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Field-scale risk assessment for diffuse-source pesticide inputs into German surface waters

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Table of Contents

List of Figures

List of Tables

List of Abbreviations and Acronyms

Abbreviation/ Acronym	full name or explanation
a.i.	**a**ctive **i**ngredient
ADAS	**A**gricultural **D**evelopment and **A**dvisory **S**ervice (UK)
ANOVA	**An**alysis **o**f **Va**riance
ARS	**A**gricultural **R**esearch **S**ervice (USA)
BBA	**B**iologische **B**undes**a**nstalt = Federal Biological Agency
BD	dry **b**ulk **d**ensity
BUEK	**B**oden**ü**bersichts**k**arte = German soil map
BVL	**B**undesamt für **V**erbraucherschutz und **L**ebensmittelsicherheit = Federal Agency for Consumer Protection and Food Safety
CEC	**C**ation **E**xchange **C**apacity
CN	runoff **c**urve **n**umber
CSL	**C**entral **S**cience **L**aboratory
CORINE	**Co**ordination of **In**formation on the **E**nvironment
CREAMS	**C**hemicals, **R**unoff and **E**rosion from **A**gricultural **M**anagement **S**ystems
DBU	**D**eutsche **B**undesstiftung **U**mwelt = German Environment Foundation
DRIPS	**D**rainage-**R**unoff-Spraydrift **I**nput of **P**esticides in **S**urface Waters
DT_{50}	dissipation half-life; the time, when 50 % of the initial amount of a substance can no longer be analytically detected
DWD	**D**eutscher **W**etter**d**ienst = German Weather Service
EC_{50}	**e**ffect **c**oncentration 50 = the exposure concentration that causes an observable adverse effect on 50 % of the test organisms in an ecotoxicological study
EPA	**E**nvironmental **P**rotection **A**gency (USA)
EPIC	**E**rosion **P**roductivity-**I**mpact **C**alculator
EU	**E**uropean **U**nion
EVA	**E**xposure **V**ia **A**ir
EXAMS	**Ex**posure **A**nalysis **M**odeling **S**ystem
FA	**F**raction **A**ffected
FAO	**F**ood and **A**gricultural **O**rganization
FC	**F**ield **C**apacity
FEMVTF	**F**IFRA **E**nvironmental **M**odel **V**alidation **T**ask **F**orce
FIFRA	**F**ederal **I**nsecticide, **F**ungicide and **R**odenticide **A**ct (USA)
FOCUS	**Fo**rum for the **C**oordination of Pesticide Fate Models and their **Us**e
GIS	**G**eographical **I**nformation **S**ystem
GLEAMS	**G**roundwater **L**oading **E**ffects of **A**gricultural **M**anagement **S**ystems
HC	**H**azardous **C**oncentration
HYPRES	**Hy**draulic **Pr**operties of **E**uropean **S**oils
ILR	**I**nstitute of **L**andscape Ecology and **R**esources Management
IME	Fraunhofer **I**nstitute for **M**olecular Biology and Applied **E**cology
ISIP	**I**nformation **S**ystem on **I**ntegrated **P**lant Production
IPU	isoproturon
K_{oc}	Freundlich sorption coefficient normalized to soil organic carbon content
LC_{50}	**l**ethal **c**oncentration 50 = the exposure concentration that kills 50 % of the test organisms in an ecotoxicological study
LHS	**L**atin **H**ypercube **S**ampling
LOD	**l**imit **o**f **d**etection
m	Freundlich exponent
MLR	**M**ultiple **L**inear **R**egression
MUSLE	**M**odified **U**niversal **S**oil **L**oss **E**quation

NEPTUN	**N**etzwerk zur **E**rmittlung des **P**flanzenschutzmitteleinsa**t**zes in **u**nterschiedlichen, landwirtschaftlich genutzten **N**aturräumen Deutschlands = Network for determining pesticide application in different agriculturally used regions of Germany
NOEC	**N**o **O**bserved **E**ffect **C**oncentration = the highest concentration of a substance that causes no observable adverse effects on the test organisms
OC	**o**rganic **c**arbon content
OM	**o**rganic **m**atter content
PAT	**P**esticide **A**pplication **T**imer
PEARL	**P**esticide **E**mission **A**ssessment at **R**egional and **L**ocal Scales
p-EMA	**p**esticide component of the system "**E**nvironmental **M**anagement for **A**griculture"
PEC_{sed}	**P**redicted **E**nvironmental **C**oncentration in **sed**iment
PEC_{sw}	**P**redicted **E**nvironmental **C**oncentration in **s**urface **w**ater
PEST	**P**arameter **Est**imation (software)
PET	**P**otential **E**vapo**t**ranspiration
POPPIE	**P**rediction **o**f **P**esticide **P**ollution **i**n the **E**nvironment
PRZM	**P**esticide **R**oot **Z**one **M**odel
PSD	**P**esticides **S**afety **D**irectorate (UK)
PSM	**P**flanzen**s**chutz**m**ittel
Q_{10}	factor of increase of the degradation rate with an increase in temperature of 10 °C
r	Pearson product-moment correlation coefficient
r^2	coefficient of determination
RZWQM	**R**oot **Z**one **W**ater **Q**uality **M**odel
SCS	**S**oil **C**onservation **S**ervice (USA)
SCR	**s**oil-**c**limate **r**egion (Boden-Klima-Region, BKR)
SENSAN	**Sens**itivity **An**alysis (software)
SLU	Swedish University of Agricultural Sciences
SRC	**S**tandardized **R**egression **C**oefficient
SSD	**S**pecies **S**ensitivity **D**istribution
TER	**T**oxicity/**E**xposure **R**atio
SWAT	**S**oil **W**ater **A**ssessment **T**ool
SWATCATCH	**S**urface **W**ater **At**tenuation **Catch**ment model
TOXSWA	**Tox**ic Substances in **S**urface **Wa**ter
UBA	**U**mwelt**b**undes**a**mt = Federal Environment Agency
USDA	**U**nited **S**tates **D**epartment of **A**griculture
USLE	**U**niversal **S**oil **L**oss **E**quation
WFD	**W**ater **F**ramework **D**irective (2000/60/EC)
WP	**W**ilting **P**oint

Abstract

The contamination of surface water bodies with agricultural pesticides can pose a significant threat to aquatic ecosystems. The aim of this work was to develop a field- and use-specific risk assessment approach for pesticide inputs into surface waters via the diffuse input paths drainage and runoff. This approach constitutes the basis for a web-based decision support tool for farmers and advisors with respect to aquatic ecology.

Drainflow calculations were performed with MACRO 4.3b. A scenario-based approach was used with 8 drainage-relevant soil classes and 19 soil/climate scenarios. Simulations were performed for 109 different active ingredients and 229 uses registered in Germany. For the runoff simulations (185 a.i. and 446 uses) the model PRZM 3.21β was employed. Again, a scenario-based approach was chosen, comprising 5 soil classes with different runoff susceptibility, 8 climate scenarios with different probability of high-intensity rainstorms, and 20 different weather years per climate. The maximum daily pesticide loss over the simulation period (+ the corresponding date and drainflow/runoff volume), together with regional variables (land use, pesticide application practice, river discharge, and extent of tile drainage) served as the basis for the calculation of maximum initial PEC_{sw} (Predicted Environmental Concentrations in surface water). The PEC_{sw} obtained refer to the outlet of a small catchment with about 10 (1-100) km^2 area. The higher of both concentrations ($PEC_{sw,Runoff}$ and $PEC_{sw,Drainage}$) is compared with the acute aquatic "maximum tolerable concentration" for the respective pesticide.

In most cases, $PEC_{sw,Runoff}$ were higher than $PEC_{sw,Drainage}$ for the same use. There were large differences in PEC_{sw} not only between different uses and input paths, but also between different regions in Germany. As the developed risk assessment approach includes the influence of regional factors on the predicted concentrations, it allows to create risk maps for Germany as well as to carry out a Germany-wide probabilistic risk assessment for a given use. The approach can therefore provide a viable basis for improving the regulatory practice in Germany.

Keywords: pesticides, runoff, drainage, surface water, risk assessment

Kurzfassung

Die Kontamination von Oberflächengewässern mit Pflanzenschutzmitteln (PSM) kann eine ernsthafte Bedrohung für aquatische Ökosysteme darstellen. Ziel dieser Arbeit war die Entwicklung eines schlag- und anwendungsspezifischen Ansatzes zur Risikoabschätzung für PSM-Einträge in Oberflächengewässer über die Eintragspfade Runoff (Oberflächenabfluss) und Drainage, als Basis für ein Online-Werkzeug zur Entscheidungsunterstützung für Berater und Landwirte im Hinblick auf die Gewässerökologie.

Die Drainage-Rechnungen wurden mit dem Modell MACRO 4.3b durchgeführt. Hierbei wurde ein szenarienbasierter Ansatz mit 8 drainagerelevanten Bodenklassen und 19 Boden/Klima-Szenarien verwendet. Simulationen wurden für 109 verschiedene Wirkstoffe mit 229 in Deutschland zugelassenen Anwendungen durchgeführt. Für die Runoff-Simulationen (185 Wirkstoffe und 446 Anwendungen) wurde das Modell PRZM 3.21β verwendet. Auch hier wurde ein szenarienbasierter Ansatz gewählt, der 5 Bodenklassen, 8 Klimaszenarien und 20 verschiedene Wetterjahre pro Klimaszenario umfasste. Das Maximum des täglichen PSM-Austrags über den Simulationszeitraum (+ das dazugehörige Datum und Drainage- bzw. Runoffvolumen) bildete zusammen mit regionalen Variablen (Landnutzung, Praxis des PSM-Einsatzes, flächenspezifischer Abfluss, Anteil drainierten Ackerlands) die Grundlage für die Berechnung maximaler initialer PEC_{sw} (Predicted Environmental Concentrations in surface water). Die PEC_{sw} beziehen sich auf den Auslass eines kleinen Einzugsgebiets mit etwa 10 (1-100) km^2 Fläche. Die höhere der beiden Konzentrationen ($PEC_{sw,Runoff}$ und $PEC_{sw,Drainage}$) wird mit der akuten aquatischen “maximalen tolerablen Konzentration” für den entsprechenden Wirkstoff verglichen.

In den meisten Fällen waren für die gleiche Anwendung die $PEC_{sw,Runoff}$ höher als die $PEC_{sw,Drainage}$. Nicht nur zwischen verschiedenen Anwendungen und Eintragspfaden waren große Unterschiede bzgl. der PEC_{sw} festzustellen, sondern auch zwischen verschiedenen Regionen in Deutschland. Da der entwickelte Risk-Assessment-Ansatz den Einfluss regionaler Faktoren auf die vorhergesagten Konzentrationen beinhaltet, ermöglicht er die Erstellung von Risikokarten sowie die Durchführung einer deutschlandweiten probabilistischen Risikoabschätzung für eine bestimmte Anwendung. Der Ansatz kann daher eine brauchbare Grundlage liefern, um die Zulassungspraxis in Deutschland zu verbessern.

Schlagwörter: Pflanzenschutzmittel, Oberflächenabfluss, Drainage, Oberflächengewässer, Risikoabschätzung

1 Introduction

The use of pesticides to control weeds, pests and fungal diseases is an integral component of modern agricultural production. The steep increase of agricultural productivity during the last century could only be achieved due to an intensive use of pesticides and fertilizers (Cheng, 1990). Negative side effects of modern agriculture on non-target organisms and off-site ecosystems became evident in the 1950s, when mass mortalities of water birds were observed in the USA (Clear Lake, California) due to the accumulation of organochlorine pesticides in the food chain, and the population of falcons in the UK collapsed for the same reason.

The contamination of surface water bodies with agricultural pesticides and their metabolites can pose a significant threat to aquatic ecosystems and, where surface water is used for drinking water production, also to human health. An attempt towards a more sustainable agriculture is the so-called integrated crop production, which tries to achieve a balance between maximization of economic return and protection of the environment, and thus to reduce the environmental impact by crop protection measures as far as possible.

To offer the farmers in Germany an online advisory system for integrated plant production, the Deutsche Bundesstiftung Umwelt (DBU; German Environment Foundation) has initiated the ISIP project (**I**nformation **S**ystem on **I**ntegrated **P**lant Production). ISIP is a web-based information system directed to both farmers and plant protection advisors (www.isip.de). It contains, for instance, pest infestation surveys, up-to-date weather data, individual infestation forecasts and recommendations. ISIP is intended to provide the farmers with the necessary information to make optimal field- and application-specific decisions about fertilizing and crop protection measures. The ecological component of ISIP (more precisely: the environmental risk assessment component) is provided by the Institute of Landscape Ecology and Resources Management (ILR) at the University Gießen.

The task of this work was to develop a field- and use-specific risk assessment approach for pesticide inputs into surface waters via the diffuse input pathways runoff/erosion and drainage. This approach should constitute the basis for a decision support tool for farmers and advisors with respect to aquatic ecology. This tool will finally be integrated into the ISIP website.

The risk assessment approach to be developed shall help farmers and advisors to decide whether a given use (e.g. autumn application on winter cereals) of a given pesticide on the farmer's field poses an unacceptable risk to aquatic life or not. Moreover, it is intended to raise environmental awareness among farmers and offer the farmer an opportunity to do something beneficial for the environment.

2 State of the Art

2.1 Input Pathways of Pesticides into Surface Waters

Pesticides can enter surface water bodies via diffuse or via point sources. Diffuse input paths for pesticides into surface waters are drain outflow, surface runoff, and soil erosion from treated fields, spraydrift at application, and deposition after volatilization. Point sources are mainly farmyard runoff (either directly into streams or into the sewer system), sewage plants, sewer overflows, and accidental spills. It has been shown that at least in some regions of Germany point-source inputs contribute the majority to the observed pesticide loads in rivers (Müller et al., 2002; Fischer et al., 1998; Seel et al., 1996). However, Kreuger (2004) demonstrated that point-source inputs can be relatively easily mitigated by increasing awareness of the farmers with regard to pesticide handling and application, and encouraging them to implement loss-reducing measures such as sprayer cleaning only on the field or on biobeds, and no application of pesticides on the farmyard. In contrast, diffuse-source inputs result from the normal pesticide application on the field, and are therefore not as easily reduced as point-source inputs. Hence, in the following the focus will exclusively lie on diffuse sources of pesticide inputs into surface waters.

Drainflow

The purpose of installing artificial drains is to remove excess water that otherwise would impair crop development or soil trafficability and workability. This water can either be shallow groundwater or stagnant water resulting from slowly permeable horizons in the subsoil or overall heavy texture. Consistent research findings have demonstrated that preferential flow phenomena are key contributors to the rapid transfer of pesticides to drainage systems (Kladivko et al., 1991; Harris and Catt, 1999; Funari et al., 1998; Novak et al, 2001; Accinelli et al., 2002). Preferential flow includes all phenomena where water and solutes move along certain pathways, while bypassing a fraction of the porous matrix (Hendrickx and Flury, 2001). It can be broadly distinguished into i) macropore flow along cracks, fissures, root channels and earthworm burrows (e.g. Schwartz et al., 1998; Flury et al., 1994), and ii) finger flow, which occurs in sandy soils (Ghodrati and Jury, 1990; Wang et al., 2003) and is mainly caused by the physical fluid properties of water (Jury et al., 2003). For pesticide displacement in soils along preferential flow pathways the observation is characteristic that strongly adsorbing pesticides reach tile drains or lysimeter bottoms at the same time as mobile compounds; however, the amounts lost are still ranked according to the mobility characteristics of the pesticides (Flury, 1996). Pesticide transport by preferential flow to drains can cause high transient concentrations in agricultural ditches and rivers (Williams et al., 1996; Brown et al., 2004). This is due to the fact that the relatively rapid movement of pesticide-loaded water through only a portion of the available pore space while bypassing a significant portion of the soil matrix decreases the residence time of the pesticide in the upper soil layers, where sorption is usually stronger and degradation faster than in the subsoil. In other words, the infiltrating water does not have sufficient time to equilibrate with slowly moving resident water in the soil matrix (Jarvis, 1998). Although pesticide displacement by preferential flow was traditionally considered to be an issue restricted to heavy clay soils (Harris and Catt, 1999; Johnson and Haria, 1996), it has been demonstrated that it also plays an important role in lighter textured loamy or silty soils (Beven and Germann, 1982; Brown et al., 1995; Zehe and Flühler, 2001) and even occurs in poorly structured, homogeneous sandy soils (Hendrickx et al., 1993; Ghodrati and Jury, 1992). Yet, it is also evident from the literature that pesticide losses via drainflow are generally higher in heavy, structured soils than in sandy, weakly structured soils (Accinelli et al., 2002; Traub-Eberhard et al., 1995), unless the latter have a very shallow groundwater table. The most important factors affecting pesticide inputs into surface waters via drainage are

- soil: texture, structure
- site: permeability of subsoil and vadose zone, height of groundwater table
- drainage system: drain depth and spacing
- compound properties: sorption and degradation behaviour, volatility
- weather: temperature, rainfall distribution (especially the first weeks after application), to a lesser extent total amount of rainfall
- application rate
- application date: spring, summer or autumn.

Surface runoff and erosion

Surface runoff can in principle occur on almost every arable field, even in nearly flat terrain (Leonard, 1988; Wauchope, 1978). It is generated when both infiltration capacity and surface storage capacity of the soil are exceeded by the incoming precipitation. Surface runoff usually starts as laminar sheet flow and after a certain travel length channelizes to concentrated, turbulent flow (Hillel, 1980). Soil erosion consists of two processes: i) the detachment of soil particles from the soil surface, and ii) their subsequent transport downslope. Detachment is caused by raindrop impact and also by the abrasive power of surface runoff, especially when the runoff water flow has concentrated (Morgan, 2001). The downslope transport of detached particles occurs mainly with runoff water, to a lesser extent also by rainsplash. Whereas the tendency of soils to surface runoff increases with decreasing infiltration capacity and thus mostly with increasing clay content, soil erosion by water is highest for soils with a high percentage of silt and fine sand, e.g. loess soils (Schwertmann et al., 1987). Runoff susceptibility and soil erodibility are enhanced by silting and crusting of the soil surface due to raindrop impact and splash during high-intensity rainfalls (Le Bissonais et al., 1995).

Several studies have been published on pesticide transport via surface runoff and erosion (e.g. White et al., 1976; Rohde et al., 1980; Haider, 1994; Klöppel et al., 1997; Lennartz et al., 1997; Spatz, 1999; Rübel, 1999; Wauchope et al., 1999; Louchart et al., 2001). Pesticides lost in runoff and erosion events leave the field either dissolved in runoff water or adsorbed to eroded soil particles. However, for most pesticides losses via runoff are considered far more important than losses via erosion, because the amount of eroded soil lost from a field is usually small compared with the runoff volume (Leonard, 1990). Only for strongly sorbing substances with a K_{oc} (Freundlich sorption coefficient normalized to soil organic carbon content) greater than ca. 1000 L kg^{-1}, erosion is considered as the main loss pathway (Kenaga, 1980; Haider, 1994; Spatz, 1999). Compounds with intermediate sorption are more prone to being lost with surface runoff than weakly sorbing compounds, because the latter are quickly leached away from the soil surface by the infiltrating rainfall (Burgoa and Wauchope, 1995).

A measure to reduce pesticide inputs into surface waters via both runoff and erosion is the use of vegetated buffer strips. However, it must be clearly distinguished here between buffer strips directly adjacent to the field at its lower edge, and bank vegetation along streams and rivers. The effectiveness of grassed buffer strips at the lower edges of fields has been demonstrated in a lot of studies (e.g. Rohde et al., 1980; Arora et al., 1996; Klöppel et al., 1997; Patty et al., 1997; Spatz, 1999). The reduction in pesticide load is mainly due to infiltration and sedimentation in the buffer strip (Spatz, 1999); however, for strongly sorbing compounds also sorption processes in the buffer strip play a role (e.g. Rohde et al., 1980). In contrast, bank vegetation along surface water bodies has been found rather ineffective in reducing chemical inputs via runoff and erosion. Fabis et al. (1994) found that a large portion of water and solutes that had infiltrated into the bank vegetation filter strips nevertheless reached the stream via rapid interflow. Parsons et al. (1995) observed that the resistance of natural bank vegetation to surface runoff entering the strip as concentrated flow was very low. Bach et al. (1994) demonstrated for a typical German low mountain agricultural area that only

1 to 6 % of the river length adjacent to agricultural fields were sufficiently protected by bank vegetation filter strips against pesticide runoff and erosion inputs. The main reasons for this were that i) surface runoff entered the bank vegetation strips mainly as concentrated flow (as opposed to laminar sheet flow), which greatly diminishes the filter efficiency, and ii) most bank vegetation strips were not suitable to effectively reduce pesticide runoff and erosion inputs even for sheet flow, because they were either too narrow or too sparsely vegetated. Other possibilities for mitigating pesticide runoff and erosion inputs into surface waters are common measures to reduce surface runoff and erosion from the field, such as conservation tillage or mulching.

Spraydrift

During pesticide application by spraying, it is regularly observed that a certain portion of the applied amount is deposited outside the target area (Ganzelmeier et al., 1995), e.g. on soil, plant, and water surfaces. The extent of spraydrift losses from the target area depends on weather conditions, technical equipment, application method, and target crop (Huber, 1998). In contrast to the loss pathways runoff, erosion and drainage, spraydrift losses are independent from the pesticide properties. Pesticide inputs into surface waters by spraydrift can be mitigated by the use of drift-reducing nozzles, by vegetated buffer strips along field edges and water bodies (i.e., hedges and bank vegetation), or by simply keeping a sufficient distance to the nearest water body when spraying. In the current regulatory practice in Germany, for each plant protection product there is a legally prescribed minimum spraying distance between 1 and 20 meters (in some cases dependent on the employed spraying equipment) that must be kept by the farmer. Simulations by Huber et al. (2000) and Röpke et al. (2004) suggested that total spraydrift inputs into German surface waters are much lower than inputs by surface runoff or drainage.

Other diffuse sources

Further diffuse input pathways for pesticides into surface waters are atmospheric deposition after volatilization, and aeolian deposition of pesticide-loaded soil particles previously eroded by wind. The former pathway, which is active on a longer range than spraydrift, may be relevant for some very volatile pesticides. The latter should have at most spot-wise importance, since wind erosion is not an area-wide problem in Germany.

2.2 Existing Modelling and Risk Assessment Approaches for Pesticide Inputs into Surface Waters

Due to the large numbers of existing pesticide fate models developed for various scales and purposes, a comprehensive overview cannot be given here. Models exclusively designed for simulating leaching to groundwater will not be mentioned either.

Prominent examples of drainflow models are the dual-porosity (two domains: one mobile, one immobile) model CRACK-NP (Armstrong et al., 2000b) and the dual-permeability (two flow domains with different flow velocities) MACRO (Jarvis, 2003; Larsbo and Jarvis, 2003). Due to the dual-porosity nature of the model (i.e., water flow occurs only in cracks between aggregates and in macropores; cf. Šimůnek et al., 2003), the use of CRACK-NP is restricted to heavy clay soils (e.g., Armstrong et al., 2000a). In contrast, MACRO can be applied to nearly any soil type. The PEARL leaching model (Tiktak et al., 2000) also contains routines for simulating pesticide losses to drains, but does not consider preferential flow yet (only one-domain equilibrium flow based on the Richards equation). However, the next PEARL version, which is announced for 2006, will include a description of macropore flow. A comprehensive model capable to simulate pesticide losses via drainage, leaching, runoff and erosion is RZWQM (Ahuja and Hebson, 1992). RZWQM is, like MACRO, a dual-permeability model and thus able to simulate preferential flow. However, RZWQM has a large number of model parameters and requires extensive calibration (Hanson et al., 1999). Another model able to handle drainflow and associated pesticide losses is the two-dimensional code HYDRUS-2D (Šimůnek et al., 1999). The current version (2.x) of HYDRUS-2D is not able to simulate preferential flow, but a suite of options for modelling preferential flow is in preparation (Šimůnek et al., 2003).

One of the first models predicting runoff, erosion and associated chemical losses from agricultural fields was CREAMS (Knisel, 1980). Extending CREAMS with a component for pesticide leaching yielded GLEAMS (Leonard et al., 1987). CREAMS/GLEAMS simulate surface runoff with the empirical SCS curve number approach (Soil Conservation Service, 1972) and soil erosion with an extension of the Universal Soil Loss Equation (Wischmeier and Smith, 1978). Due to problems with the representation of soil hydrology and an outdated description of pesticide fate (e.g., Rekolainen et al., 2000), GLEAMS is no longer considered up-to-date and is also no longer supported by the USDA (FEMVTF, 2001). Nevertheless, several of the equations developed for CREAMS/GLEAMS have been used or modified within other models such as EPIC (Singh and Williams, 1995) and the catchment-scale models SWRRB (Arnold et al., 1990), SWAT (Arnold et al., 1998), and SWIM (Krysanova et al., 1998). Further models able to simulate pesticide losses via runoff and erosion are e.g. OPUS (Smith, 1992) and RZWQM (Ahuja and Hebson, 1992; see above). The most widely used model to simulate pesticide runoff and erosion losses from agricultural fields is probably PRZM (Carsel et al., 2003; FOCUS, 2001). Very similar to PRZM is the model PELMO (Klein, 1995; Jene, 1998; FOCUS, 2000), which is based on the first PRZM version (Carsel et al., 1984). The advantage of these two models in comparison with many other runoff and erosion models is that they are almost exclusively intended for pesticides, and hence (at least the current versions) have rather sophisticated descriptions of pesticide fate.

Spraydrift inputs into surface waters are commonly modelled using drift tables based on measurements made under defined conditions, e.g. the German BBA drift tables (Ganzelmeier et al., 1995; Rautmann et al., 2001) or the Dutch drift tables (Van de Zande et al., 2001).

Pesticide concentrations and fate in water and sediment of surface water bodies adjacent to fields can be simulated with the model TOXSWA (Adriaanse, 1997; Beltman and Adriaanse, 1999). The current version FOCUS-TOXSWA 1.1.1 (FOCUS, 2001) is able to simulate varying water levels and discharges, and can handle pesticide inputs calculated by other models via runoff and erosion, drainage and spraydrift. The U.S. equivalent to TOXSWA with similar capabilities is the model EXAMS (USEPA, 2005).

The models mentioned above were, if not indicated otherwise, all field-scale models. At the catchment scale, pesticide inputs into surface waters can be simulated with spatially distributed hydrological models such as SWAT (Arnold et al., 1998) and MIKE SHE (Refsgaard and Storm, 1995). However, so far no successful application of SWAT with respect to pesticide inputs into surface waters has been reported. Another spatially distributed approach for calculating pesticide concentrations in surface waters is the GIS-based model DRIPS (Röpke et al., 2004). DRIPS is a further development of the approach of Huber et al. (2000). It is an ArcView 3.2 extension and simulates on a daily basis pesticide inputs via surface runoff, drainflow and spraydrift for pixels of 1 km × 1 km size, based on spatially distributed input variables. Dispersion of the pesticide peak during transport in the river is accounted for in DRIPS by a convection-dispersion approach proposed by Gustafson et al. (2004).

Existing risk assessment approaches for surface water are, for instance, POPPIE and p-EMA. POPPIE (Hollis et al., 1996) is used by the Environment Agency for England and Wales to optimize monitoring strategies within the context of the implementation of the Water Framework Directive (WFD). POPPIE is a combination of the semi-empirical, spatially distributed model SWATCATCH (Brown et al., 2002) with databases within a GIS. SWATCATCH predicts river discharge at the catchment outlet and associated pesticide concentrations on a weekly basis. The tool p-EMA (Brown et al., 2003) is a risk assessment system to guide the optimization of pesticide use at the farm level. p-EMA combines a field-scale exposure estimation for surface water with a pesticide ecotoxicity database (Hart et al., 2003). **P**redicted **E**nvironmental **C**oncentrations in **s**urface **w**ater (PEC_{sw}) due to spraydrift are calculated using the already mentioned BBA drift tables, while PEC_{sw} due to drainage inputs are based on MACRO simulations for a range of soil types and K_{oc} classes. Moreover, p-EMA predicts pesticide leaching to groundwater with a meta-model based on MACRO simulations for several combinations of soil, climate, K_{oc} and dissipation half-life DT_{50}. Further examples of risk assessment approaches for pesticide inputs into surface waters are SYNOPS (Gutsche and Roßberg, 1997), which has recently been upgraded with a runoff and a drainflow component (Strassemeyer, pers. comm., 2005), and EXPOSIT (Winkler, 2001), which will be discussed in the following section.

2.3 Current Practice of Aquatic Exposure and Risk Assessment for Pesticide Registration in the EU and Germany

Newly developed active ingredients have to pass the EU registration procedure (cf. FOCUS, 2000; FOCUS, 2001), which is based on Council Directive 91/414/EEC of 15.07.1991 and its numerous amendments, in order to be placed on a list of substances authorized for use within the European Union. Afterwards, the substances have to pass national registration procedures before being permitted for use in the respective member states. All pesticides already registered at a member state level before the EU registration procedure came into force have undergone or are currently undergoing a reevaluation at the EU level, which will be completed by 2008 (European Commission, 2005).

For pesticide inputs into surface waters, the FOCUS (**Fo**rum for the **C**oordination of Pesticide Fate models and their **Us**e) working group on surface water scenarios established a step-wise or tiered risk assessment approach at the EU level (FOCUS, 2001). There are four possible steps, with decreasing worst-case nature and increasing realism from step 1 to step 4 (Fig. 2.1). All steps consider pesticide inputs into surface water via spraydrift, drainflow, runoff, and erosion. If the substance to be registered fails the first step for the intended use, the risk assessment proceeds with the second step, and so on. The first step in the tiered approach is to estimate surface water exposure based on an “extreme worst case loading” scenario. The estimated exposure is then compared to the relevant ecotoxicological endpoints, i.e. the lethal (LC_{50}) or effect concentration (EC_{50}), or the no-effect concentration (NOEC) of the aquatic test organisms (FOCUS, 2001). Step 2 assumes surface water loading based on sequential application patterns, taking into account the degradation of the substance between successive applications. Both step 1 and 2, which are implemented in the FOCUS step 1,2 calculator (FOCUS, 2001), calculate concentrations for a standard water body and are not specific to climate, crop, topography or soil type (Fig. 2.1). In step 3, more sophisticated exposure estimations are undertaken using a set of 10 agro-pedo-climatic scenarios representing “realistic worst case” situations for surface water within Europe. The FOCUS step 3 scenarios comprise 6 drainage scenarios, 4 runoff scenarios and three water body types (ditch, stream and pond). For the calculation of spraydrift inputs the 90^{th} percentiles of the German BBA drift tables (Rautmann et al., 2001) are used. The PRZM and MACRO models calculate the water and substance fluxes that enter the water body via runoff/erosion and drainage, respectively. TOXSWA simulates pesticide fate in the water body following loading resulting from spraydrift deposition and either runoff/erosion or drainage. Step 3 risk assessments may also incorporate higher-tier ecotoxicity data generated from micro- or mesocosm studies (FOCUS, 2001). The final step 4 is in principle a higher-tier exposure assessment. This may include various refinement options of different complexity, such as risk mitigation measures (e.g. no-spray zones, drift-reducing nozzles, grassed buffer strips), refinement of pesticide fate input parameters, or regional and landscape-level approaches using GIS. By its nature, step 4 is a case-by-case process, depending on the properties of the compound, its use pattern, and the areas of potential concern identified in the lower tier assessments (FOCUS, 2001). The upcoming report of the FOCUS landscape and mitigation working group will include recommendations for step 4 exposure assessments.

In the national registration procedure in Germany, risk assessment for surface water is performed with the tool EXPOSIT 1.1 (Winkler, 2001). EXPOSIT 1.1 calculates PEC_{sw} due to pesticide inputs via drainage, runoff and spraydrift in MS Excel spreadsheets. EXPOSIT assumes a 1 ha field and an adjacent standard ditch (100 m length × 1 m width × 30 cm depth). Runoff/erosion and drainage inputs are calculated as fixed percentages of the applied amount, which are orientated at measured values from the literature (e.g. Klöppel et al., 1997). Peak pesticide losses via runoff and erosion combined are set to 0.5 % of the applied amount, irrespective of soil type, climate, crop or compound properties. EXPOSIT applies reduction factors to runoff volumes, eroded sediment and associated pesticide losses when grassed buffer strips are present. The reduction factors employed are 50 % reduction for 5 m, 90 % for 10 m, and 97.5 % for 20 m buffer width. The calculation of pesticide drainage inputs is differentiated with respect to application season and the “mobility class” of the compound, but again independent of soil, crop, and climate. Grouping into a “mobility class” is done by the water solubility, K_{oc} and DT_{50} of the compound. For application from November to March, peak drainage losses are set to 0.0125 % of the applied amount for “low mobility” compounds (K_{oc} >> 500 L kg^{-1}) and to 0.25 % for the other mobility classes. The corresponding values for application from April to October are 0.00125 % and 0.025 % of the applied amount, respectively. Spraydrift is again calculated using the 90^{th} percentile values of the BBA drift tables. Additional to EXPOSIT, the tool EVA 1.1 (**E**xposure **V**ia **A**ir; Koch and Winkler, 2002) has been established to calculate combined PEC_{sw} due to pesticide inputs via spraydrift and deposition after volatilization. The pesticide volatilization rates used in EVA 1.1 are based on Kördel et al. (1999). It can be seen from the very simple approaches used for the calculation of drainage and runoff inputs, that the emphasis in the German pesticide registration with respect to surface water has clearly been on spraydrift inputs so far. In contrast to the fixed percentages for drainage and runoff losses used in EXPOSIT, which essentially serve the purpose of enabling cut-off decisions, in this work differentiated approaches with respect to soils, climates, crops and compounds will be pursued in the drainage and runoff calculations.

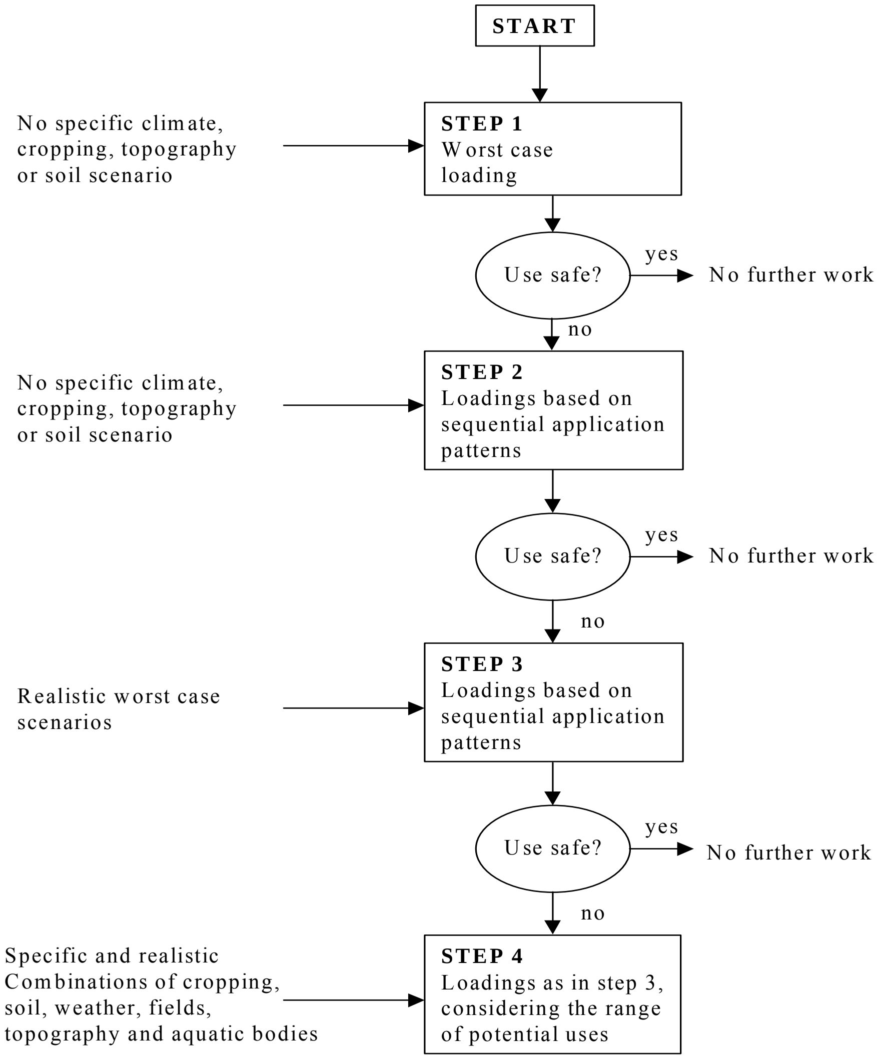

Fig. 2.1: The $FOCUS_{sw}$ tiered approach in pesticide exposure and risk assessment (taken from FOCUS, 2001).

2.4 Critical Terms in Environmental Modelling

“Things should be made as simple as possible, but not any simpler.” Albert Einstein

Before presenting the approaches used for model testing and predictive modelling, some critical terms in environmental modelling have to be discussed and clarified briefly.

Model **calibration** is basically varying model input parameters to achieve a better fit to measured data. It may be undertaken for a range of purposes which broadly fall under four categories (Dubus et al., 2002): i) model parameterization, ii) model evaluation, iii) model extrapolation, and iv) targeted parameter estimation (also called inverse modelling).

The decision to perform a calibration or not depends on the intended purpose. In the context of model evaluation (see below), calibrated simulations reflect the model's inherent capability to represent a particular field situation. This can also be interpreted as the flexibility of the model. In contrast, uncalibrated ("blind") simulations assess the model as well as the employed parameterization, such as the data that were used to derive input values, the modeller's expert judgement and the quality of the pedotransfer functions (Dubus et al., 2002). Uncalibrated simulations are therefore better suited for model testing exercises when a later use without calibration, e.g. simulations of generic scenarios, is expected.

The testing of the capacity of a model to describe or predict reality is commonly referred to as "**validation**" (Dubus et al., 2002). However, it has been demonstrated that complex environmental models (like hypotheses in general) cannot be validated, but only tested and invalidated (Konikow and Bredehoeft, 1992; Oreskes et al., 1994). The former authors therefore suggest to use the terms "model testing" or "model evaluation" rather than "validation". The term "verification" is even more misleading and should be used only with respect to the correct implementation of the model theory and equations in the model code (Refsgaard and Henriksen, 2004). Nevertheless, confidence in a model can be established by "confirming observations" (Oreskes et al., 1994), i.e. successful predictions of measured data. The greater the number and diversity of confirming observations, the higher the probability is that the model concept is not flawed.

Model **extrapolation** is the transfer of model parameters or parameter sets from one set of conditions to another, e.g. from one year to other years at the same field site, to other climate scenarios, to other soil types or to other crops. However, extrapolations to radically different scenarios (e.g. between contrasting soil types or different climatic regions) are questionable given the uncertainty they introduce into the modelling (Dubus et al., 2002).

With respect to extrapolation from calibrated simulations, there are two contrary views. Whereas for some, successfully calibrating a model demonstrates its ability to simulate a specific set of conditions and allows one to extrapolate to other points in space and time (Durborow et al., 2000), others feel that the calibration of complex deterministic models tends to be specific to the conditions at the site for which the experimental data were collected and no calibration should be carried out. For instance, Vanclooster et al. (2000) stated that the extrapolative capacity of a model can only be demonstrated with independent modelling results, and calibration should therefore be avoided as much as possible.

Pesticide sorption and degradation parameters can vary considerably between different sites and soil types (Wauchope et al., 2002; Coquet and Barriuso, 2002; Barriuso and Calvet, 1992; Laabs et al., 2002; Sims and Cupples, 1999), e.g. due to different quality of the organic matter and different degradation capacities of microbial populations. Moreover, soil hydraulic parameters are variable even within the same soil type, for instance due to differences in land-use and tillage history. Hence, it can be concluded that in pesticide fate modelling, calibrated parameter sets are hardly transferable from one site to another, and both model testing and extrapolation should better be done with uncalibrated simulations. The “predictive capability” of a pesticide fate model can therefore be defined as its ability to achieve good agreement with observations without prior calibration, thus allowing "predictive modelling" without measured data (e.g. scenario-based modelling). On the basis of the considerations above, in this work both the model evaluation and the predictive modelling were carried out without calibration (cf. chapters 3 and 4).

Closely related to model validation and extrapolation is the problem of **uncertainty**. There are several sources of uncertainty in pesticide fate modelling (Dubus et al., 2003). They can be broadly divided into model error, input error, and parameter error (Loague and Green, 1991). Model error is the inability of the model to adequately describe reality even if provided with appropriate input parameter sets. It mostly results from oversimplified or wrong process descriptions or non-inclusion of important processes in the model (FOCUS, 2001). Input error is the result of errors in the source terms, e.g. chemical application rates or measured meteorological data. Parameter error encompasses two types of uncertainty: incertitude (the true value of the parameter is not known) and variability (the parameter is spatially and/or temporally variable). Incertitude arises from incomplete knowledge (Moore, 2001), e.g. due to limited sample size or simply lack of measurements. Typical examples for incertitude in the context of pesticide fate modelling are lack of measured bulk density or soil structure for a soil profile to be modelled (cf. section 3.2). Examples for variability are variability of soil texture and structure over a field, variability of sorption and degradation parameters within and between sites, or annual variability of rainfall patterns.

3 Modelling Drainage Inputs with MACRO

For the simulation of pesticide losses to drains, the model MACRO 4.3b (Jarvis, 2003) was selected for the following reasons:

- MACRO accounts for preferential flow, which is crucial for drainflow modelling.
- MACRO is a "mechanistic" or "physically based" model (i.e. it tries to describe the processes involved as realistically as possible), while still having a reasonable number of model parameters.
- MACRO has widely been used for pesticide leaching and drainflow simulations (e.g. Larsson and Jarvis, 1999; Armstrong et al., 2000a; Balderacchi et al., 2002; Brown et al., 2004) and has a high "validation" status. It is widely recognized as the most appropriate model at this time for dealing with the observed rapid leaching of pesticides through soil.
- MACRO (version 4.3) is officially used as drainage model in the European pesticide registration procedure (FOCUS surface water scenarios).
- Although preferential flow models are generally difficult to parameterize (Šimůnek et al., 2003), pedotransfer functions for calculating the soil hydraulic properties (water retention and conductivity functions) from basic soil data (texture, OC content, bulk density, structure) exist for MACRO (Jarvis and Stenemo, 2002).

3.1 Description of the MACRO Model

MACRO is a physically-based, one-dimensional, dual-permeability numerical model of water flow and reactive solute transport in field soils (Jarvis, 1994). The first version of the MACRO model was released in 1991 (Jarvis, 1991). Version 4.3b is used in the context of the FOCUS surface water scenarios (FOCUS, 2001) as the drainage model. It is also used as one of the official leaching models in one of the nine FOCUS groundwater scenarios (FOCUS, 2000). MACRO is able to simulate tile drain outflow, leaching, decay, plant uptake, and foliar washoff of pesticides. In the following, the processes of MACRO relevant for drainflow modelling are explained briefly. For a more detailed description the reader is referred to Jarvis (2003).

3.1.1 Water Transport

The preferential flow model MACRO calculates coupled unsaturated-saturated water flow in cropped soil, including the location and extent of perched water tables, and can also deal with saturated flow to field drainage systems. The model accounts for macropore flow, with the soil porosity divided into two flow systems or domains (macropores and micropores). MACRO is not able to simulate the preferential flow processes of finger flow and funnel flow that occur in coarse-textured soils.

In the macropores, gravity flow of water is assumed. The hydraulic conductivity function in the macropores is given as a simple power law expression of the degree of saturation in the macropores S_{ma}. This approach to describe water flow in macropores is the numerical equivalent of the analytical kinematic wave approach described by Germann (1985):

$$K_{ma} = K_{s(ma)} \; S_{ma}^{n*} \qquad \text{(eq. 3.1)}$$

with

$$S_{ma} = \frac{\theta_{ma}}{e_{ma}} \qquad \text{(eq. 3.2)}$$

where

K_{ma}	actual hydraulic conductivity of the macropores (mm h^{-1})
$K_{s(ma)}$	saturated conductivity of the macropores (mm h^{-1})
S_{ma}	relative saturation of the macropores (dimensionless)
$n*$	kinematic exponent reflecting macropore size distribution and tortuosity (dimensionless)
θ_{ma}	macropore water content (m^3 m^{-3})
e_{ma}	macropore volume (m^3 m^{-3})

It is recognized that macroporosity and macropore hydraulic conductivity may not be constant, but instead vary due to swelling and shrinkage. To account for this, simple relationships are assumed (Messing and Jarvis, 1990):

$$e_{ma} = e_s + p\left(\theta_b - \theta_{mi}\right)$$

$$K_{s(ma)} = \left(K_{s(\min)} - K_b\right)\left(\frac{e_{ma}}{e_s}\right)^{m*} \qquad \text{(eq. 3.3)}$$

where

e_s	minimum value of macroporosity ($m^3\ m^{-3}$)
p	slope of the shrinkage characteristic (dimensionless)
θ_b	saturated water content of the micropores ($m^3\ m^{-3}$)
θ_{mi}	actual water content of the micropores ($m^3\ m^{-3}$)
$K_{s(min)}$	minimum saturated hydraulic conductivity (mm h^{-1}) of a swelling soil, attained when $e_{ma} = e_s$, i.e. in the non-shrunk state
K_b	boundary hydraulic conductivity (hydraulic conductivity when the micropores are saturated and the macropores are empty; mm h^{-1})
m^*	empirical exponent (dimensionless)

A change in macroporosity due to swelling and shrinkage also implies a change in microporosity, because the soil is treated as macroscopically rigid and the total porosity in any layer is held constant. In MACRO, the soil hydraulic properties of the micropores (eq. 3.5 and 3.7) are not affected by soil shrinkage. In the micropores, Richards' equation is used to calculate vertical water fluxes:

$$\frac{\partial\theta}{\partial t} = \frac{\partial}{\partial z}\left(K\left(\frac{\partial\psi}{\partial z} + 1\right)\right) - \sum R_i \qquad \text{(eq. 3.4)}$$

where

θ	volumetric water content ($m^3\ m^{-3}$)
ψ	soil water pressure head (matric potential; mm)
t	time (h)
z	depth (mm)
K	hydraulic conductivity of the micropores (mm h^{-1})
R_i	source/sink terms for water exchange with macropores, drainage and root water uptake (h^{-1})

Soil water retention in the micropores is calculated using the Brooks-Corey equation (Brooks and Corey, 1964). Thus, the soil water pressure head ψ_{mi} is given by:

$$\psi_{mi} = \psi_b\, S_{mi}^{-1/\lambda} \qquad \text{(eq. 3.5)}$$

with

$$S_{mi} = \frac{\theta_{mi} - \theta_r}{\theta_b - \theta_r} \qquad \text{(eq. 3.6)}$$

where

S_{mi}	effective saturation in the micropores ($m^3\ m^{-3}$)
ψ_b	"boundary tension" (mm), i.e. soil water pressure head when the micropores are saturated and the macropores are empty
λ	pore size distribution index (dimensionless)
θ_r	residual water content ($m^3\ m^{-3}$; often set to zero)

Mualem's (1976) model is used to describe unsaturated hydraulic conductivity in the micropores K:

$$K = K_b\ S_{mi}^{\ n+2+2/\lambda} \qquad \text{(eq. 3.7)}$$

with

n	tortuosity factor in the micropores (dimensionless; usually set to 0.5)

Water exchange from macropores to micropores (R_w) is treated as an approximate first-order process, neglecting the influence of gravity (Booltink et al., 1993) and assuming a rectangular-slab geometry for the aggregates (Van Genuchten and Dalton, 1986):

$$R_w = \left(\frac{3\, D_w \gamma_w}{d^2}\right)\left(\theta_b - \theta_{mi}\right) \qquad \text{(eq. 3.8)}$$

where

d	effective "diffusion" pathlength (i.e. half the aggregate width; mm)
D_w	effective water diffusivity ($mm^2\ s^{-1}$)
γ_w	scaling factor introduced to match the approximate and exact solutions to the diffusion problem (dimensionless; fixed to 0.8)

This equation only describes flow from macro- to micropores and not in the reverse directions. If the micropore domain is saturated, flow from micro- to macropores may be generated. This may occur, for example, if micropore hydraulic conductivity decreases with depth in the soil. In this situation, the excess water instantaneously starts to fill the macropores.

The boundary condition for water flow at the soil surface is critical because it determines the partitioning of net precipitation between the flow domains (Beven and Germann, 1981). In MACRO, water will flow into surface-vented macropores if the rainfall intensity exceeds the boundary conductivity K_b and the matric potential ψ is greater (i.e. less negative) than the boundary tension ψ_b at the soil surface. The surface boundary condition in MACRO is therefore chosen such that oversaturation in the micropores in the surface soil layer is prevented. The calculated net precipitation in a given time interval (P_n) is divided into an amount taken up by the micropores I_{mi} and an excess amount flowing into macropores I_{ma} :

$$\begin{aligned} I_{mi} &= P_n \,; P_n \leq I_{\max} \\ I_{ma} &= 0 \\ \\ I_{mi} &= I_{\max} \,; P_n > I_{\max} \\ I_{ma} &= P_n - I_{mi} \end{aligned} \qquad \text{(eq. 3.9)}$$

where I_{max} is the infiltration capacity of the micropores (mm h^{-1}) given by :

$$I_{\max} = K_b \left(\left(\frac{2(\psi_b - \psi_1)}{\Delta z_1} \right) + 1 \right) \Delta t \qquad \text{(eq. 3.10)}$$

where the subscript 1 refers to the surface soil layer. If the macropores in the surface layer become saturated, then any excess water is lost as surface runoff.

To describe the bottom boundary condition for water flow, five different options are available in MACRO. For simulating tile-drained fields, which are subject to waterlogging due to stagnant water or shallow groundwater, the most appropriate option of these is a vertical seepage rate calculated as an empirical linear function of the height of the water table in the soil profile. This bottom boundary condition is therefore used in the FOCUS surface water scenarios and also in this study.

Lateral flow from saturated soil layers to field drains is given as a sink term to the vertical one-dimensional flow equation. The drains are assumed to be overlain by fully penetrating seepage surfaces (i.e. ditches or drains with permeable backfill). Flux rates from saturated layers above the drainage depth are predicted using seepage potential theory for layered soils (Youngs, 1980; Leeds-Harrison et al., 1986). Water flow to drains from layers below the drainage depth is calculated using the first term of the Hooghoudt drainage equation (Hooghoudt, 1940). It should be noted that the macropores have to be saturated for drainflow to occur. If both macro- and micropores are saturated, also the micropores contribute to drainflow.

Evapotranspiration in MACRO is composed of evaporation from crop interception, evaporation from soil and transpiration from the crop. Potential evapotranspiration is calculated internally from daily meteorological input variables (maximum and minimum temperature, solar radiation, water vapour pressure and wind speed) according to the Penman-Monteith method (Monteith, 1965). Alternatively, potential evapotranspiration (PET) can be directly provided by the user.

3.1.2 Pesticide Transport and Fate

Sorption within MACRO is described using the Freundlich isotherm, with the sorption sites partitioned between the two flow domains. An instantaneous sorption equilibrium between solution phase and sorbed phase is assumed in each of the two domains:

$$S' = K_f \cdot C_{ref} \left(\frac{C'}{C_{ref}} \right)^m$$

(unit-corrected version) (eq. 3.11)

where:

S'	concentration of adsorbed pesticide in the solid phase (either micro- or macropores; mg kg^{-1})
C'	concentration of dissolved pesticide in the water phase (either micro- or macropores; mg L^{-1})
K_f	Freundlich coefficient (same value in both domains; L kg^{-1})
m	Freundlich exponent (same value in both domains; dimensionless)
C_{ref}	reference concentration in dissolved phase; per convention 1 mg L^{-1} (the value of the Freundlich coefficient depends on the reference concentration)

Where site-specific sorption data are not available, the Freundlich coefficient can be obtained by calculating back from a generic Freundlich coefficient normalized to soil organic carbon (however, this works only when organic matter is the main sorbent for the compound):

$$K_{oc} = K_f OC \qquad \text{(eq. 3.12)}$$

with

K_{oc}	Freundlich coefficient normalized to soil organic carbon content (L kg^{-1})

OC fraction of soil organic carbon (kg kg^{-1})

Pesticide degradation rates in each of the four pools (liquid and solid phase, micro- and macropores) are predicted assuming first-order kinetics:

$$\frac{\partial C}{\partial t} = -\mu \cdot t = -\frac{\ln 2}{T_{1/2}} t \qquad \text{(eq. 3.13)}$$

where

C pesticide concentration in one of the four pools (mg L^{-1} or mg kg^{-1})

μ degradation rate coefficient (d^{-1})

$T_{1/2}$ degradation half-life (d) corresponding to μ

In the case of first-order kinetics, and in the absence of other dissipation pathways (e.g. volatilization), the DT_{50} (**d**issipation **t**ime 50; the time, when 50 % of the initial amount can no longer be analytically detected) is equal to the degradation half-life $T_{1/2}$. Each pool has a separate, user-defined reference degradation rate coefficient μ_{ref}. Actual degradation rate coefficients in the field μ are predicted from reference values obtained under standardized conditions, using correction functions F_w and F_t to account for the effects of soil moisture and temperature (Boesten and van der Linden, 1991):

$$\mu = \mu_{ref} \; F_w \; F_t \qquad \text{(eq. 3.14)}$$

where the moisture-correction function F_w in the micropores is given by the Walker equation (Walker, 1974):

$$F_w = \left(\frac{\theta}{\theta_{ref}} \right)^B \qquad \text{(eq. 3.15)}$$

where

θ volumetric soil moisture (m^3 m^{-3})

θ_{ref} reference soil moisture for degradation (m^3 m^{-3})

B empirical exponent (dimensionless)

In MACRO, θ_{ref} is equal to the boundary water content θ_b where the micropores are saturated and the macropores are empty. In the macropore domain, F_w is always 1. B is usually set to 0.7, which is the geometric mean of a number of values found in the literature (Gottesbüren, 1991). The temperature-correction function F_t is given by a numerical approximation of the Arrhenius equation (Boesten and van der Linden, 1991) modified for low soil temperatures :

$$F_t = e^{\alpha (T - T_{ref})} \quad ; \quad T > 5^oC$$

$$F_t = \left(\frac{T}{5}\right) e^{\alpha (5 - T_{ref})} \quad ; \quad 0 \leq T \leq 5^oC \qquad \text{(eq. 3.16)}$$

$$F_t = 0 \quad ; \quad T < 0^oC$$

with

T	soil temperature (°C),
T_{ref}	reference temperature for degradation (°C)
α	composite parameter (h^{-1}) dependent on T, T_{ref}, the gas constant and the molar activation energy (Boesten and van der Linden, 1991)

Solute transport is predicted using the convection-dispersion equation with source/sink terms U_i to represent mass exchange between flow domains, solute uptake by the crop, biodegradation and lateral leaching losses to drains and/or regional groundwater:

$$\frac{\partial A}{\partial t} = \frac{\partial}{\partial z}\left(D\,\theta_{mi(m)} \frac{\partial C}{\partial z} - qC \right) - \sum U_i \qquad \text{(eq. 3.17)}$$

where

A	solute content (mg m^{-3})
z	depth (mm)
$\theta_{mi(m)}$	mobile water content (m^3 m^{-3}), which in the micropores accounts for an inaccessible soil volume due to anion exclusion
C	solute concentration in the liquid phase (mg m^{-3})
q	water flow rate (mm h^{-1})
U_i	source/sink term (mg m^{-3} h^{-1})
D	dispersion coefficient (mm^2 h^{-1}) given by:

$$D = D_v v + D_o f^*$$

with

D_o	diffusion coefficient in free water (mm^2 h^{-1})
f^*	impedance factor (dimensionless; assumed constant)
D_v	dispersivity (= dispersion length; mm)
v	pore water velocity (mm h^{-1})

In the macropores, dispersion is neglected (i.e. D is set to zero), since solute transport is assumed to be dominated by convection. At the soil surface, the solute concentration in water routed into the macropores is calculated by assuming instantaneous local equilibrium and complete mixing of incoming net rainfall with the water stored in a shallow surface soil layer or "mixing depth" (Steenhuis and Walter, 1980).

The source/sink term for mass transfer of solute between micropores and macropores U_e is given by a combination of a diffusion component (Van Genuchten and Dalton, 1986; Valocchi, 1990) and a mass flow component:

$$U_e = \left(\frac{3\, D_e\, \theta_{mi(m)}}{d^2} \right) \left(C_{ma} - C_{mi} \right) + S_w C' \qquad \text{(eq. 3.18)}$$

where the prime notation indicates either macropore or micropore water depending on the direction of water flow S_w (i.e., $C' = C_{ma}$ if water flows from macropores to micropores) and D_e (mm^2 h^{-1}) is an effective diffusion coefficient approximated by:

$$D_e = D_o\, f^*\, S_{ma} \qquad \text{(eq. 3.19)}$$

where the relative saturation of the macropores S_{ma} is included to account for incomplete wetted contact area between the flow domains. The loss of solute to the drains is calculated assuming complete mixing within a flow domain in the horizontal dimensions. Thus, the drainage sink term U_t is simply given by:

$$U_t = \frac{q_d}{\Delta z} C' \qquad \text{(eq. 3.20)}$$

with

U_t solute flow to drains from the respective flow domain (mg m^{-3} h^{-1})

q_d water flow to drains from the respective flow domain (mm h^{-1})

Δz layer thickness (mm)

Finally, the solute uptake rate by roots U_c is modelled as a passive process as a function of root water uptake and the solute concentration:

$$U_c = f_c R_r C' \qquad \text{(eq. 3.21)}$$

with

U_c solute uptake by roots (mg m^{-3} h^{-1})

R_r water uptake by roots (h^{-1})

f_c empirical “concentration factor” (dimensionless) varying from zero to unity; Boesten and van der Linden, 1991)

FOCUS (2001) recommends to set the plant uptake concentration factor f_c to 0.5 for systemic pesticides (i.e. pesticides which are translocated within the plant) and to 0 for non-systemic pesticides. However, since also non-systemic compounds can usually be taken up to some extent by plant roots, it can be justified to set f_c to 0.5 for nearly all organic pesticides. MACRO is not able to simulate pesticide volatilization or pesticide losses by surface runoff or erosion. Processes of foliar interception, dissipation and washoff of pesticides are treated in the same way as in the model PRZM (Carsel et al., 2003; cf. section 4.1.2).

3.2 Testing MACRO Against Measured Data

MACRO has to be used in this work in a purely predictive way, i.e. without measured data for comparison, and without prior calibration (cf. section 2.4). Hence, the predictive capability of the MACRO model under these circumstances had to be tested extensively irrespective of its good validation status. Additionally, the pedotransfer functions of MACRO_DB2 had to be tested for their usefulness. Therefore, several European drainage studies, covering a wide range of different soils and climates, were modelled with MACRO 4.3b, and the modelling results were compared with measured data.

Before comparing simulated and measured data, three things have to be done. Firstly, it has to be decided which model output variables shall be used to evaluate the quality of the fit.

Secondly, criteria have to be defined or selected to quantitatively evaluate how well the simulation results match the measurements (“goodness-of-fit criteria”). Thirdly, it has to be defined which value of a goodness-of-fit criterion shall be the acceptability limit, i.e. what is the border between an acceptable and an inacceptable quality of the simulation (“performance criterion”, Refsgaard and Henriksen, 2004).

In the case of drainage studies, the most important output variables are i) tile drain outflow, and ii) pesticide loss via drainflow, because they govern the resulting pesticide concentration in the receiving surface water body. With respect to surface waters, the pesticide concentration in tile drain outflow itself is of smaller importance, since the surface water body probably does not receive water exclusively from the drains.

A widely used goodness-of-fit criterion for time series is, for instance, the model efficiency or Nash-Sutcliffe index (Nash and Sutcliffe, 1970). Physically, the model efficiency is the ratio of the mean square error to the variance in the observed data, subtracted from unity (Legates and McCabe, 1999). However, calculating the model efficiency is only meaningful if the time series are continuous and if measured and simulated data are of the same type (in the case of drainflow simulations, daily rates). It turned out that the measured data from the drainage studies used often did not fulfill these requirements. Other, more simple criteria are the ratios of simulated and measured total tile drain outflow and simulated and measured total pesticide losses via drainage. For the purpose of aquatic risk assessment, however, peak losses are often more important than total pesticide losses, since the acute or sub-acute ecotoxicity of a pesticide to aquatic organisms is mostly more critical than the chronic ecotoxicity. Another criterion for the goodness of fit is the match between simulated and measured timing of drainflow events. If the timing is well matched, this suggests that the process descriptions of the model are reasonable. However, for the purpose of aquatic risk assessment a good fit of the timing of events is not that crucial. Nevertheless, it makes a difference whether the highest simulated pesticide losses occur in the same season as in the experiment or not, because the river discharge varies between seasons and also the sensitivity of aquatic organisms may vary over the year. On the basis of these considerations, the following criteria were chosen for testing the performance of MACRO:

- ratio of simulated and measured total drainflow volume
- ratio of simulated and measured maximum daily drainflow
- ratio of simulated and measured total pesticide loss via drainflow
- ratio of simulated and measured maximum daily pesticide loss via drainflow
- timing of events (visual inspection)

As regards the limits of acceptability, a universal, scientifically justified limit for the deviation between measured and simulated values does not exist (Refsgaard and Henriksen, 2004). The maximum acceptable deviation depends on the model output variable of concern and the intended purpose of the simulations. Hence, the acceptability limits were defined pragmatically. For the water flux variables, i.e. total and maximum daily drainflow, a factor of 2 was selected as the maximum acceptable deviation between simulated and measured values. It was felt that a rather strict limit was needed here to establish confidence in the MACRO_DB2 pedotransfer functions. The solute flux variables, i.e. total and maximum daily pesticide loss via drainflow, are affected by uncertainty (model error and parameter error) from both water transport and solute transport simulation. Moreover, in the aquatic risk assessment for pesticides usually a safety factor (the Toxicity/Exposure Ratio, TER) of 10 or 100 is used to account for uncertainty on both the exposure and the effect side (cf. section 5.1.3). Therefore, the acceptability limit for the deviation between simulated and measured pesticide losses was set to a factor of 10. To further differentiate the quality of “acceptable” simulations, in the following a deviation of not more than 20 % from the measurements will be called “slightly”, and a deviation by not more than a factor of 2 from the measurements will be referred to as “moderately”.

3.2.1 Test Sites and Simulations

The datasets of 9 European drainflow studies (Table 3.1), which have been kindly made available by several parties, were used for model testing.

Table 3.1: Drainage studies used for model testing

study site	source	site location	soil	field size (ha)	compounds measured and used for modelling
Lanna	Nick Jarvis, SLU, Sweden	SW-Sweden	silty clay	0.4	bentazone
Cadriano	Ettore Capri, Catholic University Piacenza, and	N-Italy	loam	0.33	atrazine
Carpi	Alberto Vicari, University Bologna, Italy	N-Italy	silty clay	1.85	atrazine
Brimstone	Adrian Armstrong, Graham Harris, ADAS, UK	S-England	clay	0.2	isoproturon
Mill Farm	M.-A. Reding, Monsanto Europe	M-England	clay loam	7.7	sulfonylurea herbicide
Cockle Park	Colin Brown, University of York, formerly Cranfield Centre for Ecochemistry, UK	NE-England	loam	0.25	isoproturon
La Bouzule	Sandra Novak, France	NE-France	silty clay	1.85	metolachlor
		NE-France	silty clay loam	2.83	metolachlor
Beetz	W. Kördel, IME, Schmallenberg, Germany	NE-Germany	sand	ca. 4	isoproturon, metolachlor

As reasoned in section 2.4, no model calibration was performed. Only the meteorological data, site and experimental characteristics were site-specific in the simulations. For compound properties (DT_{50}, K_{oc}, Freundlich exponent, water solubility), intentionally generic instead of site-specific values were used (Table 3.2). This approach, which is also called “blind validation” (Trevisan et al., 2003), integrates the uncertainty arising from model error and parameter error (Loague and Green, 1991; cf. section 2.4).

Table 3.2: Generic compound properties used for MACRO model testing (cf. Appendix A)

compound	K_{oc}	Freundlich exponent m	DT_{50} (topsoil)	water solubility @ 20/25 °C
	L kg^{-1}		d	mg L^{-1}
bentazone	29	1	14	not used[1)]
atrazine	147	0.9	60	not used[1)]
isoproturon	71	0.88	11	70.2
sulfonyl urea herbicide	25	0.9	25	1626.8
metolachlor	201	0.9	30	488.0

[1)] not used, since application on bare soil and thus no crop interception

Crop properties and depth reduction factors for the degradation rate were chosen according to the FOCUS surface water scenarios (FOCUS, 2001). The parameter settings used in all simulations are shown in Table 3.3.

Table 3.3: MACRO settings used for all simulations

parameter	description	value
AEXC	excluded water content for solute transport due to anion exclusion (%)	0
ALBEDO	albedo	0.25
ATTEN	attenuation factor for solar radiation in crop canopy	0.6
CONC	pesticide concentration in rainfall (mg m^{-3})	0
CONCIN	pesticide concentration at bottom boundary (mg m^{-3})	0
CRITAIR	critical soil air content for root water uptake (%)	5
DIFF	diffusion coefficient in free water (m^2 s^{-1})	5.0 E-10
DV	dispersivity (cm)	1
EXPB	exponent in the moisture response function for degradation	0.7
FRACMAC	fraction of sorption sites in macropores	0.02
FSTAR	solute concentration factor for plant uptake	0.5
RINTEN	rainfall intensity (mm h^{-1})	2
SNOWMF	snowmelt factor (mm ^{o}C d^{-1})	4.5
SOLINIT	initial pesticide concentration (mg m^{-3})	0
TREF	reference temperatur for degradation rate (°C)	20
TRESP	exponent in the temperature response function for degradation	0.079
ZA	exponent (only relevant if shrinkage is to be modelled)	1
ZM	tortuosity factor (micropores)	0.5
ZMIX	mixing depth (mm)	0.1
ZP	slope of shrinkage characteristic	0[1)]

[1)] i.e., no shrinkage was modelled in the test simulations

The critical tension for root water uptake (*WATEN*) was calculated according to the method used for the FOCUS surface water scenarios (FOCUS, 2001). For the estimation of all other soil hydraulic parameters (water retention and conductivity characteristics) the pedotransfer functions of MACRO_DB2 (Jarvis and Stenemo, 2002) were used. The MACRO_DB2 pedotransfer functions require the following basic soil properties as input variables for each soil horizon:

- sand (50-2000 µm), silt (2-50 µm) and clay (< 2 µm) content
- organic carbon content
- dry bulk density
- a structural description according to FAO (1990): aggregate size, degree of structural development and aggregate shape (e.g. coarse / moderate / blocky).

The equations of the pedotransfer functions can be found in Jarvis and Stenemo (2002). The MACRO input files (.par) used for the test simulations are given in Appendix B on the attached CD-ROM.

3.2.1.1 Lanna

The Lanna dataset is a standard data set for testing pesticide fate models, especially models accounting for preferential flow and tile drainage. The Lanna site is located in SW-Sweden (58° 21' N, 13° 08' E) on a flat plain. The experimental plot has an area of 0.4 ha and is equipped with tile drains at 1 m depth and 13.5 m spacing. The basic soil properties of the profile are shown in Table 3.4.

Table 3.4: Soil properties of the Lanna site (Larsson and Jarvis, 1999)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density[1)]	pH	structure (strength/size/shape) (FAO, 1990)
cm		%		%	kg dm^{-3}		
0-30	46.5	46.2	7.3	2.0	1.41	7.2	strong coarse subangular blocky
30-60	56.1	40.6	3.3	0.8	1.52	7.4	strong fine to medium angular blocky
60-100	60.6	37.4	2.0	0.3	1.51	7.4	strong coarse angular blocky
105-175	66.6	30.5	2.9	0.2	n.i.[2)]	n.i.	n.i.[2)]

[1)] average over three measurements between 10/1994 and 3/1995; averaged over 10 cm depth increments
[2)] no information available

A detailed description of the site and the experiment is given in Larsson and Jarvis (1999). The experiment included an autumn application (18.10.1994) of 2.508 kg ha^{-1} bentazone to bare soil on a zero-tillage plot. In the following season, spring rape was sown on 06.05.1995 and harvested on 08.09.1995. Tile drainage outflow was measured daily and analysed for bentazone from 12.10.1994 to 30.11.1995.

Soil texture was given as 0-2, 2-60 and 60-2000 µm fractions (Table 3.4). Yet, the MACRO_DB2 pedotransfer functions require the fractions of 2-50 µm and 50-2000 µm as input for silt and sand content, respectively. Since no translation of particle size fractions from one system to another was available at that time, the given 2-60-2000 percentages were entered *as is* in MACRO_DB2 as clay, silt and sand contents. This causes a slight underestimation of the sand content and thus a slight input error for the MACRO_DB2 pedotransfer functions. However, a major difference between the 2-50 µm and 2-60 µm fractions is expected only for soils rich in loess, which is not the case for the Lanna soil.

The available site-specific weather data comprised all meteorological input variables required by MACRO: daily maximum and minimum temperature, solar radiation, water vapour pressure and wind speed. Precipitation was available as hourly values. In addition to a simulation with generic sorption and degradation parameters for bentazone (Table 3.2), also a run with the bentazone parameters used by Larsson and Jarvis (1999) for a MACRO 4.1 simulation was performed.

Table 3.5 shows the cumulative measured and simulated values of drainflow volumes and bentazone losses via drainflow. In analogy, table Z shows the measured vs. simulated maximum daily drainflow volumes and bentazone losses. In Fig. 3.1-3.3, measured and simulated time series of drainflow volumes and bentazone drainage losses are presented.

During the study period (12.10.1994 – 30.11.1995) 362 mm tile drain outflow were recorded. The simulation using the pedotransfer functions of MACRO_DB2 moderately underestimated the cumulative drainflow volume by 29 % and the maximum daily drainflow by a factor of two. Fig. 3.1 shows that the timing of events was mostly simulated well. The calculated model efficiency (also called Nash-Sutcliffe index; Nash and Sutcliffe, 1970) for the drainflow time series was 0.48, which supports the conclusion that drainflow was adequately simulated.

The observed cumulative bentazone drainage losses over the study period totalled 8.4 % of the applied amount, the maximum daily bentazone loss 0.28 % of the applied amount. For the simulation with generic sorption and degradation parameters for bentazone (K_{oc} = 29 L kg^{-1}, Freundlich exponent m = 1, DT_{50} = 14 d) derived from several measured values (European Commission, 2004a; UBA, 1997) and the depth dependence of degradation according to FOCUS (2001), cumulative bentazone losses via drainflow were underestimated by 37 %, and maximum daily bentazone losses overestimated by a factor of two. Fig. 3.2 reveals that bentazone drainage losses were overpredicted in the first two drainflow events, and underpredicted in the later events. Model efficiency for the bentazone outflow time series was rather poor with 0.08. Nevertheless, the results can still be considered adequate for the purpose of aquatic risk assessment.

Larsson and Jarvis (1999) had used the following parameter settings for bentazone: K_{oc} = 5 L kg^{-1} (based on measurements in a Dutch soil; Van der Pas, 1994), m = 1, DT_{50} = 12.5 d in the top 30 cm, no degradation in the subsoil (based on laboratory measurements for the Lanna soil; Bergström et al., 1994). Here, the simulation with the bentazone parameterization according to Larsson and Jarvis (1999) slightly underpredicted cumulative bentazone losses by 13 % and overpredicted maximum daily losses by 37 %. The measured and simulated time series of bentazone losses (Fig. 3.3) matched reasonably well, which is confirmed by a model efficiency of 0.31.

The simulation results using generic bentazone parameters were clearly worse than those using the original parameterization by Larsson and Jarvis (1999). Apparently, both sorption and degradation of bentazone were much better described with the original parameter settings. For degradation, this is obvious because Larsson and Jarvis used site-specific degradation data. As regards sorption, the better suitability of the K_{oc} value of 5 L kg^{-1} from a Dutch site compared with the generic K_{oc} of 29 L kg^{-1} based on several measurements was probably just by chance. This is another example for the large uncertainty of the K_{oc} value (or the invalidity of the K_{oc} concept) for non-ionic compounds. Since Bentazone (pK_a = 3.3) is anionic at the pH of agricultural soils, it is not likely to adsorb to soil organic matter to great extent. Therefore, K_{oc} values for bentazone have no real physical meaning, and a generic K_{oc} for bentazone has only statistical relevance.

The original simulation of Larsson and Jarvis (1999), which was calibrated against measured hydrology and bromide data, with the older MACRO version 4.1 yielded a total drainflow volume of 325 mm and a total bentazone loss of 228 g ha^{-1}. These results are only slightly better than those of the uncalibrated MACRO 4.3 simulation with the original bentazone parameterization (Table 3.6). This implies that the drop in quality resulting from using the MACRO_DB2 pedotransfer functions instead of calibrated hydraulic parameters was not substantial here.

It can be summarized that MACRO, using the pedotransfer functions of MACRO_DB2, was able to predict timing and magnitude of drainflow volumes and bentazone drainage losses reasonably well for the Lanna dataset.

Table 3.5: Measured vs. simulated cumulative drainflow volumes and bentazone losses over the study period (12.10.1994 – 30.11.1995) for Lanna

simulation	dose	measured values (acc.)		simulated results (acc.)		ratio predicted/ observed		model efficiency[1)]	
of bentazone		drainflow	drainage loss	drainflow	drainage loss	drain-flow	drainage loss	drain-flow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	mm	g ha^{-1}				
Larsson / Jarvis[2)]	2.51	361.6	209.9	258.4	183.4	0.71	0.87	0.48	0.31
generic[3)]	2.51	361.6	209.9	258.4	132.8	0.71	0.63	0.48	0.08

[1)] Nash and Sutcliffe (1970)

[2)] bentazone parameters according to Larsson and Jarvis (1999): K_{oc} = 5 L kg^{-1}, linear sorption, DT_{50} = 12.5 d; no degradation below 30 cm

[3)] generic parameters for bentazone: K_{oc} = 29 L kg^{-1}, linear sorption, DT_{50} = 14 d; depth-dependence of degradation rate according to FOCUS (2001)

Table 3.6: Measured vs. simulated maximum daily drainflow volumes and bentazone losses over the study period (12.10.1994 – 30.11.1995) for Lanna

simulation	dose	measured values (max.)		simulated results (max.)		ratio predicted/ observed		model efficiency[1)]	
of bentazone		drainflow	drainage loss	drainflow	drainage loss	drain-flow	drainage loss	drain-flow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	mm	g ha^{-1}				
Larsson / Jarvis[2)]	2.51	10.78	7.02	5.30	9.63	0.49	1.37	0.48	0.31
generic[3)]	2.51	10.78	7.02	5.30	15.09	0.49	2.15	0.48	0.08

[1)] Nash and Sutcliffe (1970)

[2)] bentazone parameters according to Larsson and Jarvis (1999): K_{oc} = 5 L kg^{-1}, linear sorption, DT_{50} = 12.5 d; no degradation below 30 cm

[3)] generic parameters for bentazone: K_{oc} = 29 L kg-1, linear sorption, DT_{50} = 14 d; depth-dependence of degradation rate according to FOCUS (2001)

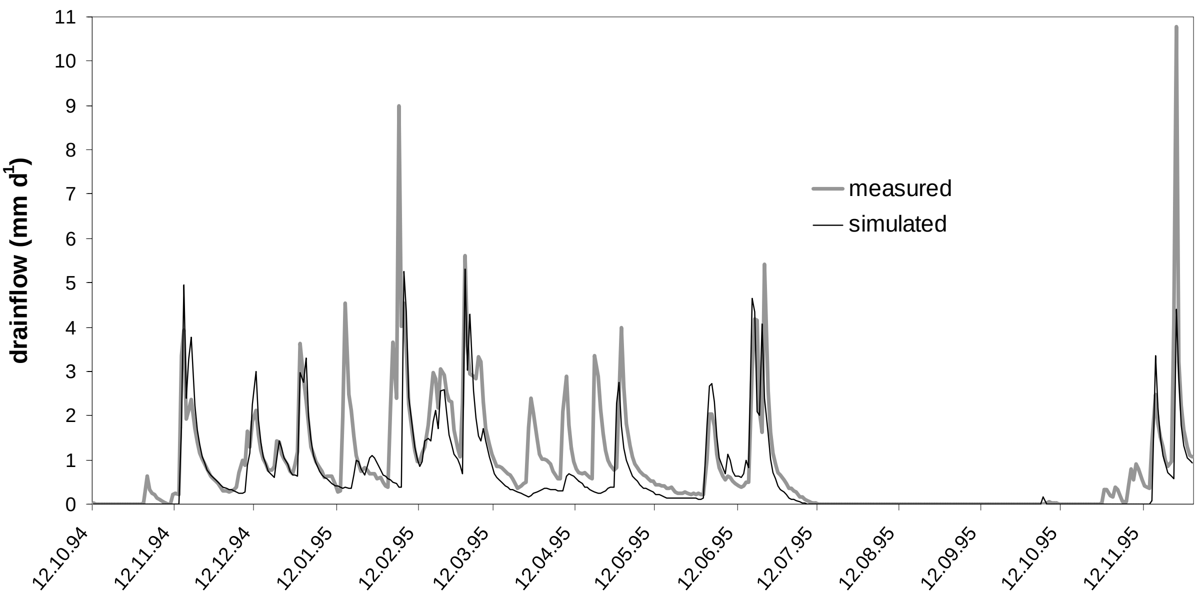

Fig. 3.1: Measured vs. simulated drainflow volumes for Lanna.

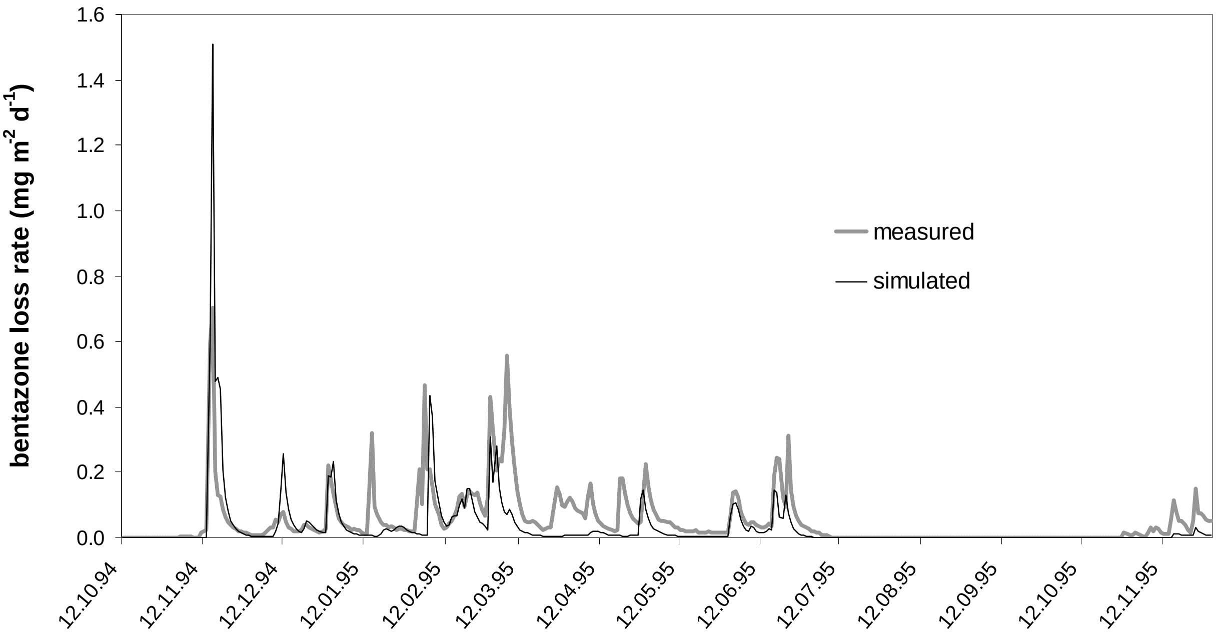

Fig. 3.2: Measured vs. simulated bentazone losses via drainflow for Lanna (generic bentazone parameters)

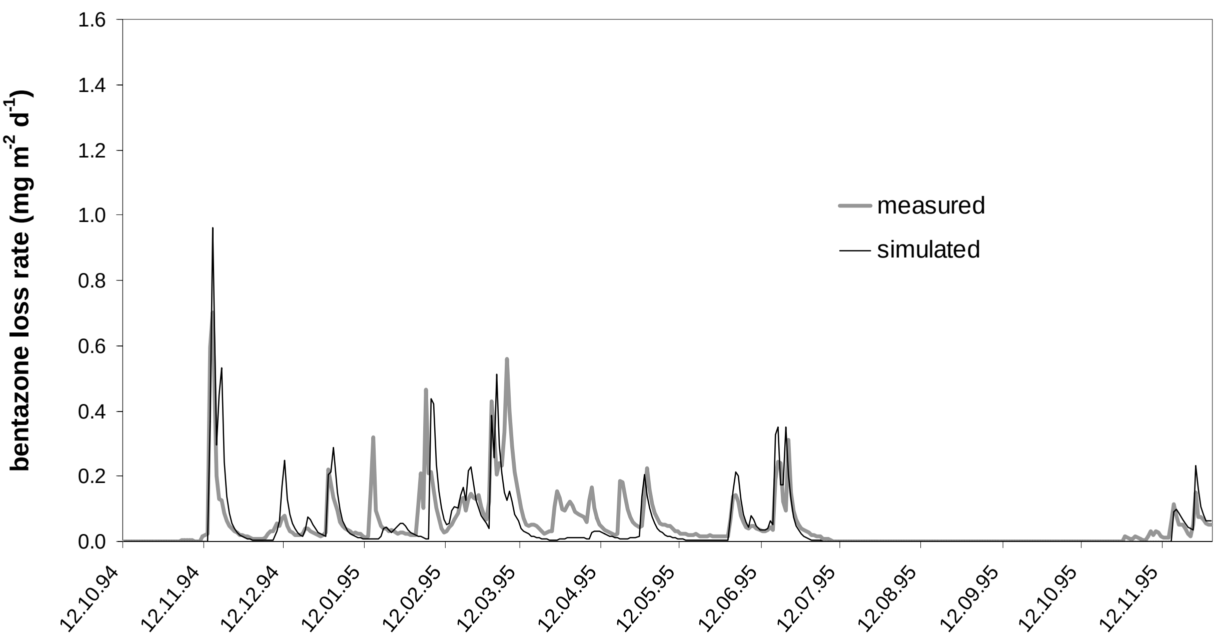

Fig. 3.3: Measured vs. simulated bentazone losses via drainflow for Lanna (bentazone parameters according to Larsson and Jarvis, 1999)

3.2.1.2 Cadriano

The Cadriano and Carpi sites are situated in two different agricultural areas of the Po Valley, Northern Italy. Details of the field experiments are given in Accinelli et al. (2002). As for Lanna, both drainage studies have already been modelled with a previous version of MACRO before. Balderacchi et al. (2002) modelled Cadriano and Carpi with MACRO 4.2, using the pedotransfer functions of MACRO_DB v. 1.0 (Jarvis et al., 1997).

The experimental plot at the Cadriano site, located in the southeastern Po valley, has an area of 0.33 ha and plastic drain tubes installed at ca. 0.9 m depth and 2.5-7.5 m spacing. The basic soil properties of the profile are shown in Table 3.7.

Table 3.7: Soil properties of the Cadriano site (Accinelli et al., 2002; Balderacchi, pers. comm)

depth	clay (0-2 µm)	silt (2-50 µm)	sand (50-2000 µm)	OC[1]	pH (water)	CEC_{pot}[2] cmolc kg^{-1}	structure (FAO, 1990)
cm		%		%			
0-50	24.5	37.5	38.0	0.85	7.96	17.75	weak coarse blocky
50-75	28.5	40.3	31.2	0.60	7.86	20.02	strong medium prismatic
75-135	22.0	56.8	21.2	0.47	8.38	17.34	moderate coarse blocky

[1] values calculated from the OM content in the original profile description; OM/OC = 1.724

[2] potential cation exchange capacity

The experiment included a spring application of atrazine (11.04.1996) to a maize/winter wheat crop rotation at a rate of 1 kg ha^{-1}. Maize was sown on 11.04.96 and harvested on 16.09.96. Wheat was sown in late October. Drainage outflow was measured and analyzed for atrazine from 01.03.1996 to 28.02.1997.

No measured data were available for bulk density, which is an input variable for all MACRO_DB2 pedotransfer functions (except for the ptf that calculates the effective diffusion pathlength ASCALE). Therefore, bulk density was calculated for each horizon according to the method proposed by Rawls (1983). This method estimates soil bulk density from the organic matter content and a diagram based on a database of 2721 soil horizons relating mineral bulk density to sand and clay contents. As Rawls (1983) reported an average overprediction of bulk density for topsoils of 0.05 g cm^{-3} and an average underprediction for subsoils of 0.03 g cm^{-3} with the proposed method, the estimated bulk densities were subsequently corrected here by these average deviations.

The available site-specific weather data comprised daily values of temperature, relative humidity (maximum and minimum values each) and precipitation. Potential evapotranspiration was estimated according to the Haude equation (Klein, 1995).

In Table 3.8 the cumulative measured and simulated values of drainflow volumes and atrazine losses via drainflow are presented, while Table 3.9 shows the measured vs. simulated maximum daily drainflow volumes and atrazine losses. In Fig. 3.4 and 3.5, measured and simulated time series of drainflow volumes and atrazine drainage losses are presented. The drainflow samples were not always taken daily; instead, they often collected water over two, three or more days. Therefore, presenting measured and simulated time series as daily rates is misleading here, and a cumulative presentation was chosen instead. For the same reason, a calculation of the model efficiency as a goodness-of-fit criterion is not meaningful here.

During the study period (01.03.1996 – 28.02.1997) 236 mm tile drain outflow were recorded. The simulation using the pedotransfer functions of MACRO_DB2 slightly overestimated the cumulative drainflow volume by 11 %. The overestimation mainly occurred in the winter months December and January (Fig. 3.4) and was probably due to partial soil freezing, which is not accounted for in MACRO. The maximum daily drainflow was moderately overpredicted by 24 %; however, the maximum measured and simulated daily drainflow volumes did not belong to the same drainflow event (12.05.1996 vs. 10.12.1996). For the largest observed drainflow event on 12.05.1996, MACRO underestimated drainflow by 27 %. Nevertheless, Fig. 3.4 shows that the timing of events was mostly simulated well. It can be concluded that tile drain outflow was adequately simulated for Cadriano.

The observed cumulative atrazine drainage losses over the study period totalled 0.62 % of the applied amount (Table 3.8), most of which (0.54 %) occurred on a single day (12.05.1996; Table 3.9; Fig. 3.5). Cumulative atrazine losses via drainflow were moderately underpredicted by 24 %. However, maximum daily atrazine losses were underestimated by a factor of six, which could be critical with respect to peak concentrations in receiving surface water bodies and thus to acute aquatic risk assessment. Fig. 3.5 shows that the overall magnitude of the major loss event in May, caused by 70 mm rainfall within three days (10.-12.05.1996), was underpredicted only by a factor of about two, but also that the event was distributed in MACRO over several days.

However, it has to be noted that the sample taken on 12.05.1996 actually integrated tile drain outflow and associated atrazine losses over three days (10.-12.05.1996), and it can only be speculated how drainflow and atrazine loss were distributed between these three days. Hence, the actual underestimation of maximum daily atrazine loss by the MACRO simulation was possibly much smaller than a factor of six.

Table 3.8: Measured vs. simulated cumulative drainflow volumes and atrazine losses over the study period (01.03.1996 – 28.02.1997) for Cadriano

	measured values (acc.)			simulated results (acc.)			ratio predicted / observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
1.00	235.56	6.24	0.624	262.08	4.76	0.476	1.11	0.76

Table 3.9: Measured vs. simulated maximum daily drainflow volumes and atrazine losses over the study period (01.03.1996 – 28.02.1997) for Cadriano

	measured values (max.)			simulated results (max.)			ratio predicted / observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
1.00	26.65[1)]	5.44[1)]	0.544[1)]	32.93	0.86	0.086	1.24	0.16

[1)] integrates drainflow and atrazine loss over three days (10.-12.05.1996)

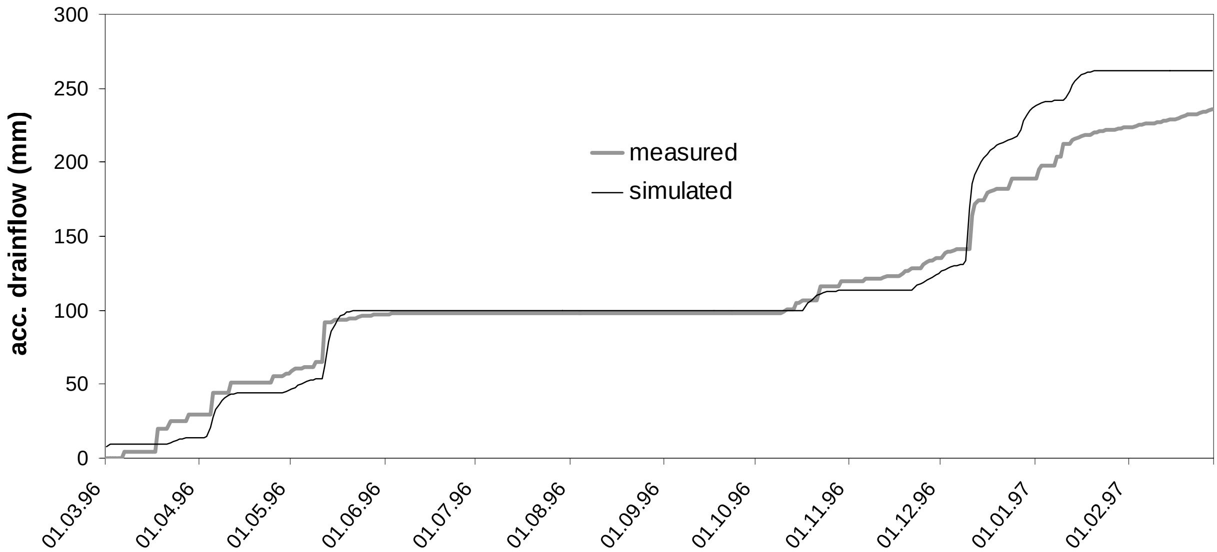

Fig. 3.4: Measured vs. simulated drainflow volumes for Cadriano (cumulative values).

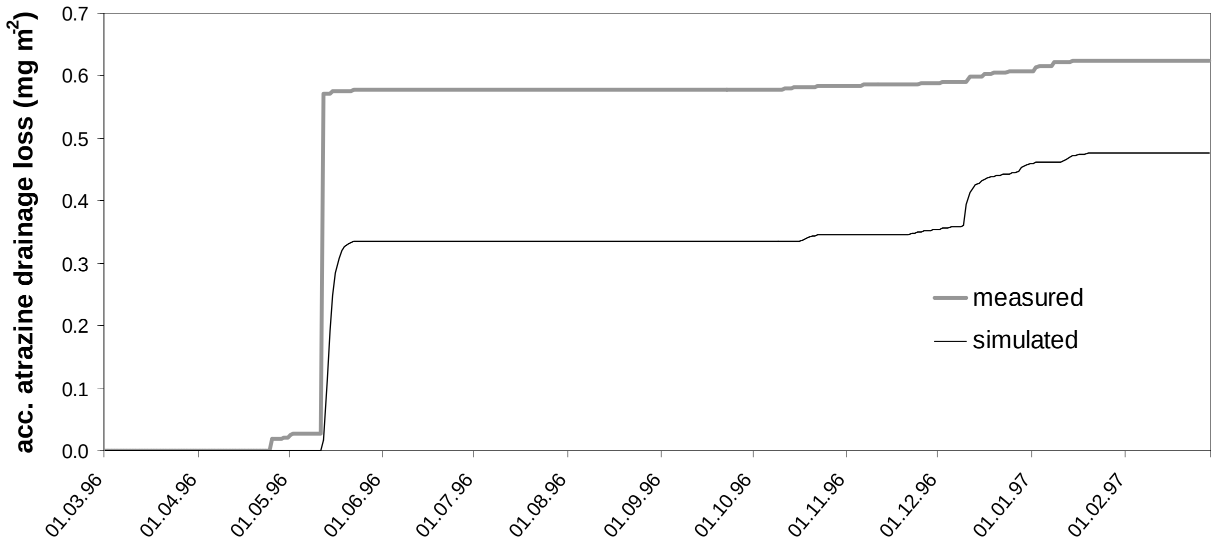

Fig. 3.5: Measured vs. simulated atrazine losses via drainflow for Cadriano (cumulative values).

The predictions could probably be significantly improved if the bulk densities of the soil horizons were known: Rawls (1983) reported a standard error of 0.17 g cm^{-3} for bulk density estimates with the method proposed by him. Since bulk density is a crucial input variable for the MACRO_DB2 pedotransfer functions (Jarvis and Stenemo, 2002), the uncertainty in the bulk density value of a horizon will propagate to nearly all soil hydraulic parameters.

Given the uncertainty in soil bulk density, it can be summarized that MACRO, using the pedotransfer functions of MACRO_DB2, was able to predict timing and magnitude of drainflow volumes and atrazine drainage losses acceptably for the Cadriano dataset.

3.2.1.3 Carpi

The experimental plot at Carpi, situated in the central Po valley, has an area of 1.85 ha and plastic drain tubes installed at a depth of ca. 0.9 m and a spacing of 5-20 m. The basic soil properties of the profile are shown in Table 3.10.

Table 3.10: Soil properties of the Carpi site (Accinelli et al., 2002; Balderacchi, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-50 µm)	sand (50-2000 µm)	OC[1)]	pH (water)	CEC_{pot}[2)] cmolc kg^{-1}	structure FAO
cm	%	%	%	%			
0-25	43	52	5	1.4	7.7	23.68	weak medium blocky
25-60	42	53	5	1.2	7.8	23.01	moderate coarse blocky
60-95	38	57	5	0.9	8.0	19.31	strong medium prismatic
95-120	25	56	19	0.5	8.0	13.46	moderate coarse blocky
120-135	20	49	31	0.4	8.0	12.04	moderate coarse blocky
135-170	15	33	52	0.4	8.1	9.50	weak coarse blocky

[1)] values calculated from the OM content in the original profile description; OM/OC = 1.724
[2)] potential cation exchange capacity

The experiment included a spring application of atrazine (16.04.96) to a maize/winter wheat crop rotation at a rate of 1 kg ha^{-1}. Maize was sown on 15.04.96 and harvested on 20.09.96. Wheat was sown in early November. Drainage outflow was measured and analyzed for atrazine from 01.03.1996 to 28.02.1997.

Also for the Carpi site, data on soil bulk density were missing, and bulk densities were therefore calculated with the same method as for the Cadriano test site. The available site-specific weather data comprised daily values of temperature, relative humidity (maximum and minimum values each) and precipitation. Potential evapotranspiration was estimated according to the Haude method (Klein, 1995).

Table 3.11 shows the cumulative measured and simulated values of drainflow volumes and atrazine losses via drainflow. In analogy, Table 3.12 shows the measured vs. simulated maximum daily drainflow volumes and atrazine losses. In Fig. 3.6 and 3.7, measured and simulated time series of drainflow volumes and atrazine drainage losses are presented as cumulative values (for the same reasons as for Cadriano).

During the study period (01.03.1996 – 28.02.1997) 196 mm tile drain outflow occurred. The simulation using the pedotransfer functions of MACRO_DB2 moderately overestimated the cumulative drainflow volume by 64 %. A large part of the overestimation occurred in December and January and may again be attributed to partial soil freezing. The maximum daily drainflow was slightly overestimated by 20 %. However, the maximum measured and simulated daily drainflow volumes did not belong to the same drainflow event (07.01.1997 vs. 13.05.1996. Fig. 3.6 shows that timing and magnitude of events were not always simulated well. For instance, drainflow was underpredicted by a factor of three for the event of 13.05.1996. In contrast, a major drainflow event in October was missed by the simulation.

The observed cumulative atrazine drainage losses over the study period totalled 2.14 % of the applied amount, most of which (1.36 %) occurred on a single day (13.05.1996). Cumulative atrazine losses via drainflow were slightly underpredicted by 7 %. Maximum daily atrazine losses were moderately underestimated by 40 %. However, the overall magnitude of the major loss event in May, caused by 62 mm rainfall within two days (12.-13.05.1996), was matched well (Fig. 3.7).

Also for the Carpi dataset, the lack of measured bulk density data is probably the largest source of error in the simulations. Another possible source of error is the fact that MACRO 4.3 does not consider tillage operations, e.g. between maize harvest and wheat sowing, and the resulting temporary changes in soil physical and hydraulic properties.

Table 3.11: Measured vs. simulated cumulative drainflow volumes and atrazine losses over the study period (01.03.1996 – 28.02.1997) for Carpi

	measured values (acc.)			simulated results (acc.)			ratio predicted / observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
1.00	196.50	21.37	2.14	322.66	19.95	1.99	1.64	0.93

Table 3.12: Measured vs. simulated maximum daily drainflow volumes and atrazine losses over the study period (01.03.1996 – 28.02.1997) for Carpi

	measured values (max.)			simulated results (max.)			ratio predicted/ observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm d	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
1.00	28.65	13.56[1)]	1.36[1)]	34.44	8.20	0.820	1.20	0.60

[1)] integrates atrazine loss over five days (09.-13.05.1996)

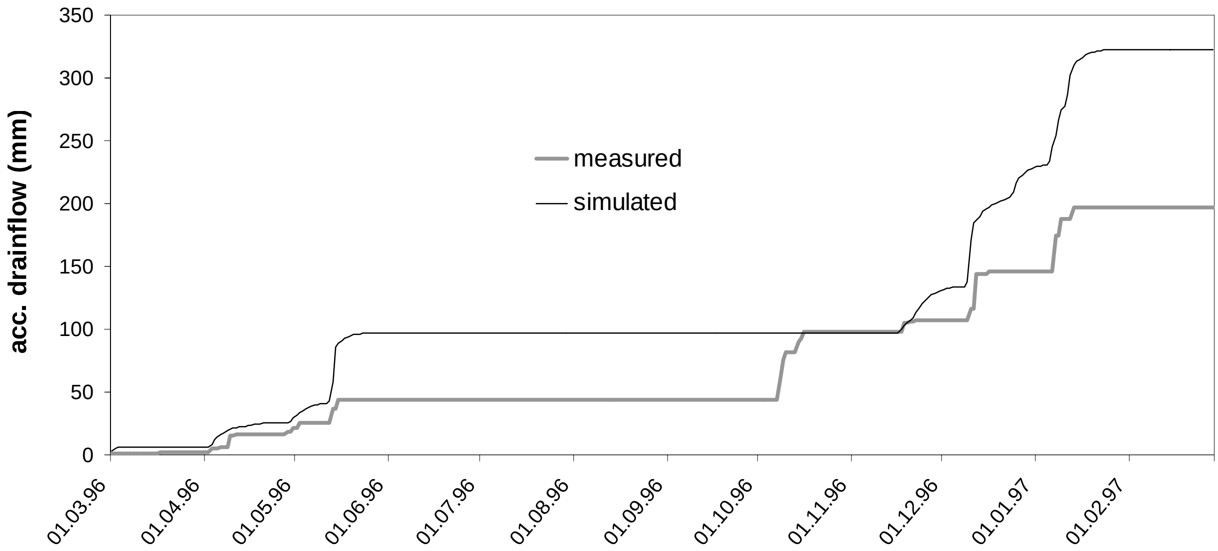

Fig. 3.6: Measured vs. simulated drainflow volumes for Carpi (cumulative values).

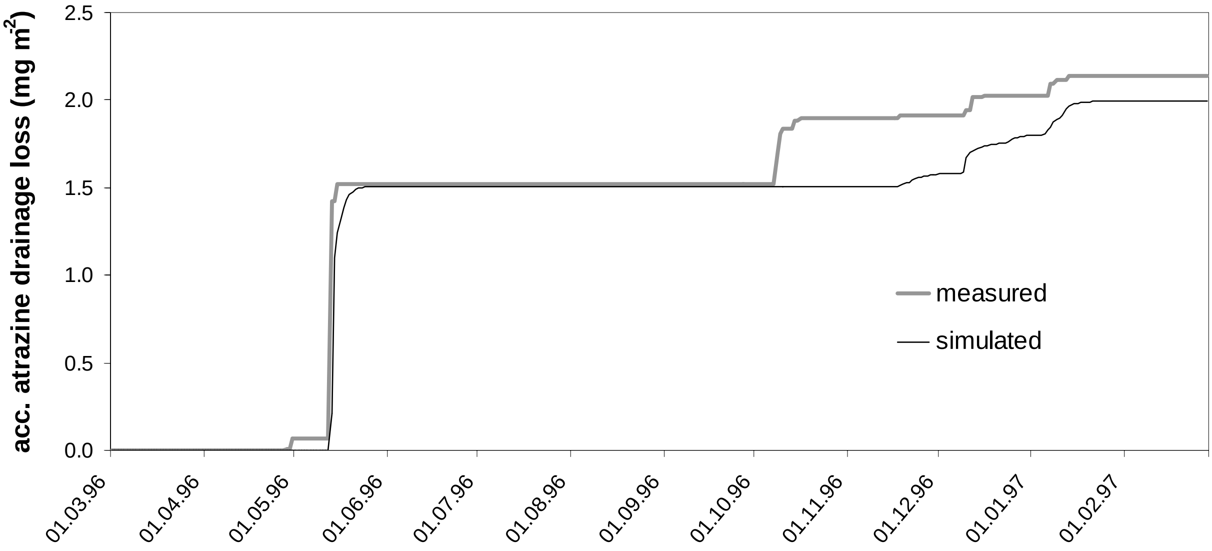

Fig. 3.7: Measured vs. simulated atrazine losses via drainflow for Carpi (cumulative values).

Overall, it can be concluded that the combination of MACRO 4.3b and the pedotransfer functions of MACRO_DB2 was able to predict the magnitude, and with reservations also the timing, of drainflow volumes and atrazine drainage losses reasonably well for the Carpi dataset.

3.2.1.4 Brimstone

The Brimstone Farm experimental facility comprises a set of plot scale lysimeters for the study of water and solute movement through a cracked clay soil. The major characteristics of the site are given by Cannell et al. (1984) and Harris et al. (2000). The site is located in southern England (51°35’ N, 1°39’ W) and has a mean annual precipitation of 686 mm. The soil is classified as Verti-Eutric Gleysol according to FAO (1988). Basic soil parameters are given in Table 3.13. Although this soil situation is extreme, representing a soil in which macropore flow is almost the sole mode of transport, it is typical of much lowland clay in arable use in England (Goss et al., 1988). When the soil of the site dries out in the summer, large vertical cracks develop, which close again in winter when the soil wets up.

The experimental facility consists of 20 hydrologically isolated plot lysimeters, each 0.2 ha in size. The plot with the most suitable dataset for model testing was plot 9. This plot is drained with 50 mm pipes at 0.55 m depth and with a spacing of 2 m (Armstrong, pers. comm., 2002). The pipes thus simulate the effects of mole drains but without the gradual decrease in efficiency that is characteristic of mole drains.

Table 3.13: Soil properties of the Brimstone site (Cannell, 1984; Armstrong, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density	pH (water)	structure
cm	%			%	kg dm^{-3}		
0-20	54	39	7	3.3	1.05	6.9	moderate medium blocky
20-35	56	39	6	0.8	1.34	7.8	strong coarse blocky
35-62	60	37	3	0.7	1.32	7.9	strong medium prismatic
62-89	62	36	2	0.6	1.43	7.9	strong medium prismatic
89-112	62	37	1	0.6	1.46	8.1	moderate coarse prismatic

Isoproturon was applied to a cereal rotation with mostly winter wheat in seven successive seasons from 1993 to 2000 (Table 3.14).

Table 3.14: Isoproturon applications, dates and doses at the Brimstone site (Armstrong, pers. comm., 2002)

season	crop	application date	IPU dose
			g ha^{-1}
1993/94	winter wheat	02.11.93	2488.5
1994/95	winter wheat	17.11.94	2500
1995/96	winter oats	30.10.95	250
1996/97	winter wheat	30.10.96	1500
1997/98	winter wheat	23.10.97 + 09.03.98	1500 + 1000
1998/99	spring oats	12.02.99	250
1999/00	winter wheat	26.10.99	1500

Drain outflow was measured continuously in half-hourly intervals. Isoproturon concentrations in drainflow were monitored only during the first 3-5 key drainflow events of each season. Total drainflow losses of isoproturon per season were thus obtained by extrapolation. The available site-specific weather data comprised daily values of temperature (maximum and minimum values), precipitation, and potential evapotranspiration calculated using the standard MORECS model (Thompson et al., 1981).

Table 3.15 shows the cumulative measured and simulated values of drainflow volumes and isoproturon losses via drainflow, while Table 3.16 shows the corresponding maximum daily values. In Fig. 3.8, measured and simulated time series of daily drainflow volumes are presented for the season 1993/94 as an example. In Fig. 3.9, measured and simulated time series of cumulative drainflow volumes are compared for the whole study period. Since only the first key drainflow events of each season were sampled and analyzed for isoproturon, a graphical comparison of measured and simulated IPU losses would have been misleading and is therefore not presented here.

1557 mm tile drain outflow were recorded during the study period (01.11.1993 – 31.07.2000). The simulation using the pedotransfer functions of MACRO_DB2 well matched the cumulative drainflow volume (Table 3.15, Fig. 3.9) and overestimated the maximum daily drainflow slightly by 12 % (Table 3.16). As can be seen in Fig. 3.8 as an example for one cropping/drainage season, the timing of events was mostly simulated well. However, the calculated model efficiency for the whole drainflow time series was only 0.07, which is in part due to an overestimation of drainflow during the exceptionally dry winter of 1996/97 (Table 3.15, Fig. 3.9). Also, occasionally the simulation missed measured drainflow events in late spring, summer or early autumn (e.g. in May 1994, cf. Fig. 3.8).

Table 3.15: Measured vs. simulated cumulative drainflow volumes and isoproturon losses for Brimstone

		measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[2)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (93-00)	10.99	1557.17	152.42	1.39	1605.73	446.18	4.06	1.03	2.93
93-94	2.49	245.55	136.90	5.50	263.90	147.99	5.95	1.07	1.08
94-95	2.50	252.44	9.37	0.37	234.34	165.48	6.62	0.93	17.67
95-96	0.25	166.28	0.25	0.10	206.25	16.31	6.52	1.24	66.28
96-97	1.50	17.68	0.001	6.7E-05	60.88	7.15	0.48	3.44	7152.8
97-98	1.50	135.86	0.21	0.014	168.33	38.67	2.58	1.24	187.70
spring 98[3)]	1.00	367.68	0	0	345.25	45.38	4.54	0.94	-
98-99 [3)]	0.25	143.69	0.38	0.15	83.94	0.92	0.37	0.58	2.40
99-00	1.50	227.99	5.32	0.35	242.83	24.29	1.62	1.07	4.57

1) Total seasonal drainflow and IPU losses refer to time period between two applications.

2) Total losses per season were extrapolated from sampled events (Armstrong, pers. comm., 2002). The exact time periods of the seasons were not specified.

3) spring application

Table 3.16: Measured vs. simulated maximum daily drainflow volumes and isoproturon losses for Brimstone

		measured values (max.)			simulated results (max.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[1)2)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm d^{-1}	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (93-00)	10.99	18.16	21.42	0.19	20.42	66.20	0.60	1.12	3.09
93-94	2.49	12.84	21.42	0.86	19.99	45.03	1.81	1.56	2.10
94-95	2.50	12.84	7.66	0.31	16.64	66.20	2.65	1.30	8.65
95-96	0.25	18.16	0.096	0.038	20.42	4.48	1.79	1.12	46.72
96-97	1.50	6.99	0.0016	1.1E-04	13.11	1.86	0.12	1.87	1159.4
97-98	1.50	12.05	0.085	5.7E-03	13.07	8.54	0.57	1.09	100.13
spring 98[3)]	1.00	11.44	0	0	19.74	12.30	1.23	1.73	-
98-99 [3)]	0.25	5.76	0.18	0.072	6.02	0.29	0.12	1.04	1.61
99-00	1.50	9.95	1.26	0.084	12.36	4.40	0.29	1.24	3.49

[1)] Maximum daily drainflow rates and IPU losses refer to time period between two applications.

[2)] Calculated as an approximation from daily mean concentrations and daily drainflow volumes.

[3)] spring application

The observed cumulative isoproturon drainage losses over the whole study period totalled 1.39 % of the applied amount, the maximum daily isoproturon loss 0.19 % of the applied amount. The simulation overestimated both cumulative and maximum daily losses of isoproturon over the whole study period by a factor of three, which can be considered acceptable for the purpose of aquatic risk assessment. In some seasons, however, the overprediction was considerably larger (Tables 3.15 and 3.16). For example, after spring application in 1998, where no isoproturon losses were measured at all, MACRO predicted losses of 4.5 % of the applied amount. Since drainflow volumes were matched fairly well, possible explanations for the overestimation are that either the sorption and degradation behaviour of isoproturon at the Brimstone site was significantly different from the generic values used for the simulation, or that kinetic sorption processes, which are not accounted for in MACRO 4.3b, played a major role in the Brimstone soil. The latter possibility is also supported by the fact that overestimation of isoproturon losses was higher for dry winter seasons.

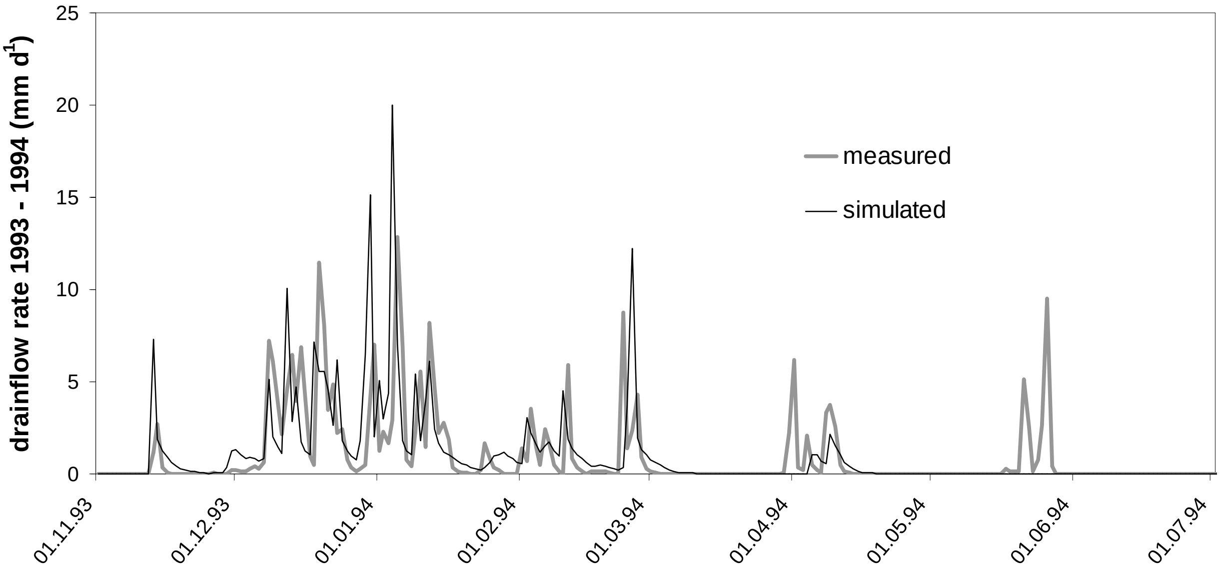

Fig. 3.8: Measured vs. simulated daily drainflow volumes for Brimstone, season 1993-1994.

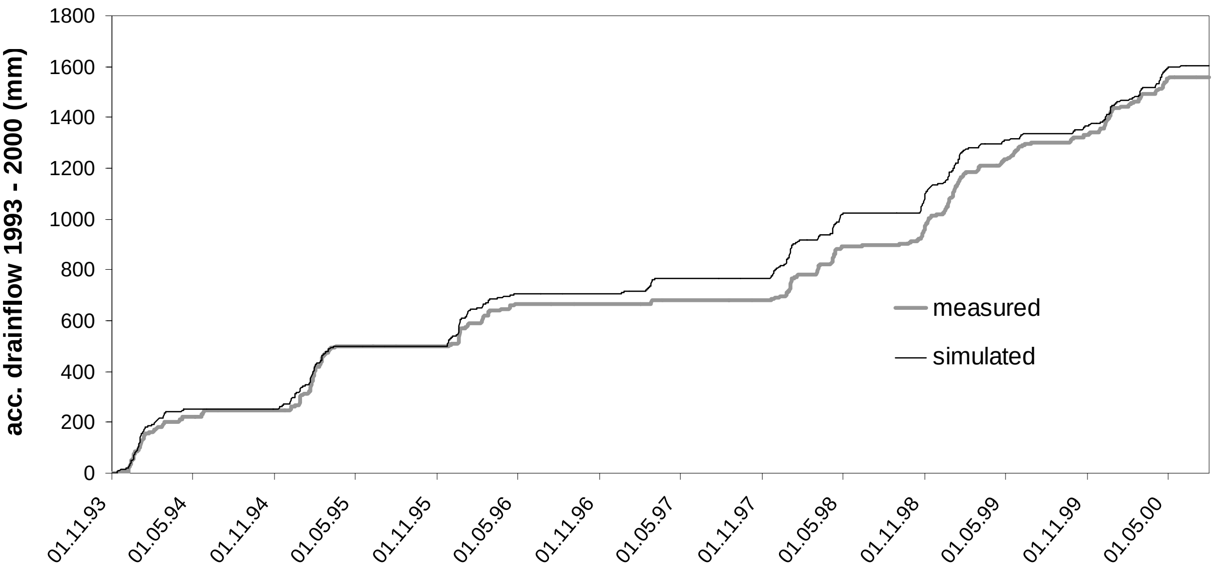

Fig. 3.9: Measured vs. simulated drainflow volumes (cumulative values) for Brimstone over the whole simulation period (1993-2000).

Given the uncertainty in measured isoproturon losses (mainly due to the fact that not all drainflow events of a season were sampled), it can be summarized that MACRO, using the pedotransfer functions of MACRO_DB2, was able to predict timing and magnitude of drainflow volumes and isoproturon drainage losses reasonably well even for the somewhat extreme heavy clay soil at Brimstone Farm.

3.2.1.5 Mill Farm

This study was conducted on behalf of Monsanto. The experimental site is located in Central England (52°14’ N, 0°33’ W) on a chalky boulder clay soil. Basic soil properties are shown in Table 3.17. The field has an area of 7.7 ha and is equipped with pipe drains at 0.8 m depth and 20 m spacing. Moreover, it is mole drained at a depth of 0.50-0.55 m and with a spacing of 2 m. A sulfonyl urea herbicide was applied in spring (16.05.2000) to a winter wheat crop at a rate of 19.8 g ha^{-1}. Drain outflow was recorded on an hourly basis from 16.05.2000 to 28.02.2001 and sampled for herbicide analysis till 13.11.2000.

Table 3.17: Soil properties of the Mill Farm site (source: Monsanto; Fogg, pers. comm., 2003**)**

depth	clay (0-2 µm)	silt (2-63 µm)	sand (63-2000 µm)	OC	dry bulk density	pH (water)	CEC_{pot} [1)] cmolc kg^{-1}	structure (FAO, 1990)
cm		%		%	kg dm^{-3}			
0-30	27.63	34.52	37.85	1.2	1.5	7.1	24.4	moderate medium blocky
30-56	29.21	33.76	37.03	0.3	1.6	7.2	16.8	moderate medium blocky
56-97	29.19	40.80	30.01	0.4	1.7	8.3	12.8	strong medium blocky
97-120	37.78	39.33	22.89	0.4	1.8	8.5	12.6	massive, occasional cracks

[1)] potential cation exchange capacity

The available site-specific weather data comprised hourly values of precipitation, air temperature, relative humidity, solar radiation, and wind speed. Thus, the weather data contained all necessary input variables required by MACRO for internal calculation of potential evapotranspiration.

Table 3.18 shows the cumulative measured and simulated values of drainflow volumes and sulfonyl urea losses via drainflow. In analogy, Table 3.19 shows the measured vs. simulated maximum daily drainflow volumes and bentazone losses. In Fig. 3.10-3.12, measured and simulated time series of drainflow volumes, herbicide concentrations in drainflow, and herbicide drainage losses are presented.

During the study period (16.05.2000 – 28.02.2001), 296 mm tile drain outflow were recorded, and 113 mm till the end of pesticide sampling (13.11.2000). The simulation using the pedotransfer functions of MACRO_DB2 moderately overestimated the cumulative drainflow volume by 38 % for the pesticide sampling period and slightly by 11 % for the whole study period. The maximum daily drainflow rate, which occurred on 06.11.2000 both in reality and in the simulation, was moderately underestimated by 29 %. Fig. 3.10 shows that the timing of events was mostly simulated well, although peak recession was apparently slower in the simulation than in reality. This may be in part due to the fact that only one of the two installed drainage systems could be simulated with the chosen lower boundary condition. Neglecting the wider-spaced pipe drain system and simulating only the more important mole drains may have led to slower drainflow recession in the simulation than in reality. Moreover, bulk density, which is a crucial input variable for the MACRO_DB2 pedotransfer functions, was only imprecisely known (one digit after the decimal point). Through the pedotransfer functions, this uncertainty propagates to nearly all soil hydraulic parameters. Still, the calculated model efficiency for the drainflow time series was 0.68, which supports the conclusion that drainflow was adequately simulated.

The observed cumulative drainage losses of the sulfonyl urea herbicide over the sampling period totalled 0.54 % of the applied amount (Table 3.18). The maximum daily herbicide loss, which occurred 12 days after application and was caused by 48 mm rainfall within three days, totalled 0.40 % of the applied amount (Table 3.19, Fig. 3.12). Cumulative herbicide losses via drainflow were overpredicted by a factor of four, maximum daily losses by a factor of three. The magnitude of pesticide concentrations in drainflow was matched relatively well (Fig. 3.11). However, MACRO simulated the largest pesticide concentration on the day of the simulated and measured drainflow peak (28.05.2000), whereas in the experiment the highest concentration occurred 2 days before, together with only little drainflow. Hence, the overestimation of pesticide loads (Fig. 3.12) can largely be attributed to the offset between simulated and measured pesticide concentrations in drainflow. A major source of uncertainty in the simulation of pesticide transport was here that the sulfonyl urea herbicide is anionic in agricultural soils (pK_a = 3.5), and the K_{oc} value is therefore uncertain for this compound (cf. the bentazone simulation in section 3.2.1.1).

Brown et al. (2004) conducted a simulation with MACRO 4.1 for the same dataset. They made use of site-specific water retention and pesticide dissipation data for model parameterization and also performed a slight calibration. However, their simulation did not perform better than the simulation conducted here: Pesticide drainage losses for the whole study period and for the major loss event in May 2000 were overpredicted by a factor of 5 each. In summary, it can be concluded that the combination of MACRO 4.3 and the pedotransfer functions of MACRO_DB2 was able to predict timing and magnitude of drainflow volumes and sulfonyl urea drainage losses acceptably well for the Mill Farm dataset.

Table 3.18: Measured vs. simulated cumulative drainflow volumes and herbicide losses for Mill Farm over the pesticide sampling period (16.05.2000 – 13.11.2000)

	measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
0.0198	113.41	0.108	0.54	156.00	0.444	2.24	1.38	4.12

Table 3.19: Measured vs. simulated maximum daily drainflow volumes and herbicide losses for Mill Farm over the pesticide sampling period (16.05.2000 – 13.11.2000)

	measured values (max.)			simulated results (max.)			ratio predicted/ observed	
dose	drainflow	drainage loss		drainflow	drainage loss		drainflow	drainage loss
kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
0.0198	30.02	0.080	0.40	21.43	0.269	1.36	0.71	3.38

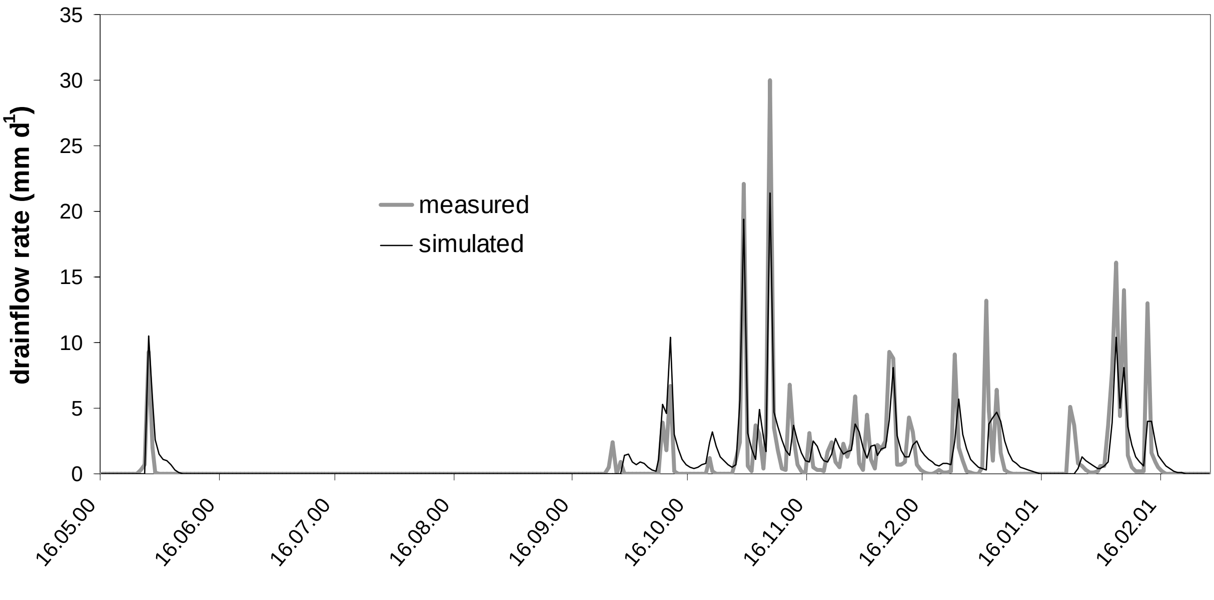

Fig. 3.10: Measured vs. simulated daily drainflow volumes for Mill Farm.

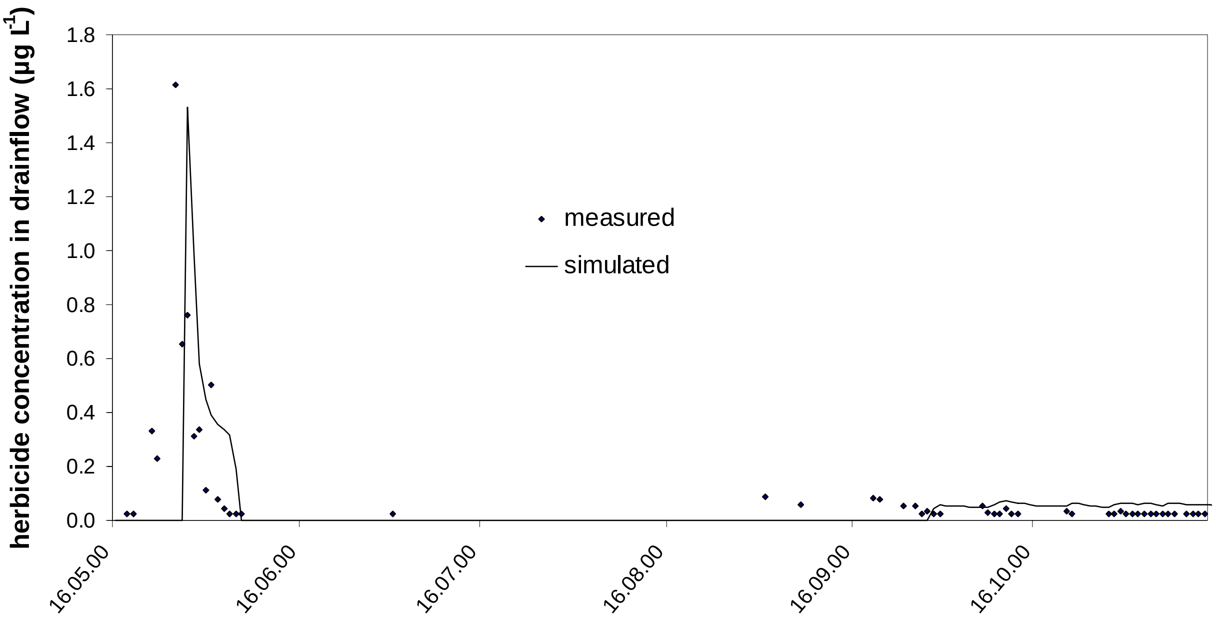

Fig. 3.11: Measured vs. simulated herbicide concentrations in drain outflow for Mill Farm.

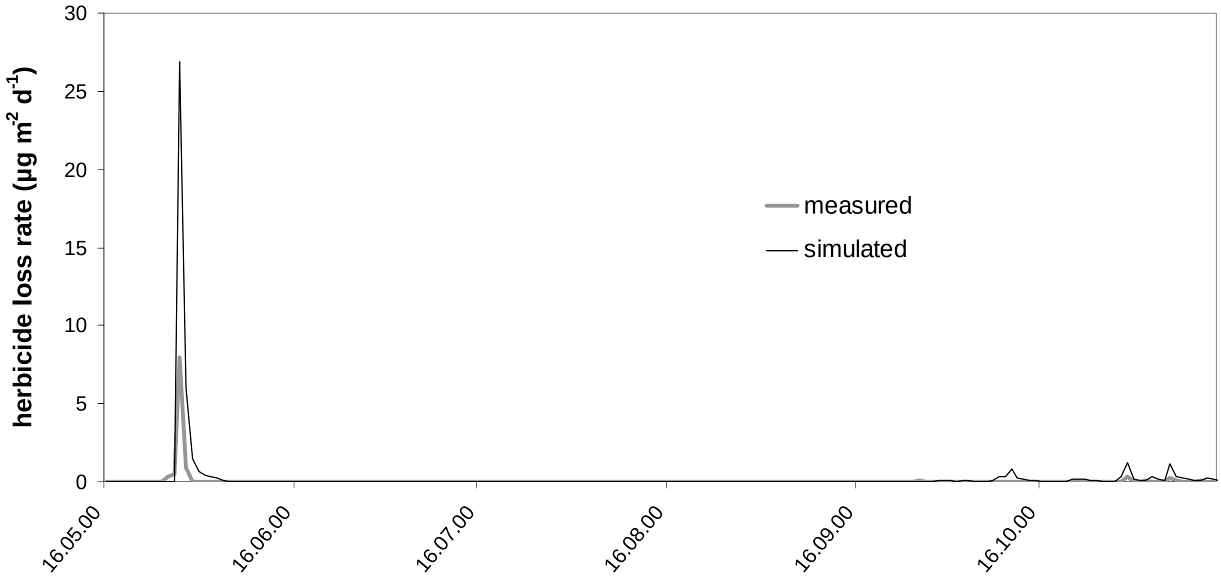

Fig. 3.12: Measured vs. simulated sulfonyl urea losses via drainflow for Mill Farm.

3.2.1.6 Cockle Park

The Cockle Park study was conducted by Colin Brown (now University of York, UK) and is described in detail in Brown et al. (1995). The site is located in NE-England and contained three plots with 0.25 ha (25 m × 100 m) each and 2 % slope. The soil is a Stagno-Gleyic Luvisol (FAO, 1988) and is characterized by a sharp transition between a finely structured, permeable topsoil (sandy loam) and a massively prismatic, only slowly permeable subsoil (clay loam). Basic soil properties are given in Table 3.20. A perched water table is present over the whole year within the top 100 cm of the soil and can rise almost to the surface in absence of drains.

Table 3.20: Soil properties of the Cockle Park site (source: Brown, pers. comm., 2002 and 2003; Beulke et al., 1998)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density	pH (water)	structure (FAO, 1990)
cm	%	%	%	%	kg dm^{-3}		
0-15	22	31	47	3.27	1.12 [1]	5.80	moderate medium blocky[4]
15-30	22	31	47	2.48	n.a.[2]	6.39	moderate medium blocky[4]
30-45	24	32	44	1.10	n.a.	7.08	moderate coarse blocky[4]
45-60	37	36	27	0.94	1.50 [2]	7.22	moderate coarse blocky[4]
60-75	37	36	27	0.89	n.a.	7.03	moderate coarse blocky[4]
75-90	32	37	31	0.79	n.a.	7.29	weak coarse prismatic[4]

1) at 10 cm depth

2) n.a. = not available

3) at 60 cm depth

4) not determined in the field; descriptions are based on posterior expert judgement by Colin Brown

Two of the plots were mole-drained at 50 cm depth and with 1.8 m spacing, the third plot was an undrained control. While the undrained plot C was used for runoff modelling with PRZM (cf. section 4.2.1.5), the mole-drained plot A was used for MACRO testing.

Isoproturon was applied to a winter wheat crop in two successive seasons. On 27.11.1989, 1.96 kg ha^{-1} isoproturon were applied by spraying to plot A. On 13.11.1990, 2.50 kg ha^{-1} isoproturon were applied. Sampling for pesticide analysis was done automatically, using a scheme which biased the sampling towards the upward limb of the hydrograph. As a consequence, not on every day with occurrence of drainflow water samples for IPU analysis were taken.

The available site-specific weather data comprised daily maximum and minimum temperature and precipitation. Potential evapotranspiration was estimated with Linacre's method (Linacre, 1977) and, as the estimate seemed too high, subsequently scaled down to an average annual PET of 600 mm. The corresponding scaling factor was 0.73.

Table 3.21 shows the cumulative measured and simulated values of drainflow volumes and isoproturon losses via drainflow, while Table 3.22 shows the corresponding maximum daily values. In Fig. 3.13 and 3.14, measured and simulated time series of daily drainflow volumes are presented for the first and the second simulation year, respectively. Since not on all days with drainflow water samples were taken and analyzed for isoproturon, a graphical comparison of measured and simulated IPU losses would have been misleading and is therefore not presented here. Fig. 3.15 shows measured vs. simulated isoproturon concentrations in drainflow.

During the study period (01.09.1989 – 31.08.1991) 361 mm tile drain outflow were recorded. The first study year (01.09.1989 – 31.08.1990) was exceptionally dry with 471 mm rainfall, and thus only little drainflow occurred (Table 3.21). The simulation using the pedotransfer functions of MACRO_DB2 well matched the cumulative drainflow volume in the first year and underestimated it in the second year by 23 % (Table 3.21). The maximum daily drainflow was slightly underestimated in both years by 20 % (Table 3.22). Fig. 3.13 and 3.14 show that also the timing of events was simulated well except for the beginning of the drainage season (overestimation of drainflow in the first, and underestimation in the second year). The calculated model efficiency for the drainflow time series was 0.50, which supports the conclusion that drainflow was acceptably simulated.

Table 3.21: Measured vs. simulated cumulative drainflow volumes and isoproturon losses for Cockle Park

		measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[1)2)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (89-91)	4.46	360.58	1.66	0.037	298.59	8.79	0.20	0.83	5.88
89-90	1.96	83.88	0.25	0.013	85.51	2.11	0.11	1.02	8.07
90-91	2.50	276.71	1.41	0.056	213.09	6.68	0.27	0.77	5.42

[1)] Total seasonal drainflow and IPU losses refer to time period between two applications.

[2)] Total losses per season were interpolated between sampling events (Brown, pers. comm., 2003).

Table 3.22: Measured vs. simulated maximum daily drainflow volumes and isoproturon losses for Cockle Park

		measured values (max.)			simulated results (max.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[1)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (89-91)	4.46	14.57	0.29	6.5E-03	11.68	0.97	0.022	0.80	3.36
89-90	1.96	9.80	0.15	7.5E-03	7.82	0.38	0.020	0.80	2.61
90-91	2.50	14.57	0.29	0.012	11.68	0.97	0.039	0.80	3.36

[1)] Maximum daily drainflow rates and IPU losses refer to time period between two applications.

[2)] Calculated as an approximation from daily mean concentrations and daily drainflow volumes.

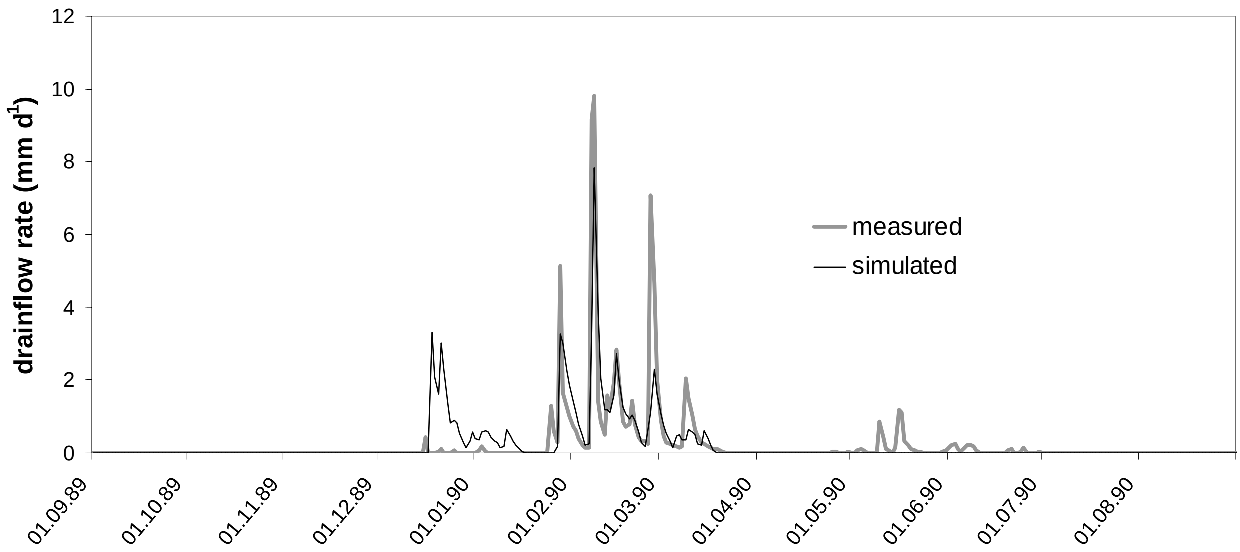

Fig. 3.13: Measured vs. simulated daily drainflow volumes for Cockle Park, 1st simulation year.

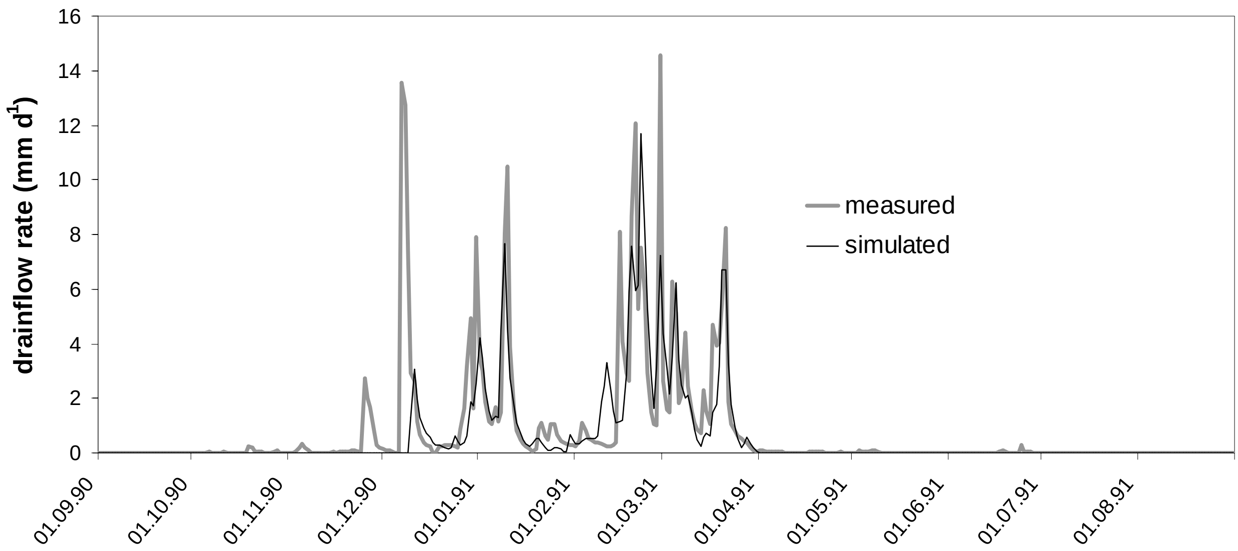

Fig. 3.14: Measured vs. simulated daily drainflow volumes for Cockle Park, 2nd simulation year.

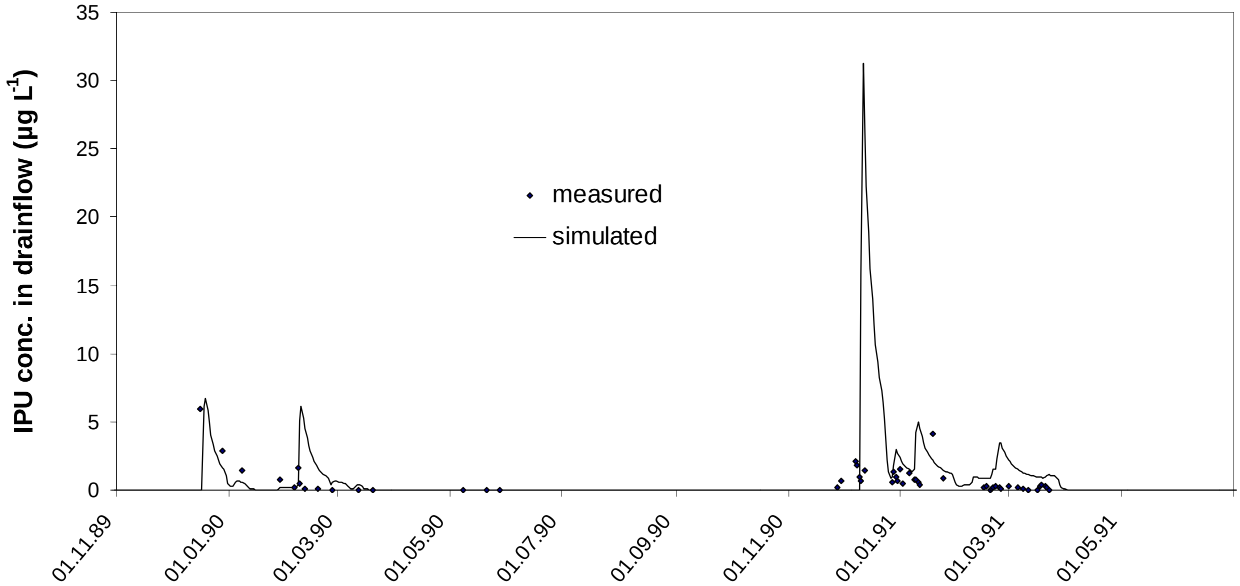

Fig. 3.15: Measured vs. simulated isoproturon concentrations in drain outflow for Cockle Park.

The observed cumulative isoproturon drainage losses over the whole study period totalled 0.037 % of the applied amount, the maximum daily isoproturon loss 0.0065 % of the applied amount. The simulation overestimated cumulative IPU losses over the whole study period by a factor of six, and in the first year even by a factor of eight. The maximum daily losses of isoproturon were overpredicted in both years by a factor of three, which can be considered acceptable for the purpose of aquatic risk assessment.

There are several possible explanations for the overestimation of both cumulative and maximum daily IPU drainage losses. First, since not on all days with drainflow water samples were taken (e.g., no measured concentration exists for the day with the maximum simulated IPU concentration, 11.12.1990, Fig. 3.15), cumulative pesticide loads over the study period had to be calculated by interpolation between sampling events (Brown et al., 1995). The interpolation procedure introduces uncertainty into both total and maximum daily measured losses. Secondly, the overprediction of drainflow volume few weeks after application (27.11.1989) in the first simulation year (Fig. 3.13) also caused too high simulated isoproturon losses in that period. Thirdly, the sorption and degradation behaviour of isoproturon at the Cockle Park site was possibly significantly different (e.g. faster degradation) from the generic values used for the simulation.

It also has to be noted that, apart from the substance properties, a lot of input for the MACRO simulation was rather uncertain: Potential evapotranspiration had to be estimated rather crudely with Linacre's method, and measured bulk density was lacking for most horizons. Moreover, the structural description of the soil horizons, affecting both saturated hydraulic

conductivity (KSATMIN) and the effective diffusion pathlength (ASCALE), which governs water and solute exchange between the two flow domains, was not determined in the field. It was then estimated by expert judgement of the data owner (Brown, pers. comm., 2003).
In view of the considerable uncertainty both in model input and in measured pesticide losses, it can be concluded that MACRO, using the pedotransfer functions of MACRO_DB2, was able to predict timing and magnitude of drainflow volumes and isoproturon drainage losses acceptably well for the Cockle Park dataset.

3.2.1.7 La Bouzule

The La Bouzule site is located near Nancy in north-eastern France. The experimental field contains two different soil types in a toposequence: a Stagnic Luvisol (FAO, 1988; silty clay loam) in a level position and downslope a Vertic Cambisol (silty clay) with a slope of 5-6 %. The basic soil properties of the profiles are shown in Table 3.24 and 3.23, respectively. The Vertic Cambisol covers an area of 1.85 ha and is drained with pipe drains at 90 cm depth and with 8 m spacing. In the Stagnic Luvisol area (2.83 ha), pipe drains are installed at the same depth and with 12 m spacing.

Table 3.23: Soil properties of the Vertic Cambisol at La Bouzule (Novak et al., 2001; Novak, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-50 µm)	sand (50-2000 µm)	OC	bulk density	pH (water)	CEC_{pot}	structure[1)] (FAO, 1990)
cm	%			%	kg dm^{-3}		cmolc kg^{-1}	
0-20	54.2	40.5	5.3	1.90	1.17	8.2	20.7	moderate medium blocky
20-60	54.1	42.8	3.1	0.88	1.30	8.2	21.0	strong medium prismatic
60-100	53.0	43.0	4.0	0.51	1.40	8.3	21.6	massive

[1)] derived from original profile description

A detailed description of the experiment is given in Novak et al. (2001). The field was cropped in rotation with maize and winter cereals. Metolachlor was applied pre-emergence to maize on 07.05.1996 at 3.053 kg ha-1 and on 14.05.1998 at 3.926 kg ha-1. Drain outflow from each soil area was measured continuously over the whole study period (01.03.1996 – 31.08.1998). Metolachlor in drainflow was monitored from 07.05.1996 to 28.02.1997 and from 14.05.1998 to 31.08.1998, with samples taken automatically on a flow-proportional basis (i.e., no sampling on days with only small drainflow). The available site-specific weather data comprised daily values of temperature (maximum and minimum values), precipitation, and potential evapotranspiration.

Table 3.24: Soil properties of the Stagnic Luvisol at La Bouzule (Novak et al., 2001; Novak, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-50 µm)	sand (50-2000 µm)	OC	bulk density	pH (water)	CEC_{pot}	structure [1] (FAO, 1990)
cm	%	%	%	%	kg dm^{-3}		cmolc kg^{-1}	
0-25	26.0	52.0	21.9	1.36	1.28	6.6	17.2	weak medium blocky
25-40	31.2	52.1	16.7	n.i.[2]	1.37	n.i.	n.i.	moderate fine blocky
40-60	37.2	48.8	14.0	0.41	1.55	5.8	21.5	moderate medium blocky
60-80	40.2	49.0	10.8	n.i.	1.53	n.i.	n.i.	strong medium prismatic
80-100	39.8	52.6	7.6	0.32	1.58	5.2	24.4	strong coarse prismatic

1) derived from original profile description
2) n.i. = no information available

Measured flow data and pesticide losses were available only on an aggregated basis (i.e., as cumulative values for days on which samples for pesticide analysis were taken), so that daily drainflow rates and pesticide losses cannot be calculated. Therefore, a comparison of measurements and simulation results can only be made with cumulative data. Table 3.25 shows the cumulative measured and simulated values of drainflow volumes and metolachlor losses via drainflow for the Vertic Cambisol, while Table 3.26 shows the corresponding data for the Stagnic Luvisol. Fig. 3.16-3.18 show time series of measured and simulated cumulative drainflow volume, metolachlor drainage loss and metolachlor concentration in drainflow, respectively, for the Cambisol. In Fig. 3.19-3.21, the corresponding measured and simulated data for the Luvisol are presented.

During the study period (01.03.1996 – 31.08.1998), 268 mm drain outflow were recorded for the Vertic Cambisol, and 309 mm for the Stagnic Luvisol. The simulations slightly overestimated the total drainflow volume by 19 % for the Cambisol (Table 3.25) and by 9 % for the Luvisol (Table 3.26). From Fig. 3.16 and 3.19 it can be seen that also the timing of drainflow events was simulated well for both soils.

Table 3.25: Measured vs. simulated cumulative drainflow volumes and isoproturon losses for La Bouzule, Vertic Cambisol

		measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[1)2)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (96-98)	6.979	267.93	33.86	0.49	317.97	24.63	0.35	1.19	0.73
96 - 05/98	3.053	260.49	17.94	0.59	304.33	24.47	0.80	1.17	1.36
05-08/98	3.926	7.44	15.92	0.41	13.64	0.16	4.1E-03	1.83	0.010

1) Total seasonal drainflow and metolachlor losses refer to time period between two applications.

2) Metolachlor was not monitored from 01.03.1997 to 13.05.1998. However, possible metolachlor losses within this period can be considered negligible.

Table 3.26: Measured vs. simulated cumulative drainflow volumes and isoproturon losses for La Bouzule, Stagnic Luvisol

		measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
season	dose	drainflow[1)]	drainage loss[1)2)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
all (96-98)	6.979	309.18	9.47	0.14	337.45	10.58	0.15	1.09	1.12
96 - 05/98	3.053	296.49	2.38	0.078	320.98	10.55	0.35	1.08	4.43
05-08/98	3.926	12.69	7.09	0.18	16.47	0.036	9.1E-04	1.30	5.0E-03

1) Total seasonal drainflow and metolachlor losses refer to time period between two applications.

2) Metolachlor was not monitored from 01.03.1997 to 13.05.1998. However, possible metolachlor losses within this period can be considered negligible.

The observed cumulative metolachlor drainage loss over the study period totalled 0.49 % of the applied amount for the Cambisol, and 0.14 % for the Luvisol. As expected, pesticide losses were higher for the heavier, more structured soil. In the Vertic Cambisol, metolachlor drainage losses were moderately overestimated by 36 % after the first application in 1996, and strongly underestimated after the second application in May 1998 (Table 3.25). For the Stagnic Luvisol, the contrast between the two seasons was even more extreme (Table 3.26). Fig. 3.17 shows that for the Cambisol, the magnitude of the first loss event in 1996 three weeks after application, was underestimated by the simulation by a factor of 2.5, while losses over the following autumn and winter were strongly overpredicted. The major losses that occurred in June 1998 a few weeks after the second application were almost completely missed by the simulation. Similarly, for the Stagnic Luvisol the measured losses in June 1998 were missed (Fig. 3.20); however, the first loss event in 1996 was overestimated by a factor of 10. As drain outflow itself was simulated relatively well for both soils (Fig. 3.16 and 3.19), the problem most probably lies in the simulation of pesticide transport. Fig. 3.18 and 3.21 show that for both soils, measured and simulated metolachlor concentrations in drainflow were at least comparable for the first loss event in 1996, but that the very high measured drainflow concentrations in June 1998 (up to 282 µg L^{-1} metolachlor for the Cambisol and up to 101 µg L^{-1} for the Luvisol) could not be reproduced with the simulations.

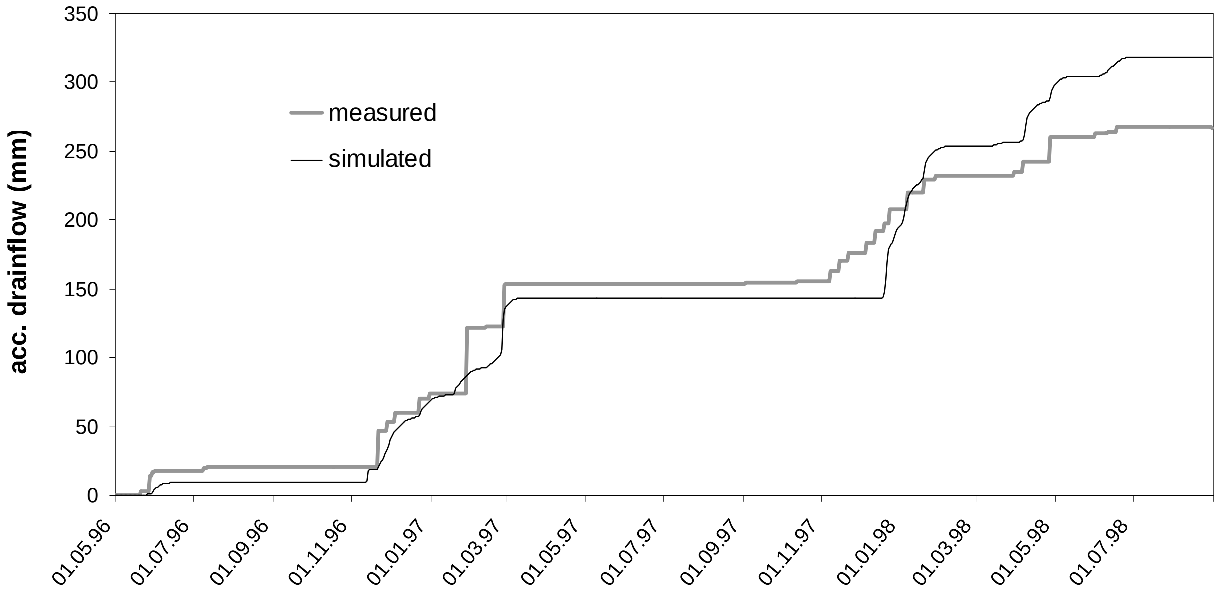

Fig. 3.16: Measured vs. simulated drainflow volumes for La Bouzule, Vertic Cambisol (cumulative values).

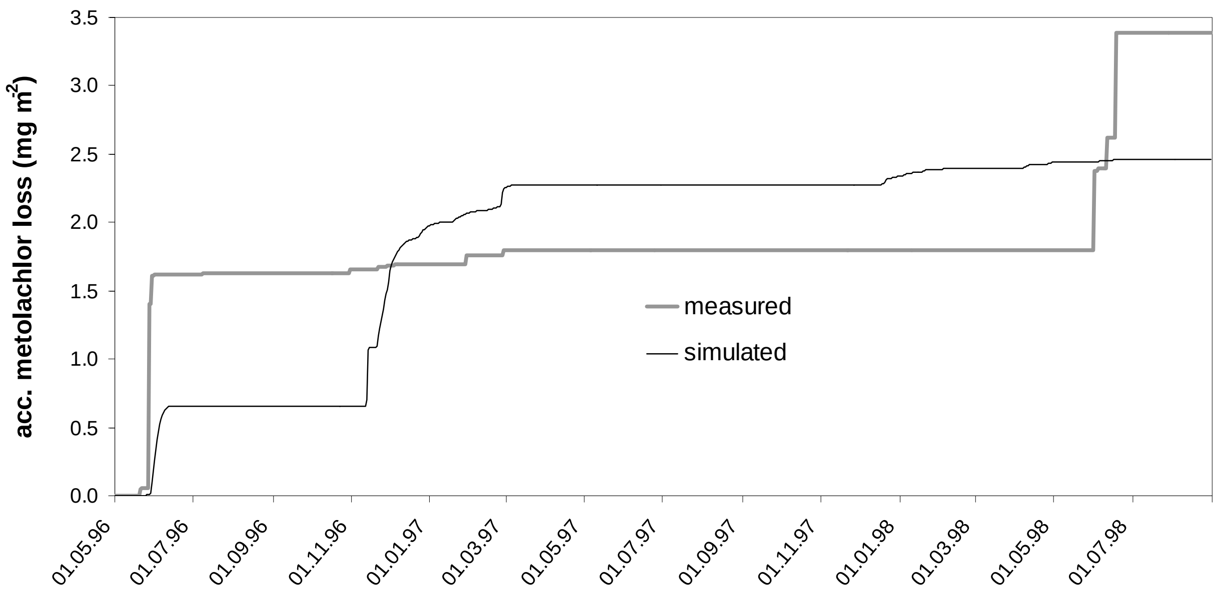

Fig 3.17: Measured vs. simulated metolachlor losses via drainflow for La Bouzule, Vertic Cambisol (cumulative values).

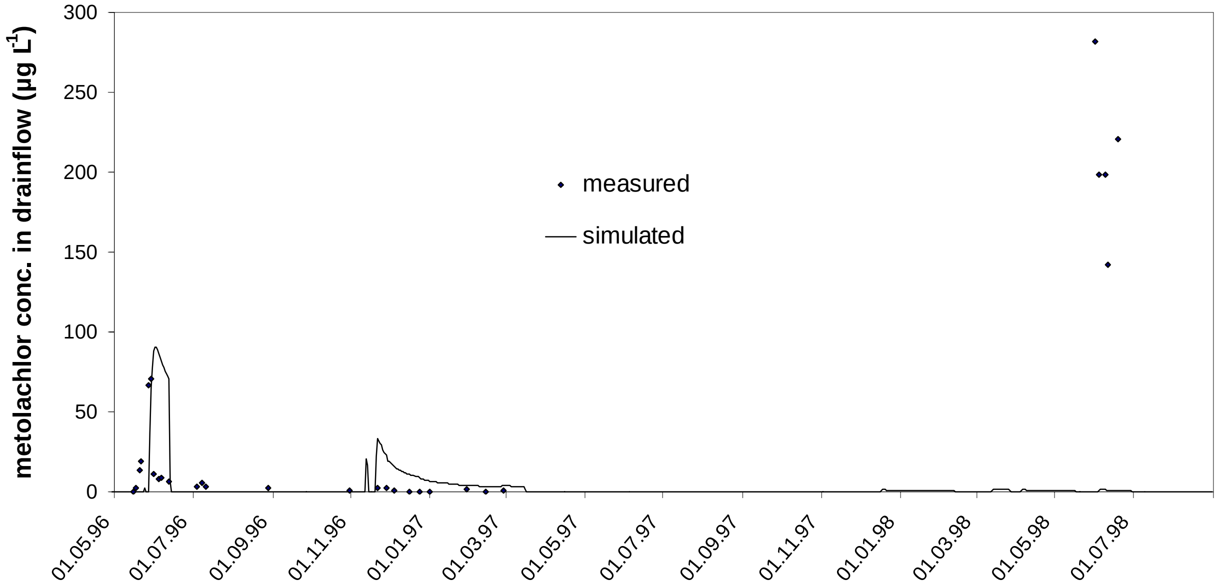

Fig. 3.18: Measured vs. simulated metolachlor concentrations in drain outflow for La Bouzule, Vertic Cambisol.

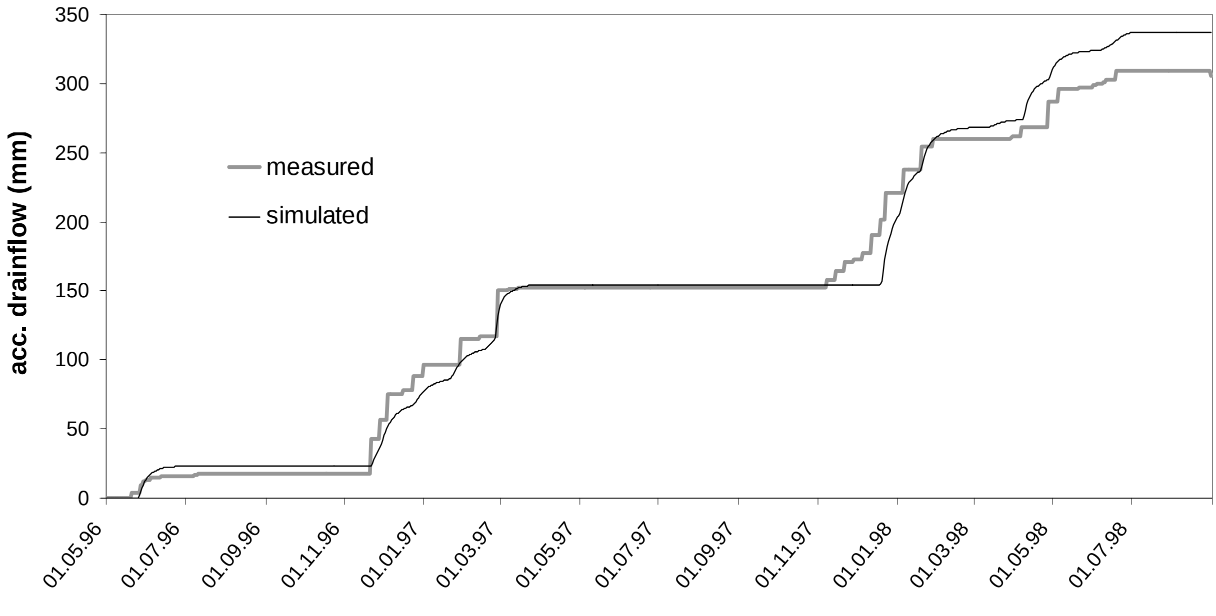

Fig. 3.19: Measured vs. simulated drainflow volumes for La Bouzule, Stagnic Luvisol (cumulative values).

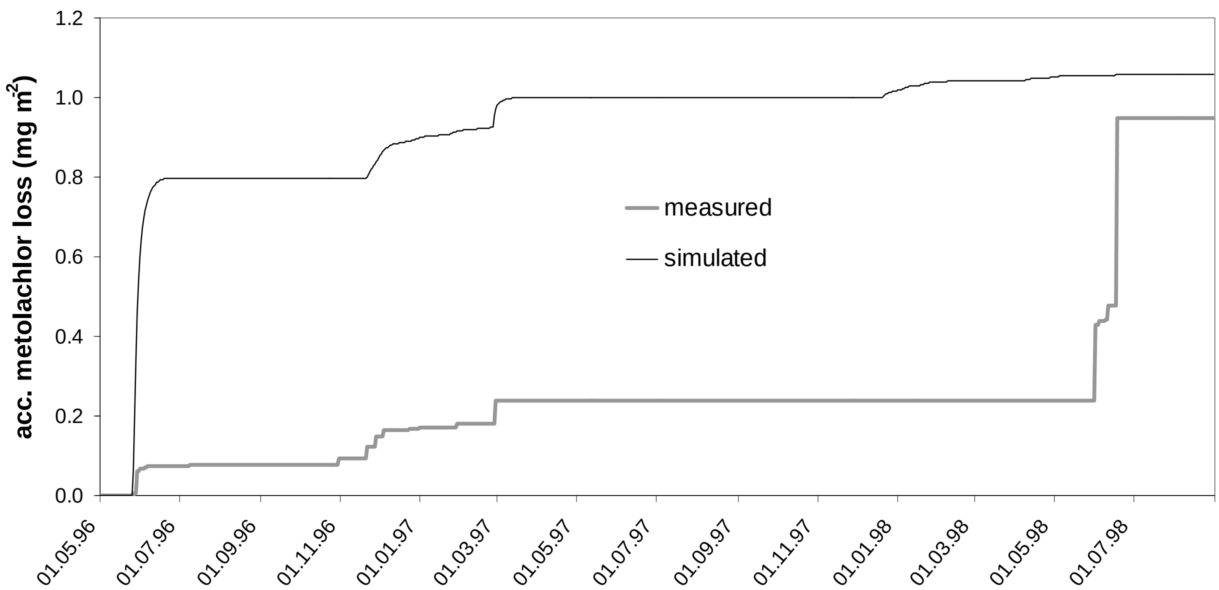

Fig. 3.20: Measured vs. simulated atrazine losses via drainflow for La Bouzule, Stagnic Luvisol (cumulative values).

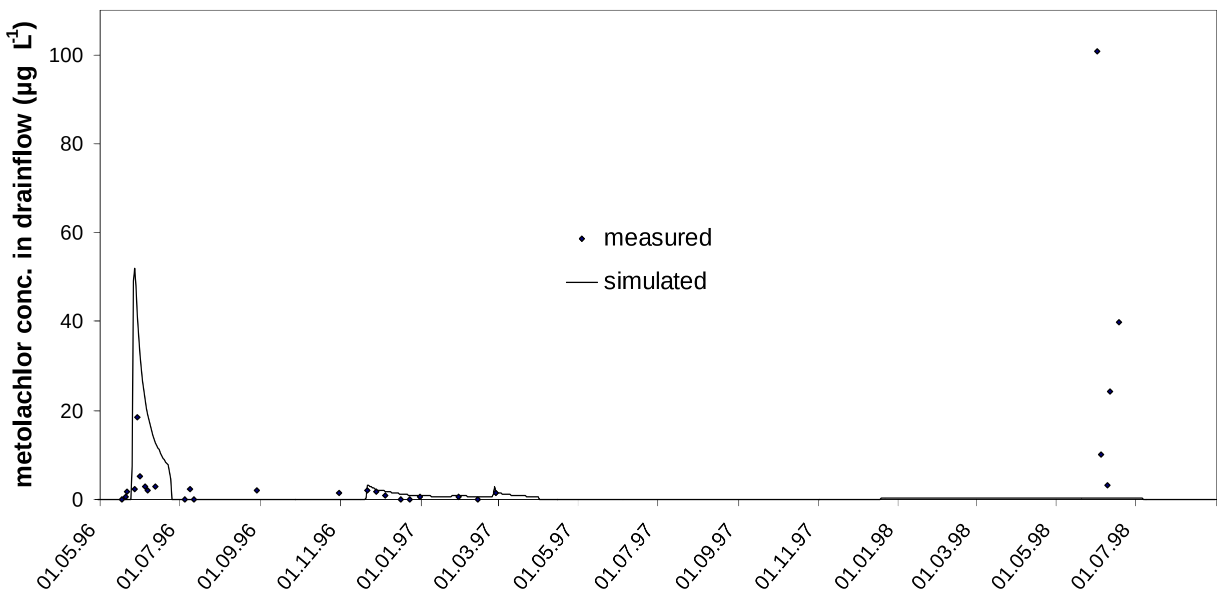

Fig. 3.21: Measured vs. simulated metolachlor concentrations in drain outflow for La Bouzule, Stagnic Luvisol.

Since the site-specific measured sorption and degradation parameters of metolachlor were not substantially different from the generic parameters used in the simulation, input of inappropriate compound properties can be excluded here as a source of error. However, it may be possible that the high application rate in 1998 of almost 4 kg ha^{-1} had toxic effects on the metolachlor-degrading microbial community and thus retarded dissipation of metolachlor. Another possible explanation for the mismatch between measured and simulated metolachlor concentrations in drainflow is nonequilibrium sorption, which is not accounted for in

MACRO 4.3. The occurrence of nonequilibrium sorption was also suggested by Novak et al. (2003) as result of a modelling study.
It can be summarized that for the two soils at La Bouzule, MACRO was able to predict drainflow adequately, but not pesticide losses via drainflow. These may be affected here by processes not accounted for in MACRO 4.3.

3.2.1.8 Beetz

The experimental site is located in Brandenburg, north-eastern Germany, north-west of Berlin. The climate is rather continental with a mean annual precipitation of only 537 mm. The field has an area of ca. 4 ha and has 3 single pipe drains installed at a depth of 70-90 cm and an average spacing of ca. 110 m. The pipes drain separately into a ditch. Basic soil properties are shown in Table 3.27. Information on bulk density, soil structure, and subsoil horizons deeper than 65 cm was not available. Bulk density was then estimated according to Rawls' method (Rawls, 1983).

Table 3.27: Soil properties of the site Beetz (Kördel et al., 1996)

depth	clay (0-2 µm)	silt (2-63 µm)	sand (63-2000 µm)	OC	pH	CEC_{pot}
(cm)		%		%		cmolc kg^{-1}
0-25	4.0	7.0	89.0	2.5	6.3	7.3
25-45	1.0	1.0	98.0	0.2	5.8	3.6
45-65	2.0	2.0	96.0	0.6	5.2	4.7

Detailed descriptions of the field experiments are given in Traub-Eberhard et al. (1995) and Kördel et al. (1996). Among several applications of various pesticides, 1.67 and 2.0 kg ha^{-1} metolachlor were applied post-emergence to maize on 05.06.1992 and 19.05.1993, respectively. Furthermore, 1.5 kg ha^{-1} isoproturon were applied to bare soil on 17.11.1992. During the whole study period (May 1992 – March 1994), drainflow was measured and analyzed for pesticides at least on a daily basis. It has to be noted that drainflow was monitored only at the outlet of one of the three pipe drains. This drain had an estimated catchment of about 1 ha.
The available site-specific weather data comprised only daily rainfall. Temperature, vapour pressure and wind speed were substituted with data for the same time period from the DWD

station Neuruppin, solar radiation was taken from the radiation station Potsdam (both stations are also situated in Brandenburg).

Table 3.28 shows the cumulative measured and simulated values of drainflow volumes and metolachlor losses via drainflow, while Table 3.29 shows the corresponding maximum daily values. In Fig. 3.22 and 3.23, measured and simulated time series of drainflow volumes and metolachlor drainage losses are presented.

During the whole study period (01.05.1992 – 31.03.1994), only very little drainflow occurred (13.6 mm; Table 3.28). In the first year, between the two applications of metolachlor, only 2.3 mm drainflow were recorded. The simulation underestimated the cumulative drainflow volume for the first study year by a factor of 3 and overpredicted it by a factor of 7 in the second year. The maximum daily drainflow rate was underestimated in both years by a factor of 11 in the first, and by a factor of 2.5 in the second year (Table 3.29). Fig. 3.22 shows that the starting point of drainflow events was matched relatively well, but subsequently drainage ceased only slowly in the simulation. The too "smooth" simulated drainage behaviour of this very sandy soil may be explained by the fact that MACRO simulates only macropore flow as a preferential flow mechanism, which usually does not play a major role in sandy, weakly structured soils. MACRO does not account for the preferential flow phenomenon of "finger flow", which commonly occurs in sandy soils. However, in view of the very small drainflow that occurred at this site, and the fact that all meteorological variables except rainfall had to be obtained from other, more distant meteorological stations, the simulation of drain outflow can be considered adequate.

Table 3.28: Measured vs. simulated cumulative drainflow volumes and metolachlor losses for Beetz

		measured values (acc.)			simulated results (acc.)			ratio predicted/ observed	
period	dose	drainflow[1)]	drainage loss[1)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
05/92 - 03/94	3.67	13.64	0.019	5.3E-04	78.10	0.024	6.4E-04	5.73	1.22
05/92 - 05/93	1.67	2.32	2.5E-05	1.5E-06	0.80	0	0	0.34	0
05/93 - 05/94	2.00	11.32	0.019	9.7E-04	77.30	0.024	1.2E-03	6.83	1.22

1) Total seasonal drainflow and IPU losses refer to time period between two applications.

Table 3.29: Measured vs. simulated maximum daily drainflow volumes and metolachlor losses for Beetz

		measured values (max.)			simulated results (max.)			ratio predicted/ observed	
period	dose	drainflow[1)]	drainage loss[1)]		drainflow[1)]	drainage loss[1)]		drainflow	drainage loss
	kg ha^{-1}	mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
05/92 - 03/94	3.67	2.78	9.5E-03	2.6E-04	1.10	1.0E-03	2.8E-05	0.39	0.11
05/92 - 05/93	1.67	0.52	2.5E-05	1.5E-06	0.046	0	0	0.089	0
05/93 - 05/94	2.00	2.78	9.5E-03	4.8E-04	1.10	1.0E-03	5.2E-05	0.39	0.11

[1)] Maximum daily drainflow rates and IPU losses refer to time period between two applications.

The observed cumulative drainage losses of metolachlor over the study period (01.05.1992 – 31.03.1994) were small with 5.3E-04 % of the applied amount (Table 3.28); the maximum daily loss equalled 2.6E-04 % of the total applied amount (Table 3.29). While in the first simulation year (i.e., between the first and second application of metolachlor) MACRO did not simulate any metolachlor drainage loss, metolachlor losses were moderately overpredicted by 22 % in the second year. However, neither maximum daily metolachlor losses (Table 3.29) nor timing of loss events (Fig. 3.23) were matched well by the simulation.

The relative measured losses of isoproturon (monitored from 01.11.1992 till 31.05.1993) totalled 2.6E-05 % of the applied amount. Simulated isoproturon losses in the monitoring period were practically zero; however, by the end of the simulation period (31.03.1994) they reached the same level as the observed losses.

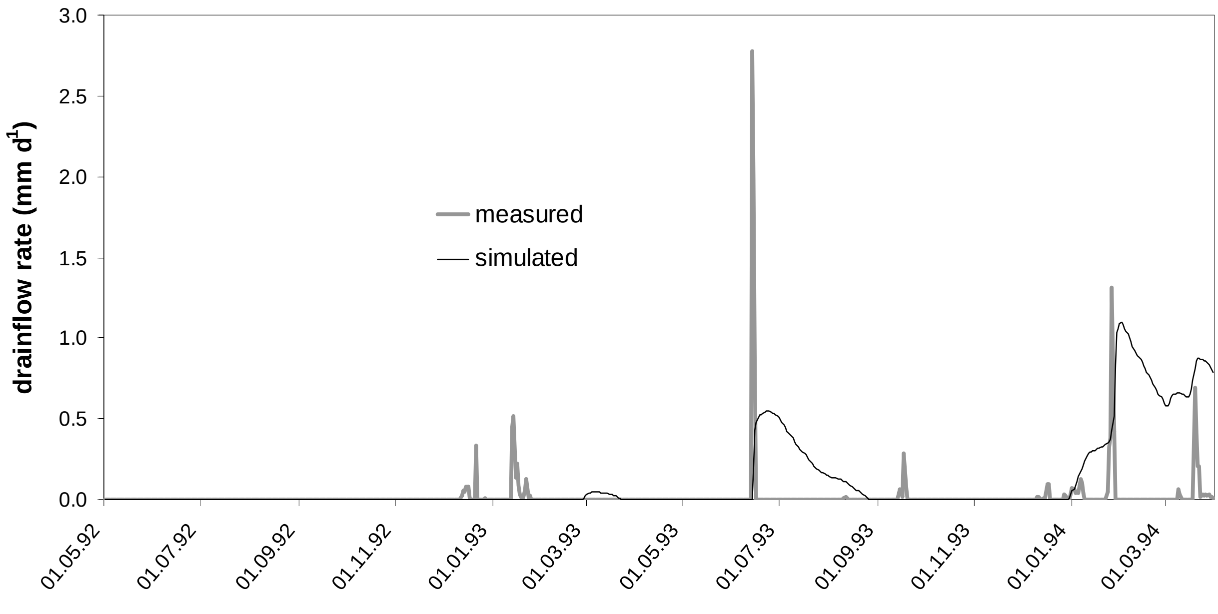

Fig. 3.22: Measured vs. simulated daily drainflow volumes for Beetz.

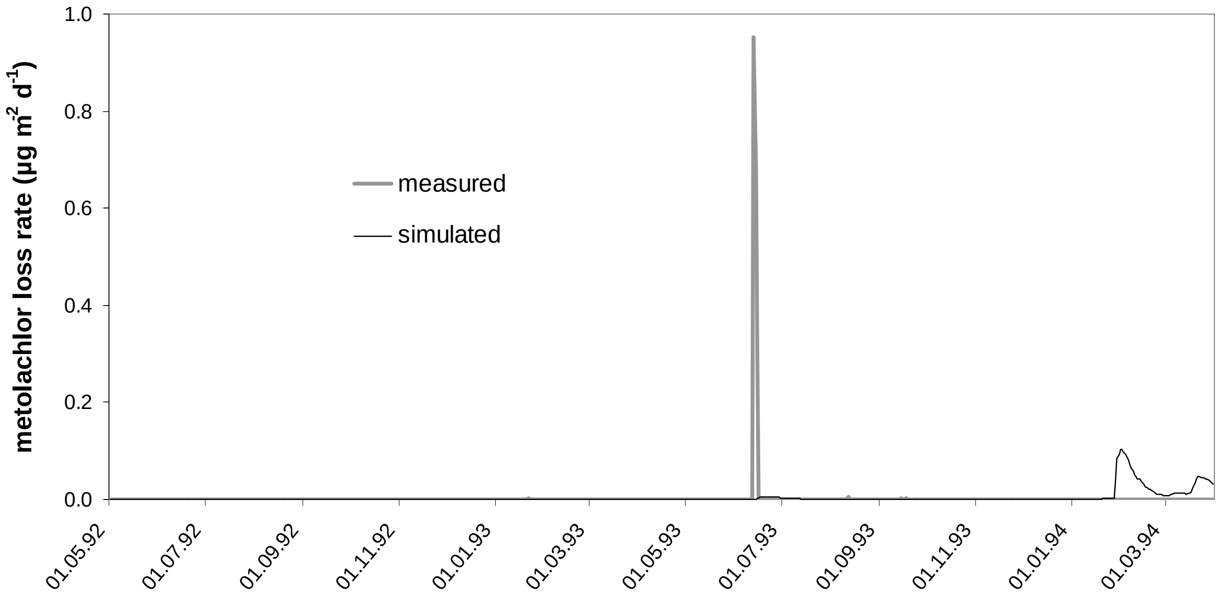

Fig. 3.23: Measured vs. simulated metolachlor losses via drainflow for Beetz.

It has to be emphasized that, apart from the meteorological input data, also the soil properties introduced considerable uncertainty into the simulation. Bulk density and soil structure, which are both crucial input for the MACRO_DB2 pedotransfer functions, had to be estimated. In addition, subsoil horizons deeper than 65 cm and their properties had to be obtained by expert judgement. As the measurements were only done at the outlet of one single drain, the drain spacing was very large and the area hydraulically influenced by the monitored drain was not known, also the measured drainflow and pesticide loss data are substantially uncertain when expressed in relation to an area.

Given the considerable uncertainty both in model input and in measured data, and the very little drainflow and small pesticide losses that occurred at this continental and very sandy site, it can be concluded that MACRO, using the pedotransfer functions of MACRO_DB2, was able to predict drainflow volumes and pesticide drainage losses acceptably for the Beetz dataset.

3.2.2 General Discussion and Conclusions

The following diagrams (Fig. 3.24-3.27) provide a summary of the quality of the simulations for the nine drainage test data sets, comparing measured and simulated values of total drainflow, maximum daily drainflow, total pesticide loss and maximum daily pesticide loss, respectively.

Fig. 3.24 shows that total drainflow was in most cases matched closely by the simulation. Deviations between simulated and measured total drainflow by more than the previously defined factor of 2 occurred only for the heavy clay Brimstone site (one season of 8) and the sandy, dry Beetz site (both seasons). The maximum daily drainflow (Fig. 3.25) was also acceptably predicted in most cases. Only for the Beetz and the Lanna site, maximum daily drainflow was underpredicted by more than 50 % (51 % for Lanna). Also the timing of drainflow events was mostly well simulated (except for the Beetz and in part for the Carpi site).

Total pesticide losses via drainflow (Fig. 3.26) were acceptably predicted, i.e. within a factor of 10 from the measurements, in 13 of 21 cases. Overpredictions beyond a factor of 10 occurred for 5 of 8 seasons of the Brimstone site. Underpredictions by more than a factor of 10 occurred for the Stagnic Luvisol at La Bouzule (2nd season) and for isoproturon and metolachlor at the Beetz site (1st season). Comparing measured and simulated maximum daily pesticide losses via drainflow (Fig. 3.27) yields a similar result: Predictions were acceptable in 11 of 17 cases (measured losses as daily rates were not available for La Bouzule). Overpredictions by more than a factor of 10 occurred for 4 seasons at Brimstone, and underpredictions by more than a factor of 10 again for isoproturon and metolachlor at Beetz (1st season). It has to be noted that in all of these cases where the acceptability limit regarding pesticide loss was exceeded, there was at least one additional source of uncertainty, either i) uncertainty in measured data (Beetz, Brimstone), ii) very small measured losses (Beetz, in part Brimstone), or iii) incomplete soil profile and meteorological data (Beetz, La Bouzule). Moreover, at La Bouzule and Brimstone there was possibly a sorption mechanism active not accounted for in MACRO 4.3. In general, MACRO tended to overestimate total and maximum daily pesticide losses to drains. However, it is impossible to determine whether this tendency was due to the model itself, the pedotransfer functions, the uncertainty in model input data or the uncertainty in the measured pesticide losses.

A model testing exercise was performed with a number of measured drainflow datasets, covering the whole range of soil textures from sand to heavy clay. The results of the exercise lead to the conclusion that the model MACRO 4.3b, using the pedotransfer functions of MACRO_DB2, is capable to simulate water flow and pesticide losses to drains adequately and without prior calibration, for a wide range of different soils. Thus, MACRO can be used with sufficient confidence for predictive modelling of pesticide losses from agricultural fields via drains to surface water.

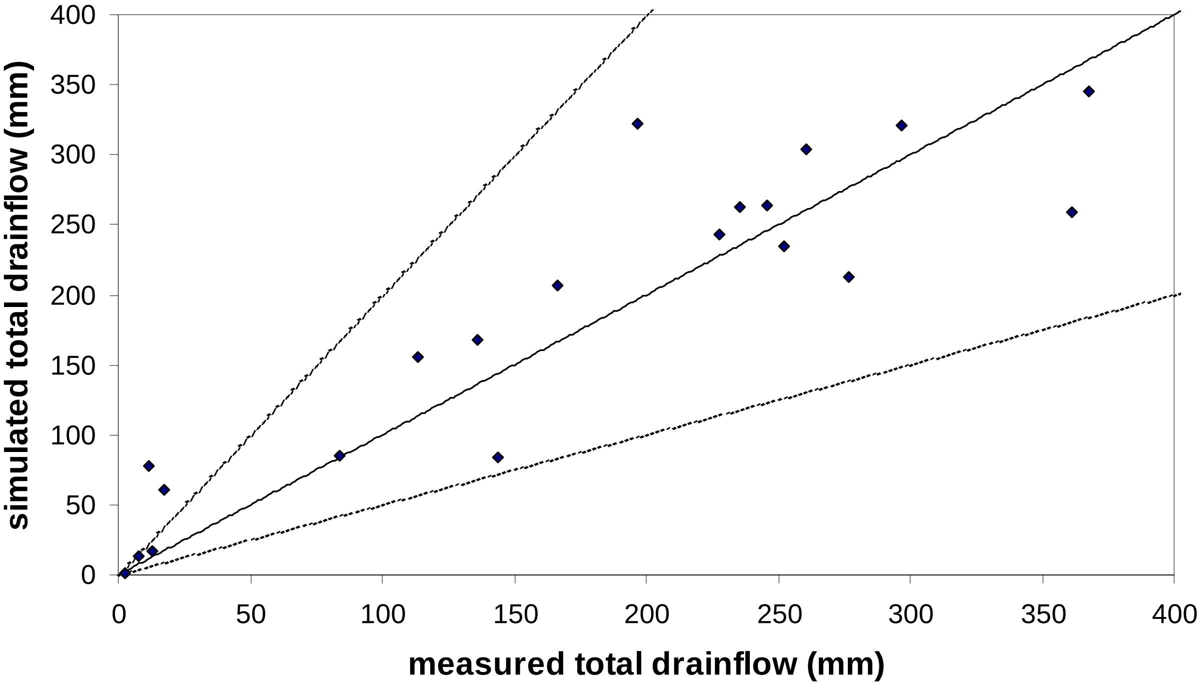

Fig. 3.24: Measured vs. simulated values of total drainflow over the study period for the nine test data sets. When a simulation comprised more than one season, measured and simulated values are compared for each season rather than for the whole simulation period. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 2.

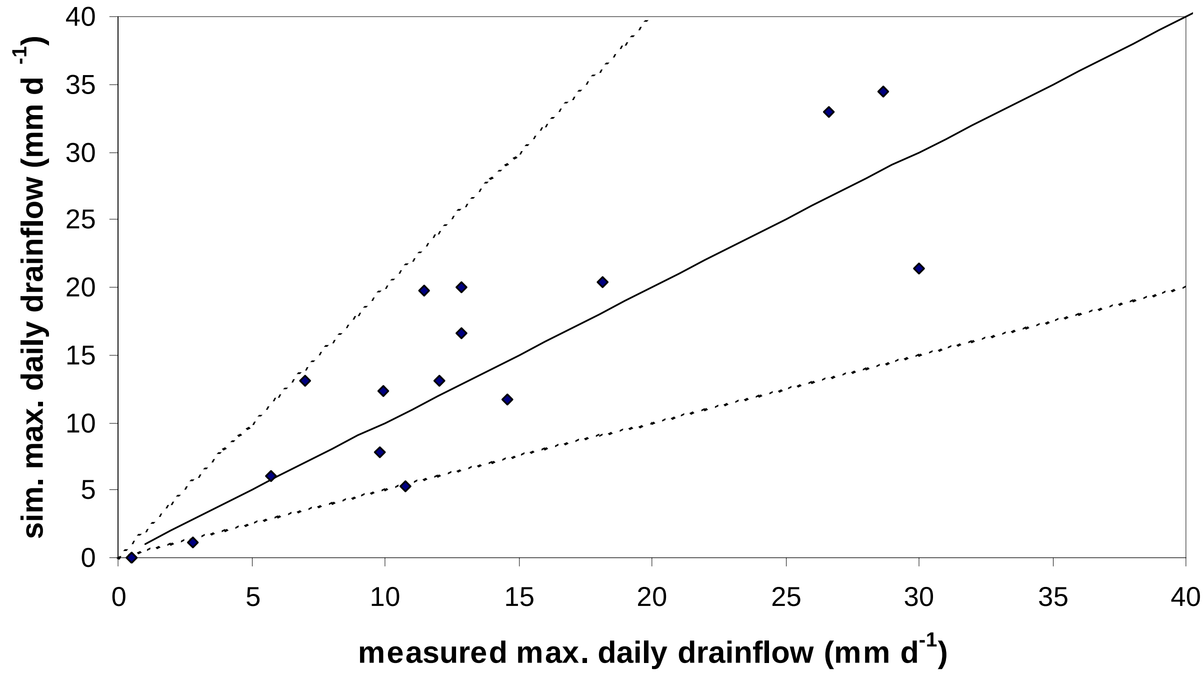

Fig. 3.25: Measured vs. simulated values of maximum daily drainflow over the study period for the nine test data sets. When a simulation comprised more than one season, measured and simulated values are compared for each season rather than for the whole simulation period. No daily measured data were available for the two La Bouzule datasets. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 2.

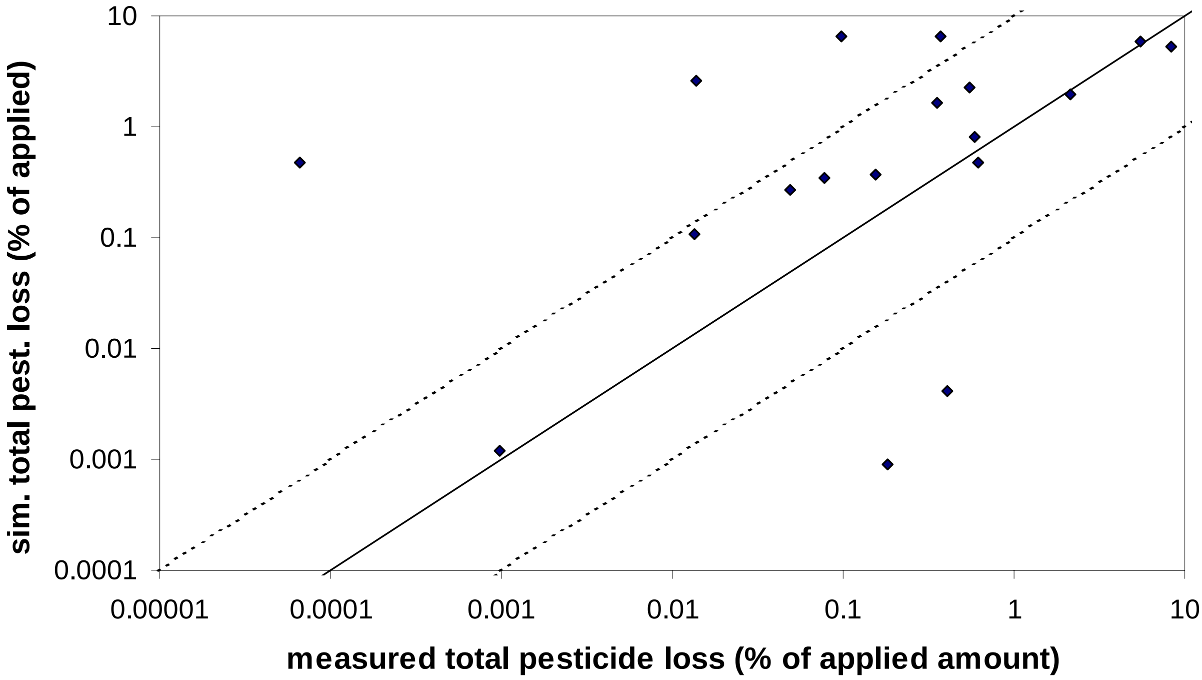

Fig. 3.26: Measured vs. simulated values of total pesticide loss (relative to the applied amount) over the study period for the nine test data sets. When a simulation comprised more than one season, measured and simulated values are compared for each season rather than for the whole simulation period. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data points (0; 4.5376) (IPU, Brimstone, spring 1998), (2.65E-05; 3.15E-21) (IPU, Beetz) and (1.49E-06; 0) (metolachlor, Beetz) cannot be shown due to the logarithmic plot.

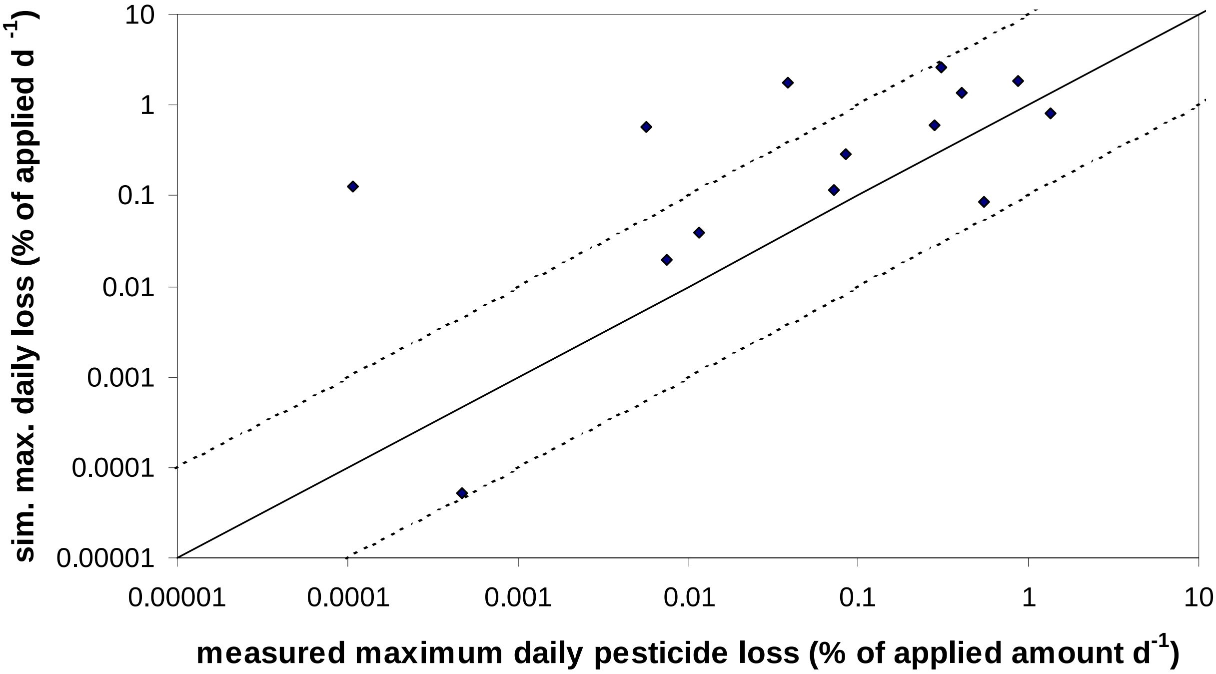

Fig. 3.27: Measured vs. simulated values of maximum daily pesticide loss (relative to the applied amount) over the study period for the nine test data sets. When a simulation comprised more than one season, measured and simulated values are compared for each season rather than for the whole simulation period. No daily measured data were available for the two La Bouzule datasets. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data points (0; 1.2298) (IPU, Brimstone, spring 1998), (2.46E-05; 3.14E-22) (IPU, Beetz) and (1.49E-06; 0) (metolachlor, Beetz) cannot be shown due to the logarithmic plot.

3.3 Predictive Modelling with MACRO

3.3.1 Setup and Parameterization of Basis Scenarios

For a meaningful prediction of diffuse-source pesticide inputs into surface waters a modelling approach is necessary that is differentiated with respect to

- soils
- climates
- crops
- compounds.

From the land-use-differentiated German soil map 1 : 1000000 (*nutzungsdifferenzierte BUEK 1000;* BGR, 1999; Hartwich et al., 1995), all main soil types (the dominant soil types of the soil mapping units) under agricultural use which were likely to be drained were identified and selected. Criteria were the presence of hydromorphic (gleyic or stagnic) genetic horizons and the probability of stagnant water in the profile during some time of the year. The 17 soil types selected were further condensed to 8 soil classes (Table 3.30; Table C.2, Appendix C). The geographical distribution of the soil classes is shown in Fig.3.28.

Table 3.30: Soil scenarios for predictive MACRO modelling

soil class	soil type[1)]	FAO soil type[2)]	represented BUEK soil units	texture of soil profile	reason for drainage[4)]
1	Kalkmarsch	Calcaric Fluvisol	3	silty-loamy	G
2	Gley-Vega	Fluvisol	8, 9, 11	loamy-silty	G
3	Paternia	Fluvisol	10, 13	sandy	G
4	podsol. Gley-Braunerde	Gleyic Cambisol	12, 17	sandy	G
5	Pseudogley	Stagnic Cambisol	22, 23, 24	sandy-loamy	S, G
6	Fahlerde-Pseudogley	Stagnic Podzoluvisol	28, 29	sandy-loamy	S
7	Pseudogley	Stagnic Cambisol + Stagnic Luvisol	43, 48	silty	S
8	Pelosol-Braunerde	Vertic Cambisol	51, 66	clayey	S

[1)] AG Boden (1994)
[2)] FAO (1988)
[4)] G = shallow groundwater; S = stagnant water in the profile

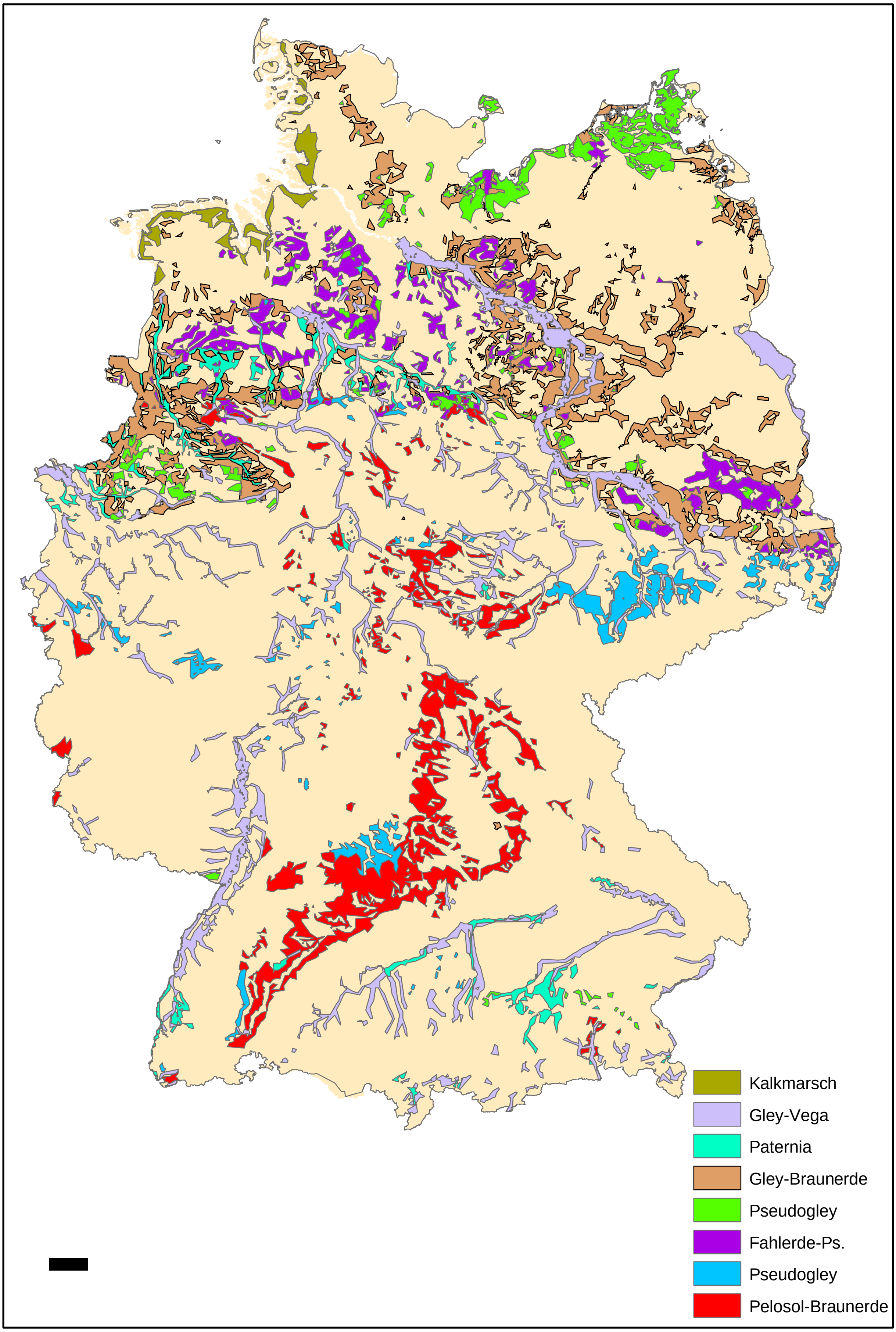

Fig. 3.28: Spatial distribution of the 8 soil classes for drainflow modelling, derived from the land-use-differentiated German 1 : 1 000 000 soil map (nutzungsdifferenzierte BUEK 1000; BGR, 1999). Note that the BUEK 1000 displays only dominant soil types. Hence, the map shown in this figure was only used for the purpose of visualization.

Fig. 3.28 reveals that the drainage-relevant soils are concentrated in river floodplains (soil mapping units 2 and 3), the North Sea coastal area (unit 1), lowland basins (unit 4) and certain types of geological substrate (units 5, 6, 7, 8). A large proportion of the agricultural land in Germany is therefore not relevant for tile drainage. However, it must be noted that the BUEK 1000 displays only dominant soil types. This implies that a soil situated in e.g. the red area of the map (class 8) does not necessarily belong to this soil class. On the other hand, soil class 8 can also occur outside the red area, although not as dominant soil. Therefore, the map shown in Fig. 3.28 was only used for the purpose of visualization. The assignment of a farmer's field to a soil class within the ISIP risk assessment module is exclusively done on the basis of user input (cf. chapter 6; Table C.1, Appendix C).

In accordance with the BUEK, all profiles were parameterized to a depth of 200 cm. Soil hydraulic parameters were obtained for each horizon using the pedotransfer functions of the tool MACRO_DB2. The pedotransfer function of MACRO_DB2 require particle size fractions of < 2 µm (clay), 2-50 µm (silt), and 50-2000 µm (sand). To obtain these values, first the mean textures (sand: 63-2000 µm, silt: 2-63 µm, clay: < 2 µm) of the German soil textural classes (e.g., weakly sandy loam Ls2) were calculated by taking the centres of gravity of the classes in the textural triangle (AG Boden, 1994). In a second step, the textures were converted from the German system to the USDA/FAO system (silt = 2-50 µm). The interpolation of the 2-50 µm fraction was kindly performed by Attila Nemes (USDA-ARS Hydrology & Remote Sensing Lab, Beltsville, MD, USA) and Henk Wösten (Alterra, NL) using the similarity procedure described in Nemes et al. (1999) on the HYPRES database (Wösten et al., 1998). Bulk density was obtained by taking the class mean of the bulk density class (AG Boden, 1994) of each horizon. Analogously, the OC content was obtained by dividing the class mean of the humosity (organic matter content) class (AG Boden, 1994) by 1.724. The structural description (size / strength / shape) according to FAO (1990), which is mainly used for estimating the effective diffusion pathlength (ASCALE) in MACRO, was obtained by expert judgement, thereby considering the soil type, the texture and bulk density of the respective horizon and its genetic horizon designation (e.g. Bt-Sd). Depth and spacing of the drains were estimated from the real drainage studies used for model testing (see section 3.2) and from the FOCUS surface water drainflow scenarios (FOCUS, 2001).

To account for the different climates in Germany, the 8 soil classes were subdivided into geographically and climatically different subunits. This resulted in 19 soil/climate subunits which represent the base scenarios for the MACRO simulations. For each subunit, the average yearly precipitation was determined by overlaying the soil polygons with a precipitation map

(DWD, 1996). From a set of agriculturally relevant weather stations in Germany (30-year meteorological data from 122 synoptic stations had been purchased from the German Weather Service (DWD); for Bavaria, data from several agro-meteorological stations were downloaded for free from the Bavarian ministry of agriculture; StmLF, 2003), the stations situated in the same region as the soil/climate subunits were checked for weather years with approximately the same measured precipitation as the median annual rainfall in each subunit (Table 3.31). Also in the FOCUS surface water scenarios, the selection of representative weather years for drainflow calculations has been made according to annual rainfall totals (FOCUS, 2001). The following weather data were used for the MACRO input files:

- daily precipitation (mm)
- max. daily temperature (°C)
- min. daily temperature (°C)
- global radiation (W m^{-2})
- water vapour pressure (kPa)
- wind speed (m s^{-1})

Since in Germany the network of stations where global radiation is measured (45 stations) is different from the net of meteorological stations, only in a few cases radiation data and climatic data exist for the same location. Thus, global radiation for the meteorological input files was taken from radiation stations nearby the meteorological stations. Table 3.31 shows the chosen meteorological stations and weather years for each scenario (soil/climate subunit).

Normally, a period of three years (the same weather year was repeated twice) was simulated, to ensure that the peak of pesticide drainage loss is captured by the simulation. However, for compounds which are both strongly sorbing and persistent, preliminary tests revealed that the maximum daily pesticide loss may be reached even later than in the first three years after application. Therefore, for compounds with a K_{oc} > 1000 L kg^{-1} and a DT_{50} > 60 d seven subsequent years were simulated. Pesticide application always took place in the first simulation year only.

Since in some regions meteorological stations were rare, and for some stations there were considerably less than 30 years of measurements, the choice of the weather year is a source of uncertainty as concerns the representativity of model predictions, because a "typical" weather year often does not exist among the available weather years.

Table 3.31: Weather/radiation stations and years chosen for the soil/climate subunits

soil/ climate subunit	target annual rainfall (median of subunit)	chosen weather station and year	annual rainfall chosen year	max. daily rainfall chosen year	T_{mean} chosen year	chosen global radiation station (same year)
	mm		mm	mm d^{-1}	°C	
1	780	Jever 1983	786.7	30.9	9.5	Bremen
2 NW	711	Kassel 1993	719.2	38.4	8.8	Kassel
2 OR	715	Karlsruhe 1983	711.9	31.3	11.0	Mannheim
2 S	812	Haar 1996	820.4	33.7	7.1	Haar
2 NO	547	Halle 2001	545	55.2	9.7	Halle
3 N	717	Diepholz 1980	703.4	25.2	8.5	Osnabrück
3 S	880	Haar 1993	883.1	37.6	8.5	Haar
4 O	564	Potsdam 1988	567.9	19.3	9.5	Potsdam
4 W	755	Osnabrück 1997	758.7	54.1	9.8	Osnabrück
5 NW	765	Bad Sassendf.-O. 1978	786.5	69.5	8.7	Osnabrück
5 S	946	Moosinning 1995	963.8	56.4	8.3	Moosinning
5 NO	612	Rostock 1995	627.3	60.5	9.3	Heiligendamm-Rostock
5 SB	577	Wittenberg 1993	590.9	35.6	9.1	Halle
6 W	750	Soltau 1973	757.7	27.2	8.6	Hamburg-Sasel
6 O	606	Doberlug-Kirchhain 2001	619.1	26.2	9.4	Dresden
7 S	855	Oehringen 1980	871.1	23.0	8.5	Stuttgart
7 N	687	Chemnitz 1999	689.2	39.7	9.1	Chemnitz
8 S	770	Mittelstetten 1995	774.2 [1)]	31.8 [1)]	9.0	Nürnberg
8 N	714	Leinefelde 1988	733.2	40.3	8.4	Kassel

[1)] The original annual rainfall of 823.6 mm was scaled down with a factor of 0.94 to 774.2 mm

3.3.2 Crop Properties

The parameters of the crops considered (maize, sugar beets, winter cereals, spring cereals, oilseed rape (winter), oilseed rape (spring), potatoes), e.g. crop height and rooting depth, were set according to the FOCUS surface water scenarios (FOCUS, 2001) or estimated from them. The crop calendar (emergence, harvest, etc.) was obtained by FOCUS scenarios, literature search, and expert judgement. The crop calendars for each crop were too variable between the different data sources to allow a regionally differentiated setting of crop dates. Hence, for each crop, the crop dates were set equal for all scenarios (Table 3.32), which is certainly an oversimplification.

Table 3.32: Crop dates for predictive MACRO modelling

crop type	emergence date *IDSTART*	intermediate crop development *ZDATEMIN*	max. leaf area development *IDMAX*	harvest date *IHARV*
	dd.mm.			
winter cereals	10.10.	01.04.	07.07.	15.08.
spring cereals	01.04.	02.04.	12.06.	23.08.
maize	05.05.	06.05.	14.08.	20.09.
oilseed rape, winter	02.09.	01.03.	01.06.	28.07.
oilseed rape, spring	15.04.	16.04.	16.06.	28.08.
potatoes	16.05.	17.05.	05.08.	19.09.
sugar beet	30.04.	01.05.	27.07.	22.10.

[1)] removal of residues and tillage

The critical tension for root water uptake *WATEN* (where the plant starts reducing transpiration due to increasing drought stress) was calculated with the same formula as it is done for the FOCUS surface water scenarios. Also, the crop interception fraction *ZFINT* was calculated with the same formula as for $FOCUS_{sw}$:

$$ZFINT = ZFINTMAX * LAI/LAIMAX \qquad \text{(eq. 3.22)}$$

where

ZFINTMAX maximum interception fraction (dimensionless)

LAI current (total) leaf area index ($m^2\ m^{-2}$)

LAIMAX maximum leaf area index of the crop ($m^2\ m^{-2}$)

It should be noted that within MACRO, the total *LAI* does not decrease between maturity and harvest, in contrast to the green leaf area.

3.3.3 Pesticide Use Scenarios

From the database of registered uses in Germany (BBA, 2002), for each registered pesticide its uses in winter cereals, spring cereals, maize, sugar beets, oilseed rape (winter), oilseed rape (spring), and potatoes were selected. Vegetables and special cultures (hops, wine, orchards) were not considered in this first step. For each particular use (i.e. combination of compound, target crop and application season), the highest registered dose was chosen for the simulations. Since MACRO would not have calculated significant drainage losses for other pesticides anyway, only pesticides with a K_{oc} < 20000 L kg^{-1} and a $DT_{50} \geq 1$ d were simulated.

The resulting 229 uses (pesticide/crop/application combinations; comprising 109 pesticides) were run for every base scenario, which gives 229 * 19 = 4351 simulations in total. Pesticide application windows were obtained from the NEPTUN 2000 database (Roßberg et al., 2002), which was kindly provided by the Federal Biological Agency (Biologische Bundesanstalt, BBA). For each agriculturally relevant soil/climate region (SCR; Kaule and Schulzke, 1998) within NEPTUN 2000, the calendary month with the highest total applied amount of the respective pesticide for the respective use was selected. Subsequently, since the soil/climate subunits in this study mostly contained shares of several SCR, the final application month for each subunit was obtained by averaging these maximum-dose months of the SCR contained in or overlapping with the soil/climate subunits.

Pesticide application days were finally obtained with the Pesticide Application Timer (PAT) in MACRO_DB2. The PAT is also used within the FOCUS surface water scenarios. In the following there is a brief description of the rules implemented in the PAT (FOCUS, 2001):

PAT automatically determines pesticide application dates which satisfy pre-set criteria, based on the daily rainfall file for the simulation period, together with the following user-defined information:

- An application "window" (defined by a first possible day of application and a last possible day of application; here: one calendary month).
- The number of applications (up to a maximum of five; here: one).
- The minimum interval between applications (for multiple applications).

Initially, the pre-set criteria state that there should be at least 10 mm of rainfall in the ten days following application and at the same time, there should be no more than 2 mm of rain each day in a five day period, starting two days before application, extending to two days following the day of application. PAT then steps through the "application window" to find the first day which satisfies these requirements. For multiple applications, the procedure is carried out for each application, respecting the minimum interval specified between applications.

Depending on the rainfall pattern in the application window defined by the user, it is quite possible that no application day exists which satisfies the two basic criteria defined above. In this case, the criteria are relaxed and the procedure repeated until a solution is found, as follows:

- The five-day period around the day of application is reduced first to a three day period (one day either side of the application day), and then if there is still no solution, to just the day of application. Relaxing these criteria makes the resulting leaching estimates potentially more conservative.
- If PAT still fails to find a solution, then the second criterion is relaxed, such that 10 mm of rain is required to fall in a 15-day period following application, rather than 10 days. Relaxing these criteria makes the leaching estimates less conservative.
- If a solution is still not forthcoming (for example, for dry periods, such that the total rainfall during the entire application window is less than 10 mm), then the minimum rainfall requirement is reduced 1 mm at a time, to zero.
- If PAT still fails to find a solution (this will be the case if the application window is very wet, with more than 2 mm of rain every day), then the amount of rain allowed on the day of application is increased 1 mm at a time, until a solution is found.

Following this procedure, the program always finds a solution.

3.3.4 Pesticide Properties

Sorption and degradation parameters, and solubility in water were obtained from UBA (1997), UBA (2002), EU review reports (European Commission, 2004a; European Commission, 2004b), and several online resources, mainly ARS database (ARS, 2004) and WIN-PST database (NRCS, 2002). A list of the substance properties as used for the simulations is given in Appendix A. Where two or more values representing single measurements were given, K_{oc} values were averaged geometrically, and Freundlich exponents m arithmetically. Under the assumption that K_{oc} is log-normally and m is normally distributed, this corresponds to a median Freundlich isotherm. Analogously, where more than two values from single measurements were given, DT_{50} values were averaged geometrically. The geometric mean of DT_{50} values has the advantage that it makes no difference whether degradation rates or half-lives are averaged. Geometrically averaged half-lives are slightly less conservative (smaller) than arithmetically averaged ones, whereas the geometric mean of the K_{oc} is slightly more conservative (smaller) than the arithmetic mean. Therefore, the obtained DT_{50}/K_{oc} combinations are neither too lax nor unrealistically conservative. Since MACRO is not able to calculate volatilization, field half-lives were preferredly used if present, because they already account for this dissipation path. Nevertheless, temperature and moisture dependence of the dissipation half-lives were not switched off because the simulations also included winter periods, where it would not have been appropriate to use the same half-life as in spring or summer. It should be noted that MACRO uses the water content at saturated micropores (XMPOR; usually at around 10 cm tension) as reference moisture for degradation, whereas usually the water content at pF 2 (i.e., 100 cm tension) is used. This makes the calculations slightly more conservative. For temperature dependence of degradation, the reference temperature was always set to 20 °C; the depth dependence of degradation was set according to FOCUS (0-30 cm depth: full degradation rate, 30-60 cm depth: degradation rate reduced to 50 % of topsoil, 60-100 cm: degradation rate reduced to 30 % of topsoil, below 100 cm depth: no degradation).

Since metabolites cannot be simulated in MACRO within the same model run, and since not all active substances have environmentally relevant metabolites, metabolites were not simulated. However, there were three special cases where the applied pesticide rapidly degrades in the environment to a metabolite which is also a registered active substance (iodosulfuron → metsulfuron-methyl, benomyl → carbendazim, thiophanate-methyl → carbendazim). In these cases, the application rate was corrected by the ratio of molar masses of metabolite and parent and the metabolite was applied (assuming a formation fraction of 100 %), and the sorption and degradation properties of the metabolite was used for the simulation.

3.3.5 Running MACRO with SENSAN

MACRO was run in batch mode by coupling it with the tool SENSAN, a utility for sensitivity analysis included in the PEST package (Doherty, 2002). The flow chart of the MACRO-SENSAN coupling is given in Appendix D, the SENSAN template files (.tpl) for all 19 soil/climate scenarios in Appendix E.

For the whole simulation period, for each simulation year, and for each calendary month, the maximum value of the daily drainage loss rate (*DSOLTOSS*) was extracted from the SENSAN output files together with the corresponding date and drain flow rate (*SSEEP*). Additionally, the cumulative drainflow (*TSEEP*) and pesticide loss via drainage (*DRAINLOS*) were recorded.

3.3.6 Results and Discussion

The following Tables 3.33-3.36 show rankings of pesticide drainage losses simulated with MACRO. The ranking was always performed according to the median value of the target variable. In Tables 3.33 and 3.34, the 19 soil/climate scenarios are ranked according to relative total 3-year pesticide losses and relative maximum daily pesticide losses, respectively, over the 229 simulated uses. Inversely, Tables 3.35 and 3.36 show the top 20 rankings according to relative total 3-year pesticide losses and relative maximum daily losses over the 19 soil/climate scenarios. In addition, Tables 3.33-3.36 contain mean and median absolute pesticide losses as well as mean relative losses.

Table 3.33 reveals that cumulative pesticide losses over three years simulation period were highest for the two heaviest and most structured soils, the *Pelosol-Braunerde* (soil class 8) and the *Gley-Vega* (soil class 2; Table 3.30, section 3.3.1). In contrast, cumulative pesticide losses were lowest for the two sandiest and least structured soils, the *Paternia* (soil class 3) and the *podsol. Gley-Braunerde* (soil class 4). For the dry climate scenarios from East Germany, losses were generally lower than for the moister West German scenarios (cf. Table 3.31). In Table 3.34, the same tendency can be observed for the maximum daily drainage losses; the ranking is very similar to Table 3.33. The high losses for the scenario 2 OR (*Gley-Vega*, weather station Karlsruhe), especially in comparison with the equally moist 2 NW and the even moister 2 S scenario for the same soil, can be explained by the occurrence of two periods with very large rainfalls within a few days (78 mm in 3 days in April, 75 mm in 3 days in May). The maximum daily rainfall over the simulation period (Table 3.31), however, turned out to give no indication on predicted peak or total pesticide losses. From the large differences between median and mean losses it can be seen that the distributions of total and maximum daily losses over the 229 uses are strongly skewed to the right. This implies that for a lot of uses, very little or no pesticide losses via drainflow were predicted, while for a few uses high losses were simulated.

Table 3.35 reveals that cumulative losses over 3 years were highest for weakly sorbing compounds with moderate degradability (cf. Appendix A), e.g. the herbicide amidosulfuron with a K_{oc} of 11 L kg^{-1}, a Freundlich exponent m of 1 and a DT_{50} of 21 days. Also a few compounds with moderately low sorption and relatively high persistence (e.g. fluroxypyr acid with K_{oc} = 66 L kg^{-1}, m = 0.92, DT_{50} = 38 d) occur in the top 20 ranking. Of course, the highest losses would be predicted for compounds which are both weakly sorbing and persistent; however, such compounds would not pass the registration process. Between different uses of the same pesticide (dicamba or amidosulfuron), losses were larger after autumn application than after spring application. Table 3.36 yields essentially the same picture for the maximum daily losses over the simulation period. The considerable differences between median and mean maximum daily losses again point to the differences in losses between the 19 soil/climate scenarios (cf. Table 3.34).

Fig. 3.29 and 3.30 show cumulative drainage losses over 3 years of two example compounds, the herbicides dichlorprop-P and terbutryn, after autumn application in winter cereals, for all 19 soil/climate scenarios. In analogy, Fig. 3.31 and 3.32 show the corresponding maximum daily drainage losses for the two compounds. Relative cumulative losses of the weakly sorbing dichlorprop-P (K_{oc} = 21 L kg^{-1}, m = 1, DT_{50} = 19 d) in autumn on winter cereals ranged from 0.026 to 34.9 % (mean = 4.9 %) of the applied amount (Fig. 3.29), which corresponds to absolute losses of 4.3-523 g ha^{-1} (mean = 73 g ha^{-1}). Maximum losses of dichlorprop-P ranged from 0.0026 to 9.6 % (mean = 0.75 %) of the applied amount (Fig. 3.31). For the relatively strongly sorbing and persistent compound terbutryn (K_{oc} = 775 L kg^{-1}, m = 0.76, DT_{50} = 52 d) and autumn application on winter cereals, cumulative loss of 0-0.63 % (mean = 0.13 %) of the applied amount (Fig. 3.30) and maximum daily losses of 0-0.25 % (mean = 0.037 %; Fig. 3.32) were calculated. Again, these figures demonstrate large differences in losses between the 19 scenarios, both between different soils and between different climates for one soil.

It can be summarized that the predictive MACRO simulations yielded large differences in pesticide drainage losses between different compounds, different soils and different weather scenarios. Both total and peak losses can under certain circumstances reach substantial fractions of the applied dose, which suggests that the importance of drainflow as an input pathway of pesticides into surface waters might have been underestimated in the German pesticide registration process so far.

Table 3.33: Ranking of soil/climate scenarios according to *median cumulative* 3-year *drainage* losses (*relative* to applied amount, over all 229 uses**)**

rank		scenario	soil type	soil type	**rel. acc. drainage loss**		**abs. acc. drainage loss**	
rel. loss	abs. loss	name	(AG Boden, 1994)	(FAO, 1988)	median	mean	median	mean
					% of applied		$g\ ha^{-1}$	
1	1	8S	Pelosol-Braunerde	Vertic Cambisol	0.832	4.949	1.217	21.21
2	2	2OR	Gley-Vega	Fluvisol	0.564	1.996	0.664	27.99
3	5	5NW	Pseudogley	Stagnic Cambisol	0.313	1.077	0.284	14.80
4	4	5S	Pseudogley	Stagnic Cambisol	0.305	1.478	0.349	11.45
5	3	7S	Pseudogley	Stagnic Cambisol + Stagnic Luvisol	0.302	0.992	0.485	4.120
6	6	2S	Gley-Vega	Fluvisol	0.139	0.756	0.148	6.705
7	7	8N	Pelosol-Braunerde	Vertic Cambisol	0.079	1.866	0.115	7.674
8	8	2NW	Gley-Vega	Fluvisol	0.011	0.312	0.033	1.271
9	9	7N	Pseudogley	Stagnic Cambisol + Stagnic Luvisol	8.8E-03	0.205	0.012	1.014
10	10	2NO	Gley-Vega	Fluvisol	5.5E-04	0.027	1.4E-03	0.106
11	11	1	Kalkmarsch	Calcaric Fluvisol	2.3E-04	0.180	2.5E-04	0.658
12	12	6W	Fahlerde-Pseudogley	Stagnic Podzoluvisol	2.8E-06	0.509	3.5E-06	1.885
13	13	5SB	Pseudogley	Stagnic Cambisol	5.6E-13	0.010	3.5E-12	0.026
14	14	3S	Paternia	Fluvisol	7.9E-14	0.200	3.3E-13	0.629
15	15	5NO	Pseudogley	Stagnic Cambisol	2.1E-17	3.7E-03	1.3E-16	9.2E-03
16	16	4W	podsol. Gley-Braunerde	Gleyic Cambisol	6.6E-22	0.136	2.0E-21	0.397
17	17	6O	Fahlerde-Pseudogley	Stagnic Podzoluvisol	4.3E-31	0.011	4.1E-30	0.025
18	18	3N	Paternia	Fluvisol	0	0.033	0	0.081
19	19	4O	podsol. Gley-Braunerde	Gleyic Cambisol	0	0.017	0	0.035

Table 3.34: Ranking of soil/climate scenarios according to *median maximum daily drainage* losses (*relative* to applied amount, over all 229 uses)

rank relative	rank absolute	scenario name	soil type (AG Boden, 1994)	soil type (FAO, 1988)	rel. max. daily drainage loss median	rel. max. daily drainage loss mean	abs. max. daily drainage loss median	abs. max. daily drainage loss mean
					% of applied d^{-1}		g ha-1 d^{-1}	
1	1	2OR	Gley-Vega	Fluvisol	0.190	0.896	0.215	13.14
2	2	8S	Pelosol-Braunerde	Vertic Cambisol	0.158	1.382	0.189	6.186
3	4	5NW	Pseudogley	Stagnic Cambisol	0.107	0.351	0.086	5.337
4	3	7S	Pseudogley	Stagnic Cambisol + Stagnic Luvisol	0.061	0.135	0.118	0.597
5	5	5S	Pseudogley	Stagnic Cambisol	0.048	0.169	0.051	1.579
6	6	2S	Gley-Vega	Fluvisol	0.024	0.112	0.024	1.861
7	7	8N	Pelosol-Braunerde	Vertic Cambisol	0.015	0.423	0.021	1.892
8	8	2NW	Gley-Vega	Fluvisol	2.8E-03	0.026	6.0E-03	0.111
9	9	7N	Pseudogley	Stagnic Cambisol + Stagnic Luvisol	1.1E-03	0.038	1.6E-03	0.214
10	10	2NO	Gley-Vega	Fluvisol	4.9E-04	0.012	9.3E-04	0.048
11	11	1	Kalkmarsch	Calcaric Fluvisol	1.5E-05	4.5E-03	2.0E-05	0.016
12	12	6W	Fahlerde-Pseudogley	Stagnic Podzoluvisol	4.5E-07	0.025	8.8E-07	0.075
13	13	5SB	Pseudogley	Stagnic Cambisol	7.2E-14	6.2E-04	5.7E-13	1.6E-03
14	14	3S	Paternia	Fluvisol	5.6E-15	3.4E-03	4.8E-14	9.6E-03
15	15	5NO	Pseudogley	Stagnic Cambisol	4.6E-18	2.2E-04	1.4E-17	6.1E-04
16	16	4W	podsol. Gley-Braunerde	Gleyic Cambisol	2.9E-22	3.8E-03	7.5E-22	1.3E-02
17	17	6O	Fahlerde-Pseudogley	Stagnic Podzoluvisol	1.3E-29	3.6E-04	3.2E-29	9.3E-04
18	18	3N	Paternia	Fluvisol	0	1.4E-03	0	3.9E-03
19	19	4O	podsol. Gley-Braunerde	Gleyic Cambisol	0	5.1E-04	0	1.1E-03

Table 3.35: Ranking of uses according to the median *cumulative* 3-year *drainage* losses (*relative* to applied amount, over all 19 soil/climate scenarios)

rank				application		**rel. acc. drainage loss**		**abs. acc. drainage loss**	
rel. loss	abs. loss	compound	crop	season	dose[1]	median	mean	median	mean
					g ha^{-1}	% of applied		g ha^{-1}	
1	14	amidosulfuron	winter cereals	autumn	30	4.593	7.606	1.378	2.282
2	4	dicamba	winter cereals	autumn	120	4.123	6.823	4.947	8.188
3	2	mecoprop-P	winter cereals	autumn	1200	1.630	4.720	19.56	56.63
4	1	dichlorprop-P	winter cereals	autumn	1500	1.592	4.877	23.88	73.16
5	32	azadirachtin (neem)[2]	potatoes	summer	25	1.523	2.477	0.381	0.619
6	37	amidosulfuron	winter cereals	spring	30	0.906	2.296	0.272	0.689
7	13	fluroxypyr[3]	winter cereals	autumn	180	0.895	3.582	1.610	6.448
8	59	metsulfuron	winter cereals	autumn	7.71	0.862	3.991	0.066	0.308
9	80	iodosulfuron[4]	winter cereals	autumn	1.73 [4]	0.783	3.694	0.014	0.064
10	17	clopyralid	maize	spring	120	0.760	2.191	0.912	2.629
11	62	triasulfuron	winter cereals	autumn	6.0	0.755	3.825	0.045	0.230
12	50	sulfosulfuron	winter cereals	autumn	20	0.738	3.699	0.148	0.740
13	11	dicamba	maize	spring	360	0.679	2.114	2.446	7.610
14	20	clopyralid	oilseed rape, winter	spring	120	0.592	1.784	0.711	2.141
15	21	clopyralid	sugar beet	spring	120	0.581	2.457	0.697	2.948
16	47	amidosulfuron	spring cereals	spring	30	0.538	1.930	0.161	0.579
17	9	metribuzine	potatoes	spring	700	0.516	1.802	3.613	12.62
18	3	bentazone	winter cereals	autumn	999	0.499	3.145	4.988	31.42
19	29	haloxyfop-R	oilseed rape, winter	autumn	104	0.461	3.069	0.479	3.192
20	28	dicamba	winter cereals	spring	120	0.405	0.734	0.486	0.881

[1] a.i. equivalents without ester groups or counterions
[2] available physico-chemical properties doubtful (cf. Appendix A)
[3] Due to rapid breakdown of the fluroxypyr-meptyl ester, fluroxypyr (acid) was simulated.
[4] applied and simulated as its primary metabolite metsulfuron-methyl

Table 3.36: Ranking of uses according to the median *maximum daily drainage* losses (*relative* to applied amount, over all 19 soil/climate scenarios**)**

rank				application		**rel. max. daily drainage loss**		**abs. max. daily drainage loss**	
rel. loss	abs. loss	compound	crop	season	dose[1]	median	mean	median	mean
					$g\ ha^{-1}$	% of applied d^{-1}		$g\ ha^{-1}\ d^{-1}$	
1	5	dicamba	winter cereals	autumn	120	0.187	0.784	0.224	0.940
2	25	amidosulfuron	winter cereals	autumn	30	0.153	0.843	0.046	0.253
3	1	dichlorprop-P	winter cereals	autumn	1500	0.076	0.745	1.144	11.18
4	10	fluroxypyr[2]	winter cereals	autumn	180	0.071	0.600	0.128	1.080
5	92	iodosulfuron[3]	winter cereals	autumn	1.73	0.068	0.726	0.001	0.013
6	2	mecoprop-P	winter cereals	autumn	1200	0.068	0.667	0.814	8.007
7	58	metsulfuron	winter cereals	autumn	7.71	0.063	0.759	0.005	0.058
8	49	sulfosulfuron	winter cereals	autumn	20	0.058	0.732	0.012	0.146
9	51	azadirachtin (neem)[4]	potatoes	summer	25	0.044	0.375	0.011	0.094
10	26	haloxyfop-R	oilseed rape, winter	autumn	104	0.042	0.464	0.044	0.483
11	27	haloxyfop-R	potatoes	spring	104	0.040	0.631	0.042	0.656
12	75	triasulfuron	winter cereals	autumn	6.0	0.039	0.632	0.002	0.038
13	24	clopyralid	maize	spring	120	0.039	0.255	0.047	0.306
14	3	MCPA	winter cereals	autumn	1360	0.037	0.538	0.507	7.318
15	4	bentazone	winter cereals	autumn	999	0.037	0.667	0.370	6.667
16	20	metalaxyl	potatoes	summer	200	0.034	0.241	0.068	0.482
17	18	flurtamone	winter cereals	autumn	250	0.030	0.714	0.074	1.786
18	52	amidosulfuron	spring cereals	spring	30	0.028	0.347	0.008	0.104
19	55	amidosulfuron	winter cereals	spring	30	0.027	0.825	0.008	0.248
20	34	clopyralid	sugar beet	spring	120	0.026	0.473	0.032	0.568

[1] a.i. equivalents without ester groups or counterions

[2] Due to rapid breakdown of the fluroxypyr-meptyl ester, fluroxypyr (acid) was simulated.

[3] applied and simulated as its primary metabolite metsulfuron-methyl

[4] available physico-chemical properties doubtful (cf. Appendix A)

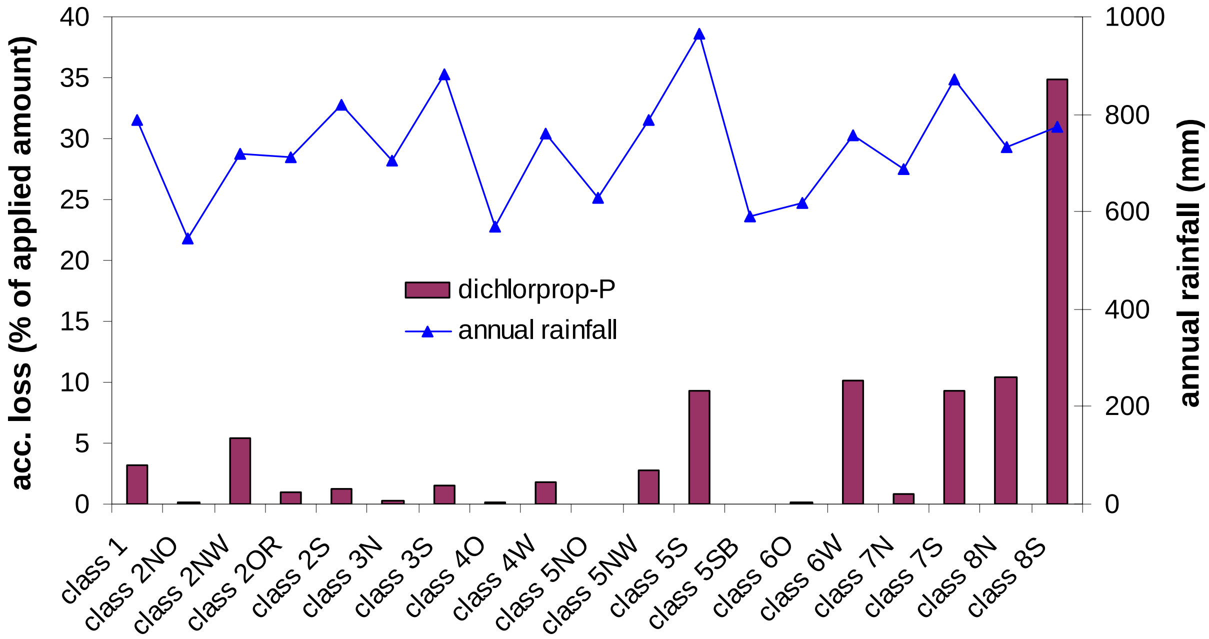

Fig. 3.29: Predicted total 3-year drainflow losses of dichlorprop-P in winter cereals (autumn application) for all 19 soil/climate scenarios.

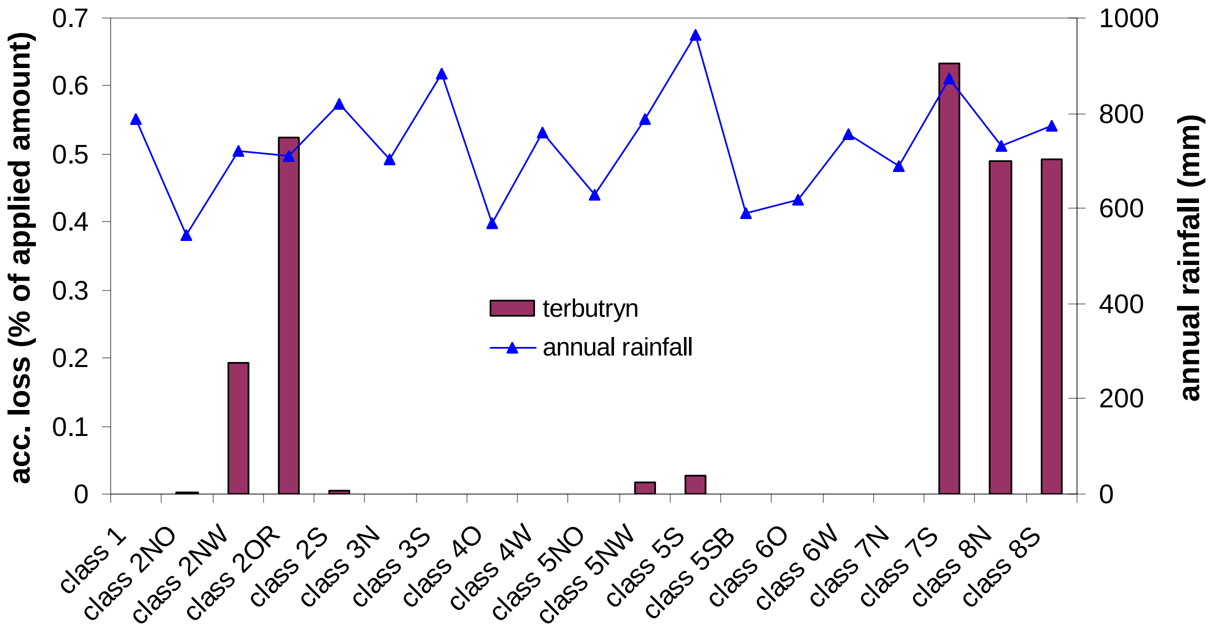

Fig. 3.30: Predicted total 3-year drainflow losses of terbutryn in winter cereals (autumn application) for all 19 soil/climate scenarios.

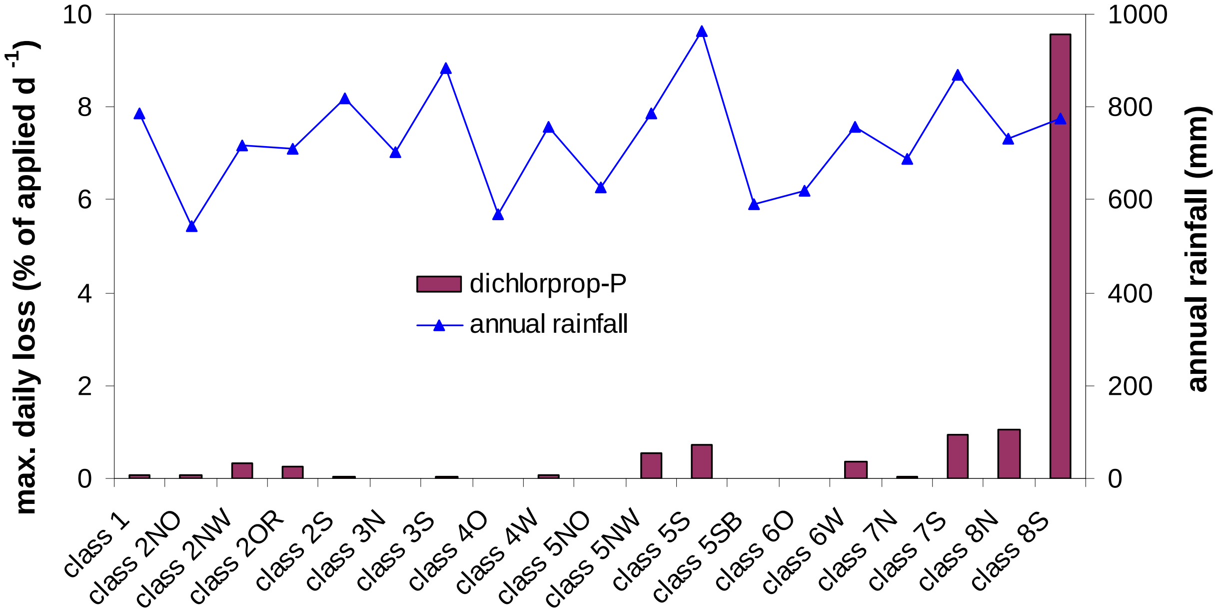

Fig. 3.31: Predicted maximum daily drainflow losses of dichlorprop-P in winter cereals (autumn application) for all 19 soil/climate scenarios.

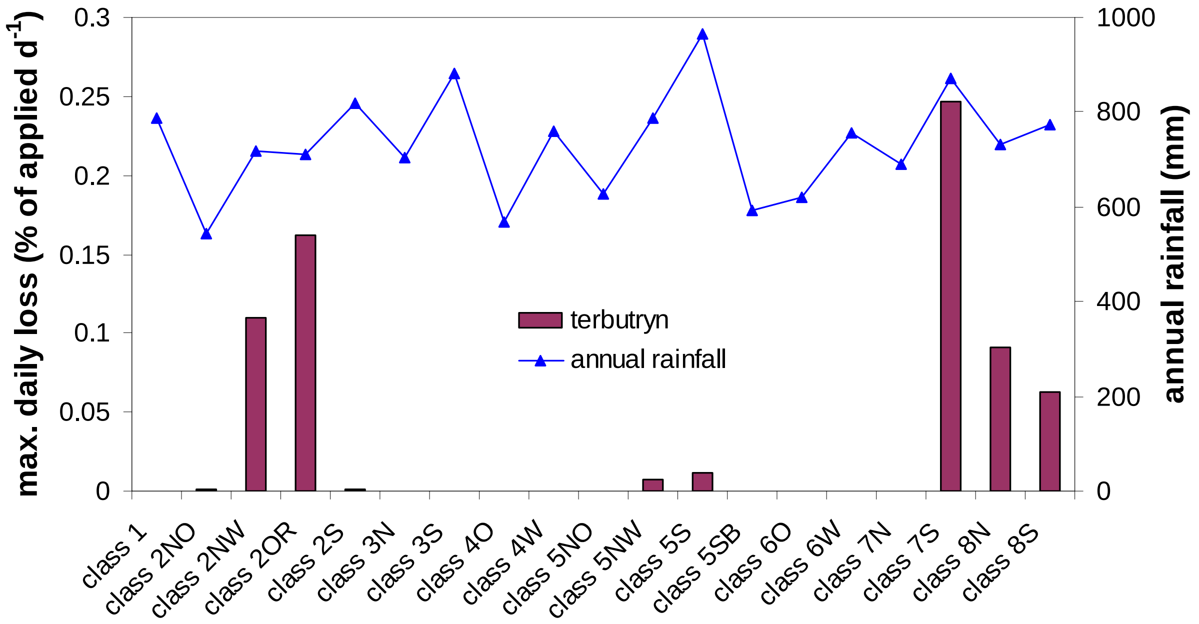

Fig. 3.32: Predicted maximum daily drainflow losses of terbutryn in winter cereals (autumn application) for all 19 soil/climate scenarios.

3.3.7 Uncertainty Analysis

There is always the question how much confidence can be put into the results of predictive simulations. In the case of predictive drainage simulations, the following questions emerge:

1. How uncertain are the pesticide losses predicted with MACRO?
2. What is the relative importance of the various sources of uncertainty:
    - annual variability of the weather (e.g., occurrence of periods with large rainfalls)?
    - uncertainty of the compound properties (K_{oc}, Freundlich exponent, DT_{50})?
    - choice of the application day?
    - parameterization of soil scenarios (soil hydraulic properties, OC content etc.)?

Due to the long computation time of MACRO runs, it was not possible in this study to conduct a Monte Carlo analysis in order to assess the sensitivity of MACRO input parameters (especially substance properties and soil hydraulic parameters). However, as the sensitivity of MACRO input parameters with regard to pesticide leaching is roughly known (Dubus and Brown, 2002), one can make inferences on the sensitivity of the input parameters with regard to drainflow losses. For pesticide leaching, which is a relatively continuous process, the sorption and degradation properties are the most sensitive input variables for MACRO (Dubus and Brown, 2002). They are followed by the soil hydraulic properties, which become more important with increasing soil structure. For pesticide losses via drainage, which is a more event-driven process, the application date and the rainfall distribution, especially shortly after application, will become more important, whereas the substance properties will lose some of their sensitivity. Therefore, and because the amount and quality of sorption and degradation data was different for each compound, an extensive uncertainty analysis with respect to the compound properties was not performed. Moreover, once better K_{oc}, m, or DT_{50} values for a given pesticide are known, the pesticide database can be quickly updated and new model runs for that pesticide can be conducted.

There is also a comprehensive discussion in the FOCUS surface water scenario report (FOCUS, 2001) on the uncertainty in pesticide drainage losses calculated with MACRO that results from model and parameter error. However, the “blind validation” test simulations (cf. section 3.2) have shown that the predictive capability of MACRO 4.3, using the pedotransfer functions of MACRO_DB2, is good. Model and parameter error are therefore not the main problem here. The remaining major uncertainty issues are related to representativity:

- How representative are the soil scenarios?

- How representative are the weather scenarios, i.e. the selected weather stations and years?
- How reliable can the assignment of a field to one of the 19 soil/climate scenarios be?
- How representative is the choice of the application date?

The soil scenarios were carefully constructed from real "main soil type" profiles of the German soil map and thus should at least not produce results that are unrealistic. As regards the representativity of the soil classes: Since the area of a BUEK soil mapping unit is not covered entirely by the main soil type (it is only the dominant, i.e. most frequent soil type in that unit), and the main soil type of a given unit can (and mostly will) also occur outside this unit, the representativity of the eight soil classes for the total drained agricultural area of Germany can hardly be estimated.

As the differences in total and peak pesticide losses between scenarios with the same soil, but different meteorological input files were often larger than the differences between scenarios with different soils (cf. section 3.3.6), the influence of the employed weather data deserves larger attention. The choice of the weather year for a soil/climate scenario is a quite difficult and error-prone task for the following reasons:

- All weather years have extremes (very cold or hot periods, droughts, or heavy rainfalls), which are not necessarily "representative" for the region they shall represent.
- The only available and feasible criterion for the choice of a year was the annual rainfall as compared to the median rainfall of the respective subunit.
- In some regions (e.g., Lower Saxony), meteorological stations were rather scarce, which resulted in only little choice for weather years.
- Moreover, some stations did not cover a full 30-year period, which further limited the choice.

Since the selection of a weather year for a given scenario is most likely the largest source of uncertainty, the first part of the uncertainty analysis focused on the influence of the weather year on pesticide drainage losses. For three selected soil/climate scenarios with comparatively large simulated drainage losses (8N, 8S, 2OR; cf. Table 3.31), two compounds with contrasting physico-chemical properties (dichlorprop-P (K_{oc} = 21 L kg^{-1}, m = 1, DT_{50} = 19 d) , and terbutryn (775 L kg^{-1}, m = 0.76, DT_{50} = 52 d)), and four selected uses,

- dichlorprop-P on winter cereals, spring application
- dichlorprop-P on winter cereals, autumn application
- terbutryn on maize, spring application

- terbutryn on winter cereals, autumn application,

3-year simulations were performed for all weather years of the respective station where the necessary data were available (24 years for scenarios 2 OR and 8 N, 13 years for 8 S). This gives 244 simulations in total. Analogously to the predictive simulations (cf. section 3.3.1), pesticide application took place in the first year only, and the same weather year was repeated twice. The pesticide application date was determined with the PAT separately for each weather year.

In the second part of the uncertainty analysis, the influence of the application day on pesticide losses was investigated. According to FOCUS (2001), the criteria implemented in the Pesticide Application Timer (PAT) result in selection of application dates which are the 60th to 70th percentile wettest days for non-irrigated crops. This exercise should give information about whether PAT also yields application dates of intermediate to slightly worst-case conditions with respect to pesticide losses via drains. Simulations were performed for the same three soil/climate scenarios and four selected uses as above, with the application day varying from 15 days before to 15 days after the original application date calculated by the Pesticide Application Timer. The same weather years were employed as for the predictive simulations. In total, this part of the uncertainty analysis encompassed 372 simulation runs.

As examples, Fig. 3.33-3.35 show the variation in maximum daily drainflow losses over the available weather years for

- dichlorprop-P, winter cereals, spring application, scenario 2 OR
- dichlorprop-P, winter cereals, spring application, scenario 8 N
- terbutryn, maize, spring application, scenario 8N

It can be seen from the diagrams and from Table 3.37 that the variation in maximum daily drainflow losses over the different weather years was generally quite high and reached up to 4 orders of magnitude between the lowest and the highest loss. A correlation of maximum daily pesticide losses with the annual rainfall amount is not evident. The large variability of maximum daily losses between years can be explained by the different rainfall distribution in each year, especially the occurrence or non-occurrence of large rainfall events or rainy periods shortly after application. For the cumulative drainflow losses, the loss patterns over the years were similar to those for the peak losses; however, the variation was generally smaller.

Of course, high or low pesticide drainage losses are not inherent to each weather year. The loss pattern over the different years also depends on the application month of the pesticide.

For instance, the year 1983 in the 2 OR scenario yielded the by far highest peak losses of all 24 years for spring application of dichlorprop-P (Fig. 3.33), but for autumn application of dichlorprop-P only losses close to the median value of all years (not shown). This leads to the conclusion that there is no such thing as a representative weather year for simulating pesticide losses via drainage, and that the results of the predictive drainflow modelling bear considerable uncertainty. However, it has to be noted that the soils selected for the uncertainty analysis were the worst cases of the 8 soil scenarios with respect to pesticide losses via drainflow. The uncertainty caused by annual weather variability is probably considerably smaller for the soil scenarios less prone to preferential flow, e.g. the sandy soil scenarios 3 and 4 (cf. section 3.3.6).

The variability in pesticide losses due to variation of the application date (see Fig. 3.36 as an example) was much smaller than the variability between weather years. A large effect only occurred when the last drainage event before the summer fell in the range of the application dates (PAT date ± 15 days) and the pesticide was largely dissipated when drainage resumed in late autumn or winter (Fig. 3.37).

Table 3.37: Variation in *maximum daily* drainage losses (*relative* to applied amount) between different weather years of one weather station

soil/ climate scenario	compound	crop	application season	maximum daily pesticide loss over the simulation period min.	max.	median	mean	std. dev.
				% of applied amount d^{-1}				
2 OR	dichlorprop-P	winter cereals	spring	2.8E-05	0.64	4.4E-03	0.056	0.15
			autumn	3.1E-03	1.11	0.24	0.32	0.30
	terbutryn	maize	spring	9.2E-21	0.29	0.027	0.049	0.072
		winter cereals	autumn	8.1E-23	0.56	0.12	0.14	0.15
8 N	dichlorprop-P	winter cereals	spring	3.9E-03	9.22	1.14	1.58	2.34
			autumn	0.32	20.87	4.16	5.59	5.49
	terbutryn	maize	spring	5.2E-04	0.12	7.9E-03	0.019	0.029
		winter cereals	autumn	2.5E-03	0.42	0.022	0.060	0.11
8 S[1)]	dichlorprop-P	winter cereals	spring	6.8E-03	21.58	7.10	7.70	8.23
			autumn	0.36	30.66	6.38	9.47	9.49
	terbutryn	maize	spring	3.5E-04	0.13	0.020	0.043	0.047
		winter cereals	autumn	2.5E-03	0.59	0.042	0.15	0.19

[1)] The original weather year 1995 (824 mm rainfall) was used here rather than the one with downscaled rainfall.

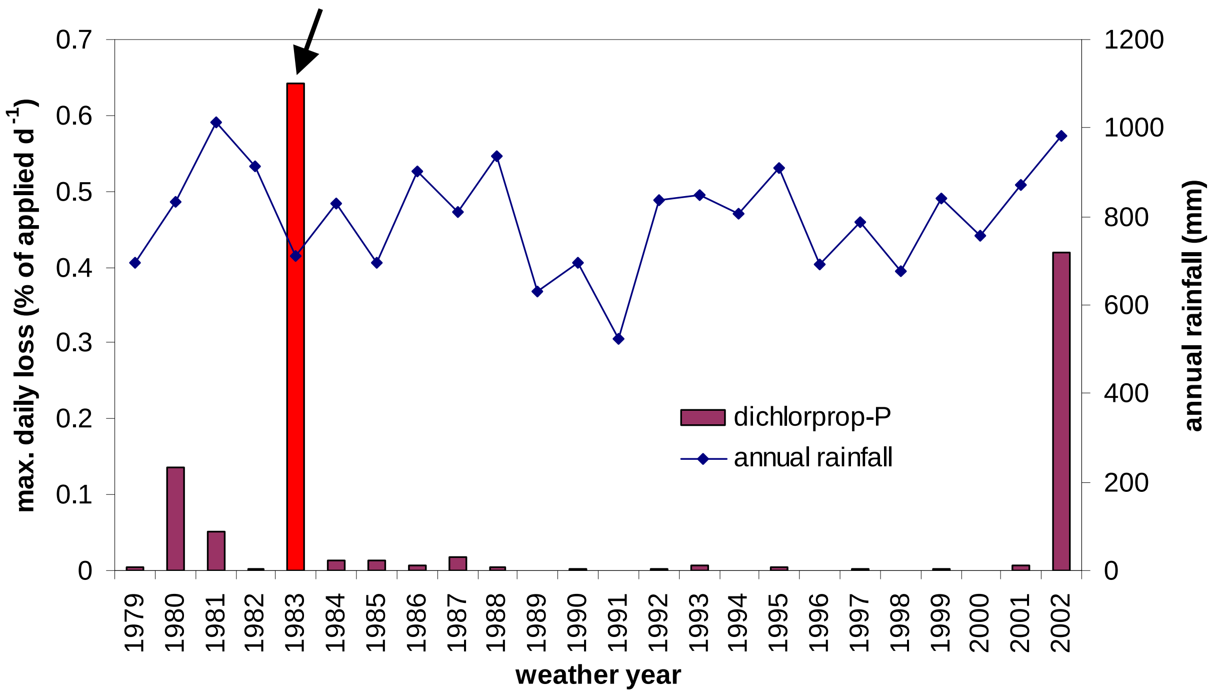

Fig. 3.33: Predicted maximum daily drainflow losses of dichlorprop-P in winter cereals (spring application) for 24 different weather years, soil/climate scenario 2 OR (Gley-Vega, weather station Karlsruhe). The arrow indicates the weather year (1983) used for the predictive modelling.

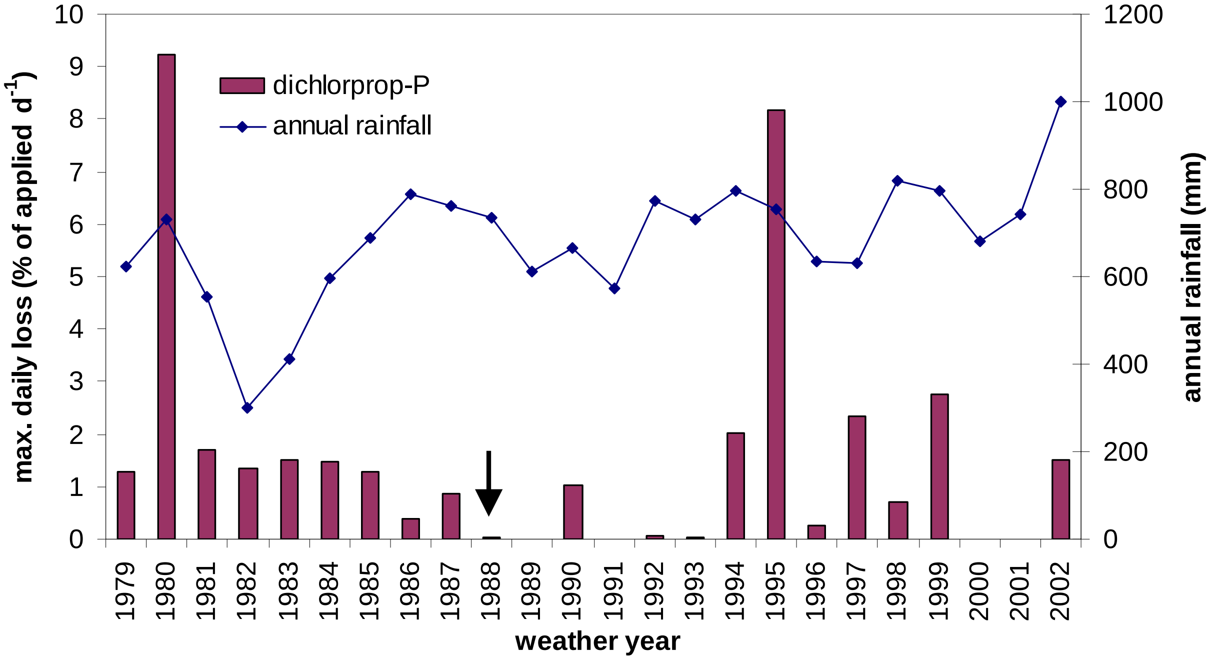

Fig. 3.34: Predicted maximum daily drainflow losses of dichlorprop-P in winter cereals (spring application) for 24 different weather years, soil/climate scenario 8N (Pelosol-Braunerde, weather station Leinefelde). The arrow indicates the weather year (1988) used for the predictive modelling.

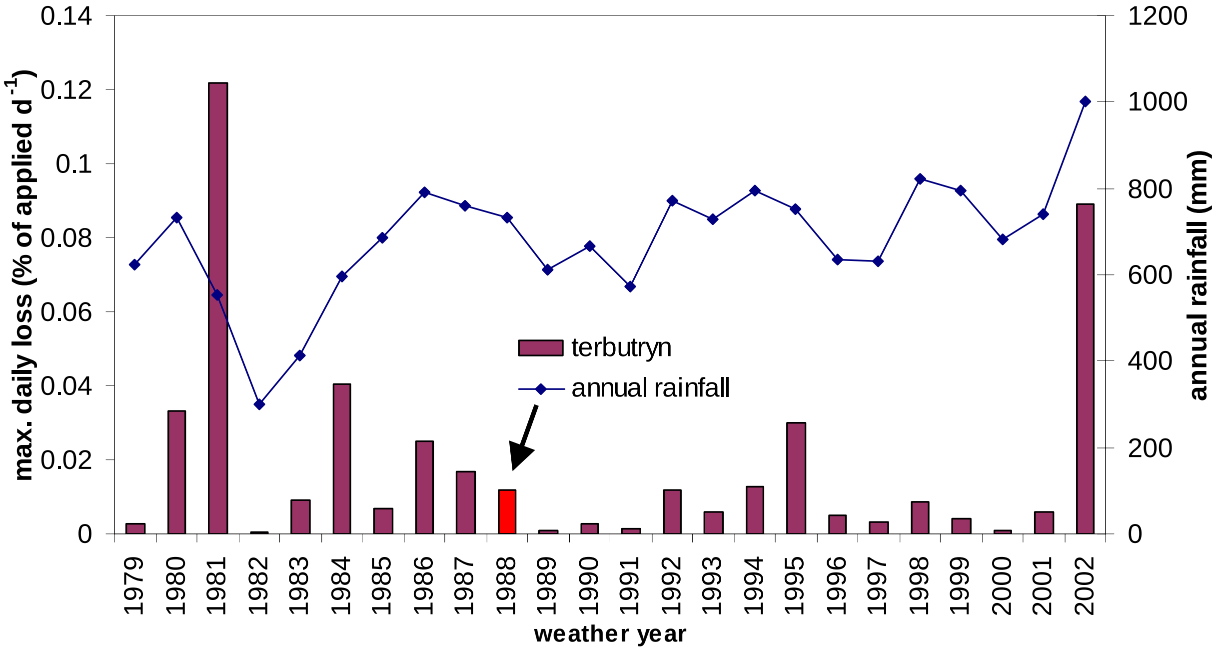

Fig. 3.35: Predicted maximum daily drainflow losses of terbutryn in maize (spring application) for 24 different weather years, soil/climate scenario 8N (Pelosol-Braunerde, weather station Leinefelde). The arrow indicates the weather year (1988) used for the predictive modelling.

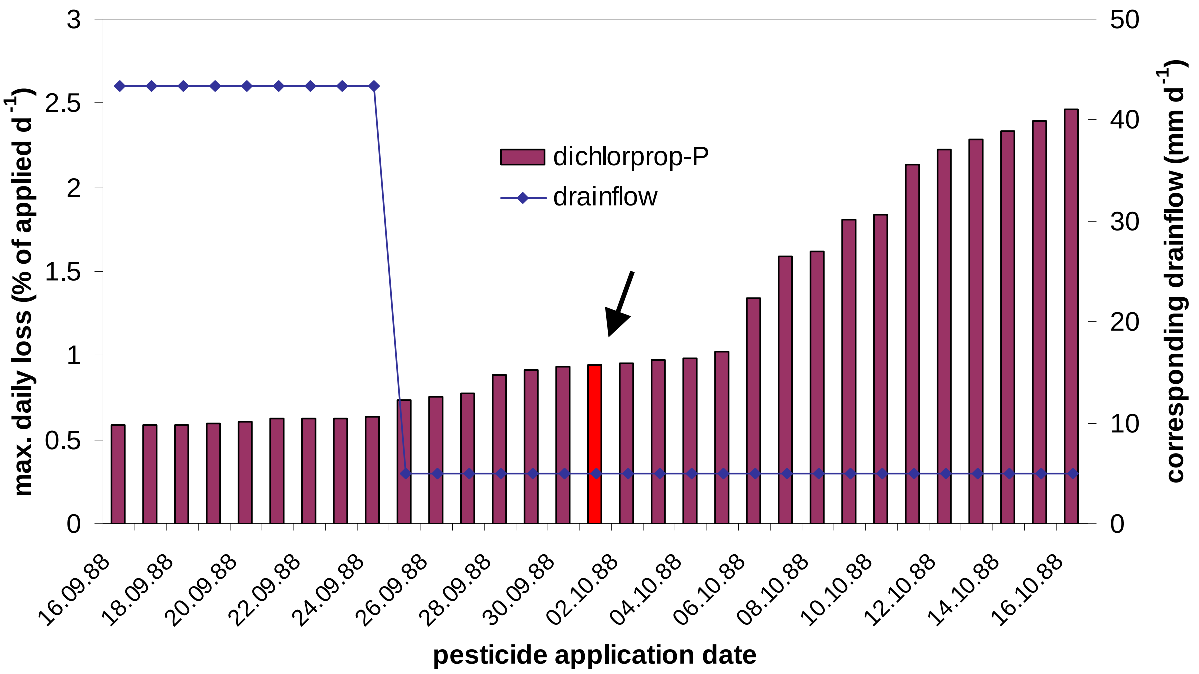

Fig. 3.36: Predicted maximum daily drainflow losses of dichlorprop-P in winter cereals (autumn application) for 31 different application dates (range: PAT date ± 15 days), soil/climate scenario 8N (Pelosol-Braunerde, weather station Leinefelde). The arrow indicates the PAT-calculated date (01.10.1988), which was used for the predictive modelling.

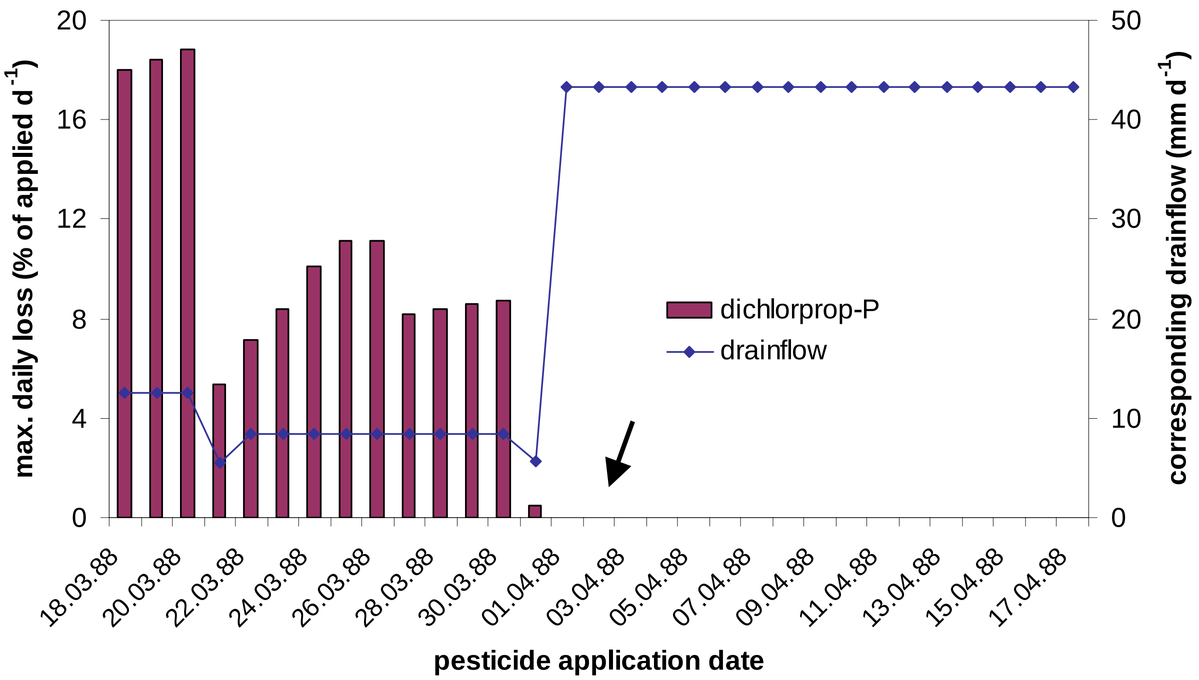

Fig. 3.37: Predicted maximum daily drainflow losses of dichlorprop-P in winter cereals (spring application) for 31 different application dates (range: PAT date ± 15 days), soil/climate scenario 8N (Pelosol-Braunerde, weather station Leinefelde). The arrow indicates the PAT-calculated date (02.04.1988), which was used for the predictive modelling.

3.3.8 Conclusions and Recommendations

Although the model testing exercises (section 3.2) revealed that the predictive capability of MACRO 4.3 in combination with the pedotransfer functions of MACRO_DB2 is good, the uncertainty analysis (section 3.3.7) has shown that both peak and total pesticide losses strongly depend on the weather year employed. The results of the predictive simulations bear therefore considerable uncertainty due to annual weather variability, especially for the soils prone to preferential flow. The only possibility to capture this uncertainty would be to simulate several different weather years per climate scenario. Given the long computation time required by MACRO 4.3 and the large number of different uses to be simulated, however, this is hardly feasible. An option would be to switch to the faster new version MACRO 5 (Larsbo and Jarvis, 2003), which is now available. As the performance of the new built-in pedotransfer functions in MACRO 5 has not been tested yet, this would require a new model testing exercise like in section 3.2.

4 Modelling Surface Runoff and Erosion Inputs with PRZM

For the runoff and erosion simulations the model PRZM 3.21β (FOCUS, 2001) was selected because it

- is officially used within the European pesticide registration procedure (FOCUS surface water, step 3 calculations),
- yields satisfactory results (tested with 12 real data sets, cf. section 4.2), while relatively easy to parameterize,
- needs only little computation time, which facilitates the use of probabilistic methods.

4.1 Description of the PRZM model

PRZM (**P**esticide **R**oot **Z**one **M**odel) is a one-dimensional, dynamic, compartmental finite-difference model that can be used to simulate chemical movement in unsaturated soil systems within and immediately below the root zone (Carsel et al., 2003). The original version of the PRZM model was released in 1984 (Carsel et al., 1984). The model has been continuously improved since then. The latest, Windows-based version PRZM 3.21β is used in the context of the FOCUS surface water scenarios (FOCUS, 2001) as runoff and erosion model. A version with only minor differences is also used as one of the official leaching models in the FOCUS groundwater scenarios (FOCUS, 2000).

The PRZM model is able to simulate surface runoff, erosion, leaching, decay, plant uptake, foliar washoff, and volatilisation of pesticides. It has two major components – water and chemical transport. In the following, the processes of PRZM relevant for runoff and erosion modelling are explained briefly.

4.1.1 Water Transport

PRZM is a capacity-type model with a daily time step. Water movement is simulated with a rather simple approach. The soil profile is divided into several layers. A soil layer is characterized by three hydraulic parameters: field capacity (usually reported as the amount of water the soil can hold against the influence of gravity), wilting point (the soil moisture content below which plants can no longer extract water from the soil), and saturated water content (pore volume). If the soil water content of a soil layer exceeds field capacity, the excess water drains to the next layer. The whole soil profile drains within one day to field capacity. Thus, PRZM is not able to simulate waterlogging. As PRZM is also unable to simulate preferential flow, its application should be restricted to well-drained soils without strongly developed soil structure if leaching estimates are required. However, since waterlogging rarely occurs in the topsoil and leaching by preferential flow does not significantly affect bulk pesticide concentrations in the topsoil, these limitations do not affect the general applicability of PRZM to runoff and erosion problems.

Evapotranspiration in PRZM is composed of evaporation from crop interception, evaporation from soil and transpiration from the crop. Potential evapotranspiration is obtained from direct input of daily pan evaporation, multiplied with a crop-specific correction factor.

PRZM is not able to simulate upward water movement due to hydraulic potential gradients induced by evapotranspiration. This can lead to an underestimation of actual evapotranspiration.

Surface runoff is described by a modification of the empirical USDA Soil Conservation Service (SCS) Curve Number technique (Haith and Loehr, 1979):

$$Q = \frac{(P + SM - 0.2S)^2}{P + SM + 0.8S} \qquad \text{for } (P + SM - 0.2\ S) > 0 \qquad \text{(eq. 4.1)}$$

$$Q = 0 \qquad \text{for } (P + SM - 0.2\ S) \leq 0$$

where

Q surface runoff (cm d^{-1})

P precipitation as rainfall, minus crop interception (cm d^{-1})

SM snowmelt (cm d^{-1})

S daily watershed retention parameter (cm d^{-1}); 0.2 S is also referred to as “initial abstraction”

The daily watershed retention parameter *S* is estimated by

$$S = \frac{1000}{CN} - 10 \qquad \text{(eq. 4.2)}$$

with

CN SCS runoff curve number ($0 < CN \leq 100$)

Curve numbers are a function of soil type, soil drainage properties, crop type and management practice (Carsel et al., 2003). The higher the curve number, the more frequently runoff will occur, and the higher the runoff volume per event will be. In PRZM, the curve numbers are adjusted daily as a function of the soil water status in the upper soil layers, following the algorithms developed and reported by Haith and Loehr (1979). Runoff curve numbers are tabulated for different crops and soil hydrologic groups in the PRZM 3.12.1 Manual (Carsel et al., 2003). Curve numbers and thus runoff susceptibility increase from group A (light, sandy soils) to D (heavy, clayey soils). Note that although PRZM considers the effect of snowmelt in the runoff equation, the curve numbers are not adjusted to account for the effects of snowpack or frozen ground on runoff generation.
Soil loss by sheet and rill erosion is also modelled empirically using the Modified Universal Soil Loss Equation (MUSLE; Williams, 1975) or one of its modifications (MUSS, MUST). MUSS was specifically designed for small watersheds and is used in the PRZM calculations in the FOCUS surface water scenarios.

MUSLE: $$X_e = 1.586\ (V_r\ q_p)^{0.56}\ A^{0.12}\ K\ LS\ C\ P \quad \text{(eq. 4.3)}$$

MUSS: $$X_e = 0.79\ (V_r\ q_p)^{0.65}\ A^{0.009}\ K\ LS\ C\ P \quad \text{(eq. 4.4)}$$

where

X_e	event soil loss (t d^{-1})
V_r	volume of event (daily) runoff (mm)
q_p	peak storm runoff rate (mm h^{-1})
A	field size (ha)
K	soil erodibility factor (dimensionless)
LS	length-slope factor (dimensionless)
C	soil cover factor = crop management factor (dimensionless)
P	conservation practice factor (dimensionless)

While A, K, LS, C and P are user input, q_p is calculated internally in PRZM, using a generic storm hydrograph. The rainfall intensity is assumed to occur according to "design storm distributions" or rainfall regimes. The rainfall regime is entered by the PRZM user. For Western and Middle Europe, type II, which covers the largest part of the USA without the Atlantic, Pacific and southern regions, is the most appropriate rainfall regime.

4.1.2 Pesticide Transport and Fate

In contrast to the older PRZM version 3.12 used by the US Environmental Protection Agency (USEPA), the latest version 3.21β is also capable of modelling non-linear sorption and temperature- and moisture-dependent degradation (FOCUS, 2001). Sorption is described identically as in MACRO using a Freundlich isotherm (eq. 3.11, section 3.1.2). Degradation is by default described by single first-order kinetics; however, there is also a possibility to specify biphasic degradation with a "hockey-stick" model, which switches from a fast first-order kinetic to a slower one at a user-defined time point.

The temperature dependence of degradation is based on a Q_{10} equation, which is mathematically equivalent to the formula used in MACRO (cf. eq. 3.16, section 3.1.2) as an approximation of the Arrhenius equation. The moisture-dependence of degradation is also in PRZM described with the Walker formula (eq. 3.15, section 3.1.2). However, in PRZM the reference moisture can be freely chosen, either as absolute volumetric moisture or in percent of field capacity.

The extraction of pesticides from soil with runoff water follows an empirical approach, where the runoff-availability of a compound decreases with depth ("non-uniform extraction model"; Carsel et al., 2003):

$$DRI_i = 0.7 \cdot \left(\frac{1}{2.0 \cdot Midtot_i + 0.9} \right)^2 \qquad \text{(eq. 4.5)}$$

where

DRI_i	fraction of dissolved-phase chemical present in compartment i available for runoff (dimensionless)
$Midtot_i$	depth to midpoint of compartment i (cm)
0.7	efficiency factor
0.9	depth-reduction coefficient

Calculations are performed for all compartments *i* from the surface to a depth of 2 cm; the thickness of the topsoil compartments is usually set to 0.1 cm. Thus, the runoff-available fraction decreases from 70 % of the dissolved chemical in the uppermost compartment to 3 % in the 20th compartment. Below 2 cm depth the runoff availability of chemicals is zero. Pesticide runoff loss from compartment *i* is then obtained as

$$J_{r,i} = DRI_i \cdot C_i \cdot Q \cdot 10 \qquad \text{(eq. 4.6)}$$

with

$J_{r,i}$	pesticide runoff loss from compartment i (mg m^{-2} d^{-1})
C_i	concentration of dissolved pesticide in the water phase (mg L^{-1})
10	unit correction factor

During erosion events, apart from losses dissolved in surface runoff, pesticides can also leave the field adsorbed to eroded topsoil material. Because erosion is a selective process, eroded soil material is, compared with the topsoil from which it was eroded, enriched in smaller particles and organic matter (the main sorbent for non-ionic pesticides). In PRZM, the enrichment ratio for organic matter r_{om} is calculated empirically according to the following equation:

$$\ln (r_{om}) = 2 - 0.2 \ln (1000\ X_e/A) \qquad \text{(eq. 4.7)}$$

Thus, larger erosion events are less selective and will result in lesser enrichment of organic matter. Pesticide loss from the field via erosion is calculated as

$$J_e = \frac{X_e \cdot r_{om} \cdot S_1}{10 \cdot A} \qquad \text{(eq. 4.8)}$$

with

J_e	pesticide erosion loss (mg m^{-2} d^{-1})
S_1	concentration of adsorbed pesticide in the solid phase (mg kg^{-1}) in the uppermost compartment
10	unit correction factor

In contrast to MACRO, PRZM is also able to model pesticide losses via volatilization. PRZM explicitly simulates vapour phase diffusion in soil, volatilization from soil and plant surfaces, and volatilization flux through the plant canopy. A detailed process description cannot be given here, but can be found in Carsel et al. (2003).

Pesticide washoff from the crop canopy to the soil surface is modelled using an empirical extraction coefficient. In the FOCUS surface water scenario report (FOCUS, 2001) an extraction coefficient based on water solubility is suggested:

$$FEXTRC = 0.0160 \cdot SOL^{0.3832} \qquad \text{(eq. 4.9)}$$

with

FEXTRC	foliar extraction coefficient (cm^{-1})
SOL	pesticide aqueous solubility ($mg\ L^{-1}$)

The amount of pesticide washed off from the crop canopy is obtained as

$$J_{fw} = FEXTRC \cdot P_r \cdot M_f \qquad \text{(eq. 4.10)}$$

where

J_{fw}	pesticide washoff from crop canopy ($mg\ m^{-2}\ d^{-1}$)
P_r	daily rainfall depth ($cm\ d^{-1}$)
M_f	pesticide mass on foliage, per plant surface projected area ($mg\ m^{-2}$)

Pesticide uptake by roots is treated in the same way as in MACRO (cf. eq. 3.21, section 3.1.2) as a passive process with a plant uptake concentration factor between 0 and 1.

4.2 Testing PRZM Against Measured Data

Since PRZM is to be used in this project in a purely predictive way and without prior calibration, the predictive capabilities of PRZM had to be tested extensively (cf. section 3.2). Therefore, a number of European runoff and erosion studies was modelled with PRZM 3.21β, and the modelling results were compared with measured data.

The predictive capability of PRZM 3.21β was tested by comparison of model results (simulated target variables) with the corresponding measured values from the runoff studies. Target variables for runoff were:

- runoff volume
- pesticide runoff loss (pesticide load dissolved in runoff water).

The corresponding target variables for erosion were:

- soil loss
- pesticide erosion loss (pesticide load adsorbed to eroded soil material).

Also, the timings of measured and simulated surface runoff events were compared visually. In analogy to the drainage test simulations (cf. section 3.2), the ratios of simulated and measured values were compared for both total and maximum daily values of runoff volume, soil loss and pesticide runoff and erosion losses, respectively. Most runoff and erosion models (including PRZM) still rely on simple, empirical process descriptions of runoff and erosion. Moreover, runoff and erosion experiments are difficult to conduct. Considerable uncertainty in the measured data and problems of comparability of measured and simulated values can thus be expected. Therefore, the average deviation between measured and simulated target variables will probably be larger than for the drainflow test simulations. On the basis of these considerations, the acceptability limit for the deviation between simulated and measured values was set to a factor of 10 for both surface runoff and eroded sediment yield. The simulated pesticide runoff losses are affected by uncertainty from both water transport and chemical transport simulation. For simulated pesticide erosion losses, the situation is analogous. The deviation between simulated and measured values can thus be expected to be on average higher for pesticide runoff or erosion losses than for the corresponding runoff volumes or eroded sediment yields. However, for the purpose of aquatic risk assessment (cf. section 5.1.3), an under– or overprediction of pesticide inputs into a surface water body by more than a factor of 10 cannot be considered acceptable. Therefore, in analogy to the drainflow test simulations, also for pesticide losses via runoff or erosion the acceptability limit was set to a factor of 10 between simulated and measured values.

4.2.1 Test Sites and Simulations

After extensive literature research and negotiations with the data owners, a number of qualitatively acceptable datasets of field runoff studies could be obtained (Table 4.1).
On the basis of the considerations in section 2.4 and analogously to the MACRO test simulations (cf. section 3.2), no model calibration was performed. Only the meteorological data, site and experimental characteristics were site-specific in the simulations. For compound properties (DT_{50}, K_{oc}, Freundlich exponent m, water solubility, Henry's Law constant), intentionally no site-specific, but generic values were used (Table 4.2).

Table 4.1: Runoff and erosion studies used for model testing

study site	number of datasets	source	site location	soil	crop	compounds measured and used for modelling
Temple Balsall	4	Neil Adams, Monsanto Europe; Colin Brown, CSL York, formerly Cranfield Centre for Ecochemistry, UK	Middle England	sandy loam	maize	alachlor, atrazine, pendimethalin
				clay loam	maize	alachlor, atrazine, pendimethalin
				sandy loam	oilseed rape	alachlor
				clay loam	oilseed rape	alachlor
Schmallen-berg	1	W. Kördel, H. Klöppel, Fraunhofer IME Schmallenberg, Germany	Middle-German low mountain ranges	silt loam	triticale	isoproturon, dichlorprop-p, bifenox
Kleinhohen-heim	3	Robert Spatz, Syngenta, formerly University of Hohenheim, Germany	S-Germany	clay silt	maize	terbuthylazin, pendimethalin
					maize	terbuthylazin, pendimethalin
					spring barley	isoproturon
Rosemaund	1	R.J. Williams, Centre for Ecology and Hydrology, Wallingford, UK	W-England	strongly silty clay	winter wheat	trifluralin
Cockle Park	1	Colin Brown, CSL York, formerly Cranfield Centre for Ecochemistry, UK	NE-England	sandy loam over clay loam	winter wheat	isoproturon, trifluralin
Freising	2	Josef Haider, Landesumweltamt NRW, formerly Technical University Munich, Germany	S-Germany	sandy loam over loamy sand	fallow	isoproturon, dichlorprop-p, bifenox
					spring barley	isoproturon, dichlorprop-p, bifenox

Table 4.2: Generic compound properties used for PRZM model testing (cf. Appendix A)

compound	K_{oc}	Freundlich exponent m	DT_{50} (topsoil)	water solubility at 20/25 °C	vapour pressure at 20 °C	Henry's Law constant at 20 °C
	L kg^{-1}		d	mg L^{-1}	Pa	(dimensionless)
alachlor	137	0.9	18	240	2.90E-03	1.315E-06
atrazine	147	0.9	60	33	3.80E-05	1.002E-07
bifenox	4949	1	7	0.398	1.30E-05	4.508E-06
dichlorprop-P	21	1	19	900000	1.30E-05	1.393E-12
isoproturon	71	0.88	11	70.2	3.15E-06	3.798E-09
pendimethalin	14000	0.9	146	0.275	1.94E-03	6.671E-04
terbuthylazine	247	0.83	88	8.5	1.50E-04	1.635E-06
trifluralin	7795	0.97	155	0.32	6.70E-03	2.880E-03

Crop properties and depth reduction factors for the degradation rate were chosen according to the FOCUS surface water scenarios (FOCUS, 2001). The parameter settings used in all simulations are shown in Table 4.3.

Table 4.3: PRZM parameter settings used for all simulations

parameter	description	value
ALBEDO	monthly values of soil surface albedo	0.18
ANETD	largest depth from which evaporation is extracted (cm)	15
APPEFF	application efficiency (fraction)	1
B-VALUE	exponent for moisture correction of degradation rate	0.7
DAIR	molecular diffusion coefficient for the pesticide in air (cm^2 d^{-1})	4300
DGRATE(i)	vapour phase pesticide degradation rate in horizon i (d^{-1})	0
DISP(i)	pesticide hydrodynamic dispersion coefficient in soil horizon i	0
DPN(i)	thickness of compartments in soil horizon i (cm)	0.1 (top 10 cm) 5 (rest)
DRFT	spray drift (fraction)	0
EMMISS	emissivity of soil surface for longwave radiation (0.96)	0.96
ENPY	vaporization enthalpy of the pesticide (kcal mol^{-1})	22.7
IPSCND	condition for disposition of foliar pesticide after harvest	2
IREG	rainfall regime	3
MNGN	Manning's roughness coefficient for the field	0.10
PLDKRT	pesticide decay rate on plant foliage (d^{-1})	0.0693
PLVKRT	pesticide volatilization rate on plant foliage (d^{-1})	0
QFAC	factor for increase of degradation rate when temperature increases by 10°C	2.2
REFMOIST	reference soil moisture relative to field capacity (%)	100
SFAC	snow melt factor (cm per °C above freezing)	0.46
TBASE	reference temperature for degradation (°C)	20
UPTKF	plant uptake factor (describes uptake as a fraction of transpiration × dissolved phase concentration)	0.5

Soil parameters (curve numbers, field capacity, wilting point, USLE factors) were obtained from the PRZM 3.12 Manual (Carsel et al., 2003). The curve numbers are tabulated there for each soil hydrologic group and for different crop types. Field capacity (*FC*) and wilting point water content (*WP*) for each soil layer were calculated using multiple regression equations:

$$FC = 0.3486 - 0.0018\,SAND + 0.0039\,CLAY + 0.0228\,OM - 0.0738\,BD \qquad \text{(eq. 4.11)}$$

$$WP = 0.0854 - 0.0004\,SAND + 0.0044\,CLAY + 0.0122\,OM - 0.0182\,BD \qquad \text{(eq. 4.12)}$$

where

FC	water content at pF 2.5
WP	water content at pF 4.2
SAND	sand content (%)
CLAY	clay content (%)
OM	organic matter content (%)
BD	dry bulk density (kg dm^{-3})

The PRZM input files (.inp) used for the test simulations are included in Appendix G on the attached CD-ROM. For the sake of the readibility of section 4.2.1, only diagrams for the One Oak and Firs Farm datasets are shown in the text body as examples. However, all diagrams for the PRZM testing datasets are included in Appendix H on the CD-ROM.

4.2.1.1 Temple Balsall

The Temple Balsall studies were conducted on behalf of Monsanto Company. The site is located in Middle England (52°23’ N), 10 km southeast of Birmingham. Four runoff studies were conducted on different fields. Samples of surface runoff and soil water were collected following major rainfall events. Further details on the experiments can be found in Brown and Hollis (1996).

One Oak, sandy loam

Alachlor, atrazine and pendimethalin were applied in spring 1993 to a fodder maize crop on a sandy loam soil (FAO soil type: Eutric Cambisol). The field slope was 3.5 %. Groundwater depth was below 1.3 m; no drains were installed. Basic soil properties are shown in Table 4.4. Soil hydrologic group B-C was assigned to this profile.

The field was rolled on 03.05.1993, and on 15.05.1993 fodder maize was drilled. On 18.05.1993 alachlor (1.92 kg a.i.ha^{-1}), atrazine (1.15 kg ha^{-1}) and pendimethalin (1.30 kg ha^{-1}) were applied by surface spray. Runoff and soil water were sampled triggered by rainfall events over a period of 3 months after application. The surface runoff samples were collected from three runoff traps (1 m^2) with 5.5 m^2 catchment area.

Table 4.4: Soil properties of Temple Balsall, One Oak (Brown, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	organic carbon	dry bulk density	pH (H_2O)
cm		%		%	kg dm^{-3}	
0-33	18	23	59	3.2	1.45	6.5
33-51	8	19	73	0.6	1.51	7.0
51-79	3	16	81	0.2 [1)]	1.54	6.9
79-105+	2	19	79	0.1 [1)]	1.20	7.0

[1)] estimated

The available site-specific weather data (06.05.1993 - 08.08.1993) comprised daily precipitation as well as daily maximum and minimum temperatures. The missing meteorological variables (pan evaporation, wind speed and solar radiation) were obtained as follows. For wind speed and solar radiation long-term monthly averages of the FOCUS$_{sw}$ scenario Brimstone were used. Pan evaporation, which can be considered equal to potential evapotranspiration for grass (FOCUS, 2001), was obtained using Linacre's (1977) method and the same correction factor of 0.73 for downscaling as for the Cockle Park drainflow study (cf. section 3.2.1.6).

Firs Farm, clay loam

Alachlor, atrazine and pendimethalin were applied in spring 1993 to a fodder maize crop on a clay loam soil. The soil type according to FAO (1988) was Stagno-Gleyic Luvisol. The field slope was 4 %. A transient perched water table was noted at 35 cm depth on 21.05.1993 and 14.06.1993. The true groundwater table appeared at 60-78 cm depth towards the end of the study (14.06.1993 - 05.08.1993). Historical tile and horseshoe drains were present at approximately 70 cm depth. Basic soil properties are given in Table 4.5. This soil was grouped into soil hydrologic group C.

The field was rolled on 03.05.1993, and fodder maize drilled on the same day. On 06.05.1993 alachlor (1.92 kg a.i. ha^{-1}), atrazine (1.15 kg ha^{-1}), and pendimethalin (1.30 kg ha^{-1}) were applied by surface spray. Runoff and soil water were sampled triggered by rainfall events over a period of 3 months after application. The surface runoff samples were collected from runoff traps (1 m^2) with 5.5 m^2 catchment area.

Table 4.5: Soil properties of Temple Balsall, Firs Farm (Brown, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	organic carbon	dry bulk density	pH (H_2O)
cm		%		%	kg dm^{-3}	
0-24	21	31	48	2.3	1.51	6.9
24-48	22	32	46	0.6	1.65	7.0
48-89	38	37	25	0.3 [1)]	1.73	7.4
89-100+	29	35	36	0.2 [1)]	1.86	7.5

[1)] estimated

The site-specific weather data were the same as for One Oak.

Temple House Farm, sandy loam

Alachlor was applied in autumn 1992 to an oilseed rape crop on a sandy loam soil. The field slope was 1.5 %. The groundwater table was at 1.0-1.2 m depth. Basic soil properties are shown in Table 4.6. This profile was grouped into soil hydrologic group B.
The field was rolled on 15.09.1992, and oilseed rape drilled on the same day. On 21.09.1992 alachlor (1.92 kg a.i. ha^{-1}) was applied by surface spray. Runoff and soil water were sampled triggered by rainfall events over a period of 6 weeks after application. The surface runoff samples were collected from one runoff trap (1 m^2) with 5.5 m^2 catchment area.

Table 4.6: Soil properties of Temple House Farm, sandy loam (Brown, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density	pH (H_2O)
cm		%		%	kg dm^{-3}	
0-29	15	17	68	1.7	1.45	7.0
29-47	6	5	89	1.0	1.63	7.0
47-110	10	2	88	0.8	1.59	7.3

The available site-specific weather data (21.09.1992 - 29.10.1992) comprised daily mean temperature, precipitation, daily means of solar and net radiation, wind speed and direction. The missing potential evapotranspiration was again calculated by Linacre's method and a correction factor of 0.73.

Temple House Farm, clay loam

Alachlor was applied in autumn 1992 to an oilseed rape crop on a clay loam soil. The field slope was 3.5 %. The groundwater table was at 80 cm depth at start of study. A perched water table at 35 cm depth appeared at beginning of October; by the end of October, a single water table was observed at 35 cm depth. Historical tile and horseshoe drains were present at approximately 70 cm depth. Basic soil properties are shown in Table 4.7. This soil was grouped into soil hydrologic group C.

The field was rolled on 15.09.1992, and oilseed rape drilled on the same day. On 21.09.1992 alachlor (1.92 kg a.i. ha^{-1}) was applied by surface spray. Runoff and soil water were sampled triggered by rainfall events over a period of 6 weeks after application. The surface runoff samples were collected from two runoff traps (1 m^2) with 5.5 m^2 catchment area. The site-specific weather data were the same as for Temple House Farm (sandy loam).

Table 4.7: Soil properties of Temple House Farm, clay loam (Brown, pers. comm., 2002)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density	pH (H_2O)
cm		%		%	kg dm^{-3}	
0-37	20	28	52	1.9	1.49	6.6
37-53	19	25	56	1.8	1.68	6.9
53-82	16	15	69	1.7	1.81	7.2
82-92	27	14	59	0.8	1.75	7.4
92-105+	56	27	17	1.3	1.47	7.6

Since erosion was not investigated in the four studies, only simulated and measured runoff results can be compared. In Table 4.8 the cumulative measured and simulated values of runoff volumes and pesticide runoff losses are shown. In analogy, Table 4.9 shows the measured vs. simulated maximum runoff volumes and pesticide losses per event. In Fig. 4.1-4.4, time series of measured vs. simulated runoff volumes and pesticide runoff losses are presented for One Oak and Firs Farm to visualize timing and magnitude of the simulated events with respect to daily precipitation and observed events. In all four studies, no extremely heavy rainfalls occurred (the largest daily rainfall was 23.4 mm for One Oak / Firs Farm), and hence the runoff events were rather small. The observed cumulative pesticide runoff losses ranged from zero to 0.047 % of the applied amount; maximum losses per event totalled up to 0.032 % of the applied amount. For the same experimental periods, measured runoff volumes and pesticide runoff losses were higher for the heavier clay loam soils than for the lighter sandy loam soils. The PRZM simulations yielded the same result.

Apart from One Oak runoff trap 2, where no runoff was observed in the field, the cumulative simulated runoff volumes were within factors of 0.19 and 10.2 (median: 2.5) of the measured volumes; for the maximum runoff volumes, the simulated values were within factors of 0.44 and 7.8 (median: 2.9) of the measured ones. Given the small amounts of runoff that occurred in the field and the fact that potential evapotranspiration had to be estimated rather crudely, this can be considered as a good agreement between simulated and measured results.

Table 4.8: Measured vs. simulated cumulative runoff volumes and pesticide runoff losses for the four Temple Balsall studies

dataset	replicate	dose	compound	measured values (acc.) runoff	measured values (acc.) pest. runoff loss	simulated results (acc.) runoff	simulated results (acc.) pest. runoff loss	ratio predicted/ observed runoff	ratio predicted/ observed pest. runoff loss
		$kg\ ha^{-1}$		mm	$g\ ha^{-1}$	mm	$g\ ha^{-1}$		
One Oak [1)]	trap 1	1.92	alachlor	0.18	0.0085	1.83	1.180	10.2	138.6
	trap 3	1.92	alachlor	2.19	0.118	1.83	1.180	0.84	10.00
	trap 1	1.15	atrazine	0.18	0.00018	1.83	0.730	10.2	4053
	trap 3	1.15	atrazine	2.19	0.257	1.83	0.730	0.84	2.84
	trap 1	1.30	pendimethalin	0.18	0	1.83	0.021	10.2	-
	trap 3	1.30	pendimethalin	2.19	0.0084	1.83	0.021	0.84	2.51
Firs Farm	trap 1	1.92	alachlor	0.71	0.205	5.60	2.539	7.89	12.4
	trap 2	1.92	alachlor	1.81	0.204	5.60	2.539	3.10	12.4
	trap 3	1.92	alachlor	1.09	0.155	5.60	2.539	5.14	16.4
	trap 1	1.15	atrazine	0.71	0.511	5.60	1.669	7.89	3.27
	trap 2	1.15	atrazine	1.81	0.542	5.60	1.669	3.10	3.08
	trap 3	1.15	atrazine	1.09	0.367	5.60	1.669	5.14	4.55
	trap 1	1.30	pendimethalin	0.71	0.0053	5.60	0.086	7.89	16.1
	trap 2	1.30	pendimethalin	1.81	0.0042	5.60	0.086	3.10	20.4
	trap 3	1.30	pendimethalin	1.09	0.0080	5.60	0.086	5.14	10.7
THF, SL [2)]	trap 1	1.92	alachlor	0.25	0.016	0.048	0.015	0.19	0.97
THF, CL [3)]	trap 1	1.92	alachlor	1.40	0.079	1.49	1.095	1.06	13.8
	trap 2	1.92	alachlor	0.78	0.129	1.49	1.095	1.90	8.52

[1)] No runoff was observed in trap 2.
[2)] Temple House Farm, sandy loam
[3)] Temple House Farm, clay loam

Pesticide runoff losses were substantially overestimated for One Oak trap 1, where only one small runoff event with 0.18 mm occurred in the field. Not considering One Oak traps 1 and 2, the simulated pesticide runoff losses were within factors of 0.97 and 20.4 (cumulative values; median: 10.0) and 1.39 and 13.9 (maximum values; median: 4.7) of the measured losses. With One Oak trap 1, the median predicted/observed ratios were 10.7 for the cumulative losses and 5.5 for the maximum losses. Considering that only generic substance properties were used for the simulation, and considering the uncertainty coming from the simulated runoff volumes, also the simulation of pesticide runoff losses can be judged as adequate.

Table 4.9: Measured vs. simulated maximum daily runoff volumes and pesticide runoff losses for the four Temple Balsall studies

dataset	replicate	dose	compound	measured values (max.)[1) runoff	measured values (max.)[1) pest. runoff loss	simulated results (max.)[1) runoff	simulated results (max.)[1) pest. runoff loss	ratio predicted/ observed runoff	ratio predicted/ observed pest. runoff loss
		$kg\ ha^{-1}$		mm	$g\ ha^{-1}$	mm	$g\ ha^{-1}$		
One Oak[2)]	trap 1	1.92	alachlor	0.18	0.0085	0.66	0.489	3.67	57.4
	trap 3	1.92	alachlor	0.73	0.073	0.66	0.489	0.90	6.71
	trap 1	1.15	atrazine	0.18	0.00018	0.66	0.281	3.67	1563
	trap 3	1.15	atrazine	0.73	0.202	0.66	0.281	0.90	1.39
	trap 1	1.30	pendimethalin	0.18	0	0.66	0.0077	3.67	-
	trap 3	1.30	pendimethalin	0.73	0.0044	0.66	0.0077	0.90	1.75
Firs Farm	trap 1	1.92	alachlor	0.2	0.185	1.56	1.053	7.79	5.69
	trap 2	1.92	alachlor	0.45	0.162	1.56	1.053	3.46	6.50
	trap 3	1.92	alachlor	0.45	0.146	1.56	1.053	3.46	7.20
	trap 1	1.15	atrazine	0.2	0.371	1.56	0.654	7.79	1.77
	trap 2	1.15	atrazine	0.45	0.325	1.56	0.654	3.46	2.01
	trap 3	1.15	atrazine	0.45	0.350	1.56	0.654	3.46	1.87
	trap 1	1.30	pendimethalin	0.2	0.0044	1.56	0.024	7.79	5.48
	trap 2	1.30	pendimethalin	0.45	0.0036	1.56	0.024	3.46	6.74
	trap 3	1.30	pendimethalin	0.45	0.0079	1.56	0.024	3.46	3.05
THF, SL[3)]	trap 1	1.92	alachlor	0.11	0.0098	0.048	0.015	0.44	1.53
THF, CL[4)]	trap 1	1.92	alachlor	0.64	0.043	1.02	0.599	1.59	13.9
	trap 2	1.92	alachlor	0.45	0.128	1.02	0.599	2.26	4.69

[1)] Note that measured maximum values are on an event basis (between 1 and ca. 3 days), while simulated values are always on a daily basis.

[2)] No runoff was observed in trap 2.

[3)] Temple House Farm, sandy loam

[4)] Temple House Farm, clay loam

The diagrams (Fig 4.1-4.4; H.1-H.12 in Appendix H) reveal that there is often an offset of a few days between simulated and measured events. This can be explained by a delay in sampling in the field: Usually, the runoff samples were taken when the rainfall/runoff event was over. Thus, an offset of two or three days between simulated events (and rainfall) and observed events is not unusual, and it can be concluded that the timing of the runoff events was also predicted fairly well.

Given that only very small runoff events occurred during the experiments, it can be summarized that PRZM was able to predict runoff volumes, pesticide runoff losses and the timing of runoff events reasonably well for the 4 Temple Balsall datasets.

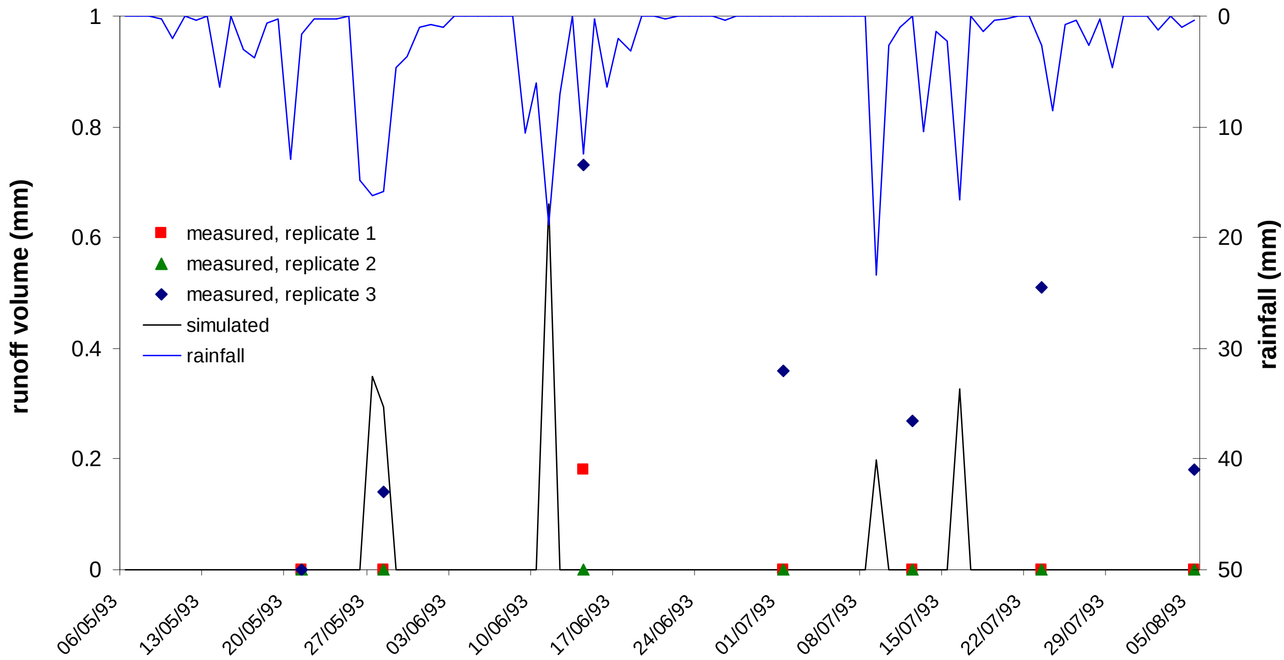

Fig. 4.1: Measured vs. simulated runoff volumes for One Oak (sandy loam).

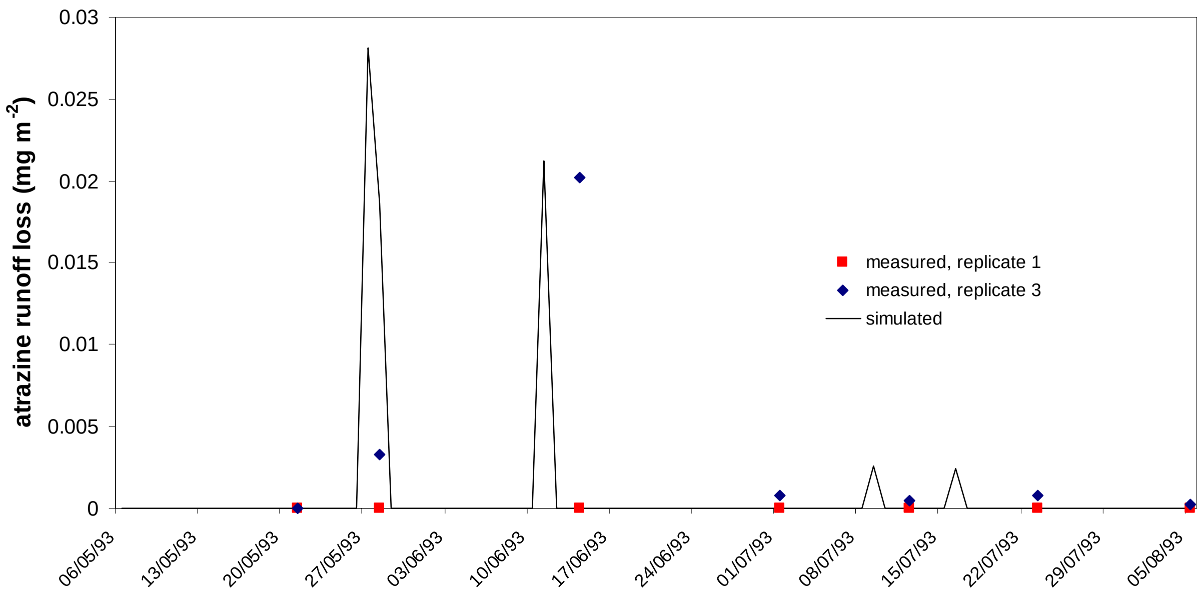

Fig. 4.2: Measured vs. simulated atrazine runoff losses for One Oak (sandy loam).

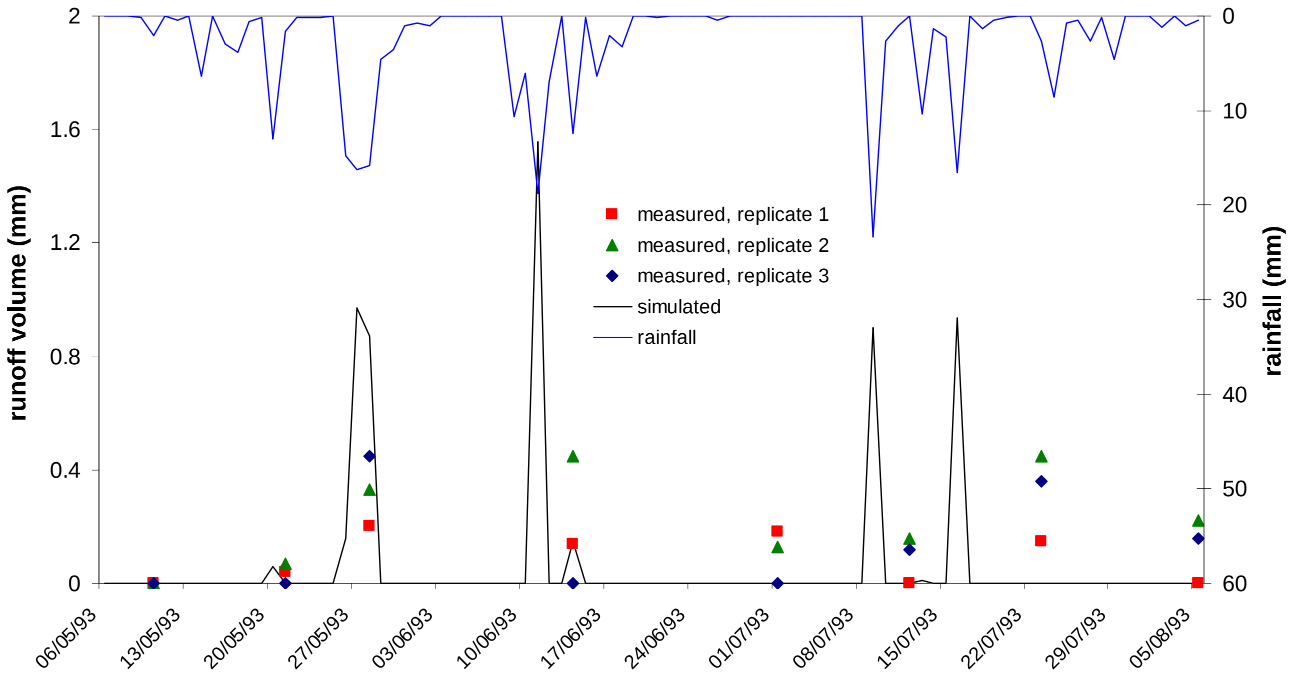

Fig. 4.3: Measured vs. simulated runoff volumes for Firs Farm (clay loam)

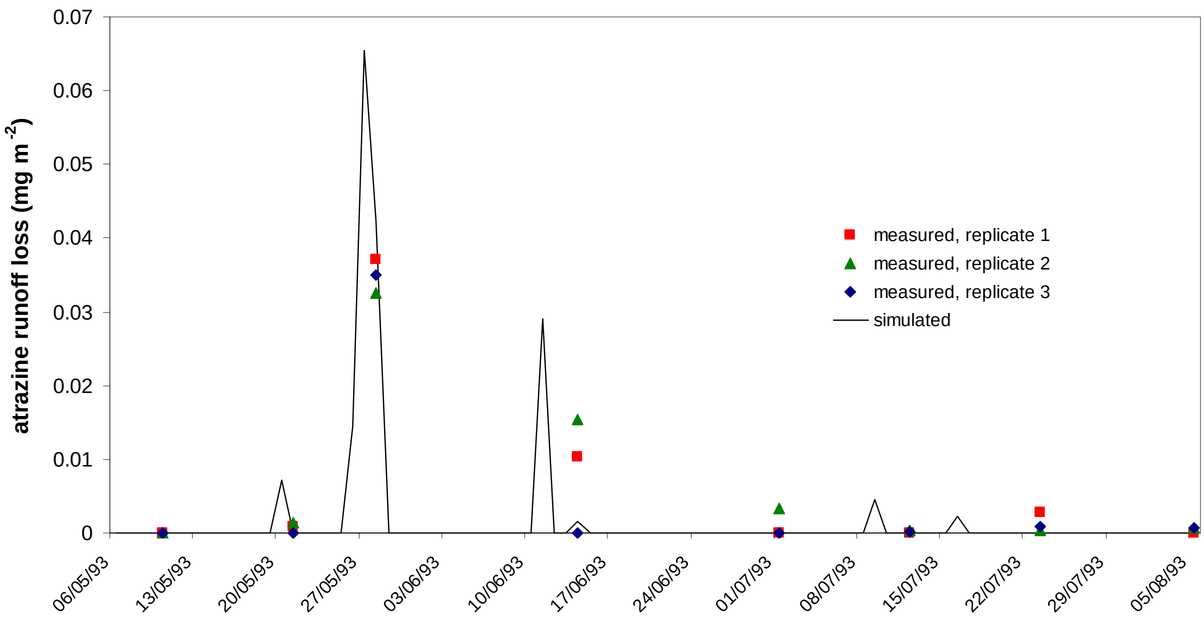

Fig. 4.4: Measured vs. simulated atrazine runoff losses for Firs Farm (clay loam).

4.2.1.2 Schmallenberg

The Schmallenberg runoff study was conducted in spring 1993 by the Fraunhofer Institute for Molecular Biology and Applied Ecology (IME, formerly IUCT). The site is located in the German lower mountain range area. The soil is a Cambisol (FAO, 1988) derived from a mixture of loess and periglacial solifluction layers. The experimental plot has an area of 1200 m^2, a slope length of 60 m and a slope of 8 %. The available soil properties are shown in Table 4.10. The soil was grouped into soil hydrologic group B by expert judgement. Due to the high content of coarse rock fragments ("Bodenskelett"), the pore volume of this soil is substantially reduced compared to a stone-free soil. Hence, for the PRZM simulations the calculated field capacity and wilting point water content were corrected by a factor of (1-(fraction of rock fragments)).

Table 4.10: Soil properties of Schmallenberg (silt loam; Klöppel et al., 1997**)**

	fine earth fraction (< 2 mm diameter)				coarse rock	
depth	clay (0-2 µm)	silt (2-63 µm)	sand (63-2000 µm)	organic carbon	fragments (> 2 mm)	pH ($CaCl_2$)
cm	% of fine earth fraction				%	
0-22	21	53	26	2.7	50-75	5.3
25-35	19	55	26	0.76	70-80	5.5
35-80+	11	50	39	n.d.[1)]	80-90	5.4

[1)] not determined

The field was cropped with triticale, with a plant cover of 42.3 % at the time of the experiment. On 13.04.1993 a mixture of isoproturon (1.16 kg ha^{-1}), dichlorprop-P (1.20 kg ha^{-1}) and bifenox (0.58 kg ha^{-1}) were applied by spraying. One day later the plot was irrigated with artificial rain at a rate of 14 mm h^{-1} for 2.5 hours. Runoff samples were collected at different points in the tractor lanes of the plot and in a central outlet with half of the plot as catchment. Eroded sediment was not measured at the outlet. Further experimental details can be found in Klöppel et al. (1997) and Kördel and Klöppel (1994).

Since erosion was not quantitatively measured in the Schmallenberg study, only simulated and measured runoff results can be compared. However, although some erosion was observed within the plot (tractor lanes), virtually no eroded material reached the plot outlet. Runoff from the plot started relatively late after ca. 8 mm cumulative rainfall, although it started earlier in the compacted tractor lanes (Kördel and Klöppel, 1994). Due to the high infiltration capacity of this soil, cumulative runoff was rather low (Table 4.11). The observed cumulative pesticide runoff losses were 0.04 % of the applied amount for isoproturon and dichlorprop-P; the strongly adsorbing herbicide bifenox was not detected in runoff water.

Table 4.11: Measured vs. simulated runoff volumes and pesticide runoff losses (cumulative values) for Schmallenberg (silt loam)

			measured values			simulated results			ratio predicted/ observed	
dataset	dose	compound	runoff	pest. runoff loss		runoff	pest. runoff loss		runoff	pest. runoff loss
	kg ha^{-1}		mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
Schmallen-berg	1.20	dichlorprop-P	0.343	0.48	0.04	0.883	2.184	0.182	2.573	4.55
	1.16	isoproturon	0.343	0.46	0.04	0.883	0.827	0.071	2.573	1.78
	0.58	bifenox	0.343	0	0	0.883	0.012	0.0021	2.573	-

PRZM overestimated the runoff volume by a factor of 2.5 (Table 4.11). This can be considered relatively good. However, if soil hydrologic group C (and the corresponding curve numbers) had been chosen as it is suggested by the soil texture, runoff would have been considerably overestimated by a factor of 11. Pesticide runoff losses were moderately overestimated for isoproturon by 78 %, and for dichlorprop-p by a factor of 4.6 (Table 4.11). In contrast to the measurements, PRZM predicted small runoff losses for bifenox with an average bifenox concentration of 1.38 µg L^{-1} in runoff water.

It can be concluded that PRZM was able to predict runoff volumes and pesticide runoff losses for the Schmallenberg study reasonably well, especially in view of the somewhat unusual soil at the test site.

4.2.1.3 Kleinhohenheim

This study was conducted in 1994 and 1995 at the University of Hohenheim, Germany (Spatz, 1999). The site is located in a loess area of Southern Germany. The soil is a Stagnic Luvisol according to FAO (1988) nomenclature. Topsoil properties are given in Table 4.12. According to the available properties, the soil was grouped into soil hydrologic group C. The field is tile-drained and has a slope of 9-11 %. The two experimental plots each had an area of 9000 m^2 and a slope length of 100 m.

Table 4.12: Topsoil properties of Kleinhohenheim (clay silt; Spatz, 1999)

depth (ca.)	clay (0-2 µm)	silt (2-63 µm)	sand (63-2000 µm)	organic carbon	CEC_{eff} [1)]	pH ($CaCl_2$)
cm		%		%	$cmol_c\ kg^{-1}$	
0-30	24	70	6	0.8	12	6.6

[1)] effective cation exchange capacity

In 1994, the first plot was cropped with maize, the second with spring barley. Spring barley was sown on 30.03.1994, and maize on 03.05.1994. On 17.05.1994., terbuthylazine (0.98 kg ha^{-1}) and pendimethalin (2.0 kg ha^{-1}) were applied on the maize plot, and isoproturon (1.50 kg ha^{-1}) on the barley plot. Runoff and eroded sediment were trapped with 1 m wide steel tubs; the traps did not have defined catchments.

In 1995 the crop pattern was reversed, and the runoff traps had catchments of 2.5 m width defined by sheet metal strips. Spring barley was sown on 25.03.1995, and maize on 24.04.1995. Pesticides were applied on 04.05.1995 at the same rate as the year before. Further details on the experiments are given in Spatz (1999).

The available site-specific meteorological data comprised hourly values of precipitation, maximum and minimum temperature and relative humidity. For the PRZM simulations, potential evapotranspiration was calculated according to the Haude equation (Klein, 1995); wind speed and solar radiation were obtained by using long-term monthly means of the FOCUS runoff scenario Weiherbach (FOCUS, 2001).

This study allows comparison of simulations and measurements for both runoff (Tables 4.13 and 4.15) and erosion (Tables 4.14 and 4.16). In Fig. H.13-H.27 in Appendix H, time series of measured vs. simulated runoff volumes and pesticide runoff losses are shown to visualize timing and magnitude of the simulated events with respect to daily precipitation and observed events.

1994 (experimental period: 17.05.94 – 20.09.94):

On 08.06.1994 an extreme rainfall event (max. 30-minute intensity: 52 mm h^{-1}, max. 5-minute intensity: 144 mm h^{-1}) occurred leading to the formation of deep erosion gullies in both plots, especially the maize plot. The gullies changed the hydrologic behaviour of the plots substantially and irreversibly. Furthermore, heavy surface sealing occurred on the maize plot. Five of eight runoff traps flew over on 08.06.1994; for these traps, runoff volumes and eroded sediment yields could only be extrapolated (Spatz, 1999). Since the runoff traps had no defined catchment, the size of the actual catchment had to be estimated in order to be able to calculate losses per area. Finally, the catchment area of each trap was assumed here as 50 m^2, in analogy to the 1995 experiments. Due to analytical problems, isoproturon could not be quantified in 1994; hence, only the maize plot can be used for a comparison between measured and simulated results.

Simulated and measured runoff volumes and pesticide runoff losses show relatively good agreement, both for cumulative and maximum values (Table 4.13 and 4.15, resp.). Eroded sediment yield was underpredicted by a factor of 5 (cumulative values, Table 4.14) and 10 (maximum values, Table 4.16). Pendimethalin losses via erosion were acceptably underestimated by a factor of 5 (both cumulative and maximum values), whereas terbuthylazine erosion losses were strongly underestimated by PRZM. The underestimation of soil erosion can be explained by the occurrence of deep gully formation and surface sealing at the extreme event of 08.06.1994, which greatly enhanced soil erodibility for the rest of the study period; this increase in erodibility could not be accounted for in PRZM. The timing of the events was simulated adequately, but not their magnitude (Fig. H.13-H.18, Appendix H).

1995 (experimental period: 04.05.95 - 25.09.95 for maize, 04.05.95 - 09.08.95 for barley):

Due to unusually few thunderstorms, rainfall intensities were comparatively low in this year. Only 4 runoff events occurred in both plots.

For the maize plot, total and peak runoff and soil loss were overestimated within the acceptable range by factors between 2 and 8 for two of the three replicate traps (Tables 4.13-4.16). In the third replicate, almost no runoff occurred in the experiment. The analogous was found for pesticide losses via runoff and erosion, with pendimethalin losses consistently more overpredicted than terbuthylazine losses. Although PRZM predicted some more runoff events than were actually observed, the timing of events was acceptably simulated (Fig. H.19-H.24, Appendix H).

For the barley plot, total and peak runoff volume and eroded sediment yield were heavily overestimated, and isoproturon runoff losses even more (Tables 4.13-4.16). Isoproturon could not be detected in eroded sediment. However, this was probably due to the insensitive analytical detection method employed (limit of detection (LOD) was 0.164 mg kg^{-1}). Also in runoff water, LOD was rather poor with 1.83 µg L^{-1}. Similar to the maize plot in this year, PRZM predicted more runoff events than occurred (Fig. H.25-H.27, Appendix H).

It can be summarized that PRZM underpredicted soil erosion and pesticide erosion losses in the year with an extreme rainfall event, and overpredicted runoff, erosion and pesticide losses in the year without heavy rainfalls. This may largely be due to the daily calculation time step of PRZM. Actual rainfall intensities are not considered in PRZM (only the general rainfall regime for erosion calculations). Hence, PRZM is likely to underestimate runoff and erosion for short, high-intensity rainfalls (e.g. thunderstorms) and to overestimate runoff and erosion for longer, low-intensity rainfalls ("Landregen").

Table 4.13: Measured vs. simulated runoff volumes and pesticide runoff losses (cumulative values) for Kleinhohenheim (clay silt)

				measured values (acc.)[1)]			simulated results (acc.)			ratio predicted / observed	
dataset	repli-cate	dose	compound	runoff	pest. runoff loss		runoff	pest. runoff loss		runoff	pest. runoff loss
		kg ha^{-1}		mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
maize, 1994	1	0.98	terbuthylazine	24.25	16.69	1.70	32.55	7.688	0.78	1.34	0.46
	2	0.98		27.85	19.64	2.00	32.55	7.688	0.78	1.17	0.39
	3	0.98		23.66	12.47	1.27	32.55	7.688	0.78	1.38	0.62
	4	0.98		36.41	8.385	0.86	32.55	7.688	0.78	0.89	0.92
	1	2.00	pendimethalin	24.25	1.591	0.08	32.55	2.652	0.13	1.34	1.67
	2	2.00		27.85	1.988	0.10	32.55	2.652	0.13	1.17	1.33
	3	2.00		23.66	1.073	0.05	32.55	2.652	0.13	1.38	2.47
	4	2.00		36.41	0.594	0.03	32.55	2.652	0.13	0.89	4.46
maize, 1995	1	0.98	terbuthylazine	4.92	3.550	0.36	26.48	6.981	0.71	5.39	1.97
	2	0.98		4.79	1.918	0.20	26.48	6.981	0.71	5.53	3.64
	3	0.98		0.037	0.016	0.002	26.48	6.981	0.71	723	446
	1	2.00	pendimethalin	4.92	0.131	0.007	26.48	2.102	0.11	5.39	16.1
	2	2.00		4.79	0.079	0.004	26.48	2.102	0.11	5.53	26.7
	3	2.00		0.037	6.8E-04	3.4E-05	26.48	2.102	0.11	723	3078
spring barley, 1995	1	1.50	isoproturon	0.31	3.7E-03	2.5E-04	20.97	7.031	0.47	67.6	1883
	2	1.50		1.02	0.077	0.005	20.97	7.031	0.47	20.6	91.6
	3	1.50		1.38	0.451	0.03	20.97	7.031	0.47	15.2	15.6

[1)] Measured values for 1994 are only estimates because the runoff traps did not have defined catchments and substantial overflow of the traps occurred on 08.06.1994.

Table 4.14: Measured vs. simulated soil erosion and pesticide erosion losses (cumulative values) for Kleinhohenheim (clay silt)

dataset	repli-cate	dose	compound	measured values (acc.)[1)]			simulated results (acc.)			ratio predicted / observed	
				sedi-ment yield	pest. erosion loss		sedi-ment yield	pest. erosion loss		sedi-ment yield	pest. erosion loss
		$kg\ ha^{-1}$		$g\ m^{-2}$	$g\ ha^{-1}$	% of applied	$g\ m^{-2}$	$g\ ha^{-1}$	% of applied		
maize, 1994	1	0.98	terbuthylazine	2415.6	26.13	2.67	502.7	0.142	0.015	0.21	0.005
	2	0.98		2822.6	23.64	2.41	502.7	0.142	0.015	0.18	0.006
	3	0.98		2400.6	21.57	2.20	502.7	0.142	0.015	0.21	0.007
	4	0.98		3307.8	29.99	3.06	502.7	0.142	0.015	0.15	0.005
	1	2.00	pendimethalin	2415.6	61.50	3.08	502.7	14.22	0.71	0.21	0.23
	2	2.00		2822.6	69.55	3.48	502.7	14.22	0.71	0.18	0.20
	3	2.00		2400.6	56.55	2.83	502.7	14.22	0.71	0.21	0.25
	4	2.00		3307.8	86.29	4.31	502.7	14.22	0.71	0.15	0.16
maize, 1995	1	0.98	terbuthylazine	50.32	0.035	0.004	205.8	0.093	0.009	4.09	2.66
	2	0.98		25.96	0.074	0.008	205.8	0.093	0.009	7.93	1.26
	3	0.98		3.82	n.d.[2)]	0	205.8	0.093	0.009	53.8	-
	1	2.00	pendimethalin	50.32	0.172	0.009	205.8	4.031	0.20	4.09	23.4
	2	2.00		25.96	0.327	0.016	205.8	4.031	0.20	7.93	12.3
	3	2.00		3.82	8.4E-04	4.2E-05	205.8	4.031	0.20	53.8	4827
spring barley, 1995	1	1.50	isoproturon	1.79	n.d.[3)]	-	136.3	0.015	0.001	76.0	-
	2	1.50		5.37	n.d.[3)]	-	136.3	0.015	0.001	25.4	-
	3	1.50		19.40	n.d.[3)]	-	136.3	0.015	0.001	7.03	-

[1)] Measured values for 1994 are only estimates because the traps did not have defined catchments and substantial overflow of the traps occurred on 08.06.1994.

[2)] n.d. = not detected

[3)] very high detection limit for isoproturon; isoproturon erosion loss is probably > 0

Table 4.15: Measured vs. simulated runoff volumes and pesticide runoff losses (maximum values) for Kleinhohenheim (clay silt)

				measured values (max.)[1)]			simulated results (max.)			ratio predicted / observed	
dataset	repli-cate	dose	compound	runoff	pest. runoff loss		runoff	pest. runoff loss		runoff	pest. runoff loss
		kg ha^{-1}		mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
maize, 1994	1	0.98	terbuthylazine	13.34	13.11	1.34	7.11	7.103	0.72	0.53	0.54
	2	0.98		15.62	14.48	1.48	7.11	7.103	0.72	0.46	0.49
	3	0.98		15.70	10.31	1.05	7.11	7.103	0.72	0.45	0.69
	4	0.98		14.68	4.522	0.46	7.11	7.103	0.72	0.48	1.57
	1	2.00	pendimethalin	13.34	1.297	0.06	7.11	0.686	0.03	0.53	0.53
	2	2.00		15.62	1.518	0.08	7.11	0.686	0.03	0.46	0.45
	3	2.00		15.70	0.884	0.04	7.11	0.686	0.03	0.45	0.78
	4	2.00		14.68	0.244	0.01	7.11	0.686	0.03	0.48	2.81
maize, 1995	1	0.98	terbuthylazine	2.66	3.032	0.31	10.23	6.691	0.68	3.85	2.21
	2	0.98		2.70	1.231	0.13	10.23	6.691	0.68	3.79	5.43
	3	0.98		0.024	0.016	0.002	10.23	6.691	0.68	426	432
	1	2.00	pendimethalin	2.66	0.110	0.005	10.23	0.739	0.04	3.85	6.74
	2	2.00		2.70	0.049	0.002	10.23	0.739	0.04	3.79	15.1
	3	2.00		0.024	5.7E-04	2.9E-05	10.23	0.739	0.04	426	1296
spring barley, 1995	1	1.50	isoproturon	0.14	3.7E-03	2.5E-04	7.72	6.861	0.46	55.2	1838
	2	1.50		0.98	0.051	0.003	7.72	6.861	0.46	7.88	133.3
	3	1.50		1.22	0.420	0.03	7.72	6.861	0.46	6.33	16.3

Measured values for 1994 are only estimates because the traps did not have defined catchments and substantial overflow of the traps occurred on 08.06.1994.

Table 4.16: Measured vs. simulated soil erosion and pesticide erosion losses (maximum values) for Kleinhohenheim (clay silt)

dataset	repli-cate	dose	compound	measured values (max.)[1)]			simulated results (max.)			ratio predicted / observed	
				sedi-ment yield	pest. erosion loss		sedi-ment yield	pest. erosion loss		sedi-ment yield	pest. erosion loss
		kg ha^{-1}		g m^{-2}	g ha^{-1}	% of applied	g m^{-2}	g ha^{-1}	% of applied		
maize, 1994	1	0.98	terbuthylazine	1494.7	23.32	2.38	149.5	0.133	0.014	0.10	0.006
	2	0.98		1890.1	21.36	2.18	149.5	0.133	0.014	0.08	0.006
	3	0.98		1569.0	19.30	1.97	149.5	0.133	0.014	0.10	0.007
	4	0.98		1467.3	23.18	2.37	149.5	0.133	0.014	0.10	0.006
	1	2.00	pendimethalin	1494.7	48.88	2.44	149.5	10.81	0.54	0.10	0.22
	2	2.00		1890.1	58.59	2.93	149.5	10.81	0.54	0.08	0.18
	3	2.00		1569.0	46.76	2.34	149.5	10.81	0.54	0.10	0.23
	4	2.00		1467.3	56.05	2.80	149.5	10.81	0.54	0.10	0.19
maize, 1995	1	0.98	terbuthylazine	46.02	0.032	0.003	110.6	0.093	0.009	2.40	2.87
	2	0.98		14.46	0.039	0.004	110.6	0.093	0.009	7.65	2.38
	3	0.98		3.30	n.d.[2)]	0	110.6	0.093	0.009	33.5	-
	1	2.00	pendimethalin	46.02	0.138	0.007	110.6	2.573	0.13	2.40	18.6
	2	2.00		14.46	0.144	0.007	110.6	2.573	0.13	7.65	17.9
	3	2.00		3.30	8.4E-04	4.2E-05	110.6	2.573	0.13	33.5	3081
spring barley, 1995	1	1.50	isoproturon	0.844	n.d.[3)]	-	70.14	0.014	0.001	83.1	-
	2	1.50		5.20	n.d.[3)]	-	70.14	0.014	0.001	13.5	-
	3	1.50		15.12	n.d.[3)]	-	70.14	0.014	0.001	4.64	-

[1)] Measured values for 1994 are only estimates because the traps did not have defined catchments and substantial overflow of the traps occurred on 08.06.1994.

[2)] n.d. = not detected

[3)] very high detection limit for isoproturon; isoproturon erosion loss is probably > 0

4.2.1.4 Rosemaund

The Rosemaund pesticide transport study (Williams et al., 1996) was carried out over the period 1987 to 1993 at the ADAS Rosemaund Research Centre in Herefordshire, UK. The objectives of this study were to monitor pesticide transport from an agricultural catchment under conditions of normal agricultural practice, and to increase understanding of the processes that control pesticide movement. In the framework of this study, also runoff experiments were conducted. The runoff study site was located at the border of two soil mapping units (Table 4.17); hence, the soil properties were interpolated for the PRZM modelling. The soil was grouped into soil hydrologic group C. On 06.11.1992 trifluralin was applied pre-emergence to winter wheat at a rate of 1.10 kg ha^{-1}. Surface runoff samples were collected from 06.11.1992 to 01.05.1993 using 1 m wide steel troughs as runoff traps. The traps did not have defined catchments. Eroded sediment was not measured.

Table 4.17: Soil properties at the Rosemaund runoff site (strongly silty clay; Williams et al., 1996)

soil series	depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	organic carbon	pH (water)
	cm	%	%	%	%	
Bromyard series, normal phase	0-30	31	60	9	1.66	6.3
	30-48	32	58	10	0.91	6.8
	48-67	43	52	5	0.66	6.7
	67-83	46	50	4	0.37	6.7
Bromyard series, shallow phase	0-22	28	70	1	1.80	6.3
	22-31	30	66	3	1.35	6.5
	31-60	28	71	3	0.30	6.2
	60-78	26	73	1	0.28	5.8
	78-112	20	79	1	0.29	5.8

The available site-specific meteorological data comprised hourly values for precipitation, solar radiation, wind speed and soil temperature (as a surrogate for air temperature), as well as daily potential evapotranspiration according to Penman.

As the runoff traps did not have defined catchments, the measured runoff volumes and pesticide losses could not be related to an area. Hence, only measured and simulated trifluralin concentrations in runoff water could be compared (Fig. H.28, Appendix H).

The predicted trifluralin concentrations (4-5 µg L^{-1}) were well in the range of the measured concentrations (0.15-86 µg L^{-1}). However, PRZM failed to reproduce the sharp observed decline of trifluralin concentrations in runoff water from the first to the following runoff events.

The timings of simulated and measured runoff events matched only poorly (Fig. H.28, Appendix H). This might be explained by the fact that the meteorological station was situated at about 1 km distance from the runoff study site. The true rainfall was possibly different from that used in the simulations.

4.2.1.5 Cockle Park

The Cockle Park study was conducted by Colin Brown (now CSL York, UK) and is described in detail in Brown et al. (1995). The site is located in NE-England and contained three plots with 0.25 ha (25 m × 100 m) each and 2 % slope. The soil is a Stagno-Gleyic Luvisol (FAO, 1988) and is characterized by a sharp transition between a finely structured, permeable topsoil (sandy loam) and a massively prismatic, only slowly permeable subsoil (clay loam). Basic soil properties are given in Table 4.18. A perched water table is present over the whole year within the top 100 cm of the soil and can rise almost to the surface in absence of drains. The soil was grouped into soil hydrologic group C.

Table 4.18: Soil properties of the Cockle Park site (Brown, pers. comm., 2002; Beulke et al., 1998)

depth	clay (0-2 µm)	silt (2-60 µm)	sand (60-2000 µm)	OC	dry bulk density	pH (water)
cm		%		%	kg dm^{-3}	
0-15	22	31	47	3.27	1.12 [1)]	5.80
15-30	22	31	47	2.48	n.a.[2)]	6.39
30-45	24	32	44	1.10	n.a.	7.08
45-60	37	36	26	0.94	1.50 [3)]	7.22
60-75	37	36	26	0.89	n.a.	7.03
75-90	32	37	31	0.79	n.a.	7.29

[1)] at 10 cm depth
[2)] n.a. = not available
[3)] at 60 cm depth

Two of the plots were mole-drained, the third plot was an undrained control. While the mole-drained plot A was used for drainflow modelling with MACRO (cf. section 3.2.1.6), the undrained plot C was used for PRZM testing.

Isoproturon and trifluralin were applied to a winter wheat crop in two successive seasons (01.09.89 – 31.08.91). On 27.11.1989, 1.96 kg ha^{-1} isoproturon and 0.96 kg ha^{-1} trifluralin were applied by spraying to plot C. On 13.11.1990, 2.50 kg ha^{-1} isoproturon and again 0.96 kg ha^{-1} trifluralin were applied. Surface layer flow (surface runoff + lateral flow through the topsoil) was collected by an interceptor drain to a depth of 30 cm at the bottom of the plot. Sampling for pesticide analysis was done automatically on the basis of flow rate. Water samples were split into aqueous phase and sediment by filtering through a 0.7 µm filter. Both phases were analyzed for pesticides. The sampling method implies that only the eroded sediment was captured that had not settled in the interceptor drain before sampling.

The available site-specific weather data comprised daily maximum and minimum temperature and precipitation. The missing meteorological variables were obtained as follows. Potential evapotranspiration was obtained using Linacre's method (Linacre, 1977) and the same correction factor of 0.73 as for the Cockle Park drainflow study (cf. section 3.2.1.6). For wind speed and solar radiation long-term monthly averages of the FOCUS surface water scenario Brimstone were used.

This study allows comparison of simulations and measurements for both runoff (Table 4.19 and 4.21) and erosion (Tables 4.20 and 4.22). In Fig. H.29-H.34 (Appendix H), time series of measured vs. simulated runoff volumes, sediment yields and pesticide runoff and erosion losses are shown to visualize timing and magnitude of the simulated events with respect to daily precipitation and observed events. The comparability of measured and simulated values is impaired by some circumstances though:

- The interceptor drains did not exclusively capture runoff (overland flow), but integrated runoff and shallow interflow (lateral flow through the topsoil). However, PRZM only simulates surface runoff.
- Since sampling was not fully continuous, cumulative pesticide loads and sediment yield over the study period had to be calculated by interpolation between sampling events (Brown et al., 1995). This adds further uncertainty to the measured pesticide runoff and erosion losses.
- Only the eroded sediment was captured that was still suspended in the runoff/interflow water at the time of sampling and had not settled in the interceptor drain before. Therefore, the measured values may underestimate the actual sediment yield and pesticide erosion loss from the plot.

The cumulative simulated runoff volumes were about ten times smaller than the measured surface runoff + shallow interflow volumes (Table 4.19), while the simulated and measured maximum daily runoff volumes differed only by a factor of 2 (Table 4.21). As the ratio of runoff to interflow volumes will increase with increasing rainfall intensity, the simulation results can be considered realistic in this respect.

PRZM overestimated total and maximum eroded sediment yields by a factor of 2 for the first study year, where only very little erosion occurred (Tables 4.20 and 4.22). In the second year, total and peak sediment yields were underestimated by factors of 7 and 4, respectively. Thus, the simulated sediment yields were within the acceptable range for both years. However, it has to be kept in mind that the measured sediment yields were probably too low and also rather uncertain.

For both cumulative and maximum values, isoproturon runoff losses were substantially overestimated in the first year (01.09.1989 – 31.08.1990), where only small IPU losses were observed. In the second study year (01.09.1990 – 31.08.1991), total and peak IPU runoff losses were underestimated by 76 and 19 %, respectively. Trifluralin runoff losses were overestimated in both years (Tables 4.19 and 4.21).

Pesticide erosion losses were considerably overestimated for both compounds in the first year, where only very little erosion occurred (Tables 4.20 and 4.22). In the second study year, isoproturon erosion losses were underestimated by a factor of 250 for cumulative values and 50 for maximum values, while trifluralin losses were acceptably overpredicted by factors of 1.4 and 2.4, respectively.

Although the timing of the events was acceptably simulated, the magnitude of the single events was generally predicted badly by PRZM (Fig. H.29-H.34, Appendix H). PRZM was neither able to reproduce the observed differences in runoff volumes, sediment yields and pesticide runoff and erosion losses between the two study years. The most probable explanation for these findings is that the hydrology at the Cockle Park site (a soil prone to waterlogging with a permeable over a slowly permeable layer and a permanent perched water table) is too complex to be emulated with the simple PRZM hydrology, where neither waterlogging nor lateral flow occur.

Although the agreement between PRZM simulations and measurements was relatively poor for the Cockle Park study, the restricted comparability of measured and simulated results (see above) does not allow to finally judge the performance of PRZM in this case as inadequate. Due to this insufficient comparability, the Cockle Park study was not included in the general discussion of the model evaluation exercise (section 4.2.2).

Table 4.19: Measured vs. simulated runoff volumes and pesticide runoff losses (cumulative values) for Cockle Park (sandy loam over clay loam), undrained plot

			measured values (acc.)			simulated results (acc.)			ratio predicted / observed	
period	dose	compound	runoff[1)]	pest. runoff loss[2)]		runoff	pest. runoff loss		runoff	pest. runoff loss
	kg ha^{-1}		mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
89-91	4.46		242.62	12.01	0.27	23.16	8.307	0.19	0.10	0.69
89-90	1.96	isoproturon	66.89	0.732	0.04	8.73	5.624	0.29	0.13	7.68
90-91	2.50		175.73	11.28	0.45	14.43	2.683	0.11	0.08	0.24
89-91	1.92		242.62	0.158	0.008	23.16	0.662	0.034	0.10	4.19
89-90	0.96	trifluralin	66.89	0.024	0.003	8.73	0.202	0.021	0.13	8.29
90-91	0.96		175.73	0.134	0.014	14.43	0.460	0.048	0.08	3.44

1) includes also lateral flow through the topsoil

2) interpolated values (Brown et al., 1995)

Table 4.20: Measured vs. simulated sediment yield and pesticide erosion losses (cumulative values) for Cockle Park (sandy loam over clay loam), undrained plot

			measured values (acc.)			simulated results (acc.)			ratio predicted / observed	
period	dose	compound	sediment yield[1)]	pest. erosion loss[2)]		sediment yield	pest. erosion loss		sediment yield	pest. erosion loss
	kg ha^{-1}		g m^{-2}	g ha^{-1}	% of applied	g m^{-2}	g ha^{-1}	% of applied		
89-91	4.46		26.11	0.080	0.002	5.89	0.0035	7.7E-05	0.23	0.04
89-90	1.96	isoproturon	1.19	4.0E-05	2.0E-06	2.33	0.0031	1.6E-04	1.96	77.9
90-91	2.5		24.93	0.080	0.003	3.56	3.4E-04	1.3E-05	0.14	0.004
89-91	1.92		26.11	0.076	0.004	5.89	0.206	0.011	0.23	2.72
89-90	0.96	trifluralin	1.19	0.0048	5.0E-04	2.33	0.107	0.011	1.96	22.3
90-91	0.96		24.93	0.071	0.007	3.56	0.098	0.010	0.14	1.39

1) only sediment contained in samples for pesticide analysis

2) interpolated values (Brown et al., 1995)

Table 4.21: Measured vs. simulated runoff volumes and pesticide runoff losses (maximum values) for Cockle Park, undrained plot

			measured values (max.)			simulated results (max.)			ratio predicted / observed	
period	dose	compound	runoff[1)]	pest. runoff loss[2)]		runoff	pest. runoff loss		runoff	pest. runoff loss
	kg ha^{-1}		mm	g ha^{-1}	% of applied	mm	g ha^{-1}	% of applied		
89-91	4.46		8.91	2.745	0.06	4.76	4.066	0.09	0.53	1.48
89-90	1.96	isoproturon	8.91	0.156	0.008	3.85	4.066	0.21	0.43	26.1
90-91	2.5		7.99	2.745	0.11	4.76	2.212	0.09	0.60	0.81
89-91	1.92		8.91	0.014	7.4E-04	4.76	0.106	0.006	0.53	7.47
89-90	0.96	trifluralin	8.91	0.0037	3.9E-04	3.85	0.087	0.009	0.43	23.4
90-91	0.96		7.99	0.014	0.001	4.76	0.106	0.011	0.60	7.47

1) includes also lateral flow through the topsoil

1) When two or more samples were taken on the same day, daily mean pesticide concentrations were used for calculation of loads.

Table 4.22: Measured vs. simulated sediment yield and pesticide erosion losses (maximum values) for Cockle Park, undrained plot

			measured values (max.)			simulated results (max.)			ratio predicted / observed	
period	dose	compound	sediment yield[1)2)]	pest. erosion loss[2)]		sediment yield	pest. erosion loss		sediment yield	pest. erosion loss
	kg ha^{-1}		g m^{-2}	g ha^{-1}	% of applied	g m^{-2}	g ha^{-1}	% of applied		
89-91	4.46		6.22	0.011	2.5E-04	1.60	0.0016	3.5E-05	0.26	0.14
89-90	1.96	isoproturon	0.54	0	0	1.19	0.0016	8.0E-05	2.19	-
90-91	2.5		6.22	0.011	4.5E-04	1.60	2.6E-04	1.1E-05	0.26	0.02
89-91	1.92		6.22	0.023	0.001	1.60	0.072	0.004	0.26	3.08
89-90	0.96	trifluralin	0.54	0.0012	1.2E-04	1.19	0.072	0.008	2.19	62.34
90-91	0.96		6.22	0.023	0.002	1.60	0.056	0.006	0.26	2.39

[1)] only sediment contained in samples for pesticide analysis

[2)] When two or more samples were taken on the same day, daily mean pesticide and sediment concentrations were used.

4.2.1.6 Freising

This study was conducted by the Technical University of Munich, Germany (Haider, 1994). The site is located in the Bavarian tertiary hill area. The soil is a Cambisol (FAO, 1988) derived from sandy to gravelly tertiary sediments with loess cover. Basic soil properties are given in Table 4.23. As this soil contains a significant amount of coarse rock fragments, the calculated field capacity and wilting point water content were corrected by a factor of (1-(fraction of rock fragments)).

Table 4.23: Soil properties of Freising (sandy loam over loamy sand; Haider, 1994)

	fine earth fraction (< 2 mm diameter)				coarse rock	
depth	clay (0-2 µm)	silt (2-63 µm)	sand (63-2000 µm)	total carbon	fragments (> 2 mm)	pH ($CaCl_2$)
cm	% of fine earth fraction				%	
0-25	21	36	43	1	7-13	6.6
25-55	22	35	47	0.2	n.a.[1)]	6.6
55-80	11	14	73	0.1	n.a.	6.5
80-100	4	11	83	0.1	n.a.	6.5

[1)] n.a. = not available

The experimental field contained two plots with 187 m^2 each (34 m × 5.5 m), one cropped with spring barley (sown on 01.07.1991) and the other fallow. On 22.07.1991, the herbicides dichlorprop-P (1.20 kg ha^{-1}), isoproturon (1.17 kg ha^{-1}) and bifenox (0.58 kg ha^{-1}) were applied to both plots. Runoff and eroded sediment were captured by steel funnels at the bottom of the plots. Further experimental details are given in Haider (1994). Since the plots already showed considerable surface sealing due to high-intensity rainstorms before pesticide application, the soil was grouped into hydrologic group D instead of C for the simulations.

The available site-specific weather data comprised daily precipitation, maximum, minimum and mean temperature, relative humidity at 14.00 h and solar radiation. For the PRZM simulations, potential evapotranspiration was calculated according to Haude (Klein, 1995). Wind speed was obtained by using long-term monthly means of the FOCUS runoff scenario Weiherbach.

Apart from cumulative runoff volumes and sediment yields (Table 4.24), only cumulative total pesticide losses (runoff + erosion losses integrated) were available in Haider (1994) for a comparison with simulation results (Table 4.25). Measured values were available for both the whole study period and the first runoff event, which occurred two days after pesticide application.

The experimental period is characterized by high precipitation (120 mm rainfall fell between pesticide application on 22.07.1991 and the end of the study on 02.08.1991; 100 mm fell alone in the last three days of the study), large runoff volumes and eroded sediment yields, and high pesticide losses especially from the fallow plot.

For the fallow plot, total runoff volumes were slightly underestimated by 16 % for the whole study period, and by 59 % for the first runoff event (Table 4.24). For the barley plot, the underestimation of runoff volumes was a bit more pronounced. Following the same trend as the runoff volumes, eroded sediment yield was overpredicted by a factor of 2 for the whole study period, but for the first runoff event underestimated by factors of 3.5 (fallow plot) and 30 (barley plot). Here again a tendency of PRZM to underestimate runoff and soil erosion for high-intensity rainstorms is visible (cf. section 4.2.1.3).

Table 4.24: Measured vs. simulated runoff volumes and eroded sediment yields (cumulative values) for Freising (sandy loam over loamy sand)

		measured values (acc.)		simulated results (acc.)		ratio predicted / observed	
dataset	period	runoff	sediment yield	runoff	sediment yield	runoff	sediment yield
		mm	g m^{-2}	mm	g m^{-2}		
Freising, fallow	24.07. - 02.08.[1)]	78.0	2600	65.20	5278.2	0.84	2.03
	24.07. - 27.07.[2)]	9.5	640	3.87	179.8	0.41	0.28
Freising, spring barley	24.07. - 02.08.	47.0	260	34.77	469.2	0.74	1.80
	24.07. - 27.07.	2.5	40	0.50	1.27	0.20	0.03

[1)] all runoff events

[2)] first runoff event

Total pesticide losses (i.e., runoff and erosion losses combined) were underestimated for the fallow plot by factors of 2.5 to 5 (Table 4.25) and by factors around 2 for the barley plot and the whole study period. In contrast, losses of dichlorprop-P and isoproturon were moderately overpredicted for the first runoff event in the barley plot. As could be expected from the sorption properties of the three herbicides, PRZM predicted that runoff was the clearly dominant loss pathway for dichlorprop-P and isoproturon, whereas for the strongly sorbing bifenox larger erosion than runoff losses were simulated.

In summary, it can be stated that PRZM was able to predict runoff volumes, eroded sediment yields and pesticide runoff and erosion losses for the Freising study acceptably well.

Table 4.25: Measured vs. simulated total pesticide losses (cumulative values) for Freising

				measured losses (acc.)		simulated pesticide losses (acc.)				ratio predicted / observed
dataset	period	dose	compound	total pest. loss		runoff loss	erosion loss	total pest. loss		total loss
		$kg\ ha^{-1}$		$g\ ha^{-1}$	% of applied	$g\ ha^{-1}$	$g\ ha^{-1}$	$g\ ha^{-1}$	% of applied	
Freising, fallow	24.07. - 02.08.[1)]	1.20	dichlorprop-p	108.0	9	38.81	0.311	39.13	3.26	0.36
		1.17	isoproturon	187.2	16	52.57	0.850	53.42	4.57	0.29
		0.58	bifenox	58.0	10	4.891	19.11	24.01	4.14	0.41
	24.07. - 27.07.[2)]	1.20	dichlorprop-p	84.0	7	24.85	0.308	25.16	2.10	0.30
		1.17	isoproturon	105.3	9	19.42	0.774	20.19	1.73	0.19
		0.58	bifenox	17.4	3	0.342	4.543	4.885	0.84	0.28
Freising, spring barley	24.07. - 02.08.	1.20	dichlorprop-p	12.0	1	6.813	0.0050	6.818	0.57	0.57
		1.17	isoproturon	35.1	3	13.80	0.070	13.87	1.19	0.40
		0.58	bifenox	11.6	2	2.064	4.423	6.487	1.12	0.56
	24.07. - 27.07.	1.20	dichlorprop-p	< 1.20	< 0.1	2.650	0.0046	2.655	0.22	> 2.21
		1.17	isoproturon	< 1.17	< 0.1	1.651	0.0097	1.661	0.14	> 1.42
		0.58	bifenox	< 0.58	< 0.1	0.034	0.074	0.108	0.02	> 0.19

[1)] all runoff events

[2)] first runoff event

4.2.2 General Discussion and Conclusions

The following logarithmic scatterplots provide a summary of the quality of the simulations for the runoff test data sets, comparing measured and simulated values of total and maximum daily surface runoff (Fig. 4.5 and 4.6, resp.), total and maximum daily eroded sediment yield (Fig. 4.7 and 4.8), and total and maximum daily pesticide loss via runoff (Fig. 4.9 and 4.10) and erosion (Fig. 4.11 and 4.12). Since not all target variables were available for all 12 test datasets, the scatterplots contain measured and simulated data only for 3 to 10 test datasets. Measured values from replicate runoff traps in the Temple Balsall and Hohenheim experiments were averaged before comparison with the corresponding simulated value. For the Cockle Park study, sufficient comparability of measured and simulated values was not given (cf. section 4.2.1.5). Hence, the results from this study were not included in the scatterplots. For the Freising study, measured and simulated values for both the whole study period and the first runoff event (cf. section 4.2.1.6) are included.

Fig. 4.5 shows that, except in one case, the deviations between simulated and measured cumulative runoff volumes were smaller than a factor of 10. No systematic over- or underestimation of runoff volumes was observed. The predicted maximum daily runoff volumes (Fig. 4.6) were all within a factor of 10 of the measurements. However, Fig. 4.6 reveals that PRZM tends to overestimate small runoff events (cf. section 4.2.1), which constitute the majority of data points. The only data point available for a major observed runoff event (ca. 15 mm, cf. Table 4.15, section 4.2.1.3) furtermore suggests that large runoff events are underestimated by PRZM. Except for the Rosemaund dataset, the timing of runoff events was simulated adequately.

Although simulated total and maximum eroded soil losses were in most cases (5 of 7 and 2 of 3, respectively) within a factor of 10 of the measurements (Fig. 4.7 and 4.8), soil loss predictions were generally worse than surface runoff predictions. This seems logical as the MUSS-simulated daily soil loss (cf. section 4.1.1) is a function of the daily runoff volume and several other USLE factors introducing further uncertainty. It has also to be noted that the USLE approach was originally intended for yearly or seasonal losses, and not for a daily time scale (Wischmeier, 1976). Due to the limited number of available data points, Fig. 4.7 and 4.8 do not allow to identify possible systematic deviations between measured and simulated eroded sediment yields. However, the three data points in Fig. 4.8 all come from the same study (Kleinhohenheim), for which the simulation yielded an underprediction of soil loss in the year with an extreme rainfall event and overprediction of soil loss in the year without heavy rainfalls (cf. section 4.2.1.3).

Cumulative pesticide runoff losses were acceptably predicted in 9 of 16 cases (Fig. 4.9). In the remaining 7 cases, all with a measured loss equal to or smaller than 0.01 % of the applied amount, pesticide losses were overpredicted by more than a factor of 10. Generally, the cumulative runoff losses tended to be overestimated. The maximum daily runoff losses (Fig. 4.10) yield a very similar picture, with acceptable predictions in 10 of 13 cases and three small loss events overpredicted by a factor greater than 10. Also the maximum daily runoff losses were overestimated in general.

Only 5 data points (all from the Kleinhohenheim study, cf. section 4.2.1.3) were available to compare measured and simulated values of pesticide erosion losses. For both cumulative and maximum daily losses (Fig. 4.11 and 4.12, resp.), only in 2 of 5 cases the simulated value was within the acceptable range. Since the simulated pesticide erosion losses integrate the uncertainty propagating from surface runoff, soil erosion, and chemical fate and transport simulation, the low quality of the predictions seems plausible. Also here it is visible that PRZM underpredicted pesticide erosion losses in a year with an extreme rainfall event (Kleinhohenheim, 1994) and overpredicted pesticide erosion losses in a year without heavy rainfalls (Kleinhohenheim, 1995; cf. section 4.2.1.3).

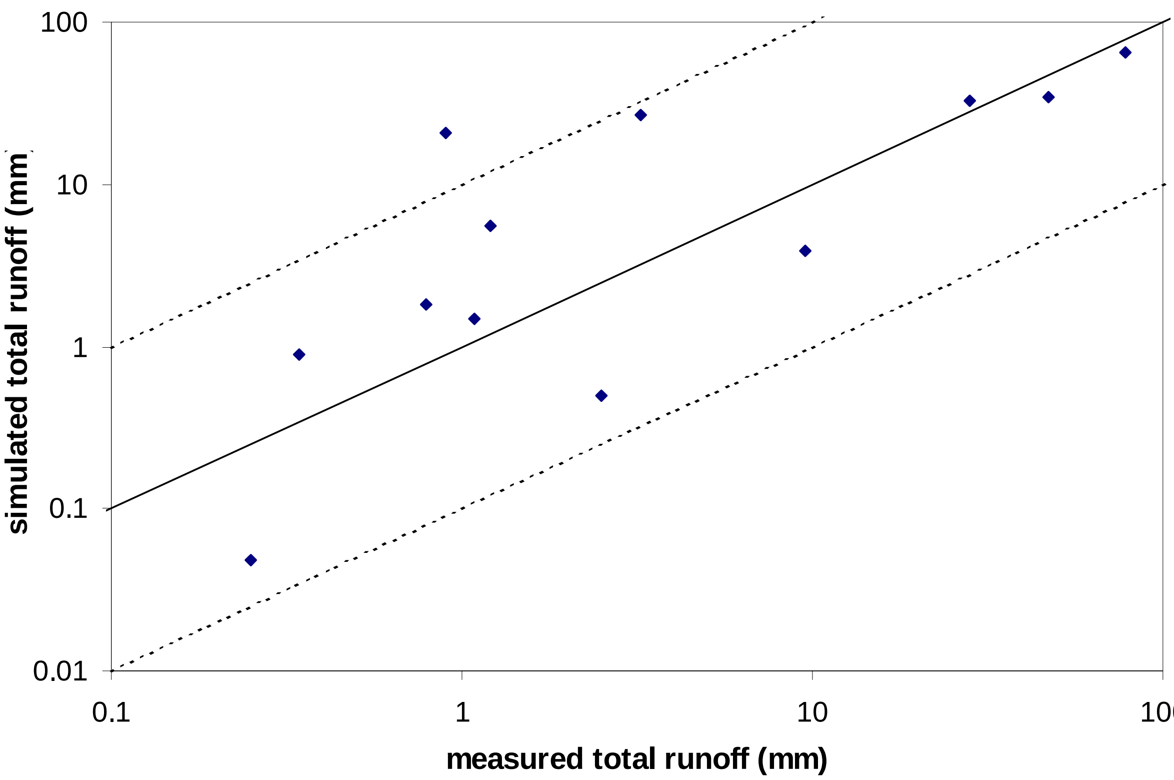

Fig. 4.5: Measured vs. simulated values of total runoff volume over the study period for 10 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10.

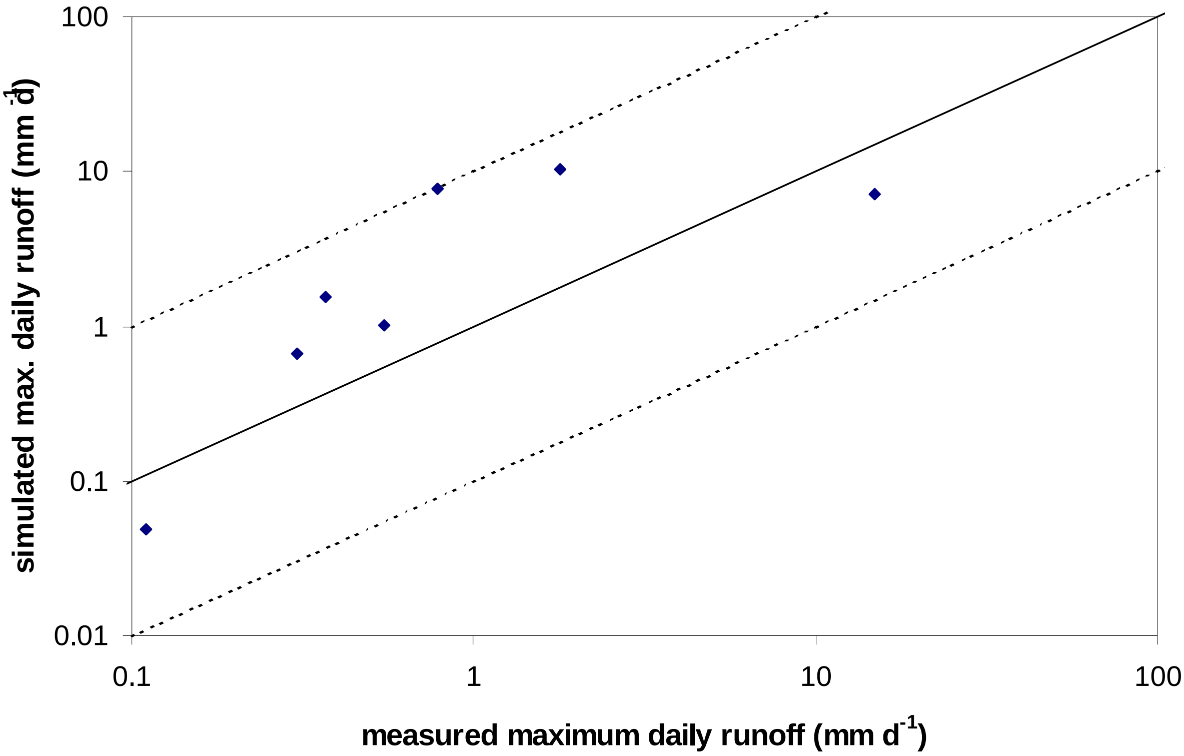

Fig. 4.6: Measured vs. simulated values of maximum daily runoff volume over the study period for 7 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10.

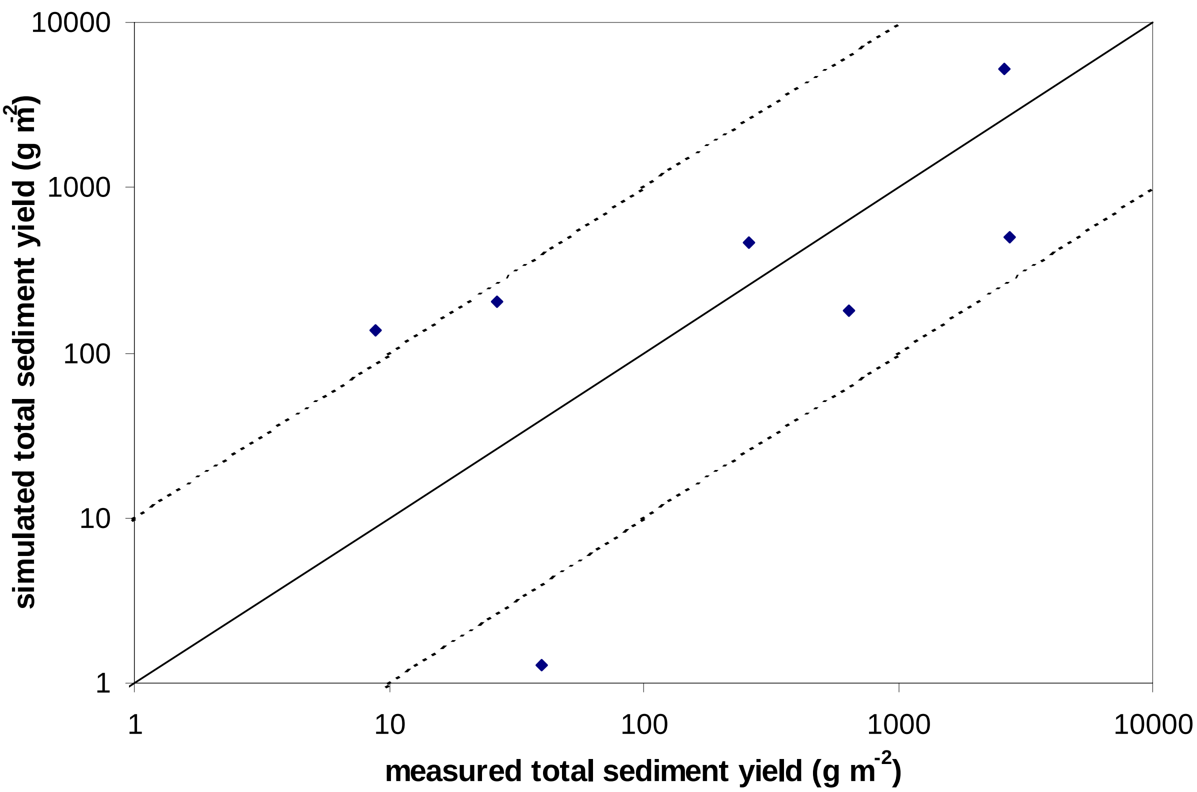

Fig. 4.7: Measured vs. simulated values of total eroded sediment over the study period for 5 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10.

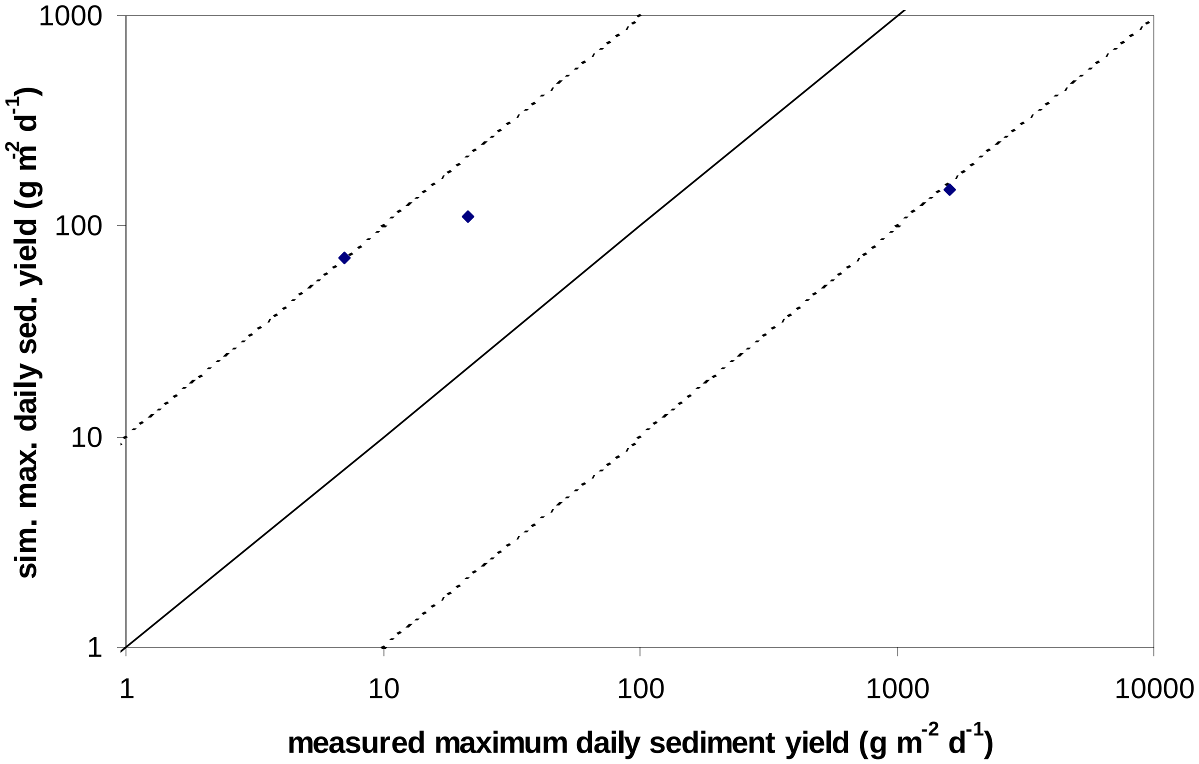

Fig. 4.8: Measured vs. simulated values of maximum daily eroded sediment yield over the study period for 3 test data sets (all from Kleinhohenheim). Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data point on the right belongs to the study year 1994, the two data points on the left to 1995.

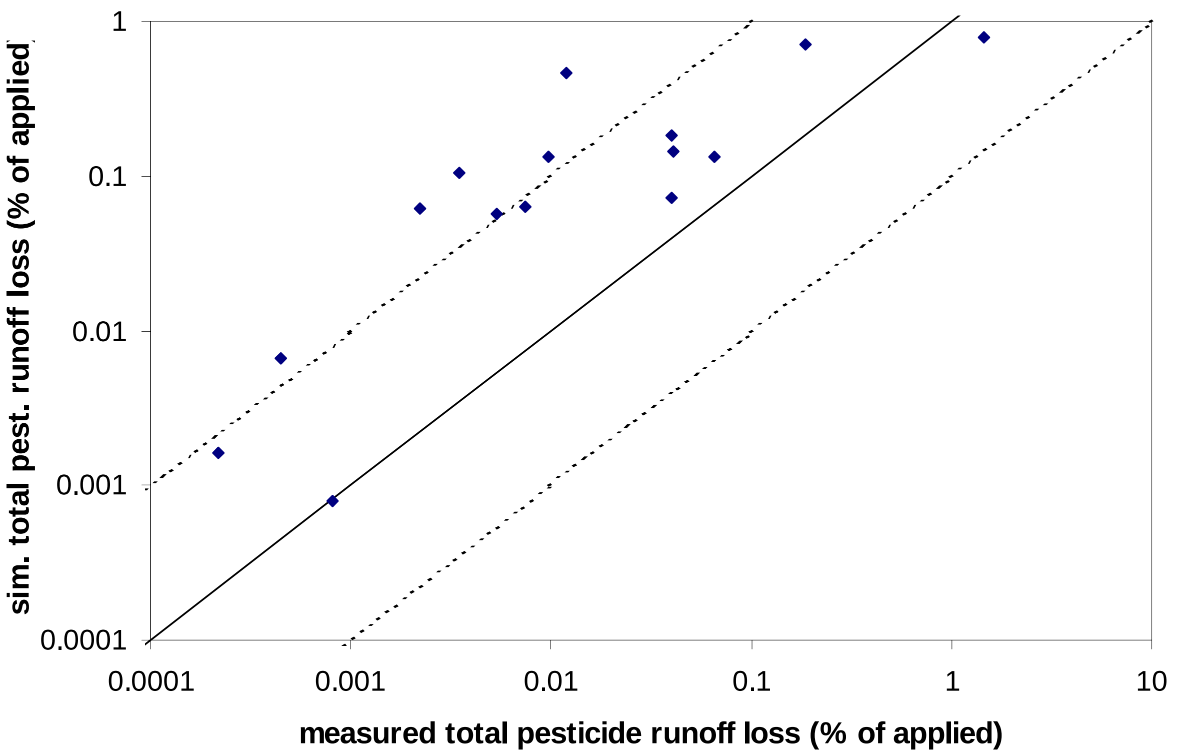

Fig. 4.9: Measured vs. simulated values of total pesticide runoff loss (relative to the applied amount) over the study period for 8 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data point (0; 0.0021) (Bifenox, Schmallenberg) cannot be shown due to the logarithmic plot.

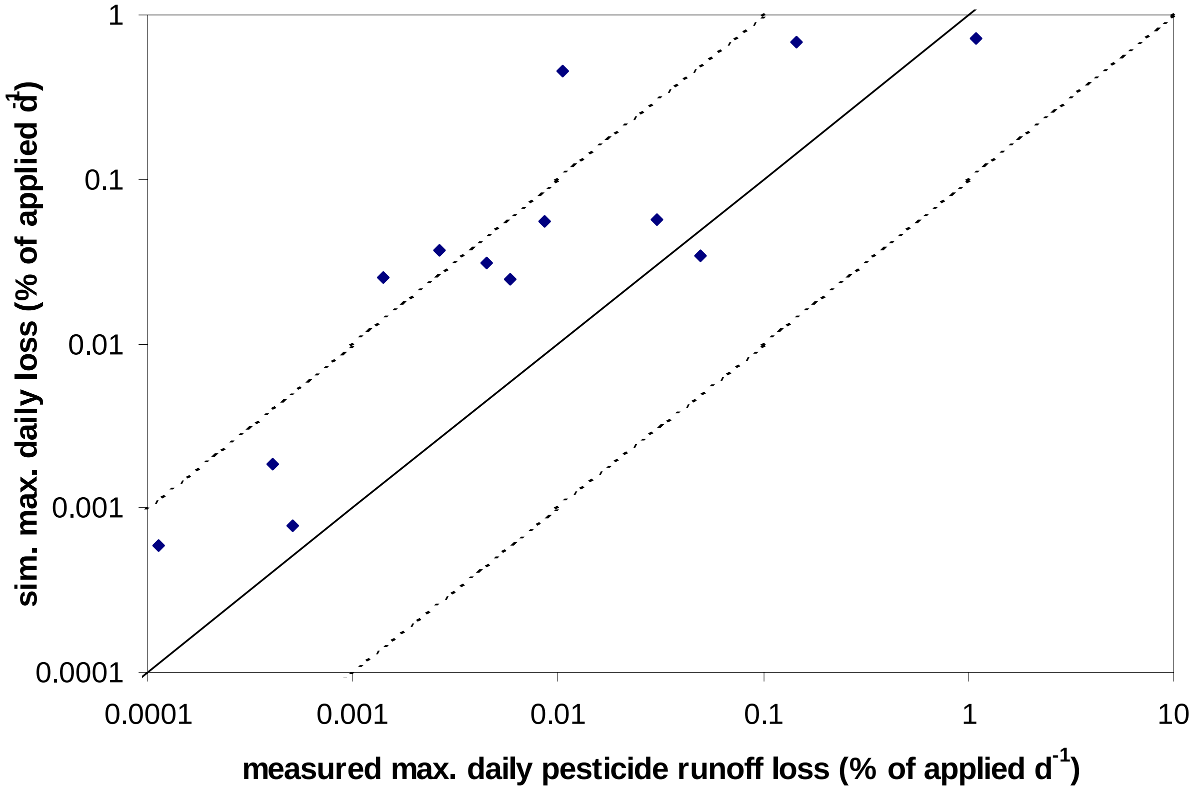

Fig. 4.10: Measured vs. simulated values of maximum daily pesticide runoff loss (relative to the applied amount) over the study period for 7 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10.

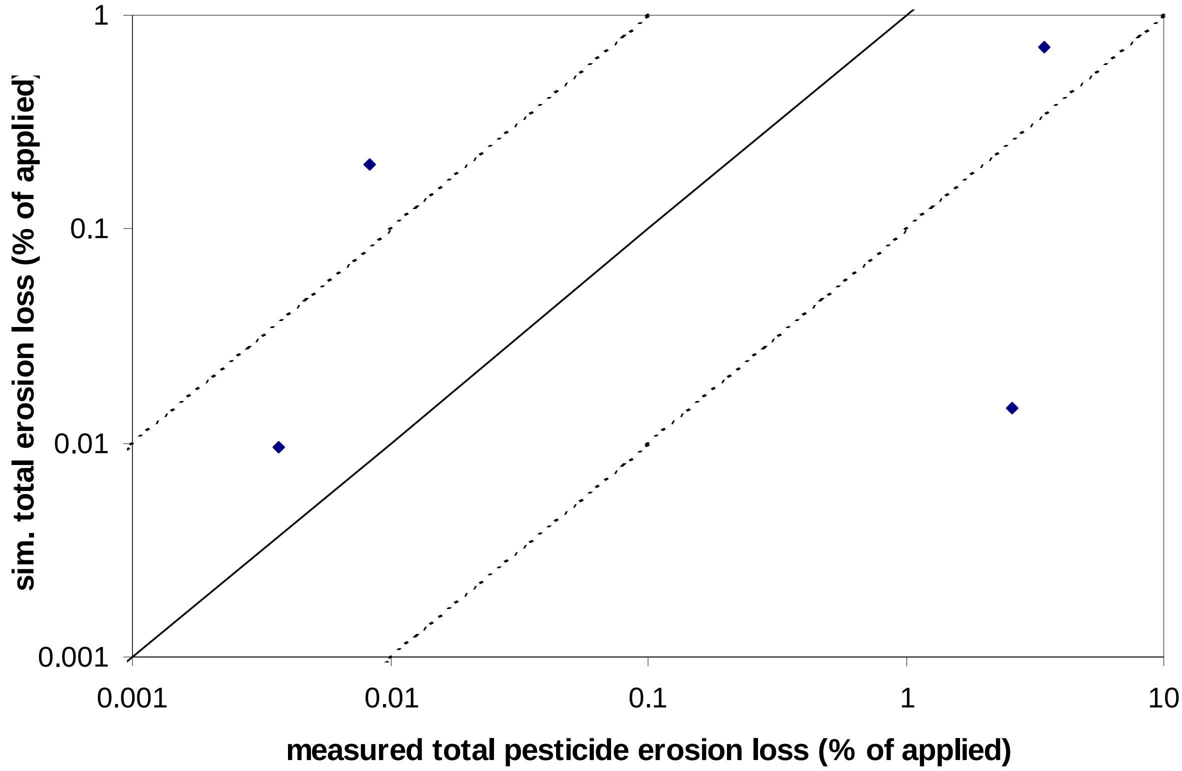

Fig. 4.11: Measured vs. simulated values of total pesticide erosion loss (relative to the applied amount) over the study period for 3 test data sets (all from Kleinhohenheim). Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data point (0; 0.00101) (IPU, Kleinhohenheim) cannot be shown due to the logarithmic plot. The data points on the left belong to the study year 1995, the data points on the right to 1994.

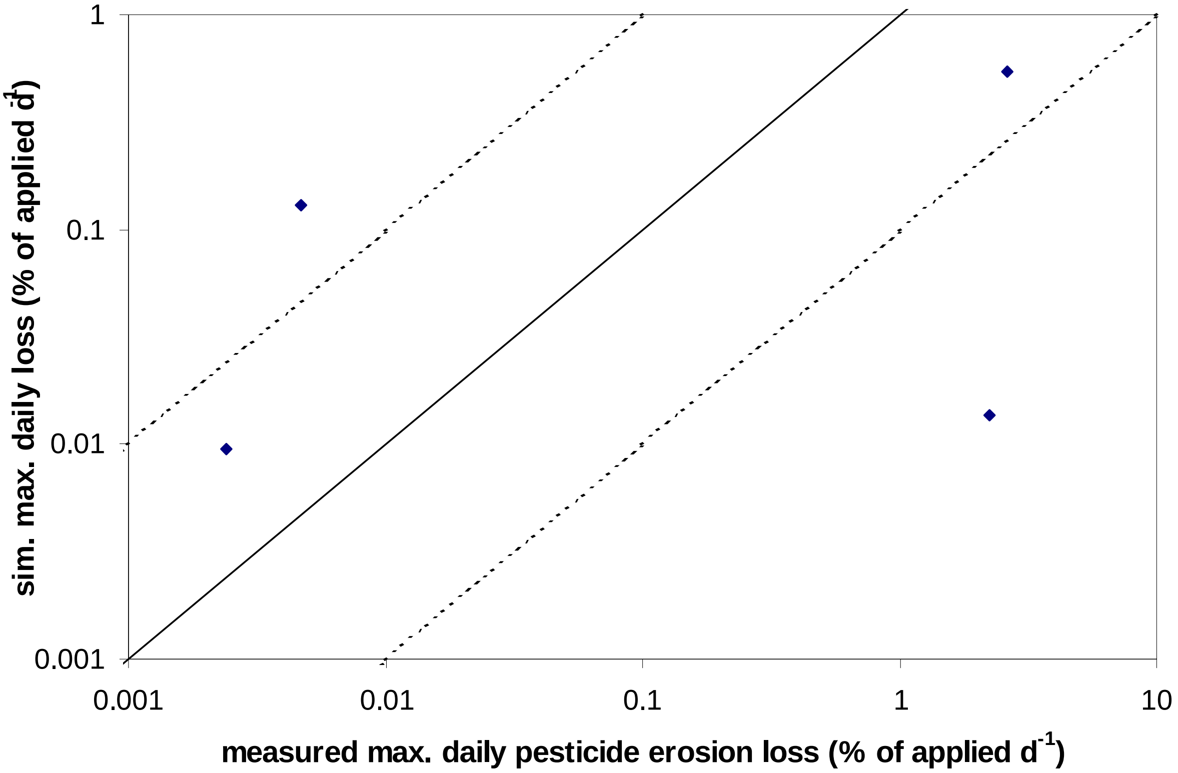

Fig. 4.12: Measured vs. simulated values of maximum daily pesticide erosion loss (relative to the applied amount) over the study period for 3 test data sets. Replicate runoff traps have been averaged. The solid line denotes the 1:1 line, the dashed lines over- and underprediction, resp., by a factor of 10. The data point (0; 9.39E-04) (IPU, Kleinhohenheim) cannot be shown due to the logarithmic plot. The data points on the left belong to the study year 1995, the data points on the right to 1994.

Concerning the 12 measured runoff and erosion datasets, it can be summarized that

- in many cases, there was considerable uncertainty in the measured data
- comparability between measured and simulated target variables was not always given
- there is considerable spatial variability in the field, which is suggested by the scatter observed between replicate runoff traps (cf. Tables 4.8, 4.9 and 4.13-4.16)
- there is also a large temporal variability in runoff volumes, eroded sediment yields and pesticide losses between different years at the same site (cf. Tables 4.13-4.16 and 4.19-4.22).

From this model testing exercise comprising soils from all runoff-relevant soil hydrologic groups (B to D), the following conclusions can be drawn:

- Weaknesses of PRZM with respect to more complex soil hydrologies in the field (e.g. soils prone to waterlogging and/or lateral flow) are evident. These are probably caused by the simplistic description of hydrology.
- PRZM predicted total and peak runoff volumes adequately, i.e. within the defined acceptability limit of a factor of 10 from the measurements. Peak runoff volumes were mostly overestimated. The timing of runoff events was simulated adequately in most cases.
- In general, PRZM predicted total and maximum eroded soil losses adequately. Yet, soil loss predictions were generally worse than surface runoff predictions.
- Total and maximum pesticide runoff losses were predicted acceptably in the majority of the cases. PRZM usually overestimated total and peak runoff losses, especially for small measured losses equal to or less than 0.01 % of the applied amount.
- There is evidence that PRZM tends to overpredict runoff, soil erosion and pesticide runoff and erosion losses for low-intensity rainfalls and small runoff events, and to underpredict them for high-intensity rainfalls and large runoff events. This is probably due to the daily calculation time step of PRZM and the non-consideration of actual rainfall intensities.
- In summary, PRZM 3.21β (using the parameterization help in the PRZM 3.12 Manual and in the FOCUS surface water report) is able to predict surface runoff, soil erosion and pesticide runoff losses for soils with moderate to very high runoff susceptibility acceptably well and without prior calibration. Thus, it can be used for predictive modelling of pesticide runoff losses from agricultural fields to surface water bodies with sufficient confidence.
- The number of measured data points on pesticide erosion losses available for a comparison with simulation results was not sufficient to draw general conclusions on the predictive capability of PRZM 3.21β with respect to pesticide losses via erosion.

4.3 Predictive Modelling with PRZM

4.3.1 Setup and Parameterization of Basis Scenarios

Due to the decisively shorter computation time of PRZM (few seconds per run) compared with MACRO 4.3b (3-4 hours per run), PRZM allows to perform substantially more simulation runs than possible with MACRO and also to consider probabilistic aspects of pesticide exposure.

Soil scenarios:

The 57 main soil types under agricultural use in the land-use-differentiated German soil map 1 : 1000 000 (*nutzungsdifferenzierte BUEK 1000*; BGR, 1999; Hartwich et al., 1995) were divided into five soil classes. These classes correspond to the soil hydrologic groups in PRZM for which the runoff curve numbers are tabulated. The criterion for attribution of a soil type to one of the five classes was the texture of the topsoil. Subsequently, for each class a representative, intermediate soil profile (Table 4.26; Table I.2, Appendix I) was created from the soil profiles of the class members. Runoff susceptibility increases from class 1 to 5, i.e. from soil hydrologic group A to D (cf. section 4.1.1).

Table 4.26: Soil scenarios for predictive PRZM modelling. Runoff susceptibility increases from soil hydrologic group A to group D.

class	soil hydr. group	representative soil type[1)]	FAO soil type[2)]	topsoil particle size class[1)]	number of represented BUEK units[3)]
1	A	Podsol	Podzol	sand	5
2	B	Braunerde-Pseudogley	Stagnic Cambisol	loamy sand	12
3	B-C	Parabraunerde	Luvisol	strongly loamy sand / sandy loam	9
4	C	Parabraunerde	Luvisol	clay silt / silty loam	28
5	D	Pelosol-Braunerde	Vertic Cambisol	clay / clay loam	3

[1)] according to AG Boden (1994)
[2)] FAO (1988)
[3)] soil mapping units represented by the respective scenario

Fig. 4.13 shows the spatial distribution of the five runoff susceptibility classes among the 57 agriculturally used BUEK main soil types over Germany. The map reveals that in Northern Germany the majority of agricultural soils exhibits only low or moderate runoff susceptibility, whereas in Middle and Southern Germany most soils are strongly or very strongly prone to

runoff (soil hydrologic groups C and D). However, it must be pointed out that the BUEK 1000 displays only dominant soil types. This implies that a soil situated in e.g. the red area of the map does not necessarily belong to soil hydrologic group D. On the other hand, group D soils can also occur outside the red area. Therefore, the map shown in Fig. 4.13 was only used for the purpose of visualization, and the assignment of a farmer’s field to a soil class within the ISIP risk assessment module is exclusively done on the basis of user input (cf. chapter 6).
The soil parameters for the predictive PRZM modelling were obtained analogously to the test simulations (cf. section 4.2).

Climate scenarios:

The probability of runoff occurrence is decisively influenced by the frequency of high-intensity rainstorms. The frequency of extreme rainfall events is commonly described by the Gumbel distribution (Gumbel, 1958). A grid map containing the two parameters (u, w) of the Gumbel distribution for 24-h periods (KOSTRA-Atlas, 1997) was obtained from the German Weather Service (DWD). For each pixel the recurrence interval T (in d) of a rainstorm with at least 10 mm precipitation within 24 h was calculated. Although there is no theoretical justification, 10 mm in 24 hours is widely used as a threshold for runoff generation.
Afterwards, the T map was clipped with the area of arable land and orchards according to CORINE Land Cover (Statistisches Bundesamt, 1997) to remove non-agriculturally used pixels (e.g. woodland). The remaining agriculturally relevant pixels were divided into 10 climate classes with different probability of high-intensity rainstorms. Later, as a consequence of the results of the uncertainty analysis performed (cf. section 4.3.7), the climate classes were reduced to 8 (Fig. 4.14) for the predictive modelling.
To obtain the climate scenarios for PRZM modelling, Gumbel parameters for 94 single DWD weather stations were purchased and the recurrence interval T was calculated. From these stations a representative weather station with long-term weather records available was chosen for each climate class. The resulting 10 (8) climate scenarios with 11 (22) to 30 available weather years each are shown in Table 4.27. In the predictive calculations, for each of the 8 climate scenarios the same number of weather years (20) and the same time period (years 1981-2000) were employed, in order to ensure best possible comparability between the climate scenarios.

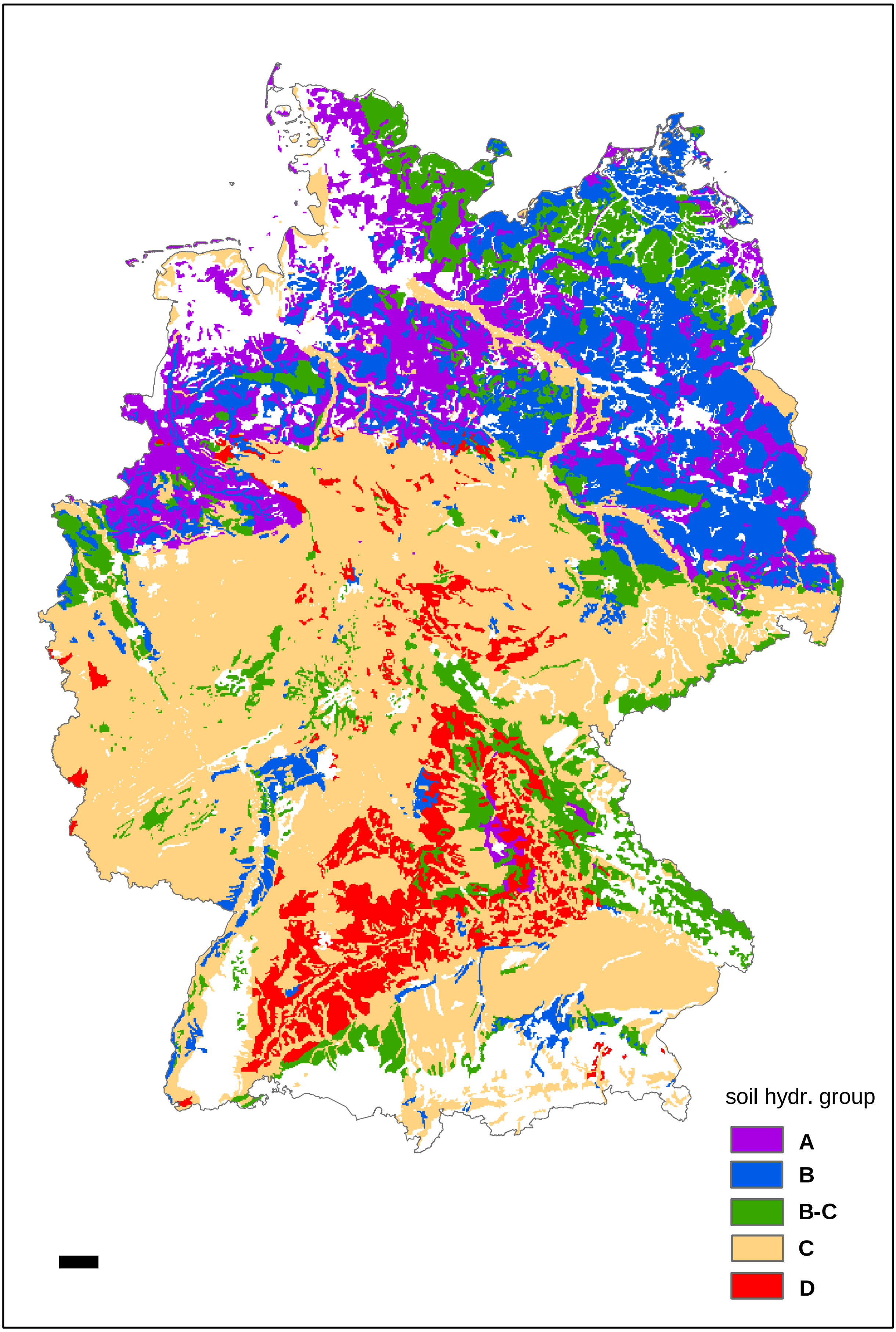

Fig. 4.13: Spatial distribution of the 5 soil classes for surface runoff modelling, derived from the German 1 : 1 000 000 soil map (BUEK 1000). Note that the BUEK 1000 displays only dominant soil types. Hence, the map shown in this figure was only used for the purpose of visualization.

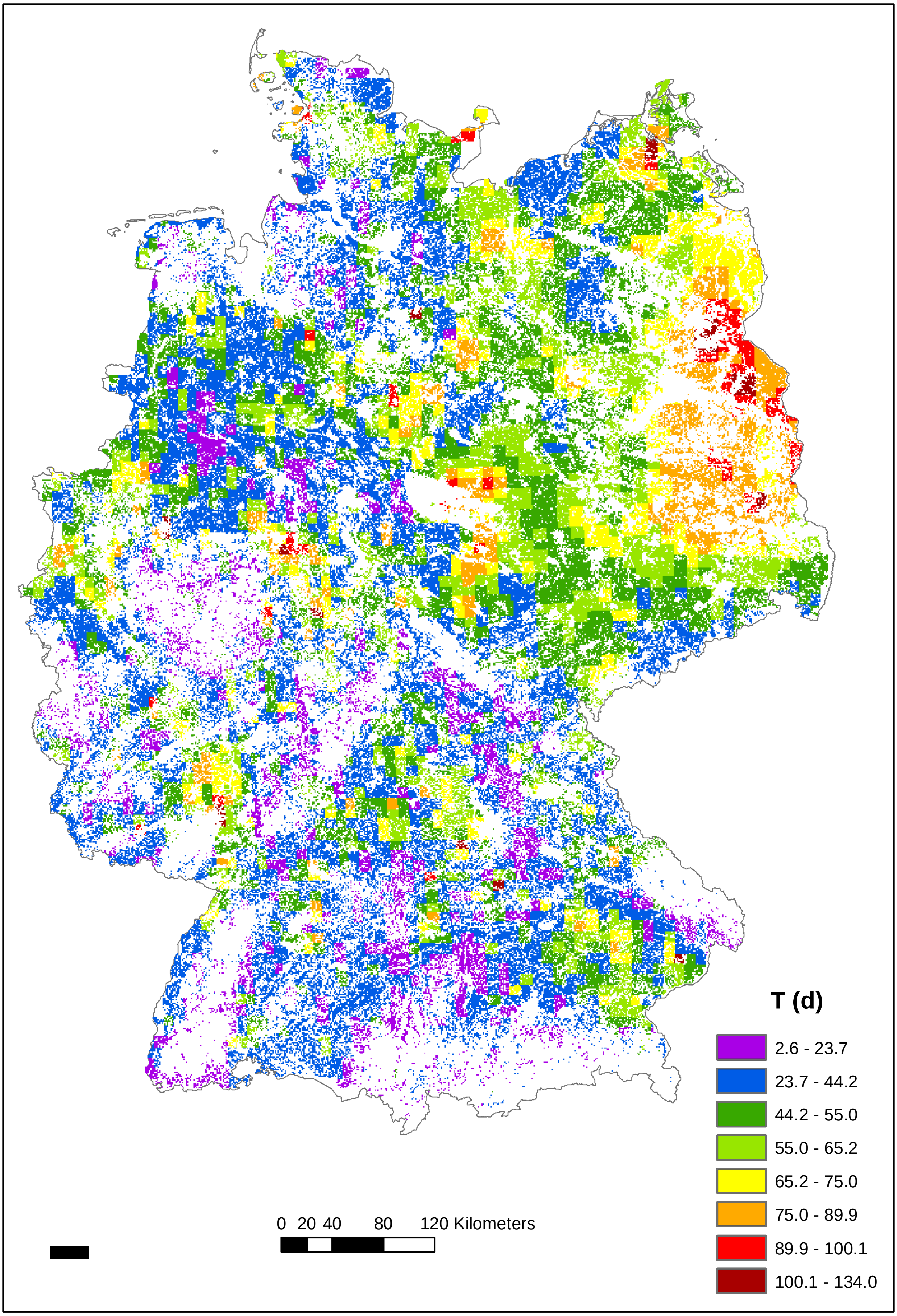

Fig. 4.14: Frequency classes for runoff-producing rainfall events. T (d) = recurrence interval of a high-intensity rainstorm (>= 10 mm in 24 h) for arable land and orchards according to CORINE Land Cover (Statistisches Bundesamt, 1997).

Table 4.27: Climate scenarios for PRZM modelling

climate scenario	weather station	number of weather years	recurrence intervall T	mean annual precipitation	global radiation station
			d	mm	
1	Freiburg	30	14	955.8	Freiburg
2	Haar[1)]	13	30	833.3	Haar
3	Saarbrücken	22	39	911.2	Saarbrücken
4	Bremen	26	51	700.9	Bremen
5	Chemnitz	22	60	709.6	Chemnitz
6	Gera	30	70	636.5	Weimar
7	Bad Salzuflen	25	78	832.0	Osnabrück
8	Mannheim	24	95	698.2	Mannheim
9	Berlin-Schönefeld	30	106	522.0	Potsdam
10	Angermünde[1)]	11	136	534.3	Neubrandenburg

[1)] The climate scenarios Haar and Angermünde were later dropped as a consequence of the uncertainty analysis (section 4.3.7) and not used for predictive modelling.

For all compounds and uses, a period of 2 years was simulated (the weather year was repeated once), to ensure that the maximum daily loss was captured by the simulation. Pesticide application took place in the first year only.

4.3.2 Crop Properties

Plant parameters (e.g. crop height, root depth) for the different crops were directly taken or estimated from the FOCUS surface water scenarios (FOCUS, 2001). Crop dates (emergence, maturity, harvest; Table 4.28) for PRZM modelling were also taken from FOCUS or set with expert knowledge.

Table 4.28: Crop dates for predictive PRZM modelling

crop type	emergence date	maturation date	harvest date	fallow date[1)]
	dd.mm.			
winter cereals	10.10.	07.07.	15.08.	22.08.
spring cereals	01.04.	12.06.	23.08.	30.08.
maize	05.05.	14.08.	20.09.	27.09.
oilseed rape, winter	02.09.	01.06.	28.07.	04.08.
oilseed rape, spring	15.04.	16.06.	28.08.	04.09.
potatoes	16.05.	05.08.	19.09.	26.09.
sugar beet	30.04.	27.07.	22.10.	29.10.
orchards[2)]	15.04	01.07	30.10	01.11
hops[2)]	15.04	27.08	01.09	01.11
strawberries[2)]	02.01	03.01	30.12	31.12

[1)] removal of residues and tillage
[2)] perennial crops

4.3.3 Pesticide Use Scenarios

From the database of registered uses in Germany (BBA, 2004), for each registered pesticide its uses in winter cereals, spring cereals, maize, sugar beets, oilseed rape (winter), oilseed rape (spring), and potatoes were selected. Additionally to these crops, which were also considered in the drainage modelling, the registered uses in the special cultures hops, orchards (separately for pome, stone and nut fruit) and strawberries were selected, as application data for these crops from the NEPTUN 2001 database (Roßberg, 2003) were now available. For each particular use (i.e. combination of compound, target crop and application season), the highest registered dose was chosen for the simulations. A second extensive research on substance parameters (e.g. European Commission, 2004a and 2004b; PSD, 2004) increased the number of compounds that could be simulated with PRZM to 185. Correspondingly, the number of uses (pesticide/crop/application combinations) that could be modelled increased to 446.

The 446 uses were run for every base scenario, which gives 446 uses × 5 soils × 8 climates × 20 weather years per climate = 356800 simulations in total. As for MACRO, pesticide application windows and percentages of crop area treated were obtained from the NEPTUN database. However, as the climate scenarios for PRZM were all strongly fragmented and scattered all over Germany, the application months were chosen uniformly for the entire area of Germany:

- arable land: For each soil-climate region (SCR) within NEPTUN 2000 (Roßberg et al., 2002), the month with the highest total applied amount of the respective pesticide/crop combination was selected. From these maximum-dose months the application month for the PRZM simulation was then obtained as crop-area-weighted mean over all SCR.
- hops, orchards and strawberries: An analogous method was followed in NEPTUN 2001 (Roßberg, 2003) as for arable land, with the difference that within NEPTUN 2001, which was conducted specifically for these special cultures, there are cultivation regions instead of SCR.

For other special cultures (e.g. vines) no NEPTUN application data were available, and thus simulations could not be conducted for these crops. After the application months had been determined, the final application dates were obtained for each climate scenario and weather year by applying the rules of the Pesticide Application Timer (PAT) used within the FOCUS surface water scenarios (FOCUS, 2001) to the precipitation time series of each scenario (cf. section 3.3.3).

4.3.4 Pesticide Properties

Sorption and degradation parameters, water solubility and vapour pressure were obtained from UBA (1997), UBA (2002), EU review reports (European Commission, 2004a; European Commission, 2004b), PSD evaluation documents (PSD, 2004), online databases (ARS, 2004; NRCS, 2004) or other web resources, e.g. EXTOXNET (2004). A list of the substance properties as used for the simulations and their sources is given in Appendix A. Water solubility is used for calculating the foliar washoff coefficient, and both water solubility and vapour pressure are used for calculating the dimensionless Henry's Law constant for volatilization from the soil surface.

As for the MACRO simulations, where two or more values representing single measurements were given, K_{oc} and DT_{50} values were averaged geometrically, and Freundlich exponents arithmetically. When both field and laboratory half-lives were available, the choice between field and laboratory half-life was made as follows:

1. DT_{50} field > DT_{50} lab → DT_{50} field chosen

   In field dissipation studies volatilization is already implicitly included (lumped dissipation half-life), whereas laboratory degradation studies mostly do not include volatilization (closed vessels). Here, the field half-life (which includes volatilization) is larger than the lab half-life, despite the fact that the laboratory studies probably did not include volatilization. This means that there are factors or processes in the field slowing down pesticide dissipation that are not accounted for in the laboratory. Therefore, the field DT_{50} is more appropriate here.

2. DT_{50} field << DT_{50} lab → DT_{50} field chosen

   The field half-life is much shorter than the lab half-life, and the difference is too large too be explained by volatilization alone. This means that there are factors or processes in the field accelerating pesticide dissipation that are not accounted for in the laboratory. Therefore, the field DT_{50} is also more appropriate here.

3. DT_{50} field < DT_{50} lab → DT_{50} lab chosen

   The field half-life is somewhat shorter than the laboratory half-life, and the difference is of a magnitude to be likely due to volatilization. Thus, using lab DT_{50} might give a more exact picture because volatilization can be explicitly modelled under daily changing weather conditions.

4. DT_{50} field ≈ DT_{50} lab → more reliable value chosen

   If field and lab values were similar, the more reliable value (more single values, less scatter) was chosen.

When field half-lives were chosen, volatilization was switched off by setting Henry's Law constant to zero. Nevertheless, temperature and moisture dependence of the field degradation rates were not switched off because the simulations also included winter periods, where it would not have been appropriate to use the same half-life as in spring or summer.
For depth, temperature and moisture dependence of the degradation rate the FOCUS (2001) default settings were used.

4.3.5 Running PRZM with SENSAN

PRZM was run in batch mode by coupling it with the tool SENSAN (Doherty, 2002). The corresponding flow chart is given in Appendix J, and the SENSAN template files (.tpl) for all 5 soil scenarios in Appendix K.

Target variables were:

- cumulative runoff volume (*RUNF*) and pesticide loss via runoff (i.e., in the dissolved phase; *RFLX1*)
- cumulative soil loss (*ESLS*) and pesticide loss via erosion (i.e., adsorbed to eroded soil material; *EFLX1*)
- maximum daily pesticide runoff loss (*RFLX1*) for the whole simulation period, for each simulation year and for each calendary month (+ corresponding date and runoff volume *RUNF*)
- maximum daily pesticide erosion loss (*EFLX1*) for the whole simulation period, for each simulation year and for each calendary month (+ corresponding date and eroded soil material *ESLS*)

4.3.6 Results and Discussion

The following Tables 4.30-4.33 and L.1-L.12 in Appendix L show top 20 rankings of pesticide runoff and erosion losses simulated with PRZM. Ranking was performed for all 16 possible combinations of group aggregation level, target variable and type of values to be ranked (Table 4.29).

Table 4.29: Overview over ranking tables for pesticide losses predicted by PRZM

PRZM output variable	type of ranked values		aggregation level	Table	section
	relative or absolute values	maximum daily or cumulative values	use[1] or use/soil combination[2]		
pesticide runoff loss	relative to the applied amount	max. daily	use use/soil	4.30 L.5	4.3.6 Appendix L
		cumulative	use use/soil	4.31 L.6	4.3.6 Appendix L
	absolute	max. daily	use use/soil	L.1 L.2	Appendix L Appendix L
		cumulative	use use/soil	L.3 L.4	Appendix L Appendix L
pesticide erosion loss	relative to the applied amount	max. daily	use use/soil	4.32 L.11	4.3.6 Appendix L
		cumulative	use use/soil	4.33 L.12	4.3.6 Appendix L
	absolute	max. daily	use use/soil	L.7 L.8	Appendix L Appendix L
		cumulative	use use/soil	L.9 L.10	Appendix L Appendix L

[1] 446 uses with n = 800 (5 soils × 8 climates × 20 weather years per climate)
[2] 2230 use/soil combinations with n = 160 (8 climates × 20 weather years each)

The ranking of the groups was always performed according to the median value of the target variable within each group, i.e. one use or one use/soil combination. When uses (combinations of pesticide, crop and application season) were compared, the groups comprised 800 simulation runs each (5 soils × 8 climates × 20 weather years). When use/soil combinations were compared, each group comprised 160 simulation runs (8 climates × 20 weather years). The full rankings containing all simulated uses and use/soil combinations can be found on the attached CD-ROM. In the following, I focus on the relative values and the comparison of uses, to eliminate the influence of the applied dose and the soil type on the ranking.

Table 4.30 shows that the simulated relative maximum daily pesticide runoff losses were highest for moderately sorbing, relatively persistent compounds which are used in row crops (maize, potatoes, sugar beet) and are applied in late spring or early summer. The highest median maximum daily loss reached 0.067 % of the applied amount (quizalofop-P in potatoes). The findings can be explained this way:

- Moderately to relatively strongly sorbing compounds with a K_{oc} between ca. 200 and 900 L kg^{-1} are only little prone to leaching. Even after larger amounts of rainfall, the largest proportion of the pesticide remains at or near the soil surface, where it is still within reach of surface runoff (in PRZM, chemicals within the top 2 cm of the soil can be extracted by runoff water). The adsorption of these compounds is, on the other hand, not too strong, so that there is enough pesticide present in the dissolved phase, where it is available for surface runoff. In comparison, weakly sorbing compounds have an even higher potential availability for runoff extraction (i.e. a higher proportion in the dissolved phase), but are more likely to be leached beyond 2 cm depth before a runoff-producing rainfall event occurs.
- Slow degradation rates increase the amount of pesticide available for runoff when a runoff-producing rainfall event occurs.
- For row crops, higher runoff curve numbers are tabulated in the PRZM manual than for cereals or rape. This implies that surface runoff will start earlier and the runoff volume will be higher in row crops than in cereals or rape, which is in accordance with observations.
- In Germany, heavy rainstorms occur most frequently in late spring and early summer. If pesticides are applied in May or June, the probability of heavy rainstorm events occurring in the next few days or weeks after application is higher than in other seasons of the year.

Similar observations can be made for the (relative) cumulative runoff losses (Table 4.31). The pesticides listed are, on average, more strongly sorbing than those in Table 4.30. The highest median cumulative loss totalled 0.17 % of the applied amount (terbutryn in maize). Apparently, for high cumulative losses it is even more important that the pesticide remains in the top 2 cm of the soil for a long time than for maximum daily losses. The high ranks for April and March applications of triallate in maize, spring cereals and sugar beet can be explained by the fact that these applications took place before crop emergence (cf. Table 4.28), i.e. on bare soil with a higher runoff curve number than cropped soil. Over all simulated uses, soils, climates and weather years (356800 simulation runs), the highest simulated relative runoff losses were 5.4 % of the applied amount for total loss (indoxacarb, summer application in pome fruit) and 4.2 % for maximum daily loss (clethodim, autumn application in winter oilseed rape).

The rankings for losses via erosion, where the pesticides are removed from the field adsorbed to eroded soil particles, yield a completely different picture. Both the rankings for relative maximum daily erosion losses (Table 4.32) and for relative cumulative losses over 2 years (Table 4.33) exclusively contain extremely strongly sorbing pesticides such as pyrethroids (e.g. deltamethrin and alpha-cypermethrin) and bipyridinium herbicides (paraquat, deiquat). Crop type and application month apparently did not have a major influence on the erosion rankings. The highest median maximum daily erosion loss (0.17 % d^{-1} of the applied amount) and cumulative erosion loss (0.65 %), both for spring application of paraquat in maize, were higher than the corresponding highest runoff losses by factors of 2.5 and 4, respectively. As soil material is eroded only from the uppermost PRZM layer (the top 0.1 cm of the soil), high pesticide losses via erosion only occur if most of the pesticide remains at the soil surface and the largest proportion of the compound is adsorbed to soil particles. Hence, strong sorption is a prerequisite for high pesticide losses via erosion. Over all simulated uses, soils, climates and weather years (356800 simulation runs), the highest simulated relative erosion losses were 4.4 % of the applied amount for total loss, and 2.1 % d^{-1} for maximum daily loss (both for paraquat, spring application in maize).

Absolute pesticide runoff losses (Appendix L) were highest for the fungicide metam in potatoes, which is however registered with a high and probably unrealistic maximum dose of 126 kg ha^{-1}. If metam is not considered, the highest median maximum daily loss totalled 1.80 g ha^{-1} d^{-1}, and the highest median cumulative loss 5.30 g ha^{-1} (both for prosulfocarb, spring application in potatoes). The highest median absolute pesticide erosion losses (cf. Appendix L) were 1.06 g ha^{-1} d^{-1} for maximum daily loss (pendimethalin, spring application in maize) and 3.87 g ha^{-1} for cumulative loss (paraquat, spring application in maize).

The rankings of use/soil combinations (Appendix L) reveal that pesticide losses via runoff were highest for the most runoff-susceptible soil class 5 (Pelosol-Braunerde, hydrologic group D). The highest median (relative) maximum daily runoff loss totalled 0.22 % of the applied amount (metalaxyl-M, summer application in potatoes, soil class 5), and the highest median cumulative runoff loss 0.49 % (terbuthylazine, spring application in maize, soil class 5). Pesticide erosion losses were highest for the soil classes 5 and 4 (Parabraunerde, hydrologic group C), the latter being the soil most prone to soil erosion (USLE soil erodibility factor K = 0.37). The median of relative pesticide erosion losses reached 0.44 % of the applied amount for the maximum daily loss and 1.71 % for the cumulative loss (both for spring application of paraquat in maize, soil class 4).

Fig. 4.15-4.22 show, for some example uses, frequency distributions of maximum daily pesticide losses over all 800 simulations performed for the respective use (5 soils × 8 climates × 20 weather years per climate). From the frequency distributions for runoff losses (Fig. 4.15-4.18), it can be seen that all distributions are skewed to the right (= positively skewed). This means that losses much larger than the median loss occur, but much less frequently than small losses. Skewness and also the proportion of zero losses (represented by the leftmost column) decrease in the order dichlorprop-P → isoproturon → quizalofop-P → trifluralin, which corresponds to the order of increasing sorption and roughly also to the order of increasing persistence (cf. Appendix A). Zero losses imply that either no surface runoff occurred after pesticide application for the rest of the simulation, or that there was no more pesticide left in the uppermost 2 cm of the soil when the first runoff event occurred. Apart from runoff and erosion losses, pesticide dissipation from these uppermost 2 cm occurs by leaching, degradation and volatilization. Therefore, strong sorption and high persistence of a pesticide will (as already mentioned above) prolong the time period of its presence in the top 2 cm of the soil and thus of its runoff availability, and hence will cause a less skewed frequency distribution. Nevertheless, strong sorption of a pesticide leads to overall lower runoff losses (Fig. 4.18) than for pesticides with intermediate sorption (Fig. 4.17), due to the decrease in extractability by runoff water.

Similarly to the runoff loss distributions, the example frequency distributions for erosion losses (Fig. 4.19-4.22) reveal a decrease in skewness and of zero losses with increasing sorption and persistence of the pesticides (cf. Appendix A). In contrast to surface runoff, stronger sorption led (as expected) to higher pesticide erosion losses. However, the simulated maximum daily erosion losses for trifluralin (Fig. 4.21) and for quizalofop-P (Fig. 4.20) were comparable, despite the stronger sorption and persistence of the former. This can be explained by the higher runoff susceptibility of potatoes compared with oilseed rape, and by the high volatility of trifluralin (cf. Appendix A), which probably leads to depletion of trifluralin in the top 0.1 cm of the soil.

It can be summarized that the predictive PRZM simulations yielded considerable differences in pesticide runoff and erosion losses between different uses, soils, and meteorological input (climate scenarios and weather years). In vulnerable soils, both total and peak losses can under certain circumstances reach significant fractions of the applied dose.

Table 4.30: Ranking of uses according to the median *maximum daily runoff* losses (*relative* to applied amount, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	rel. max. daily runoff loss median[3)]	mean[3)]
			g ha^{-1}		L kg^{-1}		d	% of applied d^{-1}	
1	quizalofop-P	potatoes	92.6	5	540	0.90	60	0.067	0.107
2	propamocarb	potatoes	831.2	6	315	0.90	30	0.064	0.120
3	methiocarb	sugar beet	100	5	572	1.00	18	0.064	0.108
4	quizalofop-P	sugar beet	92.6	5	540	0.90	60	0.064	0.102
5	terbutryn[4)]	maize	1960	5	775	0.76	56	0.062	0.097
6	metosulam	maize	30	5	202	0.90	31	0.062	0.122
7	terbuthylazine	maize	750	5	247	0.83	46	0.061	0.120
8	flufenacet	maize	600	5	266	0.90	32	0.061	0.120
9	propaquizafop	sugar beet	125	5	400	0.90	15	0.060	0.103
10	clomazone	potatoes	90	5	235	0.90	87	0.059	0.120
11	phenmedipham	sugar beet	960	5	870	0.85	31	0.057	0.087
12	flutriafol	maize	50	4	231	0.90	500	0.056	0.115
13	methiocarb	maize	100	6	572	1.00	18	0.056	0.093
14	dimethomorph	potatoes	400	6	404	0.90	42	0.054	0.095
15	imidacloprid	sugar beet	119	4	183	0.80	145	0.054	0.111
16	S-metolachlor	maize	1250	5	201	0.90	26	0.052	0.121
17	metolachlor	maize	1500	5	201	0.90	38	0.052	0.121
18	propiconazole	winter cereals	125	5	675	0.90	91	0.051	0.085
19	propaquizafop	potatoes	125	6	400	0.90	15	0.050	0.085
20	methiocarb	oilseed rape, spring	100	4	572	1.00	18	0.050	0.092

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 800 (5 soils × 8 climates × 20 weather years per climate)

[4)] no longer registered in Germany

Table 4.31: Ranking of uses according to the median *cumulative runoff* losses (*relative* to applied amount, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	rel. acc. runoff loss median[3)]	rel. acc. runoff loss mean[3)]
			g ha^{-1}		L kg^{-1}		d	% of applied	% of applied
1	terbutryn[4)]	maize	1960	5	775	0.76	56	0.173	0.245
2	triallate	maize	1200	4	2400	0.90	46	0.168	0.209
3	triallate	sugar beet	1440	4	2400	0.90	46	0.160	0.200
4	phenmedipham	sugar beet	960	5	870	0.85	31	0.158	0.218
5	quizalofop-P	potatoes	92.6	5	540	0.90	60	0.156	0.241
6	quizalofop-P	sugar beet	92.6	5	540	0.90	60	0.151	0.232
7	triallate	spring cereals	1200	3	2400	0.90	46	0.135	0.176
8	methiocarb	sugar beet	100	5	572	1.00	18	0.134	0.216
9	prosulfocarb	potatoes	4000	5	1637	0.96	13	0.133	0.178
10	propaquizafop	sugar beet	125	5	400	0.90	15	0.129	0.209
11	propiconazole	sugar beet	112.5	6	675	0.90	91	0.122	0.177
12	pymetrozine	maize	200	6	1196	0.90	14	0.121	0.161
13	propamocarb	potatoes	831.2	6	315	0.90	30	0.121	0.218
14	pymetrozine	potatoes	150	6	1196	0.90	14	0.119	0.159
15	methiocarb	maize	100	6	572	1.00	18	0.114	0.187
16	zoxamide	potatoes	149.4	6	1201	0.90	17	0.111	0.150
17	dimethomorph	potatoes	400	6	404	0.90	42	0.110	0.187
18	flusilazole	sugar beet	150	6	1603	0.90	141	0.109	0.145
19	metosulam	maize	30	5	201.5	0.90	31	0.109	0.224
20	fluquinconazole	winter cereals	150	5	750	0.90	135	0.108	0.166

1) a.i. equivalents without ester groups or counterions

2) 1 = Jan, 2 = Feb, etc.

3) n = 800 (5 soils × 8 climates × 20 weather years per climate)

4) no longer registered in Germany

Table 4.32: Ranking of uses according to the median *maximum daily erosion* losses (*relative* to applied amount, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	**rel. max. daily erosion** loss median[3)]	mean[3)]
			g ha^{-1}		L kg^{-1}		d	% of applied d^{-1}	
1	paraquat	maize	600	4	234000	0.90	5000	0.169	0.249
2	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	0.161	0.232
3	paraquat	sugar beet	600	4	234000	0.90	5000	0.160	0.222
4	deltamethrin	sugar beet	7.5	5	460000	0.90	36	0.125	0.178
5	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	0.121	0.169
6	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	0.113	0.162
7	deltamethrin	potatoes	5	6	460000	0.90	36	0.111	0.162
8	lambda-cyhalothrin	sugar beet	7.5	5	131052	0.90	20	0.108	0.155
9	alpha-cypermethrin	oilseed rape, spring	10	5	61904	0.90	35	0.107	0.149
10	deiquat	potatoes	1000	9	1600000	0.90	5000	0.105	0.176
11	lambda-cyhalothrin	oilseed rape, spring	7.5	5	131052	0.90	20	0.102	0.142
12	lambda-cyhalothrin	potatoes	7.5	6	131052	0.90	20	0.093	0.140
13	lambda-cyhalothrin	maize	7.5	6	131052	0.90	20	0.086	0.127
14	pyrethrins	potatoes	36.68	6	100000	0.90	12	0.077	0.117
15	pendimethalin	maize	1600	5	14000	0.90	146	0.066	0.118
16	deiquat	oilseed rape, winter	400	7	1600000	0.90	5000	0.065	0.133
17	quinoxyfen	sugar beet	125	6	23020	0.90	374	0.059	0.091
18	deltamethrin	winter cereals	7.5	6	460000	0.90	36	0.056	0.119
19	deltamethrin	oilseed rape, winter	7.5	5	460000	0.90	36	0.056	0.121
20	alpha-cypermethrin	oilseed rape, winter	10	5	61904	0.90	35	0.050	0.114

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 800 (5 soils × 8 climates × 20 weather years per climate)

Table 4.33: Ranking of uses according to the median *cumulative erosion* losses (*relative* to applied amount, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	**rel. acc. erosion** loss median[3)]	**rel. acc. erosion** loss mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d	% of applied	% of applied
1	paraquat	maize	600	4	234000	0.90	5000	0.645	0.954
2	paraquat	sugar beet	600	4	234000	0.90	5000	0.572	0.845
3	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	0.495	0.754
4	deltamethrin	sugar beet	7.5	5	460000	0.90	36	0.420	0.660
5	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	0.398	0.588
6	deltamethrin	potatoes	5	6	460000	0.90	36	0.386	0.582
7	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	0.367	0.594
8	lambda-cyhalothrin	sugar beet	7.5	5	131052	0.90	20	0.356	0.564
9	alpha-cypermethrin	oilseed rape, spring	10	5	61904	0.90	35	0.346	0.520
10	lambda-cyhalothrin	oilseed rape, spring	7.5	5	131052	0.90	20	0.329	0.494
11	lambda-cyhalothrin	potatoes	7.5	6	131052	0.90	20	0.318	0.498
12	deiquat	potatoes	1000	9	1600000	0.90	5000	0.315	0.569
13	lambda-cyhalothrin	maize	7.5	6	131052	0.90	20	0.292	0.454
14	pyrethrins	potatoes	36.68	6	100000	0.90	12	0.258	0.406
15	pendimethalin	maize	1600	5	14000	0.90	146	0.198	0.390
16	deltamethrin	oilseed rape, winter	7.5	5	460000	0.90	36	0.192	0.405
17	quinoxyfen	sugar beet	125	6	23020	0.90	374	0.180	0.313
18	deiquat	oilseed rape, winter	400	7	1600000	0.90	5000	0.178	0.395
19	deltamethrin	winter cereals	7.5	6	460000	0.90	36	0.175	0.371
20	lambda-cyhalothrin	oilseed rape, winter	7.5	5	131052	0.90	20	0.168	0.355

1) a.i. equivalents without ester groups or counterions

2) 1 = Jan, 2 = Feb, etc.

3) n = 800 (5 soils × 8 climates × 20 weather years per climate)

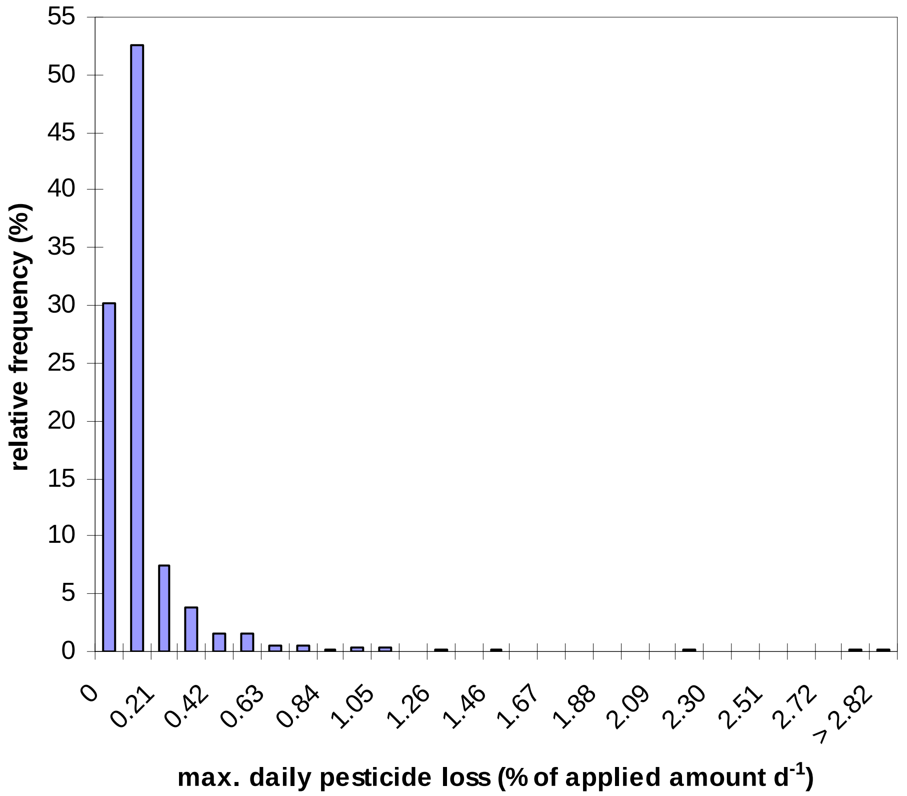

Fig. 4.15: Frequency distribution of maximum daily **runoff** losses of isoproturon in winter cereals (autumn application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

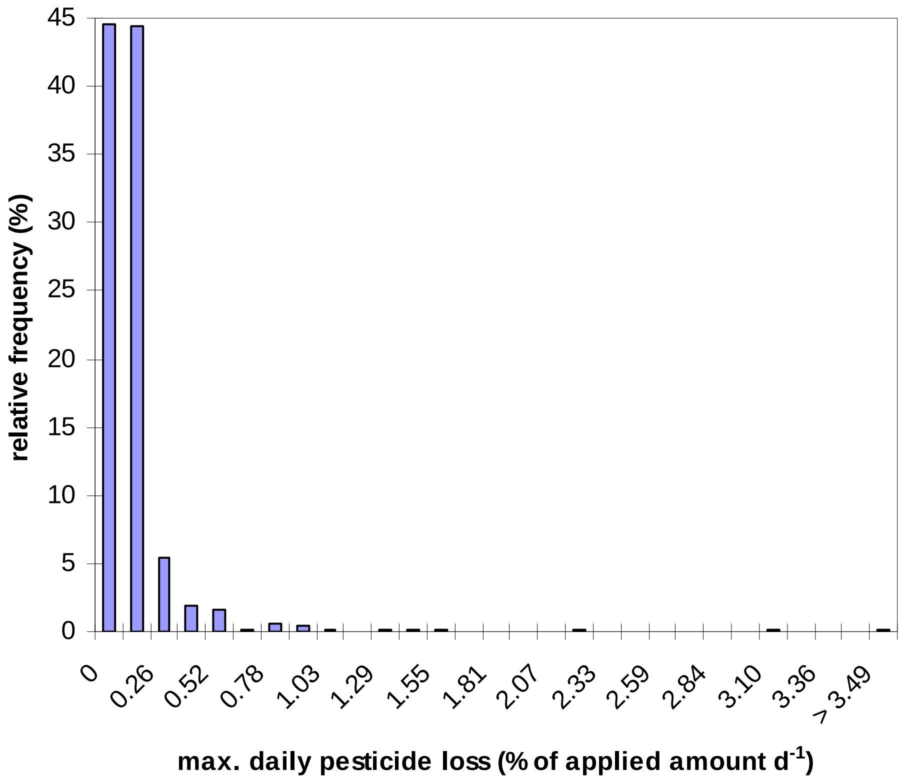

Fig. 4.16. Frequency distribution of maximum daily **runoff** losses of dichlorprop-P in winter cereals (autumn application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

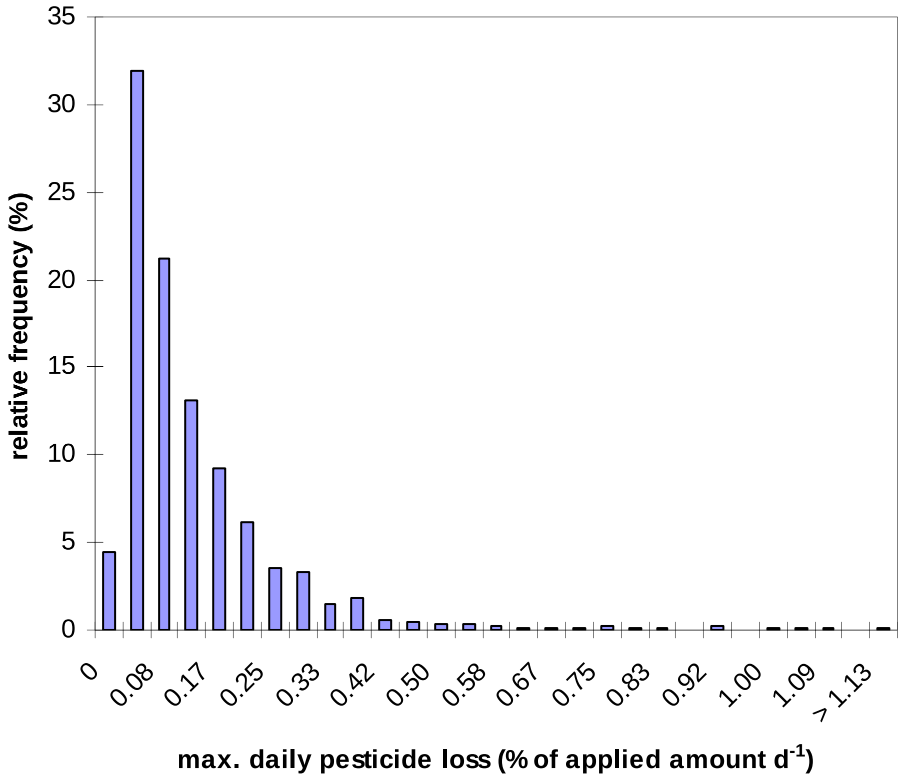

Fig. 4.17: Frequency distribution of maximum daily **runoff** losses of quizalofop-P in potatoes (spring application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

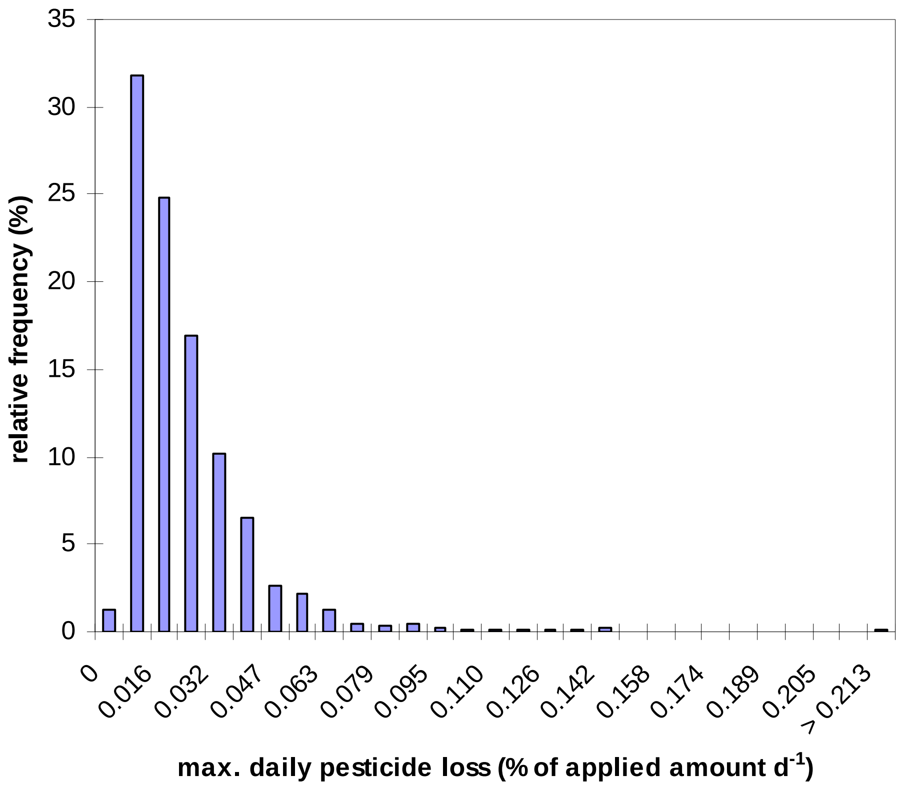

Fig. 4.18: Frequency distribution of maximum daily **runoff** losses of trifluralin in spring oilseed rape (spring application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

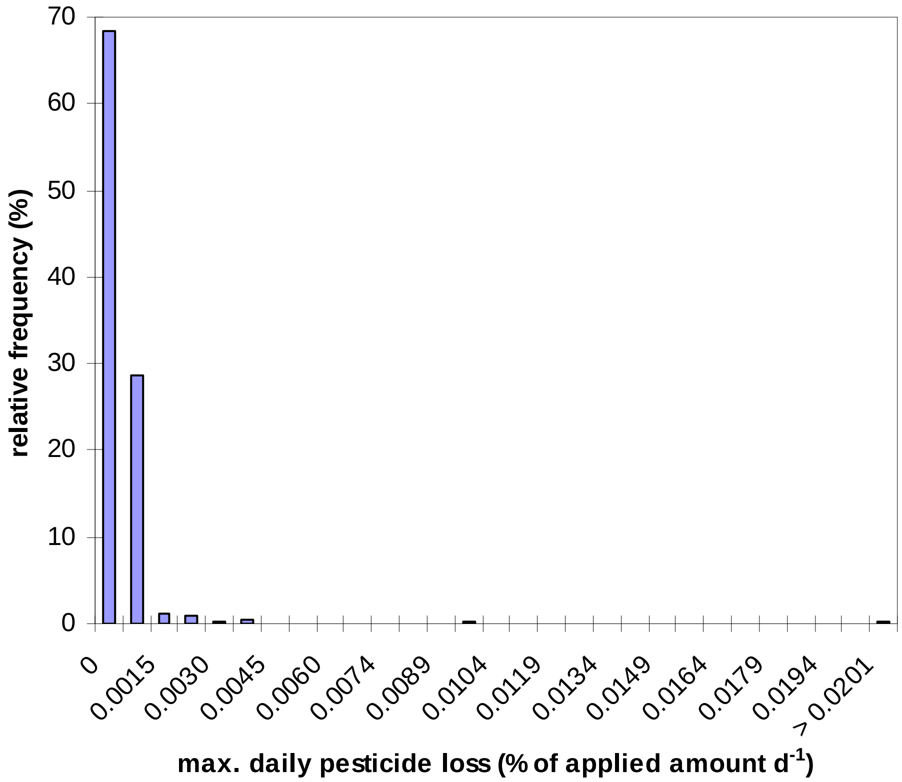

Fig. 4.19: Frequency distribution of maximum daily **erosion** losses of isoproturon in winter cereals (autumn application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

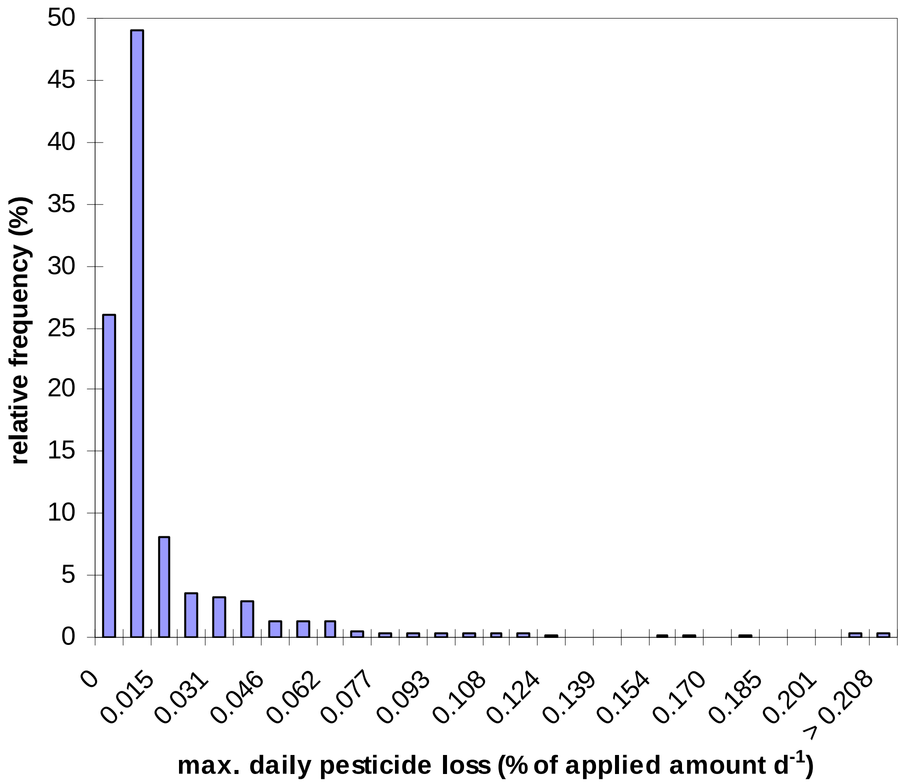

Fig. 4.20: Frequency distribution of maximum daily **erosion** losses of quizalofop-P in potatoes (spring application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

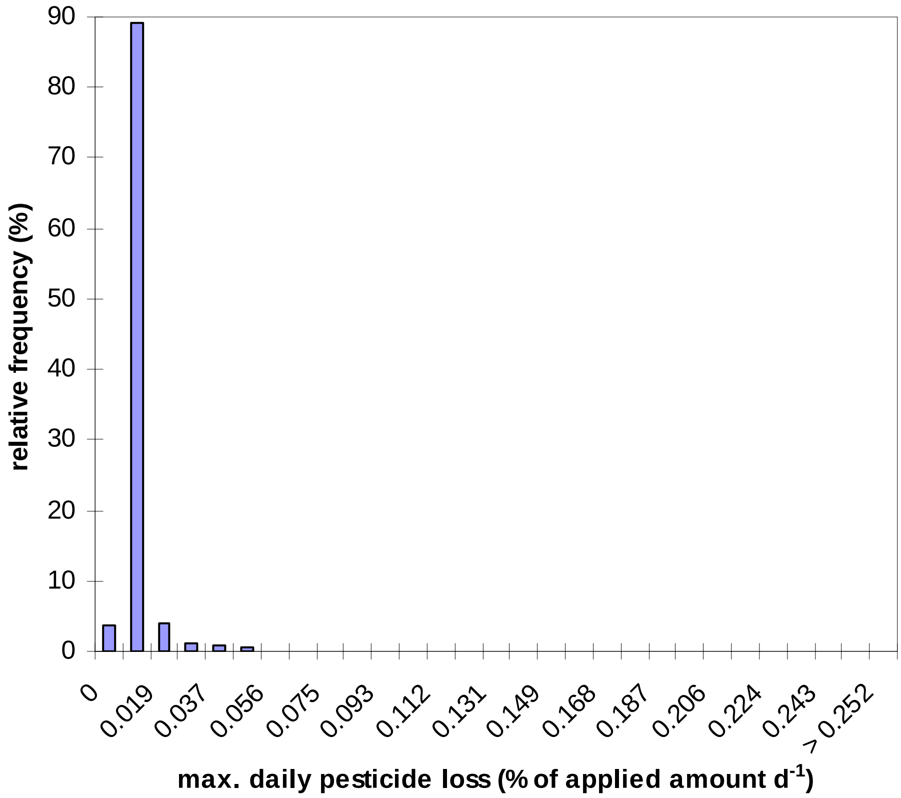

Fig. 4.21: Frequency distribution of maximum daily **erosion** losses of trifluralin in spring oilseed rape (spring application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

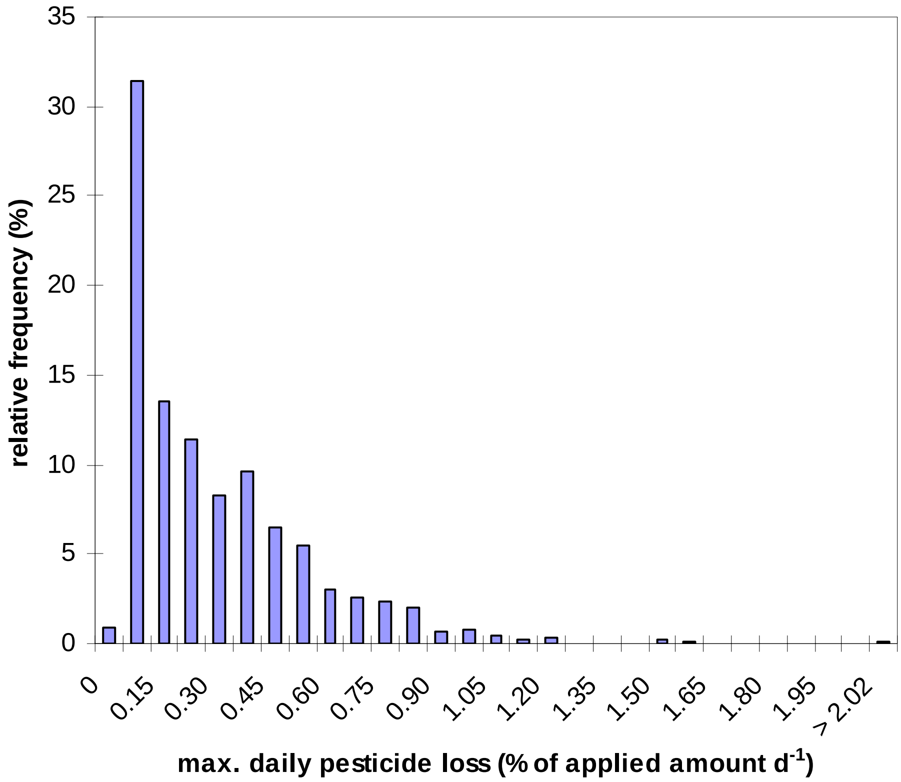

Fig. 4.22: Frequency distribution of maximum daily **erosion** losses of paraquat in maize (spring application). n = 800 (5 soils × 8 climates × 20 weather years per climate).

4.3.7 Uncertainty Analysis

Before starting the actual predictive modelling, an extensive uncertainty analysis was performed to answer the following questions:

1. How uncertain are the results predicted with PRZM?
2. What is the largest source of uncertainty:
   - annual variability of the weather (occurrence of heavy rainstorms, very wet or dry periods etc.)?
   - uncertainty of the compound properties (K_{oc}, Freundlich exponent, DT_{50})?
   - choice of the application day?
   - parameterization of soil scenarios (curve numbers, OC content, bulk density etc.)?
3. What is the most favourable design for the predictive modelling (uncertainty smallest as possible and well to describe, with as few model runs as possible)?

The sensitivity of PRZM with respect to pesticide losses via runoff and erosion is to a large extent known (FEMVTF, 2001). In the FEMVTF study, the runoff curve numbers CN for crop-covered and bare soil clearly turned out as the most sensitive input parameters, followed by the sorption coefficient K_d (non-linear sorption was not available in PRZM at that time), degradation rates and bulk density (the latter being the most important input for field capacity and wilting point calculation). These results already give a good hint which input parameters should be included in an uncertainty analysis. However, in the FEMVTF study the influence of the “driving data” (the weather file) was not investigated.

In the uncertainty analysis done here, the following model input was varied:

- 10 climate scenarios with different recurrence intervals of high-intensity rainstorms
- 11 to 30 weather years per climate scenario
- 5 soil scenarios with differing runoff susceptibility (cf. section 4.3.1)
- 6 uses (3 compounds with different properties), with 4 of them also used for the MACRO uncertainty analysis (cf. section 3.3.7):
  - dichlorprop-p (K_{oc} = 21 L kg^{-1}, m = 1, DT_{50} = 19 d),
    winter cereals / spring application + winter cereals / autumn application
  - isoproturon (K_{oc} = 71 L kg^{-1}, m = 0.88, DT_{50} = 11 d)
    winter cereals / spring application + winter cereals / autumn application
  - terbutryn (K_{oc} = 775 L kg^{-1}, m = 0.76, DT_{50} = 56 d),
    maize / spring application + winter cereals / autumn application

- The 9 most sensitive soil and substance parameters were varied by Latin Hypercube Sampling (LHS) with realistic parameter ranges and distributions (Table 4.34), n = 70.

In total, this gives

6 uses × 5 soils × 233 weather years × 70 LHS combinations = 489300 simulation runs.

Table 4.34: Input for Latin Hypercube Sampling (LHS)

input variable	distribution type	range relative to basis scenario
CN (cropping period)	uniform	+/- difference to next soil class
CN (fallow)	uniform	+/- difference to next soil class
bulk density BD	uniform	+/- 0.1 g cm^{-3}
organic matter OM	uniform	+/- 1/3
application date	uniform	+/- 10 d[1)]
Normalized Freundlich coefficient K_{oc}	log-normal, truncated[2)]	*/: factor 2
Freundlich exponent m	normal, truncated[2)]	+/- 20 %
Degradation rate	log-normal, truncated[2)]	*/: factor 2
slope[3)]	uniform	+/- 5 % slope

[1)] deviation from the application date calculated with the Pesticide Application Timer (PAT)

[2)] truncation at the 2.5th percentile (lower end) and the 97.5th percentile (upper end)

[3)] only used for erosion calculations

Target variables were:

- maximum daily pesticide surface runoff loss over the simulation period of 2 years, relative to the applied amount
- maximum daily pesticide erosion loss over the simulation period of 2 years, relative to the applied amount

First, it was investigated how much variance was introduced into the target output by the different factors that were varied: use (i.e. combination of compound, crop and application season combination), soil scenario, climate scenario, weather year, and sensitive model parameters. As examples, the following example diagrams compare frequency distributions of maximum daily pesticide runoff loss at different levels of aggregation: between different uses (Fig. 4.23), between different soils for the same use (Fig. 4.24), between different climates for the same use and soil (Fig. 4.25), and between selected different weather years for the same climate, soil and use (Fig. 4.26). Since the target output variables were not distributed homoskedastically (i.e. the different groups, for instance the 6 uses, did not have the same variance), it was not possible to conduct an ANOVA (**An**alysis **o**f **Va**riance). However, it was still possible to analyze the variances "manually". The variances (more precisely: the sums of the squared residuals) of the two target variables were separated into variance *between* groups and variance *within* groups for different aggregation levels (Table 4.35). This table reads as follows: When all 489300 simulation runs are together in one group, the variance within this group is 100 % of the total variance, and the between-group variance is zero. When the simulations are split into the 6 pesticide uses (see above), some of the variance *within* the former group of all simulations becomes variance *between* the 6 different uses (in the case of runoff: 1.47 % of the total variance). The other portion of the total variance (here: 98.53 %) constitutes the sum of variance *within* the 6 uses. The more within-group variance is eliminated at this disaggregation step, the more different the simulated losses of the 6 uses are from each other (cf. Fig. 4.23). The same holds for the next disaggregation steps. The within-group variance eliminated in a disaggregation step is equivalent to the relative uncertainty contribution of the respective factor used in this disaggregation step (e.g. soil scenario or climate scenario) to the simulation results.

Table 4.35: Eliminated within-group variance with decreasing level of aggregation

agg. level	description	variance is eliminated between	relative eliminated within-group variance[1)] runoff loss	erosion loss
			%	%
5	all runs together in one group	-	0	0
4	uses separate	6 uses	1.47	8.46
3	uses + soils separate	5 soils	6.52	14.17
2	uses + soils + climates separate	10 climates	4.20	2.80
1	uses + soils + climates + weather years separate	available weather years	50.98	35.81
0	all runs separate	70 runs within a LHS	36.84	38.76

[1)] reduction of within-group sum of squares (QSZ) / total sum of squares (TSS)

The separation of variances as described above revealed (Table 4.35):

- For both surface runoff and erosion, the uncertainty caused by the different weather years, i.e. the annual weather variability (cf. Fig. 4.26), is by far larger than the uncertainty caused by the choice of the climate scenario (cf. Table 4.27, section 4.3.1). This implies that it is better to model fewer climate scenarios, but as many weather years as possible for each climate scenario.
- For runoff, the uncertainty caused by the annual variability of the weather is also larger than the uncertainty caused by sensitive model parameters (CN, OM, K_{oc}, m,...). For erosion, the magnitudes of the two uncertainty sources are comparable. Due to computational limitations, it is not possible here to do LHS in the predictive PRZM modelling. Hence, it is advantageous that the unconsidered uncertainty introduced by sensitive model parameters will not be larger than the uncertainty from the other sources accounted for in the predictive simulations.

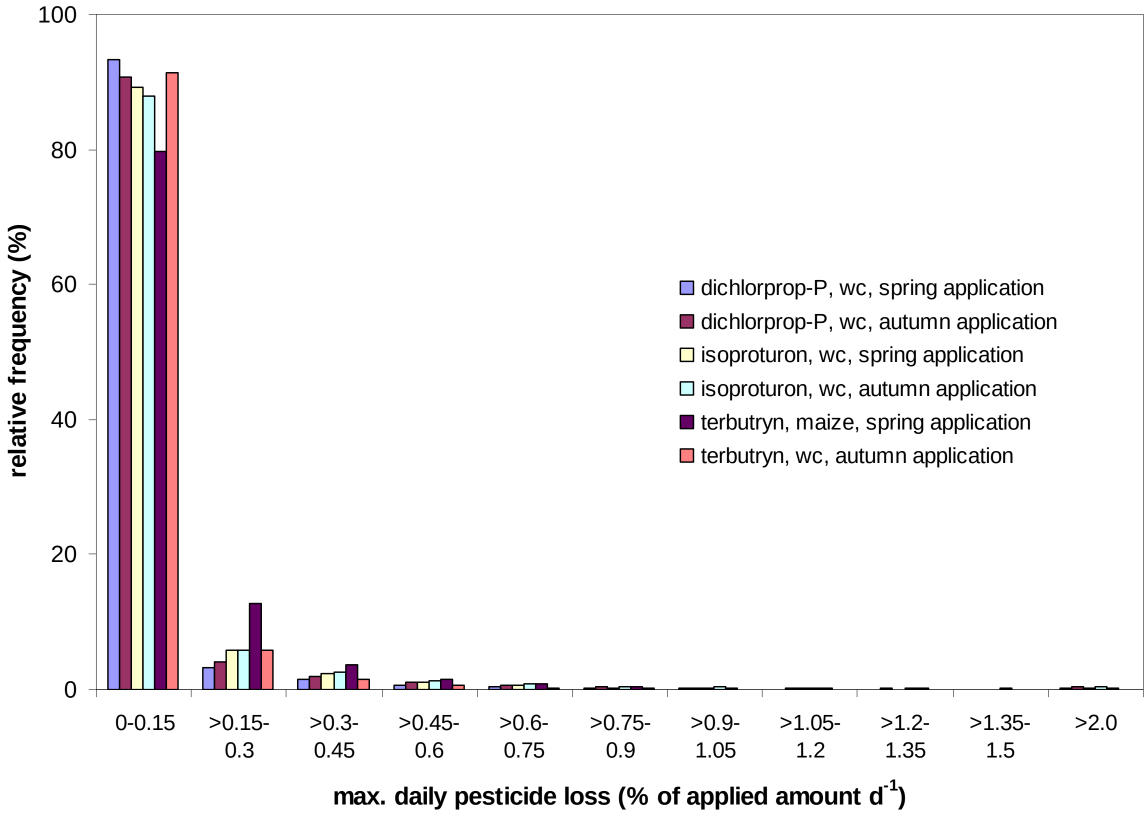

Fig. 4.23: Frequency distribution of maximum daily **runoff** losses for all 6 uses included in the uncertainty analysis. n = 81550 for each use (5 soils × 10 climates with 233 weather years in total × 70 LHS runs). wc = winter cereals.

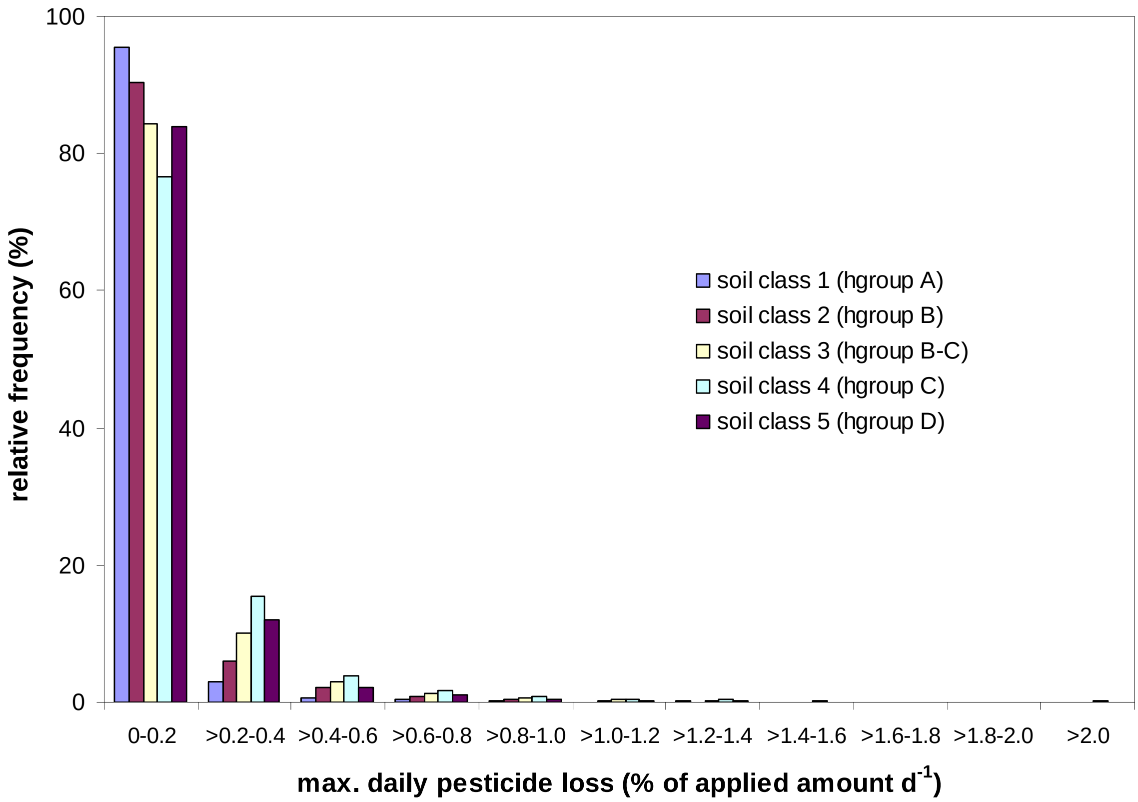

Fig. 4.24: Frequency distribution of maximum daily **runoff** losses for terbutryn in maize (spring application) and the five different soils. n = 16310 for each soil (10 climates with 233 weather years in total × 70 LHS runs).

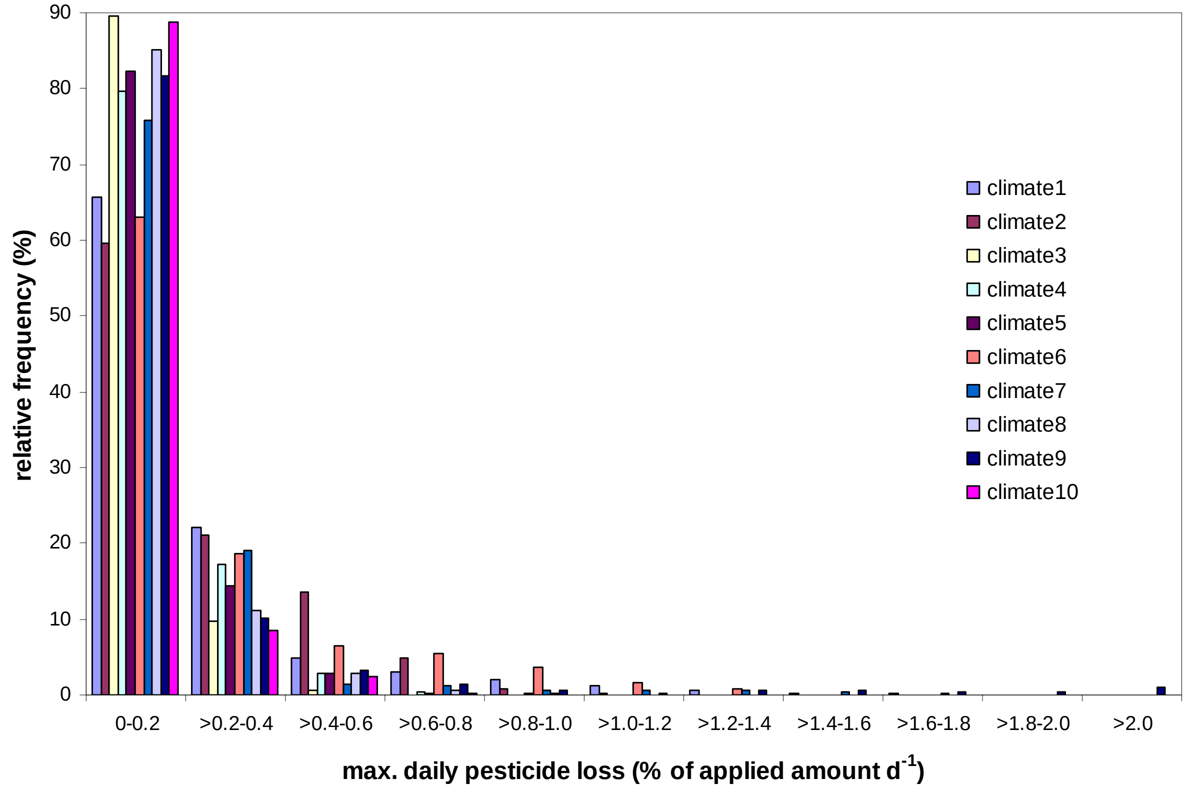

Fig. 4.25: Frequency distribution of maximum daily **runoff** losses for terbutryn in maize (spring application), soil class 4 (hydrologic group C), and the 10 climate scenarios. n = 770-2100 for each climate (11-30 available weather years × 70 LHS runs).

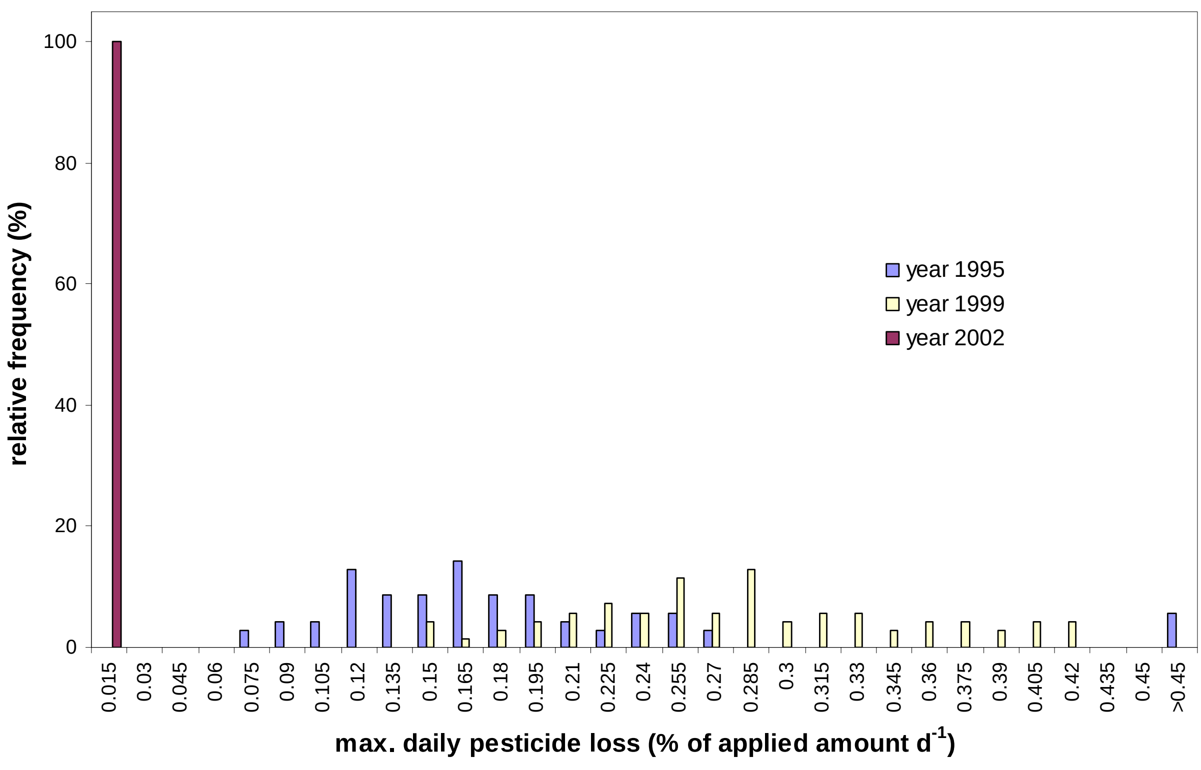

Fig. 4.26: Frequency distribution of maximum daily **runoff** losses for terbutryn in maize (spring application), soil class 4 (hydrologic group C), climate scenario 3 (Saarbrücken), and 3 selected weather years (out of 22 simulated years) with extremely low (2002), extremely high (1999) and intermediate (but with extreme outliers up to 1.2 % of applied amount d^{-1}; 1995) terbutryn runoff losses. n = 70 for each year (70 LHS runs).

The example diagram Fig. 4.26 displays not only the variation of the peak terbutryn runoff losses between the 3 selected weather years (for the same climate, soil and use), but also the variation within each weather year due to the LHS-varied sensitive model parameters. This variation differs from year to year. For the worst-case year 1999, maximum daily terbutryn losses of 0.14-0.42 % of the applied amount were predicted. For the intermediate year 1995, which however exhibited some extreme outliers, predicted peak terbutryn losses ranged from 0.07 to 1.21 % (mean = 0.20 %, median = 0.16 %), and for the nearly best-case year 2002 from zero to 7.6E-06 %. For the year 2001, zero losses were predicted for all 70 LHS runs. It can be seen that under certain circumstances, the model parameters varied with LHS can considerably affect the simulated maximum daily pesticide losses (cf. Table 4.35).

To identify the most sensitive of the LHS-varied model input parameters, a multiple linear regression analysis (MLR) was performed with all 8 (for runoff) and 9 (for erosion) model parameters for all 6990 simulated LHS blocks (70 runs each). For each regression, the standardized regression coefficients (SRC) of each variable were ranked according to their magnitude, and the ranks were averaged for each use. The MLR revealed that, except in one case, the most sensitive input parameter was the runoff curve number during the cropping period (Table 4.36). Hence, care must be taken when selecting the soil hydrologic group and thus the curve numbers to be used, as this governs the frequency of occurrence and the magnitude of runoff events. The second most sensitive model input parameters differed between the three compounds and the two loss paths, but were mostly those governing sorption (K_{oc}, Freundlich exponent, OM). However, for the weakly sorbing and very mobile compound dichlorprop-P the application date became more sensitive than sorption-related parameters. For erosion losses of the relatively strongly sorbing and persistent compound terbutryn the field slope was important, which influences the magnitude of erosion events.

Table 4.36: Most sensitive PRZM parameters with respect to maximum daily pesticide losses

compound	crop	application period	target output R/E[1]	most sensitive model parameters 1	most sensitive model parameters 2	LR[2] mean r^2	2LR[3] mean r^2	n (valid)[4] of 1165
dichlorprop-P	winter cereals	spring	R	CN in_crop[5]	appl. date	0.186	0.295	978
dichlorprop-P	winter cereals	autumn	R	CN in_crop	appl. date	0.220	0.321	902
isoproturon	winter cereals	spring	R	CN in_crop	OM	0.255	0.333	1040
isoproturon	winter cereals	autumn	R	CN in_crop	OM	0.285	0.332	1017
terbutryn	maize	spring	R	CN in_crop	K_{oc}	0.543	0.669	1070
terbutryn	winter cereals	autumn	R	CN in_crop	K_{oc}	0.431	0.575	1059
dichlorprop-P	winter cereals	spring	E	CN in_crop	appl. date	0.050	0.118	848
dichlorprop-P	winter cereals	autumn	E	CN in_crop	appl. date	0.063	0.141	771
isoproturon	winter cereals	spring	E	CN in_crop	Freundlich m[6]	0.059	0.122	998
isoproturon	winter cereals	autumn	E	CN in_crop	K_{oc}	0.080	0.134	944
terbutryn	maize	spring	E	slope	K_{oc}	0.251	0.347	1071
terbutryn	winter cereals	autumn	E	CN in_crop	slope	0.116	0.327	1061

1) R = runoff, E = erosion

2) Simple linear regression with the most sensitive model parameter for the LHS blocks with valid MLR runs. r^2 gives a rough indication of the variance explained by this model parameter alone.

3) Multiple linear regression with the two most sensitive model parameters for the blocks with valid MLR runs. r^2 gives a rough indication of the variance explained by these two model parameters.

4) Multiple linear regressions with a coefficient of determination $r^2 \geq 0.15$ were considered valid.

5) curve number in cropping period (from emergence to harvest)

6) Freundlich exponent

4.3.8 Conclusions and Recommendations

The model testing exercise (section 4.2) revealed that there are some limitations of PRZM due to the simplistic hydrology and the daily calculation timestep. This model-inherent error cannot be reduced by the user. An uncertainty analysis including different uses, soils, climates, weather years, and sensitive model parameters (section 4.3.7) showed that the annual weather variability is the most important source of uncertainty with respect to pesticide runoff losses, and also plays an important role with respect to erosion losses. Thus, a major part of the uncertainty due to parameter and input error can be captured by simulating several weather years. The results of the uncertainty analysis and of the predictive PRZM modelling also suggest that the uncertainty introduced by the annual weather variability is larger than the model error. Thus, the probabilistic component (simulating 20 weather years per climate scenario) in the predictive modelling ensures that sufficient confidence can be put in the predicted pesticide losses via runoff and erosion.

5 Calculation of Predicted Environmental Concentrations (PEC_{sw}) in Surface Water Bodies and Aquatic Risk Assessment

"Risk assessment should therefore be a scientific process and not some sort of black art."
Mick Hamer (2000)

To establish confidence in the results of a risk assessment procedure, transparency with respect to the methodologies and assumptions used in the exposure and risk assessment is essential. In this chapter, first the methods used for the PEC_{sw} calculation and the subsequent aquatic risk assessment are described in detail. Subsequently, results are presented and discussed for a number of important uses as examples. Finally, the uncertainty in the exposure and risk estimates and its sources are discussed.

A question that has to be clarified before comparing exposure and effect is the likelihood that maximum daily drainage and runoff/erosion inputs occur on the same day. In most cases, the highest daily drainage losses from agricultural fields were simulated in the typical drainflow season from late autumn to early spring, when the soils are wet. In contrast, the highest daily pesticide losses via runoff and erosion were mostly predicted for late spring, early summer and early and mid-autumn, when heavy rainfalls are more frequent than in the winter period. Hence, the probability that peak runoff and drainage inputs coincide on the same day is low, although it is somewhat higher for autumn-applied pesticides than for spring-applied pesticides. It was therefore felt that adding the peak inputs from drainage and surface runoff for the exposure estimate would constitute an unrealistic worst case. Moreover, it has to be considered that pesticide inputs via both pathways are associated with water flow (drain outflow and runoff water, respectively) into the stream (cf. eq. 5.1 and 5.2, section 5.1). Thus, even if the maximum daily drainflow and runoff inputs occurred on the same day, the resulting concentration in surface water would be considerably lower than the sum of PEC_{sw} due to drainage and PEC_{sw} due to runoff inputs. On the basis of these considerations, in the following the assessment of exposure is performed separately for pesticide inputs via drainage and surface runoff.

5.1 Materials and Methods

Due to the requirements of a web-based application in ISIP and the lack of regionalized data on surface water body characteristics, simple, but nevertheless scientifically valid approaches had to be identified for the calculation of PEC_{sw} (**P**redicted **E**nvironmental **C**oncentrations in **s**urface **w**ater) and the subsequent aquatic risk assessment.

The pesticide losses via drainflow (calculated with MACRO) and via runoff and erosion (calculated with PRZM) were stored in lookup tables. However, because of software limitations and computer performance problems, it was not feasible to store all possible PEC_{sw}, which depend on both the model results and the municipality in which the respective field is located, in a lookup database for the use in ISIP. Therefore, PEC_{sw} calculation and risk assessment have to be performed online and input-specifically within the ISIP risk assessment module. Because of the need for a quick online calculation of PEC_{sw}, it is only possible to calculate acute exposure concentrations, i.e. maximum initial PEC_{sw}. Chronic exposure of aquatic organisms cannot be considered at the moment, as the calculation of long-term PEC_{sw} would be computationally very expensive and take too much time for a web-based application. The same holds true for the concentrations of pesticides adsorbed to the stream bed sediment (PEC_{sed}). However, in the pesticide registration process the risk assessment for sediment dwelling organisms is performed with the long-term PEC_{sw} anyway, not with PEC_{sed}. Thus, a calculation of PEC_{sed} is not necessary for the risk assessment.

5.1.1 Calculation of PEC_{sw} Caused by Drainflow

After calculation of pesticide losses via drainage using MACRO and creation of a lookup table, the correct simulation result must be assigned online to the respective input of the farmer/advisor in order to calculate PEC_{sw} and conduct an aquatic risk assessment.

First, the field is assigned to one of the 8 soil classes (cf. Appendix C). The user can enter the soil properties either according to the current German soil classification system (*Bodenkundliche Kartieranleitung*; AG Boden, 1994) or according to the German soil appraisal (*Reichsbodenschätzung*; Pfeiffer et al., 2003). Subsequently, the climate scenario is determined by the geographical position of the municipality. Afterwards, the user enters the target crop (winter cereals, spring cereals, oilseed rape (winter), oilseed rape (spring), maize, sugar beet or potatoes) and optionally compound, product or target organism. With these inputs, the model run/result pertaining to this soil/climate/use-combination can be identified. The maximum initial pesticide concentration in the receiving surface water body can, as an approximation, be calculated with the following formula:

$$PEC_{\,sw,D} = \frac{[\text{drainloss}] * [\%\ \text{crop area}] * [\%\ \text{treated}] * [\text{tile drain density}]}{[\text{discharge } 75] + [\%\ \text{arable land}] * [\text{tile drain density}] * [\text{drainflow}]} \qquad \text{(eq. 5.1)}$$

where

$PEC_{sw,D}$: predicted maximum initial pesticide concentration in the receiving surface water body at the catchment outlet (µg L^{-1}) due to drainage inputs

drainloss: maximum daily pesticide drainage loss in the simulation period (mg km^{-2} d^{-1}) (MACRO output)

% crop area: proportion of the municipality area covered by the respective crop (*Agrarstrukturerhebung*; Statistisches Bundesamt, 1999)

% treated: proportion of the area of the respective crop (NEPTUN 2000; Roßberg et al., 2002) treated with the pesticide of concern; when no application data were availabe, “% treated” was set to 50 %.

tile drain density: tile- or mole-drained proportion of the arable land of the municipality (assumed equal for all field crops; Huber, 1998)

discharge 75: 75^{th} percentile of the long-time month-specific discharge (m^3 km^{-2} d^{-1}) of the receiving water body (each municipality belongs to one of 350 non-overlapping watersheds; Behrendt et al., 2002)

% arable land: proportion of the municipality area covered by arable land (*Agrarstrukturerhebung*; Statistisches Bundesamt, 1999). Here the simplifying assumption is made that the area-specific drainflow volumes from the different crop types are similar.

drainflow: area-specific drainflow (m^3 km^{-2} d^{-1}) at the day of the maximum daily pesticide drainage loss (m^3 km^{-2} d^{-1}) (MACRO output)

This formula basically dilutes the maximum daily pesticide drainage input in the sum of drainflow volume and stream discharge on that day and yields a daily average flux concentration. The PEC_{sw} obtained refer to the outlet of a small watershed with about 10 km^2 area, approximately covering the area of a small municipality. They are neither intended for edge-

of-field estimates nor for large watersheds (> 100 km^2). In large watersheds, not all water entering the streams would reach the catchment outlet within one day.
The 75th percentile of the month-specific water body discharge was used in the PEC equation as opposed to the 50th percentile, because larger drainflow events usually occur when the soil is relatively wet and thus also the stream discharge in the catchment is higher than for average soil moisture conditions.
The variable ”% treated“ reflects both the plant protection intensity in this culture and the area-related market share of the pesticide in this use. As a consequence, it is possible that for a compound with a high market share and relatively advantageous sorption and degradation properties a higher PEC is calculated than for a compound with less advantageous properties, but only a small market share.

5.1.2 Calculation of PEC_{sw} Caused by Surface Runoff and Erosion

The assignment of the correct PRZM simulation result to the user’s input is done analogously to the MACRO simulations (cf. section 5.1.1). In contrast to the drainage simulations, however, the 8 climate scenarios are independent from the 5 soil scenarios. The key to the runoff soil scenarios is given in Table I.1, Appendix I.
For strongly sorbing compounds with a K_{oc} greater than ca. 1000 L kg^{-1} it is frequently observed in reality (e.g. Spatz, 1999; Haider, 1994), that the pesticide loss via erosion (bound to eroded soil material) is higher than the surface runoff loss (dissolved in the runoff water). In this PRZM modelling exercise this was the case in 15.4 % of 356800 simulation runs. Unfortunately, accounting for pesticide erosion inputs in the PEC_{sw} calculation would be problematic for the use in ISIP because of the considerable computational expense and the general lack of regionalized data on stream bed sediment properties (depth, bulk density, organic carbon content etc.). To clarify the relevance of pesticide erosion inputs for acute exposure concentrations in surface water, a very conservative estimate was made with the following assumptions: no stream bed sediment present, instantaneous sorption equilibrium between the surface water body and the eroded soil particles, and linear sorption of the pesticides. For *discharge 75* (analogously to drainflow, the 75th percentile of the month-specific discharge was chosen, because larger runoff events usually occur when the soil is already pre-wetted and also the stream discharge in the catchment is higher than for average soil moisture conditions) and the proportion of agricultural land exclusive of grassland (it is assumed that runoff only occurs on arable land and special cultures such as vines and hops),

the unweighted mean over all German municipalities was used. The estimate revealed that the maximum initial concentration in surface water resulting from erosion inputs was in 14.5 % of the simulations higher than the concentration caused by runoff inputs, and in 5.6 % higher by a factor greater than 10. As the assumptions made in the estimate (especially the absence of bed sediment) are very conservative and lead to considerable overestimation of the pesticide fraction in the water phase, it can therefore be justified to consider only pesticide inputs via surface runoff for the calculation of initial PEC_{sw}. In the case of a later use of the data where computation time plays a less important role than for the ISIP web page, and with more and better data on real water bodies in the landscape, the predicted runoff and erosion losses can be directly used as input for a more sophisticated aquatic pesticide fate model (e.g. TOXSWA) or for self-developed equations accounting for water flow velocity and water-sediment interactions.

As a consequence of the considerations above, the maximum initial pesticide concentration in the receiving surface water body can, as an approximation, be calculated with the following equation:

$$PEC_{sw,R} = \frac{[\text{runoff loss 90}] * [\text{\% crop area}] * [\text{\% treated}]}{[\text{discharge 75}] + [\text{\% (agricultural land - grassland)}] * [\text{runoff}]} \qquad \text{(eq. 5.2)}$$

where

$PEC_{sw,R}$:	predicted maximum initial pesticide concentration in the receiving surface water body at the catchment outlet (µg L^{-1}) due to runoff inputs
runoff loss 90:	90^{th} percentile of maximum daily pesticide runoff loss in the simulation period (mg km^{-2} d^{-1}) (PRZM output) Here, the 90^{th} percentile corresponds to the weather year with the second highest maximum loss of the 20 simulated years.
% treated:	proportion of the area of the respective crop treated with the pesticide of concern (NEPTUN 2000, Roßberg et al., 2002; NEPTUN 2001, Roßberg, 2003). When no application data were availabe, the “% treated” was set to 50 %.
% (agricultural land - grassland):	proportion of the municipality area covered by agricultural land exclusive of grassland (*Agrarstrukturerhebung*; Statistisches Bundesamt, 1999). Here it is assumed that surface runoff only

occurs on arable land and special cultures like hops or vines, but not on grassland. Furthermore, it is assumed that the area-specific runoff volumes from the different crop types are similar.

runoff: area-specific surface runoff volume (m^3 km^{-2} d^{-1}) at the day of the maximum daily pesticide runoff loss (m^3 km^{-2} d^{-1}) (PRZM output)

Analogously to the calculation of PEC_{sw} due to drainage (cf. section 5.1.1), this formula dilutes the maximum daily pesticide runoff input in the sum of runoff volume and stream discharge on that day and yields a daily average flux concentration. Because PRZM tends to underestimate runoff volume and pesticide losses for high-intensity rainstorms (cf. section 4.2), which are in most cases responsible for the maximum daily losses in a simulation period, it was decided to calculate the PEC from the 90^{th} percentile of maximum daily runoff loss and not from e.g. the 50^{th} percentile. This way a possibly too low level of protection for the aquatic community is avoided. Nevertheless, outside of ISIP pesticide concentrations in surface water due to runoff can also be calculated from any other percentile of maximum daily loss.

5.1.3 Aquatic Risk Assessment Based on Calculated PEC_{sw}

As risk is a function of both exposure and effect (e.g. FOCUS, 2001), PEC_{sw} alone do not say much about the risk a compound poses to the aquatic ecosystem. The risk for the aquatic community is decisively influenced by the ecotoxicity of the different compounds. As within ISIP it is not possible to calculate long-term PEC_{sw}, a chronic risk assessment (required for fish, invertebrates and sediment dwelling organisms) cannot be performed here. Hence, only acute exposure and effect concentrations are compared.

As the probability that peak drainage and peak runoff inputs occur on the same day is low (see above), PEC_{sw} are calculated separately for drainage and for runoff inputs (cf. section 5.1.1 and 5.1.2). Subsequently, the higher of both PEC_{sw} is compared with the acute aquatic “maximum tolerable concentration” for the respective pesticide. The acute “maximum tolerable concentration” is defined here as the minimum over all test species of the ratio of the acute ecotoxicological endpoint (EC_{50} or LC_{50}) and the legally required safety factor (TER = Toxicity/Exposure Ratio) of 10 (algae and higher aquatic plants) or 100 (fish and invertebrates). In other words, the “maximum tolerable concentration” is the highest concentration at which for all test taxa the required TER is met and thus no risk is to be expected for any of the test species. If higher-tier studies such as mesocosm experiments are carried out by the registrant (the company applying for the registration of a certain use), the required TER for the use of concern may be reduced to a value smaller than 10 or 100, respectively. However, since this information was not available here, the standard TER values of 10 and 100 were employed for all simulated uses. The required TER can be easily updated in the ISIP database though, if registrants provide the author with eventual reduced values.

Ecotoxicity data were chiefly obtained from EU review reports (European Commission, 2004a and 2004b), the EPA Pesticide Ecotoxicity database (USEPA, 2004) and PSD evaluation documents (PSD, 2004). The risk for the aquatic community is evaluated as follows in ISIP:

- If the simulated PEC_{sw} is lower than the maximum tolerable concentration, it can be expected that there is no significant risk for the aquatic community.
- If the simulated PEC_{sw} is higher than the maximum tolerable concentration, a danger to the aquatic community cannot be excluded.

The outcome of the risk assessment (no significant risk or possible danger) is shown to the user on the screen (cf. chapter 6), as well as whether the risk originates from runoff or drainage inputs.

Apart from selecting a single pesticide for the risk assessment, the ISIP user is also able to choose a certain product or a certain target organism. If he chooses a plant protection product which contains more than one active ingredient, PEC_{sw} calculation and subsequent risk assessment are conducted separately for each compound. The appraisal of the product is then based on the compound which yields the highest risk. If the user chooses a certain target organism (weed, pest or fungal disease), PEC_{sw} calculation and risk assessment are performed for each product that is registered for the use against this target organism in the respective crop.

It has to be noted that the simulation results and the resulting PEC_{sw} are always based on the **maximum** registered a.i. doses for this use ("use" in the sense of compound/crop/application season combination; not in the regulatory sense of product/crop/application season). That means, if the user chooses a plant protection product with a lower registered dose (e.g. 1.0 kg ha^{-1}) of a certain a.i., the PEC_{sw} will nevertheless correspond to the maximum dose mentioned above (e.g. 1.5 kg a.i. ha^{-1}) and the risk will be slightly overestimated. A linear loss correction for lower doses has deliberately not been included in ISIP because pesticide sorption behaviour is usually nonlinear, and thus a dose reduction by e.g. 50 % by no means implies that losses are also reduced by 50 %.

5.2 Results and Discussion: Predicted Environmental Concentrations in Surface Water (PEC_{sw}) and Aquatic Risk

In the following the PEC_{sw} distributions for runoff and for drainage over the ca. 13000 German municipalities and the different soil scenarios are presented and discussed for selected important uses in each crop type. Furthermore, for each of these uses the PEC_{sw} are compared with the maximum tolerable concentration of the respective pesticide. Also, example PEC maps for isoproturon are shown.

In the case of drainage, there are 8 soil scenarios that can be assigned to a field. The climate scenario is determined by the soil scenario and the geographical position of the municipality in which the field is located. In the case of runoff, the climate scenario is exclusively determined by the municipality in which the field is situated and thus independent from the 5 soil scenarios. The number of resulting soil/municipality combinations (and PEC_{sw}) per simulated use is 92456 for drainage und 65720 for runoff. Of course, not all combinations occur in reality, since not each municipality will contain all soil classes. Table 5.1 shows the distribution of simulated PEC_{sw} due to drainage and runoff inputs over all municipality/soil combinations for some typical uses, all with a rather large area-specific market share, which is an input in the PEC calculations (cf. section 5.1). A table containing PEC_{sw} for some more compounds and uses is given in Appendix M on the attached CD-ROM. Since for the special cultures hops, orchards and strawberries no drainflow simulations were performed, only PEC_{sw} due to runoff are available for uses in these crops.

Table 5.1: Distribution of PEC_{sw} over all soil/municipality combinations[1)] for some typical uses

compound	crop	application month[1)]	dose	max. tol. conc.[2)]	input path	mean	median	75th perc.	95th perc.	99th perc.	maximum
		1-12	g ha^{-1}	µg L^{-1}	D / R[3)]	µg L^{-1}					
captan	pome fruit	7	1556.3	0.262	R	0.036	0.0039	0.018	0.105	**0.344**	**6.514**
cyprodinil	strawberries	5	375	0.32	R	5.3E-04	2.4E-04	4.6E-04	0.0020	0.0056	0.016
dichlorprop-P	spring cereals	5 or 4	1500	410	D	0.123	0.0053	0.032	0.710	2.088	16.63
		5	1500	410	R	1.766	0.641	1.955	7.528	16.06	41.78
	winter cereals	4 or 3	1500	410	D	0.443	0.0044	0.035	0.864	11.73	202.1
		4	1500	410	R	1.617	0.126	1.090	7.954	25.10	61.17
		10	1500	410	D	5.137	0.321	1.702	29.73	102.2	250.7
		10	1500	410	R	13.76	8.048	20.17	49.37	75.09	109.9
diflufenican	winter cereals	10	187.5	0.2	D	0.0019	0	3.4E-04	0.012	0.031	0.096
		10	187.5	0.2	R	0.102	0.064	0.138	**0.356**	**0.518**	**0.973**
		3	66.6	0.2	D	3.0E-04	0	7.7E-05	0.0016	0.0050	0.017
		3	66.6	0.2	R	0.018	0.011	0.022	0.059	0.110	**0.295**
dithianon	hops	7	1000	0.23	R	0.0017	2.5E-04	4.2E-04	0.0037	0.038	0.120
ethofumesate	sugar beet	5 or 4	1000	110	D	0.201	0	0.041	0.985	3.877	14.00
		5	1000	110	R	0.880	0.206	1.137	3.826	7.087	17.34
fenpropi-morph	winter cereals	5 or 6	750	24	D	1.7E-04	0	0	5.8E-04	0.0047	0.019
		5	750	24	R	0.368	0.261	0.496	1.055	1.673	2.826
fluazinam	potatoes	7	200	0.36	R	0.0058	0.0016	0.0048	0.022	0.080	0.186
isoproturon	spring cereals	5 or 4	1500	1.3	D	0.064	0	6.1E-04	0.328	**1.330**	**10.04**
		5	1500	1.3	R	1.174	0.488	**1.341**	**4.724**	**10.48**	**24.74**
	winter cereals	4 or 3	2000	1.3	D	0.037	0	0.0011	0.205	0.800	**4.311**
		4	2000	1.3	R	**2.636**	0.657	**3.068**	**11.92**	**21.61**	**61.95**
		10 or 9	1500	1.3	D[4)]	1.253	3.5E-05	0.123	**8.067**	**23.07**	**103.7**
		10	1500	1.3	R	**6.664**	**2.015**	**8.621**	**30.09**	**47.72**	**81.21**
mancozeb[5)]	potatoes	6	552.6	264	R	0.242	0.056	0.195	0.977	3.417	10.14
	stone fruit	5	767.5	264	R	0.0059	6.1E-05	0.0017	0.022	0.106	1.588
metamitron	sugar beet	5 or 4	3600	22	D	0.586	0	0.041	1.625	10.42	**154.2**
		5	3600	22	R	3.752	0.868	4.983	15.90	**32.30**	**85.74**
metazachlor	oilseed rape, spring	4	1250	0.47	D	0.0012	0	1.0E-06	0.0061	0.035	0.091
		4	1250	0.47	R	0.099	0.021	0.101	**0.512**	**0.825**	**1.297**
	oilseed rape, winter	8 or 9	750	0.47	D	0.036	0	0.0026	0.140	**0.888**	**6.645**
		8	750	0.47	R	**1.653**	**0.525**	**2.072**	**7.238**	**13.19**	**24.01**
metribuzine	potatoes	5 or 4	700	0.81	D	0.073	0.0019	0.020	0.263	**1.239**	**40.96**
		5	700	0.81	R	0.402	0.064	0.274	**1.685**	**5.920**	**27.48**
nicosulfuron	maize	5	40	0.17	D	0.0091	5.7E-05	0.0024	0.041	0.166	**0.931**
		5	40	0.17	R	0.054	0.020	0.073	**0.211**	**0.409**	**1.499**
pirimicarb	stone fruit	5	312.5	0.065	R	0.0026	3.0E-04	0.0014	0.012	0.040	**0.334**
propiconazole	spring cereals	6 or 5	125	5.1	D	0.0064	0	0.0031	0.039	0.081	0.215
		6	125	5.1	R	0.031	0.019	0.038	0.106	0.169	0.306
tebuconazole	oilseed rape, spring	5	376.8	4.9	R	0.0085	0.0058	0.012	0.023	0.040	0.086
	oilseed rape, winter	4 or 5	376.8	4.9	D	2.0E-04	0	5.0E-06	6.4E-04	0.0051	0.031
		4	376.8	4.9	R	0.087	0.058	0.118	0.259	0.457	1.251
		9 or 10	376.8	4.9	D	4.7E-04	0	1.5E-05	0.0021	0.010	0.054
		9	376.8	4.9	R	0.099	0.064	0.138	0.309	0.460	0.822
terbuthylazine	maize	5	750	0.32	D	0.234	0	0.110	**1.195**	**3.716**	**12.66**
		5	750	0.32	R	**1.193**	**0.674**	**1.756**	**3.871**	**6.692**	**19.22**

[1)] For the drainage simulations, the application month for a given use may vary between the 19 soil/climate scenarios (cf. section 3.3.3).
[2)] maximum tolerable concentration (cf. section 5.1.3)
[3)] D = drainage (MACRO); R = runoff (PRZM)
[4)] Autumn application on tile-drained fields is currently not allowed in Germany for most IPU-containing products.
[5)] Because of the rapid hydrolytical breakdown of Mancozeb, dose, PEC_{sw} and maximum tolerable concentration refer to the main metabolite of Mancozeb, ethylene thiourea (ETU).
bold: The maximum tolerable concentration is exceeded.

For the use of the fungicide captan in pome fruit, the maximum tolerable concentration was exceeded only in very few cases (1.4 %). This can be attributed to the rapid dissipation of captan (cf. Appendix A).

No exceedance of the maximum tolerable concentration (0.32 µg L^{-1}; Table 5.1) was found for cyprodinil in strawberries, which is probably mainly due to the relatively small crop area covered by strawberries.

Although partly very high concentrations in surface water were simulated for the highly mobile herbicide dichlorprop-P, especially for autumn application in winter cereals (up to 251 µg L^{-1} for drainflow), neither for surface runoff nor for drainage inputs exceedances of the maximum allowed concentration were observed. This is due to the low acute ecotoxicity of dichlorprop-P (Table 5.1). Analogous results were observed for all registered uses of bentazone, which are therefore not listed in Table 5.1.

For autumn application of the herbicide diflufenican in winter cereals, in 14 % of the soil/municipality combinations the maximum tolerable concentration was exceeded due to runoff inputs. Due to the slow degradation and relatively strong sorption of diflufenican (Appendix A), a large proportion of the applied dose is still present in the uppermost 2 cm of the soil when a runoff event occurs. Yet, the strong sorption has also the effect that the availability of diflufenican for extraction by runoff water is comparatively low. No exceedance was observed for drainage inputs, which are generally limited for strongly sorbing compounds. The lower diflufenican concentrations for spring application compared to the autumn application can be explained by the lower dose and by the faster degradation at higher temperatures.

No exceedance was simulated for the fungicide dithianon in hops. This can be attributed both to the strong sorption of the compound, which limits the availability for extraction by runoff water, and accelerated degradation in the summer months. Growing of hops is concentrated in very few regions of Germany. Outside these regions, the proportion of the municipality area covered by hops was set to 0.01 %. Therefore, significant concentrations in surface waters are only predicted for the main hop-growing regions.

For the herbicide ethofumesate in sugar beet, no exceedance of the maximum tolerable concentration was observed by either drainage or runoff inputs, although rather high surface water concentrations (up to 17 µg L^{-1} for runoff) were simulated for both input paths. This result can be attributed to the low acute ecotoxicity of ethofumesate.

No exceedance either was simulated for the fungicide fenpropimorph in winter cereals, which is strongly sorbing and has relatively low acute ecotoxicity.

Also, for the fungicide fluazinam in potatoes no exceedance of the maximum tolerable concentration (0.36 µg L^{-1}) was predicted. This is probably due to the relatively low dose of fluazinam of 200 g ha^{-1}.

For the spring application of isoproturon in winter cereals, in 40 % of the cases exceedances are predicted for runoff, but only in 0.3 % for drainflow. For the autumn application, in 57 % of the cases an exceedance caused by runoff inputs, and in 12 % caused by drainflow inputs is predicted. Apart from the large market share of isoproturon in winter cereals (the region-specific proportion of the area cropped with winter cereals that is treated with isoproturon totals up to 85 %), the relatively high dose of isoproturon in combination with its mobility are mainly responsible for the exceedances. The difference in the PEC_{sw} distributions between spring and autumn application (here: April and October, resp.) reflects the slower degradation due to low temperatures in late autumn compared to spring. The PEC_{sw} for IPU in spring cereals (exceedance in 1.0 and 26 % of the cases for drainflow and runoff, resp.) are of similar magnitude as those for spring application in winter cereals. With regard to the risk posed to aquatic ecosystems by inputs of isoproturon, it has to be noted that the application of isoproturon on soils with more than 30 % clay content is not allowed in Germany. This applies to all soils of runoff soil class 5 and a few of soil class 4, which are both very prone to the occurrence of surface runoff, and also to drainage soil class 8, which is very prone to drainflow. Actually, the purpose of this restriction is to avoid leaching of IPU via macropores to groundwater, but also the risk of IPU inputs into surface waters via runoff and drainage is substantially reduced this way.

For the fungicide mancozeb neither in potatoes nor in stone fruit exceedances were simulated. Note that because of the rapid hydrolytical breakdown of mancozeb upon contact with water, PEC_{sw} and maximum tolerable concentration refer to the main metabolite of mancozeb, ethylene thiourea (ETU), which is of low acute ecotoxicity (Appendix A).

For the herbicide metamitron in sugar beet, despite the high dose only in few cases exceedances due to runoff (2.4 %) and drainage inputs (0.4 %) were predicted. This can be attributed to the relatively low acute ecotoxicity of metamitron.

For the use of metazachlor in winter rape in 52 % of the municipality/soil combinations an exceedance of the maximum tolerable concentration caused by surface runoff inputs was predicted. Both the high market share of metazachlor in rape (the region-specific proportion treated can reach 88 %) and the relatively low maximum tolerable concentration (0.47 µg L^{-1}) play a role here. In contrast, only few exceedances (6 %) were predicted for spring application in spring rape, which is grown quite rarely in Germany and thus holds only low proportions of the crop area (as the statistical data available did not distinguish between winter and spring rape, the crop area of spring rape within a municipality was conservatively assumed as 10 % of the total oilseed rape area).

For the weakly sorbing herbicides metribuzine (in potatoes) and nicosulfuron (in maize) an exceedance by runoff inputs was simulated in 10 and 7.5 % of the cases, respectively. The reason that, despite the low sorption of metribuzine and nicosulfuron, PEC_{sw} due to surface runoff were higher than PEC_{sw} due to drainflow is probably the application month. Usually in May a lot of runoff-producing rainstorms occur, but there is only little drainflow because the soils are already rather dry.

Despite high acute ecotoxicity, in only 0.4 % of the cases exceedances of the maximum tolerable concentration due to runoff inputs were predicted for the insecticide pirimicarb in stone fruit. This can be attributed to the relatively small proportions of the crop area held by stone fruit orchards (Statistisches Bundesamt, 1999).

For the fungicide propiconazole, which should be prone to runoff losses due to its sorption and degradation properties (Appendix A), the maximum tolerable concentration of 5.1 $\mu g\ L^{-1}$ was not exceeded in any of the soil/municipality combinations. This is probably mainly due to the low dose of 125 $g\ ha^{-1}$, the moderate acute toxicity of propiconazole and a rather narrow distribution of simulated runoff losses over the different soil classes (cf. section 4.3.6).

No exceedances either were predicted for the fungicide tebuconazole in winter and spring rape. Although the median absolute tebuconazole runoff losses calculated with PRZM are higher than those for metazachlor in the corresponding crops (Appendix L), the $PEC_{sw,R}$ in Table 5.1 for tebuconazole are consistently lower than those for metazachlor. As the crops are the same and the overall market share of tebuconazole in oilseed rape is only slightly lower than that of metazachlor (Roßberg et al., 2002), there are only two possible explanations for these findings: i) the market shares of tebuconazole and metazachlor have different spatial distributions over Germany (this is relevant with respect to climate scenarios and river discharges), or ii) the distributions of absolute simulated runoff losses over soils, climates and weather years are narrower and less skewed for the strongly sorbing, persistent tebuconazole than for the moderately sorbing, readily dissipating metazachlor (cf. section 4.3.6). Both possibilities are indeed the case.

In contrast to the former two compounds, for the use of the herbicide terbuthylazine in maize in 65 % of the cases an exceedance caused by runoff inputs was predicted. Also, in 17 % of the soil/municipality combinations, PEC_{sw} due to drainage inputs exceeded the maximum tolerable concentration of terbuthylazine. Apart from the high market share (the region-specific proportion of the maize area that is treated totals up to 100 %), the comparatively disadvantageous sorption and degradation properties of terbuthylazine (intermediate sorption with a K_{oc} of 247 L kg^{-1}, which implies relatively low leaching tendency with still good availability for runoff, and sufficient mobility to reach tile drains through macropores in significant amounts; relatively high persistence; cf. Appendix A) are responsible for these results.

In summary, it is evident from Table 5.1 that initial PEC_{sw} not only varied strongly between the different uses, but also over the soil/municipality combinations within a given use. This spread reflects both the differences in simulated maximum daily losses (due to soil, climate and weather year) and of regional differences in river discharge, crop area and proportion treated. From a comparison of mean and median PEC_{sw} values (Table 5.1) it can be seen that all distributions are more or less skewed to the right. However, the skew, the range and also the percentage of zero simulated losses varied strongly between different uses (cf. Appendix M) and also between input paths for the same use (Fig. 5.1). Generally, distributions of PEC_{sw} due to drainage were wider and more skewed than those of runoff PEC_{sw} for the same use.

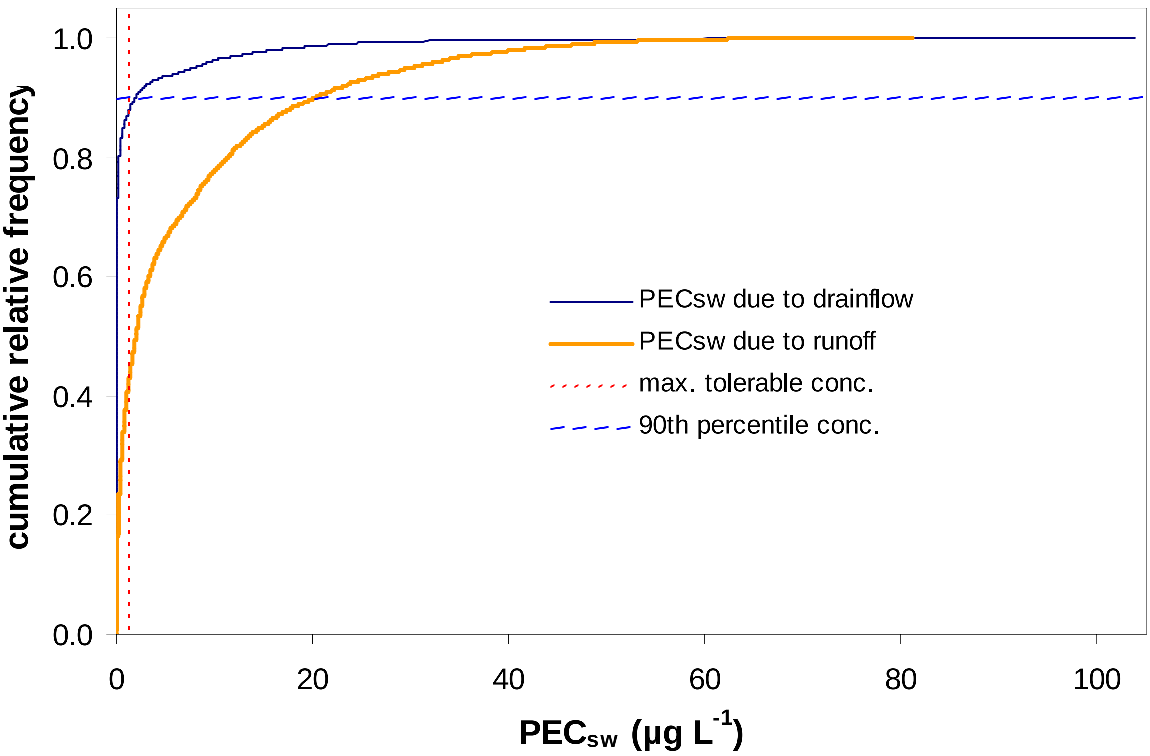

Fig. 5.1: Cumulative frequency distribution of PEC_{sw} due to drainage and surface runoff for isoproturon in winter cereals, autumn application. The vertical dashed line indicates the maximum tolerable aquatic IPU concentration (1.3 µg L^{-1}), and the horizontal dashed line the 90th percentile of the distributions.

In most cases, PEC_{sw} due to runoff were higher than PEC_{sw} due to drainage for the same use, which is in accordance with the results of Huber et al. (2000) and Röpke et al. (2004). It might be argued that the higher concentrations caused by surface runoff as compared with drainage are mainly due to the fact that the 90th percentile of maximum daily runoff losses (i.e. the second worst weather year of the 20 years simulated) was used for $PEC_{sw,R}$ calculation, whereas for MACRO only one “average” weather year was simulated. However, even if the PEC_{sw} caused by runoff inputs are calculated with the 50th percentile of maximum daily losses (i.e. the year with the 10th highest maximum daily loss), these $PEC_{sw,R}$ are in most cases still higher than the PEC_{sw} caused by drainage inputs (cf. Table M.1, Appendix M).
The following example maps (Fig. 5.2-5.5) show PEC_{sw} for drainage and runoff inputs of isoproturon applied to winter cereals. To create the maps, the soil- and municipality-specific PEC_{sw} (Table 5.1) were combined with the land-use-differentiated German soil map 1 : 1000000 (BGR, 1999) according to the following method:

1. Each municipality has several ”potential“ PEC_{sw}, one for each soil class (8 for drainage, 5 for surface runoff)
2. The 8 MACRO soil classes represent the 17 drainage-relevant soil mapping units (cf. section 3.3.1); the 5 PRZM soil classes represent all 57 agriculturally used soil units in Germany (cf. section 4.3.1).
3. The German municipality map (IfAG, 2000) was intersected with the land-use-differentiated soil map (BGR, 1999). Both input maps were polygon layers (shapefiles).
4. Within each municipality, the soil- and municipality-specific PEC were assigned to the resulting soil polygons according to the soil unit / soil class they belonged, separately for drainage and runoff.

It has to be pointed out that, as the BUEK displays only dominant soil types, the maps reflect the PEC_{sw} based on isoproturon losses for the **dominant** soil type in each soil polygon. Also, no PEC_{sw} due to drainage or runoff are shown for areas outside the areas covered by the drainage- or runoff-relevant soil classes in the BUEK. However, the white “no data” areas in the maps do not mean that there are no drainage-relevant soils (in the case of drainage) or no agricultural soils at all (in the case of surface runoff). These restrictions of the maps have to be kept in mind. Moreover, for the PEC_{sw} calculation it was assumed that the farmers always apply the maximum allowed dose. It must be stressed that the purpose of the maps is to identify **areas at risk** of damage to the aquatic ecosystem (under the current cropping and application conditions), not to depict the pesticide concentrations occurring in reality.

Fig. 5.2 reveals that for autumn application in winter cereals the maximum tolerable isoproturon concentration (1.3 $\mu g\ L^{-1}$) is basically only exceeded by the $PEC_{sw,D}$ in areas in southern and middle Germany covered by soil class 8 (Pelosol-Braunerde), which occurs only on a few geological substrates, e.g. mesozoic shale strata. Since the heavy clay soils represented by this soil class contain more than 30 % clay, the application of isoproturon on these soils is not allowed. Moreover, for most IPU-containing products autumn application on artificially drained fields is currently not allowed in Germany at all. Hence, if the former restriction is observed by the farmers, drainage inputs from autumn application of isoproturon to winter cereals should not pose a significant risk to aquatic ecosystems (provided that the agricultural and application statistics used for PEC calculation are still valid), and consequently the latter restriction is in principle not necessary. After soil class 8, the highest $PEC_{sw,D}$ occurred in areas covered with soil class 7 (Pseudogley, silty) and class 2 (Gley-Vega, loamy-silty), which also represent relatively heavy and structured soils.

For spring application of isoproturon in winter cereals (Fig. 5.3), $PEC_{sw,D}$ exceeded the maximum tolerable concentration only in a few spots in Southern Germany belonging to the scenarios 2 S and 2 OR (cf. Table 3.31, section 3.3.1). These spots reflect coincidences of disadvantageous values of two region-specific variables used in the PEC calculation (eq. 5.1): the proportion of the municipality area covered with winter wheat and the tile drain density.

PEC_{sw} due to runoff after application in spring (April) exceeded the maximum tolerable concentration of isoproturon for large areas in Southern and middle Germany (Fig. 5.4), while markedly less exceedances were predicted for Northern Germany. This pattern corresponds rather well with the spatial distribution of soil classes of different runoff susceptibility (Fig. 4.13, section 4.3.1).

For autumn application of IPU in winter cereals, the relation of the $PEC_{sw,R}$ to the soil class is less obvious (Fig. 5.5). Although most predicted exceedances of the maximum tolerable concentration occur in Southern and middle Germany on soils belonging to the runoff-prone hydrologic groups C and D, exceedances are also occasionally predicted for group B soils with little runoff susceptibility, e.g. in the northeast of Germany in Mecklenburg. In these areas, very high proportions of the municipality area (> 30 %) are cropped with winter cereals. For nearly all regions of Germany, at least spotwise exceedances of the maximum tolerable IPU concentration were predicted. Apart from the soil class and the area cropped with winter cereals, also the effect of the frequency of high-intensity rainstorms (cf. Fig. 4.14, section 4.3.1) on the $PEC_{sw,R}$ distribution is visible. For instance, comparatively low $PEC_{sw,R}$ and few exceedances of the maximum tolerable concentration were predicted for the drier east of Germany with long recurrence intervals of runoff-producing rainstorms.

The PEC distributions have shown that predicted pesticide concentrations in surface water can vary strongly between different regions. These results point out the necessity of regionally differentiated exposure and risk assessment approaches for pesticide inputs into surface waters.

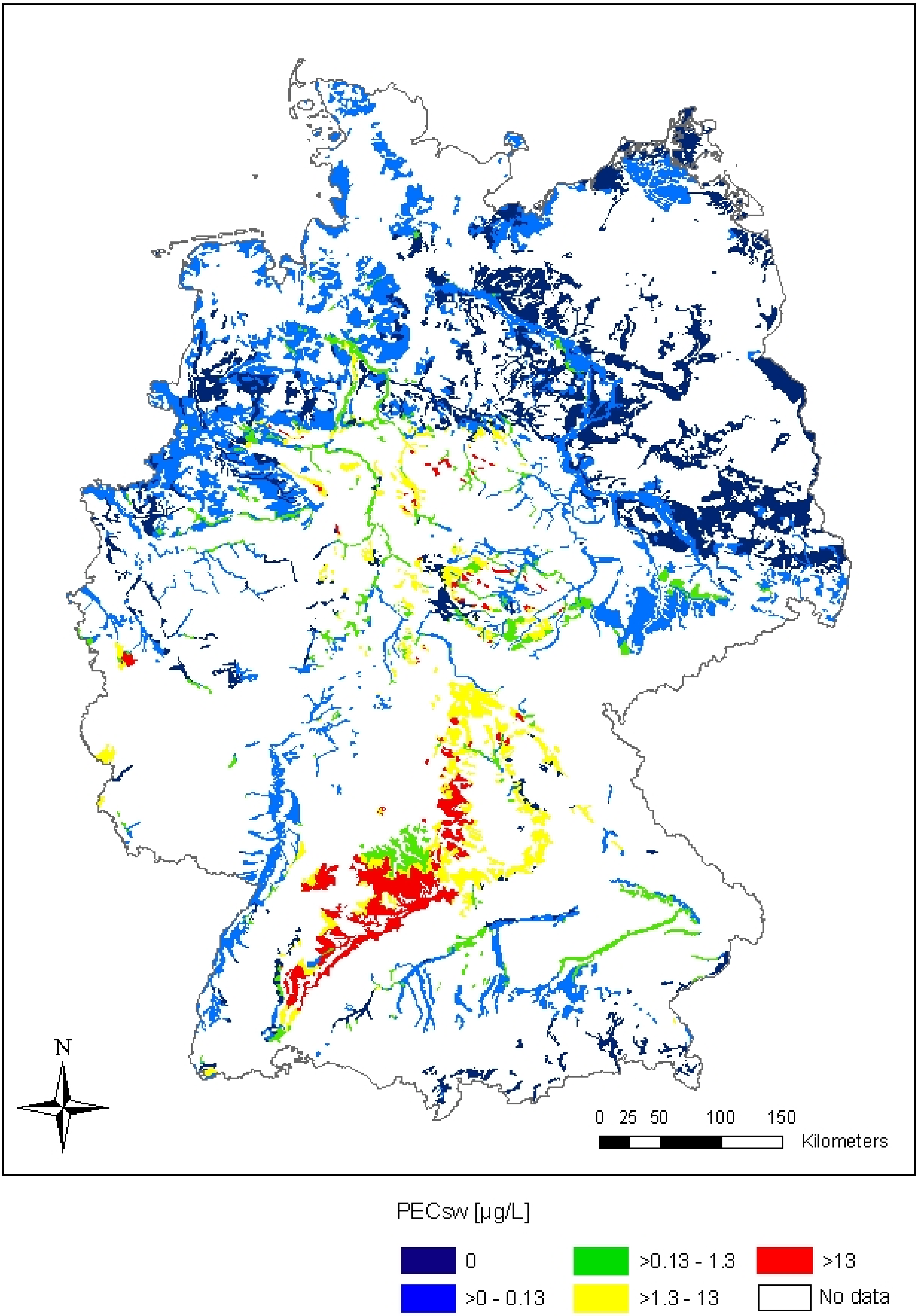

Fig. 5.2: PECsw (maximum initial concentrations in the receiving surface water body) due to drainage inputs for isoproturon in winter cereals, autumn application.

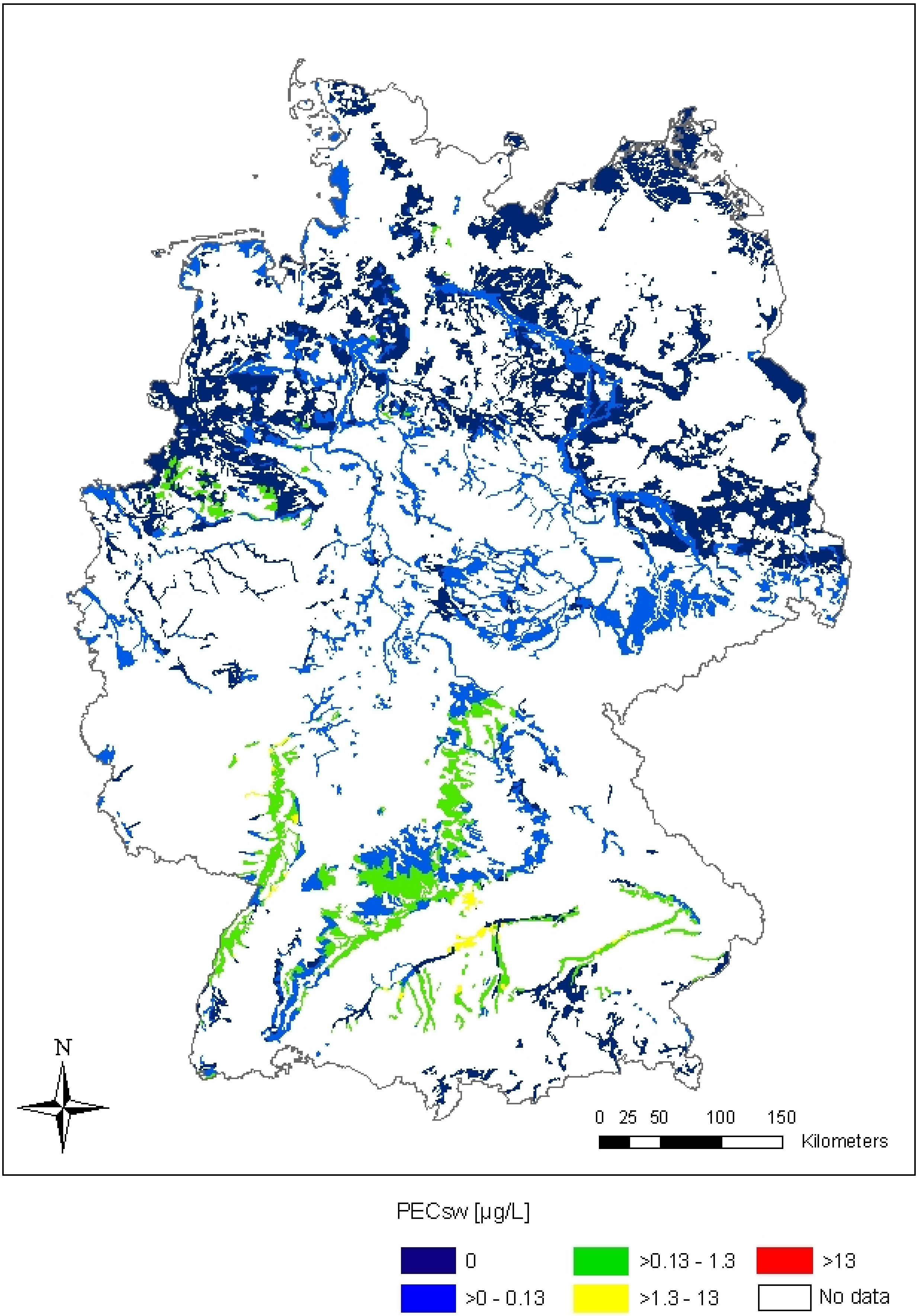

Fig. 5.3: PECsw (maximum initial concentrations in the receiving surface water body) due to drainage inputs for isoproturon in winter cereals, spring application.

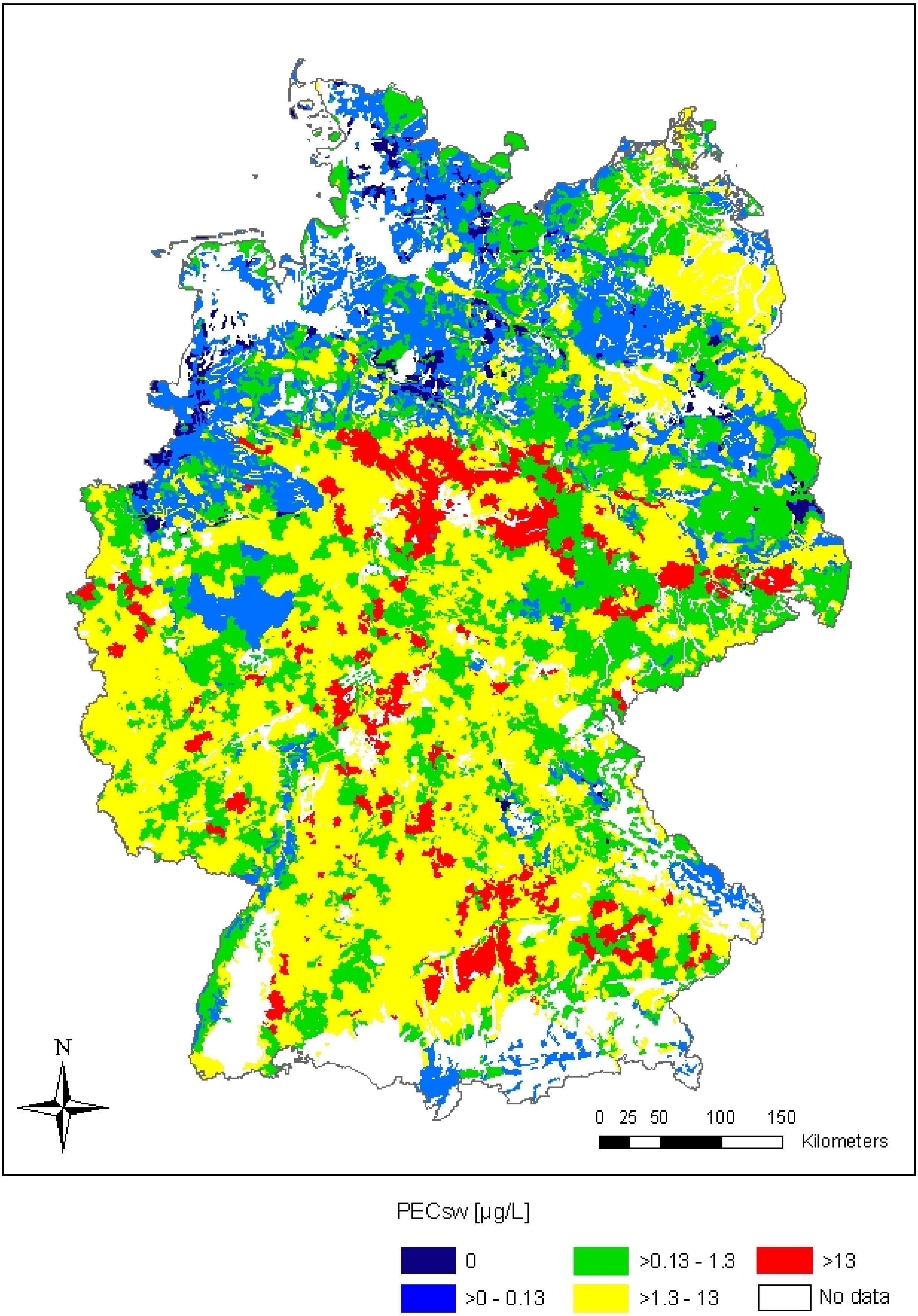

Fig. 5.4: PECsw (maximum initial concentrations in the receiving surface water body) due to runoff inputs for isoproturon in winter cereals, spring application. The PEC are based on the 90th percentile year with respect to maximum daily runoff loss.

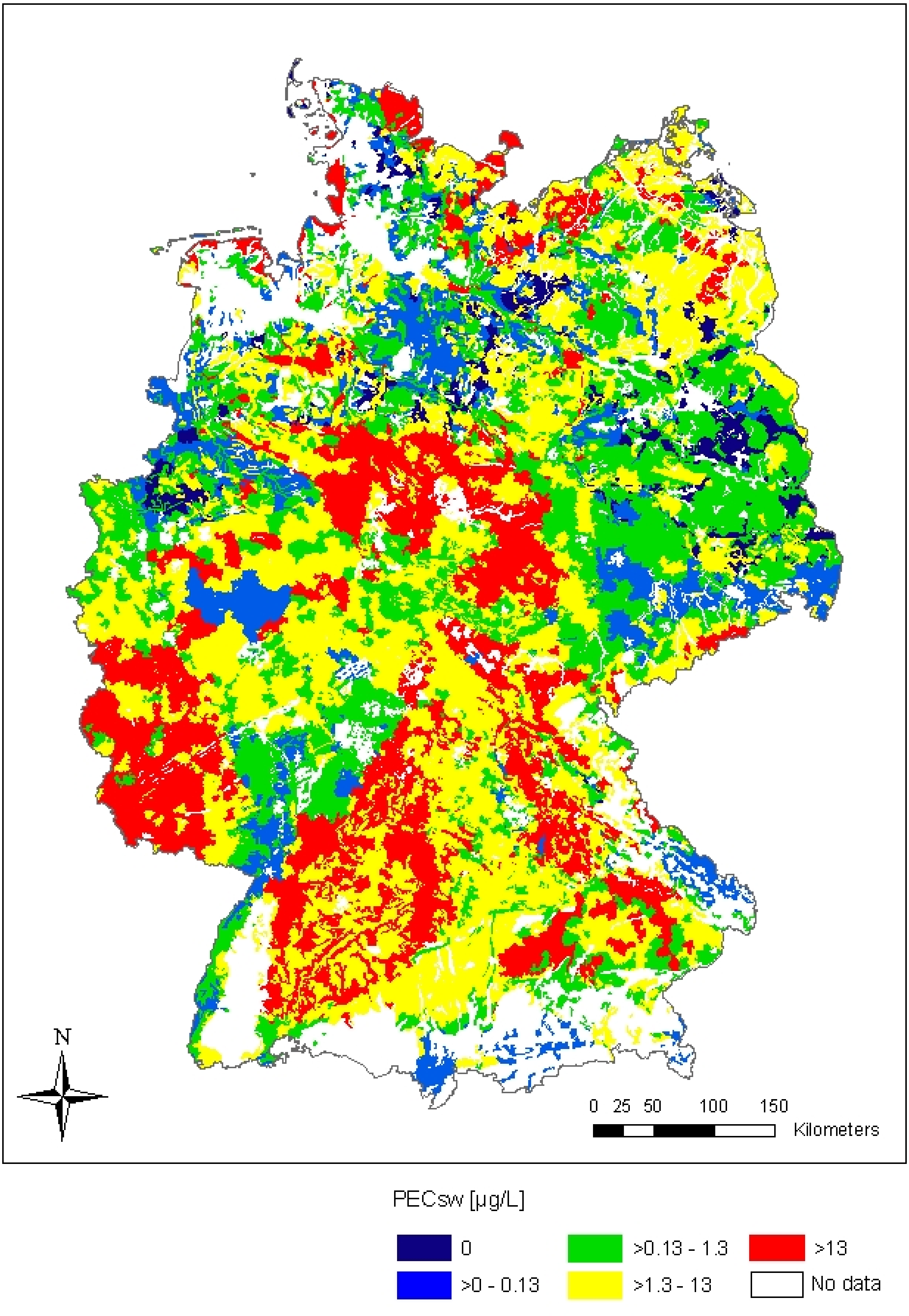

Fig. 5.5: PECsw (maximum initial concentrations in the receiving surface water body) due to runoff inputs for isoproturon in winter cereals, autumn application. The PEC are based on the 90th percentile year with respect to maximum daily runoff loss.

5.3 Uncertainty Considerations

Predicted environmental concentrations are often misunderstood as absolute, “true” values. However, the uncertainty sources contributing to the overall uncertainty of the PEC_{sw} and the outcome of the subsequent risk assessment are numerous. In the following, the uncertainty inherent in the different steps of the ISIP risk assessment approach and its sources are discussed.

First of all, the farmer’s field has to be assigned to a runoff- and a drainage soil/climate scenario based on user input. The hierarchical keys to the soil scenarios have been carefully designed to be simple and unequivocal (cf. Appendix C and I). Moreover, they offer the possibility to the user to enter the soil properties according to either the German soil classification system (AG Boden, 1994) or the German soil appraisal (*Reichsbodenschätzung*, Pfeiffer et al., 2003). Basic soil properties according to one of the two systems should normally be known to the farmer. However, a part of the uncertainty remains, since the assignment of a wrong soil scenario due to wrong user input can never be completely excluded. Assignment of a wrong climate scenario due to wrong user input is nearly impossible, since this is done by the municipality in which the farmer’s field is located. However, in the case of runoff climate scenarios, it is still possible that the particular field has, due to its aspect or slope position, high-intensity rainfall patterns different from the municipality average. Also for the drainage climate scenarios, the local climate, especially the amount of rainfall, might be different from the “representative” climate due to differences in altitude or luff/lee-situation.

The uncertainty in the calculated pesticide losses from the field via drainflow has several sources. First, MACRO is not able to simulate pesticide volatilization, which can be considered as model error. However, this problem was alleviated by the preferential use of field half-lives if available, because they already account for this dissipation path. Another problem is the uncertainty of the sensitive parameter ASCALE (effective diffusion pathlength), which governs the water and solute exchange between the micro- and the macropores. The structural description (which determines the value of ASCALE) of the soil horizons in the 8 soil scenarios was derived by expert knowledge. However, even within the same field, soil properties are strongly variable, both spatially and temporally. The temporal variability of soil structure is further enhanced by tillage operations, and these effects cannot be easily accounted for in MACRO 4.3. The most important source of uncertainty in the drainage simulations is that the annual variability of the weather is not captured (cf. section

3.3.7), since only one weather year per climate scenario could be simulated due to the long computation time of MACRO 4.3.

For the pesticide losses via runoff and erosion calculated with PRZM, the situation is somewhat different. In contrast to the MACRO simulations, a probabilistic approach to capture the annual weather variability was feasible. However, there is a relatively large model error inherent in the pesticide losses predicted with PRZM (cf. section 4.2). First, the empirical methods used for simulating surface runoff and erosion are being used beyond their original scope. Both SCS curve number technique for runoff calculation and the USLE/MUSLE/MUSS approach for erosion calculation have been developed in the USA and are based on experimental data from the US. Because of the empirical nature of both approaches, the transferability of their parameter values to European conditions is questionable. Moreover, the USLE approach was originally intended for yearly or seasonal soil losses, not for calculations on a daily basis (Wischmeier, 1976). In fact, this method is basically a statistical summary of measured erosion data (one could also say, a metamodel based on experimental data). Secondly, the USLE actually calculates soil loss from the slope segments of a field and not the sediment leaving the field, because it does not account for deposition of eroded soil material in e.g. depressions or at the bottom of the slope (Wischmeier, 1976). This leads to overestimation of sediment inputs into surface water bodies; however, this overestimation may be corrected in PRZM by the parameterization of the MUSS equation (eq. 4.4, section 4.1.1), which was specifically designed for small watersheds. Thirdly, as already mentioned (cf. section 4.2), the daily calculation time step leads to overestimation of runoff and erosion for low-intensity rainstorms (small runoff events) and to underestimation for high-intensity rainstorms (large runoff events). This underestimation of large runoff events was alleviated by taking the 90^{th} percentile year (with respect to maximum daily pesticide loss) of the 20 simulated years for the PEC calculations. The runoff curve numbers are the most sensitive input parameters for PRZM; they are tabulated for the different soil hydrologic groups, different crop types and good or bad status of the crop (Carsel et al., 2003). However, also other factors not considered here influence runoff susceptibility, like crusting, presence of cracks, or increased surface roughness after tillage operations. Thus, both the starting point of surface runoff and the total runoff volume can be easily mispredicted. It must also be mentioned here that although PRZM considers the effect of snowmelt in the runoff equation, the curve numbers are not adjusted to account for the effects of snowpack or frozen ground on runoff generation. This might lead to overestimation (in the case of snowpack) or underestimation (in the case of frozen ground) of surface runoff and is critical for autumn-applied pesticides.

Further uncertainty is introduced by the PEC_{sw} calculation method itself. First of all, the PEC calculation method employed here does not consider pesticide inputs via erosion. Although the neglect of erosion inputs is justifiable for the calculation of initial PEC_{sw} (cf. section 5.1.2), it is nevertheless unsatisfactory from a scientific point of view.

Secondly, PEC_{sw} are calculated separately for drainage and runoff inputs, and the possibility that peak drainage and runoff inputs occur on the same day is neglected. However, it has been shown that the probability of a coincidence is low (cf. introduction to chapter 5). Moreover, even if the maximum daily drainflow and runoff inputs did occur on the same day, the resulting concentration in surface water would be lower than the sum of $PEC_{sw,D}$ and $PEC_{sw,R}$. Thus, it is preferable to evaluate pesticide drainage and runoff inputs separately.

Thirdly, it has to be noted that MACRO and PRZM simulations yield edge-of-field estimates for pesticide losses. For the PEC calculation it was conservatively assumed that all pesticide lost from the field will enter the surface water body. However, not all pesticides entering the tile drains might reach the surface water body, due to losses during transport in the drains, e.g. by infiltration, sorption to macrophytes or to the walls of the collector drain. Yet, this reduction in pesticide input is hardly predictable and probably not significant. A more important issue is the possible reduction of pesticide runoff and erosion losses by vegetated buffer strips and topography effects. Grassed buffer strips directly adjacent to the lower edges of agricultural the fields have indeed been shown to effectively reduce surface runoff, erosion, and associated pesticide losses from these fields (cf. section 2.1). However, such buffer strips are not commonly used by farmers in Germany. In contrast, bank vegetation along surface water bodies cannot be considered as effective in reducing chemical inputs via runoff and erosion (cf. section 2.1). With regard to the effects of topography, e.g. for fields in hollow positions or fields far away from a surface water body: There is no experimental evidence that under Middle European conditions, once generated concentrated surface runoff will reinfiltrate into the soil before reaching a surface water body. Moreover, in most regions of Germany (except for e.g. karst landscapes) the surface water network density is larger than 1 km km^{-2} (Huber, 1998), so that a large distance of a field of several hundred meters to the nearest surface water body is unlikely. It can be concluded that neither the mere distance of a field to a surface water body nor the presence of bank vegetation is sufficient to apply reduction factors to pesticide runoff and erosion inputs. Hence, the use of edge-of-field pesticide losses for PEC_{sw} calculation is justified and can be considered as not too conservative.

The PEC_{sw} calculated according to eq. 5.1 (section 5.1.1) for drainage and eq. 5.2 (section 5.1.2) for runoff do not reflect only the pesticide application of the farmer, but of all farmers in a small catchment. As a consequence of the variable *% treated* (the proportion of the area of the respective crop treated with the pesticide of concern) in the PEC_{sw} equations, it is possible that the use of a pesticide with relatively advantageous sorption and degradation properties, but a high market share, might yield a higher PEC than the use of a pesticide with disadvantageous properties, but a small market share. Therefore, the market share of a pesticide for a given use has to be kept up-to-date. Otherwise, there is a danger of putting some pesticides at a disadvantage. It is also inherent in the PEC_{sw} equations that applications of the same pesticide in other crops, which might also cause pesticide inputs into the surface water body, are not considered. Moreover, the agricultural statistics (*Agrarstrukturerhebung*; Statistisches Bundesamt, 1999) are only differentiated at the county (*Landkreis*) level. Hence, there may be deviations in the area proportions covered by arable land or the different crops between single municipalities and the county average. Finally, it has to be emphasized that pesticide inputs via spraydrift are not considered in the PEC_{sw} calculations. It is assumed that the farmer will follow the label restrictions! Also point-source inputs of pesticides into surface waters are explicitly not considered here (cf. section 2.1).

A major source of uncertainty in the risk assessment process is the uncertainty on the effect side. Of course, it would have been desirable to consider this uncertainty with a probabilistic approach like the one suggested by Aldenberg and Jaworska (2000). This approach uses Species Sensitivity Distributions (SSD), which are cumulative distributions of the ecotoxicological endpoints of several test species belonging to the same taxonomic group. The method proposed by Aldenberg and Jaworska (2000) allows to calculate Fractions Affected FA_x (i.e., what percentage x of species will be affected at a given pesticide concentration) as well as Hazardous Concentrations HC_x (i.e., at which concentration a given percentage x of species will be affected) for each taxonomic group, both with confidence intervals. However, even if enough data points for each taxonomic group had been available to create reliable SSD, the outputs from a risk assessment based on SSD would not be understandable for most ISIP users (e.g. farmers, agricultural advisors), who are not familiar with complex statistical concepts. Hence, we chose a simple Toxicity/Exposure Ratio (TER) approach for the risk assessment as opposed to a SSD approach.

Since long-term PEC_{sw} could not be calculated, a chronic risk assessment cannot be performed. Although the acute toxicity of a compound to a test species is in most cases more critical than the chronic toxicity, in some cases the risk is underestimated by comparing only initial PEC and acute ecotoxicological endpoints.
Finally, it must be pointed out that the PEC calculated here are intended for small catchments of ca. 10 km^2 size. Exposure and thus risk to aquatic organisms may be higher at “hot spots” directly adjacent to drain outlets or agricultural fields.

5.4 Conclusions and Recommendations

The results of the PEC_{sw} calculations have revealed that there are large differences in predicted concentrations not only between different uses and input paths, but also between different regions in Germany. The need for a regionally differentiated exposure and risk assessment is therefore evident.
A large number of uncertainty sources contribute to the overall uncertainty in the calculated pesticide concentrations in surface water. It becomes clear that at least the major sources of uncertainty, e.g. the annual weather variability, have to be accounted for in the risk assessment process to create a reliable basis for decisions. The use of probabilistic methods in aquatic risk assessment for pesticides is therefore highly recommended.

6 The Risk Assessment Module in ISIP

In the following the user interface of the risk assessment module is briefly presented as it exists in MS Access and also as it will appear in ISIP for the user. The risk assessment module was programmed by Jukka Höhn and Björn Röpke in VBA (Visual Basic for Applications).

6.1 The Input Dialogues

The user (farmer or plant protection advisor) has to fill in 3 different dialogues, so that for his individual field and his individual use the appropriate simulation run can be identified. In the first dialogue *Gemeindeauswahl* the municipality is chosen, which is unequivocally determined by state / administrative district / name of the municipality (Fig. 6.1).

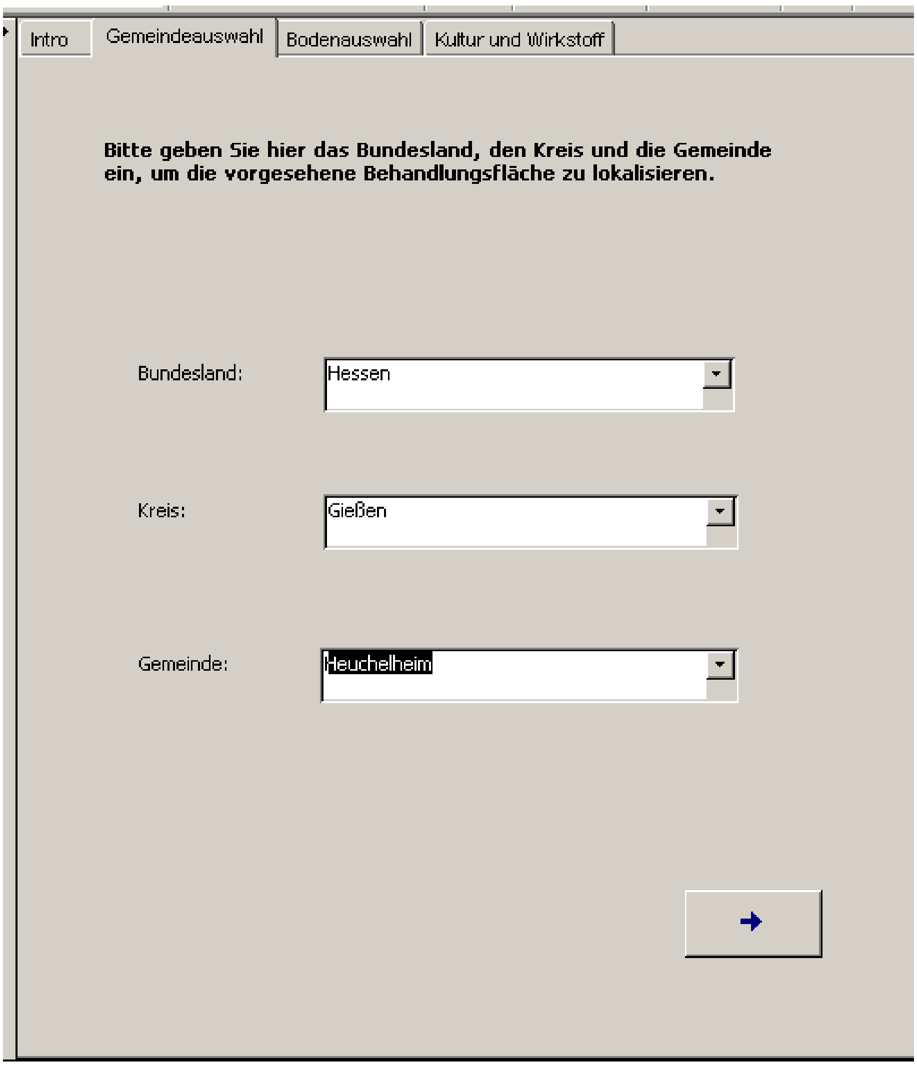

Fig. 6.1: The dialogue *Gemeindeauswahl* (choice of municipality)

In the next dialogue *Bodenauswahl* (choice of soil; Fig. 6.2) the user is first requested to indicate whether his field is artificially drained or not. Only in the first case a risk assessment for drainage inputs is performed.

When selecting the soil, the user has the possibility to enter, depending on his status of knowledge, either

a) particle size class (Bodenart) and type of soil genesis (Entstehungsart) according to the German soil appraisal (*Reichsbodenschätzung*; Pfeiffer et al., 2003) or

b) particle size class (Bodenart) of the topsoil according to the German soil classification system (*Bodenkundliche Kartieranleitung*; AG Boden, 1994) and the statement ”marsh soil“, ”alluvial soil“, “soil with slowly permeable subsoil horizon” or ”don’t know“

to identify the soil scenario.

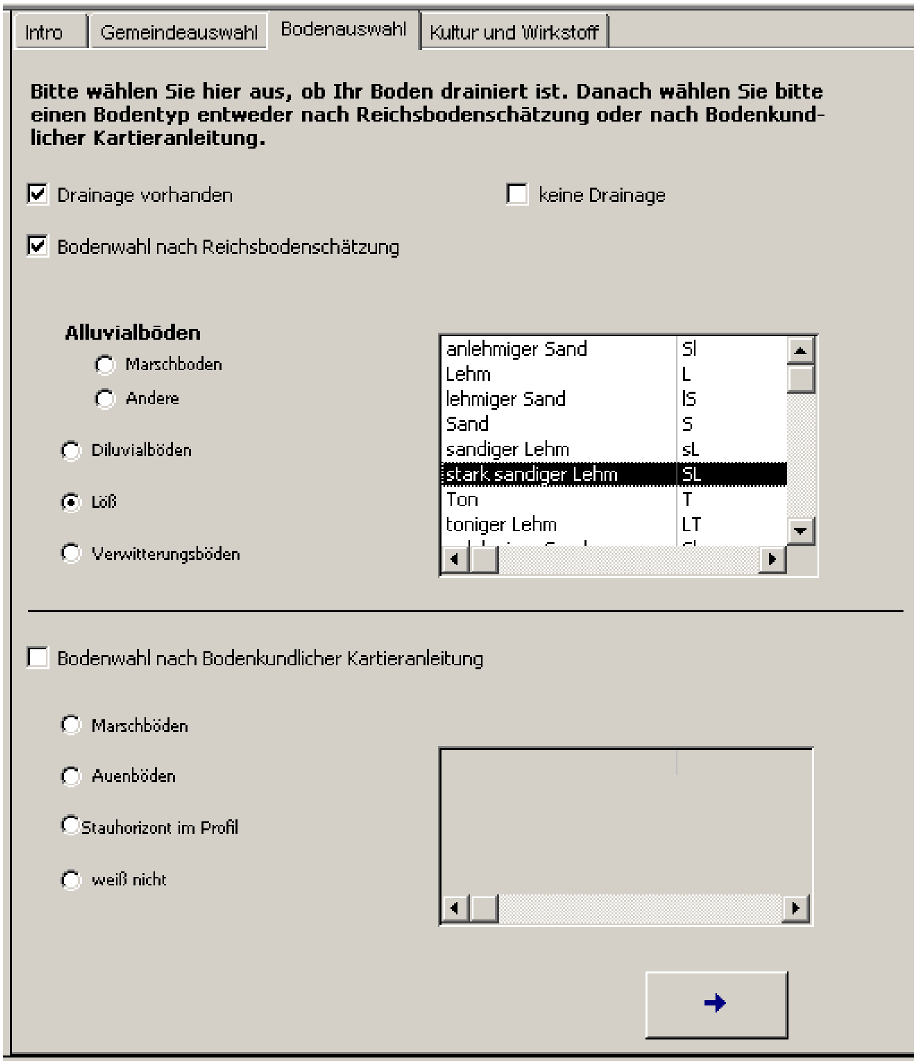

Fig. 6.2: The dialogue *Bodenauswahl* (choice of soil)

In the dialogue *Kultur und Wirkstoff* (Fig. 6.3) the user first selects the crop to be treated and then the intended application season (spring, summer, autumn or winter). Subsequently, the user has the possibility to choose a certain plant protection product, a certain compound or a certain target organism. In the first two cases the user will get exactly one result, in the latter case usually several (mostly several products / pesticides are registered for the use against one certain target organism).

After filling in these 3 dialogues the input necessary for starting the risk assessment is available. The internal course of action is: identification of the pertaining simulation runs → querying the model results → PEC calculation → risk assessment.

Thereby the user input is assigned in the background to both the corresponding drainage simulation (MACRO) and the corresponding runoff simulation (PRZM). An uncomfortable double data entry is avoided.

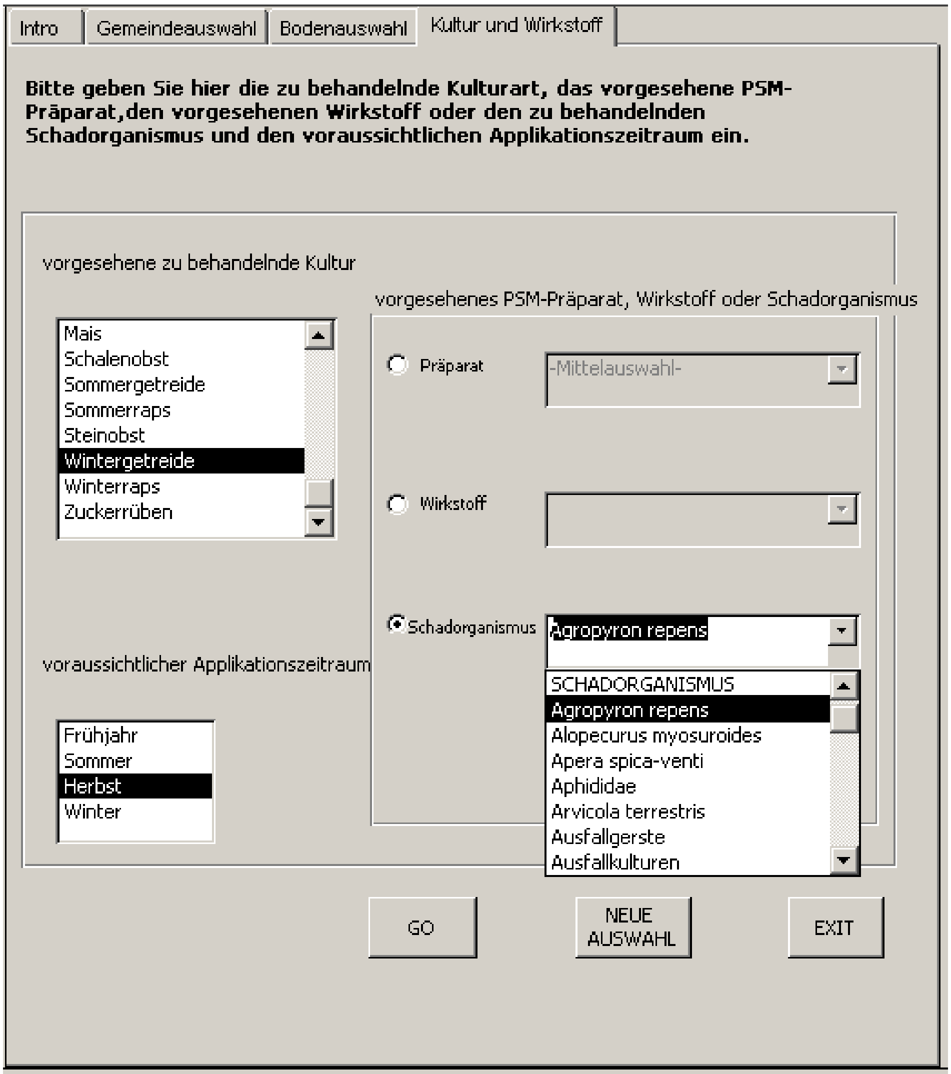

Fig. 6.3: The dialogue *Kultur und Wirkstoff* (crop and pesticide)

6.2 Display of Results

Fig. 6.4 shows the output window in the case of the choice of a target organism. If a single pesticide or a plant protection product has been chosen, the window is analogous but simpler. In the lower field the crops are listed for which the respective product / crop type combination is registered; this is only relevant for the crop types winter and spring cereals, which contain several plant species (wheat, rye, barley etc.).

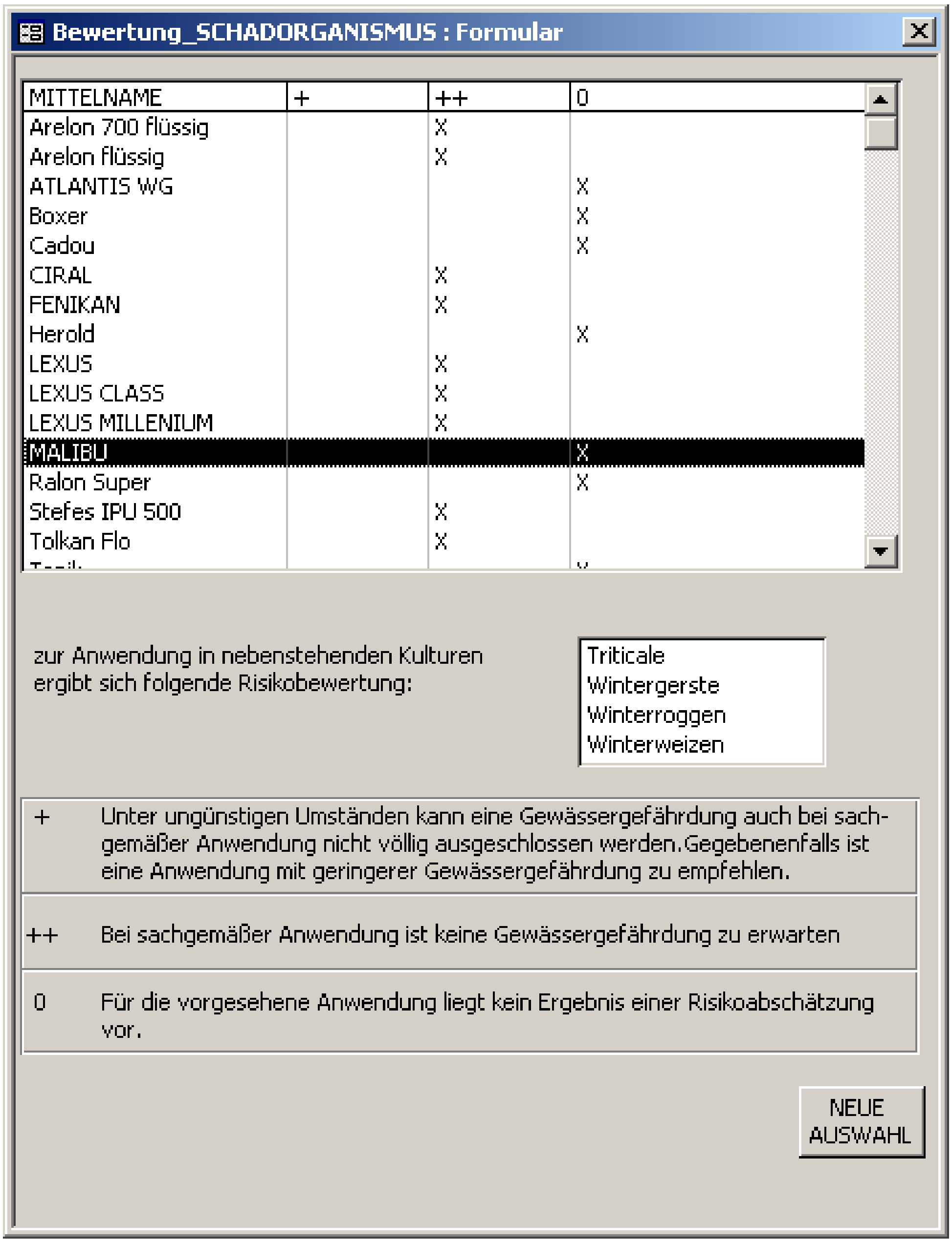

Fig. 6.4: The output window for the risk assessment if a target organism was chosen

In the ISIP risk assessment procedure, the simulated PEC_{sw} is compared with the maximum tolerable concentration of the pesticide. If the PEC_{sw} exceeds this threshold, the compound is rated with ”+“ (a danger to the aquatic community cannot be excluded). If the PEC_{sw} is lower than the threshold, the compound is rated with ”++“ (no significant risk for the aquatic community). If no ecotoxicity data are available or, for any reason, no simulation run exists for this registered use, this case is labelled with ”0“.

7 General Discussion

In this chapter the limitations and the plausibility of the predictions of the developed risk assessment approach are discussed. Also the benefits, possible risks, and wider implications of the approach are addressed.

Like all modelling and risk assessment approaches, the approach developed in this study has of course limitations. As was discussed in detail in section 5.3, the calculated PEC_{sw} carry considerable uncertainty. The most important source of uncertainty for the PEC_{sw} due to drainflow is the annual variability of the weather, which could not be accounted for in the MACRO calculations. For PEC_{sw} due to runoff, the most important sources of uncertainty are the limitations of the PRZM model and the non-consideration of erosion inputs in the PEC_{sw} calculation. Also the applicability of the calculated PEC_{sw} is limited to the **outlet of small catchments** between ca. 1 and 100 km^2. For “hot spots” in the catchment directly adjacent to treated fields, peak concentrations in surface water would be underestimated by the PEC_{sw}. For catchments larger than ca. 100 km^2, the assumption used in the PEC_{sw} equations that all water entering the streams reaches the catchment outlet within one day does not hold any more. Therefore, PEC calculation for larger watersheds would require the use of a catchment hydrology model. It must also be noted that the catchments for which the PEC_{sw} are calculated are hypothetical. The PEC calculation formula (eq. 5.1) for drainage inputs implies the assumption that all drained arable fields belong to the same soil class. Analogously, the PEC_{sw} equation for runoff inputs (eq. 5.2) assumes that all areas in the catchment covered with arable land and special cultures belong to the same soil class. These assumptions may hold for some, but certainly not for all small catchments under agricultural use in Germany. However, it must be pointed out that the intention of the approach employed here was not to predict **real** concentrations, but to provide a site- and use-specific risk assessment.

Of course, the predicted losses and pesticide concentrations have to be **realistic** in order to allow a reliable risk assessment. For this reason, in the following a comparison is done with some examples of measured data from the literature which were not used for model testing. It must be stressed, however, that measured literature values and calculated losses and concentrations are, strictly speaking, not comparable at all. Firstly, measurements and simulations are not based on the same conditions (soil, climate, dose, crop area proportions etc.). Secondly, the loss or PEC distribution for a given use does not represent a single set of conditions, but a wide range of different soils, climates etc. Thirdly, measured concentrations in surface water mostly cannot distinguish between runoff and drainage inputs. Moreover, the observed pesticide concentrations are often substantially influenced by point sources. Hence, a comparison between literature data and simulation results can only give an indication of the realism or the credibility of the predictions.

Flury (1996) reviewed the available literature on field drainage studies. He reported cumulative (annual or seasonal) losses of less than 0.003 % of the applied amount for strongly sorbing compounds (trifluralin, pendimethalin) and up to 3.6 % for more mobile, moderately sorbing compounds (atrazine, metolachlor). These ranges correspond well to the cumulative 3-year losses predicted with MACRO: For metolachlor in maize, losses of 0 to 7.1 % (median = 0.04 %) of the applied amount were simulated over the 19 soil/climate scenarios, and for pendimethalin in maize 0 to 0.004 % (Appendix F). Also the cumulative metolachlor drainage loss of 0.02 % reported by Funari et al. (1998) from a silt loam soil fits well into the simulated range. From a literature survey, FOCUS (2001) concluded that mass losses via drainage were largest in well-structured clay soils, and somewhat less in loamy soils. Sandy soils with shallow groundwater seemed to pose a smaller risk than soils exhibiting macropore flow. Also these observations are in accordance with the MACRO simulations (Tables 3.33 and 3.34, section 3.3.6). After autumn application on winter cereals, Kördel et al. (1996) found total seasonal drainage losses of 0.36 % of the applied amount for isoproturon and 0.001 % for pendimethalin in a silt loam soil in northwestern Germany. The corresponding peak losses of these herbicides were 0.12 % and 0.0002 % of the applied amount, respectively. For autumn application in winter cereals, the 3-year drainage losses predicted with MACRO range from practically zero to 23 % (median = 0.026 %) of the applied amount for isoproturon and from 0 to 0.0048 % for pendimethalin over the 19 soil/climate scenarios. The simulated maximum daily losses range from practically zero to 4.6 % (median = 0.0026 %) of the applied amount for IPU and from 0 to 0.0009 % for pendimethalin (Appendix F). Thus, for both herbicides, and for both total and maximum losses, the measurements were well within the predicted range. Kördel et al. (1996) also monitored a stream in the same agriculturally intensively used region for five months (March to August) and observed peak concentrations in surface water of 0.72 μg L^{-1} for isoproturon and and 0.62 μg L^{-1} for bentazone. These values fall in the upper percentile ranges of the simulated PEC_{sw} for these compounds due to drainflow (Appendix M), which was probably the most important diffuse source of pesticide inputs for this stream. In a long-term monitoring study (1990-1996) in the Vemmenhög catchment (9 km^2) in Sweden, which is tile-drained and dominated by sandy loam soils, Kreuger (1998) found in part very high peak concentrations in surface water at the catchment outlet. For instance, the maximum observed concentrations of metamitron and metazachlor totalled 60 and 200 μg L^{-1}. These concentrations are beyond the 99th percentile of the simulated $PEC_{sw,D}$

for metamitron and far higher than the maximum of $PEC_{sw,D}$ for metazachlor (Appendix M). However, since the major proportion of the pesticide load measured at the catchment outlet was probably due to point sources such as spills and farmyard runoff, these results suggest that the simulated $PEC_{sw,D}$ are realistic. Another long-term monitoring study was conducted in the Rosemaund catchment (1.5 km^2 area) in the UK (Williams et al., 1996). In the stream draining the catchment, the authors observed peak concentrations in the stream of 1 µg L^{-1} for dichlorprop after spring application and 16.2 µg L^{-1} for isoproturon after autumn application, predominantly due to drainage inputs. For both compounds, these values lie between the 95^{th} and 99^{th} percentile of the simulated $PEC_{sw,D}$, which seems plausible given the heavy, structured soils in this catchment. In summary, the magnitudes of calculated pesticide losses via drainage (Appendix F) and the resulting $PEC_{sw,D}$ (Table 5.1, section 5.2; Appendix M) appear reasonable, which increases the confidence that can be put in the approach employed for the drainage exposure assessment.

From his review of available pesticide runoff studies (all from the US), Wauchope (1978) concluded that i) total runoff and erosion losses from agricultural fields are usually less than 5 % of the applied amount even under worst case conditions, and ii) for the majority of commercial pesticides, losses are 0.5 % or less of the amount applied, unless severe rainfall conditions occur within 1-2 weeks after application. The results of the predictive PRZM simulations (Appendix L) agree with these rules of thumb. For a 2-year runoff study in Northern Italy, Rossi Pisa et al. (1994; in Miao et al., 2004) reported total losses via surface runoff of 0.08 % of the applied amount for metolachlor and 0.14 % for terbuthylazine from a conventionally tilled, loamy soil with 15 % slope. The corresponding losses via erosion were 0.03 % of the applied amount for metolachlor and 0.08 % for terbuthylazine. The measured runoff losses correspond well with the median PRZM runoff losses over all soils, climates, and weather years (0.08 % for metolachlor and 0.10 % for terbuthylazine, respectively; Appendix L). In contrast, the measured erosion losses were beyond the 95^{th} percentile of the predicted erosion losses for metolachlor, and beyond the 99^{th} percentile for terbuthylazine. This can be attributed to the steep slope of the experimental field, which led to increased soil erosion compared with the slope of 6 % used in the predictive PRZM simulations. Patty et al. (1997) observed total runoff losses of 0.03 % of the applied amount for isoproturon and 0.18 % for diflufenican after application in January to winter wheat. These values lie between the 50^{th} and 75^{th} percentiles of the simulated IPU and between the 75^{th} and 95^{th} percentiles of simulated diflufenican runoff losses after autumn application to winter wheat over all soils, climates and weather years (n= 800). Müller et al. (2002) investigated pesticide concentrations and loads in surface water for a low mountain range catchment of 50 km^2 area in

Germany, with only a small extent of tile drainage, but a strong influence of point sources (sewage plants and sewer overflows). They measured, among other substances, peak concentrations of 1.95 µg L^{-1} for carbetamide, 1.75 µg L^{-1} for dichlorprop-P (after application in spring), 23.18 µg L^{-1} for isoproturon, 1.28 µg L^{-1} for metamitron, 6.12 µg L^{-1} for metazachlor, 2.09 µg L^{-1} for metolachlor, and 1.59 µg L^{-1} for terbuthylazine. For all these compounds, the measured concentrations are in the middle or upper percentile range of the simulated PEC_{sw} due to runoff inputs (Appendix M). From the comparisons made above, it can be concluded that the magnitudes of the calculated pesticide losses via runoff and erosion (Appendix L) and of the $PEC_{sw,R}$ (Table 5.1, section 5.2; Appendix M) seem reasonable.

Leu et al. (2004a) measured pesticide losses and surface water concentrations after controlled application in the Greifensee catchment, Switzerland. This catchment has a size of 2.1 km^2, predominantly loamy soils, and parts of it are tile-drained. Both drainflow and surface runoff were active as input pathways for pesticides into surface water. After application in May on maize, total observed losses of metolachlor and dimethenamid to the receiving stream were 0.41 % and 0.27 % of the applied amount, respectively. Point sources like farmyard runoff contributed less than 20 % to the total loads. For comparison, total drainage losses from the predictive modelling ranged from practically zero to 7.1 % (median = 0.04 %) of the applied amount for metolachlor and from 0 to 5.5 % (median = 0.0002 %) for dimethenamid (Appendix F). The simulated total runoff losses ranged from 0 to 2.0 % (median = 0.08 %) for metolachlor and from 0 to 1.9 % (median = 0.08 %) for dimethenamid. Measured peak concentrations in the stream from diffuse sources were 1.5 µg L^{-1} for dimethenamid and 0.9 µg L^{-1} for metolachlor. For both compounds, these concentrations lie slightly above the median of the simulated PEC_{sw} due to runoff and in the upper range of the PEC_{sw} due to drainflow (Appendix M; as explained before in chapter 5, $PEC_{sw,R}$ and $PEC_{sw,D}$ are not to be added). Although it was not possible to separate the contributions of runoff and drainage inputs to the pesticide load in the stream (Leu et al., 2004b), the pesticide losses and concentrations observed in the Greifensee catchment further confirm that the predicted pesticide losses via runoff and drainage and the resulting PEC_{sw} are reasonable and realistic.

In the following, the benefits and possible risks of the risk assessment approach and the corresponding software module in ISIP are addressed. The primary benefit of the ISIP risk assessment module is that it offers the farmers the possibility to include the risk to the aquatic environment in their decision which pesticide to apply. Moreover, it is hoped that the risk assessment module will increase the general environmental awareness among the users. The integration into the ISIP website ensures that the module will reach a large audience of farmers and plant protection advisors. A further benefit of the risk assessment approach is that it includes the influence of regional factors (climate, land use, pesticide application practice, river discharge, extent of tile drainage) on the predicted pesticide concentrations in surface water. Together with a soil map of sufficient resolution, this regional differentiation allows to create PEC_{sw} maps for Germany (cf. Fig. 5.2-5.5, section 5.2) and also to carry out a Germany-wide probabilistic risk assessment for a given use.

A possible risk of the module is that the outcome of the risk assessment might be misunderstood by the user. It is clear that modelling results must not be seen as absolute "truth", but as inherently uncertain. Therefore, the wording used in the output window displayed to the ISIP user (cf. Fig. 6.4, section 6.2) has to be chosen carefully. Moreover, it might be criticized that the module may – for the specific conditions of a farmer's field - judge a certain use as "unsafe", although this use has passed the registration procedure and is therefore legally considered as "safe". However, one must be aware that *per se* "safe" or "unsafe" uses do not exist. Risk is always a probability between 0 and 1. For certain worst case situations (e.g. the coincidence of a heavy clay soil with a high frequency of runoff-inducing rainstorms and a large area proportion treated with the pesticide of concern), it is logical that the calculated PEC can be higher than the PEC estimated in the registration procedure for a "realistic worst case", which usually corresponds to the 90^{th} percentile of exposure. In summary, it can be concluded that the benefits of the ISIP risk assessment module and the underlying approach outweigh possible disadvantages by far.

The risk assessment approach developed here also bears some implications for the regulatory practice in Germany. As already shown by Huber et al. (2000) and Röpke et al. (2004), the importance of pesticide inputs into surface waters via drainage and runoff has been underestimated in the German regulatory practice so far. Moreover, their strong regional variability has been neglected. Although the currently used tool EXPOSIT 1.1 considers drainage and runoff/erosion inputs, it operates with standard loss percentages without any regional differentiation. Hence, the EXPOSIT approach is likely to overestimate pesticide concentrations in surface water in most cases, but also to underestimate pesticide concentrations in some disadvantageous cases, which nevertheless occur in reality. This problem can be easily overcome with a regionally differentiated approach like the one developed in this study. In the author's opinion, the scenario-based modelling approach and the soil- and municipality-specific PEC_{sw} calculation method proposed here can provide a viable basis for improving the regulatory practice in Germany.

8 Overall Conclusions and Outlook

In this work, a field- and use-specific risk assessment approach was developed for pesticide inputs into surface waters via the diffuse input pathways surface runoff and drainage. The approach will be integrated as a software module in the online information system ISIP (**I**nformation **S**ystem on **I**ntegrated **P**lant Production) directed to farmers and plant protection advisors. Beyond its primary objective, this study led to the following conclusions:

- Model evaluation exercises with several measured datasets from field studies have demonstrated that the models MACRO 4.3b (using the pedotransfer functions of MACRO_DB2) and PRZM 3.21β can be used with sufficient confidence for predictive simulations of pesticide losses from agricultural fields via drainage and surface runoff, respectively.
- There are large differences in predicted pesticide concentrations in surface water not only between different uses and input paths, but also between different regions in Germany. The need for a regionally differentiated exposure and risk assessment is therefore evident.
- A large number of uncertainty sources contribute to the overall uncertainty in the calculated pesticide concentrations in surface water. At least the major sources of uncertainty, e.g. the annual weather variability, have to be accounted for in the risk assessment process to create a reliable basis for decisions. The use of probabilistic methods in aquatic risk assessment for pesticides is therefore highly recommended.
- The demonstrated strong need for regional differentiation and probabilistic assessments is contradictory to the current risk assessment practice in the German pesticide registration procedure.
- The risk assessment approach developed here allows the creation of risk maps and facilitates a Germany-wide probabilistic risk assessment. Thus, it can provide a viable basis for improving the regulatory practice in Germany.

Of course, there is still a lot of room for further improvements of this risk assessment approach. Firstly, it has not been possible so far to account for the annual weather variability in the drainflow calculations. This could be achieved by switching from MACRO 4.3b to the faster new version MACRO 5. Secondly, some of the regionalized data used in the PEC_{sw} calculation could still be improved, e.g. the tile drain density map. Furthermore, it has not been possible so far to account for pesticide erosion inputs in the PEC_{sw} calculation, and neither to perform a chronic risk assessment. If regionalized data on real surface water bodies in the landscape and their bed sediment properties can be obtained, it will be possible to use the predicted pesticide losses via drainage, runoff, and erosion directly as input for an aquatic pesticide fate model (e.g. TOXSWA) or for self-developed equations accounting for water flow velocity and water-sediment interactions. This would also allow to calculate long-term PEC and to consider chronic exposure and effect in the risk assessment procedure.

Another potential field of use for the risk assessment approach developed here is the implementation of the Water Framework Directive 2000/60/EC (WFD, *Wasserrahmen-richtline*). The WFD demands from the EU member states to establish river basin management plans, for which knowledge about the sources and quantities of pesticide inputs into surface water is essential. Due to the scarcity of surface water monitoring data and the high costs associated with monitoring programmes, in most watersheds the estimation of pesticide inputs and concentrations will have to rely on modelling. A modelling approach to be used within this context should allow to i) identify areas with surface water bodies at risk of diffuse-source pesticide contamination and damage to the aquatic ecosystem, ii) calculate potential pesticide exposure for unmonitored surface water bodies, and iii) estimate the potential effect of mitigation measures. All this is possible with the proposed methodology, at least after slight modifications if necessary. The target audience of the risk assessment approach developed in this study are therefore both ISIP users, i.e. farmers and plant protection advisors (risk assessment of crop protection measures with respect to aquatic ecosystems), and water managers (model-based assessment of pesticide inputs from diffuse sources into small catchments as part of watershed management concepts). All in all, the author hopes that this risk assessment approach will help to improve surface water quality.

9 Summary

The contamination of surface water bodies with agricultural pesticides and their metabolites can pose a significant threat to aquatic ecosystems. An attempt towards a more sustainable agriculture is the so-called integrated plant production, which tries to reduce the environmental impact by crop protection measures as far as possible. To offer the farmers in Germany an online advisory system for integrated plant production, the Deutsche Bundesstiftung Umwelt (DBU) has initiated the ISIP project (**I**nformation **S**ystem on **I**ntegrated **P**lant Production). ISIP is a web-based information system directed to both farmers and plant protection advisors.

The task of this work was to develop a field- and use-specific risk assessment approach for pesticide inputs into surface waters via the diffuse input pathways runoff/erosion and drainage. This approach should constitute the basis for a decision support tool for farmers and advisors with respect to aquatic ecology. This tool will finally be integrated into the ISIP website.

The risk assessment approach will help farmers and advisors to decide whether a given use (e.g. autumn application on winter cereals) of a given pesticide on the farmer's field poses an unacceptable risk to aquatic life or not.

Drainflow calculations were performed with the preferential flow model MACRO 4.3b, which is used in the European pesticide registration procedure (FOCUS surface water scenarios; FOCUS, 2001) as the drainage model. A model evaluation exercise with several European drainage datasets revealed that MACRO 4.3b, using the pedotransfer functions of MACRO_DB2, can be used with sufficient confidence for predictive modelling of pesticide losses from agricultural fields via drains to surface waters without prior calibration.

For the predictive modelling of drainage inputs into surface waters, a scenario-based approach was used with 8 drainage-relevant soil classes, 19 soil/climate scenarios, and one "representative" weather year per climate. Simulations were performed for 109 different active ingredients and 229 uses (pesticide/crop/application season combinations) registered in Germany and. The maximum daily pesticide loss over the simulation period (+ the corresponding date and drainflow volume) was extracted from the MACRO output as basis for the calculation of pesticide concentrations in surface water.

The predictive MACRO simulations yielded large differences in pesticide drainage losses between different compounds, soils and climate scenarios. For certain soil/climate combinations, both total and maximum daily pesticide losses can reach substantial fractions of the

applied dose. These results suggest that the importance of pesticide inputs via drainflow into surface waters has been underestimated in the German pesticide registration procedure so far, where drainage inputs are still calculated as standardized percentages of the applied amount. An uncertainty analysis identified the annual weather variability as the most important source of uncertainty with respect to pesticide losses via drainage. A possibility to account for this variability in the exposure assessment would be to switch from MACRO 4.3 to the faster new version MACRO 5 (Larsbo and Jarvis, 2003), which would facilitate to simulate not only one, but several different weather years per climate scenario.

For the runoff and erosion simulations the model PRZM 3.21β was selected, which is used in the European pesticide registration procedure (FOCUS surface water scenarios; FOCUS, 2001) as runoff and erosion model. A model testing exercise with a number of European runoff and erosion studies revealed that PRZM 3.21β can be used for predictive modelling of pesticide runoff losses from agricultural fields to surface water bodies with sufficient confidence. Analogously to the drainage modelling, a scenario-based approach was chosen for the runoff and erosion predictions, comprising 5 soil classes with different runoff susceptibility, 8 climate scenarios with different probability of high-intensity rainstorms, and 20 different weather year per climate. Simulations were performed for 185 different active ingredients and 446 registered uses. The maximum daily pesticide runoff loss for the whole simulation period (+ the corresponding date and runoff volume) was extracted from the PRZM output. The analogous was done for pesticide erosion losses.

The predictive PRZM simulations yielded considerable differences in pesticide runoff and erosion losses between different uses, soils, and meteorological input (climate scenarios and weather years). On vulnerable soils, both total and peak losses can reach significant fractions of the applied dose. An uncertainty analysis revealed that also with respect to runoff losses, the annual weather variability is the most important source of uncertainty. The probabilistic component (simulating 20 weather years per climate scenario) in the predictive PRZM modelling makes it possible to capture this uncertainty and to account for the annual weather variability in the exposure assessment.

Due to the requirements of the web-based application in ISIP, the calculation of PEC_{sw} (**P**redicted **E**nvironmental **C**oncentrations in **s**urface **w**ater) and the subsequent risk assessment have to be performed online and input-specifically within the ISIP risk assessment module. Because of the need for a quick online calculation of PEC_{sw}, it is only possible to calculate acute exposure concentrations, i.e. maximum initial PEC_{sw}. Moreover, due to the considerable computational expense required and the lack of regionalized data on stream bed sediment properties, it was neither possible within ISIP to account for pesticide erosion inputs in the PEC_{sw} calculation. However, a conservative estimate revealed that it can be justified to consider only pesticide runoff inputs for the calculation of initial PEC_{sw}. The PEC_{sw} obtained refer to the outlet of a small catchment with about 10 km^2 area, which approximately corresponds to the area of a smaller municipality. The higher of both PEC_{sw} (PEC_{sw} resulting from runoff and PEC_{sw} resulting from drainage inputs) is compared with the acute aquatic "maximum tolerable concentration" for the respective pesticide, which is the highest concentration at which for all test taxa the required Toxicity/Exposure Ratio (TER) is met and thus no risk is expected for any of the test species. The risk for the aquatic community is evaluated in ISIP as follows:

- If the calculated PEC_{sw} is lower than the maximum tolerable concentration, it can be expected that there is no significant risk for the aquatic community.
- If the calculated PEC_{sw} is higher than the maximum tolerable concentration, a danger to the aquatic community cannot be excluded.

In most cases, PEC_{sw} due to runoff were higher than PEC_{sw} due to drainage for the same use. There were large differences in PEC_{sw} not only between different uses and input paths, but also between different regions in Germany. The need for a regionally differentiated exposure and risk assessment is therefore evident.

A large number of uncertainty sources contribute to the overall uncertainty in the calculated PEC_{sw}. At least the major sources of uncertainty, e.g. the annual variability of the weather, have to be accounted for in the risk assessment process to create a reliable basis for decisions. The use of probabilistic methods in aquatic risk assessment for pesticides is therefore strongly recommended.

The primary benefit of the ISIP risk assessment module is that it offers the farmers the possibility to include the risk to the aquatic environment in their decision which pesticide to apply.

A further benefit of the risk assessment approach is that it includes the influence of regional factors (climate, land use, pesticide application practice, river discharge, extent of tile drainage) on the predicted pesticide concentrations in surface water. This regional differentiation allows to create risk maps for Germany as well as to carry out a Germany-wide probabilistic risk assessment for a given use. Hence, the scenario-based modelling approach and the soil- and municipality-specific PEC_{sw} calculation method developed here can provide a viable basis for improving the regulatory practice in Germany.

10 Zusammenfassung

Die Kontamination von Oberflächengewässern mit Pflanzenschutzmitteln und ihren Metaboliten kann eine ernsthafte Bedrohung für aquatische Ökosysteme darstellen. Ein Schritt in Richtung einer nachhaltigeren Landwirtschaft ist die sog. integrierte Pflanzenproduktion, die versucht, die Beeinträchtigung der Umwelt durch Pflanzenschutzmaßnahmen so weit wie möglich zu vermindern. Um den Landwirten in Deutschland ein Online-Beratungssystem zur integrierten Pflanzenproduktion anzubieten, hat die Deutsche Bundesstiftung Umwelt (DBU) das ISIP-Projekt (**I**nformations**s**ystem **I**ntegrierte **P**flanzenproduktion) initiiert. ISIP ist ein web-basiertes Informationssystem, das sich sowohl an Landwirte als auch an Pflanzenschutzberater wendet.

Die Aufgabenstellung der vorliegenden Arbeit war die Entwicklung eines schlag- und anwendungsspezifischen Ansatzes zur Risikoabschätzung für Pflanzenschutzmitteleinträge in Oberflächengewässer über die diffusen Eintragspfade Runoff (Oberflächenabfluss), Erosion und Drainage. Dieser Ansatz sollte die Basis für ein Werkzeug zur Entscheidungsunterstützung für Berater und Landwirte im Hinblick auf die Gewässerökologie darstellen, welches schließlich in die ISIP-Website eingebunden werden soll.

Der Ansatz zur Risikoabschätzung wird den Landwirten und Pflanzenschutzberatern bei der Entscheidung helfen, ob eine bestimmte Anwendung (z.B. Herbstapplikation in Wintergetreide) eines bestimmten Wirkstoffs auf dem Schlag des Landwirts ein inakzeptables Risiko für aquatische Organismen darstellt oder nicht.

Die Drainage-Rechnungen wurden mit dem Preferential-Flow-Modell MACRO 4.3b durchgeführt, das auch im europäischen Zulassungsverfahren (FOCUS surface water scenarios; FOCUS, 2001) als Drainagemodell eingesetzt wird. Die Evaluierung des Modells anhand einer Reihe von Datensätzen aus europäischen Drainagestudien ergab, dass MACRO 4.3b, unter Benutzung der Pedotransferfunktionen von MACRO_DB2, mit hinreichender Vorhersagegüte ohne vorhergehende Kalibrierung für die Schätzung von Pflanzenschutzmitteleinträgen über Drainagen in Oberflächengewässer eingesetzt werden kann.

Für die prädiktive Modellierung der Drainageeinträge wurde ein szenarienbasierter Ansatz mit 8 drainagerelevanten Bodenklassen, 19 Boden/Klima-Szenarien und jeweils einem "repräsentativen" Wetterjahr verwendet. Für 109 verschiedene Wirkstoffe mit 229 in Deutschland zugelassenen Anwendungen (hier: Kombinationen von Wirkstoff, Kulturpflanze und Applikationssaison) wurden MACRO-Simulationen durchgeführt. Das Maximum des täglichen Wirkstoffaustrags über den Simulationszeitraum, das dazugehörige Datum und der dazugehörige Drainagefluss wurden aus dem MACRO-Output extrahiert, als Grundlage für die spätere Berechnung der Wirkstoffkonzentrationen im Oberflächengewässer.

Die MACRO-Simulationen ergaben große Unterschiede bzgl. der Drainageausträge zwischen verschiedenen Wirkstoffen, Böden und Klimaszenarien. Für bestimmte Boden/Klima-Kombinationen können sowohl der Gesamtaustrag als auch der maximale Tagesaustrag bedeutende Anteile der Aufwandmenge erreichen. Diese Ergebnisse legen den Schluss nahe, dass die Bedeutung von Pflanzenschutzmitteleinträgen in Oberflächengewässer über Drainagen im deutschen Zulassungsverfahren, in dem Drainageeinträge immer noch als standardisierte Prozentzahlen der Aufwandmenge berechnet werden, bisher unterschätzt worden ist. Eine Unsicherheitsanalyse identifizierte die jährliche Variabilität des Wetters als bedeutendste Unsicherheitsquelle in Bezug auf Drainageausträge von Pflanzenschutzmitteln. Eine Möglichkeit, die jährliche Variabilität des Wetters bei der Expositionsabschätzung zu berücksichtigen, wäre ein Wechsel von MACRO 4.3 zur neuen, schnelleren Version MACRO 5 (Larsbo and Jarvis, 2003), mit der nicht nur ein Wetterjahr pro Klimaszenario, sondern mehrere verschiedene Jahre gerechnet werden könnten.

Für die Simulation von Runoff- und Erosionsausträgen wurde das Modell PRZM 3.21β ausgewählt, das auch im europäischen Zulassungsverfahren (FOCUS surface water scenarios; FOCUS, 2001) als Runoff- und Erosionsmodell eingesetzt wird. Eine Modellevaluierung anhand einer Reihe von europäischen Datensätzen ergab, dass PRZM 3.21β mit hinreichender Vorhersagegüte für die Schätzung von Runoffeinträgen in Oberflächengewässer verwendet werden kann. Analog zur Drainage-Modellierung wurde ein Ansatz auf Szenario-Basis für die Runoff-Vorhersagen gewählt, der 5 Bodenklassen mit unterschiedlicher Anfälligkeit für Oberflächenabfluss, 8 Klimaszenarien mit unterschiedlicher Starkniederschlagshäufigkeit und 20 verschiedene Wetterjahre pro Klimaszenario umfasste. PRZM-Simulationen wurden für 185 verschiedene Wirkstoffe mit 446 zugelassenen Anwendungen durchgeführt. Das Maximum des täglichen Runoffaustrags über den Simulationszeitraum, das dazugehörige Datum und das dazugehörige Runoffvolumen wurden aus dem PRZM-Output extrahiert; analoges gilt für die Erosionsausträge.

Die PRZM-Simulationen ergaben beträchtliche Unterschiede bzgl. der Runoff- und Erosionsausträge zwischen verschiedenen Anwendungen, Böden und meteorologischen Inputdaten (Klimaszenarien und Wetterjahre). Auf runoff- und erosionsanfälligen Böden können sowohl der Gesamtaustrag als auch der maximale Tagesaustrag signifikante Anteile der applizierten Menge erreichen. Eine Unsicherheitsanalyse ergab, dass, wie für die Drainageausträge, auch für die Runoffausträge die jährliche Variabilität des Wetters die

wichtigste Unsicherheitsquelle ist. Durch die probabilistische Komponente (Simulation von 20 Wetterjahren pro Klimaszenario) in der vorhersagenden PRZM-Modellierung kann diese Unsicherheit erfasst und die jährliche Variabilität des Wetters in der Expositionsabschätzung berücksichtigt werden.
Aufgrund der Anforderungen der web-basierten Anwendung in ISIP müssen die Berechnung der PEC_{sw} (**P**redicted **E**nvironmental **C**oncentrations in **s**urface **w**ater) und die anschließende Risikoabschätzung online und eingabespezifisch im ISIP Risk-Assessment-Modul durchgeführt werden. Weil die Online-Berechnung der PEC_{sw} schnell vor sich gehen muss, ist es nur möglich, initiale PEC_{sw} für akute Exposition zu berechnen. Außerdem war es aufgrund des erheblichen Rechenaufwandes und des Fehlens regionalisierter Daten zu Sedimenteigenschaften von Vorflutern ebenfalls nicht möglich, im Rahmen von ISIP Pflanzenschutzmitteleinträge über Erosion bei der PEC_{sw}-Berechnung zu berücksichtigen. Es konnte jedoch mit einer konservativen Abschätzung gezeigt werden, dass es zu rechtfertigen ist, für die Berechnung initialer PEC_{sw} nur PSM-Einträge über Runoff zu berücksichtigen. Die erhaltenen PEC_{sw} beziehen sich auf den Auslass eines kleinen Einzugsgebiets mit etwa 10 km^2 Fläche, was ungefähr der Fläche einer kleineren Gemeinde entspricht. Die höhere der beiden PEC (PEC_{sw} durch Runoffeinträge und PEC_{sw} durch Drainageeinträge) wird mit der akuten aquatischen "maximalen tolerablen Konzentration" für den entsprechenden Wirkstoff verglichen. Dies ist die höchste Konzentration, bei der für alle Test-Taxa die geforderte Toxicity/Exposure Ratio (TER) eingehalten wird und daher für keine der Test-Spezies ein Risiko erwartet wird. Die schlag- und anwendungsspezifische Risikobewertung für das aquatische Ökosystem wird in ISIP schließlich folgendermaßen vorgenommen:

- Ist die berechnete PEC_{sw} niedriger als die maximale tolerable Konzentration, so kann man erwarten, dass kein signifikantes Risiko für die aquatische Lebensgemeinschaft besteht.
- Ist die berechnete PEC_{sw} höher als die maximale tolerable Konzentration, so kann eine Gefährdung der aquatischen Lebensgemeinschaft nicht ausgeschlossen werden.

In den meisten Fällen waren, für die gleiche Anwendung, die PEC_{sw} durch Runoffeinträge höher als die PEC_{sw} durch Drainageeinträge. Es waren nicht nur zwischen verschiedenen Anwendungen und Eintragspfaden große Unterschiede bzgl. der PEC_{sw} festzustellen, sondern auch zwischen verschiedenen Regionen in Deutschland. Die Notwendigkeit eines regional differenzierten Ansatzes zur Expositions- und Risikoabschätzung ist daher offensichtlich.

Viele Unsicherheitsquellen tragen zur Gesamtunsicherheit in den berechneten PEC_{sw} bei. Zumindest die bedeutendsten Unsicherheitsquellen, z.B. die jährliche Variabilität des Wetters, müssen im Prozess der Risikoabschätzung berücksichtigt werden, um eine verlässliche Grundlage für Entscheidungen zu schaffen. Der Einsatz probabilistischer Methoden in der aquatischen Riskoabschätzung für Pflanzenschutzmittel wird daher nachdrücklich empfohlen.

In erster Linie ist der Nutzen des ISIP Risk-Assessment-Moduls darin zu sehen, dass es den Landwirten die Möglichkeit anbietet, das Risiko für die aquatische Umwelt in ihre Entscheidung, welchen Wirkstoff sie einsetzen sollen, mit einzubeziehen.

Ein weiterer Nutzen des Risk-Assessment-Ansatzes besteht darin, dass er den Einfluss regionaler Faktoren (Klima, Landnutzung, Praxis des PSM-Einsatzes, flächenspezifischer Abfluss, Anteil drainierten Ackerlands) auf die vorhergesagten Wirkstoffkonzentrationen im Oberflächengewässer beinhaltet. Diese regionale Differenzierung ermöglicht die Erstellung von Risikokarten für Deutschland sowie weiterhin die Durchführung einer deutschlandweiten probabilistischen Risikoabschätzung für eine bestimmte Anwendung. Deshalb können der szenarienbasierte Modellierungsansatz und die boden- und gemeindespezifische PEC_{sw}-Berechnungsmethode, die hier entwickelt wurden, eine brauchbare Grundlage liefern, um die Zulassungspraxis in Deutschland zu verbessern.

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Appendix

The following pages show selected tables from Appendix L and M. The complete Appendix is included in the attached CD-ROM. The titles of the Appendix sections (A to M) and the figures and tables on the CD are listed in the "Table of Contents", "List of Figures" and "List of Tables" sections, respectively.

Appendix L: Results of the predictive PRZM modelling (use rankings)

Runoff losses, absolute

Table L.1: Ranking of uses according to the median *maximum daily runoff* losses (*absolute* values, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	**abs. max. daily runoff** loss median[3)]	**abs. max. daily runoff** loss mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d	$g\ ha^{-1}\ d^{-1}$	$g\ ha^{-1}\ d^{-1}$
1	metam	potatoes	126000	5	272	1.00	4.5	61.24	134.9
2	prosulfocarb	potatoes	4000	5	1637	0.96	13	1.797	2.655
3	terbutryn[4)]	maize	1960	5	775	0.76	56	1.219	1.901
4	metamitron	strawberries	4500	8	156	0.81	26	1.208	3.993
5	metamitron	sugar beet	3600	5	156	0.81	26	1.190	3.884
6	prosulfocarb	spring cereals	4000	5	1637	0.96	13	0.904	1.429
7	prosulfocarb	winter cereals	4000	10	1637	0.96	13	0.901	1.624
8	metolachlor	maize	1500	5	201	0.90	38	0.777	1.815
9	dimethenamid	maize	1440	5	95	0.93	8.0	0.708	1.653
10	S-metolachlor	maize	1250	5	201	0.90	26	0.650	1.507
11	glyphosate-trimesium[4)]	maize	2400	10	4556	0.93	20	0.608	0.829
12	triallate	sugar beet	1440	4	2400	0.90	46	0.582	0.848
13	phenmedipham	sugar beet	960	5	870	0.85	31	0.549	0.838
14	propamocarb	potatoes	831.2	6	315	0.90	30	0.533	0.999
15	aclonifen	potatoes	2400	5	6749	0.92	117	0.522	0.717
16	chloridazone	sugar beet	2000	4	177	0.90	43	0.497	1.578
17	triallate	maize	1200	4	2400	0.90	46	0.486	0.702
18	chlorothalonil	winter cereals	1050	5	547	0.90	17	0.469	0.894
19	dimethenamid-P	maize	1008	5	189	1.00	7.4	0.462	1.160
20	terbuthylazine	maize	750	5	247	0.83	46	0.458	0.903

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 800 (5 soils × 8 climates × 20 weather years per climate)

[4)] no longer registered in Germany

Table L.2: Ranking of use/soil combinations according to the median *maximum daily runoff* losses (*absolute* values, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**abs. max. daily runoff** loss median[3)]	mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		$g\ ha^{-1}\ d^{-1}$	
1	metam	potatoes	126000	5	272	1.00	4.5	5	214.4	266.3
2	metam	potatoes	126000	5	272	1.00	4.5	4	124.4	192.1
3	metam	potatoes	126000	5	272	1.00	4.5	3	65.29	126.0
4	metam	potatoes	126000	5	272	1.00	4.5	2	28.93	76.20
5	metamitron	sugar beet	3600	5	156	0.81	26	5	7.085	9.688
6	metamitron	strawberries	4500	8	156	0.81	26	5	4.967	7.749
7	fosetyl	strawberries	37300	5	79	0.90	0.04	5	4.073	17.79
8	fosthiazate	potatoes	3000	4	65	0.89	13	5	3.163	5.968
9	metolachlor	maize	1500	5	201	0.90	38	5	3.125	4.052
10	prosulfocarb	potatoes	4000	5	1637	0.96	13	4	3.045	4.211
11	chloridazone	sugar beet	2000	4	177	0.90	43	5	3.036	4.140
12	metamitron	strawberries	4500	8	156	0.81	26	4	2.949	5.831
13	dimethenamid	maize	1440	5	95	0.93	8.0	5	2.824	3.555
14	S-metolachlor	maize	1250	5	201	0.90	26	5	2.564	3.331
15	prosulfocarb	potatoes	4000	5	1637	0.96	13	5	2.434	3.041
16	metamitron	sugar beet	3600	5	156	0.81	26	4	2.255	4.935
17	prosulfocarb	potatoes	4000	5	1637	0.96	13	3	2.084	2.964
18	dimethenamid-P	maize	1008	5	189	1.00	7.4	5	2.050	2.598
19	terbutryn[4)]	maize	1960	5	775	0.76	56	4	2.037	3.009
20	diuron	pome fruit	4050	5	474	0.90	63	5	2.017	3.082

[1)] a.i. equivalents without ester groups or counterions
[2)] 1 = Jan, 2 = Feb, etc.
[3)] n = 160 (8 climates × 20 weather years each)
[4)] no longer registered in Germany

Table L.3: Ranking of uses according to the median *cumulative runoff* losses (*absolute* values, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	**abs. acc. runoff** loss median[3)]	**abs. acc. runoff** loss mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d	$g\ ha^{-1}$	$g\ ha^{-1}$
1	metam	potatoes	126000	5	272	1.00	4.5	90.91	220.5
2	prosulfocarb	potatoes	4000	5	1637	0.96	13	5.304	7.114
3	terbutryn[4)]	maize	1960	5	775	0.76	56	3.384	4.808
4	prosulfocarb	spring cereals	4000	5	1637	0.96	13	2.581	3.771
5	aclonifen	potatoes	2400	5	6749	0.92	117	2.509	3.193
6	glyphosate-trimesium[4)]	maize	2400	10	4556	0.93	20	2.493	3.225
7	triallate	sugar beet	1440	4	2400	0.90	46	2.299	2.879
8	triallate	maize	1200	4	2400	0.90	46	2.017	2.513
9	prosulfocarb	winter cereals	4000	10	1637	0.96	13	2.003	3.688
10	metamitron	strawberries	4500	8	156	0.81	26	1.966	5.886
11	metamitron	sugar beet	3600	5	156	0.81	26	1.657	5.969
12	triallate	spring cereals	1200	3	2400	0.90	46	1.626	2.116
13	phenmedipham	sugar beet	960	5	870	0.85	31	1.514	2.097
14	aclonifen	maize	1500	5	6749	0.92	117	1.506	1.927
15	glyphosate	maize	1800	4	9890	0.96	23	1.361	1.733
16	metolachlor	maize	1500	5	201	0.90	38	1.169	3.056
17	glyphosate-trimesium[4)]	winter cereals	2400	8	4556	0.93	20	1.139	1.759
18	dimethenamid	maize	1440	5	95	0.93	8.0	1.108	2.748
19	propamocarb	potatoes	831.2	6	315	0.90	30	1.002	1.815
20	S-metolachlor	maize	1250	5	201	0.90	26	0.981	2.540

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 800 (5 soils × 8 climates × 20 weather years per climate)

[4)] no longer registered in Germany

Table L.4: Ranking of use/soil combinations according to the median *cumulative runoff* losses (*absolute* values, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**abs. acc. runoff** loss median[3)]	**abs. acc. runoff** loss mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		$g\ ha^{-1}$	$g\ ha^{-1}$
1	metam	potatoes	126000	5	272	1.00	4.5	5	419.5	549.9
2	metam	potatoes	126000	5	272	1.00	4.5	4	187.2	282.0
3	metam	potatoes	126000	5	272	1.00	4.5	3	99.24	165.0
4	metam	potatoes	126000	5	272	1.00	4.5	2	41.70	91.88
5	metamitron	sugar beet	3600	5	156	0.81	26	5	13.90	17.83
6	prosulfocarb	potatoes	4000	5	1637	0.96	13	5	12.50	13.57
7	metamitron	strawberries	4500	8	156	0.81	26	5	10.31	14.10
8	prosulfocarb	potatoes	4000	5	1637	0.96	13	4	9.174	10.75
9	terbutryn[4)]	maize	1960	5	775	0.76	56	5	8.920	9.791
10	metolachlor	maize	1500	5	201	0.90	38	5	6.913	8.555
11	chloridazone	sugar beet	2000	4	177	0.90	43	5	6.528	7.782
12	prosulfocarb	spring cereals	4000	5	1637	0.96	13	5	6.008	6.858
13	dimethenamid	maize	1440	5	95	0.93	8.0	5	5.885	7.421
14	prosulfocarb	winter cereals	4000	10	1637	0.96	13	5	5.805	6.755
15	terbutryn[4)]	maize	1960	5	775	0.76	56	4	5.724	6.934
16	S-metolachlor	maize	1250	5	201	0.90	26	5	5.678	7.056
17	fosthiazate	potatoes	3000	4	65	0.89	13	5	5.419	8.188
18	prosulfocarb	spring cereals	4000	5	1637	0.96	13	4	5.248	6.348
19	prosulfocarb	potatoes	4000	5	1637	0.96	13	3	4.908	6.303
20	glyphosate-trimesium[4)]	maize	2400	10	4556	0.93	20	4	4.740	5.534

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 160 (8 climates $\times$ 20 weather years each)

[4)] no longer registered in Germany

Runoff losses, relative

Table L.5: Ranking of use/soil combinations according to the median *maximum daily runoff* losses (*relative* to the applied amount, over all climates and weather years**)**

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**rel. max. daily runoff** loss median[3)]	mean[3)]
			g ha^{-1}		L kg^{-1}		d		% of applied d^{-1}	
1	metalaxyl-M	potatoes	96.8	6	96	0.90	46	5	0.218	0.287
2	metalaxyl	potatoes	200	6	96	0.90	46	5	0.211	0.291
3	mesotrione	maize	150	5	81	0.90	13	5	0.209	0.286
4	metolachlor	maize	1500	5	201	0.90	38	5	0.208	0.270
5	S-metolachlor	maize	1250	5	201	0.90	26	5	0.205	0.266
6	dimethenamid-P	maize	1008	5	189	1.00	7.4	5	0.203	0.258
7	metamitron	sugar beet	3600	5	156	0.81	26	5	0.197	0.269
8	dimethenamid	maize	1440	5	95	0.93	8.0	5	0.196	0.247
9	ethofumesat	sugar beet	1000	5	150	0.89	61	5	0.196	0.260
10	desmedipham	sugar beet	62.5	5	120	0.90	30	5	0.195	0.255
11	haloxyfop-R	potatoes	104	5	75	0.90	55	5	0.194	0.288
12	pirimicarb	potatoes	225	6	111	0.90	10	5	0.193	0.259
13	haloxyfop-R	sugar beet	104	5	75	0.90	55	5	0.188	0.270
14	fluroxypyr[4)]	maize	270	5	66	0.92	38	5	0.185	0.289
15	fluazifop-P	potatoes	214	5	70	0.90	20	5	0.184	0.285
16	metosulam	maize	30	5	202	0.90	31	5	0.178	0.238
17	pirimicarb	sugar beet	150	6	111	0.90	10	5	0.178	0.242
18	triflusulfuron	sugar beet	19.4	5	59	0.90	7.1	5	0.177	0.259
19	bromoxynil (phenol)	maize	500	5	183	0.81	8.0	5	0.176	0.228
20	terbuthylazine	maize	750	5	247	0.83	46	5	0.176	0.236

[1)] a.i. equivalents without ester groups or counterions

[2)] 1 = Jan, 2 = Feb, etc.

[3)] n = 160 (8 climates $\times$ 20 weather years each)

[4)] Due to the rapid breakdown of the applied methylheptyl ester, fluroxypyr was simulated as fluroxypyr-acid.

Table L.6: Ranking of use/soil combinations according to the median *cumulative runoff* losses (*relative* to applied amount, over all climates and weather years)

rank	compound	crop	dose[1]	application month[2]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	rel. acc. erosion loss median[3]	rel. acc. erosion loss mean[3]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		% of applied	% of applied
1	terbuthylazine	maize	750	5	247	0.83	46	5	0.492	0.575
2	flutriafol	maize	50	4	231	0.90	500	5	0.485	0.560
3	metosulam	maize	30	5	202	0.90	31	5	0.483	0.571
4	quizalofop-P	potatoes	92.6	5	540	0.90	60	5	0.478	0.533
5	flufenacet	maize	600	5	266	0.90	32	5	0.475	0.563
6	imidacloprid	sugar beet	119	4	183	0.80	145	5	0.468	0.538
7	clomazone	potatoes	90	5	235	0.90	87	5	0.465	0.555
8	metolachlor	maize	1500	5	201	0.90	38	5	0.461	0.570
9	terbutryn[4]	maize	1960	5	775	0.76	56	5	0.455	0.500
10	S-metolachlor	maize	1250	5	201	0.90	26	5	0.454	0.564
11	propamocarb	potatoes	831.2	6	315	0.90	30	5	0.452	0.521
12	imidacloprid	potatoes	180	4	183	0.80	145	5	0.446	0.519
13	quizalofop-P	sugar beet	92.6	5	540	0.90	60	5	0.440	0.496
14	methiocarb	sugar beet	100	5	572	1.00	18	5	0.423	0.479
15	metalaxyl-M	potatoes	96.8	6	96	0.90	46	5	0.409	0.515
16	dimethenamid	maize	1440	5	95	0.93	8.0	5	0.409	0.515
17	propaquizafop	sugar beet	125	5	400	0.90	15	5	0.405	0.456
18	dimethenamid-P	maize	1008	5	189	1.00	7.4	5	0.401	0.509
19	bromoxynil (phenol)	maize	500	5	183	0.81	8.0	5	0.398	0.504
20	ethofumesate	sugar beet	1000	5	150	0.89	61	5	0.397	0.499

[1] a.i. equivalents without ester groups or counterions
[2] 1 = Jan, 2 = Feb, etc.
[3] n = 160 (8 climates × 20 weather years each)
[4] no longer registered in Germany

Erosion losses, absolute

Table L.7: Ranking of uses according to the median *maximum daily erosion* losses (*absolute* values, over all soils, climates and weather years)

rank	compound	crop	dose[1]	application month[2]	K_{oc}	Freundlich exponent m	DT_{50}	**abs. max. daily erosion** loss median[3]	mean[3]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d	$g\ ha^{-1}\ d^{-1}$	
1	pendimethalin	maize	1600	5	14000	0.90	146	1.062	1.896
2	deiquat	potatoes	1000	9	1600000	0.90	5000	1.046	1.759
3	paraquat	maize	600	4	234000	0.90	5000	1.016	1.496
4	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	0.963	1.390
5	paraquat	sugar beet	600	4	234000	0.90	5000	0.961	1.334
6	aclonifen	potatoes	2400	5	6749	0.92	117	0.715	1.799
7	glyphosate	maize	1800	4	9890	0.96	23	0.583	1.395
8	aclonifen	maize	1500	5	6749	0.92	117	0.477	1.164
9	glyphosate	sugar beet	1088	4	9890	0.96	23	0.377	0.839
10	pendimethalin	winter cereals	2000	10	14000	0.90	146	0.363	0.867
11	deiquat	oilseed rape, winter	400	7	1600000	0.90	5000	0.260	0.533
12	glyphosate	spring cereals	1800	8	9890	0.96	23	0.245	0.697
13	glyphosate	winter cereals	1800	8	9890	0.96	23	0.210	0.715
14	glyphosate-trimesium[4]	maize	2400	10	4556	0.93	20	0.196	0.600
15	glyphosate	oilseed rape, winter	1800	8	9890	0.96	23	0.190	0.702
16	bromoxynil (octanoate)	maize	450	5	10000	0.90	7.0	0.158	0.361
17	glyphosate-trimesium[4]	winter cereals	2400	8	4556	0.93	20	0.142	0.682
18	triallate	sugar beet	1440	4	2400	0.90	46	0.120	0.459
19	triallate	maize	1200	4	2400	0.90	46	0.110	0.396
20	fenpropimorph	winter cereals	750	5	4179	0.90	42	0.103	0.367

[1] a.i. equivalents without ester groups or counterions
[2] 1 = Jan, 2 = Feb, etc.
[3] n = 800 (5 soils × 8 climates × 20 weather years per climate)
[4] no longer registered in Germany

Table L.8: Ranking of use/soil combinations according to the median *maximum daily erosion* losses (*absolute* values, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**abs. max. daily erosion** loss median[3)]	mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		$g\ ha^{-1}\ d^{-1}$	$g\ ha^{-1}\ d^{-1}$
1	metam	potatoes	126000	5	272	1.00	4.5	5	3.555	10.34
2	deiquat	potatoes	1000	9	1600000	0.90	5000	4	3.000	3.374
3	pendimethalin	maize	1600	5	14000	0.90	146	5	2.936	3.711
4	aclonifen	potatoes	2400	5	6749	0.92	117	5	2.787	3.924
5	paraquat	maize	600	4	234000	0.90	5000	4	2.611	2.840
6	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	4	2.444	2.586
7	pendimethalin	maize	1600	5	14000	0.90	146	4	2.309	3.395
8	paraquat	sugar beet	600	4	234000	0.90	5000	4	2.275	2.610
9	glyphosate	maize	1800	4	9890	0.96	23	5	2.206	2.904
10	deiquat	potatoes	1000	9	1600000	0.90	5000	5	2.192	2.532
11	paraquat	maize	600	4	234000	0.90	5000	5	2.051	2.194
12	aclonifen	potatoes	2400	5	6749	0.92	117	4	1.903	3.108
13	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	5	1.853	1.996
14	paraquat	sugar beet	600	4	234000	0.90	5000	5	1.852	1.996
15	aclonifen	maize	1500	5	6749	0.92	117	5	1.811	2.490
16	glyphosate	maize	1800	4	9890	0.96	23	4	1.556	2.481
17	glyphosate	spring cereals	1800	8	9890	0.96	23	5	1.505	1.704
18	pendimethalin	winter cereals	2000	10	14000	0.90	146	5	1.471	2.012
19	deiquat	potatoes	1000	9	1600000	0.90	5000	3	1.395	1.892
20	paraquat	maize	600	4	234000	0.90	5000	3	1.312	1.602

1) a.i. equivalents without ester groups or counterions

2) 1 = Jan, 2 = Feb, etc.

3) n = 160 (8 climates × 20 weather years each)

Table L.9: Ranking of uses according to the median *cumulative erosion* losses (*absolute* values, over all soils, climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	**abs. acc. erosion** loss median[3)]	mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d	$g\ ha^{-1}$	
1	paraquat	maize	600	4	234000	0.90	5000	3.870	5.726
2	paraquat	sugar beet	600	4	234000	0.90	5000	3.435	5.072
3	pendimethalin	maize	1600	5	14000	0.90	146	3.173	6.237
4	deiquat	potatoes	1000	9	1600000	0.90	5000	3.146	5.695
5	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	2.967	4.523
6	aclonifen	potatoes	2400	5	6749	0.92	117	1.616	4.468
7	glyphosate	maize	1800	4	9890	0.96	23	1.480	3.634
8	aclonifen	maize	1500	5	6749	0.92	117	1.132	2.987
9	glyphosate	sugar beet	1088	4	9890	0.96	23	0.884	2.102
10	pendimethalin	winter cereals	2000	10	14000	0.90	146	0.795	2.026
11	glyphosate	spring cereals	1800	8	9890	0.96	23	0.721	2.206
12	deiquat	oilseed rape, winter	400	7	1600000	0.90	5000	0.714	1.581
13	glyphosate-trimesium[4)]	maize	2400	10	4556	0.93	20	0.519	1.809
14	bromoxynil (octanoate)	maize	450	5	10000	0.90	7.0	0.452	0.930
15	glyphosate	winter cereals	1800	8	9890	0.96	23	0.402	1.386
16	glyphosate	oilseed rape, winter	1800	8	9890	0.96	23	0.364	1.312
17	quinoxyfen	winter cereals	250	6	23020	0.90	374	0.270	0.622
18	glyphosate-trimesium[4)]	winter cereals	2400	8	4556	0.93	20	0.238	1.120
19	bromoxynil (octanoate)	spring cereals	470	5	10000	0.90	7.0	0.237	0.526
20	triallate	sugar beet	1440	4	2400	0.90	46	0.226	0.891

[1)] a.i. equivalents without ester groups or counterions
[2)] 1 = Jan, 2 = Feb, etc.
[3)] n = 800 (5 soils × 8 climates × 20 weather years per climate)
[4)] no longer registered in Germany

Table L.10: Ranking of use/soil combinations according to the median *cumulative erosion* losses (*absolute* values, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**abs. acc. erosion** loss median[3)]	**abs. acc. erosion** loss mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		$g\ ha^{-1}$	$g\ ha^{-1}$
1	pendimethalin	maize	1600	5	14000	0.90	146	5	14.65	15.64
2	aclonifen	potatoes	2400	5	6749	0.92	117	5	11.47	13.01
3	paraquat	maize	600	4	234000	0.90	5000	4	10.25	11.01
4	paraquat	sugar beet	600	4	234000	0.90	5000	4	9.733	9.993
5	deiquat	potatoes	1000	9	1600000	0.90	5000	4	9.721	11.27
6	paraquat	maize	600	4	234000	0.90	5000	5	9.501	10.27
7	glyphosate	maize	1800	4	9890	0.96	23	5	9.244	10.02
8	pendimethalin	maize	1600	5	14000	0.90	146	4	8.655	9.892
9	paraquat	sugar beet	600	4	234000	0.90	5000	5	8.641	9.089
10	deiquat	potatoes	1000	9	1600000	0.90	5000	5	8.431	9.934
11	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	4	8.375	8.885
12	aclonifen	maize	1500	5	6749	0.92	117	5	7.681	8.516
13	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	5	6.972	7.617
14	glyphosate	spring cereals	1800	8	9890	0.96	23	5	6.335	6.477
15	glyphosate-trimesium[4)]	maize	2400	10	4556	0.93	20	5	5.606	6.087
16	metam	potatoes	126000	5	272	1.00	4.5	5	5.160	12.39
17	glyphosate	sugar beet	1088	4	9890	0.96	23	5	5.057	5.635
18	aclonifen	potatoes	2400	5	6749	0.92	117	4	4.677	6.071
19	pendimethalin	winter cereals	2000	10	14000	0.90	146	5	4.532	5.198
20	glyphosate	maize	1800	4	9890	0.96	23	4	4.232	5.308

[1)] a.i. equivalents without ester groups or counterions
[2)] 1 = Jan, 2 = Feb, etc.
[3)] n = 160 (8 climates, 20 weather years each)
[4)] no longer registered in Germany

Erosion losses, relative

Table L.11: Ranking of use/soil combinations according to the median *maximum daily erosion* losses (*relative* to applied amount, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**rel. max. daily erosion** loss median[3)]	mean[3)]
			g ha^{-1}		L kg^{-1}		d		% of applied d^{-1}	
1	paraquat	maize	600	4	234000	0.90	5000	4	0.435	0.473
2	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	4	0.407	0.431
3	paraquat	sugar beet	600	4	234000	0.90	5000	4	0.379	0.435
4	paraquat	maize	600	4	234000	0.90	5000	5	0.342	0.366
5	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	5	0.309	0.333
6	paraquat	sugar beet	600	4	234000	0.90	5000	5	0.309	0.333
7	deltamethrin	sugar beet	7.5	5	460000	0.90	36	4	0.307	0.353
8	deiquat	potatoes	1000	9	1600000	0.90	5000	4	0.300	0.337
9	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	4	0.283	0.316
10	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	4	0.282	0.318
11	deltamethrin	potatoes	5	6	460000	0.90	36	4	0.271	0.312
12	lambda-cyhalothrin	sugar beet	7.5	5	131052	0.90	20	4	0.271	0.308
13	alpha-cypermethrin	oilseed rape, spring	10	5	61904	0.90	35	4	0.239	0.277
14	deltamethrin	sugar beet	7.5	5	460000	0.90	36	5	0.236	0.262
15	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	5	0.230	0.248
16	lambda-cyhalothrin	oilseed rape, spring	7.5	5	131052	0.90	20	4	0.228	0.267
17	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	5	0.224	0.250
18	lambda-cyhalothrin	potatoes	7.5	6	131052	0.90	20	4	0.223	0.269
19	deiquat	potatoes	1000	9	1600000	0.90	5000	5	0.219	0.253
20	paraquat	maize	600	4	234000	0.90	5000	3	0.219	0.267

1) a.i. equivalents without ester groups or counterions

2) 1 = Jan, 2 = Feb, etc.

3) n = 160 (8 climates × 20 weather years each)

Table L.12: Ranking of use/soil combinations according to the *median cumulative erosion* losses (*relative* to applied amount, over all climates and weather years)

rank	compound	crop	dose[1)]	application month[2)]	K_{oc}	Freundlich exponent m	DT_{50}	soil class	**rel. acc. erosion** loss median[3)]	mean[3)]
			$g\ ha^{-1}$		$L\ kg^{-1}$		d		% of applied	
1	paraquat	maize	600	4	234000	0.90	5000	4	1.708	1.835
2	paraquat	sugar beet	600	4	234000	0.90	5000	4	1.622	1.665
3	paraquat	maize	600	4	234000	0.90	5000	5	1.583	1.712
4	paraquat	sugar beet	600	4	234000	0.90	5000	5	1.440	1.515
5	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	4	1.396	1.481
6	deltamethrin	sugar beet	7.5	5	460000	0.90	36	4	1.275	1.318
7	deiquat	oilseed rape, spring	600	7	1600000	0.90	5000	5	1.162	1.269
8	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	4	1.128	1.162
9	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	4	1.109	1.160
10	lambda-cyhalothrin	sugar beet	7.5	5	131052	0.90	20	4	1.100	1.123
11	deltamethrin	sugar beet	7.5	5	460000	0.90	36	5	1.093	1.158
12	deltamethrin	potatoes	5	6	460000	0.90	36	4	1.080	1.134
13	alpha-cypermethrin	sugar beet	10	5	61904	0.90	35	5	1.018	1.094
14	alpha-cypermethrin	oilseed rape, spring	10	5	61904	0.90	35	4	0.978	1.009
15	deiquat	potatoes	1000	9	1600000	0.90	5000	4	0.972	1.127
16	lambda-cyhalothrin	oilseed rape, spring	7.5	5	131052	0.90	20	4	0.956	0.977
17	deltamethrin	potatoes	5	6	460000	0.90	36	5	0.950	1.027
18	deltamethrin	oilseed rape, spring	7.5	5	460000	0.90	36	5	0.937	1.008
19	lambda-cyhalothrin	sugar beet	7.5	5	131052	0.90	20	5	0.921	1.003
20	pendimethalin	maize	1600	5	14000	0.90	146	5	0.915	0.977

1) a.i. equivalents without ester groups or counterions

2) 1 = Jan, 2 = Feb, etc.

3) n = 160 (8 climates × 20 weather years each)

Appendix M: PEC_{sw} distributions

Table M.1: Distribution of PEC_{sw} due to runoff over all soil/municipality combinations[1)] for some typical uses, calculated with the **50^{th} percentile** of *maximum daily runoff* losses

compound	crop	application month	dose	max. tolerable conc.	maximum initial PEC in surface water: mean	median	75^{th} perc.	95^{th} perc.	99^{th} perc.	maximum
		1-12	g ha^{-1}	µg L^{-1}	µg L^{-1}					
captan	pome fruit	7	1556.3	0.262	0.0062	6.1E-05	0.0020	0.019	0.079	**2.439**
cyprodinil	strawberries	5	375	0.32	3.7E-04	1.6E-04	3.1E-04	0.0014	0.0037	0.012
dichlorprop-P	spring cereals	5	1500	410	0.474	0.011	0.260	2.631	6.794	21.88
	winter cereals	4	1500	410	0.153	4.5E-04	0.026	0.741	2.978	21.34
		10	1500	410	1.847	0.043	0.848	11.40	25.57	63.72
diflufenican	winter cereals	10	187.5	0.2	0.045	0.029	0.062	0.155	**0.257**	**0.658**
		3	66.6	0.2	0.015	0.0090	0.018	0.054	0.094	0.174
dithianon	hops	7	1000	0.23	7.4E-04	7.7E-05	2.4E-04	6.3E-04	0.022	0.074
ethofumesate	sugar beet	5	1000	110	0.437	0.042	0.443	2.115	4.818	15.59
fenpropimorph	winter cereals	5	750	24	0.282	0.194	0.400	0.835	1.193	1.803
fluazinam	potatoes	7	200	0.36	0.0043	0.0010	0.0031	0.016	0.066	0.200
isoproturon	spring cereals	5	1500	1.3	0.417	0.097	0.414	**1.998**	**4.434**	**12.47**
	winter cereals	4	2000	1.3	0.597	0.059	0.437	**3.209**	**6.813**	**27.45**
		10	1500	1.3	**1.325**	0.199	1.116	**7.013**	**16.01**	**37.58**
mancozeb[1)]	potatoes	6	552.6	264	0.030	0.0019	0.013	0.141	0.458	4.744
	stone fruit	5	767.5	264	3.1E-04	2.1E-07	3.6E-05	9.4E-04	0.0053	0.174
metamitron	sugar beet	5	3600	22	1.394	0.125	1.175	6.930	17.18	**57.99**
metazachlor	oilseed rape, spring	4	1250	0.47	0.030	0.0034	0.022	0.161	0.401	**1.084**
	oilseed rape, winter	8	750	0.47	0.377	0.049	0.361	**1.857**	**3.918**	**8.433**
metribuzine	potatoes	5	700	0.809	0.098	0.0014	0.029	0.443	**1.741**	**15.69**
nicosulfuron	maize	5	40	0.17	0.016	0.0011	0.0090	0.093	**0.236**	**0.896**
pirimicarb	stone fruit	5	312.5	0.065	9.0E-04	1.6E-06	3.6E-04	0.0035	0.015	**0.186**
propiconazole	spring cereals	6	125	5.1	0.013	0.0078	0.018	0.047	0.076	0.161
tebuconazole	oilseed rape, spring	5	376.8	4.9	0.0045	0.0028	0.0061	0.015	0.025	0.037
	oilseed rape, winter	4	376.8	4.9	0.061	0.036	0.084	0.209	0.337	0.547
		9	376.8	4.9	0.041	0.021	0.052	0.152	0.286	0.504
terbuthylazine	maize	5	750	0.32	**0.723**	**0.345**	**1.028**	**2.554**	**4.661**	**12.58**

1) Because of the rapid hydrolytical breakdown of Mancozeb, dose, PEC_{sw} and max. tolerable concentration refer to the main metabolite of Mancozeb, ethylene thiourea (ETU).

bold: The maximum tolerable concentration is exceeded.

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