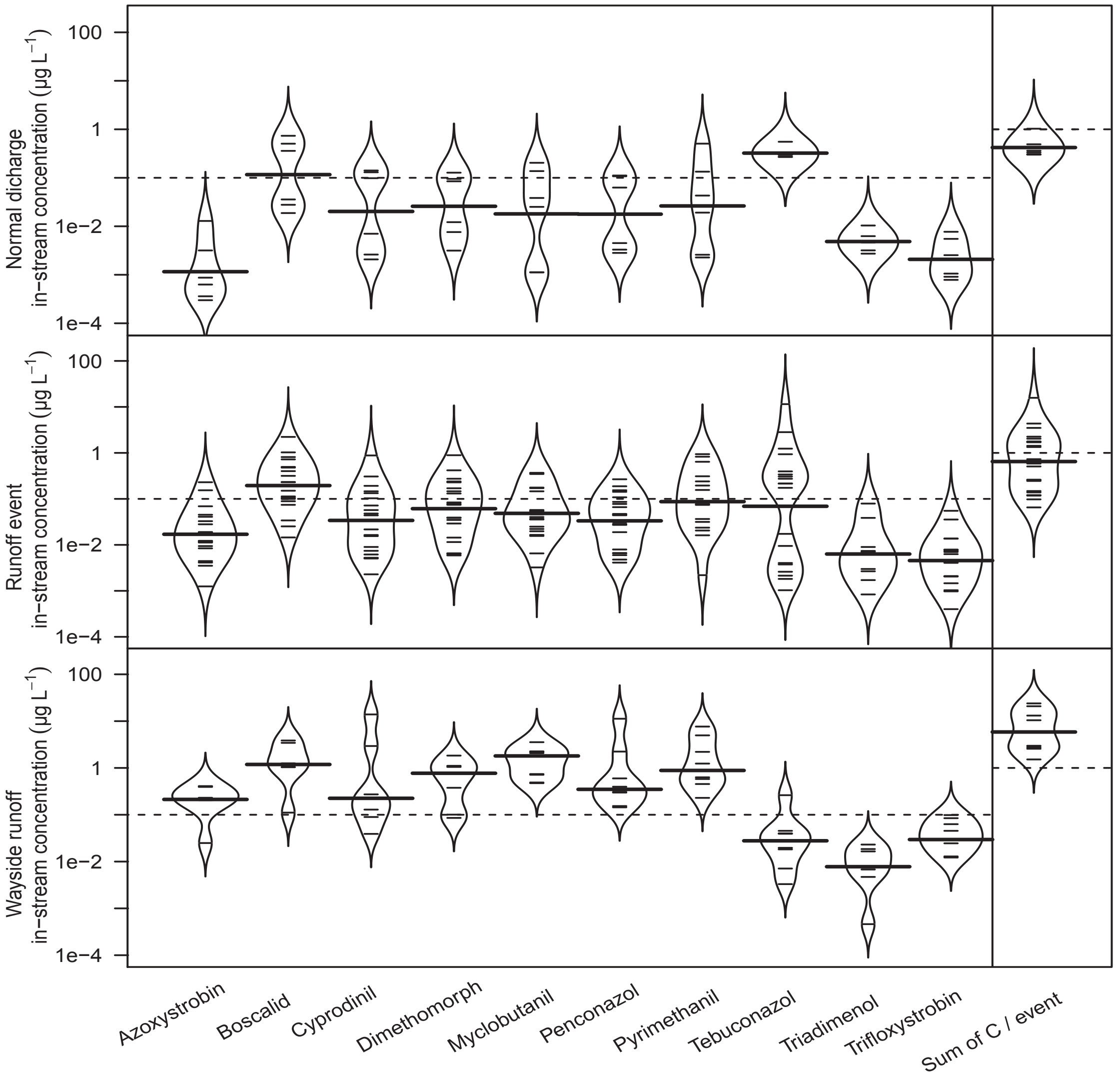

Figure 3.1.8: In-stream inlet peak concentrations of ten fungicides at normal discharge 2007-2009 (upper graph), during runoff events (middle graph) and concentration in wayside runoff 2008-2009 (lower graph). Beanplot "Sum of C / event" shows the distribution of inlet concentration sums of the ten fungicides within single samples. The dotted line is the EU drinking water benchmark of 0.1 µg/L for single fungicides and 1 µg/L for the sums of concentrations (Elsaesser et al., 2011).

Median reduction of concentrations was 25% in detention ponds and 53% in vegetated ditches. Median reduction of potential toxicity was 38% in detention ponds and 56% in vegetated ditches. Mean retention in the VD1 systems increased from a median value of 32% in the 165 m (VD1a) with plant density 40% to a median value of 58% in the shortened ditch (VD1b) with higher plant density of 90%.

Parameters influencing the mitigation

Multiple regression analysis was performed with data of vegetated ditches and detention ponds separately in order to identify variables with highest explanatory power for the response variable pesticide retention performance. Relative importance of the explanatory variables was assessed using hierarchical partitioning (Chevan & Sutherland, 1991). An overview of the relative importance of the variables in the experimental results and the monitoring is provided in figure 3.1.9.

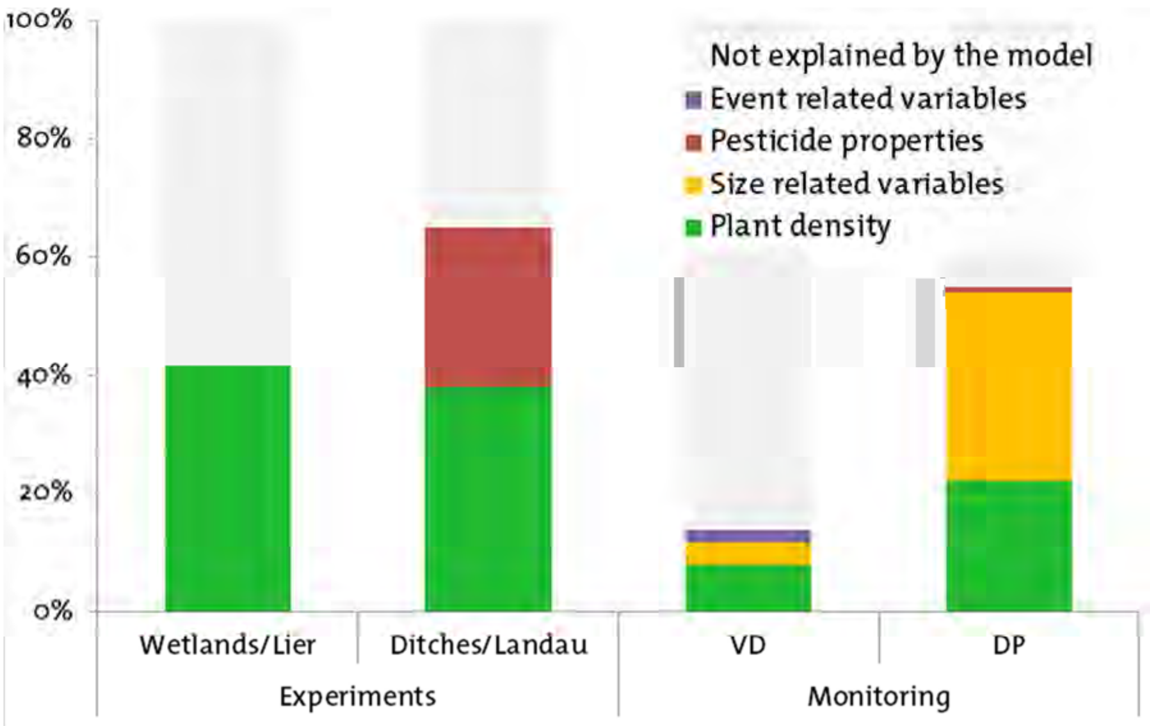

Figure 3.1.9: Weighting of the explanatory variables for the response variable reduction of peak concentrations for experimental and monitoring sites.

4. Simulation at European Scale

4.1 Risk of runoff-related pesticide exposure – the ArtWET exposure tool

Contents of this chapter are published in the articles "Risk map of runoff-related pesticide pollution in small rivers of the European agricultural landscape" (Elsaesser, 2011e)(Appendix III) and "A spatial decision support system for mitigation of runoff-related pesticide pollution in surface waters across Europe" (Elsaesser & Schulz, 2011c)(Appendix III)

Database

A geodata layer, which contains all agricultural areas within a buffer zone of 50 m around European streams was built with current data. Data was chosen by spatial accuracy and availability for Central, Southern and Eastern Europe. Most of the source data was taken from freely accessible data portals of the European Commission Joint research center (Table 4.1.1)

Table 4.1.1: Geodata included in the database. a.: + - data was modified or converted to meet the standards for the database. -: data was taken as is into the database.

Attribute	Unit	Conversion[a]	Source	Reference
Type of agriculture		-	Corine Land cover	(Büttner, 2007)
Hydrological soil type		+	Soil database	(Panagos, 2006)
Slope	%	+	SRTM	(Farr et al., 2007)
Discharge	L/s	-	Hydrosheds	(Lehner et al., 2008)
OC in topsoil	%	-	Soil Database	(Panagos, 2006)
Length of Riversegments	m	+	EC-JRC, IES	(Vogt et al., 2007)
Curve Number		+	USDA	(Zhan & Huang, 2004)
Plant interception	%	-		(Linders et al., 2000)

Structure of the model

The simulation tool was programmed in ESRI ArcGIS Model builder.

It consists of five consecutive models (Figure 4.1.1). The amount of rainfall contributing to surface runoff was calculated with Runoff Curve number model (Zhan & Huang, 2004). The percentage of applied amount within the surface runoff is calculated using the modified REXTOX model (Probst et al., 2005), that was proposed by the OECD (OECD, 2000).

$$L_{\mathrm{Runoff}} = \left(\frac{\mathrm{Q}_{\mathrm{Runoff}}}{(P * 10)}\right) * \mathrm{e}^{-3*\frac{\ln 2}{Dt_{50}}} * \frac{1}{1+Kd} * \left(1-\frac{Pli}{100}\right) * slope * \ 0.83^{Buffer} * 100$$

where L_{Runoff} is the percentage of applied substance in runoff, *Dt50* is the half life of applied substance in soil (days), *Kd* is the soil-water partitioning coefficient, *Pli* is the interception on plant tissue, *slope* is the slope factor, calculated using the methods of Probst (2005) and *Buffer* is the mean width of densely vegetated buffer strips.

Concentration of the substance in stream is calculated with the second part of the REXTOX model:

$$PEC = L_{\mathrm{Runoff}} * PA * \frac{1}{Q_{\mathrm{Stream}} * T * 60}$$

where *PEC* is the predicted in stream peak concentration in μg/L, *PA* is the amount of substance applied in the simulation area in μg, Q_{Stream} is the discharge in stream in L/s and *T* is the duration of rain event in minutes.

Acute toxicity data of the substances for fish, algae and aquatic invertebrates can be used to assess potential toxicity of the substance based on toxic units (TU). Toxic units are calculated for each peak concentration of the substance. Specific LC_{50} or EC_{50} values for acute toxicity to *Oncorhynchus mykiss* (fish LC_{50} 96 hours), *Daphnia magna* (aquatic invertebrate EC_{50} 48 hours) and algae (EC_{50} growth 72 hours) can be found in the Footprint Pesticide Properties database (PPDB, 2011). The TUs are calculated using the TU approach (Peterson, 1994; Junghans et al., 2006):

$$PTU = \frac{PEC}{EC_{50}}$$

where *PTU* is the potential toxicity in toxic units and EC_{50} is the lowest concentration causing acute effects to selected species.

Acute toxicity data of the substances for fish, algae and aquatic invertebrates can be used to assess potential toxicity of the substance based on toxic units. Toxic units (TU) are calculated for each peak concentration of the substance. Specific LC_{50} or EC_{50} values for acute toxicity to *Oncorhynchus mykiss* (fish LC_{50} 96 hours), *Daphnia magna* (aquatic invertebrate EC_{50} 48 hours) and algae (EC_{50} growth 72 hours) can be found in the Footprint Pesticide Properties database (PPDB, 2011). The TUs are calculated using the TU approach (Peterson, 1994; Junghans et al., 2006). The PTU value is to derive a target retention factor

(TRF). The TRF describes a percentage of reduction of peak concentration, which is needed to mitigate the simulated pollution below pollution threshold. After the TRF calculation the resulting shapefile is split into polygon layers, each containing the areas of different type of agriculture.

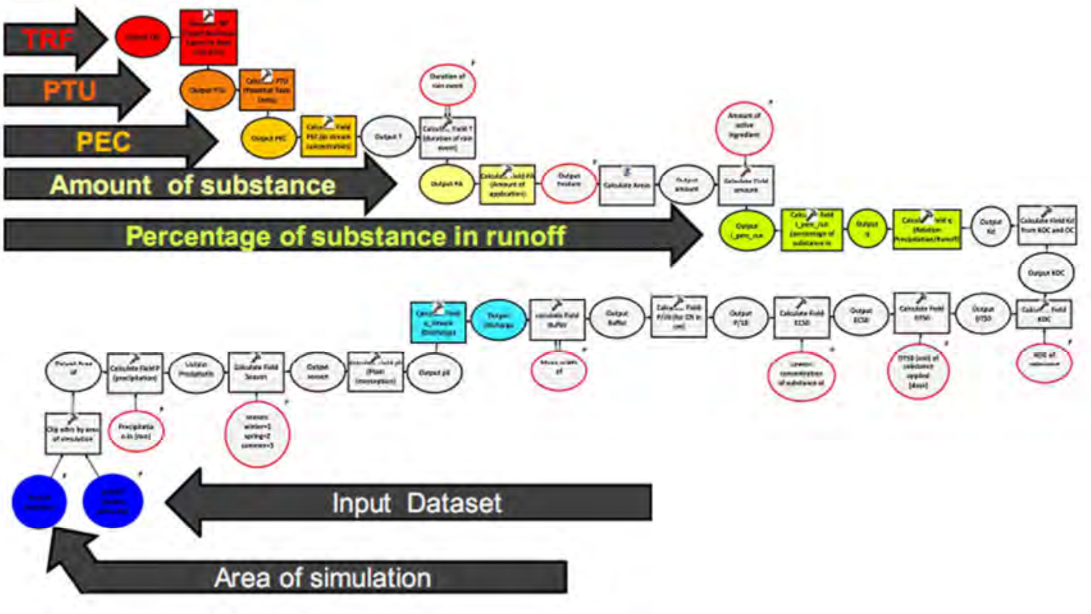

Figure 4.1.1: Structure of the risk tool with five consecutive models.

Risk map

The ArtWET exposure tool was used to create a risk map on European scale (Sopporting material). Runs with worst-case dummy substances are base for the map.

4.2 Simulation of mitigation measures – The ArtWET mitigation simulator

Contents of this chapter are published in the article “A spatial decision support system for mitigation of runoff-related pesticide pollution in surface waters across Europe” (Elsaesser & Schulz, 2011c)(Appendix IV.b)

Structure of the model

The mitigation tool was built to quantify the resources needed for the implementation of possible mitigation measures. Based on the review of Schulz et al. (2004) and Reichenberger et al. (2007) three types of mitigation measures were integrated into the tool. As preventive measure, the amount of pesticide substances applied can be reduced to meet the mitigation target, as edge of field measure, the vegetated buffer strip can be broadened to retain the pollutant and as end of pipe measure VTS can be installed to mitigate the pollution before it reaches the receiving aquatic ecosystem. Total costs for mitigation can be calculated with information on the spatial extent of the mitigation measures and costs for implementation of the measures.

The tool is structured in five intertwining modules (Figure 4.2.1). In modules **a**, **b** and **c** the mitigation measures are simulated, in module **d** costs are calculated, in module **e** results are combined in a table and in module f the polygons representing VTS are built.

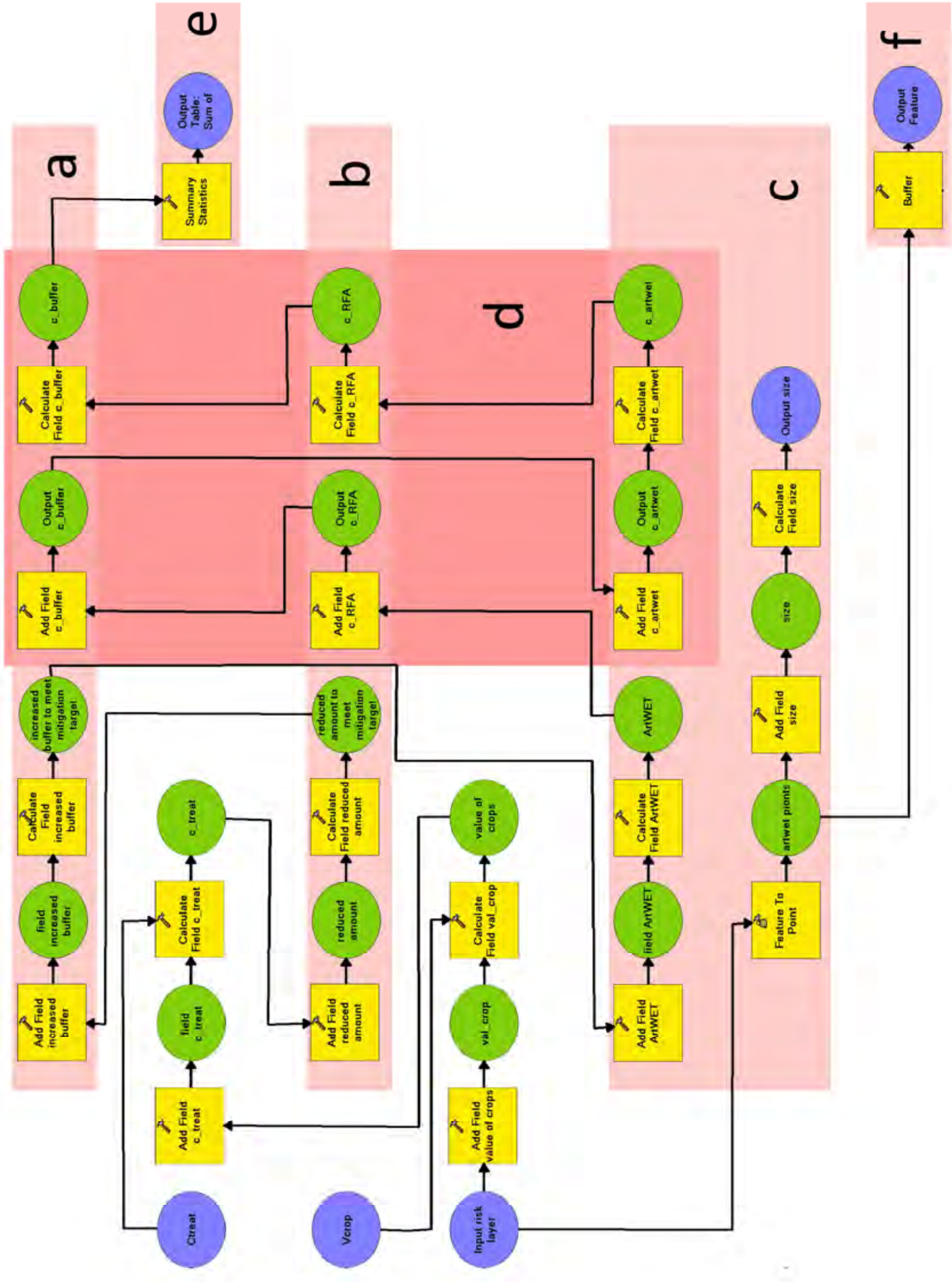

Figure 4.2.1: Structure of the mitigation DSS.

Simulation of mitigation measures

The reduction of amount applied on the field is calculated by rearranging the PTU-calculation with a PTU of 0.01 for all segments of the waterbody where the PTU exceeds the 0.01 benchmark:

$$RFA = \frac{EC_{50} * Q_{\text{Stream}} * T * 60}{L_{\text{Runoff}}} - \frac{PA}{100 * A}$$

RFA is the reduction of amount of pesticides applied on the crop in g/ha and PA is the amount applied on the crop in the segment calculated in µg and A is the area of the segment in m².

The broadening of existing densely vegetated buffer strips between the waterbody and the agricultural area is easily implemented by rearranging the runoff equation of the REXTOX model with a PTU of 0.01 for all segments of the waterbody where the PTU exceeds the 0.01 benchmark.

$$Buffer = \log_{0.38}\left(\frac{P * (1 + Kd) * Q_{Stream} * EC50}{60 * Q_{Runoff} * \mathrm{e}^{-3*\frac{\ln 2}{Dt50}} * \left(1 - \frac{Pli}{100}\right) * slope * PA * T}\right)$$

Buffer is the width of densely vegetated buffer between the sprayed area and the waterbody that is needed to decrease the potential toxicity in stream to a value below 0.01 toxic units.

To calculate the size of optimised VTS that is needed to meet the mitigation target, a model was built with experimental and monitoring data of the ArtWET project (chapter 2.1, 2.2, 3.1, Gregoire et al. 2010, Stehle et al. 2011). Influence of system, pesticide and event properties were analysed regarding their influence in reduction of pesticide peak. Linear regression analysis identified plant density and size-related variables of vegetated treatment systems as central predictors. Based on those results the surface area of VTSs with a depth of 50 cm and an optimised plant density of more than 90% is calculated. The VTS surface area is calculated by multiplying the flow length with a width of 3 m. The areas of the VTS for each subwatershed are summed up and a circular polygon representing the size of the resulting wetland is built.

The correction factor for optimised plant density was calculated with results of a linear regression of all ArtWET prototypes (Figure 4.2.2, systems without vegetation were excluded) and applied to fit the whole database to a plant density of 90%.

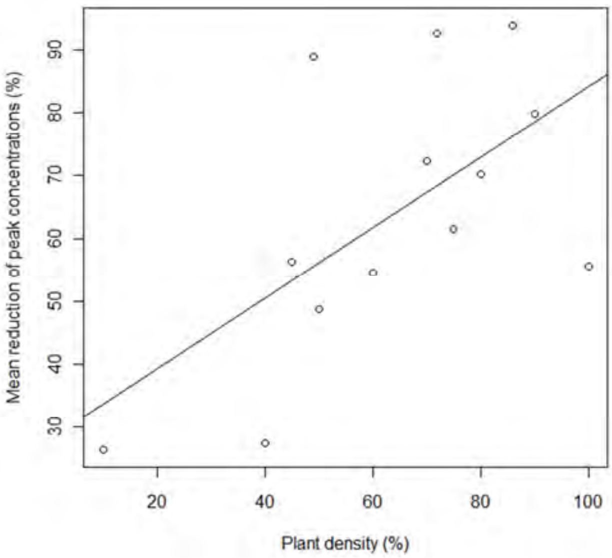

Figure 4.2.2: linear regression of plant density with mean reduction of concentrations. R^2=0.33 p=0.02 y=28.04*0.56x.

The correction factor for plant density was applied to the database:

$$R_c = R_m\, 1.78 * (90 - P_m)$$

Where R_c is the corrected reduction value, R_m is the measured reduction of peak concentrations and P_m is the plant density recorded.

Flow length was identified as the variable with the highest explanatory power. Linear regression analysis was used to derive a flow length factor for calculation of size for simulated VTS (Figure 4.1.3).

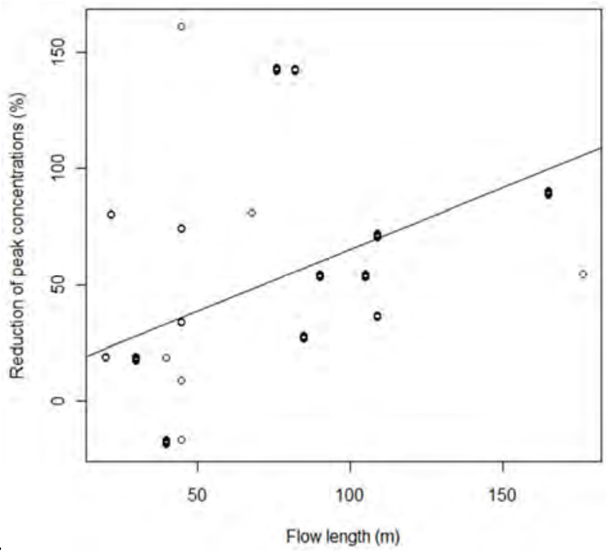

Figure 4.1.3: Linear regression of corrected reduction values for plant density of 90%. R^2=0.24, p<0.0001 y=11.9+0.53x

Size of VTS as mitigation measure was implemented in the model:

$$\text{VTS-Factor} = \frac{1}{0.53} * 3 = 5.63$$

$$VTS = \sum TRF * 5.63$$

where *VTS* is the modeled surface area in m² of the VTS with an plant density of 90% .

Calculation of implementation costs and feasibility (spatial decision support system)

The cost for the reduced field amount is calculated with the annual cost for pesticide treatment and the annual contribution margin for crop, which is the value of crops minus fixed costs, as variables.

$$C_{RFA} = \left(0.6 * TRF * V_{crop} * \frac{A}{10000}\right) - \left(RFA * C_{treat} * \frac{A}{10000}\right)$$

C_{RFA} is the profit setback following the reduction of applied amount,

V_{crop} is the annual contribution margin for crop in €/ha and

C_{treat} are the annual costs for pesticide treatment €/ha.

Those input variables differ for each crop and region and may be obtained from national and international statistical offices. A loss of 30% of the yield is assumed when no pesticides are applied. This mean loss of yield was estimated by comparing yields of conventional agriculture and organic farming for ten different crops (Paller & Prankl, 2008) and adding a security of 40% relative loss (Table 4.2.1).

$$L_{\mathrm{crop}} = \frac{\sum\left(1.4 * 100 - \frac{Y_{\mathrm{o}}}{0.01 * Y_{\mathrm{c}}}\right)}{n_{\mathrm{crops}}}$$

L_{crop} is the loss of yield without pesticide application (%), Y_o is the yield of crop with organic agricultural practice (kg/ha), Y_c is the yield of crop with conventional agricultural practice (kg/ha) and n_{crops} is the number of different crops.

Table 4.2.1: Calculation of loss through crop shortfall without pesticide application. Based on yield data for organic and conventionally produced crops in Austria (Paller & Prankl, 2008).

	Crop	Organic (O)	Conventional (C)	O/(C/100)	loss from C to O	factor f (*1.4)
		dt/ha	dt/ha	%	%	%
	wheat	50	70	71	29	40
Maximal	grapes	81	122	66	34	47
Yield	corn	99	111	89	11	15
	apples	204	347	59	41	58
	potatoes	325	400	81	19	26
	wheat	30	35	86	14	20
Minimal	grapes	45	52	87	13	19
Yield	corn	64	70	91	9	12
	apples	87	130	67	33	46
	potatoes	150	175	86	14	20
			mean	78	22	30
			range	59-91	9-41	12-58

The cost for the widening of the existing buffer strip is calculated based on the area lost for these buffers and the building and maintaining costs which are implemented as fixed annual amount of 1 €/m².

The cost for VTSs are also calculated based on the area loss and implementation and maintenance costs. Here an annual amount of 2 €/m² for depreciation and management is used in the model.

All costs and the area need for the different measures are summed up and stored as database-file (.dbf) in the project folder.

5. Conclusion

5.1 Synthesis of the results

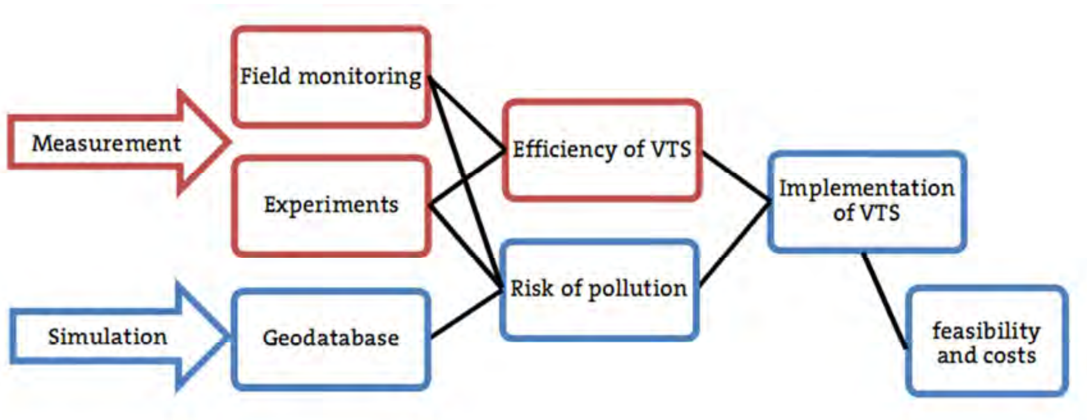

Figure 5.1: Synthesis of the results.

The aim of the study was the assessment of VTS as mitigation measure for nonpoint-source pesticide pollution. To attain this overall target interlocked tasks were completed. Efficiencies of optimised experimental VTS, regional field efficiencies and literature data were joined to perform an assessment of feasibility and calculation of costs on large scale. Product is a spatial decision support system for measures mitigating the risk of adverse effects caused by nonpoint-source pesticide pollution.

Findings of optimised VTS were combined with the results of the monitoring campaign to assess efficiency of VTS. If the focus is set on the monitoring results, the heterogeneity in performance of the VTS becomes obvious. Variability in reduction of peak concentrations is very high. With the controlled conditions of the experiments, reduction of peak concentrations showed less variability and was much higher. Regarding the retention of loads within the systems the values were low. The experiment in the Lier wetland cells reported mass retention below 5% for the pesticide mixture with moderately mobile substances. The tracer studies in two vegetated ditches in Landau reported mass retention of 35% for the highly sorptive Sulforhodamine B (Lange et al., 2011).

Literature data reported high efficiencies for both experiments and field studies (Dabrowski et al., 2006; Moore et al., 2001; Budd et al., 2009; Stehle et al.2011; Lizotte et al., 2011; Moore et al., 2009). On the one hand, compounds studied wer often higly sorptive insecticides, on the other hand this trend in literature can be explained with the "filedrawer problem" (Borenstein, 2009). Low reduction values and especially negative values are not published by the researchers and studies with monitoring data may not be accepted for publication (Sutton, 2009). Stehle et al. (2011) performed a comparison of literature data on retention performance of pesticides in VTS with literature data and data from ArtWET prototypes (DP1, DP2 and DP3 were included in the analysis) and reported differences in median reduction values of 25% between literature (median reduction: 81%) and project data (median reduction: 56%).

Although only a few of the commonly applied fungicides were analyzed, exceedance of toxicity thresholds was observed. For the monitoring results the strong influence of plant density in reduction of peak concentrations could be confirmed. From results of the monitoring campaign in Landau size related variables hydraulic retention time, length of flow through the system and hydraulic loading rate showed influence on reduction performance. Combined with results from other project partners the size variable length of flow through the VTS was identified as variable with the strongest influence on assessment of the efficiency of VTS with experiments and field studies. These results were input for the simulation of mitigation measures.

The tools were built with geodata in the best spatial resolution available. With the modified REXTOX indicator realistic risk maps were created for all small rivers within agricultural area of Europe. The DSS for mitigation measures produces intuitive estimation of costs and need of space. Simulated sizes of VTS needed to mitigate the risk are drawn for each watershed. A table with summarised costs and space helps deciding on which mitigation measure or combination is feasible for the region studied. It has to be taken into account that efficiency of buffer strips as mitigation measure is discussed controversially in literature (Bereswill et al., 2011; Reichenberger et al., 2007; Schulz, 2004). For the implementation of this mitigation measure, decision-makers have to consider that the buffer term in the present model is based on preconditions of absence of preferential flow through the strip, absence of gutters and paved paths as drainage systems and uniform distribution of the runoff water into as well as laminar sheet flow within the buffer strip.

A good qualitative and quantitative status of all water bodies is the aim of the Water Framework Directive. In order to achieve this goal, pollution has to be remediated before it reaches surface waters. External costs of the pollution can be equalized with costs for remediation. On a large scale, the tools on the one hand can help to compute external costs of pesticide use with simulation of mitigation costs on three levels, on the other hand feasible measures mitigating or remediating the effects of nonpoint-source pollution can be identified for implementation.

5.2 Outlook

A large step was taken with the present study in understanding the efficiency of VTS in reducing concentrations of pesticides in the water, and the risk of adverse effects. Nevertheless, there are several tasks arising from the results:

Field monitoring revealed, that pesticide pollution is very variable. Concentration levels for single substances showed several orders of magnitude. Regarding the reduction performance of the VTS some of the variance was unexplained. For future studies the focus has to be set on the whole bandwidth of pesticides. Especially pollution with mixtures of many different pesticides with low toxicity and low or medium sorptivity may pose a risk to receiving aquatic systems. The toxicity of the different compounds is likely to behave synergistic and adverse effects may occur. Pesticides with low sorptivity and high solubility in water are likely to be transported with rainfall-related runoff into the waters. These substances and their mixtures have to be identified and the toxicity of the mixtures needs to be quantified.

Further studies with VTS have to be performed to assess the long term operational reliability of the VTS and the impact on the aquatic ecosystem with changing not only the hydraulics, but also the pollution patterns in stream.

The Risk map and the calculation of mitigation measures have to be validated with data from large monitoring campaigns for different regions.

6. References

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Appendix

I. Papers: Experiments

Paper 1: Experimental vegetated ditches

Influence of vegetation density on mitigation of a pesticide mixture in experimental stream mesocosms

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Submitted to Water Science and Technology

Abstract

Vegetated treatment systems have the ability to reduce the risk of adverse effects of nonpoint source pesticide pollution in agricultural surface waters. A large scale (45 m length) vegetated ditch mesocosm was built to study the influence of pesticide properties and plant density on retention performance.

Concentrations of a mixture of six common insecticides and fungicides (dimethoate, indoxacarb, pyrimethanil, tebuconazole, thiacloprid and trifloxystrobin) were reduced to less than 10 % within the 44 m of the ditch mesocosms (reduction between 90.1 and 99.9%). Vegetated ditches performed significantly better than the ditch without vegetation. Median reduction in the non-vegetated ditch was 91.1%; median in the vegetated ditches was 97.3%. Highly sorptive compounds are also significantly better retained. Linear regression analysis identified plant density and K_{OC} as variables with the highest explanatory power for the response variable reduction of peak concentration ($R^2 = 0.67$, $p < 0.001$). Optimized vegetated ditches can be highly effective in reduction of runoff related pesticide peak concentrations.

Keywords: pesticide;mitigation;pollution;mesocosm;elodea;ditch

Introduction

Intensive agriculture may lead to adverse effects when pesticides are transferred to aquatic non-target ecosystems (Schäfer et al., 2011). Nonpoint-sources (runoff, drainage and spray drift) account for a majority of all surface water pollution (Zaring, 1996). During peak application of pesticides in agricultural watersheds, a mixture of numerous substances may be transported to the waterbodies (Battaglin & Goolsby, 1999; Thomas et al., 2001). As a result relevant concentrations of pesticides are found in the aquatic environment (Schulz, 2004; Suess et al., 2006).

The need for mitigation of pesticide pollution in surface waters it has been pointed out in recent regulatory frameworks like the European Water Framework Directive (European-Commission, 2000) or the EU-framework for sustainable use of pesticides (European-Commission, 2009). Mitigation measures were proposed and discussed in several reviews and numerous original research studies (Reichenberger et al., 2007; Schulz, 2004; Stehle et al.,2011; Zhang et al., 2010). Vegetated treatment systems (VTS) in agricultural waters are proposed as an end-of-pipe technology for inevitable pollution (Gregoire et al., 2009; Schulz, 2004). As part of the EU Life project ArtWET (Gregoire et al., 2009), we focused in the present study on the role of vegetation in optimizing the potential of agricultural ditches and detention ponds for pesticide mitigation. Effectiveness of vegetated artificial wetland ecosystems in retaining loads and peak concentrations of pesticides has been studied within ArtWET in various experiments and tracer studies (Elsaesser et al., 2011; Gregoire et al., 2010; Lange et al., 2011; Stehle et al, 2011.; Blankenberg et al., 2007) In the present study, the focus was on the influence of plant density in small experimental ditches following a simulated runoff event with six commonly used insecticides and fungicides. The two main aims of the present study were (1) to quantify the effectiveness of vegetated ditches in mitigating potential risks and (2) to identify variables explaining this effectiveness.

Material and Methods

Experimental ditches

Six concrete channels with a length of 45 m and a width of 0.4 m were built at the campus of the university at Landau (south-western Germany) (Figure 1, Figure 2). The outdoor stream mesocosm system has an average water depth of 0.28 m on a 10 cm sediment layer and is fed by spillways attached to a water reservoir. Sediment is a medium loamy sand with a total organic carbon (TOC) content of 0.78%. Discharge can be controlled by manual water taps. The water in the 230 m^3 reservoir derives from communal water supply and has drinking water quality. Three month prior to the pesticide amendment, the ditches were planted with the submerged macrophyte *Elodea nutallii* (Planch). Plant density was manually adjusted in order to provide a regression design with a ditch without plants and ditches with 50%, 62.5%, 75%, 87.5% and 100% plant density at the date of the pesticide amendment (Aug. 7. 2009). Following the experiment (Sept. 10. 2009) in each ditch plant samples of 0.8 m^2 were removed to quantify plant density.

Two sampling sites were established within each channel, one 2 m downstream of the inlet (s1) and the second 1 m upstream of the outlet (s2) (Figure 1)., thus providing a channel stretch of 42 m between the two sites.

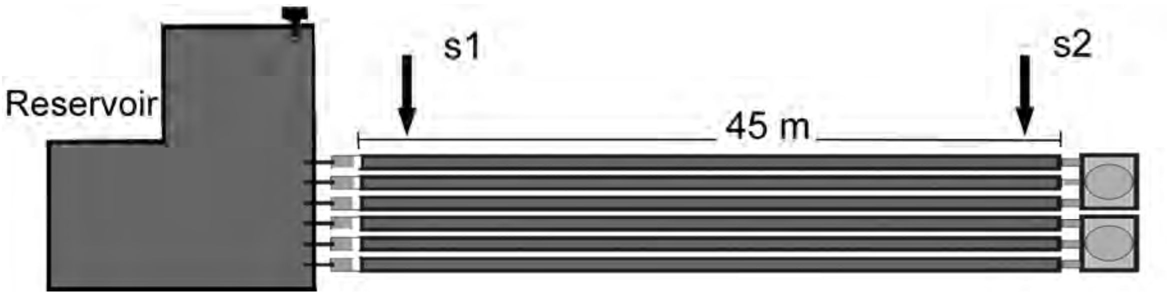

Figure 1: Layout of the experimental ditches

Figure 2: Arial photograph of the ditches with the water reservoir and the inlet in the foreground.

Experimental setup

In order to define travel times and mixing of the water within cells, two sodium chloride tracer experiments were performed three and six days prior to the main experiment. A total of 60 g of sodium chloride were injected at the inlet weir of the ditches. Sampling times at the sampling stations were defined by this tracer experiment in order to sample the same water parcel at the sampling stations based on a discharge of 1 L/s per ditch. The calculated hydraulic loading rates (HLR) and hydraulic retention time (HRT) were fixed by the discharge of 1 L/s to 4.8 m/d and 84 minutes respectively. A mixture of six pesticides commonly used in the EU, three fungicides and three insecticides, was prepared for injection (Table 1). Target concentrations after injection in 96 L of water at the inlet ranged between 5 and 20 µg/L.

Table 1: Properties and injected concentrations of the compounds used for the experiments.

Pesticide	Pesticide type	Substance group	K_{OC}[1] (mL/g)	Solubility[1] (mg/L)	Log P[1]	DT_{50} water[1] (d)	DT_{50} water-sediment[1] (d)	Load injected (µg)	LOQ (ng/L)
Dimethoate	Insecticide	Organophosphate	30	39800	0.704	45.3	15.2	960	0.2
Indoxacarb	Insecticide	Oxadiazine	6450	0.2	4.65	1.4	6	960	0.4
Pyrimethanil	Fungicide	Anilinopyrimidine	301	121	2.84	16.5	80	1920	0.1
Tebuconazole	Fungicide	Triazole	769	36	3.7	42.6	365	960	0.30
Thiacloprid	Insecticide	Neonicotinoid	615	184	1.26	8.5	28	1920	0.4
Trifloxystrobin	Fungicide	Strobilurin	2377	0.61	4.5	1.1	2.4	480	0.21

Plant densities were randomly assigned to the six ditches and manually adjusted. The ditch with highest plant density was set as 100% and density of the five other ditches was calculated by means of the dry weight of plants that were removed from 0.8 m² of each ditch (Table 2). Results of the ditch with manually adjusted plant density of 62.5 % were not taken into account for this experiment due to a technical failure with water supply prior to the experiment.

Sampling and Analysis

Water samples were taken at the time with expected peak concentration at the respective site in the center of the ditch. All water samples were taken in 1 L brown glass bottles and stored in the fridge at 4° C until extraction. Pesticide extraction was with 500 mL of the samples using method described in Elsaesser et al. (2011). SPE cartridges (SPE Column: Chromabond C18, 500 mg, 6 mL; conditioning solvent: MeOH) were dried with nitrogen and stored in a freezer at -18°C until elution. SPE cartridges were eluted with MeOH. Analysis was performed by LC MS/MS. The HPLC system used was a Model 1100 liquid chromatograph (Hewlett Packard, PaloAlto, CA, USA). Chromolith Performance columns (Merck RP-18e 100 x 4.6 mm, 5 µm) were used at a flow rate of 0.6 mL/min. Aliquots of 20 µL of solutions were injected by the HP 1100 autosampler. Electrospray data were acquired by Multiple Reaction Monitoring using an Applied Biosystems 4000 Q Trap Linear Ion Trap Quadrupole mass spectrometer (Sciex, Concord, ON, Canada). Limits of quantification (LOQ) are listed in Table 1.

Data Analysis

Efficacy of the experimental ditches in pesticide peak reduction was calculated for each substance and sampling station as follows:

[1]

$$RP\ (\%) = \left[\frac{(c_{in} - c_{Sx})}{c_{in}} \right] \times 100$$

where *RP* is the reduction of concentration peaks, c_{in} is the target concentration of the substance injected at the inlet and c_{Sx} is the corresponding pesticide concentration detected at the sampling stations s1 or s2.

Statistical analysis and graphics were computed using the free software package R x64 V. 2.13 (www.r-project.org). Difference between paired reduction values for plant densities and substances were statistically tested with Wilcoxon signed rank test, since reduction values were not normally distributed. Normal distribution was tested using the Kolmogoroff-Smirnoff test.

Linear models were used to explain the influence of pesticide properties (KOC, LogP and solubility in water) and plant density on peak reduction within the first two metres and the whole length of the ditches. Due to short hydraulic retention times of less than 0.05 days DT50 values were not considered for statistical analysis. Possible interactions of pesticide properties with plant density were tested. Stepwise regression with backward selection based on "Akaike's An Information Criterion" (Akaike, 1974) was used to select the best fit model. Intercorrelated variables were identified and the variable with lower plausibility to explain the variation in the response variable based on expert opinion was removed.

The assumptions of the regression models regarding linearity were verified with residual plots and normal distribution of residuals by visual inspection of scatterplots and P-P plots. Influence of single observations was excluded by residual-leverage plots and Cook's distance plots. Additionally, tests for heteroscedasticity, linearity and autocorrelation (r-package: lmtest; gqtest and package: car; reset, bgtest) were performed. Hierarchical partitioning (r-package: gtools and hier.part) was applied to the results to determine the percentage of relative importance of explanatory variables (Chevan & Sutherland, 1991).

All distributions of either concentrations or toxic units were visualized using beanplots (r-package: beanplot). This alternative to box- or violinplots has the advantage to show all possible information on density, anomality and range of the distributions (Kampstra, 2008).

Results and Discussion

Although *Elodea* is present in the many small rivers and ditches all over the world, densities used in this experiment are the upper end of those common in agricultural drainage ditches due to regular cleaning and management of the systems. Dry masses of *Elodea* spec. in densely vegetated areas of North American lakes range between 450 and 600 g m^{-3} (Duarte & Kalff, 1990; Nichols & Shaw, 1986).

Table 2: Plant densities of the experimental ditches

Ditch Nr.	Dry mass (g m^{-3})	Plant density in %	
		Manually adjusted	Calculated[1]
3	960	100	100
4	821	87.5	85.6
2	687	75	71.6
6[2]	670	62.5	69.8
5	469	50	48.8
1	0	0	0

1: calculated with dry mass of ditch 3 = 100%. 2: Ditch 6 was removed from analysis, due to technical problems with water supply.

According to the results of the salt tracer experiments, the water was completely exchanged within 71 to 85 minutes (peak after 42 to 56 min) in the ditches. Sampling times were fixed in order to sample the peak concentrations (Fig 2).

The Pesticide mixture (Table 1) was injected into 96 L of water at the inlet of the ditch. Based on the injected loads a total of 16.7 % of the concentrations injected at the inlet weir in the non-vegetated ditch and 63.8 % in the vegetated ditch were diluted and retained rapidly in the first two metres. After 44 metres at sampling station s2 the concentrations decreased in all ditches to less than 10 % of the concentrations injected (Figure 3, Figure 4). Median reduction in the non-vegetated ditch was 91.1%. Median reduction for vegetated ditches was 97.3%. Peak concentrations at the first sampling station between 0.828 µg/L and 18.46 µg/L is comparable to peak concentration levels of pesticide detected in agricultural surface waters following runoff or spray drift events (Figure 3)(Berenzen et al., 2005a; Berenzen et al., 2005b; Gregoire et al., 2010; Rabiet et al., 2010).

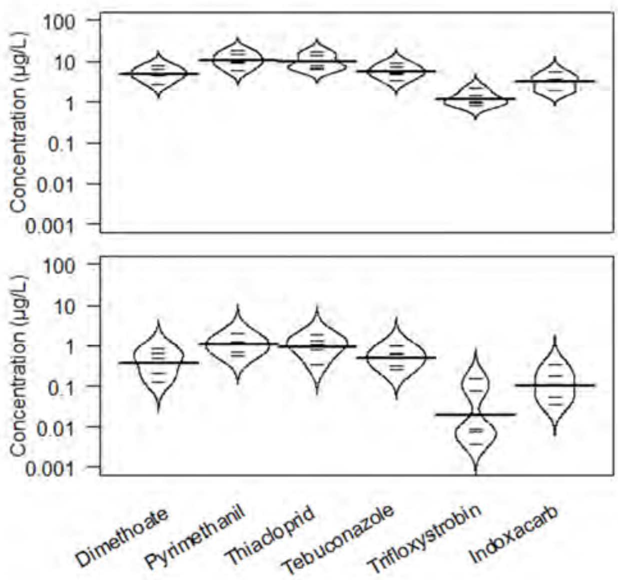

Figure 3: Concentrations at sampling station 1 (upper graph) and after 44 m at sampling station 2 (lower graph

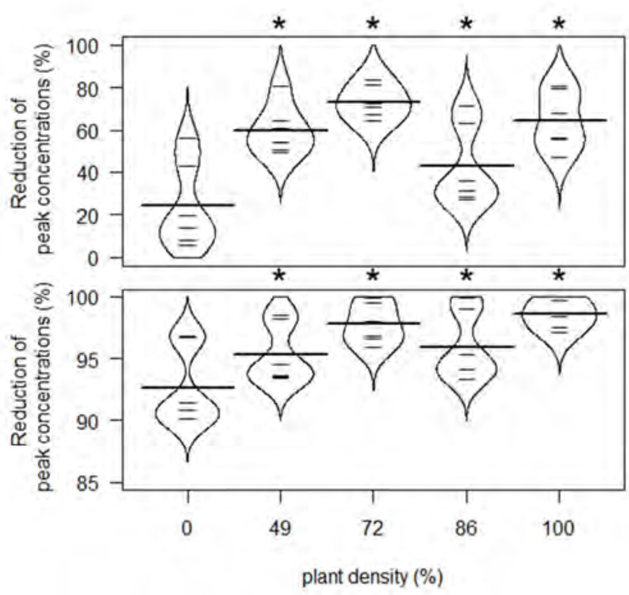

Figure 4: Reduction of peak concentrations in the first two metres (upper graph) and for the whole length of 44 m (lower graph) at different plant densities. All experimental ditches with plants reduced peak concentrations significantly better than the ditch without plants. Significance testing was performed with paired Wilcoxon signed rank test (p=0.016 for all plant densities at both sampling sites). Short horizontal lines indicate values for each of the six single substances, long horizontal lines are the median values and the outer shape represents the density of values.

Former studies on pesticide retention within in larger vegetated treatment systems showed slightly lower reduction of peak concentrations. A study on the insecticide azinphos-methyl in a vegetated stream of 180 m (water volume: 61-200 m³) observed 61–90% peak retention (Dabrowski et al., 2006), however the hydraulic retention time was also lower (33-44 min). In a study on atrazine and lambda-cyhalothrin in 40 m (water volume: 97 m³) of a ditch with a discharge of 1 L/s, reduction of peaks was 92% and 76%, respectively (Moore et al., 2001). An experiment in two vegetated and one wetland cell without vegetation of 30 m³ each showed reduction of concentrations for 6 pesticides of 89% and 91% in the vegetated and 73% in the cell without vegetation at a discharge of 0.6 L/s (Elsaesser et al., 2011). Nevertheless all of those values are not directly comparable due to fundamental differences in system layout and plant species. Plant densities were far lower in those studies than in the least densely vegetated ditch of this experiment and are thus rather comparable to the non-vegetated ditch. Values were < 75 g m^{-3} (Moore et al., 2001), a central unvegetated channel (Dabrowski et al., 2006) and plant coverage at the water surface of 60% (Elsaesser et al., 2011).

Multiple regression analysis was performed with reduction of peak concentrations between inlet and s1 and between inlet and s2 separately in order to identify efficiency of plant density and influence of pesticide properties. Modell A (inlet to s1) and B (inlet to s2) contained the variables plant density and K_{OC} and explained 41 % (Model A) and 65 % (Model B) of total variability. Log P, solubility in water and possible interactions between the pesticide properties and plant density showed no significant correlation with reduction (Table 3).

Table 3: Multiple linear regression analysis results including most important factors predicting pesticide retention performance (n=30) in the first two metres of the experimental ditches (Model A) and over the full length of 44 m (Model B).

Model A: s1	Estimate	Std. Error	t value	Significance		Relative importance (%)
(Intercept)	25.0	6.9	3.6	<0.01	**	
Plant coverage (%)	0.3	0.1	3.7	<0.001	***	63
K_{OC} (ml/g)	0.004	0.001	2.8	<0.01	**	37
Model B: s2						
(Intercept)	91.5	0.7	129.6	<0.001	***	
Plant coverage (%)	0.1	0.01	5.8	<0.001	***	59
K_{OC} (ml/g)	0.001	0.0001	4.8	<0.001	***	41

Model A summary: $R^2 = 0.45$; adjusted R^2: 0.41; p<0.001. Excluded factors were: Log P, solubility in water (mg/L), water-sediment DT_{50} (d), water DT_{50} (d), photolytic DT50 (d). Model B summary: $R^2 = 0.67$; adjusted R^2: 0.65; p<0.001. Excluded factors were: Log P, solubility in water (mg L-1), water-sediment DT50 (d), water DT_{50} (d), photolytic DT_{50} (d).

Regression model assumptions of linearity, homoscedasticity and absence of autocorrelation were met. Hierarchical partitioning showed that plant density and KOC are positively correlated with reduction of concentrations. Results of model A might be influenced by incomplete dilution of the injected pesticides. It has been documented that plant density is the most important variable influencing pesticide peak reduction within vegetated treatment systems (Budd et al., 2009; Cooper et al., 2004; Gill et al., 2008; Moore et al., 2002; Schulz et al., 2003). The increasing reduction of peak concentrations with increasing plant density was quantified in several studies. For the insecticides permethrin and diazinon, reduction increased between non-vegetated and vegetated wetlands between 29 and 62 % respectively (Lizotte et al., 2011). An experiment at vegetated and non-vegetated wetland cells in Norway showed a significant increase in efficiency of 16-18 % for six common pesticides (Elsaesser et al., 2011). On the one hand the increasing reduction of peak concentrations in vegetated systems can be explained with sorption to plant material, on the other hand, retention can be indirectly influenced by the plants through altered water chemistry (pH, oxygen), flow patterns, flow velocity and residence time.

Influence of K_{OC} as the other important explanatory variable regarding the reduction of peak concentrations can be explained by the fact that hydrophobic pesticides are more effectively retained in wetlands due to adsorption of molecules to plants and sediments (Imfeld et al., 2009; Moore et al., 2001; Stehle et al.,2011). A study with Elodea densa and the sorptive insecticide chlorpyrifos showed, that Elodea has the ability to sorp large amounts of chlorpyrifos from highly contaminated water (Karen et al., 1998; Brock et al., 1992). Other variables and all possibly relevant interactions of centered variables showed no significant correlation with reduction.

In this experiment other variables such as discharge, size, pH and temperature were excluded. Significance of differences in plant density and KOC were tested with nonparametric statistics. Although reduction of peak concentration was high in the ditch without vegetation, all vegetated ditches reduced peak concentrations significantly better

(Figure 4). This increase of reduction could be on the one hand a further dilution of the contaminated water due to hydraulic effects of the plants, on the other hand pesticide compounds could be adsorbed to plant surface. The retention of substances through sorption was assessed by focusing on the K_{OC}. K_{OC} values were classified to three classes of two substances each: mobile compounds (<500 mL/g), medium sorptive compounds (500-1000 mL/g) and compounds with strong adsorption to organic carbon (>1000 mL/g) (PPDB, 2011). Concentrations of highly sorptive substances are significantly better reduced within the ditches (Figure 5).

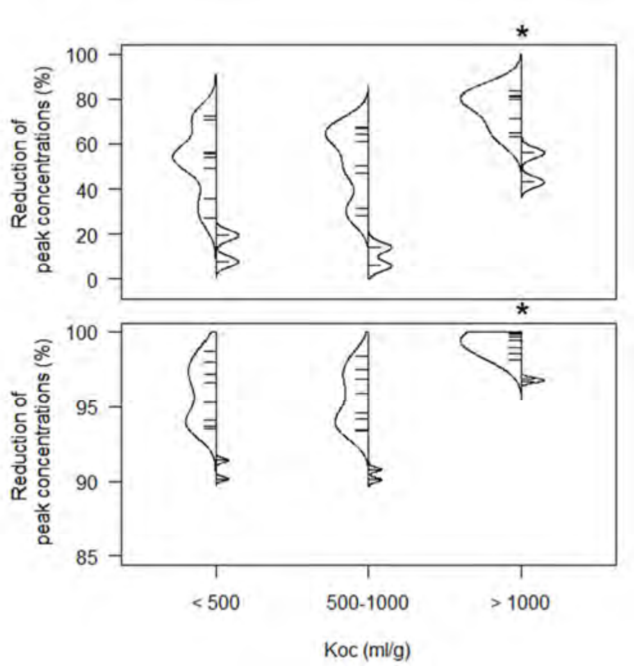

Figure 5: Reduction of peak concentrations in the first two metres (upper graph) and for the whole length of 45 m with classified K_{OC} (n=2 compounds in each class) levels. Horizontal lines left of the vertical center line represent the values for vegetated ditches and horizontal lines at the right side of the centerline represent the two values for the non-vegetated ditch. Highly sorptive compounds are reduced significantly better. Significance testing was performed with paired Wilcoxon signed rank test (p=0.016 for highly sorptive group at both sampling sites).

Conclusions

Overall, the reduction of peak concentrations was remarkably high within the small mesocosms. *Elodea nutaIlii* as a submerged plant with very high leaf surface below the water surface improves the reduction. In further experiments, the influence of different plants, discharge, hydraulic retention times, level of inlet concentrations and different physico-chemical water properties have to be studied in order to quantify the influence of those properties. In comparison with field studies, these optimized experimental systems showed a higher performance in reduction of peak concentrations. It can be concluded, that optimized, densely vegetated systems are a feasible and effective end of pipe technology to reduce the risk of adverse effects caused by inevitable non-point source pesticide pollution upstream of ecologically sensitive receiving water courses.

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Paper 2: Experiments at the Lier wetlands

Assessing the influence of vegetation on reduction of pesticide concentration in experimental surface flow constructed wetlands: Application of the toxic units approach

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Abstract

In summer 2008, an experiment on retention of a mixture of five pesticides in the Lier experimental wetland site (Norway) was performed. Two vegetated cells with hydraulic retention times (HRT) of 280 min and 330 min and one cell without vegetation (HRT of 132min) of 120 m² surface area each were investigated regarding their ability to reduce peak concentrations, pesticide masses and predicted adverse effects. Discrete water, plant and sediment samples were taken and analysed. The inlet peak concentrations of the pesticides dimethoate, dicamba, trifloxystrobin and tebuconazole ranged from 18 ng/L up to 5904 ng/L. The mean reduction of peak concentration was 72% in the non-vegetated cell and up to 91% the vegetated cells. Less than 5% of the masses were retained within the wetlands. Uptake and sorption by plants was low (up to 4%), however, higher for the vegetated cell dominated by *Phalaris arundinacea* L. than for the one with *Typha latifolia* L. as dominant plant. The toxic units (TU) approach was used to describe the potential reduction of toxicity within the wetland cells. Calculated toxicity of the substances decreased by 79% in the non-vegetated cell and by 95% in the two vegetated cells. Despite the low mass retention, the vegetated wetland system reduced the toxic effects, expressed as toxic units from values of 0.24 to 0.01, i.e. a concentration two orders of magnitude below the acute toxicity threshold, within a distance of 40 m while the non-vegetated would need to be about 64 m long for the same efficiency.

1. Introduction

Pesticides are widely used in agriculture, but adverse effects may be observed when the substances are transferred to natural ecosystems (Schulz, 2004). Nonpoint-source pollution through runoff, drainage and spray drift accounts for a majority of all surface water pollution (Zaring, 1996). Constructed wetlands have the ability to mitigate pesticide pollution deriving from various agricultural nonpoint sources (Baker, 1992; Schulz and Liess, 2001; Schulz and Peall, 2001; Schulz et al., 2001a). Dense vegetation increases the effectiveness in remediating pesticide pollution (Susarla et al. 2002; Braskerud and Haarstad, 2003; Imfeld et al., 2009; Moore et al., 2002, 2006, 2009b; Rogers and Stringfellow, 2009). Retention of pesticide loads is driven by physico-chemical characteristics of the substances, inserted masses and the hydraulic retention time as well as physical properties of the wetland filter (Baker, 1992; Gregoire et al., 2009; Schulz, 2004). Nonetheless, our knowledge about the processes which lead to decreasing concentrations in those systems is limited (Gregoire et al., 2009; Schulz, 2004).

During peak application of pesticides in a watershed, a mixture of numerous substances may be transported to the waterbodies (Battaglin and Goolsby, 1999; Schulz, 2004; Thomas et al., 2001). Adverse effects are driven by exposure time and concentration levels of the substances. High peak concentrations in water and suspended solids may occur during exposure events (Schulz, 2004). Even if there is low risk of adverse effects with low concentrations of the single substances, the mixture may lead to severe impacts in the receiving waterbody. Junghans et al. (2006) proposed to sum up the toxicity of the single substances as toxic units to describe the effects of pesticide mixtures within the receiving ecosystem.

The toxic units (TU) approach is a feasible method to predict adverse effects of complex chemical mixtures on the structure and functioning of aquatic ecosystems (Junghans et al., 2006; Peterson, 1994; Sprague, 1970). However, this approach so far was never used to assess the potential positive effects artificial wetlands may have on aquatic surface water quality.

As an integrated part of the EU Life project ArtWET (Gregoire et al., 2009) we focus on the role of vegetation in optimising the potential of agricultural ditches and detention ponds for pesticide mitigation. In the present wetland experiment, the focus was on a surface flow system with low discharge and high plant densities, but also very short hydraulic retention times of 132–280 min. The fate of a pesticide mixture in water and suspended sediment phase was followed during the passage to assess differences between reduction of pesticide peak concentrations and adverse effects through sorption and hydraulic processes.

2. Materials and methods

2.1. Study area and design of the wetland cells

The Lier experimental wetland site is located 40km south of Oslo (Blankenberg et al., 2006). Eight parallel wetland cells are approximately 40m in length, 3 m in width and depth varies from 0.05 to 0.5 m. The 1200 m^2 of the wetland area (cells and sedimentation pond), which is located directly upsteam of the inlet weirs (Fig. 1), cover 0.15% of the watershed. Total area of the watershed is 0.8 km^2 of which 0.15 km^2 are used for christmas tree breeding, 0.2 km^2 for growing vegetables, 0.35 km^2 for cereals and about 0.1 km^2 is urban. The wetland system is gravity fed through pipelines with stream and drainage water (Braskerud et al., 2005; Blankenberg et al., 2006). Water at the outlet is collected in a pond, which discharges into a ditch. Three of the eight surface flow wetland cells were used for the present experiment. Discharge at the inlet and outlet of the cells and the bypass were controlled with vnotches. Three sampling stations were located 2 m (SSt1) and 20 m downstream from the inlet (SSt2) and directly at the outlet (SSt3) (Fig. 1).

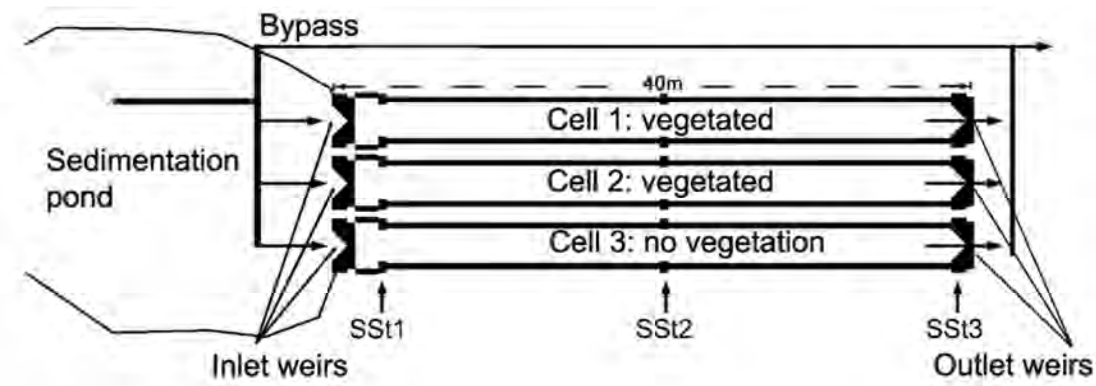

Fig. 1. Layout of the Lier experimental wetland cells (40m length) with the three sampling stations SSt1, SSt2 and SSt3.

Two of the cells were densely vegetated with submerged and emergent local aquatic plants. Optical top view coverage of vegetation was 90% while the measured coverage at the water surface was 60%. Species with the highest coverage were the poaceae *Phalaris arundinacea* L. (cell 1: 72%, cell 2: 27%), *Typha latifolia* L. (cell 1: 9%, cell 2: 54%) and *Phragmites australis* (Cav.) Trin. ex Steud. (cell 1: 4.5%, cell 2: 4.5%). In the vegetated cells there were also *Lemna* spec., *Solanum dulcamara* L., *Glyceria fluitans* L., *Sparganium erectum* L. emend Rchb. and *Ranunculus repens* L. In cell 3 the plants and roots were completely removed. Sediment is a sandy silt covered by a sediment layer of fine silt.

Thickness of this layer, especially in the downstream area of the sedimentation pond, is partially greater than 20 cm. Due to the retaining influence of vegetation, the mean water depth of the two vegetated cells (cell 1: 9.7 cm, cell 2: 13 cm) was larger than in cell 3 (6.5 cm).

2.2. Monitoring

Discharge, pH, temperature, and specific conductivity were monitored twice a day from 22 July until 23 September and air temperature and precipitation were monitored constantly with a weather station. In order to define travel times and mixing of the water within cells, a sodium chloride tracer experiment was performed two days prior to the main experiment. 100 g of sodium chloride were injected into the inlet of cell 1 and cell 2 and 75 g into cell 3. Sampling times at each of the nine sampling stations were defined by this tracer experiment in order to sample the same water parcel at all three sampling stations based on a discharge of 0.6 L/s per cell. The hydraulic loading rates (HLR) at the day of the experiment, the hydraulic retention time (HRT), pH, conductivity, and water temperature are listed in Table 1.

Table 1
Physical and chemical water parameters and hydraulic characteristics of the three single wetland cells and all three cells together. pH, conductivity and temperature of the water were measured at the inlet of the cells.

	Discharge (L/s)	HLR (m^3/day)	HRT (min)	pH	Conductivity (μS/cm)	Temperature (°C)	Dominant plant species
Wetland total	1.8	0.582	241	7.7	446	17.6	
Cell 1	0.6	0.505	280	7.7	446	17.6	*Phalaris arundinacea* L.
Cell 2	0.6	0.568	330	7.7	446	17.6	*Typha latifolia* L.
Cell 3	0.6	0.710	132	7.7	446	17.6	No vegetation

2.3. Experimental setup

A mixture of five commonly used pesticides in the EU was prepared for injection. Advised nominal concentrations of the substances directly at the inlet weir were chosen to be below the lowest acute aquatic effect concentration (EC50: half maximal effective concentration). Target concentrations at the inlet ranged between 5 and 50 μg/L. The target concentration in the suspended solids was equivalent to an additional μg/L in the suspension (Table 2). Following rapid dilution in the inlet basin of each cell, concentrations of each single substances were expected to be at least a factor of two below the EC50.

Table 2
Properties of the pesticides used in the experiment and a metabolite of trifloxystrobin. K_{OC}: organic-carbon sorption constant, DT_{50}: half-life in water phase, EC_{50}: half maximal effective concentration.

Type	Substance	$K_{OC}^{(1)}$ (mL/g)	$DT_{50}^{(1)}$ water (days)	Lowest EC_{50}[a] (μg/L)	Target concentration	
					Water (μg/L)	Suspended solids (μg/L)
Herbicide	Dicamba	12	40	1800	50	1
Insecticide	Dimethoate	30	45	2000	10	1
Fungicide	Trifloxystrobin	2377	1.1	5.3	5	1
Herbicide	Metamitron	81	11	400	10	1
Fungicide	Tebuconazole	769	43	100	10	1
Metabolite	CGA321113	121	245	49200	-	-

[a] Data from the Footprint Pesticide Properties database (PPDB, 2009).

2.3.1. Preparation of spiked suspended particles

For the experiment, a mixture of contaminated water and suspended solids was prepared to simulate contaminant entry through runoff or drainage. Suspended solids were prepared based on the methods described in Schulz and Liess (2001). 2 kg of wet sediment without roots and algae were removed from the sedimentation pond upstream of the wetland cells and dried to constant weight in an oven to calculate a factor between dry and wet mass. Target mass of TSS (total suspended solids) was 1 µg/L (dry weight). Target concentration of the pesticides in TSS was 1 µg/g dry weight (equivalent to 1 g/L in the target suspension). Using the factor of weight loss during drying, three portions of wet sediment (65.7 g wet sediment for cell 1 and cell 2 and 49.28 g wet sediment for cell 3) were used to prepare the spiked suspended particles. One sixth of the wet sediment for each cell was dried and spiked with the pesticide mixture. Afterwards, the three contaminated particle suspensions were again mixed with the rest of the wet sediment and 1 L of water from the inlet of the wetlands. The suspended mixture was stirred for 24 h in glass jars wrapped in aluminum foil to avoid photodegradation.

2.3.2. Preparation of spiked water

A dilution of the pesticide mixture in 5 L of water from the inlet of the wetland was prepared for injection. The target concentration in µg/L was multiplied by 40 for cell 1 and 2 and by 30 for cell 3 to take into account the volume difference, in liters, in the inlet basin. The 5 L of water for each cell were mixed with the suspended particles 30 s before the injection at the inlet weir of the cells.

2.3.3. Sampling procedure and analysis

On the 22nd of September 2008, water and suspended particles spiked with the mixture of five pesticides were added to the falling water at the inlet weirs directly into the inlet basin of each of the three cells. Discrete samples of plants (n = 3), sediments (n=3) and water (n = 5) were taken at each sampling station during the following 17 h. Sampling times for water were fixed to represent the whole peak flow at each sampling station, plant and sediment samples were taken at rising concentration, during peak concentration and after the passage of the pesticide mixture. Plant samples from 225 cm^2 densely vegetated area were cut with acetone rinsed scissors directly at the ground and below the water surface. Sediment samples were taken with molds of 225 cm^2 by hand from the top 5 mm of non vegetated ground sediment. Plant and sediment samples were wrapped in aluminum foil and stored in the freezer at –18 °C until extraction. Water samples were taken in 1 L brown glass bottles and stored in the fridge at 4 °C until extraction. 500 mL of each water sample were solid phase extracted (SPE Column: Chromabond C18, 500 mg, 6 mL; conditioning solvent MeOH). Before passing the C18 cartridges, water was pumped through filter floss to remove large particles and prevent sorbent clogging.

Sediment samples were treated as described in Schulz et al. (2001a). Samples were centrifuged and the supernatant water was discarded. After adding 30 mL MeOH, samples were vortexed until complete resuspension. Following centrifugation, the supernatant MeOH was collected in a glass jar. Another 30 mL of MeOH was added, and the sample was vortexed, sonicated for 30 min and centrifuged. MeOH was mixed with the first 30 mL and diluted in 150 mL of deionised water. 70 mL of the 210 mL were solid phase extracted using Chromabond C18 columns.

Plants were pestled. 30 mL of MeOH were added and the sample was sonicated for 10 min. After centrifugation and collection of the supernatant MeOH, the procedure was repeated. MeOH was diluted in 150 mL of pure water and 105 mL were solid phase extracted using Chromabond C18 columns. C18 columns were eluted with 5mL of MeOH: NH3 (95:5) and divided in two samples of 2.5 mL.

Samples were analysed by two methods. For analysing dicamba and trifloxystrobin, eluate derivatisation was necessary (Bioforsk method M15). All other substances were analysed without derivatisation (Bioforsk method M60). Ditalimfos, isofenphos, quintozene, triphenyl phosphate and deltamethrin were used for the M60 method and fenoprop was used for the M15 method as internal standards to calculate recovery.

Derivation for M15: Eluate was spiked with 200 µL internal standard for the M15 method (0.2 µg fenoprop on 1 mL phosphate buffer). After evaporisation under a stream of nitrogen, the sample was diluted in 4 mL of phosphate buffer. Following the addition of 150 µL THA (0.015 M tetrahexylammoniumhydrogensulfate in phosphate buffer and 2.0 mL PFB (0.10% pentafluorobenzylbromide in dichlormethane), the sample was mixed for 20 min. 1.4 mL of the solution were dried under a stream of nitrogen and rediluted in 1.4 mL isooctane before GC/MS analysis.

GC/MS method for M15: MeOH solutions of water samples were analysed using Column Chrompack CP-SIL 5CB MS2, 50m×0.25mm i.d., 0.40 m film. Detector temperature was 280° C with helium as carrier gas. Flow was constant at approximately 30 cm/s. 5 µL were injected splitless with a pulsed pressure program. Temperature programmes: 80° C/1 min→20° C/min→160° C/0 min→5° C/min→280° C/5 min [Dwell = 150 ms for both substances, EMV= ca. 2300–2800 V (EM Offset = +800 V), Tune file: atunemax.u].

Concentration for M60: Eluate was spiked with internal standard and decane to avoid volatilisation before drying under a stream of nitrogen. After drying, the sample was rediluted in 500 µg toluole: isoctane (10:19) and analysed by GC/MS.

GC/MS method for M60: MeOH solutions of water samples were analysed using Column: HP-5MS, 30 µm 0.25 mm i.d., 0.25 mg and as precolumn fused silica 2–10 µm, 0.25 mm i.d.

Detector temperature was 260° C with helium as carrier gas. Flow was constant with approx. 26 cm/s. 15µL were injected (PTV injector). Temperature programmes: 80° C/1 min→20° C/min→250° C/5 min (MS-detektor i SIM-mode: dicamba: 400, 402 fenoprop: 448, 450, Dwell = 150ms for both substances, EMV= ca. 2300–2800 V, EM Offset = +800 V, Tune file: atunemax.u).

Calibration samples and blanks were added for every run of 15 samples. Limits of quantification (LOQ) were 25 ng/L for dicamba and dimethoate, 50 ng/L for tebuconazole and 150 ng/L for metamitron in the water phase.

LOQs for sediment and plant samples were dependent on the weight of the samples. LOQ for sediment samples ranged from 0.097 ng/kg dry weight (minimum for dicamba and dimethoate) to 1.32 ng/kg dry weight (maximum for metamitron). LOQ of plant samples ranged from 0.014 ng/kg dry weight (minimum for dicamba and dimethoate) to 0.41 ng/kg dry weight (maximum for metamitron).

2.4. Reduction of peak concentration, calculation of toxic units and mass partition

Absolute concentrations in water, plants and sediment were calculated from analytical results. Reduction factors in the water phase were calculated for the pairs of SSt1/SSt3. Reduction values in % were calculated using formula 1.

$$RED\% = \frac{100 \cdot (C_{SSt1} - C_{SSt3})}{C_{SSt1}} \tag{1}$$

RED: % reduction of peak concentration; C_{SSt1}: peak concentration at SSt1; C_{SSt3}: peak concentration at SSt3.

Acute toxicity data of the substances for fish, algae and aquatic invertebrates were used to analyse the reduction of potential toxicity of the mixture based on toxic units (TUs). TUs were calculated for each peak concentration of the substances with the specific LC_{50} or EC_{50}. Values for acute toxicity to *Oncorhyncus mykiss* (fish LC_{50} 96 h), *Daphnia magna* (aquatic invertebrate EC_{50} 48 h), *Skeletonema costatum, Raphidocelis subspicata, Pseudokirchneriella subspicata* and *Desmodesmus subspicatus* (algae EC_{50} growth 72 h) were taken from the Footprint Pesticide Properties database (PPDB, 2009). TUs were calculated for each water sample using formula 2 (Junghans et al., 2006; Peterson, 1994).

(2)

$$TU = \sum_{i}^{n} \frac{C_i}{C_{EC50_i}}$$

TU: toxic unit; C: concentration of substance; C_{EC50} : concentration of substance at the EC_{50} or LC_{50} level.

In order to calculate the distance from the inlet in which the TU decreases to an appreciable level, a non-linear regression with the highest TU of the most sensitive species at the three sampling stations and the inlet was performed. Functions of the non-linear regression were solved with TU = 0.01 (y) to calculate the wetland length in meter (x) required to reduce the TU to the 0.01 level. Differences of the peak concentration reduction were analysed and plotted using Origin software. Significance testing was done with the non-parametric Paired sample Wilcoxon Signed Rank test for the combinations cell 1–cell 2, cell 1–cell 3 and cell 2–cell 3. The highest concentration in plant and sediment samples at each sampling station was used as peak concentration for the calculation of the masses sorbed to sediment and plants between the sampling stations. The total mass of the pesticides in plants was estimated using the wetland surface area of each cell and defined sampling area of the single plant samples using formula 3.

(3)

$$M_{pt} = \frac{A \times M_{pm} \times C_p \times D_s}{A_p \times D_m}$$

M_{pt}: total mass of pesticide in plants at sampling site in ng; A: area of sampling site in m^2; M_{pm}: mean mass of plant samples in g; C_p: pesticide concentration in plant sample in ng/g; D_s: depth at sampling area (center of the cell) in m; A_p: area of plant sample in m^2; D_m: mean depth of cell in m.

The total mass of the pesticides in sediment was estimated using the wetland surface area of each cell and defined sampling areas of the single plant and top sediment samples using formula 4. Masses of pesticides in water were calculated by subtracting the masses in plants and sediment from inserted loads. Masses in the three compartments were compaired for the surface area of the first 2 m, the first 20 m and the whole length of the wetland cells.

(4)

$$M_{st} = \frac{A \times M_{sm} \times C_s}{A_s}$$

M_{st}: total mass of pesticide in sediment at sampling site in ng; A: area of sampling site in m²; M_{sm}: mean mass of sediment samples in g; C_s: pesticide concentration in sediment sample in ng/g; As: area of sediment sample in m².

3. Results

3.1. Concentrations

The zero reference water samples, which were taken at the inlets prior to the experiments, showed concentrations below the LOQ of (E,E)-trifloxystrobin acid CGA 321113, a metabolite of trifloxystrobin. All other substances were below limit of detection in the reference samples. The zero reference samples in sediment and plants showed concentrations up to 1.4 ng/kg of CGA 321113, which was in the range of the measured concentrations during the experiment. For this reason the concentrations ofCGA321113 were not considered in the mass balance calculation.

Experimental samples of the five main substances showed maximum concentrations between 117 ng/L and 5.9 µg/L in the water phase. In plants and sediment, peak concentrations ranged from 0 ng/g to 6.6 ng/g. Dicamba, the substance with the lowest KOC was not detected in any plant or sediment sample. Only 13 of the 54 concentrations in water samples (cell 1: 7, cell 2: 1, cell 3: 5) of metamitron were above the LOQ. For this reason, metamitron was not considered in analysis of peak retention and reduction of toxicity. Inserted masses, maximum concentrations and outlet peak concentrations are shown in Table 3. Differences of the maximum concentrations at SSt1 among the cells were caused by incomplete dilution due to laminar flow and absence of plants in the first 2m of the wetland cells.

3.2. Mass partition

Estimation of mean mass partitioning between water and the sum of plants plus sediment was below 5% (Fig. 2). No difference in sorption and sedimentation to bulk sediment was observed among the three cells. Nevertheless a trend of higher sorption to plants was observed in cell 1. Highest mass of a single substance sorbed to plants was 95.775 µg of tebuconazole in cell 1. Highest mass of a single substance sorbed to sediments was 21 µg of dimethoate in cell 3. Trifloxystrobin, the substance with the highest KOC summed up to 26 µg in plants of cell 1 and 42 µg in cell 2. Sample masses of plants showed no significant differences between the cell 1 and cell 2. Standard deviation of the masses of sediment plus plant samples are below 1.5%.

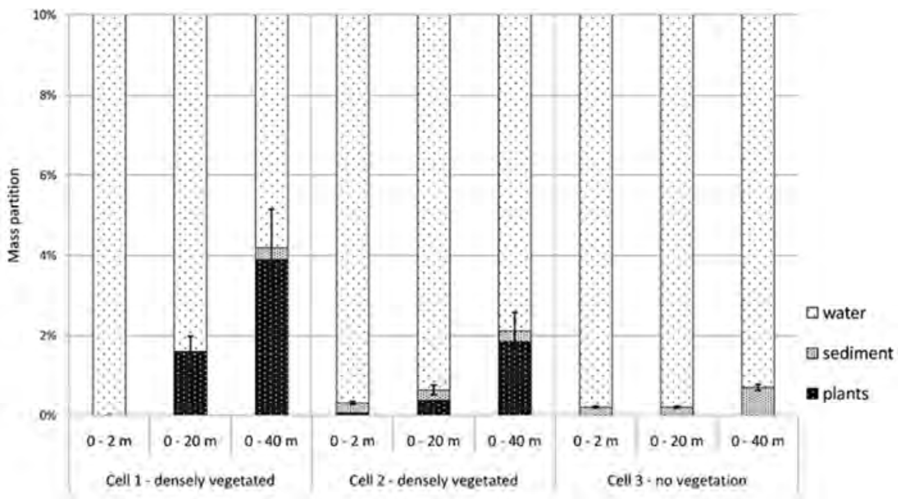

Fig. 2. Mass partitioning of the inserted pesticides, based on inserted masses and maximal concentrations in bulk sediment and plants. Error bars show SD for plant plus SD for sediments. For clarity, the y axis is only shown using the first 10%. The remaining 90% belong to the water phase.

Table 3
Injected masses and peak concentrations of the five substances in the waterphase.

	Dicamba	Dimethoate	Trifloxystrobin	Tebuconazole	Metamitron	CGA321113
Injected mass	µg	µg	µg	µg	µg	
Cell 1	2040	440	240	440	440	–
Cell 2	2040	440	240	440	440	–
Cell 3	1530	330	180	330	330	–
Peak concentration						
SSt1	ng/L	ng/L	ng/L	ng/L	ng/L	
Cell 1	4039	158	821	1929	1921	6410
Cell 2	5904	18	892	1494	1335	6321
Cell 3	4190	244	1062	2038	1851	7179
Peak concentration						
SSt3	ng/L	ng/L	ng/L	ng/L	ng/L	
Cell 1	1360	<LOQ	36	<LOQ	<LOQ	423
Cell 2	596	<LOQ	38	354	116	499
Cell 3	2237	61	246	709	485	1371

3.3. Reduction of peak concentration

Reduction of pesticide peak concentrations in water ranged from 46% to 100%. Mean reduction of peak water concentrations was 89% in cell 1, 91% in cell 2 and 73% for cell 3 (no vegetation). Both vegetated cells showed significantly larger reduction of peak concentrations than the cell without vegetation (Fig. 3).

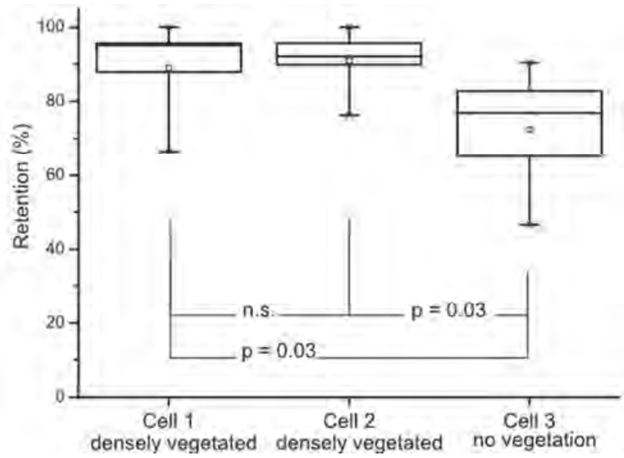

Fig. 3. Reduction of the pesticide peak concentration in water between SSt1 and SSt3. Retention for cell 1 and cell 2 was significantly larger than for cell 3 (Wilcoxon signed rank test at the 0.05 level).

3.4. Toxic units

Potential pollutant effects, expressed as toxic units, showed levels between 0.2 and 0.3 at SSt1 (Fig. 4). At SSt3, the mean reduction of toxicity was 95% for the two vegetated cells and 79% for the nonvegetated wetland cell. Outlet values at SSt3 of the two vegetated cells were ≤0.01 TU, whereas the TU at the outlet of the nonvegetated cell was 0.06. Fig. 5 shows a regression of the decreasing toxicity within the three wetland cells. The calculated length of the wetland that decreases the TU below 0.01 was 32 m for cell 1, 39 m for cell 2 and 64 m for cell 3.

4. Discussion

The range of peak concentrations of this experiment (0.1–7 μg/L) was realistic in comparison to high concentration levels of pesticides detected in agricultural surface water following runoff or spray drift events (Berenzen et al., 2005a,b; Schulz, 2004).

Efficiency of mass retention of pesticides in wetlands is linked to the inlet load and type of pollutant (Agudelo et al., 2010; Moore et al., 2000, 2001; Schulz and Liess, 2001). Retention of pesticide loads in a surface flow wetland is also influenced by several characteristics of the wetland. Possible non-uniform dispersion of the contaminated water within the cells and influence of the masses in samples below LOQ were not taken into account for the mass balance. This could have lead to an underestimation of sorbed masses. Estimated low sorption of pesticide masses to sediment and plants can be explained as a result of both physico-chemical parameters of the substances, i.e. the relatively low K_{OC} (Table 2, the low sorptivity and low carbon content of the silty bulk sediment and the short HRT of the wetland system (Table 1). In this context several studies on pesticide retention in wetlands showed similar ranges of load reduction. Those studies used composite samples to quantify the mass inflow and outflow of the systems. Experimental data from 2003 at the Lier wetland showed low reduction of loads of the pesticides fenpropimorph, linuron, metalaxyl, metamitron, metribuzin, propachlor and propiconazole, with a mean measured mass reduction of 14% (median 7%) (Blankenberg et al., 2006). In another study from 2000 to 2001 at a smaller, but deeper wetland near Stavanger, mean load reductions of 21% (median 21%) were achieved (Braskerud and Haarstad, 2003). For non-mobile pyrethroids in wetlands and vegetated ditches, retention ranged from 47 to 65% at wetland lengths up to 36 m (Moore et al., 2002). Larger wetlands with higher storage capacity and longer HRTs increase the reduction of masses. With a flow length of more than 500 m, reduction rates were above 98% (Bouldin et al., 2004; Budd et al., 2009; Cooper et al., 2004).

In the two vegetated cells, the masses sorbed to the plants were 13-fold and 7-fold, respectively, higher than the masses sorbed to bulk sediment. A similar trend was observed in vegetated wetlands with up to 86% of the measured insecticide esfenvalerate sorbed to plants (Cooper et al., 2004). Higher sorption of pesticide masses to plants in cell 1 than in cell 2 is possibly caused by the different plant communities within the cells. In cell 3, sorption to bulk sediment was larger than in the two vegetated cells. The substance with highest sorption to sediments was dimethoate, which has a relatively low K_{OC}. A study assessing the effectivity of rice ponds in reducing diazinon loads showed a significant role of sediment in the non-vegetated wetland. Mass partition to Sediment in the non-vegetated wetland was 8-fold higher than in vegetated wetlands (Moore et al., 2009b). The carbon content of the sediment combined with the K_{OC} of the substance is supposably the most important factor for sorption to bulk sewdiment. In the present study, sorption to sediment in the non vegetated ditch was only 2-fold higher than in the non vegetated ditch. Possible causes for the slight increase in sorption are the lower water level, different texture of the sediment surface and a coarser particle size of the top sediment, due to higher flow velocity. Sorption to plants and the biofilm on the surface of the vegetation is dependend on the surface area below the water level (Tanner, 1996). *P. arundinacea*, which is dominant plant in cell 1 has compared to the major plant in cell 2 *T. latifolia* smaller stems and a larger leaf surface area below the water surface. Plant type thus seemed to be more important for the partitioning than HRT which was lower in wetland cell 1 than in cell 2.

Even though reduction of loads may be relatively low, the concentration peaks can be reduced to a much greater extent. Peak retentions observed in this experiment were between 46% and 100%, thus about a factor of 10 higher than mass retention. Mean peak retentions in the vegetated wetland cells were caused mainly by dispersion. With low discharge of 0.6 L/s and a width of 3 m, the dense vegetation forced the water to flow across the whole width of the cells. The results are also supported by the results of the tracer studies (Fig. 4). The peak retention is comparable to results from other studies with wetlands of a similar size and density of vegetation. A study on the slightly mobile insecticide azinphos-methyl in a vegetated stream of 180 m observed 61–90% peak retention (Dabrowski et al., 2006). In a study on atrazine and lambda-cyhalothrin in a 40 m ditch with a discharge of 1 L/s, reduction of peaks was 92% and 76%, respectively (Moore et al., 2001). Interestingly, although many constructed wetlands studies show relatively high retention based on peak concentrations and the toxicity of many pesticides is driven by short term peaks (Hosmer et al., 1998; Schulz and Liess, 2000), the performance of constructed wetlands has so far never been evaluated using a toxic units based approach. To assess the ecological impact of pesticide retentions, a closer look at the effects is required. Even if there is only a small amount of the substance retained in the wetland, the reduction of the peak could be relevant for minimising potential adverse effects.

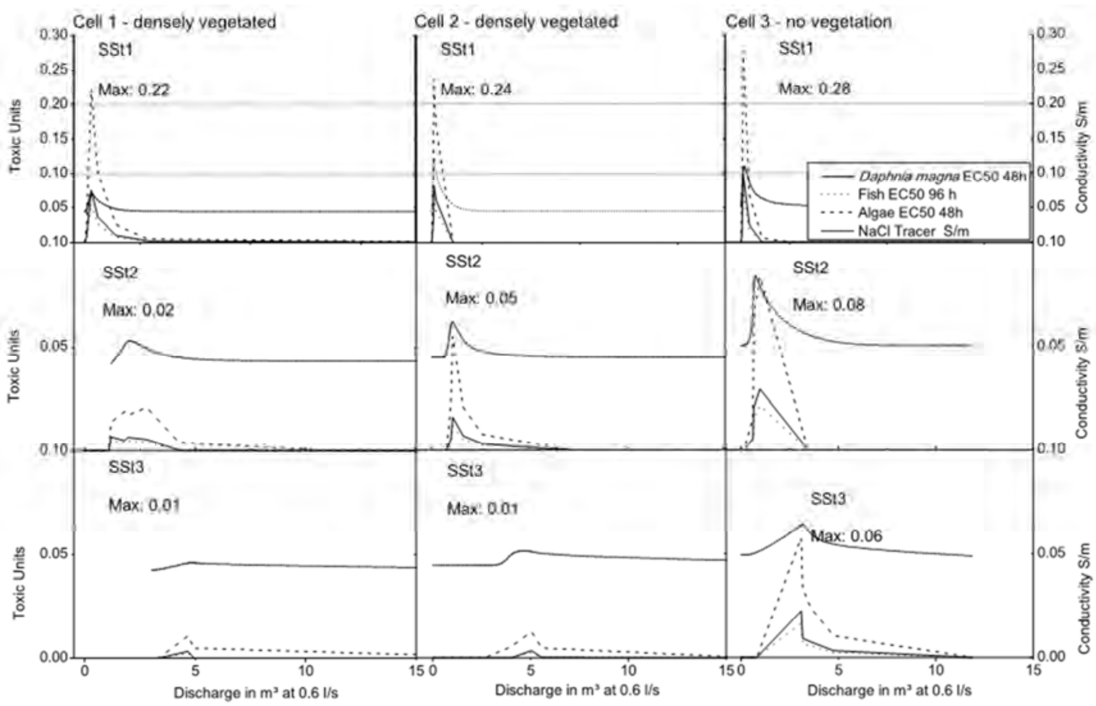

Fig. 4. Temporal pattern and maxima of the pesticide peaks at different sampling stations (SSt1–SSt3) in all three wetlands expressed as toxic units calculated based on acute toxicity data for algae, daphnids and fish. NaCl-tracer data were recorded two days prior to the pesticide experiment.

The toxic units approach is a good way to describe the ecological impact of pesticide mixtures. The difference of 16–18% mean reduction of peak concentrations in the vegetated cells and the cell without vegetation translates to a difference in reduction of effects of 15%. More importantly though, the TU was at the 0.01 level at the outlet of the two vegetated cells. In the nonvegetated cells the TU at the outlet was more than 5 times higher. This is the first study using the toxic units approach to evaluate the potential of constructed wetlands for mitigating pesticide risks.

The observed differences between vegetated and non-vegetated cells are mainly caused by different hydraulic conditions of the cells. Nevertheless there is some reduction through uptake and sorption to the plants within the vegetated wetland cells. Both sorption and hydraulic differences are caused by the dense vegetation.

The few previous studies looking at toxicity in wetlands using bioassays showed high reduction of effects in wetlands. Toxicity of pesticides, measured with in situ bioassays was reduced by 89% in a vegetated wetland in the Lourens River catchment, South Africa (Schulz and Peall, 2001; Schulz et al., 2001b). A study of a simulated worst case runoff scenario with the insecticide methyl parathion was reduced significantly during passage of the wetland. The vegetated wetland showed a complete reduction of concentrations in the first 20m of the wetland, while in the non vegetated wetland the concentration of the samples at the furthest station were still above the LOQ. Toxicity measured in situ and in laboratory tests with water from the vegetated and non-vegetated wetland cells also showed significant reduction with increasing distance from the inlet. The mortality in the nonvegetated wetland was more than 60% higher than in the vegetated wetland at the furthest sampling station. The autors identified the difference in transport caused by the dense vegetation as main cause for the reduction of toxicity (Schulz et al., 2003a,b).

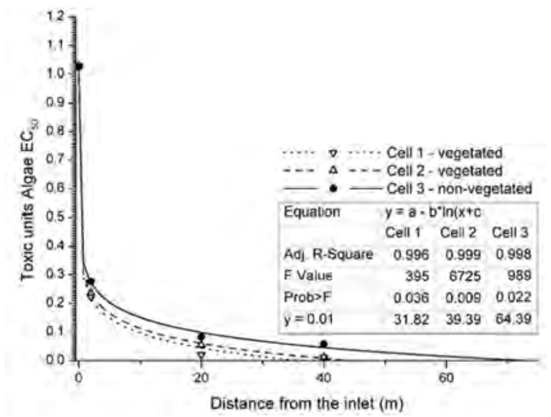

Fig. 5. "Non-linear" regression of the maximum observed toxic units (algae EC50 48 h) versus distance from the inlet in the three wetland cells. Values at 0m were calculated with target concentrations at the inlet.

5. Conclusions

Constructed surface flow wetlands have an ability to reduce peak concentrations and adverse effects of pesticide pollution. Reduction of peak concentrations, masses and potential effects differ due to hydraulic conditions, concentration levels, pesticide properties and vegetation. Hydraulic modification of the wetland cells 1 and 2 with dense vegetation improves the reduction of peak concentrations (89% and 91%) significantly, although this study also shows a 72% reduction of peak concentrations in cell 3. Concentrations, that were injected during this experiment, were reduced to an appreciable amount by the 40 m vegetated wetland cells. For short passage times of less than 3 h, only minor retention of masses through sorption on plant surface, sedimentation and photolytic decay can be expected. Nevertheless, the potential toxicity decreased to 0.01 toxic units within the 40m length of cells 1 and 2. By transferring these results to the landscape level, it can be stated that artificial vegetated wetland systems could be an effective end of pipe technology to reduce the risk of adverse effects caused by inevitable non-point source pesticide pollution upstream of ecologically sensitive receiving water courses.

Acknowledgements

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II. Paper: Field monitoring

Paper 3: Fungicides in detention ponds and vegetated ditches

Mitigation of agricultural nonpoint-source fungicide pollution in detention ponds and vegetated ditches

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Submitted to Chemospere

Abstract

Large amounts of fungicides are commonly applied in winegrowing areas and may lead to adverse effects when they are transported to agricultural surface waters. In this study aquatic fungicide exposure at normal discharge and during rainfall-related runoff events as well as mitigation performance of five vegetated detention ponds (DP) and two vegetated ditches (VD) in Southern Palatinate (SW-Germany) was assessed. At all sites and in all of the 81 samples taken between 2006 and 2009, mixtures of four to eleven different fungicide compounds were detected. During runoff events, ecotoxicological potential of this mixture exceeded EU-thresholds based on toxic units. Concentrations of the studied fungicides and potential adverse effects of the mixtures were reduced significantly within VD (Median 56%) and DP (Median 38%) systems. Using multiple regression analysis, plant density and size related properties of the mitigation systems were identified as variables with highest explanatory power for the response variable fungicide reduction during runoff events.

Keywords: Viticulture, pesticide, wetland, mitigation

1 Introduction

Pesticides and particularly fungicides are commonly applied to vineyards throughout Europe. In regions with intensive agriculture adverse effects may be observed when the substances are transferred to non-target ecosystems (Schäfer et al., 2011). During peak application of pesticides in a watershed, a mixture of numerous substances may be transported to the waterbodies (Battaglin & Goolsby, 1999; Thomas et al., 2001). Various studies reported pesticide residues in the aquatic environment even at ecotoxicological relevant concentrations (Schulz, 2004; Suess et al., 2006). Nonpoint-sources (runoff, drainage and spray drift) account for a majority of all surface water pollution (Zaring, 1996). As steep slopes of more than 2% are common in winegrowing areas of southwestern Germany and the northeast of France, the risk of runoff pollution is higher than in many other cultures (Ohliger & Schulz, 2010). Fungicide applications account for 96% of all pesticide treatments in vineyards of this region (Rossberg, 2009). Although many fungicides have relatively low acute toxicity to aquatic invertebrates, the mixture of fungicides commonly applied at substantial application rates may lead to adverse effects in surface water. Nevertheless, there are only few studies focusing on fungicide pollution after rainfall-related runoff events (Bermúdez-Couso et al., 2007; Gregoire et al., 2010; Hildebrandt et al., 2008; Rabiet et al., 2010; Schäfer et al., 2011).

Recent regulatory frameworks like the European Water Framework Directive (European-Commission, 2000) or the EU-framework for sustainable use of pesticides (European-Commission, 2009) fortify the need for mitigation measures to control amongst others also the pesticide pollution in surface waters. There are more than ten reviews and numerous original research studies (Moore et al., 2011; Otto et al., 2008; Pätzold et al., 2007; Reichenberger et al., 2007; Schulz, 2004; Stehle et al., 2011; Zhang et al., 2010) dealing with mitigation measures to reduce runoff-related pesticide entries into surface waters. Vegetated areas within agricultural headwaters were proposed as best management practice mitigating pollution that already reached the waterbodies (Gregoire et al., 2009; Schulz, 2004). As part of the EU Life project ArtWET (Gregoire et al., 2009), we focused in the present study on the role of vegetation in optimising the potential of agricultural ditches and detention ponds for pesticide mitigation. Effectiveness of vegetated artificial wetland ecosystems in retaining loads and peak concentrations of pesticides was studied within ArtWET in several experiments and tracer studies (Elsaesser et al., 2011; Gregoire et al., 2010; Lange et al., 2011; Stehle et al., 2011).

In the present study, the focus was on the monitoring of fungicide pollution in small waterbodies following heavy rainfall-related runoff events and the assessment of reduction of fungicide concentrations and toxicity within partly optimised vegetated ditches and detention ponds. The two main aims of the present study were (1) the assessment of patterns of pesticide exposure linked to effectiveness of vegetated areas within the agricultural waterbodies in mitigating potential risks and (2) the identification of variables explaining this effectiveness.

2 Material and Methods

2.1 Study area and sites

In the present field study, vegetated systems in the winegrowing area of the Southern Palatinate in southwestern Germany (Figure 1) were monitored between 2006 and 2009.

Sections of densely vegetated ditches (VD1 and VD2) and stormwater detention ponds (DP1-DP5) were selected as independent sampling sites (Table 1). With approximately 23,000 ha the southern palatinate is the second-largest winegrowing region in Germany.

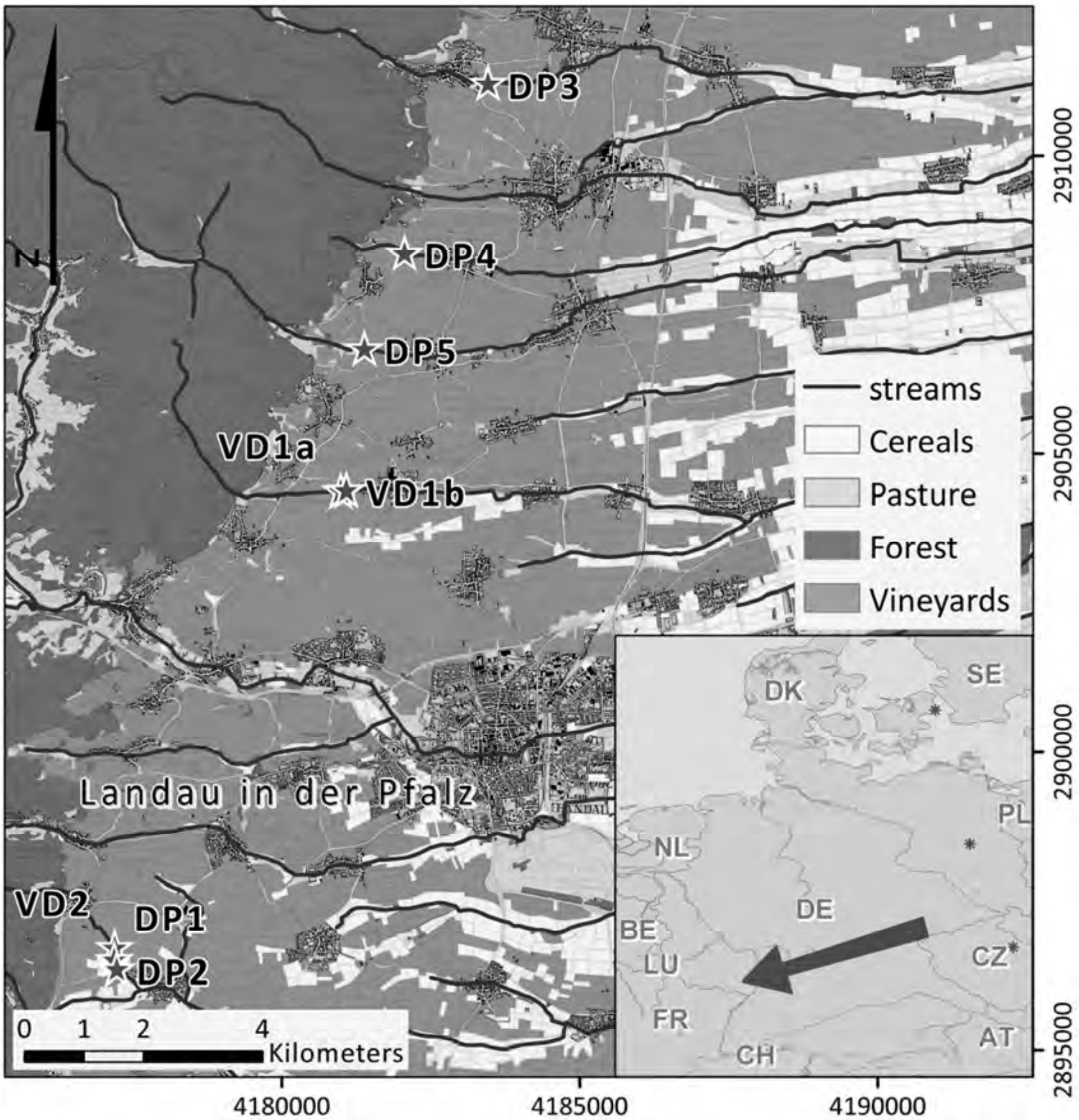

Fig 1: Study area in the southern Palatinate. Coordinate system: ETRS 1989 LAEA.

Table1: Study sites in a winegrowing area in southern palatinate in southwestern Germany.

Location	Study period	Site	Surface area (m^2)	Depth (m)	Flow length (m)	Plant density (%)
Hainbach	2006-07	VD1a	165	0.2	165	40
Hainbach	2008-09	VD1b	105	0.25	105	60
Krottenbach	2007-09	VD2	51	0.1	85	75
Krottenbach	2008-09	DP1	26	0.15	22	45
Krottenbach	2008-09	DP2	1300	0.45	68	45
Kropsbach	2006-07	DP3	644	0.8	76	10
Leiselgraben	2006-07	DP4	980	0.135	82	90
Modenbach	2006-07	DP5	1720	0.2	176	60

2.2 Fungicide Application

Fungicides were selected for this study based on the following considerations. The substance is detectable with the LC MS/MS multimethod used and the substance was detected in all four seasons of monitoring. Properties of the ten fungicides that met both conditions are listed in Table 2. Concentrations of other pesticides detected in the water samples can be found in the appendix. Nine of the target fungicide substances were listed in the local annual recommendations of application for vineyards (DLR, 2009).

Table 2: Characteristics and toxicity threshold values (i.e. toxic endpoint divided by respective assessment factor, for *Daphnia*, fish and algae) of fungicide substances monitored during the present study.

Substance	Chemical Group	K_{OC}[a] (mL g^{-1})	Log P[a]	DT50[a,b] (d)	Application rate (g ha^{-1}) / number of applications[c]	LOQ[d] (ng L^{-1})	Acute Toxicity[a] *Daphnia* (µg L^{-1})	Acute Toxicity[a] fish (µg L^{-1})	Acute Toxicity[a] algae (µ L^{-1})	Chronic Toxicity[a] *Daphnia* (µg L^{-1})	Chronic Toxicity[a] fish (µg L^{-1})	Chronic Toxicity[a] algae (µg L^{-1})
Azoxystrobin	Strobilurin	482	2.5	46	1600 / 3	0.18	2.3	7.4	36	4.4	14.7	80
Boscalid[e]	Carboxamide	809	2.96	9	600 / 1	0.18	53.3	27	375	130	14	375
Cyprodinil[f]	Anilinopyrimidine	1706	4	12.5	360 / 2	0.26	0.33	24.1	260	0.88	8.3	260
Dimethomorph[f]	Morpholine	348	2.68	10	234 / 3	0.22	106	34	2920	0.5	5.6	980
Myclobutanil	Triazole	517	2.89	12	72 / 4	0.28	170	20	266	100	20	266
Penconazol[f]	Triazole	2205	3.72	2	24 / 6	0.32	67.5	11.3	200	6	32	200
Pyrimethanil[f]	Anilinopyrimidine	301	2.84	16.5	1000 / 2	0.1	29	105.6	120	94	160	120
Tebuconazol[f]	Triazole	769	3.7	42.6	400 / 3[g]	0.30	27.9	44	196	1	1.2	10
Triadimenol[f]	Triazole	273	3.18	53	-/0[h]	0.4	510	213	960	10	313	100
Trifloxystrobin	Strobilurin	2377	4.5	1.1	120 / 3	0.21	0.11	0.15	0.53	0.3	0.8	1

a: based on the Pesticide Properties Database (PPDB, 2011) b: water phase only c: (BVL, 2011) d: Limit of quantification e: substance in suspect for endocrine activity (Orton et al., 2011) f: Substance with endocrine activity (Orton et al., 2011) g: Tebuconazole approval in vineyards was withdrawn 2007 h: Triadimenol was not approved for use in vineyards.

Table 3: Multiple linear regression analysis results including most important factors predicting pesticide retention performance of detention pond systems (n = 68, Model A) and of vegetated ditch systems (n = 143, Model B).

Model A: DP	Estimate	Std. Error	t value	Significance		Relative importance (%)
(Intercept)	-0.09	0.1	-0.6	0.6		-
Plant coverage (%)	0.01	0.002	5.3	<0.001	***	40
Hydraulic retention time (h)	0.001	2.E-04	5.7	<0.001	***	37
Flow length (m)	0.004	0.001	4.2	<0.001	***	21
Log P	-0.09	0.04	-2	0.05	*	2
Model B: VD						
(Intercept)	-0.6	0.2	-2.5	0.01	*	-
Plant coverage (%)	0.01	0.003	4.7	<0.001	***	50
Precipitation (mm)	0.04	0.01	2.8	<0.01	**	9
Hydraulic retention time (h)	0.002	0.001	2.5	0.01	*	19
Hydraulic loading rate (m d^{-1})	-0.02	0.01	-2.3	0.02	*	8
Inlet concentration (μg L^{-1})	0.1	0.04	2.4	0.02	*	7
Solubility in water (mg L^{-1})	-0.001	0.0006	-1.9	0.06	.	8

Model A summary: R^2 = 0.57; adjusted R^2: 0.55; p<0.001. Excluded factors were: K_{OC} (ml g^{-1}), solubility in water (mg L^{-1}), pesticide inlet concentration (μg L^{-1}), water-sediment DT_{50} (d), water DT_{50} (d), photolytic DT50 (d), precipitation (mm), peak discharge (L/s), total water inflow during event (m^3), System surface area (m^2) and hydraulic loading rate (m d^{-1}). Model B summary: R^2 = 0.19; adjusted R^2: 0.15; p<0.001. Excluded factors were: Log P, K_{OC} (ml g^{-1}), water-sediment DT50, water DT_{50} (d), photolytic DT_{50} (d), peak water inflow during event (L s^{-1}), total water inflow during event (m^3), System surface area (m^2), depth (m) and flow length through the system (m).

2.3 Sampling and Analysis

At each site, a sampling station was installed at the inlet and outlet of the wetland or the respective vegetated stretch of the ditch. Water levels were recorded at the sampling stations. In 2006 and 2007 composite water samples representing the contamination levels during runoff were accomplished using bottles stored in the stream or river with the opening fixed at a water level typically reached after heavy rainfall events (Schulz et al., 2001). During rainfall-induced surface runoff, the rising water level fills the bottles passively. In 2008 and 2009 the samples were taken manually at peak level after heavy rain events 5 cm below water surface in the center of the stream. Between 2007 and 2009, a total of 22 inlet-outlet pairs of samples were collected during 17 rainfall-runoff events. Additional samples (in total 14 inlet-outlet pairs) were taken during normal discharge at least four days after the last rainfall. In 2008 and 2009 an additional total of nine samples of the runoff water were collected on paved waysides directly before entering the waterbody. All water samples were taken in 1 L brown glass bottles and stored in the fridge at 4° C until extraction. Pesticide extraction was performed after centrifugation with 500 mL of the samples using method described in Elsaesser et al. (2011) (SPE Column: Chromabond C18, 500 mg, 6 mL; conditioning solvent: MeOH). SPE cartridges were dried with nitrogen and stored in a freezer at -18°C until elution. SPE cartridges were eluted with

MeOH. Analysis was performed by LC MS/MS. The HPLC system used was a Model 1100 liquid chromatograph (Hewlett Packard, PaloAlto, CA, USA). Chromolith Performance columns (Merck RP-18e 100 x 4.6 mm, 5 µm) were used at a flow rate of 0.6 mL min-1. Aliquots of 20 µL of solutions were injected by the HP 1100 autosampler. Electrospray data were acquired by Multiple Reaction Monitoring using an Applied Biosystems 4000 Q Trap Linear Ion Trap Quadrupole mass spectrometer (Sciex, Concord, ON, Canada). Limits of quantification (LOQ) are listed in Table 2.

2.4 Data Analysis

Data was analysed with a focus on reduction of concentrations and possible adverse effects within the wetlands or vegetated ditches. Efficacy of the wetlands in pesticide peak reduction was calculated as follows:

$$RP\ (\%) = \left[\frac{(c_{in} - c_{out})}{c_{in}} \right] \times 100 \qquad [1]$$

where RP is the reduction of concentration peaks during a particular hydrological event in percent, cin is the concentration of a pesticide measured at the inlet and cout the corresponding pesticide concentration detected at the outlet. From data pairs showing a 100% retention performance, only those inlet concentrations were used, which exceeded the LOQ at least by a factor 10 to preclude methodological artifacts. Negative reductions of low concentrations in water samples during runoff, deriving from increasing concentrations between inlet and outlet (n=21) were set to zero (all concentration values are listed in the supplementary material).

A toxic unit (TU) concept was used to evaluate reduction of toxicity of the mixtures of fungicides detected. Toxic units were calculated based on the Uniform Principle (UP) criterion, which was established within the standard European Tier I pesticide risk assessment to define a maximum acceptable field concentration of a pesticide (European-Commission, 1997). Acute and chronic UP threshold values were chosen for the samples taken during runoff events and normal discharge, respectively, to assess potential adverse effects on aquatic communities. UP-concentrations were calculated with toxic endpoints and the respective assessment factors according to the European Council Directive 97/57/ec (European-Commission, 1997): Acute Daphnia magna EC50 48 h*0.01, acute Oncorhynchus mykiss LC50 96 h*0.01, acute algae EC50 72 h*0.1 and chronic NOEC of either Daphnia magna 21 d, fish 21 d or algae 96 h*0.1. (Table 2).

Subsequently, UP-threshold values were transformed to toxic units (TU) (Liess & von der Ohe, 2005; Sprague, 1970). In order to compare ecotoxicity between inlet and outlet samples, TUs were calculated by summing up the quotients of aqueous-phase pesticide concentrations and the respective Uniform Principle criteria for each substance within a water sample using formula 2 (Junghans et al., 2006; Peterson, 1994).

$$TU_{UP} = \sum_{i}^{n} \left(\frac{C_i}{C_{UP\,i}} \right) \qquad [2]$$

TU_{UP} is the total toxic unit of the n pesticides in the sample, Ci is the concentration (µg L-1) of the pesticide i and CUPi is the UP- toxicity value (µg L-1) of pesticide i for the respective test species.

Statistical analysis and graphics were computed using the free software package R x64 V. 2.13 (www.r-project.org). Difference between paired inlet and outlet toxicity levels were statistically tested with Wilcoxon signed rank test, since variables were not normally distributed. Normal distribution was tested using the Kolmogoroff-Smirnoff test.

Linear models were used to explain variation in fungicide peak reduction within the two different types of waterbodies (DP and VD) and 13 explanatory variables characterizing the mitigation systems, events and pesticide properties. Possible interactions of main predictors with other variables were tested. Stepwise regression with backward selection based on "Akaike's An Information Criterion" (Akaike, 1974) was used to select the best fit model. Autocorrelated variables were identified and the variable with lower plausibility to explain the variation in the response variable based on expert opinion was removed.

The assumptions of the regression models regarding linearity were verified with residual plots and normal distribution of residuals by visual inspection of scatterplots and P-P plots. Influence of single observations was excluded by residual-leverage plots and Cook's distance plots. Additionally, tests for heteroscedasticity, linearity and autocorrelation (r-package: lmtest; gqtest and package: car; reset, bgtest) were performed. Hierarchical partitioning (r-package: gtools and hier.part) was applied to the results to determine the percentage of relative importance of explanatory variables (Chevan & Sutherland, 1991).

All distributions of either concentrations or toxic units were visualized using beanplots (r-package: beanplot). This alternative to box- or violinplots has the advantage to show all possible information on density, anomality and range of the distributions (Kampstra, 2008).

3 Results and discussion

3.1 Fungicide exposure

A total of 22 pairs of watersamples with 399 separate fungicide concentration values arising from runoff events were included in the analysis. Furthermore 11 pairs of watersamples with 222 concentration values at normal discharge and 9 samples with 85 concentration values of wayside runoff water were collected and analysed. The full database with excluded substances is provided as supporting material.

Maximal concentrations for single substances during runoff events ranged from 0.05 µg L-1 (trifloxystrobin) to 11.49 µg L-1 (tebuconazole). At normal discharge maximum concentrations ranged from 0.008 µg L-1 (trifloxystrobin) to 0.73 µg L-1 (boscalid). Samples of wayside runoff showed maximum concentrations between 0.02 µg L-1 (triadimenol) and 13.9 µg L-1 (cyprodinil). Median values of total concentration of fungicides within the samples were 0.65 µg L-1 during runoff events, 0.49 µg L-1 at normal discharge and 5.86 µg L-1 in wayside runoff (Figure 2). The range of peak concentrations of this study is comparable to concentration levels of fungicides detected in agricultural surface waters following runoff or spray drift events (Berenzen et al., 2005a; Berenzen et al., 2005b; Gregoire et al., 2010; Rabiet et al., 2010). Gregoire et al. (2010) detected pesticide concentrations in the range of 0.1-5.8 µg L-1 following runoff events in a french winegrowing region. Rabiet et al. (2010) who investigated five fungicides in a small water course within a vineyard area in Fran and detected total fungicide concentrations at a range of up to 8.3 µg L-1 at normal discharge. After rainfall-runoff events, fungicide concentrations reached maximum values up to 14.4 µg L-1 (Rabiet et al., 2010). Although drinking water thresholds are not directly relevant for surface waters, they may be used as benchmark to estimate possible risks for subsequent drinking water reservoirs based on total concentrations. European drinking water threshold value for total pesticides of 1 µg L-1 was exceeded in more than 35% of all samples. At least six of the ten substances studied and thus 72% of all detections show endocrine activity (Table 2).

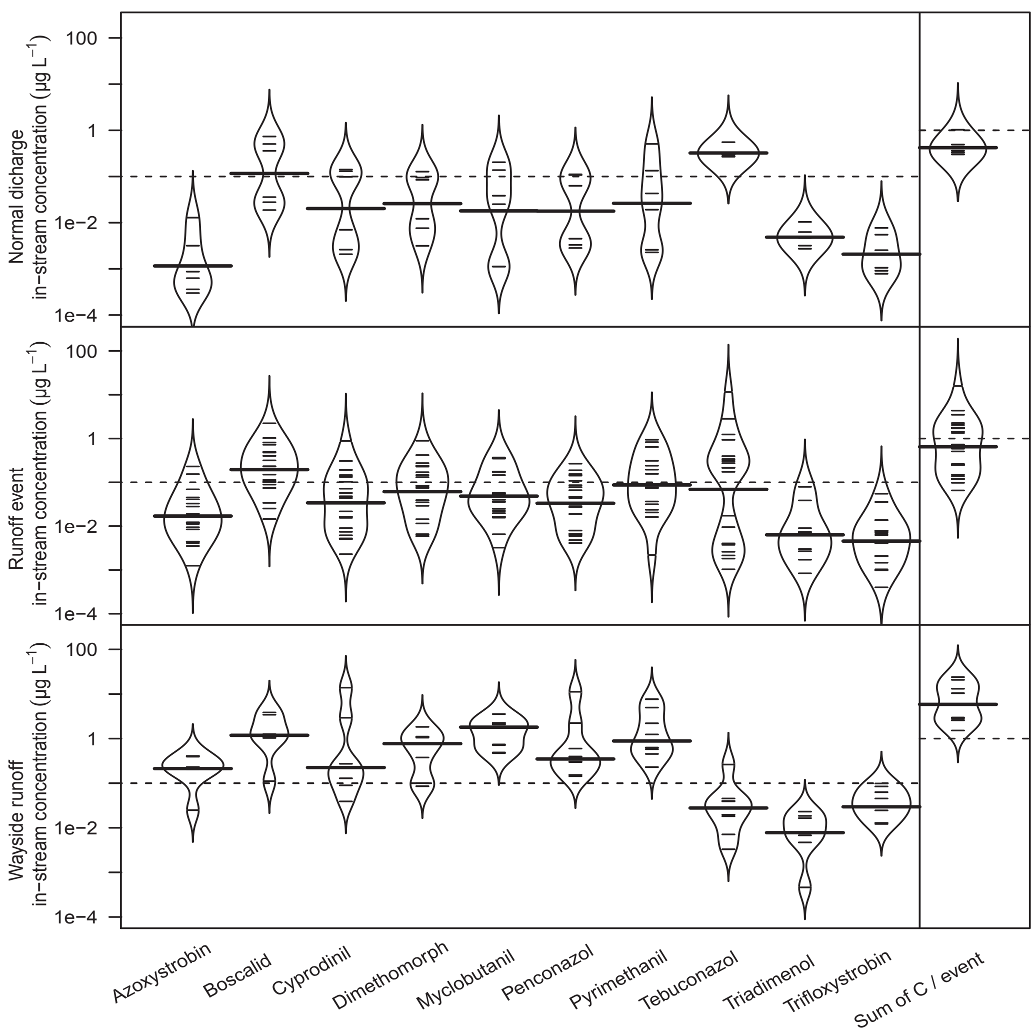

Fig 2: In-stream inlet peak concentrations of ten fungicides at normal discharge 2007-2009 (upper graph), during runoff events (middle graph) and concentration in wayside runoff 2008-2009 (lower graph). Beanplot “Sum of C / event” shows the distribution of inlet concentration sums of the ten fungicides within single samples. The dotted line is the EU drinking water benchmark of 0.1 µg L-1 for single fungicides and 1 µg L-1 for the sums of concentrations.

3.2 Reduction of peak concentrations and risk of adverse effects to aquatic communities

Reduction of peak concentrations was calculated for each pair of inlet and outlet concentrations of in-stream water samples after rainfall-related runoff events. Reduction of toxicity was calculated using TUs for aquatic organisms. Median reduction of concentrations was 25% in detention ponds and 53% in vegetated ditches. Median reduction of toxicity was 38% in detention ponds and 56% in vegetated ditches.

Distributions of the reduction of toxicity and concentrations within detention ponds and vegetated ditches are plotted in Figure 3.

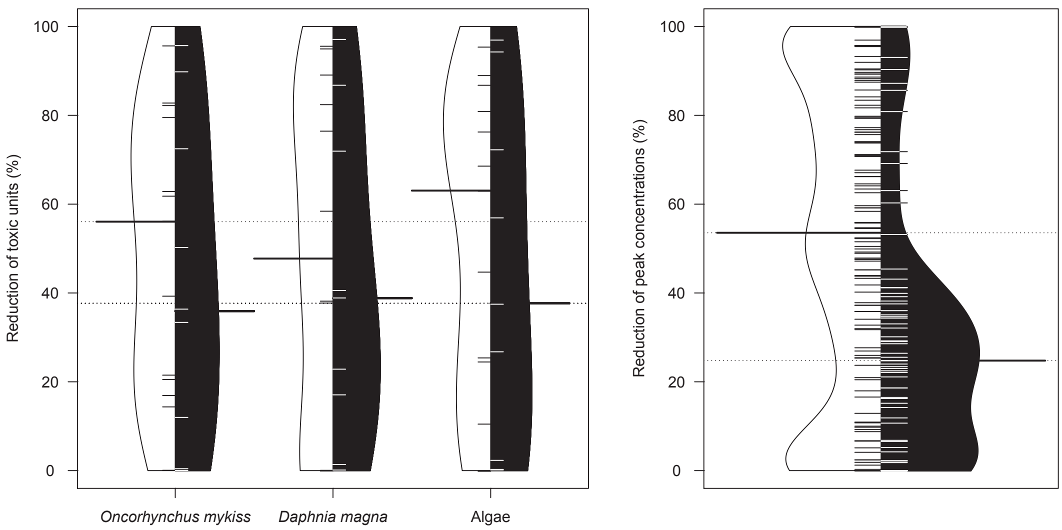

Fig 3: Reduction of toxicity (n = 22; left graph) and peak concentrations (n = 214; right graph) from inlet to outlet within the detention ponds (black) and vegetated ditches (white) after rainfall-runoff events. Short bars represent single events (left graph) and paired concentration values (right graph), long bars are median values and the shape represents the distribution of reduction values.

Former studies on pesticides within vegetated treatment systems with comparable size showed better retention performance. A study on the slightly mobile insecticide azinphos-methyl in a vegetated stream of 180 m observed 61–90% peak retention (Dabrowski et al., 2006). In a study on atrazine and lambda-cyhalothrin in a 40 m ditch with a discharge of 1 L/s, reduction of peaks was 92% and 76%, respectively (Moore et al., 2001). Another study on retention of organophosphate and pyrethroid insecticides showed 22%-90% reduction of concentrations (Budd et al., 2009). Nevertheless those values are not directly comparable due to fundamental differences in substance properties (e.g. solubility, Log P, KOC and application rates). Stehle et al. (2011) recently conducted a meta-analysis on performance of constructed wetland systems in mitigating nonpoint source pesticide pollution. With 14 studies using experimental exposure setups and 10 studies with pesticide entries originating from normal farming practices, in the majority of cases retention performances were greater than 80%, with only a small proportion of the pesticide trapping efficacies below 40%. The difference in performance in reduction of peak concentration to the present study can be explained with the selection of pesticides studied and their physico-chemical properties. Most of the substances are mobile, water phase decomposition times are moderate and extreme values are not present for both, KOC and DT50 values.

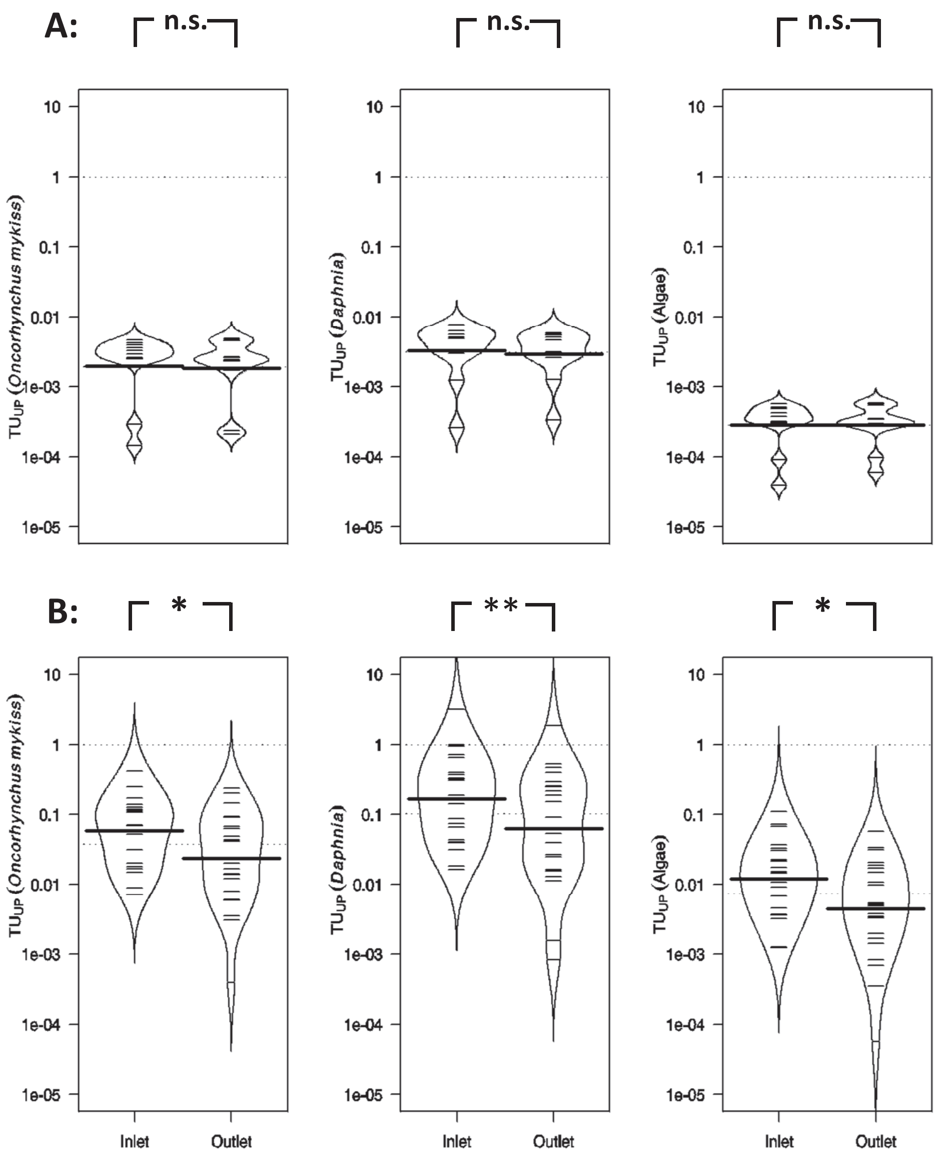

Figure 4: A: UP Toxic units of ten fungicides at normal discharge 2007-2009 (n=14). Based on NOEC*0.1. Samples were taken at inlet and outlet of the mitigation systems. Significance testing was performed with Wilcoxon signed rank test (p=0.4, p=0.4, p=0.5). B: UP Toxic units during runoff events 2006-2009 (n=22). Based on L(E)C50*0.01 for *Oncorhynchus mykiss* (Fish) and *Daphnia magna* and EC50*0.1 for algae. Samples were taken at inlet and outlet of the mitigation systems. Significance testing was performed with Wilcoxon signed rank test (p=0.001, p<001, p=003).

At normal discharge conditions, potential effects on the aquatic community were below 0.1 toxic units based on chronic UP values. No significant reduction of concentrations and toxicity was observed during normal flow conditions within the systems (Figure 4). Following runoff events, acute UP thresholds were exceeded in three samples for *Daphnia* *magna*. Toxicity was significantly reduced within the wetlands (Figure 4). Median Daphnia magna TU_{UP} decreased from 0.2 at the inlet to 0.07 at the outlet. Due to the fact, that toxicity of many pesticides is driven by short term peaks (Hosmer et al., 1998) the performance of the systems was evaluated using a toxic unit based approach with acute toxicity values for runoff events and chronic toxicity for normal discharge. At normal discharge conditions with toxic units below 0.01 it can be assumed, that the risk of adverse effects of the fungicides is relatively low. After rainfall-runoff events toxicity threshold values were exceeded and risk of adverse effects is very high. The risk of adverse effects after rain events was reduced significantly in the wetland systems by factors up to 35. High performance of vegetated mitigation systems in reducing possible adverse effects of pesticides pollution was observed in several recent studies (Elsaesser et al., 2011; Lizotte et al., 2011; Moore et al., 2009).

3.4 Identification of parameters influencing the reduction of effects after runoff events

Multiple regression analysis was performed with data of vegetated ditches and detention ponds separately in order to identify variables with highest explanatory power for the response variable pesticide retention performance after runoff events. Modell A (detention ponds) contained the variables plant coverage, depth of water, hydraulic retention time (HRT), flow length of the system and Log P and explained about 55% of the variability. About 15% of the variability in model B (vegetated ditches) was explained by the variables plant coverage, hydraulic retention time, precipitation, hydraulic loading rate, inlet concentration and solubility in water (Table 3). Two outliers in DP Data and one outlier in VD data were identified using Cook's distance and removed (see supporting material). Regression model assumptions of linearity, homoscedasticity and absence of autocorrelation were met. Reduction of peak concentration was driven by plant density as a functional variable of the VD and DP systems. Hierarchical partitioning showed that in DP systems size related variables such as flow length and hydraulic retention time accounted for 58% of total varability, whereas in VD systems, hydraulic retention time and hydraulic loading rate as size related variables explained only 27% of total variability.

Plant density as the most important variable influencing pesticide retention has been documented extensively within scientific literature (Budd et al., 2009; Cooper et al., 2004; Gill et al., 2008; Moore et al., 2002; Schulz et al., 2003). Lizotte et al. (2011) observed an increase in efficiencies for diazinon (8%) and permethrin (35-70%) between non-vegetated and vegetated wetlands. Experimental exposure in vegetated and non-vegetated wetland cells showed a significant increase in efficiency of 16-18% for six common pesticides (Elsaesser et al., 2011). Increasing efficiency with increasing plant density can be explained by sorption to plant material, altered water chemistry (pH, oxygen) and physical effects like influence in flow pattern, flow velocity and residence time.

Hydraulic loading rate as a size related variable, defined as water inflow divided by system surface area is inversely related to reduction of effects in model B. Hydraulic retention times ranged between 400 seconds (VD2, August 11. 2008) and 500 min (DP2, July 3. 2009). Due to retention times of less than 25% of the lowest DT50 value, the DT50 variables were excluded from analysis (Table 2). HLR and HRT are linked to mitigation values in constructed wetlands by studies of Stearman et al. (2003) and Blankenberg et al. (2006; 2007). An increase of reduction of concentrations with increasing flow length was also observed in studies of Bennett et al. (2005) and Cooper et al. (2004).

Generally, hydrophobic pesticides with high KOC, high Log P and low solubility in water are more effectively retained in wetlands due to adsorption of molecules to plants and sediments (Imfeld et al., 2009; Moore et al., 2001). Fungicide properties included in the models were Log P, which showed a relative importance of 2% in DP and the non-significant solubility in water, which showed a relative importance of 8% in model B. In this model, the event related variables of fungicide inlet concentration and precipitation intensity were significantly positively correlated but have also a relatively low explanatory importance.

Other variables and all possibly relevant interactions of centered variables showed no significant correlation with reduction. Although model B left 85% of the variance unexplained, this relatively low percentage of the six explanatory variables in VD systems is presumably not caused by missing variables, but by small variability in the fungicide properties and the size and structure related properties of the three VD systems.

4 Conclusion

Although common fungicides have mostly a low or moderate toxicity on aquatic organisms, they are applied in amounts and mixtures that may lead to adverse effects in aquatic ecosystems. To avoid under- or overestimation of the risk for receiving waters, a closer look on the presence and mixture of fungicide compounds in further agricultural headwaters and assessment of mixture toxicity of fungicides with appropriate test species is needed. Analysis of properties influencing the mitigation performance showed that vegetation density and size are the most important properties reducing concentrations and potential adverse effects within the systems. In order to quantify the influence of size related system properties further studies, especially in vegetated ditches, are needed. Optimisation of vegetation and size could be easily implemented in a cost-efficient way to further detention ponds and ditches in agricultural areas. Optimised, densely vegetated systems can be an effective end of pipe technology to reduce the risk of adverse effects caused by inevitable non-point source fungicide pollution upstream of ecologically sensitive receiving water courses.

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III. Papers: GIS-tools

Paper 4: Risk Map

Risk map of runoff-related pesticide pollution in small rivers of the European agricultural landscape

David Elsaesser

Submitted to Journal of Maps

Abstract

As an integrated part of the EU Life project ArtWET, a tool was built to model pesticide pollution in surface waters following rainfall runoff events at the European scale. The geodata used for simulation is taken from freely available sources. The OECD-REXTOX and USDA Curve Number models were combined to calculate predicted concentrations in stream. The potential effects are modeled with the toxic units approach. Runs with worst-case dummy substances are base for a risk map on European scale. The whole approach was realized using Esri ArcView 9.1 and ArcGIS model builder.

Introduction

Pesticides are widely used in agriculture, but adverse effects may be observed when the substances are transferred to natural ecosystems (Schulz, 2004). Nonpoint-source pollution through runoff, drainage and spray drift accounts for the majority of all surface water pollution (Zaring, 1996).

During peak application of pesticides in a watershed, a mixture of numerous substances may be transported to the waterbodies (Schulz, 2004; Battaglin & Goolsby, 1999; Thomas et al., 2001)

In the present study, the focus was set on mapping the risk of pesticide pollution after rainfall-related runoff events in small streams on European scale.

Methods

The simulation for the map is based on a geodata layer, which contains all agricultural area within a buffer zone of 50 m around European streams. Most of the source data was taken from freely accessible data portals of the European Commission Joint research center. Attributes of the database are described in Table 1.

Table 1: Geodata included in the database. a.: + - data was modified or converted to meet the standards for the database. -: data was taken as is into the database.

Attribute	Unit	Conversion[a]	Source	Reference
Type of agriculture		-	Corine Land cover	(Büttner, 2007)
Hydrological soil type		+	Soil database	(Panagos, 2006)
Slope	%	+	SRTM	(Farr et al., 2007)
Discharge	L/s	-	Hydrosheds	(Lehner et al., 2008)
OC in topsoil	%	-	Soil Database	(Panagos, 2006)
Length of Riversegments	m	+	EC-JRC, IES	(Vogt et al., 2007)
Curve Number		+	USDA	(Zhan & Huang, 2004)
Plant interception	%	-		(Linders et al., 2000)

To run the simulation further parameters of the substance and rain event need to be defined (Table 2).

Table 2: Parameters for simulation

Parameter	unit	Source	Simulated event
season	-	selection	summer
Width of buffer strips	m	-	3
Precipitation amount	mm	Weather or climate data	15
Precipitation duration	minutes	Weather or climate data	30
Pesticide applied amount	g/ha	Pesticide registration	1500
Pesticide: DT_{50}	days	PPDB (2011)	10
Pesticide: K_{OC}	mL/g	PPDB (2011)	10
Pesticide: toxicity	µg/L	PPDB (2011)	0.1

The simulation tool was programed in ESRI ArcGIS Model builder. Risk of pesticide pollution after rainfall-related runoff is calculated with four consecutive models. The amount of rainfall contributing to surface runoff was calculated with Runoff Curve Number model (Zhan & Huang, 2004):

$$\mathrm{Q}_{\mathrm{Runoff}} = \frac{25.4 * \left(CN * \left(\frac{P}{2.54} + 2\right) - 200\right)^2}{CN * \left(CN * \left(\frac{P}{2.54} - 8\right) + 800 \right)}$$

where Q_{Runoff} is the amount of rainfall contributing to runoff in mm, *CN* is the Curve Number and *P* is the precipitation in mm

The percentage of applied amount within the surface runoff is calculated using the modified REXTOX model (Probst et al., 2005), that was proposed by the OECD(OECD, 2000):

$$L_{\mathrm{Runoff}} = \left(\frac{\mathrm{Q}_{\mathrm{Runoff}}}{(P * 10)}\right) * \mathrm{e}^{-3*\frac{\ln 2}{Dt_{50}}} * \frac{1}{1 + Kd} * \left(1 - \frac{Pli}{100}\right) * slope * 0.83^{Buffer} * 100$$

where L_{Runoff} is the percentage of applied substance in runoff, *Dt50* is the half life of applied substance in soil (days), *Kd* is the soil-water partitioning coefficient, *Pli* is the interception on plant tissue, *slope* is the slope factor, calculated using the methods of Probst (2005) and *Buffer* is the mean width of densely vegetated buffer strips.

Concentration of the substance in stream is calculated with the second part of the REXTOX model:

$$PEC = L_{\mathrm{Runoff}} * PA * \frac{1}{Q_{\mathrm{Stream}} * T * 60}$$

where *PEC* is the predicted in stream peak concentration in μg/L, *PA* is the amount of substance applied in the simulation area in μg, Q_{Stream} is the discharge in stream in L/s and *T* is the duration of rain event in minutes.

Acute toxicity data of the substances for fish, algae and aquatic invertebrates can be used to assess potential toxicity of the substance based on toxic units (TU). Toxic units are calculated for each peak concentration of the substance. Specific LC_{50} or EC_{50} values for acute toxicity to *Oncorhynchus mykiss* (fish LC_{50} 96 hours), *Daphnia magna* (aquatic invertebrate EC_{50} 48 hours) and algae (EC_{50} growth 72 hours) can be found in the Footprint Pesticide Properties database (PPDB, 2011). The TUs are calculated using the TU approach (Peterson, 1994; Junghans et al., 2006):

$$PTU = \frac{PEC}{EC_{50}}$$

where *PTU* is the potential toxicity in toxic units and EC_{50} is the lowest concentration causing acute effects to selected species.

Conclusions

Runs of the model with several commonly used pesticides show a realistic range of runoff pollution and potential toxicity values for the exposure model. The range of peak concentrations is comparable to concentration levels of fungicides detected in agricultural surface water following runoff or spray drift events (Berenzen et al., 2005b; Gregoire et al., 2010; Rabiet et al., 2010; Schäfer et al., 2011). Particularly small streams with low discharge show a high risk of adverse effects within the waterbody. To perform a validation of the model further monitoring data for all regions of the European Union is needed. Nevertheless the risk of pollution after runoff events is clearly displayed.

Software

The whole approach of simulation, mapping and publishing was done with Esri ArcView 9.1 and the extension Spatial Analyst.

Acknowledgements

This study is part of the European LIFE ENVIRONMENT project ArtWET (LIFE 06 ENV/F/000133).

Map Design

Aim of the design was an intuitive illustration of the risk. Symbology of the risk with a "traffic light labeling", i.e. a color ramp from green (low risk) to red (high risk) was chosen. Further Elements are neutrally colored to attract attention to the main information.

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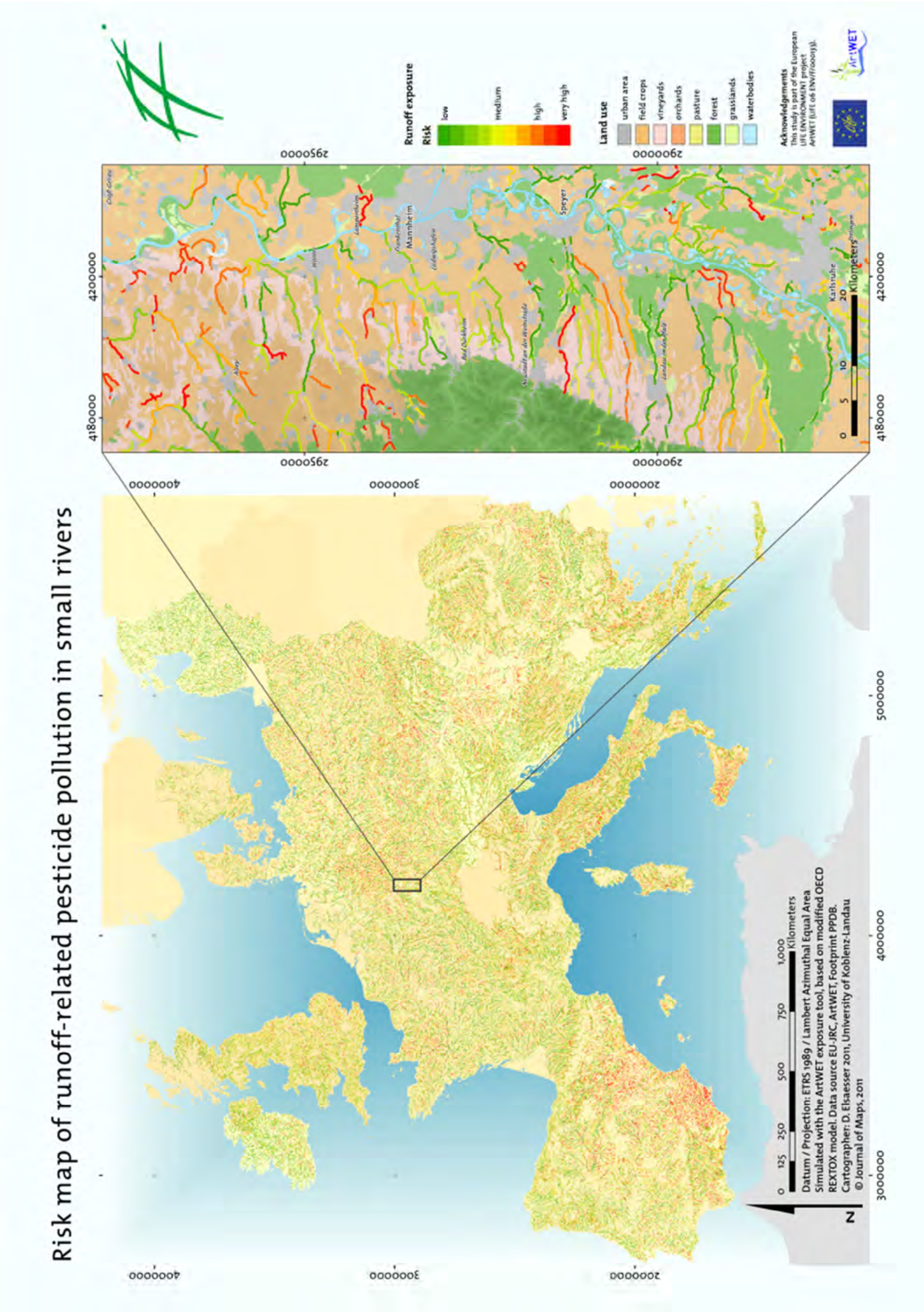
Next Page:

Figure 1: Risk map of runoff-related pesticide pollution in small rivers on European scale. Original size A1 (594x841 mm)


Risk map of runoff-related pesticide pollution in small rivers
Runoff exposure
Risk
low
medium
high
very high
Land use
urban area
field crops
vineyards
orchards
pasture
forest
grasslands
waterbodies
Acknowledgements
This study is part of the European LIFE ENVIRONMENT project ArtWET (LIFE 06 ENV/F/000133).
ArtWET
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Datum / Projection: ETRS 1989 / Lambert Azimuthal Equal Area
Simulated with the ArtWET exposure tool, based on modified OECD REXTOX model. Data source EU-JRC, ArtWET, Footprint PPDB.
Cartographer: D. Elsaesser 2011, University of Koblenz-Landau
© Journal of Maps, 2011
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Paper 5: Spatial DSS

A spatial decision support system for mitigation of runoff related pesticide pollution in surface waters across Europe

David Elsaesser and Ralf Schulz

Submitted to ijgis

Abstract

Two tools were built to model both pesticide pollution in surface waters following rainfall-related runoff events and possible mitigation measures at the European scale to help decision making in risk mitigation for aquatic ecosystems. Geodata for simulation at the European scale was collected and joined. The OECD-REXTOX and USDA Curve number models were combined and extended to calculate predicted concentrations in streams. Potential effects are modeled using the toxic units approach. In the second tool three possible mitigation measures on field, at the edge of field and in the headwaters as well as costs and landuse for implementation of those measures are assessed. The whole approach was realised using ArcGIS model builder and visual basic scripts.

Keywords: Pesticide; exposure; rainfall runoff; risk mitigation; model builder

1. Introduction

Pesticides are widely used in agriculture, but adverse effects may be observed when the substances are transferred to natural ecosystems (Schulz 2004). Nonpoint-source pollution through runoff, drainage and spray drift accounts for a majority of all surface water pollution (Zaring 1996). During peak application of pesticides in a watershed, a mixture of numerous substances may be transported to the waterbodies (Schulz 2004, Battaglin and Goolsby 1999, Thomas *et al.* 2001).

As an integrated part of the EU Life project ArtWET (Gregoire *et al.* 2009), we focus on the role of vegetation in optimizing the potential of agricultural ditches and detention ponds for pesticide mitigation. In the present study, the focus was set on the development of a simple and user-friendly tool to assess the risk of pesticide pollution in small streams

following a rainfall-related runoff event and possible mitigation measures to reduce this risk.
To assess the exposure and potential risk of adverse effects, modified OECD-REXTOX and USDA Curve number models were combined. The REXTOX (Ratio of EXposure to TOXicity) indicator is a mechanistic model, using direct, unscored values for all its input variables. It was developed from european indicators to assess trends in acute risk to aquatic ecosystems and is proposed by the OECD (Organisation for Economic Co-operation and Development)(Probst *et al.* 2005, OECD 2000).
SCS Curve number (CN) model is commonly used to predict the division of precipitation in surface runoff and infiltration (Mockus *et al.* 2004). The CN is a function of Landuse and hydrologic soil type. High CN represents areas with high runoff and low infiltration (Zhan and Huang 2004). Risk of adverse effects can be assessed with toxic units.
The toxic units (TU) approach is a feasible method to predict adverse effects of single substances and complex chemical mixtures on the structure an functioning of aquatic ecosystems (Junghans *et al.* 2006, Peterson 1994, Sprague 1970) and act as a basis for benchmarking mitigation measures.
There are several mitigation measures reducing effects of pesticide pollution in the aquatic ecosystem. Reduction of the pesticide amounts applied in the agricultural area is a simple and effective measure to reduce risk of exposure. Vegetated buffer strips belong to the best studied management measures (e.g. Schulz 2004, Reichenberger *et al.* 2007, Zhang *et al.* 2010, Pätzold *et al.* 2007, Otto *et al.* 2008). Vegetated buffer strips as risk mitigation measure for runoff-related pesticide pollution are part of the regulatory framework in several European countries (FOCUS 2007). In Germany for 5 m, 10 m and 20 m wide densely vegetated buffers, a 50%, 90% and 97.5% pesticide reduction is assumed (Grossmann 2008). The width of densely vegetated buffer strips as parameter influencing the pesticide runoff are already included in the REXTOX model as an exponential term. Vegetated areas within agricultural headwaters were proposed as best management practice mitigating pollution that already reached the waterbodies (Schulz 2004, Gregoire *et al.* 2009). Effectiveness of vegetated treatment systems (VTS) was studied in several experiments and tracer studies (Lange *et al.* 2011, Gill *et al.* 2008, Gregoire *et al.* 2010, Elsaesser *et al.* 2011, Stehle *et al.* 2011). Based on the results of the ArtWET Project and the meta-analysis by Stehle *et al.* (2011) this measure is implemented in the mitigation module.

2. Data and methods

2.1. *Geodata*

Basis of the simulation is a geodata layer, which contains all agricultural areas within a buffer zone of 50 m around European streams. Most of the source data is available from the open access data portals of the European Commission Joint research center. The edges of the resulting polygons are the intersection of all attribute layers. The attributes are described in Table 1.

The type of agriculture was extracted from the landuse information of the Corine Land Cover Database (Büttner 2007). Geometric accuracy of the CLC data is better than 100 m, thematic accuracy is greater than 85%. The Data was reclassified to the classes of the ArcCN-Runoff tool (Zhan and Huang 2004).
Hydrological soil types are not available directly from the European soil database. Nevertheless all information needed to classify the european soils are given. Layers of the

Table 1. Geodata

Attribute	Unit	Conversion	Source	Reference
Type of agriculture		n	Corine Land cover	Büttner (2007)
Hydrological soil type		y	Soil database	Panagos (2006)
Slope	%	y	SRTM	Farr *et al.* (2007)
Discharge	L/s	n	Hydrosheds	Lehner *et al.* (2008)
OC in topsoil	%	n	Soil Database	Panagos (2006)
Length of river segments	m	y	EC-JRC, IES	Vogt *et al.* (2007)
CN		y	USDA	Zhan and Huang (2004)
Plant interception	%	n		Linders *et al.* (2000)

soil database (ESDB) from the European Commission's Joint Research Centre, Institute for Environment and Sustainability (Panagos 2006) were reclassified and joined to meet the classification of the Natural Resources Conservation Service of the U.S. Department of Agriculture (NRCS) (Mockus *et al.* 2004, Neilsen and Allen T. Hjelmfelt 1998). The weighting of the different layers was done by the attributes of ESDB described in Table 2. To meet the classification of the NRCS the reclassified soil texture was weighted with factor 3 and the three attributes of depth were weighted with factor one each. The hydrological soil group of areas with an existing drainage system and fine or very fine surface texture was upgraded to the group with the next lower runoff potential using the information from the layer of the water management system (Table 2).

Table 2. Input data for the classification of the hydrological soil type

Attribute	Layer of the sdb	classes	Weight
Dominant surface texture	TEXT	7	3
Depth to an impermeable layer	DIMP	2	1
Depth to a gleyed horizon	DGH	4	1
Soil water regime	WR	5	1
Water management system	WM1	8	-

Slope data was modeled with ArcGIS Spatial Analyst (esri ArcGIS 9.3) based on SRTM elevation data (Farr *et al.* 2007). The mean slope values in percent of all squared 100 m cells which intersect the polygons of the 50 m buffer were written to the geodatabase.
Discharge values were taken from the Hydrosheds database (Lehner *et al.* 2008). Maximum, minimal and mean discharge values in hectoliters per second were written in separate columns to the geodatabase.
Percentage of organic carbon in topsoil was extracted from the ESDB (Panagos 2006).
The Polyline river Database (Vogt *et al.* 2007) was dissolved to one single line and divided everey 1000 m. The resulting polyline was buffered with a width of 50 m and the ArtWET Database was clipped with the resulting layer. The lengths of segments were calculated within the divided river polyline and joined by spatial location to the clipped ArtWET dataset.
Curve numbers (CN) were calculated based on landuse and hydrogroup using the ArcCN-Runoff tool (Zhan and Huang 2004) with the curve number databases of the AnnAG-NPSmodel (Bingner *et al.* 2010).

2.2. *Pesticide and Event Data*

To run the simulation, some further parameters of the pesticide compound to be used and the rain events under consideration needed to be defined as input variables for the model (Table 3).

Table 3. Pesticide and rainfall-related variables for simulation

Variable	unit	Source
Season	-	-
Width of buffer strips	m	-
Precipitation amount	mm	Weather or climate data
Precipitation duration	minutes	Weather or climate data
Pesticide: applied amount	g/ha	Pesticide registration
Pesticide: DT_{50}	days	PPDB (2011)
Pesticide: K_{OC}	mL/g	PPDB (2011)
Pesticide: toxicity	μg/L	PPDB (2011)

2.3. *Exposure model*

The models were programed in ESRI ArcGIS Model builder. The exposure model consists of ten consecutive modules (Figure 1). In module a the input Dataset is clipped with a selected area of simulation. After calculating fields of the parameters precipitation and season, the plant interception based on Linders *et al.* (2000) is calculated with the information of crop type and season in module b. The discharge in the waterbody is calculated in module c, based on season and data taken from hydrosheds (Lehner *et al.* 2008). After writing the fields for the parameters bufferstrips, toxicity, DT_{50} , and K_{OC} , the Kd is calculated in module d by dividing the K_{OC} by the Content of organic carbon in topsoil. The amount of rainfall contributing to surface runoff (QRunoff) is calculated in module e (Eqn. 1).

$$Q_{Runoff} = \frac{25.4 * (CN * (\frac{P}{2.54} + 2) - 200)^2}{CN * (CN * (\frac{P}{2.54} - 8) + 800)} \qquad (1)$$

Q_{Runoff} is the contribution of rainfall to surface runoff in mm, CN is the runoff Curve Number (Zhan and Huang 2004) and P is the precipitation in mm

The percentage of applied peticide amount within the surface runoff is calculated in module f using the modified REXTOX model (Probst *et al.* 2005), that was proposed by the OECD(OECD 2000):

$$L_{Runoff} = \frac{Q_{Runoff}}{P * 10} * e^{-3 * \frac{\ln 2}{DT_{50}}} * \frac{1}{1 + Kd} * (1 - \frac{Pli}{100}) * slope * 0.83^{Buffer} * 100 \qquad (2)$$

L_{Runoff} is the percentage of applied substance in runoff, DT_{50} is the half life in days of applied substance in soil, Kd is the soil-water partitioning coefficient, Pli is the plant interception. Values were extracted from literature for combinations of crop types and growing stages (Linders *et al.* 2000), *slope* is the slope factor calculated using the methods of Probst *et al.* (2005) and *Buffer* is the mean width of a buffer strip, which is assumed to be densely vegetated. A fixed time intervall of three days between

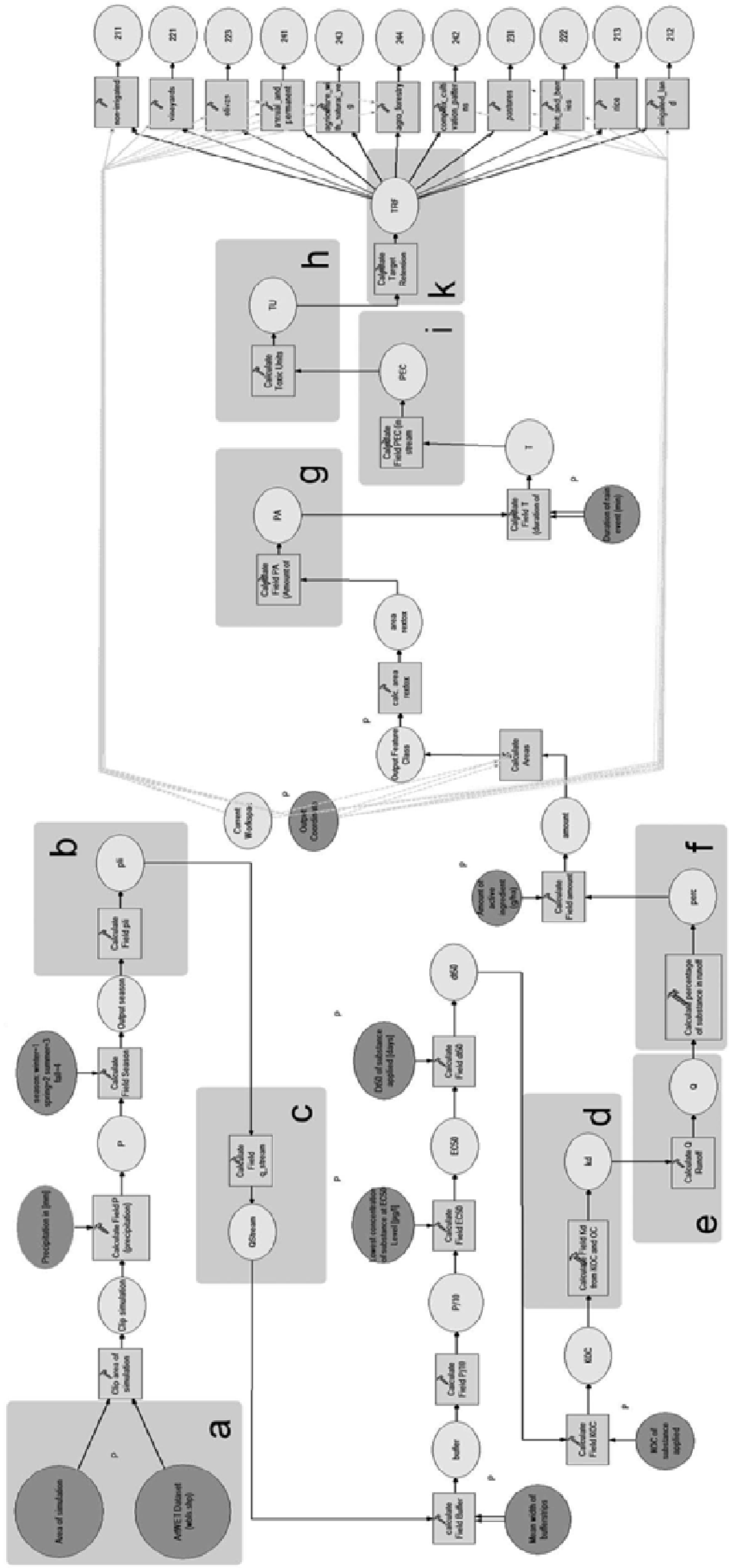

Figure 1: Structure of the exposure tool.

application of the pesticide and rain-related runoff is implemented in the exponent of the second term of the equation.

The parameter "amount of active ingredient" and the calculated areas of the single polygons of the dataset, are used to calculate the amount of substance applied on field in module g. In module h the concentration of the substance in stream is calculated with the second part of the REXTOX model(Eqn. 3) The percentage of applied amount within the surface runoff is calculated in module f using the modified REXTOX model (Probst *et al.* 2005):

$$PEC = L_{Runoff} * PA * \frac{1}{Q_{Stream} * T * 60} \tag{3}$$

PEC is the predicted in stream peak concentration in g/L, PA is the amount of substance applied in the simulation area in g, Q_{Stream} is the discharge of waterbody in L/s and T is the duration of rain event in minutes

Acute toxicity data of the substances for fish, algae and aquatic invertebrates can be used to assess potential toxicity of the substance based on toxic units. Toxic units are calculated in module i for each peak concentration of the substance. Specific LC50 or EC50 values for acute toxicity to *Oncorhyncus mykiss* (Walbaum)(fish LC50 96 hours), *Daphnia magna* (Straus)(aquatic invertebrate EC50 48 hours), algae (EC50 growth 72 hours) can be found in the Footprint Pesticide Properties database (PPDB 2011). The TUs are calculated using Eqn. 4 (Peterson 1994, Junghans *et al.* 2006):

$$PTU = \frac{PEC}{EC_{50}} \tag{4}$$

where PTU is the potential toxicity in toxic units and EC_{50} is the lowest effect concentration

The PTU value is used in module k to derive a target retention factor (TRF). The TRF describes a percentage of reduction of peak concentration, which is needed to reduce the simulated pollution to a value below 0.01 toxic units. After the last calculation the result is split into polygon layers each containing the areas of different crop types to allow the use of the mitigation tool for single crops.

2.4. *Mitigation model*

The mitigation tool was built to quantify the resources needed for the implementation of possible mitigation measures. Based on the review of Schulz (2004) and Reichenberger *et al.* (2007) three types of mitigation measures were integrated into the tool. As on-site mitigation measure the amount applied can be reduced to meet the mitigation target, as edge of field measure the vegetated buffer strip can be broadened to retain the pollutant and as end of pipe measure vegetated treatment systems (VTS) can be installed to mitigate the pollution before it reaches receiving aquatic ecosystem (Figure 2).

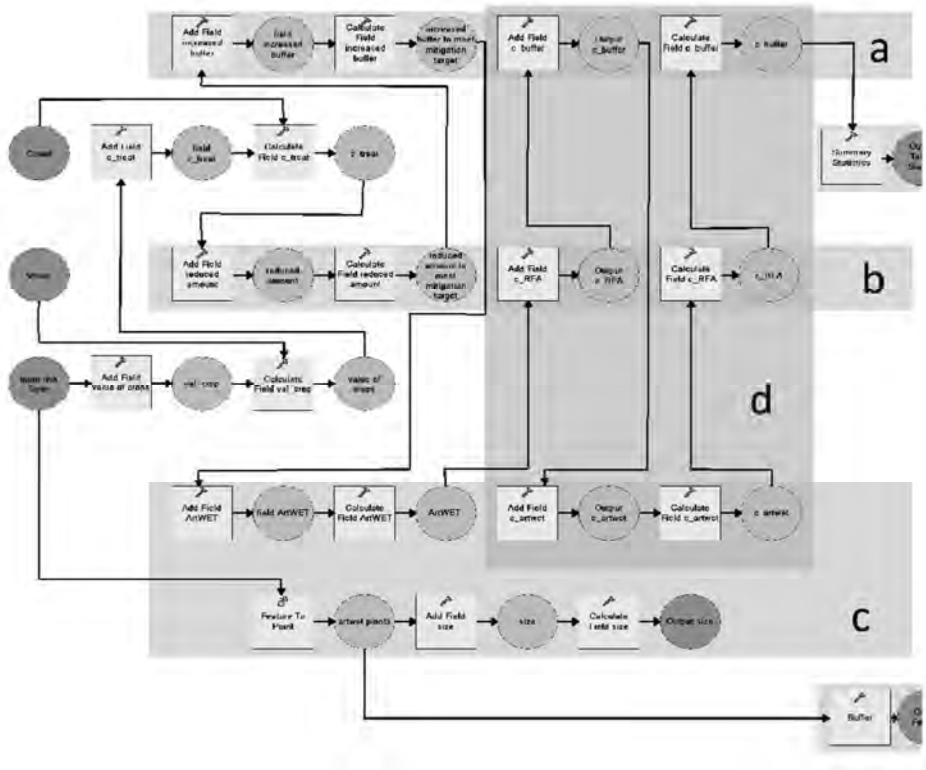

Figure 2. Structure of the mitigation tool.

mark (Eqn. 5).

$$RFA = \frac{EC_{50} * Q_{Stream} * T * 60}{L_{Runoff}} \tag{5}$$

RFA is the reduced amount of pesticides applied on the crop in g/ha and A is the area of the segment in m^2

The broadening of existing densely vegetated buffer strips between the waterbody and the agricultural area is easily implemented by rearranging formula 4 with a PTU of 0.01 for all segments of the waterbody where the PTU exceeds the 0.01 benchmark (Eqn. 6).

$$Buffer_{increased} = \log_{0.38} \frac{0.06 * P * (1 + Kd) * Q_{Stream} * T * EC_{50}}{Q_{Runoff} * e^{-3 * \frac{ln2}{DT_{50}}} * (1 - \frac{Pli}{100}) * PA * slope} \tag{6}$$

$Buffer_{increased}$ is the width of densely vegetated buffer strips to mitigate the simulated pesticide pollution.

To calculate the size of optimised VTS that is needed to meet the mitigation target, a model was built with experimental and monitoring data of the ArtWET project. Influence of system, pesticide and event properties were analysed regarding their influence in reduction of pesticide peak concentration for demonstration prototypes of the project ArtWET (Gregoire *et al.* 2009, Stehle *et al.* 2011). Linear regression analysis identified plant density and size-related variables of vegetated treatment systems as central predictors. Based on those results the surface area of VTSs with a depth of 50 cm and a plant density of more than 90% is calculated with Eqn. 7. The areas of the VTS for each subwatershed are summed up and a circular polygon representing the size of the resulting wetland is built.

$$VTS = \sum TRF * 187 * 3 \tag{7}$$

VTS is the modelled surface area in m of the VTS with an plant density of 90% and a depth of 50 cm.

2.5. *Mitigation model: costs*

The costs for each mitigation measure at all segments exceeding the 0.01 PTU are calculated using the equations 8 -10.
The cost for the reduced field amount is calculated with the annual cost for pesticide treatment (C_{treat}) and the annual contribution margin for crop (V_{crop}), which is the value of crops minus fixed costs, as variables (Eqn. 8).

$$C_{RFA} = ((1 - \frac{L_{crop}}{100}) * TRF * V_{crop} * A/10000) - (RFA * C_{treat} * A/10000) \tag{8}$$

C_{RFA} is the profit setback following the reduction of applied amount,L_{crop} is the factor for loss of yield without pesticide application, V_{crop} is the annual contribution margin for crop €/ha and C_{treat} are the annual costs for pesticide treatment €/ha.

Those input variables differ for each crop and region and may be obtained from national and international statistical offices. A loss of 30 % of the yield is assumed when no pesticide is applied. This mean loss of yield was estimated by comparing yields of conventional agriculture and organic farming for ten different crops (Paller and Prankl 2008). A security factor of 1.4 was applied (Eqn. 9)(see supporting material).

$$L_{crop} = \frac{\sum 1.4 * (100 - Y_o/(0.01 * Y_c))}{n_{crops}} \tag{9}$$

Y_o is the yield of crop with organic agricultural practice (kg/ha), Y_c is the yield of crop with conventional agricultural practice (kg/ha) and n_{crops} is the number of different crops.

The cost for the widening of the existing buffer strip is calculated based on the area lost for these buffers and the building and maintaining costs which are implemented as fixed annual amount of 1 €/m^2 in the last term of Eqn. 10

$$C_{buffer} = (V_{crop} * Buffer_{increased}/10) - (C_{treat} * Buffer_{increased}/10) + Buffer_{increased} \tag{10}$$

where C_{buffer} are costs and profit setback following the increasing of buffer strips in €.

The cost for VTSs are also calculated based on the area loss and implementation and maintainance costs. Here an annual amount of 2 €/m^2 for depreciation and management is used in the last term of Eqn. 11

$$C_{VTS} = (VTS * V_{crop}/10000) - (VTS * C_{treat}/10000) + (VTS * 2) \tag{11}$$

where C_{VTS} are costs and profit setback for the installation of VTS in €.

All costs and the area need for the different measures are summed up and stored as database-file (.dbf) in the project folder.

2.6. *Graphical user interface*

The stylesheets of the user interface and the documentation are clearly stuctured and all variables are explained to simplify the application of the tool(Figure 3 and Figure 4). The documentation and help files were translated in English, German, French and Italian (Figure 3).

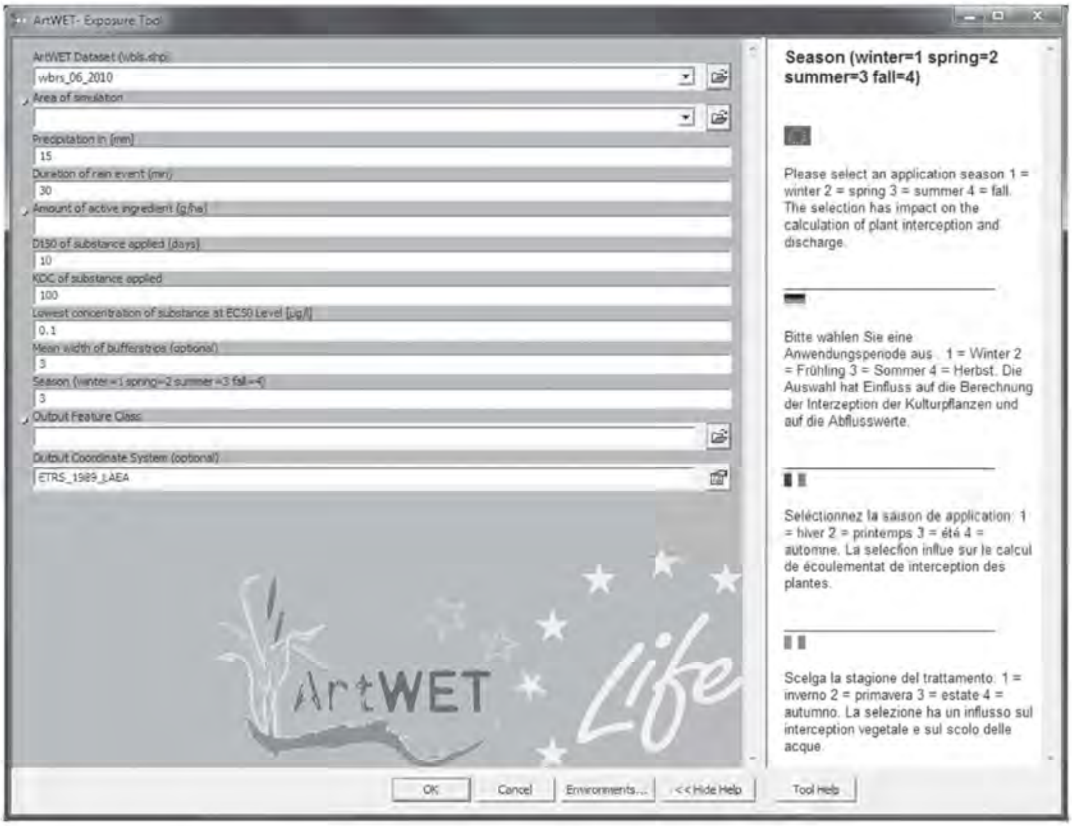

Figure 3. Graphical user interface of the exposure simulation tool.

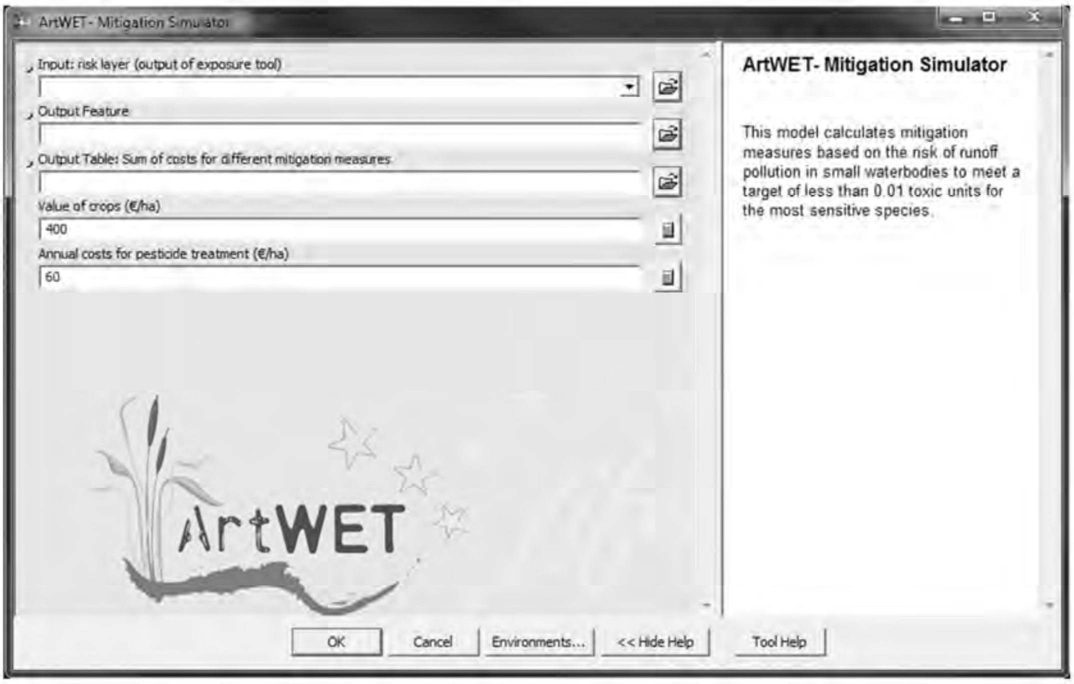

Figure 4. Graphical user interface of the mitigation simulation tool

3. Results and discussion

Verification of all modules was done.
Sensitivity index (Jorgensen 1995) was calculated for the REXTOX model by Probst *et al.* (2005) when it is used to predict losses from one homogenous patch of arable land. Parameters buffer width and plant interception showed highest sensitivity. Regarding the high sensitivity of the model on the buffer width it has to be taken into account that use of a buffer value in simulation runs may lead to underestimation of risk. Efficiency of buffer strips as mitigation measure is discussed contoversely in literature (Bereswill *et al.* 2011, Reichenberger *et al.* 2007, Schulz 2004). The buffer term in the present model is based on preconditions of absence of preferential flow through the strip, absence of gutters and paved paths as drainage systems and uniform distribution of the runoff water into as well as laminar sheet flow within the buffer strip.

Runs with several commonly used pesticides show a realistic range of runoff pollution and potential toxicity values for the exposure model. The range of peak concentrations are comparable to concentration levels of fungicides detected in agricultural surface water following runoff or spray drift events (Berenzen *et al.* 2005, Gregoire *et al.* 2010, Rabiet *et al.* 2010, Schäfer *et al.* 2011). Particularly small streams with low discharge show a high risk of adverse effects figure 3). To perform a validation further monitoring data for all regions of the European Union is needed. Nevertheless the risk of pollution after runoff events is clearly displayed (Figure 6).
Effectiveness of mitigation measures show a dependance on magnitude of pollution and properties of the waterbodies.
Due to their relatively low need of space but high cost for installation VTS are reasonable in areas of high-value crops like orchards and vinyards. For crops with lower contribution

margins widening of buffer strips and reduction of amounts are the better options. An example of results for mitigation measures is showed in Figure 5.

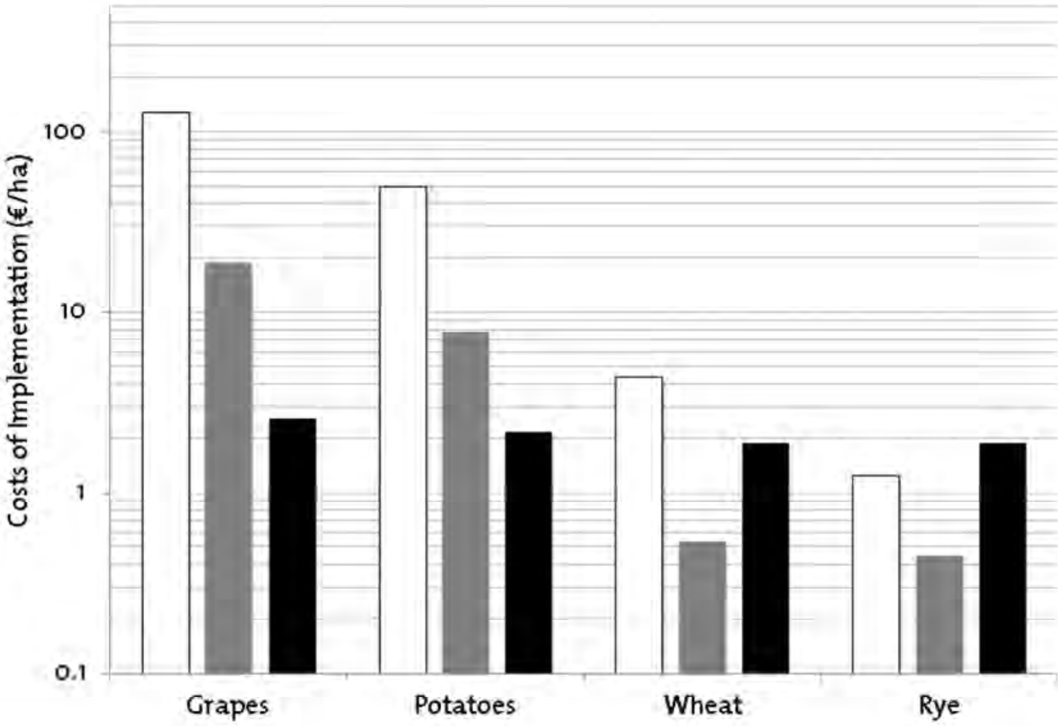

Figure 5. costs of the mitigation measures for crops with different contibution margins. The white bars represent reduced amount applied, the gray bars represent the widening of densely vegetated buffer strips and the black bars represent the implementation of VTS.

Limitations of the model are mainly given by the quality of the source data. Especially the low resoluted landuse data (approx. 90x90 m raster cells) and values for the discharge in small streams during rain events could lead to inaccurate results. To deal with these uncertainties the database has to be updated regularly and ground truthing for selected regions has to be performed. The mitigation tool gives an estimation of size and costs of possible measures. The user has the resposibility to interpret the results. Depending on the input dataset mitigation measures are calculated for different land uses with full application on all agricultural areas. The results for the costs of the vegetated buffer strips and VTS are affected by the annual maintainance and building costs of the structures. If there are a lot of roads along the streams, the costs for building new structures can easily exceed the amount of 1, respectively 2 €that are implemented in the model. In addition to the uncertaincies in the costs, there are also differences in the performance of the buffer strips. The model calculation is based on densely vegetated bufferstrips without any preferential flow paths or gaps. Moreover, implementation of the measures may lead to higher or lower costs, depending on the location. VTS and buffer strips don't necessarily have to be located within agricultural land.

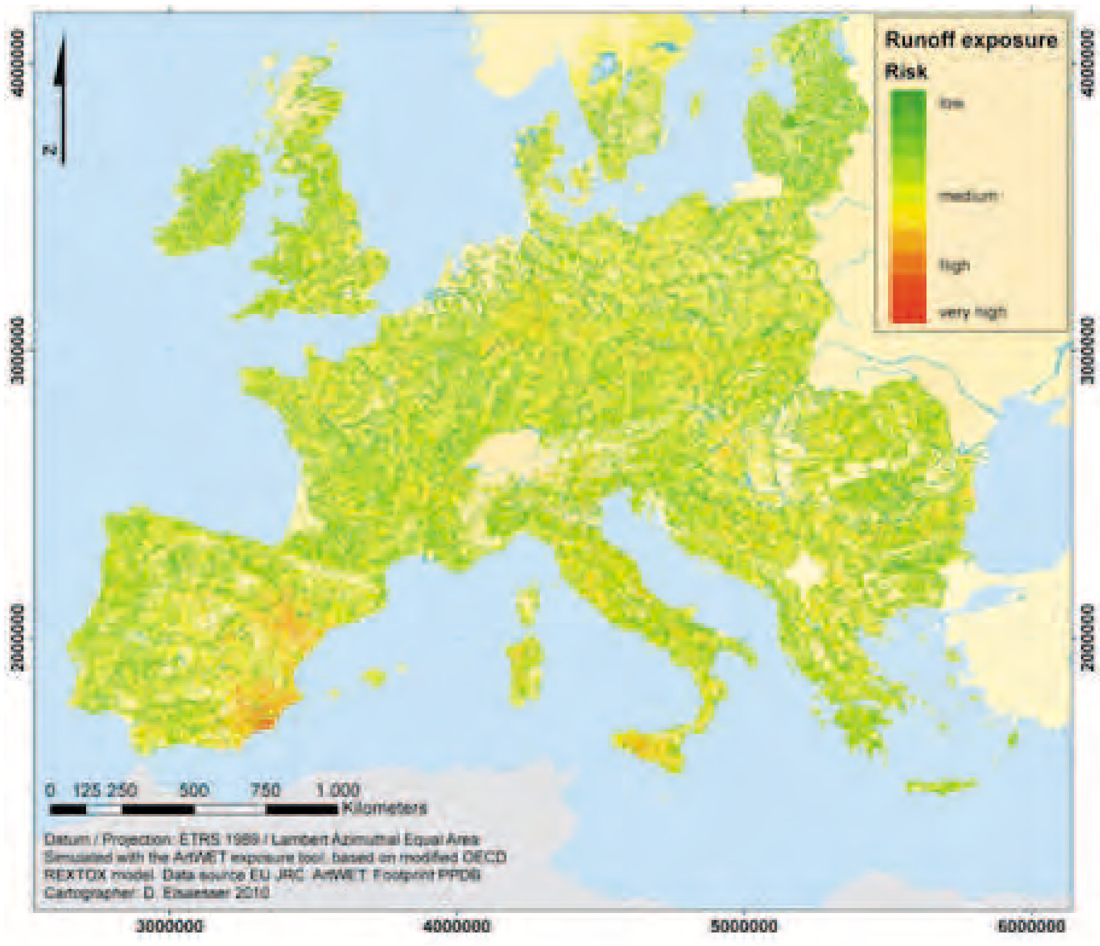

Figure 6. Run of the tool with the herbicide isoproturon: application amount of 700 g/ha, precipitation of 10 mm in 30 minutes and season summer

4. Conclusions

The ArtWET risk of runoff exposure model is a promising tool to assess runoff derived pesticide pollution in regional scale. At this stage the model gives a clear output of runoff risk. To validate the quantitative results of simulations with the model on European level an extensive study has to be performed with data from runoff monitoring for all European regions.

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IV. Publication record

Peer reviewed Publications related to the study

Elsaesser, D. and R. Schulz (2010), The ArtWET tool: a Georeferenced Approach Assessing Runoff Related Pesticide Pollution in Surface Waters across Europe, In: Behr, Franz-Josef, Pradeepkumar, A. P., Beltrán Castanón, C. A., Applied Geoinformatics for Society and Environment, Stuttgart University of Applied Sciences, Volume 109, 65-70.

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Elsaesser, D., C. Stang, R. Schulz (2011), Influence of vegetation density on mitigation of a pesticide mixture in experimental stream mesocosms. **submitted to** Water Science and Technology

Elsaesser, D., C. Stang, R. Schulz (2011), Mitigation of agricultural nonpoint-source fungicide pollution in detention ponds and vegetated ditches, **submitted to** Chemosphere.

Elsaesser, D. (2011), Risk map of runoff-related pesticide pollution in small rivers of the European agricultural landscape. **submitted to** Journal of Maps.

Elsaesser, D., R. Schulz (2011), A spatial decision support system for mitigation of runoff related pesticide pollution in surface waters across Europe, **submitted to** International Journal of Geographical Information Science.

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Conference contributions

Elsaesser, D., E. Hauck and R. Schulz (2007): Mitigation of Pesticide Pollution in Vegetated Agricultural Surface Waters: The Role of Vegetation. Oral presentation at the Wetland Pollutant Dynamics and Control Conference, Tartu, Estonia, September 2007.

Elsaesser, D. A. Geist and R. Schulz (2009): Mitigation of pesticide pollution in an experimental vegetated surface flow constructed wetland system. Oral presentation at the Wetland Pollutant Dynamics and Control Conference, Barcelona Spain 2009.

Elsaesser, D. and R. Schulz (2010): A spatial decision support system for mitigation of runoff related pesticide pollution in surface waters across Europe. Oral Presentation at the Scientific Meeting: Mitigation of agricultural nonpoint-source pollution and phytoremediation in artificial wetland ecosystems in Landau, Germany, June 2010.

Elsaesser, D. and R. Schulz (2010): The ArtWET tool: a Georeferenced Approach Assessing Runoff Related Pesticide Pollution in Surface Waters across Europe. Oral presentation at the AGSE Conference in Arequipa, Peru August 2010.

Stang, C., Elsaesser D., Schulz R (2009): Flow-through vegetated ditch mesocosm for estimating mitigation potentials of agricultural non-point source pollution. Poster presentation at the Wetland Pollutant Dynamics and Control Conference, Barcelona, Spain, September 2009.

V. Erklärung

Hiermit versichere ich, dass ich die eingereichte Dissertation

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David Elsaesser

Landau, 13.10.2011

VI. Curriculum vitae

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April 2002 – Mar 2007	Studies of environmental sciences at the University of Koblenz-Landau, Campus Landau, Germany. Diploma thesis: GIS-gestützte Spätfrostanalyse –Möglichkeiten der Geländegestaltung im Rahmen der Rebflurbereinigung Neustadt Duttweiler
Dec 2006 – Apr 2007	Contract work at the University of Koblenz-Landau: Geodata-Based Probabilistic Risk Assessment and Management of Pesticides in Germany
Since Jul 2007	Scientist at the Institute for Environmental Sciences at the University of Koblenz-Landau. Project ArtWET: Mitigation of agricultural nonpoint-source pesticides pollution and phytoremediation in artificial wetland ecosystems

VII. Supporting material on DVD

- Digital version of the thesis
- GIS-Dataset (V. 2.1, Oct. 2011).
- ArcGIS Toolbox: ArtWET-DSS with Exposure Tool and Mitigation Simulator (V. 2.1, Sept. 2011).
- Risk map of runoff related pesticide pollution in small surface waters across Europe.
- Pesticide monitoring Data for detention ponds and vegetated ditches in the Southern Palatinate/Germany (2006-2009).
- R-Statistics Scripts
- Digital Versions of all related publications.