



Environmental behaviour of selected Herbicides in a lowland catchment in Northern Germany

**Relevance of inputs via surface runoff and
drainage systems into surface water**

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M.Sc. Uta Ulrich**

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Referentin: Prof. Dr. Nicola Fohrer

Koreferent: Prof. Dr. Hans-Rudolf Bork

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ABSTRACT

In order to gain high production levels and product quality, pesticides are employed for the protection of plants and plant products. By their very nature, however, most pesticides create harmful risks to humans, animals and the environment. As an example for pesticide behaviour in lowland conditions, losses of selected pesticides from fields into surface water were observed in the catchment of the Kielstau river. These areas are characterized by flat topography, shallow groundwater, high proportion of artificial drainages, and a low hydraulic gradient causing low flow velocities. Hence, they are sensitive to alterations that result in changes of the natural water balance and in-stream water quality. The herbicides Terbutylazine, Metazachlor and Flufenacet, used for corn, rape and winter grain, were monitored on the scales of field, subcatchment and catchment, each in a single period during spring 2008, autumn 2008 and autumn 2009, respectively. The objective of these observations was the assessment of the relevance of field drainage to herbicide losses. In daily samples, herbicide concentrations were determined in drainage and groundwater on a drained field, as well as in the Kielstau and one of its tributaries, the Moorau. Furthermore, precipitation, and discharges of the tile drainages, of the Kielstau and Moorau were continuously observed. To assess herbicide losses in relation to amounts applied, catchment land use was mapped and local farmers were interviewed for herbicide application data. Results from drainage, groundwater, and surface water in the rivers show concentrations of $> 25 \text{ ng/l} - 301 \text{ ng/l}$ for Terbutylazine, $> 25 \text{ ng/l} - 576 \text{ ng/l}$ for Metazachlor and $> 30 \text{ ng/l} - 170 \text{ ng/l}$ for Flufenacet. Losses at all scales were determined as $< 0.01 \% - 0.01 \%$ of the amount applied for Terbutylazine, $0.02 - 0.3 \%$ of the amount applied for Metazachlor and $0.02 - 0.04 \%$ of the amount applied for Flufenacet. The pattern of the herbicide concentrations reveal that the compounds were transported into the drainage and then into surface water during rainfall-induced discharge peaks. Highest concentrations were observed during first discharge event(s) after application, but highest daily loads occurred 6 -12 days after application for Terbutylazine, 32 – 71 days for Metazachlor and 50 – 53 days for Flufenacet. On the field scale, the relevance of herbicide relocation via drainage was clearly assessed. On the catchment and subcatchment scales, however, it was impossible to evaluate all potential pathways. It is assumed that the detected loads came mainly from drainage systems whereas inputs from other pathways were of lesser relevance.

In addition, as a dislocator of pesticides from fields to water bodies, rainfall-induced surface runoff was evaluated as a further possible pathway in a laboratory experiment. Representing lowland characteristics, soil-filled containers with a slope of 6 % were exposed to intermittent artificial rainfall of 13 mm, with six days of rainless period between rainfall events. This cycle was repeated six times. During one-hour rainfall events, surface runoff was sampled at 10-minute intervals. The samples were analyzed for volume of the water phase, sediment weight, and herbicide concentration of the water phase. Fates of Metazachlor, Terbutylazine and Flufenacet were observed. Maximum concentrations in the water phase of the surface runoff were 3184 µg Metazachlor/l, 661 µg Terbutylazine/l and 207 µg Flufenacet/l. Discharged herbicide losses amounted to 345 - 440 µg Metazachlor/0.2 m² (plot), 310 - 318 µg Terbutylazine/0.2 m² and 87 - 111 µg Flufenacet/0.2 m². These loads correspond to 1.92 % and 2.5 % (Metazachlor), 5.7 – 6.6 % (Terbutylazine) and 2.1 – 3.8 % (Flufenacet) of the amount applied. The results show that highest concentrations were observed during the first interval(s) of surface runoff. But highest loads occurred during the second rainfall event after surface runoff was generated the first time, when surface runoff volume increased, and herbicide concentrations were below the maximum. The artificial set up of intermittent rainfall revealed that, with every new rainfall event after a rainless period, a higher amount of herbicides was released from the plot than was released during the last interval of the previous rainfall event. During the rainless periods, soil surface alterations occurred that caused this effect.

Keywords: herbicides, lowland catchment, drainage systems, surface runoff, intermittent rainfall

ZUSAMMENFASSUNG

Pflanzenschutzmittel werden weltweit eingesetzt, um einen hohen Ernteertrag, aber auch um eine gute Produktqualität zu gewährleisten. Aufgrund ihrer Eigenschaften stellen sie jedoch ein Gefährdungspotenzial für Mensch, Tier und Umwelt dar. Daher wurde das Austragsverhalten ausgewählter Herbizide von landwirtschaftlichen Flächen in Oberflächengewässer in einem Einzugsgebiet der Norddeutschen Tiefebene exemplarisch im Kielstau-Einzugsgebiet untersucht. Charakteristisch für das Tiefland sind eine flache Topographie, oberflächennahes Grundwasser, ein hoher Anteil an künstlichen Drainagen und ein niedriger hydraulischer Gradient, der nur geringe Fließgeschwindigkeiten hervorruft. Aufgrund dieser Merkmale reagieren Tieflandgebiete sensibel auf (anthropogene) Veränderungen, die sich dann auf die Wasserbilanz und die Gewässerqualität auswirken. Die Herbizide Terbuthylazin, Metazachlor und Flufenacet, die in Mais-, Raps- und Wintergetreidekulturen eingesetzt werden, wurden in verschiedenen Größenskalen (Feld, Teileinzugsgebiet, Einzugsgebiet) untersucht. Dazu wurden Messkampagnen im Frühjahr 2008 (Terbuthylazin), Herbst 2008 (Metazachlor) und Herbst 2009 (Flufenacet) durchgeführt. Ziel dieser Beobachtungen war es, die Relevanz des Eintragspfades Drainage für Herbizide in Oberflächengewässer abzuschätzen. Die Herbizide wurden in Tagesmischproben aus der Drainage und dem Grundwasser eines drainierten Feldes, aus der Kielstau und einem ihrer Nebenflüsse, der Moorau, bestimmt. Weiterhin wurden die Niederschläge, die Grundwasserstände und die Abflüsse der Drainage, der Moorau und der Kielstau kontinuierlich erfasst. Um den prozentualen Herbizidaustrag, gemessen an der applizierten Menge, zu bestimmen, wurde die Landnutzung im Einzugsgebiet kartiert und die Landwirte über ihre Applikationsdaten befragt. Die Ergebnisse aus den Drainageproben, dem Grundwasser und den beiden Oberflächengewässern Moorau und Kielstau lieferten Konzentrationen von $> 25 \text{ ng/l} - 301 \text{ ng/l}$ für Terbuthylazine, $> 25 \text{ ng/l} - 576 \text{ ng/l}$ für Metazachlor und $> 30 \text{ ng/l} - 170 \text{ ng/l}$ für Flufenacet. Die Herbizidausträge in Abhängigkeit von der applizierten Menge betragen auf den verschiedenen Skalen $< 0,01 \text{ \%} - 0,01 \text{ \%}$ für Terbuthylazin, $0,02 - 0,3 \text{ \%}$ für Metazachlor und $0,02 - 0,04 \text{ \%}$ für Flufenacet. Die Verläufe der Herbizidkonzentrationen zeigen, dass die Wirkstoffe mit niederschlagsbedingten Anstiegen des Abflusses in die Drainage verlagert und von dort in die Oberflächengewässer eingetragen werden. Die höchsten Herbizidkonzentrationen wurden nach dem/den ersten Niederschlags-

ereignis/sen nach Applikation detektiert, die höchsten Tagesfrachten wurden jedoch bei Terbuthylazin 6 – 12 Tage, bei Metazachlor 32 – 71 Tage, und bei Flufenacet 50 – 53 Tage nach der Applikation beobachtet. Auf der Feldskala konnten die Herbizidausträge eindeutig dem Drainagepfad zugeordnet werden, während es auf Teileinzugs- und Einzugsgebietsskala nicht möglich war, alle potenziellen Eintragspfade abzuschätzen, da dort Mischsignale erfasst wurden. Es wird jedoch angenommen, dass die erfassten Herbizidausträge überwiegend über den Drainagepfad in die Oberflächengewässer eingetragen wurden und dass andere Eintragspfade von geringerer Relevanz sind.

Weiterhin wurde der niederschlagsinduzierte Oberflächenabfluss als möglicher Eintragspfad in einem Laborversuch mit einem Regensimulator abgeschätzt. Um die Gegebenheiten in einem Tieflandeinzugsgebiet nachzubilden, wurden mit Boden gefüllte Container mit 6 % Hangneigung einem intermittierenden Niederschlag von 13 mm ausgesetzt, auf den eine sechstägige regenfreie Periode folgte. Dieser Zyklus wurde insgesamt sechsmal wiederholt. Während der einstündigen Beregnung wurde der Oberflächenabfluss in 10-Minuten Intervallen aufgefangen und das Volumen der Wasserphase, der Sedimentanteil und die Herbizidkonzentration darin bestimmt. Wie in den Messkampagnen im Kielstaugebiet wurde das Austragsverhalten der Herbizide Terbuthylazin, Metazachlor und Flufenacet untersucht. Die maximalen Herbizidkonzentrationen in der wässrigen Phase des Oberflächenabflusses betrugen 3184 µg Metazachlor/l, 661 µg Terbuthylazin/l und 207 µg Flufenacet/l. Die ausgetragenen Frachten lagen bei 345 – 440 µg Metazachlor/0,2 m² (plot), 310 – 318 µg Terbuthylazine/0,2 m² und 87 – 111 µg Flufenacet/0,2 m². Diese Frachten entsprechen 1,92 % und 2,5 % (Metazachlor), 5,7 % – 6,6 % (Terbuthylazine) und 2,1 % - 3,8 % (Flufenacet) der applizierten Mengen. Die Ergebnisse zeigen, dass die höchsten Konzentrationen im ersten Intervall, in dem Oberflächenabfluss auftrat, zu beobachten waren. Die höchsten Frachten traten jedoch erst eine Beregnung nach dem ersten beobachteten Oberflächenabfluss auf, wenn das Abflussvolumen bereits angestiegen war und die Herbizidkonzentrationen sich noch auf einem hohen Level bewegten. Das Laborexperiment mit intermittierendem Niederschlag zeigt, dass nach einer trockenen Phase im ersten Intervall der neuen Beregnung eine größere Menge Herbizid frei gesetzt wurde als im letzten Intervall der vorherigen Beregnung. Während der trockenen Phasen veränderte sich die Bodenoberfläche und verursachte diesen Effekt.

Stichworte: Herbizide, Tieflandeinzugsgebiet, Drainagen, Oberflächenabfluss, intermittierender Niederschlag

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ABBREVIATIONS

A	Area
a.a.	after application
a.s.l.	above sea level
Corg	Organic Carbon
DAD	Diode Array Detector
DT ₅₀	Dissipation Time 50 %: time required for one-half of the initial quantity or concentration of a pesticide to dissipate from a system
EC ₅₀	Effect Concentration at 50%: statistically derived concentration of a substance in an environmental medium expected to produce a certain effect in 50% of test organisms in a given population under a defined set of conditions
EQS	Environmental Quality Standard
EQS-AA	Environmental Quality Standard expressed as Annual Average
EQS-MAC	Environmental Quality Standard expressed as Maximum Allowable concentration
EU-WFD	European Water Framework Directive
F1-3	Soil containers treated with Flufenacet
GUS	Groundwater Ubiquity Score
GW	Groundwater well
HPLC	High Performance Liquid Chromatography
ID	Inner diameter
IUPAC	International Union of Pure and Applied Chemistry
k	Extension factor in the assessment process of pesticide analysis uncertainty
K _d	Partition coefficient
k _f	Saturated hydraulic conductivity
k _{fb}	Conductivity in the vadose zone
K _{oc}	Organic-carbon sorption coefficient
log Pow	logarithm n-octanol/partition coefficient
M1,2	Soil containers treated with Metazachlor
NOEC	No observed Effect Concentration
OMC	Organic Matter Content
PVC	Polyvinylchloride
T1,2	Soil containers treated with Terbutylazin
TDR	Time Domain Reflective
X 1 - 6	Measuring point

1 INTRODUCTION

Pesticides are agrochemicals which are applied to protect plants and plant products against any kind of constraints. Significant damages to agricultural crops caused by varieties of pests lead to crop losses, and, hence, losses of income. Agricultural progress has been a crucial factor in worldwide socio-economic change. From a socio-economic point of view, prevention of crop loss and crop quality decrease are of particular importance in assuring food supplies of the world population, and to warrant farm profitability. The first synthetic pesticide was the insecticide Dinitrocresol, developed by the Bayer chemical company in 1892 (Dittmeyer et al., 2004). By their very nature, however, most pesticides create harmful risks to humans, animals or the environment because they are designed to kill or adversely affect living organisms. Macrophytes in aquatic systems which present the primary producers in an ecosystem are most vulnerable. Pesticide concentrations in surface water bodies cause direct effects on biomass and species abundance, and effect whereby changes in habitat structure occur. High pesticide concentrations have pronounced long-term effects on aquatic biota and ecosystem function (Mohr et al., 2007; Mohr et al., 2008). Besides these effects to organisms, the chemical water quality of water bodies is reduced by pesticides. These water resources are used for drinking water supply, and, hence, they have to be cleaned extensively to meet the thresholds of drinking water legislation. Therefore, in recent years, there has been increasing interest in the impact of pesticides on ground and surface water quality. Though the detection of pesticides in the environment has been reported by many studies, the frequency and magnitude of contamination must be monitored for exposure assessments. To evaluate mitigation strategies and to restrict the hazards to non-target organisms and non-target areas, it is essential to understand alterations, degradation and migration. In brief, it is necessary to understand the fate of these agents in the environment.

The present thesis shall contribute to improvement of the state of knowledge concerning the fate of pesticides in the environment. The focus is put on the transport of pesticides into surface water via agricultural drainage systems and surface runoff.

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2.1 Pesticides

Pesticides are defined as substances or mixtures of substances intended for preventing, destroying, repelling, or mitigating any pest (EPA , 2006). Pests can be insects, mice and other animals, unwanted plants (weeds), fungi, or microorganisms such as bacteria and viruses. Pesticides are employed to protect plants or other plant products from harmful organisms; to regulate the growth of plants; to give protection against harmful creatures; or to render such creatures harmless (FEPA, 1985; Pflanzenschutzgesetz, 2009). At the same time, most pesticides may be harmful to humans, animals and the environment because of their ecotoxicity, their potential bioaccumulating properties or their hormone disrupting effects. When pesticides are applied on the field, only a certain percentage of the applied dose will reach the target crop. The remaining fraction will enter the soil, air, surface and groundwater via various pathways, or will be affected by various alterations that can occur to the pesticide (Fig. 1).

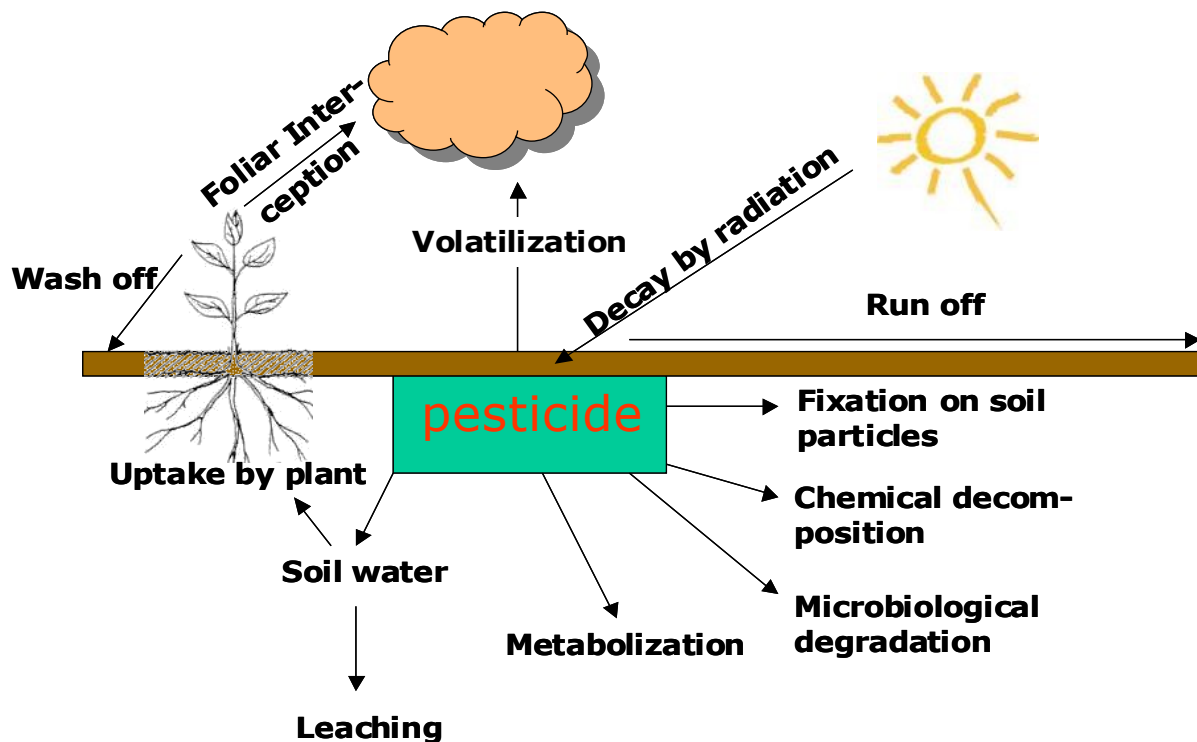


Fig. 1: Fate of pesticides in the environment

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Applied to fields, a compound volatilizes from soil or plants into the air, depending on its vapor pressure. The volatilization can begin to occur during the application, the gaseous portion of the pesticide is then capable of being transported by wind and air masses. Solar radiation activates photolysis, meaning that components are split into smaller molecules. If rainfall events occur after the application in such an intensity that infiltration or surface storage capacity of the soil is exceeded, water including soluble pesticide and particle bonded pesticide is discharged from the field as runoff or surface runoff. In the soil, the compound can be fixed to the organic matter to a degree of reversibility that accords to its capability of adsorption to the organic matter. Furthermore, it is metabolized and decomposed chemically and microbiologically. The dissolved part of the pesticide can be taken up by plants or moves downward. The compound leaches through the soil and may reach the groundwater or further leach to surface water. In regions with subsurface drains, the compound may also reach the drainage systems and be transported into surface water (Börner et al., 1994; Heinisch et al., 1976).

For the mobility of the pesticide and, hence, its distribution in the environment, the following properties are crucial (Claver et al., 2006):

Tab. 1: Crucial properties influencing the mobility of pesticides

Water solubility	ability to dissolve in water
Octanol/water partition coefficient $\log P_{ow}$	distribution between polar phase (water) and nonpolar phase (humic substance). The parameter indicates the pesticide's potential to adsorb to lipophilic (nonpolar) humic substances in the soil.
Organic carbon sorption coefficient K_{oc}	ability to be fixed to the organic carbon of the soil by different types of binding
Vapor pressure	ambient pressure at which the compound changes from liquid to gas phase
Dissipation time DT_{50}	time span in which 50 % of the initial amount is dissipated by any of the degradation processes

2.1.1 Sources and transport pathways in the environment

As demonstrated in Fig. 1, there are a variety of alterations and migration possibilities for pesticides when they enter the environment. Focussing on surface water, two kinds of entry

sources are distinguished relative to how the agents are released into water bodies: via diffuse (or non-point) sources, or via point sources. Several authors have defined these terms, but often unequally (Akkan et al., 2003; Carter, 2000b; Jaeken & Debaer, 2005; Werner & Wodsak, 1994). The definitions according to Carter (2000b) will be the ones used in this thesis. The terms are explained as follows:

Pesticides from diffuse (non-point) sources enter water indirectly as inputs originating in agricultural fields. Active substances can be transported through the soil layers as solubles, or as adsorbed to soil particles, before entering water via artificial drainage systems, surface or sub-surface flow, leaching or by-pass flow. Spray drift and pesticides in precipitation are also considered as diffuse sources of surface water contamination.

Pesticides from point sources enter water directly as inputs derived from a localized situation and may enter a water body at a specific or restricted number of locations. Approved point source contamination exists in the form of consented discharges, such as from vegetable washing plants. Non-approved spillage is caused by poor practice, illegal operations or mismanagement.

Taking these definitions into account, the following attributions of sources can be conducted Tab 2:

Tab 2: Sources of pesticide entry into water (Carter, 2000a, altered)

diffuse/non-point entry sources	point entry sources
spray drift	farmyards
volatilization and precipitation	waste water treatment plants
surface runoff	accidental release e.g. spilling, tank filling
leaching	
interflow	
drain flow	
groundwater flow	

Spray drift occurs when a spray application is conducted in the close vicinity of surface water. The amount of pesticide entering the water body depends on technical equipment employed, distance to the surface water, weather conditions (e.g. wind speed and direction), bankside vegetation, and sprayed crop. Due to taller plants, in orchard and wine regions the spray drift is higher than in wheat, horticultures, or on bare soil. Spray drift can cause high and short-lived pesticide concentrations in surface water (FOCUS, 2004b; Huber et al., 1998).

Volatilization describes the process whereby volatile pesticides turn from the liquid phase into the gas phase and are deposited on non-target areas and organisms. Due to volatile properties, several pesticides have also been detected in rainfall (Asman et al., 2003; Carter, 2000b).

Surface runoff is defined as the movement of water, or water and eroded soil particles over soil surface. It occurs when the infiltration and/or storage capacity of the soil is exceeded and the water including pesticides is discharged via soil surface to proximate surface water (Carter, 2000b; Fohrer, 1995).

Leaching is a major process for the vertical downward transport of water and solubles. They percolate through the soil profile and the unsaturated zone, reaching the groundwater or a drainage system, if existing. The leaching process depends on soil and pesticide properties, weather and hydrological conditions, as well as on the application procedure (Carter, 2000a; Reichenberger et al., 2007). Besides vertical water movement in soils, there is also lateral movement. **Interflow** describes water moving vertically into the soil without reaching groundwater and laterally until it is discharged as overland flow at the change of slope or where the profile has been disrupted, by ploughing, for example (Amerman, 1965; Stevens et al., 1999). If the leachate enters a drainage system, it is displaced via **drain flow** through the pipe system to surface water. The contamination of the water body is mostly event-based. Although it is possible that contaminated **groundwater** can seep into surface water, this pathway is not considered significant for pesticide entry (Groenboek, 2002; Carter, 2000a).

In general, point sources are related to the handling of pesticides. **Accidental releases** during the filling of tanks, or spillage, are causes of contamination, as is the cleaning of application equipment in the farmyard. If cleaning of the application equipment is conducted in the **farmyard**, the contaminated waste water flows directly into the surface water at the point where the waste pipe of the farmyard ends. If the farmyard is connected to the **waste water treatment plant**, the pesticides are transported to the plant, but cannot be removed. Microorganisms in waste water treatment plants do not have the ability to degrade pesticides, and pesticides adsorb to sewage sludge only to a limited extent. Hence, pesticides are discharged into a recipient stream (Carter, 2000a; Reichenberger et al., 2007, Fig. 2).

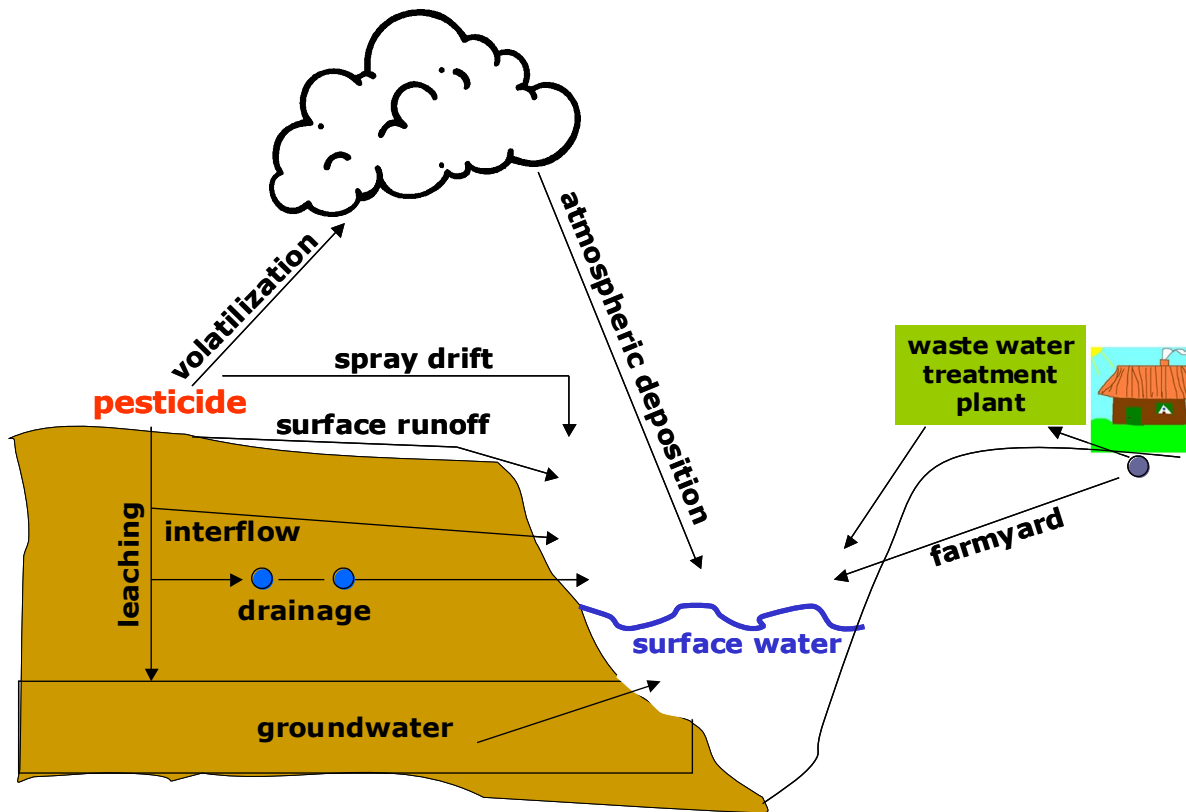


Fig. 2: Potential entry routes of pesticides into surface water

2.1.2 Processes during pesticide transport

Surface runoff and interflow are important pathways for pesticides to be dislocated from a field. Hence, it is necessary to understand the mechanisms taking place during these processes and how they are influenced.

After application, a pesticide strikes the soil surface directly, or indirectly by washing down from plants. Sorption and biological or chemical degradation are the possible interactions between soil and compound. The sorption behaviour is governed by K_{oc} , water solubility of the compound and by soil organic matter content, C_{org} (see chapter 2.3.3). The water solubility of the compound depends on its functional groups, polarity and polarizability, acidity or basicity, and molecular size (McDowell et al., 2002). Other factors such as soil pH can also effect leaching indirectly by influencing the sorption process: Changes in the soil pH cause alterations of the ionic soil molecules and therewith the binding locations for the pesticides (Bureaul & Führ, 2000; Scheuner & Reuter, 2000). Subject to the pesticide properties, the sorption to the soil organic matter is dominated by specific bonds, such as hydrogen bonds to carboxylic and phenolic groups for compounds with higher polarity and charged functional

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groups. The interaction is strongest, when the functional groups of the molecules closely match with the active sites of the soil surface (Laird & Koskinen, 2008; Oren & Chefetz, 2005). Pesticides with low polarity and neutral functional groups, however, adsorb to the soil matrix mainly by unspecific hydrophobic interactions with the aromatic and/or aliphatic domains of the soil. In general, these types of bonds count as weak adsorption mechanisms and are therefore likely to be detached (Boivin et al., 2005; Calderbank, 1989; Chefetz et al., 2004). Hence, the compound can be desorbed relatively easily and is available for relocation in a higher or lower amount, depending on the strength of these bindings (Gottesbüren et al., 1994; Haider & Auerswald, 1997). The main factor influencing the desorption of the pesticides is the time available for soil and water interactions (Nash et al., 2002). The sorption and desorption processes in general need time to develop a steady-state, so that the pesticides have time to reach the sorption locations and adsorb there. During rainfall events, it is not possible to reach a steady-state situation because the transporting water moves too quickly over the surface or into the soil for sorption to occur, thus, the pesticides are deposited elsewhere. Hence, not every potential binding place is fulfilled. With ongoing rainfall, the loosely bonded pesticides are desorbed from the soil first. High pesticide concentrations in the water phase can be assumed. Later on, the pesticides bound more strongly to humic matter molecules, or to the interior of the humic matter molecules, are released from the sorption locations, resulting in a lower concentration of pesticides in the water phase (Chiou, 1989; Gottesbüren et al., 1994; Haider, 1994). Calderbank (1989) and Gottesbüren et al. (1994) observed that after several hours, a meta-stable equilibrium between water and soil develops. In time, the pesticides strengthen their bonds to the soil organic matter, or even diffuse into soil aggregates, and are less available for dislocation (Boesten, 1986; Bunte, 1991).

Surface runoff can occur on almost any arable field, even in nearly flat terrain (Leonard, 1988; Wauchope, 1978). A distinction is made between two types of runoff. Infiltration excess, or Hortonian runoff, refers to the rate of rainfall on a surface exceeding the rate at which water can infiltrate the ground after all depression storages have been filled. This more commonly occurs in arid and semi-arid regions, where rainfall intensities are high and the soil infiltration capacity is reduced because of surface sealing, or in paved areas. Saturation excess runoff, on the other hand, refers to additional water that is discharged at the surface, due to the rising of groundwater levels to the soil surface (Beven, 2004).

Several factors influence the process of pesticide loss via surface runoff (Fig. 3). The determining parameters include properties of the compound and of the soil, management measures, characteristics of the precipitation, topography, and the elapsed time between application and the first rainfall event (Wolfe, 2001). The contribution of each parameter to this process is a point of debate.

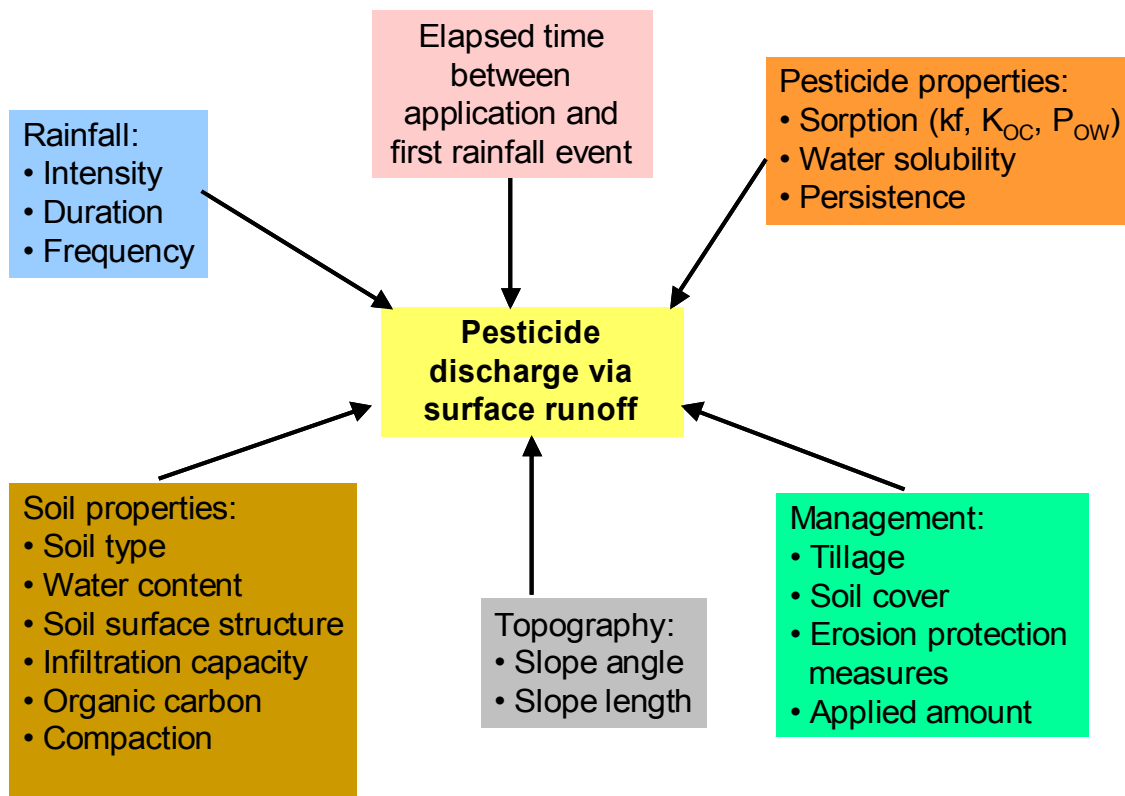


Fig. 3: Factors influencing the release of pesticides via surface runoff

Focussing on soil properties, soil surface structure is an important factor for the infiltration process. During a rainfall event, aggregates on the soil surface are gradually slaked and smoothed by the energy of the raindrops, but particles are not relocated. Hence, water can still infiltrate into the soil. Secondly, the transport of fine soil particles starts and these are deposited with the infiltrating water into the upper few millimeters of the soil. The pores beneath the surface are clogged, therefore, with ongoing rainfall, the particles wash into the pores and seal the surface (Abu Hamad et al., 2006; Agassi et al., 1995; Le Bissonnais & Singer, 1992; Loch & Foley, 1994). The developed crust consists of an upper skin caused by compaction of the raindrops and a zone of decreased porosity generated by the fine soil particles washed into the pores. This reduces the hydraulic conductivity and infiltration rate, as well as enhancing

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the surface runoff and therewith the loss of pollutants (Fohrer, 1995; Fohrer et al., 1999; Truman & Bradford, 1990; Zeiger, 2007; Zeiger & Fohrer, 2009).

The physical-chemical properties of a pesticide significantly determine its transport from the target area as described above. Water solubility and adsorption to organic matter are key parameters in this context. Compounds highly dissolved in water are removed mainly by the infiltrating water from the soil surface and, hence, are less available for surface runoff. In contrast, compounds of lower solubility are transported into the soil in lower amounts, but stay on the soil surface and can be released by runoff (Calderbank, 1989; Lang & Hurle, 1997). Compounds with higher adsorption coefficient K_{oc} are more likely to be adsorbed to eroded particles, and thus released from the field (Burgoa & Wauchope, 1995; Huber et al., 1998). The disappearance time DT_{50} , as a further parameter, affects the speed at which a pesticide can be degraded. Short DT_{50} times effect that the pesticide is available for discharge for a limited time and in limited amounts only, while long DT_{50} times cause the opposite effect.

Subsurface drainage is an important component of successful agricultural water management in regions with shallow groundwater, slowly permeable horizons in the subsoil, or with a generally heavy texture. Inadequate drainage results in delayed planting and a shorter growing season, hindered plant root growth, and, possibly, crop failure due to excessive water stress. Therefore, drainage systems are successful at removing excess water and achieving the soil water quantity goals of agriculture management. Generally, drainage increases infiltration, which subsequently decreases surface runoff (Kladivko et al., 2001). In Germany, two million hectares, i.e., 17 % of the overall 11.8 million hectares arable land (plant production only, excluding pasture), are drained and discharge their drainage water into recipients such as ditches, lakes and streams (LUA-NRW, 1999). The main draining method is de-watering by perforated subsurface pipes. In general, the fields are partly equipped with drainage systems (tile drainage), but their locations are often unclear or unknown due to constructions of former generations and a lack of documentation. There are concerns about the rapid transport of water soluble agents such as nutrients and pesticides via drains into surface water.

Pesticides reach the drainage pipes by means of leaching processes of percolating water. This downward movement depends on the physical-chemical properties of the compound, application, and soil characteristics:

- soil: texture, structure
- site: permeability of subsoil and vadose zone, depth 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), and, to a lesser extent, total amount of rainfall
- application rate and application season: spring, summer or autumn (as for surface runoff, the time between application and the first drain flow event is critical) (Reichenberger et al., 2007).

Sorption affinity to the soil constituents is of particular importance. In general, the more a pesticide is sorbed, the less it is available for leaching.

Drained sites show special hydrological conditions. Frequently, in the subsoil are water impermeable layers resulting in high groundwater levels or standing water according to the hydrological situation (e.g., after intensive precipitation). The regulation of the water budget by drainage causes a fast exchange of the soil water throughout the entire profile. Hence, the degradation of compounds is reduced, due to the short residence time of the percolating water in unsaturated zone. Furthermore, under conditions when the groundwater level exceeds the depth of the drainage pipes, the hydraulic gradient from groundwater level to drainage pipe increases. The groundwater flows not laterally, but more vertically, to the isolines of the hydraulic potential into the drainage pipe (Fig. 4). Pesticides bound to soil particles above the drainage can be dissolved and transported by the increased groundwater level (Lennartz et al., 1994; Wichtmann, 1994; Widmoser, 1990).

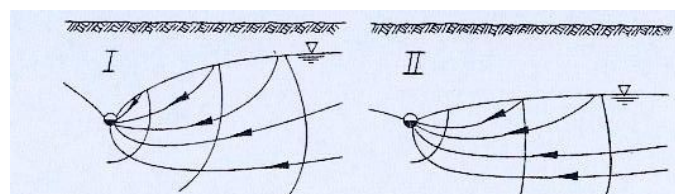


Fig. 4: Isolines of the hydrological potential and flow lines (arrows) flowing towards a drain pipe (I) rise of groundwater level after rainstorm (II) followed by groundwater level decrease in dry period (Wichtmann, 1994)

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Beside matrix flow, when a bulk of soil is involved into transport, rapid transport of pesticides to drains was observed (Brown et al., 2004; Leu et al., 2004b; Williams et al., 1996). This "preferential flow" includes phenomena where water and dissolved compounds move along certain macropore pathways such as cracks, fissures, root channels and earthworm burrows or finger flows while bypassing a fraction of the porous matrix (Hendrickx & Flury, 2001). This transport process causes high transient concentrations in the downstream ditches and rivers after rainfall events. The rapid percolation of water and pesticides decreases the residence time of the compound in the upper soil layers where, usually, sorption is stronger and degradation is faster than in the subsoil. Hence, the infiltrating water does not have sufficient time to equilibrate with slow moving resident water in the bulk of the soil matrix (Jarvis, 1998; Simunek et al., 2003). Brown et al. (1995) and Zehe & Flühler (2001) observed that the problem of preferential flow occurs not only in heavy clay soils, but in lighter-textured loamy or silty soils as well.

2.1.3 Pesticide selection for this study

As there are numerous pesticides available to farmers, in this study it was decided to focus on single agents. Therefore, out of the group of pesticides that includes among others the insecticides, fungicides, nematicides, molluskicides, rodenticides, and viricides, the herbicides were chosen.

Herbicides are not only the most often applied pesticide group, with an annual mean sales volume of approximately 15,000 t/year in Germany (Fig. 5) (BMELF, 2003; BMELF, 2006), but also have the highest potential to be released from a field. The requested effect of a herbicide is the suppression of weeds before germination, in order to eliminate competitors of crops for nutrients, water and sunlight. Thus, herbicides are applied mainly to soil without vegetation or with very little vegetation. This enhances the pesticide relocation from the sprayed area, because mechanical obstacles to agent retardation are few, and because possibilities for plant uptake are very low.

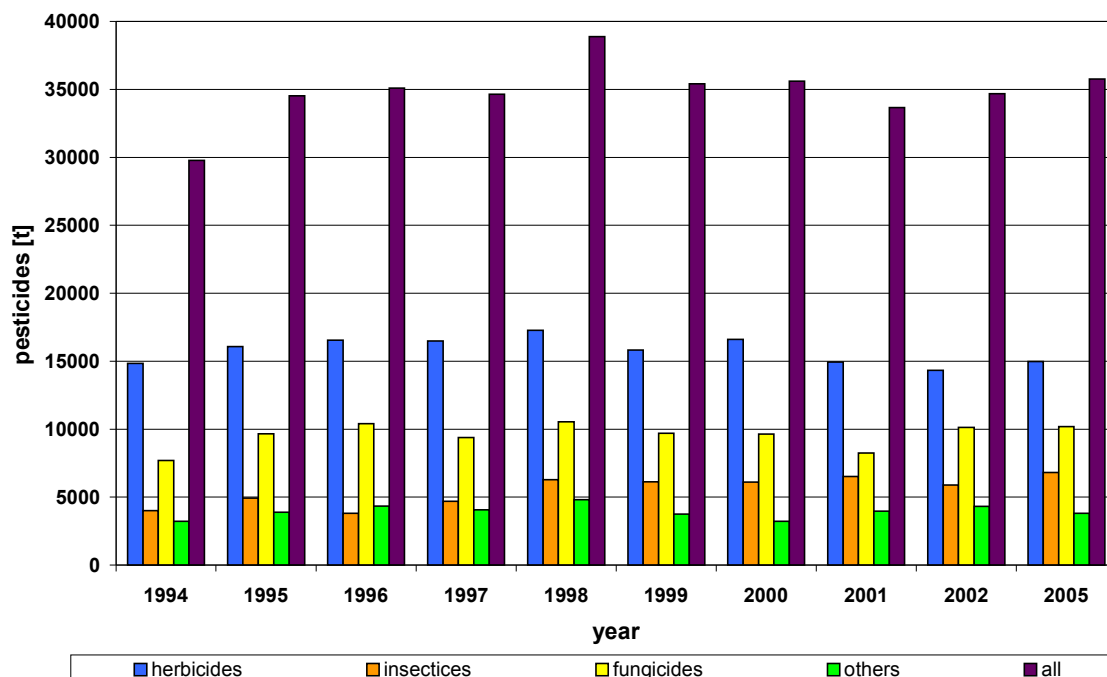


Fig. 5: Sales volume of pesticides in Germany [data source: BMELF (2003); BMELF (2006)]

Among the crops to which herbicide agents are applied, the dominant crops of winter grain, corn and rape were selected (Statistisches Bundesamt, 2010). With increasing area of application the potential for unintended displacement to non-target areas enlarges. The selected herbicides (Tab. 3) are widely used agents for these crops and are distributed in large amounts (LK-SH, 2008). They also meet the requirements for analysis by High Performance Liquid Chromatography and Diode Array Detection (HPLC/DAD) and, due to their physical-chemical properties, show a high potential for vertical and lateral transport from the target area.

Tab. 3: Selected herbicides and application

herbicide	crop
Metazachlor	rape
Terbutylazine	corn
Flufenacet	grain

Metazachlor is an agent with high water solubility and leaching potential. It is stable in the water phase and moderately mobile in soil (footprint, 2009). Therefore, the potential for being released from the fields to the environment and causing adverse effects is significant. Metazachlor is listed in the German ordinance for protecting surface waters (OgewV) annex 5

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(OgewV, 2010), and is restricted to a MAC-EQS (Maximum Acceptable Concentration Environmental Quality Standard) of 0.4 µg/l.

Like Metazachlor, Terbutylazine demonstrates pronounced leachability, though it is less water soluble and moderately mobile in soil. Degradation in the water phase is assessed as "moderately fast" and in soil as "moderately consistent" (footprint, 2009). It is listed in the OgewV annex 5 (OgewV, 2010) and restricted to a MAC-EQS of 0.5 µg/l.

Flufenacet is classified as a substance of moderate water solubility, moderate mobility in soil and in leaching potential. It is stable in the water phase, but degrades moderately fast in soil (footprint, 2009). It is not listed in annex 5 of OgewV, though the German Länder-Arbeitsgruppe Wasser (LAWA) recommends an AA-EQS (Annual Average Environmental Quality Standard) in lakes and rivers of 0.04 g/l and a MAC-EQS of 0.2 µg/l (LAWA (Bund-/Länder-Arbeitsgemeinschaft Wasser), 2010). Flufenacet is an agent that is applied most prevalently to grains. It undermines no environmental quality standards and has no restrictions. It can be described as an herbicide whose effect on water quality is caused more by its high rates of application than by its physical-chemical properties.

Selected physical-chemical properties of the three herbicides are plotted in detail in Tab. 4:

Tab. 4: Selected physical-chemical properties of the three herbicides (footprint 2009)

	Metazachlor	Terbutylazine	Flufenacet
IUPAC name	2-chloro- <i>N</i> -(pyrazol-1-ylmethyl)acet-2',6'-xylidide	<i>N</i> 2-tert-butyl-6-chloro- <i>N</i> 4-ethyl-1,3,5-triazine-2,4-diamine	4'-fluoro- <i>N</i> -isopropyl-2-[5-(trifluoromethyl)-1,3,4-thiadiazol-2-yloxy]acetanilide
CAS number	67129-08-2	5915-41-3	142459-58-3
Chemical formular	C ₁₄ H ₁₆ ClN ₃ O	C ₉ H ₁₆ CN ₅	C ₁₄ H ₁₃ F ₄ N ₃ O ₂ S
Water solubility at 20 °C	450 mg/l	6.6 mg/l	56 mg/l
Log P _{ow} (Octanol-water partition coefficient) at pH 7, 20 °C	2.49	3.4	3.2
Vapor pressure at 25 °C	0.093 mPa	0.15 mPa	0.09 mPa
Henry's law constant at 20 °C	1.8 x 10 ⁻⁷	1.64 x 10 ⁻⁶	2.4 x 10 ⁻⁶
K _{oc} (organic-carbon sorption coefficient)	53.8 – 220 ml/g	151 – 333 ml/g	202 – 401 ml/g
Photolysis in water DT ₅₀ at pH 7	stable	stable	stable

	Metazachlor	Terbuthylazine	Flufenacet
Hydrolysis in water DT ₅₀ at pH 7, 20 °C	stable	stable	stable
DT ₅₀ in soil (field experiments)	3 – 21 days	10 – 36 days	38 – 43 days
DT ₅₀ in water phase	216 days	6 days	54 days
GUS leaching potential (groundwater ubiquity score)	3.53	3.13	2.71
Aquatic plants acute dose over 7 days , EC ₅₀ , biomass	0.0023 mg/l <i>Lemna gibba</i>	0.0128 mg/l <i>Lemna gibba</i>	0.002 mg/l <i>Lemna gibba</i>
Algae acute dose over 72 hours EC ₅₀ , growth	0.0162 mg/l <i>Pseudokirchneriella subcapitata</i>	0.012 mg/l <i>Pseudokirchneriella subcapitata</i>	0.00204 mg/l <i>Raphidocelis subcapitata</i>
Aquatic invertebrates acute dose over 48 hours EC ₅₀	33 mg/l <i>Daphnia magna</i>	21.2 mg/l <i>Daphnia magna</i>	30.9 mg/l <i>Daphnia magna</i>
Aquatic invertebrates acute dose over 21 days, NOEC	0.1 mg/l <i>Daphnia magna</i>	0.019 mg/l <i>Daphnia magna</i>	3.26 mg/l <i>Daphnia magna</i>

None of the pesticides have legal constraints in application, except Metazachlor, which is permitted to be sprayed only once a year on the same field. All of them are assessed as toxic to algae, water plants and fish (BVL, 2010).

2.2 Selected pesticide legislation

2.2.1 Selected European pesticide legislation

The **European water framework directive (EU-WFD)** became effective on 23/10/2000 and is a tool to unify legal settings in water policy within Europe with the aim of a sustainable and ecological use of water (EU Water Framework Directive, 2000). The directive takes a broad view of water management, setting the prevention of any further deterioration of water bodies and the protection and enhancement of the status of aquatic ecosystems as key objectives (Coquery, M., Morin, A., Becue, A., Lepot, B., 2005). Strategies against chemical pollution of surface waters are undertaken on two levels. Particularly agents with a high potential of hazard, so-called "priority substances," are under intense observation regulated in the **Directive**

on priority substances (European Commission, 2008): “Chemical pollution of surface water presents a threat to the aquatic environment with effects such as acute and chronic toxicity to aquatic organisms, accumulation in the ecosystem and losses of habitats and biodiversity, as well as a threat to human health. As a matter of priority, causes of pollution should be identified and emissions should be dealt at source, in the most economically and environmentally effective manner”. On the community level, a selection of priority substances is made and community-wide measures will be defined. Thirty three substances or groups of substances are on the list of priority substances in annex X, including selected existing chemicals, biocides, metals and other groups such as Polyaromatic Hydrocarbons, Polybrominated Biphenylethers and pesticides. In addition, eleven “substances subject to review for possible identification as priority substances or priority hazardous substances” (annex III (European Commission, 2008)) are taken into account. It is required that compliance to the Environmental Quality Standards (EQS) set for priority substances and other pollutants be monitored on a monthly basis (Annex V 1.3 EU-WFD). They are expressed as annual average values (AA-EQS) and maximum allowable concentrations (MAC-EQS) in inland and other surface waters in annex I part A of (European Commission, 2008). Annex IX and X of the EU-WFD, as well as European Commission (2008), regulate the chemical state of the water bodies community wide, while the ecological state is administered by EQS of biological parameters and stream specific contaminants. These EQS are set by the EU member states themselves. The aim is to establish measures to assist in reaching the quality status and other environmental objectives of the EU-WFD (article 4), and also to achieve phase-out or cessation of emissions, losses and discharges of priority hazardous substances. Indisputably, within the context of the EU-WFD, the reduction of substances harming the aquatic environment is fixed.

The Chemicals Regulation Directorate of the Health and Safety Executive, an executive agency of the Department of the Environment, Food and Rural Affairs, regulates pesticides in agriculture, horticulture, forestry, food storage, recreational parks, and domestic gardens on behalf of the EU. The approval of pesticides in the EU falls under a dual system of national and European legislation. Any company seeking approval of a substance must undergo the procedures of **Directive 91/414/EEC concerning the placing of plant protection products on the market** (European Commission, 2005), and must apply for approval of conformance to national legislation. A comprehensive dossier documenting all risk and safety issues must be filed. This is evaluated by a "rapporteur" member state and then is considered by all mem-

ber states, the European Food Safety Authority and the European Commission. If the active ingredient meets the specific standards, it is approved and listed in annex I of the Directive. Plant protection products containing an active ingredient listed in annex I are then authorized at a national level as long as acceptable use is proven, taking into consideration formulation, climatic and agronomic factors.

2.2.2 Selected pesticide legislation in Germany

The EU-WFD became effective as **Wasserrahmenrichtlinie (EG-WRRL)** in Germany as it did in all other EU member states on 22/12/2000. It amends the German **Wasserhaushaltsgesetz (WHG)** (Wasserhaushaltsgesetz, 2009) that regulated the protection and usage of water and water bodies before that date. In Germany, the legislation of water-related issues belongs to the jurisdiction of the single federal states of Germany and not to the federal government. Therefore, the federal states enacted laws in terms of legal ordinances called "Landesverordnung" which set the guidelines for implementation of the EU-WFD (LV, 2003). Similarly, the implementation of Directive 2008/105/EC in all EU states was inaugurated in June of 2010. In Germany, the **Ordinance for Protection of Surface Water (OgewV)** (Oberflächengewässerverordnung, 2010) was drafted for determining the MAC-EQS and AA-EQS for the 33 priority substances as well as for the list of 173 stream specific contaminants compiled by the German experts of the Länder-Arbeitsgruppe Wasser (LAWA). As the German Constitution (GG, 2009) was changed in July 2006, all jurisdiction concerning the EU-WFD has been turned into national law and will be applied to all federal states of Germany.

The German **Plant Protection Act (PflSchG)** (Pflanzenschutzgesetz, 2009) is the main law concerning all issues of pesticides. Its intention is the protection of cultivated plants and plant products against pests, but also the prevention of threats to humans, animals and the environment. Furthermore, laws on European Community level dealing with pesticides are implemented by regulations in the PflSchG or with subordinated directives.

The authorization of pesticides, changes in the supplements and prolongation of authorizations are regulated on the national level in Germany by the **Ordinance on Plant Protection Products and Plant Protection Equipment (PflSchV)** (Pflanzenschutzmittelverordnung, 2005). The responsible authority for this procedure is the Federal Agency for Consumer Protection and Food Safety (BVL). The BVL cooperates with three assessment authorities in the

authorisation procedure. The Julius Kühn-Institut (JKI) evaluates efficiency, crop tolerance, practical applications and benefits. The Federal Institute for Risk Assessment (BfR) assesses the impact on human and animal health, and the Federal Environment Agency (UBA) evaluates the product with regard to possible effects on the environment. At the BVL, the composition and the physico-chemical characteristics of the product in question are assessed.

The limitations and restrictions in pesticide usage are the scope of the **Plant Protection Use Ordinance (PflSchAnwV)** (Pflanzenschutzmittel-Anwendungsverordnung, 2009). Banned agents are listed in this ordinance as well as detailed prescriptions where and how pesticides can be applied.

People working with pesticides, selling pesticides or advising others in the use of pesticides need a special and approved qualification. Therefore, the legal basis was set by the implementation of the **Ordinance Governing Specialist Qualifications in Plant Protection (PflSchSachkV)** (Pflanzenschutz-Sachkundeverordnung, 2010).

The following table summarizes the selected legislation in the European Union and in Germany (Tab. 5).

Tab. 5: summary of the selected legislation in the European Union and in Germany

legislation	European Union	Germany
overall framework	2000/60 EC (EU-WFD)	EG-WRRL
environmental quality standards	2008/105/EC	OgewV (draft)
Superior law governing all pesticide related concerns		PflSchG
approval of pesticides	91/414/EEC	PflSchV
restrictions and prescriptions of use		PflSchAnwV
qualification of user		PflSchSachkV

2.3 Literature review on pesticides transport behaviour

Pesticides are accepted as essential to society because of their ability to exterminate disease-causing organisms and control insects, weeds and other pests. At the same time, most pesticides have the potential to harm humans, animals and the environment because of their ecotoxicity, their bioaccumulating properties or their hormone disrupting effects (Akkan et al., 2003). Hence, the concern about the fates of plant-protecting products that endanger water resources has been growing in the last decades.

The observation and detection of pesticides are difficult, expensive and time consuming. The suitable points of time and place of monitoring have to be met to generate representative and significant samples. The analysis itself requires technical equipment of high standards and the preparation of the samples includes several steps of enrichment because of low pesticide concentrations. Most essential is the cooperation with farmers.

Pesticide contamination of surface waters has been documented worldwide. Claver et al. (2006) monitored the Ebro river basin in Spain on 17 sampling dates from 2001 – 2004 during pesticide application periods, and detected 44 compounds in concentrations of 30 – 1078 ng/l. In the Weida river, Germany, Eyring et al. (2009) determined 21 pesticides in continuous (56 samples) and event-based (19 samples) sampling set ups. Nine of them had concentrations above the German drinking water limit of 100 ng/l. Griffini et al. (1997) quantified herbicide concentrations up to 3680 ng/l in the Arno river, Italy, while in the Netherlands, in the Scheldt river, maximum concentrations of 1350 ng/l were found (Steen, 2002; Steen et al., 2001). In Greek rivers, Konstantinou et al. (2006) detected 4850 ng/l as the highest concentration of a pesticide. They observed that Atrazine, Simazine, Metolachlor, Alachlor and Molinate were the five most commonly encountered compounds in European freshwaters. S-Triazine herbicides are widely applied herbicides in Europe for pre- and post-emergence weed control among various crops. High levels of Terbutylazine and/or Metolachlor in fresh waters may be related to the use of these herbicides as substitutes for Atrazine, as all three compounds have overlapping herbicidal properties (Tomlin, 1995).

The results of the exemplarily selected studies reveal that under certain circumstances, high concentrations of pesticides can be detected. In general, highest concentrations corresponded to agricultural applications with event-based peaks correlating to meteorological and hydrological events such as rainstorms and flooding (Riise et al., 2004; Vryzas et al., 2009; Zonta et al., 2005). Findings in streams, however, must be taken as mixed signals which cannot easily provide information about the entry routes of the pesticides. Studies focussing on single pathways are therefore essential. In the following chapters, the state of the art concerning the entry routes of pesticides released to surface water is summarized.

2.3.1 Pathway spray drift

Because pesticides are generally applied as sprays to fields, there is the potential of aerial transport outside the target areas on plants, soil and surface water, according to the spray physical properties and formulation. Drift can appear as vapour spray drift and/or droplet spray drift (De Schamphelleire et al., 2007; Gil & Sinfort, 2005). Apart from the weather conditions of wind speed and direction, important roles are played by air pressure, saturation deficit, wet bulb temperature depression and the application equipment. Therefore, implementation of machinery standards for safety (European Commission, 2009), for environmental protection (European Commission, 2001), and for inspections (European Commission, 2003b) were implemented. Drift-reducing nozzles are mandatory, as are shielded and band sprayers or spray additives to coarsen the droplet size distribution (FOCUS, 2004a). The height of target crops also influences spray drift. In taller crops, such as wine or orchards, the height of the vertical spray column increases in proportion with the height of the crop, thus enlarging the potential for drift (FOCUS, 2004b). Increasing the spray application distance from a water body reduces the amount of spray drift entering it (Carter, 2000b), therefore, in regard both to good agricultural practice and to legislation, farmers are urged to respect safety margins of distance to proximate surface waters.

Ultimately, airborne polluting agents are removed from the atmosphere by dry (gas and particle) and wet (precipitation by rain and snow) deposition (Kumar, 2001). The German pesticide registration authority has elaborated table values to calculate spray drift losses; in this study, for field crops, a mean distance to the adjacent water body of 5 m during the application was assumed, corresponding to a spray drift loss rate of 0.57 % (90th-percentile) of the active ingredients applied (Ganzelmeier et al., 1995; Rautmann et al., 2001). Röpke et al. (2005) simulated with the DRIPS model a pesticide loss of 38 kg by spray drift appropriate to 0.0003 % of the applied amount. In experiments in Schleswig-Holstein on field scale, Rexilius (2004) observed maximum concentrations of 4985 µg Terbutylazine/m² and 11114 µg Metazachlor/m² within one meter of a field border after application of common supplements (Artett[®] containing 150 g Terbutylazine/l and Nimbus CS[®] containing 250 g Metazachlor/l). Even in the opposite wind direction of the prevailing winds, amounts of up to 38 µg Terbutylazine/m² and 39 µg Metazachlor/m², were determined. Though several authors consider pesticide inputs to surface water via spray drift to be inconsequential (Asman et al., 2003;

Bach et al., 2005b; Huber et al., 2000; Neumann et al., 2002), the results of Rexilius (2004) show the importance of spray drift in regions with higher wind speed, e.g. in coastal regions.

2.3.2 Atmospheric deposition

Atmospheric deposition is the pathway of volatilized pesticides, atmospherically-transported pesticides and wind-eroded, pesticide-loaded soil particles into surface water. Typical losses during application for volatilization are reported in the range of 5 – 26 %, depending on the observation period and the compound properties (Taylor, 1995). Under certain weather conditions, the short-range transport can become as important as spray drift (Asman et al., 2003; Loubet et al., 2006; Siebers et al., 2003). Dubus et al. (2000) reviewed studies of pesticide concentrations in rainfall in Europe in the 90's and reported positive findings of 100 ng/l concentrations or more among almost every monitored compound. Of major concern were findings of the long banned insecticide, Lindane (HCH) in 90 – 100 % of analyzed samples. Like spray, atmospheric deposition is not among the main entry pathways of pesticides into surface water (Brown & van Beinum, 2009; Carter, 2000b; Reichenberger et al., 2007).

2.3.3 Pathway surface runoff

Conducting runoff experiments according to uncertainties which arise from the set up is a challenge. If experiments are accomplished at field scale, they provide more realistic results due to the scale size and the natural rainfall situation. On the other hand, opportune timing of occurrences of weather conditions in the field, upon which the scientist is dependent for his data, can not be influenced. The rainfall events must be in an adequate range for sampling and at a suitable point of time after application so that the pesticides are still available for runoff. If studies are carried out on a micro-plot scale in a laboratory, with soil boxes and rainfall simulator, they have the advantage of good reproducibility and controlled parameters whose variations can be observed (Fohrer et al., 1999; Zeiger & Fohrer, 2009). The disadvantage is that the scale is small and the extrapolation to realistic conditions is challenging (Wauchope et al., 1995). Hence, in comparing data from surface runoff studies, it should be mentioned whether they were determined in field experiments under natural conditions, or in micro-scale experiments with a rainfall simulator under controlled boundary conditions.

2 State of the Art

Values of pesticide loss via surface runoff ascertained in several field studies vary according to site characteristics as well as to the amount and intensity of rainfall. Citing only a selection of the diverse results, we find Erlach et al. (2004); Gomides Freitas (2005); Klein (2004); Ng & Clegg (1997); Patty et al. (1997) and Frick et al. (2000) determined losses of up to 2 % of the amount applied, whereas loss values up to 5 % were reported by Klik et al. (2001) Wauchope (1978) and Rosner & Klik (2001), or even higher losses by Haider (1994) and Reddy et al. (2001).

Experiments with rainfall simulators were conducted mainly with a single and very intensive rainfall event (e.g. 70 mm/h, 111 mm/h, 25 – 100 mm/h) in order to gain sufficient runoff (Haider & Auerswald, 1997; Kördel & Klöppel, 1997; Müller et al., 2002; Warnemuende et al., 2007), though this does not represent natural conditions. The values for pesticide loss determined in these studies are in the range of 0.04 – 7 % (Kördel & Klöppel, 1997; Müller et al., 2006; Müller et al., 2002). Studies carried out under subsequent rainfall conditions are rare and do not focus on pesticide discharge via surface run off, but on soil crusting and erosion processes (Hardy et al., 1983; Le Bissonnais & Singer, 1992; Levy et al., 1986; Fohrer et al., 1999).

Investigations independent of field or laboratory set ups, focussing on selected parameters of surface runoff of pesticides, have been conducted. According to Müller et al. (2006), Zhang et al. (1997), Spatz (1999) and Hurlle (1982), the initial soil water content during the pesticide application affects the sorption processes of the agents and, hence, their discharge. Higher initial soil water contents cause a 60 – 80 % lower dislocation of pesticides than dryer conditions. Rainfall intensity is another important factor influencing pesticide loss. In general, a higher surface run off is observed with increasing rainfall intensity (Assouline & Ben-Hur, 2006; Parsons & Stone, 2006; Pot et al., 2005). Arnaez et al. (2007) even determined a runoff increasing linearly with the rainfall intensity. The physical-chemical properties of the selected pesticide affect the adsorption and desorption processes on the soil surface, so that more water-soluble agents are transported with the infiltrating water into the soil and are less available for surface runoff than are those agents which are less water-soluble (Burgoa & Wauchope, 1995; Gomides Freitas, 2005; Müller et al., 2002; Truman & Bradford, 1990). In other studies, the influence of tillage systems was investigated (Erlach, 2005; Hall et al., 1991; Klik et al., 2001; Reddy et al., 2001; Warnemuende et al., 2007). Their results reveal that the higher

the intensity of tillage management (conventional tillage > conservation tillage > no tillage), the higher the pesticide loss from fields.

2.3.4 Pathway drainage systems

Though a substantial percentage of arable land in Germany is drained (see chapter 2.1.2), Bach et al. (2001) and Ritter (2001) count the loss of pesticides via drainage as unimportant and of issue in specific orchard regions only. They do not consider, however, its relevance in regions of heavy soils and flat topography, where artificial drainage is common. De la Cueva (2006) determined the extent of drained arable land in different European countries, accounting for 0.5 % in Spain to 93 % in Finland. Several authors observed the pathway via drainage and reported pesticide losses in the range of 0.001 – 4 % of the applied amount (e.g., Kladi-vko et al. (1991) in the USA, Michaelsen (1999), Traub-Eberhard et al. (1994) and Neumann et al. (2002) in Germany, Novak et al. (2001) in France and Accinelli et al. (2002) in Italy). Brown & van Beinum (2009) reviewed 23 field experiments across Europe and determined in drain flow maximum pesticide concentrations that varied between "undetectable" (generally 0.02 µg/l) and 15470 µg/l. They determined seasonal losses of "undetectable" to 10.6 % of the applied amount. More than half of the losses were below 0.1 %.

Table 1
Summary of European studies on pesticide transport in drainflow.

Reference	Site	Field size ^a (ha)	Topsoil texture	Topsoil %OC ^a (%)	Topsoil %Clay ^a (%)	Years of study	Pesticides studied
Accinelli et al. (2002)	Po Valley, Italy	0.19	Silty clay	0.74	42.5	1996	Triasulfuron, prosulfuron, metolachlor, atrazine
Brown et al. (1995)	Po Valley, Italy	0.31	Silty loam	0.85	24.5	1996	Triasulfuron, prosulfuron, metolachlor, atrazine
Brown et al. (2004)	Cadriano, Po Valley, Italy	0.3	Silt loam	0.85	24.5	2000	Inazamethabenz-methyl, isoproturon, diflufenican
Dousset et al. (2004)	Cockle Park, Northumberland, UK	0.25	Clay loam	2.70	25	1989-1991	Mecoprop, isoproturon, Iomofos, trifluralin
Fletcher et al. (2004)	Maidwell, Northants, UK	7.7	Clay loam	1.20	28	2000	Sulfosulfuron
Catzweiler et al. (1999)	La Bouzule, France	2.83	Silt loam	1.5	26	1992-1993	Alachlor, bentazone
Hardy (1997)	Essex Coast (south of Harwich), UK	1.85	Silty clay	2	54.2	1992-1994	Alachlor, bentazone
Harris and Hollis (1998)	Wöllstadt, Hesse, Germany	1	Sandy loam	2	n.a.	1993	Mecoprop
Harris and Pepper (1999)	Städtkirchen, Northrhine-Westfalia, Germany	1	Silty loamy sand	1.00	16.5	1997	Isoproturon
Heppell et al. (1999)	Boarded Barns Farm, Ongar, UK	1.6	Sandy loam	1.30	20.8	1997	Isoproturon
Johnson et al. (1994, 1995)	Boarded Barns Farm, Ongar, UK	1.45	Clay loam	1.20	20.2	1994	Diflufenican, isoproturon
Kammer et al. (1999)	Boarded Barns Farm, Ongar, UK	1.3	Clay loam	1.50	31.2	1994	Diflufenican, isoproturon
Kier et al. (2003)	Rosemannund, Herefordshire, UK	n.a.	Silty clay loam	1.70	36.1	1994	Flutrisafol, isoproturon, propiconazole, trifluralin
	Knappwell Field, Boxworth, Cambs, UK	1.89	Clay	2.20	43	1994-1996	Flutrisafol, isoproturon, propiconazole, trifluralin
	Brimstone Farm, Oxon, UK	n.a.	Clay	3.60	60	1994-1998	Chlorotoluron, isoproturon, triasulfuron
	Wytham, Oxon, UK	n.a.	Clay	3.10	57	1994	Isoproturon
	Wytham, Oxon, UK	0.18	Clay	2.57	57	1993-1994	Isoproturon
	Bohkurst, Schleswig-Holstein, Germany	0.5	Sandy loam	n.a.	18.4	1993-1994	Carbetamide, dimetofuron, isoproturon, pendimethalin
	Estrup, Vejlen, Jutland, Denmark	1.26	Sandy loam	4.5	15	2000-2002	Amidosulfuron, bentazone, bromoxynil, flamprop-n-isopropyl, glyphosate, ioxynil, mcpa, metsulfuron-methyl, pendimethalin, pirimicarb
	Faarstrup, Slagelse, Zealand, Denmark	2.33	Sandy loam	1.4	14.5	1999-2002	Bromoxynil, dimethoate, flamprop-n-isopropyl, fluroxypyr, glyphosate, ioxynil, mcpa, pirimicarb, propiconazole
	Silstrup, Thisted, Jutland, Denmark	1.69	Sandy clay loam	2.2	22	2000-2001	Dimethoate, flamprop-n-isopropyl, glyphosate, pirimicarb
	Slaeggerup, Roskilde, Zealand, Denmark	2.17	Clay loam	1.4	22	2000-2002	Amidosulfuron, bentazone, bromoxynil, dimethoate, flamprop-n-isopropyl, glyphosate, ioxynil, metsulfuron-methyl, pendimethalin, pirimicarb
Novak et al. (2001a)	La Bouzule, Lorraine, France	2.83	Silt loam	1.36	26	1996, 1998	Metolachlor
Peterson et al. (2003)	Near Copenhagen, Denmark	1.85	Clay	1.90	54.2	1996, 1998	Metolachlor
Ritse et al. (2004)	Syverud, Norway	0.16	Sandy loam	3.10	11.2	1999-2000	Ioxynil, pendimethalin
Scorza et al. (2004)	Askim, Norway	0.0402	Silt loam	3.2	n.a.	2001	Bentazone, propiconazole
Smelt et al. (2003)	Andelst, Netherlands	0.0324	Silty clay loam	1.3	n.a.	2001	Bentazone, propiconazole
Traub-Eberhard et al. (1995)	Central Netherlands	0.8	Silty clay loam	2.1	28	1998	Bentazone, imidacloprid
Vilhoth et al. (2000)	Brandenburg, nr Berlin, Germany	n.a.	Silty clay loam	2.10	28	1998	Imidacloprid
Williams et al. (1996)	Gelbæk, Central Jutland, Denmark	0.0025	Sand	2.50	4	1992	Isoproturon, metolachlor, pendimethalin, terbutylazine
	Rosemannund, Herefordshire, UK	5.94	Sandy loam	1.55	15.5	1997	Prochloraz
	Rosemannund, Herefordshire, UK	n.a.	Silty clay loam	1.70	23	1989-1993	Atrazine, carbosulfuron, chlorpyrifos, dimethoate, isoproturon, fenpropimorph, lindane, mcpa, trifluralin
	Speckhacker, Wehrhach, SW Germany	0.09	Silt loam	0.80	14	1997	Aldicarb, atrazine, chlorpyrifos, dimethoate, isoproturon, lindane, trifluralin
	Zehe and Fühler (2001)	0.09	Silt loam	0.80	14	1997	Isoproturon

^a n.a. = not available.

Fig. 6: Studies about pesticide loss via drainage systems in Europe (Brown & van Beinum, 2009)

Brown & van Beinum (2009) used the statistical technique residual maximum likelihood (REML), to identify a combination of factors that best explain the values for maximum concentrations and seasonal loss. Thus, they determined the four most important factors influencing maximum pesticide concentrations in drain flow: (i) elapsed time between application and first subsequent drainage event, (ii) strength of sorption of the compound to the soil, (iii) the clay content and the half-life of the compound in soil (DT₅₀). For the seasonal pesticide loss, nearly the same factors are most influential: (i) strength of sorption of the compound to the soil, (ii) percentage of compound remaining after the first drainage event, (iii) the soil clay content and (iv) the distance between subsurface drainage pipes. Kladvko et al. (2001) reviewed results of 30 studies observing pesticide transport to subsurface drains in North America. They identified the same factors influencing the seasonal loss of pesticides via drainage. In further studies, the importance of rainfall patterns (timing, magnitude, intensity) (Beulke et al., 2001; McGrath et al., 2010) and antecedent soil water content (Jarvis, 2007; Kahl et al., 2008) is stressed. High initial soil water content enhances macropore flow, and, thus, pesticide leaching into deeper soil. Pesticide relocation was observed at different soils and revealed highest losses in clay, due to a higher extent of preferential flow (Jarvis, 1994; Novak et al., 2001) Besides the influencing parameters listed above, several investigations focussed on the effect of different management procedures. Oquist et al. (2007) found that organic farming reduces the subsurface drainage discharge by 41 % and, hence, diminishes pollutant loss, too. According to Malone et al. (2003) and Watts & Hall (1996), the transport of water and dissolved compounds through the soil is retarded by conservation tillage, providing the pesticides additional time for sorption or degradation.

2.3.5 Pathways from farmyards

Water contamination sources have also originated from farmyards in connection to handling of pesticides before and after application to fields. Spillages during filling of tanks, disposal of waste spray remains and incorrect storage of canisters account for accidents and mismanagement. Cleaning procedure for spray equipment is a focus of observation. Out of convenience, farmers often clean their equipment in the farmyard instead of in the field (Carter, 2000a; Jaeken & Debaer, 2005). Appropriate technical equipment to simplify cleaning of sprayers (an additional freshwater tank) is available but not affordable for all farmers.

2 State of the Art

The de-watering of paved farmyard areas can take place in several ways (Blarr et al., 2009):

- farmyard – channel – waste water treatment plant – recipient (combined sewage system)
- farmyard – separation channel – recipient (separate sewage system)
- farmyard – in-house receiver (e.g. slurry basin) – output on the field – infiltration into soil
- farmyard – direct discharge into the proximate recipients

The prevailing de-watering situation depends on locations of farms. They can be situated in villages or outside villages between the fields, according to the historical development of the region. In the first case, connection to a waste water treatment plant is more likely than in the second case (Huber et al., 1998). However, degradation of pesticides in water does not occur to a great extent in waste water treatment plants; there they are merely sorbed to solid and sludge particles. Accurate figures of amounts adsorbed in waste water treatment plants are not available. Hence, pesticides tend to be released back into the environment. Data concerning farmyards connected to waste water plants are largely from the southern and western regions of Germany; data from the northern and eastern regions are not available. (Blarr et al., 2009; Reichenberger et al., 2007; Seel et al., 1994).

In Germany, several authors report the significance of pesticide losses from farmyards via waste water treatment plants of up to 90 % of the total load of a stream (Müller, 2000; Neumann et al., 2003). Fischer et al. (1998) observed concentrations of up to 130 µg/l in the recipient stream. Studies on the EU level state similar values of loss via waste water treatment plants in the range of 30 – 90 % of the total load in the recipient stream (Kreuger (1998) in Sweden, Leu et al. (2004b) in Switzerland, Beernaerts et al. (2002) in Belgium and Mason (2003) in the UK).

2.3.6 Pesticide fate in catchment-scale studies

Within the last few years, there has been shift from the simple monitoring of pesticide concentrations in surface water to more integrated catchment-scale studies. Monthly monitoring of concentrations in surface water throughout the year provides an overview of contamination and seasonal variations, but cannot deliver proper information about sources and pathways of

the pesticides. Edge-of-the-field studies try to evaluate losses via single pathways, usually via surface runoff (e.g. Haider, 1994; Hall, J. K., Mumma, R. O. & Watts, D. W., 1991; Klein, 2004)) and rarely via drainage systems (Brown & van Beinum, 2009; Gaynor et al., 2002; Kladvik et al., 2001). On the catchment scale, the total pesticide load of an entire hydrological unit can be determined in relation to the applied amount. The variations in loss, caused by the individual characteristics of the single fields, are balanced at the catchment scale, hence, extreme values are evened to more representative values. Data of high temporal and spatial resolution are the basis for further models simulating the single processes of pesticide alterations and movements in a watershed. By means of more detailed information, it is possible to differentiate between diffuse and point sources or even between single pathways and to obtain effective mitigation measures for the pesticide loss (Bärlund et al., 2007; Behera & Panda, 2006; Santhi et al., 2006). Several detailed projects about the fates of herbicides in small catchments (2-50 km²) have been realized (Fischer, 1996). A selection is reported in Tab. 6.

Tab. 6: Data of selected reviewed studies on pesticide fate in catchments

catchment	size [km ²]	length of stream [km]	slopes	drained areas	farmyards connected to wwtp*	application data
Nil, Belgium (Holvoet, 2006)	32	14	hilly 110 – 167 m a.s.l. ^o	not quantified	no	yes
Zwester Ohm, Germany (Müller, 2000)	50	11	low mountain range	23%	yes	yes
Lake Greifensee, Switzerland (Leu et al. 2004)	2.1	7.2	5 – 10 %	12%	yes	yes
Nette & Pletschbach, Germany (Neumann et al., 2002)	1550; 1080	4; 5.7	0.8 – 4 %	not mentioned	yes	no
Vemmenhög, Danmark (Kreuger, 1998)	9		plain	> 40 %	not mentioned	yes

* wwtp = waste water treatment plant ° a.s.l. = above sea level

In the catchment of the Zwester Ohm, Germany, Müller (2000) determined pesticide losses between 0.1 % and 0.67 %. Runoff from farmyards via waste water treatment plant were iden-

tified as the main entry pathway, accounting for 77% of the total load. Losses from non-point sources were relevant only during the winter season. Neumann et al. (2002) distinguished between point and diffuse sources and quantify the relevance of point sources with 30 - 90 % of the total load in the stream. Five different sources for pesticide runoff in the catchment were determined in this study: field runoff, farmyard runoff, rainwater sewers, waste water treatment plants, and sewage sewers. The highest proportions of 84 % and 66 % of the total load in the stream was attributed to herbicide inputs from farmyard runoff via waste water treatment plants. On a catchment-scale, without regard to pathways, as a sum of all pathways, Kreuger (1998) observed pesticide losses in the range of 0.06 to 0.68 % of the applied amount. Gomides Freitas (2005) focussed on the spatial and temporal variations of herbicide losses into surface water within a catchment. The spatial variability was attributed in higher extent to system characteristics of the catchment, and in lesser extent to the herbicide characteristics (degradation, sorption and mobilization potential). Single fields are assumed to contribute significantly to herbicide loss due to their hydrological conditions (Freitas et al., 2008).

2.3.7 Models simulating the fate of pesticides

Computer models provide the possibility to simulate the fate and pathways of pesticides. One advantage of modelling a system consists of the reduction of monitoring costs. Furthermore, single processes that are sometimes difficult to measure, can be observed in detail. Reliable data are required to gain sufficient simulation results, however. Computer models can demonstrate the effects of different scenarios and clarify the relevance of single parameters or processes. The results of simulations can be used to assess the risks for the environment. The effectiveness of different pesticide mitigation measures can be displayed, thus aiding decision makers in their evaluations (Holvoet, 2006). Moreover, models are used in the process of pesticide registration to simulate certain processes in the fate of the pesticide. In the European Commission, the FOCUS organisation (Forum for the Coordination of Pesticide Fate Models and their Use) was constituted to develop guidance for notifiers and member states concerning appropriate methods for calculating exposure concentrations for plant protection products (FOCUS, 2004a). Two models were selected to determine pesticide losses from a field. These "edge-of-the-field" models simulate the loss of a compound via surface runoff from a field and into a stream (PRZM) (Carsel et al., 1984). The second model (MACRO) simulates the

loss via subsurface drainage from a field into surface water (Jarvis, 1994). MACRO is a mechanistic, dual-porosity model of pesticide fate and mobility in soils which accounts for non-equilibrium flow in macropores (Jarvis, 1994). Both models calculate the pesticide concentrations in the stream over time spans of up to 20 years and under different climatic conditions (FOCUS, 2004a; FOCUS, 2004b).

As several models have been developed to simulate the different pathways of pesticides on different size scales, only a selection of applied models in Germany and their is properties given in Tab. 7.

Tab. 7: Selection of applied models for pesticide transport in Germany (Dietrich, 2010)

Model	Pathway				Scale	References
	SR	LEA	D	P		
DRIPS	o	o	o		macro scale	(Röpke et al., 2004)
EVA			o		micro scale	(Koch & Winkler, 2004)
EXPOSIT	o	o	o		micro scale	(Winkler, 2001)
HYDRUS (1D, 2D)		o			micro scale	(Simunek et al., 1998))
LEACHM (LEACHP)		o			micro scale	(Hutson & Wagenet, 1992)
MACRO (DB)		o			micro scale	(Jarvis, 1994)
PELMO		o			micro scale	(Klein, 1994)
PESTLA		o			micro scale	(Boesten, 1993)
PRZM (2, 3)	o	o			micro scale	(Carsel et al., 1984)
QuickTrift			o		micro scale	(Kohlschütter et al., 2005)
REXTOX (SFIL)	o				macro scale	(OECD, 2000)
SIMULAT		o			micro scale	(Diekkrüger, 1996)
SWAT	o	o		o	meso- to macro scale	(Arnold et al., 1998)
SYNOPS	o	o	o		meso scale	(Gutsche & Rossberg, 1997)
VARLEACH		o			micro scale	(Walker, 1987)
RP	o				meso scale	(Schriever et al., 2007)

SR= surface runoff; LEA = leaching; D = drift; P = point sources

Several models work with the one-dimensional vertical dislocation of pesticides in the soil (HYDRUS 1D, LEACHP, VEARLEACH) at the field scale. Simulating on larger scales demands a high amount of input data in order to describe the more complex physical, biological and chemical processes (Krysanova et al., 1998). According to Arnold & Fohrer (2005) and

2 State of the Art

Hörmann et al. (2005), the available hydrological models are suitable to answer ecological and economical questions (Dietrich, 2010).

3 RESEARCH DEFICITS AND OBJECTIVE OF THIS STUDY

Research on the fate of pesticides and their harm to non-target organisms and areas have been investigated for decades. For the most part, concentrations and loads have been monitored; but long-term studies in surface water and groundwater have been conducted as well. On the basis of these data, conclusions are drawn about the sources, interrelations and dependencies of water and pesticide transport. There are still uncertainties concerning the relevance of the single pathways of pesticides entering surface and groundwater, however, regional differences of watersheds make it impossible to extrapolate measured pesticide loadings to unmonitored river basins. Hence, it is necessary to quantify the contribution of every single pathway of pesticide losses so that total loads can be predicted and the regional importance of the known non-point and point sources of pollution can be assessed (Huber et al., 1998).

Until the present, no investigations have been accomplished on the fate of pesticides in lowland catchments. These areas are characterized by a flat topography, shallow groundwater, high proportion of drainage and a low hydraulic gradient causing low flow velocities. They are sensitive to alterations in drainage systems or changes due to river regulations that result in changes of the natural water balance and in-stream water quality (Krause et al., 2007; Lam et al., 2009; Schmalz & Fohrer, 2010). An attempt to fill this research gap was exemplarily conducted in a catchment of the North German Lowlands.

The objective of this study is the assessment in a lowland catchment of the relevance of field drainage to losses of herbicides used for corn, rape and winter wheat. Among others, the following significant questions are to be answered:

1. What herbicide concentrations will be detected in drainage water and groundwater on field plots, and in surface water?
2. What herbicide loads will be discharged into surface water?
3. How high are the potential discharges as they relate to scale?
4. Which losses will be detected according to the initial application amount?
5. Will there be differences according to scale sizes?

3 Research deficits and objective of this study

6. Is it possible to compare the amount of discharge and the discharge pattern of the single herbicides in spite of varying hydrological conditions, sites and physical-chemical properties of the herbicides?

In addition, as a dislocator of pesticides from fields to water bodies, rainfall-induced surface runoff was evaluated as a further possible pathway. Diverse studies on this topic have been conducted with rainfall simulators, but none have taken the effects of intermittent rainfall into account. Under natural conditions, at field scale these effects are difficult to observe, as the complexity of the surface runoff processes is high and single parameters can not be influenced.

The second objective of this thesis is the investigation of the impact of intermittent rainfall on the fate of herbicides applied to the prevalent crops corn, rape and winter grain. Laboratory experiments under defined conditions representing Northern Lowland conditions are conducted with a capillary rainfall simulator to answer the following questions:

1. What herbicide concentrations will be detected in the water phase of the runoff?
2. What herbicide loads will be discharged from the plot with the water phase of the runoff?
3. What patterns will the discharge of the herbicides show?
4. What losses will be detected in the water phase according to the initial application amount?
5. Will there be differences in discharge and discharge pattern of the herbicides due to their physical-chemical properties?

As the analytic process of pesticide quantification was not instituted in the chemical laboratory of the institute, it was part of this thesis to establish the guideline DIN EN ISO 11369 (1997) for the determination of selected plant treatment agents using high performance liquid chromatography with UV detection after solid-liquid extraction.

4 CHARACTERIZATION OF THE STUDY AREAS

4.1 Kielstau catchment

The study area is the catchment of the river Kielstau. It is located in the northernmost region of Germany in Schleswig-Holstein, 10 km south east of the town of Flensburg, near the Danish border. An area of 50 km² drains into the 17 km long river, which is part of the drainage area of the Treene, the most important tributary of the Eider river. The Kielstau originates at Hargesby at a height of ca. 45 m above sea level and flows westerly with a mean slope of 1 %. After 3 km, it flows through the Winderatter See, then joins the river Bondenau after 17 km, west of the village of Soltfeld, and leads into the Treßsee. Both streams, Kielstau and Bondenau, are the headwaters of the river Treene, which begins at the outlet of the Treßsee (Lam et al., 2009; Schmalz & Fohrer, 2010).

Various small tributaries, several open agricultural drainage ditches and drainage pipes contribute to the main stream water flow. There are two important tributaries from the north: the Moorau, joining the Kielstau ca. 400 m behind the outlet of the Winderatter See, and the Hennebach. A third tributary, the Levensau, is mainly piped (Schmalz et al., 2008a).

4 Characterization of the study areas

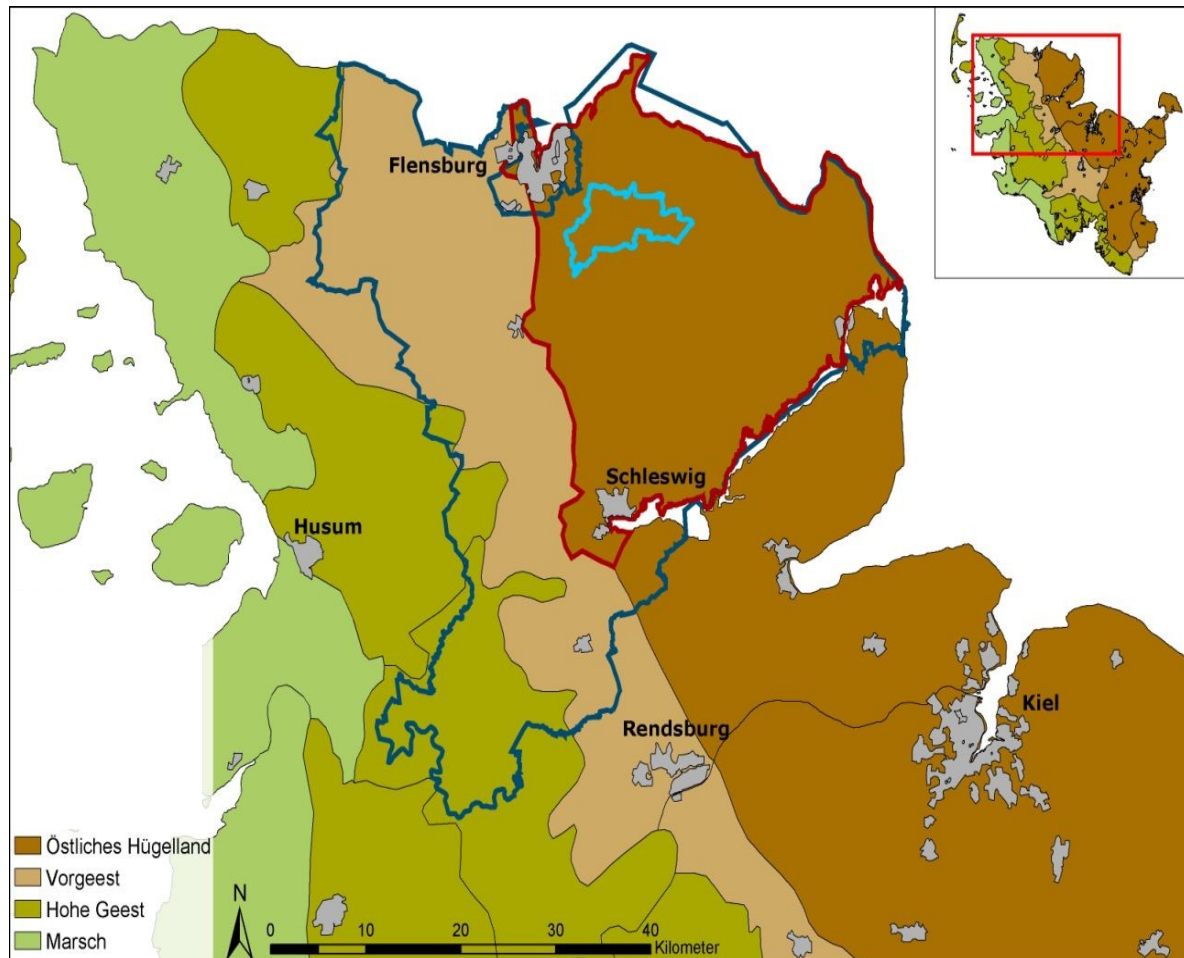


Fig. 7: Location of the Kielstau catchment [data source: Landesvermessungsamt (2005)]

The catchment represents typical characteristics of the North German Lowlands with a high proportion of drained fields, moderate slopes ($< 10\%$), and with farms located outside villages, their farmyards unconnected to waste water treatment plants. The North German Lowlands cover an area of approximately 140,000 km², an area equivalent to 39 % of the entire area of Germany, and are part of the Middle European Lowland Belt (BfN, 2008, Fig. 8).

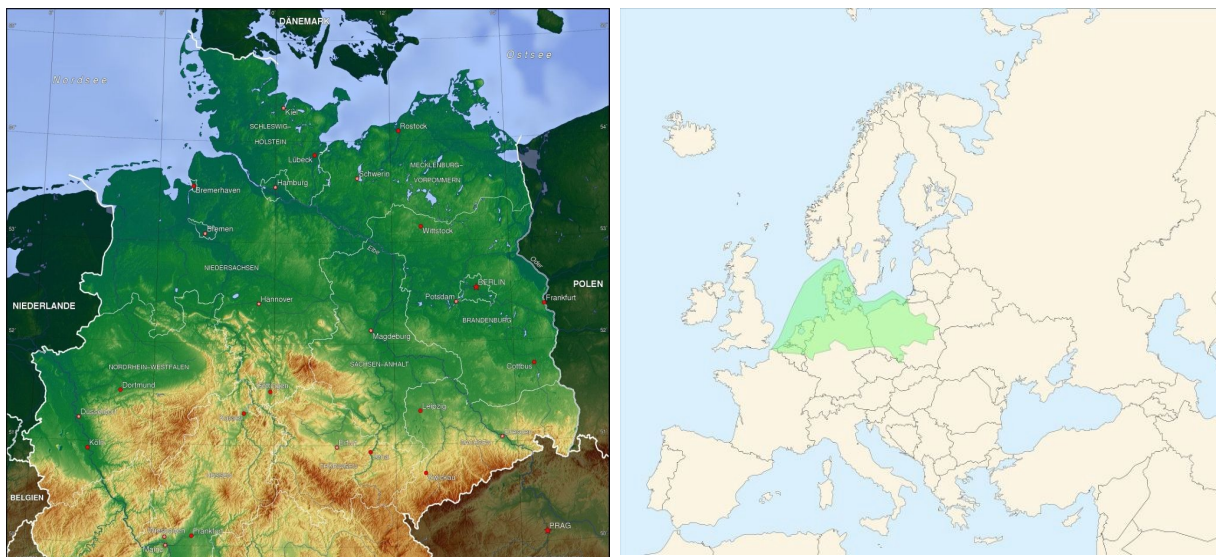


Fig. 8: Location of the North German Lowlands (left) and the Lowlands of Middle-Europe (right) in green colour [data source: Deutschland topo, 2006 (l); BfN, 2008 (r)]

Climate

The climate of Schleswig-Holstein and therewith the catchment is determined mainly by the proximity of the sea. Maritime air masses provide a year-round mild and humid climate with temperatures of limited variability. The dominating west wind conditions deliver humid air masses from the Atlantic and North Sea. According to the rising roughness of the landscape, the humid air results in orographic rain which varies greatly during the seasons and years. Compared to other locations at the same latitude, many frost-free days and limited snow fall events lasting only several days can be observed (Wagner, 1998). The annual mean precipitation (1985-2008) at the Satrup station shows a value of 820 mm (LLUR, 2009), which is in the range of average precipitation for the entire state of Schleswig-Holstein. The mean annual temperature in this region varies from a minimum of 0.6° C in January to 16.0° C in July, resulting in an annual mean amplitude of 15.4° C. In Fig. 9, the distribution of the annual precipitation and temperature are shown. In spite of frequent low-pressure areas causing clouds and precipitation, the annual mean sunshine duration (1961-1990) is 1482.9 h in Flensburg (DWD, 2007b).

4 Characterization of the study areas

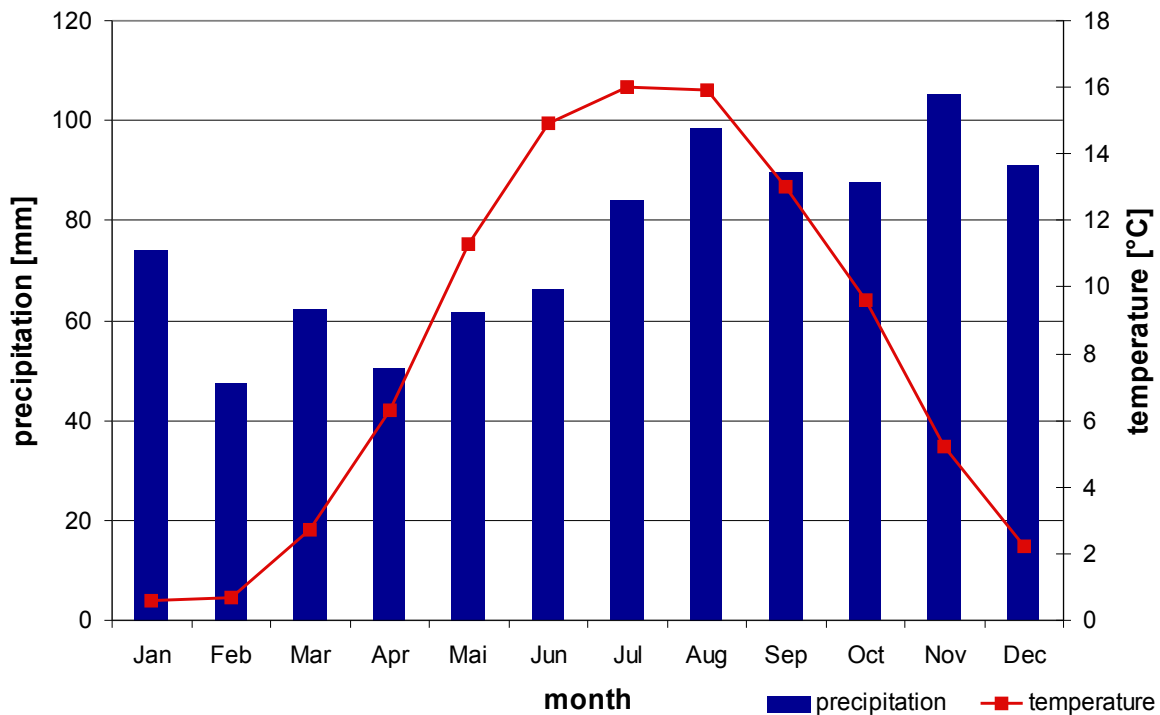


Fig. 9: Average monthly precipitation and temperature, Station Flensburg 1428, period 1961-1990 [chart by Bieger (2007), data source: DWD (2007a)]

Geomorphology and soils

The Kielstau is located in the landscape unit of the “Östliches Hügelland” (eastern hilly moraine landscape). This landscape unit is one of the three predominant nature areas, along with the “Geest” and the “Marsch” areas in Schleswig-Holstein. The three last glacial periods in northern Europe, the Elster, Saale and Weichsel periods formed the contemporary landscape resulting in flat hills and a high variability of depressions and rolling hills. The elevation ranges from 27 to 78 m a.s.l.. The prevalent soils in the east and south are fertile brown soils and luvisols of up to 56 points for soils, while gley soils and groundwater dependent peat soils dominate river valleys and depressions (Beuck, 1996; LW, 1990, Fig. 10)

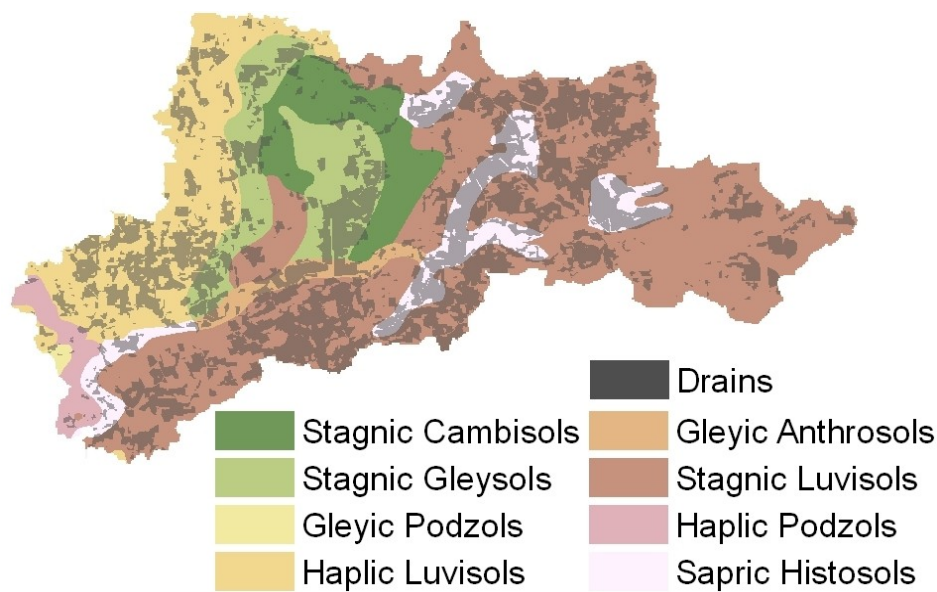


Fig. 10: Soil types of the Kielstau catchment [data source: BGR, 1999]

Land use and population

In the Kielstau catchment, the land use is dominated by arable land and pasture occupying 83% of the surface area. Forests are scattered and in limited extension, covering only 9 %. The urban land and fallow land take 3 % and 6 %, respectively, of the catchment (Schmalz et al., 2008b). The main crops are grain, rape and corn (Stat. Landesamt S-H, 2005). Extensive drainage measures have been implemented during the reallocation of land, mainly from the 1950s to the late 1970s (MELF, 1980). The drained area has been estimated by Fohrer et al. (2007) to be 38 %.

At the upper part of the catchment area, the nature conservation zone *Stiftungsland Winderatter See* is located. The nature protection foundation, Naturschutz Schleswig-Holstein, is owner of a 155 ha area around the Winderatter See and downstream of the Moorau, and leases the fields to farmers for extensive cultivation. The foundation aims to conserve and advance the biodiversity by supporting the coexistence of habitats. Furthermore, the *Stiftungsland Winderatter See* and the Kielstau belong to the European Network NATURA 2000-Protectorates (Stiftung Naturschutz, 2007; Janßen, 2005).

Population of the study area is marginal. Only eight municipalities are located here (Husby, Freienwill, Hürup, Ausacker, Großsolt, Grundhof, Maasbüll and Sörup) with scattered farms in between. There are no industrial areas, but there is a gravel pit. Transportation infrastruc-

4 Characterization of the study areas

ture includes the railway line Kiel-Flensburg, district road K 190, as well as several small rural roads.

Six waste water treatment plants are located in the region and discharge treated sewage water into the Kielstau and its tributaries (Tab. 8). Frequent, isolated farms and scattered houses are not connected to the waste water treatment plants, but to a domestic sewage treatment system whose effluents likewise reach the waters of the catchment.

Tab. 8: Waste water treatment plants in the Kielstau catchment
[data source:Schleswig, 2006]

waste water treatment plant	inhabitants served	discharge [m ³ /a]	recipient stream
Husby	3000	329000	Moorau
Ausacker	1880	max. 45000	Kielstau
Hürup Süd	461	max. 101000	Hennebach
Hürup Nord	447	max. 98000	Hennebach
Hürup-Weseby	240	max. 52500	Hennebach
Freienwill	350	17500	Kielstau

Characterization of the river Kielstau

The Kielstau belongs to rivers of Type 16 according to the typification of the EU-WFD. This refers to a gravel-dominated lowland stream characterized by frequent changes between fast and calmed passages (Bieger, 2007; Sommerhäuser & Schuhmacher, 2003; Thiemann, 2008). Due to artificial alterations, the Kielstau is considered nowadays to be more a canal than a natural river. In several sections, the course has been artificially straightened and the profile has been lowered.

The water quality of the Kielstau and its tributaries has been the topic of several monitoring campaigns in the last few years (Beyersdorf, 2008; Bieger, 2007; Jelinek, 2008). Interest was focussed mainly on physical parameters and chemical compounds originating from agricultural management practices. In overview, the results of six sampling days between 03/2006 and 01/2007 at 15 sampling points along the Kielstau are shown in Tab. 9 (Bieger, 2007). The values describe the maximum and minimum medians during this period. The assessment of the water quality is performed with the mean of all data of the parameter, and according to the LAWA water quality classification (LAWA, 1998). This classification consists of seven categories with I signifying *unpolluted* and IV *excessively contaminated*.

Tab. 9: Water quality of the Kielstau at 6 dates at 15 sampling points along the Kielstau [data source: Bieger (2007)]

parameter	Median		classification according to LAWA (LAWA, 1998)
	minimum	maximum	
electrical conductivity [$\mu\text{S}/\text{cm}$]	445	698	no classification
pH	7.1	7.8	no classification
Oxygen [mg/l]	5.85	11.75	I
Ammonium-N [mg/l]	0.07	0.52	II, II-III
Nitrate-N [mg/l]	2.83	8.18	III
Phospahte-P [mg/l]	0.11	0.42	III
Total Phosphorous[mg/l]	0.18	0.56	mainly III
Chloride [mg/l]	22.35	48.1	I-II
Sulfate [mg/l]	26.85	52.9	I-II

Concerning the physical parameters of oxygen, chloride and sulfate, the Kielstau is in good ecological condition, but especially the nutrient related parameters show that the input of nitrogen and phosphorous compounds have to be reduced severely to meet the demands of the WFD by 2015.

The pesticide contamination of the Kielstau has been observed since 1994 at the gauge in Soltfeld by the Landesamt für Landwirtschaft, Umwelt und Ländliche Räume (LLUR) once a month during the spring and autumn application of pesticides. The concentrations of the measured pesticides were mainly below the quantification limit of $0.03 \mu\text{g}/\text{l}$ or $0.05 \mu\text{g}/\text{l}$, depending on the compound. Single maximum values amounted for $12.5 \mu\text{g}$ Carbofuron/l, $4.4 \mu\text{g}$ Diuron/l, and $3.5 \mu\text{g}$ Metazachlor/l (LLUR, 2010).

4.2 Subcatchment of the Moorau tributary

The Moorau is the largest tributary of the Kielstau, joining it 400 m behind the Winderatter See. It has a length of 5 km and drains an area of approx. 747 ha. This subcatchment represents 15 % of the entire Kielstau catchment. The Moorau is characterized mainly by unpaved but steep banks. Though the stream describes a curvature, the course is straight and only the underflow meanders. The stream bed is flanked in general by Planosols and fens areas. Several drainage pipes, ditches and the waste water treatment plant of Husby discharge into the Moorau. Notably, the waste water treatment plant causes adverse effects in the Moorau, due to high loads of nitrogen and phosphorous compounds. These loads, however, are diluted by the

4 Characterization of the study areas

discharge of the stream and decrease downstream (Beyersdorf, 2008; Jelinek, 2008). In general, the water quality of the river Moorau is in a bad state. Its water can be classified as water quality class III “heavily contaminated“ or worse according to the LAWA water classification (LAWA, 1998). Occasionally, the river can be placed in water quality class IV “very heavily contaminated“, especially after the sewage inputs. Merely in regard to chloride and sulfate can it be classified in water quality class I “unpolluted“ or water quality class I-II “lightly polluted“ (Beyersdorf, 2008; Jelinek, 2008). Investigation of pesticide concentrations have not been conducted up to the present point.

4.3 Field plots

For the monitoring of the three herbicides, two different sites were observed to represent the field scale.

In spring 2008, the drained field 1 was investigated from 16/5 - 30/6/2008 in order to determine the amount of pesticides applied to corn and discharging via the drainage system into surface water. The field is located in the community of Hürup next to the district road K 190 and has a size of 13.2 ha (Fig. 11). The tile drainage comprises one pipe of ca. 170 m length at a depth of 1.2 m below surface, which discharges into the Hennebach after crossing the adjacent field. The drainage is situated in a depression almost in the middle of the field so that water from the upper parts move to this area. The pipe discharges in general from September/October to June/July, depending on the hydrological conditions. The drained field 1 is cultivated under conventional farming management with crop rotations. During the 2008 season, corn was cultivated, and, due to the practiced crop rotations, winter wheat was grown there in 2006 and rape in 2007, so that residues of pesticides previously applied to corn could not be observed. On 30/4/2008, corn was sowed on the field; application of the pesticide took place on 16/5/2008. During the monitoring period, no additional management practices were necessary according to the guidelines of good management practices.



Fig. 11: Drained field 1 [Google Earth, 2009]

Drained field 2 was under investigation during the autumns of 2008 and 2009 in observation of discharged pesticides into surface waters via the drainage system, which are applied to rape and winter grain. The monitoring campaigns lasted from 1/9/2008 - 27/11/2008 and from 24/9/2009 - 5/12/2009. The field is situated in the Ausacker community next to the K 190 district road (Fig. 12). It has an area of 5.4 ha and contains tile drainage of a main and a side pipe with an overall length of 180 m. The tile drainage lies 1.5 m below surface and crosses the K 190 before discharging into the Levensau, one of the Kielstau's tributaries.

4 Characterization of the study areas



Fig. 12: Drained field 2 [Google Earth, 2009]

The drained field 2 is also cultivated under conventional farming management with crop rotations. During the monitoring campaign, in autumn 2008, rape was grown there, and in autumn 2009, winter wheat. According to the crop rotations, barley was cultivated in 2007. Analogous to drain field 1, no residues from former applied pesticides in rape or wheat could be observed. Drain flow is available in general all through the year. The dates of sowing were on 26/8/2008 and of pesticide application on 1/9/2008, as well as 17/9/2009 and 24/9/2009. Additional management practices during this time were not necessary according to the guidelines of good agricultural management practices.

5 MATERIAL AND METHODS

5.1 Experimental set up of herbicide monitoring in the Kielstau catchment

During monitoring campaigns that lasted six and ten weeks, soil and hydrological parameters and herbicide concentrations were observed. The dates of the monitoring phases are listed in Tab. 10.

Tab. 10: Periods of herbicide monitoring

monitoring phase	date	number of weeks
Terbuthylazine	16/5/2008 - 29/6/2008	6.5
Metazachlor	1/9/2008 - 27/11/2008	12.5
Flufenacet	24/9/2009 - 5/12/2009	10

For three periods, three areas of separate scale, nested within each other, were monitored:

- 2 agricultural fields (13.2 and 5.4 ha)
- subcatchment of the Moorau tributary (747 ha)
- catchment of the Kielstau (5000 ha)

Locations of the sampling points are plotted in Fig. 13.

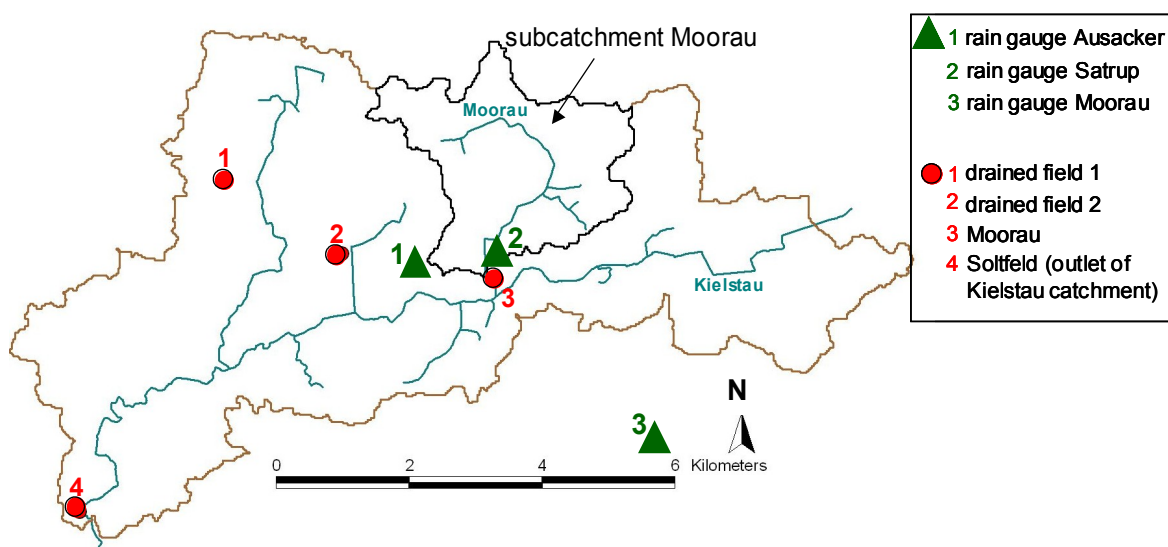


Fig. 13: Sampling points in the Kielstau catchment

5 Material and methods

Collection of soil samples was conducted once for drained field 1 and once for drained field 2 to characterize the sites.

During the monitoring period, on drained fields 1 and 2, groundwater level, tile drainage discharge and soil moisture were observed. Drainage water and groundwater were sampled for herbicide analysis (Fig. 14).

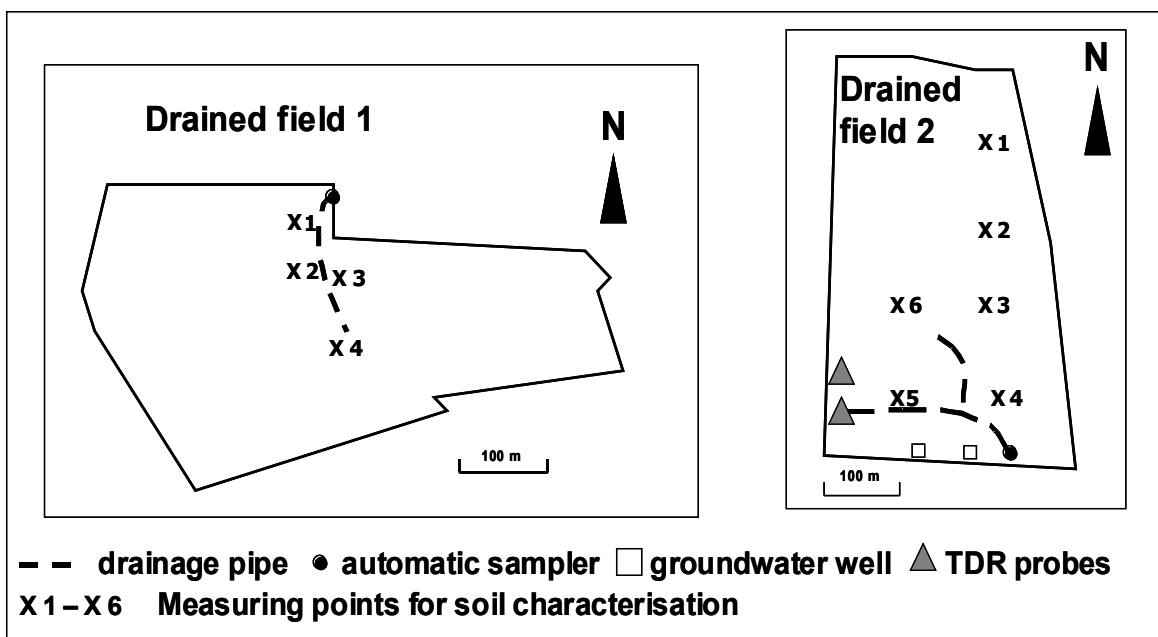


Fig. 14: Installations on drained field 1 (left) and drained field 2 (right)

At the sampling points of the Moorau subcatchment and of the Kielstau catchment at Soltfeld, discharge measurements were recorded and water samples were collected for the herbicide analysis.

Daily precipitation was monitored at stations within and near the catchment, and land use within the entire Kielstau catchment was mapped.

5.1.1 Herbicide application on drained fields 1 and 2

The applied supplements are pre-emergence herbicides and are sprayed before the crops reach the bifolium stage. Butisan Top® and Herold SC® contain further agents (Quinmerac and Diflufenican) which were not in the focus of the observations. Application data of drained fields 1 and 2 in each monitoring period are reported in Tab. 11.

Tab. 11: Application data on drained fields 1 and 2

date	field	supplement	agent(s)	applied concentration of supplement [l/ha]	amount of herbicide [g/ha]
16/05/2008	1	Calaris®	Terbuthylazine	1	330
01/09/08	2	Butisan Top®	Metazachlor, Quinmerac	2	750 (Metazachlor)
24/9/2009	2	Herold SC	Flufenacet, Diflufenican	0.6	240 (Flufenacet)

5.1.2 Soil parameters

To characterize the sites, soil parameters were determined according to standard guidelines, which are explained as follows:

Soil type was defined in the field with soil drill and finger probe methods, according to the German KA 5 guidelines (AG Boden, 2005). The soil type was then transferred into the international FAO classification system (WRB, 2006).

Particle size was determined in the laboratory in line with (DIN ISO 11277, 2002). An amount of 20 g air dried soil was sieved through varying mesh sizes, and the clay fraction was determined by sedimentation. For validation of results, the analysis was conducted with three parallels.

Organic matter content (OMC) was determined after (DIN 19684-3, 2000), using weight differences before and after ignition. The humic content was then calculated, by multiplying the OMC by a factor of 1.76.

The saturated hydraulic conductivity k_f under transient conditions was determined with a hood permeameter according to DIN 19683-9 (1998). Cylindrical core-cutters with an undisturbed soil volume of 100 m³ were used. For validation of the results, the analysis was conducted with seven parallels.

During monitoring for Flufenacet, soil water content was measured at depths of 20 and 40 cm at the position of the drainage pipe and 10 m north of it, to include spatial variations (Fig. 14). The soil water content was measured with Time Reflective Domain (TDR) probes (Trime It, range: 0 – 100 %; Imko, Ettlingen/Germany) in hourly intervals. The data were recorded with a data logger (Delta-T Devices, Cambridge, UK) and aggregated to daily mean values.

The catchment size of the drainage system on drained field 2 was determined by the water conductivity in the vadose zone K_{fb} (after DIN 19682-8, 2007). Rise velocity of the groundwater level was measured in a drilled hole after initial pumping off, thus providing the groundwater flow velocity. This parameter was then used to determine the drain pipe distance in soils wetted by groundwater according to DIN 1185-2 (1973). The calculated drain pipe distance was multiplied by the length of the drain pipes, thus providing the catchment size of the drainage system. The discharge/precipitation ratio was applied as a second method to determine the catchment size of the drainage. This determination was conducted under the following assumed conditions: the soil water storage was saturated, evapotranspiration was negligible, and the total precipitation was discharged as drain flow. The size of the drained area was calculated by dividing the discharge of the drainage by the sum total of precipitation.

5.1.3 Hydrological Parameters

5.1.3.1 Precipitation

Precipitation data from three different locations were available (see Fig. 13). The distances of the rain gauges are reported in Tab. 12:

- at the Satrup station, precipitation was registered every minute with an automatic rain gauge (Ott Pluvia, Ott, Kempten/Germany) and aggregated to the daily precipitation total; data were provided by the LLUR.
- at Moorau, an automatic rain gauge (type 506301, Thiess Clima, Göttingen/Germany) monitored hourly values, which were aggregated to a daily precipitation total.
- at the village of Ausacker, a Hellmann rain gauge was used and provided daily precipitation totals (Janßen 2008, Janßen 2009).

Tab. 12: Distance of rain gauges to the sampling points

rain gauge	drained field 1	drained field 2	Moorau	Soltfeld (Kielstau)
Satrup	10 km	8 km	8km	8km
Moorau	3.5 km	2 km	0 km	8 km
Ausacker	3.5 km	1.5 km	1 km	7 km

During the first monitoring in spring 2008 the Moorau rain gauge had not been installed, and precipitation records from Ausacker were not available. Within the observations in autumn 2008 and 2009 all rain gauges provided data, but in autumn 2009, the Moorau rain gauge did not record precipitation data, due to technical problems. Gauges used during each monitoring campaign are listed in Tab. 13.

Tab. 13: Use of rain gauges in the single monitoring campaigns

monitoring campaign	Satrup	Moorau	Ausacker
Terbuthylazine	X	-	-
Metazachlor	X	X	X
Flufenacet	X	-	X

5.1.3.2 Discharge of the tile drainage

A pressure sensor was located on the bottom of the drainage pipe where the horizontal drainage pipe enters and empties into the bottom of the vertical inspection shaft (Fig. 15). The bottom of the sensor was placed on the bottom on the drainage pipe. At continuous 10-minute intervals, an integrated measuring cell measured the pressure of the hydrostatic head above. Pressure data were converted automatically into cm of water level. The recorded data were aggregated into daily mean values.

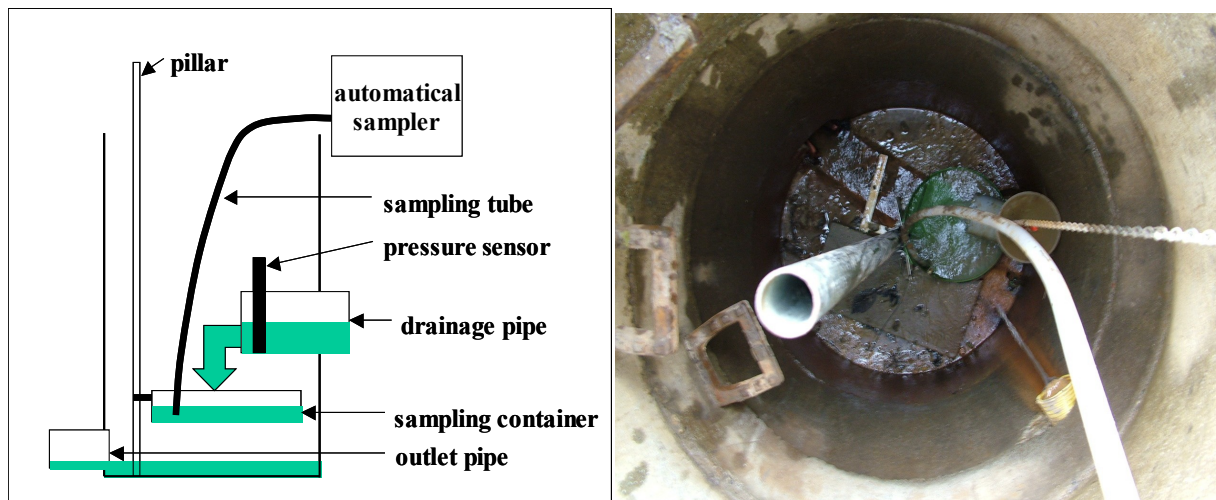


Fig. 15: Scheme and photo of the installations in the drain pipe inspection shaft

Twice a week, discharge and water level at the drainage pipe were measured manually. By means of these data, a rating curve was generated, so that the recorded water level data were randomized into the discharge data.

5 Material and methods

For the monitoring of Terbutylazine and Metazachlor, a pressure sensor (Driesen & Kern, Bad Bramstedt/Germany) was employed. For the Flufenacet monitoring, it was replaced by a pressure sensor of type MDS Dipper-T3, range 0-2 m (SEBA Hydrometrie, Kaufbeuren/Germany).

5.1.3.3 Groundwater level

During the monitoring of Metazachlor and Flufenacet, groundwater levels were measured twice a week in both temporary groundwater measuring points, GW1 and GW2, with a light plummet (type 025, Hydrotechnik, Obergünzburg/Germany). Furthermore, at GW2, the water level was determined continuously at 10-minute intervals with a pressure sensor (MDS Dipper-T3, range 1-10 m, SEBA Hydrometrie, Kaufbeuren/Germany). These data were aggregated to daily mean values. The sensor was installed at the end of the monitoring in autumn 2008, hence, data were provided for the last 15 days. During the monitoring of Flufenacet in autumn 2009, groundwater level data were missing from 9/10/2009 to 11/10/2009 and 17/11/2009 to 22/11/2009, due to technical problems.

5.1.3.4 Discharge of the Moorau

Water levels of the Moorau were determined by means of a mechanical water level recorder (Ott, Kempten/Germany). Using a rating curve, daily mean values were aggregated and converted into discharge. Once a month, over a two-year period, 2006-2008, the discharge was determined with a flow meter (Flowsens 801, Seba GmbH, Kaufbeuren/Germany), thus delivering data for the rating curve.



Fig. 16: Sampling point Moorau with mechanical water level recorder (1) and automatic sampler (2).

5.1.3.5 Discharge of the Kielstau

Discharge of the Kielstau was monitored with a flow sensor (flow sense 750 AV ultrasonic sound doppler, Teledyne Isco, Lincoln/USA) recording hourly data during the Terbutylazine monitoring. The data were aggregated to daily mean values.

Hourly discharge data for the two other herbicide periods were provided from the environmental agency, Staatliches Umweltamt (StUA) Schleswig, and aggregated to daily mean values. The water level is measured by the agency with a mechanical water level recorder (Ott, Kempten/Germany). Once a month, the discharge is determined against the water level with a flow sensor (Nautilus, Ott, Kempten/Germany). With these data, a rating curve is generated that enables a determination of the hourly discharge.



Fig. 17: Sampling point at the Kielstau with water level recorder (1) and automatic sampler (2). (3) indicates position underneath bridge of flow meter in the Kielstau.

5.1.4 Collection of water samples

For pesticide detection, on drained fields 1 and 2, at the Moorau and at the Kielstau, Soltfeld station, automatic samplers (ISCO 6712, Teledyne Isco, Lincoln/USA) collected a daily sample mixture composed of 20 samples, each 50 ml in volume, at continuous, 1:12 h intervals. The sampling bottles of the automatic sampler were of plastic, however, further transport and treatment were conducted in glass jars.

During the Metazachlor monitoring in autumn 2008, technical problems of the automatic sampler in the Kielstau at Soltfeld gauge occurred, and several daily mixed samples were not available (see Appendix A 2).

Twice a week, the groundwater was sampled during the monitoring of Metazachlor and Flufenacet at the temporary groundwater measuring point, GW1. Water residing in the pipe was pumped out, and the groundwater flowing in was sampled after reaching the initial water level.

5.1.5 Land use mapping

Land use in the entire catchment of the Kielstau was mapped in early summer 2008 for the Terbutylazine monitoring, and at the beginning of the years 2009 and 2010 for the monitoring of Metazachlor and Flufenacet, respectively. Each field crop was mapped with mobile mapping software (ArcPad 6.0.3, ESRI), using a GPS receiver and a Microsoft Windows driven personal digital assistant (Dell Axim). The system allowed mapping while the receiver indicated actual position. The output maps of ArcPad were compatible for input in ESRI ArcGIS, a geographic information system software. With ArcGIS 3.3, the areas of the single land use classes could be calculated (Golon, 2009). In a second step, the land use map was joined in ArcGIS with a drainage map of the region developed by Golon (2006). On the basis of this work, the portion of each crop area in the catchment, as well as the portion of each drained crop area in the catchment, could be determined and used for further assessment of potential discharge.

5.1.6 Assessment of the applied herbicide amount

To assess the the loads released from the agricultural areas into surface water, it was necessary to gain as much information as possible from the farmers about their application procedures. In cooperation with the local plant protection service, a group of farmers who usually meet every 14 days from April to July to discuss possible applications of nutrients and pesticides was interviewed. During the following monitoring campaigns, the number of farmers contributing to the projects increased to 55 persons, due to intense cooperation with the Schleswig-Holstein chamber of agriculture and the local farmers' association. In meetings, information was provided to the farmers about the monitoring activities in the catchment and their purpose (Fig. 18). Questionnaires were then sent via mail. The response rate of the questionnaires amounted to 100 %, due to intense communication and inquiries. But it was not possible to contact all farmers growing corn, rape and winter grain during the respective monitorings. Results of the observations were presented to the farmers at the end of each year.

The farmers were asked the following questions:

- date of application

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- product applied
- herbicide concentration of the sprayed solution
- size of the sprayed field
- portions of treated fields that are drained



Fig. 18: Meeting with the local farmers for information exchange (27/5/2010)

5.2 Experimental set up of the surface runoff experiment with rainfall simulator

In a rainfall experiment, soil containers treated with pesticides were exposed to intermittent precipitation. To generate surface runoff, a slope of 6 % was adjusted. The experiment was conducted in seven day cycles (six times): Every seven days, 13 mm precipitation fell on the soil containers within one hour. This represents a strong, but common rainfall event in northern Germany (LLUR, 2009). The surface runoff resulting from each rainfall event was sampled and analyzed at 10-minute intervals. Throughout the six days between simulated rainfall events, the containers were stored in the rainfall tower at 14 – 18°C, and dried with fans to simulate evaporation under natural conditions (Fig. 19). The experiment was conducted with a set up already developed in a previous project by (Zeiger, 2007).



Fig. 19: Experimental set up in the rainfall tower

5.2.1 Rainfall simulation

A capillary rainfall simulator is placed in a former silo to simulate natural rainfall under laboratory conditions. It comprises a square tank of durable PVC, with a base area of 1.20 m^2 and a wall height of 40 cm, hung at a height of 9 m. The core of the tank's drop plate (1.00 m^2) includes 2500 capillaries, each with an external diameter of 2.5 mm and an internal diameter of 0.5 mm, and each with a wire (diameter = 0.3 mm, length = 2.6 cm) inside to reduce water tension (Fig. 20). Raindrops form at the capillaries, and, due to their own weight, release and fall freely downwards. Depending on the water level in this box, the simulated rainfall intensity can vary. Therefore, a float device maintains a constant water level in the tank. A net of 2 mm mesh size is placed 30 cm below the rainfall simulator to ensure uniform drop size. The drop size is in the range of $< 1 \text{ mm}$ to 4 mm, and the majority of drops are within the range of 1 - 2 mm. The fall velocity of the raindrops is within 0.8 to 4.2 m/s, most drops falling at 1.4 m/s. The drop size and fall velocity are comparable to natural rainfall (Schmidt, 2005). Drinking water stored in a reservoir serves as rain water for this experiment.

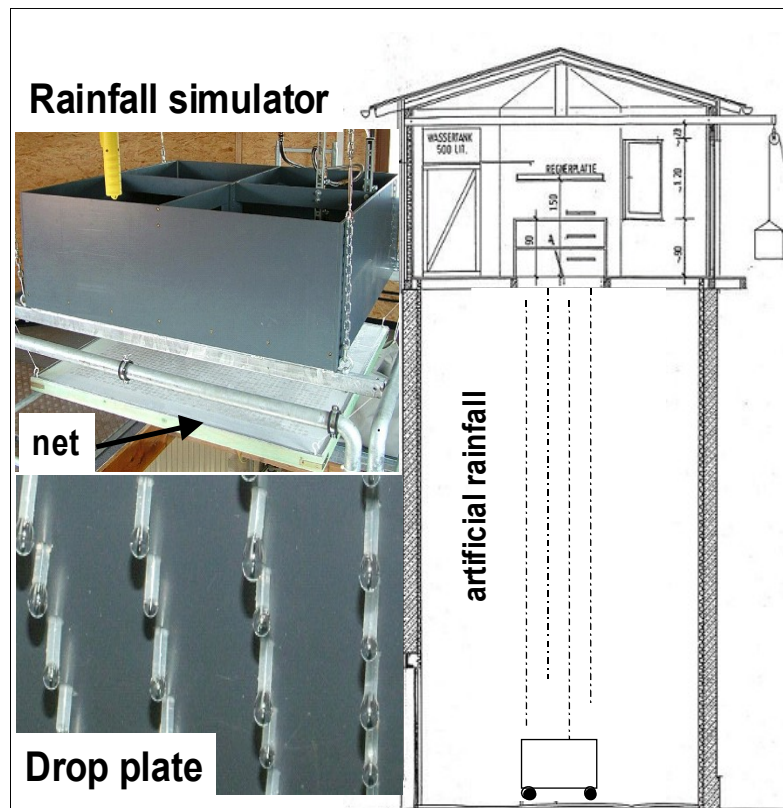


Fig. 20: Rainfall tower, rainfall simulator (drop plate) and net [Zeiger & Fohrer (2009) altered]

5.2.2 Soil container set up

Six mobile containers sized 90 x 80 x 40 cm were used for this experiment. At a depth of 36 cm, a suction plate (EcoTech, Bonn/Germany) was installed to control the soil water content in the soil box between rainfall events. For optimal drainage, the plate was embedded into gravel. Soil from the upper 20 cm of the AP horizon from drained field 2 was dug with an excavator bucket and air-dried to a soil moisture of approximately 12 – 14 %. It was poured through a screen with a mesh size of 2 cm onto a gravel layer on the floor of each container, and compacted to a bulk density of 1.4 g/m³. Furthermore, Time Domain Reflector probes (TDR) (range: 0 to 100 %; Trime It, Imko, Ettlingen/Germany) were installed at depths of 30 and 20 cm to monitor the water content in each soil container. After four weeks of natural settling, the containers were filled to the top, and a further TDR probe was installed at a depth of 7 cm depth (Fig. 21).

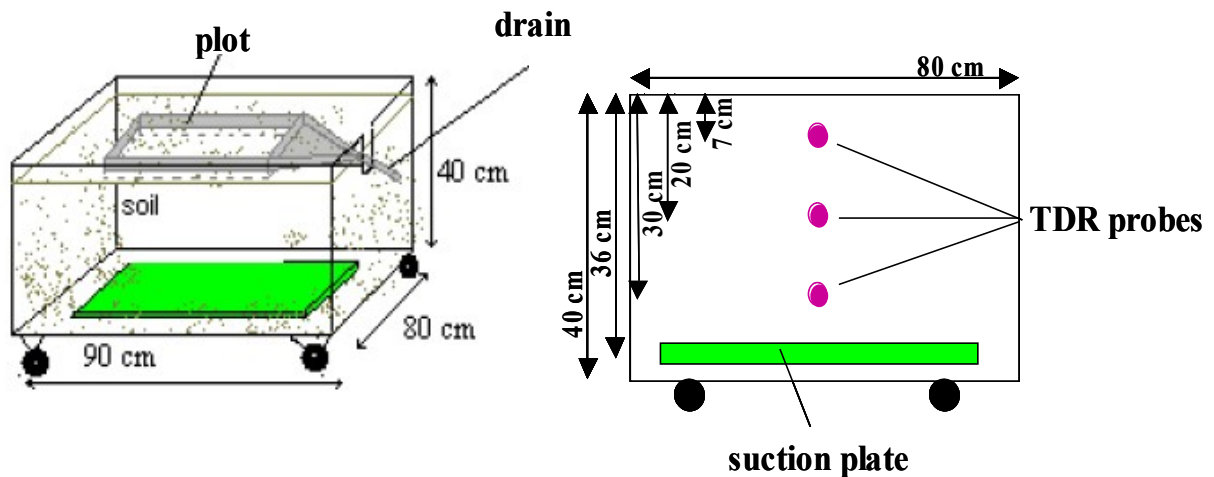


Fig. 21: Diagram of the soil container set up [Fohrer et al. (1999) altered]

According to the field situation, a micro-relief was created by compacting the soil slightly and placing aggregates ($A=2-16 \text{ cm}^2$) on top. Thus, the irregularity of a seed bed was simulated. Under field conditions, herbicides are applied to bare soil, therefore the soil boxes were kept free of vegetation Fig. 22.



Fig. 22: Soil surface of the field (l); installation of the sensors (m); soil surface of a container (r)

To prevent potential boundary effects, a rectangular inner plot unit of 40 x 50 cm was placed on the surface of each soil container so that only the runoff of the enclosed area was the object of observations.

During the six days between the rainfall events, a vacuum of 200 mbar was applied to the suction plates to simulate the percolation of the leaching water, and to prevent water from standing in the soil containers.

5.2.3 Application of the pesticides

The soil boxes were exposed one time to a precipitation of 4 mm. This procedure simulated a rainfall event between sowing and application of pesticides. As the time span between sowing and application varies within the range of one week (grain) to three weeks (corn), it is therefore supposed that precipitation will occur at least once during that period.

The pesticides were applied according to the accreditation and to guidelines of the producer. The amounts are shown in Tab. 14.

Tab. 14: Agent application data

	Butisan[®]	Calaris[®]	Herold SC[®]
agent concentration	500 g Metazachlor/l	330 g Terbuthylazine/l	400 g Flufenacet/l
amount	1.5 l/ha	0.8 l/ha	0.6 l/ha

According to these amounts, the application was conducted with a plot sprayer (Baumann, 2 bar, 0,3 anti-drift nozzles, 50 cm distance to soil surface). Two soil boxes were sprayed with the same pesticide Fig. 23. To control the application amount of the plot sprayer, six petri dishes (d=4.5 cm) were placed on the soil surface outside the plot. The collected volume of the application solution was determined gravimetrically, and the amount of pesticide applied to each plot was documented. (Tab. 15).

Tab. 15: Amount of herbicide/plot (0.2 m²)

container	M1	M2	T1	T2	F1	F2	F3
herbicide/plot [mg]	18.0	17.5	4.5	5.4	4.4	2.9	2.9
herbicide	Metazachlor		Terbuthylazine		Flufenacet		

In accordance to the statement of good agricultural practice that pesticide application should be avoided before or during precipitation, the first rainfall simulation was initiated four days after the application of pesticide.

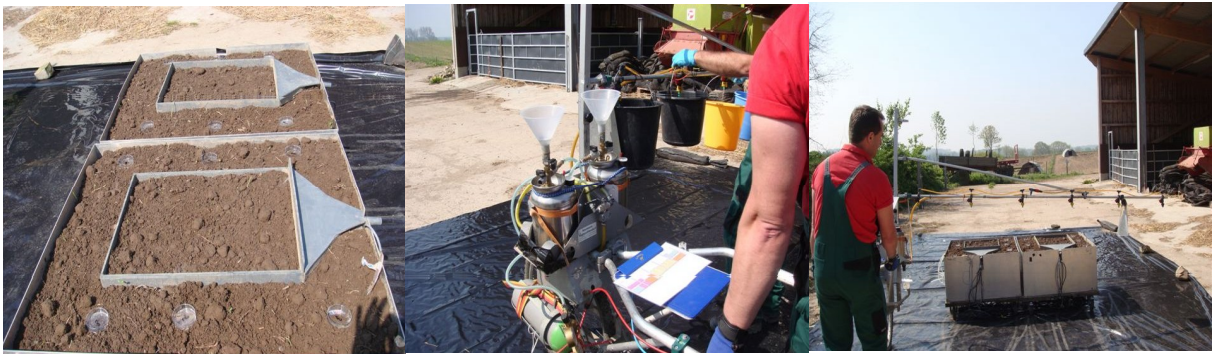


Fig. 23: Application of the pesticides by members of the Institute of Phytopathology, Kiel University

5.2.4 Monitored parameters during the surface runoff experiment

The soil used for this experiment was removed from the upper 20 cm of drained field 2. Soil type was determined in the field with soil drill and finger probe methods, according to German guidelines KA 5 (AG Boden, 2005). Determination of particle size was conducted via sieving and sedimentation according to DIN ISO 11277 (2002). Organic matter content was determined according to DIN 19684-3 (2000), measuring weight differences before and after ignition.

Soil water content

Time Domain Reflector probes (TDR) (range: 0 bis 100 %; Trime It, Imko, Ettlingen/Germany) were installed at 7, 20, and 30 cm depths to measure soil water content. They were connected to a data logger (Delta-T Devices, Cambridge, UK) for power supply and monitoring. The soil water content was detected at five-minute intervals.

Precipitation

The amount and intensity of the simulated rainfall was monitored with a distrometer (Laser Niederschlags-Monitor; Thies Clima, Göttingen/Germany), located approximately 40 cm above the soil box. In addition, the rainfall intensity was checked before and after simulation with Hellmann rain gauges. Within each rainfall event, the containers were exposed to 13 mm of artificial rainfall. The intensity varied between 10 – 15 mm/h.

Surface runoff

For analytical reasons, the runoff of each interval was filtered through a cellulose-nitrate filter with a pore size of 2 μm (Sartorius, Göttingen/Germany), and then determined gravimetrically.

Sediment

To determine sedimentation, the cellulose-nitrate filter, pore size 2 μm (Sartorius, Göttingen/Germany) (see surface runoff), and the sampling glasses, were weighed before usage. After filtering the runoff volume, each filter with the residue and the corresponding sampling glass were dried for 24 hours at 105°C in an oven, and afterwards weighed again. The difference provided the sediment amount.

5.3 Chemical analysis of the pesticides

The analyses of the chemical agents Metazachlor, Terbutylazine and Flufenacet in the water phase of the surface runoff of the laboratory experiment and in the water samples of the monitoring campaigns were carried out according to DIN EN ISO 11369 (1997), with solid phase extraction and determination by High Performance Liquid Chromatography (HPLC) and Diode Array Detection (DAD).

The following devices are components of the system. A draft of the HPLC system is presented in Fig. 24.

- Low pressure gradient LC22 (Bruker)
- Autosampler Marathon Basic (Spark Holland)
- Oven CTO-6A (Shimadzu)
- Diode array detector Smartline 2600 (Knauer)
- Degaser Ultimate (Resteck)
- Column: Hypersil ODS 250 mm, 3 μm particle size, 3 mm ID (MZ Analysentechnik, Mainz/Germany)
- Precolumn: Hypersil ODS 30 mm, 3 μm particle size, 3 mm ID (MZ Analysentechnik, Mainz/Germany)
- Cleanup extraction columns: CUC18 octadecyl, unendcapped (UCT, Bristol/USA)

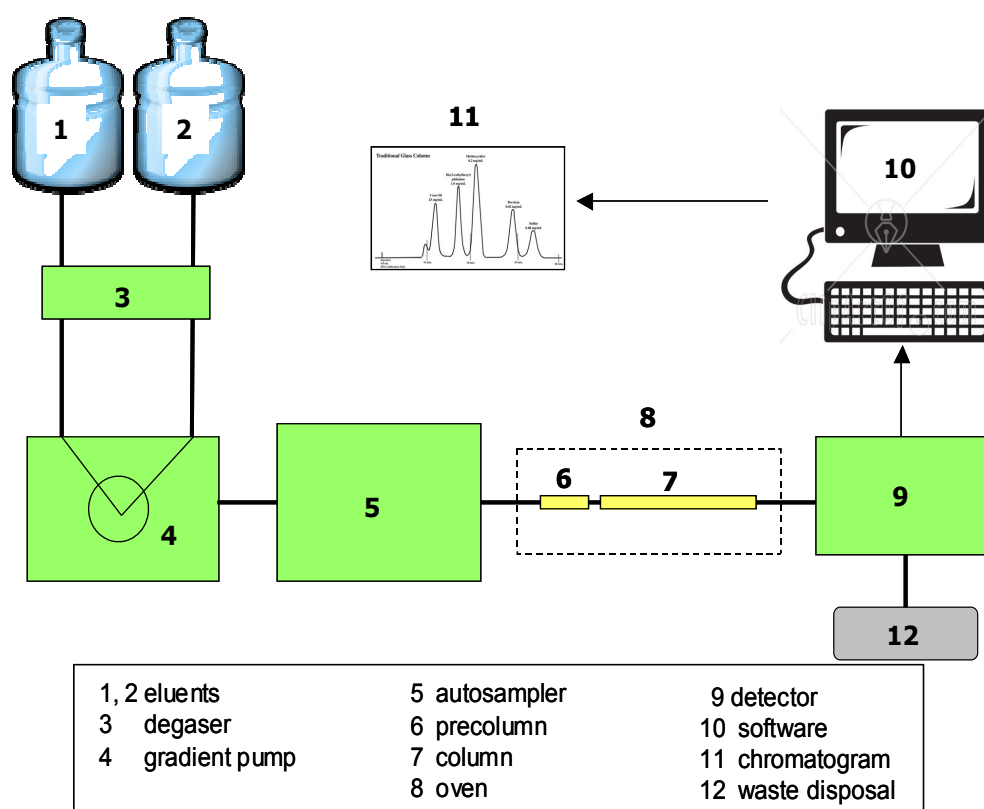


Fig. 24: Scheme of a High Pressure Liquid Chromatography (HPLC) system

5.3.1 Determination of pesticides with HPLC/DAD

The solid phase column was conditioned with 8 ml Acetone and 6 ml double-distilled water. After percolation of 800 ml sample through the column, the column was dried for 30 minutes in a nitrogen gas flow. The pesticides were then eluted with Acetone (8 x 2 ml each with 10 minutes residence time) and the eluate concentrated with an evaporation rotator. The residue was dissolved in 800 μ l of an Acetonitrile/1 mmol Ammonium Acetate buffer solution (10:90) and analyzed by HPLC (Fig. 25). In the rainfall experiment, the surface runoff samples of the rainfall experiment were filtrated at first (see Chapter 5.2.4). Besides, the sample volume varied according to the generated runoff volume. Instead of 800 ml, the available sample volume percolated through the solid phase. In the last step, the concentrate was dissolved in 1000 μ l of Acetonitrile/1 mmol Ammonium Acetate buffer solution (10:90) and analyzed by HPLC. Due to variations of the sample volumes from the runoff, the concentration factor had to be determined for each sample.

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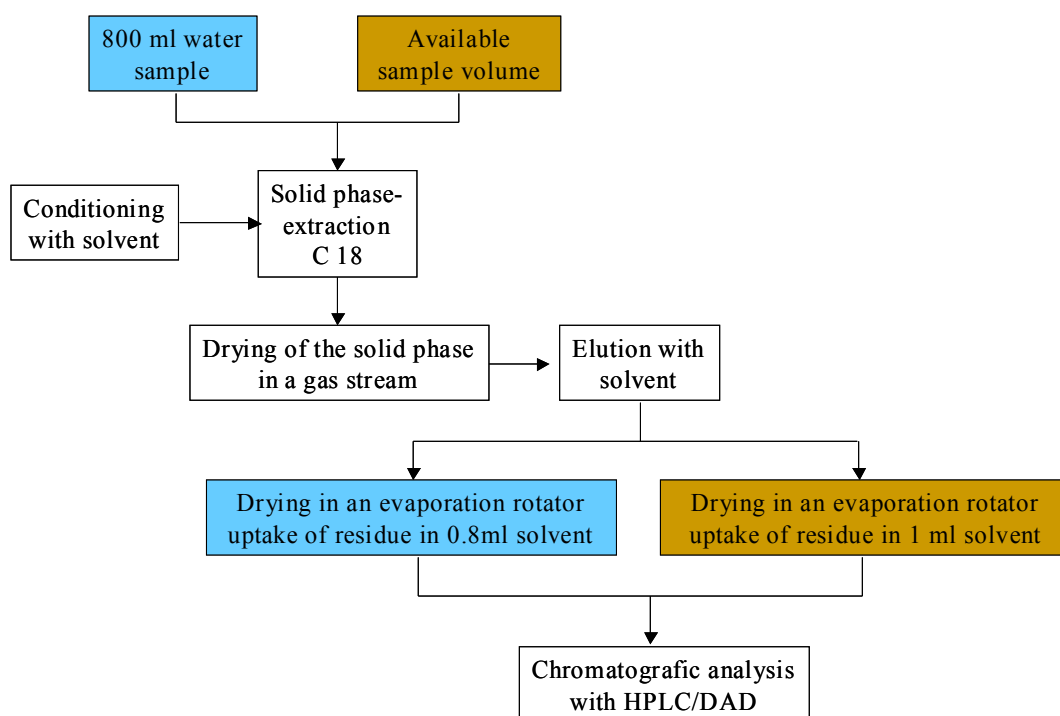


Fig. 25: Scheme of sample preparation; water samples (blue); water phase from surface runoff samples (brown)

The analysis with HPLC/DAD was conducted following the subsequent gradient schedule (Tab. 16):

Tab. 16: Gradient schedule of the pesticide analysis with HPLC/DAD, flow 0.55 ml/min

time [min]	Acetonitrile [%]	1 mmol Ammonium Acetate buffer
0	20	80
0.1	20	80
45	55	45
46	55	45
47	80	20
48	90	10
58	90	10
59	20	80
79	20	80
83	20	80

5.3.2 Quality control of the analysis

To assure the accuracy of the measured pesticide data, several procedures were followed:

The sample preparation was controlled by an internal standard. Due to often small and variable sample volumes, the recovery rate of the internal standard was in the range of 92 – 106 %, and 82 – 112 % in the runoff experiment.

For external quality control, samples and designed samples with known concentration (spiked samples) were analysed by the independent laboratory of Schleswig-Holstein Landeslabor Neumünster with High Performance Liquid Chromatography and Gas Chromatography. So the preparation of the samples and the quality of the analysis with the HPLC were controlled.

The standard deviation of the reproducibility of the herbicide values accounted in average for 9 % (Terbuthylazine), 14 % (Metazachlor), and 16 % (Flufenacet). The tests were conducted in double-distilled water spiked with concentrations from 100 – 500 ng/l.

The recovery rate of Terbuthylazine was 95 %; of Flufenacet 97 %; and of Metazachlor 107 %, in double-distilled water, spiked with 250 ng/l of the agents for the drainage measurement range. The recovery rates in drinking water, spiked with 1400 ng/l of the agents for the runoff measurement range, are 87-94 % for Terbuthylazine, 96-99 % for Metazachlor and 90 - 94 % for Flufenacet.

For Metazachlor and Terbuthylazine, the quantification limit is 70 ng/l and the detection limit is 25 ng/l. For Flufenacet the limits are 90 ng/l and 30 ng/l.

The quantification of the concentrations was carried out via multi-calibration. The correlation factor as a quality criterion of the calibration curve was in the range of 0.9957 and 0.9999.

The measurement was linear in the range of 50 – 1000 ng/l for drainage samples, and in the range of 500 – 2000 ng/l for surface runoff samples.

The stability of the HPLC system was checked with control standards which were inserted and analysed after every fifth sample (control card system).

The uncertainty of the overall analysis was determined according to the guidelines of Nordtest (2004). The extended measurement uncertainty with an extension factor of $k=2$ was 31.21 % for Terbuthylazine, 28.15 % for Metazachlor, and 31.53 % for Flufenacet.

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In the presented figures, all measured concentrations up to the detection limit are printed, and qualification and detection limits are drawn in. A higher uncertainty of the concentrations between detection and quantification limits must be taken into account.

For determinations of loads, pesticide concentrations and flows were multiplied. Concentration values above the detection limit were recorded as measured, and values below the detection limit were set to half of the detection limit (12.5 ng/l for Metazachlor and Terbutylazine, 15 ng/l for Flufenacet). The proceeding of the EU-WFD (EU Water Framework Directive, 2000) was not followed, where all concentration values below the quantification limit must be set to half of the quantification limit. High loads are caused in spite of concentrations below the detection limit, hence, overestimates are likely to occur. The loading effect is more enhanced during periods of high discharge.

6 RESULTS

6.1 Monitoring of Terbutylazine in spring 2008

6.1.1 Soil parameters on drained field 1

The soil texture on drained field 1 was analyzed for two horizons at each measuring point. The variations between locations were low, ranging from 57 – 66 % sand, 19 – 26 % silt and 5 – 9 % clay (Tab. 17). Hence, the soil texture differed between silty and loamy sand, whereas loamy sand occurred twice in the upper layer (X1 and X2) and once in the lower layer (MP4).

Tab. 17: Results of soil texture determination on drained field 1

sampling point	depth [cm]	horizon	sand [%]	silt [%]	clay [%]	soil texture (AG Boden, 2005)
X 1	0-15	Ap	62.83	22.73	5.54	SI2 / Su3
X 1	15-70		65.63	20.88	5.07	Su2
X 2	0-45	Ap	60.99	26.13	6.15	Su3
X 2	45-90		65.99	23.23	6.88	SI2 / Su3
X 3	0-35	Ap	63.04	24.9	5.43	Su3
X 3	35-90		56.78	25.77	6.43	Su3
X 4	0-40	Ap	60.97	26.5	5.97	Su3
X 4	40-90		65.13	18.95	9.06	SI2 / Su3

The organic matter content on this field was in the range of 1.1 – 3.5 %, showing higher contents in the upper layer than in the horizon below (Tab. 18). The humic content varied from 1.9 – 6.2 % and can be assessed as very humic in the upper layer, and in the lower depths of X3 and X4, as middle and slightly humic, according to KA 5 (AG Boden, 2005).

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Tab. 18: Results of the organic matter and humic content determination on drained field 1

sampling point	depth [cm]	Corg [%]	humus [%]	KA 5 (AG Boden, 2005)
X 1	0-15	3.5	6.2	very humic
X 1	15-70	3	5.3	very humic
X 2	0-45	3.4	6.0	very humic
X 2	45-90	3.1	5.5	very humic
X 3	0-35	3	5.3	very humic
X 3	35-90	1.3	2.3	middle humic
X 4	0-40	3.3	5.8	very humic
X 4	40-90	1.1	1.9	slightly humic

The saturated hydraulic conductivity was determined at the same measuring points, but at depths of 0 – 20 cm and 20 – 40 cm Tab. 19. The results accounted for 49 cm/d to 96 cm/d, and showed higher conductivities in the upper depth (61 – 96 cm/d) than in the lower one (49 – 65 cm/d). X4 is an exception, as the conductivity is higher at 20 – 40 cm depth (89 cm/d) than at 0 – 20 cm (77 cm/d). According to the German guidelines of DVWK (1999), the hydraulic conductivity can be classified as high, only the conductivity of X3 is classified as middle.

Tab. 19: Results of the determination of the saturated hydraulic conductivity on drained field 1 (n=10)

sampling point	depth [cm]	saturated conductivity [cm/d]	DVWK (1999)
X 1	0-20	96.35	high
X 1	20-40	65.31	high
X 2	0-20	60.78	high
X 2	20-40	55.09	high
X 3	0-20	76.59	high
X 3	20-40	48.71	middle
X 4	0-20	77.23	high
X 4	20-40	89.33	high

An average value of 71 cm/d was determined after considering the data from all sampling points and both depths. A water drop and a therein dissolved pesticide would need approx. 1.7 days to reach the drainage pipes in 1.2 m depth. For this calculation, saturated hydraulic conditions were assumed; the real track speed of the water drop and adsorption effects of the pesticide were neglected.

6.1.2 Hydrological Parameters in spring 2008

6.1.2.1 Precipitation

During the monitoring period 16/05/2008 – 30/06/2008, the first two rainfall events occurred on 25 and 26/05/2008 with 2 and 11 mm, 12 days after application (Fig. 26). A rainless period of about two weeks followed, and in the second half of June, numerous rainfall events took place. In sum, 54 mm of precipitation were determined in the monitored period. Precipitation data from 1984 to 2009 show that this value is significantly lower than the mean precipitation during the other years. It amounts to 50 % of the mean precipitation (DWD, 2007b; LLUR, 2009).

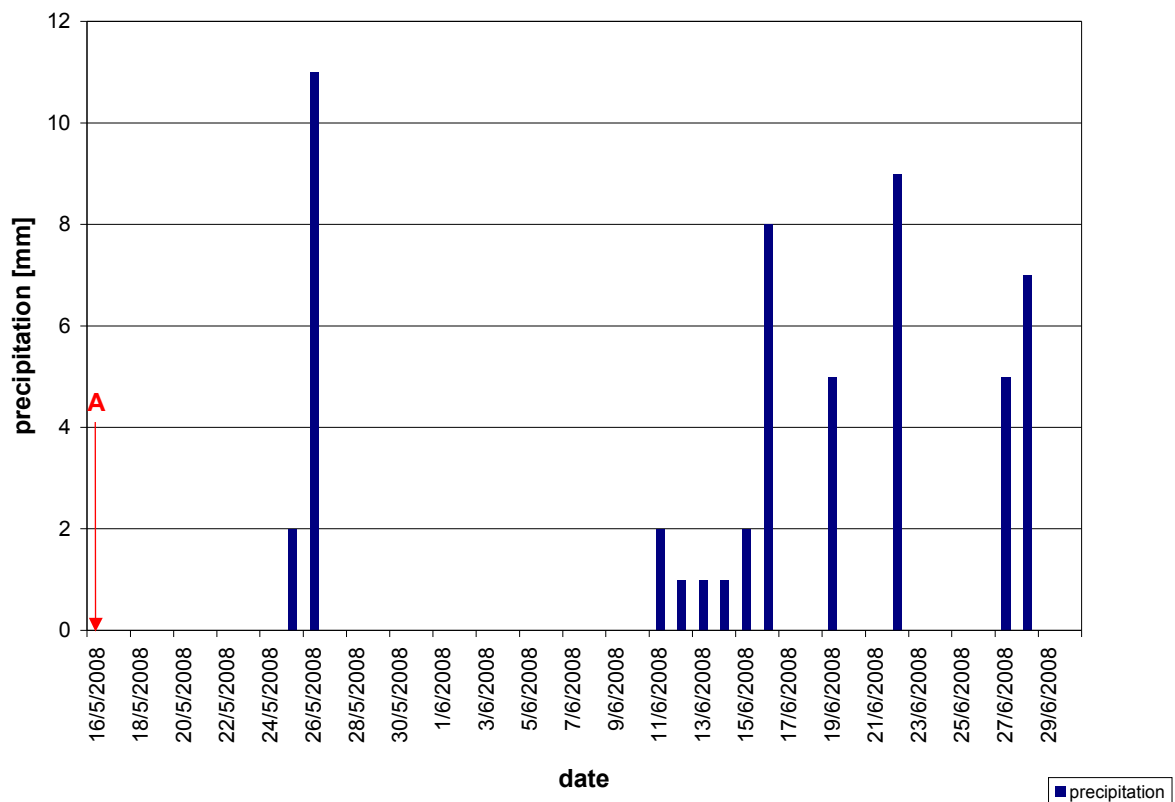


Fig. 26: Precipitation in the Kielstau region in spring 2008 (daily total)[data source: LANU (2008)]; **A**=application date on drained field 1

6.1.2.2 Discharge of the tile drainage

According to the few rainfall events, the discharge in the drainage was very low. From visual observations, there were no more than single drops or a slight trickle. Hence, the water level in the drain pipe was below the potential measure of 0.5 cm, which corresponds to approx. $11.5 \cdot 10^{-8} \text{ m}^3/\text{s}$. On 7/06/2008 the drainage ran dry.

6.1.2.3 Discharges of the Moorau and the Kielstau at Soltfeld

The beginning of the monitoring period was characterized by a rainless period. Hence, the discharge of the Kielstau decreased continuously while that of the Moorau remained constant at $0.028 \text{ m}^3/\text{s}$ (Fig. 27). The rainfall amounts on 25/5/2008 and 26/5/2008 of 2 mm and 11mm caused an increase of the discharge in the Kielstau on 26/5/2008. The discharge of the Moorau increased on 26/5/2008 as well, but peaked one day later. Within the following rainless period, the Kielstau discharge decreased to the minimum of the monitoring, to $0.050 \text{ m}^3/\text{s}$, and to $0.026 \text{ m}^3/\text{s}$ in the Moorau. Subsequently, a rainy period began on 11/6/2008, with rainfall measures of up to 9 mm/d, resulting in a maximum discharge of $0.139 \text{ m}^3/\text{s}$ in the Kielstau on 25/6/2008, and $0.031 \text{ m}^3/\text{s}$ in the Moorau on 24/6/2008, 27/6/2008 and 28/6/2008. The mean discharges during the monitoring were $0.105 \text{ m}^3/\text{s}$ in the Kielstau and $0.027 \text{ m}^3/\text{s}$ in the Moorau. Kielstau discharge data from long-term observations (1987-2005) for the months May and June indicate $0.16 \text{ m}^3/\text{s}$ (Land Schleswig-Holstein, 2009). The results of the discharge monitoring in May and June 2008 show significantly lower values than those of the long-term observations and reveal the dry conditions of the observation period. Long-term data for the Moorau discharge are not available.

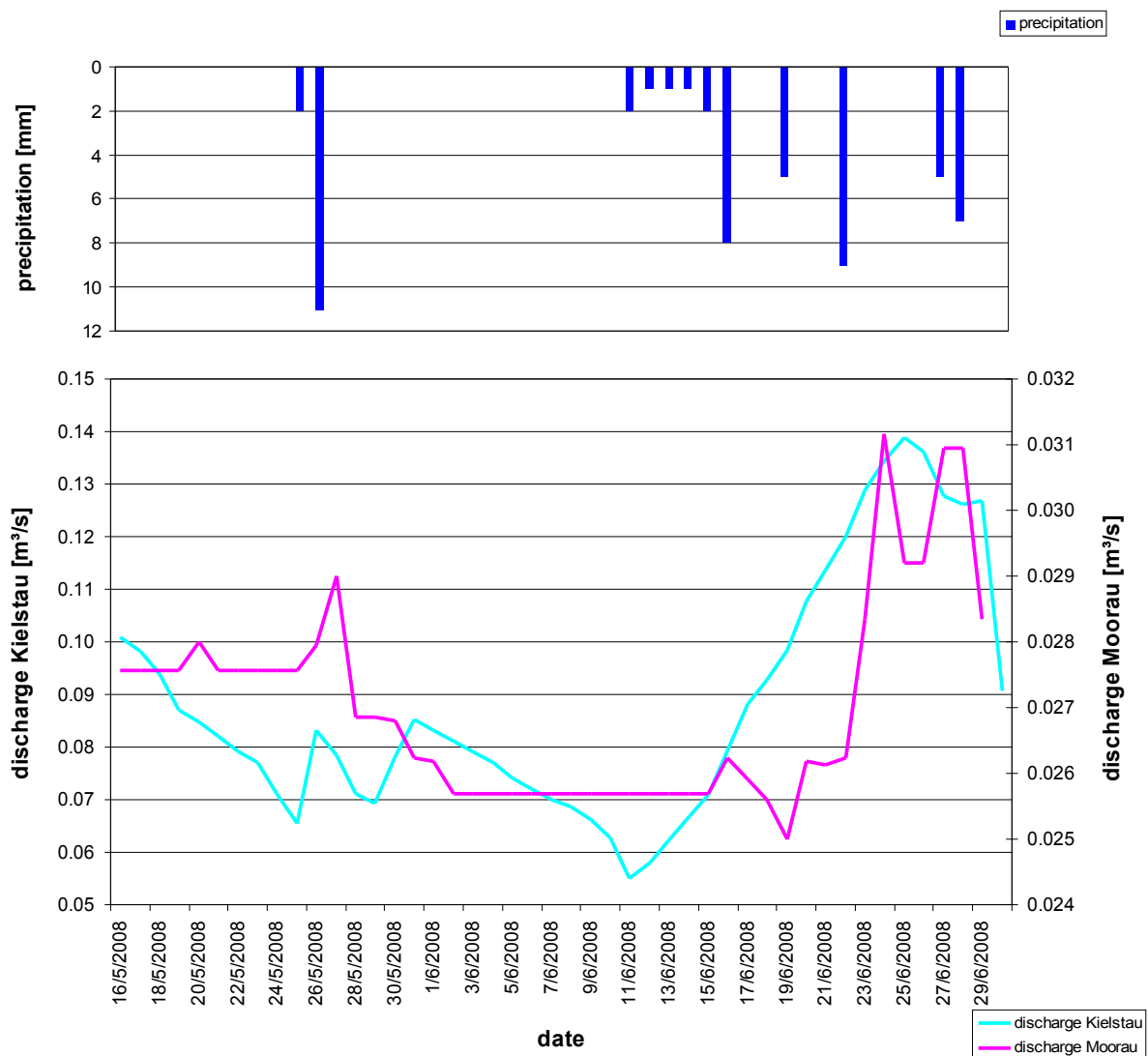


Fig. 27: Discharges of the Kielstau at Soltfeld and the Moorau in spring 2008 (daily mean values)

6.1.3 Terbutylazine concentrations

Drainage

Though it was not possible to determine the discharge of the drainage, drainage water could be sampled for pesticide analysis, due to the technical set up. The water for sampling was collected in a sampling container in the drain pipe inspection shaft (see Fig. 15), and comprised a sufficient volume for the analysis until the drainage fell dry on 9/6/2008.

On 22/5/2008, six days after application of Terbutylazine, the first positive result was detected in the drainage, showing a concentration of 93 ng/l. Similar Terbutylazine concentra-

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tions of 85 ng/l and 91 ng/l followed the two subsequent days (Fig. 28). The transport of Terbutylazine took place independently from the observed precipitation during these three days. Simultaneous to the first rainfall event of 2 mm on 25/5/2008, the Terbutylazine concentrations increased to 132 ng/l, and to 250 ng/l on 26/5/2008 after 11 mm of precipitation. The maximum value of the observation period occurred two days after this rainfall event, on 28/5/2008, and accounted for 301 ng/l. Subsequently, the concentrations diminished to a range of 81 ng/l to 151 ng/l, and below the detection limit of 25 ng/l on the last two days (7/6/2008 and 8/6/2008), before the drainage ran dry on 9/6/2008.

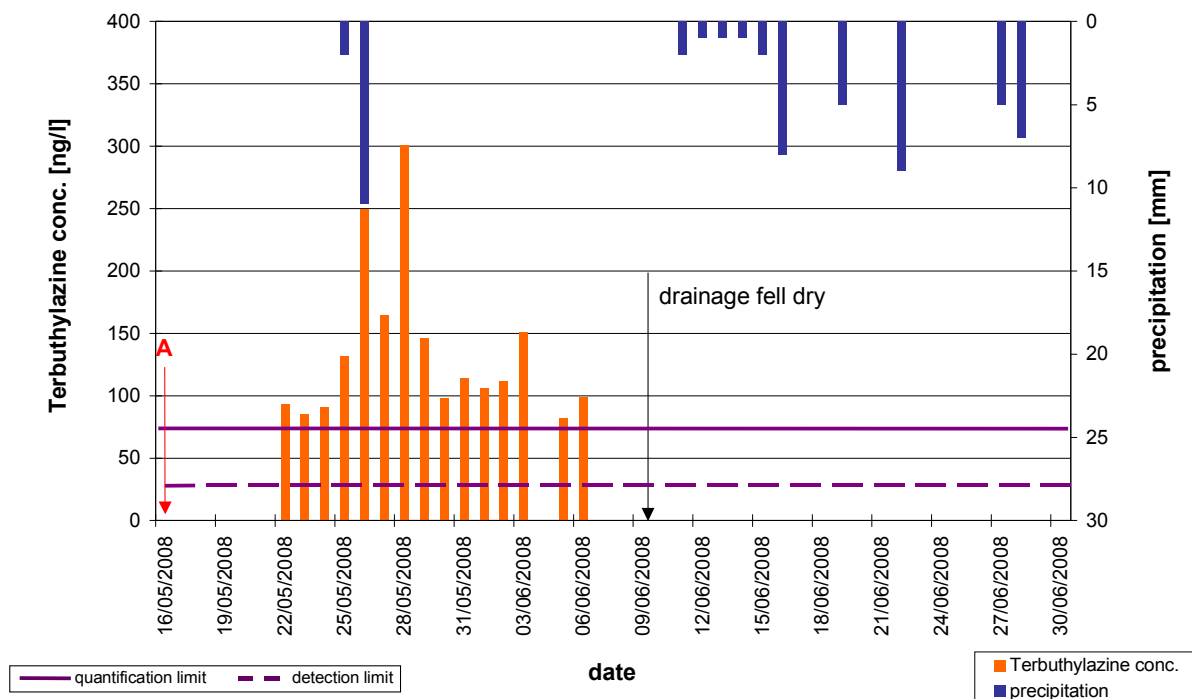


Fig. 28: Terbutylazine concentrations in the drainage on drained field 1 in spring 2008 (daily mixed samples); **A**=application date on drained field 1

Moorau

The Moorau samples of the second day of observation (17/5/2008) revealed Terbutylazine concentrations of 87 ng/l (Fig. 29). The maximum value was reached on 21/5/2008 with 96 ng/l, and was followed by three additional findings in the range of 75 ng/l, independent of observed precipitation. Simultaneously, with the decrease of the first discharge peak which responded to the 11 mm of precipitation on 26/5/2008, the Terbutylazine concentrations diminished to 32 ng/l until 8/6/2008. From 9/6/2008 to 15/6/2008, Terbutylazine was not observed. From 16/6/2008 until the end of observation, the herbicide was determined again with

37 ng/l, on average, following roughly the pattern of discharge. Though the discharge increased to the maximum value of 0.03 m³/s on 24/6/2008 and 27, 28/6/2008 the Terbutylazine concentrations did not rise. Except for the seven findings at the beginning of the monitoring, all values were below the quantification limit.

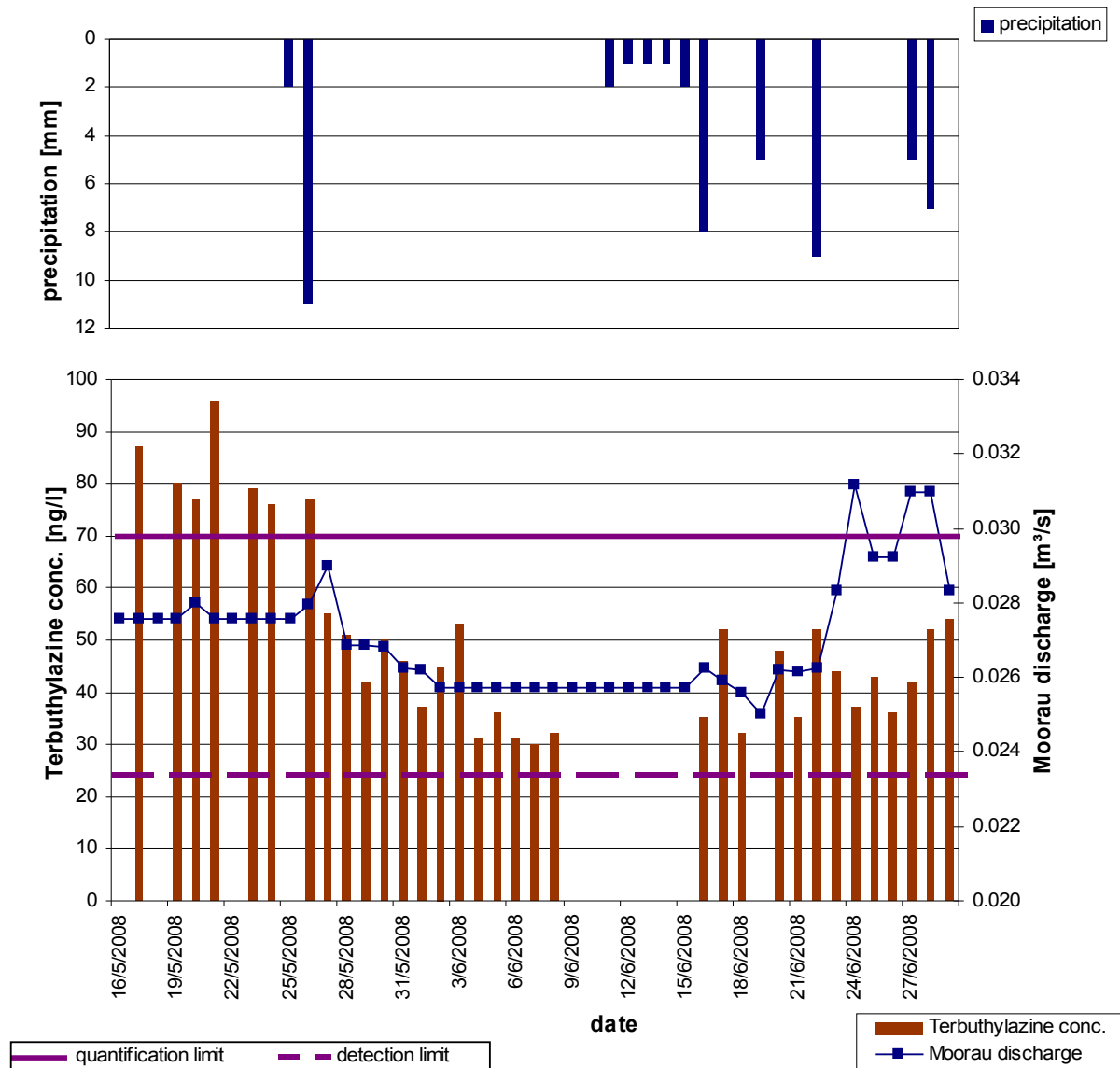


Fig. 29: Terbutylazine concentrations in the Moorau tributary in spring 2008 (daily mixed samples)

Kielstau

The first detections of Terbutylazine in the Kielstau at the Soltfeld gauge were made from 21/5/2008 – 24/5/2008 with 79 – 86 ng/l (Fig. 30). In this period, the discharge of the Kielstau constantly decreased, due to the rainless period. On 27/5/2008, the maximum concentration of

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147 ng/l was monitored on the recession limb of a discharge peak, which was a response to the precipitation on 26/5/2008. Equivalent to the Moorau data, the Terbutylazine concentrations declined to 57 ng/l until 8/6/2008, following the decrease of the Kielstau discharge. From 9/6/2008 to 15/6/2008, no concentrations were detected. During several days of rainfall (16/6/2008 - 23/6/2008), rising Terbutylazine concentrations of up to 118 ng/l were monitored during increasing discharge. However, within the period of maximum discharge (23/6/2008 – 27/6/2008), the concentrations decreased to approximately 65 ng/l on average.

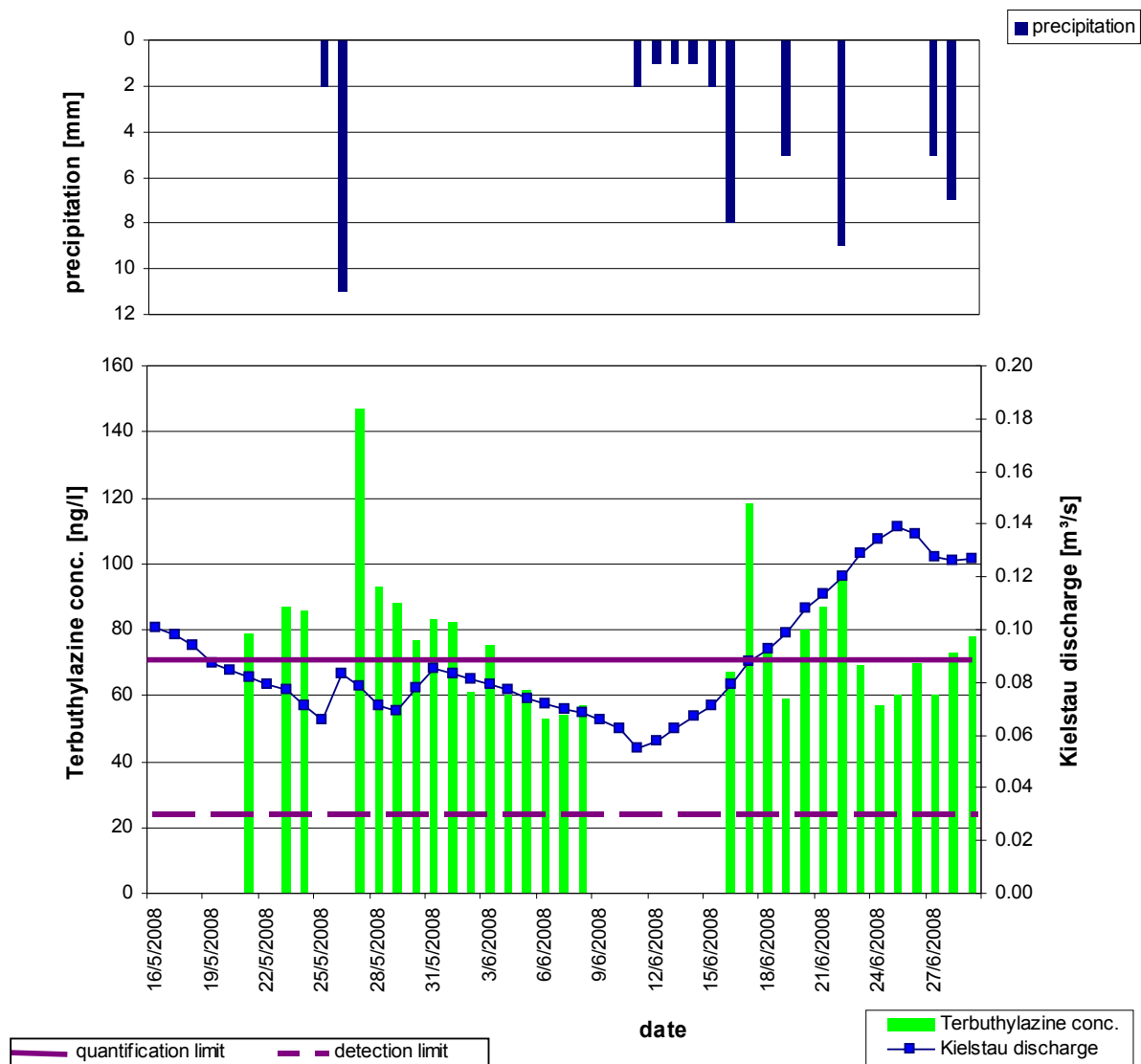


Fig. 30: Terbutylazine concentrations in the Kielstau at Soltfeld in autumn 2008 (daily mixed samples)

6.1.4 Terbutylazine loads

Drainage

Terbutylazine loads released from the drainage of drained field 1 could not be determined, because of the low discharge beneath the potential measure which could not be quantified.

Moorau

The pattern of the cumulated loads observed in the tributary Moorau showed a sharp increase until 25/5/2008, including the daily maximum load of 232 mg Terbutylazine on 21/5/2008, though the first rainfall event of the monitoring phase appeared on 24/5/2008 (Fig. 31). The subsequent period was characterized by a less sharper incline until 9/6/2008, when a plateau occurred, due to concentrations below the detection limit. This plateau lasted until 15/6/2008. The time until the end of observation showed a constant but steeper incline than the period from 9/6/2008 – 15/6/2008, due to several rainfall events causing increased discharge. The total Terbutylazine load discharged during the monitoring phase into the Moorau was 4.4 g.

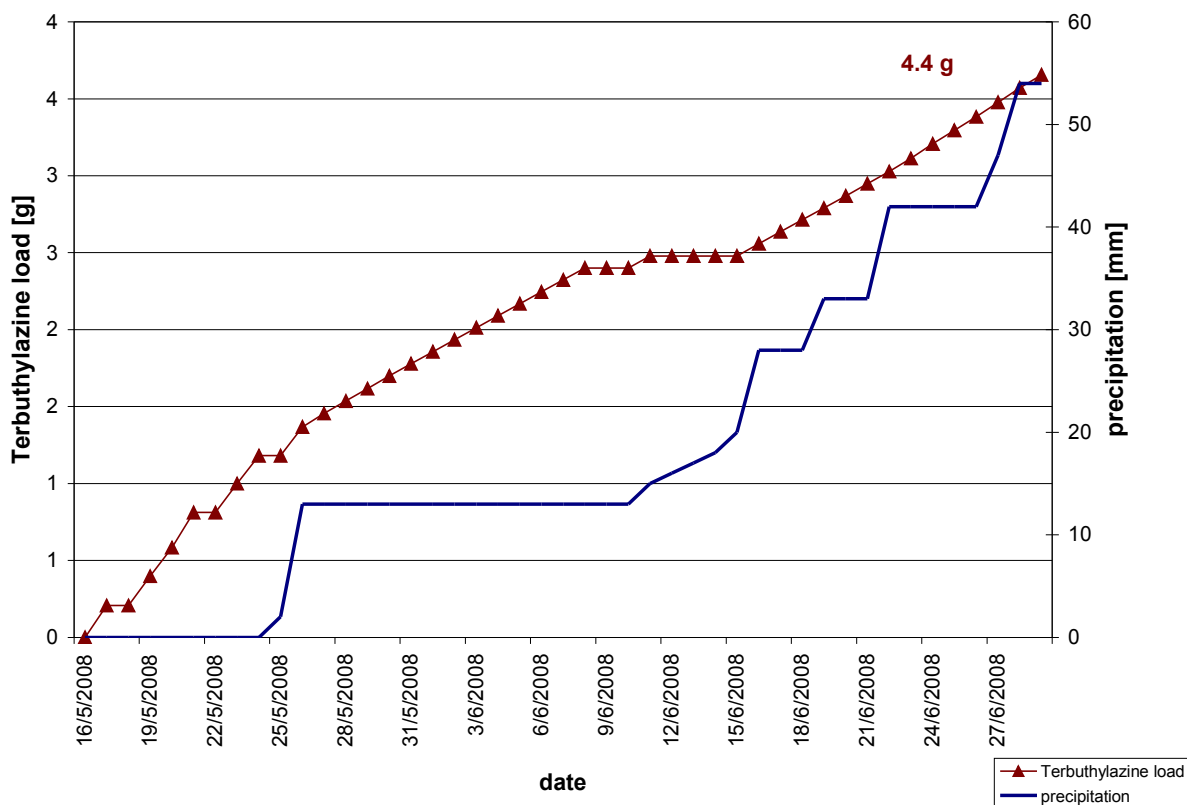


Fig. 31: Cumulated Terbutylazine loads in the Moorau (daily values)

Kielstau

The first monitored Terbutylazine load in the Kielstau at Soltfeld occurred on 26/5/2008, and the cumulated load curve increased stepwise until 26/5/2008 (Fig. 32). One day after the 11 mm rainstorm of 26/5/2008, the maximum daily value of 1.06 g Terbutylazine was detected on 27/5/2008. Then a period of constant rise followed, and lasted until 8/6/2008. Equivalent to the pattern of the Moorau curve, a plateau followed, according to Terbutylazine concentrations below the detection limit from 9/6/2008 to 15/6/2008. A span of steeper incline followed, due to several rainfall events and increasing discharge. The total Terbutylazine load discharged during the monitoring phase into the Kielstau at Soltfeld amounted to 20 g. Overall, the curves of the cumulated Terbutylazine loads released to the Moorau and the Kielstau showed consistent patterns.

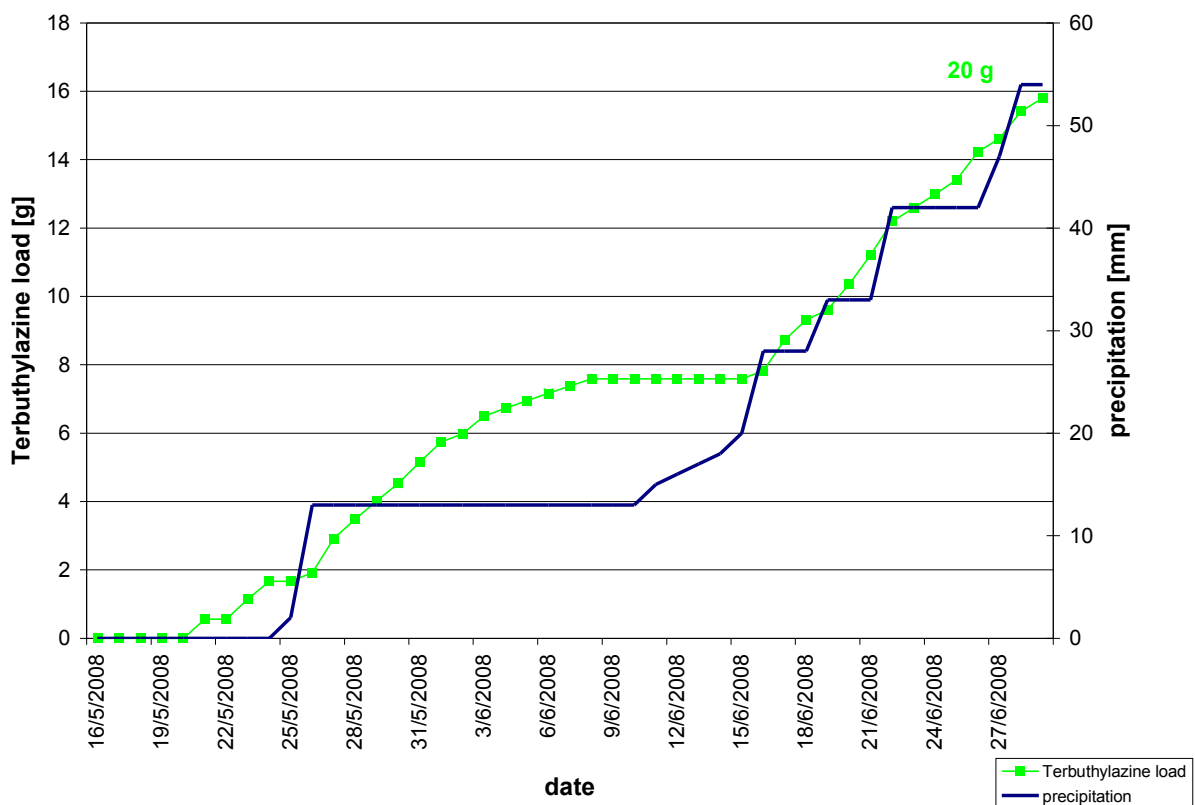


Fig. 32: Cumulated Terbutylazine loads in the Kielstau at Soltfeld (daily values)

6.1.5 Land use in spring 2008

In May and June 2008, the land use of the Kielstau catchment was mapped at field scale. The actual field crops for that time are given in Fig. 33.

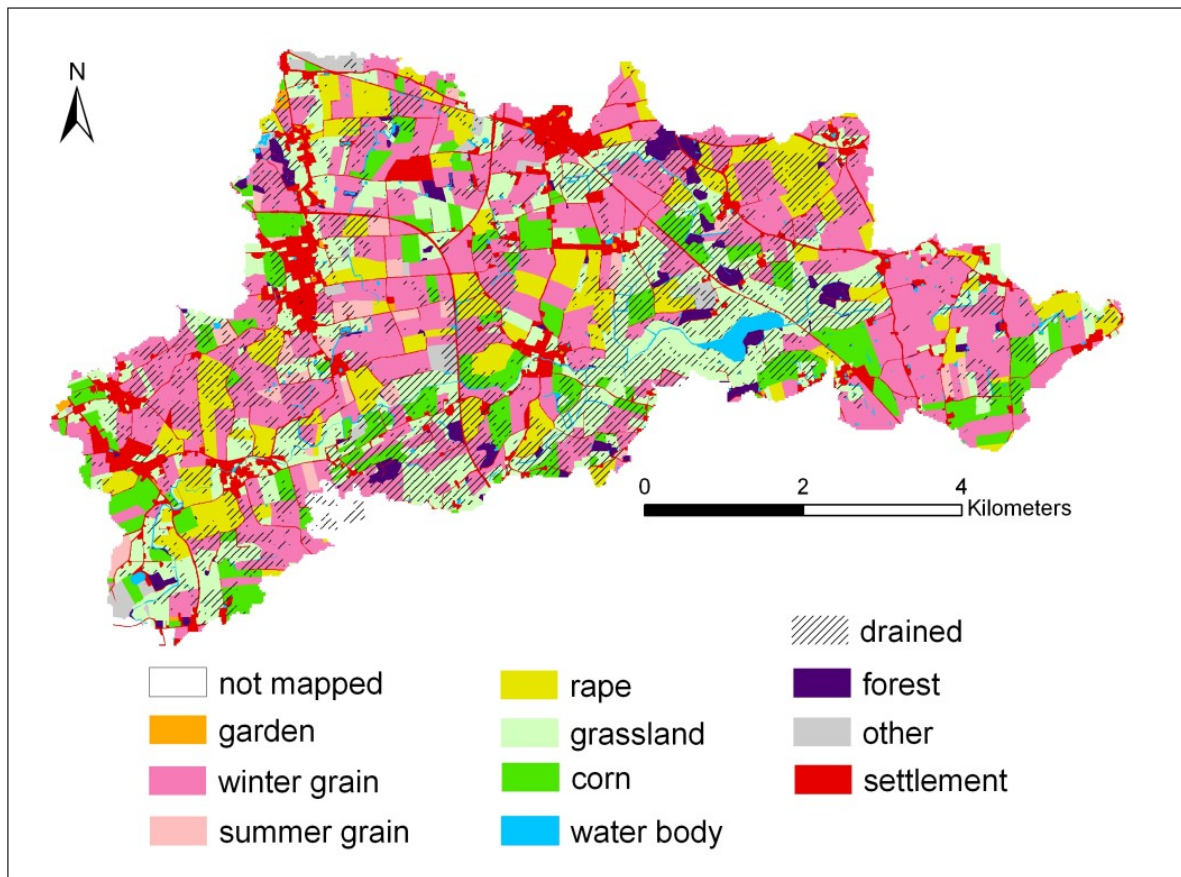


Fig. 33: Land use map of the Kielstau catchment (May/June 2008) (Golon, 2006)

The catchment was dominated by the cultivation of winter grain amounting to 1752 ha (41 % of the catchment area). Grassland covered 1048 ha (22 %), followed by rape with 618 ha (13 %) and corn with 517 ha (11 %).

In the subcatchment of the Moorau, the distribution of the crops was equivalent to that of the entire catchment. Winter grain predominated the region and was cultivated on 266 ha (36 %), followed by grassland with 148 ha (20 %), rape with 112 ha (15 %), and corn with 52 ha (7 %). The proportion of corn was lower than in the Kielstau catchment. Crop proportions are reported in detail in Tab. 20.

Tab. 20: Proportion of crops in the Kielstau catchment and Moorau subcatchment in spring 2008

crop	catchment Kielstau		subcatchment Moorau	
	area [ha]	percentage of catchment [%]	area [ha]	percentage of subcatchment [%]
fallow	10	< 0.5	0	< 0.5
garden	15	< 0.5	3	< 0.5
water body	71	1	8	1
grassland	1048	22	148	20
corn	517	11	52	7
rape	618	13	112	15
other	65	1	16	2
forest	125	3	38	5
winter grain	1752	41	266	36
summer grain	107	2	12	2
settlement	502	10	92	12
not mapped	71	1	4	1
sum	4840	100	747	100

In a second step, the digital land use map was joined with a digital drain map Golon (2006) showing the areas with drainage systems in the Kielstau catchment as black hatching in Fig. 33. Of the total 517 ha corn, 187 ha were drained, corresponding to 36 % of the corn areas and 3.9 % of the entire catchment.

In the Moorau subcatchment, the portion of corn amounted to 52 ha, including 32 ha of drained corn fields. These 32 ha correspond to 4.3 % of the entire subcatchment and to 62 % of the corn areas in the subcatchment.

6.1.6 Terbutylazine application in the catchment

In corn fields, a number of herbicides can be used to suppress the growth of weeds. Common supplements are Dual Gold[®], Gardo Gold[®], Callisto[®] and Calaris[®]. Some of them contain agents other than Terbutylazine. Interviews with local farmers provided information concerning 122 ha of corn area, corresponding to 24 % of the corn fields in the catchment. An area of 97 ha of these 122 ha were sprayed with a Terbutylazine containing supplement. The application period for the corn field lasted from 1/5/2008 – 13/6/2008, according to the in-

formation provided (Fig. 34). During this period, only a few rainfall events occurred, so that the application of the herbicides was accomplished mainly on rainless days.

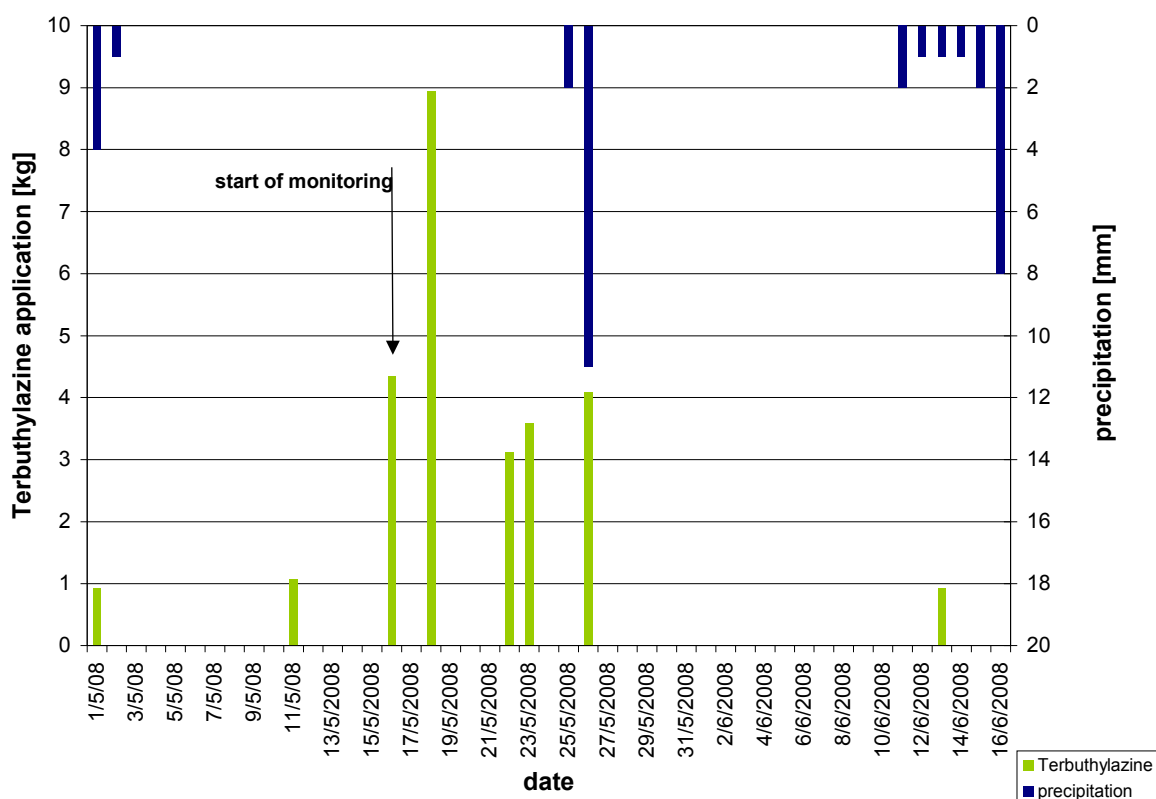


Fig. 34: Distribution of Terbutylazine application in the Kielstau catchment in spring 2008

Taking the information of the farmers and the amount of mapped corn areas into account, enabled the determination of the potential quantity of Terbutylazine applied in the catchment and subcatchment. In total, 114 kg Terbutylazine were possibly sprayed on the fields in the entire catchment, and 11.5 kg were sprayed in the subcatchment Moorau and potentially discharged to non-target areas. An amount of 41 kg was allotted to the drained corn fields in the catchment, and, of that, 7.1 kg to the subcatchment (Tab. 21).

Tab. 21: Potential Terbutylazine discharge from corn fields

	Area [ha]	Terbutylazine [kg]	Moorau	Area [ha]	Terbutylazine [kg]	Kielstau	Area [ha]	Terbutylazine [kg]
Data of corn fields (farmers)	122	27	Extrapolation subcatchment corn	52	11.5	Extrapolation catchment corn	517	114
Data of drained corn fields (farmers)	No data	No data	Extrapolation subcatchment corn drained	32	7.1	Extrapolation catchment corn drained	187	41

6.2 Monitoring of Metazachlor in autumn 2008

6.2.1 Soil parameters on drained field 2

From the more elevated north end of the field to the south end of the field, the soil on drained field 2 is characterized by a decrease in the sand fraction and an increase of the loamy substrate. With increasing depth, the clay content rose, causing stagnant moisture effects in the subsoil, which could be observed in the profile as patches of oxidized iron (eh), manganese (es), and spots of discolouration (rb) that result from reducing conditions in the soil (Fig. 35). According to KA 5 classification, the soil type has been determined to be a Pseudogley (AG Boden, 2005), which corresponds to a Planosol after FAO classification (WRB, 2006). Detailed results of the soil type determination are shown in Tab. 22.



Fig. 35: Soil type determination with soil drill (l) and stagnant moisture characteristics in the subsoil (r)

Tab. 22: Results of the soil type determination of drained field 2 according to the German KA 5 (AG Boden, 2005)

sam- pling points	geogr. location		depth [cm]		horizon	soil texture	humic content	soil colour	hydro- morpho- logical characte- ristics	soil type
	easting	northing	from	to						
X 1	3535871	6068891	0	30	Ap	SI2-3	h2	10 YR 3/2	-	BB- SS
			31	75	Bv-Sw	SI3	h1	10 YR 3/6	eh; es	
			76	110	Sd	SI4	h1	10 YR 3/3	eh; es; rb	
			> 111		Cv	Ss	h1	10 YR 4/6	-	
X 2	3535884	6068833	0	30	Ap	SI3	h2	10 YR 3/2	-	SS- BB
			31	> 135	Sw-Bv	SI4	h1	10 YR 4/6	eh; es	
X 3	3535897	6068757	0	30	Ap	SI3	h2	10 YR 3/2	eh	SS
			31	110	(Bv)-Sw	SI3	h1	2,5 Y 4/3	eh; es; rb	
			> 111		Sd	SI4	h1	2,5 Y 4/3	eh; rb	
X 4	3535910	6068674	0	30	Ap	SI2-3	h2	10 YR 3/2	eh	SS
			31	60	Sw	Ls3	h1	2,5 Y 4/3	eh; es; rb	
			61	> 120	Sd	Ls2	h1	2,5 Y 4/3	eh; rb	
X 5	3535846	6068668	0	30	Ap	SI2-3	h2	10 YR 3/2	eh	SS
			31	80	Sw	SI4	h1	2,5 Y 5/4	eh; es; rb	
			81	> 120	Sd	Ls3	h1	2,5 Y 5/3	eh; rb	
X 6	3535833	6068748	0	30	Ap	SI2-3	h2	10 YR 3/2	eh	SS
			31	> 120	(Bv)-Sw	SI3	h1	2,5 Y 4/3	eh; es; rb	

Laboratory analysis of particle sizes confirmed that sand content diminished with depth. From north to south, the clay fraction increases gradually (Tab. 23), hence, soil texture changed from strong silty sand (Su4) to silty loam (Lu) (after AG Boden, 2005).

Tab. 23: Results of soil texture determination on drained field 2

sampling point	depth [cm]	horizon	sand [%]	silt [%]	clay [%]	soil* texture
X1	0-20	Ap	38.36	42.19	6.01	Su4
X1	20-40	Bv-Sw	37.43	46.09	6.45	Su4
X2	0-20	Ap	28.58	51.12	8.48	Uls
X2	20-40	Sw-Bv	25.05	50.67	9.89	Uls
X3	0-20	Ap	21.39	49.02	15.37	Slu
X3	20-40	(Bv)-Sw	14.21	49.14	22.27	Ls2
X4	0-20	Ap	15.59	54.53	18.18	Lu
X4	20-40	Sw	9.81	56.31	24.34	Lu
X5	0-20	Ap	23.20	48.82	15.15	Slu
X5	20-40	Sw	9.11	55.54	26.23	Lu
X6	0-20	Ap	26.33	49.54	10.48	Slu
X6	20-40	(Bv)-Sw	15.86	56.55	14.66	Uls

* according to KA 5 (AG Boden, 2005)

The organic matter content varied within the range of 0.95 to 2.43 %, and the humic content varies between 1.63 and 4.17 %. The soil can therefore be classified after KA 5 (AG Boden, 2005) as slightly humic to very humic. At all sampling points, the organic matter and humic contents were higher at the 0 – 20 cm depth than at the 20 – 40 cm depth (Tab. 24). It was observed that the distribution of organic matter and the humus over the entire field is relatively constant between the two depths.

Tab. 24: Results of the organic matter and humic content determination on drained field 2

sampling point	depth [cm]	Corg%	humus %	KA 5 (AG Boden, 2005)
X1	0-20	2.06	3.54	middle humic
X1	20-40	1.13	1.94	slight humic
X2	0-20	2.12	3.64	middle humic
X2	20-40	1.40	2.41	middle humic
X3	0-20	2.43	4.17	very humic
X3	20-40	1.69	2.91	middle humic
X4	0-20	2.57	4.42	very humic
X4	20-40	1.53	2.64	middle humic
X5	0-20	2.32	3.99	middle humic
X5	20-40	1.51	2.59	middle humic
X6	0-20	2.10	3.61	middle humic
X6	20-40	0.95	1.63	slight humic

The results of the saturated hydraulic conductivity were in the range of 14 to 722 cm/d and classified according to German guidelines (DVWK, 1999) as average to very high hydraulic conductivity (Tab. 25). Only the X5 value of 7 cm/d in the depth of 20 – 40 cm was lower.

The sample X2 showed crucial differences to the other sampling points and had extremely high values (722 and 368 cm/d). This can be explained by a localized inhomogeneity of the soil. Overall, the results showed no significant discrepancies of saturated hydraulic conductivity in the two depths, hence, a change in the saturated hydraulic conductivity from the permeable to the impermeable horizon could not be observed.

An average value of saturated hydraulic conductivity of 63 cm/d was determined by considering the data from all sampling points and both depths (the data of X2 being significantly out of the range were not included). A water drop and a therein dissolved pesticide would require approximately two days to reach drainage pipes at a depth of 1.5 m. For this calculation, saturated hydraulic conditions were assumed, and the real track speed of the water drop and adsorption effects of the pesticide were neglected.

Tab. 25: Results of the determination of the saturated hydraulic conductivity k_f on drained field 2 (n=10)

sampling point	depth [cm]	saturated conductivity [cm/d]	(DVWK, 1999)
X1	0-20	33.32	middle
X1	20-40	58.28	high
X2	0-20	722.07	extremely high
X2	20-40	368.49	extremely high
X3	0-20	134.51	very high
X3	20-40	88.54	high
X4	0-20	61.74	high
X4	20-40	18.88	middle
X5	0-20	14.42	middle
X5	20-40	7.09	marginal
X6	0-20	95.98	high
X6	20-40	122.14	very high

The conductivity in the vadose zone was determined at the four sampling points X3 – X6. The investigated data accounted for 0.26 – 0.4 m/d, except for X4, which showed a value of 0.81 m/d (Fig. 34). According to Kuntze et al. (1994), the hydraulic conductivity for X3, X5 and X6 can be classified as average and for X4 as good.

According to the guidelines, the samples used for the determination of the saturated hydraulic conductivity (DIN 19683-9, 1998) represent a volume of 100 m³ and do not display influences of the surrounding. But the determination of the conductivity in the vadose zone is a field method in naturally saturated soil layers. Furthermore, effects of the area surrounding the borehole are integrated into the results and, therewith, provide representative conditions of the water flow at the depth of the drainage pipes. The average results of saturated hydraulic conductivity (63 cm/d) according to DIN 19683-9 (1998) and of conductivity in the vadose zone (DIN 19684-3, 2000) (46 cm/d) in this study are in a similar range.

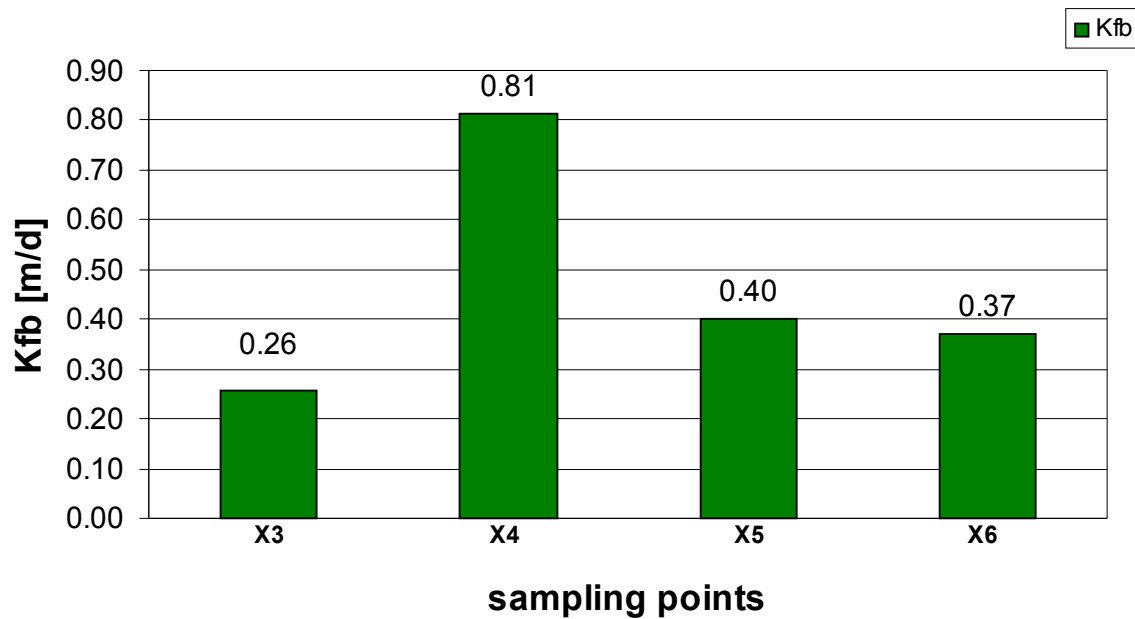


Fig. 36: Hydraulic conductivity in the vadose zone k_{fb} on drained field 2

The catchment size of the drainage system on drained field 2 could therewith be assumed to be approximately 3500 m². Applying the discharge-precipitation ratio with a discharge of 309744 l and a precipitation of 218 l/m², the catchment size was estimated to be approximately 1400 m². For further calculations the size of the potential drainage catchment is set to 1000 m² – 4000 m².

Data of the soil characterization allow classification as a soil with medium permeability according to KA 5 standards (AG Boden, 2005). This soil shows the typical properties of a Planosol under agricultural conditions.

6.2.2 Hydrological parameters in autumn 2008

6.2.2.1 Precipitation

As soon as monitoring was begun, on September 1st, 2008, it began to rain, and continued raining for seven days. Three subsequent dry weeks were followed by four days of continuous rain with a maximum intensity of 31 mm/d. These rainfall events and subsequent rain periods in October and November caused an increase in water levels throughout the catchment, so that water was retained and drained off slowly (Fig. 37). In sum, 215 mm of precipitation were determined for the monitored period. This corresponds to 125 % of the long-term mean precipit-

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ation of the months October and November, from 1984 to 2009 (DWD, 2007b; LLUR, 2009). Monitoring at the Ausacker gauge began on 8/10/2008. The data of the three gauges showed a high consistency in spite of different locations. This resulted in a standard deviation between the gauges of 14 %.

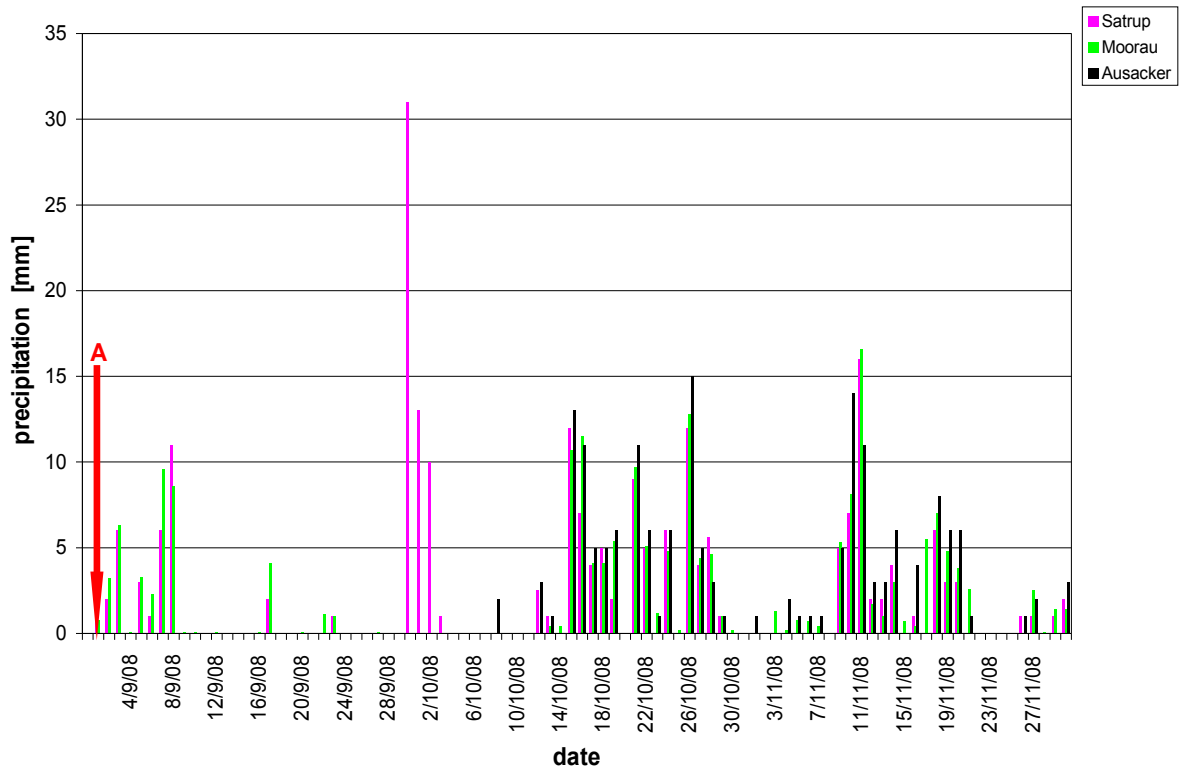


Fig. 37: Precipitation in the Kielstau region in autumn 2008 (daily total)

In the following figures of Metazachlor monitoring, precipitation at the Satrup rain gauge is depicted.

6.2.2.2 Discharge of the tile drainage

As the discharge of the drain pipe was measured indirectly, via water level, the following rating curve was determined. This allows a calculation of discharge at any monitored time interval (Fig. 38).

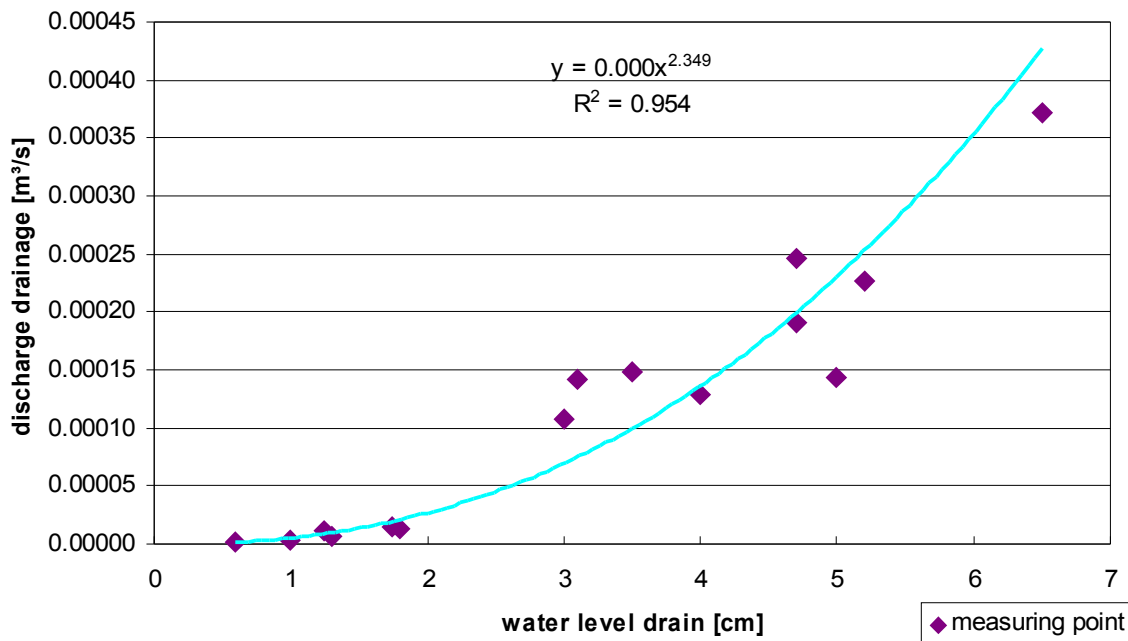


Fig. 38: Rating curve of the drainage pipe on drained field 2 in autumn 2008

In Fig. 39, the daily mean drain flow calculated with the rating curve is presented. The drainage discharge varied between $7.9 \cdot 10^{-7}$ and $6.9 \cdot 10^{-4}$ m³/s during the monitoring. The release of water increased immediately with the first rainfall events of 1/9/ to 8/9/2008, but, overall, remained at low levels. Further significant rainstorms during this period, occurring on 30/9/ - 2/10/2008, 15/10/ - 29/10/2008 and 9/11/ - 11/11/2008 enhanced discharges immediately or within one day. Similarly, the drain flow decreased in the rainless time spans of 9/9 - 29/9/2008, 4/10/ - 11/10/2008 and 30/10/ - 10/11/2008. The pattern of the discharge reveals its correlation to rainfall. A linear trend line indicates the overall increase in discharge during the monitoring period and corresponds to the numerous rainfall events. The water level in the entire catchment rose as a response to the intensive and numerous rainfall events at the end of September and the beginning of October. Hence, water could not discharge sufficiently and flooding occurred at several places in the catchment, like on drained field 2 (Fig. 40).

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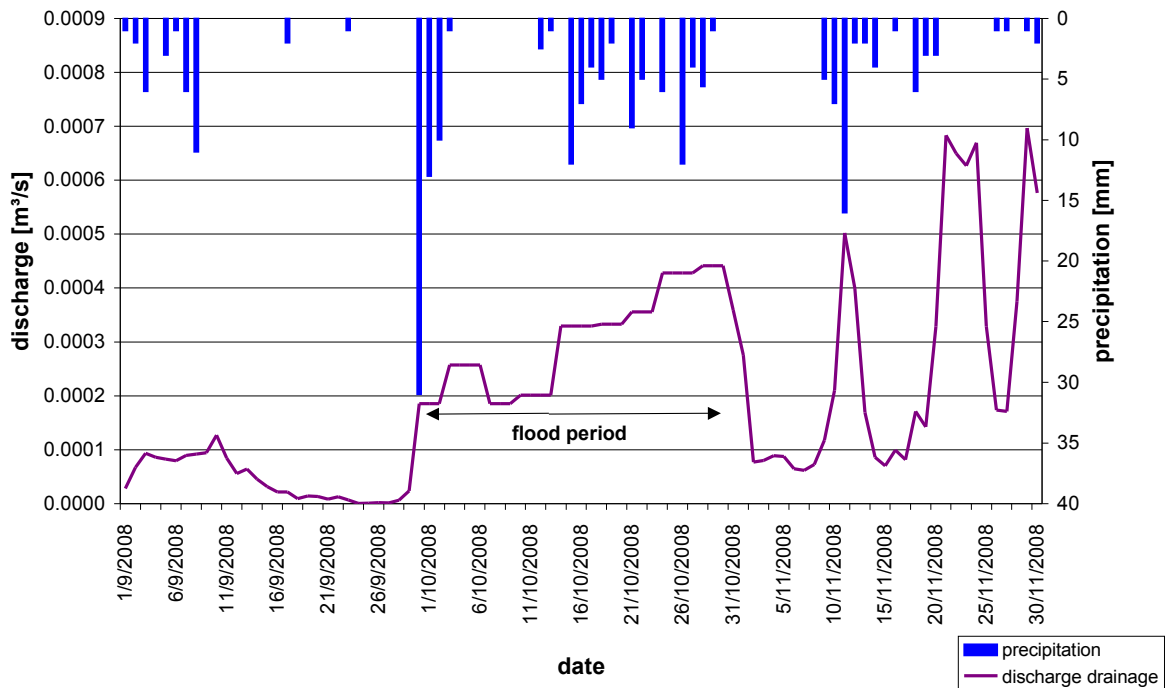


Fig. 39: Discharge of the tile drainage on drained field 2 in autumn 2008 (daily mean values); **A**=application date on drained field 2



Fig. 40: Flood situation on drained field 2, drain pipe inspection shaft (l) and field (r)

6.2.2.3 Groundwater levels

Groundwater levels measured in the two wells, located 17 m (GW1) and 35 m (GW2) distant from the drain pipe inspection shaft, indicated dry conditions at the beginning of the monitoring period. The first rainfall events did not cause significant alterations in groundwater levels. With the rainstorms at the beginning of October, the water level rose from 1.9 m to 1.0 m below the surface and stabilised at approximately 0.6 m below surface, according to numerous

showers in October and November (Fig. 41). The dry periods between rainfall events caused decreases in groundwater levels. The fluctuations in groundwater levels revealed direct responses of groundwater to precipitation and were consistent with patterns of drain flow.

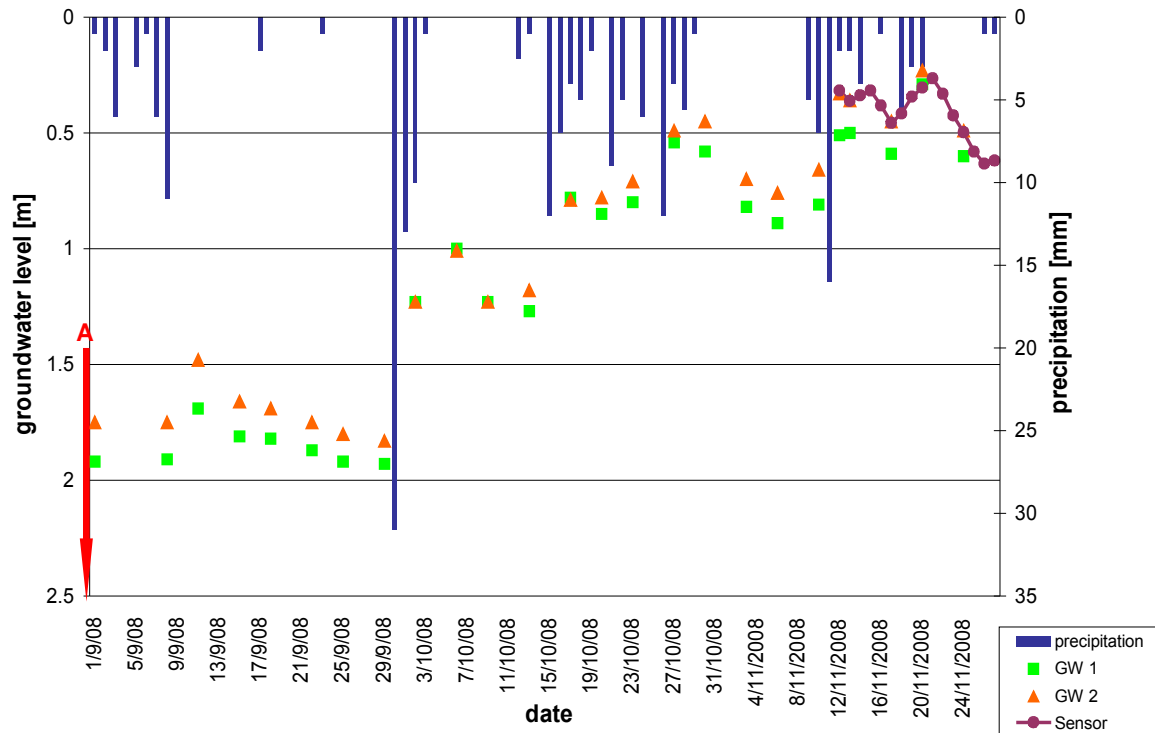


Fig. 41: Groundwater levels on drained field 2 in autumn 2008; **A**=application date on drained field 2

6.2.2.4 Discharges of the Moorau and the Kielstau in Soltfeld

The discharge of the Kielstau at the outlet of the catchment in Soltfeld and of the Moorau tributary are illustrated in Fig. 42. Similar to discharge from the drained field, discharges of both streams increased after the rainfall events in the first days of September, 30/9 - 3/10/2008, 12/10 - 29/10/2008 and 9/11/ - 20/11/2008, with a delay of up to three days, the time the water needed to reach the gauges at the Moorau and in Soltfeld. With every additional rainstorm, the discharges enlarged, and reached their maximum at Soltfeld on 12/11/2008 with $1.32 \text{ m}^3/\text{s}$, and in the Moorau on 11/11/2008 with $0.174 \text{ m}^3/\text{s}$. The daily mean discharge of the Kielstau in Soltfeld during the monitoring phase accounted for $0.44 \text{ m}^3/\text{s}$. This matches the long-term average of $0.42 \text{ m}^3/\text{s}$ over the year (1987 - 2005), and exceeds the averages of $0.32 \text{ m}^3/\text{s}$ for September through November periods (Land Schleswig-Holstein, 2009). The average discharge of the Moorau of $0.052 \text{ m}^3/\text{s}$ is higher than that measured in spring 2008, when the average discharge was $0.027 \text{ m}^3/\text{s}$ (see Chapter 6.1.2.3) upon seasonal variations. However, the

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mean discharge from 1993 – 2008 amounted for 0.43 m³/s what is almost ten times higher than the observed discharge during the Terbutylazine monitoring (Lam et al., 2010).

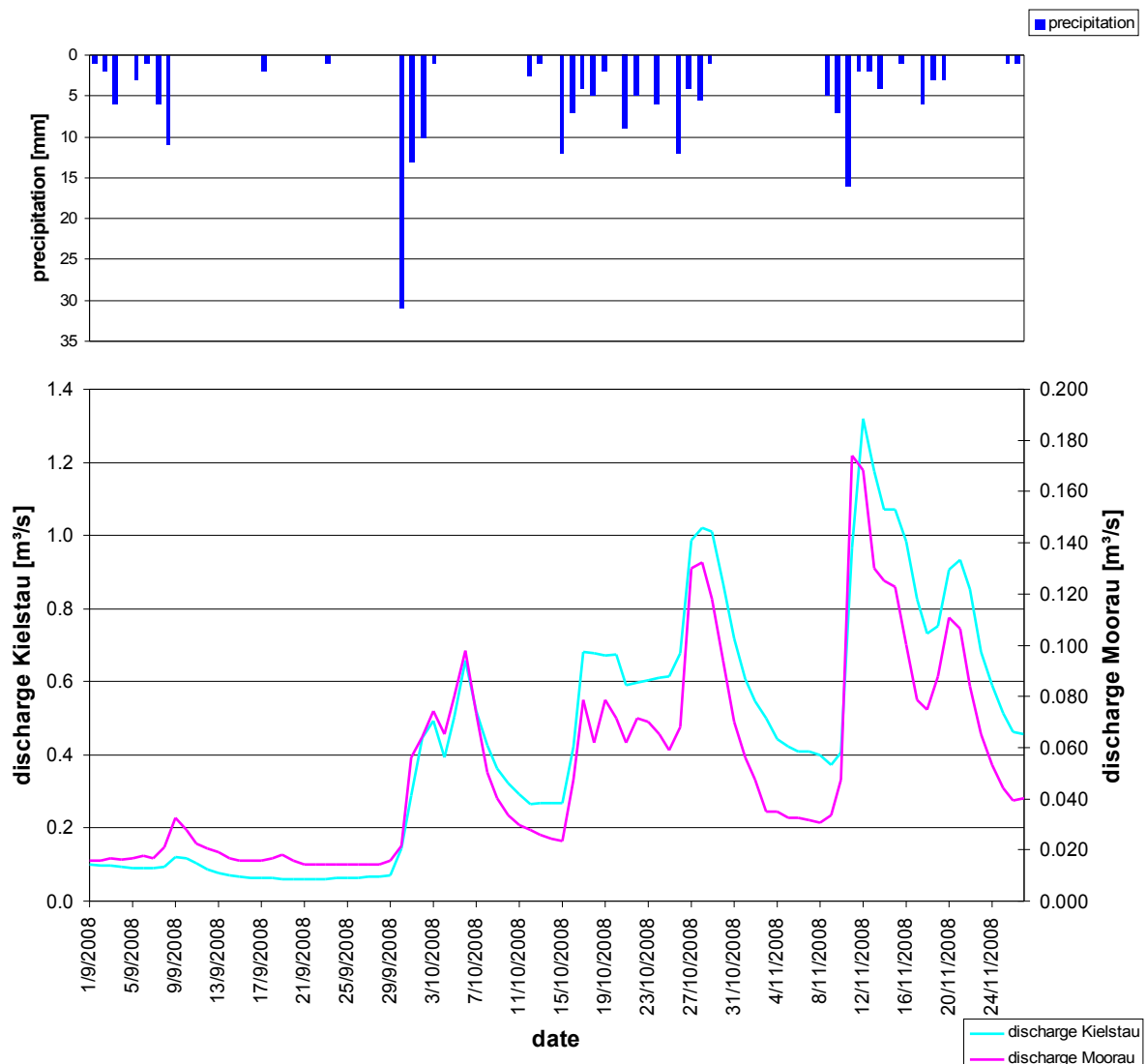


Fig. 42: Discharge of the Kielstau at Soltfeld and the Moorau in autumn 2008 (daily mean values) [data source Kielstau: StJA Schleswig (2009)]

6.2.3 Metazachlor concentrations

Drained field 2

Immediately after application of Butisan Top[®] to drained field 2, rain fell. This caused the first positive result of 131 ng/l in the drainage five days later, on 6/9/2008 (Fig. 43). At the end of this precipitation period, Metazachlor concentrations from 558 – 70 ng/l were detected. In the

subsequent eight days, these concentrations appeared on the descending slope of the discharge peak. During the following September dry phase, the agent was no longer transported to the drainage. In the rainless phase, at the beginning of November, concentrations below the quantification limit of 70 ng/l (40 – 68 ng/l) were detected. From the high rainfall events at the end of September/beginning of October, the percolating water with dissolved Metazachlor required four days to enter the drainage and produced values of 70 – 576 ng/l. The concentrations from 1/10/ - 31/10/2008 were analysed in water samples collected from accumulations in the drain pipe inspection shaft during flooding. The samples 23/10/2008 29/10/2008 were unified to a mixed weekly sample because of expected dissolving effects, due to the flood of October 2008. However, the dissolving effects did not occur. The rainfall events from 9/11/2008 – 11/11/2008 again caused transport of Metazachlor showing concentrations of up to 444 ng/l. The findings were detected when discharge increased.

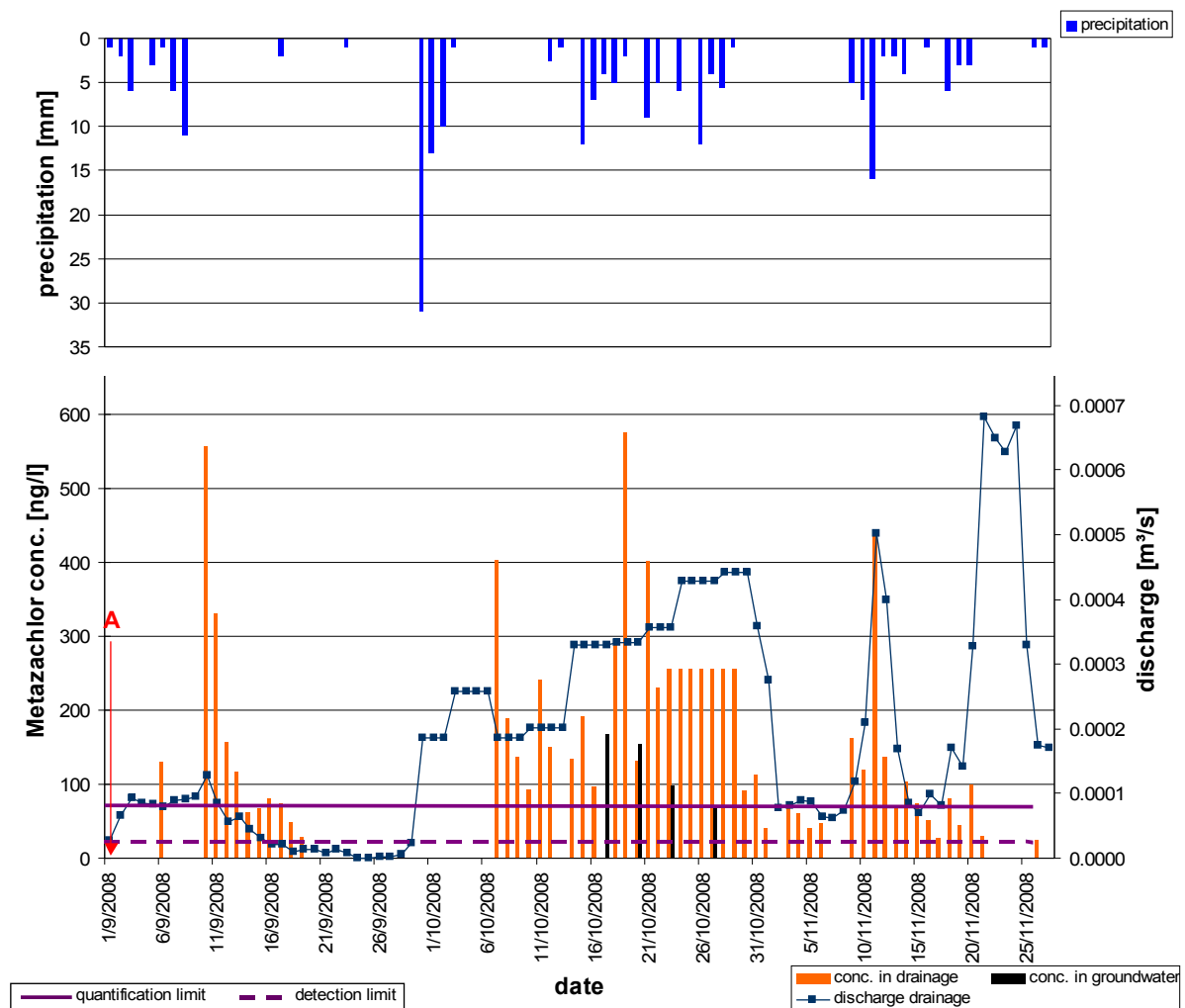


Fig. 43: Metazachlor concentrations in drainage and groundwater and the discharge on drained field 2 in autumn 2008 (daily mixed samples in the drainage);
A=application date on drained field 2

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Metazachlor results in the groundwater were detected 46 days after application from 17/10/2008 to 27/10/2008 in concentrations of 70 – 168 ng/l. The groundwater level rose from 2.0 m below surface at the commencement of monitoring to 0.8 m below surface at that time (17/10/ to 27/10/2008) (Fig. 43).

Moorau

During the entire monitoring phase, no Metazachlor findings above the detection limit of 25 ng/l were reported from the Moorau.

Kielstau

In the Kielstau samples, the first observed Metazachlor peaks occurred on 8/9/2008 and 11/9/2008 with 80 ng/l and 29 ng/l, respectively, caused by the precipitation of the previous days. During the rainless period in the second half of September, no Metazachlor was detected above detectable limits. The rainstorms on 30/9/ - 2/10/2008 led to concentrations in the range of 35 – 88 ng/l that appeared immediately at the time of rainfall. One more finding of 48 ng/l was observed on 16/10/2008 after the rainfall event on 15/10/2008. No Metazachlor was detected in the Kielstau water thereafter (Fig. 44). The Metazachlor concentrations occurred mainly during the rising limb of discharge. Overall, the concentrations were in the range of the quantification limit and half of the findings were below this threshold.

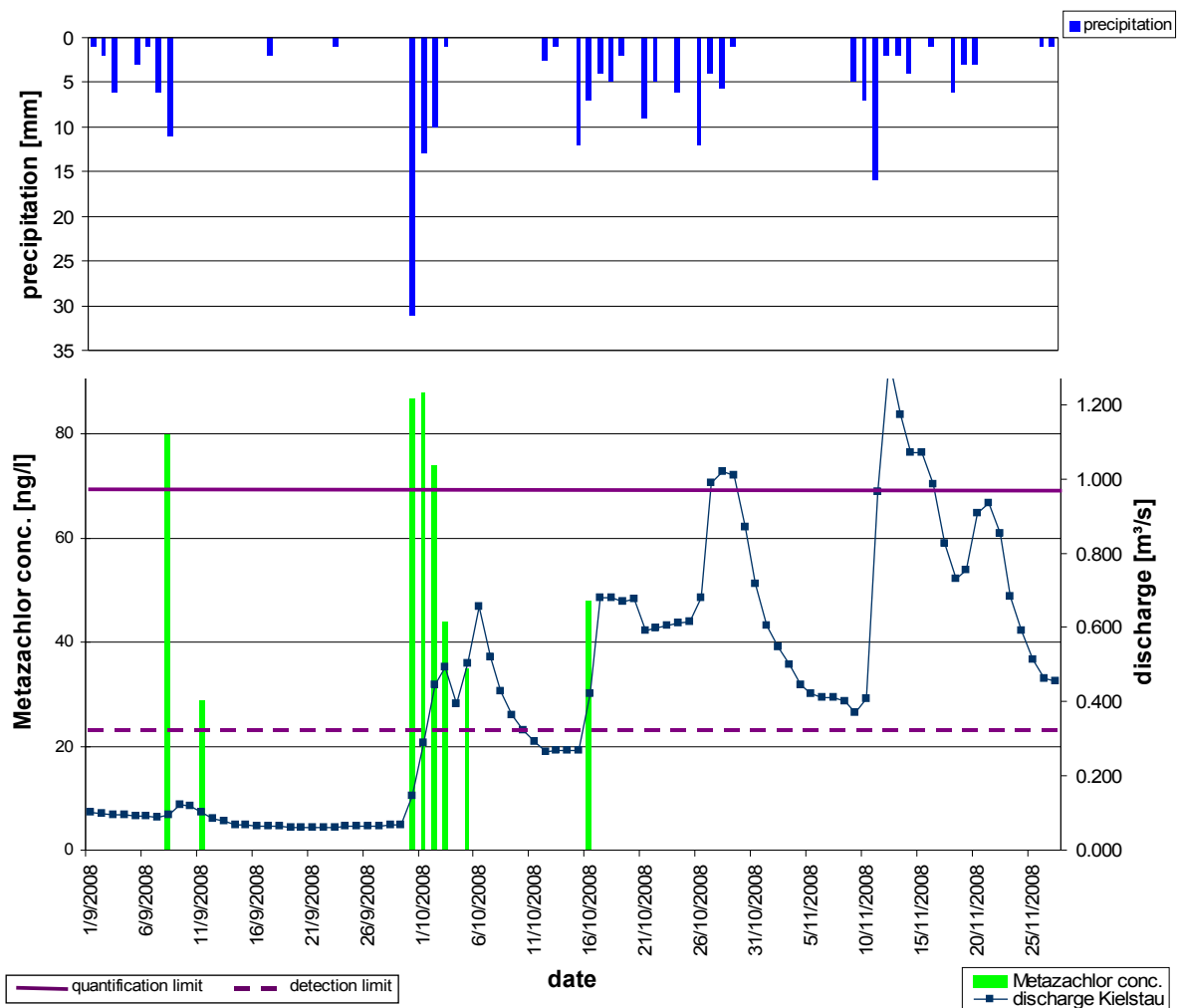


Fig. 44: Metazachlor concentrations in the Kielstau at Soltfeld in autumn 2008 (daily mixed samples)

6.2.4 Metazachlor loads

Drainage

The discharged loads of Metazachlor from drained field 2 via drainage illustrate the strong correlation to precipitation. The cumulated daily values of both parameters show similar patterns (Fig. 45). In the beginning of September, precipitation reached a plateau on 8/9/2008; the first observed Metazachlor load, however, arrived three days later. Similarly, precipitation increased on 29/9/2008, and the load rose eight days later. The delayed response time of discharge load levels to precipitation gradually shortened, until, finally, on October 29th, load level rise and fall was observed to react immediately and in direct proportion to rainfall meas-

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urements. Summing up the loads, a total of 219 mg Metazachlor was detected during the monitoring period.

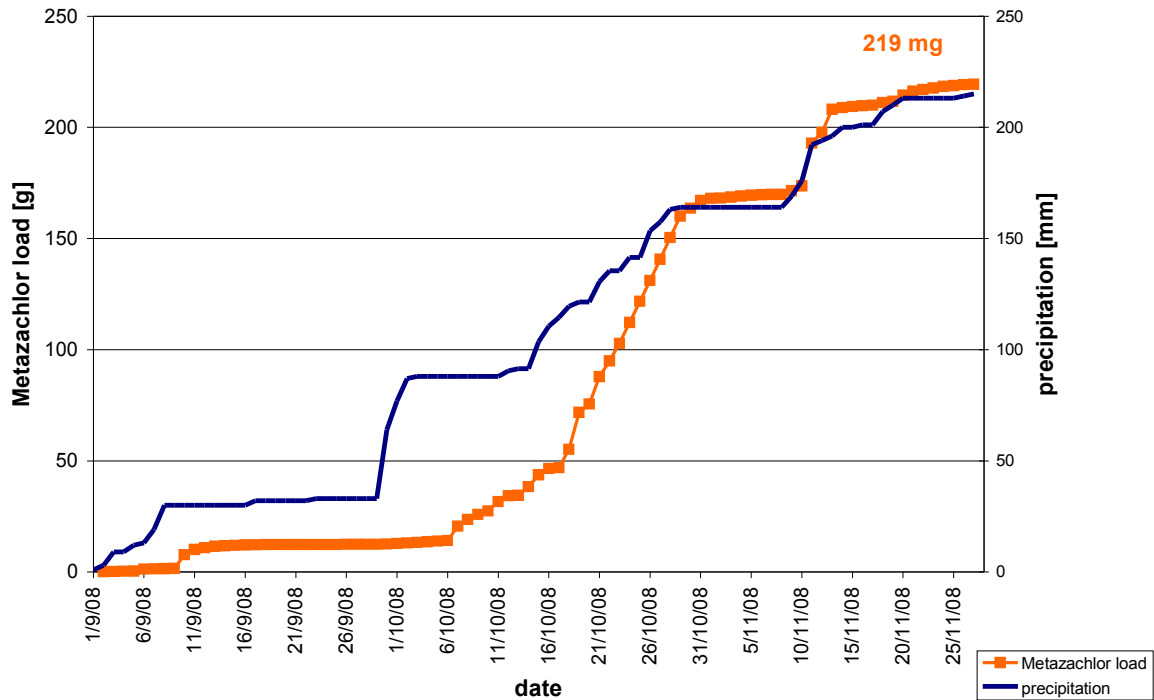


Fig. 45: Cumulated Metazachlor loads in the drainage of drained field 2 in autumn 2008 (daily values)

Moorau

As Metazachlor was not detected above the detection limit of 25 ng/l in the Moorau, loads could not be determined.

Kielstau

In Soltfeld, phenomena were observed that were comparable to those in the drainage. At the beginning of September, the Metazachlor load in the Kielstau increased to the first plateau three days after precipitation. As shown in Fig. 46, on 29/9/2008, the graphs of cumulated loads and cumulated precipitation rose simultaneously and maintained the same patterns until 16/10/2008, when the last Metazachlor observation occurred. In total, a load of 50.9 g was determined in the Kielstau during the monitoring period.

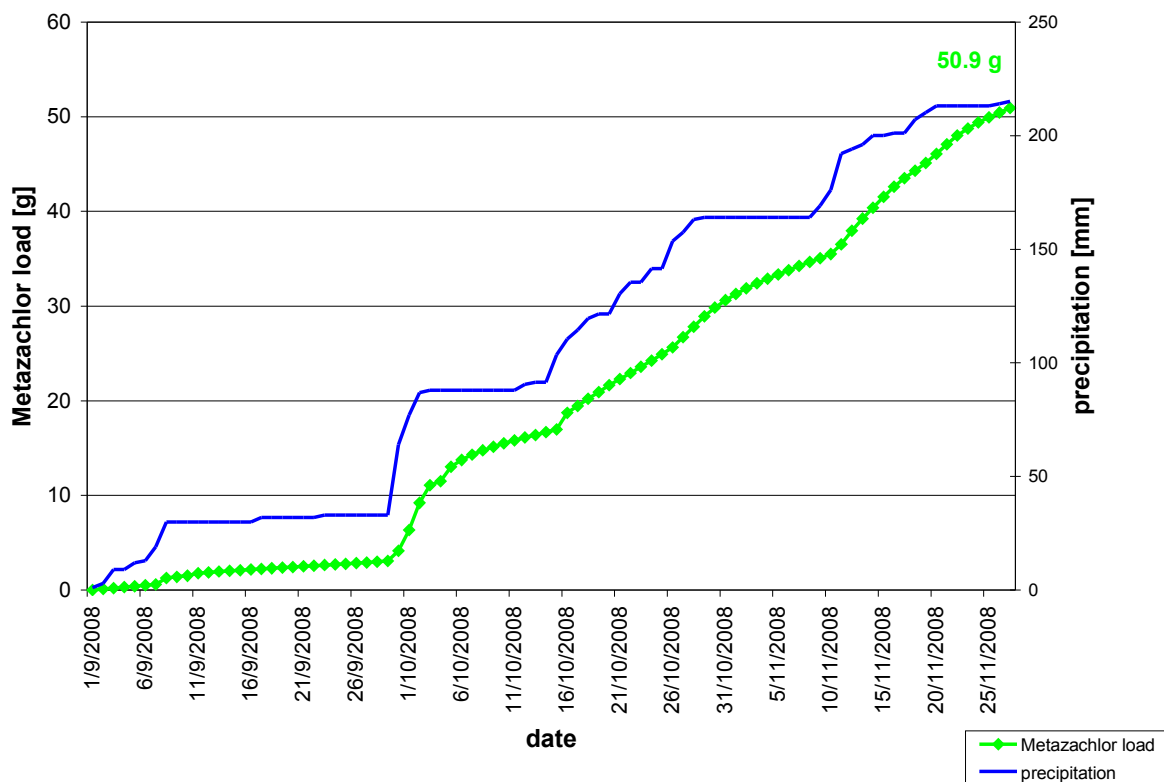


Fig. 46: Cumulated Metazachlor loads in the Kielstau at Soltfeld (daily values)

6.2.5 Land use in autumn 2008

The land use of the Kielstau catchment was mapped at field scale in November and December, 2008. The actual field crops during that time are given in Fig. 47. White areas of the map correspond to areas where summer crops were being cultivated. They could not be mapped in November and December because they had not been sown in autumn or winter.

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In Fig. 47, the dominance of winter grain (41 %) in the Kielstau catchment can be observed, followed by grassland (22 %), corn (11 %) and rape (10 %). Detail of areas and proportions of single crops are reported in Tab. 26.

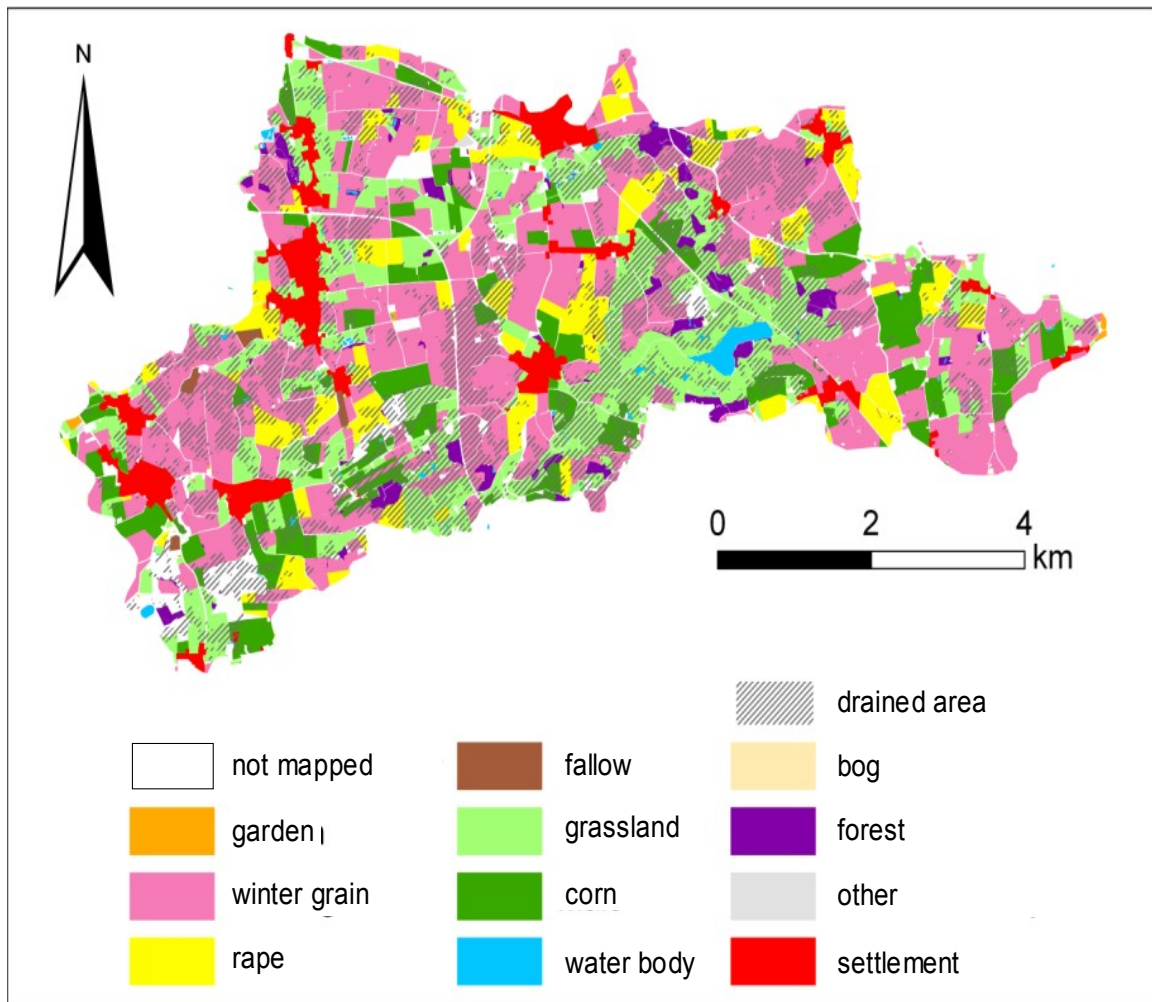


Fig. 47: Land use map of the Kielstau catchment (Nov./Dec. 2008)

Tab. 26: Proportion of crops in the Kielstau catchment and Moorau subcatchment autumn 2008

crop	catchment Kielstau		subcatchment Moorau	
	area [ha]	percentage of catchment [%]	area [ha]	percentage of subcatchment [%]
fallow	15	< 0.5	0	< 0.5
garden	13	< 0.5	2	< 0.5
water body	71	1	8	1
grassland	1070	22	150	20
corn	543	11	39	5
rape	455	10	119	16
other	38	1	8	1
forest	132	3	38	5
winter grain	1937	41	271	36
settlement	502	10	92	12
not mapped	71	1	20	3
sum	4840	100	747	100

In the subcatchment of the Moorau, winter grain was also the prevailing crop (36 % ha), followed by grassland (20 %), then rape (16 %) and corn (5 %).

The black hatching in Fig. 47 illustrates areas with drainage systems in the catchment, and is derived from the joining of the digital land use map with a digital drain map (Golon, 2006). From the total 455 ha of rape cultivation, 148 ha were drained, thus, 33 % of the rape area and 3.4 % of the entire catchment was drained.

In the subcatchment, the area of rape amounted to 119 ha and includes 42 ha of drained rape fields. The 42 ha correspond to 5.7 % of the entire subcatchment and 36 % of the rape areas in the subcatchment.

6.2.6 Metazachlor application in the catchment

Interviews with farmers of the catchment indicated that, for the most part, supplements containing Metazachlor as an active ingredient were the ones applied (Nimbus[®], Butisan[®], Butisan Top[®]). Overall, information on 238 ha of rape field was available, i.e., 52 % of the total 455 ha rape area in the catchment. Since interviews were anonymous, dates and amounts of application could not be spatialized. On 7.5 % (34 ha) of the rape area, a supplement (Colzor trio[®]) containing active ingredients other than Metazachlor was applied. As application of

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Colzor trio[®] closer than 5 to 10 meters to hedges is prohibited, on three fields a combination of Colzor trio[®] and Butisan Top[®] was sprayed. For the last meters Butisan Top[®] had to be applied there, because it is allowed. In autumn 2008, 120 kg of Metazachlor were applied to the 238 ha of rape fields belonging to the interviewed farmers of the Kielstau catchment. The daily amounts were in the range of 2.6 to 17.8 kg with an average of 4.7 kg/d. The time span of Metazachlor application was 27 days, from 25/8/ to 20/9/2008 (Fig. 48), and the main part of Metazachlor was sprayed from 30/8 to 5/9/2008. The monitoring began on 1/9/2008. On 13 days of this period rainfall occurred, in amounts mainly below 6 mm. A rainstorm depositing 11 mm of rainfall took place on 8/9/2008, before application of Metachlor could be accomplished.

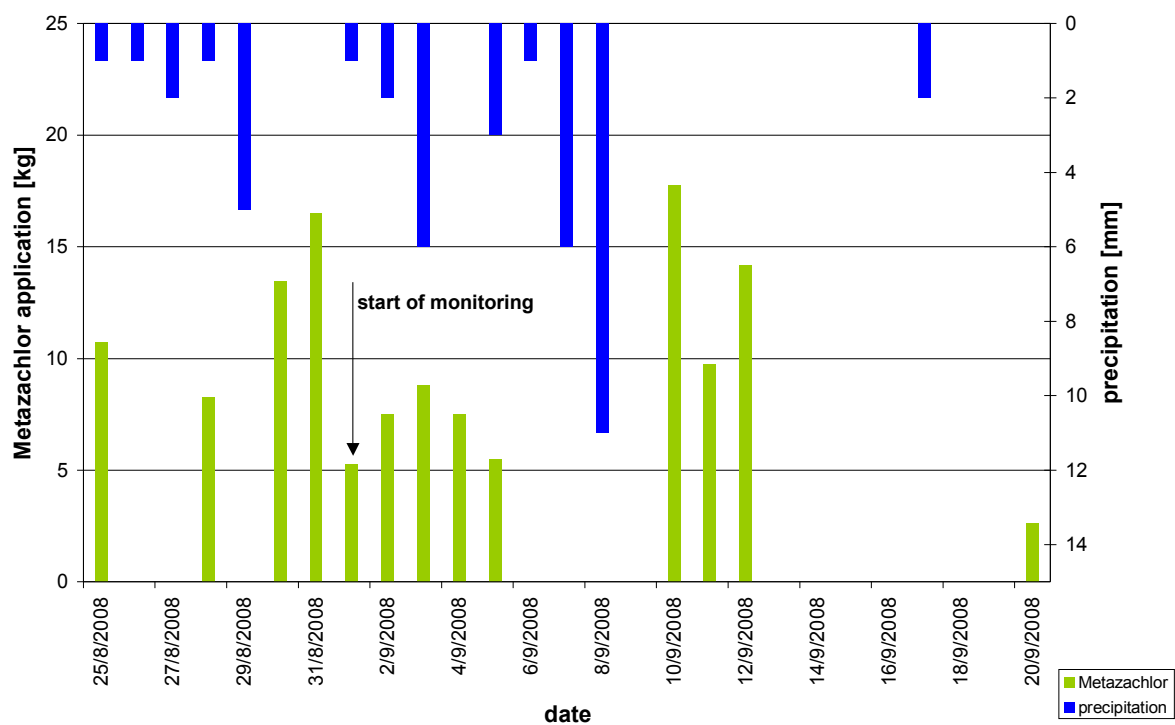


Fig. 48: Distribution of Metazachlor application in the Kielstau catchment in autumn 2008

Taking the farmers' information and the mapped rape areas into account, the potential quantity of Metazachlor applied in the catchment/subcatchment was determined. In the entire catchment, 229 kg of Metazachlor were probably spread on the fields, and 60 kg of that amount was applied in the subcatchment of the Moorau. From the 229 kg Metazachlor, 84 kg were allotted to the drained rape fields in the catchment, and from those 84 kg, 24 kg were allotted to drained rape fields in the subcatchment (Tab. 27). Hence, the amount of potential discharge of Metazachlor into non-target areas was 229 kg.

Tab. 27: Potential Metazachlor discharge from rape fields

	Area [ha]	Metazachlor [kg]	Moorau	Area [ha]	Metazachlor [kg]	Kielstau	Area [ha]	Metazachlor [kg]
Data of rape fields (farmers)	238	120	Extrapolation subcatchment Moorau rape	119	60	Extrapolation Kielstau catchment rape	455	229
Data of drained rape fields (farmers)	68	39	Extrapolation subcatchment Moorau rape drained	42	24	Extrapolation Kielstau catchment rape drained	148	84

6.3 Monitoring of Flufenacet in autumn 2009

6.3.1 Monitored soil parameters

The monitoring of Flufenacet at field scale was accomplished on drained field 2. The parameters characterizing the soil are reported in Chapter 6.2.1.

The soil water content was measured at two locations at the side of the field: at the drainage pipe (S), and at a distance of 10 m to the north (N). The maximum variations between both locations ranged within 6 % at 20 cm depth, and 4 % at 40 cm depth. The soil water content at 20 cm depth was generally higher than at 40 cm depth. The values were in the range of 11.1 – 47 (75) % at 20 cm and 11.1 – 26 % in 40 cm (Fig. 49). Until the first rainstorm on 3/10/2008, the soil water content was low and similar in both depths. All sensors showed the same response to rainfall events. The soil water content increased with rainfall, or, at the latest, a day after an event (e.g., 3/19/2009, 10/10/2009 - 13/10/2009, 2/11/2009, 10/11 - 13/11/2009, 28/11/2009). On 29/11/2009, the sensors at 20 cm depth responded distinctively to the rainfall observed one and two days before (23 mm), indicating that soil water content had increased to 45 and 75 %. As both 20 cm TDR probes reacted, the soil water content at 40 cm depth increased and the discharge of the drainage rose, the high values were not artifacts.

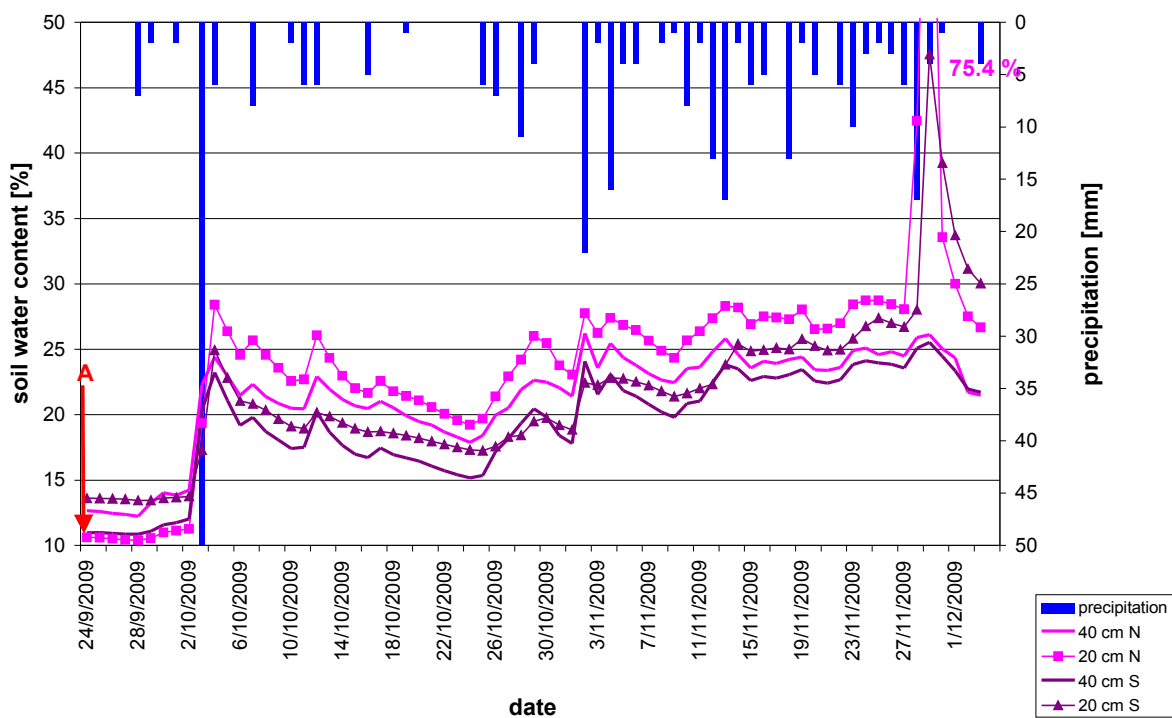


Fig. 49: Soil water content of drained field 2 in autumn 2009 (daily mean values);
A=application date on drained field 2

6.3.2 Hydrological parameters in autumn 2009

6.3.2.1 Precipitation

The precipitation was monitored at the rain gauges in Ausacker and Satrup. Four days after the herbicide application, on 28/9/2009, the first rainfall event occurred with an amount of 7 mm (Fig. 50). The rainstorm of 3/10/2009 with 50 mm can be classified as a significant event that appeared maximally once a year, according to long term observations from 1984 – 2009 (DWD, 2007a; LLUR, 2009). The monitoring phase is characterized by continuous rainfall, exceeding occasionally the 15 mm bench mark (2/11/, 4/11/, 13/11/ and 28/11/2009), and by one rainless period from 17/10/ to 24/10/2009. The total of precipitation during the observation amounted to 313 mm in Ausacker and 262 mm in Satrup. Of that, 114 mm/m (Ausacker) and 99 mm/m (Saturp) fell in October, and 176 mm/m (Ausacker) and 144 mm/m (Saturp) fell in November. These values correspond to 122 % (Ausacker) and 106 % (Saturp) of the long-term averages from 1984 to 2004 for October, and to 248 % (Ausacker) and 144 %

(Satrup) of the long-term averages from 1984 to 2009 for November (DWD, 2007b; LLUR, 2009). The record at both locations varied by a standard deviation of 26 %.

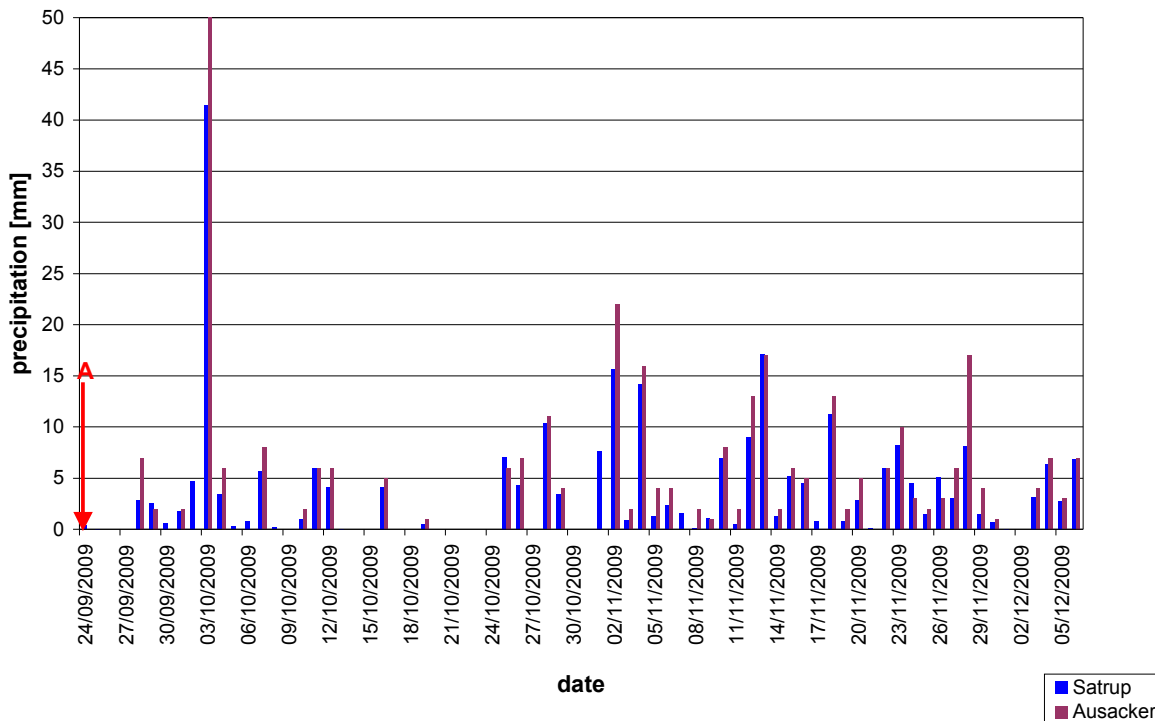


Fig. 50: Precipitation in the Kielstau region in autumn 2009 (daily total); **A**=application date on drained field 2

In the following figures of the Flufenacet monitoring, the precipitation of the rain gauge in Ausacker is depicted.

6.3.2.2 Discharge of the tile drainage

The rating curve of the drainage pipe is presented in Fig. 51, allowing the calculation of the discharge for every monitored time interval.

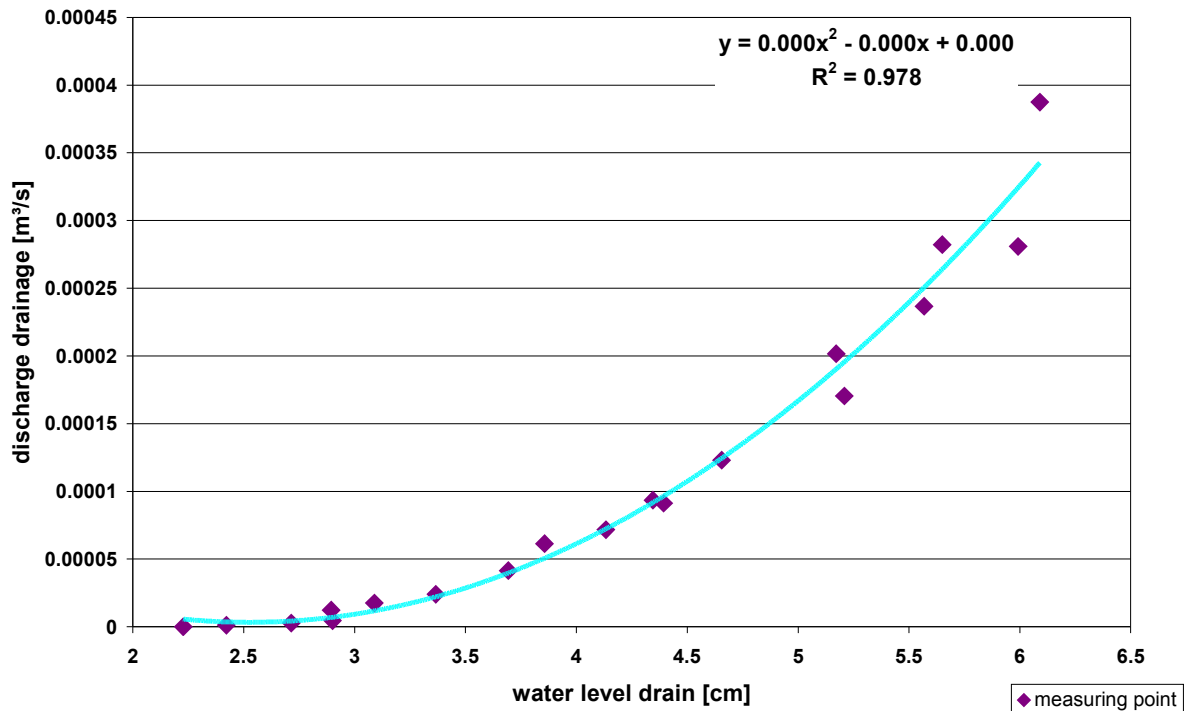


Fig. 51: Rating curve of the drainage pipe on drained field 2 in autumn 2009

The values of the discharge accounted for $3,3 \cdot 10^{-6}$ m³/s on 25/9/2009 and $5,4 \cdot 10^{-4}$ m³/s on 29/11/2009 (Fig. 52). The beginning of the monitoring period was characterized by low discharge due to a rainless period during September. The rainstorm on 3/10/2009 generated a significant increase in drainage discharge. The discharge responded with one day of delay to the rainfall events (2/11/2009, 4/11/2009, 14/11/2009, 29/11/2009). As an effect of the continuous and abundant rainfall, the discharge rose constantly from the beginning of November.

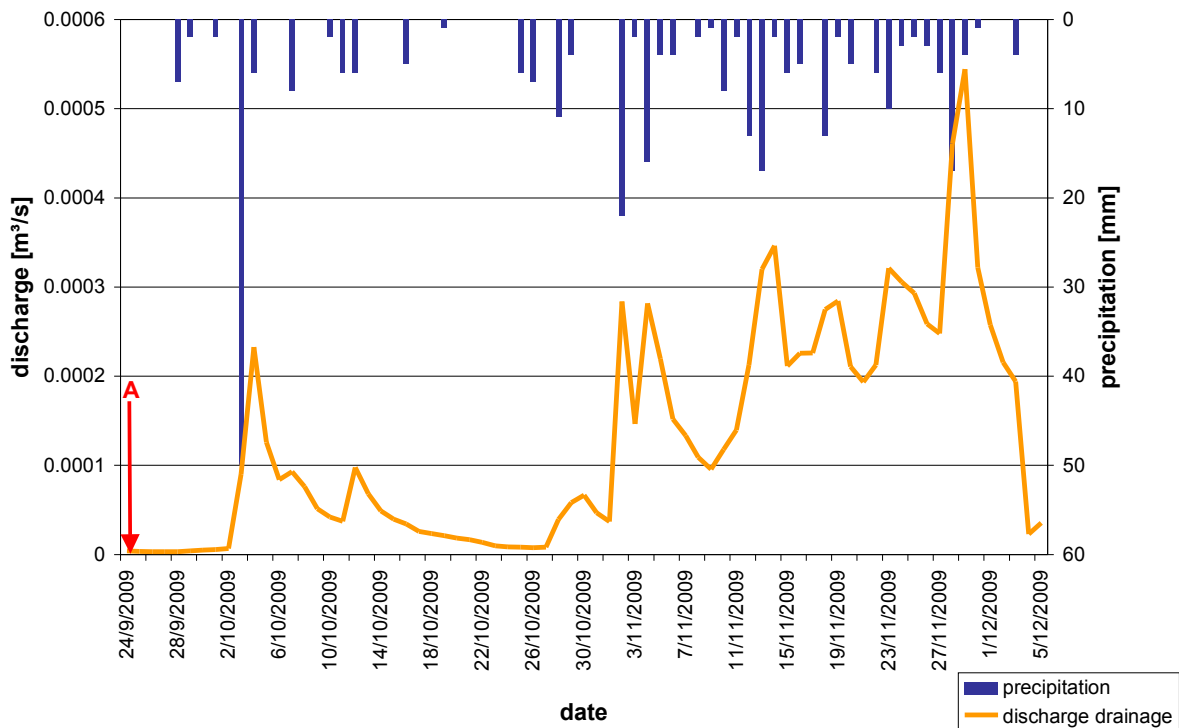


Fig. 52: Discharge of the tile drainage on drained field 2 in autumn 2009 (daily mean values); **A**=application date on drained field 2

6.3.2.3 Groundwater levels

The groundwater level was measured manually in two wells (GW1 and GW2), and a pressure sensor detected the water level in GW2 continuously. At the beginning of the observation, the water level was around 1.5 m below surface, rising up to 0.3 m below surface in November. The groundwater level reacted immediately to rainfall events on 5/10/2009, 28/10/2009, 2/11/2009, 13/11/2009, and 18/11/2009. Both wells show the same dynamic, and the sensor in GW2 delivered similar data to the manual determination in GW2 (Fig. 53).

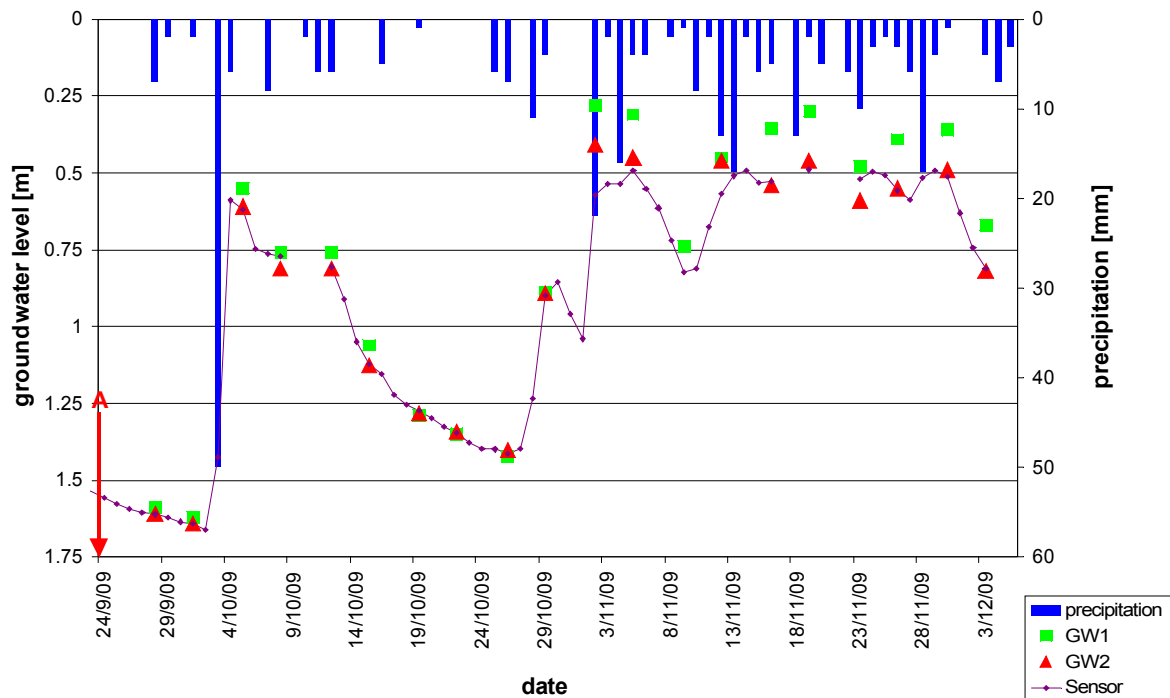


Fig. 53: Groundwater levels on drained field 2 in autumn 2009; **A**=application date on drained field 2

6.3.2.4 Discharges of the Moorau and the Kielstau in Soltfeld

During the two weeks before the monitoring campaign started, 1 mm of rainfall occurred. Hence, at the beginning of the observation, the discharge of the Moorau and the Kielstau at the Soltfeld gauge was at a low level of flow ($0.02 \text{ m}^3/\text{s}$ and $0.07 \text{ m}^3/\text{s}$). Caused by the rainstorm on 3/10/2009, the Moorau discharge rose immediately to $0.2 \text{ m}^3/\text{s}$ and that of the Kielstau to $0.4 \text{ m}^3/\text{s}$ one day later. They leveled off afterwards at $0.03 \text{ m}^3/\text{s}$ (Moorau) and $0.16 \text{ m}^3/\text{s}$ (Kielstau), due to only four smaller rainfall events of 5 - 6 mm (11/10/2009, 12/10/2009, 25/10/2009, 26/10/2009). The rainstorms on 2/11/2009 and 4/11/2009 increased water flow, accounting for $0.27 \text{ m}^3/\text{s}$ in the Moorau and $0.98 \text{ m}^3/\text{s}$ in the Kielstau. On 14/11/2009 there were flows of $0.39 \text{ m}^3/\text{s}$ and $1.42 \text{ m}^3/\text{s}$. In the Moorau, the maximum discharge of $0.46 \text{ m}^3/\text{s}$ was determined on 29/11/2009, and one day later, on 30/11/2009, a maximum value of $1.71 \text{ m}^3/\text{s}$ in the Kielstau at Soltfeld (Fig. 54).

The mean discharge of the Moorau amounted to 0.14 m³/s. It was significantly higher than that of autumn 2008, accounting for 0.052 m³/s, but was only a fourth of the mean discharge from 1993 – 2008 (0.43 m³/s) (Lam et al., 2010). The mean discharge of the Kielstau of 0.63 m³/s during the monitoring exceeded the value of autumn 2008 of 0.437 m³/s and the long-term average of 0.424 m³/s of the years 1987 – 2005 (Land Schleswig-Holstein, 2009). Nevertheless, the maximum of 1.71 m³/s was below detected maxima of ca. 2.5 m³/s, which could be observed in the months of September until November of the long-term surveillance.

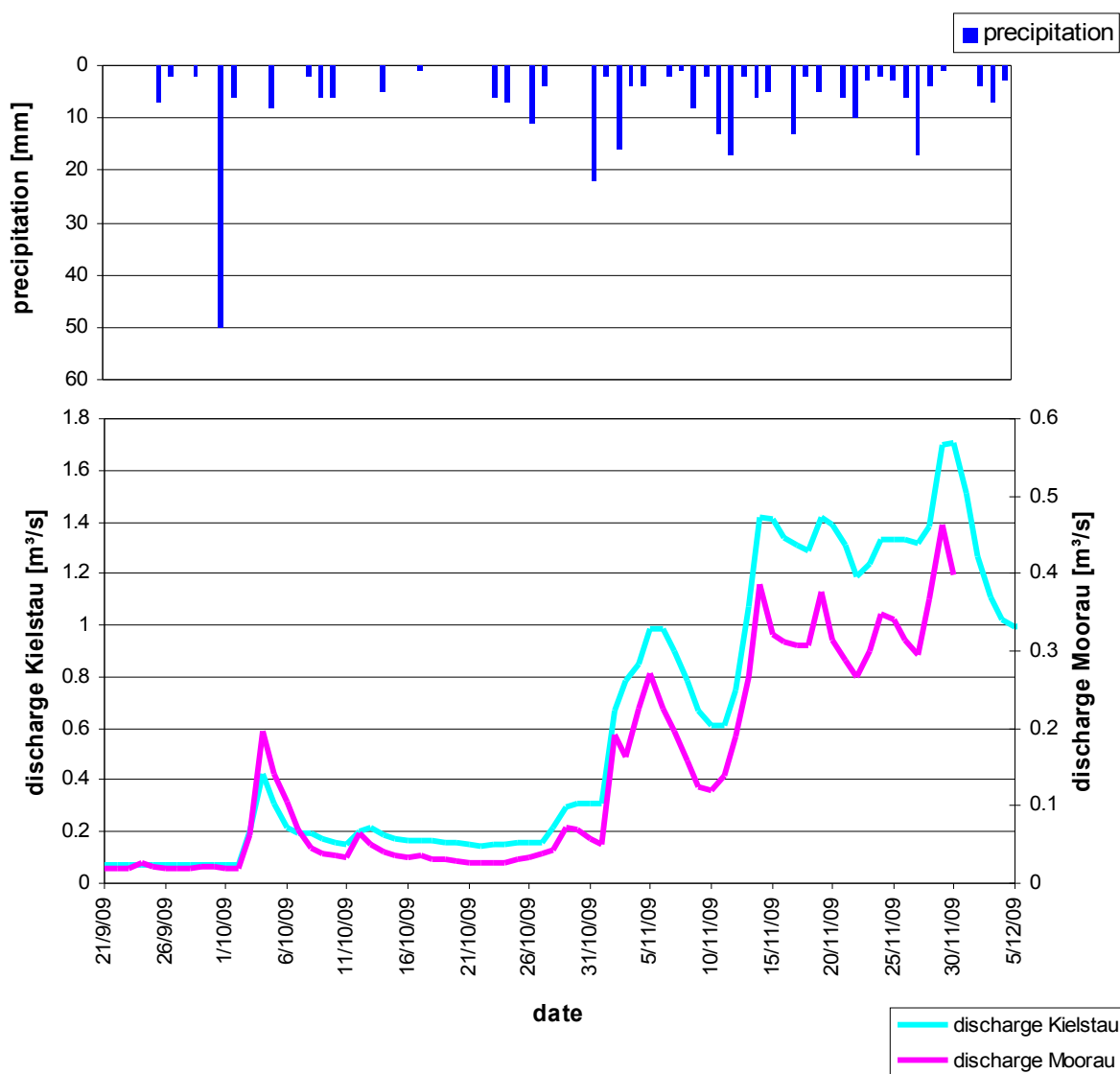


Fig. 54: Discharge of the Kielstau at Soltfeld and the Moorau in autumn 2009 (daily mean values) [data source Kielstau: LKN S-H (2009)]

6.3.3 Flufenacet concentrations

Drained field 2

In the drainage water, Flufenacet concentration in the range of > 30 ng/l – 170 ng/l were detected from 24/9/2009 – 5/12/2009 (Fig. 55). The first Flufenacet peak was determined on 3/10/2009 on the same day that a rainstorm of 50 mm was recorded. The Flufenacet concentration in the drainage water was 170 ng/l, the highest concentration during the monitoring. In the following dry period, the herbicide was not transported to the drainage. Again on 30/10/2009 and 1/11/2009, findings of 83 ng/l and 106 ng/l could be observed as a result of several days of precipitation (25 – 29/10/2009). Though November and December were characterized by continuous rainfall, merely the rainstorms on 13/11/2009 and 17/11/2009 with amounts of 17 mm resulted in Flufenacet concentrations in the range of 60 – 138 ng/l (13/11/2009) and 81 – 76 ng/l (17/11/2009). All findings occurred with the rising or maximum discharge of the drainage.

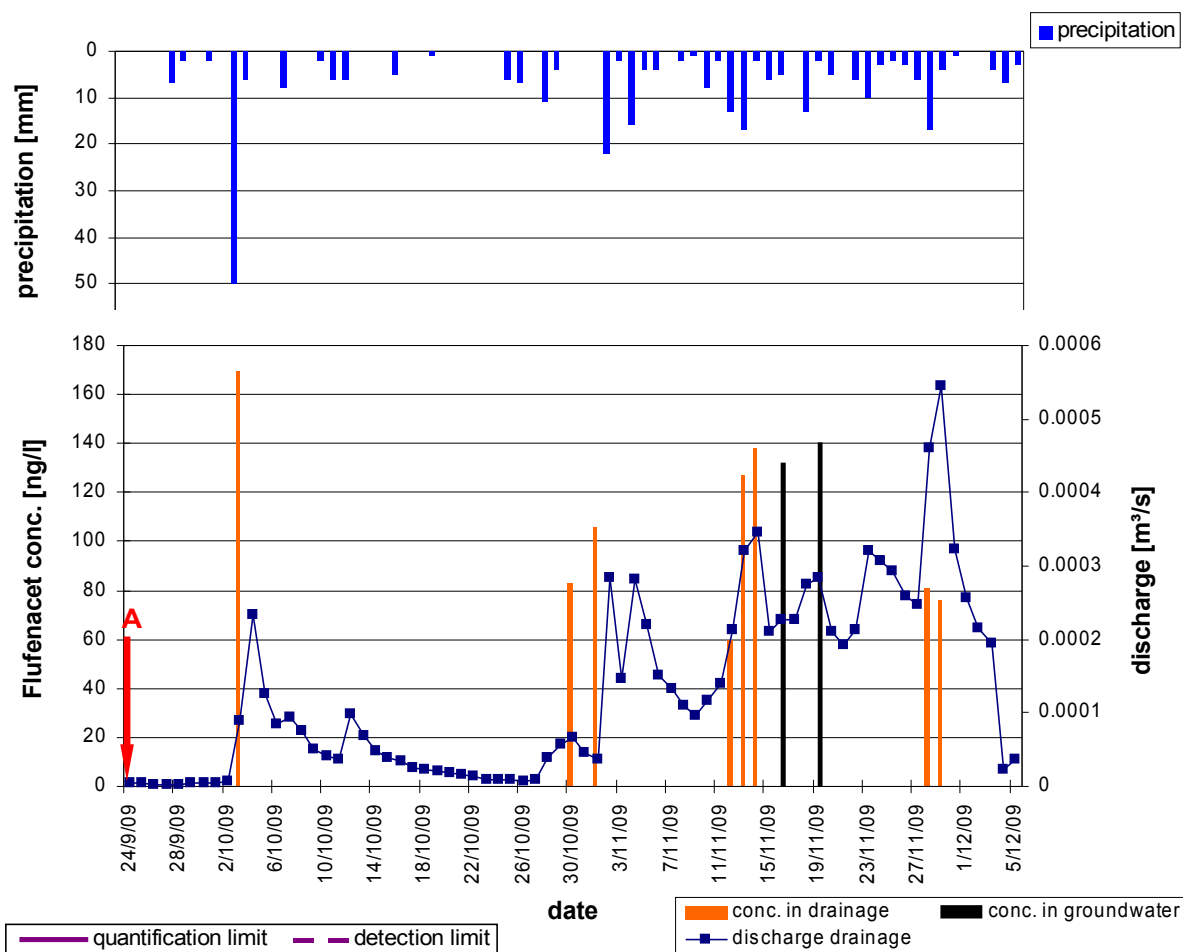


Fig. 55: Flufenacet concentrations in drainage and groundwater on drained field 2 in autumn 2009 (daily mixed samples in the drainage); **A**=application date on drained field 2

In the groundwater well GW2, Flufenacet was detected 53 days after application on two subsequent sampling days, on 16/11/2009 and 19/11/2009, in amounts of 132 ng/l and 140 ng/l (Fig. 55). The groundwater level was in the range of 0.3 – 0.54 m below surface at that time, but started at 1.6 m below surface at the beginning of the monitoring.

Moorau

In the water samples of the Moorau tributary, seven peaks of Flufenacet were determined during the ten weeks showing values between 40 ng/l and 96 ng/l (Fig. 56). The first peak of 84 ng/l occurred on 5/10/2009 two days after the intensive rainfall event of 50 mm along the falling limb of the hydrograph. The findings on 12/10/ and 13/10/2009 were also detected in the phase of diminished discharge, while those on 2/11/ - 4/11/2009 and 14/11/2009 were observed during the rising of the discharge, or with its maximum. Subsequently, no more Flufenacet was monitored in the Moorau.

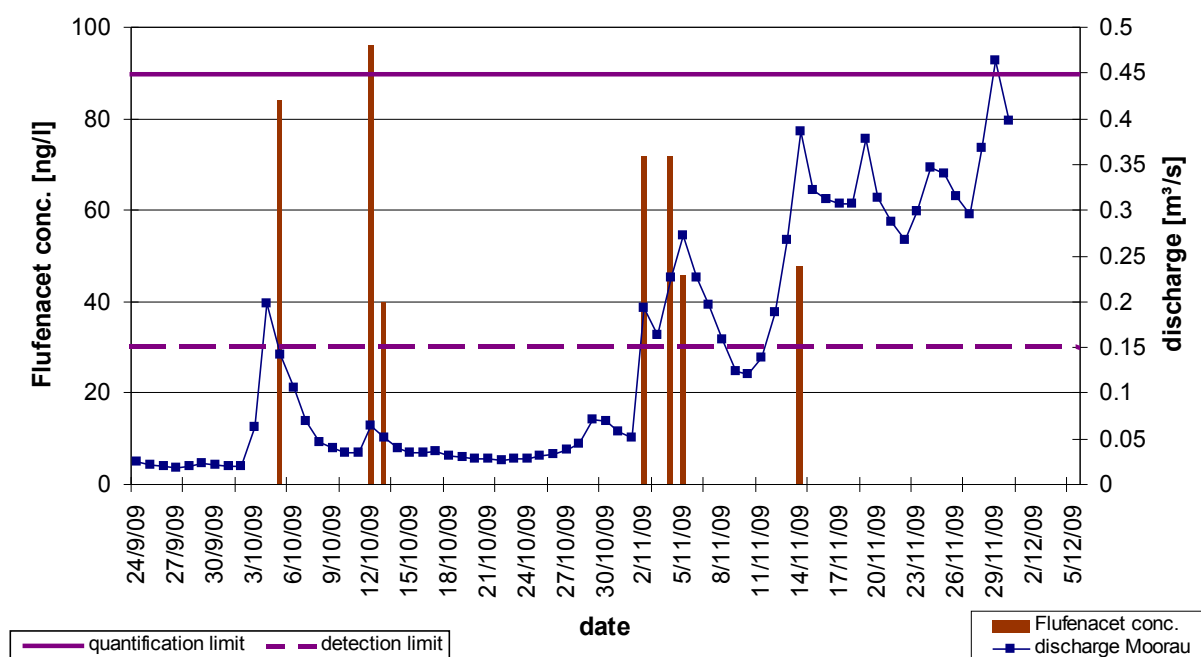


Fig. 56: Flufenacet concentrations in the Moorau in autumn 2009 (daily mixed samples)

Kielstau

At the outlet of the catchment (Soltfeld), Flufenacet concentrations were determined in the Kielstau that amounted from > 30 ng/l to 160 ng/l (Fig. 57). Similar to drainage and Moorau, the rainstorm on 3/10/2009 caused a relocation of the agent from fields into the water of the Kielstau. Findings from 3/10/2009 – 5/10/2009 and 7/10/2009 were observed, including the maximum value during the monitoring of 160 ng/l as second positive result.

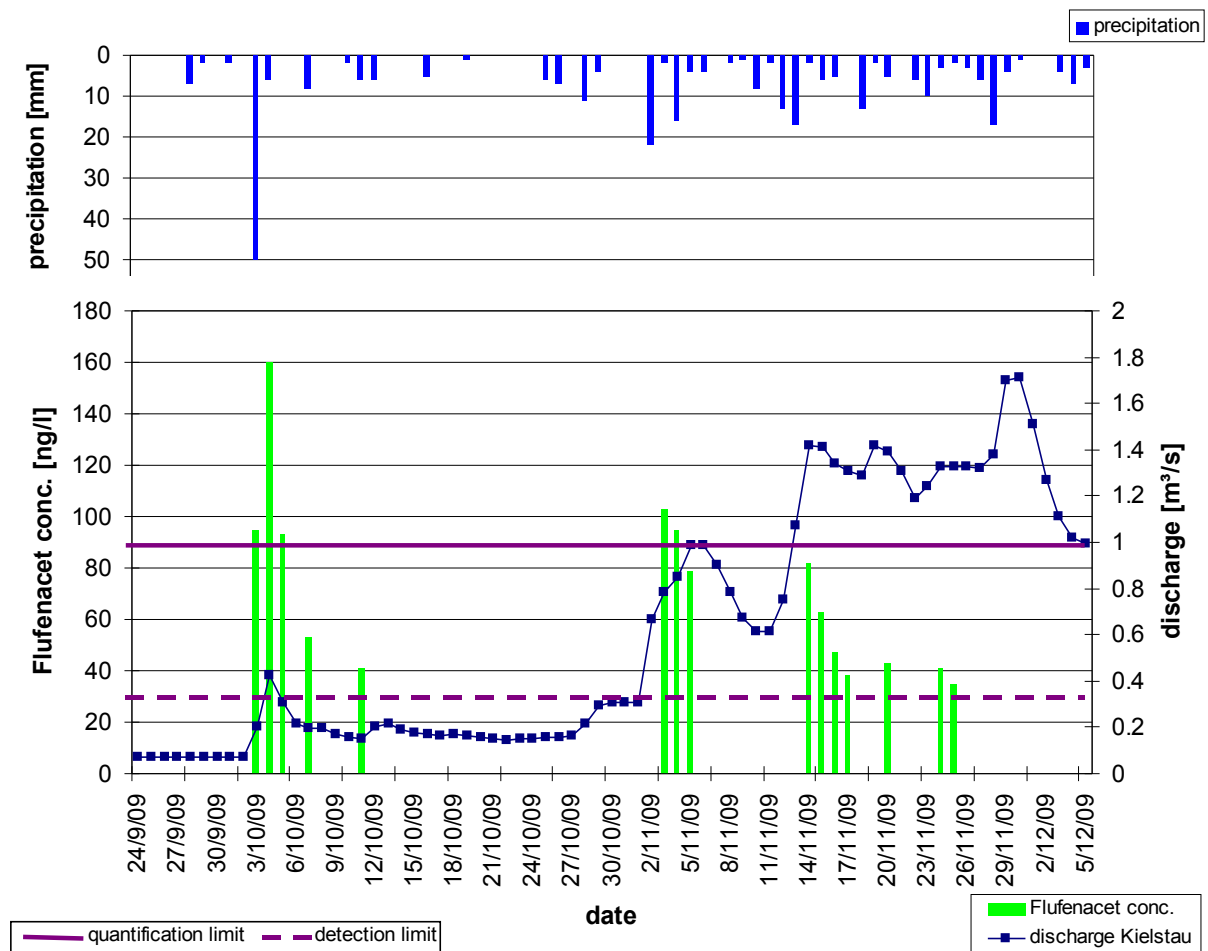


Fig. 57: Flufenacet concentrations in the Kielstau at Soltfeld in autumn 2009 (daily mixed samples)

The Flufenacet peaks occurred on the rising as well as the falling limb of the discharge peak. A single finding was documented on 11/10/2009 that accounted for 41 ng/l. Following this, Flufenacet was monitored on 3/11/2009 – 5/11/2009 in concentrations of 103 ng/l – 79 ng/l, after the rainfall event of 22 mm on 2/11/2009 with rising discharge. From 14/11/2009 to 25/11/2009, Flufenacet was measured in the Kielstau in the range of 82 ng/l – 35 ng/l, and diminished continuously. All values of this period were below the quantification limit and five

of them were close to the detection limit. Overall, the tendency of decreasing Flufenacet concentrations in the water samples of the Kielstau could be observed during the ten weeks of monitoring.

6.3.4 Flufenacet loads

Drainage

The graph of the cumulated precipitation rose continuously. The ascents were characteristic on 3/10/2009, 28/10/2009 – 29/10/2009 and 2/11/2009 – 6/11/2009 marking the start of a steeper slope equivalent to higher precipitation.

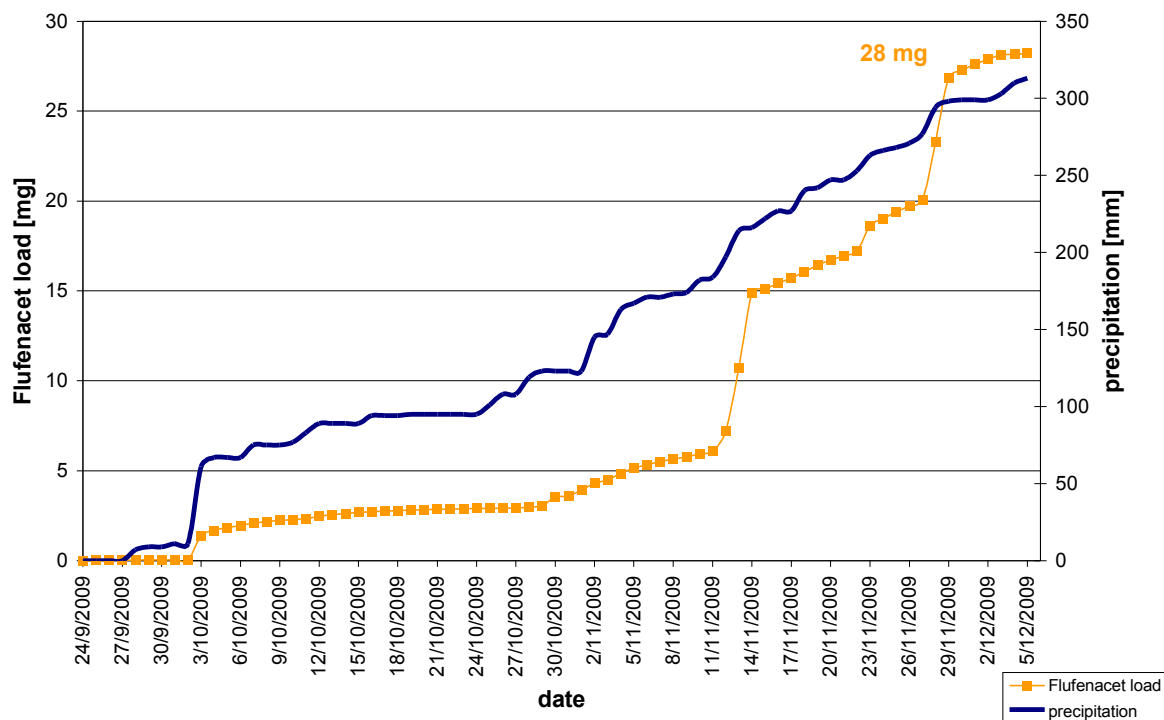


Fig. 58: Cumulated Flufenacet loads on drained field 2 in autumn 2009 (daily values)

The first load released from the drainage appeared simultaneously with the rainstorm on 3/10/2009 that amounted to 1.3 mg. Following that, Flufenacet was discharged on 30/10/2009 – 1/11/2009 as a response to the precipitation of 25/10/2009 – 29/10/2009, but delayed by four days (Fig. 58). The rainstorms in the first days of November were without response as Flufenacet was not detected in these days. The main load of 8.5 mg during the monitoring was

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determined from 12/11/2009 – 14/11/2009, after several days of intensive rainfall. Due to the continuous rainfall, the delay between rainfall event and detected load could be determined only on several dates. The total load in the drainage water of the ten week observation period accounted for 28 mg Flufenacet.

Moorau

The pattern of the graph of loads in the Moorau followed that of the precipitation. A sharp incline of the loads graph was detected on 4/10/2009, followed by a second on 2/11/2009 – 5/11/2009 and a third one on 14/11/2009 (Fig. 59). The rises of the precipitation graph occurs coincidentally. The main load in the Moorau catchment was discharged on 2/11/2009 – 5/11/2009 amounting to 3.22 g after several rainfall events. Summing up the loads, 18 g Flufenacet were released to the Moorau from 24/9/2009 to 5/12/2009.

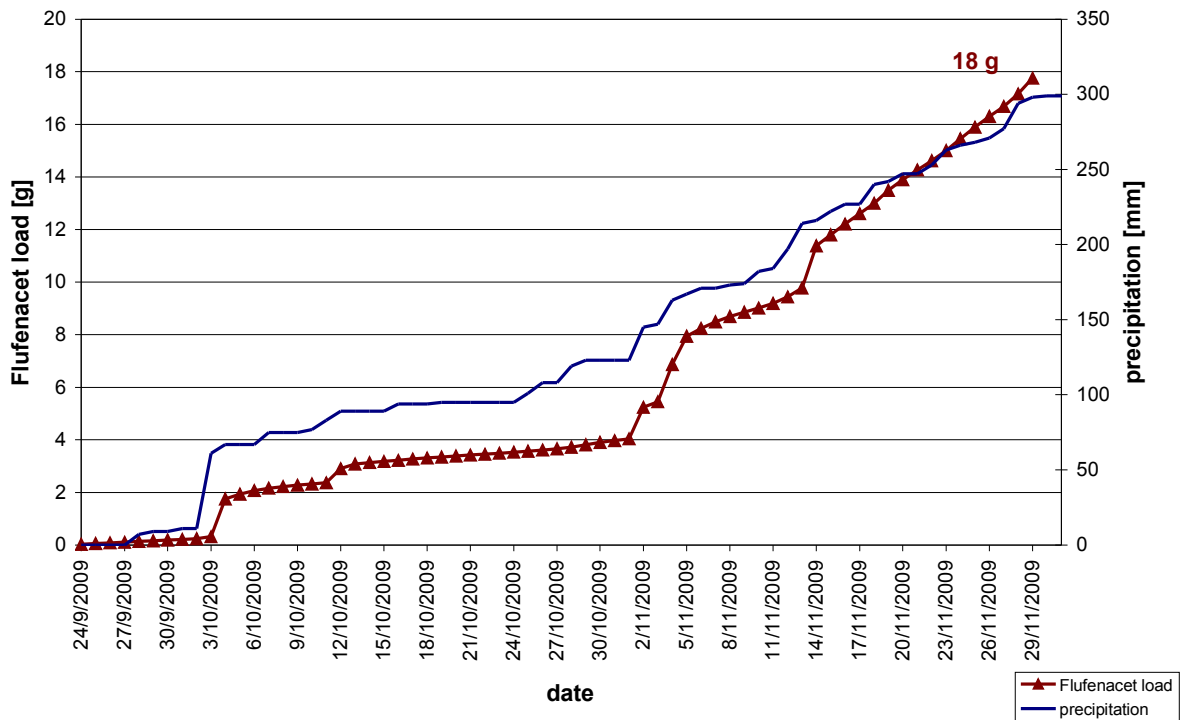


Fig. 59: Cumulated Flufenacet loads in the Moorau in autumn 2009 (daily values)

Kielstau

In the Kielstau, the first rise of the loads included the daily inputs of 3/10/2009 – 5/10/2009 and responded immediately to the rainstorm on 3/10/2009 (Fig. 60). During 3/11/2009 – 5/11/2009, the second significant incline was observed, one day later than the rise of the precipitation graph on 2/11/2009. But the load graph did not respond to 28 mm of precipitation (25/10/2009 – 29/10/2009), hence, an increase of the load graph was not detectable. The total load determined in the Kielstau at Soltfeld amounted to 115 g Flufenacet.

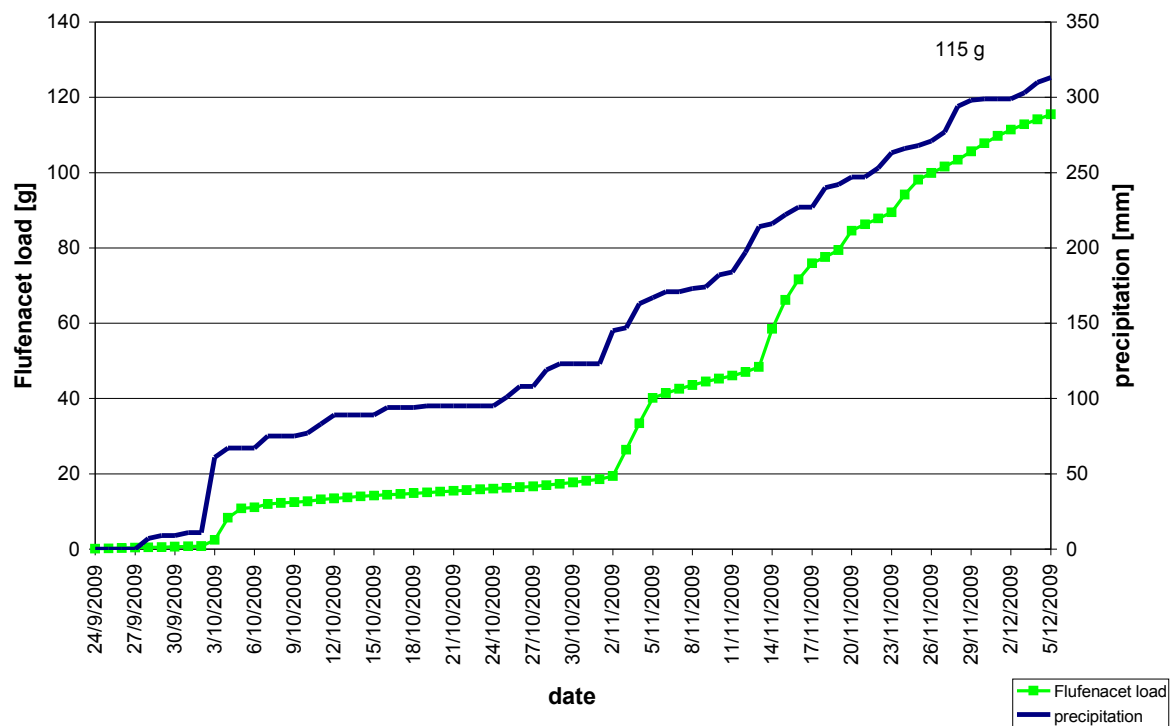


Fig. 60: Cumulated Flufenacet loads in the Kielstau at Soltfeld gauge in autumn 2009 (daily values)

6.3.5 Land use in autumn 2009

In February 2010, the land use of the Kielstau catchment was mapped using a digital map with a resolution of field scale. The cultivated field crops are presented in Fig. 61. White marks show areas which could not be mapped in that time, due to cultivation of summer crops on these fields, which were not sown in winter.

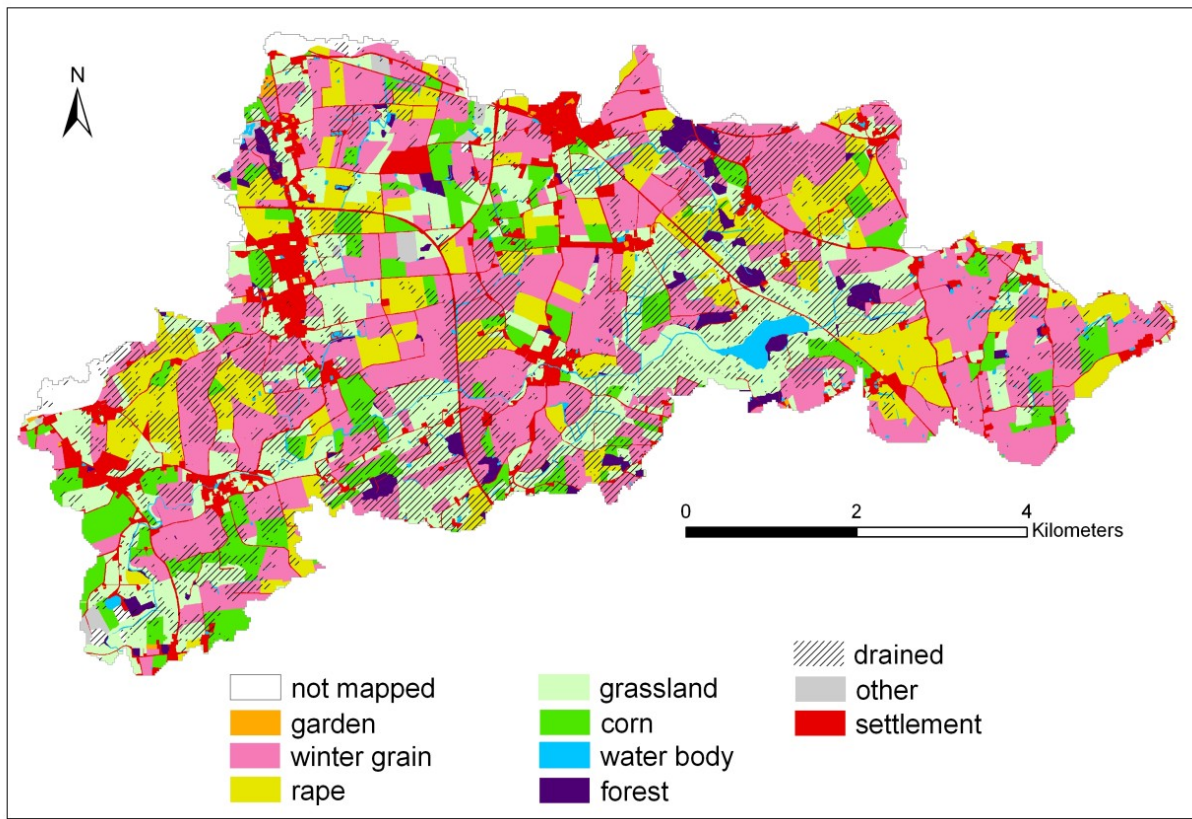


Fig. 61: Land use map of the Kielstau catchment (Jan./Feb. 2010)

Analogous to the previous vegetation periods, winter grain was the dominant crop in 2009/2010 in the Kielstau catchment with 1748 ha (36 %), followed by grassland with 1097 ha (23 %), rape with 689 ha (14 %) and corn with 491 (10 %). The detailed areas and proportions of the single crops are presented in Tab. 28.

Tab. 28: Proportions of crops in the Kielstau catchment and the Moorau subcatchment in autumn 2009

crop	catchment Kielstau		subcatchment Moorau	
	area [ha]	percentage of catchment [%]	area [ha]	percentage of subcatchment [%]
fallow	15	< 0.5	0	< 0.5
garden	14	< 0.5	2	< 0.5
water body	71	1	8	1
grassland	1097	23	151	20
corn	491	10	35	5
rape	689	14	99	13
other	31	1	10	1
forest	125	3	38	5
winter grain	1748	36	295	39
settlement	502	10	92	12
not mapped	58	1	17	2
sum	4840	100	747	100

In the subcatchment of the Moorau, winter grain was also prevailing in 2009/2010. The areas of the most frequent crops were 295 ha (39 %) winter grain, 151 ha (20 %) grassland, 99 ha (13 %) rape and 35 ha (5 %) corn.

In a second step, the digital land use map was joined with a digital drain map (Golon 2009) showing the areas with drainage systems in the catchment as black hatching in Fig. 61. From the total of 1748 ha winter grain, 630 ha were drained, corresponding to 36 % of the winter grain and 13 % of the entire catchment.

In the Moorau subcatchment, the proportion of winter grain accounted for 295 ha, including 130 ha of drained winter grain fields. The 130 ha correspond to 44 % of the winter grain areas in the subcatchment, and to 17.4 % of the entire subcatchment.

6.3.6 Flufenacet application in the catchment

The farmers of the Kielstau catchment were questioned in the same way as in the monitoring of the other herbicides. They provided information about an area of 764 ha of winter grain, which was 47 % of the entire winter grain area. The supplements were mainly Herold SC[®], Bacara[®] and Cadou[®], all containing Flufenacet as the active agent. Except for one field of 10

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ha, the agent Flufenacet was applied to each field. The application period lasted 42 days, from 18/9/2009 – 30/10/2009, depending on the harvest of the previous crop. The chronological distribution of the application is presented in Fig. 62. The highest amount of Flufenacet, 16.9 kg, was sprayed on 2/10/2009, followed by 13 kg on 29/9/2009, and 12.8 kg on 27/10/2009. The mean application amounted to 2.3 kg Flufenacet/d. During the time of application, several rainfall events > 8 mm and one rainstorm of 50 mm on 3/10/2009 took place. Up to this rainstorm, 61 % (62.4 kg) of the requested applied amount was sprayed.

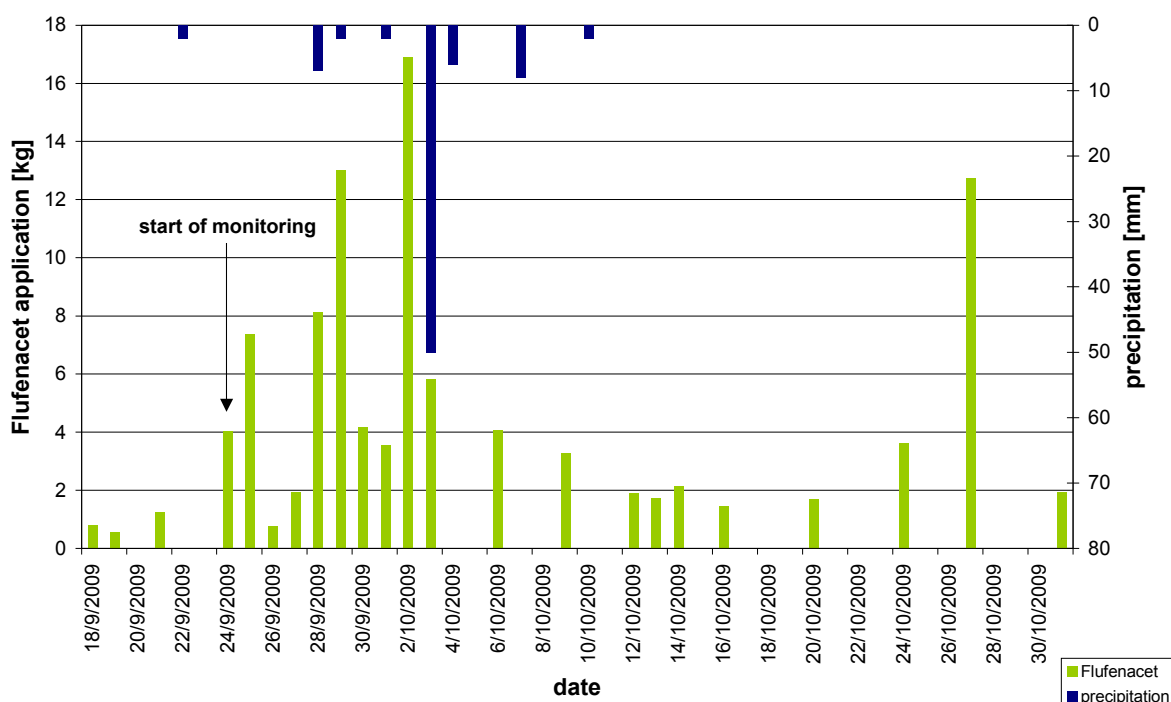


Fig. 62: Distribution of Flufenacet application in the Kielstau catchment in autumn 2009

It is assumed that the data of the farmers are representative for the catchment and can be extrapolated on the 1748 ha winter grain area. Hence, 236 kg Flufenacet were possibly applied on catchment scale, and 40 kg on subcatchment scale (Tab. 29). These 236 kg of Flufenacet describe the maximum potential discharge from the fields into non-target areas. From this, 86 kg were applied to drained winter grain fields on catchment scale, and 18 kg on drained winter grain fields in the Moorau subcatchment.

Tab. 29: Potential discharge of Flufenacet from winter grain fields in autumn 2009

	Area [ha]	Flufenacet [kg]	Moorau	Area [ha]	Flufenacet [kg]	Kielstau	Area [ha]	Flufenacet [kg]
Data of winter grain fields (farmers)	764	103	Extrapolation subcatchment winter grain	295	40	Extrapolation catchment winter grain	1748	236
Data of drained winter grain fields (farmers)	308	42	Extrapolation subcatchment winter grain drained	130	18	Extrapolation catchment winter grain drained	630	86

6.4 Surface runoff experiment with rainfall simulator

6.4.1 Soil characterization

The data of the soil characterization (Tab. 30) allows the classification as a soil with medium permeability according to German classification standards KA 5 (AG Boden, 2005). It shows the typical properties of a Pseudogley with agricultural use. The soil type Pseudogley corresponds to a Planosol after FAO classification (WRB, 2006). Further characteristics of the soil determined within the monitoring campaign in autumn 2008 are reported in Chapter 6.2.1.

Tab. 30: Characterization of the soil

parameter	soil
soil type	Pseudogley/Planosol
particle size distribution	61 % sand, 25 % silt, 5 % clay
organic matter content	4.5 %

6.4.2 Soil water content

The soil water content in the upper soil layer has a significant influence on the generation of surface runoff, hence, only the results from this depth are depicted. In Fig. 65, the vertical lines mark the beginning and end of one rainfall cycle, including one hour of precipitation with a mean intensity of 13 mm/h on the first day, and six following days as a drying period.

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The soil water content increased to 21 – 25 % when the artificial rainfall was begun and decreased in the following six dry days to the initial values of 18 – 22 %.

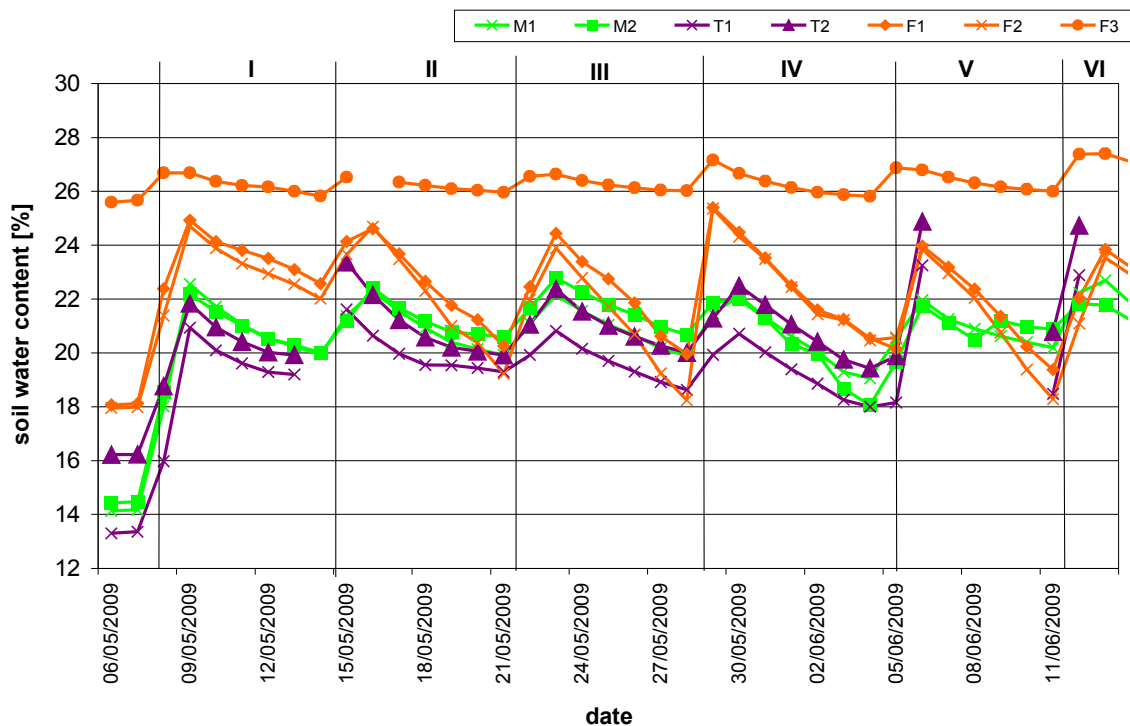


Fig. 63: Soil water content of the containers at 7 cm depth (daily mean values) with M1, M2 = soil containers with Metazachlor; T1, T2 = soil containers with Terbutylazine; F1; F2, F3 = soil containers with Flufenacet

The containers showed similar pattern of soil water content dynamics, except of container F1. Due to technical problems with the TDR probe, the initial water content was adjusted too high, hence, the soil water content was higher in F1 than in all other containers, and showed less dynamic between dry and wet conditions.

At 20 and 30 cm depth, the amplitude between minimum and maximum soil water content decreased, and the total soil water content rose with increasing depth. Results of this observation are given exemplarily of container M1 in Fig. 64.

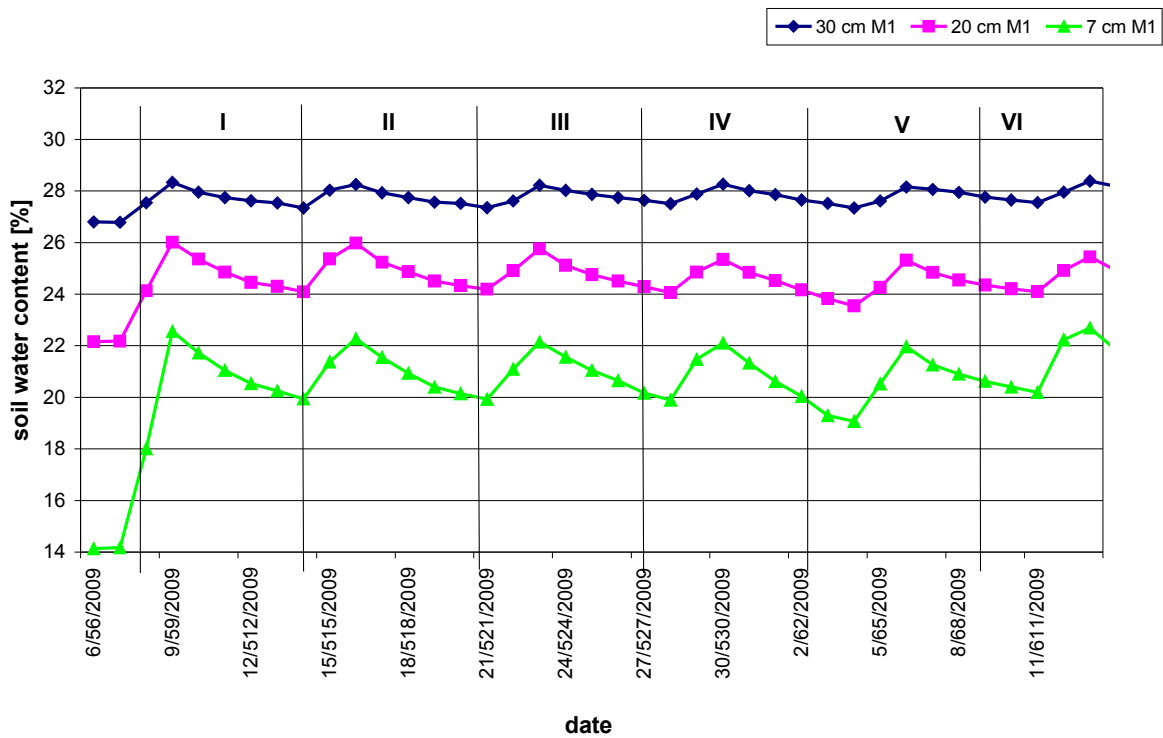


Fig. 64: Soil water content of container M1 at 7 cm, 20 cm and 30 cm dept (daily mean values)

6.4.3 Surface runoff

In the containers M1, M2, T1 and T2, the surface runoff began during the first rainfall event and reached values up to 14 % of the total precipitation (Fig. 65) The infiltration of the rain was constrained by sealing of the soil surface with proceeding rainfall (Fohrer et al., 1999). The runoff in the other containers occurred in the second cycle. It is notable that the precipitation in the third and fourth rainfall events was discharged almost completely (max. 95 %) via surface runoff, due to the developed impermeable crust on top of the soil (Dietrich, 2010*). This pattern appeared in all containers, except container F2 and F3, where this pattern occurred only in the fourth cycle. From the fifth rainfall event, the infiltration of the precipitation increased and runoff decreased because cracks arose, due to changing soil water content conditions (Fohrer et al., 1999).

6 Results

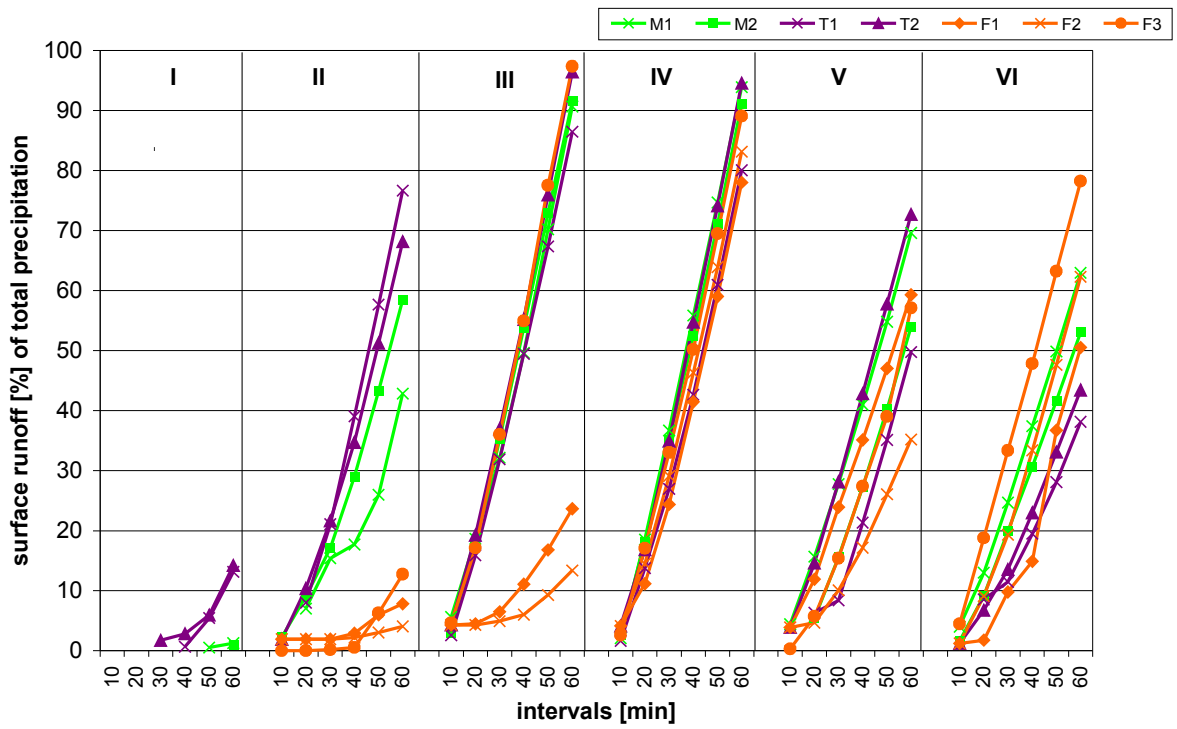


Fig. 65: Cumulated surface runoff from the plots during rainfall events with M1, M2 = soil containers with Metazachlor; T1, T2 = soil containers with Terbutylazine; F1; F2, F3 = soil containers with Flufenacet

6.4.4 Sediment discharge in surface runoff

The sediment in the runoff was determined in order to estimate the sediment related transport of the herbicides. As the sediment discharge depends on the runoff, similar discharge pattern of sediment and surface runoff can be noticed (Fig. 66) (Dietrich, 2010*). The amount of eroded sediment increased with each rainfall event and reached the maximum discharge in rainfall events III and IV. During the rainfall events III and IV, the sediment was eroded at rates of up to 60 g/m². In prior and later cycles, the results are lower, due to higher infiltration. The mean sediment discharge of all containers over the entire experiment of six cycles amounted to 142 g/m² and varied by a standard deviation of 56 g/m².

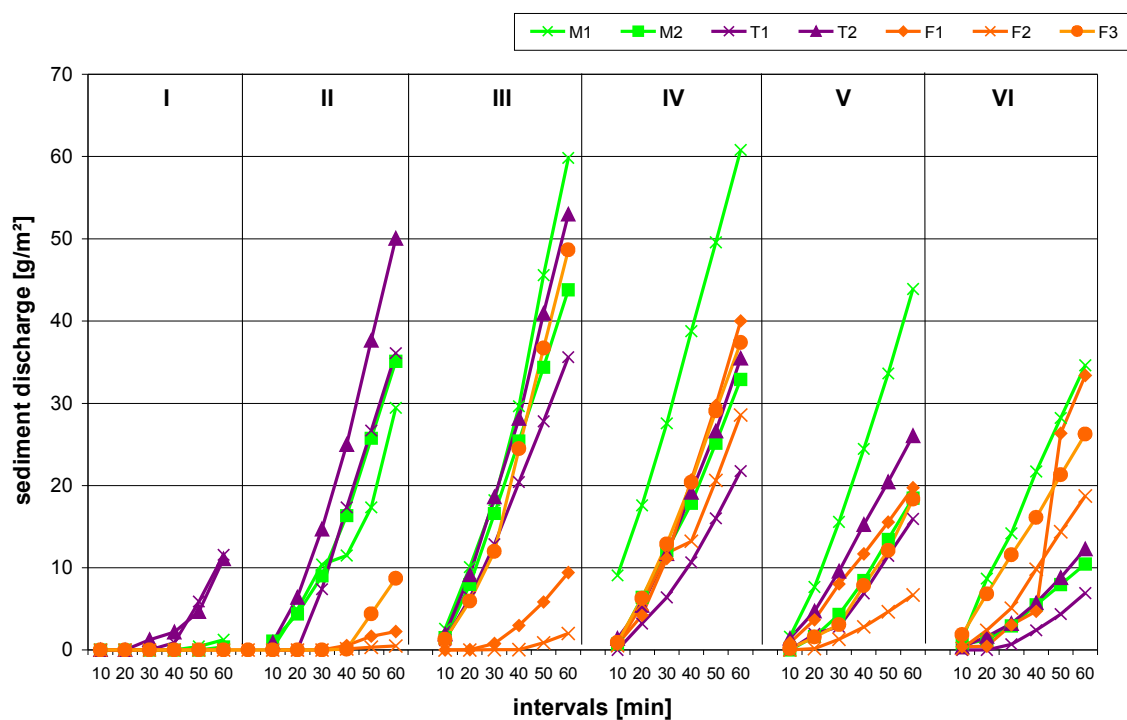


Fig. 66: Cumulated sediment discharge from the plots during the artificial rainfall events with M1, M2 = soil containers with Metazachlor; T1, T2 = soil containers with Terbutylazine; F1; F2, F3 = soil containers with Flufenacet

6.4.5 Herbicide concentrations in surface runoff

The concentrations of Metazachlor in the water phase of the 10-minute intervals were in the range of 5 to 3184 $\mu\text{g/l}$. The highest concentration was detected in the fifth interval (40-50 min.) of the first cycle, where the first surface runoff was generated. In the following intervals, the concentrations decreased exponentially. At all times, the concentration in the first interval was highest within that cycle (Fig. 67).

Terbuthylazine concentrations of 10 to 660 $\mu\text{g/l}$ were detected in the water phase. Container T1 showed the same concentration pattern as M1 and M 2 with highest concentration in the first runoff interval. In container T2, the concentrations of the second to fourth intervals (10-20, 20-30 and 30-40 min.) were 137 - 194 $\mu\text{g/l}$ and therewith significantly lower than in T1 (Fig. 67).

In the Flufenacet containers, runoff was initiated only in the second cycle. The concentrations in the water phase amounted from 1.7 to 207 $\mu\text{g/l}$. Among these containers, a different development of the concentration can be observed (Fig. 67): The pattern of concentration in F3 followed those of M1, M2, T1 with highest concentration of 207 $\mu\text{g/l}$ in the first interval, when surface runoff occurred. The concentrations of container F1 and F2 showed the development of container T2 with significantly lower concentrations in the range of 31 and 41 $\mu\text{g/l}$. It was observed that container F1 showed this characteristic also in the third cycle. Besides, the concentrations of Flufenacet in container F2 were remarkably higher in the first interval (0-10 min.) of cycle III and V than in the last interval of the previous cycle.

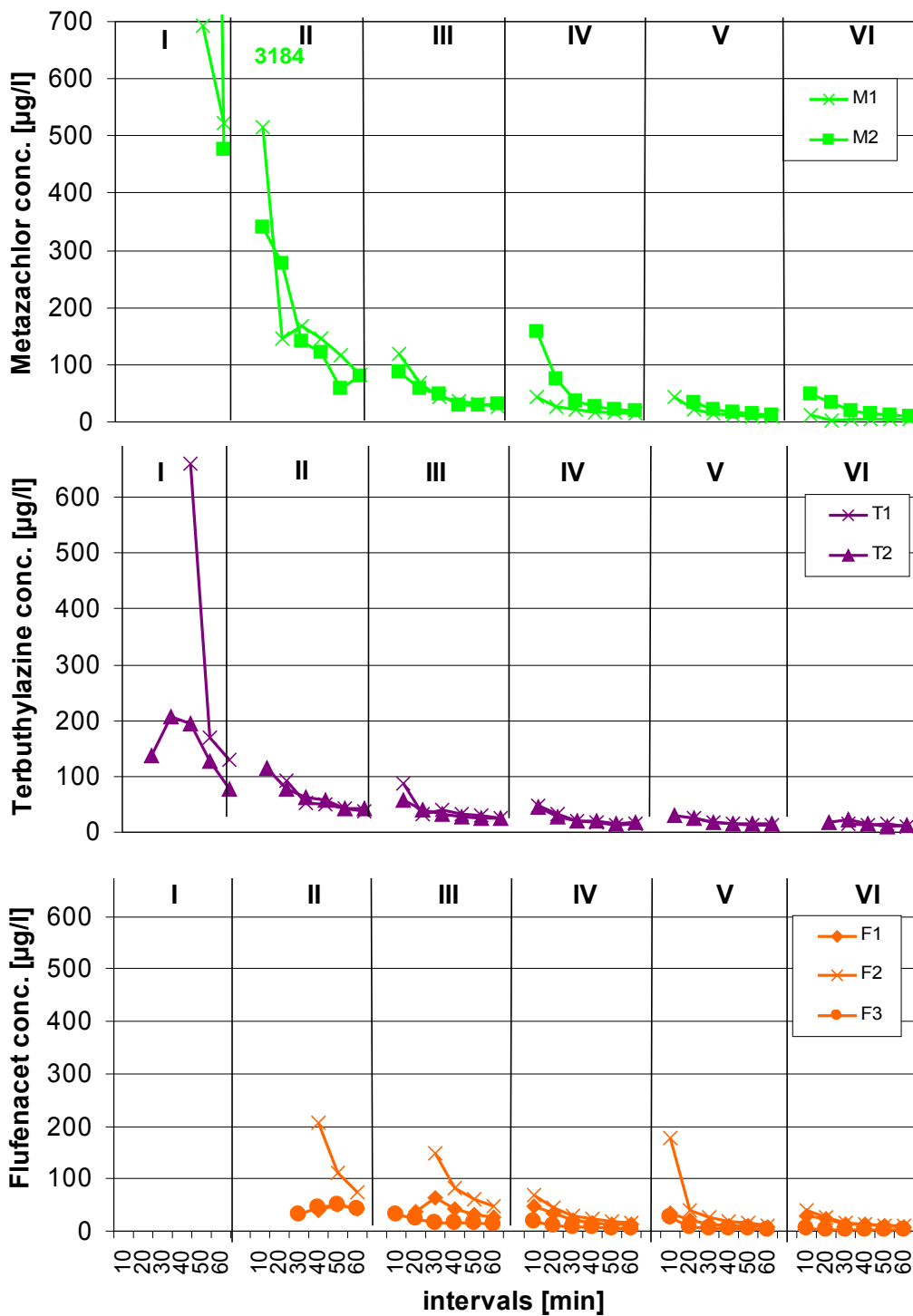


Fig. 67: Herbicide concentrations in the water phase of the surface runoff with M1, M2 = soil containers with Metazachlor; T1, T2 = soil containers with Terbutylazine; F1, F2, F3 = soil containers with Flufenacet

6.4.6 Herbicide loads in surface runoff

The pattern of the loads, discharged with the surface runoff, began slowly in the first cycle, then increased exponentially during the second to fourth cycle and ended in a saturation phase in cycle V/VI (Fig. 68). The slope of the limb and the point of time, when the phase of constant loss set in, varied for the three herbicides. For Metazachlor (M1, M2) and Flufenacet (F3) the discharged load stagnated during the last cycle, while it was still increasing for the other containers. The total load of the six cycles from the 0.2 m² plot was 345 µg (M1) and 440 µg (M2) Metazachlor, 1.9 % (M1) and 2.5 % (M2) of the amount applied. For Terbutylazine, loads of 318 µg (T1) and 310 µg (T2) were determined, corresponding to 6.6 % (T1) and 5.7 % (T2) of the amount applied. The loads in containers F1, F2 and F3 accounted for 94 µg, 111 µg and 87 µg Flufenacet; 2.1 %, 3.8 % and 3.0 % of the amount applied.

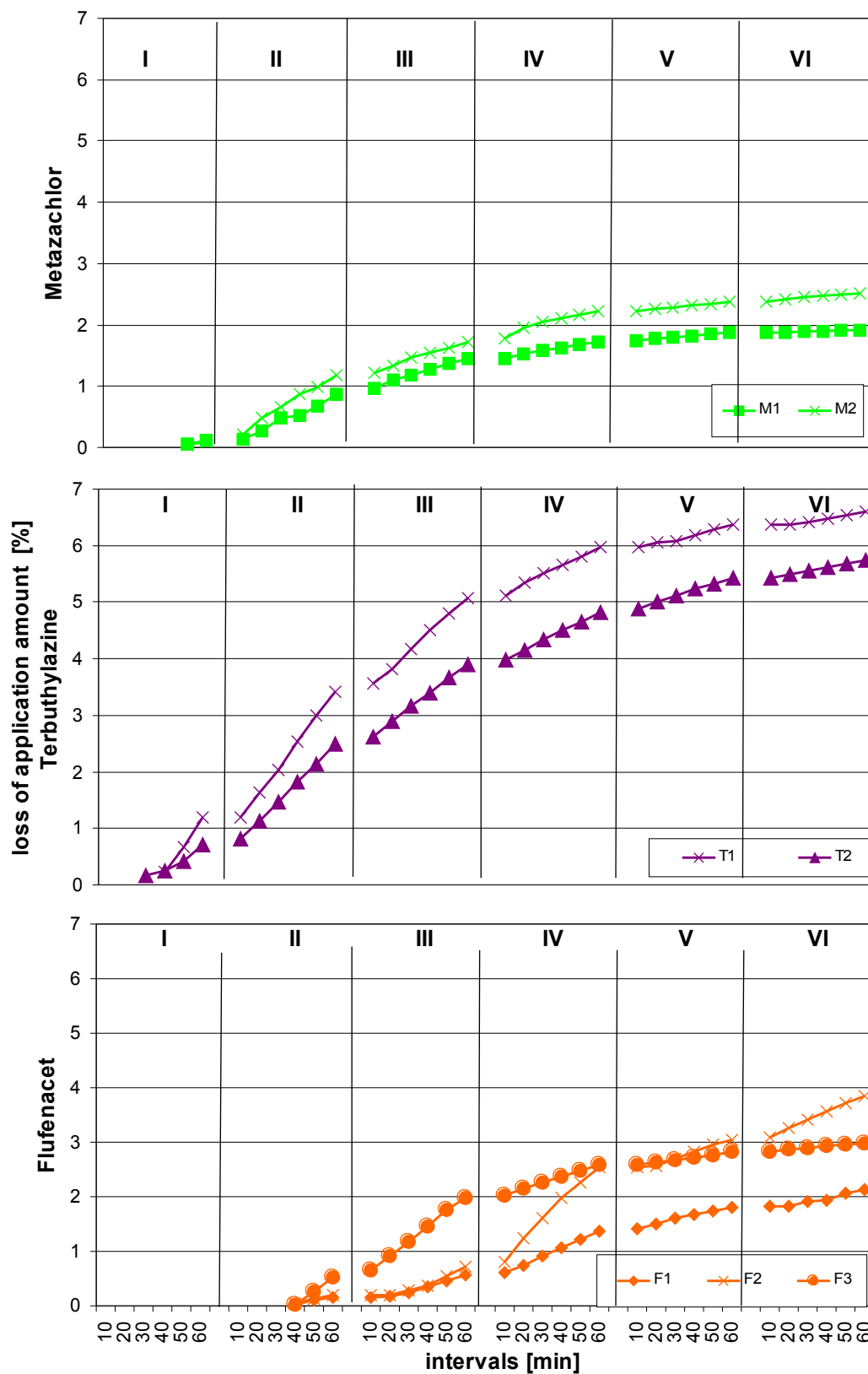


Fig. 68: Cumulated herbicide loss in the water phase of the runoff/plot in [% of herbicides applied] with M1, M2 = soil containers with Metazachlor; T1, T2 = soil containers with Terbutylazine; F1; F2, F3 = soil containers with Flufenacet

7 DISCUSSION

7.1 Terbutylazine monitoring in spring 2008

7.1.1 Hydrological parameters in spring 2008

The monitoring period was characterized by low precipitation. Hence, the discharges of the Moorau and the Kielstau were lower than the long-term averages, and the discharge of the drainage was below the potential measure, stopping 22 days after the beginning of the observations.

The Moorau flow reacted simultaneously to the precipitation events of 26/5/2008, 16/6/2008, 27/6/2008 and 28/6/2008 and peaked with two days of delay to the rainfall at 22/6/2008. The average travel time of water in the Moorau subcatchment can therefore be assumed to be in the range of one to two days. Jelinek (2008) determined average flow velocities in the Moorau of approximately 0.06 m/s, hence, the travel time of water along the 5 km long course of the Moorau takes approximately one day. The flow of the Kielstau responded on the same day to the rainfall events on 26/5/2008, and with a delay of one day to the rainy days beginning at 11/6/2008. The maximum discharge within the monitoring was reached four days after the last rainstorm on 22/6/2008. Flow velocities in the Kielstau were determined at average values of approximately 0.1 m/s (Tavares, 2006), and indicate the travel time of water along the 17 km long course of the Kielstau to be approximately two days. These data reveal a broad range in travel time, of one to four days, through the entire catchment of the Kielstau. As the Kielstau catchment is more than six times larger than the subcatchment, the distribution of rainfall is spatially higher, resulting in a long period of water transport from throughout the catchment to the outlet in Soltfeld. Therefore, peaks of discharge are less sharp and tend to tail (Holvoet, 2006). Nevertheless, there are uncertainties regarding the discharges of the two streams and the observed precipitation. The discharge of the Moorau increased on 20/5/2008 without an observed rainfall event at Satrup gauge, for example. Furthermore, the

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discharge first decreased after the rainstorm on 26/5/2008, but remained at 0.028 m³/s for two days before decreasing again. From 2/6/2008 to 15/6/2008, the Moorau discharge stayed constant at 0.026 m³/s. The waste water treatment plant in Hürup discharges into the Moorau, and its discharge may overlay that of the Moorau during this low flow period causing the constant flow over almost two weeks. On 31/5/2008, the discharge of the Kielstau rose to a value similar to that after the 11 mm rainstorm on 26/5/2008, but precipitation was not monitored at Satrup gauge. Moreover, the discharge increased continuously during the rainy period from 6/6/2008 to 22/6/2008, though larger rainfall events of 5 – 9 mm occurred three days after each other. Rainstorms of this intensity caused a stepwise and irregular rise of the discharge, that was observed during the monitoring of Metazachlor and Flufenacet. These examples reveal that the rainfall distribution in the catchment may have varied to a great extent, and that precipitation at the single sampling points may have differed from the observed data at the rain gauge in Satrup. The distances of the rain gauge to the single sampling points are roughly 8 km to those of the Moorau and the Kielstau at Soltfeld, and 10 km to drained field 1 (see Chapter 5.1.3.1). The variability of rainfall can already be observed in areas smaller than the Kielstau catchment. Within an area of 0.25 km² in southern Denmark, the coefficient of rainfall variability amounted to 26 % (Jensen & Pedersen, 2005; Pedersen et al., 2010). The simulations of Mandapaka et al. (2009) revealed that heterogeneity in rainfall has a larger impact for smaller scale basins whose pattern of peak flow were dominated by the rainfall intensity and spatial distribution. The hydrological response of larger scale basins was driven by rainfall volume and river characteristics.

7.1.2 Terbutylazine concentrations

Drained field 1

The concentrations in the drainage water, varying between > 25 ng/l and 301 ng/l, showed that Terbutylazine was relocated in the beginning of the investigation period independently from observed precipitation. During the time that drain flow occurred, the only rainfall events appeared on 25/5/2008 and 26/5/2008. They caused an increase of the Terbutylazine concentrations on the same day (26/5/2008) and two days later (28/5/2008), to the maximum values of the monitoring. The enhanced amount of percolating water enabled a higher quantity of pesticide to be dissolved and transported more rapidly via drainage (Czapar et al., 1994; Kla-

divko et al., 1991). As explained in chapter 2.1.2, the herbicide can adsorb to the organic matter of the soil after application. The strength of these bondings and further desorption is crucial for the leaching behaviour. Terbutylazine as a non-polar compound belonging to the Triazine group, is adsorbed specifically by hydrogen bonds and unspecifically by hydrophobic interactions to the organic matter of the soil. Basically, the bonds by hydrophobic interactions are counted as weak adsorption mechanisms, and hence are likely to be separated. During the contact between water and soil matrix, the compound can be desorbed from the organic matter and a considerable amount can consequently be released. By further leaching, the compound is transported with the water to drains and groundwater (Boivin et al., 2005; Chefetz et al., 2004; Haider & Auerswald, 1997). Terbutylazine is classified as moderately mobile, due mainly to its water solubility of 6.6 mg/l and organic carbon sorption coefficient of 151 – 333 ml/g.

It can not be explained which water volume transported the Terbutylazine downwards, as its release began before precipitation. Michaelsen (1999) also detected herbicide concentrations in tile drains on dry topsoil seven days before the first rainfall event, assuming that restricted areas of higher soil water content caused by compressed lanes or depressed location enabled a detectable transport. In a study by Bergström & Jarvis (1993), higher concentrations of Dichlorprop were found in the leachate from a clay soil under a low irrigation regime than from one under an intense irrigation regime. They attributed this to macropore flow in the soil. Due to the low discharge beneath the potential measure, the course of the drain water is not known. These data could have provided useful information about the pesticide transport. If the pore water movement was forced by the gradient, and if gravity flow drew water into cracks, then some of the pesticides could have moved through the topsoil to the tile drains. Furthermore, the possibility must be considered that precipitation occurred at the location of drained field 1, but not at the rain gauge in Satrup. Analysis of samples taken before application showed no Terbutylazine concentrations, hence, contaminations from the year(s) before can be excluded.

In other studies, the Terbutylazine concentrations in drain water are reported with 45 µg/l (Kreuger, 1998) and 1.4 µg/l (Traub-Eberhard et al., 1995).

Moorau

In the Moorau, the maximum concentration (96 ng Terbuthylazine/l) was detected on 21/5/2008, one day after a discharge peak. However, the first rainfall events were observed four days later on 25/5/2008 and 26/5/2008. It is possible that precipitation occurred in a very small spatial distribution in the area of the Moorau, as the flow of the Kielstau did not rise at that time. The concentration maximum did not differ significantly from the other concentrations of that period (76 – 87 ng/l). Hence, it can not be ascertained that this small peak of discharge led to the highest concentration during the observation, or that these fluctuations represent common variations. It is observed that the concentrations decline with decreasing flow of the Moorau (27/5/2008 – 8/6/2008) as indicated in other studies e.g. (Neumann et al., 2002). They did not incline significantly, however, with increasing discharge that began on 16/6/2008. The maximum and minimum discharge values of the Moorau fluctuated approx. 22 % from the mean discharge while those of the Kielstau fluctuated approx. 89 % from the Kielstau mean discharge. It is possible that the antecedent soil water content in the subcatchment was lower than in the entire catchment, and that rainfall was stored in the soils to a greater extent than in the entire catchment. Most of the rainfall beginning on 11/6/2008 was retained by soil, therefore, the discharge of the herbicide was low.

Kielstau

In the Kielstau, the Terbuthylazine findings on 21/5/2008, 23/5/2008 and 24/5/2008 appeared before rainfall was recorded, and similarly in the Moorau samples. These findings are detected during decreasing discharge, therefore, are not rainfall induced. Hence, a relocation with water as transport medium does not seem to be likely, since alone the presence of water in the soil pores could have supported vertical movement. Within this period, the application of 3.1 kg and 3.6 kg Terbuthylazine on 22/5/2008 and 23/5/2008 took place (Fig. 23), so that an entry of Terbuthylazine during and/or after the application (i.e, drift or cleaning procedures) can be considered. Kreuger (1998) attributed non-rainfall associated pesticide findings to handling mistakes and mismanagement. The rainfall on 26/5/2008 caused an immediate increase of the discharge and the maximum Terbuthylazine concentration was detected one day later on the recession limb of the Kielstau discharge. The concentration diminished with decreasing flow rate, as was likewise reported by Leu et al. (2004b), who observed higher concentrations during high flow situations and lower concentrations in low flow situations fol-

lowing rainfall events. From 16/6/2008 to 22/6/2008, the Terbutylazine concentrations increased during rising discharge. It is assumed that during the period of 8/6/2008 to 15/6/2008, water was standing in soil pores. Therefore, an equilibrium between adsorbed Terbutylazine and dissolved Terbutylazine in the pore water could have been established. An increasing amount of Terbutylazine was desorbed from the soil matrix and transported to the surface water. However, this coincidence ended on 23/6/2008, when the discharge was still increasing, but the concentrations had already dropped.

Regarding the transport mechanisms, the simultaneous incidence of Terbutylazine concentrations and increased flow implies that the herbicide was transported with rainwater and not held back during the transport. Hence, it can be attributed to preferential pathways into subsurface drains. The findings in the catchment support the concept of a rapid transport mechanism in areas with subsurface drainage networks. These networks increase drainage, either by facilitating the removal of infiltrating water or by collecting surface runoff water (Schottler et al., 1994).

Comparing the monitored Terbutylazine findings at all scales, it can be observed that they follow generally the same pattern (Fig. 69). At all sampling points, the first findings were detected before the earliest observed rainfall. The maxima occurred as a direct response to the rainstorms on 25 and 26/5/2008, and decline with reduced flow. While the drainage fell dry on 7/6/2008, no findings were monitored in both rivers during the low flow period from 9/6/2008 – 15/6/2008. The subsequent Terbutylazine results were higher in the beginning than those before the break. This indicates that the change between rainy and rainless period led to changes of the soil properties and a higher release of pesticides. The phenomenon of similar concentration patterns on different scales was observed in other studies as well (Leu et al., 2005; Michaelsen, 1999).

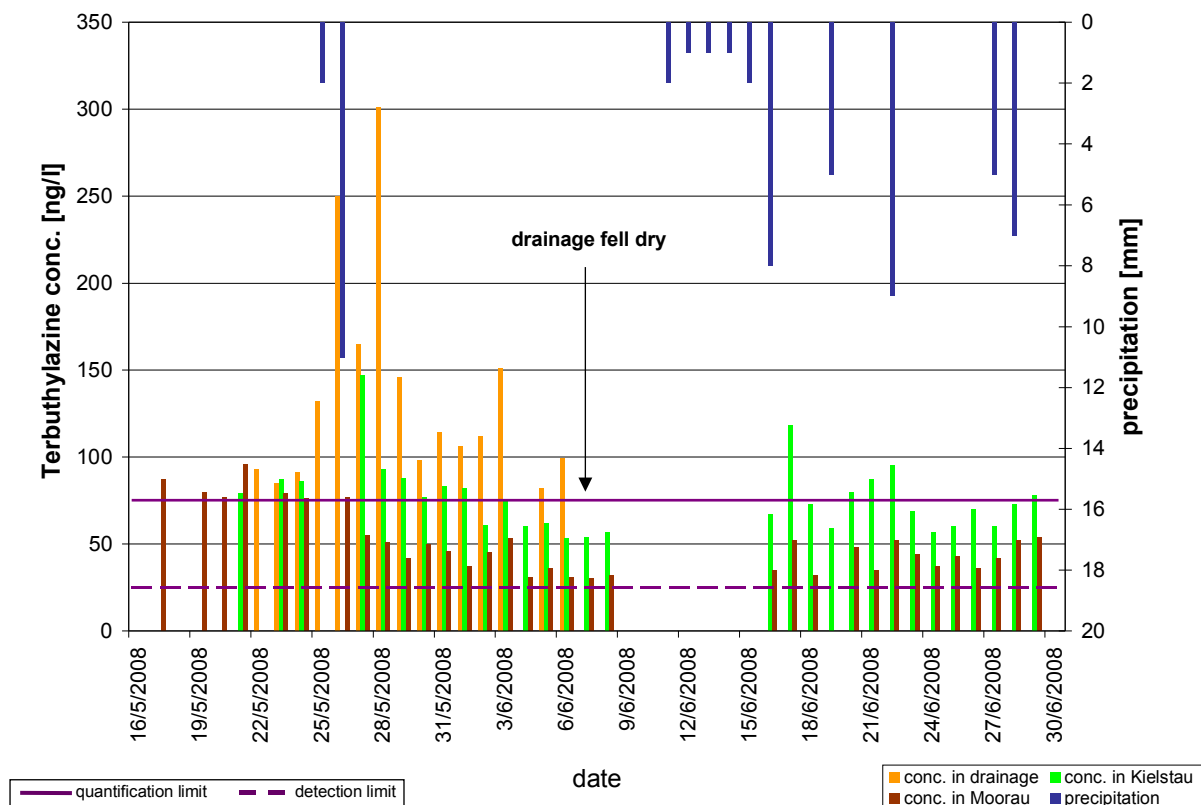


Fig. 69: Pattern of Terbutylazine concentrations on the drained corn field, in Moorau and in the Kielstau at Soltfeld in spring 2008 (daily values)

In general, highest concentrations are expected on the smallest scale, due to lowest dilution by flows. In fact, the concentrations on drained field 1 were the highest, with a range of 85 – 250 ng/l. The concentrations in the Moorau subcatchment were lower (30 – 96 ng/l) than in the entire catchment (53 – 147 ng/l). The proportion of corn fields in the subcatchment is 4 % (7 %) less than in the entire catchment (11%). This can result in lower Terbutylazine concentrations in the Moorau than in the Kielstau. Furthermore, the corn fields in the subcatchment are located further away from the sampling point than they are in the other parts of the catchment. These two aspects may explain the lower concentrations in the subcatchment.

Comparing the Terbutylazine concentration of the Moorau (30 – 96 ng/l) and the Kielstau (85 – 250 ng/l) with those from other studies, they are in the lower range of the following examples: 45 ng/l (Palma et al., 2009), 50 – 250 ng/l (Müller, 2000), 220 ng/l (Hildebrandt et al., 2008) and 1200 ng/l (Neumann et al., 2002). Depending on several factors, such as amount applied, characteristics of the area, soil properties, rainfall duration and rainfall intensity, the concentrations may vary in a wide range.

7.1.3 Potential discharge and losses

Herbicide loads in the drainage of drained field 1 could not be quantified, due to discharge values below the potential measure.

The loads transported in the Moorau and Kielstau showed no significant increase after the first discharge triggering rainfall events on 25 and 26/5/2008. In contrast, the maximum daily load determined in the Moorau appeared on 21/5/2008 and accounted for 0.232 g Terbutylazine, corresponding to 6.5 % of the total Terbutylazine applied to the subcatchment. Instead, the rainfall on 25 and 26/5/2008 caused a continuous enhancement of the cumulated load curves lasting from 26/5/2008 to 8/6/2008 in the Moorau, and from 27/5/2008 to 8/6/2008 in the Kielstau. Loads of 1.04 g (29 % of total 3.58 g) originated in the Moorau, and 4.70 g (29 % of total 16.21 g) in the Kielstau. Numerous small rainfall events commencing on 11/6/2008 effected, at least, a slight enhancement of the Kielstau flow. However, until 16/6/2008, no loads were observed in both rivers. It is possible that within these five days, rapid transport mechanisms by preferential flow probably were not dominant but matrix flow, including a larger volume of the soil matrix (Michaelsen, 1999). Hence, the relocation of Terbutylazine took several days. Overall, the cumulated loads increased continuously in the remaining time span with numerous rainfall events, leading to a partial load of 1.09 g Terbutylazine (31 % of total) in the Moorau, and 8.49 g (51 % of total) in the Kielstau. Basically, both rivers showed similar patterns of observed cumulated loads.

Information from local farmers concerning their applications, in conjunction with land use mapping, enabled the determination of amounts of Terbutylazine sprayed on the fields, and that potentially could be dislocated into the Moorau and Kielstau. In total, 11.5 kg herbicide were applied in the subcatchment of the Moorau and a load of 4.4 g herbicide was detected at the outlet of the Moorau during the six weeks of monitoring. This amount corresponds to a proportion of < 0.01 % of the applied Terbutylazine. Considering the entire catchment of the Kielstau, 114.5 kg of Terbutylazine were applied to the fields and 20.1 g were observed at the outlet of the catchment in Soltfeld, the latter an amount equal to 0.01 % of the total amount applied. In the literature, values for the Terbutylazine loss in comparison to the applied amount are not available. Müller (2000) determined losses of 52.5 mg Terbutylazine/ha, which is in the same range as the losses of 37 mg/ha in the Moorau subcatchment and of 44 mg/ha in the Kielstau catchment. Terbutylazine, like Atrazine, is counted among the group of Triazines, therefore, percentaged losses of Atrazine and, additionally,

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of the Phenylurea Isoproturon are cited. Nevertheless, it should be mentioned that they differ in their properties. As examples, the differences in water solubility (Terbutylazine 6.6 mg/l, Atrazine 35 mg/l, Isoproturon 157 mg/l), organic-carbon sorption constant (Terbutylazine 231 ml/g, Atrazine 100 ml/g, Isoproturon 122 ml/g) and $DT_{50\text{soil}}$ (Terbutylazine 75 d, Atrazine 75 d, Isoproturon 12 d) are reported (footprint, 2009). Atrazine losses vary from 0.33 % (Ng et al., 1995), 0.27 – 1.14 % (Accinelli et al., 2002), and up to 1,6 % -1,8 % (Ng et al., 1995) of the applied amount. Michaelsen (1999) determined 2.1% loss of Isoproturon in a set up similar to this monitoring, while Harris et al. (1994) detected 0.5 % loss from drained fields. The cited loss values show a broad range not only by variables influencing pesticide losses, but also by variables in monitoring periods, selection of compounds, and precipitation conditions.

7.2 Metazachlor monitoring in autumn 2008

According to KA 5 standards, data of the soil characterization allow classification as a soil with medium permeability (AG Boden, 2005). The soil shows the typical properties of an agricultural Planosol.

7.2.1 Hydrological parameters in autumn 2008

The monitoring period was characterized by large amounts of precipitation (215 mm) leading to high water levels in the entire catchment and a flood situation on drained field 2 in October. On all scales, the discharge responded to rainstorms within one day, and displayed increasing values. Highest discharge values were observed in November, though the rainfall intensity was lower than in October. The degree of saturation of the soil water storage in the catchment increased with time, due to numerous rainfall events. Hence, rainstorms of 10 – 12 mm induced significant increases of discharge. The groundwater level on drained field 2 also responded immediately to rainstorms and corresponded to the fluctuations in drain flow. The overall rising groundwater level also confirmed the increasing saturation of the soil water storage on the field scale.

7.2.2 Metazachlor concentrations

Drained field 2

Metazachlor was first observed in the drainage water of drained field 2 five days after application, without an increase in drain flow, and in a single finding. As several authors have observed rapid transport of pesticides by preferential flow on a field scale to subsurface drains (e.g. Köhne et al., 2009; Kördel et al., 2008) (see Chapter 2.1.2), this phenomenon must be considered as a possible explanation for the observed concentration peak. Only ten days after application, the water of the rainfall events from 1/9/2008 – 8/9/2008, percolating through a large soil volume (matrix flow), reached the drainage and displaced the Metazachlor. Metazachlor concentrations were observed for several days, with the highest value (558 ng/l) at the beginning of this Metazachlor flush, and then, due to effects of dilution, decreasing exponentially (Kladivko et al., 1991). Highest concentrations during the first drainage event(s) after application are often observed (e.g. Kladivko et al., 2001; Shipitalo et al., 2000). The second flush of Metazachlor reached the drainage on 7/10/2008 three days after the rainstorms from 30/9/2008 to 3/10/2008. Due to this delay, herbicide transport by matrix flow is assumed to be more likely than by preferential flow. In a pattern similar to the first flush, the highest concentration occurred in the beginning, then decreased exponentially on the descending limb of the discharge peak. Further results during the flooding of the drain pipe inspection shaft could not be explained with certainty, because the samples were taken from the accumulated water in the drain pipe inspection shaft. Nevertheless, Metazachlor was detected in high concentrations during the entire flood period. During the discharge peak from 9/11/2008 to 15/11/2008 Metazachlor was detected in the drainage water with concentrations up to 444 ng/l, while almost no Metazachlor was observed during the following discharge peak ten days later. It can be assumed that degradation had proceeded, and that Metazachlor molecules were bonding strongly to the soil organic matter, hence, free Metazachlor molecules were removed in concentrations below detectable limits. For verification of this hypothesis, the monitoring period had to be prolonged. Reviewing the literature, Kreuger (1998) observed Metazachlor in subsurface drains. The detected concentrations were up to 200 µg/l in a culvert of a subsurface drain.

In the groundwater on drained field 2, 46 days after application, Metazachlor was detected for a limited time of 10 days only. The findings coincided with the flood situation on the field,

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and a rise of groundwater level, but the groundwater level was not highest during this period of Metazachlor findings. It is possible that, during the flood situation, due to cracks and leaks, surface water with dissolved Metazachlor passed the sealing on top of the groundwater pipe, and moved downward outside the pipe. Hence, Metazachlor could enter the shallow groundwater during this specific time span. Another explanation might lie in the exchange processes of water and Metazachlor that occur between the upper soil layer and the shallow groundwater, which was only 49 to 79 cm below surface during that time.

Moorau

In the Moorau water, Metazachlor was not detected in concentrations above the detection limit of 25 ng/l during the monitoring phase, though the proportion of rape in the subcatchment (16 %) was higher than in the Kielstau catchment (10 %). It is possible that the rape fields were located sufficiently away from the Moorau, that detectable amounts of Metazachlor were not discharged into the Moorau. Sorption and degradation processes on the way to the Moorau could have reduced the transport of the herbicide. Secondly, the application period of Metazachlor could have lasted for several weeks and not all of the catchment was treated on the same day, but probably one after another. Hence, Metazachlor was available for transport only in small amounts over a longer time and resulted in Metazachlor concentrations below 25 ng/l (Leonard, 1990). Furthermore, Leu et al. (2004a) and Gomides Freitas (2005) observed in a small catchment, that single fields contribute differently to pesticide discharge in spite of similar weather conditions and location in the same type of landscape. But also within small areas the intrinsic field properties can vary significantly and result in diverse pattern of pesticide loss.

Kielstau

In the Kielstau, the observed Metazachlor findings were rare and the concentrations ranged close to and below the quantification limit of 70 ng/l (29 – 88 ng/l). Four of the eight findings were below the quantification limit. As most findings occurred at the beginning of event driven discharge peaks, a rapid transport of Metazachlor through the soil into the Kielstau can be assumed. However, on 11/9/2008, a single Metazachlor peak was observed two days after the last rainstorm, which could have originated from farmyards, because, according to farmers' information, most applications in the catchment were conducted on 10/9/2008. Müller (2000) determined Metazachlor concentrations in the river Zvester Ohm between 0.05

and 6.12 $\mu\text{g/l}$, and Kreuger (1998) observed similar concentrations up to 5.1 $\mu\text{g/l}$ at the outlet of the Vemmenhög catchment.

Comparing the Metazachlor concentrations on drained field 2 and in the Kielstau, it is observed, that Metazachlor was detected in the Kielstau in direct response to a rainstorm. On drained field 2, the herbicide reached the drain with two and four days delay to a rainfall event (Fig. 70). The results reveal that dislocation on the field scale was slower than on the catchment scale, meaning more transport by matrix flow than by preferential flow (Michaelsen, 1999). Furthermore, the variation in ranges of concentration can be observed. The concentrations in the Kielstau catchment were approximately three times smaller than on the field scale. This can be attributed to dilution effects of river discharge caused by the meteorological and hydrological conditions, such as precipitation amount, discharges and groundwater levels, during monitoring.

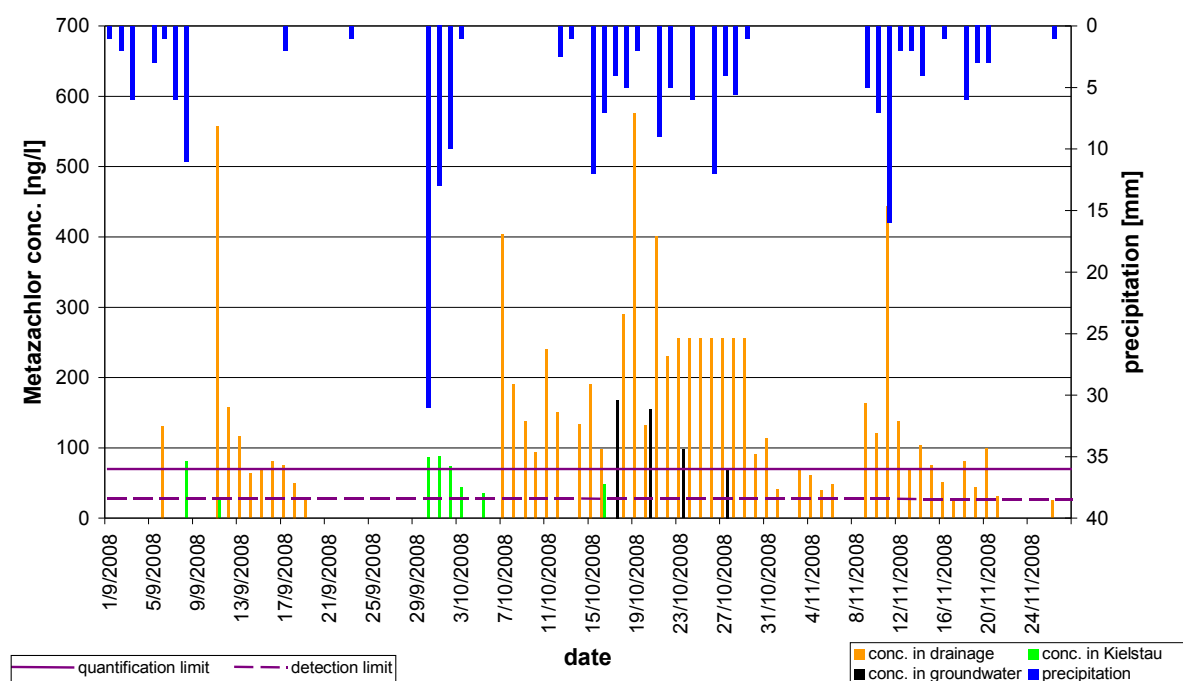


Fig. 70: Pattern of Metazachlor concentrations on drained field 2 and in the Kielstau at Soltfeld in autumn 2008 (daily values)

7.2.3 Potential discharge and losses

Drainage

The daily loads observed in the drainage water were in the range of 0.01 – 19.3 mg Metazachlor, and the daily mean value amounted to 2.5 mg. Though the highest concentration was detected on 11/9/2008, the daily load accounted for 6.1 mg Metazachlor (2.8 % of 219 mg total load), due to lower drain flow. During the flood situation, significantly higher daily loads were determined (0.6 – 16.5 mg), resulting from increasing drain flow. But these values include a higher uncertainty due to technical problems in the flooded drain pipe inspection shaft. The highest daily load of 19.3 mg Metazachlor (8.8 % of total load) was observed 71 days after application, on 11/11/2008, when both drain flow and concentration showed high values. Using the model MACRO, Lewan et al. (2009) simulated the loss of pesticides to subsurface drains with scenario D4, the climatic conditions of Skousbo, Denmark. They observed that in autumn, the medium-term precipitation (30 – 90 days after application), and not the immediate precipitation after application, is one of the most sensitive variables controlling pesticide transport. The observed rainfall events starting at the end of September and lasting until the end of monitoring can be counted to this medium-term precipitation. The level of the cumulated daily Metazachlor loads rose 2 days (9/9/2008) and four days (6/10/2008) later than the precipitation level. At the beginning of the monitoring period, the soil water content on drained field 2 was low. It rose at the end of September due to numerous rainfall events after the end of September. The soil water storage could retain more water until the beginning of October, hence, water and dissolved Metazachlor needed two and four days of travel time to enter the drain pipe. Over time, the soil water storage was saturated to an amount sufficient for Metazachlor to be discharged in coincidence with rainstorms on 29/10/2008 and 11/11/2008.

The drainage system on drained field 2 drains only a part of the field, therefore the catchment of the drainage system was estimated to be between 1000 and 4000 m². From the applied amount of 750 g Metazachlor/ha, it was calculated that 75 g Metazachlor were sprayed on 1000m² and 300 g Metazachlor on 4000m² of the catchment, if the drained area was that large. Therefore, the determined total Metazachlor load released via drainage amounted to 219 mg and corresponds to 0.29 % of the applied amount on 1000 m² or 0.07 % of the applied amount

on 4000 m². A loss of 0.5 – 2 g Metazachlor per hectare of rape area via drainage can be extrapolated, on the basis of the assumed size of the drainage catchment.

Kielstau

In the Kielstau, at the Soltfeld gauge the daily loads ranged from 0.07 – 2.8 g/d and the average was 0.58 g/d. The main loads were discharged into the Kielstau from 30/9/2008 – 5/10/2008 as a response to the rainstorms on 30/9/2008 – 2/10/2008. It accounted for 8.8 g Metazachlor and corresponds to 17 % of the total load of 51 g. The Metazachlor concentrations on 8/9/2008 and 2/10/2008 were in the same range (80 ng/l and 74 ng/l, respectively), but the loads varied significantly (0.66 g and 2.8 g, respectively), due to their ranges of discharge (0.1 m³/s and 0.4 m³/s, respectively). These results reveal that, in spite of high pesticide concentrations in surface water after rainstorms that occur soon after application, the loads can be low because of reduced discharge. High discharges, however, that appear farther away from the application, can effect high loads in spite of low concentrations. Hence, in general, highest loads can not be expected immediately after application. Equivalent to the drainage, the increasing saturation of the soil water storage shortened the delayed response time of discharge load to precipitation, which was three days at the beginning of September and was compensated at the end of September.

The total load of 51 g Metazachlor, discharged into the Kielstau during the monitoring, corresponds to 0.02 % of 229 kg applied to the rape fields of the catchment. A loss of 110 mg Metazachlor/ha could be derived from determined loads and applied amounts in the catchment. On the catchment scale, Kreuger (1998) observed significantly higher Metazachlor losses of 0.32 – 0.44 %, depending on seasonal fluctuations, while Müller (2000) determined losses of 77.5 – 160 mg/ha on a subcatchment scale similar to the one of this study. In another study losses from 0.16 % to 0.0004 % for numerous pesticides. The losses of Metazachlor were assessed as important (Müller et al., 2003).

The Metazachlor loss, given in percentage and the amount discharged per hectare, differ significantly between field and catchment scale. In general, extrapolating results from field scale to larger scale includes uncertainties (Wauchope et al., 1995). Leu et al. (2004a) reported significant differences between three subcatchments and catchment scales and attributed them to hydrological soil groups, subsoil texture, topography and the location of tile drains. Furthermore, on the field scale, the pathway drainage was the focus (no surface runoff was observed due to the flat topography of the field), while the relevance of the single entry routes

can only be assumed on a catchment scale. Nevertheless, on both scales, similar patterns were observed. For example, (i) highest loads were not detected at highest concentrations, and (ii) delayed response time of load to precipitation shortened over time, due to increasing soil water content.

7.3 Monitoring of Flufenacet in autumn 2009

7.3.1 Soil parameters and hydrological parameters in autumn 2009

During the monitoring, a total of 313 mm rainfall was observed; the sum of precipitation in November significantly exceeded the long-term averages of November (1984 – 2009) (DWD, 2007a; LLUR, 2009). On the field scale, the measured parameters, soil water content, groundwater level and drain flow reacted simultaneously within one day to rainstorms. Hence, increases of these parameters were event-driven. The overall trend of these parameters rose over time during the monitoring period. During the two weeks before Flufenacet was sprayed to drained field 2, 1 mm of rainfall occurred so that the antecedent soil water content during application was on a low level.

The discharges of the Moorau and the Kielstau showed dependencies on rainfall that were similar to the drain flow on drained field 2. After rainstorms, the discharges peaked within one day and remained constant during rainless periods and periods of low precipitation. In both streams, the discharge generally rose, especially in November. The abundant rainfall events in November caused an increase in soil water saturation within the catchment, hence, less rainfall was stored in the soils but was discharged into surface water bodies. The average discharge in the Kielstau of $0.63 \text{ m}^3/\text{s}$ is five times higher than in the Moorau, which accounted for 0.14 m^3 . As the Kielstau catchment is more than six times larger than the subcatchment, the distribution of rainfall is spatially higher, resulting in long water transport times from all areas of the catchment to the outlet in Soltfeld. Hence, peaks of discharge are less sharpened than in the Moorau tributary (Fig. 54) (Holvoet, 2006).

7.3.2 Flufenacet concentrations

Drained field 2

Flufenacet concentrations were determined in the drainage water of drained field 2 to be in the range of > 30 ng/l to 170 ng/l. Within the eight detected findings, four concentrations were below the quantification limit of 90 ng/l. Flufenacet was observed on drained field 2 in five times, and each time the concentration peak appeared on the rising limb or at the maximum of a rainfall induced discharge peak. The sudden increase of pesticide concentrations in subsurface drains, in general, is coincidental with the beginning of a discharge event (Kladivko et al., 2001). As the soil water content values on drained field 2 showed the same run as the drain flow values, it is concluded, that Flufenacet was relocated from the upper soil layer to the drain pipe during periods of increased soil water content. The first observed Flufenacet peak showed the highest concentration of the entire monitoring, a phenomenon, which is confirmed in other studies (e.g. Kalita et al., 2006; Kladivko et al., 2001; Kreuger, 1997; Leu et al., 2004b; Traub-Eberhard et al., 1994). The Flufenacet findings on 3/10/2009, 30/11/2009 and 1/11/2009 occurred as single peaks at the beginning of discharge peaks. This indicates that the amount of Flufenacet available for transport decreased quickly, due to a limited time span in which the herbicide could be dissolved in the rapidly percolating water (Traub-Eberhard et al., 1994). Consequently, the concentrations dropped below the detection limit. From 12/11/2009 to 14/11/2008, the concentrations rose with increasing discharge. Instead of dilution effects on the Flufenacet concentrations, the concentration daily increased. It is assumed that before 12/11/2009, the soil water standing in the pores had time sufficient for an equilibrium to develop between Flufenacet molecules bonded to soil organic matter and Flufenacet molecules dissolved in the soil water. The rainstorm occurring after this period of establishment of equilibrium, on 21/11/2008, led to release of Flufenacet concentrations in increasing amounts.

Flufenacet is an herbicide first registered in Europe in July, 2003 (European Commission, 2003a). Results from studies focussing on Flufenacet in drainage systems are not available so far, due possibly to this short time of usage, and because thresholds or EQS are not constituted. However, Flufenacet was determined in a further study on a wheat field in leachate samples in 80 cm below soil surface with suction cups. Concentrations up to 600 ng/l and a loss of 21 – 24 mg/ ha, corresponding to 0.01 – 0.18 % of the applied amount, were observed

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five to eight weeks after autumn application (Hüwing, 2008). Furthermore, the Flufenacet values determined in our study are compared with Terbutylazine values from other investigations, because their mobility is assessed in a similar range (footprint, 2009). As reported in Table 2, these two herbicides show similar partition coefficients $\log P_{OW}$ values, but Flufenacet is water soluble to a higher extent, shows a slightly higher adsorption coefficient K_{OC} and has a higher DT_{50} than Terbutylazine. During the monitoring of Terbutylazine on drained field 2 in spring 2008, Terbutylazine concentrations in the range of > 25 ng/l to 301 ng/l were observed in drainage water, while significantly higher Terbutylazine maximum concentrations of 45 μ g/l were determined in another study in a culvert of a drained field (Kreuger, 1997; Kreuger, 1998).

Flufenacet concentrations in the groundwater well GW1 were observed only on 16/11/2009 and 19/11/2008 and amounted to 132 ng/l and 140 ng/l. The groundwater level showed maximum values to these points of time. It is assumed that a singular exchange of Flufenacet between the upper soil layer and the shallow groundwater took place, hence, the herbicide was detected for a limited time in the groundwater. The phenomenon of pesticide occurrence for only several days in the groundwater was also observed during the monitoring of Metazachlor on the same field in autumn 2008 (see Chapter 6.2.3).

Moorau

In the Moorau, Flufenacet concentrations ranged from > 30 ng/l – 96 ng/l. Only one concentration value of the seven findings was above the quantification limit of 90 ng/l. The first finding on 5/10/2009 was detected within two days after the rainstorm of 3/10/2009, and on the recession limb of the discharge peak. Hence, rapid transport processes were not dominant. It is more likely that large parts of the soil volume are involved in the vertical movement of water and dissolved compounds (matrix flow). The following Flufenacet concentrations on 12/10/2008 and 2/11/2008 had already occurred with the maximum discharge of the Moorau, and the subsequent concentrations were actually observed on the recession limb of the discharge peak (4/11/2009 and 14/11/2009). With progressing time and accumulating precipitation, Flufenacet was more quickly released to the Moorau. This can be attributed to an increasing soil water content in the subcatchment caused by abundant rainfall.

Kielstau

In the Kielstau at the Soltfeld gauge, Flufenacet concentrations were observed in the range of > 30 ng/l to 160 ng/l, and five of the 15 findings were above the quantification limit. During the first Flufenacet flush (3/10/2009 – 7/10/2009) and at the beginning of November (3/11/2009 – 5/11/2009), preferential pathways can be assumed to dominate the transport of Flufenacet, because the findings occurred on the rising limb of the discharge peak. Overall, from 3/11/2009, the observed concentrations decreased continuously due to dilution by the Kielstau discharge, degradation and sorption to soil, riverine vegetation and sediments of the Kielstau.

Flufenacet was one of 37 pesticides observed over three years in the Mississippi River. While it was not detected in the Mississippi River within the period of 1999 - 2000 Flufenacet (Zimmerman et al., 2002), concentrations between > 50 ng/l and 120 ng/l were determined in the period of 2000 – May 2001 (Rebich et al., 2004). These values confirm the results of the monitoring in the Kielstau catchment. Comparing the results of Flufenacet concentrations in streams with Terbutylazine concentrations, Terbutylazine was detected in stream concentrations of 50 ng/l to 1200 ng/l (Hildebrandt et al., 2008; Müller, 2000; Palma et al., 2009), i.e. the Flufenacet values of this study were in the lower range of the interval detected in the cited studies.

The concentrations of all sampling points are presented in Fig. 71. Clearly, Flufenacet was transported most rapidly in the drainage. Like those in the drainage, concentrations in the Kielstau responded immediately to the rainstorm of 3/10/2009. Two days later, Flufenacet was detected in the Moorau, and then again after seven days (12/10/2009). During the Flufenacet discharge from 30/10/2009 to 5/11/2009, concentrations were first observed in the drainage, then in the Moorau and the Kielstau. The same pattern of concentration appeared on 12/11/2009 – 17/11/2009, when first Flufenacet findings in the drainage were determined and followed by findings in the Moorau and the Kielstau two days later. The Flufenacet was able to reach the drainage pipes at 1.5 m depth due to the shorter transport way. In the Moorau subcatchment, changes occurred which caused, from the beginning of the monitoring, slower transport of Flufenacet than in the Kielstau, and from the beginning of November, transport of the same velocity. It is assumed that different values of the initial soil water content in the subcatchment and in the Kielstau catchment caused the varying transport velocities in the beginning, and that their soil water content figures came to match each other over time. Hence,

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over time, the transport velocities also matched. The similar concentration patterns on the three scales are ascertained by a study in the catchment of Lake Greifensee, Switzerland, where similar concentration dynamics were monitored in three subcatchments (Leu et al., 2005).

The concentrations at the different scale sizes did not vary significantly. In fact, the drainage samples showed the highest concentration values, and a dilution of the concentrations in the Moorau can be observed. However, the concentrations in the Kielstau water were in the same range as the values of the drainage until 5/11/2009. Flufenacet was applied predominantly to the fields of the catchment. Hence, it is possible, that dilution effects caused by the discharge of the Kielstau were obscured by high amounts of applied Flufenacet.

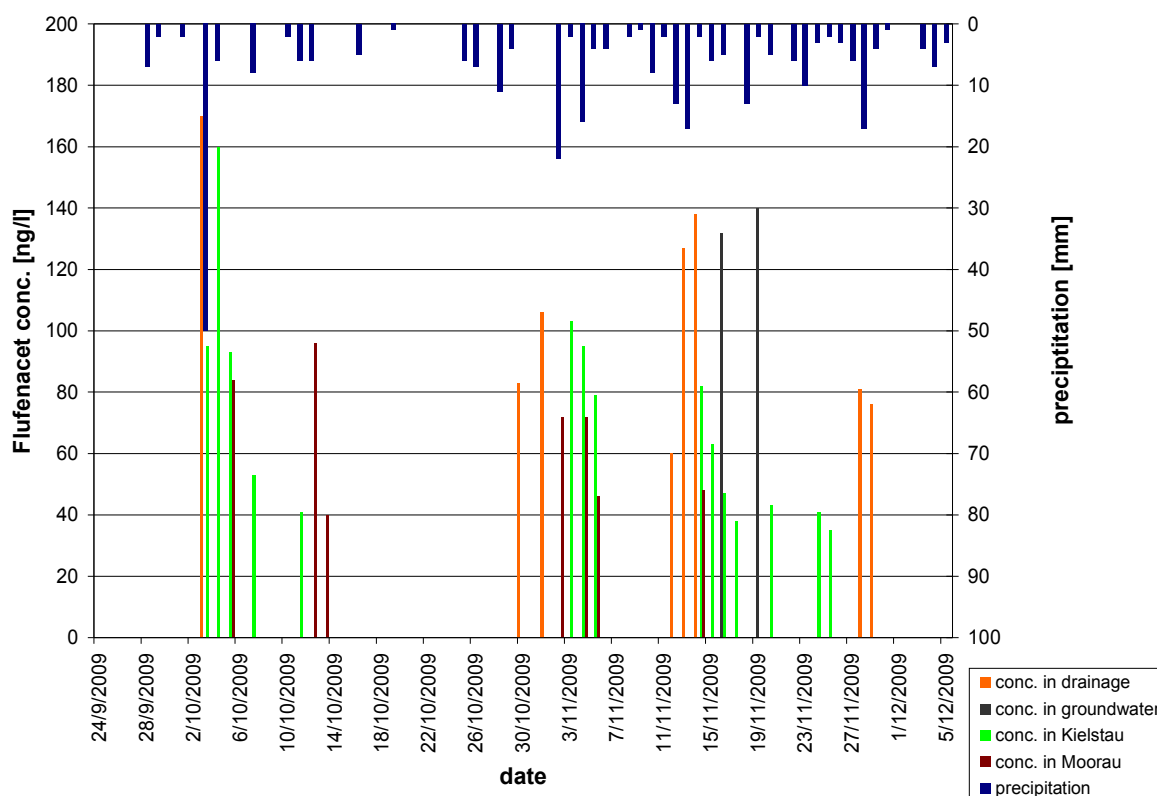


Fig. 71: Pattern of Flufenacet concentrations on drained field 2, in the Moorau and in the Kielstau at Soltfeld in autumn, 2009 (daily values)

7.3.3 Potential discharges and determined losses

Drainage

In the drainage, within the total load of 28 mg Flufenacet, the highest daily loads of 3.5 mg and 4.1 mg were observed on 13/11/2009 and 14/11/2009. The high values result from high Flufenacet concentrations as well as high drain flow. The daily load on 3/10/2009, where the highest Flufenacet of the monitoring was observed, amounted to 1.3 mg Flufenacet, due to a lower drain flow. Overall, the pattern of the cumulated load graph equals the one of the cumulated precipitation graph. However, the slope of the load graph was significantly higher than that of the precipitation graph on 13/11/2009, 14/11/2009, 28/11/2009 and 29/11/2009, when the highest daily loads due to high drain flow were observed.

In autumn 2009, the catchment of the drainage had a size of approximately 3000 -5000 m². Amounts of 72 g and 120 g Flufenacet were sprayed on these catchment areas, so that the

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total loss via drainage of 28 mg corresponds to 0.04 % (3000 m²) and 0.02 % (5000 m²) of the applied amount. Depending on the drainage catchment size, a loss of 60 mg – 90 mg Flufenacet/ha is determined. In other studies, losses of 0.08 -0.18 % of Metolachlor (Novak et al., 2001) and 0.27 % of Metolachlor as well as 0.67 % of Atrazine (Accinelli et al., 2002) were reported. It has to be stressed that Metalochlor and Atrazine show a higher potential for relocation than Flufenacet, due to their physical-chemical properties (footprint, 2009) Losses of Flufenacet via subsurface drains at field scale have not been reported.

Moorau

The loads in the Moorau showed their highest daily value of 1.6 g Flufenacet on 14/11/2009. Further high loads were observed on 4/10/2009 and 4/11/2009, each with 1.4 g Flufenacet. All of them are reactions to rainstorms, which can be seen from the graphs of cumulated load and cumulated precipitation, which show the same run. Only on 4/10/2009, the rise of the load appeared one day after the increase of the precipitation. This can be caused by a lower soil storage saturation in the beginning of the monitoring period, which increased over time due to rainfall, and then led to faster percolation of the water through the soils and into the Moorau. The total load released into the Moorau during the ten weeks of observation amounted to 17.8 g Flufenacet, which corresponds to 0.04 % of the applied amount in the subcatchment and to a loss of 60 mg/ha.

Kielstau

In the Kielstau, the total load of the monitoring period accounted for 115 g Flufenacet. The daily maximum loads were detected with 10 g Flufenacet on 14/11/2009, followed by a load of 7 g on 4/11/2009, and 6 g on 4/10/2009. Equivalent to the determined loads in the Moorau, the highest daily loads in the Kielstau occurred on the same days and as a response to rainstorms. The total load of 115 g Flufenacet corresponds to 0.05 % of the 236 kg Flufenacet applied in the Kielstau catchment. A loss of 66 mg Flufenacet/ ha was determined.

Losses of Flufenacet on the catchment scale, given in percentage or in discharged per hectare, are not yet published in the reviewed literature. Alternatively, results from studies with other herbicides are consulted: Terbutylazine losses of 53 mg/ha were reported in the Zwest-er Ohm catchment in Germany (Müller, 2000). Atrazine losses of 0.004 % to 1.0 % were observed, differing between subcatchment and catchment scale and within single rainstorms (Leu et al., 2004a). In terms of these results and of the Metazachlor monitoring in autumn

2008 (see chapter 7.2.3), the Flufenacet losses in the monitoring of autumn 2009 show similar values on all scales.

7.4 Surface runoff experiment with rainfall simulator

7.4.1 Soil physical parameters

The energy of a rain drop hitting the soil surface destroys the soil aggregates by initiating air slaking. Small breakdown products, “splash material” is formed and can be easily transported with the infiltrating water into the upper millimetres of the soil and clog the pores beneath the surface. This causes a sealing of the soil surface and the development of a crust so that the infiltration rate decreases with increasing cumulated rainfall energy (Le Bissonnais et al., 1989; Truman & Bradford, 1990). Furthermore, the breakdown of the aggregates into small particles leads to a levelling of the surface and resulted in higher runoff velocities and higher transport of sediment. The soil water content has an important influence on the development of the sealing. The higher the initial water content of the soil, the more stable are the aggregates. Hence, they are crushed into bigger particles than under initially dryer soil conditions, and less soil material is released (Le Bissonnais et al., 1989). The sealing is more permeable and the potential for infiltration remains longer than in soils with lower initial soil moisture (Fohrer, 1995; Zeiger & Fohrer, 2009; Zhang et al., 1997). The delayed runoffs of the containers F1, F2; F3 can be explained with the higher initial water contents. Furthermore, unequal compaction of the upper soil layer or different structure of the soil surface as well as the heterogeneity of the soil itself can be responsible for the variations of the first runoff event.

High initial infiltration rates were observed during each rainfall event of the experiment. Under intermittent rainfall conditions, the high infiltration rate at the beginning of each rainfall event reoccurred in every cycle. Alterations of the texture and morphology of the soil surface appeared in the dry period in between the rainfall events and caused cracks in the upper soil layer, due to the changing soil water content. Following, the initial high infiltration rate decreased significantly because the cracks were again closed by splash material or by swelling of the soil itself. Consequently, the surface runoff increased considerably and resulted in maximum runoff of 80 – 95 % of the total rainfall of one rainfall event. The already pre-sealed

soil surface in later cycles enhanced earlier start and higher runoff. Similar effects can be observed at Fohrer et al. (1999), Zeiger (2007) and Zeiger & Fohrer (2009).

In cycle V and VI, the runoff decreased. The cracks that formed during the drying periods between the rainfall events IV – VI were not sealed by splash material or swelling of the soil to the extent of the former cycles. The decrease of the sediment part in the surface runoff within cycle V and VI documented a lower transport of soil material than in the previous cycles and confirmed this process. Hence, the infiltration rate increased while the proportion of runoff decreased. A dense and compact crust was generated due to the evaporation during the dry period and air slaking of the dry aggregates on the soil surface at the beginning of the rainfall event (Agassi et al., 1995; Boiffin & Monnier, 1986; Fohrer, 1995). The stability of the crust is influenced by the number of drying and wetting cycles as well as by the intensity and duration of the rainfall. Hence, different processes of crust forming and types of crust morphology appear resulting in different properties of the crust (Hardy et al., 1983; Levy et al., 1986).

The sediment discharge amounted to maximum values of 60 g/m² during a single rainfall event, and to 56 – 230 g/m² over the entire experiment with six cycles. Sediment values of other studies vary from 10 g/m² to 532 g/m² and express the wide range of the results, due to the various influencing parameters and different set ups (Fohrer, 1995; Müller et al., 2002; Roth & Helming, 1992). The determination of the pesticide loads adsorbed to the sediment was not part of this study. However, considering the partition coefficient K_d from the literature or studies and the amount of the discharged sediment, enables the calculation of the pesticide load adsorbed to soil particles.

7.4.2 Herbicides concentrations in surface runoff

The maximum herbicide concentrations in the surface runoff were in different ranges, due to the herbicide concentration of the applied solution. Hence, they varied between 3184 µg Metazachlor/l, 661 µg Terbuthylazine/l and 207 µg Flufenacet/l. Two concentration patterns were observed during the first generated samples: (i) maximum concentration in a small runoff volume and (ii) lower concentration in the three samples with larger runoff volume. During a rainfall event, water comes into contact with the herbicides which are adsorbed to the soil matrix in variable bond-strengths. If surface runoff occurs, the herbicide can be dissolved

in the discharged water, due to its physical-chemical properties. The volume in which the herbicide is dissolved influences the concentration. In addition, the velocity of the draining water has an impact on the solution of the herbicide and hence, also on the concentration. In fast-flowing water, there is only a short time for creating a steady state between dissolved and adsorbed agent. Thus, only a small amount of it can be dissolved (Sparks & Suarez, 1991). Müller et al. (2002) assume that a rapid initial desorption of the pesticide causes the high concentrations in the beginning of the rainfall. It is then followed by slower desorption, due to stronger bonds of the agent to the soil matrix, and effected lower concentrations. Gottesbüren et al. (1994) determined an increase of the partition coefficient K_d with the duration of the experiment. This increase was caused by the change of the equilibrium between pesticide and sorption places. In the beginning of the experiment, the pesticides were adsorbed to the sorption places with weaker bonds than at the end of the experiment, when they are adsorbed with strong bonds or even absorbed into the soil aggregates.

Notably, the herbicide concentrations in the first interval of each simulated rainfall was as high or even higher than the concentration in the last interval of the previous rainfall. During the six-day dry period, potentials for changing desorption and adsorption may have developed. As the properties of the organic matter varies according to the soil moisture, the bonding capacities for the herbicides also differ (Gottesbüren et al., 1994). Additionally, soil aggregates are destroyed in the drying process, offer new surface for desorption of the agents and cause the higher concentrations in the first intervals of the each rainfall.

Over time, the herbicide concentrations in the runoff diminished exponentially. As the herbicides were discharged via runoff and infiltrated into the pores of the soil with increasing rainfall duration, the amount of agent, which is available for discharge, is reduced. The changes of the agents from sorption places of weak bonds to those with stronger bonds enhances this effect (Gottesbüren et al., 1994; Lang & Hurle, 1997; Müller et al., 2002). Furthermore, the herbicides underlied degradation processes within the experiment, thus, over time lower amounts could be relocated.

7.4.3 Herbicide loads in surface runoff

The determined total loads of herbicide loss amounted to 345 and 440 μg Metazachlor/ 0.2 m^2 (plot), 1.92 % (M1) and 2.5 % (M2) of the amount applied. For Terbutylazine, the loads dis-

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charged via surface runoff were 318 and 310 μg Terbutylazine/0.2 m^2 , equivalent to 6.6 % and 5.7 % (T1, T2), Loads of 94, 111 and 87 μg Flufenacet/0.2 m were determined, corresponding to 2.1 %, 3.8 % and 3.0 % (F1, F2, F3) of the amount applied. Reviewing the literature, it is notable that results for Flufenacet have not been published yet. For Terbutylazine loads of 0.15 – 1 % of the applied amount are determined in the water phase of the surface runoff (Erlach, 2005; Erlach et al., 2004; Müller et al., 2002) and 0.15 – 0.31 % of the Metazachlor applied (Erlach, 2005; Erlach et al., 2004). It has to be pointed out that these results of total herbicide loss are lower than in this study, due to the different set ups of the experiments. However, Wauchope et al. (1995) indicated that the value of the results' variation might account for one range due to the multiple variables in this process.

Focussing on the loads of the single rainfall events, it is observed that the loads of the containers M1, M2, T1, T2 are not highest in the first cycle when concentrations were highest, but in the second cycle (Tab. 31). The load is the product of concentration and runoff volume. To that point of time, the combination of high but not maximum herbicide concentration and runoff volume, which had already increased, caused part-loads of 31 % and 43 % of the total load for Metazachlor and Terbutylazine. Due to delayed runoff generation, the maximum part-load of 49 % in container D occurred in the third cycle. Containers F1 and F2 showed highest part-loads of 37 % and 47 % in the fourth cycle because the surface runoff volume was highest, then.

Tab. 31: Discharged herbicide loads in each rainfall event in [μg] and [%] of total load

Cycle	I		II		III		IV		V		VI	
Containers	[μg]	[%]	[μg]	[%]	[μg]	[%]	[μg]	[%]	[μg]	[%]	[μg]	[%]
M1	19	6	138	40	103	30	48	14	28	8	8	2
M2	16	4	190	43	96	22	89	20	25	6	24	6
T1	54	18	100	34	74	25	40	14	19	6	10	3
T2	38	12	96	31	76	25	50	16	33	11	16	5
F1	0	0	7	7	18	19	35	37	20	21	15	16
F2	0	0	6	5	15	14	53	47	15	13	23	21
F3	0	0	15	17	43	49	17	20	7	8	5	5

The results of this experiment with intermittent simulated rainfall give an overview of the relevance of surface runoff in the transport of pesticide from the field into surface water. However, they can not be transferred by implication from this small scale to macro scale. The in-

fluence of soil surface structure, machine tracks, length of the slope and runoff dynamics at field scale must be considered.

7.5 Influence of herbicide properties on herbicide transport

In this chapter, the results of the monitoring campaigns of Terbutylazine, Metazachlor and Flufenacet are compared and conclusions regarding the herbicide properties are discussed.

On the field scale, comparable fates of Metazachlor and Flufenacet were observed on drained field 2. As Terbutylazine was monitored on drained field 1, the site conditions and the hydrological conditions during that observation already differ from those of Metazachlor and Flufenacet on drained field 2. A comparison of Terbutylazine with the other two herbicides is not appropriate because differences could be related to variable site conditions and not to the properties of the herbicides.

Metazachlor and Flufenacet were monitored in autumn. The total precipitation of the monitoring periods at the Satrup rain gauge was accounted by 215 mm in 2008 (Metazachlor) and 261 mm in 2009 (Flufenacet). Metazachlor concentrations were observed more frequently and in higher concentrations than Flufenacet (Fig. 72). This can be attributed to higher application amounts, as Metazachlor was sprayed in amounts of 750g/ha while Flufenacet was sprayed in amounts of 240g/ha. For several pesticides, a good correlation between amounts used and occurrence in water samples is observed (Kreuger, 1998; Kreuger & Törnqvist, 1998). Regarding the properties of the two herbicides, Metazachlor shows a higher water solubility and GUS leaching potential, but lower $DT_{50\text{soil}}$ and K_{oc} than Flufenacet (see chapter 2.1.3). The higher and more frequent Metazachlor concentrations can also be explained by the enhanced mobility of Metazachlor, due to its chemical-physical properties. Flufenacet, however, is characterized as a substance of high retention in soils (Gupta et al., 2000). Despite influences of the herbicide properties on transport processes, similar patterns of discharge are observed. Independently from observed rainstorms, both herbicides were detected 10 days after application (a.a.) in the drainage samples coincidentally with rising discharge. This phenomenon can not be attributed to the herbicide properties because coincident findings, in spite of different characteristics, are not likely. On tile drained sites preferential flow is frequently discussed to be a further transport mechanism beside the matrix flow. Whereas the bulk soil is involved in matrix flow, only macropores are used during preferential flow (Flury, 1996; Kördel et al.,

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2008). During matrix flow, the sorption properties of pesticides are relevant because this kind of transport is slower and enables adsorption and desorption processes of the pesticide to and from the soil organic matter. Hence, pesticides with higher affinity to the soil matrix are retarded. In contrast, preferential flow is a rapid transport where the rate of transport exceeds the rate of adsorption so that even pesticides with high sorption capability are rarely retarded. The time available for equilibrium between dissolved and bound pesticide molecules is attained to be too short (Kördel et al., 2008; Traub-Eberhard et al., 1994). Hence, the pesticide properties during preferential flow transport are of secondary relevance (Goss et al., 2010). In this study, Metazachlor and Flufenacet were detected on the same days a.a. in the drainage water, but in different concentrations. It is assumed that the transport velocity in macropores is independent from the pesticide properties, hence, they occur at the same time in the drainage. However, the concentration and the amount of a pesticide discharged via preferential flow are influenced by its properties: Mobile herbicides are released in higher concentrations and in higher amounts than less mobile ones (Flury, 1996; Malone et al., 2004).

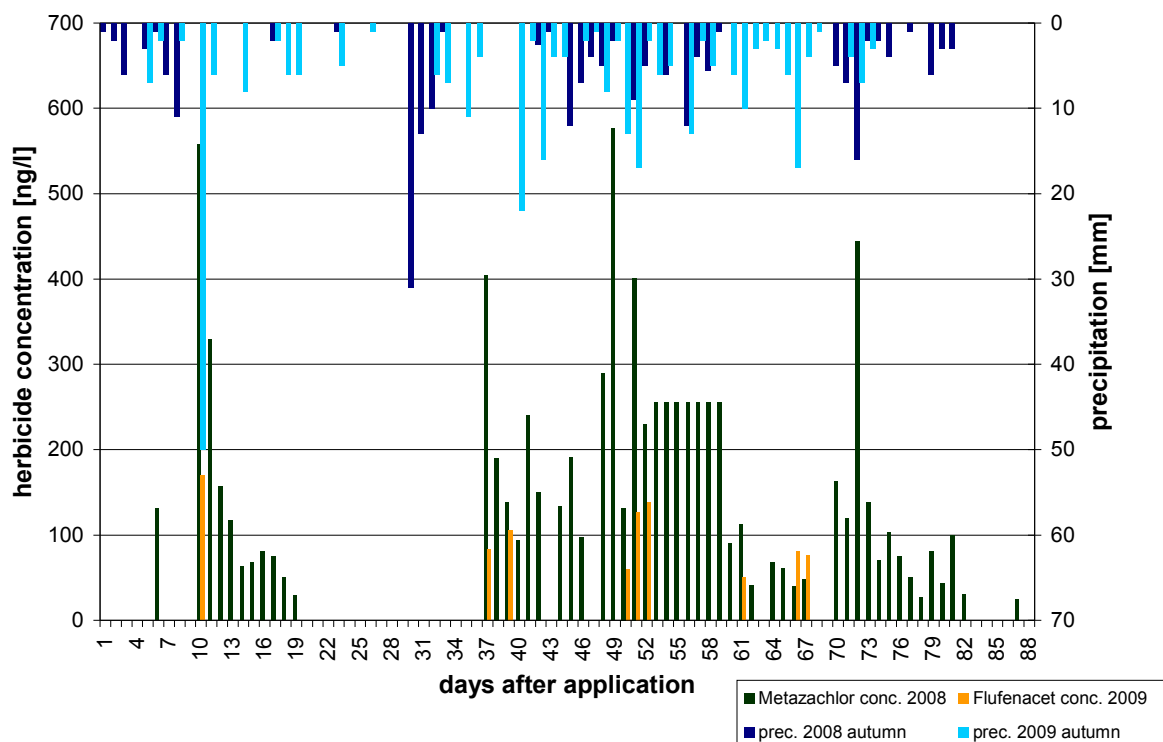


Fig. 72: Herbicide concentrations on drained field 2 in autumn 2008 and 2009 (daily values)

In the groundwater similar patterns of herbicide concentrations were observed (Fig. 73). Both compounds occurred within 48 days to 58 days a.a. and neither before nor after this time, though rainfall intensity and rainfall distribution, groundwater levels and herbicide properties differed. Though the processes taking place at that time and transporting the herbicide into the shallow groundwater can not be explained sufficiently, they may be related to the soil texture. Kamra et al. (1999) and Lennartz (1999) stated that physical soil properties forming the flow path system are more relevant to pesticide adsorption and mobility than their chemical-physical properties that are directly related to the adsorption process. They observed the comparable occurrence of main concentration peaks despite of notable differences in rainfall, drain flow and areas of application.

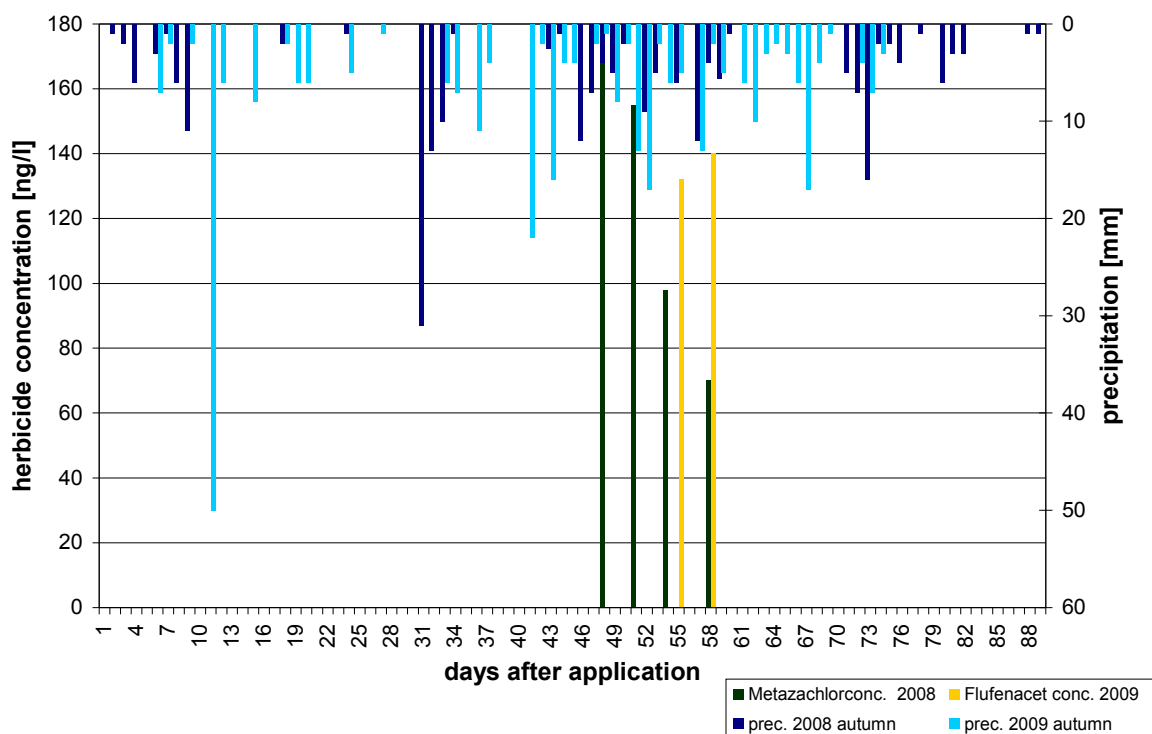


Fig. 73: Herbicide concentrations in the groundwater of drained field 2 in autumn 2008 and 2009 (daily values)

All three herbicides were monitored in the Moorau, but Metazachlor was not observed in concentrations above detectable limits. In the following, Terbutylazine and Flufenacet are compared (Fig. 74). Terbutylazine was monitored for six weeks in the Moorau in spring 2008 whereas Flufenacet was observed for ten weeks in autumn 2009. The total sum of precipita-

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tion accounted for 54 mm in spring 2008 and 261 in autumn 2009 at the Satrup rain gauge and the mean discharges of the Moorau were 0.027 m³/s (2008) and 0.138 m³/s (2009). Notably, Terbutylazine was observed more frequently than Flufenacet but the concentrations of both herbicides were in the same range. Terbutylazine and Flufenacet do not differ as much in their properties as Metazachlor and Flufenacet, but Flufenacet appears to be less mobile than Terbutylazine due to its lower leaching potential (footprint, 2009). Gupta et al. (2000) and Rouchaud et al. (1999) observed that Flufenacet desorption is extremely difficult, requiring 33 mm of precipitation to be transported to 35 cm depth in a soil column. That aspect may explain the less frequent Flufenacet concentrations. Nevertheless, the different hydrological conditions also influence the concentration patterns and have to be considered. Seasonal variations such as higher precipitation and lower evaporation during autumn time than in spring time can cause higher discharges and therewith dilution of herbicide concentrations (Holvoet, 2006; Kreuger, 1998). It is assumed that the soil water content of the soils in the Moorau subcatchment was lower during Terbutylazine monitoring in spring 2008 than during Flufenacet monitoring in autumn 2009. As soil water content measurements were not conducted in spring 2008, the influence of different soil water contents can not be assessed. But it can be pointed out that this parameter may have influenced the herbicide transport. The application amounts of the herbicides in the subcatchment (approx. 12 kg Terbutylazine, approx. 40 kg Flufenacet) is assumed to be of minor relevance, otherwise Flufenacet concentrations should have been higher. Similar concentration patterns, as observed on drained field 2, due rather to physical soil properties and less to chemical features of herbicides, were not noticed on the subcatchment scale.

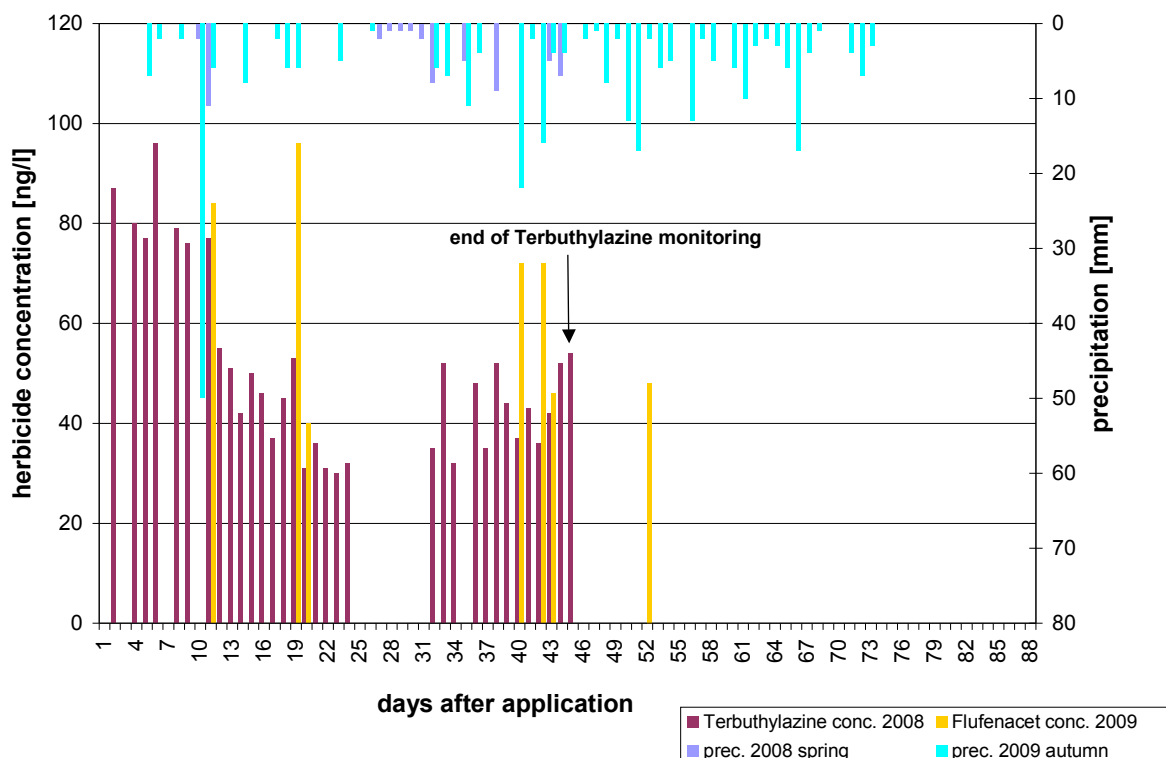


Fig. 74: Herbicide concentrations in the tributary Moorau in spring 2008 and autumn 2009 (daily values)

In the Kielstau at the Soltfeld gauge all herbicides were detected during their monitorings. The mean discharge of the Kielstau varied between $0.11 \text{ m}^3/\text{s}$ (Terbutylazine), $0.44 \text{ m}^3/\text{s}$ (Metazachlor) and $0.63 \text{ m}^3/\text{s}$ (Flufenacet) during the single observations. Equivalent to the Moorau, Terbutylazine was detected more frequently than Flufenacet, which can be attributed to its higher mobility (Fig. 75). Metazachlor, as the herbicide with the highest mobility potential of the investigated herbicides (see Chapter 2.1.3), was determined only four times and in lower concentrations than Flufenacet and Terbutylazine.

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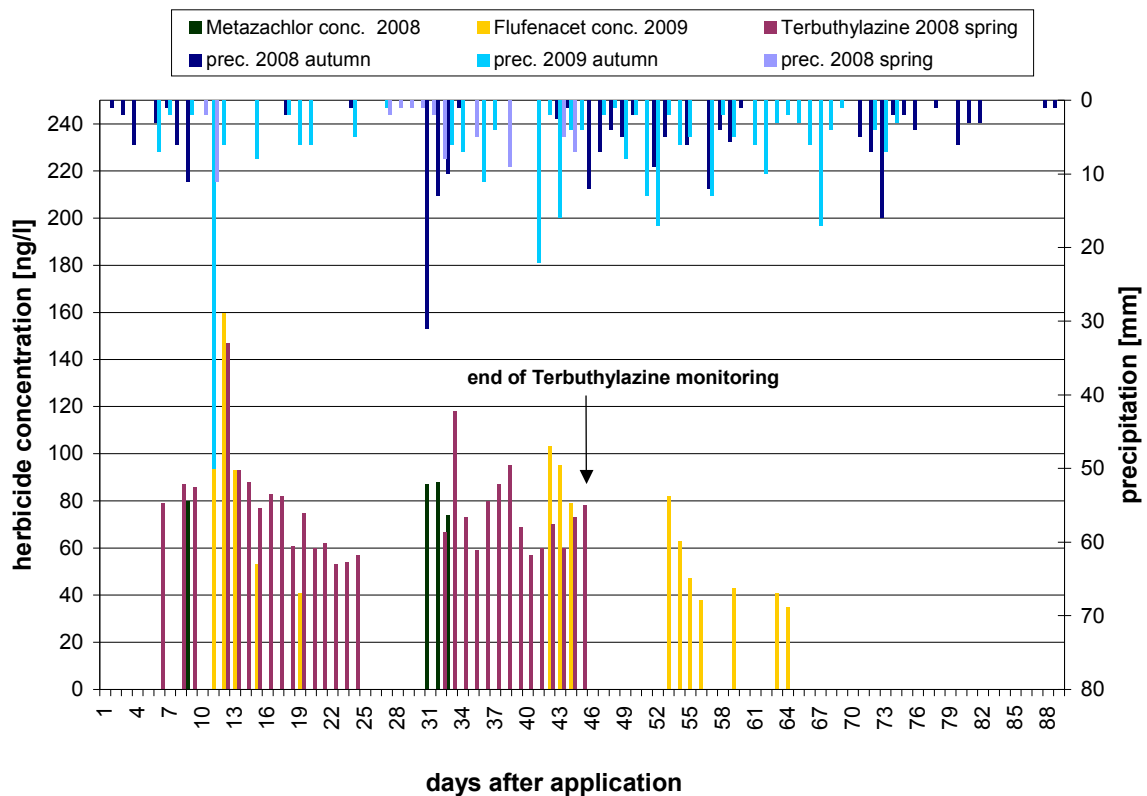


Fig. 75: Herbicide concentrations in the Kielstau at Soltfeld in spring 2008, autumn 2008 and 2009 (daily values)

The degradation of Metazachlor must be considered when explaining its rare findings. It is inferred that Metazachlor was partly metabolized in soil to daughter compounds leading to few detections above detectable limits (footprint, 2009). During monthly monitoring from 2007 - 2010, the LLUR observed Metazachlor significantly less frequent than the other two herbicides in surface water bodies in Schleswig Holstein (LLUR, 2010*) (Tab. 32). This reveals that, on larger scales, Metazachlor is retained or degraded to a higher extent than Flufenacet and Terbutylazine.

Tab. 32: Pesticide concentrations in surface water bodies in Schleswig-Holstein 2007 - 2010 [data source: LLUR (2010*)]

$\mu\text{g/l}$	> 0.05	> 0.1	maximum	number of samples
Flufenacet*	160	91	2.2	1761
Metazachlor	23	12	6	1305
Terbutylazine	38	19	1.2	1305

In addition to the properties of the herbicides, the different hydrological conditions of the monitorings influenced the transport of the herbicides. Higher mean discharges induced by higher precipitation amounts like in autumn 2009 are more likely to dilute concentrations than lower ones like in spring 2008, for example (Kladivko et al., 2001). The applied amount of herbicides in the catchment appear to be of less dominance regarding the herbicide transport. Approximate amounts of 236 kg Flufenacet, 229 kg Metazachlor and 114 kg Terbutylazine were spread at catchment scale. If these distributions had a relevant influence on the herbicide transport Terbutylazine would have been detected to a lower extent. In the Kielstau, similar concentration patterns of the three herbicides independent from herbicide properties but dependent on soil texture were not observed. This was in agreement with observations in the Moorau.

The influence of the herbicide properties on transport processes was observed on the field scale. During herbicide transport via preferential flow on the field scale, the herbicide properties seemed to be unimportant, because of the short water-soil contact, which did not provide sufficient time to develop an equilibrium between dissolved and bonded herbicides. With increasing of scale, the influence of the hydrological conditions such as the discharge also increased and overshadowed the property related processes of the herbicide relocation. Furthermore, the amounts applied and the varying antecedent soil water contents, especially between spring and autumn monitoring, may have influenced the herbicide relocation to an unknown extent.

Comparing scales, it is noticed that the herbicide concentrations do not follow the common scheme of decreasing concentrations per size increase of the river (Holvoet, 2006). For all herbicides, lowest concentrations were observed in the Moorau tributary subcatchment scale so that this effect must be attributed to individual processes taking place in the subcatchment. In other studies, comparing herbicide relocation in different catchments and subcatchments, the single catchment or field properties, such as hydrological soil properties and connectivity of fields to surface water, are determined to be the main factor influencing pesticide discharge (Blanchard & Lerch, 2000; Leu et al., 2005; Leu et al., 2004a). The Moorau is embedded in a fen which is framing the river on both sides with an average of 150 m (Fig. 10). Fens are characterized to have a high sorption potential (Blume et al., 2010) which can cause the retardation of the herbicides and therewith result in lower concentrations in the Moorau than in the Kielstau.

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The herbicide losses given in percentage of the amount applied vary from < 0.01 % to 0.3 % on the three scales (Tab. 33). It must be pointed out that the monitoring of Terbutylazine was four weeks shorter than those of the other herbicides, which probably caused lower loads. The values in Tab. 1 reveal that the losses do not differ significantly among the herbicides so that the influence of the herbicide properties on loss is not clearly ascertained. For Terbutylazine and Flufenacet, there is marginal variation between the losses on the different scales though their findings differed in frequency and concentrations.

Tab. 33: Discharged loads of amount applied [%] on all scales

herbicide	drained field	subcatchment Moorau	catchment Kielstau
Terbutylazine	-	0.01	< 0.01
Metazachlor	0.07- 0.3	-	0.02
Flufenacet	0.02 – 0.04	0.04	0.04

The concentration and discharge data from all monitorings were analyzed for a correlation between these two parameters. But in agreement with Laroche & Gallichand (1995) and Kreuger (1998), neither in the Moorau nor in the Kielstau, there was a correlation between pesticide concentration and the magnitude of stream flow. Exemplarily, for all monitorings the concentration-discharge volume-correlation of Terbutylazine in spring 2008 is shown in Fig. 76. Actually, a correlation of pesticide concentration in leachate to any environmental parameter was not observed by Brown & van Beinum (2009).

Considering the physical-chemical properties of the applied herbicides in the surface runoff experiment, the Koc values of the three selected herbicides differ from 53 to 401 ml/g, but also merge up to a certain degree while the water solubility varies more. Though Metazachlor is the most water soluble (450 mg/l) of them, the discharged load by runoff is the lowest. Furthermore, Terbutylazine with the lowest water solubility (6.6 mg/l) generated the highest loads. Burgoa & Wauchope (1995), Müller et al. (2002) and Freitas et al. (2008) also determined that pesticides of higher water solubility are less discharged via surface runoff. Agents with higher water solubility are transported faster in vertical direction with the infiltrating water and hence, are available for surface runoff in a smaller proportion. Agents with lower water solubility do not percolate that fast with the infiltrating water and are more available for surface runoff. The results of the monitorings in the Kielstau catchment and of the surface runoff experiment confirm these observations.

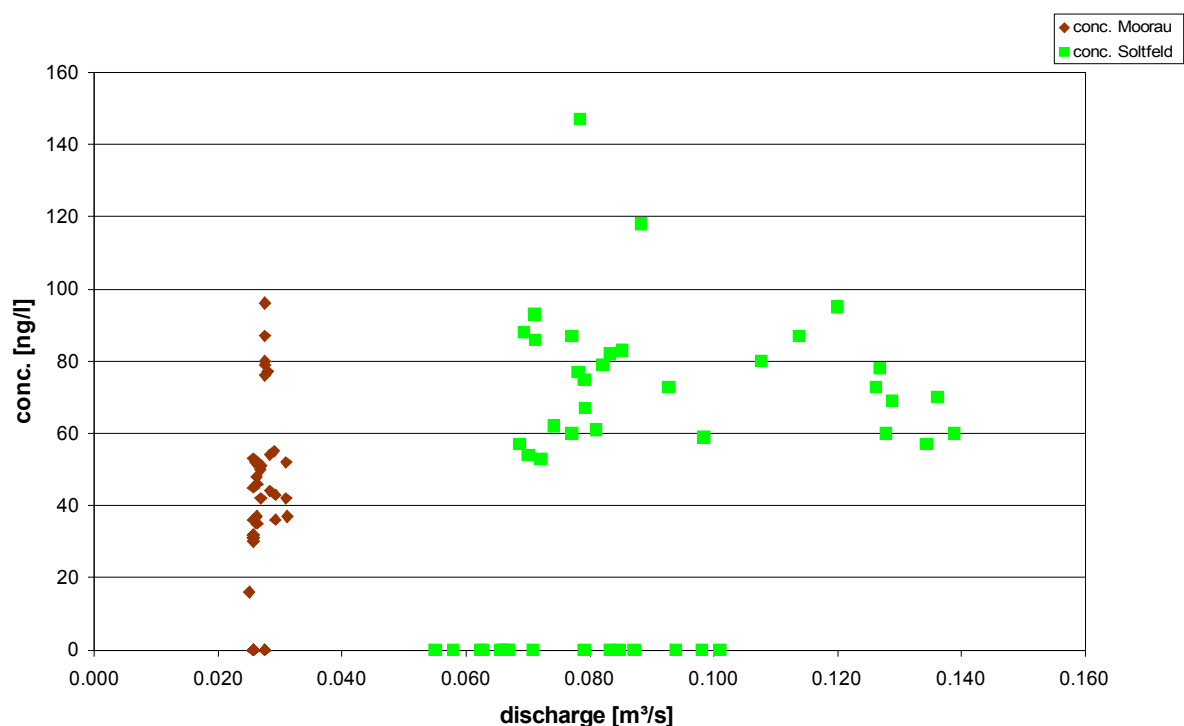


Fig. 76: Pesticide concentration-discharge volume-correlation of analyzed water samples in spring 2008

7.6 Final discussion

Precipitation patterns are one of the main factors influencing pesticide transport, relocating pesticides as solutes or bonded to field soil particles (Arnaez et al., 2007; Klavivko et al., 2001; Lewan et al., 2009). Within the three herbicide monitoring campaigns in the Kielstau catchment, the dependence of herbicide transport on precipitation was clearly observed in autumn 2008 and autumn 2009. Rainfall events increased discharges of artificial drainages and the Moorau and Kielstau rivers; herbicides were detected mainly during these discharge peaks. Within the monitoring of spring 2008, there was little effect on Terbutylazine relocation by the observed precipitation. Records were available only from the rain gauge at Satrup, 8 – 10 km away from the field site. It is assumed that the spatial variability of precipitation is higher in spring 2008 than in autumns 2008 and 2009 within the catchment.

With an experimental set up on the monitored drained fields, the herbicide loss could be traced directly to the artificial drainage, however, on the larger subcatchment and catchment scales, it was not possible to sufficiently distinguish the relevance of individual pathways for pesticides into surface water. The findings in the Moorau and in the Kielstau are a mixture of

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losses from all potential pathways. One may limit the relevance of single entry routes, such as drift and atmospheric deposition, that are generally assumed to be negligible (Asman et al., 2003; De Schampheleire et al., 2007; Loubet et al., 2006). A general attribute of point sources, from farmyards, for example, is that they are triggered by small rainfall events and recede very fast. In contrast, discharge from fields, e.g., via surface runoff and drainage, requires more precipitation, but lasts much longer. Nevertheless, it is likely that inputs from both sources appear in a short period at the beginning of discharge events (Leu et al., 2004b). Leu et al. (2004a) observed that surface runoff-related losses show a shorter and more pronounced concentration peak than drainage losses. Data in a higher temporary resolution are necessary for this distribution and cannot be derived from the daily values of this investigation. The proportion of surface runoff effect on the total discharge at the outlet of the Kielstau catchment is evaluated as low. Estimated results accounted for an average proportion of 5 % of the total discharge for surface runoff and, hence, it is not substantial (Kiesel et al., 2010; Kiesel et al., 2009). It can be inferred that the herbicide concentrations and loads which were detected in the Moorau and the Kielstau originated mainly from drainage systems and farmyards. It was not possible to quantify the loss of herbicides from fields via drainage with sufficient accuracy on subcatchment and catchment scale, because scope of a drainage's catchment changes on field scale according to hydrological conditions and is therefore difficult to ascertain. Hence, there is wide variability in application/loss ratios. It is not appropriate to extrapolate these values of already higher uncertainty to the scales of subcatchment and catchment, because the drained areas in the catchment determined by Golon (2006) also include over- and underestimations. In addition, it can not be assumed that the drainage systems in the entire catchment discharge the same proportion of herbicide as they do from the observed drained fields. An extrapolation would result in an educated guess instead of scientifically ascertained values. However, the extrapolation of herbicide amounts applied to the fields of the subcatchment and the catchment implies an uncertainty which has to be taken into account when looking at the rate of herbicide losses on these scales. They provide an order of magnitude but must be confirmed by further studies.

Similar to the results of the herbicide monitorings in the Kielstau catchment, the herbicide losses via surface runoff determined in the laboratory experiment with the rainfall simulator should not be transferred by implication from micro-scale (plot) to macro-scale (catchment). Micro-plots are research tools especially useful for process investigations, but the influence of

soil surface structure, machine tracks, length of the slope and dynamic of the runoff at field scale or larger must be considered. Hence, these experiments give an overview of the relevance of surface runoff in the transport of pesticide from the field into surface water. The herbicide loss via surface runoff (2 - 7 %) is by the magnitude of one to two orders higher than that via drainage (< 0.01 – 0.3 %), despite uncertainties of the values determined in the monitorings and the laboratory experiment. In other studies, similar proportions between losses from surface runoff and drainage systems are documented from field and catchment observations (Bach et al., 2005a; Kreuger, 1998; Reichenberger et al., 2007).

8 CONCLUSION AND OUTLOOK

The loss of selected herbicides from agricultural fields to non-target areas was investigated in drain water, groundwater and surface water in a lowland catchment in northern Germany. Analysis of monitoring observations revealed that herbicide compounds were relocated mainly during discharge peaks after rainfall events that induced rises in rates of discharge. Highest concentrations were observed during the first discharge peak(s) after herbicide application, but highest loads occurred later, when, due to numerous rainfall events, discharge increased, though herbicide concentrations had diminished. Rapid transport of herbicides via preferential flow is assumed to be an important mechanism for their relocation and was observed on the scales of field, subcatchment and catchment. During this kind of transport, the physical-chemical properties of the herbicides are of minor relevance. At field scale, the influence of the herbicide properties was clearly observed, but increasingly obscured by hydrological parameters at the scales of subcatchment and catchment.

Regarding the pathways of herbicides into surface water, drainage systems and farmyards are assessed to be the dominant entry routes, whereas surface runoff is of minor relevance. The loss via drainage systems could not be quantified with a sufficient exactness because extrapolations from field to catchment scale are inappropriate. The portion of herbicide loss from farmyards could not be determined, due to the infrastructure of waste water connections. The farmyard outlets are not connected to the waste water treatment plants, but discharge their outflow somewhere into a recipient stream. It is not possible to observe the high number of potential farmyard outlets in spatial and temporal distribution during application periods, but it must be questioned whether the inputs of herbicides into surface water from today's farmyards has decreased in comparison to those of years ago. A new generation of farmers has been raised with environmental education, so that a higher sensitivity for environmental threats from agriculture can be assumed. Furthermore, the plant protection services and the chambers of agriculture undertake intensive trainings for farmers, regarding the handling and use of pesticides. Spraying equipment with an additional fresh water tank for cleaning procedures on the field relieve the farmers' work. Finally, the prices of pesticide supplements have

risen to an extent that farmers must now be more economically conscious in application of these supplements.

The experimental set up for intermittent simulated rainfall shows that pesticide loads were discharged from a soil surface via surface runoff in significant amounts of 2 – 7 % of the amount applied. It was observed that the first samples after application contained in fact the highest concentrations, but that loads were highest during the second rainfall event of runoff generation, when the runoff volume was larger, due to crusting of the soil surface. Even small amounts of rainfall can initiate surface runoff if sealing and crusting of the soil surface develop rapidly. Furthermore, the herbicides were released by alterations of the soil surface during the rainless period and by air slaking of the dry soil aggregates in the beginning of the rainfall events. Hence, a repeating increase of the pesticide concentration in the first interval of each rainfall event was noticed.

Improvements for further studies:

The size of a drainage's catchment is an essential factor in determining the proportion of the pesticide loss. Dimensions of the surface area of the catchment affecting or affected by a drainage system are crucial for determination of pesticide losses, however, such figures vary relative to hydrological conditions and must be determined with proper methodology. The monitoring campaigns of this study show wide variability in the portion of catchment area that may relate to a drainage system. Therefore, for the purpose of higher accuracy, the installation of further groundwater points in the vadose zone, and the application of tracers such as Bromide or color tracers is suggested.

In the groundwater samples on drained field 2, herbicide concentrations were observed in the temporary groundwater measuring point GW1 for a limited time, but without explanation. Additional temporary groundwater measuring points would have provided a better understanding of this and of the groundwater flow direction that changes often in regions of flat topography and shallow groundwater. By sampling several groundwater measuring points, how and whether herbicide findings are temporally or spatially relevant can be determined with greater accuracy.

A question concerning the extent to which the physical-chemical properties of the selected herbicides explain the herbicide transport arose during the monitoring campaigns. If this topic had been of major interest at the beginning of the monitorings, the herbicides would have been applied in one application solution, so that results that varied according to different hy-

drological conditions or different sites would not have occurred. Furthermore, herbicides of pronounced differences in physical-chemical properties would have been chosen.

Precipitation is an important factor influencing pesticide transport. During the monitoring of Terbutylazine, data from one rain gauge at 8 – 10 km distance from the sampling points were available. Discharge peaks could not be explained with the observed patterns of precipitation. Hence, several rain gauges should be installed at different locations in the catchment to record the spatial distribution of rainfall events within the catchment.

In further surface runoff experiments with the rainfall simulator, multiple pesticides can be sprayed together in one application solution. In several studies, this approach was observed, and interactions between the compounds appeared negligible. This set up offers the opportunity of clearer comparison of pesticide discharges, since variations of the conditions in the soil containers are omitted.

To calculate herbicide balance in the soil containers, the volume of water drained from the containers by the suction plates should be measured and analyzed for pesticide concentration. The subsequent determination of pesticide content of the soil would complete the balance.

Recommendations for authorities:

Derived from the investigations in the catchment and in the laboratory is that highest herbicide loss occurred 5 to 71 days after application during the monitoring in the Kielstau catchment, and within the second rainfall event in the laboratory experiment. Hence, aquatic ecosystems are not only endangered immediately after application when highest herbicide concentrations were observed, but are threatened over a longer period, due to future high discharges that may augment the herbicide loads of surface waters. This circumstance should be taken into account when discussing mitigation strategies for the two pathways drainage systems and surface runoff.

The results of this monitoring of herbicides in the Kielstau catchment reveal that drainage systems contribute significantly to herbicide loss, especially in lowland catchments with a high proportion of artificially drained areas. Therefore, loss reducing measures other than placing the application date into rainless periods must be gathered. Farmers need a certain soil water content for the efficiency of the supplement so that they do not spray the pesticides on dry soil. The collection of drainage water in natural or artificial ponds may be a step into the right direction, because, there, a residence time can be provided for pesticide degradation.

8 Conclusion and outlook

For a better understanding of the processes taking place in a catchment, it is necessary to take samples in high resolution during the application period and the first weeks after it, instead of grab sampling in monthly intervals throughout the year. It must be recognized that the timing and duration of application periods varies, depending on the harvest of the previous crops. Hence, monitoring periods should be adapted to these facts.

The validity of the results provided from the monitoring campaigns and the laboratory experiment has limitations which can be improved by a more complex monitoring set up that more thoroughly covers aspects and variations of pesticide loss. In general, this is associated with high technical, personnel and financial effort. The alternative is the implementation of a model which displays transport processes and proportions. The gained data are suitable to be integrated into such a model. In a current project, the simulation of herbicide transport in the Kielstau catchment is accomplished with these data.

The results of this dissertation show that there are present needs for extended knowledge about the fate and transport of pesticides. Complex processes take place and many interrelations have not been observed, or can not be sufficiently explained. Hence, intensive cooperation of environmental agencies, researchers and industries is imperative, in order to enhance the understanding of pesticide fate and create a strategy of pesticide use that preserves ecosystems and further generations from unwanted side-effects.



Fig. 77: Kielstau river

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10 APPENDIX

A 1 Monitoring of Terbutylazine in spring 2008

A 2 Monitoring of Metazachlor in autumn 2008

A 3 Monitoring of Flufenacet in autumn 2009

A 4 Surface runoff experiments with rainfall simulator

MONITORING OF TERBUTHYLAZINE IN SPRING 2008

Discharges in spring 2008

Daily mean values [m³/s]

date	Moorau	Kielstau
1/5/2008	0.031	0.208
2/5/2008	0.032	0.198
3/5/2008	0.032	0.197
4/5/2008	0.031	0.191
5/5/2008	0.030	0.184
6/5/2008	0.029	0.175
7/5/2008	0.029	0.160
8/5/2008	0.029	0.154
9/5/2008	0.028	0.144
10/5/2008	0.028	0.134
11/5/2008	0.027	0.131
12/5/2008	0.027	0.126
13/5/2008	0.027	0.117
14/5/2008	0.027	0.114
15/5/2008	0.028	0.108
16/5/2008	0.028	0.101
17/5/2008	0.028	0.098
18/5/2008	0.028	0.094
19/5/2008	0.028	0.087
20/5/2008	0.028	0.085
21/5/2008	0.028	0.082
22/5/2008	0.028	0.079
23/5/2008	0.028	0.077
24/5/2008	0.028	0.071
25/5/2008	0.028	0.066
26/5/2008	0.028	0.083
27/5/2008	0.029	0.078

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date	Moorau	Kielstau
28/5/2008	0.027	0.071
29/5/2008	0.027	0.069
30/5/2008	0.027	0.078
31/5/2008	0.026	0.085
1/6/2008	0.026	0.083
2/6/2008	0.026	0.081
3/6/2008	0.026	0.079
4/6/2008	0.026	0.077
5/6/2008	0.026	0.074
6/6/2008	0.026	0.072
7/6/2008	0.026	0.070
8/6/2008	0.026	0.069
9/6/2008	0.026	0.066
10/6/2008	0.026	0.063
11/6/2008	0.026	0.055
12/6/2008	0.026	0.058
13/6/2008	0.026	0.062
14/6/2008	0.026	0.067
15/6/2008	0.026	0.071
16/6/2008	0.026	0.079
17/6/2008	0.026	0.088
18/6/2008	0.026	0.093
19/6/2008	0.025	0.098
20/6/2008	0.026	0.108
21/6/2008	0.026	0.114
22/6/2008	0.026	0.120
23/6/2008	0.028	0.129
24/6/2008	0.031	0.134
25/6/2008	0.029	0.139
26/6/2008	0.029	0.136
27/6/2008	0.031	0.128
28/6/2008	0.031	0.126
29/6/2008	0.028	0.127
30/6/2008		0.091

Precipitation records in spring 2008

Daily total [mm]

date	Satrup
13/5/2008	0
14/5/2008	0
15/5/2008	0
16/5/2008	0
17/5/2008	0
18/5/2008	0
19/5/2008	0
20/5/2008	0
21/5/2008	0
22/5/2008	0
23/5/2008	0
24/5/2008	0
25/5/2008	2
26/5/2008	11
27/5/2008	0
28/5/2008	0
29/5/2008	0
30/5/2008	0
31/5/2008	0
1/6/2008	0
2/6/2008	0
3/6/2008	0
4/6/2008	0
5/6/2008	0
6/6/2008	0
7/6/2008	0
8/6/2008	0
9/6/2008	0
10/6/2008	0
11/6/2008	2
12/6/2008	1
13/6/2008	1

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date	Satrup
14/6/2008	1
15/6/2008	2
16/6/2008	8
17/6/2008	0
18/6/2008	0
19/6/2008	5
20/6/2008	0
21/6/2008	0
22/6/2008	9
23/6/2008	0
24/6/2008	0
25/6/2008	0
26/6/2008	0
27/6/2008	5
28/6/2008	7
29/6/2008	0
30/6/2008	0

Terbutylazine concentrations in spring 2008

Daily mixed samples [ng/l]

date	drainage	Moorau	Kielstau
16/5/2008	< 25	< 25	< 25
17/5/2008	< 25	87	< 25
18/5/2008	< 25	< 25	< 25
19/5/2008	< 25	80	< 25
20/5/2008	< 25	77	< 25
21/5/2008	< 25	96	79
22/5/2008	93	< 25	< 25
23/5/2008	85	79	87
24/5/2008	91	76	86
25/5/2008	132	< 25	< 25
26/5/2008	250	77	< 25
27/5/2008	165	55	147
28/5/2008	301	51	93

date	drainage	Moorau	Kielstau
29/5/2008	146	42	88
30/5/2008	98	50	77
31/5/2008	114	46	83
1/6/2008	106	37	82
2/6/2008	122	45	61
3/6/2008	151	53	75
4/6/2008	< 25	31	60
5/6/2008	82	36	62
6/6/2008	99	31	53
7/6/2008	< 25	30	54
8/6/2008	< 25	32	57
9/6/2008	drainage ran	< 25	< 25
10/6/2008	dry	< 25	< 25
11/6/2008		< 25	< 25
12/6/2008		< 25	< 25
13/6/2008		< 25	< 25
14/6/2008		< 25	< 25
15/6/2008		< 25	< 25
16/6/2008		35	67
17/6/2008		52	118
18/6/2008		32	73
19/6/2008		16	59
20/6/2008		48	80
21/6/2008		35	87
22/6/2008		52	95
23/6/2008		44	69
24/6/2008		37	57
25/6/2008		43	60
26/6/2008		36	70
27/6/2008		42	60
28/6/2008		52	73
29/6/2008		54	78

Terbutylazine loads in spring 2008

Daily loads

date	Moorau [mg/d]	Kielstau [g/d]
13/5/2008	29	0.126
14/5/2008	29	0.123
15/5/2008	30	0.117
16/5/2008	30	0.109
17/5/2008	207	0.106
18/5/2008	30	0.101
19/5/2008	190	0.094
20/5/2008	186	0.092
21/5/2008	229	0.561
22/5/2008	30	0.085
23/5/2008	188	0.579
24/5/2008	181	0.529
25/5/2008	30	0.071
26/5/2008	186	0.090
27/5/2008	138	0.995
28/5/2008	118	0.571
29/5/2008	97	0.527
30/5/2008	116	0.519
31/5/2008	104	0.611
6/1/2008	84	0.590
6/2/2008	100	0.427
6/3/2008	118	0.513
6/4/2008	69	0.400
6/5/2008	80	0.397
6/6/2008	69	0.330
6/7/2008	67	0.327
6/8/2008	71	0.338
6/9/2008	28	0.071
6/10/2008	28	0.068
6/11/2008	28	0.059
6/12/2008	28	0.063
13/6/2008	28	0.067

date	Moorau [mg/d]	Kielstau [g/d]
14/6/2008	28	0.072
15/6/2008	28	0.077
16/6/2008	79	0.459
17/6/2008	116	0.899
18/6/2008	71	0.585
19/6/2008	35	0.502
20/6/2008	109	0.745
21/6/2008	79	0.855
22/6/2008	118	0.985
23/6/2008	108	0.768
24/6/2008	100	0.662
25/6/2008	108	0.720
26/6/2008	91	0.824
27/6/2008	112	0.663
28/6/2008	139	0.796
29/6/2008	132	0.855

Application of Terbutylazine in the Kielstau catchment in spring 2008

date	Terbutylazine [kg/d]
1/5/2008	0.93
2/5/2008	0.00
3/5/2008	0.00
4/5/2008	0.00
5/5/2008	0.00
6/5/2008	0.00
7/5/2008	0.00
5/8/2008	0.00
9/5/2008	0.00
10/5/2008	0.00
11/5/2008	1.07
12/5/2008	0.00
13/5/2008	0.00
14/5/2008	0.00
15/5/2008	0.00
16/5/2008	4.36

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date	Terbutylazine [kg/d]
17/5/2008	0.00
18/5/2008	8.94
19/5/2008	0.00
20/5/2008	0.00
21/5/2008	0.00
22/5/2008	3.12
23/5/2008	3.60
24/5/2008	0.00
25/5/2008	0.00
26/5/2008	4.09
27/5/2008	0.00
28/5/2008	0.00
29/5/2008	0.00
30/5/2008	0.00
31/5/2008	0.00
1/6/2008	0.00
2/6/2008	0.00
3/6/2008	0.00
4/6/2008	0.00
5/6/2008	0.00
6/6/2008	0.00
7/6/2008	0.00
8/6/2008	0.00
9/6/2008	0.00
10/6/2008	0.00
11/6/2008	0.00
12/6/2008	0.00
13/6/2008	0.93
14/6/2008	0.00
15/6/2008	0.00
16/6/2008	0.00

Uncertainty of Terbutylazine analyses

Messunsicherheitsabschätzung	
zur Bestimmung von	Terbutylazin
in	Wasser
mittels	SPE - HPLC/DAD
für den Konzentrationsbereich:	50-1000 ng/l
auf der Basis des Nordtest-Handbooks	
"Handbook for calculation of measurement uncertainty in environmental laboratories"	
Bearbeitung:	Uta Ulrich
Datum:	Unterschrift:
Reproduzierbarkeit innerhalb des Labors	
u_{Rw}	8.47%
A) Kontrollprobe, die den gesamten Prozess abdeckt	
Standardabweichung:	10
bei Konzentration:	118
rel Standardabweichung:	8.47%
B) Kontrollprobe, die nicht den gesamten Prozess abdeckt	
B.1 Kontrollprobenergebnis	
Standardabweichung:	
bei Konzentration:	
rel Standardabweichung:	
B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)	

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>
Kombination:	<input type="text"/>

C) Instabile Kontrollproben

C.1 Wiederholbarkeit

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>

C.2 "Langzeit"-Komponente

Schätzwert für die Standardabweichung	<input type="text"/>
basierend auf:	<input type="text"/>
Kombination:	<input type="text"/>

Methoden- und Laborabweichung

u_{bias} **4.14%**

A) Mehrfache Analytik eines zertifizierten Referenzmaterials

zertifizierter Wert	<input type="text"/>	Einheit:	<input type="text" value="mg/kg"/>
Konfidenzintervall +/-	<input type="text"/>		
Konfidenzniveau	95%		
relative Standardunsicherheit:	<input type="text"/>		
Mittelwert der ZRM-Analytik:	<input type="text"/>	mg/kg	
Mittlere Abweichung	<input type="text"/>		
Mittlere Abweichung in %	<input type="text"/>		

Std.-abweichung der ZRM-Analytik:	<input type="text"/>	mg/kg
rel.Std.-abweichung der ZRM-Analytik:	<input type="text"/>	
Anzahl der Messwerte:	<input type="text"/>	
Standardunsicherheit:	<input type="text"/>	

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interva I	Konf.-niv.	Mittelwert
ZRM 1	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 2	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 3	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 4	<input type="text"/>	<input type="text"/>	95%	<input type="text"/>
	$u(c_{ref})$		Abw.	Abw.quadrat
ZRM 1	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 2	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 3	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 4	<input type="text"/>		<input type="text"/>	<input type="text"/>
Mittel	<input type="text"/>	RMS _{bias}	<input type="text"/>	
Standardunsicherheit:	<input type="text"/>			

C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw- quadrat	s _R (%)	N Werte	u(c _{ref})
Probe 1	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>
Probe 2	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>	<input type="text"/>

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Probe 3		
Probe 4		
Probe 5		
Probe 6		
Probe 7		
Probe 8		
Probe 9		
Probe 10		
Probe 11		
Probe 12		
	RMS _{bias}	
		u(c _{ref})
Standardunsicherheit:		

D) Wiederfindungsexperiment

Unsicherheit der Konzentration der Aufstocklösung:

Konzentration der Aufstocklösung:	250
Konfidenzintervall +/-	5
Konfidenzniveau:	
u _{conc}	1.02%

Unsicherheit des zugegebenen Volumens:

max. Abweichung [%] (Rechteckverteilung)	0.01%	Std-abw.:	0.01%
Wiederholbarkeit [%] (als Standardabw.)	0.01%		

		u_{vol}	0.01%			
Unsicherheit der Aufstockung:		$u_{recovery}$	1.02%			
Wiederfindung:						
	Aufstockung	Messdiffere nz	Wiederfindun g	Abweichun g	Abw-quadrat	
1	250	5	98.00%	2.00%	0.04%	
2	250	9	96.40%	3.60%	0.13%	
3	250	14	94.40%	5.60%	0.31%	
4						
5						
6						
7						
8						
9						
10						
11						
12						
					RMS_{bias}	4.01%
Standardunsicherheit:		4.14%				
Kombinierte Standardunsicherheit				u	9.43%	
Erweiterte Unsicherheit U		k-Faktor	2	18.86%		

MONITORING OF METAZACHLOR IN AUTUMN 2008

Rating curve of the drain pipe on drained field 2 in autumn 2008

water levels in drain pipe[m]	discharge [m ³ /s]
1.8	1.33E-05
1.74	1.46E-05
1.25	1.11E-05
1.3	7.00E-06
1	3.33E-06
0.6	2.44E-06
3.1	1.42E-04
3	1.08E-04
4.7	1.90E-04
5.2	2.27E-04
3.5	1.48E-04
5	1.44E-04
4	1.28E-04
4.7	2.47E-04
6.5	3.72E-04

Discharges in autumn 2008

Daily mean values [m³/s]

date	drainage	Moorau	Kielstau
1/9/2008	2.81E-05	0.016	0.102
2/9/2008	6.68E-05	0.016	0.098
3/9/2008	9.34E-05	0.017	0.096
4/9/2008	8.59E-05	0.016	0.094
5/9/2008	8.23E-05	0.017	0.092
6/9/2008	7.96E-05	0.018	0.091

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date	drainage	Moorau	Kielstau
7/9/2008	8.96E-05	0.017	0.089
8/9/2008	9.18E-05	0.021	0.095
9/9/2008	9.41E-05	0.033	0.121
10/9/2008	1.27E-04	0.028	0.117
11/9/2008	8.45E-05	0.023	0.103
12/9/2008	5.58E-05	0.020	0.086
13/9/2008	6.40E-05	0.019	0.077
14/9/2008	4.53E-05	0.017	0.070
15/9/2008	3.16E-05	0.016	0.067
16/9/2008	2.17E-05	0.016	0.065
17/9/2008	2.20E-05	0.016	0.064
18/9/2008	9.38E-06	0.017	0.063
19/9/2008	1.43E-05	0.018	0.062
20/9/2008	1.35E-05	0.016	0.062
21/9/2008	8.10E-06	0.014	0.061
22/9/2008	1.29E-05	0.014	0.061
23/9/2008	7.10E-06	0.014	0.062
24/9/2008	2.03E-07	0.014	0.063
25/9/2008	7.87E-07	0.014	0.063
26/9/2008	1.86E-06	0.014	0.064
27/9/2008	1.53E-06	0.014	0.066
28/9/2008	6.24E-06	0.015	0.067
29/9/2008	2.35E-05	0.016	0.069
30/9/2008	1.85E-04	0.022	0.15
1/10/2008	1.85E-04	0.056	0.289
2/10/2008	1.85E-04	0.064	0.45
3/10/2008	2.57E-04	0.074	0.493
4/10/2008	2.57E-04	0.065	0.394
5/10/2008	2.57E-04	0.080	0.504
6/10/2008	2.57E-04	0.098	0.657
7/10/2008	1.85E-04	0.073	0.520
8/10/2008	1.85E-04	0.050	0.427
9/10/2008	1.85E-04	0.040	0.362
10/10/2008	2.02E-04	0.034	0.322
11/10/2008	2.02E-04	0.030	0.293
12/10/2008	2.02E-04	0.028	0.266

date	drainage	Moorau	Kielstau
13/10/2008	2.02E-04	0.026	0.268
14/10/2008	3.30E-04	0.024	0.270
15/10/2008	3.30E-04	0.024	0.270
16/10/2008	3.30E-04	0.048	0.423
17/10/2008	3.30E-04	0.079	0.681
18/10/2008	3.33E-04	0.062	0.679
19/10/2008	3.33E-04	0.079	0.670
20/10/2008	3.33E-04	0.072	0.676
21/10/2008	3.56E-04	0.062	0.590
22/10/2008	3.56E-04	0.072	0.599
23/10/2008	3.56E-04	0.070	0.605
24/10/2008	4.28E-04	0.065	0.611
25/10/2008	4.28E-04	0.059	0.616
26/10/2008	4.28E-04	0.068	0.679
27/10/2008	4.28E-04	0.130	0.988
28/10/2008	4.41E-04	0.133	1.020
29/10/2008	4.41E-04	0.118	1.009
30/10/2008	4.41E-04	0.094	0.869
31/10/2008	3.59E-04	0.070	0.719
1/11/2008	2.75E-04	0.056	0.606
2/11/2008	7.69E-05	0.048	0.547
3/11/2008	8.04E-05	0.035	0.499
4/11/2008	8.93E-05	0.035	0.444
5/11/2008	8.77E-05	0.033	0.422
6/11/2008	6.48E-05	0.033	0.410
7/11/2008	6.19E-05	0.032	0.410
8/11/2008	7.27E-05	0.031	0.401
9/11/2008	1.18E-04	0.034	0.372
10/11/2008	2.10E-04	0.048	0.407
11/11/2008	5.02E-04	0.174	0.966
12/11/2008	4.00E-04	0.168	1.320
13/11/2008	1.69E-04	0.130	1.174
14/11/2008	8.61E-05	0.125	1.070
15/11/2008	7.01E-05	0.123	1.070
16/11/2008	9.93E-05	0.100	0.985
17/11/2008	8.18E-05	0.079	0.827

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date	drainage	Moorau	Kielstau
18/11/2008	1.71E-04	0.075	0.731
19/11/2008	1.42E-04	0.088	0.753
20/11/2008	3.28E-04	0.111	0.906
21/11/2008	6.83E-04	0.107	0.933
22/11/2008	6.50E-04	0.084	0.854
23/11/2008	6.27E-04	0.065	0.683
24/11/2008	6.69E-04	0.053	0.590
25/11/2008	3.29E-04	0.044	0.515
26/11/2008	1.74E-04	0.039	0.463
27/11/2008	1.71E-04	0.040	0.456
	calculated		

Precipitation records in autumn 2008

Precipitation (daily total) [mm]

date	Satrup	Moorau	Ausacker
1/9/2008	1	1	
2/9/2008	2	3	
3/9/2008	6	6	
4/9/2008	0	0	
5/9/2008	3	3	
6/9/2008	1	2	
7/9/2008	6	10	
8/9/2008	11	9	
9/9/2008	0	0	
10/9/2008	0	0	
11/9/2008	0	0	
12/9/2008	0	0	
13/9/2008	0	0	

date	Satrup	Moorau	Ausacker
14/9/2008	0	0	
15/9/2008	0	0	
16/9/2008	0	0	
17/9/2008	2	4	
18/9/2008	0	0	
19/9/2008	0	0	
20/9/2008	0	0	
21/9/2008	0	0	
22/9/2008	0	1	
23/9/2008	1	1	
24/9/2008	0	0	
25/9/2008	0	0	
26/9/2008	0	0	
27/9/2008	0	0	
28/9/2008	0	0	
29/9/2008	0	0	
30/9/2008	31	0	
1/10/2008	13	0	
2/10/2008	10	0	
3/10/2008	1	0	
4/10/2008	0	0	
5/10/2008	0	0	
6/10/2008	0	0	
7/10/2008	0	0	
8/10/2008	0	0	2
9/10/2008	0	0	0
10/10/2008	0	0	0
11/10/2008	0	0	0
12/10/2008	2.5	0	3
13/10/2008	1	0	1
14/10/2008	0	0	0
15/10/2008	12	11	13
16/10/2008	7	12	11
17/10/2008	4	4	5
18/10/2008	5	4	5
19/10/2008	2	5	6
20/10/2008	0	0	0

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date	Satrup	Moorau	Ausacker
21/10/2008	9	10	11
22/10/2008	5	5	6
23/10/2008	0	1	1
24/10/2008	6	5	6
25/10/2008	0	0	0
26/10/2008	12	13	15
27/10/2008	4	4	5
28/10/2008	5.6	5	3
29/10/2008	1	1	1
30/10/2008	0	0	0
31/10/2008	0	0	0
1/11/2008	0	0	1
2/11/2008	0	0	0
3/11/2008	0	1	0
4/11/2008	0	0	2
5/11/2008	0	1	1
6/11/2008	0	1	1
7/11/2008	0	0	1
8/11/2008	0	0	0
9/11/2008	5	5	5
10/11/2008	7	8	14
11/11/2008	16	17	11
12/11/2008	2	2	3
13/11/2008	2	1	3
14/11/2008	4	3	6
15/11/2008	0	1	0
16/11/2008	1	0	4
17/11/2008	0	6	0
18/11/2008	6	7	8
19/11/2008	3	5	6
20/11/2008	3	4	6
21/11/2008	0	3	1
22/11/2008	0	0	0
23/11/2008	0	0	0
24/11/2008	0	0	0
25/11/2008	0	0	0
26/11/2008	1	0	1

date	Satrup	Moorau	Ausacker
27/11/2008	1	3	2

Groundwater levels on drained field 2 in autumn 2008

values (GW1 und 2) und daily mean values (sensor) [m]

date	GW 1	GW 2	GW Sensor
1/9/2008	1.92	1.75	
2/9/2008			
3/9/2008			
4/9/2008			
5/9/2008			
6/9/2008			
7/9/2008			
8/9/2008	1.91	1.75	
9/9/2008			
10/9/2008			
11/9/2008	1.69	1.48	
12/9/2008			
13/9/2008			
14/9/2008			
15/9/2008	1.81	1.66	
16/9/2008			
17/9/2008			
18/9/2008	1.82	1.69	
19/9/2008			
20/9/2008			
21/9/2008			
22/9/2008	1.87	1.75	
23/9/2008			
24/9/2008			
25/9/2008	1.92	1.8	
26/9/2008			
27/9/2008			
28/9/2008			
29/9/2008	1.93	1.83	

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date	GW 1	GW 2	GW Sensor
30/9/2008			
1/10/2008			
2/10/2008	1.23	1.23	
3/10/2008			
4/10/2008			
5/10/2008			
6/10/2008	1	1.01	
7/10/2008			
8/10/2008			
9/10/2008	1.23	1.23	
10/10/2008			
11/10/2008			
12/10/2008			
13/10/2008	1.27	1.18	
14/10/2008			
15/10/2008			
16/10/2008			
17/10/2008	0.78	0.79	
18/10/2008			
19/10/2008			
20/10/2008	0.85	0.78	
21/10/2008			
22/10/2008			
23/10/2008	0.8	0.71	
24/10/2008			
25/10/2008			
26/10/2008			
27/10/2008	0.54	0.49	
28/10/2008			
29/10/2008			
30/10/2008	0.58	0.45	
31/10/2008			
1/11/2008			
2/11/2008			
3/11/2008	0.82	0.7	
4/11/2008			
5/11/2008			

date	GW 1	GW 2	GW Sensor
6/11/2008	0.89	0.76	
7/11/2008			
8/11/2008			
9/11/2008			
10/11/2008	0.81	0.66	
11/11/2008			
12/11/2008	0.51	0.33	0.32
13/11/2008	0.5	0.36	0.36
14/11/2008			0.34
15/11/2008			0.32
16/11/2008			0.38
17/11/2008	0.59	0.45	0.46
18/11/2008			0.42
19/11/2008			0.34
20/11/2008	0.29	0.23	0.30
21/11/2008			0.27
22/11/2008			0.33
23/11/2008			0.43
24/11/2008	0.6	0.49	0.50
25/11/2008			0.58
26/11/2008			0.63
27/11/2008			0.62

Metazachlor concentrations in autumn 2008

Daily mixed samples in the drain pipe and in the Kielstau [ng/l]

date	drainage	groundwater	Kielstau
1/9/2008	application		< 25
2/9/2008	< 25		no sample
3/9/2008	< 25		no sample
4/9/2008	< 25		no sample
5/9/2008	< 25		no sample
6/9/2008	131		no sample
7/9/2008	< 25		no sample

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8/9/2008	< 25	< 25	80
9/9/2008	< 25		no sample
10/9/2008	558		no sample
11/9/2008	330	< 25	29
12/9/2008	157		< 25
13/9/2008	117		no sample
14/9/2008	63		no sample
15/9/2008	68	< 25	no sample
16/9/2008	81		no sample
17/9/2008	75		no sample
18/9/2008	50	< 25	no sample
19/9/2008	29		no sample
20/9/2008	< 25		no sample
21/9/2008	< 25		no sample
22/9/2008	< 25	< 25	no sample
23/9/2008	< 25		< 25
24/9/2008	< 25		< 25
25/9/2008	< 25	< 25	< 25
26/9/2008	no results		< 25
27/9/2008	no results		< 25
28/9/2008	no results		< 25
29/9/2008	no results	< 25	< 25
30/9/2008	< 25		87
1/10/2008	< 25		88
2/10/2008	< 25	< 25	74
3/10/2008	< 25		44
4/10/2008	< 25		< 25
5/10/2008	< 25		35
6/10/2008	< 25	< 25	no sample
7/10/2008	404		no sample
8/10/2008	190		no sample
9/10/2008	138	< 25	no sample
10/10/2008	94		no sample
11/10/2008	240		no sample
12/10/2008	151		no sample
13/10/2008	< 25	< 25	no sample
14/10/2008	134		< 25
15/10/2008	191		< 25

16/10/2008	97		48
17/10/2008	< 25	168	< 25
18/10/2008	290		< 25
19/10/2008	576		< 25
20/10/2008	132	155	< 25
21/10/2008	401		< 25
22/10/2008	230		< 25
23/10/2008	256	98	< 25
24/10/2008	256		< 25
25/10/2008	256		< 25
26/10/2008	256		< 25
27/10/2008	256	70	< 25
28/10/2008	256		< 25
29/10/2008	256		< 25
30/10/2008	91	< 25	< 25
31/10/2008	113		< 25
1/11/2008	41		< 25
2/11/2008	< 25		< 25
3/11/2008	68	< 25	< 25
4/11/2008	61		< 25
5/11/2008	40		< 25
6/11/2008	48	< 25	< 25
7/11/2008	< 25		< 25
8/11/2008	< 25		< 25
9/11/2008	163		< 25
10/11/2008	120	< 25	< 25
11/11/2008	444		< 25
12/11/2008	138		< 25
13/11/2008	70	< 25	< 25
14/11/2008	104		< 25
15/11/2008	75		< 25
16/11/2008	51		< 25
17/11/2008	27	< 25	< 25
18/11/2008	81		< 25
19/11/2008	44		< 25
20/11/2008	100	< 25	< 25
21/11/2008	31		< 25
22/11/2008	< 25		< 25

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23/11/2008	< 25		< 25
24/11/2008	< 25		< 25
25/11/2008	< 25	< 25	< 25
26/11/2008	25		< 25
27/11/2008	< 25	< 25	< 25
		weekly mixed	sample

Metazachlor loads in autumn 2008

date	drainage [mg]	Kielstau [g]
1/9/2008	application	
2/9/2008	0.072	0.106
3/9/2008	0.101	0.104
4/9/2008	0.093	0.102
5/9/2008	0.089	0.099
6/9/2008	0.900	0.098
7/9/2008	0.097	0.096
8/9/2008	0.099	0.659
9/9/2008	0.102	0.131
10/9/2008	6.118	0.127
11/9/2008	2.409	0.259
12/9/2008	0.757	0.093
13/9/2008	0.647	0.083
14/9/2008	0.247	0.075
15/9/2008	0.186	0.072
16/9/2008	0.152	0.070
17/9/2008	0.142	0.069
18/9/2008	0.041	0.068
19/9/2008	0.036	0.067
20/9/2008	0.015	0.067
21/9/2008	0.009	0.066
22/9/2008	0.014	0.066
23/9/2008	0.008	0.067
24/9/2008	0.000	0.068
25/9/2008	0.001	0.068
26/9/2008	0.002	0.069
27/9/2008	0.002	0.071
28/9/2008	0.007	0.072
29/9/2008	0.025	0.074
30/9/2008	0.200	1.086
1/10/2008	0.200	2.196
2/10/2008	0.200	2.852
3/10/2008	0.278	1.874

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date	drainage [mg]	Kielstau [g]
4/10/2008	0.278	0.426
5/10/2008	0.278	1.524
6/10/2008	0.278	0.710
7/10/2008	6.467	0.561
8/10/2008	3.041	0.461
9/10/2008	2.209	0.391
10/10/2008	1.638	0.348
11/10/2008	4.182	0.317
12/10/2008	2.631	0.287
13/10/2008	0.218	0.289
14/10/2008	3.815	0.292
15/10/2008	5.438	0.291
16/10/2008	2.762	1.753
17/10/2008	0.356	0.735
18/10/2008	8.338	0.734
19/10/2008	16.562	0.724
20/10/2008	3.795	0.730
21/10/2008	12.325	0.637
22/10/2008	7.069	0.646
23/10/2008	7.868	0.653
24/10/2008	9.463	0.660
25/10/2008	9.463	0.665
26/10/2008	9.463	0.734
27/10/2008	9.463	1.067
28/10/2008	9.754	1.102
29/10/2008	9.754	1.090
30/10/2008	3.467	0.938
31/10/2008	3.505	0.776
1/11/2008	0.975	0.655
2/11/2008	0.083	0.591
3/11/2008	0.472	0.539
4/11/2008	0.470	0.479
5/11/2008	0.303	0.455
6/11/2008	0.269	0.443
7/11/2008	0.067	0.443
8/11/2008	0.078	0.433

date	drainage [mg]	Kielstau [g]
9/11/2008	1.657	0.402
10/11/2008	2.178	0.440
11/11/2008	19.262	1.043
12/11/2008	4.764	1.426
13/11/2008	10.393	1.268
14/11/2008	0.774	1.156
15/11/2008	0.454	1.156
16/11/2008	0.438	1.064
17/11/2008	0.191	0.894
18/11/2008	1.198	0.789
19/11/2008	0.541	0.813
20/11/2008	2.836	0.979
21/11/2008	1.829	1.008
22/11/2008	0.702	0.922
23/11/2008	0.677	0.738
24/11/2008	0.723	0.637
25/11/2008	0.355	0.556
26/11/2008	0.375	0.500
27/11/2008	0.185	0.493

Application of Metazachlor in the Kielstau catchment in autumn 2008

date	Metazachlor [kg/d]
25/8/2008	10.75
26/8/2008	0.00
27/8/2008	0.00
28/8/2008	8.25
29/8/2008	0.00
30/8/2008	13.47
31/8/2008	16.50
1/9/2008	5.25
2/9/2008	7.50
3/9/2008	8.78
4/9/2008	7.50
5/9/2008	5.48

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date	Metazachlor [kg/d]
6/9/2008	0.00
7/9/2008	0.00
8/9/2008	0.00
9/9/2008	0.00
10/9/2008	17.78
11/9/2008	9.75
12/9/2008	14.17
13/9/2008	0.00
14/9/2008	0.00
15/9/2008	0.00
16/9/2008	0.00
17/9/2008	0.00
18/9/2008	0.00
19/9/2008	0.00
20/9/2008	2.62

Uncertainty of Metazachlor analyses

Messunsicherheitsabschätzung	
zur Bestimmung von	Metazachlor
in	Wasser
mittels	SPE - HPLC/DAD
für den Konzentrationsbereich:	50-1000 ng/l
auf der Basis des Nordtest-Handbooks	
"Handbook for calculation of measurement uncertainty in environmental laboratories"	
Bearbeitung:	Uta Ulrich
Datum:	09.06.2009
Unterschrift:	
Reproduzierbarkeit innerhalb des Labors	
	u_{Rw} 8,47%
A) Kontrollprobe, die den gesamten Prozess abdeckt	
Standardabweichung:	10
bei Konzentration:	118
rel Standardabweichung:	8,47%
B) Kontrollprobe, die nicht den gesamten Prozess abdeckt	
B.1 Kontrollprobenergebnis	
Standardabweichung:	
bei Konzentration:	
rel Standardabweichung:	
B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)	

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>
Kombination:	<input type="text"/>

C) Instabile Kontrollproben

C.1 Wiederholbarkeit

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>

C.2 "Langzeit"-Komponente

Schätzwert für die Standardabweichung	<input type="text"/>
basierend auf:	<input type="text"/>
Kombination:	<input type="text"/>

Methoden- und Laborabweichung

u_{bias} **9,62%**

A) Mehrfache Analytik eines zertifizierten Referenzmaterials

zertifizierter Wert	<input type="text"/>	Einheit:	<input type="text" value="mg/kg"/>
Konfidenzintervall +/-	<input type="text"/>		
Konfidenzniveau	<input type="text" value="95%"/>		
relative Standardunsicherheit:	<input type="text"/>		
Mittelwert der ZRM-Analytik:	<input type="text"/>	<input type="text" value="mg/kg"/>	
Mittlere Abweichung	<input type="text"/>		
Mittlere Abweichung in %	<input type="text"/>		

Std.-abweichung der ZRM-Analytik:	<input type="text"/>	mg/kg
rel.Std.-abweichung der ZRM-Analytik:	<input type="text"/>	
Anzahl der Messwerte:	<input type="text"/>	
Standardunsicherheit:	<input type="text"/>	

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interva I	Konf.-niv.	Mittelwert
ZRM 1	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 2	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 3	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 4	<input type="text"/>	<input type="text"/>	95%	<input type="text"/>
	$u(c_{ref})$		Abw.	Abw.quadrat
ZRM 1	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 2	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 3	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 4	<input type="text"/>		<input type="text"/>	<input type="text"/>
Mittel	<input type="text"/>	RMS _{bias}	<input type="text"/>	
Standardunsicherheit:		<input type="text"/>		

C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw- quadrat	s _R (%)	N Werte	u(c _{ref})
Probe 1	404	404	0,00%	0,00%	0%	1	0,00%
Probe 2	120	100	-16,67%	2,78%	0%	1	0,00%

			u_{vol}	0,01%	
Unsicherheit der Aufstockung:			$u_{recovery}$	1,02%	
Wiederfindung:					
	Aufstockung	Messdiffere nz	Wiederfindun g	Abweichun g	Abw-quadrat
1	250	-30	112,00%	-12,00%	1,44%
2	250	-17	106,80%	-6,80%	0,46%
3	250	5	98,00%	2,00%	0,04%
4					
5					
6					
7					
8					
9					
10					
11					
12					
				RMS_{bias}	8,05%
Standardunsicherheit:		8,11%			
Kombinierte Standardunsicherheit				u	12,82%
Erweiterte Unsicherheit U			k-Faktor	2	25,64%

FLUFENACET MONITORING IN AUTUMN 2009

Rating curve of the drain pipe on drained field 2 in autumn 2009

water levels in drain pipe[cm]	discharge [m ³ /s]
2.9	4.61E-06
2.7	2.83E-06
2.4	1.13E-06
2.2	4.58E-08
4.7	1.23E-04
4.1	7.18E-05
4.3	9.35E-05
3.7	4.15E-05
3.4	2.40E-05
3.1	1.74E-05
2.9	1.23E-05
3.9	6.13E-05
6.1	3.88E-04
5.2	2.02E-04
4.4	9.13E-05
5.7	2.82E-04
5.6	2.37E-04
6.0	2.81E-04
5.2	1.71E-04

Discharges in autumn 2009

Daily mean values [m³/s]

date	drainage	Moorau	Kielstau
21/9/2009	5.72E-06	0.019	0.074
22/9/2009	5.29E-06	0.019	0.074
23/9/2009	4.51E-06	0.019	0.073
24/9/2009	4.11E-06	0.025	0.071
25/9/2009	3.59E-06	0.021	0.07
26/9/2009	3.32E-06	0.019	0.069
27/9/2009	3.30E-06	0.019	0.069
28/9/2009	3.35E-06	0.019	0.069
29/9/2009	3.93E-06	0.022	0.069
30/9/2009	5.08E-06	0.021	0.069
1/10/2009	5.70E-06	0.019	0.069
2/10/2009	7.04E-06	0.019	0.07
3/10/2009	9.04E-05	0.062	0.201
4/10/2009	2.33E-04	0.198	0.425
5/10/2009	1.26E-04	0.141	0.307
6/10/2009	8.39E-05	0.106	0.217
7/10/2009	9.28E-05	0.070	0.198
8/10/2009	7.64E-05	0.047	0.197
9/10/2009	5.13E-05	0.039	0.171
10/10/2009	4.21E-05	0.035	0.156
11/10/2009	3.75E-05	0.034	0.152
12/10/2009	9.78E-05	0.065	0.203
13/10/2009	6.81E-05	0.051	0.214
14/10/2009	4.91E-05	0.040	0.189
15/10/2009	3.96E-05	0.035	0.174
16/10/2009	3.42E-05	0.034	0.167
17/10/2009	2.59E-05	0.036	0.164
18/10/2009	2.35E-05	0.032	0.168
19/10/2009	2.14E-05	0.030	0.162
20/10/2009	1.85E-05	0.029	0.158
21/10/2009	1.68E-05	0.028	0.148
22/10/2009	1.37E-05	0.027	0.147

date	drainage	Moorau	Kielstau
23/10/2009	9.89E-06	0.027	0.15
24/10/2009	8.86E-06	0.027	0.152
25/10/2009	8.30E-06	0.031	0.155
26/10/2009	7.80E-06	0.033	0.157
27/10/2009	8.29E-06	0.038	0.161
28/10/2009	3.95E-05	0.044	0.214
29/10/2009	5.84E-05	0.071	0.297
30/10/2009	6.66E-05	0.069	0.309
31/10/2009	4.68E-05	0.057	0.31
1/11/2009	3.73E-05	0.051	0.308
2/11/2009	2.84E-04	0.193	0.668
3/11/2009	1.46E-04	0.164	0.786
4/11/2009	2.82E-04	0.227	0.851
5/11/2009	2.19E-04	0.272	0.989
6/11/2009	1.52E-04	0.227	0.984
7/11/2009	1.33E-04	0.196	0.903
8/11/2009	1.09E-04	0.158	0.786
9/11/2009	9.56E-05	0.124	0.671
10/11/2009	1.18E-04	0.121	0.615
11/11/2009	1.40E-04	0.139	0.615
12/11/2009	2.13E-04	0.189	0.751
13/11/2009	3.20E-04	0.267	1.07
14/11/2009	3.46E-04	0.387	1.42
15/11/2009	2.11E-04	0.321	1.41
16/11/2009	2.26E-04	0.312	1.34
17/11/2009	2.26E-04	0.307	1.31
18/11/2009	2.75E-04	0.306	1.29
19/11/2009	2.85E-04	0.378	1.42
20/11/2009	2.11E-04	0.314	1.39
21/11/2009	1.93E-04	0.288	1.31
22/11/2009	2.13E-04	0.267	1.19
23/11/2009	3.21E-04	0.299	1.24
24/11/2009	3.06E-04	0.347	1.33
25/11/2009	2.93E-04	0.340	1.33
26/11/2009	2.59E-04	0.315	1.33
27/11/2009	2.48E-04	0.295	1.32
28/11/2009	4.60E-04	0.368	1.38

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date	drainage	Moorau	Kielstau
29/11/2009	5.44E-04	0.464	1.7
30/11/2009	3.22E-04	0.398	1.71
1/12/2009	2.57E-04		1.51
2/12/2009	2.16E-04		1.27
3/12/2009	1.94E-04		1.11
4/12/2009	2.30E-05		1.02
5/12/2009	3.56E-05		0.992

Precipitation records in autumn 2009

Precipitation (daily total) [mm]

date	Satrup	Ausacker
7/9/2009	0	0
8/9/2009	0	0
9/9/2009	0	0
10/9/2009	0	0
11/9/2009	0	0
12/9/2009	0	0
13/9/2009	0	0
14/9/2009	0	0
15/9/2009	0	0
16/9/2009	0	0
17/9/2009	0	0
18/9/2009	0	0
19/9/2009	0	0
20/9/2009	0	0
21/9/2009	0	0
22/9/2009	1	2
23/9/2009	0	0
24/9/2009	0	0
25/9/2009	0	0
26/9/2009	0	0
27/9/2009	0	0
28/9/2009	3	7
29/9/2009	3	2

date	Satrup	Ausacker
30/9/2009	1	0
1/10/2009	2	2
2/10/2009	5	0
3/10/2009	41	50
4/10/2009	3	6
5/10/2009	0	0
6/10/2009	1	0
7/10/2009	6	8
8/10/2009	0	0
9/10/2009	0	0
10/10/2009	1	2
11/10/2009	6	6
12/10/2009	4	6
13/10/2009	0	0
14/10/2009	0	0
15/10/2009	0	0
16/10/2009	4	5
17/10/2009	0	0
18/10/2009	0	0
19/10/2009	0	1
20/10/2009	0	0
21/10/2009	0	0
22/10/2009	0	0
23/10/2009	0	0
24/10/2009	0	0
25/10/2009	7	6
26/10/2009	4	7
27/10/2009	0	0
28/10/2009	10	11
29/10/2009	3	4
30/10/2009	0	0
31/10/2009	0	0
1/11/2009	8	0
2/11/2009	16	22
3/11/2009	1	2
4/11/2009	14	16
5/11/2009	1	4

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date	Satrup	Ausacker
6/11/2009	2	4
7/11/2009	2	0
8/11/2009	0	2
9/11/2009	1	1
10/11/2009	7	8
11/11/2009	1	2
12/11/2009	9	13
13/11/2009	17	17
14/11/2009	1	2
15/11/2009	5	6
16/11/2009	5	5
17/11/2009	1	0
18/11/2009	11	13
19/11/2009	1	2
20/11/2009	3	5
21/11/2009	0	0
22/11/2009	6	6
23/11/2009	8	10
24/11/2009	5	3
25/11/2009	2	2
26/11/2009	5	3
27/11/2009	3	6
28/11/2009	8	17
29/11/2009	2	4
30/11/2009	1	1
1/12/2009	0	0
2/12/2009	0	0
3/12/2009	3	4
4/12/2009	6	7
5/12/2009	3	3

Groundwater levels on drained field 2 in autumn 2009

Values (GW1 und 2) und daily mean values (sensor) [m]

date	GW 1	GW 2	sensor in GW 2
24/9/2009			1.56
25/9/2009			1.58
26/9/2009			1.59
27/9/2009			1.61
28/9/2009	1.59	1.61	1.61
29/9/2009			1.62
30/9/2009			1.64
1/10/2009	1.62	1.64	1.64
2/10/2009			1.66
3/10/2009			1.42
4/10/2009			0.59
5/10/2009	0.55	0.61	0.62
6/10/2009			0.75
7/10/2009			0.76
8/10/2009	0.76	0.81	0.77
9/10/2009			
10/10/2009			
11/10/2009			
12/10/2009	0.76	0.81	0.81
13/10/2009			0.91
14/10/2009			1.05
15/10/2009	1.06	1.125	1.12
16/10/2009			1.15
17/10/2009			1.22
18/10/2009			1.25
19/10/2009	1.29	1.28	1.27
20/10/2009			1.30
21/10/2009			1.32
22/10/2009	1.35	1.34	1.34
23/10/2009			1.38
24/10/2009			1.40
25/10/2009			1.40

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date	GW 1	GW 2	sensor in GW 2
26/10/2009	1.42	1.4	1.41
27/10/2009			1.40
28/10/2009			1.23
29/10/2009	0.89	0.89	0.90
30/10/2009			0.86
31/10/2009			0.96
1/11/2009			1.04
2/11/2009	0.28	0.41	0.57
3/11/2009			0.54
4/11/2009			0.54
5/11/2009	0.31	0.45	0.49
6/11/2009			0.55
7/11/2009			0.61
8/11/2009			0.72
9/11/2009	0.74	82.5	0.82
10/11/2009			0.81
11/11/2009			0.67
12/11/2009	0.45	0.46	0.57
13/11/2009			0.51
14/11/2009			0.49
15/11/2009			0.53
16/11/2009	0.355	0.54	0.53
17/11/2009			
18/11/2009			
19/11/2009	0.3	0.46	0.49
20/11/2009			
21/11/2009			
22/11/2009			
23/11/2009	0.48	0.59	0.52
24/11/2009			0.49
25/11/2009			0.51
26/11/2009	0.39	0.55	0.56
27/11/2009			0.59
28/11/2009			0.52
29/11/2009			0.49
30/11/2009	0.36	0.49	0.51
1/12/2009			0.63

date	GW 1	GW 2	sensor in GW 2
2/12/2009			0.74
3/12/2009	0.67	0.82	0.81
4/12/2009			
5/12/2009			

Soil water content on drained field 2 in autumn 2009

Daily mean values [%]

date	40 cm N	20 cm N	40 cm S	20 cm S
21/9/2009	12.6	10.6	10.9	13.3
22/9/2009	12.6	10.6	10.8	13.6
23/9/2009	12.6	10.6	10.8	13.6
24/9/2009	12.6	10.6	11.0	13.6
25/9/2009	12.6	10.6	11.0	13.6
26/9/2009	12.5	10.5	10.9	13.6
27/9/2009	12.4	10.4	10.9	13.5
28/9/2009	12.2	10.4	10.8	13.4
29/9/2009	13.2	10.6	11.1	13.5
30/9/2009	14.0	11.0	11.6	13.6
1/10/2009	13.8	11.1	11.7	13.7
2/10/2009	14.2	11.3	12.0	13.7
3/10/2009	22.3	19.3	20.3	17.3
4/10/2009	24.4	28.4	23.2	24.9
5/10/2009	22.9	26.4	21.1	22.8
6/10/2009	21.5	24.6	19.2	21.0
7/10/2009	22.3	25.7	19.8	20.8
8/10/2009	21.4	24.6	18.7	20.3
9/10/2009	20.9	23.6	18.1	19.7
10/10/2009	20.5	22.6	17.4	19.1
11/10/2009	20.5	22.7	17.5	18.9
12/10/2009	22.9	26.1	20.2	20.2
13/10/2009	21.9	24.3	18.7	19.9
14/10/2009	21.2	23.0	17.6	19.4
15/10/2009	20.7	22.0	17.0	18.9
16/10/2009	20.5	21.6	16.7	18.7

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date	40 cm N	20 cm N	40 cm S	20 cm S
17/10/2009	21.0	22.6	17.5	18.7
18/10/2009	20.5	21.8	16.9	18.6
19/10/2009	19.9	21.4	16.7	18.4
20/10/2009	19.5	21.1	16.5	18.2
21/10/2009	19.2	20.6	16.1	18.0
22/10/2009	18.7	20.1	15.7	17.7
23/10/2009	18.3	19.6	15.4	17.5
24/10/2009	17.9	19.2	15.2	17.3
25/10/2009	18.4	19.7	15.4	17.2
26/10/2009	20.0	21.4	17.2	17.6
27/10/2009	20.5	22.9	18.2	18.3
28/10/2009	21.9	24.2	19.3	18.4
29/10/2009	22.6	26.0	20.4	19.5
30/10/2009	22.5	25.5	19.8	19.8
31/10/2009	22.0	23.8	18.4	19.2
1/11/2009	21.4	23.1	17.8	18.9
2/11/2009	26.2	27.8	24.1	22.4
3/11/2009	23.6	26.2	21.6	22.3
4/11/2009	25.4	27.4	23.1	22.8
5/11/2009	24.4	26.9	21.8	22.8
6/11/2009	23.8	26.4	21.4	22.5
7/11/2009	23.1	25.7	20.8	22.2
8/11/2009	22.7	24.9	20.2	21.8
9/11/2009	22.5	24.3	19.8	21.4
10/11/2009	23.5	25.7	20.8	21.6
11/11/2009	23.6	26.4	21.0	22.0
12/11/2009	24.8	27.4	22.5	22.3
13/11/2009	25.8	28.3	23.8	23.8
14/11/2009	24.6	28.2	23.5	25.4
15/11/2009	23.6	26.9	22.6	24.9
16/11/2009	24.1	27.5	22.9	25.0
17/11/2009	23.9	27.4	22.8	25.1
18/11/2009	24.2	27.3	23.1	25.0
19/11/2009	24.4	28.0	23.5	25.8
20/11/2009	23.4	26.5	22.6	25.2
21/11/2009	23.4	26.6	22.4	24.9
22/11/2009	23.6	27.0	22.7	25.0

date	40 cm N	20 cm N	40 cm S	20 cm S
23/11/2009	24.9	28.4	23.8	25.8
24/11/2009	25.1	28.7	24.1	26.8
25/11/2009	24.6	28.7	24.0	27.4
26/11/2009	24.8	28.5	23.8	27.0
27/11/2009	24.5	28.0	23.6	26.7
28/11/2009	25.9	42.5	25.1	28.0
29/11/2009	26.1	75.4	25.5	47.5
30/11/2009	25.0	33.6	24.5	39.3
1/12/2009	24.3	30.0	23.4	33.7
2/12/2009	21.7	27.5	21.9	31.1
3/12/2009	21.5	26.7	21.7	30.0

Flufenacet concentrations on autumn 2009

Daily mixed samples in the drainage, in the Moorau and in the Kielstau [ng/l]

date	drainage	groundwater	Kielstau	Moorau
24/9/2009	< 30		< 30	< 30
25/9/2009	< 30		< 30	< 30
26/9/2009	< 30		< 30	< 30
27/9/2009			< 30	< 30
28/9/2009	< 30	< 30	< 30	< 30
29/9/2009	< 30		< 30	< 30
30/9/2009	< 30		< 30	< 30
10/1/2009	< 30	< 30	< 30	< 30
10/2/2009	< 30		< 30	< 30
10/3/2009	170		95	< 30
10/4/2009	< 30		160	< 30
10/5/2009	< 30	< 30	93	84
10/6/2009	no sample		< 30	< 30
10/7/2009	< 30		53	< 30
10/8/2009	< 30	< 30	< 30	< 30
10/9/2009	< 30		< 30	< 30
10/10/2009	< 30		< 30	< 30
10/11/2009	< 30		41	< 30
10/12/2009	< 30	< 30	< 30	96

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date	drainage	groundwater	Kielstau	Moorau
13/10/2009	< 30		< 30	4< 30
14/10/2009	< 30		< 30	< 30
15/10/2009	< 30	< 30	< 30	< 30
16/10/2009	< 30		< 30	< 30
17/10/2009	< 30		< 30	< 30
18/10/2009	< 30		< 30	no sample
19/10/2009	< 30		< 30	< 30
20/10/2009	< 30		< 30	< 30
21/10/2009	< 30		< 30	< 30
22/10/2009	< 30	< 30	< 30	< 30
23/10/2009	< 30		< 30	< 30
24/10/2009	< 30		< 30	< 30
25/10/2009	< 30		< 30	< 30
26/10/2009	< 30	< 30	< 30	< 30
27/10/2009	< 30		< 30	< 30
28/10/2009	< 30		< 30	< 30
29/10/2009	< 30	< 30	< 30	< 30
30/10/2009	83		< 30	< 30
31/10/2009	< 30		< 30	< 30
11/1/2009	106		< 30	< 30
11/2/2009	< 30	< 30	< 30	72
11/3/2009	< 30		303	< 30
11/4/2009	< 30		95	72
11/5/2009	< 30	< 30	79	46
11/6/2009	< 30		< 30	< 30
11/7/2009	< 30		< 30	< 30
11/8/2009	< 30		< 30	< 30
11/9/2009	< 30	< 30	< 30	< 30
11/10/2009	< 30		< 30	< 30
11/11/2009	< 30		< 30	< 30
11/12/2009	< 30		< 30	< 30
13/11/2009	127		< 30	< 30
14/11/2009	138		82	48
15/11/2009	< 30		63	< 30
16/11/2009	< 30	132	47	< 30
17/11/2009	< 30		38	< 30
18/11/2009	< 30			< 30

date	drainage	groundwater	Kielstau	Moorau
19/11/2009	< 30	140		< 30
20/11/2009	< 30		43	< 30
21/11/2009	< 30			< 30
22/11/2009	< 30			< 30
23/11/2009	< 30	< 30		< 30
24/11/2009	< 30		41	< 30
25/11/2009	< 30		35	< 30
26/11/2009	< 30	< 30	< 30	< 30
27/11/2009	< 30		< 30	< 30
28/11/2009	81		< 30	< 30
29/11/2009	76		< 30	< 30
30/11/2009	< 30	< 30	< 30	< 30
01/12/09	< 30		< 30	< 30
2/12/2009	< 30		< 30	< 30
3/12/2009	< 30	< 30	< 30	< 30
4/12/2009	< 30		< 30	< 30
5/12/2009	< 30		< 30	< 30

Flufenacet loads in autumn 2009

Daily loads

date	drainage [mg]	Moorau [g]	Kielstau [g]
24/9/2009	0.01	0.033	0.092
25/9/2009	0.00	0.028	0.091
26/9/2009	0.00	0.025	0.089
27/9/2009	0.00	0.024	0.089
28/9/2009	0.00	0.025	0.089
29/9/2009	0.01	0.029	0.089
30/9/2009	0.01	0.027	0.089
1/10/2009	0.01	0.025	0.089
2/10/2009	0.01	0.025	0.091
3/10/2009	1.33	0.081	1.650
4/10/2009	0.30	1.436	5.875
5/10/2009	0.16	0.183	2.467

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date	drainage [mg]	Moorau [g]	Kielstau [g]
6/10/2009	0.11	0.137	0.281
7/10/2009	0.12	0.090	0.907
8/10/2009	0.10	0.061	0.255
9/10/2009	0.07	0.050	0.222
10/10/2009	0.05	0.045	0.202
11/10/2009	0.05	0.044	0.538
12/10/2009	0.13	0.539	0.263
13/10/2009	0.09	0.176	0.277
14/10/2009	0.06	0.052	0.245
15/10/2009	0.05	0.046	0.226
16/10/2009	0.04	0.044	0.216
17/10/2009	0.03	0.046	0.213
18/10/2009	0.03	0.041	0.218
19/10/2009	0.03	0.039	0.210
20/10/2009	0.02	0.037	0.205
21/10/2009	0.02	0.036	0.192
22/10/2009	0.02	0.035	0.191
23/10/2009	0.01	0.036	0.194
24/10/2009	0.01	0.035	0.197
25/10/2009	0.01	0.040	0.201
26/10/2009	0.01	0.043	0.203
27/10/2009	0.01	0.049	0.209
28/10/2009	0.05	0.057	0.277
29/10/2009	0.08	0.093	0.385
30/10/2009	0.48	0.089	0.400
31/10/2009	0.06	0.074	0.402
1/11/2009	0.34	0.066	0.399
2/11/2009	0.37	1.199	0.866
3/11/2009	0.19	0.212	6.995
4/11/2009	0.37	1.411	6.985
5/11/2009	0.28	1.079	6.751
6/11/2009	0.20	0.294	1.275
7/11/2009	0.17	0.254	1.170
8/11/2009	0.14	0.205	1.019
9/11/2009	0.12	0.160	0.870
10/11/2009	0.15	0.156	0.797
11/11/2009	0.18	0.180	0.797

date	drainage [mg]	Moorau [g]	Kielstau [g]
12/11/2009	1.10	0.245	0.973
13/11/2009	3.51	0.346	1.387
14/11/2009	4.13	1.604	10.060
15/11/2009	0.27	0.417	7.675
16/11/2009	0.29	0.405	5.441
17/11/2009	0.29	0.398	4.301
18/11/2009	0.36	0.397	1.672
19/11/2009	0.37	0.489	1.840
20/11/2009	0.27	0.407	5.164
21/11/2009	0.25	0.373	1.698
22/11/2009	0.28	0.346	1.542
23/11/2009	1.39	0.388	1.607
24/11/2009	0.40	0.450	4.711
25/11/2009	0.38	0.440	4.022
26/11/2009	0.34	0.409	1.724
27/11/2009	0.32	0.382	1.711
28/11/2009	3.22	0.477	1.788
29/11/2009	3.57	0.601	2.203
30/11/2009	0.42		2.216
1/12/2009	0.33		1.957
2/12/2009	0.28		1.646
3/12/2009	0.25		1.439
4/12/2009	0.03		1.322
5/12/2009	0.05		1.286

Application of Flufenacet in the Kielstau catchment in autumn 2009

date	Flufenacet [kg/d]
18/9/2009	0.80
19/9/2009	0.56
20/9/2009	0.00
21/9/2009	1.26
22/9/2009	0.00
23/9/2009	0.00
24/9/2009	4.05

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date	Flufenacet [kg/d]
25/9/2009	7.37
26/9/2009	0.76
27/9/2009	1.92
28/9/2009	8.13
29/9/2009	13.01
30/9/2009	4.16
1/10/2009	3.54
2/10/2009	16.90
3/10/2009	5.83
4/10/2009	0.00
5/10/2009	0.00
6/10/2009	4.06
7/10/2009	0.00
8/10/2009	0.00
9/10/2009	3.26
10/10/2009	0.00
11/10/2009	0.00
12/10/2009	1.90
13/10/2009	1.73
14/10/2009	2.12
15/10/2009	0.00
16/10/2009	1.47
17/10/2009	0.00
18/10/2009	0.00
19/10/2009	0.00
20/10/2009	1.68
21/10/2009	0.00
22/10/2009	0.00
23/10/2009	0.00
24/10/2009	3.63
25/10/2009	0.00
26/10/2009	0.00
27/10/2009	12.76
28/10/2009	0.00
29/10/2009	0.00
30/10/2009	0.00
31/10/2009	1.94

Uncertainty of Flufenacet analyses

Messunsicherheitsabschätzung	
zur Bestimmung von	Flufenacet
in	Wasser
mittels	SPE - HPLC/DAD
für den Konzentrationsbereich:	50-1000 ng/l
auf der Basis des Nordtest-Handbooks	
"Handbook for calculation of measurement uncertainty in environmental laboratories"	
Bearbeitung:	Uta Ulrich
Datum:	Unterschrift:
Reproduzierbarkeit innerhalb des Labors	uRw 9,60%
A) Kontrollprobe, die den gesamten Prozess abdeckt	
Standardabweichung:	72
bei Konzentration:	750
rel Standardabweichung:	9,60%
B) Kontrollprobe, die nicht den gesamten Prozess abdeckt	
B.1	
Kontrollprobenergebnis	
Standardabweichung:	
bei Konzentration:	
rel Standardabweichung:	

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B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)		
mittlere Spannweite:		
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	3	
Standardabweichung:		
Kombination:		
C) Instabile Kontrollproben		
C.1 Wiederholbarkeit		
mittlere Spannweite:		
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	2	
Standardabweichung:		
C.2 "Langzeit"-Komponente		
Schätzwert für die Standardabweichung		
basierend auf:		
Kombination:		
Methoden- und Laborabweichung	ubias	6,48%
A) Mehrfache Analytik eines zertifizierten Referenzmaterials		
zertifizierter Wert		Einheit: mg/kg
Konfidenzintervall +/-		
Konfidenzniveau	95%	
relative Standardunsicherheit:		
Mittelwert der ZRM-Analytik:		mg/kg
Mittlere Abweichung		
Mittlere Abweichung in %		
Std.-abweichung der ZRM-Analytik:		mg/kg
rel.Std.-abweichung der ZRM-Analytik:		

Anzahl der Messwerte:

Standardunsicherheit:

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interval	Konf.-niv.	Mittelwert
ZRM 1			St.-Abw.	
ZRM 2			St.-Abw.	
ZRM 3			95%	
ZRM 4			95%	
	u(cref)		Abw.	Abw.quadrat

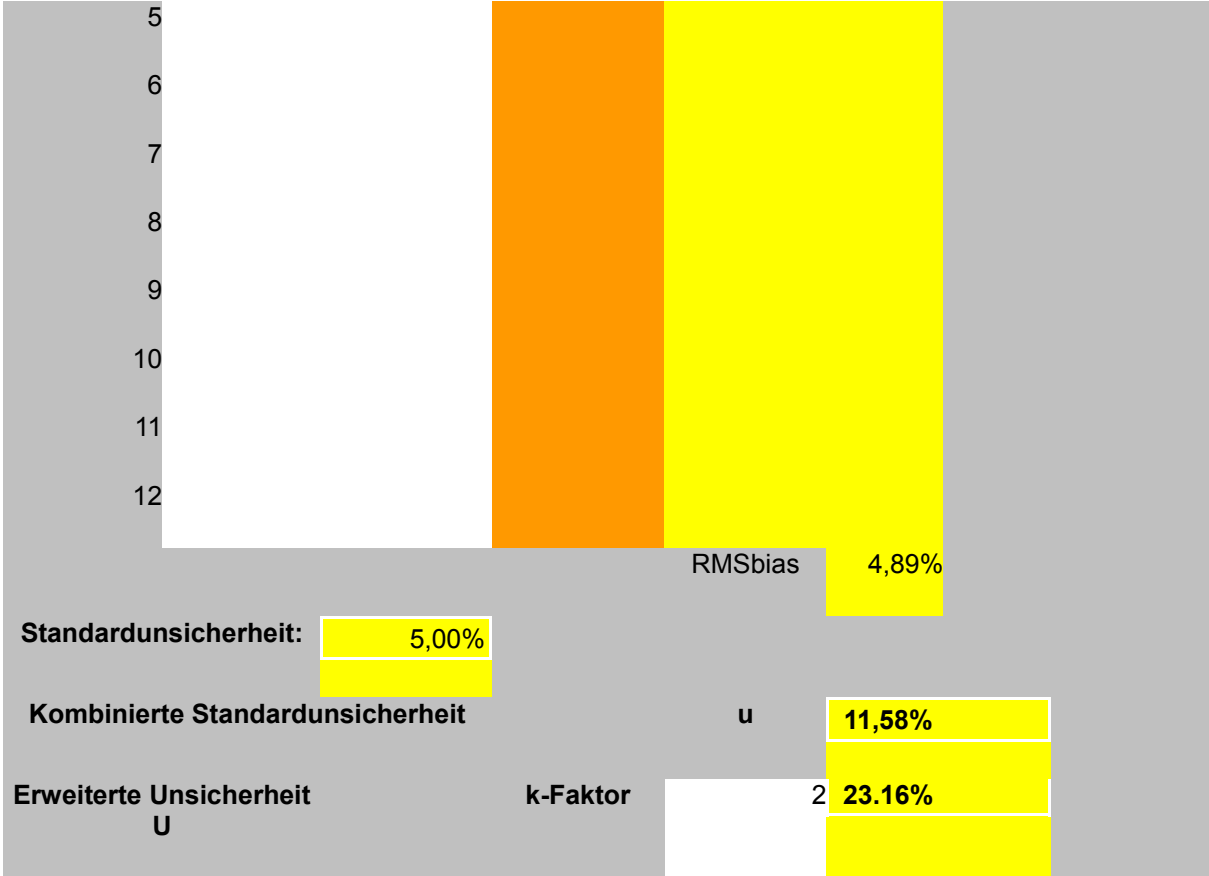
ZRM 1			
ZRM 2			
ZRM 3			
ZRM 4			
Mittel		RMSbias	

Standardunsicherheit:

C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw-quadrat	sR (%)	N Werte	u(cref)
Probe 1	100	101	1,00%	0,01%	0%	1	0,00%
Probe 2	300	269	-10,33%	1,07%	0%	1	0,00%
Probe 3	400	383	-4,25%	0,18%	0%	1	0,00%
Probe 4							
Probe 5							
Probe 6							
Probe 7							

Probe 8					
Probe 9					
Probe 10					
Probe 11					
Probe 12					
		RMSbias	6,48%	u(cref)	0,00%
Standardunsicherheit:	6,48%				
D) Wiederfindungsexperiment					
Unsicherheit der Konzentration der Aufstocklösung:					
Konzentration der Aufstocklösung:	250				
Konfidenzintervall +/-	5				
Konfidenzniveau:	95%				
uconc	1,02%				
Unsicherheit des zugegebenen Volumens:					
max. Abweichung [%] (Rechteckverteilung)	0,01%	Std-abw.:	0,01%		
Wiederholbarkeit [%] (als Standardabw.)	0,01%				
uvol	0,01%				
Unsicherheit der Aufstockung:	urecovery	1,02%			
Wiederfindung:					
	Aufstockung	Messdifferenz	Wiederfindung	Abweichung	Abw-quadrat
1	250	-5	102,00%	-2,00%	0,04%
2	250	10	96,00%	4,00%	0,16%
3	250	18	92,80%	7,20%	0,52%
4					



SURFACE RUNOFF EXPERIMENT WITH RAINFALL SIMULATOR

Soil water content in containers

Container M1, M2 (Metazachlor) [%] (daily mean values)

date		M1				M2			
		30 cm M1	20 cm M1	7 cm M1	Ten-sio	30 cm M2	20 cm M2	7 cm M2	Ten-sio
5/6/2009		26.81	22.16	14.13	2.67	25.20	19.21	14.43	2.71
5/7/2009		26.78	22.18	14.17	2.67	25.21	19.20	14.48	2.71
5/8/2009		27.55	24.13	18.01	2.50	26.18	21.17	18.55	2.51
5/9/2009		28.34	26.01	22.56	2.44	27.21	22.65	22.18	2.46
5/10/2009		27.96	25.36	21.72	2.51	26.94	22.07	21.54	2.53
5/11/2009	1. rainfall	27.75	24.86	21.05	2.57	26.75	21.77	20.99	2.60
5/12/2009		27.62	24.46	20.54	2.61	26.56	21.51	20.53	2.62
13/5/2009		27.54	24.30	20.25	2.64	26.47	21.41	20.29	2.66
14/5/2009		27.35	24.09	19.94	2.67	26.35	21.27	20.00	2.67
15/5/2009		28.04	25.37	21.37	2.48	26.67	22.07	21.20	2.50
16/5/2009		28.26	25.98	22.27	2.44	26.91	22.69	22.42	2.46
17/5/2009		27.93	25.24	21.55	2.52	26.66	22.10	21.68	2.54
18/5/2009	2. rainfall	27.75	24.88	20.93	2.58	26.53	21.80	21.17	2.61
19/5/2009		27.57	24.51	20.40	2.62	26.46	21.64	20.79	2.64
20/5/2009		27.53	24.34	20.14	2.64	26.45	21.57	20.69	2.64
21/5/2009		27.35	24.19	19.93	2.66	26.33	21.49	20.59	2.66
22/5/2009		27.62	24.91	21.10	2.48	26.48	21.72	21.66	2.50
23/5/2009		28.23	25.75	22.15	2.42	26.90	22.37	22.79	2.44
24/5/2009		28.03	25.12	21.56	2.50	26.67	21.95	22.26	2.52
25/5/2009	3. rainfall	27.87	24.76	21.05	2.56	26.53	21.69	21.78	2.58
26/5/2009		27.75	24.51	20.65	2.60	26.45	21.57	21.42	2.62
27/5/2009		27.64	24.30	20.17	2.66	26.35	21.39	20.98	2.69
28/5/2009		27.51	24.06	19.89	2.71	26.17	21.46	20.68	2.72
29/5/2009		27.89	24.86	21.47	2.47	26.44	21.73	21.87	2.50

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date		M1				M2			
		30 cm M1	20 cm M1	7 cm M1	Ten- sio	30 cm M2	20 cm M2	7 cm M2	Ten- sio
30/5/2009		28.27	25.34	22.11	2.43	26.87	22.25	22.00	2.45
31/5/2009		28.02	24.85	21.33	2.52	26.68	21.90	21.29	2.55
6/1/2009	4. rainfall	27.87	24.52	20.62	2.61	26.50	21.57	20.32	2.68
6/2/2009		27.65	24.17	20.04	2.68	26.30	21.27	19.96	2.43
6/3/2009		27.53	23.83	19.29	2.80	26.12	20.89	18.67	0.00
6/4/2009		27.34	23.55	19.06	2.85	25.88	20.76	18.05	0.00
6/5/2009		27.61	24.26	20.52	2.59	25.90	20.96	19.66	0.90
6/6/2009		28.16	25.32	21.96	2.42	26.51	21.91	21.74	2.44
6/7/2009		28.07	24.84	21.26	2.51	26.40	21.65	21.10	2.53
6/8/2009	5. rainfall	27.95	24.55	20.90	2.57	26.33	21.45	20.50	2.58
6/9/2009		27.76	24.35	20.62	2.60	26.23	21.36	21.20	2.61
6/10/2009		27.66	24.21	20.40	2.62	26.21	21.28	20.97	2.62
6/11/2009		27.55	24.10	20.20	2.66	26.18	21.20	20.87	2.66
6/12/2009		27.95	24.92	22.23	2.71	26.53	21.77	21.83	2.46
13/6/2009		28.39	25.45	22.69	2.72	26.99	22.43	21.77	2.42
14/6/2009	6. rainfall	28.18	24.91	21.83	2.72	26.78	22.04	21.20	2.50
15/6/2009		28.10	24.36	16.56	2.10	26.65	21.60	15.18	1.38
16/6/2009		27.76	23.73	13.34	1.49	26.31	21.03	13.17	2.86
17/6/2009		27.55	23.64	13.92	1.52	26.15	20.93	14.12	2.81
18/6/2009		27.50	23.63	14.41	1.32	26.06	20.91	14.98	2.77
19/6/2009		27.40	23.64	14.76	1.25	26.02	20.91	16.08	2.76

Containers T1, T2 (Terbutylazine) [%] (daily mean values)

date		30 cm T1	20 cm T1	7 cm T1	Ten- sio	30 cm T2	20 cm T2	7 cm T2	Ten- sio
5/6/2009		27.49	17.19	13.30	2.66	23.18	23.49	16.22	2.73
5/7/2009		27.51	17.20	13.36	2.67	23.18	23.49	16.23	2.73
5/8/2009		27.74	18.48	15.98	2.52	23.48	24.45	18.76	2.55
5/9/2009		29.23	20.38	20.94	2.39	24.67	25.54	21.83	2.44
5/10/2009		29.27	19.63	20.10	2.48	24.68	25.17	20.95	2.52
5/11/2009	1. rainfall	29.18	19.30	19.61	2.54	24.65	24.93	20.41	2.58
5/12/2009		29.07	19.06	19.29	2.56	24.55	24.73	20.02	2.60
13/5/2009		29.03	18.99	19.20	2.57	24.51	24.67	19.92	2.61
14/5/2009									
15/5/2009		29.62	21.41	21.61	2.22	25.29	26.29	23.36	2.30

date		30 cm T1	20 cm T1	7 cm T1	Ten- sio	30 cm T2	20 cm T2	7 cm T2	Ten- sio	
16/5/2009		29.85	20.40	20.64	2.38	25.18	25.63	22.15	2.44	
17/5/2009		29.69	19.81	19.97	2.47	24.96	25.10	21.22	2.53	
18/5/2009	2. rainfall	29.50	19.51	19.56	2.52	24.85	24.93	20.57	2.58	
19/5/2009		29.49	19.32	19.54	2.55	24.71	24.73	20.21	2.61	
20/5/2009		29.45	19.16	19.44	2.57	24.67	24.64	20.06	2.62	
21/5/2009		29.38	19.02	19.30	2.59	24.67	24.58	19.92	2.64	
22/5/2009		29.43	19.75	19.93	2.47	24.96	25.00	21.05	2.49	
23/5/2009		29.92	20.61	20.82	2.39	25.58	25.66	22.37	2.42	
24/5/2009		29.72	19.87	20.15	2.48	25.29	25.16	21.54	2.52	
25/5/2009	3. rainfall	29.58	19.51	19.70	2.54	25.15	24.87	21.01	2.58	
26/5/2009		29.50	19.30	19.31	2.57	25.09	24.74	20.61	2.61	
27/5/2009		29.42	19.09	18.92	2.61	25.01	24.63	20.27	2.67	
28/5/2009		29.22	18.87	18.63	2.65	24.83	24.52	20.01	2.71	
29/5/2009		29.49	20.15	19.93	2.45	25.11	24.88	21.28	2.52	
30/5/2009		30.03	20.61	20.72	2.39	25.79	25.48	22.50	2.41	
31/5/2009		29.78	19.98	20.03	2.49	25.59	25.12	21.79	2.52	
6/1/2009	4. rainfall	29.63	19.59	19.39	2.56	25.45	24.91	21.06	2.61	
6/2/2009		29.50	19.37	18.86	2.62	25.28	24.66	20.42	2.69	
6/3/2009		29.39	19.11	18.26	2.71	25.01	24.38	19.75	2.83	
6/4/2009		29.22	19.11	18.00	2.75	24.87	24.22	19.43	2.86	
6/5/2009		29.11	19.19	18.15	2.72	24.77	24.09	19.88	2.73	
6/6/2009		29.28	21.86	23.25		24.78	24.01	24.88		
6/7/2009										
6/8/2009	5. rainfall									
6/9/2009										
6/10/2009										
6/11/2009		29.54	19.4	18.48		25.08	25.78	20.78	2.59	
6/12/2009		29.79	24.27	22.89	2.46	25.6	26.87	24.73	2.40	
13/6/2009										
14/6/2009	6. rainfall									
15/6/2009										
16/6/2009										
17/6/2009										
18/6/2009										
19/6/2009		29.85	19.74	18.59	2.58	25.49	24.65	21.26	2.88	
			actual value							

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Containers F1, F2, F3 (Flufenacet) [%] (daily mean values)

date		F1				F2				F3			
		30 cm F1	20 cm F1	7 cm F1	Ten-sio	30 cm F2	20 cm F2	7 cm F2	Ten-sio	30 cm F3	20 cm F3	7 cm F3	Ten-sio
9/9/09		29.39	17.67	18.07	1.24	24.27	23.26	17.95	1.14	30.32	21.13	25.59	0.89
9/10/09		29.39	17.68	18.12	1.29	24.22	23.31	17.99	1.13	30.37	21.26	25.67	1.52
9/11/09	1	30.55	20.21	22.39	1.29	24.68	24.99	21.38	1.12	31.90	23.00	26.69	0.35
9/12/09	rain-	31.49	21.54	24.93	1.28	25.77	26.23	24.70	1.17	30.64	22.48	26.69	1.15
13/9/09	fall	31.16	20.89	24.13	1.25	25.57	25.51	23.89	1.19	30.29	22.02	26.37	1.17
14/9/09		30.82	20.53	23.81	1.30	25.52	25.10	23.31	1.20	30.06	21.77	26.21	1.36
15/9/09		30.60	20.28	23.51	1.27	25.52	24.85	22.94	1.18	29.85	21.63	26.16	1.25
16/9/09		30.40	20.04	23.09	1.25	25.47	24.68	22.55	1.18	29.76	21.49	26.00	1.25
17/9/09		30.22	19.73	22.57	1.35	25.26	24.45	22.02	1.30	29.53	21.18	25.82	1.25
18/9/09	2	30.55	21.16	24.14	1.32	25.43	25.63	23.65	1.27	29.94	22.56	26.53	1.27
19/9/09	rain-	31.44	21.37	24.61	1.23	26.18	26.20	24.69	1.21				
20/9/09	fall	31.23	20.44	23.68	1.22	26.04	25.37	23.48	1.18	29.99	22.22	26.34	1.22
21/9/09		30.85	19.79	22.66	1.30	25.91	24.78	22.30	1.21	29.91	22.12	26.23	1.24
22/9/09		30.44	19.44	21.77	1.28	25.67	24.23	21.01	1.21	29.80	21.90	26.10	1.23
23/9/09		30.21	19.11	21.23	1.25	25.40	23.98	20.37	1.17	29.71	21.80	26.04	1.22
24/9/09		30.04	18.80	20.26	1.31	25.10	23.70	19.22	1.24	29.64	21.73	25.96	1.21
25/9/09	3	29.88	20.44	22.46	1.37	24.98	25.12	21.98	1.27	29.95	22.33	26.56	1.23
26/9/09	rain-	30.39	21.40	24.44	1.29	25.34	25.63	23.90	1.24	30.13	22.55	26.63	1.26
27/9/09	fall	30.40	20.50	23.39	1.27	25.38	24.81	22.78	1.21	29.94	22.17	26.40	1.25
28/9/09		30.22	19.94	22.75	1.17	25.31	24.27	21.74	1.16	29.87	21.97	26.24	1.25
29/9/09		30.09	19.50	21.86	1.24	25.16	24.03	20.69	1.20	30.13	21.83	26.14	1.22
30/9/09		29.85	19.12	20.63	1.32	24.99	23.54	19.24	1.27	30.24	21.73	26.05	1.26
10/1/09		29.59	18.81	19.96	1.28	24.78	23.38	18.25	1.27	30.15	21.79	26.02	1.27
10/2/09	4	30.39	22.83	25.4		25.07	27.12	25.36	1.31	31.28	23.43	27.16	1.26
10/3/09	rain-	30.57	21.69	24.48		25.63	25.63	24.32		30.84	22.68	26.67	1.21
10/4/09	fall	30.47	20.94	23.53		25.77	24.86	23.49		30.64	22.25	26.38	1.20
10/5/09		30.26	20.28	22.51		25.63	24.26	22.44		30.48	21.95	26.14	1.19
10/6/09		29.98	19.75	21.6		25.56	23.75	21.43		30.31	21.72	25.96	1.18
10/7/09		29.8	19.48	21.25		25.33	23.52	21.22		30.12	21.65	25.88	1.25
10/8/09		29.67	19.19	20.55		25.21	23.27	20.46		29.92	21.46	25.81	1.28
10/9/09	5	29.65	19.07	20.15		25.17	23.71	20.58		30.32	22.51	26.88	1.29
10/10/09	rain-	30.33	20.88	23.97		25.87	25.44	23.85		30.60	22.71	26.79	1.25
10/11/09	fall	30.23	20.25	23.18		25.85	24.73	22.96		30.49	22.30	26.52	1.25

date		F1				F2				F3			
		30 cm F1	20 cm F1	7 cm F1	Ten-sio	30 cm F2	20 cm F2	7 cm F2	Ten-sio	30 cm F3	20 cm F3	7 cm F3	Ten-sio
10/12/09		30.19	19.72	22.37		25.71	24.18	22.05		30.41	22.06	26.31	1.25
13/10/09		29.93	19.3	21.36		25.42	23.75	20.75		30.30	21.90	26.17	1.23
14/10/09		29.71	18.82	20.23		25.23	23.2	19.39		30.24	21.81	26.07	1.22
15/10/09	6	29.58	18.43	19.38		24.94	22.97	18.28		30.14	21.71	26.00	1.23
16/10/09	rain-	29.57	19.91	22.04		24.86	23.35	21.09		30.77	23.06	27.38	1.25
17/10/09	fall	29.95	20.67	23.84		25.31	24.2	23.54		30.86	22.90	27.40	1.23
18/10/09		30.03	20.17	23.17		25.45	24.1	22.88		30.59	22.40	27.09	1.21
19/10/09		30	19.85	22.79		25.45	23.99	22.45		30.48	22.18	26.94	1.19
20/10/09		29.9	19.6	22.5		25.4	23.83	22.11		30.35	22.02	27.05	1.19
21/10/09		29.79	19.36	22.04		25.31	23.66	21.84		30.25	21.99	26.95	1.19
22/10/09		29.67	19.17	21.65		25.2	23.5	21.54		30.24	21.83	26.86	1.16
23/10/09		29.59	19.05	21.41		25.12	23.4	21.34		30.31	21.80	26.83	1.16

Surface runoff

container	interval	in ml/10 min and plot					
		1. rainfall	2. rainfall	3. rainfall	4. rainfall	5. rainfall	6. rainfall
M1	10	0	11	146	54	115	103
M1	20	0	171	339	427	292	234
M1	30	0	218	351	472	315	304
M1	40	0	60	454	498	344	331
M1	50	14	216	535	490	359	324
M1	60	19	438	532	500	384	341
M2	10	0	59	77	67	0	42
M2	20	0	175	381	405	140	196
M2	30	0	211	460	440	265	279
M2	40	0	308	481	451	305	281
M2	50	2	372	496	487	336	285
M2	60	21	394	485	519	356	297
T1	10	0	0	67	42	0	0
T1	20	0	208	346	316	165	222

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container	interval	in ml/10 min and plot					
		1. rainfall	2. rainfall	3. rainfall	4. rainfall	5. rainfall	6. rainfall
T1	30	0	340	416	343	53	76
T1	40	16	467	456	407	337	209
T1	50	115	484	465	477	358	224
T1	60	184	494	497	496	380	262
T2	10	0	50	111	107	101	32
T2	20	0	220	390	331	279	144
T2	30	41	293	461	471	351	176
T2	40	26	340	474	515	383	246
T2	50	75	429	538	504	388	263
T2	60	199	440	533	531	388	269
F1	10				32	59	36
F1	20			6	183	208	14
F1	30			52	343	313	208
F1	40		25	119	444	291	133
F1	50		81	149	457	309	567
F1	60		47	178	493	319	359
F2	10				36	1	21
F2	20				270	20	205
F2	30			17	380	141	265
F2	40		7	29	448	184	366
F2	50		22	85	457	232	370
F2	60		27	106	500	237	382
F3	10	0	0	120	67	8	116
F3	20	0	0	326	376	140	372
F3	30	0	4	491	415	252	379
F3	40	0	9	492	446	313	376
F3	50	0	149	588	502	302	400
F3	60	0	168	515	510	470	390

Herbicide concentrations in the water phase of surface runoff

interval	Metazachlor [$\mu\text{g/l}$]		Terbuthylazine [$\mu\text{g/l}$]		Flufenacet [$\mu\text{g/l}$]		
	M1	M2	T1	T2	F1	F2	F3
10							
20				137			
30				207			
40			661	194			
50	693	3184	170	128			
60	522	476	129	76			
10	516	341		114			
20	146	278	93	76			
30	167	140	52	62			31
40	145	121	50	56	41	207	44
50	117	59	43	41	50	111	49
60	83	81	38	43	42	73	43
10	120	86	88	57			33
20	68	59	34	39	37		23
30	44	48	39	31	63	150	16
40	36	30	32	27	42	81	17
50	31	30	29	25	32	61	15
60	26	32	25	25	26	48	13
10	44	158	48	44	48	68	17
20	28	76	33	27	34	46	10
30	21	36	21	21	22	29	7.61
40	18	27	18	19	17	23	6.71
50	16	21	14	15	14	18	6.13
60	14	19	14	16	13	16	6.08
10	44			29	35	177	25
20	23	33	25	25	20	39	7.70
30	14	21	17	18	14	26	5.70
40	12	17	14	15	11	20	4.43
50	11	14	13	14	10	16	3.99

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	Metazachlor [$\mu\text{g/l}$]		Terbutylazine [$\mu\text{g/l}$]		Flufenacet [$\mu\text{g/l}$]		
interval	M1	M2	T1	T2	F1	F2	F3
60	10	13	11	14	8.76	12	3.52
10	11	48			28	39	4.14
20	3.49	35		19	23	26	3.02
30	4.38	19	16	23	14	17	2.41
40	5.24	14	12	14	12	13	2.07
50	4.73	12	16	10	10	11	1.96
60	4.94	8.91	10	13	8.86	9.43	1.72

Herbicide loads in the water phase of surface runoff

Loads in [$\mu\text{g}/10$ min and plot]

container	interval	1. rainfall	2. rainfall	3. rainfall	4. rainfall	5. rainfall	6. rainfall
M1	10	0.00	5.91	17.48	2.39	5.02	1.17
M1	20	0.00	24.89	23.03	11.76	6.60	0.82
M1	30	0.00	36.44	15.62	10.04	4.49	1.33
M1	40	0.00	8.64	16.51	8.88	4.30	1.73
M1	50	9.56	25.23	16.79	7.94	3.82	1.53
M1	60	9.77	36.51	13.81	7.12	3.92	1.68
M2	10	0.00	20.28	6.64	10.49	0.00	2.02
M2	20	0.00	48.69	22.44	30.91	4.62	6.87
M2	30	0.00	29.50	21.93	15.62	5.67	5.17
M2	40	0.00	37.26	14.27	12.10	5.18	4.06
M2	50	5.54	22.06	14.89	10.35	4.77	3.48
M2	60	10.13	32.01	15.32	9.91	4.67	2.65
T1	10	0.00	0.00	5.92	2.00	0.00	0.00
T1	20	0.00	19.45	11.61	10.39	4.05	0.00
T1	30	0.00	17.74	16.23	7.05	0.89	1.23
T1	40	10.60	23.40	14.60	7.31	4.81	2.60
T1	50	19.49	20.75	13.50	6.46	4.51	3.57
T1	60	23.84	18.79	12.26	7.15	4.33	2.69
T2	10	0.00	5.69	6.35	4.68	2.94	0.00

container	interval	1. rainfall	2. rainfall	3. rainfall	4. rainfall	5. rainfall	6. rainfall
T2	20	0.00	16.79	15.31	9.00	6.87	2.67
T2	30	8.51	18.07	14.50	9.88	6.39	3.99
T2	40	5.10	19.19	12.98	9.65	5.93	3.55
T2	50	9.56	17.73	13.71	7.77	5.45	2.55
T2	60	15.13	18.95	13.06	8.70	5.50	3.41
		38.30	96.42	75.91	49.68	33.09	16.17
F1	10	0.00	0.00	0.00	1.54	2.05	1.00
F1	20	0.00	0.00	0.21	6.17	4.19	0.33
F1	30	0.00	0.00	3.28	7.39	4.23	3.01
F1	40	0.00	1.02	4.96	7.40	3.20	1.66
F1	50	0.00	4.01	4.75	6.38	3.05	5.56
F1	60	0.00	1.99	4.56	6.26	2.79	3.18
F2	10	0.00	0.00	0.00	2.42	0.17	0.80
F2	20	0.00	0.00	0.00	12.32	0.78	5.28
F2	30	0.00	0.00	2.56	11.16	3.73	4.48
F2	40	0.00	1.42	2.32	10.40	3.65	4.67
F2	50	0.00	2.47	5.19	8.41	3.61	4.06
F2	60	0.00	1.96	5.13	7.97	2.78	3.60
F3	10	0.00	0.00	3.92	1.16	0.20	0.48
F3	20	0.00	0.00	7.65	3.84	1.08	1.12
F3	30	0.00	0.14	7.85	3.16	1.43	0.92
F3	40	0.00	0.42	8.39	2.99	1.39	0.78
F3	50	0.00	7.37	8.65	3.08	1.20	0.79
F3	60	0.00	7.20	6.64	3.10	1.65	0.67

Uncertainty of herbicide analyses during surface runoff experiment

Messunsicherheitsabschätzung	
zur Bestimmung von	Metazachlor Regner
in	Wasser
mittels	SPE - HPLC/DAD
für den Konzentrationsbereich:	500-2000 ng/l
auf der Basis des Nordtest-Handbooks	
"Handbook for calculation of measurement uncertainty in environmental laboratories"	
Bearbeitung:	Uta Ulrich
Datum:	Unterschrift:
Reproduzierbarkeit innerhalb des Labors	
u_{Rw}	13.64%
A) Kontrollprobe, die den gesamten Prozess abdeckt	
Standardabweichung:	150
bei Konzentration:	1100
rel Standardabweichung:	13.64%
B) Kontrollprobe, die nicht den gesamten Prozess abdeckt	
B.1 Kontrollprobenergebnis	
Standardabweichung:	
bei Konzentration:	
rel Standardabweichung:	
B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)	

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>
Kombination:	<input type="text"/>

C) Instabile Kontrollproben

C.1 Wiederholbarkeit

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	<input type="text"/>
Standardabweichung:	<input type="text"/>

C.2 "Langzeit"-Komponente

Schätzwert für die Standardabweichung	<input type="text"/>
basierend auf:	<input type="text"/>
Kombination:	<input type="text"/>

Methoden- und Laborabweichung

u_{bias} **3.49%**

A) Mehrfache Analytik eines zertifizierten Referenzmaterials

zertifizierter Wert	<input type="text"/>	Einheit:	<input type="text" value="mg/kg"/>
Konfidenzintervall +/-	<input type="text"/>		
Konfidenzniveau u	<input type="text" value="95%"/>		
relative Standardunsicherheit:	<input type="text"/>		
Mittelwert der ZRM-Analytik:	<input type="text"/>	<input type="text" value="mg/kg"/>	
Mittlere Abweichung	<input type="text"/>		
Mittlere Abweichung in %	<input type="text"/>		

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Std.-abweichung der ZRM-Analytik:	<input type="text"/>	mg/kg
rel.Std.-abweichung der ZRM-Analytik:	<input type="text"/>	
Anzahl der Messwerte:	<input type="text"/>	
Standardunsicherheit:	<input type="text"/>	

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interval	Konf.-niv.	Mittelwert
ZRM 1	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 2	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 3	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 4	<input type="text"/>	<input type="text"/>	95%	<input type="text"/>
	$u(c_{ref})$		Abw.	Abw.quadrat
ZRM 1	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 2	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 3	<input type="text"/>		<input type="text"/>	<input type="text"/>
ZRM 4	<input type="text"/>		<input type="text"/>	<input type="text"/>
Mittel	<input type="text"/>	RMS_{bias}	<input type="text"/>	<input type="text"/>
Standardunsicherheit:		<input type="text"/>		

C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw-quadrat	s_R (%)	N Werte
Probe 1	1000	994	-0.61%	0.00%	0%	1
Probe 2	1200	1170	-2.52%	0.06%	0%	1
Probe 3	1400	1323	-5.47%	0.30%	0%	1

Probe 4			
Probe 5			
Probe 6			
Probe 7			
Probe 8			
Probe 9			
Probe 10			
Probe 11			
Probe 12			
		RMS _{bias}	3.49%
			u(c _{ref})
Standardunsicherheit:			3.49%

D) Wiederfindungsexperiment

Unsicherheit der Konzentration der Aufstocklösung:

Konzentration der Aufstocklösung:

Konfidenzintervall +/-

Konfidenzniveau:

u_{conc}

Unsicherheit des zugegebenen Volumens:

max. Abweichung [%] (Rechteckverteilung)

Std-abw.:

Wiederholbarkeit [%] (als Standardabw.)

u_{vol}

Unsicherheit der Aufstockung:		u_{recovery}	0.18%
Wiederfindung:			
	Aufstockung	Messdifferenz z	Wiederfindung Abweichung Abw-quadrat
1	1400	10	99.29% 0.71% 0.01%
2	1400	35	97.50% 2.50% 0.06%
3	1400	30	97.86% 2.14% 0.05%
4	1400	29	97.93% 2.07% 0.04%
5	1400	55	96.07% 3.93% 0.15%
6			
7			
8			
9			
10			
11			
12			
			RMS_{bias} 2.49%
Standardunsicherheit:		2.50%	
Kombinierte Standardunsicherheit			u 14.08%
Erweiterte Unsicherheit U		k-Faktor 2	28.15%

Messunsicherheitsabschätzung

zur Bestimmung von	Metazachlor Regner
in	Wasser
mittels	SPE - HPLC/DAD
für den Konzentrationsbereich:	500-2000 ng/l
auf der Basis des Nordtest-Handbooks	
"Handbook for calculation of measurement uncertainty in environmental laboratories"	
Bearbeitung:	Uta Ulrich
Datum:	Unterschrift:

Reproduzierbarkeit innerhalb des Labors

u_{Rw}

13.64%

A) Kontrollprobe, die den gesamten Prozess abdeckt

Standardabweichung: 150

bei Konzentration: 1100

rel Standardabweichung: 13.64%

B) Kontrollprobe, die nicht den gesamten Prozess abdeckt

B.1 Kontrollprobenergebnis

Standardabweichung:

bei Konzentration:

rel Standardabweichung:

B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)

mittlere Spannweite:

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Zahl der Messungen für Spannweite (2, 3, 4 oder 5)		
Standardabweichung:		
Kombination:		

C) Instabile Kontrollproben

C.1 Wiederholbarkeit

mittlere Spannweite:	
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	
Standardabweichung:	

C.2 "Langzeit"-Komponente

Schätzwert für die Standardabweichung	
basierend auf:	
Kombination:	

Methoden- und Laborabweichung

u_{bias} **7.59%**

A) Mehrfache Analytik eines zertifizierten Referenzmaterials

zertifizierter Wert		Einheit:	mg/kg
Konfidenzintervall +/-			
Konfidenzniveau			
au	95%		
relative Standardunsicherheit:			
Mittelwert der ZRM-Analytik:		mg/kg	
Mittlere Abweichung			
Mittlere Abweichung in %			
Std.-abweichung der ZRM-Analytik:		mg/kg	
rel.Std.-abweichung der ZRM-Analytik:			

Anzahl der Messwerte:	<input type="text"/>
Standardunsicherheit:	<input type="text"/>

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interva I	Konf.-niv.	Mittelwert
ZRM 1	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 2	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 3	<input type="text"/>	<input type="text"/>		<input type="text"/>
ZRM 4	<input type="text"/>		95%	<input type="text"/>

	$u(c_{ref})$	Abw.	Abw.quadrat
ZRM 1	<input type="text"/>	<input type="text"/>	<input type="text"/>
ZRM 2	<input type="text"/>	<input type="text"/>	<input type="text"/>
ZRM 3	<input type="text"/>	<input type="text"/>	<input type="text"/>
ZRM 4	<input type="text"/>	<input type="text"/>	<input type="text"/>
Mittel	<input type="text"/>	RMS _{bias} <input type="text"/>	<input type="text"/>

Standardunsicherheit:	<input type="text"/>
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C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw- quadrat	s_R (%)	N Werte	$u(c_{ref})$
Probe 1	1000	939	-6.12%	0.37%	0%	1	0.00%
Probe 2	1200	1118	-6.83%	0.47%	0%	1	0.00%
Probe 3	1400	1268	-9.42%	0.89%	0%	1	0.00%

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Probe 4		
Probe 5		
Probe 6		
Probe 7		
Probe 8		
Probe 9		
Probe 10		
Probe 11		
Probe 12		
RMS_{bias}		7.59%
$u(c_{ref})$		0.00%

Standardunsicherheit: 7.59%

D) Wiederfindungsexperiment

Unsicherheit der Konzentration der Aufstocklösung:

Konzentration der Aufstocklösung:	1400
Konfidenzintervall +/-	5
Konfidenzniveau:	
u_{conc}	0.18%

Unsicherheit des zugegebenen Volumens:

max. Abweichung [%] (Rechteckverteilung)	0.01%	Std-abw.:	0.01%
Wiederholbarkeit [%] (als Standardabw.)	0.01%		
u_{vol}	0.01%		
Unsicherheit der Aufstockung:	$u_{recovery}$	0.18%	

Wiederfindung:

	Aufstockung	Messdiffere nz	Wiederfindun g	Abweichun g	Abw-quadrat
1	1400	186	86.71%	13.29%	1.77%
2	1400	88	93.71%	6.29%	0.40%
3	1400	91	93.50%	6.50%	0.42%
4	1400	79	94.36%	5.64%	0.32%
5	1400	110	92.14%	7.86%	0.62%
6					
7					
8					
9					
10					
11					
12					
				RMS _{bias}	8.39%

Standardunsicherheit: 8.39%

Kombinierte Standardunsicherheit u 15.61%

Erweiterte Unsicherheit U k-Faktor 2 31.21%

Messunsicherheitsabschätzung

zur Bestimmung von	Flufenacet Regner	
in	Wasser	
mittels	SPE - HPLC/DAD	
für den Konzentrationsbereich:	500-2000 ng/l	
auf der Basis des Nordtest-Handbooks		
"Handbook for calculation of measurement uncertainty in environmental laboratories"		
Bearbeitung:	Uta Ulrich	
Datum:		Unterschrift:

Reproduzierbarkeit innerhalb des Labors

u_{Rw}

13.64%

A) Kontrollprobe, die den gesamten Prozess abdeckt

Standardabweichung: 150

bei Konzentration: 1100

rel Standardabweichung: 13.64%

B) Kontrollprobe, die nicht den gesamten Prozess abdeckt

B.1 Kontrollprobenergebnis

Standardabweichung:

bei Konzentration:

rel Standardabweichung:

B.2 Komponente, bedingt durch wechselnde Matrices und Konzentration (aus Range)

mittlere Spannweite:

	<input type="text"/>	
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)		
Standardabweichung:		
Kombination:		<input type="text"/>

C) Instabile Kontrollproben

C.1 Wiederholbarkeit

mittlere Spannweite:	<input type="text"/>
Zahl der Messungen für Spannweite (2, 3, 4 oder 5)	
Standardabweichung:	<input type="text"/>

C.2 "Langzeit"-Komponente

Schätzwert für die Standardabweichung	<input type="text"/>
basierend auf:	<input type="text"/>
Kombination:	<input type="text"/>

Methoden- und Laborabweichung

u_{bias} **7.91%**

A) Mehrfache Analytik eines zertifizierten Referenzmaterials

zertifizierter Wert	<input type="text"/>	Einheit:	<input type="text" value="mg/kg"/>
Konfidenzintervall +/-	<input type="text"/>		
Konfidenzniveau	<input type="text" value="95%"/>		
relative Standardunsicherheit:	<input type="text"/>		
Mittelwert der ZRM-Analytik:	<input type="text"/>	<input type="text" value="mg/kg"/>	
Mittlere Abweichung	<input type="text"/>		
Mittlere Abweichung in %	<input type="text"/>		
Std.-abweichung der ZRM-Analytik:	<input type="text"/>	<input type="text" value="mg/kg"/>	

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rel.Std.-abweichung der ZRM-Analytik:		
Anzahl der Messwerte:		
Standardunsicherheit:		

B) Mehrfache Analytik *mehrerer* zertifizierter Referenzmaterialien

	zert. Wert	Konf.interva I	Konf.-niv.	Mittelwert
ZRM 1				
ZRM 2				
ZRM 3				
ZRM 4			95%	

	$u(c_{ref})$	Abw.	Abw.quadrat
ZRM 1			
ZRM 2			
ZRM 3			
ZRM 4			
Mittel		RMS _{bias}	

Standardunsicherheit:	
-----------------------	--

C) Ringversuche

	Vorgabe	Messwert	Abw.	Abw- quadrat	s_R (%)	N Werte	$u(c_{ref})$
Probe 1	1000	949	-5.07%	0.26%	0%	1	0.00%
Probe 2	1200	1118	-6.83%	0.47%	0%	1	0.00%

Probe 3	1400	1250	-10.74%	1.15%	0%	1	0.00%
Probe 4							
Probe 5							
Probe 6							
Probe 7							
Probe 8							
Probe 9							
Probe 10							
Probe 11							
Probe 12							
						RMS _{bias}	7.91%
						u(c _{ref})	0.00%

Standardunsicherheit: 7.91%

D) Wiederfindungsexperiment

Unsicherheit der Konzentration der Aufstocklösung:

Konzentration der Aufstocklösung:	1400
Konfidenzintervall +/-	5
Konfidenzniveau:	
u _{conc}	0.18%

Unsicherheit des zugegebenen Volumens:

max. Abweichung [%] (Rechteckverteilung)	0.01%	Std-abw.:	0.01%
Wiederholbarkeit [%] (als Standardabw.)	0.01%		

		u_{vol}	0.01%		
Unsicherheit der Aufstockung:		$u_{recovery}$	0.18%		
Wiederfindung:					
	Aufstockung	Messdiffere nz	Wiederfindun g	Abweichun g	Abw-quadrat
1	1400	78	94.43%	5.57%	0.31%
2	1400	84	94.00%	6.00%	0.36%
3	1400	85	93.93%	6.07%	0.37%
4	1400	82	94.14%	5.86%	0.34%
5	1400	134	90.43%	9.57%	0.92%
6	400	17	95.75%	4.25%	0.18%
7	300	31	89.67%	10.33%	1.07%
8	100	-1	101.00%	-1.00%	0.01%
9					
10					
11					
12					
					RMS_{bias} 6.67%
Standardunsicherheit:		6.67%			
Kombinierte Standardunsicherheit				u	15.76%
Erweiterte Unsicherheit U		k-Faktor	2	31.53%	

Hiermit erkläre ich, dass ich die Dissertation „Environmental behaviour of selected herbicides in a lowland catchment in Northern Germany, relevance of inputs via surface runoff and drainage systems into surface water“ selbständig verfasst habe. Es wurden keine anderen als die angegebenen Quellen und Hilfsmittel benutzt und direkt oder indirekt aus fremden Quellen übernommene Gedanken wurden als solche kenntlich gemacht.

Die Dissertation habe ich bisher keinem anderen Prüfungsamt in gleicher oder vergleichbarer Form vorgelegt. Sie wurde bisher auch nicht veröffentlicht.

Kiel, den 20.12.2010

Uta Ulrich