Using Hydrological tracers to Study Pesticide Fate and Transport on an Agricultural Field



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Abstract

Non-point source pollution from pesticide leaching and runoff has become and important environmental problem. In a study by Winchester et al. (2009) detectable levels of pesticides were found in 87 % of drinking water samples in 12 of the corn belt states. This study focuses on the assessment of dye tracers as surrogates for Smetolachlor fate and transport in the end that they be used as a possible low cost substitutes in S-metolachlor risk studies. Two experiments were performed in order to evaluate the dyes. In the first, dyes and pesticides were applied concurrently, along with sodium bromide as a conservative tracer, to the soil surface of a 5 x 15 m area and left under prevailing meteorological conditions. The progression of each constituent was monitored in surface soils and subsequent runoff events. Nominal recoveries were reported in collected runoff samples totaling 0.4, 0.06, and 0.14 % for Br-, UR and SRB. This experiment was performed from April-July, 2012 in Alteckendorf, France. After 90 days soil cores samples were extracted from the site and analyzed for tracer and pesticide residues to determine leaching depths and persistence. Approximately 87~% of Bromide was recovered in soil cores taken to a depth of $1~{\rm m}$ on the $12^{\rm th}$ fo July. Wavelength shifting of dye tracers in soil samples after the 26^{th} of June masked fluorescence analysis such that their quantification could not be made after this date. S-metolachlor analysis of water and soil samples was yet to be performed at the time of conception of this document.

In the second experiment dye and bromide tracer leaching under high intensity rainfall conditions was executed on a 2 x 4.8 m plot. Simulated rainfall equipment was used to produce rainfalls approximately equal to a two year storm for the catchment. Pesticides were not included in this study as a means of reducing pollution and obtained values were compared to results from similar studies of S-metolachlor leaching as a means of validation. All tracers were found in measurable amounts in tile drain effluent after \pm 60 mm of applied rainfall, pointing to preferential flows to field tile drains.

Keywords: Multi-tracer, S-metolachlor, fate, transport, surrogate

Zusammenfassung

Der diffuse Pestizidtransport von Ackern zu Oberflächenwassern ist zu einem wichtigen Umweltproblem geworden. In einer Studie von Winchester et al. (2009) wurden nachweisbare Konzentrationen von Pestiziden in 87 % aller Trinkwasserproben in 12 US-Bundesstaaten gefunden. Ziel dieser Arbeit ist es zu untersuchen, inwiefern Farbstofftracer als Ersatzstoffe für die Untersuchung von Pestizidverbleib und -transport verwendbar sind. Dafür wurden zwei Experimente durchgeführt. Im ersten Experiment wurden zwei Farbstofftracer (Uranin und Sulforhodamin B) gemeinsam mit Pestiziden und einem konservativen Tracer (Bromid) auf den Boden einer 5 x 15 m großen Fläche unter am Standort vorherrschenden meteorologischen Bedingungen ausgebracht. Bromid wurde verwendet, um den Abbau und die Ausbreitung der Farbstoffe und der Pestizide nachzuvollziehen. Die Ausbreitung jedes Stoffes wurde mittels Proben aus oberflächennahem Boden und oberirdischem Abfluss gemessen. Die Wiederfindung der Tracer in Abflussproben war 0.4, 0.06, und 0.14 % für Br-, UR und SRB. Dieses Experiment wurde von April bis Juli 2012 in Alteckendorf im Frankreich durchgeführt. 90 Tage nach der Ausbringung der Stoffe wurden Bodenproben aus dem Versuchsgebiet entnommen und auf Farbstofftracer- und Pestizidrückstände untersucht, um Auswaschungstiefen und Persistenz jedes Stoffes zu bestimmen. Ungefär 87 % des Bromids wurden in Bodenproben aus 1 m Tiefe am 12.7.2012 wiedergefunden. Eine Verschiebung der Fluoreszenz-Wellenlänge des Farbstofftracers am 26. Juni hat die Analyse verhindert und es wurden keine Messungen mehr nach diesem Datum gemacht. Die S-Metolachlor Analyse war bei der Fertigstellung dieser Dokuments noch nicht durchgeführt worden.

Im zweiten Experiment wurde die Farbstoff- und Bromid-Tracerversickerung auf einer 2 x 4.8 m großen Fläche bei hoher Regenintensität gemessen. Dies entspricht \pm 60 mm Regen, was der Intensität eines zweijährigen Ereignisses gleich kommt. Messungen und Proben des oberirdischen sowie des Dränageabflusses wurden genommen und davon wurde die Wiederfindung der Tracer kalkuliert. Diese Werte wurden mit der Literatur verglichen, da keine Pestizide appliziert wurden. Alle Tracer wurden im Dränageabflüssen gemessen.

To Ma and Pa

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List of Abbreviations & Symbols

Δh	Changes in water level [cm]	
ψ	Matric suction head in soils [-hPa or	DDV
	-cm of water head]	GW
$ ho_{soil}$	Bulk density of the soil $[g/cm^3]$	\mathbf{LHy}
ρ_{water}	Density of water at 20 $^{\circ}\mathrm{C}~[\mathrm{g/cm}^3]$	
A	Area $[\rm cm^2]$	$\mathbf{L}\mathbf{L}$
C	Concentration at equilibrium [mg/L	NaB
	$; \mu { m g} / { m L}]$	NLL
C_0	Initial concentration [mg/L ; $\mu {\rm g} / {\rm L}$	NOa
K_a	Langmuir adsorption coefficient	
K_d	Distribution coefficient $[cm^3/g]$	pF c
K_d	Distribution or partition coefficient	RMS
ŭ	solid/water phase $[\text{cm}^3/\text{g} ; \text{mL/g}]$	so_4
K_f	Freundlich adsorption coefficient	SRB
K_s	Saturated hydraulic conductivity	
	[cm/sec; cm/day]	\mathbf{SS}
l	Height of sample cylinder [cm]	Stde
M	Mass [g ; mg]	UR
m_{dry}	Mass of soil sample after drying at 105° C for 48 hr [g]	
m_{sample}	Mass of soil sample at field conditions [g]	VW

q	Adsorbate per unit mass of adsorbent at equilibrium [mg/g ; μ g/g]
q_m	The maximum adsorbable value of adsorbate per unit mass of absorbent $[mg/g; \mu g/g]$
t	Time [sec]
V	Volume $[mL; L; m^3]$
V_{cyl}	Volume of sampling cylinder $[\text{cm}^3]$
Br ⁻	Bromide
BTC	Breakthrough curve
CI	Confidence interval
Cl	The chemical substance Chloride
DDW	Deionized distilled water
GWC	Gravimetric water content [%]
LHyGeS	laboratory of hydrology and geo- chemistry of Strasbourg
$\mathbf{L}\mathbf{L}$	Langmuir linearization
NaBr	Sodium Bromide salt
NLLS	Nonlinear least squares regression
NO ₃ -	The chemical substance Nitrate
pF curve	Soil moisture retention curve
RMSE	Root mean squared error
so_4^{-2}	The chemical substance Sulfate
SRB	Fluorescent dye sulforhodamine B, $\rm C_{27}H_{29}N_2O_7S_2Na$
\mathbf{SS}	Statistically significant
\mathbf{Stdev}	Standard deviation
UR	Fluorescent dye uranine, $C_{20}H_{12}0_5Na_2$, also known under the name fluorescein
VWC	Volumetric water content [%]

1

Introduction - Literature Search

Non-point source runoff from agriculture activities is an ever increasing problem in the pollution of our waterways and aquifers. World use of pesticides was approximately 5.2 billion pounds (2.36 billion kg.) in both 2006 and 2007 (Grube et al., 2011), with 198 million metric tonnes of fertilizer being used in 2010 (FAO, 2010). Three sets of factors are of known importance in the fate and transport of pesticides and nutrients applied to soils; 1) management factors , 2) hydrological factors, and 3) chemical factors (Baker, 1999).

Management factors: many agricultural management practices have been examined for their usefulness in reducing non-point pollution from acreage such as: no till farming, also known as conservation farming(Andreini and Steenhuis, 1990; Olsen, 1995; Watanabe et al., 2007); reduction of soil compaction by management of sowing and harvesting times (Batey, 2009; Soane and van Ouwerkerk, 1995); alignment of rows to reduce direct runoff (USDA, 2001); buffer strips (USDA, 2000); etc. However, due to heterogeneity of natural conditions and the unpredictability of meteorological events site management practices cannot stop all cases of pesticide runoff and leaching. Thus, further management and mitigation practices, such as artificial wetlands (Lange et al., 2011), focus on the inevitability of pollutants reaching surface waters. For terseness further discussion has been excluded.

Hydrological factors: three main hydrological factors, the rate of infiltration, the route of infiltration, and quantity of runoff, are the main processes responsible for the transport of pesticides and other agrochemicals off-site (Baker, 1999; Conservation, 1993; Oliver et al., 2012). Infiltration rates are extremely site specific and dependent on

area soil properties making ameliorations difficult or economically unfeasible. Several management practices, such as mulching or no-till, have been shown to increase water absorption in the top soil layer by additions of biomass (Smets et al., 2008). This, however, does not change soil properties further down in the soil column where deep percolation occurs and possibilities of contamination exist by way of leaching pesticides and solutes.

Infiltration pathways are also heavily dependent on site characteristics; land usage; crop type, stage, and cover; and tilling practices (Mohanty et al., 1996; Wainwright, 1996; Watanabe et al., 2007). Mohanty et al. (1996) reports that nearly 91% (under corn row), 89% (under nontrafficked interrow), and 92% (under trafficked interrow) of the saturated water flux occurs through large pores and cracks in glacial till catchments, at water tension ranges of 0-0.3 hPa. Savabi et al. (2008) found higher earthworm (*Lumbricus terrestris*) activity under no-till fields and subsequent higher infiltration rates due to increased macroporosity. Increases in field macroporosity can lead to contamination of shallow aquifers during large rain events by bypassing the soil matrix, leading to deeping infiltration, and increased risk of contamination of supply wells (Cey et al., 2009; Hrudey et al., 2003).

Runoff from agricultural fields is dependent on rainfall quantity and intensity; farming practices; and site soil properties (Mohanty et al., 1996; Wainwright, 1996; Watanabe et al., 2007). In some cases runoff can exceed 70% of rainfall (Watanabe et al., 2007), with rainfall event intensity being the driving factor in the percentage of runoff measured (Wainwright, 1996). This occurs when the rainfall rate is less than the initial infiltration rate (suction driven), of the soil, but greater than the final gravity dominated rate, at this point water cannot be taken up by the soil profile as fast as it is added and ponding and runoff occur (Baker, 1999). Furthermore, the mode of pesticide transport in runoff (in the dissolved phase or in association with transported sediment) is dependent on pesticide properties (Oliver et al., 2012). Type and quantity of sediment loads also play a large role in pesticide transport (Agassi et al., 1995) and are shown to be highly correlated to tillage practices and site soil characteristics (Cogo et al., 1984).

Chemical properties: chemical properties that determine transport through the unsaturated zone depend on many factors: ion exclusion; ion exchange; volatilization; dissolution and precipitation; chemical and biological transformation; bio-degradation; adsorption; diffusion; dispersion; and persistence (Tindall et al., 1999), the four most important properties being, persistence (or resistance to transformation or degradation), soil adsorption, water solubility, and vapor pressure (volatilization) (Baker, 1999). These properties determine the most likely transport process a chemical will take. In the case of strongly adsorbed pesticides (e.g., with distribution coefficients $(K_d) > 200$), the main mode of transport is with sediment, because pesticide is not readily released to water flowing over or through the soil surface; whereas for moderately adsorbed pesticides $(1 < K_d < 20)$, pesticide is more readily released to water flowing over or through the soil surface, and runoff losses with water dominate over losses with sediment (Baker, 1999). Currently there is a good understanding of most transport processes of pesticides (Flury, 1996). There has also been extensive work done on the impact of management practices on hydrological processes in conjunction with pesticide transport (Andreini and Steenhuis, 1990; Olsen, 1995; Smets et al., 2008; Watanabe et al., 2007). However heterogeneity between sites and soils is rarely addressed and individual studies usually cannot be transfered between sites and catchments. In most cases, site specific testing must be completed in order to characterize high risk pollution pathways within individual catchments. Further complications arrive, since chemical properties of pesticides differ greatly from one to another (Hertfordshire, 2009). Moreover testing has mainly focused on the use of lysimeters or soil cores to characterize entire catchments (Fank and Harum, 1994; Vanderborght et al., 2002). This approach brings into question the validity of the transfer of observations from the small to the large scale in processes such as macroporosity given its heterogeneity (Blöschl and Sivapalan, 1995). This study's focus is to show that dye tracers can be used as a surrogate for the pesticide S-metolachlor and provide a low cost alternative in the case of site characterization while using a scale representative of the catchment as a whole.

Water tracers have been employed as a means of determining catchment hydrology for nearly 150 years (Knop, 1878). Most tracer tests focus on their use as a method to determine water transport and arrival times in surface and groundwaters (Davis et al., 1980; Haggerty et al., 2008). To that end tracers have been assessed using a set of criteria to determine if they exhibit "conservative" or "ideal" behavior (Bowman, 1984; Flury and N.N., 2003; Smart and Laidlaw, 1977). Bowman (1984) states the criteria for an effective soil water tracer are:

- 1. the tracer should not be significantly sorbed or otherwise retarded by the soil of interest
- 2. the tracer should be exotic to the soil environment, or should be present naturally at low concentrations
- 3. the tracer should be conservative in that it is not significantly degraded chemically or biologically during the course of an experiment.

Other considerations in choosing a tracer include: ease of quantitation in a soil solution matrix; cost of the tracing element; and the potential for adverse environmental impacts, particularly important if the tracer is to be used in unconfined field studies. However, only certain processes can be studied from conservative tracers such as, advection, dispersion (spreading of break through curves), and transient storage or mass transfer (tailing in break through curves) (Fank and Harum, 1994; Sánchez-Vila and Carrera, 2004).

Dye tracers have seen use as surrogates for pesticide fate and transport for upwards of 20 years. A surrogate is defined in environmental microbiology as an organism, particle, or substance used to study the fate of a pathogen in a specific environment (Sinclair et al., 2012). Uranine and rhodamine WT dye tracers have already been employed in laboratory column experiments designed to evaluate the dyes as adsorbing tracers that mimic pesticide adsorption (Sabatini and Austin, 1991). In the study Sabatini demonstrates that the tracers were able to delimit the break through of atrazine and alachlor in column experiments, with the BTC peak of uranine coming before and sulforhodamine B after the pesticides. Vanderborght et al. (2002) used brilliant blue and sulforhodamine B dyes to assess solute transport mechanisms in soil cores and Sinreich et al. (2007) used uranine and sulfrhodamine B as conservative and sorbing tracers respectively, in a comparative tracer test where both tracers passed through a thin soil layer before entry into a karst system. Most studies to date focus on the sorption properties of dyes and pesticides and the use of dyes as delimiters or indicators of pesticide leaching (Sabatini and Austin, 1991; Vanderborght et al., 2002). These works focus on pesticide and dye leaching, most commonly in association with preferential flows, during heavy rainfalls directly or shortly after application (Andreini and Steenhuis, 1990; Vanderborght et al., 2002). Very little work has been done on pesticide or dve tracer fate and transport under field conditions. Cornoi et al.

(2011) studied the fate of S-metolachlor under field conditions, but focused primarily on pesticide leaching over time. More understanding of the processes effecting pesticide dissipation in the top layer of soil need to be developed in order to better contain pollution. This is also reflected in the large range of half-life values of S-metolachlor in photodegradation studies, which range from 6.83 - 94.95 days (Costello and Hetrick, 2008); the use of organic matter and acetone as a photosensitizer being cited for the large range of values. No previous work was found in which the sorption and degradation of dyes at normal field conditions was used as a means of delimiting or determining pesticide fate.

The pesticide of focus in this study is S-metolachlor, which is shown to be moderately adsorbed, have a high water solubility and a low rate of volatilization (Bowman, 1990; Hertfordshire, 2009; University, 1993). It has been widely used for selected weed control for over 30 years and normally applied preemergence. The mean half life of S-metolachlor was demonstrated to be 23 days in dissipation studies at different European field sites (OConnell et al., 1998); where S-metolachlor persistence was shown to be correlated to the application amount, since higher application amounts increased leaching to depths were photo- and aerobic degradation were reduced (Cornoi et al., 2011). Monitoring of S-metolachlor in runoff and tile drain effluent was performed by Gaynor et al. (2002) in which 91% of total accounted pesticide loss was through the tile drainage system, with 92% being transported in the first event after herbicide application. Gish et al. (2009) reported volitalization losses of metolachlor as 19.3 - 11.4 % of applied mass for a period of 3 days after pesticide application, the larger volitization losses coming from plots with higher soil moisture contents. As before stated, there are large differences in estimations of S-metolachlor persistence with in field half-life values ranging from 11-31 days in European studies (Hertfordshire, 2009) to 6.83 - 94.95 days in American studies (Costello and Hetrick, 2008), which displays either the site specifity or conditional dependence of S-metolachlor decay.

Simulated rainfall experiments have successfully used to evaluate runoff and sediment transport from agricultural fields for many years (Grace and Eagleson, 1966; Sangesa et al., 2010; Touma and Alberge1, 1992; Wainwright, 1996). Many studies have used simulated rainfall as a means of determining solute leaching rates during

1. INTRODUCTION - LITERATURE SEARCH

large or high intensity events (Flury, 1996). Kung et al. (2000) tested deep leaching of adsorbing and non-adsorbing tracers to determine transport processes involved in leaching to field tile drains. Most rainfall simulations provide intensities well above extreme events, such as discussed in Agassi and Bradford (1999) and Dunkerley (2008) and reproduce inadequately natural rainfall. In reproducing natural rainfall the following must be considered: drop size; drop impact kinetics; uniform rainfall intensity and random drop size distribution; uniform rainfall application over the desired area; vertical angle of impact; and natural occurrence of simulated event size (Blanquies et al., 2003). The simulated rain experiment, in the case of this study, was performed to study the mass recovery of dye tracers in rain events within 24 hours after application; given that most S-metolachlor leaching is shown to occur in the first rain event (Gaynor et al., 2002) and that pesticide leachate mass is inversely proportional to the time elapsed between application and the first infiltration event (Flury, 1996). In this way, the behavior of the fluorescent dyes under certain meteorological conditions could be assessed that did not occur during the plot experiment.

It is believed that dye tracers can be effectively used as surrogates for the fate and transport of S-metolachlor under field conditions. While it is doubtful that dyes can mimic pesticide behavior completely, such that driving processes demonstrate a correlation of 100 %, it is thought that they can provide a rough estimation of these processes. It is also believed that dyes can be used as an "early warning system" or "delimiter" of pesticide peaks in catchment effluent, such as been shown in laboratory column experiments by Sabatini and Austin (1991). In this way, dye tracers that have already found use in the determination of pesticide overspray during application (Barber and Parkin, 2003) could be further monitored to delineate pesticide peaks from runoff and leaching to surface waters before they negatively impact water quality.

Aims of the project

2.1 Final aim

This study's goal is to assess the use of two dye tracers as surrogates in quantifying S-metolachlor fate and transport at the plot scale and determine their viability as such. Two experiments were performed under different conditions in order to better define individual transport processes; the aims of each are discussed below. Results from plot scale experiments are then to be applied at the catchment scale to make inferences towards driving transport processes within the catchment and the risk of pollution posed by each.

2.1.1 Aims of Plot Experiment

The plot experiment has the aims of:

- Establishing an event based mass balance for tracers (Bromide, Uranine, Sulforhodamine B) and S-metolachlor.
- Investigating the hydrological processes of sediment deposition, runoff, and infiltration, at the soil surface and in the soil column.
- Understanding sorptive properties of site soils for assessment of retention and retardation of S-metolachlor and tracers.
- Understanding the decay and transport processes of tracers compared to S-Metolachlor and their link to prevailing hydro-chemical and meteorological conditions.

2

2. AIMS OF THE PROJECT

The plot experiment was carried out under prevailing meteorological conditions as a means to better evaluate the dynamic processes of a normal spring-summer season.

2.1.2 Aims of Tile drain Experiment

The goal of the tile drain experiment is to quantify individual solute transport processes, (runoff, infiltration, and macropore flow) under high rainfall conditions. This shall be performed through the evaluation of the following points:

- Calculation of tracer mass balances under high rainfall conditions.
- Assessment of initial and final conditions and their impact on solute transport through the soil column to the tile drain.
- Quantification of a processes' contribution to solute transport.

The plot experiment utilized a simulated rainfall system with application rates similar to an extreme two year event, in order to recreate the desired meteorological conditions.

Materials & Methods

3.1 Study site

The study catchment Katzenlauf is located at 8 °51'44.136"E, 21 °53'14.189"N close to the village of Alteckendorf, France. The chosen plot area measured approximately 5 m x 15 m and was located circa 100m from the upper boundary of the catchment area in order to reduce possible downstream effects. Plot width was chosen based on the pesticide application method (sprayer boom of 6 m length), and plot length was chosen to reduce plot asymmetry. Crops planted inside of the plot area consisted of sugar beet (*Beta Vulgaris*) with the total crop makeup of the catchment comprising of 68% corn, 16% wheat 4% sugar beet (2% fallow). A slow release fertilizer was applied to the field at the end of March with pesticides and tracers being applied several weeks later on the same day in April, 2012 (exact dates are excluded for the privacy of the farmer). This was done in the interest of facilitating mass balance calculations of tracer and pesticide development over time.

900 g of uranine and sulforhodamine B along with 4.5 kg of sodium bromide (NaBr) were mixed with 30 liters of water and applied to the soil surface using a backpack sprayer. Care was taken to apply the tracers in a homogeneous manner as possible. An effort was also made to reduce the amount of soil compaction by distributing the sprayer's weight over a larger area and limiting the number of footfalls on the plot surface. Only the free anion bromide Br⁻ was analyzed, making the measurable amount of tracer equal to approximately 3.5 kg. The chemical properties of tracers are shown in table 3.1 and product information in appendix table B.1. Table 3.2 gives literature

values of Distribution coefficient (K_d) , normalized K_d to soil organic fraction value (K_{oc}) , half-life (DT50) photostability, hydrolytic stability half-life, and half-life in soils, for dye tracers and S-metolachlor. Tracer masses were chosen in consideration of the photodegradation rate of uranine and the detection limits of all tracing elements in soil and water samples. Masses per m² were 11.64 g/m² for dye tracers and 45.21 g/m² for Br⁻.

Table 3.1: Chemical properties of tracers and pesticides used in experiments at Alteckendorf, France for experiments from April-July, 2012.

Chemical	Molecular Formula	Molecular Weight	pKa	log Kow	Solubility in H20	Excit/Emit Wavelength
Sulforhodamine B^a	$\mathrm{C}_{27}\mathrm{H}_{29}\mathrm{N}_{2}\mathrm{O}_{7}\mathrm{S}_{2}\mathrm{Na}$	580.65	< 1.5	-2.02	$70 \mathrm{~g/L}$	565/590
$Uranine^{a}$	${\rm C}_{20}{\rm H}_{12}{\rm 0}_{5}{\rm Na}_{2}$	376.15	5.1	-1.33	$25~{ m g/L}$	490/520
Sodium Bromide $^{\rm b}$	NaBr	102.91			$909~{ m g/L}$	—
Metalochlor ^C	$C_{1}5H_{2}2ClNO_{2}$	283.79	omianla (201	3.05	$0.864 \mathrm{~g/L}$	266/274
Values determined from: a)Kasnavia et al. (1999) b)Roth Chemicals (2011) c)Commission (2004)						

Table 3.2: Distribution coefficient (K_d) , normalized K_d to soil organic fraction value (K_{oc}) , half-life (DT50) photostability, hydrolytic stability half-life, and half-life in soils; for UR, SRB and S-metolachlor.

Constituent	$K_d \ [cm^3/g]$	$K_{oc} \ [cm^3/g]$	Photostability water DT50	Hydrolytic stability DT50	Soil DT50
UR SRB S-metolachlor	$0 - 0.31^a$ $1.9 - 3.2^b$ $1.3 - 55.8^c$	dependent on f_{oc}^{b} dependent on f_{oc}^{b} $110 - 369^{c}$	pH dependent ^d Initial Conc. Dependent ^e $6 - 12d^c$	$_{ m stable^b}^{ m stable^b}_{ m stable^c}$	

a)Hadi et al. (1997) b)Sabatini (2000) c)Commission (2004) d)Smith and Pretorius (2002) e)Aley (2002)

3.1.1 Site description and climate

The site is characterized by circa 80% cambisols of slightly different types found in higher catchment elevations, with the remaining 20% comprising of colluvial deposists of the same cambisol soil at lower elevations. Cambisols are characterized by slight or moderate weathering of parent material and by absence of appreciable quantities of illuviated clay, organic matter, Al and/or Fe compounds. (Unesco. et al., 2006) Figure 3.1 displays the spacial distributions of the soils within the catchment.

The climate of Alteckendorf, France is considered a maritime climate according to Köppen climate classification (see Fig. 3.2). Maritime climates are defined by temperate winter and summer temperatures along with evenly distributed precipitation events



Figure 3.1: Pedology map of Alteckendorf - France (Environnement et al., 2001).



Figure 3.2: Climate graph of Alteckendorf, France - Monthly maximum, mean, and minimum temperatures (°C) with precipitation (mm), data taken from nearest weather station Strasbourg-Entzheim which is located 28 km south of Alteckendorf. The sampling period for this data covers 30 years from 1961 to 1990 (Network, 2012; NRK and NMI, 2012).

throughout the year (Köppen, 1918). Alteckendorf has more precipitation events during the months of March to July which includes most major events ie. over 20 mm/hour (Fig. 3.2). This was considered when determining experimental dates, because spring time runoff and erosion is much higher due to less or no crop cover and above stated higher rainfall intensities. Furthermore, previous studies have shown that highest pesticide losses in runoff occur during large intensity storms 1-2 weeks after application (Wauchope, 1978).

3.1.2 Plot measurement devices

A list of plot measurement devices can be found in table 3.3. Figure 3.3 displays their placement inside of the site. Values were logged at 5 min intervals for the tensiometers and soil moisture probes, with the automatic water sampler engaging on a flow dependent basis. Composite samples were produced for every 7 liters of discharge, which was measured with an Ultrasound flowmeter at an interval of 1 min in the occurrence of runoff.

Table 3.3: Equipment installed during the plot experiment Alteckendorf, France.

Equipment	Model	Evaluated parameter	Mode of measurement	
Ultrasound Flowmeter	LOGISMA	Height of water level	Continuous	
Refrigerated Automatic Sampler	Avalanche Isco Multi-Flasks NeoTek Ponsel	Water sampling	Continuous	
Tensiometers	T8 Long-term Monitoring Tensiometer UMS	Soil tension	Continuous	
Water content probes	Profile Probe Type PR2 Delta-T Devices Ltd	Volumetric water content of the soil	Continuous	

3.1.3 Catchment measurement devices

The catchment is essentially split into an upper and lower area by the department highway 25 (D25) embankment (see fig. 3.1). Continuous discharge and hydrochemistry data was collected at the upper catchment outlet, located at the culvert under D25, for the duration of both experiments. No measurements or samples were taken in the lower catchment area. Table 3.4 gives the measurement devices and their evaluated parameters installed at the catchment and drain outlets. Composite samples for every 30 L of discharge were collected by the refrigerated automatic sampler and were kept at



Figure 3.3: Map of measurement devices at the experimental plot - Alteckendorf, France.

4°C until collection to reduce degradation (biologic and photolytic) of pesticides and dye tracers. Upon collection, samples were placed in an ice box for transport to the laboratory where samples were filtered and either refrigerated or frozen depending on the elapsed time before possible analysis.

Equipment	Model	Evaluated parameter	Mode of measurement
Limnimetric scale ¹	ELPOS & ELNEG	Stream stage and sediment	Punctual
${ m Ultrasound}^1$	PCM3 NIVUS	Stream stage	Continuous
$ m Hydrochemical\ Probe^1$	AQUA Probe Acteon 3000 NeoTek Ponsel	pH, Temperature, DO, EC, Redox	Continuous
Doppler Flowmeter ¹	2150 Area Velocity Flow Module ISCO	Flow	Continuous
Refrigerated Automatic Sampler ¹	Avalanche Isco Multi-Flasks NeoTek Ponsel	Water sampling	Continuous
$CTD \ Diver^2$	Van Essen Instruments CTD-Diver	Water Depth, EC, Temperature	Continuous
BaroDiver ²	Van Essen Instruments BaroDiver	Barometric Pressure, Temperature	Continuous
Frund at 1 Catabarant aut	at 9 Desire sutlat		

Table 3.4: Equipment found at the catchment and drain outlets, evaluated parameter and type of measurement performed.

ound at 1. Catchment outlet 2. Drain outlet

3.1.4 Field sampling

Samples and data were collected from autonomous devices at the plot once every week from the 17th of April until the 10th of July. Water sampling at the catchment outlet continued from the 10th of July until the 21st of August. Punctual hydrochemistry measurements were performed at the catchment and drain outlets as a validation measure of continuous measurements. Grab samples were taken at the plot after large precipitation events when the automatic sampler was full. Water samples from the plot automatic sampler were composited to determine mean concentrations for entire runoff events. All water samples were placed on ice until arrival at the lab, where they were refrigerated at 4 °C (tracers) or frozen (pesticides) until analysis to reduce bioand photolytic degradation.

For soil sampling the plot was divided into quadrants to provide a better areal representation of the development of tracers and pesticides, with the NE corner being designated as quadrant 1, then proceeding in a clockwise manner to quadrant 4 at the NW corner (see fig. 3.4). Soil samples were taken once a week from each quadrant of the plot from the beginning of the campaign until the 29^{th} of May, at which point sampling continued at an interval of every two weeks until the discontinuation of the plot sampling campaign on the 10^{th} of July. Each sample was comprised of a composite of soil taken to a depth of 2 to 3 cm at several random locations within each quadrant. Soil samples taken in the field were placed in polyethylene bags and stored in a cooler on ice until arrival at the lab, whereupon they were frozen at -20 °C until analysis. This was done to reduce degradation in samples before analysis. In addition to disturbed surface soil samples, six 200 cm³ core samples with a depth of 5 cm, were extracted on the 3^{rd} of July in order to perform a site characterization of saturated hydraulic conductivity and soil moisture retention.

Soil core samples were taken on the 12th of July before discontinuation of sampling at the plot site using an Atlas-Copco Cobra TT percussion drill with a Van Walt soil sampling set. A total of 12 core samples were taken to the depth of one meter with a windowed sampler inside of the plot such that there was one sample for each tracer, pesticide, and soil property analyses, extracted from each quadrant. Core samples were split into sections of 0-2, 2-5, 5-10, 10-30, 30-66, and 66-99 cm. In addition to the previous samples, 8 secondary cores were extracted for tracer analysis from outside of the plot using a core sampler with polypropylene sampling tubes, also to one meter depth. Sampling sections for these cores were 0-33, 33-66, and 66-99 cm. Sample placement is shown in figure 3.4. Soil compaction was noted for all cores and transportation and storage of cores was executed in the same manner as described for surface soil samples. It was assumed that soil compaction was equally distributed throughout the core length and sample and sections were determined accordingly.



Figure 3.4: Placement of extracted core samples - taken from the plot experiment at Alteckendorf, France.

3.2 Tile Drain Experiment

A second tracer experiment was executed on a small plot of 2 x 4.8 m on the 24th - 25th of July. Tracer application was performed in the same fashion described for plot experiment, with tracer masses equal to 100 g of both UR & SRB and 500 g of NaBr; equivalent to 388.28 g of Br⁻. The tracer masses were mixed with 15 L of water and uniformly distributed on the experimental area. Masses per square meter were 10.42 g/m^2 for dye tracers and 40.45 g/m^2 for Br⁻. The tile drain experiment plot size was chosen as a scaled down area of the plot experiment, while keeping in mind the recommendation by Agassi and Bradford (1999) of plot area width to length ratios close to one. All soil and water samples were analyzed following the same procedures used during the plot experiment and are given in sections 3.3 & 3.4.

3. MATERIALS & METHODS

3.2.1 Site description

Figure 3.5 gives the site layout of the tile drain network and experiment performed in the Katzenlauf catchment. Site vegetation was comprised of alfalfa (also known as lucerne; *Medicago sativa*) with a mean height of approximately 20 cm. All vegetation was removed from the experimental site before tracer application and soil was homogenized to a depth of approximately 15-20 cm to imitate standard tilling practices employed in the rest of the catchment. The site was located circa 35 m upslope from the drain discharge point and directly over the tile drain network. TDR measurements were taken at the NW corner of the experimental area and a depth of 25 cm, with water samples and discharge measurements collected consecutively at the drain outlet.



Figure 3.5: Site of tile drain experiment - Alteckendorf, France, with description of tile drain network found in the Katzenlauf catchment.

3.2.2 Simulated rain equipment

Simulated rain equipment was constructed and used to induce infiltration and runoff at the experimental site. The device was similar to one fabricated by Sangesa et al. (2010). The design consisted of 1/2 inch (1.27 cm) galvanized pipe and pipe fittings with 4 Gardenia S-50 Pop-up Sprinkler heads (Gardena, 2012b), a manometer, and a shut off valve. Water was supplied to the system via an electric powered pump (Gardena, 2012a) and a generator, which was attached to a 1 m³ cistern. Figure 3.6 demonstrates the device set-up and its employment in the field. Water for the experiment was supplied by the Alteckendorf community. The setup was situated at a height of approximately 2.5 m directly above the center of the experimental plot, running in an east-west direction.



Figure 3.6: Diagram of simulated rain device - used in the tile drain experiment at Alteckendorf, France (Sangesa et al., 2010).

A validation of the rain equipment's homogeneity was completed before it was employed in the field. The homogeneity of spray was evaluated by two factors, the Christiansen's uniformity coefficient and the distribution value, both unitless coefficients. These are both standard measures of an irrigation system's water distribution (Camp et al., 1997; Zoldoske and Solomon, 1988). The Christiansen's uniformity coefficient (CU) (Christiansen, 1942) is characterized by the following equation:

$$CU = 100 \cdot \left(1 - \frac{\sum |x_i - \bar{x}|}{\sum x_i}\right)$$
(3.1)

where CU is Christiansen's uniformity coefficient, x_i is the observed value of precipitation in mm at point i of a uniformly spaced grid, and \bar{x} is the mean of observed values in mm. The distribution coefficient (DU) Kruse (1978) was calculated using the equation:

$$DU = 100 \cdot \left(\frac{\bar{x_4}}{\bar{x}}\right) \tag{3.2}$$

where \bar{x}_4 is the mean of the lowest 25 percent of observations in mm of precipitation and \bar{x} is the statistical mean of observed values in mm.

3.2.3 Measurement devices and Sampling

A low tech approach was used in the measurement of runoff and discharge parameters during the experiment. In the case of the drain discharge, flow was measured by the use of a graduated cylinder and a stopwatch. Runoff was measured through increases of water depth in a predefined container over a given time interval. Discharge measurements were taken every 30 min and runoff measurements every 5 min on the 24th of July during the first and second applications. The following day all measurements were done at 5 minute intervals. Water sampling of the drain effluent was conducted overnight and the following morning using an APEG automatic sampler at 7.5 min intervals during the first hour of the tailing end of the tracer break through curves, then at 30 min intervals in further measurements. During the campaign, water sampling was conducted through grab sampling of drain effluent every 30 min on the 24^{th} and every 5 min on the 25th. Soil moisture was measured at a depth of 25 cm during simulated events at a 5 min interval, using a 6050X3K1B MiniTrase Kit (SoilMoisture Equipment Corp. Santa Barbara, CA). Soil samples from the top 2-3 cm of soil were collected at the end of campaign using the same randomized sampling procedure employed for the plot experiment.

3.3 Analysis of Water Samples

Tracer analysis was performed on all samples from the plot, including samples from the catchment after the 3^{rd} of July. Water samples from the 3^{rd} until the 24^{th} of July were taken as baseline values for calculations of tracer recovery in the tile drain effluent. Hydrochemical testing was executed on all samples from both the plot and the catchment. All samples were stored at $4^{\circ}C$ in brown glass bottles until analysis to reduce decay from biotic and abiotic processes. Pesticide analysis of plot and catchment water samples was completed by the laboratory of hydrology and geochemistry of Strasbourg (LHyGeS) using internal standards.

3.3.1 Bromide tracer analysis

Bromide concentrations in water samples were measured using a Dionex DX 500 Ion-Chromatograph with the LC20 chromatography enclosure and auto-sampler (Analysis range from 140 ppb to 100 ppm with an accuracy of 8% and an effective detection limit of 0.018 mg/l (Dionex, 1993)). Samples were filtered with 0.7 μ m glass fiber filters and placed into 5 mL polypropylene vials for analysis. Given time restraints duplicate measurements could not be performed and concentrations represent single measurement values.

3.3.2 Fluorescent tracer analysis

Water samples were analyzed using a Perkin Elmer LS50B spectral fluorometer with an extinction slit of 10 nm, an emission slit of 10 nm, a delta lambda of 22 nm, and a scan speed of 600 nm/m. Hellma type 131-QS quartz glass Soprasil cuvettes with a through flow pump were employed in the analysis. Samples were filtered at 0.7 μ m with glass fiber filters prior to analysis. Samples were brought to room temperature before analyses in order to reduce temperature effects of tracer fluorescence due to different sample and calibration temperatures (Wilson et al., 1986). pH was adjusted sample dependent to reduce pH effects on uranine (Smith and Pretorius, 2002). Deionized distilled water (DDW) was used in dilutions as needed. Fluorescence of DDW was was compared with site specific blind water and showed little difference, thus no correction was needed between diluted and non-diluted samples. Calibration curves were created in accordance to the methodology explained in Wilson et al. (1986) (see appendix figure A.1). Samples were analyzed in triplicates given enough solution, otherwise duplicates were processed. Reproducibility of measurement was sample dependent and were within the range of $x \pm 0.082$ -8.87x10⁻⁴ % for UR and $x \pm 0.402$ -6.92x10⁻⁵ % for SRB. Samples with higher turbidity before filtering displayed higher deviations and background levels of fluorescence than samples with lower initial turbidity. Subsequently, detection limits were higher in such samples and sample concentrations were corrected accordingly.

3.3.3 Hydrochemistry testing

Hydrochemical analysis was performed on all plot and catchment water samples. Samples were analyzed for suspended solid flux (SS), organic matter in SS (OM), nitrogen dioxide (NO₂), nitrates (NO₃⁻), ammonium (NH₄⁺), Phosphate (PO₄⁻³), total inorganic carbon (TIC), total organic carbon (TOC), dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and Phosphorous (P). Testing was completed at LHyGeS using ISO or NF (Norme Francais) standards dependent on performed test.

3.4 Analysis of Soil Samples

All soil and core samples taken during the plot experiment were analyzed for tracer concentrations, pH, and soil moisture content using the methods described below. The six core samples taken on the 3^{rd} of July were used in soil moisture retention curve and saturated hydraulic conductivity analyses in order to characterize the physical soil properties found at the site. Samples taken before application of pesticides and tracers were used in the analyses of carbonaceous material and particle size. Pesticide analysis is to be completed by LHyGeS using internal standards for all soil samples taken from the soil surface during the tenure of the campaign and for four of the soil cores (one for each quadrant) extracted on the 12^{th} of July.

3.4.1 Soil pH

Soil pH testing was done in accordance with USEPA SW-846 method 9045 (USEPA, 2000) for the soil cores taken inside of the plot area on the 12th of July. Briefly, 20 g of soil were added to an Erlenmeyer flask and mixed with 20 mL of DDW. The mixture was then agitated by hand several times over a 30 minute period. After letting the solution sit for an hour, allowing the majority of suspended solids to settle, the pH was measured in the top portion of the solution with a WTW pH 597-S probe. For soil samples taken over the course of the sampling campaign and the soil cores taken from outside of the plot area pH testing was conducted using ISO-10390 (Carter and Gregorich, 2007; ISO, 1994) This was due to the fact that samples were frozen and had to be thawed and dried to expedite analysis procedures. In short, 10 g. of soil was mixed with 50 mL of DDW, agitated for 5 min and then allowed to sit for 2 hours. After the time had elapsed the mixture was quickly agitated and the pH was measured in the liquid portion
of the mixture. A control of the pH probe was performed with 4.01 and 7.0 pH buffer solutions before each use with the probe being calibrated as necessary.

3.4.2 Bulk Density and Field Moisture Content

Bulk Density and field moisture content were evaluated using the following equations (Klute, 1986; Schack-Kirchner et al., 2009; Terzaghi et al., 1996)

Gravimetric Water Content (GWC) =
$$\frac{(m_{sample} - m_{dry})}{m_{dry}} * 100$$
 (3.3)

$$Volumetric Water Content (VWC) = \frac{(m_{sample} - m_{dry})}{V_{cyl}} * 100$$
(3.4)

$$\rho_{soil} = \frac{m_{dry}}{V_{cyl}} \tag{3.5}$$

Where GWC and VWC are in %, m_{sample} is the mass of the sample upon arrival at the lab in g, m_{dry} is the mass of the dried sample (105 °C for 48 hr) in g, V_{cyl} is the volume of the sample cylinder in cm³, and ρ_{soil} is the bulk density of the soil in g/cm³ Volumetric water content was calculated with the aid of equation 3.6 for samples taken without defined volumes.

$$VWC = \frac{GWC * \rho_{soil}}{\rho_{water@20\,^{\circ}C}} \tag{3.6}$$

with VWC and GWC given in %, ρ_{water} in g/cm³, and ρ_{soil} in g/cm³ being equal to the mean bulk density of soils found at the plot.

3.4.3 Carbonaceous Material

Carbonaceous material analysis, both organic and inorganic, was calculated with a Wösthoff-Apparatus. The apparatus introduces a previously metered sample gas into a suitable liquid reagent of measured electrical conductivity (in this case a NaOH solution). The volumetrically proportioned streams of sample gas and liquid reagent combine, changing the conductivity of the reagent solution of which the resulting difference in conductivity of the reacted reagent solution is proportional to the concentration of the sample gas being measured. Concentrations of the solution are then determined by changes in the electrolytic conductivity of an absorbing solution. Concentrations are then converted to mg/g of substrate using mass balance considerations (Schierjott and Eikevaag, 2012; Schlichting et al., 1995).

3.4.4 Particle size

The procedure used for the analysis of soil particle size used was the Kilmer and Alexander (1949) pipette method which is the standard procedure of the USDA and Canadian Soil Survey. (Carter and Gregorich, 2007; USDA, 1996) In short, samples were oven dried at 105 °C for 24 hr., upon which they were passed through a 2 mm sieve separating the fine and coarse portions of the samples. 10 g of the fine portion of the sample was then placed in a 1 L Erlenmeyer flask and mixed with 50 mL H₂O₂ (30% volume fraction). It was then capped and left overnight at room temperature. The following day the samples were heated at 70 °C until all the organic material was destroyed, as needed more H₂O₂ was added and the procedure repeated. After this the particles were dispersed using 25 mL of Na₄P₂O₇ (C = 0.1 mol/L) and left overnight at 60 - 70 °C. The following day the sample was transfered into a sedimentation cylinder (1000 mL), shaken, and placed into a 20 °C water bath. A 10 mL sample was taken with a pipette at 10 cm depth at different times according to the particle size settling rate as determined from Stoke's law. The samples were then dried and weighed with the percentage of each particle size calculated in relation to the sample mass.

3.4.5 Saturated hydraulic conductivity

Saturated hydraulic conductivity, or K_s value, was calculated using the falling head method described in Head (1982). Samples cylinders were saturated through capillary rise overnight and the following day fitted with water tight sleeves. The sleeves were then filled with water and the time needed for the water level to move from level A to level B was recorded. On the basis of the results the K_s value was calculated using the following equation:

$$K_s = \frac{A_w}{A_{cyl}} * \frac{l}{t} * ln\left(\frac{\Delta h_0}{\Delta h_1}\right)$$
(3.7)

where A_w and A_{cyl} are the area of the sleeve and sample cylinder in cm², l is the height of the sample cylinder in cm, t is the time in seconds, and Δh_0 and Δh_1 are the water level at the beginning and end of the measurement in cm.

3.4.6 Soil Moisture Retention Curve

Analysis of six soil core samples taken on July 3rd, 2012 was done using soil water desorption and imbibition techniques. (Carter and Gregorich, 2007; Klute, 1986; Schack-Kirchner et al., 2009) The samples were saturated overnight in a wetting tank using local tap water in order to bring the matric head (ψ) of samples to 0. The sample was then weighed at saturated conditions and placed on a filter bed with a constant head burette. A given head was then applied on the core sample and allowed time to equilibrate, upon which it was weighed with the soil moisture content at the given pressure head being determined by equations 3.3 and 3.4, with the mass of the sample taken as the mass at the set pressure head. This was done for pressure head values of 0, 10, 60, 300, and 15000 hPa. A soil moisture retention curve was fit to the measured points using the RETC program. (van Genuchten et al., 1991) All curves were fit using the van Genuchten model with the assumption m = 1-1/n and K_s values determined from testing. (See section 3.4.5)

3.4.7 Bromide Tracer - Desorption from soil and analysis

Bromide was extracted from the soil using a method similar to that described in Lindau and Spalding (1984) (Herbel and Spalding, 1993; McMahon et al., 2003) In order to analyze the frozen soil samples, they were allowed to thaw for one day prior to being dried at 40 °C for 48 hr; then passed through a 2 mm sieve. 10 g of the < 2 mm substrate was combined with 100 mL of DDW, hand shaken for 1 minute and then placed on a reciprocating shaking machine at 170 rpm and 26 ± 1 °C for 24 hours. Afterwards, samples were transferred to glass centrifuge tubes and centrifuged at 3500g for 50 minutes. After centrifugation, an aliquot of the supernatant was taken and filtered using 25mm syringe filters with a 0.45m cellulose acetate membrane. Finally, bromide concentrations were measured as described in section 3.3.1. Concentrations were first calculated as mg of bromide per L in solution and then converted to mg of Br⁻ per g of substrate using mass balance considerations. Sample duplicates were performed only for core samples taken within the plot due to time constraints.

3.4.8 Fluorescent tracers - desorption from soil and analysis

Samples were prepared for analysis in the same manner stated in 3.4.7 for desorption of fluorescent dyes from soil. Filtration did not affect fluorescence measurements. Supernatant from the soil water mixture was analyzed using the procedure detailed in Section 3.3.2. Samples were brought to room temperature before analysis to reduce temperature effects of tracer fluorescence. pH was adjusted dependent on initial sample pH in order to reduce pH effects on UR. DDW was used in dilutions as needed. Calibration was executed in accordance to the methodology explained in Wilson et al. (1986) and can be found in appendix figure A.1. Triplicate measurements of each sample were taken and reproducibility of measurements were calculated. The reproducibility of measurements for soil samples was within the range of x \pm 0.039 - 9.5x10⁻⁴ % and x \pm 0.028 - 1.26⁻³ % for UR and SRB respectively.

3.5 Sorption Experiment

Batch sorption testing was performed using Alteckendorf site soil which is classified as a hydric cambisol (see section 3.1.1) with a particle distribution of (8% sand, 64% silt, 28%clay, with 0.25 mg/g of carbon). Soil taken before the application of pesticides and tracers was used in testing. Dyes were combined in batch testing to reflect conditions of field application.

3.5.1 Batch sorption tests

The experimental protocol is similar to that described in German-Heins and Flury (2000) and Mon et al. (2006). Samples were prepared by air drying them and passing them through a 2 mm sieve. Carbon was then removed using H_2O_2 following the procedure described in section 3.4.4. Eight dye concentrations were used consisting of 0.1, 1, 10, 50, 100, 200, 500, 1000 mg/l. These sample concentrations were employed since 1000 mg/l represents the applied amount of tracer on a 10 cm x 10 cm square, which is roughly equivalent to the amount taken during each sampling session. Two different solid to solution ratios were used for accurate measurement of concentration changes in solution before and after shaking (Roy, 1993). The pH and background electrolyte concentration of the batch system was adjusted with 0.1 mol/L NaOH and CaCl₂ to a pH of 9.5 and 10 mmol/L CaCl₂ in order to reduce pH and ionic

strength effects on the analysis of samples. The samples were mixed in 100 mL brown glass bottles, to reduce light induced decay of uranine, and placed on a reciprocating shaking machine at 170 rpm and $26 \pm 1 \,^{\circ}$ C for 24 hours. Mikulla et al. (1997) and German-Heins and Flury (2000) both report little difference between shaking times of 24 and 48 hr (< 1 %). Thus, 24 hr shaking times were used to expediate analysis. Samples were then transferred to glass centrifuge tubes and centrifuged at 3500g for 50 minutes. After centrifugation, an aliquot of the supernatant was taken and filtered using 25mm syringe filters with a 0.45m cellulose acetate membrane. A blank system comprising of soil without dye and dye without soil were processed in the same manner as described above. Three replicates were run of each sample including dye and soil blanks, from which mean and standard deviations of peak values were calculated. Dye concentrations were measured using a Perkin Elmer LS50B spectrophotometer with the same settings used in the analyses described in section 3.3.2. Individual sorption isotherm points were calculated from the mean concentration of triplicates according to mass balance considerations such that:

$$V * (C_0 - C) = M * (q - q_0)$$
(3.8)

where V is the volume of the sample in ml, C_0 and C are the initial and equilibrium concentrations of adsorbate in solution in mg/l, M is the mass of the substrate in g, and q_0 and q are the initial and equilibrium concentrations of adsorbate per unit mass of absorbent in mg/g.

Distribution coefficients K_d (also known as partition coefficients) were calculated for individual sorption points as a comparison to literature values for dyes and Smetolachlor. K_d was calculated using the constant partition coefficient model which is defined by the following equation:

$$K_d = \frac{q}{C} \tag{3.9}$$

where K_d is the distribution coefficient in cm³/g, q is adsorbate on the solid at equilibrium in μ g/g, and C is total dissolved adsorbate remaining in the solution at equilibrium in μ g/L (Wilhelm, 1999).

3.5.2 Sorption Isotherms

Two sorption isotherms, the Langmuir and Freundlich, were fit to the individual sorption isotherm points and evaluated for goodness of fit. The Langmuir isotherm is based on a kinetic approach and assumes that adsorption takes place on a single homogeneous layer at a constant temperature of which each site can absorb only one atom or molecule. It is also assumed that no phase transitions occur. (Czepirski et al., 2000; Langmuir, 1918) The Langmuir isotherm equation is written as:

$$q = \frac{q_m \cdot K_a \cdot C}{1 + K_a \cdot C} \tag{3.10}$$

where q is adsorbate per unit mass of absorbent in mg/g, q_m is the maximum adsorbable value of q in mg/g, K_a is a constant (function of enthalpy of adsorption and temperature), and C is the adsorbate concentration in the solution in mg/L. Kinniburgh (1986) states that linear transformations of the Langmuir isotherm for the derivation of equation parameters change the original error distribution; along with it the goodness of fit. The isotherm was parameters, K_a and q_m , were thus determined by fitting the data with two different regression methods, i.e., Langmuir linearization (LL) and non-linear least squares (NLLS) as purposed in Kinniburgh (1986) and Schulthess and Dey (1996). The linear transformation used in calculations of Langmuir coefficients is written as:

$$\frac{C}{q} = \frac{1}{K_a \cdot q_m} + \frac{1}{q_m} \cdot C \tag{3.11}$$

Weighted linear regression was not used to evaluate the Langmuir parameters. Kinniburgh (1986) states that non-weighted linear regression using the Langmuir linearization returns parameter estimates that lie somewhere between those obtained by assuming a constant absolute error and a constant relative error, which often is not an unreasonable assumption.

The Freundlich isotherm is an empirical equation, which assumes that the adsorbent has a heterogeneous surface composed of adsorption sites with different adsorption potentials. (Freundlich, 1909; Yetgin, 2006) The isotherm is explained by the equation:

$$q = K_f \cdot C^{(1/n)}$$
 (3.12)

where q is adsorbate per unit mass of absorbent in mg/g, K_f is a constant (function

of enthalpy of adsorption and temperature), C is the adsorbate concentration in the solution in mg/L, and n is a constant. When a constant relative error is assumed the Freundlich isotherm parameters can be estimated using the linearization:

$$log(q) = log(K_f) + \frac{1}{n} \cdot log(C)$$
(3.13)

Kinniburgh (1986) states linear regression based on Eq. 3.13 gives reliable estimates of the Freundlich isotherm parameters for the above assumptions.

Results

4

4.1 Plot Campaign

Several of the measurement devices at the plot malfunctioned (ie. tensiometers and soil moisture probes) during the 3 month field campaign and no data is available for these parameters for the tenure of the campaign. Results from the campaign include qualitative water samples from runoff events and quantitative soil samples for the experiment duration.

4.1.1 Plot Water Samples

Figure 4.1(a) depicts qualitative results of applied tracers (UR, SRB, Br⁻) in runoff water samples collected during the plot experiment. The results are shown as concentrations per applied tracer mass (mg/L*kg). Figure 4.1(b) displays the normalized concentrations from 0 to 1 in mg/kg*L for a representation of lower concentrations. A table of all concentrations can be found in the appendix (Table B.2). Measured concentrations in water samples show increases of all tracers after the rain event of the 22nd of May. Sample sediment flux is included in both graphs, which shows a peak value in samples taken on the 29th of May. The experimental setup for discharge measurements was inundated during large runoff events and below the least measurable flow during small events; thus, quantitative results could not be calculated from runoff water samples. Pesticide data was yet to be analyzed at the time of submission of this report. Dye tracer and pesticide data is to be compared in forthcoming reports, but is not included in this document.

As a means of tracer recovery estimation for the event of the 2^{nd} of May, measured tracer concentrations were multiplied by the volume of standing water found in the same hole as inundated devices. This can be found in Table 4.1. SRB demonstrates the highest recovery rate in samples collected on the 2^{nd} of May, with 0.032 % of applied tracer mass and UR and Br⁻ had values of 0.015 & 0.008 % respectively. The same estimation was applied to the rain event of the 22^{nd} of May. It is noted that the volume utilized in calculations underestimates runoff from the rain event of the 22^{nd} given its higher intensity; its use here is only as a means of rough estimation. Tracer recovery rates for the 22^{nd} of May, using the above assumption are: 0.39, 0.05, and 0.11% for Br⁻, UR, and SRB, respectively.

A correlation matrix of water sample constituents and available physico-chemical properties can be found in the appendix table B.5. Dye and bromide tracers show no statistically significant correlations to physico-chemical properties, though it should be noted that SRB displays a moderate positive correlation with rainfall. UR and Br⁻ demonstrate a high, statistically significant (confidence interval (CI) of 95 %), correlation with a Pearson r-value of 0.86.

Tracer	Date	Water Volume $[m^3]$	Conc. [mg/l]	Mass [mg]	% Recovered
Br	02/05/12	1.56	0.2	312.9	8.95*10-3
UR	02/05/12	1.56	$8.74*10^{-2}$	136.76	0.0152
SRB	02/05/12	1.56	0.1877	293.73	0.0326
Br	22/05/2012	1.56	8.75	13689.38	0.3917
UR	22/05/2012	1.56	0.27	419.30	0.0466
SRB	22/05/2012	1.56	0.61	961.94	0.1069

Table 4.1: Estimated tracer recovery rates for rain event of 2^{nd} of May, 2012 at Alteckendorf, France

4.1.2 Soil Samples

All soil samples during the plot experiment had measurable quantities of tracers, though fluorescence wavelength shifting occurred in both dye tracers in all samples after the 26th of June. Therefore, dye tracer quantities are only given until this date. Pesticide analysis of soil samples was not completed before conception of this document and comparisons will be made in forthcoming reports.



Figure 4.1: Normalized tracer concentrations with suspended solid flux in water samples taken at the plot in Alteckendorf from April to July 2012: (a) normalized concentrations for all events; (b) normalized concentrations from 0-1 mg/kg*L.

4.1.2.1 Soil Samples April - July

The development of anions at the soil surface for the duration of the experiment is found in figures 4.3 and 4.2. Dye tracer development is witnessed in figures 4.3(c) and 4.3(d). A reduction of nearly half of all UR and SRB is seen within the first week of the experiment reaching quantities below 0.1 mg/kg within five weeks. SRB undergoes a less drastic reduction after the first week losing approximately 25% of its mass weekly, whereas UR loses ~ 50%. Calculated half-lives for UR and SRB in surface soils are 13.81 and 18.98 days, respectively. Bromide also decreases in the soil surface during the first two weeks by more than 50%, with increases in concentrations during subsequent dry periods. This behavior is mirrored in varying degrees by all measured anions. After the rain event of the 22^{nd} -23rd of May larger differences are reported in anion and tracer concentrations between quadrants until core sampling on the 12^{th} of July.



Figure 4.2: Nitrate and sulfate development in the top 2 to 3 centimeters soil at Alteckendorf, for the period of April 17th to July 10th: (a) Nitrate (NO₃⁻); (b) Sulfate (SO₄⁻²⁾

Uranine seems to be slightly more mobile than SRB, being transported to the surface on the 29th of May, then decreasing in subsequent observations. SRB, on the other hand, shows a decline in all quadrants during the complete measurement period. Both pH and VWC exhibit decreases during dry periods and increases after rain events.



Figure 4.3: Bromide, chloride, UR, and SRB in the top 2 to 3 centimeters soil for the period of April 17^{th} to July 10^{th} , 2012: (a) Bromide (Br⁻); (b) Chloride (Cl⁻); (c) UR; (d) SRB.



Figure 4.4: The development of volumetric water content and pH in the top 2 to 3 centimeters of soil at Alteckendorf from 17^{th} April - 26^{th} June: (a) VWC; (b) pH

Minimal rainfall prior to the soil sampling campaign, approximately 12 mm during a one and a half month period, accounts for low initial VWC values.

A correlation matrix of soil constituents and physico-chemical properties can be found in appendix table B.6. All tracers show statistically significant (CI = 95 %) moderate negative correlations with precipitation with Pearson r-values of -0.40, -0.40, and -0.47 for Br⁻, UR and SRB respectively. Further correlations of note are between pH and soil anions besides sulfates, which display fairly strong negative correlations of -0.59, -0.51, and -0.65 and are also statistically significant (CI = 95 %). Also, pH and VWC have strong postive correlations (Pearson r-value = 0.75) and is statiscially significant (CI = 95 %) All tracers show high correlations (Pearson r-values over 0.90), with Br⁻ and SRB the least correlative with a Pearson r-value of 0.89.

4.1.2.2 Core Samples

Due to wavelength shifting in dye tracer samples results have been excluded. Higher concentrations of bromide in mg/g are seen to depths ranging from 5-30 cm which then decrease with depth (see fig. 4.5(a)). The same profile is observed in chloride and sulfate (fig. 4.5(b), 4.5(c)), with nitrate (fig. 4.5(d)) exhibiting inverse behavior in the



Figure 4.5: Soil anions at the Alteckendorf plot to the depth of 1 meter for soil cores extracted the 12th July, 2012:

(a) Bromide (Br⁻); (b) Chloride (Cl⁻); (c) Nitrate (NO₃⁻); (d) Sulfate (SO₄⁻²⁾.

first 40 centimeters of the soil column and then proceeding into an undefinable profile between quadrants.

Cation exchange capacity (CEC) increases rapidly until a depth of 5-10 cm (fig. 4.6(a)) at which point it continues to increase more gradually with depth. pH at the soil surface is slightly alkaline, becoming more acidic up to a depth of 5-10 cm, then progressively becoming more alkaline with depth. Soil moisture content decreases to an inflection point depth of 30 cm, where it begins to appreciate.

Table 4.2 gives the values of Bromide recovery from the plot soils. Bromide tracer was not detected in any cores extracted outside of the plot area. In order to estimate tracer masses in the soil column beneath the plot, it was assumed that all bromide tracer infiltrated normal to the surface and no lateral flow occurred. The area assigned to the plot was determined from GPS points of plot boundaries acquired by LHyGeS and was split evenly into four quadrants; one for each soil core extracted. Higher tracer masses were recovered from quadrants 3 and 4, which comprise the west side of the plot area. Quadrants 1 and 2 exhibited much lower recovery rates than the west side, with quadrant 2 returning only roughly 3% of the applied tracer mass. Plot slope runs in a plane from the extreme South-west to North-east corners. In total, $\sim 87\%$ of applied tracer mass was recovered in the soil column.

12.7.2012 Zone 1 Zone 2 Zone 3 Zone 4 Sum total Depth Bromide St. Dev. Bro

Table 4.2: Bromide tracer recovery from the soil column for soil cores extracted on

	Zoi	ne I	Zor	1e 2	Zoi	1e 3	Zor	ie 4	Sum	total
Depth	Bromide	St. Dev.								
	[8]	[8]	[8]	[8]	[8]	[8]	[B]	[8]	[8]	[8]
2	2.21	0.13	1.34	0.06	30.99	0.08	5.82	0.08	40.35	0.18
5	25.01	0.07	15.98	0.08	290.14	0.08	109.00	0.11	440.14	0.18
10	410.12	0.09	78.91	0.09	491.90	0.11	344.72	0.12	1325.65	0.20
30	105.58	0.07	0.00	0.00	34.03	0.06	57.88	4.02	197.50	4.02
66	23.91	0.02	0.00	0.00	565.46	0.02	169.35	0.05	758.72	0.06
99	0.00	0.00	0.00	0.00	24.49	0.44	244.85	0.08	269.34	0.45
Sum	566.84	0.38	96.23	0.23	1437.00	0.80	931.63	4.46	3031.70	4.55
% Recovery	16.22	0.01	2.75	0.01	41.12	0.02	26.66	0.13	86.74	0.13



Figure 4.6: Cation Exchange Capacity (CEC), pH, and gravimetric water content (GWC) with depth for the 12th July, 2012 at the Alteckendorf plot: (a) CEC; (b) pH; (c) GWC

4.2 Tile Drain Experiment

4.2.1 Simulated Rain Equipment

In all cases, 1 m³ of water was applied to the site area using the simulated rain device. The duration of each event was 42 ± 1 min with a mean precipitation rate of 0.74 mm/min, which is equivalent to a rain event of 31.1 ± 0.74 mm. Figure 4.7 displays rainfall event frequency for the months of March-July from a 4 year interval for Waltenheim sur Zorn, France; which is located approximately 7 km to the South of the Katzenlauf catchment. Most rainfall events in the area are under 5 mm for both daily and hourly intensities. Thusly, application intensities would be similar to a two year storm for the area, and multiple applications per day totaling 60 plus mm, would represent an event similar to a 20 year event (see fig. 4.8). The first application was employed as a means of wetting the area in order to reproduce conditions of a high initial VWC (similar to several days of light rain before a large event) before a large storm event, since this is when leaching is most likely to occur.



Figure 4.7: Histogram of rainfall events at Waltenheim - located 7 km to the South of Alteckendorf, for a 4 year period, comprising of the years 2008-2011, and for the months of March-July a) daily b) hourly c) 6 minute intensities. Y-axis break doesn't include all occurrences of lower intensity events for representation of larger events.

CU and DU were evaluated using equations 3.1 and 3.2. Assuming that rainfall for small areas is homogeneous a CU or DU value of 100 would be completely representative of natural rainfall, with a value below 50 indicating very heterogeneous and



Figure 4.8: Precipitation event recurrence intervals - for daily and hourly data from a 4 year period (2008-2012) and the months of March-July.

unrepresentative conditions. The Center of Irrigation Technologies Fresno, California USA rates irrigation systems with CU over 87% and DU over as 85% excellent and those below 70% and 65% as poor. (Solomon, 1990). The mean CU and DU achieved by the device was 82.16% & 73.65% respectively, which is fairly representative of natural precipitation conditions. Table 4.3 shows the statistics for the validation carried out before deployment of the device in the field.

Table 4.3: Distribution statistics of simulated rain equipment calculated from an equipment validation performed before its use in the tile drain experiment at Alteckendorf, France on the 24-25th of July, 2012.

Trial	Mean Precipitation [mm/min]	Christiansen's Uniformity Coefficient (CU)	Distribution Uniformity (DU)
1	0.77	75.20	60.90
2	0.70	84.95	80.14
3	0.75	86.33	79.91
Mean	0.74	82.16	73.65

Figure 4.9 displays the mean rainfall distribution of the device. A fairly uniform result is seen for a $2m \ge 5m$ area with a range of 0.7 to 0.9 mm/min. This correlates to the area of the tile drain experiment which was $2m \ge 4.5m$.



Figure 4.9: Distribution of simulated rain equipment - Contour plot of precipitation [mm/min] distribution of simulated rain equipment measured during the equipment validation on the 23^{rd} of July, 2012.

4.2.2 Tracer Breakthrough Curves

Tracer breakthrough curves (BTC) recovery rates as witnessed in figure 4.10(a) present tracer concentrations, normalized to the applied quantity, found in drain effluent over the period of the experiment. Br⁻ recoveries were approximately two times that of UR and eight times that of SRB, during the measurement campaign. The first BTC shows the bromide and dye tracers arriving at the same time, though dye tracer concentrations were nominal. All tracer BTCs peak at the same time, which is slightly before the end of irrigation inputs. It must be noted that the sampling interval at this time was 30 minutes and it is possible that the actual peak is not represented by the data. All data was assessed with a 5 minute time step, with missing values being evaluated through interpolation. SRB recovery during the first peak is negligent at a recovery of 0.17 % of mass. Returns for UR and Br⁻ during the first BTC were roughly 1.7 and 4.0 % of mass, respectively.

Measured anion concentrations besides Br⁻ (chloride, sulfates, and nitrates) are displayed in figure 4.10(b) with concentrations depicted as unitless normalized quantities (concentration/mean concentration). An obvious peak for all anions is seen on the 24th at approximately the same time or shortly after tracer peaks. This is followed by trough 2.5 to 3 hours later.

On the 25th of July, normalized UR and Br⁻ BTCs are similar. Approximately the same mass from the previous day was recovered in the case of Bromide and approximately 150% for UR. SRB recovery was roughly 3 times larger in comparison to the previous day, with a nominal return of 0.61% of tracer mass. Total tracer recoveries at the end of the measurement campaign were 7.69, 4.52, and 0.79%, for Br⁻, UR, and SRB. Figure 4.11 gives a comparison of BTCs from the beginning of the rain events until 180 minutes afterward. No tracer mass was measured within the period of 3 hours after the first simulated rain application, though discharge and soil moisture data are included to depict initial site conditions. Tracer BTC for the 24th of July show all tracers arriving after the discharge peak. The BTC for the 25th gives tracer arrival before peak discharge is measured, with the SRB peak exhibiting a lag of roughly 20 minutes compared to UR and Br⁻.

4.2.3 Tracer Mass Balance

Tracer recovery was calculated for the parameters measured during the tile drain experiment. Table 4.4 lists the recovery rates for each of the parameters, excluding tracers found in the soil column. Because overland flow measurements were available for only the 3rd simulated rain application, it has been assumed that recovered values for all events are similar. It is noted that this is an underestimation of the value, and is used here only as a means of evaluation. Values of tracer masses found in overland flow per single event were 0.09, 0.18, and 0.23 % for Br⁻, UR, and SRB, respectively. Total tracer recoveries for measured parameters were 9.29, 5.48, and 7.79% for Br⁻, UR, and SRB. No quantifiable tracer mass was measured in samples taken downstream at the catchment outlet after the 25th of July.

Table 4.4: Mass balance calculations of tracers for measured parameters: tile drainexperiment performed, July 24-25th, 2012 Alteckendorf, France.

Tracer	Applied mass [g]	Recovered mass outlet [g]	Overland flow [g]	Soil Surface [g]	Total Outlet + Overland flow + Surface soil [g]	% Re- covered Total
Br UR SRB	388.28 100 100	$29.86 \\ 4.52 \\ 0.79$	$0.36 \\ 0.18 \\ 0.23$	$5.12 \\ 0.43 \\ 6.29$	36.07 5.48 7.79	$9.29 \\ 5.48 \\ 7.79$



Figure 4.10: In (a) Tracer BTCs for the tile drain experiment with tracer recovery rates and discharge [L/s] from the 24-25th of July, 2012 are displayed. (b) shows Tracer BTCs with normalized anion concentrations and discharge from same experiment. Normalized anion concentrations are denoted as unitless quantities (concentration/mean concentration).



Figure 4.11: Comparison of tracer BTCs seen at the drain outlet during the tile drain experiment: (a) 1^{st} BTC after 2 simulated rain events on the 24^{th} (b) 2^{nd} BTC after 1 rain event on the 25^{th} July, 2012

4.3 Batch Sorption Experiment

Individual sorption isotherm points were evaluated using the Freundlich and Langmuir isotherms. Best fit results were obtained from the Langmuir isotherm using NLLS regression, with RMSE values of 0.00232 for UR and 0.02142 for SRB. Table 4.5 shows the results for the other isotherms evaluated. Distribution coefficients values range from 1.96 to 0.27 for UR and from 5.77 to 0.87 for SRB and show, in most cases, an inverse dependency on tracer concentration (see tab. 4.6). Higher standard deviations were calculated for lower concentrations, showing a greater imprecision in measurement, which could account for deviations from the general pattern. Figure 4.12 reproduces graphically the behavior of the evaluated isotherms. The inset windows show evaluations at lower concentrations, which in some cases demonstrate a better fit to isotherms other than the determined overall best fit.

Dye	Freund. Coeff. Kf	Freund. Coeff. n	Lang. Coeff. Ka	$\begin{array}{c} {\rm Max} \ {\rm Adsorption} \\ q_m \end{array}$	\mathbb{R}^2	RMSE	Isotherm Model
UR	0.00152	1.1862	_	_	0.0840	0.08554	Freundlich
	_	—	0.00606	0.2612	0.9989	0.00296	LL
	—	—	0.00570	0.2637	0.9993	0.00232	L-NLLS
SRB	0.01013	1.2410	—	_	0.6400	0.15572	Freundlich
	—	—	0.00647	0.9947	0.9778	0.03869	LL
	—	—	0.01198	0.8233	0.9932	0.02142	L-NLLS

 $\label{eq:table 4.5: Langmuir and Freundlich isotherm coefficients and goodness of fit criteria coefficient of determination <math display="inline">\mathrm{R}^2$ and residual root mean square error (RMSE).

Batch values	$K_d~{\rm UR}~[cm^3/{\rm g}]$	K_d SRB $[cm^3/g]$	Stdev. K_d UR	Stdev. K_d SRB
0.1	1.377	4.902	0.044	0.112
1	1.957	5.767	0.025	0.021
10	1.084	4.508	0.028	0.023
50	1.441	2.209	0.013	0.004
100	1.246	1.984	0.011	0.002
200	0.962	1.702	0.010	0.003
500	0.546	1.197	0.011	0.009
1000	0.272	0.867	0.016	0.006

Table 4.6: Distribution coefficient (K_d) $[cm^3/g]$ obtained from batch study of UR and SRB at 8 different concentrations



Figure 4.12: Calculated sorption Isotherms for UR and SRB using linearized Langmuir, NLLS Langmuir and linearized Freundlich: (a) UR; (b) SRB

Discussion

Results have been presented for tracer water & soil samples from the plot along with tile drain experiments and batch sorption tests. The aim of this study is to determine the viability of dye tracer use as surrogates for pesticide fate and transport, in particular uranine and sulforhodamine B for S-metolachlor. Since pesticide analysis was yet to be completed at the time of submission of this document, comparisons are conducted with literature values. It is noted that site specific data is needed in order to fully evaluate tracer use. This will be addressed in continuing works related to this project.

5.1 Plot Water Samples

Tracer recovery from runoff samples using the assumptions stated in the results section were nominal, with returns totaling 0.4, 0.06, and 0.14 % for Br⁻, UR and SRB. Most Br⁻ in runoff is collected during the event of the 22^{nd} of May, which can be accounted for by increases in Br⁻ concentrations in surface soils before the event. Higher observed tracer concentrations in water samples collected towards the end of the campaign can explained through the deposition of tracers at the runoff catch inlet during to the rain event of the 22^{nd} of May. This is observed in higher concentrations of Br⁻ found in quadrant 4 soil core samples from the 12^{th} of July. This behavior is seen to a lesser degree in surface soil samples namely due to the sampling technique, in which a composite samples for the total quadrant area were made, effectively diluting any tracer accumulation in one area of the quadrant.

5. DISCUSSION

None of the tracers exhibit a high correlation with suspended solids (Pearson r-values = -0.38, -0.25, -0.19; none statistically significant (SS) at 95 % CI), which means tracers are more readily released to water flowing over or through the soil surface. This is in agreement with the literature which states that runoff losses with water are the dominate mode of transport for moderately adsorbed solutes (Baker, 1999; Gilley et al., 1990). Br⁻ and UR display a strong correlation (Pearson r value = 0.86; SS at 95 % CI) in water samples, which implies similar behavior of the two tracers. In addition, both exhibit a higher correlation (Pearson r-values = 0.64, 0.65; for Br⁻ and UR; not SS) to rainfall than SRB (Pearson r-value = 0.48; not SS) being attributed to their lower K_d values. This is in accordance with the literature, which states that both Br⁻ and UR exhibit conservative behavior (non-adsorbing, non-retarded) in non-acidic soils (Goldberg and Kabengi, 2010; Smith and Pretorius, 2002).

Gaynor et al. (2002) found that runoff of metolachlor accounts for a nominal portion of total pesticide losses, comprising only 9 % of losses from measurements of leaching and runoff. Furthermore, total pesticide losses are tied to rain events occuring within the first 1 to 2 weeks after application irregardless of pesticide properties (Flury, 1996). In Gaynor et al. (2002) 67 to 77 % of all metolachlor losses occurred in the first rain event following application. Rector et al. (2003) reported S-metolachlor runoff in an event 2 days after pesticide application that was 5.3 % of applied mass. Although there is no large rain event during the first one to two weeks after application from which runoff concentrations of tracers could be compared with literature values, the data does provide insights into runoff losses even at 4-5 weeks after application. Direct comparison with pesticide concentrations is needed to further evaluate similarities of S-metolachlor and dye tracer similarity. Further examination of literature values provides a wide range of photo and aerobic degradation rates for S-metoloachlor at the soil surface, 6.83 -94.95 days for photo and 37.87 - 66 days for aerobic degradation (Costello and Hetrick, 2008). These numbers provide at least a base assumption that an increased pollution risk exists for approximately one to two months after application; however, pollution risk is extremely dependent on rain event size and intensity.

Potential sources of dye tracer measurement error exist for water samples collected during low flow events before the 26th of June due to background fluorescence increases from a high water level marking tape used prior to this date (see fig. A.2). Increases in background fluorescence for large events was assumed to be negligible. Estimated tracer recovery rates are more than likely overestimated due to water upslope of the plot entering the plot area during the two major events, biasing actual measurements. This occurred due to a failure of the boundary material. It is believed that high suspended solid flux in samples from the 29th of May are due to counter measures taken on the 22nd of May to correct erosion problems under the runoff catch on account of the same boundary breach. Counter measures led to there being more loose sediment directly at the runoff catch inlet that was easily transported in subsequent runoff events.

5.2 Plot Soil Samples

All tracers show a dissipation in surface soils until the beginning of May, at which time Br⁻ shows an increase. Br⁻ increases can attributed to the precipitation of salts in surface soils. This phenomena is caused by increases in evapotranspiration resulting in a rise of the suction force of surface soils and subsequent precipitation of salts once they have reached the soil surface (Gran et al., 2009). This behavior is mirrored in varying degrees by all measured soil anions. Both dye tracers followed first order kinetics with different decay rates. Calculated half-lives for UR and SRB were 13.81 and 18.98 days, denoting that photodegradation of UR in soils plays less of a role than one would assume given literature values (see tab. 3.2). A possible explanation for this is migration of UR with water away from the soil surface either through capillarity of smaller pores in the soil matrix, or infiltration after precipitation events. Hebert and Miller (1990) found that direct photolysis was restricted to the photic depth of soils (0.2 - 0.4 mm), while indirect photolysis depth was slightly deeper (0.6 - 0.7 mm). In all cases photolysis was limited to less than 1.0 mm. In a study of atrazine photodegradation in surface soils, soil granularity, pH value, humidity, organic content, humic acid and surface-active agents were shown to have an impact on the rate of atrazine decay (Xiaozhena et al., 2005). These factors, in turn, likely play a role in dye tracer decay.

Negative correlations of tracer masses in surface soil and rainfall indicate that other factors besides rainfall lead to their dissipation in surface soils. Negative correlations of Br⁻, Cl, and NO3 with pH can be attributed to displacement of H and Al cations on or near soil colloid surfaces during increases in salt concentration, which in turn, decreases measured soil pH (Bohn et al., 2001). This is further recognized in negative

5. DISCUSSION

correlations of soil anions with VWC; indicating anion leaching during periods of VWC increases and enrichment during decreases.

It is believed that decreases in measured soil anions in samples taken on the 12th of July are due to changes in the collection procedure, in which a large quantity of soil was taken from the soil surface in preparation for core sampling. This led to dilutions of anion masses per soil weight and also an over representation of a single area within the quadrant. Dilution is also believed to be a factor in the non detection of tracer masses in soil cores taken outside of the plot, where sampling sections were larger.

Recovered bromide masses from soil cores extracted on the 12th of July indicate that a little over one third of Br⁻ mass was found at depths of 5-10 cm. Bromide leachate was found to depths of one meter in two of the four cores (approximately 9 % of applied mass), denoting a high possibility of infiltration below this depth. The majority of Br⁻ mass was found in quadrant four, where a large volume of water entered through a breach in the boundary. Thus, the likelihood of macropore activation and resultant deep percolation in this quadrant is quite high. Similar findings for S-metolachlor were reported by Cornoi et al. (2011), in which 93 % of applied pesticide mass was recovered in the top 15 cm of soil after 90 days.

Measured peak fluorescence of soil samples after the 26th of June were at wavelengths between 508-511 nm (489-491 nm are expected absorbance wavelengths for UR). The fluorescent peak displayed no pH dependency (ie. no change in UV absorbance); where it is assumed that increasing or decreasing pH should change the UV absorbance of UR, with pH values below 3.5 effectively dampening all UR absorbance (Peterson, 2010; Smith and Pretorius, 2002). Due to this SRB was effectively quenched by peak values in the range of 508-511 nm and SRB concentrations could have been present in samples. Wavelength shifting of UR has been recorded in other studies due to colloids or organic content (Leibundgut et al., 2009), but there is no record of pH independence. Samples before the 26th of June exhibited the same fluorescence in a range of 508-511 nm, but measurable quantities of UR were found at wavelengths of 489-491 nm when solution pH was increased above 10. Also, UR fluorescence in water samples displayed only a slight wavelength shift (measured peak at 493 nm) in samples collected on the 10th and 16th of July. This leads one to believe that erroneous fluorescence peaks are from a soil constituent that has a low solubility, since it is not transported by runoff events. Other possibilities could be changes in the prevalent UR molecule. A study focusing on UR excitation spectra in different solutions found UR to exhibit fluorescence at 508 nm in methanol solutions with pHs above 6.4 attributing this behavior to a shifting of the primary UR anion from the monoanion to the dianion (Cook and Le, 2006). This phenomena needs to be studied further if UR is to be used in long term, surface application pesticide studies in the future.

5.3 Tile Drain Experiment

Tracer BTC for the 24th of July show all tracers arriving after the discharge peak with an approximate lag of 10 minutes after the second simulated rain application. Increases in discharge can either be attributed to *old water* being pushed out of the soil column, or *new water* arriving via macropores (Kung et al., 2000). This confirms piston flows from the input of irrigation water, since in the case of new water tracer peaks would be expected at the same time as the discharge peak. Furthermore, one would not expect to see the flushing effect of soil anions exhibited by the concentration increases of Cl, NO3, and SO4, whose peak values are at the same time as the tracers. If no flushing of the soil matrix occurred, it would be assumed that Cl, NO3, and SO4 concentrations would decrease with increasing discharge rates due to additions of new water. The new water from irrigation can be seen entering the system by the observed trough in anion concentrations approximately 6 hours after the initial simulated rain application, evidencing the normal infiltration of water through the soil matrix.

Calculated mean K_s values from the plot characterization returned values of 552.97 \pm 444.25 cm/day for the plot surface. Assuming conductivity decreases with increasing depth, it can be safely inferred that it would take longer than the observed 3 hour period for water to reach the outlet. Thus, tracer BTC observed 3 hours after initial irrigation application can only be attributed to preferential flows. This is affirmed by similar tracer peak arrival times in the effluent. Under normal infiltration conditions sorptive solutes show a retardation, with observed maximums taking place after less sorptive solutes. Thus, if only advective transport were responsible for tracer transport, lag times in tracer peaks should be observed, which is not the case.

SRB and UR mass recoveries from the first tracer BTC demonstrate a reduction compared to Br⁻. This denotes the occurrence of adsorption during solute transport within preferential flow pathways. If this were not the circumstance, normalized tracer

5. DISCUSSION

recoveries should be similar. This is most likely due to the interval between simulated rain events, where the inactivation of macropores allowed for sorption reactions to take place, such that in the ensuant irrigation only the unsorbed quantity of tracer was transported in the re-activation of preferential pathways.

This finding runs counter to previous studies, which show adsorption properties having no effect on tracer transport through preferential flow paths (Flury, 1996; Kung et al., 2000) and is likely attributable to differences in simulated rain quantities and durations. The assumptions made, perhaps, overestimate additions to discharge through preferential flow; exact depths of tile drain piping and K_s values are needed to truly substantiate claims. In addition, adsorption processes occurring in the interval between tracer and irrigation application and between irrigation events could account for dye tracer reductions, since in applicable studies dye and bromide tracers were applied concurrently with irrigation water.

The BTC for the 25th shows tracer arrival before peak discharge measurement, affirming the idea of piston flows. This is further substantiated through Cl and NO3 levels which drop almost directly after irrigation begin and display a slower return to baseline values after the termination of irrigation, denoting inputs of irrigation water in the effluent. SO4 levels increase for a period of approximately 30 minutes before exhibiting the same behavior as Cl and NO3. This is explained by higher sorption of SO4 compared to Cl in the soil matrix (Huber et al., 2012; Scanlon et al., 2009), leaving more SO4 to be flushed out in further events. This behavior is similar to SRB, which demonstrates a lag of roughly 20 minutes compared to UR and Br⁻ and is common of sorptive solutes during advective transport.

In a study comparing preferential flow under alfalfa and corn plot estimates from all observed data suggested that 39% more bromide was leached out of the 0-30 cm zone in the alfalfa as compared to the corn plots (Caron et al., 1996). This calls into question the validity of the application of findings from the tile drain experiment to the entire catchment. However, it should be noted that metolachlor can be readily transported towards the deeper soil layer, where less degradation of the pesticide occurs, in the presence of preferential flow (Francaviglia and Capri, 2000) and that at depths more than 5 cm S-metolachlor was found to be more persistant than EU documented values ((Commission, 2004) EU study $DT50_{soil} = 7.6-37.6$ days; (Cornoi et al., 2011) $DT50_{soil} = 69.3$ days). Thus, leaching of S-metolachlor from the soil surface via preferential flow

pathways or infiltration presents a high pollution risk to shallow aquifers or streams connected to agricultural tile drain systems regardless.

Tracer recovery rates from the experiment may be underestimated due to the sampling interval during the first BTC, though it is believed to have minimal effect on total recovered tracer mass. It is also possible that BTC peaks were not accurately recreated, because of the low sampling rates. Higher tracer concentrations seen at 8:30 on the 25th were due to a leaky hose inside of the automatic sampler and values were excluded from tracer mass recoveries. Measurements of overland flow likely overestimate discharges, because the plot area was unbound, providing a possibility for over-spray to enter the experimental area.

5.4 Batch Sorption Experiment

A quick comparison of K_d literature to measured values of dye tracers (see tab. 3.2 and 4.6) reveals comparable sulforhodamine B values, but large differences in the sorptivity of uranine. In both cases, sorption increases with decreasing concentration, which mirrors S-metolachlor behavior in a study done by Cornoi et al. (2011). High organic matter content is also a possible reason for the higher observed sorbtivity of UR. A study by Mikulla et al. (1997) showed UR having K_d values of 10.2 in the presence of 31.2 % organic matter. In a catchment characterization performed by LHyGeS organic matter contents were determined to be in the range of 4.7-7.1 %. Given these conditions it would be quite possible that higher K_d values for UR are attributed to organic matter. In a study by Shaner et al. (2006), K_d values of S-metolachlor were also found to be highly correlated to organic matter in the soil with K_d values ranging from $1.58-6.93 \text{ cm}^3/\text{g}$ for organic contents 1.5-5.6 %. This suggests that S-metolachlor would be retained in a manner closer to SRB than UR, but site specific sorption data for S-metolachlor is needed to truly evaluate the dye tracers as surrogates, due to the many facets of solute sorption. Failings of using K_d values to determine sorption in the soil column are that values from batch experiments can be high relative to the extent of sorption occurring in a real system, since water flows though the soil matrix and is not stagnant. K_d values can also over estimate desorption, because it is normally assumed adsorption and desorption processes are directly reversible, which normally is not the case (Wilhelm, 1999).

5. DISCUSSION

Langmuir isotherms for both UR and SRB provided better estimations of sorption than Freundlich isotherms for the given concentration range of batch studies. Comparable literature values of Langmuir isotherm coefficients for S-metolachlor weren't found, since pesticide application concentrations were much lower than applicable dye concentrations, and individual isotherm points were evaluated only for Freundlich isotherms. If further studies are to be done, an evaluation of the needed range of dye tracer concentration where tracers demonstrate the same sorptivity as the chosen pesticide should be performed. Also dye tracer application concentrations should be similar to their pesticide counterpart. This would increase the validity of dye tracer use as surrogates in such cases.

Conclusion

All tracers demonstrated behavior at the soil surface close to S-metolachlor values taken from a similar study by Cornoi et al. (2011) during the first two weeks of the plot experiment. However, degradation processes remain more or less unknown and similar dissipation behavior could be attributed to different processes, dependent on the constituent. Dye tracers could be used as delimiters of pesticide leaching as noted in Sabatini and Austin (1991) and concurrently applied with pesticides if a high potential of pesticide leaching exists. In this way secondary measures could be employed before the arrival of pesticide peaks, and removed after them. It must be noted that tracer masses used in this study would be cost prohibitive and further study of dye tracer use at lower concentrations must be made, especially due to sorption behavior changes of both dyes at low concentrations. Furthermore, photodegradation of UR could be under level of detection when applied in small quantities reflective of pesticide concentrations if penetration depths into the soil column are less than 0.2 mm. Bromide could also be used to delimit pesticide transport since it arrives ahead of pesticides in almost all cases, but increases in soil salt content could negatively impact crop production, and needed quantities would be cost prohibitive. Further study needs to be done on degradation and sorption processes of dye tracers if they are to be used as surrogates in pesticide transport studies.

Given the findings of the plot experiment, dye tracers are not suited for long term studies of pesticide losses from the soil surface. Fluorescence peak shifting and pH independence effectively masks the measurement of both dye tracers after approximately 80-90 days. It is possible that this behavior would not be seen in studies using only one

6. CONCLUSION

dye, but this remains unsubstantiated. Therefore, further testing comparing each dye individually to S-metolachlor are needed in order to confirm their validity as surrogates in surface application experiments.

The highest risk of pollution from S-metolachlor remains leaching during high intensity rain storms in a period of 1 to 2 weeks following application (Flury, 1996; Wauchope, 1978). This is further substantiated through drain experiment findings, which show rapid transport of both dye tracers and bromide into the tile drain system during high intensity rainfall. With effective meteorological forecasting risk of pollution can be reduced through simple measures limiting pesticide application during periods of potential precipitation within a week antecedent to pesticide application. It is noted that due heterogeneity of weather patterns, risk will continue to exist and secondary measures will be needed.
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Appendix A

Supplementary Figures



Figure A.1: Fluorescence spectroscopy calibration curves with coefficient of determination for (a) UR; and (b) SRB



Figure A.2: Background fluorescence increases from high water tape - used prior to the 26^{th} of June for the determination of runoff in the Venturi.



Figure A.3: Soil moisture curves - estimated using the Van Genuchen equation (van Genuchten et al., 1991) and the RETC program



Figure A.4: Langmuir and Freundlich linearizations - Langmuir and Freundlich linearizations used to obtain equation variables for UR and SRB with $\rm R^2$

Appendix B

Supplementary Tables

 Table B.1: Product article numbers, CAS numbers, and producers for tracers used at Alteckendorf, France

Tracing Chemical	Producer	Article number	CAS-No.
Uranine	Simon & Werner GmbH	$100982-00025 \\1A-006 \\5086$	518-47-8
Sulforhodamine B	Waldeck GmbH		3520-42-1
Sodium Bromide	Carl Roth Chemicals GmbH		7647-15-6

Table B.2: Plot water sample sediment flux and tracer concentrations; suspended solids (SS), organic matter (OM), bromide (Br), uranine (UR), and sulforhodamine B (SRB)

Sample date	SS flux [g/L]	$_{\rm [g/L]}^{\rm OM}$	%OM [%]	Conc. Br [mg/L]	Stdev. BR [mg/L]	Conc. UR $[\mu g/L]$	Conc. SRB $[\mu g/L]$	Stdev. UR $[\mu g/L]$	Stdev. SRB $[\mu g/L]$
$\begin{array}{c} 02/05/2012\\ 15/05/2012\\ 22/05/2012\\ 29/05/2012\\ 12/06/2012\\ 19/06/2012\\ 10/07/2012\\ 16/07/2012\\ \end{array}$	$1.12 \\ 0.59 \\ 2.92 \\ 7.66 \\ 0.73 \\ 0.38 \\ 0.18 \\ 0.05$	$\begin{array}{c} 0.14\\ 0.07\\ 0.40\\ 0.84\\ 0.09\\ 0.09\\ 0.08\\ 0.00\\ \end{array}$	$12.47 \\11.90 \\13.70 \\11.04 \\12.16 \\23.54 \\46.32 \\0.00$	$\begin{array}{c} 0.2\\ 0.205\\ 8.75\\ 0.68\\ 4.28\\ 19.54\\ 49.9\\ 14.4 \end{array}$	$\begin{array}{c} 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ 0.018\\ \end{array}$	$\begin{array}{c} 87.42 \\ 15.89 \\ 268.01 \\ 102.35 \\ 273.68 \\ 432.57 \\ 686.97 \\ 20.39 \end{array}$	$187.75 \\12.42 \\614.86 \\89.18 \\310.59 \\378.45 \\306.21 \\310.27$	0.70 0.26 5.93 0.80 2.01 1.74 13.64 0.40	$\begin{array}{c} 0.71 \\ 0.05 \\ 0.89 \\ 1.13 \\ 0.32 \\ 3.16 \\ 3.29 \\ 3.59 \end{array}$

Table B.3: Mass balance calculations of tracers in soil surface samples: tile drain experi-ment performed, July 24-25th, Alteckendorf, France.

	Tracer Conc. [mg/l]	Sample weight [g]	Tracer [mg/kg]	Volume $[m^3]$	$\begin{array}{c} \text{Bulk} \\ \text{density} \\ [\text{kg}/m^3] \end{array}$	Soil mass soil mass [kg]	Tracer mass [g]
Br UR SRB	$7.56 \\ 0.64 \\ 9.29$	$10.00 \\ 10.00 \\ 10.00$	$7.56 \\ 0.64 \\ 9.29$	$0.45 \\ 0.45 \\ 0.45$	$1505.12 \\ 1505.12 \\ 1505.12$	$677.30 \\ 677.30 \\ 677.30$	$5.12 \\ 0.43 \\ 6.29$

Table B.4: Saturated hydraulic conductivity (K_s) test results from plot experiment soil surface site characterization core samples

Probe	Time	h0	h1	$\rm ks\ cm/s$	ks m/s	$\rm Ks\ m/d$	Ks $\rm cm/d$
3181	115.4	10	5	0.0300	3.00E-004	25.9480	2594.7971
3202	2327.2	10	5	0.0015	1.49E-005	1.2867	128.6695
3039	80.6	9	7	0.0156	1.56E-004	13.4700	1346.9954
3039	274.40	10	5	0.0126	1.26E-004	10.9125	1091.2521
3198	968.6	10	5	0.0036	3.58E-005	3.0915	309.1468
3109	541.6	10	5	0.0064	6.40E-005	5.5288	552.8796
3178	1214	10	5	0.0029	2.85E-005	2.4666	246.6553
3178	1534	10	5	0.0023	2.26E-005	1.9520	195.2018
Mean				0.0064	6.40E-005	5.5297	552.9715
Stdev.				0.0051	5.14E-005	4.4425	444.2540

Mean and stdev. exclude values from probe 3181; it is assumed that contact with cylinder wall was broken

Table B.5: Correlation matrices (Pearson and Spearman) of water sample constituents and physico-chemical properties from samples taken during the tenure of the Alteckendorf campaign

Pearson correlation coefficients									
	SS.flux	OM	Bromide	UR	SRB	Precip.			
SS.flux	1.00	0.99	-0.38	-0.25	-0.19	-0.27			
OM	0.99	1.00	-0.32	-0.17	-0.11	-0.20			
Bromide	-0.38	-0.32	1.00	0.86	0.32	0.64			
UR	-0.25	-0.17	0.86	1.00	0.45	0.65			
SRB	-0.19	-0.11	0.32	0.45	1.00	0.48			
Precip.	-0.27	-0.20	0.64	0.65	0.48	1.00			
Poercon toot cignificance lougle									
	SS flux	OM	Bromide	UR	SBB	Precip			
SS flux	NA	0.00	0.35	0.55	0.66	0.52			
OM	0.00	NA	0.44	0.69	0.80	0.64			
Bromide	0.35	0.44	NA	0.01	0.45	0.09			
UB	0.55	0.69	0.01	NA	0.27	0.08			
SRB	0.66	0.80	0.45	0.27	NA	0.22			
Precip.	0.52	0.64	0.09	0.08	0.22	NA			
Spearman correlation coefficients									
<i></i>	SS.flux	OM	Bromide	UR	SRB	Precip.			
SS.flux	1.00	0.88	-0.62	-0.10	-0.10	-0.14			
ОМ	0.88	1.00	-0.29	0.24	0.14	-0.29			
Bromide	-0.62	-0.29	1.00	0.69	0.57	0.26			
UR	-0.10	0.24	0.69	1.00	0.55	0.24			
SRB	-0.10	0.14	0.57	0.55	1.00	0.17			
Precip.	-0.14	-0.29	0.26	0.24	0.17	1.00			
	Spe	arman t	est significar	nce levels					
	SS.flux	OM	Bromide	UR	SRB	Precip.			
SS.flux	NA	0.00	0.10	0.82	0.82	0.74			
OM	0.00	NA	0.49	0.57	0.74	0.49			
Bromide	0.10	0.49	NA	0.06	0.14	0.53			
UR	0.82	0.57	0.06	NA	0.16	0.57			
SRB	0.82	0.74	0.14	0.16	NA	0.69			
Precip.	0.74	0.49	0.53	0.57	0.69	NA			

Table B.6: Correlation matrices (Pearson and Spearman) for soil constituents and physico-chemical properties from samples taken the soil surface during the tenure of the Alteckendorf campaign.

Pearson correlation coefficients											
	Chloride	Bromide	Nitrate	Sulfate	UR	SRB	GWC	VWC	pН	Precip.	
Chloride	1.00	0.49	0.49	0.68	0.38	0.35	-0.38	-0.38	-0.59	0.14	
Bromide	0.49	1.00	0.19	0.33	0.91	0.82	-0.64	-0.64	-0.51	-0.40	
Nitrate	0.49	0.19	1.00	0.08	-0.19	-0.21	-0.56	-0.56	-0.65	-0.40	
Sulfate	0.68	0.33	0.08	1.00	0.59	0.56	-0.27	-0.27	-0.27	0.46	
UR	0.38	0.91	-0.19	0.59	1.00	0.95	-0.38	-0.38	-0.20	-0.46	
SRB	0.35	0.82	-0.21	0.56	0.95	1.00	-0.27	-0.27	-0.08	-0.47	
GWC	-0.38	-0.64	-0.56	-0.27	-0.38	-0.27	1.00	1.00	0.75	0.61	
VWC	-0.38	-0.64	-0.56	-0.27	-0.38	-0.27	1.00	1.00	0.75	0.61	
nH	-0.59	-0.51	-0.65	-0.27	-0.20	-0.08	0.75	0.75	1.00	0.35	
Precip.	0.14	-0.40	-0.40	0.46	-0.46	-0.47	0.61	0.61	0.35	1.00	
	0.2.2	0.00	0.00	0.00	0.20		0.02	0.02			
Pearson significance levels											
	Chloride	Bromide	Nitrate	Sulfate	UR	SRB	GWC	VWC	pН	Precip.	
Chloride	NA	0.00	0.00	0.00	0.04	0.07	0.02	0.02	0.00	0.40	
Bromide	0.00	NA	0.26	0.05	0.00	0.00	0.00	0.00	0.00	0.01	
Nitrate	0.00	0.26	NA	0.66	0.33	0.28	0.00	0.00	0.00	0.01	
Sulfate	0.00	0.05	0.66	NA	0.00	0.00	0.11	0.11	0.11	0.01	
UR.	0.04	0.00	0.33	0.00	NA	0.00	0.02	0.02	0.23	0.00	
SRB	0.07	0.00	0.28	0.00	0.00	NA	0.11	0.11	0.65	0.00	
GWC	0.02	0.00	0.00	0.11	0.02	0.11	NA	0.00	0.00	0.00	
VWC	0.02	0.00	0.00	0.11	0.02	0.11	0.00	NA	0.00	0.00	
nH	0.00	0.00	0.00	0.11	0.23	0.65	0.00	0.00	NA	0.02	
Precip	0.40	0.00	0.00	0.01	0.20	0.00	0.00	0.00	0.02	N A	
Treeip.	0.40	0.01	0.01	0.01	0.00	0.00	0.00	0.00	0.02	1111	
			Spearm	an correlat	ion coeff	ficients					
	Chloride	Bromide	Nitrate	Sulfate	UR	SRB	GWC	VWC	рH	Precip.	
Chloride	1.00	0.85	0.57	0.84	0.43	0.34	-0.66	-0.66	-0.72	-0.13	
Bromide	0.85	1.00	0.50	0.74	0.71	0.60	-0.67	-0.67	-0.66	-0.30	
Nitrate	0.57	0.50	1.00	0.33	-0.04	-0.17	-0.52	-0.52	-0.65	-0.31	
Sulfate	0.84	0.74	0.33	1.00	0.59	0.50	-0.61	-0.61	-0.51	0.07	
UB	0.43	0.71	-0.04	0.59	1.00	0.96	-0.20	-0.20	-0.10	-0.50	
SBB	0.34	0.60	-0.17	0.50	0.96	1.00	-0.10	-0.10	0.00	-0.44	
GWC	-0.66	-0.67	-0.52	-0.61	-0.20	-0.10	1.00	1.00	0.74	0.61	
VWC	-0.66	-0.67	-0.52	-0.61	-0.20	-0.10	1.00	1.00	0.74	0.61	
nH	-0.72	-0.66	-0.65	-0.51	-0.10	0.00	0.74	0.74	1.00	0.48	
Precip	-0.12	-0.30	-0.31	0.07	-0.50	-0.44	0.61	0.61	0.48	1.00	
Treeip.	-0.10	-0.00	-0.01	0.01	-0.00	-0.11	0.01	0.01	0.40	1.00	
			Spea	rman signif	ficance le	evels					
	Chloride	Bromide	Nitrate	Sulfate	UR	SRB	GWC	VWC	рH	Precip.	
Chloride	NA	0.00	0.00	0.00	0.02	0.07	0.00	0.00	0.00	0.44	
Bromide	0.00	NA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.08	
Nitrate	0.00	0.00	NA	0.05	0.83	0.39	0.00	0.00	0.00	0.07	
Sulfate	0.00	0.00	0.05	NA	0.00	0.01	0.00	0.00	0.00	0.70	
UB	0.02	0.00	0.83	0.00	N A	0.01	0.25	0.00	0.58	0.00	
SBB	0.02	0.00	0.39	0.00	0.00	N A	0.25	0.25	0.00	0.00	
GWC	0.07	0.00	0.00	0.01	0.00	0.57	NA NA	0.07	0.00	0.01	
VWC	0.00	0.00	0.00	0.00	0.25	0.57	0.00	N A	0.00	0.00	
5 V V C	0.00	0.00	0.00	0.00	0.20	0.07	0.00	0.00	N.A	0.00	
рп Dasaia	0.00	0.00	0.00	0.00	0.00	0.99	0.00	0.00	1NA 0.00	0.00	
Precip.	0.44	0.08	0.07	0.70	0.00	0.01	0.00	0.00	0.00	IN A	

Declaration

I herewith declare that I have produced this paper without the prohibited assistance of third parties and without making use of aids other than those specified; notions taken over directly or indirectly from other sources have been identified as such. This paper has not previously been presented in identical or similar form to any other German or foreign examination board. The thesis work was conducted from May 10th, 2012 to November 12th, 2012 under the supervision of Prof. Dr. Jens Lange at the Institut für Hydrologie; Albert-Ludwigs Universität Freiburg.

Freiburg im Breisgau, 12th November, 2012

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