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# Modeling ecological risk of runoff for benthic invertebrates in agricultural landscapes

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# Modeling ecological risk of runoff for benthic invertebrates in agricultural landscapes

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## Vorveröffentlichungen der Dissertation

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### *Tagungsbeiträge*

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Schriever, C. A., Von der Ohe, P. C. and Liess, M., 2005. Linking agricultural intensity to the observed biological quality in small streams. Oral presentation, 15$^{th}$ Annual Meeting of the Society of Environmental Toxicology and Chemistry Europe (SETAC Europe), Lille, France.

Schriever, C. A., Brown, C. D., Maltby, L., Van den Brink, P. J. and Liess, M., 2005. Untersuchung der Freilandrelevanz von aktuellen Ansätzen zur aquatischen Risikobewertung von Insektiziden. Oral presentation, 10$^{th}$ Annual Meeting of the Society of Environmental Toxicology and Chemistry Europe – German-Language-Branch (SETAC-GLB), Basel, Switzerland.

Schriever, C. A., Schäfer, R. B. and Liess, M., 2006. Mapping European risk of runoff. Poster, 16$^{th}$ Annual Meeting of the Society of Environmental Toxicology and Chemistry Europe (SETAC Europe), The Hague, The Netherlands.

Since all models are wrong, the scientist must be alert to what is importantly wrong.

G.E.P. Box, 1976

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My parents for their indispensable support and their boundless faith in me.

## Summary

Pesticide runoff from arable land is a major stressor for stream invertebrate communities and is an issue that needs to be addressed at broader scales to meet the environmental objectives of the Water Framework Directive. This thesis introduces and validates for selected regions a large-scale screening model that enables identifying both hot spots of pesticide runoff and, for the first time, hot spots of ecological risk that result from pesticide runoff. The elements of the screening approach (generic simplified runoff model, field-based exposure-response relationship for benthic macroinvertebrates considering the influence of landscape-mediated recovery potential) as well as its application and validation for the European scale are presented in four consecutive chapters. The screening model is based on a generic indicator termed runoff potential (RP) that indicates the potential exposure of stream sites to pesticide runoff due to key environmental factors of land use, precipitation, topography, and soil type. In chapter II, the indicator was validated by comparing RP values calculated for 20 small streams with runoff-induced pesticide concentrations that were measured in the streams during three years. Usually, toxicity data from lab to field studies are used to model effects of pesticide exposure. In chapter III, a case study was conducted to compare exemplarily outcomes of three current effect models with observed effects of brief, high-level insecticide exposure on a stream invertebrate community. The study underlined the value of long-term (semi)field studies, since the model outcomes based on this kind of studies predicted observations more appropriate than model outcomes based on standard toxicity data. Therefore, the screening approach presented in this thesis uses an exposure-response relationship that was established between modeled RP and monitored benthic invertebrate communities at 360 stream sites (chapter IV). A biological indicator system of species at risk from pesticides (SPEAR) was applied on the macroinvertebrate data, which revealed that the percentage SPEAR abundance decreased as RP increased. However, at sites with undisturbed upstream stretches (i.e. potential recolonization pools), the percentage SPEAR abundance at all levels of RP was equal or greater than at sites of low RP and without such stretches. Chapter V demonstrates the application of the screening model to characterize the ecological risk of runoff at the European scale with respect to landscape-mediated recovery potential. Punctual comparisons to field observations on pesticide effects from Finish, French, and German agricultural streams showed that predicted ecological risk was in good accordance with the observed field situation. In conclusion, this thesis demonstrates the value of simplified runoff modeling and field-based exposure-response relationships for an appropriate ecological risk characterization at broader scales.

## Contents

## Abbreviations

| | |
|---|---|
| %SPEAR abundance | Percentage abundance in a benthic macroinvertebrate community that is made up by SPEAR |
| $EC/LC50_{D}i$ | Median effect/lethal concentration of substance i for Daphnia magna |
| EC50 | Median effect concentration regarding immobility |
| EU-15 | European Union before the 2004 enlargement |
| FA | Fraction affected, fraction of species in a community that is affected by a given concentration of a contaminant |
| HC5 | Hazardous concentration, concentration at which 5% of SSD species will not be affected above the corresponding effect level (e.g., EC50) |
| LC50 | Median lethal concentration |
| $R_{Loss}$ | Runoff loss, measured pesticide runoff (standardized) |
| RP | Runoff potential, modeled runoff inputs at a given stream site due to environmental factors of land use, topography, soil, and precipitation |
| $R_{Toxicity}$ | Runoff toxicity, measured pesticide runoff expressed in Toxic Units |
| SPEAR | Species at risk, species that are potentially affected by pesticides due to physiological sensitivity to organic toxicants and ecological traits (generation time, migration ability, presence of aquatic stages during the main period of pesticide application) |
| $SPEAR_{(ecology)}$ | Species that are potentially at risk from pesticides when only ecological traits are considered |
| $SPEAR_{(physiology)}$ | Species that are potentially at risk from pesticides when only physiological sensitivity to organic toxicants is considered |
| SSD | Species Sensitivity Distribution |
| $TU_i$ | Toxic Unit, concentration of substance i divided by the related median effect/lethal concentration for Daphnia magna |
| $TU_{st}$ | Toxic Unit that is calculated for the most sensitive standard test organism |

# Chapter I. Introduction

## 1 Ecological effects of diffuse surface water pollution in agricultural landscapes

### 1.01 Relevance of different entry routes for agricultural pollutants

In this thesis, a screening procedure is introduced and validated for selected regions, which was developed to predict the aquatic ecological risk of agricultural runoff at the European scale. The idea of this screening procedure is to combine existing environmental data and simplified modeling for risk characterization. This introductory chapter gives the scientific background for addressing ecological risk of runoff and shortly outlines the need for a large-scale procedure to characterize ecological risk with respect to current legal framework. The challenges of field-based risk characterization at the landscape level are delineated as well as potential approaches to deal with those issues.

Diffuse pollution from agricultural sources is a major pressure on water quality of surface waters, because water bodies that drain arable land receive input of nutrients, agrochemicals and eroded sediment via different pathways (Cooper, 1993). Surface water runoff is the pathway that transports dissolved nutrients and pesticides, while erosive runoff transports both the dissolved fraction of these substances and the particle-bound fraction that is adsorbed to eroded soil. Subsurface flow is another pathway to transport dissolved nutrients and pesticides from arable land, and spray drift during application may contribute as well to diffuse pollution with pesticides. The relevance of these pathways with respect to resulting loads in water bodies varies between substances. Surface water runoff is more relevant in terms of phosphorus losses from arable land (Sharpley et al., 2001), while the gross of nitrogen losses occurs via subsurface flow (Logan et al., 1994). The gross of applied pesticides is lost from arable land via surface water runoff (Wauchope, 1978; Van der Werf, 1996), while losses via subsurface flow (Logan et al., 1994; Bach et al., 2000) or spray drift (Kreuger, 1998; Bach et al., 2000) have been reported to be less relevant. As a result, surface water runoff can be considered as the major pathway for the sum of agricultural pollutants to enter surface waters.

### 1.02 Ecological consequences of agricultural diffuse pollution

In the last decades, several monitoring studies were conducted in the field to address the potential consequences of agricultural practice for the ecological quality of surface waters. In these studies, streams without agricultural activities in their vicinity and streams draining arable land were compared concerning water quality parameters and aquatic communities. Usually, benthic macroinvertebrates were monitored as representatives of the aquatic community, since this group of freshwater organisms is widespread in streams of different size and includes important members of aquatic food webs (Cuffney et al., 1984; Wallace and Webster, 1996). Most of the studies investigated few stream sites only and long-term studies on agricultural streams (Wallace et al., 1993) are scare.

The monitoring studies showed that agricultural diffuse pollution caused deterioration of water and structural habitat quality, and that agricultural alteration promoted relatively homogeneous macroinvertebrates assemblages that were capable of tolerating agricultural nonpoint source pollution (Delong and Brusven, 1998). Benthic macroinvertebrate communities at polluted sites were demonstrated to be significantly different from sites that were undisturbed in terms of agricultural activities as is illustrated in the following studies. Increased nutrient levels were found to correlate with shifts in macroinvertebrate species composition (Dance and Hynes, 1980; Lenat, 1984; Lecerf et al., 2006) Fine sediment deposition was demonstrated to result in habitat loss due to decreased substrate stability and interstitial volume (Cobb and Flannagan, 1990; Wood and Armitage, 1997). Fine sediment suspension was suggested to cause adverse effects on macroinvertebrates, when species were long-term exposed (Newcombe and MacDonald, 1991). Pulsed short-term exposure to fine sediment suspension could not be demonstrated to affect this group of organisms (Fairchild et al., 1987; Anderson et al., 2006). Increased insecticide levels were reported to constrain population densities in comparison to less impaired sites (Leonard et al., 1999). Short-term insecticide exposure in headwater streams was reported to result in a significant reduction in the abundance of macroinvertebrates in most families of investigated communities (Sibley et al., 1991) as well as in a significant decrease in taxonomic richness (Liess and Schulz, 1999). Moreover, the macroinvertebrate community composition in streams that were characterized by measured pesticide contamination in the range of acute toxicity to *Daphnia magna* was demonstrated to differ significantly from the composition of minimally impacted sites (Berenzen et al., 2005a).

## 2 Characterizing ecological risk at large scales

### 2.01 The need for large-scale approaches due to legislative framework

Increased levels of nutrients and pesticides in water bodies as well as concerns about potential adverse effects on water quality and aquatic organisms gave rise to several legislative acts of the European Union. Examples are the Nitrate Directive 91/676/EEC (EEC, 1991a) and the Plant Protection Products Directive 91/414/EEC (EEC, 1991b) that requires risk assessment for pesticides to demonstrate that '... under field conditions no unacceptable impact on the viability of exposed organisms...' occurs. The Water Framework Directive (WFD) now incorporates the aims of earlier directives into a broader concept for the sustainable use of water resources by integrated river basin management (EC, 2000). One of the environmental objectives of the WFD is to achieve and maintain a good chemical and ecological status of surface water bodies within river basins. This objective requires to determine the chemical and ecological status of surface waters and to identify areas of concern ('hot spots'), where anthropogenic pressures on water bodies are strong and may result in deterioration of water quality. Water monitoring programs are indispensable to identify such hot spots in river basins. In addition, large-scale screening procedures can be helpful, because they enable for a first quick and cost effective location of hot spots. The outcomes of these screening procedures can help to target regional monitoring programs more efficiently.

### 2.02 Deficits of current approaches

Several screening approaches have been suggested to identify hot spots of diffuse pollution from agricultural sources at the European level. They are supposed to assess the vulnerability of landscapes to phosphorus losses (Heathwaite et al., 2003) or the nitrogen pollution of surface waters and groundwater from chemical fertilizers and manure (Giupponi and Vladimirova, 2006). Likewise, models are presented to characterize diffuse pesticide pollution of groundwater bodies (Tiktak et al., 2004) or the toxicological potential of pesticide mixtures in surface water systems (Finizio et al., 2005). These large-scale approaches characterize areas of concern with respect to potential contamination levels, but considerations about the potential ecological risk from contamination are not included yet. This owes to the instance that at broader scales little is known on exposure patterns and on exposure-response relationships, which are necessary to address ecological risks of agricultural pollution within landscapes. The results of field monitoring can provide valuable information on exposure levels and effects, but until now, there is a paucity of studies investigating the influence of agriculture on stream communities at larger scales (Liess and Von der Ohe, 2005). The scarcity of such large-scale studies may be attributed to logistical difficulties when operating at this scale and, of course, to the problems that have to be tackled in field studies at every scale:

(i) Characterizing spatio-temporal heterogeneity in exposure by appropriate monitoring programs or modeling,

(ii) the complexity of communities and the natural variation in community composition,

(iii) the difficulty of interpretation of cause and effect in the presence of a range of confounding factors (Cormier et al., 2000), an issue that was recently highlighted at a workshop of the Society for Environmental Toxicology and Chemistry (SETAC) on 'Effects of pesticides in the field' (Liess et al., 2005a).

### 2.03 Filling knowledge gaps

For assessing ecological risk at broader scales, it is necessary to bridge the knowledge gap on exposure-response relationships, which are field-based and can be considered as representative for a region of interest. One may fill this gap by making use of already existing information as described in the following. Regional authorities maintain environmental monitoring databases that contain extensive information on landscape parameters. In Germany, for example, regional authorities for surveying and mapping provide information on topography and land use that is stored in the Authoritative Topographic-Cartographic Information System (ATKIS, http://www.atkis.de). Soil data are provided by regional authorities for soil sciences, and various types of climate data can be obtained from the German Meteorological Service (DWD, http://www.dwd.de). Information from these databases (e.g., on land use patterns) can serve as a proxy for exposure levels or may be used for explicitly modeling exposure to diffuse pollutants (e.g., AGNPS (Young et al., 1989) or PRZM (Carsel et al., 1998)). Likewise, extensive aquatic biomonitoring databases for different groups of organisms are available such as for Lower-Saxony (Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz, NLWKN, http://www.nlwkn.niedersachsen.de). The biomonitoring data can be analyzed by calculating community descriptors (e.g., richness or composition measures (Barbour et al., 1999)) in order to typify the status of communities in different habitats. Combining the existing information on both exposure and aquatic communities offers the possibility for large-scale investigations on exposure-response relationships.

## 2.04 Challenges of large-scale approaches

Despite the value of large-scale investigations, the number of studies that analyze existing information is low (Potter et al., 2005; Probst et al., 2005). This may owe to the instance that these studies have to deal with the same problems that are associated with studies to collect new field data and that include in particular (i) appropriate exposure characterization and (ii) recognizing patterns in complex and variable communities.

For characterizing exposure, models are valuable tools, but modeling has to mind the scale of interest (Addiscott and Mirza, 1998). This means that highly parameterized models (e.g., PRZM (Singh and Jones, 2002)) may be well applied in small areas where extensive environmental data sets are available, while at larger scales parameter estimation may be hampered by the limited resolution and availability of required input data (Steinhardt and Volk, 2003). Thus, for larger scales the use of simplified models instead of complex ones is more appropriate. Although simplified models may not be accurate at the local scale, they enable an appropriate prediction of exposure patterns at larger scales (Klepper and Den Hollander, 1999).

For identifying effects, the complexity and natural variability of communities may obscure biological patterns and thus impede identifying links between those patterns and environmental parameters. Therefore, ways have to be found to deal with both complexity and variability. One way to recognize patterns in complex communities before the background of natural variability is to apply biological indicator systems. Such systems are built on observations that species occurrence is linked to characteristic habitat types and that species abundance increases towards the environmental optimum conditions (Braak and Prentice, 1998). Biological indicator systems use a priori knowledge on such preferences to classify selected species. The presence or abundance of the selected indicator species is then used to conclude on environmental gradients of stressors.

A simple metric that can give a general indication on levels of impairment in aquatic habitats is the presence and abundance of Ephemeroptera, Trichoptera, and Plecoptera (Ofenböck et al., 2004). These groups of macroinvertebrates were reported to be sensitive to different types of impairment: hydromorphological degradation (Hering et al., 2004), increased nutrient and sediment loads (Dance and Hynes, 1980; Harding et al., 1999), high metal and ion concentrations (Malmqvist and Hoffsten, 1999; Yuan and Norton, 2003). The earliest biological indicator system to address one particular stressor is the saprobic index (Kolkwitz, 1950) that indicates the level of organic pollution in water bodies by means of selected invertebrate species. Another example of the idea of invertebrates as indicators of specific stressors is the acidification index (Braukmann and Biss, 2004). Recently, another system based on macroinvertebrate species was developed to indicate pesticide contamination in streams (Liess and Von der Ohe, 2005). The system considers the sensitivity of species to organic toxicants including pesticides (Von der Ohe and Liess, 2004) and ecological traits (generation time, migration ability, and presence of aquatic stages during the main period of pesticide application to classify species to be at risk (SPEAR) or not at risk from pesticide exposure. By means of this classification, the system enables simplifying complex communities and reducing natural variability (e.g., due to spatio-temporal heterogeneity of habitat parameters), which can facilitate comparisons of pesticide effects between different geographical regions.

## 3 Aims of this thesis

### 3.01 Structure of the thesis

Surface water runoff is a major stressor for aquatic communities in agricultural landscapes. Among the group of runoff constituents, pesticides can be highly toxic to aquatic organisms. The environmental objectives of the WFD for European river basins require identifying hot spots, where pesticide contamination may adversely act on water quality. Therefore, the aim of this thesis is to introduce and validate for selected regions a screening model that enables the identification of hot spots of ecological risk for stream invertebrate communities that results from pesticide runoff at the European scale. The idea of the screening model is to combine existing environmental data and simplified modeling for risk characterization. The model demonstrates how existing techniques and databases allow for linking exposure assessment and ecology at large-scales. The techniques and data underlying this screening model as well as the application and validation for the European scale are presented in four consecutive chapters:

Chapter II – Predicting exposure to pesticide runoff at the landscape level
Chapter III – Comparing predicted and observed effects of insecticide runoff
Chapter IV – Establishing exposure-response relationships at broader scales
Chapter V – Predicting ecological risk of runoff at the European scale

The structure of the thesis is summarized in Figure 1 and the aims of the chapters are outlined in the following.

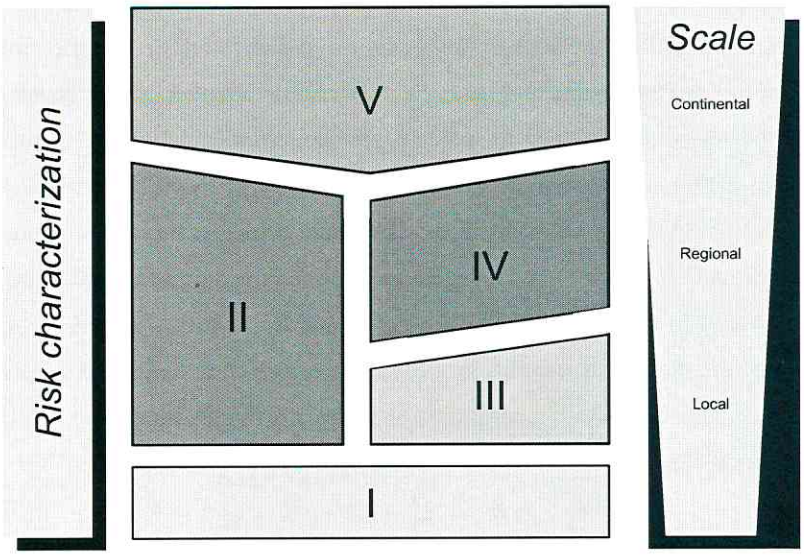


Figure 1: Structure of the thesis. Chapter I – Introduction, Chapter II – Predicting exposure to pesticide runoff at the landscape level, Chapter III – Comparing predicted and observed effects of insecticide runoff, Chapter IV – Establishing exposure-response relationships at broader scales, Chapter V – Predicting ecological risk of runoff at the European scale.

### 3.02 Predicting exposure to pesticide runoff at the landscape level

#### (i) Problem

Modeling exposure to pesticide runoff at larger scales needs to tackle the problem of limited availability and resolution of required input data. This makes it more promising to apply simplified exposure models instead of sophisticated ones, which require estimating a multitude of parameters as outlined above. However, there is a tradeoff between model complexity and uncertainty related to model outcomes. A limited number of model parameters will restrict uncertainty of model outcomes, which results from the uncertainty related to low-resolution input data for parameter estimation (Dubus et al., 2003) However, a simplified model structure also contributes to uncertainty related to model outcomes, because many processes known to influence details of exposure (Van der Werf, 1996) may not be considered.

#### (ii) Aim of the chapter

Considering these aspects the question arises, whether the results of simplified modeling produce reliable predictions on exposure. This question is addressed exemplarily in Chapter II. In this chapter, a generic indicator is introduced that is based on a simplified model to predict the potential exposure of 20 small streams to pesticide runoff. To test the reliability of the indicator and the underlying model, the indicator values are validated with runoff-induced pesticide concentrations that were measured in the 20 streams.

### 3.03 Comparing predicted and observed effects of insecticide runoff

#### (i) Problem

Characterizing ecological risk of pesticide runoff requires information on exposure and on the effects of exposure as well. While the field-based knowledge on effects is limited, mathematical models offer the possibility to predict pesticide effects. Current effect models use toxicity information that is available from studies spanning from laboratory to field conditions, which is illustrated by the following examples. Species Sensitivity Distributions (SSD) make use of standard toxicity data from laboratory tests (Kooijman, 1987; Posthuma et al., 2002a). The PERPEST model (Van den Brink et al., 2002) is a case-based reasoning methodology that uses (micro)mesocosm data. There is also a SPEAR-based model available that was recently established from field investigations (Liess and Von der Ohe, 2005). These models indicate the potential for effects or the magnitude of effects and thus they could be applied for characterizing ecological risk.

#### (ii) Aim of the chapter

However, the question arises whether the outcomes of these models, and thus underlying data, are suitable to predict field effects of pesticides. This question is addressed exemplarily in Chapter III. A case study was conducted, in which the insecticide effects that were monitored in a small agricultural stream were compared to insecticide effects that were predicted for this stream by SSDs, PERPEST, and the SPEAR-based model. The main potential of this case study is that model outcomes are compared to the results of a well-documented field study instead of being compared to effects observed under semi-field conditions or in the lab. The small sample size owes to the instance that over the last decades only few field studies were able to infer causality between insecticide exposure and observed macroinvertebrate dynamics (Schulz, 2004).

### 3.04 Establishing exposure-response relationships at broader scales

#### (i) Problem

At broader scales, knowledge is scarce how agricultural pesticide runoff affects aquatic communities, although such field-based exposure-response relationships are of great value for appropriately predicting effects and thus characterizing ecological risk of runoff (see Chapter III). This knowledge gap may be filled by making use of already existing information on environmental parameters and aquatic communities as outlined above. However, many biological databases usually contain data that result from inventory monitoring programs, which do not specifically address the issue of key determinants for communities (Sliva and Williams, 2001).

#### (ii) Aim of the chapter

Therefore, the question arises, to which extent existing data can help to make out environmental parameters influencing aquatic communities at broader scales and to identify effects of runoff in particular. This question is addressed in Chapter IV. For a set of 360 stream sites, environmental parameters were extracted from existing databases (e.g., streambed substrate, land use near streams) or calculated from these data (potential inputs via runoff – as described in Chapter II – and spray drift). Benthic invertebrate data were extracted from a governmental database on biological inventory monitoring of surface waters and various community descriptors including SPEAR-based metrics were calculated. Habitat characteristics and levels of agricultural intensity (modeled runoff and spray drift potential) were correlated with the biological metrics. This was done to investigate the relevance of agricultural intensity and habitat characteristics for the composition of benthic macroinvertebrate communities. Additionally, the aim of the chapter was to establish a relationship between agricultural intensity and community composition, which on the one hand is representative for an agricultural landscape because of a large sample size and which on the other hand incorporates the influence of landscape mediated recovery pools on the composition of macroinvertebrate communities.

### 3.05 Predicting ecological risk of runoff at the European scale

Chapter V integrates the methodologies and outcomes presented in the precedent chapters to characterize the ecological risk of runoff at the European scale. The simplified runoff model presented in Chapter II is combined with the field-based exposure-response relationship presented in Chapter IV that enables risk characterization at the European scale with respect to landscape-mediated potential for recovery. The value of such a field-based exposure-response relationship for appropriately quantifying pesticide effects in the field was assessed exemplarily in Chapter III. Chapter V presents predicted ecological risk from runoff in

Europe and shows the results of a punctual validation that was done to address the question, if it is possible to characterize risk at the European scale adequately with the limited availability and resolution of current data for this scale.

# Chapter II. Predicting exposure to pesticide runoff at the landscape level

## 1 Introduction

The amount of pesticides that is lost from arable land via surface water runoff is related to compound characteristics and spatial heterogeneity of environmental factors such as land use, topography, soils, and precipitation. In some cases, the impact of these environmental factors may override the influence of physico-chemical properties on variability in exposure (Leu et al., 2004). Characterizing the spatio-temporal variability in pesticide runoff may be challenging because this requires water-monitoring programs that are designed with respect to relevant scales and dissipation processes (Solomon, 2001). Therefore, mathematical models of varying complexity have been proposed to simulate runoff. Model outcomes are applied for exposure assessment (FOCUS, 2001) or are incorporated into the calculation of aquatic risk indicators (OECD, 2000). The spatial variability in exposure is addressed by means of Geographic Information Systems (GIS) interfacing with models. The temporal variability in exposure is usually considered by simulating long-term average losses or losses resulting from a major rainfall event (Brown et al., 2002). Highly parameterized spatial models are useful when applied to small areas, but are impractical, time-consuming, and expensive to use on broader scales, where compiling and managing enormous data sets is required (Addiscott and Mirza, 1998). In addition, modeling at broader scales has to tackle the problem of limited availability and low resolution of data, which hampers parameter estimation of sophisticated models (Steinhardt and Volk, 2003). Literature values or expert knowledge are applicable to fill in data gaps, but errors related to these values increase the uncertainty of the model outcomes (Jorgensen, 1995; Dubus et al., 2003). Therefore, in the past years, simple models have been applied at broader scales for spatially explicit prediction of exposure (Dabrowski et al., 2002;

Verro et al., 2002).

The aim of this chapter was to validate the runoff potential (RP), a generic indicator to distinguish stream sites with respect to potential runoff inputs due to key environmental characteristics. The indicator is based on a simplified mathematical model that considers the environmental factors of land use, topography, soil characteristics, and precipitation as driving forces and is characterized by a low amount of required input data. The RP differs from existing indicators in that it predicts runoff inputs of a generalized compound instead of a specific pesticide. Furthermore, predictions are based on area-specific rainfall pattern instead of a single rainfall event in order to account for the temporal variability in the interaction of precipitation and plant interception. The RP was predicted for 20 small streams and the outcomes were validated with event-controlled pesticide measurements from a triennial investigation on these streams (Liess and Von der Ohe, 2005).

## 2 Materials and methods

### 2.01 Characteristics of the investigated streams

The study area is in the Braunschweig region, Lower Saxony, Germany. The moraine landscape north of Braunschweig is characterized by low elevation (70 m above sea level) and sandy soils that merge south into typical soils of the loess hills (111 m above sea level) with comparatively low infiltration capacity. The climatic conditions are temperate oceanic, with an average annual temperature of 8.8° C and total annual rainfall of approximately 620 mm, which is distributed relatively uniformly across the seasons (Müller-Westermeier, 1996). Predicted pesticide runoff based on single compounds (Bach et al., 2000) is quite variable (very low (level 2) to high (level 5) as defined on a scale from 1 to 6). The area constitutes one of the major agricultural production areas in Germany, particularly for arable crops. Agriculture is by far the dominant land use (arable land 51%; forest 26%; pasture 10%). The major arable crops are cereals and sugar beets, which are cultivated on more than two thirds of the arable land (Keckl, 2002).

Twenty perennial streams were selected to validate predicted RP (Figure 2). The streams were selected, because they had been intensely monitored for runoff-induced pesticide contamination (Liess and Von der Ohe, 2005). Diffuse pesticide pollution from agricultural sources was assumed as major source of in-stream contamination, because near the streams arable land, pasture, and forestry were the predominant forms of land use and potential point sources of pesticide pollution had not been identified (Liess and Von der Ohe, 2005). For the present investigation, spatial information on the streams and their catchments were provided by various regional authorities (Table 1). Shape files of the stream network and land cover as well as a digital elevation model originated from the Authoritative Topographic-Cartographic Information System (ATKIS, http://www.atkis.de). These data (scale 1:25,000) were provided by the regional authority for surveying and mapping (Landvermessung und Geobasisinformation Niedersachsen, LGN, http://www.lgn.niedersachsen.de). A shape file of soil types and their characteristics (scale 1:50,000) was provided by the regional authority for soil sciences (Landesamt für Bergbau, Energie und Geologie, LBEG, http://www.lbeg.niedersachsen.de). All spatial data processing was done using Arc View 3.2 a (ESRI, Redlands, CA, USA).

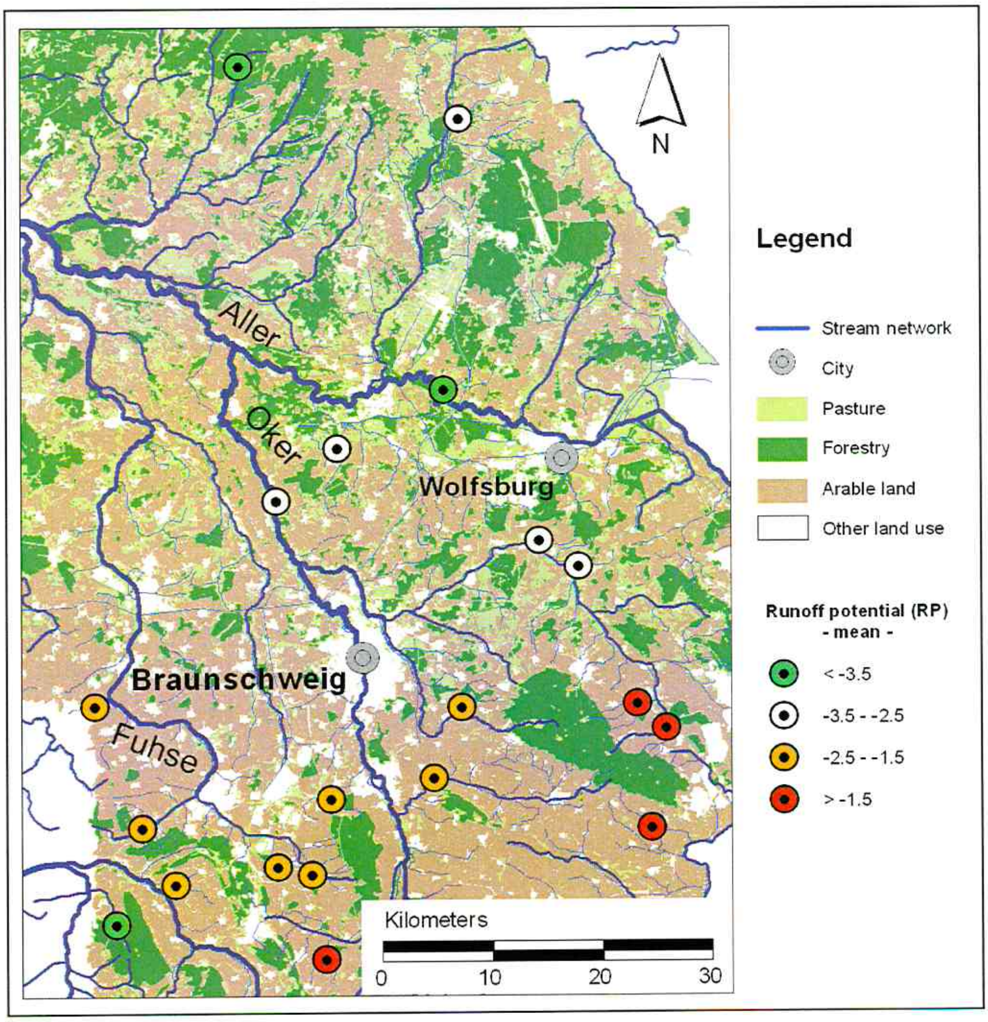


Figure 2: Predicted runoff potential (RP) of 20 stream sites in the Braunschweig region, Lower Saxony, Germany.

Table 1: Environmental characteristics of the 20 investigated stream sites and significant correlations of environmental parameters including run-off potential (RP) with observed pesticide runoff expressed as runoff loss ($R_{Loss}$) and runoff toxicity ($R_{Toxicity}$).

| | | | *Percentiles* | | *Correlation with environmental parameter - $R^2$ (p niveau)* | |
|---|---|---|---|---|---|---|
| *Category* | *Environmental parameter* | *Mean* | *$10^{th}$* | *$90^{th}$* | *$R_{Loss}$* | *$R_{Toxicity}$* |
| Surface catchment [a] | | | | | | |
| | Size [km²] | 12.59 | 6.42 | 19.22 | - | - |
| | Arable land [%] | 58.0 | 27.3 | 90.6 | 0.27 (< 0.05) | - |
| | Forest [%] | 31.9 | 2.5 | 67.9 | - | - |
| | Pasture [%] | 5.1 | 0.2 | 14.7 | - | - |
| | Slope [%] | 4.5 | 2.2 | 7.5 | - | - |
| | Precipitation [mm] | 10 | 6.3 | 16.0 | - | - |
| Near upstream environment [a b] | | | | | | |
| | Size [km²] | 0.63 | 0.31 | 1.23 | | |
| | Arable land [km²] | 0.42 | 0.02 | 0.99 | 0.34 (< 0.01) | 0.32 (< 0.01) |
| | Arable land [%] | 63.3 | 7.5 | 97.2 | 0.46 (< 0.001) | 0.30 (< 0.01) |
| | Forest [%] | 15.7 | 0.0 | 58.3 | 0.30 (< 0.01) | - |
| | Pasture [%] | 14.3 | 0.0 | 50.8 | - | - |
| | Slope of arable land [%] | 1.8 | 0.1 | 5.6 | 0.22 (< 0.05) | - |
| | Soil organic carbon content [%] | 2.2 | 0.3 | 3.8 | - | - |
| | Maximum daily rainfall [mm] | 24 | 17 | 33 | - | - |
| | Runoff potential (RP) | -0.32 | -2.0 | 0.79 | 0.75 (< 0.001) | 0.55 (< 0.001) |

[a] Analysis of digital information.
[b] A two-sided 100-m buffer of the hydrological network extending for 1,500 m upstream from a sampling site.

### 2.02 Water sampling and quantification of pesticides

Chemical water quality had been intensely monitored at each of the 20 streams (one site per stream) from April to July in the years 1998 (10 sites), 1999 (12 sites), and 2000 (13 sites) (for details see Liess and Von der Ohe (2005)). Due to the absence of potential point sources, runoff-induced short-term peak concentrations resulting from agriculture were assumed to be the dominant source of pesticide exposure (Liess et al., 1999). Thus, the sampling strategy had been to use an event-controlled runoff sampling system, which was checked weekly during the studied months. At each site two passive samplers, both consisting of a 1-l bottle, were mounted in the stream. Rising water level triggered the sampling, and each bottle was filled through a thin (5 mm) glass tube, 10 cm in length. The glass tubes were positioned 5 cm and 10 cm above the medium water level. In the laboratory, the water samples were pre-filtered (0.2 μm) and processed by solid-phase extraction with C18 columns (for a detailed description see Liess et al. (1999)).The particular pesticides to be analyzed were selected because of use information provided by the local agricultural advisory board. Pesticides were measured by GC/ECD (gas chromatograph NP 5990, Series II; Hewlett-Packard, Avondale, PA, USA). The values were confirmed by GC/MS (negative chemical ionization), using a Varian 3400 gas chromatograph (Varian, Walnut Creek, CA, USA). The GC/MS was fitted with an HP 7673 auto sampler, which was directly capillary-coupled to the quadruple mass spectrometer SSQ 700 (Finnigan, Bremen, Germany), with a quantification limit (LOQ) of 0.05 μg L-1 (for a detailed description see Liess et al. (1999)). Data on the measured pesticides are summarized in Table 2.

### 2.03 Measured runoff

The aim of this chapter was to validate predicted RP with measured levels of runoff-induced pesticide contamination. The indicator (as presented in detail further down) predicts runoff inputs of a generic compound instead of a specific pesticide. Therefore, RP was not expected to correlate with concentrations of single compounds during a specific runoff event. To enable, nevertheless, a comparison between RP and measured levels of pesticide contamination, pesticide concentrations were aggregated per site to a generalized measure. The measure, termed runoff loss ($R_{Loss}$), reflected the observed pesticide contamination of sites, irrespective of a specific compound, and was calculated as follows. For each site, measured concentrations were standardized by the applied pesticide mass per catchment and by the water solubility of the related substance (equation 1). This was done, since both applied mass and water solubility determine the level of in-stream concentrations that can occur during runoff events (Iwakuma et al., 1993; Kreuger, 1998). A standardized concentration Ci,j [$kg^{-1}$] was calculated as:

$$C_{i,j} = \frac{c_{i,j}}{D_i \cdot A(\text{catchment})_j \cdot S_i} \quad (1)$$

where

| | |
|---|---|
| $c_{i,j}$ | is the measured concentration [$\mu g\ L^{-1}$], |
| index i | refers to a specific pesticide, |
| index j | refers to a specific sampling site, |
| $D_i$ | is the recommended applied dose rate [$kg\ km^{-2}$], |
| $A(\text{catchment})_j$ | is the catchment size [$km^2$], |
| $S_i$ | is the solubility of a given compound [$\mu g\ L^{-1}$]. |

To account for possible pesticide contamination below the limit of quantification, a $C_{i,j}$ value greater than 0 was assigned to water samples without quantifiable contamination. The assigned value equaled half of the $C_{i,j}$, which reflected the annual maximum value of the least exposed stream site. For each year, values of $C_{i,j}$ were pooled per site and the log-transformed maximum values yielded the annual $R_{Loss}$ of a site. Due to the range of $C_{i,j}$ values, log-transformation was applied in order to bin values broadly into order-of-magnitude categories.

### 2.04 Measured runoff toxicity

A generalized measure termed runoff toxicity ($R_{Toxicity}$) was calculated additionally in order to compare predicted RP with the toxic pressure from runoff-induced pesticide contamination, which may adversely act on benthic macroinvertebrate communities (Liess and Von der Ohe, 2005). According to the Toxic Units concept (Sprague, 1970), toxicity was expressed by standardizing measured concentrations of all pesticides by the related median effect concentration for *Daphnia magna.* A standardized concentration $TU_i$ [-] is calculated as:

$$TU_i = \frac{c_i}{EC/LC50_{D}i} \quad (2)$$

where

| | |
|---|---|
| $c_i$ | is the measured concentration [$\mu g\ L^{-1}$], |
| index i | refers to a specific pesticide, |

$EC/LC50_{D}i$ is the median effect/lethal concentration of substance i for *Daphnia magna* [µg $L^{-1}$].

Acute (48-h) toxicity data on median lethal (LC50) and median effect concentrations regarding immobility (EC50) were extracted from the U.S. Environmental Protection Agency ECOTOXicology Database System (EPA, 2006). Values of 48-h LC50 as given in Tomlin (2001) were used, if substances were not listed in the ECOTOX database. A geometric mean of $EC/LC50_{D}i$ was calculated, when more than one toxicity value was reported for a substance. To account for possible pesticide contamination below the limit of quantification, a $TU_i$ greater than 0 was assigned to water samples without quantifiable contamination. The assigned value equaled half of the $TU_i$, which reflected the annual maximum value of the least exposed stream site. For each year, values of $TU_i$ were pooled per site and the log-transformed maximum values yielded the annual $R_{Toxicity}$ of a site. Due to the range of $TU_i$ values, log-transformation was applied in order to bin values broadly into order-of-magnitude categories.

## 2.05 Runoff potential

### (i) Model

The generic indicator RP was developed to distinguish stream sites with respect to the potential for to runoff inputs due to environmental factors. The driving forces of RP are the environmental factors of land use, topography, soil characteristics, and precipitation, which are key environmental factors for runoff. The exposure model underlying RP was developed from a model that was proposed for estimating runoff-induced pesticide losses by the Organisation for Economic Co-operation and Development (OECD) (OECD, 1998). The OECD model considers phyico-chemical properties and the key environmental factors given above to predict dissolved runoff inputs of a pesticide into a surface water body. Due to its simplified structure the OECD model helps to constrain the uncertainty of outcomes that originates from potentially low resolution of input data. Yet, the simplified model structure also contributes to the uncertainty of outcomes, since only key environmental determinants of runoff are considered.

The runoff model underlying RP was developed from this OECD model in order to estimate inherent susceptibility to runoff inputs at sites instead of arriving at a set of specific predictions for any one substance. Hence, a set of generalized compound characteristics is used in the modeling (see below) instead of specific compound properties or use patterns, which would influence absolute values of RP but would not support distinction between sites. Furthermore, the runoff model underlying the RP does not consider the presence of buffer strips between arable land and adjacent water bodies. The influence of buffer strips was not included in the model, since the resolution of data available for landscape-level exposure modeling may allow for quantify the width of buffer strips, but are usually inadequate for characterizing buffer strip quality. At larger (e.g., national scales), the available data are even too coarse for characterizing buffer strip width.

Due to the outlined simplifications, the runoff model behind the RP is based on the total amount of arable land in the near upstream environment of a stream site (i.e., in a two-sided 100 m stream corridor extending for 1,500 m upstream of the site). The near upstream environment of a stream site comprises a corridor area of 0.30 km² (i.e., 2 x 100 m x 1,500 m) unless the watercourse is branched within the upstream distance of 1,500 m. In case of a branched watercourse, the near-stream environment comprises all of the corridor area along the different branches within the upstream distance of 1,500 m and results in a corridor area of greater than 0.30 km². The amount of arable land in the near upstream environment multiplied by the application rate of a generalized substance returns a maximum estimate of the generic load that can potentially reach a stream site via runoff. This maximum generic load, however, can be decreased by site-specific environmental factors. Accordingly, the exposure model underlying RP calculates the potential loss of a generic substance (gLOAD [g]) that can be expected at a site during a rainfall event (equation 3) as:

$$gLOAD = \sum_{i=1}^{n}\sum_{j=1}^{m} A_{i,j} \cdot D_{generic} \cdot \left(1 - \frac{I_j}{100}\right) \cdot \frac{1}{1 + \frac{Koc_{generic} \cdot OC_i}{100}} \cdot f(s_i) \cdot \frac{f(P_i, T_i)}{P_i} \qquad (3)$$

where

| | |
|---|---|
| $A_{i,j}$ | is the patch size of arable land within the stream corridor [ha], |
| index i | refers to different patches of arable land |
| index j | refers to different cultivated crops, |
| $D_{generic}$ | is the applied dose rate of the generic substance, |
| $I_j$ | is the crop- and growth phase-specific plant interception at the time of the rainfall event [%], |
| $Koc_{generic}$ | is the organic carbon sorption coefficient of the generic compound, and is set to |

a value of 100 in order to maximize distinction of sites due to differences in soil organic carbon content,

$OC_i$ is the soil organic carbon content of a patch [%],

$s_i$ is the mean slope of a patch [%],

$f(s_i)$ describes the influence of slope according to Beinat and van der Berg (OECD, 1998),

$$= \begin{cases} 0.001423 \cdot s_i^{\,2} + 0.02153 \cdot s_i\,, & if \quad s_i \leq 20\% \\ 1\,, & if \quad s_i > 20\% \end{cases} \tag{4}$$

$P_i$ is the precipitation depth [mm],

$T_i$ gives the soil texture of the patch (sandy/loamy),

$f(P_i,T_i)$ is the volume of surface runoff [mm] that is specified according to results of Lutz and Maniak (OECD, 1998) for vegetated dry soils, which represent conditions in middle and late vegetation period,

$$= \begin{cases} -5.86 \cdot 10^{-6} \cdot P_i^3 + 2.63 \cdot 10^{-3} \cdot P_i^2 - 1.14 \cdot 10^{-2} \cdot P_i - 1.64 \cdot 10^{-2}\,, & if \quad T_i = Sand \\ -9.04 \cdot 10^{-6} \cdot P_i^3 + 4.04 \cdot 10^{-3} \cdot P_i^2 + 4.16 \cdot 10^{-3} \cdot P_i - 6.11 \cdot 10^{-2}\,, & if \quad T_i = Loam \end{cases} . \tag{5}$$

Runoff losses of the generic substance (gLOAD) at a given site are predicted for each rainfall during the main period of pesticide application in a study area. Such a series of rainfall events is considered instead of a single rainfall event during the main application period to account for the temporal variability in the interaction of precipitation and plant interception. The predicted maximum gLOAD during that period is log-transformed in order to categorize the runoff losses broadly into order-of-magnitude categories. The log-transformed maximum gLOAD yields the RP for a stream site, which reflects the potential for runoff inputs. It is noteworthy that assumptions about the properties of the generic substance (e.g., no degradation) represent simplifications that do not apply to most compounds. However, the described simplifications suit the aim of the RP to distinguish between sites in terms of potential runoff inputs instead of getting absolute predictions for any one substance.

### (ii) Model parameterization

Modeling generalized runoff inputs for the 20 selected stream sites, the runoff model (equation 3) was parameterized as follows. The major crops of the region that are characterized by specific temporal patterns of plant interception were supposed to be cultivated in the near upstream environment. The proportion of arable land covered by each crop was specified according to overall crop statistics of the study area (Keckl, 2002). The cropping direction was not considered. For each patch of arable land in the stream corridor, information on size $A_{i,j}$ and mean slope $s_i$ were extracted from the ATKIS database, information on soil organic carbon content $OC_i$ and texture $T_i$ were extracted from the available soil data. The application rate $D_{generic}$ was set to a constant value of 1 g ha$^{-1}$ for all crops. Values of plant interception $I_j$ were specified according to tabulated values (Linders et al., 2000). The potential loss of a generalized substance (gLOAD) was predicted for each rainfall event during the months of April, May and June, since pesticide measurement for the set of selected streams were available for this period. A time series of daily-recorded precipitation over the study period (provided by the German Meteorological Service, DWD, http://www.dwd.de) was used to specify precipitation depth $P_i$. Daily-recorded precipitation was assumed to result from one rainfall event. Assumptions about rainfall intensity were not included. A stream site potentially receive no runoff inputs, if according to the ATKIS data no arable land was located in the near upstream environment. With respect to the restricted resolution of the maps, a gLOAD value was assigned to such a stream site that indicated potential but minimum inputs. This value was equal to half of the smallest overall maximum gLOAD predicted for the set of investigated sites.

### 2.06 Sensitivity analysis

Uncertainties related to input data will propagate to model output and will increase the level of uncertainty that is related to model outcomes (Jorgensen, 1995). Therefore, it is necessary to know how robust model outcomes are to changes in each of the model parameters. Model sensitivity for gLOAD was assessed by means of the sensitivity index proposed by Jorgensen (1995). The sensitivity index S (equation 6) relates changes in parameter values to changes in model outcomes, which is done with respect to the ratio of absolute parameter values to absolute model outcomes:

$$S_{gLOAD}(K) = \left|\frac{\partial gLOAD}{\partial K}\right|_{K=K_i} \cdot \frac{K}{gLOAD(K)} \qquad (6)$$

where

K is the considered parameter and

gLOAD(K) is the model dependent on K.

Positive values of $S_{gLOAD}$ indicate that gLOAD values increase, if parameter values increase. Negative values of $S_{gLOAD}$ indicate that gLOAD values decrease, if parameter values increase. The larger $|S_{gLOAD}|$, the more the model is sensitive to changes in parameter K (i.e., the more gLOAD changes as parameter values change). If $|S_{gLOAD}|$ is a function of parameter K, then the influence of parameter changes on changes in gLOAD varies across the parameter range. If $|S_{gLOAD}|$ is a constant of 1, then the influence of parameter changes on changes in gLOAD is the same across the parameter range.

The index $S_{gLOAD}$ was calculated for each of the parameters generic application rate $D_{generic}$, precipitation P, plant interception I, slope s, arable land A and soil organic carbon content OC. The sensitivity index was calculated by varying a parameter in range according to percentiles given in Table 1, while all other parameters were kept constant at median values for the study area (P, s, A and OC) or at specified values ($D_{generic}$, $Koc_{generic}$). Plant interception was changed from 0% to 100% and mean values reflected the average situation for the major crops in the month of May (I = 80% for cereals, I = 20% for sugar beets). All computing was done with the software Mathematica 4 (Wolfram Research, Champaign, IL, USA).

### 2.07 Statistics

All statistics were carried out with Statistica® (version 6.1 for Windows®). The mean coefficient of variation (CV) in annual values of $R_{Loss}$, $R_{Toxicity}$, and predicted RP was calculated for all sites that were investigated during more than one year. Pearson's *R* was used to quantify the linear correlation between environmental parameters including RP and the measures $R_{Loss}$ and $R_{Toxicity}$. Linear regression analysis was applied to investigate significant correlations in detail. The normal distribution of data was tested with the Kolmogoroff-Smirnoff test. Equality of variances was tested using White's test for homogeneity of variance.

## 3 Results

### 3.01 Observed pesticide runoff

Over the study period, 15 pesticides were identified in the investigated streams (Table 2). Maximum concentrations were measured during May and June. The herbicides chloridazon and ethofumesate were found in most water samples and were detected at highest mean concentrations, which relates to the high total applied mass and the solubility of the two compounds (Table 2). Annual values of both $R_{Loss}$ and $R_{Toxicity}$ were frequently made up by the fungicides kresoxim-methyl and azoxystrobin as well as the insecticide parathion-ethyl. At sites investigated during more than one year, the compounds that made up both $R_{Loss}$ and

Table 2. Pesticide properties and descriptive statistics of measured concentrations equal or greater than the related limit of quantification. [a]

| *Pesticides* | | *Properties* | | | | | *Concentrations* | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | *Percentiles* | |
| | | *Solubility* [$mg\ L^{-1}$] | *Koc* [$mL\ g^{-1}$] | *EC/LC50$_{Di}$* [$\mu g\ L^{-1}$] | *D* [$g\ ha^{-1}$] | *M* [kg] | *Number of detections* | *Mean* [$\mu g\ L^{-1}$] | *10$^{th}$* [$\mu g\ L^{-1}$] | *90$^{th}$* [$\mu g\ L^{-1}$] |
| Fungicides | | | | | | | | | | |
| | Azoxystrobin | 6 | 143 | 259 | 250 | 2.7 | 42 | 1.43 | 0.1 | 2.1 |
| | Epoxiconazole | 6.63 | 442 | 8,700 | 125 | 1.2 | 43 | 0.52 | 0.1 | 0.9 |
| | Fenpropimorph | 4.3 | 804 | 2,400 | 750 | 2.2 | 4 | 0.28 | 0.2 | 0.4 |
| | Kresoxim-methyl | 2 | 421 | 332 | 125 | 0.8 | 17 | 0.46 | 0.05 | 1 |
| | Propiconazol | 100 | 650 | 3,200 | 125 | 0.1 | 3 | 0.07 | 0.06 | 0.08 |
| | Tebuconazole | 36 | 603 | 4,000 | 225 | 2.1 | 17 | 0.85 | 0.1 | 1.7 |
| Herbicides | | | | | | | | | | |
| | Bifenox | 0.35 | 1,572 | 660 | 735 | 2.2 | 8 | 0.2 | 0.04 | 0.5 |
| | Chloridazon | 340 | 30 | 132,000 | 2,000 | 23 | 43 | 3.18 | 0.2 | 6.9 |
| | Ethofumesate | 50 | 182 | 64,000 | 1,000 | 13 | 58 | 4.79 | 0.2 | 10.7 |
| | Isoproturon | 65 | 140 | 507,000 | 1,470 | 13 | 20 | 0.74 | 0.15 | 1.8 |
| | Metamitron | 1,700 | 19 | 97,000 | 700 | 5.9 | 27 | 1.23 | 0.1 | 3.5 |
| | Metribuzin | 1,050 | 60 | 4,180 | 525 | 3.4 | 8 | 0.38 | 0.1 | 1.2 |
| | Pendimethalin | 0.3 | 5,000 | 280 | 1,400 | 1 | 1 | 0.04 | 0.04 | 0.04 |
| Insecticides | | | | | | | | | | |
| | Lindane | 8.52 | 1,100 | 1,600 | 235 | 0.2 | 1 | 0.03 | 0.03 | 0.03 |
| | Parathion-ethyl | 11 | 705 | 2 | 450 | 2.1 | 7 | 0.22 | 0.05 | 0.3 |

[a] Solubility: solubility in water (Tomlin, 2001); Koc: organic carbon sorption coefficient (Hornsby et al., 1995; PAN, 2003; USDA, 2003); EC/LC50$_{Di}$: 48-h median effect/lethal concentration of substance i for *Daphnia magna* (Tomlin, 2001; EXTOXNET, 2003; EPA, 2006), a geometric mean was calculated when more than one toxicity value was reported for a substance; D: application rate (BVL, 2003); M: total applied mass, estimated from the sum of arable land in all catchments, where a substance was detected.

$R_{Toxicity}$ varied between the studied years (not shown). Except from one sampling site, $R_{Loss}$ and $R_{Toxicity}$ were only made up by concentrations measured in the months of May and June. Annual $R_{Loss}$ values of sites ranged from a value of -9.9 indicating minimum exposure to a maximum value of -4.7 that was made up by azoxystrobin. As to $R_{Toxicity}$, annual values ranged from a minimum value of -6.0 to a maximum value of -0.92 that was made up by parathion-ethyl. At six of the investigated sites, parathion-ethyl and azoxystrobin accounted for $R_{Toxicity}$ values of single years equal or greater than -1.1 (i.e., measured toxicity was in the range of 1:10 of the 48-h EC/LC50$_{Di}$). Between the investigated years, variability in $R_{Toxicity}$ was higher (CV = 40%) than variability in $R_{Loss}$ (CV = 11%).
The overall mean values of $R_{Loss}$ and $R_{Toxicity}$ were highly correlated ($R^2 = 0.77$; $p < 0.001$, $n = 20$), indicating that on average streams with high runoff-induced pesticide contamination were also characterized by high levels of toxic pressure on macroinvertebrates. Both $R_{Loss}$ and $R_{Toxicity}$ were more closely correlated with percentage arable land in the near-stream environment than with percentage arable land in the catchment (Table 1). This suggested that arable land in the near-stream environment of a site was more representative of measured runoff and related toxicity (with respect to macroinvertebrates) than characteristics of the whole catchment.

### 3.02 Comparison of predicted and observed pesticide runoff

Annual values of RP ranged from a value of -4.16, indicating potential but minimum runoff inputs, to the maximum predicted value of -1.01. Annual variability of RP was low (CV = 4%) in comparison to $R_{Loss}$ and $R_{Toxicity}$. Mean RP for the investigated streams, which is given in Figure 2, explained most of the observed variability in the mean values of $R_{Loss}$ ($R^2 = 0.75$, $p < 0.001$, $n = 20$) and $R_{Toxicity}$ ($R^2 = 0.51$, $p < 0.001$, $n = 20$). It is noteworthy that mean RP explained more of the variance in $R_{Loss}$ and $R_{Toxicity}$ between the sites than the investigated characteristics of the near-stream environment (Table 1). Figure 3 shows that RP explained 60 to 77% of the observed annual variability in $R_{Loss}$ between the sites (1998: $R^2 = 0.60$, $p < 0.01$, $n = 10$; 1999: $R^2 = 0.72$, $p < 0.001$, $n = 12$; 2000: $R^2 = 0.77$, $p < 0.001$, $n = 13$). In contrast, the correlation of RP with $R_{Toxicity}$ varied strongly between the years. RP was not correlated significantly with $R_{Toxicity}$ for the years 1998 and 1999 (1998: $R^2 = 0.08$, $p = 0.223$, $n = 10$; 1999: $R^2 = 0.26$, $p = 0.05$, $n = 12$), but RP explained 64% of the variance in $R_{Toxicity}$ in 2000 ($p < 0.001$, $n = 13$). This variability can be attributed to the comparatively high annual variability in $R_{Toxicity}$ (as demonstrated above) that is likely to result from compounds of different toxicity making up the $R_{Toxicity}$ of sites in single years.

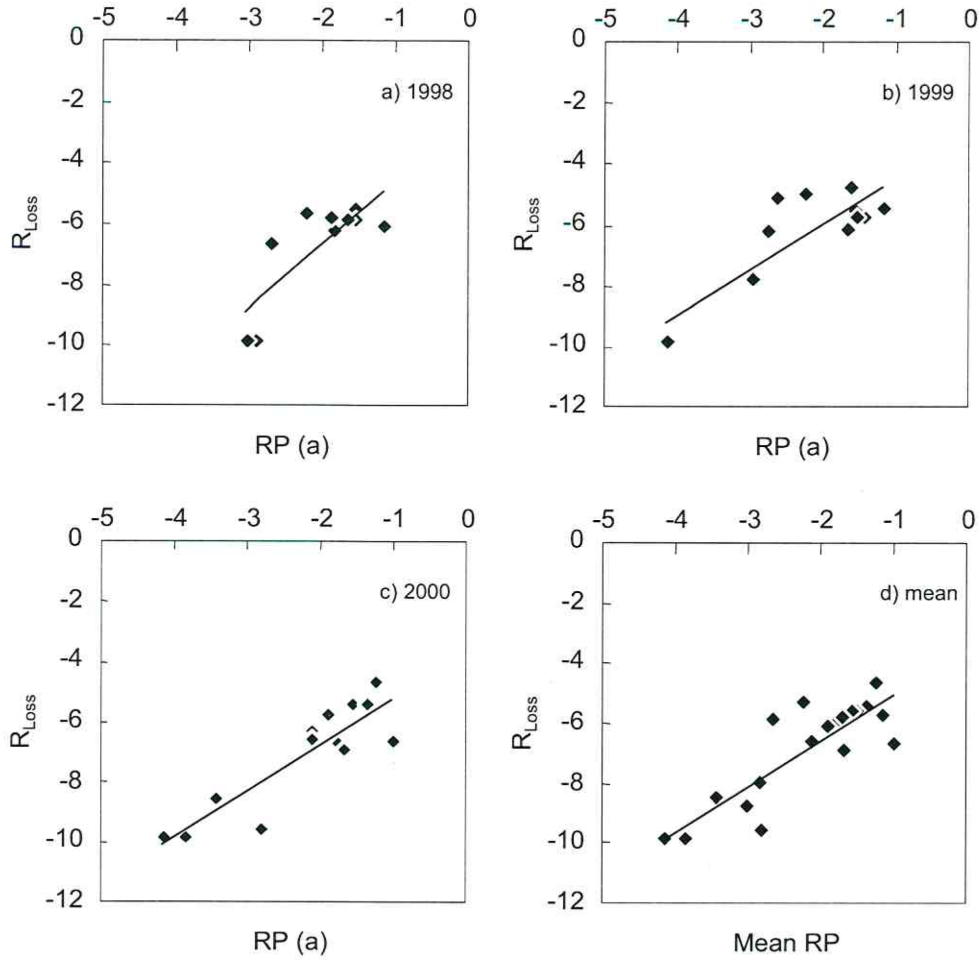


Figure 3: Linear regression plots of measured runoff loss ($R_{Loss}$) on predicted runoff potential (RP) – a) 1998 ($R^2 = 0.60$, $p < 0.01$), b) 1999 ($R^2 = 0.71$, $p < 0.001$), c) 2000 ($R^2 = 0.77$, $p < 0.001$), and d) mean ($R^2 = 0.75$, $p < 0.001$).

### 3.03 Sensitivity of the runoff model

The sensitivity index $S_{gLOAD}$ was calculated by varying each parameter in range according to percentiles given in Table 1. The $S_{gLOAD}$ calculated for precipitation ranged from 1.0 to 7.9 for and $S_{gLOAD}$ calculated for slope ranged from 1.0 to 1.3. In contrast, $S_{gLOAD}$ was a constant equal to 1 for amount of arable land and application rate. Values of $S_{gLOAD}$ were negative for the parameters plant interception and soil organic carbon content, indicating that gLOAD decreased as parameter values increased. The $|S_{gLOAD}|$ calculated for plant interception ranged from 0.0 to values 1.4, while $|S_{gLOAD}|$ calculated for soil organic carbon content ranged from 0.2 to 0.8. On average, $|S_{gLOAD}|$ was highest for parameters precipitation, slope, and plant interception demonstrating that uncertainty related to input data on these parameters had the largest influence on uncertainty related to gLOAD and, consequently, RP.

# 4 Discussion

## 4.01 The RP concept

The RP introduced in this chapter is a generic indicator that was designed to distinguish stream sites with respect to potential runoff inputs from arable land due to environmental parameters (i.e., land use, topography, precipitation, and soil). Underlying the indicator is a simplified runoff model to tackle the problem of limited data availability for modeling at larger scales. The RP uses a mathematical runoff model and in that respect is comparable to current aquatic risk indicators, such as REXTOX (OECD, 2000), EPRIP (Padovani et al., 2004), or PRISW (Finizio et al., 2001). The exposure models behind those indicators consider information on usage and physico-chemical properties of pesticides to predict aquatic exposure, which is expressed as environmental load or concentration. The RP differs from these indicators in that it was not designed to predict exposure to one substance due to one specific rainfall event. In contrast, the RP reflects environmental loads of a generic substance and thus is independent of single compounds and compound-related parameters, but representative for a variety of substances including pesticides, nutrients and other dissolved substances such as metals or humics. Furthermore, RP is based on an area-specific rainfall pattern instead of single rainfall events in order to account for the temporal variability in the interaction of precipitation and plant interception. In summary, the RP predicts potential runoff inputs due to the local combination of environmental characteristics and allows for generic runoff modeling at broader scales, since the underlying model requires a relatively small amount of input data.

## 4.02 Validation

A comparison of RP and standardized pesticide measurements showed that RP corresponded with observed pesticide runoff expressed as $R_{Loss}$ and $R_{Toxicity}$. Mean RP was a better predictor of average observed pesticide runoff than environmental characteristics of the near-stream environment or characteristics of the whole catchment of the investigated sites. Similar observations on the relevance of characteristics of the near-stream environment were made in a study on the relation between triazine flux originating from maize plots and the distance of these plots from a water channel network. The area under maize within a two-sided 50-100 m buffer on the channel network was better correlated with observed triazine fluxes at the outlet of catchments than the total area under maize within the whole catchment (Colin et al., 2000). Several studies showed that the OECD model, from which the RP was developed, produced reliable predictions of runoff-induced exposure to pesticides for different geographical regions (Dabrowski et al., 2002; Verro et al., 2002; Berenzen et al., 2005b). Nevertheless, some uncertainty is associated with RP because of the conceptual level of the underlying model, which does not consider some theoretically relevant factors such as buffer strips, soil profiles, and temperature (Larson et al., 1995; Van der Werf, 1996; Spatz et al., 1997). Differences in actual pesticide exposure due to these site-specific characteristics cannot be reflected by the RP and, consequently, reduce the predictive power of the indicator.

Model sensitivity was assessed by the sensitivity index S (Jorgensen, 1995). Probst et al. (2005a) applied this index to assess the sensitivity of the OECD model when it is used to predict losses from one homogenous patch of arable land. He found that model sensitivity was highest to the parameters buffer width and plant interception. For the current investigation, the sensitivity index was calculated for the model yielding gLOAD (i.e., generalized runoff inputs at a stream site resulting from heterogeneously cultivated fields in the near-stream environment). The model underlying RP, which did not consider the influence of buffer strips because data were not available, was found to be very sensitive to parameters precipitation, slope, and plant interception. This showed that uncertainty related to data on these parameters had the highest influence on RP and could have contributed to unexplained variance in $R_{Loss}$ and $R_{Toxicity}$. Additionally, potential sources of unexplained variance in $R_{Loss}$ and $R_{Toxicity}$ may be related to field procedures. The use of a runoff-triggered sampling technique was based on the assumption that the time of rising water level correlated with the time of pesticide peak concentrations. In cases when this assumption did not hold, measured concentrations would not represent maximum exposure values and differences in site-specific levels of runoff exposure ($R_{Loss}$, $R_{Toxicity}$) would be biased. However, these discrepancies were likely to be small in comparison to measurements based on other sampling techniques that are not event-triggered. The predicted RP produced reliable predictions, when employing data of limited resolution. Accordingly, the indicator can be applied wherever at least data of similar density are available. Due to its low data requirements, the RP enables an exposure assessment that is time- and cost-effective. Therefore, the RP is suggested as a suitable screening tool to support distributional analysis of aquatic exposure at the landscape level.

## Chapter III. Comparing predicted and observed effects of insecticide runoff

### 1 Introduction

Current models to predict the effects of pesticides on aquatic communities use existing toxicity information from single-species tests, long-term (micro)mesocosm studies of multi-species assemblages or long-term investigations on field communities. However, the question arises how such estimates correlate with field effects of the short-term exposure that frequently occurs during runoff events. Species Sensitivity Distributions (SSD) are usually based on acute toxicity data from single-species tests and predict the ecological impact of environmental contaminants on exposed communities according to the varying sensitivity of species (Kooijman, 1987; Posthuma et al., 2002a). SSDs are applied to calculate the fraction of species potentially affected by a given contaminant concentration (Van Straalen, 2002) or to determine hazardous concentrations, and hence the concentration of a contaminant at which a defined proportion of species will not be affected above the corresponding effect level. The PERPEST model (Van den Brink et al., 2002) is a case-based reasoning methodology to predict the probability of ecological effects resulting from a given pesticide concentration. Underlying the model is a case-database containing published (micro)mesocosm data on long-term effects of insecticides and herbicides on aquatic invertebrate assemblages (Van den Brink et al., 2006). Another model is based on long-term field investigations on those species in macroinvertebrate communities that are considered as species at risk (SPEAR) of being affected by pesticides due to their physiological and ecological traits (Liess and Von der Ohe, 2005). This SPEAR-based model uses a quantitative exposure-response relationship to predict the decrease in the percentage abundance of SPEAR resulting from pesticide exposure.

The aim of this chapter was to give an example of how the outcomes of the three effect models described above (SSDs, PERPEST and SPEAR-based model) match with the observed field effects of short-term insecticide exposure at high level.

## 2 Materials and methods

### 2.01 Characteristics of the investigated stream

Liess and Schulz (1999) conducted a yearlong monitoring study at the Ohebach, located in the North German Lowlands south of Braunschweig, Lower Saxony. The stream is a typical example of a watercourse highly impacted by agriculture, as fields are close to the stream without any buffer strips to reduce potential diffuse pollution.The watercourse of the Ohebach was described to be uniform in the longitudinal direction with only submerged macrophytes covering about 50% of the silty streambed. The stream (base flow 10 L $s^{-1}$) drained a slightly sloping (2-4% gradient) catchment area of 0.9 $km^2$, which is characterized by soils of loess loam and clayey marl. Agriculture is the major land use in the catchment and the only potential source of water pollution in the stream. During the study period, the insecticides parathion-ethyl, fenvalerate, and deltamethrin were applied (for further details see Liess and Schulz (1999)).

### 2.02 Measured pesticide contamination

Runoff-induced pesticide contamination in the Ohebach was intensively monitored by sampling the short-term peak contamination during runoff events (1 h peak duration assumed). Stream water samples were taken 1,000 m downstream of the spring using a runoff-triggered sampler, which provided a measurement of the maximum insecticide contamination of suspension-free water and of suspended particulates in the water. The automated active sampler was triggered by a rapid decline in conductivity in the stream water of more than 10% in 10 min. A detailed description of this method and results can be found in Liess et al. (1999). In addition, suspended particulates were monitored continuously with a suspended particle sampler, a sedimentation vessel positioned in the stream (Liess et al., 1996) that was emptied every two weeks. Water quality in the stream was measured during runoff events and at monthly intervals (Liess and Schulz, 1999). Both suspension-free water and suspended particulates were tested for various insecticide substances (Liess et al., 1999). The two insecticides parathion-ethyl (first application on May 18, 1994; application rate 101 g $ha^{-1}$) and fenvalerate (first application on June 6, 1994; application rate 20 g $ha^{-1}$) were detected in stream water and suspended particles (Table 3).

## 2.03 Observed macroinvertebrate dynamics

Macroinvertebrate dynamics in the Ohebach were investigated at the water-monitoring site, i.e. 1,110 – 1,200 m downstream of the spring of the Ohebach). Biological monitoring was conducted by randomly taking four independent samples with a Surber sampler on nine occasions in the period from March 1994 to April 1995 (for details see Liess and Schulz (1999)). The reported dynamics for 1994 are summarized in Figure 4: Nine arthropod species and two non-arthropod macroinvertebrate species were recorded frequently from March to May. Between May and June (i.e., during the time of the runoff events 2 to 4), the abundance of all species was significantly decreased by 50% and more. Six of the nine arthropod species were absent in June (i.e., three weeks after the maximum concentration of 6.0 µg $L^{-1}$ parathion-ethyl was measured). Taxonomic richness and abundance in the Ohebach remained strongly reduced in subsequent post-exposure samplings for more than eight weeks. After one year, most species with the exception of *Tubifex tubifex* and *Plectrocnemia conspersa* had fully recovered.

The causal connection between insecticide contamination and biological response was established using two in-parallel bypass microcosms each containing the dominant species *Gammarus pulex* and *Limnephilus lunatus*. The bypass microcosms allowed for assessing only the toxic potential of runoff events by eliminating increased hydraulic stress due to surface water runoff. During runoff events, one of the microcosms was disconnected from the stream and served as control, while the other one remained connected and received runoff water. Survival of *Gammarus pulex* and *Limnephilus lunatus* in the microcosms was monitored every 10 d by counting larvae and emerged individuals. Subsequent to runoff events 2 and 3, when only parathion-ethyl was detected in stream water and suspended particles, *Limnephilus lunatus* was nearly eliminated. For *Gammarus pulex*, survival was significantly reduced after events 2 and 3, but there was no appreciable further decrease after runoff event 4, when fenvalerate was measured in suspended particles. Hence, parathion-ethyl was supposed to be mainly responsible for the observed effects. For details on setup and monitoring, see Liess and Schulz (1999).

Table 3: Parathion-ethyl in stream water samples (1-h peak concentration) and sediment samples (14-d composite sample) – reported concentrations (Liess and Schulz, 1999; Liess et al., 1999) [a]

| | | *Stream water samples* | | *Sediment samples* |
|---|---|---|---|---|
| | | *Water* | *Suspended particles* [b] | *Suspended particles* |
| *No.* | *Date* | *[µg L⁻¹]* | *[µg per kg (dry weight)]* | *[µg per kg (dry weight)]* |
| 1 | 25.04.1994 | 0.04 | nm | nq (28.4.1994) |
| 2 | 19.05.1994 | 6.0 | nm | 50.8 (26.5.1994) |
| 3 | 25.05.1994 | 0.9 | nm | 50.8 (26.5.1994) |
| 4 | 08.06.1994 | 0.2 | 51.6 | 19.4 (9.6.1994) |
| 5 | 18.08.1994 | nq | nq | 2.2 (18.8.1994) |
| 6 | 24.08.1994 | nq | nq | 20.0 (1.9.1994) |

[a] nq: not quantifiable; quantification limits: 0.01 µg $L^{-1}$ for water and 1 µg $kg^{-1}$ (dry weight) for sediment; nm: not measurable, not enough sediment material for the analysis

[b] Fenvalerate was detected only during event 4 at 302 µg $kg^{-1}$ in suspended particles from stream water (no detection in water phase).

[c] Suspended particles samples consist of a composite sample collected over two weeks using a suspended particles sampler (SPS) (Liess et al., 1996). The date in brackets indicates the last day of the 2-week interval. During event 4, the insecticide fenvalerate was detected in suspended particulates at a concentration of 71µg $kg^{-1}$.

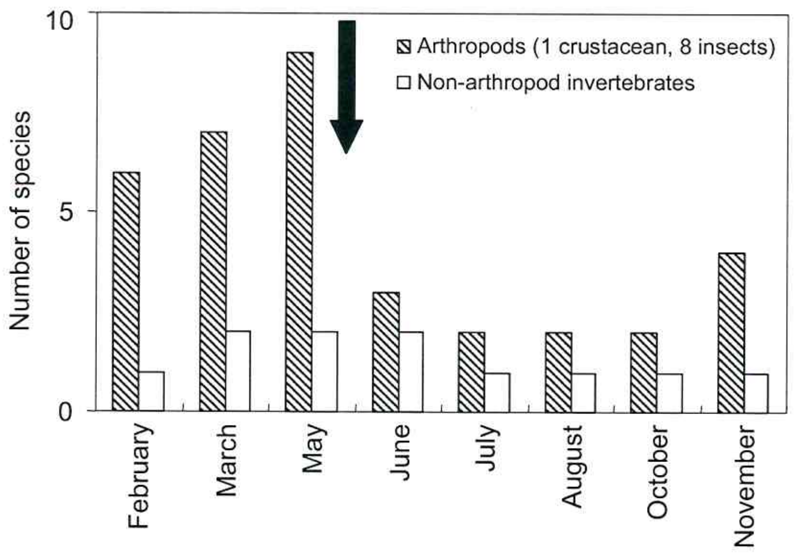


Figure 4: Summarized dynamics of the Ohebach macroinvertebrate community over the study period. The community comprised nine arthropods (*Gammarus pulex, Helodes minuta, Limnephilus lunatus, Limnephilus extricatus, Stenophylax permistus, Micropterna sequax, Plectronemia cospersa, Tipula maxima, Ptychoptera lacustris*) and two non-arthropod macroinvertebrates (*Tubifex tubifex, Dugesia gonocephala*). The black arrow indicates parathion-ethyl contaminated runoff events. For details, see Liess and Schulz (1999).

## 2.04 Effect modeling

### (i) Species Sensitivity Distribution (SSD)

In the present case study, SSDs were constructed for parathion-ethyl from results of acute toxicity tests on aquatic invertebrates (U.S. Environmental Protection Agency ECOTOXicology Database System (EPA, 2006)). For this kind of toxicity tests, exposure time equals observation time. Selected endpoints were LC50 or EC50 (regarding immobility) and test duration was 1 to 7 days. The described selection criteria were applied to in order to compare SSD estimates with the results of Maltby et al. (2005). A geometric mean was calculated, when more than one toxicity value was reported for a species or for a genus.

The selection criteria were matched by toxicity data for 24 crustaceans (5 Amphipoda, 4 Cladocera, 13 Decapoda, and 2 Isopoda), 49 insects (22 Diptera, 5 Ephemeroptera, 3 Heteroptera, 5 Plecoptera, 6 Trichoptera, 6 Coleoptera, and 2 Zygoptera) and eight non-arthropod macroinvertebrates (1 Annelida, 1 Bivalvia, 1 Pulmonata, and 5 Gastropoda). A joint SSD curve constructed from arthropod and non-arthropod data did not fit log-normal distribution. Therefore, single SSD curves were constructed from each set of arthropod and non-arthropod data by fitting log-normal distributions according to the method of Aldenberg and Jaworska (2000). Additionally, two separate SSD curves were constructed from the set of arthropod data with respect to the general presence or absence of species taxa in the investigated stream. This was done to account for the potential influence of different taxonomical composition between the SSD and the investigated community. The procedure was not applicable to the limited set of toxicity data for non-arthropod invertebrates. The SSDs were applied in a forward way (Van Straalen, 2002) to estimate the fraction of affected species (FA) at 6.0 $\mu g\ L^{-1}$ parathion-ethyl. Additionally, the SSDs were applied in an inverse way to derive the hazardous concentration of parathion-ethyl for 5% of the species (HC5). For both FA and HC5, lower (5% confidence), median (50% confidence), and upper (95% confidence) estimates were calculated. Non-overlapping confidence intervals (i.e., lower to upper limit) indicated significant differences in median estimates. All curve fitting and parameter estimation was done using the ETX 2.0 software (National Institute of Public Health and the Environment, RIVM, Bilthoven, the Netherlands, 2004). In Table 4, the types of estimates that can be obtained from SSDs (HC5 indicating potential for effects, FA indicating magnitude of effects) are compared with the type of estimates resulting from the other two effect models described further down.

### (ii) PERPEST model

The PERPEST model is a case-based reasoning methodology that uses results of long-term (micro)mesocosm studies to predict the effects of pesticides on freshwater ecosystems (Van den Brink et al., 2002). For (micro)mesocosm studies, observation time usually is a multitude of exposure time. Underlying the model is a case database with each case relating to one pesticide concentration tested in one study and to the reported biological effects of the concentration. Considered in PERPEST are one functional endpoint (community metabolism) and seven structural endpoints. Four of the structural endpoints refer to different groups of macroinvertebrates ('insects', 'macrocrustaceans', 'microcrustaceans', and 'other macroinvertebrates'). The effects are grouped into three classes (class 1 - 'no effect', class 2 - 'slight effect', class 3 - 'clear effect') according to their statistical significance and duration (Brock et al., 2000). Cases belong to the 'no effect' class when no effects were observed because of treatment. Cases belong to the 'slight effect' class when effects were observed only for individual samplings, especially shortly after treatment. Cases belong to the 'clear effects' class when sensitive endpoints showed a clear response to treatment and effects were observed at subsequent sampling dates. Given a question case, PERPEST searches the underlying database for the most similar cases. The similarity of cases can be assessed according to pesticide properties, exposure concentration expressed as Toxic Units (i.e., exposure concentration in relation to the acute LC50 for the most sensitive standard test organism, $TU_{st}$), and type of test ecosystem. According to weighted average effects reported in the most relevant cases, PERPEST predicts the probability of different effect classes to occur at the concentration of the question case. More details on the model are provided in Van den Brink et al. (2002).

In the present case study, PERPEST was applied to predict the probability of effects resulting from exposure to 6.0 $\mu g\ L^{-1}$ parathion-ethyl. The probability of class 3 effects was compared to field observations, because the significant and lasting field effects of parathion-ethyl exposure were most similar to the class 3 effects according to PERPEST criteria. Running PERPEST, only cases were taken into account that evaluated acetylcholinesterase-inhibiting substances and single pesticide applications. Because of the results of the controlled random search procedure implemented in PERPEST, furthermore only cases were taken into account that evaluated $TU_{st}$ not differing by more than a factor of 6.4 from the question case. Selected cases were given a higher weight when they evaluated the same substance (parathion-ethyl), a substance belonging to the same molecule group (organophosphates) and/or a $TU_{st}$ similar to the $TU_{st}$ of the question case. Optimized weighting coefficients were obtained by the controlled random search. In Table 4, the type of estimates given by the PERPEST model (effect probability indicating potential for effects) is compared with the types of estimates resulting from SSDs and the SPEAR-based model (described in the following).

### (iii) SPEAR-based model

The SPEAR-based model is the result of a three-year investigation on 20 small streams in the Braunschweig region, Lower Saxony, Germany (Liess and Von der Ohe, 2005). During the months of April to July, the relationship was studied between runoff-induced pesticide contamination and the presence and abundance of SPEAR. For that study, observation time was a multiple of exposure time during runoff events (1 h peak duration assumed). The SPEAR concept was applied in order to reduce variability in community composition originating from other environmental parameter than pesticides. This concept enables a firm link between exposure and effects on community composition. It also supports the separation of pesticide effects from the influence of confounding factors on community composition. Traits that defined SPEAR were sensitivity to organic toxicants including pesticides (Von der Ohe and Liess, 2004), generation time, migration ability, and presence of aquatic stages during the main period of pesticide application (Liess and Von der Ohe, 2005). During the studied months of April to July, measured toxicity expressed as log-transformed TU (logTU) ranged from -5.0 to -0.7. For details of measurements, see Liess et al. (1999). The percentage abundance of SPEAR (%SPEAR abundance) was calculated as the sum of the log-transformed SPEAR abundances in relation to the sum of the log-transformed abundances of all species. For the month of June (i.e., (post)exposure time), %SPEAR abundance was significantly lower at streams characterized by logTU equal or greater than -3 in comparison to streams with minimum detections of agrochemicals (logTU $\leq$ -4). However, the number of SPEAR in April was significantly higher when there were forested reaches upstream (i.e., undisturbed upstream sections potentially ameliorating effects of pesticides).

For the present case study, data of Liess and Von der Ohe (2005) were used to construct an exposure-response relationship reflecting the community composition in June. Measured toxicity expressed as logTU was recalculated using geometric means of acute toxicity data for *Daphnia magna* (i.e., 48-h EC/LC50$_{Di}$) from the U.S. Environmental Protection Agency database ECOTOX 4.0 (EPA, 2006). Percentage SPEAR abundance was recalculated according to the latest version of the SPEAR database (Liess et al., 2005c). In recalculating the exposure-response relationship, only those sites without undisturbed upstream sections were considered, since they were comparable to the condition at the Ohebach. The program STATIS-

TICA® 7.1 (StatSoft, Tulsa, OK, USA) was applied for linear regression analysis. In Table 4, the type of estimate resulting from the SPEAR-based model (%SPEAR abundance indicating magnitude of effects) is compared with the types of estimates resulting from SSDs and the PERPEST.

Table 4: Types of estimates given by the selected effect models (Species Sensitivity Distributions (SSD), PERPEST, and species at risk (SPEAR)-based model) with respect to the relationship between observation time and exposure time of underlying toxicity studies.

| | *Observation time vs exposure time of underlying studies* | |
|---|---|---|
| *Estimates* | *Equal duration* | *Prolonged observation time* |
| Potential for effects | SSD – endpoint 'hazardous concentration' | PERPEST – endpoint 'probability of effects' |
| Magnitude of effects | SSD – endpoint 'fraction affected' | SPEAR-based model – endpoint 'percentage SPEAR abundance' |

## 3 Results

### 3.01 Comparison of SSD estimates and observed effects

The SSD curve constructed from arthropod EC/LC50 data on parathion-ethyl is given in Figure 5. The estimated HC5 was 0.21 (0.11-0.34) µg $L^{-1}$ and suggested large potential for impacts of 6.0 µg $L^{-1}$ parathion-ethyl. This matched observed field effects and general expectations for a concentration in the range of the EC/LC50 reported for *Daphnia magna*. The predicted median FA was 57%, which means that a concentration of 6.0 µg $L^{-1}$ was larger than the EC/LC50 for 56.8 (49.2-64.18)% of the SSD species. This included *Gammarus pulex* and *Limnephilus lunatus*, two species of the Ohebach community that showed significant responses to measured parathion-ethyl exposure. In contrast to the predicted FA of 57%, a reduction in abundance (≥ of 50%) was observed for all species. Six out of the nine arthropod species were absent after exposure to 6.0 µg $L^{-1}$ parathion-ethyl. Hence, the SSD underestimated the fraction of affected arthropod species that was observed subsequent to the measured concentration of parathion-ethyl around the laboratory EC/LC50 for *Daphnia magna*. A FA corresponding to the observed effects (i.e., abundance reduced by ≥ 50% for all species)

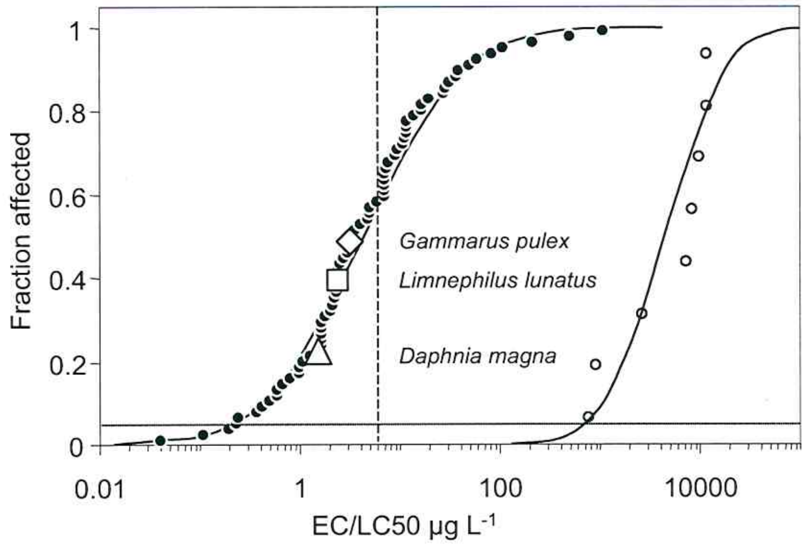


Figure 5: SSD curve for parathion-ethyl constructed from EC/LC50 data for arthropod species (filled circles) and non-arthropod macroinvertebrate species (open circles). The vertical dashed line marks the peak concentration of 6.0 µg L-1 parathion-ethyl that was measured in the Ohebach. The horizontal dotted line gives the fraction affected equal to 5%.

would result from concentrations of more than one and up to two orders of magnitude higher than the measured peak concentration.

Similar results were evident from the two arthropod SSD curves, which were constructed with respect to the general presence or absence of species taxa in the investigated stream in order to study the potential influence of different taxonomical composition between the SSD and the investigated community (not shown). The SSD curve that was adapted to the Ohebach arthropod community yielded a HC5 of 0.56 (0.31-0.90) µg $L^{-1}$ and a FA of 55.7 (45.4-65.8)%. The SSD curve that was based on arthropod taxa not recorded in the Ohebach yielded a HC5 of 0.07 (0.02-0.18) µg $L^{-1}$ and a FA of 58.7 (47.0–68.7)%. The estimates of HC5 differed between these two communities. However, no differences occurred in HC5, when the analysis was based only on insect species recorded in the Ohebach (HC5 = 0.58 (0.30-0.95) µg $L^{-1}$) and insect species not recorded in the Ohebach (HC5 = 0.67 (0.28-1.17) µg $L^{-1}$). Likewise, no significant differences occurred in HC5, when the analysis was based only on crustacean species. The HC5 estimated for Amphipoda was 0.46 (0.03-1.31) µg $L^{-1}$ (the amphipod species *Gammarus pulex* was the only crustacean taxa recorded in the Ohebach), while the HC5 estimated for crustacean taxa not being recorded in the Ohebach was 0.03

(0.00-0.12) µg $L^{-1}$. However it is noteworthy, that the median estimates of HC5 based on insects were in the same order of magnitude, while the median estimates of HC5 based on crustaceans differed by one order of magnitude.

The SSD curve based on non-arthropod data (Figure 5) did not suggest potential impact of 6.0 µg $L^{-1}$ parathion-ethyl on non-arthropod communities. The measured concentration was more than two orders of magnitude below the estimated HC5 of 645.1 (122.2-1526.7) µg $L^{-1}$ and was out of bounds for calculating FA. In contrast, field observations showed that after exposure to 6.0 µg $L^{-1}$ parathion-ethyl, both non-arthropod species decreased in abundance by 50% and more, and in the case of one of these species *(Tubifex tubifex)*, no individual survived. Hence, SSD predictions did not match the post-exposure dynamics of the two non-arthropod species in the Ohebach.

### 3.02 Comparison of PERPEST estimates and observed effects

PERPEST predicted that a concentration of 6.0 µg $L^{-1}$ parathion-ethyl was sufficient to act on arthropod communities (Figure 6). Predicted probability of clear effects (class 3) ranged from 72.9 (47.5-100.0)% for the endpoint 'macrocrustaceans' to 86.5 (73.0-96.4)% for the endpoint 'microcrustaceans' and to 89.1 (71.8-100.0)% for the endpoint 'insects'. This meant that class 3 effects on arthropod species were predicted to occur in 70 and more cases out of 100. The predicted probability of class 3 effects on the endpoint 'other macro-invertebrates' was 37.4 (3.6-67.6)%. All summed up, the PERPEST model predicted that a concentration of 6.0 µg $L^{-1}$ parathion-ethyl would cause a clear response of sensitive endpoints during several subsequent sampling dates, which was in agreement with the Ohebach observations. However, the estimated probability of effects varied considerably between the groups of arthropod and non-arthropod species.

### 3.03 Comparison of the SPEAR-based estimates and observed effects

The SPEAR-based model predicted that 6.0 µg $L^{-1}$ parathion-ethyl were sufficient to act on community composition in the Ohebach. The concentration of 6.0 µg $L^{-1}$ equals a logTU of 0.59 (i.e., for parathion-ethyl the geometric mean 48-h EC/LC50D was 1.53 µg $L^{-1}$). The relationship between logTU and %SPEAR abundance (Figure 7) indicated that at this toxicity level, %SPEAR abundance was close to 0%. This means that communities consisted mainly of species that were either ecologically robust or that were insensitive to organic toxicants, including pesticides. This was in good agreement with the observed effects at the Ohebach.

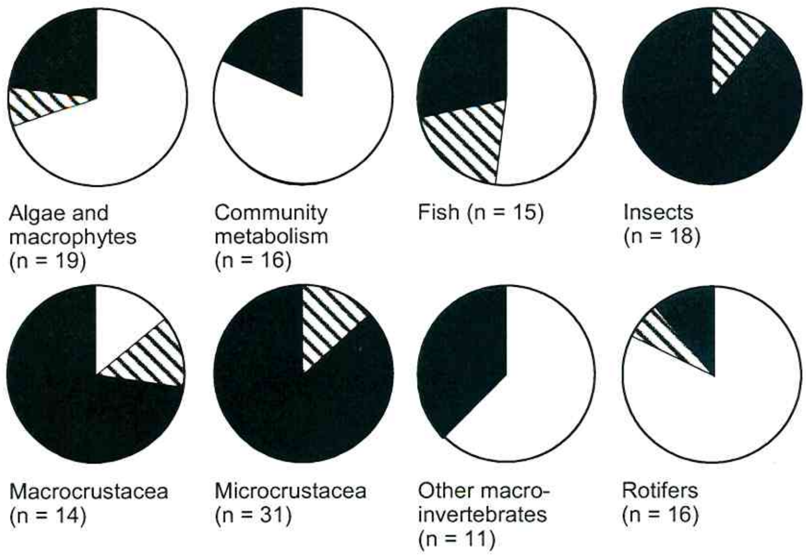


Figure 6: PERPEST predictions on the probability of effects of exposure to 6.0 µg $L^{-1}$ parathion-ethyl. Three effect classes are considered: class 1 - 'no effect' (no filling), class 2 - 'slight effect' (diagonal pattern), class 3 - 'clear effect' (black filling).

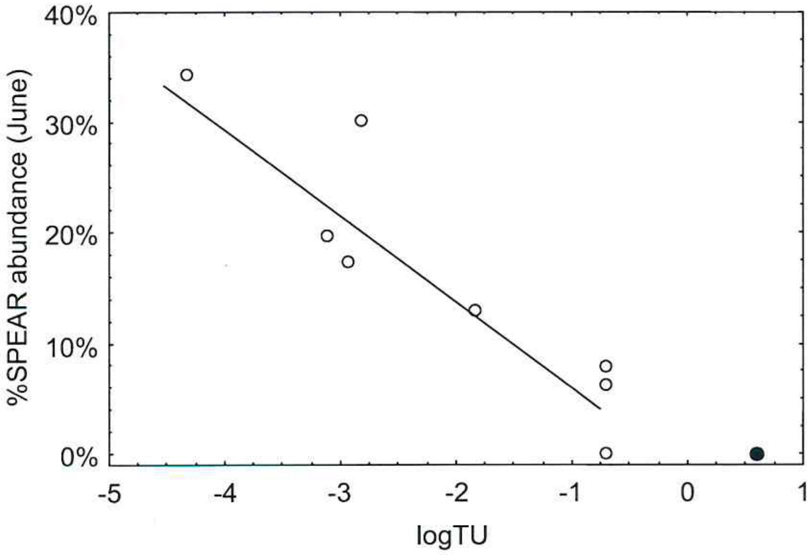


Figure 7: SPEAR-based model to predict the percentage abundance of species at risk (%SPEAR abundance) at a given log-transformed Toxic Unit (log TU). The relationship between log TU and %SPEAR abundance in June (open circles; linear regression, $R^2 = 0.84$, $p < 0.001$) is calculated from data published in Liess and Von der Ohe (2005). The filled circle marks %SPEAR abundance in the Ohebach subsequent to the measured peak concentration of 6.0 µg $L^{-1}$ parathion-ethyl.

Five of the insect species frequently recorded before exposure were SPEAR. As none of these species was recorded in post-exposure samplings, %SPEAR abundance decreased from 37% during March and May to 0% in June.

## 4 Discussion

### 4.01 Measured exposure and additional stressors

The aim of this case study was to give an example of how outcomes of current effect models correlate with observed field effects of short-term insecticide contamination at high exposure level. Therefore, three types of effect models (SSDs, PERPEST, SPEAR-based model) were used predict the effects of 6.0 μg $L^{-1}$ parathion-ethyl on aquatic macroinvertebrate communities. The outcomes were evaluated with the results of a well-documented field monitoring study (Liess and Schulz, 1999). That study on a small agrarian stream demonstrated the toxicological relevance of exposure to 6.0 μg $L^{-1}$ parathion-ethyl for the macroinvertebrate community and quantified the related effects. The toxicological relevance was well established, but the quantitative relationship between measured exposure and observed effects may have been influenced by several aspects discussed in the following.

The 1-h peak concentration of 6.0 μg $L^{-1}$ was the highest runoff-induced water concentration of parathion-ethyl in the Ohebach during a four-year period (Liess et al., 1999) and exceeded peak concentrations of parathion-ethyl by a factor of 20 that were measured in other streams in the same region (Liess and Von der Ohe, 2005). The potential discrepancy between actual exposure and measured 1-h contamination was likely to be small because of the event-triggered sampling technique.

In addition to water contamination, contamination of suspended particles could have resulted in low-level exposure that affected the community between runoff events. According to the equilibrium-partitioning concept, the concentration of 50.8 μg $kg^{-1}$ parathion-ethyl measured between rainfall event 2 and the end of the related sampling interval (Table 3) would result in a water concentration of 3 ng $L^{-1}$ (Hornsby et al., 1995). However, an aqueous concentration in this range (logTU = -2.71 based on recalculated 48-h EC/$LC50_D$) would contribute a comparatively small amount to the toxic potential of the contamination detected in suspension-free water during runoff event 2 (logTU = 0.59 based on recalculated 48-h EC/$LC50_D$). During runoff event 4, 51.6 μg $kg^{-1}$ parathion-ethyl and 302 μg $kg^{-1}$ fenvalerate were measured in suspended particles. Particle-associated fenvalerate concentrations in this range have been demonstrated to cause long-term effects (51 to 193 d after short-term exposure) on emergence and survival of species that are typical for the Ohebach (Schulz and Liess, 2001). However, the results of the microcosms operated in bypass to the Ohebach showed that significant effects on survival of *Gammarus pulex* and *Limnephilus lunatus* occurred shortly after parathion-ethyl contaminated runoff events 2 and 3, while no further significant acute effects on survival occurred shortly after runoff event 4. This suggested that the composition of the Ohebach community observed in June (i.e., three weeks after runoff event 2 and one day after runoff event 4) resulted from parathion-ethyl contaminated runoff, while the toxicological relevance of fenvalerate detected in suspended particles was low during that sampling occasion.

Toxin-induced stress may have been coupled with hydraulic stress, which potentially enhanced the impact of insecticide contamination. In contrast, hydraulic stress alone was unlikely to affect the community adversely, because Liess and Schulz (1999) found no correlation between macroinvertebrate abundance and intensity of hydraulic stress during runoff events without detectable insecticide contamination. Furthermore, the survival of *Gammarus pulex* and *Limnephilus lunatus* in the microcosms was significantly affected although the two populations were not exposed to increased hydraulic stress. Monitored standard water quality parameters were not expected to affect the benthic macroinvertebrates (Schulz and Liess, 1999).

### 4.02 Investigated community

The first post-exposure sampling of the community was done in June (i.e., three weeks after measured peak exposure of 6.0 μg $L^{-1}$ parathion-ethyl). As a result, there was a considerable difference between assumed exposure time (1 h) and observation time. Therefore, the observed post-exposure dynamics of the community may reflect both immediate and also delayed effects that were demonstrated to be able to occur long after the time of short-term exposure (Abel, 1980; Brent and Herricks, 1998; Liess, 2002).

The observed post-exposure dynamics could have also resulted from a particularly sensitive community, but there was no evidence for this. Instead, the community structure was typical of streams in the study area that are exposed to runoff-induced pesticide input. This holds for the recorded taxonomic groups (Amphipoda, Coleoptera, Diptera, Trichoptera, Oligochaeta, and Turbellaria) as well as for their relative abundance (Berenzen et al., 2005a). Also, the Ohebach community was not depauperate, since the number of 11 frequently recorded species was well in the range of five to 12 frequent species that were reported for comparable streams in the study area (Berenzen et al., 2005a).

### 4.03 Effect modeling based on standard toxicity data

SSDs were used to calculate estimates of HC5 and estimates of FA at 6.0 µg $L^{-1}$ parathion-ethyl. For arthropods, estimates of HC5 were similar to values reported by Maltby et al. (2005) and appropriately indicated large potential for effects. Also for non-arthropod macroinvertebrates, estimates of HC5 were of the same order of magnitude as values reported by Maltby et al.. However, the predicted HC5 values indicated no potential for effects, which did not match field observations. The predicted FAs at 6.0 µg $L^{-1}$ underestimated the observed effects on both arthropod and non-arthropod species. A concentration increased by one to two orders of magnitude would yield an estimated FA corresponding to observed arthropod effects, while effects on non-arthropod species would still be underestimated.

The influence of taxonomical composition on SSD distributions (Posthuma et al., 2002b; Maltby et al., 2005) was investigated by comparing an arthropod SSD adapted to the Ohebach community with a SSD based on arthropod taxa not recorded in the Ohebach. Both arthropod SSDs yielded similar estimates of FA that underestimated observed field effects. Additionally, both arthropod SSDs indicated large potential for effects (i.e., estimates of HC5 < 6.0 µg $L^{-1}$), but estimates of HC5 differed. Further analysis based on insects only showed no differences between estimates of HC5. However, the estimated HC5 from crustacean taxa recorded in the Ohebach was increased by one order of magnitude in comparison to the HC5 estimated for the group of crustaceans not recorded in the Ohebach. This suggests that differences in taxonomical composition of the group of crustaceans (due to *Gammarus pulex* as only crustacean species, the Ohebach SSD was constructed from amphipods exclusively) affected estimation of arthropod HC5s, while the predicted general trend (i.e., large potential for effects) was unchanged. In addition, taxonomical differences could have contributed to the divergence of observed and predicted effects on non-arthropod macroinvertebrates, because the two species recorded in the Ohebach, did not belong to the same taxonomical group as the species that were used to construct the SSD curve. Still, the findings for the group of arthropods suggested that a congruent taxonomic composition of SSD and field community would rather influence absolute values of estimates than the general trend of predictions (i.e., no effects on non-arthropod species).

As to the applicability of SSDs for estimation of HC or FA, the findings of this case study indicate the following. For the group of arthropods, SSDs based on acute toxicity data (1-7d EC/LC50) provide estimates of HC5 that are appropriate to indicate the occurrence of field effects of parathion-ethyl at high exposure level. Still, at least in this case study, the SSD based on acute EC/LC50 data was not suitable to provide an appropriate estimate of the arthropod FA. For the group of non-arthropod macroinvertebrates, it is difficult to draw firm conclusions, because only two species of this group were recorded in the Ohebach. The SSD approach underestimated the observed effects, though an overestimation of effects could be expected, because the exposure time in the field (1 h assumed) was shorter than the exposure time of the single species tests applied for constructing the SSD curves. These discrepancies between observed and predicted FA may be due to different aspects. Biased estimates of FA may result from the relation of exposure time and observation time in standard toxicity tests. Several studies showed that especially in standard tests at low concentrations, effects may be greatly delayed following the exposure time required to cause an effect (Abel, 1980; Brent and Herricks, 1998; Liess, 2002). Accordingly, effects may occur long after the end of exposure, which is not accounted for in standard toxicity tests. Therefore, SSDs based on such toxicity data are not suitable to reflect delayed effects. Biased estimates of FA could also result from taxonomic differences between the SSD and the field community, but in the present study, there was no evidence for this. In addition, the mean relative sensitivity of taxa determined according to Von der Ohe and Liess (2004) did not differ appreciably between the communities (SSD community: -0.27; Ohebach community: -0.23). Additionally, estimates could be biased due to biological interaction. Inter- and intraspecific interaction has the potential to amplify direct effects of toxicants on sensitive species, while single-species tests and, consequently, SSDs cannot reflect the influence of these mechanisms (Solomon and Takacs, 2002). However, the data available for this case study did not allow for addressing this aspect.

### 4.04 Effect modeling based on toxicity data from (semi)field studies

The PERPEST model predicts the probability of clear effects (Van den Brink et al., 2002). Thus, PERPEST predictions are comparable to estimates of HC5, because the outcomes of both the PERPEST model and the SSD provide information on whether a given concentration has potential to cause effects (Table 4). The PERPEST model predicted that 6.0 µg $L^{-1}$ parathion-ethyl were likely to cause clear effects on arthropods and non-arthropod macroinvertebrates, which was in agreement with the observed effects on arthropod and non-arthropod species. The HC5s estimated from the SSDs appropriately characterized the potential for effects on arthropods but underestimated the potential for effects on non-arthropods. Therefore, in this case study, the PERPEST model provided better predictions than the SSDs on the potential of concentrations to cause effects.

The SPEAR-based model predicts %SPEAR abundance for a given exposure level. Thus, model outcomes are comparable to estimates of FA, because both the SPEAR-based model and the SSD predict the magnitude of effects from a given concentration (Table 4). The SPEAR were accurately predicted as nearly eliminated due to the measured concentration of 6.0 $\mu g\ L^{-1}$ parathion-ethyl. The FA estimated from SSDs underestimated the observed FA of both arthropods and non-arthropod species. Therefore, in this case study, the SPEAR-based model provided better predictions than the SSDs on the magnitude of effects.

The good performance of the PERPEST model and the SPEAR-based model in comparison to SSDs may be mainly attributed to the fact that both the PERPEST model and the SPEAR-based model make use of the results of long-term studies. As the observation time of (micro)mesocosm and field studies is longer than the time of peak exposure, the results of these studies may reflect both immediate and delayed effects. Consequently, the outcomes of PERPEST and the SPEAR-based model are more likely to match observed effects in the Ohebach than SSD predictions that are based on standard toxicity test with identical exposure and observation time. The relevance of observation time being a multiple of exposure time may become even more important as the exposure concentration decreases. This was demonstrated in several studies, when the time to effect increased as the exposure concentration decreased (Abel, 1980; Beketov and Liess, 2005). The long-term effects of short-term exposure may be further increased in the field, since under field conditions environmental parameters (e.g., low food conditions (Beketov and Liess, 2005; Pieters et al., 2005) or UV radiation (Liess et al., 2001; Duquesne and Liess, 2003)) additionally act on exposed communities.

The present case study suggests that predicted effects correspond well to field effects of short-term exposure to high insecticide concentrations, when models are based on toxicity data that reflect both immediate and delayed effects. These findings underline the relevance of observation time in effect studies and support prolonged observation times in acute toxicity tests to provide data for a refined ecological risk assessment.

# Chapter IV. Establishing exposure-response relationships at broader scales

## 1 Introduction

The structure of macroinvertebrate communities in streams results from a combination of different environmental parameters. At undisturbed sites, stream characteristics such as morphology (Probst et al., 2005), stream chemistry (Gibbins et al., 2001), and riparian vegetation (Potter et al., 2005) may determine the occurrence and abundance of species and can provide suitable predictors of community composition (Clarke et al., 2003). Additionally, a range of anthropogenic pollutants may influence community structure, and effects have been reported e.g. from organic pollution (Kolkwitz, 1950), and heavy metals (Malmqvist and Hoffsten, 1999). For agricultural streams, pesticides (Liess and Von der Ohe, 2005), nutrients, and sediment (Cobb and Flannagan, 1990) have been demonstrated to influence macroinvertebrate communities, and runoff can be considered as the major pathway for these agricultural pollutants to enter surface water bodies. Most of the studies that investigated the influence of agricultural pollutants on the composition of stream communities focused on few sites only. Therefore, they are not of sufficient scale to be representative for the extent, to which both stream characteristics and agricultural pollutants act on macroinvertebrate communities, and to establish exposure-response relationships between the level of agricultural pollution and community composition.

This chapter presents the results of a large-scale investigation that was conducted in the North German Lowlands to extend the knowledge on agricultural influences on macroinvertebrate assemblages of small streams. Stream characteristics, agricultural intensity (potentially resulting in diffuse water pollution), and upstream habitat quality (potentially compensating for effects of agricultural activities) were related to benthic macroinvertebrate community composition. Agricultural intensity in the near-stream environment was represented by potential inputs from arable land via runoff and spray drift, which were modeled using spatial information on key environmental factors. Upstream habitat quality was assessed via the presence of forested upstream stretches. Invertebrate data from governmental monitoring programs were used to define the macroinvertebrate communities present during the main crop vegetation period (April to June). Community composition was described by standard descriptors relating to species richness and abundance as well to the SPEAR method (Liess and Von der Ohe, 2005).

## 2 Material and Methods

### 2.01 The study area

The study area is in the region of Braunschweig, Lower Saxony, Germany (for details on the study region see section 2.01 in Chapter II). A previous study on pesticide contamination of 20 small agricultural streams in this region showed that between 1998 and 2000 insecticides (organophosphates, organochlorines), fungicides (strobilurines, triazoles), and various herbicides were measured and that maximum concentrations of these compounds occurred during the months of May and June (for details see section 3.01 in Chapter II). Liess and Von der Ohe related measured toxicity in the investigated streams to the composition of benthic macroninvertebrate communities (Liess and Von der Ohe, 2005). They suggested that the insecticide parathion-ethyl, the fungicides azoxystrobin and kresoxim-methyl, as well as the herbicide ethofumesate were compounds potentially responsible for the reduction of sensitive macroinvertebrates that they observed during the main period of pesticide application (i.e., the months of May and June).

### 2.02 Characteristics of the investigated streams

A data set of 900 stream sites was available from governmental monitoring programs of benthic macroinvertebrates in Lower Saxony. From this data set, a set of 360 stream sites was selected by applying the following criteria in order to obtain a relatively harmonized data set for subsequent analysis. Firstly, the sites were monitored before (April) or during (May and June) the main period of agrochemical (and in particular insecticide) application for the study area. Secondly, the stream sites were characterized by low mean discharge ($< 0.25$ m$^3$ s$^{-1}$), thus potential pollution from agricultural sources is greatest (Probst et al., 2005), and were at a minimum distance of 1,500 m from the stream source. Thirdly, land use in the near upstream environment of stream sites was mainly arable land, pasture, and forestry, and in that respect, typical of land use in the study area. The near upstream environment was defined as a two-sided 100 m corridor extending along the hydrological network for 1,500 m upstream from sites (Table 5). The combination of low flow (low potential for dilution) and agricultural intensity provided a wide range of scenarios of agricultural input to low order streams. This included sites potentially without agricultural input and sites that were characterized by high potential for agricultural input (which in that respect represented a realistic worst-case scenario for observing potential effects of diffuse pollution from agricultural sources).

The study focused on a stream corridor, because characteristics of the near upstream environment were likely to be more relevant for the exposure of stream sites to runoff than the characteristics of the whole catchment of a site. This approach is supported by a study that showed that observed triazine fluxes at the outlet of a catchment were better correlated with arable land in a two-sided 50-100 m buffer on the channel network than with the total arable land in the catchment (Colin et al., 2000). Also, the results presented in section 3.01 of Chapter II showed that measured pesticide contamination (expressed as $R_{Loss}$) correlated better with the percentage of arable land in a two-sided 100 m corridor extending for 1,500 m upstream from sites than with the percentage of arable land in the whole catchment of the investigated sites.

The spatial data for this study were obtained from various regional authorities. Shape files of the stream network and land cover, as well as a digital elevation model originated from the Authoritative Topographic-Cartographic Information System (ATKIS, http://www.atkis.de). These data (scale 1:25,000) were provided by the regional authority for surveying and mapping (Landvermessung und Geobasisinformation Niedersachsen, LGN, http://www.lgn.niedersachsen.de). A shape file of soil types and their characteristics (scale 1:50,000) was provided by the regional authority for soil sciences (Landesamt für Bergbau, Energie und Geologie, LBEG, http://www.lbeg.niedersachsen.de). All spatial data processing used Arc Info and Arc View (ESRI, Redlands, CA, USA).

On-site habitat quality was assessed by evaluating records made by the UFZ Centre for Environmental Research in October 2002. The records included stream width and depth, discharge, conductivity, streambed substrate composition, substrate cover, and shading, and were available for 106 sites out of the selected 360 stream sites (Table 5). Assessment of habitat quality revealed that the investigated sites were typical lowland streams (Faasch, 1997). In both the moraine landscape and in the loess hills, sand was the predominant substrate of the

Table 5: Descriptive statistics of environmental parameters at the investigated stream sites.

| *Parameter (units)* | *Valid n* | *Median* | *Percentiles* *25th* | *75th* | *Min.* | *Max.* |
|---|---|---|---|---|---|---|
| Physical | | | | | | |
| Width (m) [a, b] | 106 | 1.55 | 1.10 | 2.00 | 0.50 | 4.50 |
| Depth (m) [a, b] | 106 | 0.28 | 0.18 | 0.40 | 0.05 | 1.63 |
| Current (m $s^{-1}$) [a, c] | 106 | 0.28 | 0.20 | 0.40 | 0.00 | 1.00 |
| Conductivity (mS) [a] | 106 | 701 | 420 | 1,030 | 125 | 1,974 |
| Altitude (m) [c] | 360 | 1.20 | 0.85 | 1.40 | 0.10 | 2.40 |
| Near upstream environment ($km^2$) [c, g] | 360 | 0.46 | 0.33 | 0.66 | 0.29 | 2.34 |
| Arable land (%) [c, g] | 360 | 56.5 | 23.4 | 82.5 | 0.1 | 100.0 |
| Pasture (%) [c, g] | 360 | 16.0 | 2.9 | 37.6 | 0.0 | 90.3 |
| Forest (%) [c, g] | 360 | 6.32 | 0.0 | 21.22 | 0.0 | 100.0 |
| Streambed substrate | | | | | | |
| Cobble (%) [a, d] | 106 | 0 | 0 | 10 | 0 | 90 |
| Gravel (%) [a, d] | 106 | 5 | 0 | 20 | 0 | 100 |
| Sand (%) [a, d] | 106 | 59 | 25 | 90 | 0 | 100 |
| Silt (%) [a, d] | 106 | 5 | 0 | 25 | 0 | 100 |
| Clay (%) [a, d] | 106 | 0 | 0 | 5 | 0 | 50 |
| Streambed cover | | | | | | |
| Allochtonous leaves (%) [a, d] | 106 | 5 | 0. | 10 | 0 | 90 |
| Detritus (%) [a, d] | 106 | 5 | 0 | 10 | 0 | 99 |
| Submersed plants (%) [a, d] | 106 | 2 | 0 | 5 | 0 | 60 |
| Emerged plants (%) [a, d] | 106 | 2 | 0 | 5 | 0 | 80 |
| Filamentous algae (%) [a, d] | 106 | 0 | 0 | 5 | 0 | 60 |
| Roots (%) [a, d] | 106 | 0 | 0 | 3 | 0 | 18 |
| Dead wood (%) [a, d] | 106 | 0 | 0 | 0 | 0 | 8 |
| Without cover (%) [a, d] | 106 | 70 | 40 | 85 | 0 | 100 |
| Shading trees (%) [a, d] | 106 | 5 | 0 | 40 | 0 | 98 |
| Shading plants (%) [a, d] | 106 | 6 | 2 | 15 | 0 | 95 |
| Saprobic index [f] | 347 | 2.28 | 2.13 | 2.38 | 1.35 | 3.31 |

[a] Measured in October 2002.
[b] Measured at the mean water level.
[c] Based on the time of a drifting object to travel 10 m on the water body surface.
[d] Estimated within a stretch of 100 m at the steam sites.
[e] Analysis of digital spatial data.
[f] Based on biological data from a 17 year study period (1985-2002).
[g] All of the area of a two-sided 100 m corridor of the hydrological network within a distance of 1,500 m upstream of the site.

streambed, which on average was poorly covered with plants or organic debris. Streams in the moraine landscape were on average slightly wider (1.65 m) than in the loess hills (1.35 m). Chemical water parameters such as nutrients or pH were not available. However, previous investigations showed that the variability of these parameters was reasonably low in the study area (Faasch, 1997; Liess and Von der Ohe, 2005).

Analysis of land use data showed that 69 sites out of the 360 sites had potential point sources of water pollution in the near upstream environment (i.e., within a two-sided 100 m corridor extending for 1,500 m upstream). These included water treatment plants (7 sites), sewage treatment works (20 sites), industrial sites (51 sites) and mining areas (5 sites). Community composition was compared between sites with and without such potential point sources at different levels of agricultural intensity, but statistically significant differences between the two groups of sites could not be identified. This held for overall taxonomic richness and abundance as well as for the number and abundance of sensitive species (Ephemeroptera, Plecoptera, Trichoptera, and SPEAR) and was supported by box-plots produced for each comparison (not shown). Therefore, the sites with potential point sources of water pollution were included in the analysis.

### 2.03 Measures of agricultural intensity

#### (i) Percentage of arable land

The percentage of arable land in the near upstream environment was used as an indicator of agricultural intensity and allowed comparisons between different sites (Probst et al., 2005). The near upstream environment (i.e., a two-sided 100 m stream corridor extending for 1,500 m upstream from a site) comprised a corridor area of 0.30 km² unless the watercourse was branched within the upstream distance of 1,500 m. In case of a branched watercourse within the upstream distance of 1,500 m, the near-stream environment comprised all of the corridor area along the different branches and resulted in a corridor area of greater than 0.30 km². ATKIS data were used to determine the spatial distribution of arable land in the near upstream environment and to calculate percentage arable land. As the spatial data did not indicate small patches (< 1 ha) due to low resolution, a generic value of percentage arable land was assigned, whenever the near stream environment of a site was indicated to lack this type of land use. The generic value was equal to half of the overall minimum percentage arable land calculated for the set of the investigated sites in order to reflect potential for but minimal agricultural intensity.

### (ii) Runoff potential

The RP introduced in section 2.05 (i) of Chapter II was modeled for the 360 selected stream sites. The underlying runoff model (equation 3) was parameterized in the same way as it was for modeling RP in Chapter II (for details see section 2.05 (ii)). However, the time series of daily precipitation (provided by the German Meteorological Service) covered a 17-year period analogous to the period of the investigated biological data (1985–2002). In addition to RP, relative maximum losses of the applied generalized substance (%loss) were calculated (i.e., the maximum predicted runoff load (gLOAD) was divided by the applied mass of the substance per site). It is noteworthy that the properties of the generalized substance including the assumption that it does not degrade represent simplifications that do not apply for most compounds. This means that losses of the generalized substance are overestimated. Therefore, values of predicted percentage losses can only be used to distinguish between sites instead of getting predictions for any one substance.

### (iii) Spray drift potential

The spray drift potential (SP) of the stream sites was modeled in order to compare the level of spray drift inputs from pesticide applications to field crops. The SP was based on a spatially-distributed model that used the same regression fit as the drift calculator of the Forum for Co-ordination of Pesticide Fate Models and their Use (FOCUS) (FOCUS, 2001). The model calculates the maximum drift and resulting environmental concentration of a given substance onto a water body based on the crop type and application rate. Assumptions about wind speed and dilution were in agreement with the FOCUS approach (FOCUS, 2001). The calculation used the same generic substance that was used when modeling RP (application rate 1 g $ha^{-1}$). In contrast to modeling RP, buffer strips were considered in modeling SP, because the required information on the width of buffer strips could be extracted from the available ATKIS data.

A maximum predicted concentration of the generic substance in a given direction results from drift coming from crop directly adjacent to a water body for the entire upwind direction. A concentration of the generic substance less than the maximum will result either if only a portion of the water body is potentially exposed to spray drift from that direction, or if the crop is not directly adjacent to the water body. Two ratios called the 'affected ratio' and 'drift ratio' were used to estimate these two factors. The 'affected ratio' estimates the portion of the water body that experiences spray drift from a given direction; the 'drift ratio' estimates the percentage of drift onto the water body in relation to the theoretical maximum. If crop was directly adjacent to the water body and all potentially exposed points were actually exposed for a particular wind direction, then the 'affected ratio' and 'drift ratio' would both be 1.0, yielding a load corresponding to the maximum value computed using the FOCUS drift calculator. A final drift value less than the maximum results from reductions in either the amount of water body exposed or in the degree to which it is exposed (due to a natural buffer).

A spatial link between the water body, proximate crop, and wind direction was established as follows to calculate the ratios. Sampling points were placed at regular intervals (10 m) on the water body perimeter, and a line was drawn against the direction of the wind (in each of eight directions). The number of points at which exposure of the water body could potentially occur was counted. This number was referred to as the number of potentially exposed points (NPE). The number of lines that did actually expose the water body was counted, (i.e., the line intersects crop somewhere along its length out to 60m from the water body). This number was called the number of actually exposed points (NAE). The 'affected ratio' was given by the ratio of the number of actually exposed points to the number of potentially exposed points (i.e., NAE / NPE). The 'drift ratio' with the wind in a given direction was calculated as the total calculated drift (the average of all 10m sample points potentially receiving drift from that direction) divided by the total maximum drift (i.e., the portion of the water body perimeter that does receive drift, on average receives x% of the maximum).

Exposure of a water body to spray drift was predicted by estimating the maximum generic concentration resulting from spray drift from each of eight cardinal directions (N, NE, E, SE, S, SW, W, and NW). Each of the eight predicted maximum concentrations was then multiplied by the 'affected ratio' and 'drift ratio'. A stream site was potentially not exposed to spray drift, if according to the ATKIS data no arable land was located in the near-stream environment. With respect to the restricted resolution of the maps, a spray drift concentration was assigned to these stream sites indicating potential but minimum exposure to spray drift. This concentration was set equal to half of the overall minimum concentration, which was predicted for the set of the investigated sites. For analogy with modeled RP, the predicted spray drift concentrations were binned into broadly order-of-magnitude categories by log-transformation. The resulting final SP was applied to rank sites according to potential spray drift inputs.

### 2.04 Upstream habitat quality

An analysis of the upstream habitat quality was included in this investigation in order to study the potential influences of upstream refugia on stream sites. The previous investigation of Liess and Von der Ohe had shown that stream stretches bordered by forest provided potential refugia for in-stream recolonization of downstream stretches flowing through arable land (Liess and Von der Ohe, 2005). In order to identify potentially undisturbed upstream stretches in the present data set, macroinvertebrate community composition was compared between sites that differed in the percentage of forest and pasture in the near upstream environment. Preliminary analyses showed that the number and abundance of SPEAR in relation to the overall taxonomic richness and abundance significantly increased at sites where forest covered more than 20% of the near upstream environment. Therefore, the percentage of forest in the near upstream environment according to ATKIS data was used for classifying sites to be potentially with (> 20% forest) or without (≤ 20% forest) undisturbed upstream stretches.

### 2.05 Biological data

Macroinvertebrate monitoring data from a 17-year period (1985-2002) were used to classify the biological quality of the 360 investigated stream sites (data were provided by the Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz, NLWKN, http://www.nlwkn.niedersachsen.de). The sampling program was designed to monitor the potential impacts arising from organic, deoxygenating substances, and to classify streams according to their saprobic level. Since the monitoring aimed to classify streams rather than provide a complete species inventory, the sampling frequency of sites varied from annual sampling to sampling done less than every three years. In total, 1991 records were available for the selected set of sites, of which 932 were conducted in the months of April, May, or June. The abundance of individuals per species was binned into classes ranging from 1 (one individual) to 7 (very abundant) (DIN, 1990).

Based on the overall data set of 360 sites, long-term community responses to agricultural intensity were investigated as well as the potential of upstream habitat quality for compensating effects of agricultural pressures. However, most sites in the overall data set were sampled either in the month of April (pre-application period of agrochemicals) or in the month of May or June (main application period of agrochemicals). This could have caused one of these periods to be over-represented when aggregating biological records per site and variability in the dataset could be increased due to this potential bias. To tackle this problem, a subset of 112 sites was generated that were sampled during both the pre-application and the main application period. This subset was analyzed for correlations between community structure, agricultural intensity, and on-site habitat quality as well as for seasonal trends in the data.

### 2.06 Community descriptors

For each stream site, biological records were aggregated from April, May, and June including all available years in order to reflect on average the community structure in late spring and early summer. On average, 14 species were recorded per sample, which is in accordance with the number of benthic taxa that were frequently recorded in the course of an intense monitoring program in the study area (Berenzen et al., 2005a). As to the present data, more than three species were recorded in 99% of the samples from the same month of the same year. With respect to this distribution of species per sample, single biological records per site of one to three species only, were regarded as potentially biased samples due to sampling errors and were not considered in the aggregation procedure.

The following standard community descriptors were calculated: the overall species number and abundance (i.e., the sum of the abundance classes of all species), the Shannon-Wiener diversity index, the Ephemeroptera-Plecoptera-Trichoptera (EPT) score (as number of species termed EPT number and percentage abundance of these orders termed %EPT abundance), and the saprobic index (DIN, 1990).

Furthermore, the SPEAR classification (Liess and Von der Ohe, 2005) was applied to separate the effects of diffuse water pollution from the influence of other stressors. For the present study, macroinvertebrates were classified according to the latest version of the SPEAR database (Liess et al., 2005b). In addition to the standard community descriptors described above, the following SPEAR-descriptors were calculated. The number of species at risk was termed SPEAR number, and SPEnotAR gives the number of species not at risk. The SPEAR abundance is the sum of the abundance classes of all species at risk. The percentage abundance of SPEAR (%SPEAR abundance) was calculated to reflect community composition in terms of SPEAR more comprehensive. The endpoint $\%SPEAR_{(physiology)}$ abundance gives the percentage abundance of SPEAR in case of a classification only according to potential sensitivity towards organic toxicants. Ecological traits are not considered in this endpoint. In contrast, the endpoint $\%SPEAR_{(ecology)}$ abundance gives the percentage abundance of SPEAR in case of a classification only according to life history traits and is in that respect complementary to $\%SPEAR_{(physiology)}$ abundance. The three endpoints %SPEAR abundance, $\%SPEAR_{(physiology)}$ abundance, and $\%SPEAR_{(ecology)}$ abundance were compared at different levels of agricultural intensity to investigate long-term changes in community composition. For this analysis, values of each of the three endpoints were rescaled by the respective median values of %SPEAR abundance, $\%SPEAR_{(physiology)}$ and $\%SPEAR_{(ecology)}$ at low levels of agricultural intensity.

### 2.07 Statistics

The Kolmogoroff-Smirnoff test revealed that the data were not normally distributed. Therefore, non-parametric measures and methods were used for descriptive statistics and hypothesis testing. Quartiles were used to describe the distribution of the data. The Spearman rank correlation coefficient $R$ was applied to test for correlations between community descriptors and abiotic environmental parameters. The Mann-Whitney-U test was used to compare biological endpoints between two independent groups. The Kruskal-Wallis analysis-of-variance was employed, when testing for differences in biological endpoints between several independent groups. Wilcoxon's matched pairs rank test was used to compare biological endpoints belonging to dependent groups. All statistics were carried out with STATISTICA® 7.1 (StatSoft, Tulsa, OK, USA). As is convention, strong correlation was defined as Spearman $R \geq 0.8$, moderate correlation as $0.8 >$ Spearman $R \geq 0.5$, and weak correlation as Spearman $R < 0.5$.

## 3 Results

### 3.01 Agricultural intensity at the investigated stream sites

Distributional analysis of the 360 investigated streams showed that the percentage of arable land in the near upstream environment was distributed uniformly across a range from 0% to 100%. Predicted RP for the 360 sites ranged over nearly ten orders of magnitude from -9.67 (indicating potential but minimal inputs) to a maximum value of -0.36, which equals a predicted generic load of 0.44 g per site. The majority of sites (60%) was characterized by intermediate RP ranging from greater than -3 to -1 (Figure 8a), while values of RP greater than -1 (i.e., highest predicted RP in this study) were assigned to only 12.2% of the sites. The frequency distribution of relative runoff losses (%loss) showed that at the majority of the investigated sites (69.2%), %losses ranged between greater than 0.01 and 1% (Figure 8b). The SP was modeled at 150 sites from the overall data set due to availability of data and predictions ranged from SP = -3.3 (indicating potential but minimal inputs) to a maximum value of -0.21. A predicted SP -3 or less was assigned to 8.1% of the investigated sites, while at about 30.8% of the sites predicted SP ranged from greater than -3 to -1. As a result, the majority of sites (61.1%) was characterized by high SP (> -1).

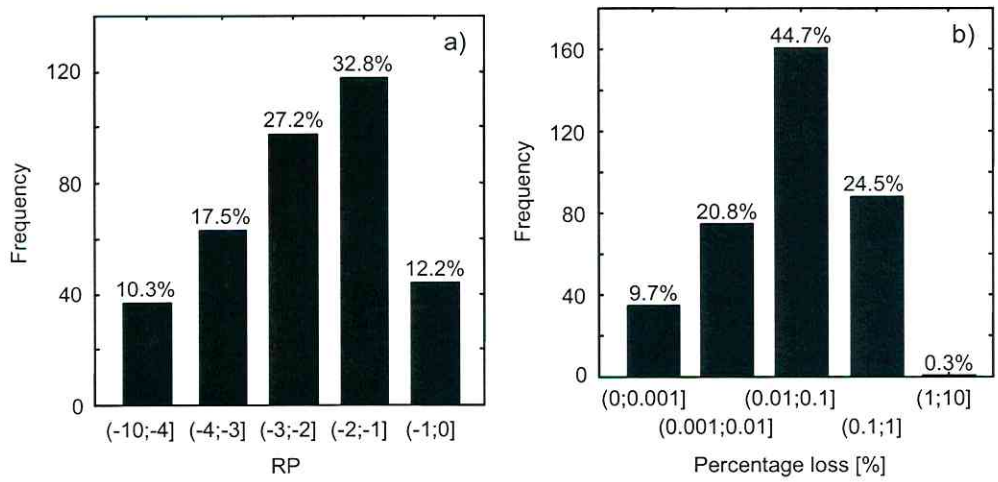


Figure 8: Frequency distribution of the investigated sites ($n$ = 360) over the range of a) predicted runoff potential (RP) and b) calculated percentage loss of the applied mass of the generalized substance.

## 3.02 Correlation between community endpoints and environmental parameters

Correlations were investigated between community structure, measures of agricultural intensity and on-site habitat quality in order to identify potential environmental correlates of community composition. For this purpose, the subset of 112 sites was analyzed, because at these sites invertebrate data were available for the month of April (pre-application period of agrochemicals) and as well for the period of May and June (main application period of agrochemicals). The various measures of agricultural intensity were intercorrelated in that the percentage of arable land moderately correlated with RP ($R = 0.68$, $p < 0.001$) and SP ($R = 0.67$, $p < 0.001$), whilst RP correlated with SP ($R = 0.65$, $p < 0.001$). As RP correlated closest with the macroinvertebrate community descriptors, further analysis was focused on RP as a surrogate measure of agricultural intensity.

For agricultural intensity, it occurred that with increasing RP there was a decrease in species number, Shannon-Wiener diversity index, EPT scores and SPEAR endpoints (for details see Table 6). For habitat quality variables, it was observed that with increasing stream width there was an increase in species number, abundance, diversity, EPT number, and SPEAR endpoints. In addition, SPEAR endpoints increased when the content of dead wood in streambed increased. In contrast, there was a decrease in EPT number and SPEAR endpoints when the

Table 6: Spearman $R$ is given for correlations of community descriptors (including descriptors based on Ephemeroptera, Plecoptera and Trichoptera, EPT, and on species at risk, SPEAR) and abiotic environmental parameters ($*p < 0.05$, $**p < 0.01$, $***p < 0.001$). The analysis is based on the subset of 112 sites; however, information on on-site habitat quality was only available for 40 sites from the subset. Environmental parameters that were described in section 2 of this chapter, but are not shown, did not correlate significantly with the investigated community endpoints. In case of intercorrelation characterized by $R \geq 0.5$, the environmental parameter correlating more closely to the community descriptors was included in the table.

| | *Environmental parameters* | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | *Runoff Potential (RP)* | | *Stream width [m]* | | *Clay [%]* | | *Dead wood [%]* | | *Detritus [%]* | |
| Community endpoints | | | | | | | | | | |
| Species number | -0.36 | (*) | 0.46 | (**) | - | | - | | - | |
| Species abundance | - | | 0.39 | (*) | - | | - | | - | |
| Shannon-Wiener diversity index | -0.39 | (*) | 0.45 | (**) | - | | - | | - | |
| EPT number | -0.44 | (**) | 0.43 | (**) | -0.37 | (*) | - | | - | |
| %EPT abundance | -0.32 | (*) | - | | - | | - | | - | |
| SPEAR number | -0.66 | (***) | 0.55 | (***) | -0.43 | (**) | 0.34 | (*) | - | |
| %SPEAR abundance | -0.65 | (***) | 0.53 | (***) | -0.44 | (**) | 0.41 | (**) | - | |
| Saprobic index | - | | - | | 0.37 | (*) | -0.37 | (*) | -0.33 | (*) |

content of clay in streambed increased. Additionally, weak intercorrelations of some environmental parameters were observed as follows. RP negatively correlated with stream width ($R$ = -0.49, $p < 0.01$) and with the percentage of dead wood ($R$ = -0.32, $p < 0.05$). However, predicted RP was not intercorrelated with the clay content of the streambed, indicating that clay content did not increase as that measure of agricultural intensity increased. Conversely, stream width was weakly negatively correlated with clay content ($R$ = -0.37, $p < 0.05$), indicating that in wider streams the clay content of the streambed was lower.

### 3.03 Short-term changes of community structure and runoff potential

The subset of 112 sites being sampled before (April) and during the main application period of agrochemicals (May to June) was evaluated in order to investigate seasonal trends in the biological data. According to the trend of community development, two groups of sites were distinguished in the set. For the first group, overall species number increased from pre- to main application period ($n$ = 59), and for the second group, overall species number decreased from pre- to main application period ($n$ = 53). For the first group, it was observed that at sites of low runoff potential (RP $\leq$ -3), the endpoint %SPEAR abundance did not change significantly from pre- to main application period. For these sites, the main to pre-application period ratio of %SPEAR abundance was 1.2. At sites of medium RP ranging from greater than -3 to -2 and at sites of high RP (> -2), this ratio did not change significantly. For the second group (decrease in overall species number), it was observed that at sites of low RP, %SPEAR abundance did not change significantly from pre- to main application period (Figure 9). However, %SPEAR abundance significantly decreased towards the main application period at sites of high RP (equivalent to predicted median %loss of 0.1%). This temporal change in community composition occurred at 54% of the sites of the subset that were characterized by high RP. For the overall dataset, this suggests similar changes at 24% of all sites, as about half of the sites of the overall set ($n$ = 162) are characterized by RP greater than -2.

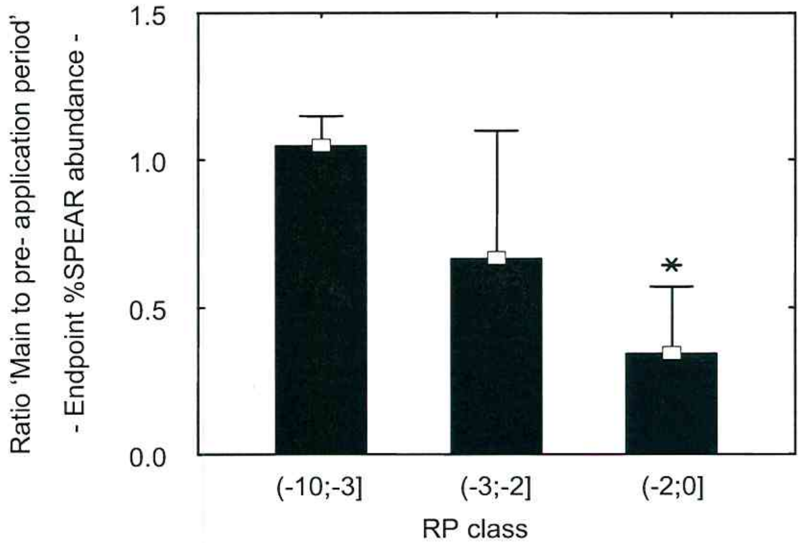


Figure 9: Decrease of percentage species at risk abundance (%SPEAR abundance) from pre- to main application period. The main to pre-application period ratio is shown with respect to predicted runoff potential (RP) ($n$ = 53). Asterisks indicate a significant difference from sites with RP of -3 or less (Kruskal-Wallis analysis-of-variance, $^*p < 0.05$). Bars give the median (50th percentile) and error bars show 25th to 75th percentile.

### 3.04 Long-term changes of community structure and runoff potential

The overall data set of 360 streams containing samples from late spring and early summer was evaluated to investigate how diversity was related to RP. At sites of low RP (≤ -3), the Shannon-Wiener diversity index, species number, EPT number and SPEAR number were reasonably high. Figure 10a shows that at sites of high RP (> -2), the diversity index was significantly decreased, but evenness remained close to 1 (i.e., community composition remained evenly spread between taxa as RP increased). Figure 10b shows the changes in diversity in more detail. At sites characterized by high RP, overall species number and EPT number were significantly decreased, while SPEAR number was significantly decreased at sites of medium RP ranging from greater -3 to -2 and higher. However, the median species number of 10 (including three EPT species and two SPEAR) suggested that macroinvertebrate communities at sites of high RP (equivalent to a median %loss of 0.12%) were still reasonably diverse.

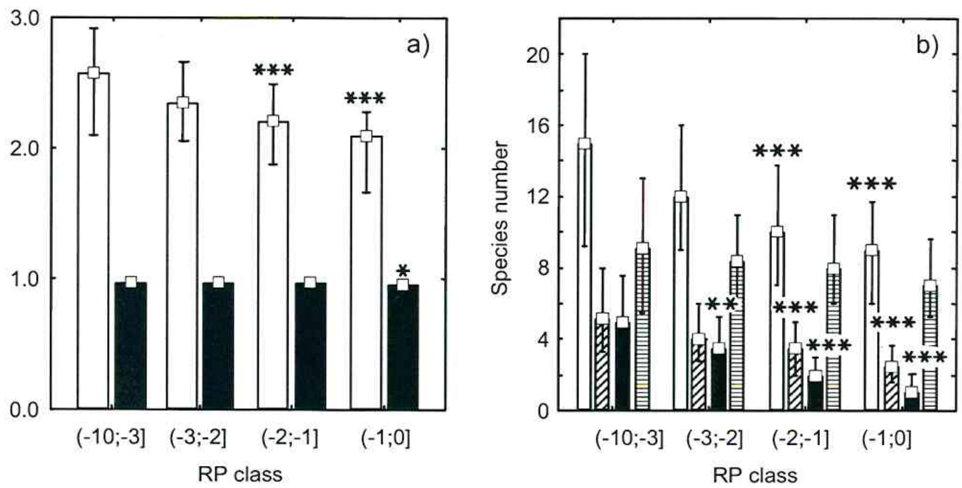


Figure 10: Relationship between predicted runoff potential (RP) and aquatic macroinvertebrate communities in late spring and early summer (April to June, $n$ = 360). Figure a gives indices of diversity (open bars) and Shannon-Wiener evenness (filled bars). Figure b shows overall species number (open bars), Ephemeroptera-Plecoptera-Trichoptera number (bars with diagonal pattern), species at risk number (filled bars), and species not at risk number (bars with horizontal pattern). Asterisks indicate significant differences from the sites with RP of -3 or less (Kruskal-Wallis analysis-of-variance, *$p < 0.05$, **$p < 0.01$, ***$p < 0.001$). Bars give the median (50th percentile) and error bars show 25th to 75th percentile.

Additionally, changes were investigated in the sensitivity of species to organic pollutants and the ecological traits of species in relation to increasing RP. For this purpose, the community endpoints %SPEAR abundance, %SPEAR$_{(physiology)}$ abundance and %SPEAR$_{(ecology)}$ abundance were compared between different levels of RP (Figure 11). At sites of medium to high RP, median values of %SPEAR abundance and %SPEAR abundance$_{(ecology)}$ were significantly decreased in comparison to sites of low RP. For the endpoint %SPEAR abundance$_{(physiology)}$, such a significant decrease was observed only at sites of high RP. When comparing the complementary endpoints %SPEAR$_{(physiology)}$ abundance and %SPEAR$_{(ecology)}$ abundance, a significant difference in median values of the two endpoints was observed only at sites of highest predicted RP (> -1). In summary, communities appeared to react in two ways in response to medium to high RP. On the one hand, there was a shift towards species that are ecologically robust (high recovery potential, emergence before the main period of agrochemical application, migration ability), and, on the other hand, there was a shift towards species that are characterized by a low sensitivity towards toxicants. In contrast, communities appeared to adapt to highest predicted RP through a shift to more ecologically robust species.

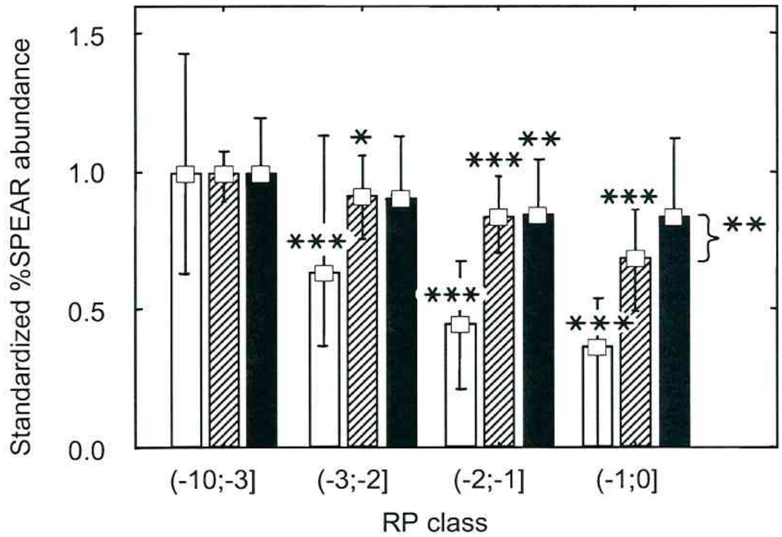


Figure 11: Relationship between predicted runoff potential (RP) and community descriptors based on species at risk (SPEAR; $n$ = 360) – percentage abundance of SPEAR (%SPEAR abundance, open bars), percentage abundance of SPEAR due to life-cycle traits (%SPEAR$_{(ecology)}$ abundance, bars with diagonal pattern), and percentage abundance of SPEAR due to physiological sensitivity (%SPEAR$_{(physiology)}$ abundance, filled bars). The data were rescaled according to median values at sites with RP of -3 or less. Asterisks indicate significant deviation from sites with RP of -3 or less (Kruskal-Wallis analysis-of-variance, $*p < 0.05$, $**p < 0.01$, $***p < 0.001$), and significant differences between %SPEAR$_{(ecology)}$ abundance and %SPEAR$_{(physiology)}$ abundance (Wilcoxon's matched pairs rank test, $**p < 0.01$). Bars give the median (50$^{th}$ percentile) and error bars show 25$^{th}$ to 75$^{th}$ percentile.

### 3.05 Influence of undisturbed upstream stretches

The overall data set was evaluated to investigate the influence of undisturbed upstream stretches on community composition. All sites were grouped according to the presence or absence of undisturbed stretches (forest cover in the near upstream environment ≤ 20% or > 20%). The relation of predicted RP and %SPEAR abundance was compared between the two resulting groups. In total, 27% of the sites had stretches within a reach of 1,500 m upstream that were undisturbed in terms of agriculture. For those sites lacking undisturbed stretches, it was observed that at high RP (> -2) %SPEAR abundance was decreased by 50% in comparison to sites of low RP (Figure 12). When sites had undisturbed upstream stretches, %SPEAR abundance did not significantly decrease as RP increased. Additionally, it was observed that %SPEAR abundance of sites with undisturbed stretches was increased by up to a factor of 2 ($p < 0.01$) in comparison to sites without such stretches. It is noteworthy that %SPEAR abundance at sites of high RP with undisturbed stretches was similar to %SPEAR abundance at sites of low RP that had no such stretches. This implied that undisturbed upstream stretches compensated for the reduction in SPEAR that was observed at high levels of RP.

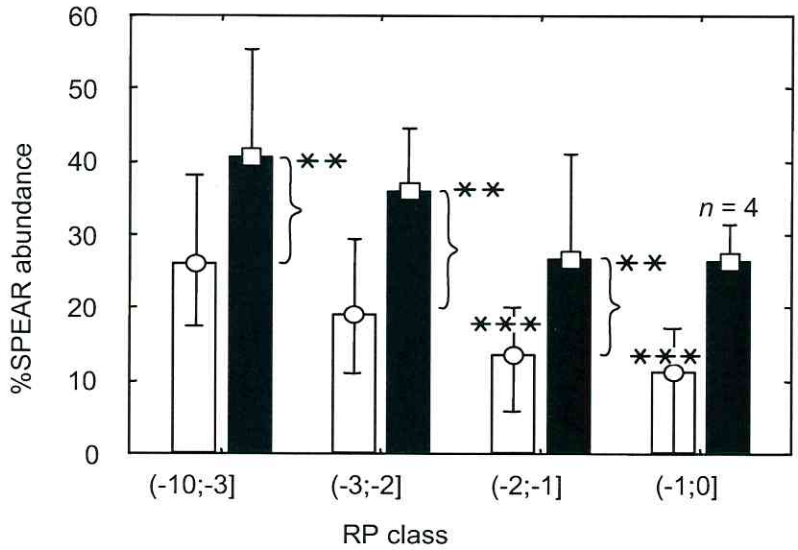


Figure 12: Relationship between predicted runoff potential (RP) and percentage abundance of species at risk (%SPEAR abundance, $n$ = 360). Sites are grouped according to the presence (filled bars) or absence (open bars) of undisturbed upstream stretches. Asterisks indicate significant deviation from sites with RP of -3 or less (Kruskal-Wallis analysis-of-variance, $***p < 0.001$), and significant differences between sites in the presence or absence of forest (Mann-Whitney-U test, $**p < 0.01$, $***p < 0.001$). Bars give the median (50$^{th}$ percentile) and error bars show 25$^{th}$ to 75$^{th}$ percentile.

Furthermore, the relation of RP and community composition was compared between sites with and without undisturbed upstream stretches in April (i.e., before the main period of pesticide application in the study area, not shown). For sites of low RP, %SPEAR abundance in April was about 40%, irrespective of the presence or absence of undisturbed upstream stretches. For sites of high RP, %SPEAR abundance was still 30% in the presence of undisturbed stretches, while the endpoint decreased to 16% ($p < 0.01$) at sites that were without undisturbed stretches. Therefore, it occurred that at sites of high RP, the endpoint %SPEAR abundance was significantly higher in the presence than in the absence of undisturbed stretches ($p < 0.01$).

## 4 Discussion

### 4.01 Environmental variables and community composition

A number of studies have investigated the influences of land use including agriculture on community composition of macroinvertebrates in the stream benthos. Sedimentation and changes in water quality were identified as potential causes for decreased macroinvertebrate taxon richness (especially for EPT species) in agricultural streams (Lenat, 1984). The effects of catchment land use (forest, agriculture, urban) on macroinvertebrate communities was investigated at three streams (Lenat and Crawford, 1994). Enhanced sediment levels and nutrient enrichment was observed in the agricultural stream, where the community was characterized by few EPT species, but many tolerant taxa in comparison to the forested stream. However, as the investigated water quality parameters could not account for all of the observed differences between the streams, some unmeasured toxicity was suggested as an additional stressor. Another study showed that along a river continuum, water quality parameters in agricultural reaches were strongly associated with the composition of benthic assemblages (Harding et al., 1999). Invertebrate species richness did not change significantly throughout the river, but EPT taxa that dominated the headwater sites were replaced in downriver agricultural reaches by molluscs, oligochaetes, and chironomids.

The findings from these previous studies echo to a certain extent the themes that arose in this chapter. Together, they also highlight a common difficulty of observational studies within a large-scale landscape, namely, to distinguish between correlation and causation. The major challenge this presents is that it is difficult to determine the precise causes of differences in community structures with a high degree of certainty when a range of potentially confounding factors are present (Manel et al., 2000). However, such studies are perhaps the only way to develop the hypotheses for further investigation of the important factors that may influence communities in ecosystems over large spatial or temporal scales. Below, some possible hypotheses are discussed for the observed correlations between macroinvertebrate communities, agricultural intensity, and on-site habitat quality in this chapter. Such hypotheses could then be tested in further focused, experimental field studies, in order to elucidate the precise causative factors, although the practical challenges of such studies would be undoubtedly substantial, as has been recognized elsewhere (Liess et al., 2005a).

Comparing agricultural intensity and habitat quality, RP and stream width (to a slightly lesser extent) correlated closely with most community descriptors. Clay content of the streambed and percentage of dead wood in the streambed cover correlated with only the community descriptors that focused on the more sensitive species variables. The parameters of agricultural intensity and habitat quality were weakly intercorrelated in that RP was negatively correlated with stream width and percentage of dead wood, but was not correlated with clay content. Among the habitat parameters, stream width was weakly negatively correlated with clay content. For stream width, the negative correlation with RP may be attributed to wider streams tending to occur in the moraine lowlands, where predicted RP was low because of sandy soils. This suggested that stream width was probably a confounding factor. However, bearing in mind that stream width correlated with most measures of taxonomic richness and abundance, the weak correlation with RP could be interpreted as well to indicate that agricultural intensity and stream width acted independently on community composition. Other studies have also found positive correlations of stream width and macroinvertebrate community composition (Heino et al., 2003; Probst et al., 2005). Increases in taxonomic richness may be attributable to species-area relationships; larger habitat area and a broader range of in-stream niches may promote higher diversity (Probst et al., 2005). Positive correlations of stream width with abundance may be also be linked to potentially increased levels of dilution in wider streams with larger catchments which may reduce peak concentrations of runoff constituents such as pesticides (Iwakuma et al., 1993). For clay content, the weak negative correlation with stream width may be attributed to wide streams in the moraine landscape with predominantly sandy soils. For percentage of dead wood, the weak negative correlation with RP may be attributed to high percentage of forest in the moraine landscape, where RP was low. Since percentage of dead wood and clay content correlated with sensitive species measures only, the observed intercorrelations suggest that these habitat parameters were probably confounding factors rather than clear environmental determinants in relation to the investigated community endpoints. However, the correlation of clay content with community descriptors that focused on the more sensitive species variables may reflect that many EPT species prefer coarse-grained, open substrates, which may be rare in agricultural streams due to sedimentation (Lenat, 1984; Harding et al., 1999).

### 4.02 Short-term community responses to predicted runoff potential

One question arising in studies on the influence of agricultural activities on benthic macroinvertebrates is the extent to which the observed changes in community structure in agriculturally intensive areas could be due agrochemicals. This investigation showed that community composition was moderately correlated with predicted RP, but was not correlated with modeled SP. Therefore, one may surmise that runoff from arable land is probably the major source of diffuse water pollution under the arable conditions in the study area. In order to address the question of the potential influence of agrochemicals, temporal trends in community composition were investigated between the broadly pre-application and main application periods of pesticides in the study area with respect to different levels of predicted RP. Herein, it is important to note that this study focused on generalized landscape mediated runoff inputs and agrochemicals as potential constituents. In contrast, it was not intend to draw inferences of the influence of any particular agrochemical.

At sites of low RP, %SPEAR abundance did not change significantly from the pre- to main application period. However, at sites characterized by high RP, %SPEAR abundance tended to decrease significantly from the pre- to main application period (i.e., from the month of April to months of May and June). This was established for half of the sites of the investigated subset. Liess and Von der Ohe (2005) showed that during the months of May and June, runoff-induced pesticide concentrations were detected in streams of the study area that might have an impact on certain aquatic invertebrates. In that study, the decrease of %SPEAR abundance from pre- to main application period was more pronounced at sites where measured pesticide residues were in the range of 1:10 to 1: 100 of the LC50 for *Daphnia magna* than at sites with the lowest measured residues. This might suggest that pesticides probably were a contributing factor to the changes in community endpoints, which were observed in the present work, although this cannot be proved due to the lack of long-term chemical monitoring data.

While pesticides may have been a contributing factor, the impact of agricultural pressure resulting from other substances than pesticides is not likely to be particularly high during the months of May and June. Runoff-related hydrodynamic stress due to increased current velocity occurs frequently throughout the year and there is no indication that it affects macroinvertebrate communities only in May and June. In addition, a previous study showed that measured intensity of hydraulic stress alone was not correlated with dynamics in macroinvertebrate abundances (Liess and Schulz, 1999).

Runoff-related input of suspended particles is most likely to occur before or early in the vegetation period, when the ground is still bare or not yet densely covered. Potentially toxic concentrations of nitrite and ammonia originating from agricultural fields are unlikely to occur between April and the period of May and June only. Rather they are expected at the beginning of the vegetation period due to application of fertilizer or manure, or late in summer due to enhanced temperature and low water levels (Kladivko et al., 1991; Chokmani and Gallichand, 1997). Regarding the observed short-term changes in %SPEAR abundance in the present study, it is noteworthy that these were reversible between the years, and complete recovery from short-term changes was observed by the following spring.

The findings imply that runoff is likely to be a significant process resulting in diffuse water pollution with pesticides. Similar conclusions on the importance of runoff in comparison to spray drift were reached for arable crops on the basis of modeled pesticides loads in German river catchments (Huber et al., 2000). However, whilst pesticide runoff may be relatively more important in arable crops, spray drift especially in terms of peak concentrations may be more significant in high crops such as orchards (Dabrowski et al., 2006). The results of a field investigation on survival rates of *Limnephilus lunatus* and *Gammarus pulex* under water conditions of a small agricultural stream (Liess and Schulz, 1999) showed that during the main period of pesticide application in the stream catchment, survival rates were lower if the species were exposed to stream water during runoff events. As no pronounced decrease was observed at other times during that study, the influence of insecticide spray drift on *Limnephilus lunatus* and *Gammarus pulex* was likely to be low in comparison to the influence of pesticide runoff.

### 4.03 Long-term community responses to predicted runoff potential

Another question addressed in this chapter was how agricultural intensity was related to diversity as well as to the sensitivity of species and their ecological traits. For diversity, it was observed that at sites characterized by low RP, the community endpoints of species number, EPT and SPEAR number were reasonably high (Berenzen et al., 2005a). In contrast, it was observed that a significant long-term decrease in these endpoints occurred at sites of high RP (45% of the investigated stream stretches). Nevertheless, macroinvertebrate communities were able to persist at this level of RP with taxonomic richness of reasonable quality. Besides these changes in taxonomic richness, it occurred that already at sites of medium RP, community composition changed towards species that are physiologically robust to organic pollutants and ecologically robust (short generation times, high migration ability and emerge before the beginning of the main application period of pesticides in the study area). In contrast, at sites characterized by the highest modeled RP (RP > -1), the shift to ecologically robust species became more pronounced than the shift to physiologically robust species.

The described long-term shifts may be attributed to the combined influence of different runoff constituents such as nutrients or suspended sediments (Lenat, 1984; Lenat and Crawford, 1994; Harding et al., 1999). Other studies found that long-term shifts in community structure also result from exposure to pesticides. A study with the caddisfly *Limnephilus lunatus,* demonstrated that several months after short-term exposure to the insecticide fenvalerate, development and mortality were adversely affected (Liess, 2002). Another investigation on the effects of short-term exposure to fenvalerate showed that during a three-year period direct effects due to the chemical were followed by shifts in interspecies relationships and differences in life history cycles, which caused long-term changes in community structure (Woin, 1998).

### 4.04 Positive effects of upstream habitat quality

The influence was investigated that undisturbed upstream stretches may have on community composition. Percentage SPEAR abundance of sites with undisturbed upstream stretches was significantly increased in comparison to sites without these stretches. In the presence of undisturbed upstream stretches, %SPEAR abundance at sites of high RP was similar to %SPEAR abundance at sites of low RP and without undisturbed stretches. Forested upstream stretches may increase the percentage of wood in substrate cover of streams which can promote invertebrate abundance (Bond et al., 2006). However, in the present study, %SPEAR abundance in April did not differ between sites with and without undisturbed upstream stretches when RP was low. This indicated that in the investigated streams potential input of allochthonous plant material from undisturbed upstream stretches did not significantly promote the macroinvertebrate communities. In contrast, when RP was medium to high, %SPEAR abundance in April was significantly higher at sites with undisturbed upstream stretches than at sites without. Therefore, one may suggest that the positive effect of undisturbed upstream sections probably resulted from in-stream recolonization. This interpretation is supported by the results of several other studies. Various species of macroinvertebrates emigrating from undisturbed stream stretches can drift several km within weeks (Hatakeyama and Yokoyama, 1997). Ephemeroptera and Plecoptera were shown to be predominant in daily fluvial downstream transport of macroinvertebrates from forested headwaters (Wipfli, 2005). A previous study (Liess and Von der Ohe, 2005) also showed that effects of recolonization in the study area are likely to be strongest in April (i.e., ten months after the period of May and June), when highest insecticide levels were measured in streams. For the period of May and June, SPEAR number did not differ significantly between sites with and without forested upstream sections. In April, however, after recovery had time to take place, SPEAR number downstream of forested stream sections was increased in comparison to sites without forested upstream sections.

### 4.05 Ecological risk assessment including landscape parameters

The results of this investigation suggested that although runoff may affect the aquatic community of sites with undisturbed upstream stretches, fluvial downstream transport of species from undisturbed sites could allow for relatively rapid recolonization of impacted sites. Therefore, one may conclude that landscape parameters such as the presence of undisturbed upstream areas could be considered, when assessing the risk of diffuse water pollution at the landscape level, which supports the recommendations made by FOCUS (FOCUS, 2005). In the following, the length of undisturbed stretches is approximated that allows such stretches to facilitate recovery of downstream habitats through recolonization.

Firstly, based on the analysis above, potentially undisturbed upstream stretches were indicated if the percentage forest cover was more than 20% within a two-sided 100 m corridor extending for 1,500 m upstream from a site. Secondly, a previous study showed that forested upstream sections may provide relevant recovery sources, if they are of a width of 50 m on both sides of the stream and extend for more than 200 m upstream within 4,000 m distance to disturbed sites (Liess and Von der Ohe, 2005). Combining these findings, undisturbed upstream stretches could be assumed for stream sites without upstream branches, if the area of a two-sided stream corridor of 50 m in width and 1,500 m in length was covered by more than 20% forest (i.e., the sum of forested area in this corridor was $\geq 0.03$ km²). Dividing the estimate of forest cover (0.03 km²) by the sum of forest width on both sides of the stream (50 m + 50 m), one arrives at an estimated length of forested reaches of 300 m. This distance is suggested as a broad estimate of the extent of undisturbed stretches that would be required within an upstream distance of 1,500 m distance from the disturbed sites in order to provide sufficient potential pools for external recovery, at least under the environmental conditions measured in this study. Herein, a width of 50 m was assumed as suitable for undisturbed stretches to facilitate downstream recovery. Yet, it appears to be possible that two-sided forested sections of less than 50 m could provide undisturbed upstream stretches, when areas are less runoff-prone because of agricultural practice (e.g., cropping direction) and environmental conditions (e.g., low slopes, soils of high infiltration capacity). In this case, the undisturbed upstream stretches could be assumed for stream sites without upstream branches, if the area of a two-sided stream corridor of less than 50 m in width and 1,500 m in length was covered by more than 20% forest (i.e., the sum of forested area in this corridor was < 0.03 $km^2$).

It is noteworthy, that macroinvertebrate communities with taxonomic richness of reasonable quality were able to persist in the study area with its relatively high levels of predicted runoff exposure. Considering this and the findings that a limited amount of forested upstream reaches appeared to substantially mitigate impacts of high runoff exposure suggests that there may be landscape management options that would allow relatively intensive agriculture to coexist with reasonable levels of aquatic macroinvertebrate biodiversity.

# Chapter V. Predicting ecological risk of runoff at the European scale

## 1 Introduction

The aim of this chapter is to combine the outcomes of chapters II to IV and to describe the screening model for characterizing ecological risk of pesticide runoff at the European scale. The model combines simplified spatial runoff modeling and existing knowledge on field-based exposure-response relationships with respect to landscape-mediated recovery potential. Predictions on ecological risk indicate to which extend runoff poses a threat to stream macro-invertebrate communities in European agricultural landscapes. Maps on predicted RP and ecological risk are presented for the European scale (EU-15 area corresponding to the European Union before the 2004 enlargement) and predicted aquatic risk is validated for selected regions with observed field effects of pesticides.

## 2 Material and Methods

### 2.01 Runoff potential at the European scale

The RP introduced in Chapter II was applied to indicate potential runoff inputs into streams at the European scale. The spatial input data of 10 km and 50 km resolution that were available (Table 7) did not allow for identifying single stream sections and the related near stream environment. Therefore, gLOAD (equation 3) was calculated from the amount of arable land in a given grid cell (x,y). This means that the rule of proportion was applied as shown in equation 7 to obtain the theoretical amount of arable land in the near upstream environment of a stream site located in the grid cell (x,y):

$$A_{stream\ i,j} = A_{cell\ i,j} \frac{E_{stream\ i,j}}{E_{cell}} \tag{7}$$

where

| | |
|---|---|
| $A_{\text{stream i,j}}$ | is the amount of arable land in the near upstream environment of a stream site located in grid cell (x,y) |
| $A_{\text{cell i,j}}$ | is the amount of arable land in cell (x,y) |
| $E_{\text{stream i,j}}$ | is the theoretical size of the near stream environment of the stream site located in grid cell (x,y); equal to 0.45 km² (i.e., the modus size of the near stream environment in case of one bifurcation of the upstream watercourse) |
| $E_{\text{cell}}$ | is the size of the grid cell (x,y) (equal to 100 km² in the present investigation) |

As a result, gLOAD reflected the potential runoff inputs into a stream section mean generic exposure of a stream section, which is located in cell (x,y) and has the same environmental characteristics as the grid cell (including percentage of arable land). Only non-irrigated arable land was considered to calculate gLOAD, since so far the RP has been only evaluated with measured runoff inputs from this type of arable land. The calculation of gLOAD based on cereals, grain maize, potatoes, sugar beets, rape and vegetables, because the majority of pesticide application in the European Union is associated with these crops (EUROSTAT, 2002). The shares of these major crops in arable land were specified per grid cell according to shares per administrative unit (Nomenclature of territorial units for statistics, NUTS III) to which a grid cell belonged. Cereals had on average the largest share in arable land per district. The application rate $D_{generic}$ reflected relative differences in pesticide use between the EU-15 countries (Figure 13) and was specified per crop and country in two steps. Firstly, the latest cumulative volumes of all pesticides applied per crop and country were divided by the amount of crop area per country. Secondly, the resulting application rates were rescaled to arrive at values of gLOAD and RP, respectively, which could be linked to the exposure-response relationship that was established in Chapter IV with respect to the presence of undisturbed upstream stretches. Since a generic application rate of 1 g ha $^{-1}$ for all major crops was inherent to that relationship, the crop-specific application rates for the EU-15 countries were rescaled in that they were divided by the application rates for Germany. The plant interception of each major crop under cool and warm climate conditions was considered according to values published in (Huber et al., 2000). For cereals as major crops, differences in plant interception between cool and warm climates were small during the months of May to July. Information on slope as well

Table 7: Input data and sources [a]

| *Data* | *Type of data* | *Resolution* | *Source* |
|---|---|---|---|
| Use of plant protections products (1999) | Tabulated | Country | EUROSTAT |
| Crop area (FSS 2000) | Tabulated | NUTS III | EU-JRC, IES |
| MARS grid | Raster map | 50 km grid | EU-JRC, IES |
| Daily recorded precipitation (2000) | Tabulated | 50 km grid | EU-JRC, IES |
| CORINE land cover data (2000) | Raster map | 10 km grid | EU-JRC, IES |
| Slope | Raster map | 10 km grid | EU-JRC, IES |
| Soil texture | Raster map | 10 km grid | EU-JRC, IES |
| Soil organic carbon content | Raster map | 10 km grid | EU-JRC, IES |
| Hydrological network | Shape file | 250 m grid | EU-JRC, IES |
| Catchments | Shape file | 250 m grid | EU-JRC, IES |

[a] EUROSTAT: Statistical Office of the European Commission; EU-JRC, IES: European Commission Joint Research Centre, Institute for Environment and Sustainability; FSS: Farm Structure Survey; NUTS: Nomenclature of territorial units for statistics; CORINE: Coordination of Information on the Environment; MARS: Monitoring Agriculture with Remote Sensing.

as on the texture and organic carbon content of soils were extracted from the data listed in Table 7. All spatial data processing used Arc View 3.2a (ESRI, Redlands, CA, USA).

Runoff losses of the generic substance (gLOAD) were predicted for each rainfall during the period April to July. This was done, since for the major crops this time was assumed to be the main application period of insecticides (Huber et al., 2000), a group of compounds that can be highly toxic to certain invertebrate species, particularly within the Arthropoda (Schulz, 2004; Liess et al., 2005a). The latest EU-15 data on daily-recorded precipitation were available for the year 2000 (Table 7). In that year, maximum values of daily rainfall for the period April to July occurred during the months of May to July. Modeling gLOAD, assumptions about rainfall intensity were not included; instead, daily-recorded precipitation was assumed to result from one rainfall event. Runoff losses (gLOAD) were predicted to be 0, when CORINE data (Table 7) did not indicate non-irrigated arable land in a grid cell. Due to spatial resolution, CORINE land use data did not allow for ruling out that arable land smaller than the minimum mapping unit (25 ha) was located in a grid cell. Therefore, if gLOAD was predicted to be 0, a generic value of gLOAD was assigned to indicate potential but minimum runoff inputs. This gLOAD value was set equal to half of the smallest gLOAD that was predicted for non-irrigated arable land indicated in the CORINE data. The maximum gLOAD predicted during the period April to July was log-transformed to obtain the RP, which reflects the potential runoff inputs at a stream site that is located in a grid cell with the specified key environmental factors. Predicted RP was binned into five classes ranging from very low to very high as shown in Table 8.

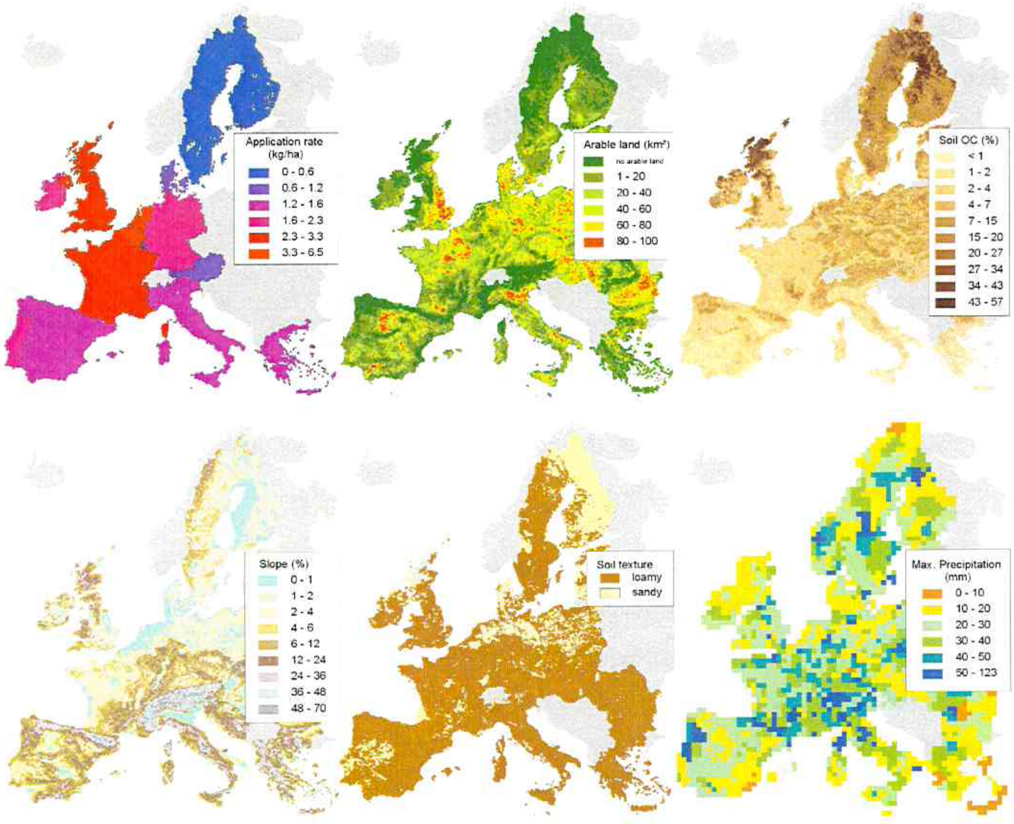


Figure 13: Raster maps of selected input data for predicting runoff potential (RP). a) application rate, b) amount of arable land, c) topsoil organic carbon content, d) slope, e) soil texture, f) maximum values of daily precipitation (April to July 2000). Data from the Statistical Office of the European Commission (EUROSTAT) and European Commission Joint Research Centre, Institute for Environment and Sustainability (EU-JRC, IES).

### 2.02 Exposure-response relationship

To predict the effects of pesticide runoff, a relationship between RP and long-term effects on benthic macroinvertebrate communities was applied, which was established for the Braunschweig region (see section 3.05 in Chapter IV). For that region, the analysis of community composition with respect to SPEAR showed that besides agricultural inputs (including pesticides), landscape structure was the other main parameter determining community structure. Community composition was compared between sites with and without forested upstream reaches representing potential sources for recolonization (Liess and Von der Ohe, 2005). Forested reaches were assumed to provide recolonization pools, if forest covered more than 20% of the near stream environment (i.e., of a two-sided 100 m corridor on the watercourse extending for 1,500 m upstream of the stream site). In the absence of forested upstream stretches, %SPEAR abundance decreased as RP increased. Downstream of forested reaches, no such significant decrease was observed. Even at sites of high RP, observed %SPEAR abundance remained significantly enhanced in comparison to sites without forested reaches.

### 2.03 Ecological risk from potential runoff exposure

The ecological risk resulting from RP was predicted in a two-step procedure. Firstly, ecological effects of RP were predicted for the EU-15 countries by combining predicted RP with the exposure-effect relationship between RP and %SPEAR abundance. This yielded the long-term ecological effect of RP for a stream site in grid cell (x,y). Secondly, this estimate was combined with the probability that stream sites in grid cell (x,y) had no forested stretches in the near upstream environment (a measure for the potential for recolonization (Liess and Von der Ohe, 2005). Instead of the ecological effect of RP at a single stream site, this yielded the ecological risk [%] of RP for the cell (x,y) as given in equation 8:

$$Ecological\ risk_{cell(x,y)} = \begin{cases} 0 \cdot x_i, \mathit{if}\ predicted\ RP \leq -3 \\ 0.25 \cdot x_i, \mathit{if}\ predicted\ RP \leq -2 \\ 1 \cdot x_i, \mathit{if}\ predicted\ RP > -2 \end{cases} \qquad (8)$$

where

| | |
|---|---|
| 0, 0.25, and 1 | are effect values resulting from predicted RP for a stream site in cell (x,y), |
| $x_i$ | gives the probability that stream sites in cell (x,y) are without forested upstream stretches, and |
| index i | is the percentage of forest in cell (x,y). |

The effect values were based on the exposure-response relationship for sites without forested upstream stretches as shown in Figure 12. The levels of predicted ecological risk are summarized in Table 8. The probability that stream sites in grid cell (x,y) had no forested upstream stretches was determined by a distributional analysis of the study area and the 360 stream sites that were investigated in Chapter IV. A 10 km grid was applied on that study area in order to relate per grid cell the percentage forest cover to the percentage number of sites that had no forested stretches upstream. The percentage of sites without forested upstream stretches decreased as the percentage of forest per cell increased. In cells with less than 10% forest cover, 98% of the stream sites had no forested stretches, while in cells with 50% and more forest cover only 25% of the stream sites were lacking forested stretches.

Table 8: Predicted ecological risk in cell (x,y) due to runoff potential (RP) and recolonization pools along hydrological networks [a].

| *Runoff inputs of a stream site in cell (x,y)* | | *Community response to RP* | *Sites in cell (x,y) with recolonization pools upstream* [b] | *Ecological risk from runoff inputs for cell (x,y)* | |
|---|---|---|---|---|---|
| *RP* | *RP class* | *Significant long-term effect (effect value)* | *Percentage recolonization pools* | *$risk_{cell(x,y)}$* | *Risk class* |
| ≤-5 | Very low [c] | - (0) | 0 - 100% | 0% | Very low |
| ≤-3 | Low | - (0) | 0 - 100% | 0% | Low |
| >-3 | Medium | - (0.25) | ≥ 50% | ≤ 10% | Low |
| >-3 | Medium | - (0.25) | < 50% | ≤ 30% | Medium |
| >-2 | High to Very high | *** (1) | ≥ 40% | ≤ 60% | Medium |
| >-2 | High to Very high | *** (1) | < 40% | ≤ 90% | High |
| >-2 | High to Very high | *** (1) | < 10% | > 90% | Very high |

[a] *** $p < 0.001$, for details see section 3.05 in Chapter IV
[b] forested upstream stretches
[c] non-irrigated arable land is not indicated according to CORINE data

### 2.04 Comparison of predicted and observed ecological risk

Predicted ecological risk of pesticide runoff for the EU-15 area was compared with field observations from selected regions on pesticide exposure in small agricultural streams and resulting effects on aquatic macroinvertebrates. The field observations were made during three studies on small streams in selected regions of France, Finland, and Germany (partly unpublished data). The streams were selected to allow for a representative investigation on the effects of different levels of pesticide exposure in the study areas. Pesticide pollution was possible, as the streams drained arable land. However, France, Finland, and Germany differ with respect to the level of pesticide use in agriculture (Figure 13a). Among the EU-15 countries, Finland is characterized by the lowest pesticide use (cumulative application rate of pesticides: 0.5 kg ha$^{-1}$ in 1999). The cumulative application rate for Germany (2.1 kg ha$^{-1}$ in 1999) was increased by a factor of 4 in comparison to Finland, while for France the cumulative application rate (3.3 kg ha $^{-1}$ in 1999) was increased by a factor of 6 in comparison to Finland and by a factor of 1.4 in comparison to Germany.

The field study in South Finland was conducted in 2005 on 13 agricultural streams in the area between Porvoo and Turku (personal communication – R.B. Schäfer, UFZ Centre for Environmental Research, Leipzig, Germany). The study included monitoring of pesticides levels (passive water sampling) and macroinvertebrate communities in the months of July and August. During these two months, measured pesticide concentrations (only fungicide Trifluralin) were five orders of magnitude below the acute median lethal concentration of *Daphnia magna* (48-h $LC50_D$) and percentage SPEAR abundance did not change significantly from July to August.

The field study in North Germany was conducted on 20 agricultural streams in the Braunschweig region (Liess and Von der Ohe, 2005). Runoff-triggered pesticide measurements and macroinvertebrate samples were taken over three years (1998 – 2000) in the months of April to June. Maximum pesticide concentrations were five orders of magnitude below the 48-h $LC50_Di$ at two of the sites, but were in the range of 1:10,000 to 1:5 of the 48-h $LC50_Di$ at the other 18 sites. During the months of May and June, measured maximum pesticide concentrations (insecticide parathion-ethyl, fungicides azoxystrobin, and kresoxim-methyl) were in the range of 1:5 to 1:70 of the 48-h $LC50_Di$. At sites with such concentrations ($n$ = 7), %SPEAR abundance significantly decreased from April to May in comparison to sites with measured concentrations less than 1:10,000 of the 48-h $LC50_Di$ ($n$ = 15). This decrease of sensitive species from pre- to main application period was attributed to measured pesticide exposure.

The field study in West France was conducted in 2005 on 16 agricultural streams in the catchments of the rivers Scorff and Illė in Brittany (personal communication – R.B. Schäfer, UFZ Centre for Environmental Research, Leipzig, Germany). The study included runoff-triggered pesticide measurements and macroinvertebrate monitoring in the months of April and May. Maximum pesticide concentrations were five orders of magnitude below the 48-h $LC50_Di$ at 5 of the sites, but were in the range of 1:10,000 to 1:10 of the 48-h $LC50_Di$ at the other 11 sites. At three out of the 11 sites, maximum measured pesticide concentrations (insecticides primicarb, carbofuran, alpha-endosulfan, and chlorfenvinphos) were one to two orders of magnitude below the 48-h $LC50_Di$ and mean %SPEAR abundance was significantly lower than for the group of five minimally contaminated sites. This significant reduction could also be attributed to measured pesticide exposure.

The observed frequency of significant reduction in %SPEAR abundance due to pesticide exposure was compared with the range of predicted ecological risk (i.e., the predicted frequency of significant reduction in %SPEAR abundance). The observed frequency of effects in each of the three studies was calculated by relating the number of contaminated streams per study, where %SPEAR abundance was significantly lower than at unimpacted sites, to the overall number of contaminated sites per study. The number of sites with forested upstream stretches was not considered in calculating the frequency of effects, because the percentage of investigated sites with forested upstream stretches was not necessarily representative for the study region and therefore could bias the calculation.

## 3 Results

### 3.01 Predicted runoff potential

Predicted RP is mapped for the EU-15 countries in Figure 14. The map reflects the variability in magnitude of RP on a continental scale, and shows areas where agricultural activities on non-irrigated arable land can result in a high exposure of stream sites to pesticide runoff. A general view of the map and the maps of input data presented in Figure 13 allows for identifying the influence of different key environmental factors on RP. For instance, RP was very low in the mountainous areas such as the Alps and the Pyrenees, because CORINE data did not indicate arable land in these regions. RP ranged from low to medium for 62% of the grid cells with arable land (low = 30%; medium = 32%). RP was low e.g. in the South of Sweden and Finland, where comparatively small amounts of arable land are combined with small slopes and low application rates. Despite high amounts of arable land and high application rates, RP was low to medium in the northern parts of Germany, which can be attributed low slopes and sandy soils. In the Po-delta, the amount of arable land was higher than in the northern parts of Germany, but still RP was medium due to low slopes. RP was characterized as high for 36% of the grid cells with arable land. RP was high e.g. in the southern parts of Germany, because of considerable amounts of arable land combined with steep slopes. Also because of considerable amounts of arable land, RP was high in large parts of France that are characterized by comparatively low slopes. In contrast, RP was high in Brittany, France because in this region rather moderate amounts of arable land are combined with comparatively steep slopes. RP was high in northwestern parts of Spain, although average application rates were comparatively small, and maximum daily precipitation as well as slope was rather low. For this region, high RP can be attributed to high amounts of arable land combined with low

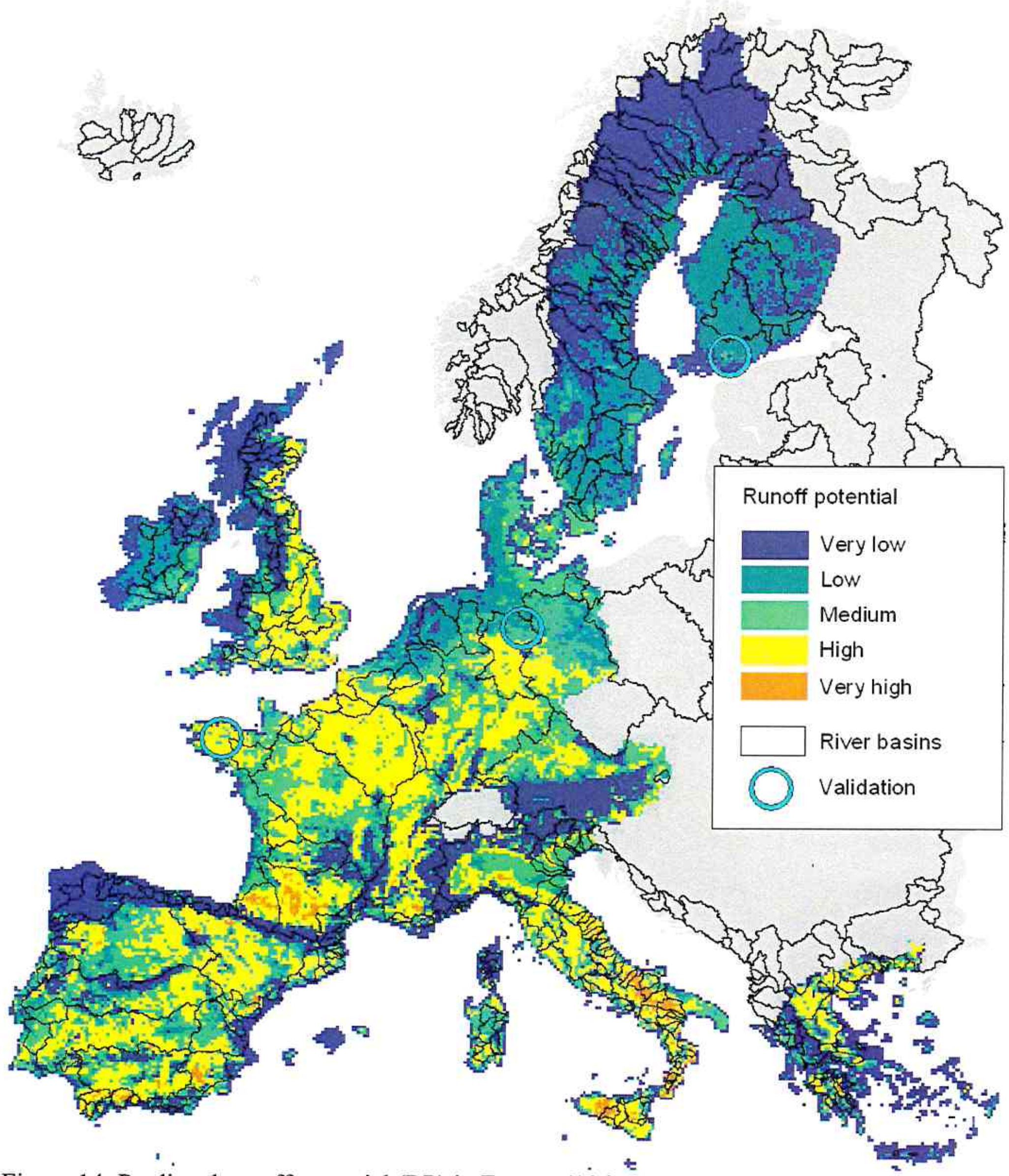


Figure 14: Predicted runoff potential (RP) in Europe (10 km raster).

soil organic carbon contents. RP was characterized as very high for only 2% of the grid cells with arable land (e.g., north of the French Pyrenees and in the Southeast of Italy). In these regions, which are characterized by predominantly loamy soils, slopes are comparatively low, but high amounts of arable land are associated with high maximum daily rainfall. Differences in RP due to plant interception could be expected between cool and warm climate regions.

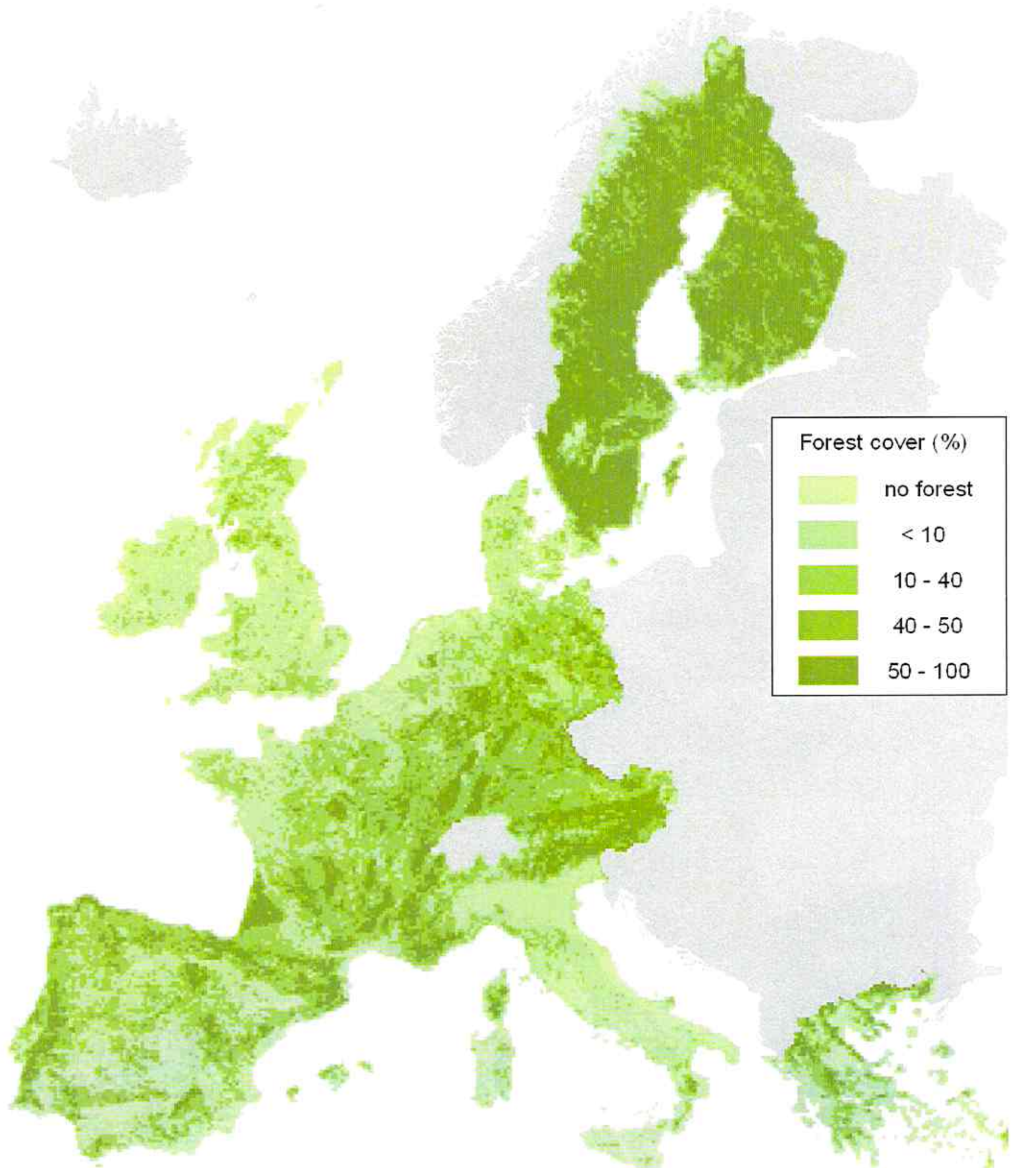


Figure 15: Percentage forest cover across Europe including deciduous, coniferous, and mixed forests. CORINE land cover data (10 km raster) from European Commission Joint Research Centre, Institute for Environment and Sustainability (EU-JRC, IES).

However, in the period of May to July (i.e., during the months of maximum daily rainfall), differences in plant interception between these regions were small, especially for cereals representing on average the major crop per district. Therefore, differences in RP between cells due to plant interception were small in comparison to the influence of the other environmental factors.

### 3.02 Predicted ecological risk

Predicted ecological risk for the EU-15 countries is mapped in Figure 16. A general view of the risk map and the forest map (Figure 15) shows the variability in ecological risk on a continental scale and indicates there runoff inputs potentially cause long-term effects on aquatic communities. Ecological risk was very low in the mountainous regions such as the Alps or the Pyrenees, because CORINE data did not indicate arable land in these regions. Predicted ecological risk was low for 34% of the grid cells with arable land (e.g., in the South of Sweden and Finland), since in these areas RP was too low to imply significant effects. Additionally, the majority of stream sites (≥ 50%) were assumed to have upstream stretches to compensate for effects of runoff exposure through recolonization. Ecological risk was medium for 32% of the grid cells with arable land (e.g., in the Po-delta and the North German Lowlands). In these regions, RP was medium and thus too low to expect significant effects. However, recolonization pools were available at less than 50% of the stream sites, which implied potential risk despite low RP. Ecological risk was high for 15% of the grid cells with arable land (e.g., in Central France and in the southern parts of Germany), because RP was high enough to imply significant effects on aquatic communities. However, forest cover in these regions indicated that at least at 10% to 40% of the stream sites forested upstream stretches were available to facilitate recolonization. Ecological risk was very high for 19% of the grid cells with arable land (e.g., in large parts of Italy, Spain, and the UK). In these regions, RP was high enough to suggest significant effects on aquatic communities and forest cover indicated that recolonization pools were available at less than 10% of the stream sites in these regions.

### 3.03 Validation for selected regions

For three selected regions in Finland, France and Germany, predicted ecological risk was compared with the results of field studies of pesticide effects on benthic macroinvertebrate communities (partly unpublished data). The predicted ecological risk in the region of South Finland was very low or low (Figure 16), because modeled RP was too low for significant long-term changes in community composition. The field study in the area between Porvoo and Turku showed that measured pesticide concentrations were very low and did not affect benthic macroinvertebrate communities (personal communication – R.B. Schäfer, UFZ Centre

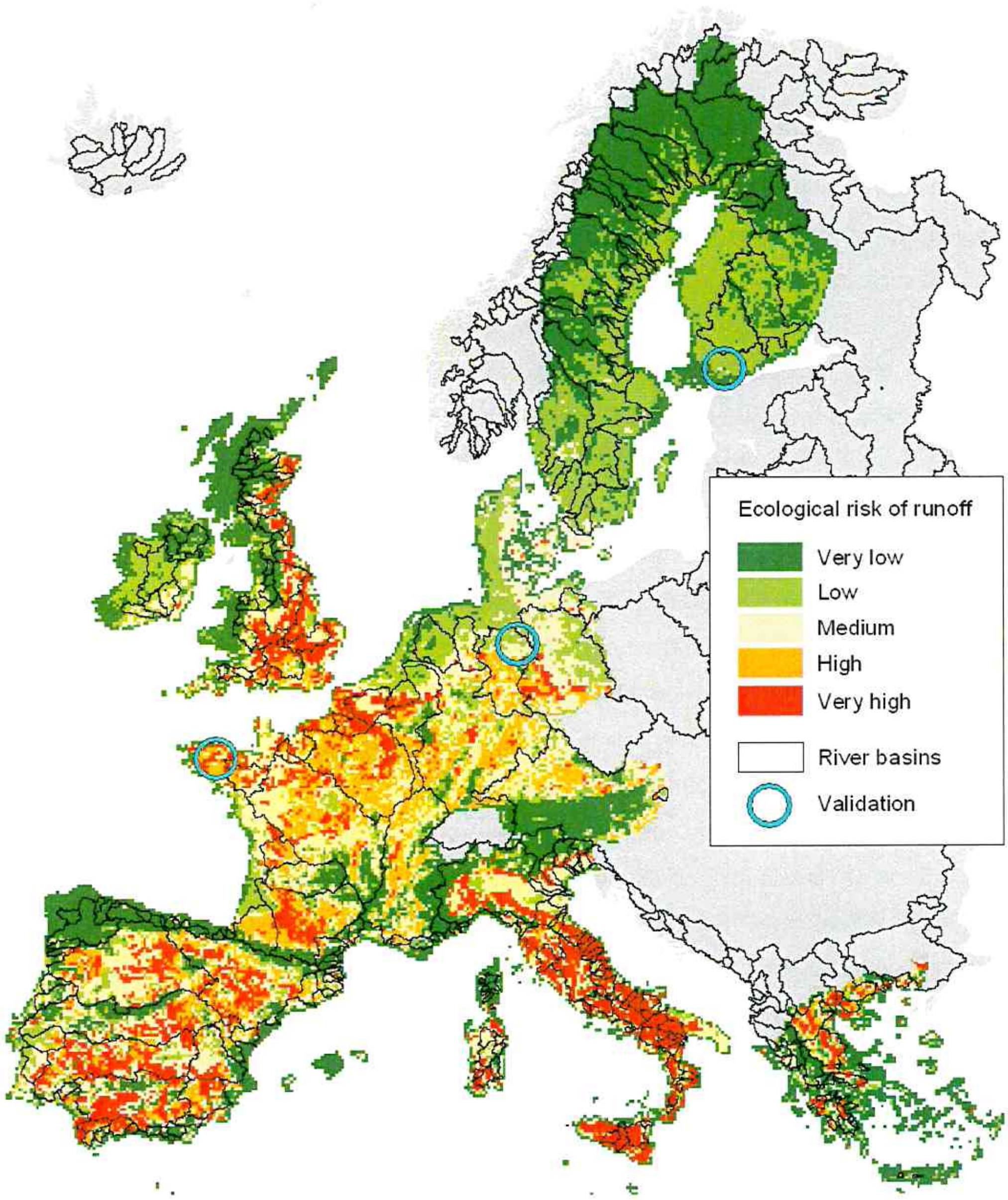


Figure 16: Predicted ecological risk of runoff in Europe (10 km raster).

for Environmental Research, Leipzig, Germany). Thus, predicted ecological risk (≤ 10%) for this area was in good agreement with the field observations.

The predicted ecological risk in the Braunschweig region in North Germany ranged from low to medium (Figure 16). This means that in some areas, RP was high enough to suggest significant long-term changes in community composition, but recolonization pools were assumed at 40% and more of the stream sites. The investigation in the Braunschweig region showed that at seven out of 15 contaminated sites there was a significant reduction of %SPEAR abundance, which was attributed to pesticides (Liess and Von der Ohe, 2005). This means that the frequency of observed effects from pesticide exposure in this region was 46% and that predicted ecological risk (i.e. predicted frequency of effects) for this region (0 – 60%) was also in good accordance with the monitoring results.

The predicted ecological risk in Brittany, France, ranged from medium to very high (Figure 16). This means that in some areas, RP was high enough to expect significant long-term changes in community composition, while recolonization pools were assumed for 40% and less of the stream sites. The field study on 16 streams in the catchments of the rivers Scorff and Ille showed that at three out of 11 contaminated sites there was a significant reduction in %SPEAR abundance, which was attributed to pesticides. Therefore, observed ecological risk from pesticide exposure was 27%, and predicted ecological risk (> 10 – 100%) was in accordance with the observed field situation. In conclusion, the comparison of predictions and observations suggested that the presented screening approach produced appropriate estimates of the ecological risk resulting from pesticide runoff in the investigated regions.

## 4 Discussion

### 4.01 Predicting ecological risk at the European scale

The aim of this chapter was to apply and validate for selected regions a screening model for aquatic ecological risk characterization of pesticide runoff at the European scale. The main potential of such a screening model is to allow for a quick and cost effective location of areas of concern and herein to provide information that can help to target regional monitoring programs with respect to the objectives of the WFD more efficiently.

Several exposure models have been suggested to identify hot spots of diffuse pollution from agricultural sources at the European scale. Heathwaite et al. (Heathwaite et al., 2003) reported the framework for a simplified screening tool to evaluate the vulnerability of landscapes to phosphorus losses based on the P index. Giupponi and Vladimirova (Giupponi and Vladimirova, 2006) presented Ag-PIE, a screening model that was applied to assess nitrogen pollution of surface waters and groundwater from chemical fertilizers and manure. For addressing diffuse pesticide pollution the European level, Tiktak et al. (Tiktak et al., 2004) presented Euro-PEARL, a spatially distributed leaching model to predict the contamination of groundwater bodies. Finizio et al. (Finizio et al., 2005) recommended a procedure to assess mixture toxicity of pesticides in surface water systems at the European level based on standard toxicity data. The approaches mentioned above differ with respect to the considered pollutants, water body types, and underlying models. However, they focused on characterization of exposure from one compound only, while none addressed the generic exposure to diffuse pollution due to environmental parameters and none addressed the ecological risk resulting from exposure.

The screening model presented in this chapter does not only indicate hot spots of runoff inputs but also provides an estimate of the related ecological risk. The underlying exposure-response relationship was based on the SPEAR concept that evaluates the sensitivity of communities to pesticides according to the ecological traits of the species that form the communities (Liess and Von der Ohe, 2005). Classifying species into SPEAR and species not at risk, the system enables simplifying community composition and reducing the difficulties of pattern recognition that result from natural variability due to habitat parameters (e.g., varying between eco-regions). Hence, the SPEAR concept facilitates distinguishing species variability due to pesticide exposure from variability resulting from differences in other determinants of community composition. Thus, the SPEAR concept makes it possible to use an exposure-response relationship established for one geographical region to characterize ecological risk of runoff in other European regions. This was well demonstrated by the outcomes of the punctual validation.

### 4.02 Calculating runoff inputs

The exposure model underlying RP was developed from a simplified model proposed by the OECD (OECD, 1998). Studies in various geographical regions showed that the OECD proposal produced reliable predictions on pesticide exposure of different stream sites (Dabrowski et al., 2002; Verro et al., 2002; Berenzen et al., 2005b), although the influence of factors such as soil profiles, and temperature (Larson et al., 1995; Van der Werf, 1996) is not considered. Since the exposure model of the RP features major characteristics of the OECD proposal, RP can be assumed to give a reliable characterization of runoff exposure as well. The exposure model underlying RP describes runoff losses of a compound with generalized properties instead of making predictions for any one substance as this is done by the OECD model. The properties of the generalized substance including the assumption that it does not degrade represent simplifications that do not apply for most compounds. However, the comparison of predicted RP and measured pesticide runoff expressed as $R_{Loss}$ for the Braunschweig region (section 3.02 in Chapter II) showed a good agreement between predicted and observed exposure. Additionally, a comparison of predicted RP and runoff losses, which were calculated for different pesticides (Bach et al., 2000) showed good agreement of designated areas of potentially high runoff for Germany.

Since modeling RP at the European scale was based on 10 km or 50 km grid information, uncertainties related to the available input data will be more relevant compared to uncertainties at the conceptual level of the model. Particular sources of uncertainty were the resolution of precipitation data and crop statistics (Table 7). Precipitation data were available in 50 km grid resolution, which was lower than the resolution of the other data. Additionally, the results of the sensitivity analysis of the runoff model (see section 3.03 in Chapter II) showed that the model underlying RP is comparatively sensitive to changes in this parameter and thus to uncertainty related to input data on precipitation. Crop statistics refer to administrative units (NUTS III), the size of which differs between EU-15 countries. This may result in considerable spatial variation in the accuracy of data on crop distribution and influences the uncertainty in application rates.

### 4.03 Calculating risk

The relationship between increasing RP and long-term changes in communities was established for streams that were potentially influenced by pesticide runoff as only stressor (section 2.02 in Chapter IV). Agriculture, forest, and pasture were the predominant land use in the near stream environment, while other potential point sources of water pollution did not appear to influence community composition. Therefore, the exposure-response relationship may change in that long-term effects potentially start to emerge at lower levels of RP, if further stressors are present (e.g., runoff from developed land along streams (Lenat and Crawford, 1994) or effluents from waste water treatment plants (Kosmala et al., 1999)). On the other hand, the exposure-response relationship may change in that long-term effects potentially start to emerge only at higher levels of RP if environmental stressors result in communities characterized by a high recovery potential. For example, drought periods have been reported to favor macroinvertebrate species with short generation times and high dispersal ability (Boulton, 2003). Hence, species with these ecological traits may be dominant in geographical regions, where periodical droughts are typical. As a result, communities in these regions may be more robust to environmental stressors including runoff. At sites with a high magnitude of environmental stressors, this would result in a specific relationship between exposure and response, which differs from the assumed relationship and may result in discrepancies between actual and predicted ecological risk.

Additionally it was assumed only forested stretches could represent pools for recolonization. While this was demonstrated under Central-European conditions (see Liess and Von der Ohe (2005) and section 3.05 in Chapter IV), further types of land use that are undisturbed by agricultural activities as well (e.g., extended grassland) may provide additional recolonization pools in other geographical regions. Regional studies on exposure-response relationships with respect to different types of recolonization pools will help to decrease the uncertainty related to this assumption.

### 4.04 Use of the results

The maps that show the results of the screening approach for the EU-15 area are relatively easy to interpret and allow for communicating areas of concern, where the need for site-specific assessment is indicated. Besides identifying areas of concern according to the current situation in the EU-15 area, the presented approach could be applied for scenario simulations such as to assess the influence of changes in land use along hydrological networks due to specific strategies of exposure management or due to effects of climate change.

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