Mobility and Mobilisation of heavy metals and PAHs in partially water repellent urban soils

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Dedicated to my family

"Wissen und Erkennen sind die Freude und die Berechtigung der Menschheit"
(Alexander von Humboldt, 1769-1859)

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Abstract

Water repellency has been found to be a crucial parameter in controlling preferential transport of water and solutes in the soil. This thesis investigates the impact of water repellency on solute and water fluxes in a contaminated former sewage site. Moreover this thesis examines the impact of water repellency on the mobilisation potential of heavy metals and PAHs by dispersion experiments. We tested the hypothesis whether preferential flow decreases the risk of groundwater contamination, since water repellent soil parts are bypassed, or if it increases, since hydraulic shear forces may cause a rapid downward transport of colloid-bound contaminants through the vadose zone (1). Moreover we assume that hydrophobic compounds are chemically inert and therefore act to a lesser extend as a source for contaminants than hydrophilic compounds (2). Furthermore we assume that the moisture-related temporal and spatial extend and severity of water repellency influences the formation and stability of preferential flow paths (3) and hence the collection performance of plate lysimeters (4).

To address the first hypothesis the long-term spatial and temporal course of solute fluxes sampled by zero-tension and tension lysimeters are analysed and physico-chemical factors which control the mobility of dissolved and colloid-bound contaminants in the soil are identified (1). The second hypothesis was tested by determining the impact of soil hydrophobicity on the mobilisation potential of contaminants using laboratory dispersion experiments (2). The influence of the initial soil moisture regime on the formation and stability of preferential flow paths was evaluated using dye tracer experiments (3). Finally the collection performance of zero-tension and tension lysimeters under natural rainfed conditions and under irrigation conditions using different initial soil moisture contents was studied (4).

The results of the lysimeter study show that the annual contaminant mass fluxes in soil solutions sampled by tension lysimeters were positive related to the mean lysimeter collection efficiencies. The contaminant concentrations in soil solutions were not related to the lysimeter collection efficiencies. This indicates that the transport of contaminants was controlled by the total cross sectional area of water flow. Results hence confirm that temporally stable preferential flow patterns decrease contaminant fluxes, since seepage water bypasses a large part of the polluted soil matrix. Hydraulic shear forces through preferential flow pathways did not contribute to an increase in colloid-bound contaminant transport. It was further demonstrated that the mobility of the Zn, Ni and Cd was positively related to soil solutions electrical conductivity. Dissolved organic matter (DOM) contributed significantly to the mobility of Cu and partly to the mobility of Cr. Due to the high sorption affinity to the

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organic matter no Pb and almost no PAHs were mobilised from the organic rich acid topsoil (1).

The results of the dispersion experiments indicate that organic hydrophobic colloids in water repellent samples were chemically inert. The mobilisation potential of colloid-bound high molecular weight PAHs (5-6 fused rings) and colloid-bound Cu in the wettable soil samples was higher than that in the adjacent water repellent soil samples, suggesting that water repellency induced aggregation of the hydrophobic organic colloids. Furthermore organic carbon dissolution was increased most likely due to microbial cell lysis in water repellent samples and contributed to the mobility of Cu through complexation reactions (2).

Results of the dye tracer experiments demonstrate that regardless on the initial soil moisture condition preferential flow took place, but the flow path cross sectional area under initially moist conditions was significantly higher than under initially dry conditions. Moreover results show that preferential flow path in partially water repellent sandy soils under high rainfall intensities and rates were persistent (3).

The results of the lysimeter studies revealed that the initial water content controlled the degree of the hydraulic gradient in preferential pathways and thus the performance of zero tension lysimeters, while the performance of tension lysimeters was not affected by the initial water content. Zero tension lysimeters performed satisfactorily only under initially moist conditions when strong rainfall events occurred and were hence more suitable for the detection of accelerated fluxes through saturated preferential flow pathways. The nearly constant relative sampling efficiency of the single tension lysimeters throughout a 18 month long period indicates that preferential flow path pattern at our study site were periodically stable (4).

Zusammenfassung

Benetzungshemmung ist eine zentrale Steuergröße für den bevorzugten Wasser- und Stofftransport im Boden. Die vorliegende Arbeit untersucht den Einfluss der Benetzungshemmung auf die Stoff- und Wasserflüsse in einem schadstoffbelasteten ehemaligen Rieselfeld. Des Weiteren untersucht diese Arbeit den Einfluss der Benetzungshemmung auf das Mobilisierungspotential von Schwermetallen und PAHs im Dispergierungsversuch.

Wir überprüften, ob der bevorzugte Fluss das Risiko einer Grundwasserbelastung senkt, da benetzungsgehemmte Bodenpartien umflossen werden, oder erhöht, da hydraulische Scherkräfte in präferentiellen Fließwegen eine Mobilisierung von kolloid-gebundenen Schadstoffen bewirken können (1). Darüber hinaus gehen wir davon aus, dass benetzungsgehemmte Bodenpartien reaktionsträge sind und daher weniger als Schadstoffquelle fungieren als benetzbare Bereiche (2). Des Weiteren nehmen wir an, dass die Ausbildung einer zeitlich stabiler Benetzungshemmung die Bildung und Stabilität der Fließwege (3) und damit die Sammeleffizienz von Platten-Lysimetern beeinflusst (4)

Die erste Hypothese wurde getestet, indem der langfristige und räumliche Verlauf der Stoffflüsse im Sickerwasser mittels freidränenden Lysimetern und Dochtlysimetern analysiert wurde und physikalisch-chemische Faktoren identifiziert wurden, die die Mobilität von gelösten und kolloid-gebundenen Schadstoffen im Boden kontrollieren (1). Die zweite Hypothese wurde getestet, indem die Auswirkungen der Boden-Hydrophobizität auf das Mobilisierungspotenzial von Schadstoffen im Labor-Dispergierungsversuch ermittelt wurden (2). Der Einfluss der Bodenfeuchte auf die Bildung und Stabilität der Fließwege wurde anhand eines Farbtracer - Experimentes bewertet (3). Schließlich wurde die Sammeleffizienz der Dochtlysimeter und freidränenden Lysimeter unter natürlichen Niederschlagbedingungen und in einem Beregnungsversuch unter unterschiedlichen anfänglichen Bodenfeuchtebedingungen bestimmt (4).

Die Ergebnisse der Lysimeterstudie zeigen, dass die jährlichen Schadstofffrachten in den Sickerwasserlösungen positiv mit den mittleren Lysimeter-Sammeleffizienzen korreliert waren. Die Schadstoffkonzentrationen waren hingegen nicht von der Sammeleffizienz abhängig. Dies deutet darauf hin, dass die Schadstofffrachten von der durchflossenen Querschnittsfläche abhängig sind. Unsere Ergebnisse bestätigen somit, dass zeitlich stabile präferenzielle Fließwege die Schadstofffrachten verringern, da das Sickerwasser einen großen Teil der schadstoffbelastet Bodenmatrix umfließt. Des Weiteren trugen hydraulische Scherkräfte in präferenziellen Fließwegen nicht zu einem erhöhten kolloid-gebundenen

Stofftransport bei. Es wurde ferner gezeigt, dass die Mobilität der Zn, Ni und Cd positiv von der elektrischen Leitfähigkeit des Sickerwassers abhängig war. Gelöster organischer Kohlenstoff (DOC) trug wesentlich zur Mobilität von Cu und teilweise zur Mobilität von Cr bei. Aufgrund der hohen Sorptionsaffinität zur organischen Substanz wurde kein Pb und fast keine PAKs aus den organisch reichen und sauren Oberböden mobilisiert (1).

Die Ergebnisse der Dispergierungsexperimente deuten darauf hin, dass die hydrophoben organischen Kolloide in den benetzungsgehemmten Bodenproben physikalisch-chemisch reaktionsträge waren und Benetzungshemmung die Aggregation der hydrophoben organischen Kolloide förderte. Es zeigte sich, dass das Mobilisierungspotential der hochmolekularen PAKs (5-6 Ringe) und des kolloid-gebundenen Cu in den benetzbaren Bodenproben höher war als in den angrenzenden benetzungsgehemmten Bodenproben. Eine Erhöhung der gelösten DOC und Cu Konzentration in den benetzungsgehemmten Bodenproben deutet darauf hin, dass Lyse von mikrobiellen Zellen stattfand, wodurch die Mobilität von Cu-DOC erhöht wurde (2).

Die Ergebnisse des Farbtracer-Experimentes zeigen, dass unabhängig von dem anfänglichen Bodenfeuchtezustand präferentieller Fluss stattfand. Dennoch war die Wasserfluss-Querschnittsfläche unter anfänglichen feuchten Bedingungen signifikant höher als unter anfänglichen trockenen Bedingungen. Ferner zeigen die Ergebnisse dass die präferentiellen Fließwege in den benetzungsgehemmten, sandigen Böden bei hohen Niederschlagintensitäten stabil blieben (3).

Schließlich deuten unsere Ergebnisse darauf hin, dass der anfängliche Bodenfeuchtezustand den hydraulischen Gradienten in präferenziellen Fließwegen steuerte und somit die Funktionsweise von freidränenden Lysimetern bestimmte, während die Funktionsweise der Dochtlysimeter unabhängig von anfänglichen Bodenfeuchtezustand war. Die nahezu konstante relative Sammel-Effizienz der verschiedenen Dochtlysimeter während einzelner Perioden zeigt, dass präferenzielle Fließwegemuster in unserem Untersuchungsgebiet saisonal persistent waren (4).

1   General Introduction

1.1   Preferential water flow in water repellent soils

The term preferential flow or nonuniform flow comprises all phenomena with a nonuniform wetting of the soil profile leading to accelerated flow along certain pathways while bypassing other parts of the bulk soil (Dekker & Ritsema, 1996; Hendrickx & Flury, 2001). One of the main factors affecting preferential solute and water flow at our research areas has been found to be caused by water repellency (Taumer, 2007). According to Ellerbrock et al. (2005) soil hydrophobicity can be considered as a material property of the soil organic matter (SOM). In general it was shown that water repellency is especially formed in undisturbed no-till arable or permanently vegetated soils such as grassland induced through the accumulation of partially decomposed plant residues that produce hydrophobic humic substances and waxy materials (Doerr et al., 2006; Hallett et al., 2001; Trojan & Linden, 1992). Furthermore the biological environment in the soil was also shown to play a role in controlling soil water repellency. While soil fungi were found to increase soil water repellency (Chan, 1992; Dekker & Ritsema, 1996) several results indicate that in dependency of the bacterial strain encountered in soil samples, bacterial biofilms can hydrophilize or hydrophobize the soil surfaces (McKenna et al., 2002; Schaumann et al., 2007). These hydrophobic compounds cover the surfaces of soil particles and render them water repellent (Mashum & Farmer, 1985). Apart from these hydrophobic compounds, the orientation of the hydrophilic and hydrophobic functional groups relative to the particle surface and hence the molecular structural conformation of soil organic matter was also assumed to influence the soil wettability (Doerr et al., 2005; Liu & Lee, 2006; Mashum & Farmer, 1985). Drying may alter also the molecular conformation of soil organic matter and may hinder rewetting of the soil (Doerr et al., 2005; Liu & Lee, 2006; Mashum & Farmer, 1985).

Water repellency and preferential flow have been found in several studies to follow a moisture-related seasonal trend (Taumer et al., 2006). Several authors reported that soil becomes water repellent when the water content decreases below a certain soil specific critical value (Dekker & Ritsema, 1996; Dekker et al., 2001; Doerr & Thomas, 2000). Further it was shown that whether preferential or matrix flow is formed depends on the rainfall intensity. Short intensive rain showers tend to trigger preferential flow, while long, steady rains tend to moisten the soil more uniformly (Taumer et al., 2006).

1.2 Mobility and mobilisation of contaminants in water repellent soils

1.2.1 Main physico-chemical factors influencing the mobility of heavy metals and PAHs

The mobility and availability of contaminants is mainly controlled by specific distribution characteristics between immobile solid phases, mobile colloidal particles and dissolved species (Bruemmer et al., 1986; Kretzschmar et al., 1999), which depend on physico-chemical soil and soil solution properties.

Main physico-chemical factors affecting heavy metals mobility in soils are the chemical bonding form, pH-value, redox potential, conductivity and ionic strength. In addition heavy metal mobility underlies seasonal fluctuations induced by climate (temperature, precipitation) and biological activity (Harter & Naidu, 2001). The pH value is one of the most important factor affecting heavy metal mobility (Dijkstra et al., 2004; Forstner & Haase, 1998; Yin et al., 2002). In general there is a negative correlation between soil pH and mobility of heavy metals. At low pH, protonisation of variably charged surfaces and repulsive charge effects lead to a higher desorption of cationic heavy metals.

Polycyclic aromatic hydrocarbons (PAHs) are hydrophobic organic contaminants that consist of more than two fused aromatic benzene rings. PAHs are mainly adsorbed due to their hydrophobicity especially to the soil organic matter (Chiou et al., 1988; Grathwohl, 1990; Karickhoff et al., 1979; Murphy et al., 1994; Petruzzelli et al., 2002) and are poorly water soluble. Factors like the chemical structure, the total concentration and the bioavailability influence the mobility of PAHs in the soil. In general low molecular weight PAHs (up to 3 fused rings) have a higher water solubility and are more chemically or microbially degradable. In contrast higher molecular weight PAHs ($4 - 6$ fused rings) have a higher hydrophobicity and toxicity, a lower solubility and persist therefore longer in the environment (Karickhoff, 1981; Marschner, 1999; Wilcke, 2000). The differences in water solubility and sorption behaviour result in a higher mobility of the low molecular weight PAHs (e.g. Naphthalene) and a lower mobility of high molecular weight PAHs (e.g. Benzo(a)pyren). Generally it has been found that the sorption of hydrophobic organic compounds to mineral-associated humic substances increases as ionic strength and pH decreases, while divalent cations increase their sorption (Murphy & Zachara, 1995; Yang et al., 2001).

Since some contaminants (e.g. Pb and PAHs) show a high sorption affinity for organic matter (solid, colloidal and dissolved), their solubility and mobility can be either reduced by binding to soil humic matter or increased by binding to soluble organic acids and organic colloids

(Bergkvist et al., 1989; Impellitteri et al., 2002; Yin et al., 2002). Several studies indicate that dissolved organic carbon (DOC) contributes significantly to the mobility of strong sorbing heavy metals such as Cu, Cr or Pb (Guggenberger et al., 1994; Impellitteri et al., 2002; Linde et al., 2007; Ponizovsky et al., 2006; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Temminghoff et al., 1997; Weng et al., 2002; Yin et al., 2002) and organic contaminants such as PAHs (de Jonge et al., 2008; Lassen & Carlsen, 1997). Various laboratory studies showed that increasing acidity decreases electrostatic repulsion through a replacement of readily dissociated counterions by H+ leading to contraction and precipitation of OC, thus reducing dissolution of OC concentration (Andersson et al., 2000; Hay et al., 1985; Godde et al., 1996; Guggenberger et al., 1994; Impellitteri et al., 2002; Jozefaciuk et al., 1996; Karlik, 1995; You et al., 1999; Shen, 1999). In contrast increasing pH enhances deprotonation of carboxylic and phenolic functional groups, which results in increasing concentrations of DOC and DOC complexed heavy metals in soil solutions. At high ionic strength, heavy metal – DOC complexes seem to be immobilised as a result of cation bridging between negatively charged DOC and negatively charged soil particles but also of DOC precipitation. This effect was shown to be more pronounced for polyvalent cations (Munch et al., 2002; Oste et al., 2002; Reemtsma et al., 1999; Shen, 1999; Temminghoff et al., 1998). While heavy metal complexation by the hydrophobic acids was shown to be lower than by hydrophilic acids (Guggenberger et al., 1994; Olsson et al., 2007; Romkens & Dolfing, 1998), several studies have shown that PAHs are mainly bound to the less mobile hydrophobic DOM fractions (Chefetz et al., 2006; Guo & Ma, 2009; Ilani et al., 2005; Polubesova et al., 2007; Raber et al., 1998; Schlautman & Morgan, 1993). Generally it has been found that increasing alkalinity, DOC become more hydrophilic through deprotonation of functional groups, resulting in decreased PAH adsorption (Guo & Ma, 2009; Marschner et al., 2005; Pan et al., 2008; Raber & KogelKnabner, 1997; Schlautman & Morgan, 1993). Discrepancies exist regarding the influence of the ionic strength on the binding capacity of DOC toward hydrophobic contaminants. Several authors reported decreased PAHs adsorption by DOC with increasing salt concentrations, when monovalent cations were prevalent (Guo & Ma, 2009; Lassen & Carlsen, 1997; Schlautman & Morgan, 1993), whereas little or no trend was found when bivalent cations were dominant (Guo & Ma, 2009; Schlautman & Morgan, 1993).

Several studies have further demonstrated that suspended in situ mobilized colloids ($\leq 1 \mu m$) can facilitate the transport of strongly sorbing contaminants such as low soluble heavy metals and PAHs (Citeau et al., 2003; Grolimund et al., 1996). In natural environments mobile subsurface colloids occur as a mixture of complex aggregates. Inorganic colloids are often

stabilized by adsorbed natural organic matter (mostly of fulvic and humic acids) by both increasing electrostatic repulsion and steric repulsive forces (Kretzschmar et al., 1998; Liang & Morgan, 1990; Ryan & Gschwend, 1990; Tiller & Omelia, 1993). Van der Waals and electrostatic interactions cause cationic contaminants to adsorb to colloids, whereas hydrophobic interactions are the reason for the adsorption of organic, nonpolar contaminants. The affinity of PAH to colloids increases with increasing molecular weight or octanol/water distribution coefficient (Kow) of single PAH reference substances and with increasing organic carbon content of the colloids (Kretzschmar et al., 1999; Villholth, 1999).

Colloids are either added to the soil surface along with other substances, or are created through detachment from the static soil matrix. Detachment and release of colloids are favoured by chemical and physical perturbations. It is well recognised that chemical perturbations may be caused through e.g. a decrease of solution ionic strength (DLVO theory), small ionic valence in the soil solution (Schulze-Hardy rule) or an increase in solution pH, resulting in an increase in electrostatic repulsion between colloids and grains (Bunn et al., 2002; Huber et al., 2000; Flury et al., 2002; Grolimund et al., 1998; McCarthy et al., 2002; Miller et al., 1990; Rousseau et al., 2004). Inconsistent results were obtained regarding physical perturbations, which may be induced by infiltration water intensity; temporal variability in moisture content, the movement of air–water interfaces (AWI) or from dissolution of cementing agents.

1.2.2 Impact of preferential flow on the mobility of contaminants

The groundwater contamination risk can be either increased or decreased by preferential flow. If preferential flow occurs from contaminated topsoils through uncontaminated sandy subsoils, the risk of groundwater pollution is increased due to a decreased filter capacity of the subsoil. On the other hand bypassing large areas of the contaminated topsoil can lead to a decreased leachability of the contaminants for a short time period, but a long-term dislocation of preferential flow pathways may result in a continuous risk of groundwater contamination (Lipsius & Mooney, 2006).

Hydraulic shear forces through preferential flow pathways may cause colloid release and a rapid downward transport of colloid-bound contaminants through the vadose zone, since no physical colloid filtration takes place (Jacobsen et al., 1997; McKay et al., 2000; Mishurov et al., 2008; Pilgrim & Huff, 1983; Ryan et al., 1998; Saiers et al., 1994).

1.2.3 Impact of soil moisture contents on the mobility of contaminants

Seasonal and periodical dynamics of the soil moisture regime may alter biological, physico-chemical and chemical soil properties, which in turn affect the release of contaminants. Wetting and drying cycles can influence the mobility of contaminants, when they are complexed to DOC or colloid-bound. Several researchers showed that DOC concentrations in soil solution increase at the beginning of a rewetting period after dry periods (Chittleborough et al., 1992; Kalbitz & Knappe, 1997; Lundquist et al., 1999; Merckx et al., 2001; Tipping et al., 1999; Totsche et al., 2007; Wehrer & Totsche, 2009; Zsolnay et al., 1999). It is therefore suggested that during dry periods microbial activity which causes decomposition of dissolved organic matter is reduced, while microbial cell lysis is enhanced, both contributing to an increased dissolution of organic carbon on wetting (Christ & David, 1996; Kalbitz & Knappe, 1997; Zsolnay et al., 1999).

Wetting–drying cycles in soils followed by intensive precipitation events may be an important trigger for the formation and redistribution of colloids in the unsaturated soil zone (Totsche et al., 2007). Also the initial soil moisture content was recognised to influence positively the transport of colloids in the unsaturated soil (Powelson et al., 1990; Rousseau et al., 2004). Wan & Tokunaga (1997) found in the conceptual model, when the water content decreases below a critical value, that colloids are immobilized because the thickness of the water films are smaller than the diameter of the colloid. This phenomenon is defined as film straining. Besides colloid removal by straining, several studies report that drying of soil leads to creation of air-water interfaces to which particles adhere strongly (El-Farhan et al., 2000; Keller & Sirivithayapakorn, 2004; Lenhart & Saiers, 2002; Wan & Wilson, 1994a; Wan & Wilson, 1994b). The importance of the air-water (AW) and air-water-soil (AWS) interface in colloid sorption was confirmed in visualization experiments by several authors (Crist et al., 2004; Wan & Wilson, 1994b; Zevi et al., 2005).

1.3 Objectives of this thesis

Water repellency has been found at our study sites to be a crucial parameter in controlling preferential transport of water and solutes in the soil.

The central topic of this thesis deals therefore with soil water repellency and its impact on contaminant release in two urban locations, a former sewage site and a municipal park, characterised both by their small scale variability in water repellency and in contaminant contents. To address this question **chapter 6** analyses the long-term spatial and temporal course of solute fluxes sampled by tension and zero-tension lysimeters, and identifies

physico-chemical factors which control the mobility of dissolved and colloid-bound contaminants in the partially water repellent topsoil. An essential requirement for the successfully monitoring of colloid-bound contaminant fluxes was to analyse if fiberglass wicks employed in tension lysimeters retained colloids (**chapter 5**). An important aspect was further to investigate if preferential flow due to water repellency increases contaminant fluxes or if it diminishes since great parts of the topsoil are bypassed. Moreover **chapter 7** evaluates the impact on soil hydrophobicity on the mobilisation potential of contaminants using laboratory dispersion experiments. It is of particular interest if the low physico-chemical reactivity of hydrophobic soil compounds in water repellent soils decreases mobilisation potential of contaminants.

Another key aspect of this thesis was to identify the formation and the stability of preferential flow paths under different moisture regimes. To address this question the collection performance of two plate lysimeter types namely zero-tension and tension lysimeter under natural rainfed conditions (**chapter 2**) and irrigation conditions using different initial soil moisture contents (**chapter 3**) was determined. A particularly important issue was to evaluate which lysimeter type is more adapted in sampling heterogeneous water fluxes. Furthermore the influence of the initial soil moisture regime on the cross sectional area of preferential flow pathways using dye tracer experiments is determined in **chapter 4**.

Finally, **chapter 8** focuses on the suitability of the batch elution test DIN 38414 part 4 (DEV S4) as an alternative to field soil water sampling for the prognosis of heavy metal concentrations in seepage water.

2 Long-term performance of tension and zero-tension lysimeters and persistence of flow pathways in a partially water repellent soil

2.1 Abstract

Assessing preferential water and solute flow in soils have been shown to pose methodological implications, because different flow paths with different flow rates and velocities are very difficult to measure and to estimate. The aim of our study was to investigate the spatial and temporal variability of the share of preferential flow pathways on water fluxes extracted by lysimeters in a partially water repellent soil. For this purpose we installed five zero-tension and five capillary fiberglass wick (tension) lysimeters side by side at 30 cm - 40 cm depth beneath the litter-Ah horizon of an organic rich sewage soil. Soil solutions were collected for 24 time intervals over a 17-month period.

Zero-tension lysimeters (ZT) collected 5 times less soil solution than tension lysimeters (TL). TL performance followed moisture-related seasonal trend and performed reasonably well under moist soil conditions and when strong rainfall events occurred. In contrast ZT only operated after strong rainfall events and might be therefore more suitable for the detection of accelerated fluxes through saturated preferential flow pathways. The nearly constant relative sampling efficiency of the single TL throughout seasonal periods indicates that preferential flow path pattern at our study site were almost stable.

2.2 Introduction

Uniform or matrix flow refers to a homogeneous moving of wetting fronts through the soil profile. The term preferential flow or nonuniform flow comprises all phenomena with a nonuniform wetting of the soil profile leading to accelerated flow along certain pathways while bypassing other parts of the bulk soil (Dekker & Ritsema, 1996; Hendrickx & Flury, 2001). Main causes leading to preferential flow are macropore flow that is created through highly conductive paths as continuous root channels, earthworm burrows, fissures, or cracks within well-structured and mostly fine-textured soils (Edwards et al., 1993; Kim et al., 2008; Nektarios et al., 2007; Ray et al., 1997), unstable flow formed by wetting front instabilities in a system with fine-over-coarse textural layers (Hill & Parlange, 1972; Glass et al., 1989; Ritsema & Dekker, 1994), air entrapment (Hendrickx et al., 1993; Raats, 1973; Wang et al., 1998), non-ponding rainfall (Raats, 1973; Selker et al., 1992) or water repellency.

One of the main factors affecting preferential solute and water flow in the contaminated organic rich sewage topsoil at the experimental test site has been found to be caused by water repellency (Taumer, 2007). Several authors have demonstrated that as a result of water repellency finger flow formation may be initiated (Bauters et al., 1998; Dekker & Ritsema, 1996; Hangen et al., 2004; Ghodrati & Jury, 1990). After Ellerbrock et al. (2005) the hydrophobicity can be considered as a material property of the soil organic matter (SOM). Water repellency under dry conditions is particularly induced through the accumulation of partially decomposed plant residues that produce hydrophobic humic substances and waxy materials at permanently vegetated soils with grassland (Doerr et al., 2006; Hallett et al., 2001; Trojan & Linden, 1992). Besides the water repellency the soil surface microtopography leading lateral redistribution of the infiltrating water from the slightly elevated positions into sinks as suggested by Kasteel et al. (2007), Mertens et al. (2007) or Wessolek et al. (2009) can also contribute to heterogenic infiltration patterns at our study site. It was shown further that whether preferential or matrix flow is formed depends on the rainfall intensity. Short intensive rain showers tend to trigger preferential flow, while long, steady rains tend to moisten the soil more uniformly (Taumer et al., 2006). Results from tracer experiments performed by Wessolek et al. (2009) at the experimental test site provided hints that flow pattern were temporally persistent. Several authors therefore suggested that preferential flow pattern may persist in water repellent sandy soils until the soil is either completely desiccated or saturated (Doerr & Thomas, 2000; Glass et al., 1988; Wessolek et al., 2009) and may be therefore very persistent over consecutive infiltration cycles for weeks, months or years (Buchter et al., 1995; Glass et al., 1988; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998).

Various in situ monitoring techniques are available to collect soil solution (Weihermuller et al., 2007) from which plate lysimeters with no or small side walls are frequently used. Plate lysimeters have been used since the mid-19th century in a wide variety of soil and environmental studies. They cause no disturbance to the soil directly above it, are low-cost and easy operable devices and require almost no maintenance (Bergstrom, 1990). In dependence of the way soil solution is extracted from the soil system the devices may be distinguished into free-drainage and suction-controlled drainage systems. Main disadvantage of free-drainage or zero-tension lysimeters (hereafter referred to as ZT) is that the soil zone directly above the lysimeter must be water-saturated having a matric head ≥ 0 before water can drain (Barbee & Brown, 1986; BrandiDohrn et al., 1996; Jemison & Fox, 1992). This leads to a large amount of water that is diverted from the soil above the lysimeter towards the

drier surrounding soil (Chiu & Shackelford, 2000; Peters & Durner, 2009; Zhu et al., 2002), so that even large lysimeters may be completely circumvented in homogeneously soils (Peters & Durner, 2009). Two possibilities to overcome this problem are to introduce sidewalls or increase pan size. However, the former enhances the risk of preferential flow along the walls and both complicate their installation (Mertens et al., 2005; Peters & Durner, 2009; Radulovich & Sollins, 1987). Fiberglass wick lysimeters, (hereafter referred to as tension lysimeters or short TL) differ from ZT in that they maintain a fixed tension at the surface and thus collect water from unsaturated soils, resulting in higher collection efficiencies (Boll et al., 1992).

Reported collection efficiencies of TL and TZ as the ratio of measured drainage to estimated drainage (obtained from the calculated water balance) vary in literature depending on the soil type, pan size and climatic conditions. For example, reported leachate collection efficiencies of TL were 59 % (Amery et al., 2008), 103 % (Boll et al., 1991), 66 % to 80 % (BrandiDohrn et al., 1996), 41 % (Haines et al., 1982), 125 % with a coefficient of variation of 36 % (Louie et al., 2000), 70 % to 103 % (Siemens & Kaupenjohann, 2004), 0 to negligible (Steenhuis et al., 1998) or 101 % with a coefficient of variation 28 % (Zhu et al., 2002). Measured leachate collection efficiencies of zero-tension lysimeters were 99 % (Barzegar et al., 2004), 27 % (Boll et al., 1991), 25 % (Haines et al., 1982), 52 % with a coefficient of variation of 43 % (Jemison & Fox, 1992), 45 % (Peters & Durner, 2009), 10 % to 36 % (Radulovich & Sollins, 1987), about 10 % (Russell & Ewel, 1985), 0 % to 55 % (Ryan et al., 1998) or 40 % with a coefficient of variation 26 % (Zhu et al., 2002).

We assume that the temporal and spatial extend of the soil water repellency, influences the formation and stability of preferential flow paths and hence the collection performance of plate lysimeters. The aim of this study is therefore to evaluate the seasonal course of collection efficiencies of TL and ZT in partially water repellent soils. Based on results obtained in a tracer experiment by Wessolek et al. (2009) on the temporary persistence stability of preferential flow path pattern at this site, this study identifies furthermore the temporal and spatial collection performance of the individual lysimeters.

2.3 Material and Methods

2.3.1 Site and soil description

Our study was performed in a 1 m by 7 m field plot located within a former sewage site in Berlin Buch, Germany. Sewage infiltration was practiced for almost 100 years and stopped in 1985. Because the former sewage farm consisted of different sewage galleries and basins the physico-chemical soil properties have pronounced small scale heterogeneities which are strongly linked to the organic matter contents (Hoffmann, 2002; Schlenther et al., 1996). The vegetation is dominated by dry grasslands (mainly couch grass; syn. Elytrigia repens). The slope of soil surface varies from 3 % to 5 %. The capillary fringe is situated at about 400 cm below the surface. The soil of the plots is classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (30 cm – 40 cm thick) over medium sized homogenous sandy subsoil. Sand is the dominant textural fraction accounting for about 98 % by mass. Table 2-1 and Table 2-2 show basic physical and chemical soil properties of the experimental test site soil.

Table 2-1: Basic physical soil properties
(-) not determined, (*) source Taumer (2007), (**) source Hoffmann (2002)

Depth	Soil horizon	Texture			Bulk density	Conductivity		Air volume	Porosity	Water content	
[m]		[%]			[g cm^{-3}]	[cm d^{-1}]		[m³/m³]	[m³/m³]	[m³/m³]	
		Sand	Silt	Clay		k_s	at 63 hPa			at 63 hPa	15 000 hPa
0.35	Ah	98.0	1.4	0.6	1.0	275 **	0.1 *	0.26 **	0.45 **	0.25	0.05 *
> 0.35	C	97.3	2.3	0.4	1.5 *	694 **	-	0.33 **	0.40 **	0.10 *	0.01*

Table 2-2: Basic chemical soil properties of the Ah horizon
(SD: standard deviation)

	pH (CaCl$_2$)	pH (H$_2$O)	Conductivity	Organic matter	C	N	S	C/N
	[-]	[-]	[µS cm^{-1}]	[g kg^{-1}]	[g kg^{-1}]	[g kg^{-1}]	[g kg^{-1}]	ratio [-]
Mean	4.4	5.0	197	86.0	44.38	4.40	1.24	10.18
SD	.4	.6	55	2.5	1.05	.12	.05	.65

2.3.2 Experimental setup

In the planning of our study it was not clear which type of lysimeter would be most suitable for the monitoring of water fluxes in this partially water repellent soil. Therefore we installed during November 2006 and April 2008 two types of lysimeters: five TL and five ZT. Respectively one ZT and one TL were installed side by side 30 cm to 40 cm beneath the litter and the Ah horizon at a distance of approximately 40 cm. Percolates from the lysimeter polycarbonate boxes (25 cm by 25 cm by 10 cm-deep) were drained through teflon (PTFE) tubes encased in polyvinylchloride (PVC) tubes into brown glass Duran bottles. A detailed description of the installation procedure is given in chapter 3.3.2.

ZT were constructed according to Jordan (1968) with little modifications. To prevent soil from collapsing into the lysimeter, each polycarbonate box was filled from the bottom to the top with a stainless steel filter screen, a stainless steel perforated plate and a 1 cm deep layer of a mixture of clean fine (0.06-0.3 mm, GEBA, Germany) and coarse (0.6-1.2 mm, DORSILIT, Germany) quartz sand. The boxes were subsequently filled with the native soil. TL were constructed according to Holder et al. (1991) with little modifications. The wicks employed were round braided fiberglass wicks (no. 1381 from Pepperell Braiding Company, Pepperell, MA), each having a diameter of 12.7 mm with a fiberglass length of 100 cm. The material was cleaned according to Knutson et al. (1993) by combustion at 400 °C for 4 h in order to remove glue and other organic materials and rinsed afterwards with 0.01 M HNO_3 and distilled–deionised water. The first 20 cm of the fiberglass wicks were separated into single filaments which were spread out on the bottom of the lysimeter boxes. The lysimeter boxes were then filled with the native soil. The wicks extended horizontally along the trench before hanging down vertically above the collection pan. The fiberglas wick length was then adjusted below the surface of a particular TL box providing a 60-cm-hanging water column and corresponding to a tension at the top of the wick of about pF value of 1.8 (Knutson et al., 1993). The fiberglass wicks were inserted into a PTFE tubes in order to isolate the wicks and to prevent contamination and evaporation.

Sampling was performed between 2006-11-1 and 2007-8-13 every 1 to 2 weeks, with the shortest intervals occurring during periods of high precipitation and with the highest interval during dry periods with low or no precipitations. From 2007-8-14 to 2008-4-8 sampling occurred monthly. Each sampling time the glass bottles with soil solution were substituted by empty bottles. In total we monitored 121 soil solution samples taken during 24 collection periods.

2.3.3 Statistical analysis

Means, medians, standard deviations, analysis of variance and correlations were computed with the statistical analysis programme SPSS. Parametric (Independent-Samples T Test, Paired-Samples T Test) and nonparametric (Wilcoxon signed-rank Test, Mann-Whitney U-Test) statistical tests were used because the data were only partly normally distributed (Kolmogorov-Smirnov statistic, Shapiro-Wilk statistic). In addition univariate data analysis inclusive post-hoc multiple comparison tests were performed. Statistical tests were performed to determine differences in leachate collection efficiencies between TL and ZT and between individual lysimeters. The probability level (p) of all tests was 95 %.

2.3.4 Calculation of the water collection efficiency

Several hydrometeorological variables, including precipitation, air temperature, relative humidity at 2 m above the soil surface, were recorded at 10-minute intervals at the nearest climate station in Berlin Buch and at the stationary station situated 20 m apart from the experimental site. Climatic data recorded at sampling date (> 9 a.m.) were attributed to the following sampling period. Potential evapotranspiration (PET) was estimated with the Haude equation (Haude, 1954), using daily values of the air temperature and the relative humidity.

In order to check if the calculated PET according to Haude were correctly, we compared those with PET according to the FAO Penman-Montheith method (Allen et al., 1998). The daily reference evapotranspiration ETo according to the FAO Penman-Montheith method was calculated by using additional daily hydrometeorological variables as wind speed, atmospheric pressure, psychometric constant and the solar radiation from the climate station Berlin Tegel situated 25 km from the test site. Besides the very dry sampling periods, where the calculated PETs using the FAO Penman-Montheith method were slightly higher than those using the Haude method, both methods results in comparable PETs. The differences between measured cumulative precipitations and calculated cumulative PET rates according to Haude (1954) were used to calculate the cumulative minimal net infiltration rates (MIR) for each sampling period. The volume of solution collected by each lysimeter was measured and normalized by the lysimeter cross-sectional area and reported in centimetres. The percentage of water collection efficiencies (computed as the ratio of the measured drainage to calculated MIR) were then calculated for each lysimeter and lysimeter type. Although we used PET rates, which may be greater than the actual evapotranspiration, we did not consider root water

uptake and infiltration losses through surface runoff, which may have compensated the potential errors regarding the calculation of the MIR and the lysimeter collection efficiencies.

2.4   Results and Discussion

2.4.1   Minimal net cumulative infiltration rates

The mean annual precipitation and temperature (1961 - 1990) for Berlin Buch are 564.3 mm and 8.8 °C (Germany's National Meteorological Service) respectively and the climate is characterised as semihumid to semiarid. The year 2007 can be described as relatively moist and warm, with a mean temperature at Berlin Buch of 10.2 °C and a precipitation of 804 mm. Starting from the sampling time November 2006 to March 2007 the MIR (161 mm) was positive due to moderate precipitation rates (230 mm) and low PET rates (Fig. 2-1). Precipitations were almost homogeneous distributed with only 10 % of the precipitations being characterised as strong rainfalls according to the nomenclature of the German Meteorological Service (DWD, > 4.1 mm h^{-1}). Prevalent water flow during this period was expected to be matrix flow. In April 2007 almost no precipitation (1.8 mm) was recorded leading to the desiccation of the soil profile. The sampling period in the summer from Mai to September 2007 was particularly wet with 513 mm rainfall being recorded at the experimental site, which was more than half of the annual sum. Precipitations during that period were not evenly distributed but were mainly characterised by several single heavy rainfall events with hourly precipitation rates from 5 mm to 28 mm. Heavy rainfall events during this period corresponded to the half (251 mm) of the total rainfall amount. In spite of particularly high precipitation rates, the MIR (85 mm) due to high PET rates was low (Fig. 2-1). Predominant water flow during this period is supposed to be preferential flow with a considerable amount of infiltration water lost through surface runoff during strong rainfall events. October 2007 was particularly dry (5 mm of precipitations) with a negative MIR. With the beginning of the winter season in November 2007 PET rates declined until the following growing season in March 2008 and precipitation rates reached 307 mm, leading to a higher MIR (204 mm) (Fig. 2-1). One third of the total precipitations within this season were characterised as strong rainfall events (5 mm h^{-1} - 8 mm h^{-1}). Predominant water flow during this period is supposed to be a mixture between preferential flow and matrix flow.

Based on the climatic characteristics and observations already made by Taumer (2007) at the experimental test site the sampling period can be divided into two non-growing seasons (November 2006 to March 2007 and October 2007 to March 2008) and a growing season

(April 2007 to September 2007) comprising each 5 to 6 month. Hereby post-hoc multiple comparison tests showed that the MIR differed significantly between all seasons.
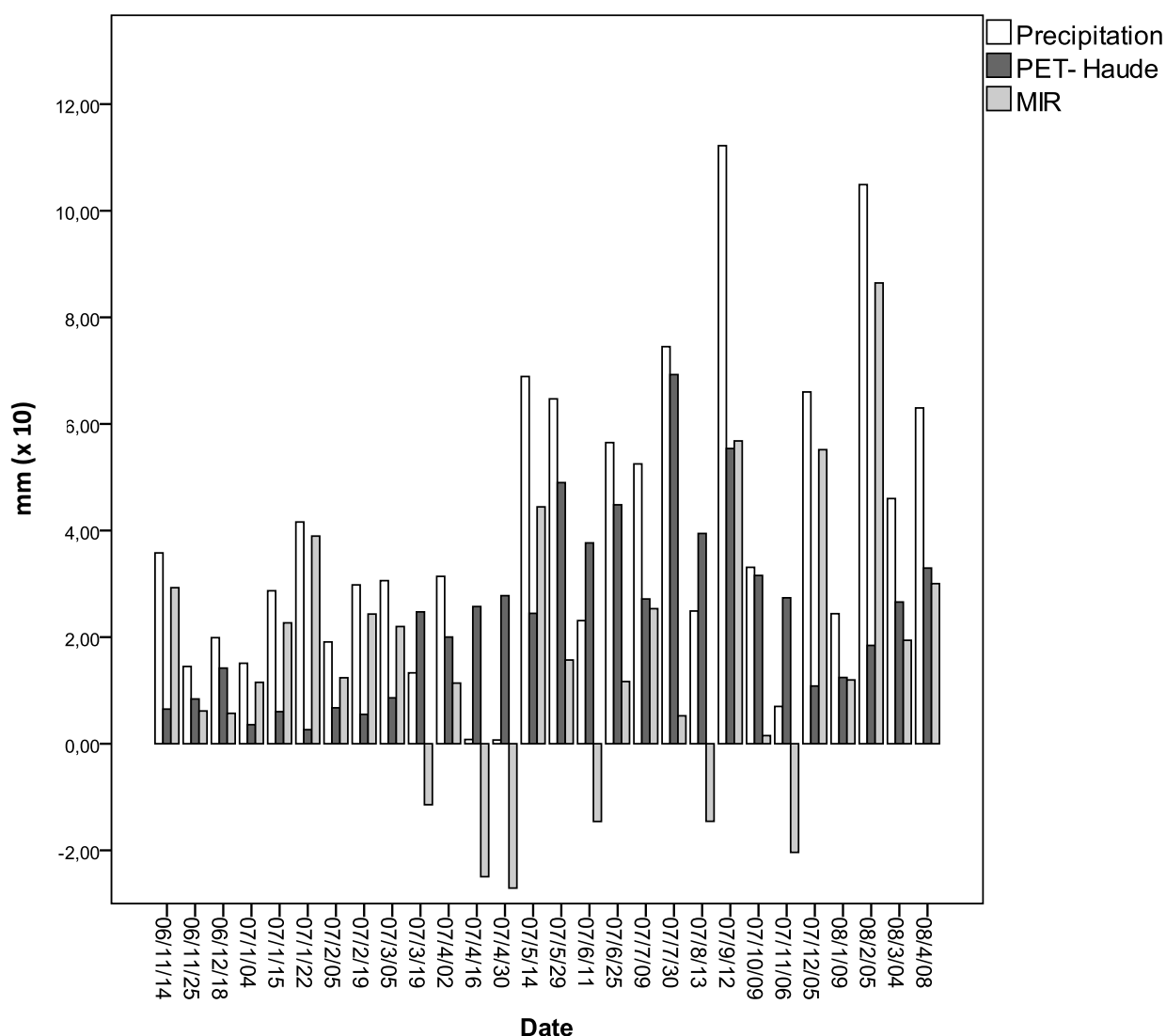
Fig. 2-1: Precipitation (mm), PET (mm) and Minimal net cumulative infiltration rates (MIR) (mm) per sampling period

2.4.2 Leachate collection efficiency of TL and ZT - seasonal trend

In the calculation of the MIR infiltration water lost by surface runoff was not included. Therefore it is likely that collection efficiencies especially during the growing period and during dry periods characterised by heavy rainfall events were even higher than collection efficiencies here reported.

Fig. 2-2 demonstrates that leachate collection efficiencies during the growing season and non-growing season differ significantly between the ZT and TL. On average, TL collected during the annual sampling period 4.6 times more leachate than ZT (27 mm) and had higher mean

collection efficiency (32 % and standard deviation of SD 24) than ZT (2 % and SD 2). Post hoc multiple comparison tests showed that the high variability of mean TL collection efficiencies (5 % - 46 %) during the whole sampling period could be largely attributed to one lysimeter (TL5) that collected more than twice as much leachate (298 mm) than the others (94 mm - 157 mm). Obviously TL5 was less affected by bypass flow. In addition in cannot be excluded that this lysimeter received surface run-off from the adjacent soil plots. Except to TL5, collection efficiencies within each lysimeter type were not significant different. Expect to TL5, TL collection efficiencies followed a seasonal trend having significant higher collection efficiencies during the non-growing seasons (Fig. 2-2).
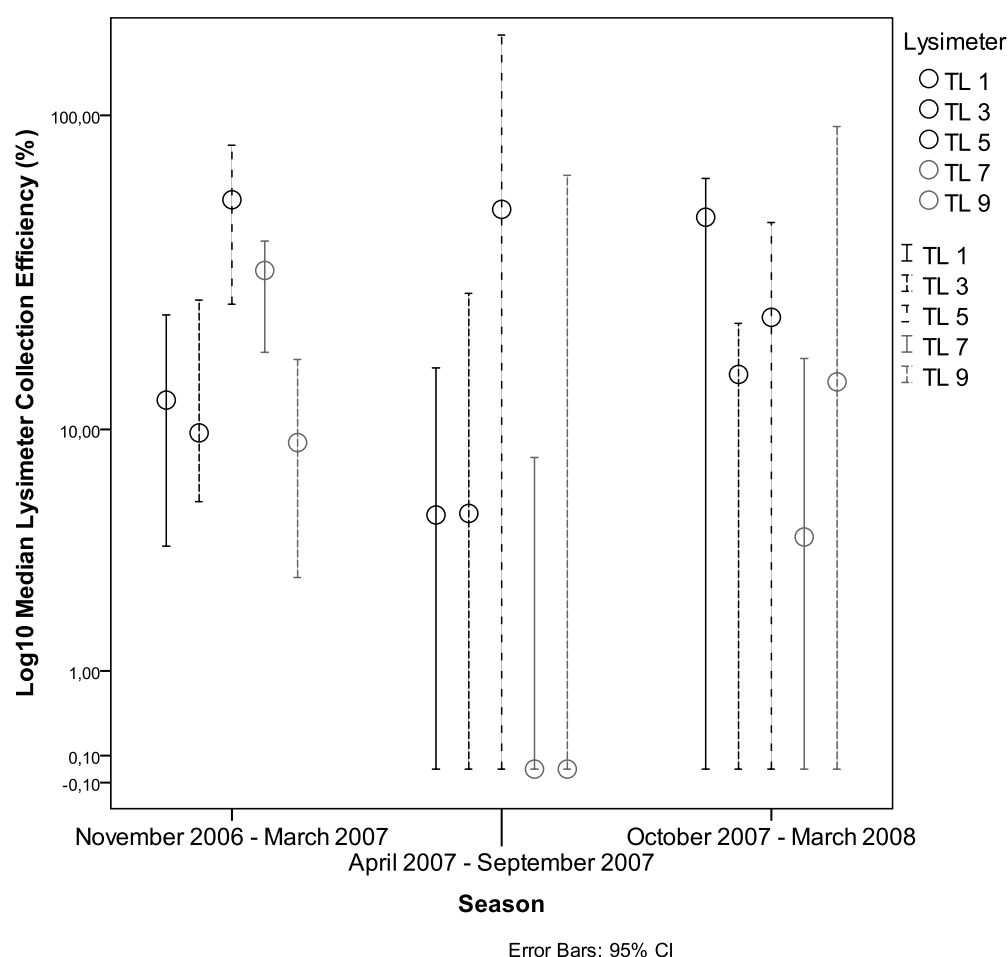
Fig. 2-2: Seasonal course of TL collection efficiencies (%) (error bars represents 95 % confidence interval of medians)

The collection efficiencies of TL5 were instead independent on the season. Collection efficiencies above 100 % during the growing season indicate that TL5 received increased surface run-off from the adjacent hydrophobic soil surface during strong rainfall events. During the sampling period from October 2007 to March 2008 collection efficiencies were

expected to be even higher than reported, due to loss of drainage water at two sampling times as a consequence of undersized collection vessels. Independent on the sampling period almost no leachate was collected when MIR was negative.

Water repellency and preferential flow has been found by Taumer et al. (2006) at the experimental test site and is well described in literature (Doerr & Thomas, 2000; Dekker et al., 2001) to follow a moisture-related seasonal trend. Preferential flow was particularly relevant during the summer due to high potential evapotranspiration rates causing soil hydrophobicity and hence inducing a decline of the total cross sectional area of water flow up to 20 % - 40 % (Taumer et al., 2006), leading to significant lower collection efficiencies (mean 12 %) in almost all TL than in the non-growing seasons (mean 29 %). Preferential flow was in the growing season favoured by intensive showers after prolonged dry periods and the existence of a microtopography leading to runoff from the slightly elevated positions into the sinks. With the beginning of the moist season more flow pathways became hydraulic active, which are reflected here by increased collection efficiencies of the TL.

In contrast to TL, ZT collection efficiencies followed no seasonal trend. Average collection efficiencies (3 %) in the growing season and in the non-growing season from October 2007 to March 2008 were almost the same. Only one of five ZT (TL6) collected in 25 % of all sampling times noteworthy soil water (> 1 mm), from which the majority of the cases were during the summer time, especially after dry periods followed by strong rainfall events with hourly recorded precipitation rates > 8 mm. In two cases notable amounts of soil solutions were collected in the winter time after heavy rainfall events. Only within two sampling periods (07/09/12 and 08/2/05), characterised by the strongest recorded daily rainfall events (≥ 38 mm) soil solutions were collected by all ZT. Within these two cases mean collected drainage water volumes and mean collection efficiencies of ZT and TL were not significant different (Fig. 2-3).
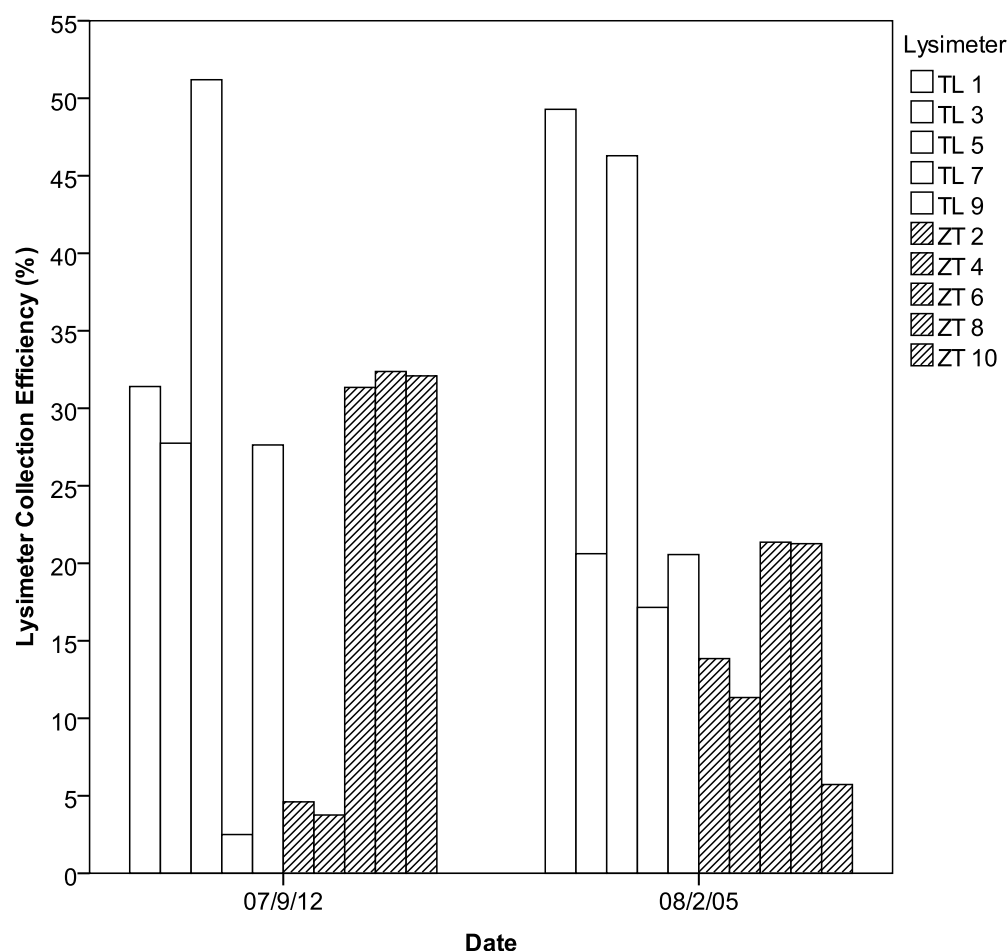
Fig. 2-3: Collection efficiency (%) of TL and ZT in sampling periods characterized by strong rainfall events (≥ 38 mm day^{-1})

The results indicate that ZT only collected soil water during strong rainfall events when water moved preferentially through macropores or through saturated pathways. In all other cases water flow bypassed ZT. Preferential flow was especially provided in the summer but could have also been created through ground frost in the winter. The evidence of preferential flow in the winter was shown within two sampling periods in the winter (08/01/09 and 08/2/05) where Collembola were presented in almost all lysimeter soil solutions. Through the high hydraulic conductivity in this sandy soil and the presence of predominantly large pores in seems unlikely that higher volumes collected in the winter time by ZT were due to saturated soil matrix conditions. The prevailing existence of unsaturated conditions was subsequently shown by mean soil water contents (mass %) after approximately 260 mm of water had been irrigated into the topsoil. Hereby it was found that only half the undisturbed steel cylinder cores sampled above the lysimeter plots reached water contents close to field capacity (pF$\equiv\log_{10}(h$ in cm$) = 1.8$), whereas in the other plots water contents were only 50 % - 60 % of field capacity (data not shown here).

While mean collection efficiencies of almost all TL followed a seasonal trend, the highest collection efficiencies of TL (mean 29 % and SD 18) and ZT (mean 18 % and SD 12) were recorded within sampling periods characterised by strong rainfall intensities (> 38 mm d^{-1}). This result is therefore in agreement with a study obtained by Peranginangin & Steenhuis (2009) reporting for both lysimeter types comparably good collection efficiencies at elevated soil moisture levels, whereas TL performed better at lower moisture contents. It is likely that both lysimeter types during strong rainfall events collected preferentially transported water through saturated finger-like pathways.

2.4.3 Preferential flow path persistence

Although the experimental test site comprised only 7 m², drainage volumes collected by TL and ZT were highly spatial variable with a coefficient of variation of 55 %. Extreme differences in total cumulative amounts of drainage water within one lysimeter type were also reported by other authors (Radulovich & Sollins, 1987; Mertens et al., 2007). Low and high variable and low collection efficiencies between individual lysimeters throughout the sampling period suggests that preferential flow pathways persisted even in the moist non-growing seasons as a consequence of low to moderate precipitation rates. Similar high variable and low collection efficiencies between individual TL were also recorded in study performed subsequently at the identical lysimeter plots using consecutive irrigation events with high irrigation intensities (30 mm h^{-1}) and rates (43 mm) (chapter 3). In addition it was shown that annual mean leachate collection efficiencies of TL in the present study were significantly correlated with irrigation water recoveries in the irrigation experiment (r² = 0.893). In contrast only net infiltrated rainwater recovered by ZT within one sampling period characterized by strong rainfall events (08/2/05) in the present study was significantly correlated to the irrigation water recovered in the irrigation experiment (r² = 0.991). The high correlation in collection efficiencies of TL between the present study and the subsequent conduced field study gives rise to the assumption that preferential flow path pattern at our study site were stable, although the cross sectional area of preferential flow pathways varied depending on net infiltration amounts and the season, which is illustrated in Fig. 2-4 by the positive correlation between leachate volumes and the MIR within individual TL.

This assumption is reinforced by the nearly constant relative sampling drainage volume C_i^{rel} of the different TL throughout the sampling seasons:

$$C_i^{rel} = \frac{C_i}{C_{all}}$$

where C_i is the collection efficiency of the i-th TL and C_{all} is the mean collection efficiency of all TL at sampling date. As an example Fig. 2-5 illustrates the relative collection efficiencies of the different TL for the non-growing season November 2006 to March 2007.
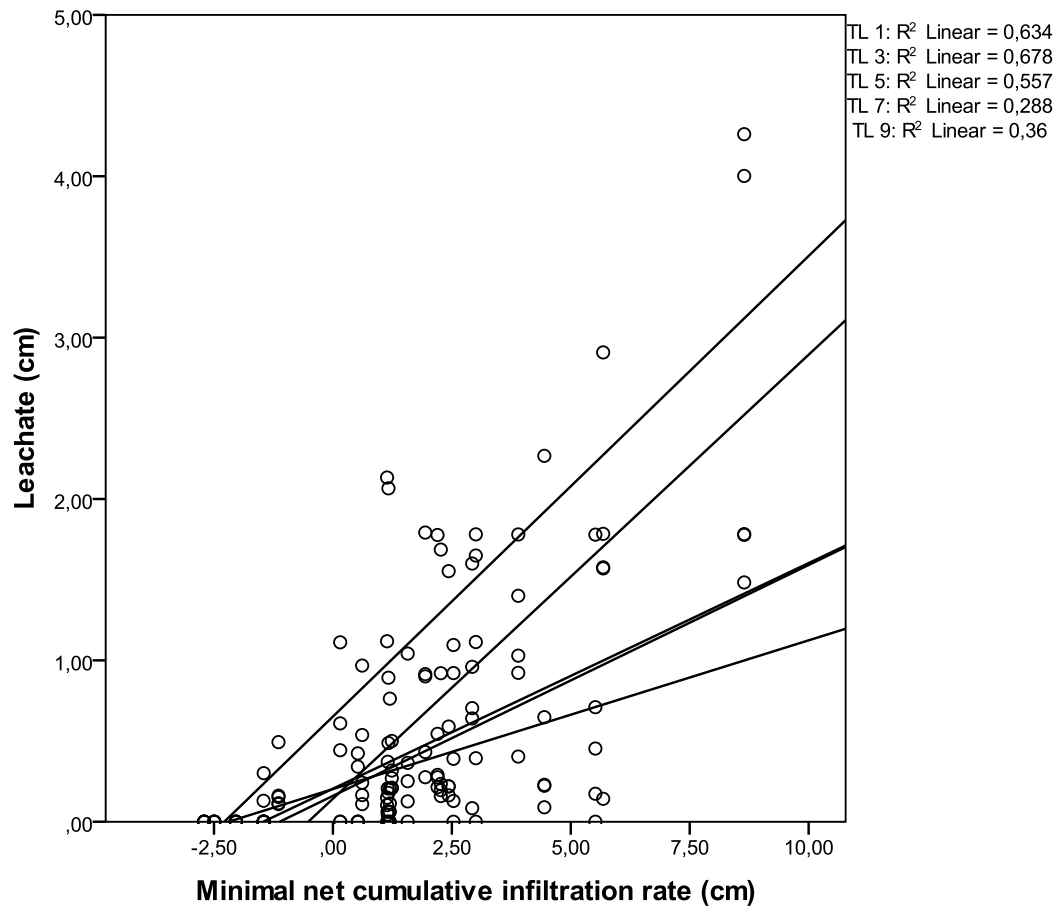
Fig. 2-4: Correlation between MIR and leachate volumes within individual TL
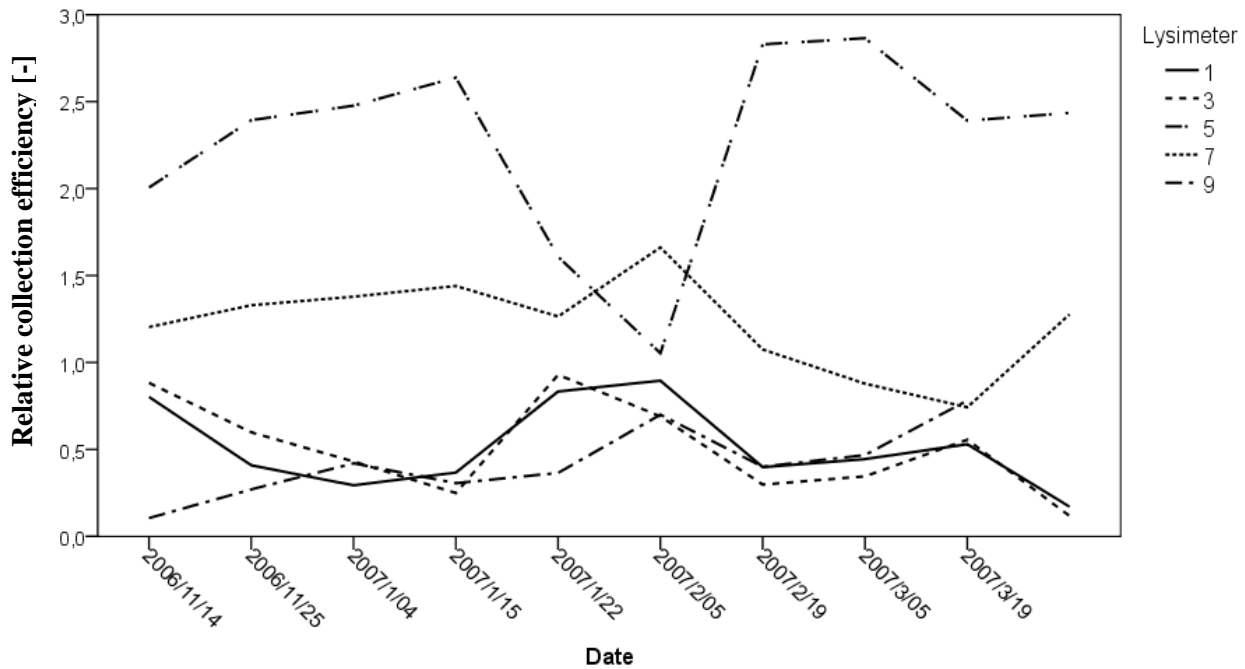
Fig. 2-5: Relative collection efficiency of individual TL in the main study under natural rainfall conditions for the non-growing season

The high correlation of collection efficiencies between the present and the subsequent conduced study supports the hypothesis that the stable performance of individual TL was caused by small scale spatial variable hydraulic properties at the partially water repellent field plots. Furthermore the soil surface microtopography leading lateral redistribution of the infiltrating water from the slightly elevated positions into sinks as suggested by Kasteel et al. (2007), Mertens et al. (2007) or Wessolek et al. (2009) may have also contributed to a different share of preferential pathways and hence heterogenic infiltration pattern above each lysimeter. Small scale spatial variable hydraulic properties may be a result of former infiltration cycles that induced higher water contents in finger pathways. Promoted water flow and finger formation through wetter soil parts has also been observed in other studies (Lennartz et al., 2008; Ohrstrom et al., 2004; Ritsema & Dekker, 1994). Because of hysteresis in the water retention curve, these previous created finger pathways may have recurred and persisted during following infiltration events (Glass et al., 1989). The measured saturated hydraulic conductivity of the topsoil at this site is about 11.5 cm h^{-1} and decreases drastically under unsaturated conditions at pF 1.8 by about three orders of magnitude to approximately 0.1 mm h^{-1} (Taumer, 2007). As a result of the higher saturated hydraulic conductivity in flow fingers it is therefore likely that consecutive infiltration events were preferably transported through the identical flow pathways.

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The predominance of preferential flow paths pattern was also supported by the subsequently conduced Brilliant Blue dye tracer experiment at the identical lysimeter plots. Although the topsoil were previously irrigated with approximately 260 mm of artificial rainwater, which was supposed to be sufficient to induce initial moist soil conditions and to rewet the soil more homogeneously, image analysis of the stained soil areas evidently indicated that the tracer solution was preferentially transported through finger like structures induced by water repellency and the microtopography (chapter 4).

2.5 Conclusion

Water repellency and preferential flow at our test site has been found by (Taumer et al., 2006) and in this study and is well described in literature (Doerr & Thomas, 2000; Dekker et al., 2001) to follow a moisture-related seasonal trend. Preferential flow was particularly relevant during the summer with high evapotranspiration rates causing soil hydrophobicity and hence inducing surface run-off and a decline of the total cross sectional area of water flow, leading to lower collection efficiencies of almost all TL than in the non-growing season. With the beginning of the moist season more flow pathways become hydraulic active, that are reflected here by increased collection efficiencies in almost all TL. However underestimated collection efficiencies compared to the calculated minimal net infiltration rate indicate that water fluxes were preferentially transported throughout the whole sampling period. TL operated as soon as the cumulative water balance at sampling date was positive. In contrast ZT only operated after strong rainfall events (> 38 mm d^{-1}) independently on the season and hence on the soil moisture regime and might be therefore more suitable for the detection of accelerated fluxes through saturated preferential flow pathways. It can be therefore concluded that unsaturated preferential flow is a common phenomenon on this partially water repellent soil, which will not necessarily lead to accelerated water and solute fluxes through the vadose zone under low to moderate rainfall intensities. Only strong rainfall intensities led to the formation of accelerated water and solute fluxes through saturated preferential flow pathways, which can pose a groundwater contamination risk. Moreover the nearly constant relative sampling efficiency of the different TL throughout the measurement indicates that preferential flow path pattern within single sampling seasons at our study site were periodically stable.

3 Performance of zero-tension and tension lysimeters in a water repellent soil - a tracer experiment

3.1 Abstract

Water repellency causes heterogeneities in the hydraulic status and thus can lead to preferential flow of water and solutes in the vadose zone. Up to date the representative water collection from undisturbed heterogeneous soils is an unresolved problem. The aim of our study was to evaluate the collection performance of two area-based collection devices, zero-tension (ZT) and wick (tension) lysimeters (TL) in a water repellent sandy soil at a former sewage site. For this purpose we installed the two lysimeter types with 5 repetitions 35 cm below the soil surface. Each lysimeter had a surface area of 25 x 25 cm. A tracer experiment using chloride under initially dry and initially moist soil conditions was conducted with intense irrigation rates (30 mm h^{-1}), simulating heavy rainfall events. Experimental recoveries of irrigation water and tracer were compared with the results of 2D numerical simulation with homogeneously distributed hydraulic properties.

The early breakthrough of the Cl tracer indicated that water was transported by preferential flow, so that point measurements with suction cups would fail to give representative results. Tension lysimeters performed comparable well under different soil moisture regimes (mean Cl recovery: 67 % and 66 %), while ZT performed satisfactorily only under initially moist conditions (mean Cl recovery: 73 %). Comparison with HYDRUS-2D simulations, indicate that water collection was in both cases enhanced by preferential water flow. Our results indicate that the initial water content controls the degree of the hydraulic gradient in preferential pathways and thus the performance of ZT lysimeters, while the performance of TL is not affected by initial water content.

3.2 Introduction

Spatial heterogeneity of hydraulic properties has been shown to strongly affect solute and water flow, by inducing preferential flow pathways. The importance of soil water repellency in causing preferential flow and its occurrence and implications has been reviewed by several authors (DeBano, 2000; Doerr et al., 2000; Doerr et al., 2007). Water repellency and preferential flow have been found in several studies to follow a moisture-related seasonal trend (Taumer et al., 2006). Several authors reported that soil becomes water repellent when the water content decreases below a certain soil specific critical value (Dekker & Ritsema, 1996; Dekker et al., 2001; Doerr & Thomas, 2000). The reversibility of the

‚hydrophobisation' of soil samples is still a matter of debate. Some studies showed that preferential flow pathways which have been induced by water repellency persisted over weeks, months or years (Buchter et al., 1995; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998; Taumer et al., 2006). Various researchers therefore suggested that intrinsic soil properties may be responsible for the formation of preferential flow pattern (Buchter et al., 1995; Hagedorn & Bundt, 2002; Ciglasch et al., 2005; Lennartz & Kamra, 1998). At our study site, a former sewage farm with large contents of organic matter, water repellency and its spatial and temporal variability results in preferential water and solute transport (Taumer, 2007).

Monitoring soil solutions in soils characterized by preferential flow paths involve methodological problems, because different flow paths with different flow rates and velocities are very difficult to measure and to estimate. Thus interpretation of point measurements e.g. by suction cups without knowing the soil structure and flow paths distribution appears questionable (Gottlein & Manderscheid, 1998; Jury & Flühler, 1992; Netto et al., 1999). The uncertainty of whether soil solution is extracted from stagnant or high-velocity preferential flow paths makes it practically impossible to determine mass-flux rates using suction cups (Hopp et al., 2006; Weihermuller et al., 2007). Contrary to suction cups plate lysimeters with no or small side walls have larger sampling area and may be more adequate for the measurement of mass fluxes in heterogeneous soils (Ciglasch et al., 2005; Weihermuller et al., 2007).

Plate lysimeters have been used since the mid-19th century in a wide variety of soil and environmental studies. They cause no disturbance to the soil directly above it, are low-cost and easy operable devices and require almost no maintenance (Bergstrom, 1990). Plate lysimeters may be distinguished into free-drainage (zero-tension) systems and suction-controlled drainage systems. Main disadvantage of zero-tension lysimeters (here referred to as ZT) is that the soil zone directly above the lysimeter must be water-saturated having a matric head ≥ 0 before water can drain (Barbee & Brown, 1986; BrandiDohrn et al., 1996; Jemison & Fox, 1992). This leads to a large amount of water diverting from the soil above the lysimeter towards the drier surrounding soil (Chiu & Shackelford, 2000; Peters & Durner, 2009; Zhu et al., 2002), so that even large lysimeters may be completely circumvented in homogeneous soils (Peters & Durner, 2009). Solutions to overcome this problem are the introduction of sidewalls or the increase of pan sizes, where the latter is less effective than the former. However, the sidewalls enhance the risk of preferential flow along the walls and both complicate their installation (Mertens et al., 2005; Peters & Durner, 2009; Radulovich &

Sollins, 1987). However since water from unsaturated pores may not be sampled, it is questionable if collected samples are representative (Barbee & Brown, 1986).

Fiberglass wick lysimeters (hereafter referred to as tension lysimeters or short TL) differ from ZT by maintaining a fixed negative matric head at the surface of the plate and thus by collecting water from unsaturated soils, resulting in higher collection efficiencies and more representative soil solute concentrations (Boll et al., 1992). Reported TL and ZT leachate collection efficiencies (measured leachate volume divided by net infiltrated water) vary widely depending on the lysimeter type, soil type, pan size or climatic conditions (Table 3-1 and Table 3-2). Several studies have shown that leachate collection efficiencies of TL are higher than of ZT (Goyne et al., 2000; Zhu et al., 2002).

Table 3-1: Leachate collection efficiencies of fiberglass wick lysimeters
(CV = coefficient of variation)

Number of lysimeter	Experimental duration	Upper boundary condition	Soil texture	Collection efficiency	Authors
32	15 months	natural rain-fed conditions	-	27 % - 41 %	Haines et al. (1982)
2	1 month	rainfall simulation	silty loam	103 %	Boll et al. (1991)
32	2 years	natural rain-fed conditions	loam	66 % to 80 %	BrandiDohrn et al. (1996)
40	-	-	sandy loam	0 % to negligible	Steenhuis et al. (1998)
30	4 years	natural rain-fed conditions	multiple	125 % (CV 36 %)	Louie et al. (2000)
18	4 years	natural rain-fed conditions	silty loam	101 % (CV 28%)	Zhu et al. (2002)
2	≈ 60 days	natural rain-fed conditions	sand	80 %	Gee et al. (2003)
10	1 month	rainfall simulation	sand	70 % to 103 %	Siemens & Kaupenjohann (2004)
4	60 days	natural rain-fed conditions	volcanic clay soils	234 % - 260 %	van der Velde et al. (2005)
18	4 months	natural rain-fed conditions	loam	59 %	Amery et al. (2008)
5	17 months	natural rain-fed conditions	sand	32 % (CV 55 %)	Matranga et. al (2010) (unpublished)

Table 3-2: Leachate collection efficiencies of zero-tension lysimeters
(CV = coefficient of variation)

Number of lysimeter	Experimental duration	Upper boundary condition	Soil texture	Collection efficiency	Authors
32	15 months	natural rain-fed conditions	-	25 % - 82 %	Haines et al. (1982)
96	-	two rainfall storm events	volcanic soil	≈10 %	Russell & Ewel (1985)
varying pan sizes	1 year	natural rain-fed conditions	volcanic soil	10 % - 36 %	Radulovich & Sollins (1987)
2	1 month	rainfall simulation	silty loam	27 %	Boll et al. (1991)
18	3 years	natural rain-fed conditions	silty loam	52 % (CV 43 %)	Jemison & Fox (1992)
	1 month	rainfall simulation	fine-loamy soils	0 % - 55%	Ryan et al. (1998)
18	4 years		silty loam	40 % (CV 26 %)	Zhu et al. (2002)
12 soil columns	-	-	-	99 %	Barzegar et al. (2004)
2	60 days	natural rain-fed conditions	volcanic clay soils	92 % - 129 %	van der Velde et al. (2005)
3 large	5 days	rainfall simulation	silty sand	45 %	Peters & Durner (2009)
1 very large	11 days	rainfall simulation	sand	100 %	Robison (2004)
5	17 months	natural rain-fed conditions	sand	2 % (CV 55 %)	Matranga et. al (2010) (unpublished)

To our knowledge, so far, no research has been conducted that compares the water and solute collection efficiencies of TL and ZT in partially water repellent sandy soils with preferential flow paths. We assume that collection performance of plate lysimeters is dependent on the moisture-related extend of water repellency and hence of the cross section of preferential flow pathways.

In order to evaluate the performance of TL and ZT in a water repellent soil a double tracer experiment using potassium chloride (KCl) was performed. Initially dry and initially moist soil conditions were used to represent the influence of the seasonal climate on the tracer transport at the experimental site, where prolonged dry periods in the summer are followed by a wet period. In order to simulate a worst case scenario of accelerated contaminant transport through preferential flow pathways an irrigation intensity of 30 mm h^{-1}, representing natural occurring strong rainfall events at this site, was applied.

3.3 Material and Methods

3.3.1 Site and soil description

Our study was performed in a 1 m by 7 m field plot located within a former sewage site in Berlin Buch, Germany. Sewage infiltration was practiced for almost 100 years and stopped in 1985. Because the sewage farm consists of different sewage galleries and basins the physico-chemical soil properties have pronounced small scale heterogeneities which are strongly linked to the organic matter contents (Hoffmann, 2002; Schlenther et al., 1996). The vegetation is dominated by dry grasslands (mainly couch grass; syn. Elytrigia repens). The slope of soil surface at the lysimeter plots varies from 3 % to 5 %. The capillary fringe is situated at about 400 cm below the surface.

The soil is classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (30 cm − 40 cm thick) over medium sized homogenous sandy subsoil (sand content 98 %). The bulk density (0.9 g·cm^{-3} to 1.1 g·cm^{-3}) is very low. The saturated hydraulic conductivity ranges from 275 cm d^{-1} in the topsoil to $\approx$ 700 cm d^{-1} in the subsoil (Hoffmann, 2002). The organic matter content of the topsoil is fairly high, ranging from 68 g kg^{1-} to 110 g kg^{1-}. The organic matter content of the subsoil is low (< 17g kg^{-1}).

3.3.2 Lysimeter installation

Ten lysimeter boxes, respectively five ZT and five TL, were installed alternately side by side 30 cm to 40 cm beneath the litter and the Ah horizon. Installation of the lysimeters was performed from a trench 7 m long, 1.2 m wide and 1.2 m deep. Ten 0.4 m long tunnels were excavated vertically from the trench, positioned at a distance of 0.4 m from each other. The lysimeter boxes were then tensioned against the roof of the tunnel using wedges. Subsequently the tunnels were refilled with the excavated soil and the trench was stabilised by a wooden construction. The lysimeter boxes (25 cm by 25 cm by 10 cm-deep) consisted of polycarbonate and contained an inclination at the bottom plate in the direction of the aperture, which was located at the site wall front, in order to drain the percolates from the lysimeters through teflon (PTFE) tubes encased in polyvinylchloride (PVC) tubes into acid washed polyethylene (PE) bottles. Silicone sealant and a black rubber stopper were used to fit the tubes.

ZT were constructed according to Jordan (1968) with little modifications. To prevent soil from collapsing into the lysimeter, each polycarbonate box was filled from the bottom to the top with a stainless steel filter screen, stainless steel perforated plate, a 1 cm deep layer of a

mixture of clean fine (0.06 mm - 0.3 mm, GEBA, Germany) and coarse (0.6 mm - 1.2 mm, DORSILIT, Germany) quartz sand and the native soil.

TL were constructed according to Holder et al. (1991) with little modifications. The wicks employed were round braided fiberglass wicks (no. 1381 from Pepperell Braiding Company, Pepperell, MA), each having a diameter of 14.5 mm and a length of 100 cm. The material was cleaned according to Knutson et al. (1993) by combustion at 400 °C for 4 h in order to remove glue and other organic materials and rinsed afterwards with 0.01 M HNO_3 and distilled–deionised water. The first 20 cm of the fiberglass wicks were separated into single filaments which were spread out on the bottom of the lysimeter boxes. The lysimeter boxes were then filled with the native soil. The wicks extended horizontally along the trench before hanging down vertically above the collection pan. Fiberglas wicks lengths were then adjusted to 60 cm below the lysimeter surface corresponding to a matric head of -60 cm at the top of the wick under unsaturated soil conditions (Knutson & Selker, 1994).

3.3.3 Irrigation simulator

In order to simulate natural rainfall allowing high uniform water and solute application onto small areas an irrigation simulator was constructed. The irrigation simulator consisted of a PVC box (100 cm by 70 cm by 30 cm-deep) containing at the bottom disposable syringe needles (Ø = 0,6 mm and 30 mm long, Braun B. Melsungen AG) placed at a distance of 1 cm apart. The irrigation simulator was levelled at about 0.1 m to 0.2 m above the soil surface. After that artificial rainwater was filled in the box, air in the needles was removed with a pressure device in order to initiate drainage. The irrigation box operated at a rainfall intensity of approximately 30 mm h^{-1}, which corresponds to strong rainfall events measured at the experimental test site. The chemical composition of the artificial rainwater was similar to that of unpolluted rainwater in Germany (51 µmol NH_4NO_3 l^{-1}, 9 µmol $(NH_4)_2SO_4$ l^{-1}, 11 µmol $CaCl_2*2$ H_2O l^{-1}, 1.5 µmol $K_2S_2O_7$ l^{-1}, 4µmol $MgSO_4*7$ H_2O l^{-1} and 12 µmol Na_2SO_4 l^{-1}) corresponding to an electrical conductivity of 23 µS cm^{-1}. The pH was adjusted to 5 with diluted HNO_3.

3.3.4 Tracer experiment

The tracer leaching experiment was conducted during the growing season of 2008. A roof construction at about 1 m above the soil surface was installed one month before the experiment started in order to prevent rainfall infiltration. Initially dry soil conditions of the soil plots were assumed after high evapotranspiration rates in Mai 2008. During that period

the cumulative reference evapotranspiration ETo according to the FAO Penman-Montheith method (Allen, 1998) was about 160 mm. We assume that this dry period was sufficient to dry the top soil to very low water contents. The atmospheric conditions for ETo calculation were obtained from the climate station Berlin Tegel situated 25 km from the test site. Initially moist soil conditions of the second experiment were represented by the soil moisture content at the end of the first experiment, after 129 mm of irrigation water had passed through the 0.3 m - 0.4 m topsoil. This was supposed to be sufficient to reached water contents close to field capacity.

A 14 mm chloride tracer pulse (11.9 g l^{-1}) with an average areal density of 170 g Cl^{-} m^{-2} was applied with the irrigation simulator on each of the 5 plots (0.7 m²) with neighbouring pairs of a TL and ZT in the soil. Chloride tracer in the initially dry soil was leached with three pulses of artificial rainwater (29 mm, 43 mm, and 43 mm). Samples were collected regularly after about every 3 mm of drainage during the first 4 hours after irrigation and thereafter the cumulative drainage was sampled after 24 hours. During drainage sample volume, breakthrough time and electrical conductivity were recorded for a 24 hour time interval before the following pulse was applied. After infiltration the plots were immediately covered with plastic planes in order to prevent soil evaporation and rainfall infiltration.

The second experiment with initially moist conditions was carried out with 5 days of delay from the first experiment. The chloride and rainwater application and sampling procedure in the second experiment was identical to the first experiment.

Cl concentrations were determined with an ion-sensitive Cl electrode (Fa. Ingold) in the laboratory. The background concentration of chloride in the soil solution was approximately 12 mg l^{-1}. Chloride mass fluxes at specific times were calculated for each lysimeter by multiplying the drainage rates with the chloride concentrations. Chloride recoveries (computed as the ratio of the sampled mass to total applied mass) and irrigation water recoveries (computed as the ratio of the measured drainage to total applied irrigation water) were calculated for each lysimeter. The recoveries were not adjusted for changes in soil-water storage above the lysimeter.

3.3.5 Numerical simulation

For simulating water flow a slightly modified version of the HYDRUS-2D software (Simunek et al., 1999), which simulates variably-saturated two dimensional water flows by solving the Richards equation, was used. The unsaturated soil hydraulic properties were characterized by the van Genuchten/Mualem model (Vangenuchten, 1980). The hydraulic parameters were

estimated with the in HYDRUS-2D incorporated Rosetta pedo-transfer function (Schaap & Leij, 1998; Schaap et al., 2001) using measured soil texture and the bulk density data. The saturated hydraulic conductivity (Ks) was adjusted to averaged data measured by Hoffmann (2002) at the test site. The hydraulic parameters were derived for two different soil horizons with the top material representing the Ah horizon above the lysimeter and the C horizon representing the material below the lysimeter (Table 3-3).

Table 3-3: Soil hydraulic properties (van Genuchten [1980]-type parameterization)

Soil	Ks (cm d^{-1})	α (cm^{-1})	n	θs (cm^3 cm^{-3})	θr (cm^3 m^{-3})
Ah horizon	275	0.040	2.966	0.400	0.048
C horizon	694	0.033	3.851	0.385	0.051

The simulation domain was 100 cm wide and 200 cm deep. The lower boundary condition was a unit-gradient type, representing a deep ground water table. Both vertical sides of the flow domain were set up as no-flow boundaries. In the horizontal centre of the flow domain at 0.35 m depth below the soil surface a 0.25 m wide lysimeter was inserted. The 10 cm high and 1 cm wide walls of the lysimeter were set up as no-flow boundaries. The upper surface of the lysimeter was set as a modified seepage face (or lysimeter) boundary condition:

$$q = 0, \qquad \text{for} \quad h_{\text{lys}} < h_{\text{seep}}$$
$$q > 0, \qquad \text{for} \quad h_{\text{lys}} \geq h_{\text{seep}}$$

where q is the boundary flux and h_{lys} is the matric head at the boundary with $h_{\text{seep}} = 0\,\text{cm}$ for the ZT and $h_{\text{seep}} = -60\,\text{cm}$ for TL.

The time variable upper boundary condition was similar to the experimental setup, i.e. high infiltration rates were followed by no flux conditions (representing the covered soil surface). The initial pressure head distribution for the initially dry soil was set to -2000 cm at the top and linear distributed to -60 cm at the bottom of the flow domain. Simulated pressure head distributions at the end of the first experiment were used for the initial condition of the second experiment. The water balance errors were in all simulations $< 0.1\,\%$.

3.3.6 Statistical analysis

Means, standard deviations (SD), analysis of variance and correlations of the normally distributed data (Kolmogorov-Smirnov statistic, Shapiro-Wilk statistic) were computed with

the statistical analysis programme SPSS. Parametric (Independent-Samples T-Test, Paired-Samples T-Test) statistical tests were performed to test for differences in measured chloride recoveries, irrigation water recoveries, initial and total breakthrough time between individual lysimeters and between lysimeter types under initially dry and moist soil conditions. Moreover measured and simulated water fluxes at corresponding depth were tested for significant differences. The probability level (p) of all tests was 95 %.

3.4 Results and Discussion

3.4.1 Irrigation water recovery

Both lysimeter types had comparable irrigation water recoveries TL (mean: 31 %, standard deviation (SD): 16) and ZT (mean: 28 %, SD 19) at elevated soil moisture levels. However at lower initial soil moisture contents TL (mean: 28 %, SD 20) performed significantly better than ZT (14 %, SD 11). These findings are supported by net infiltration water recovered after natural strong rainfall events in the growing and non-growing season in the study performed previously at the same lysimeter plots (chapter 2). Here we found that ZT only collected soil water during strong rainfall events. In all other cases the infiltrated water bypassed ZT. Due to finger flow formation, the high saturated hydraulic conductivity in these sandy soils (275 cm d^{-1}) and the presence of predominantly large pores (25 vol. %) it is unlikely that the soil matrix became saturated during the present study. The prevailing existence of unsaturated conditions was subsequently shown by mean water contents (mass %) after approximately 260 mm of water had been irrigated into the topsoil. Hereby it was found that only half the undisturbed steel cylinder cores sampled above the lysimeter plots reached water contents close to field capacity (pF = $\log_{10}(h$ in cm$)$ = 1.8), whereas in the other plots water contents were only 50 % to 60 % of field capacity (results not shown here).

Although the experimental test site comprises only 7 m², outflow water fluxes within each lysimeter type were highly spatial variable with a coefficient of variation of 55 % in the initially dry and 51 % in the initially field moist soil plots. However, the high spatial variance could be largely attributed to one TL (TL5) which recovered three fold more leachate and to one ZT (ZT8) that almost did not collect leachate (Post-Hoc multiple comparison test). Obviously TL5 was less affected by bypass flow. In addition it cannot be excluded that this lysimeter received runoff from the adjacent soil plots. In contrast surface runoff at the slightly sloping surface above ZT 8 caused that water almost completely ran off at this plot (field observations). Similar low and highly variable mean collection efficiencies (32 % and a SD 24) between the individual TL were observed in the 17 month long field lysimeter study

performed previously under natural rainfall conditions at the same lysimeter plots (chapter 2). Extreme differences in drainage water amounts within one lysimeter type were also observed in other studies (Jemison & Fox, 1992; Kasteel et al., 2007; Mertens et al., 2007; Radulovich & Sollins, 1987).

Irrigation water recoveries between initially dry and initially moist condition within each lysimeter type were significant correlated ($r^2 = 0.817$ for TL and $r^2 = 0.883$ for ZT). Furthermore annual mean collection efficiencies of net infiltrated rainwater recovered by TL in the lysimeter study performed previously were significantly correlated with irrigation water recoveries ($r^2 = 0.893$) in the current experiment. In contrast only net infiltrated rainwater recovered by ZT within one sampling period characterized by strong rainfall events in the lysimeter study performed earlier was significantly correlated to the irrigation water recovered under initially dry conditions in the present experiment ($r^2 = 0.991$). The correlations between water recoveries among subsequent realized experiments support the hypothesis that the preferential flow patterns were stable at the partially water repellent field plots. Furthermore the soil surface microtopography leading to lateral redistribution of the infiltrating water from the slightly elevated positions into sinks as suggested by Kasteel et al. (2007), Mertens et al. (2007) or Wessolek et al. (2009) may have also contributed to a different share of preferential pathways and hence of water fluxes above each lysimeter. This assumption was confirmed by the dye tracer experiment conduced hereafter. Here we reported that the dye coverage on the hydrophobic litter surface was quite low with an average of 61 %, although the dye tracer solution was evenly irrigated on the soil surface and the vegetation was reduced prior to irrigation (chapter 4).

Water repellency and preferential flow has been found by Taumer et al. (2006) at the experimental test site and in our previously conduced study (chapter 2) and is well described in literature (Doerr & Thomas, 2000; Dekker et al., 2001) to follow a moisture-related seasonal trend. Furthermore several authors reported that soil water repellency disappears when the water content increases above a certain critical value, which was found to vary widely for different soils (Dekker & Ritsema, 1996; Doerr & Thomas, 2000; Dekker et al., 2001). Therefore it was expected that in the 3 days after 129 mm of water had infiltrated into the topsoil under initially dry conditions more flow pathways would become hydraulic active and water repellency would decrease, resulting in higher and less variable irrigation water recoveries under initially moist conditions. In contrast post-hoc multiple comparison tests showed that irrigation water recoveries in TL and ZT among the six subsequent irrigation

events, ranging from 21 % to 34 % and 6 % to 34 % , respectively (Fig. 3-1) were not significant different.
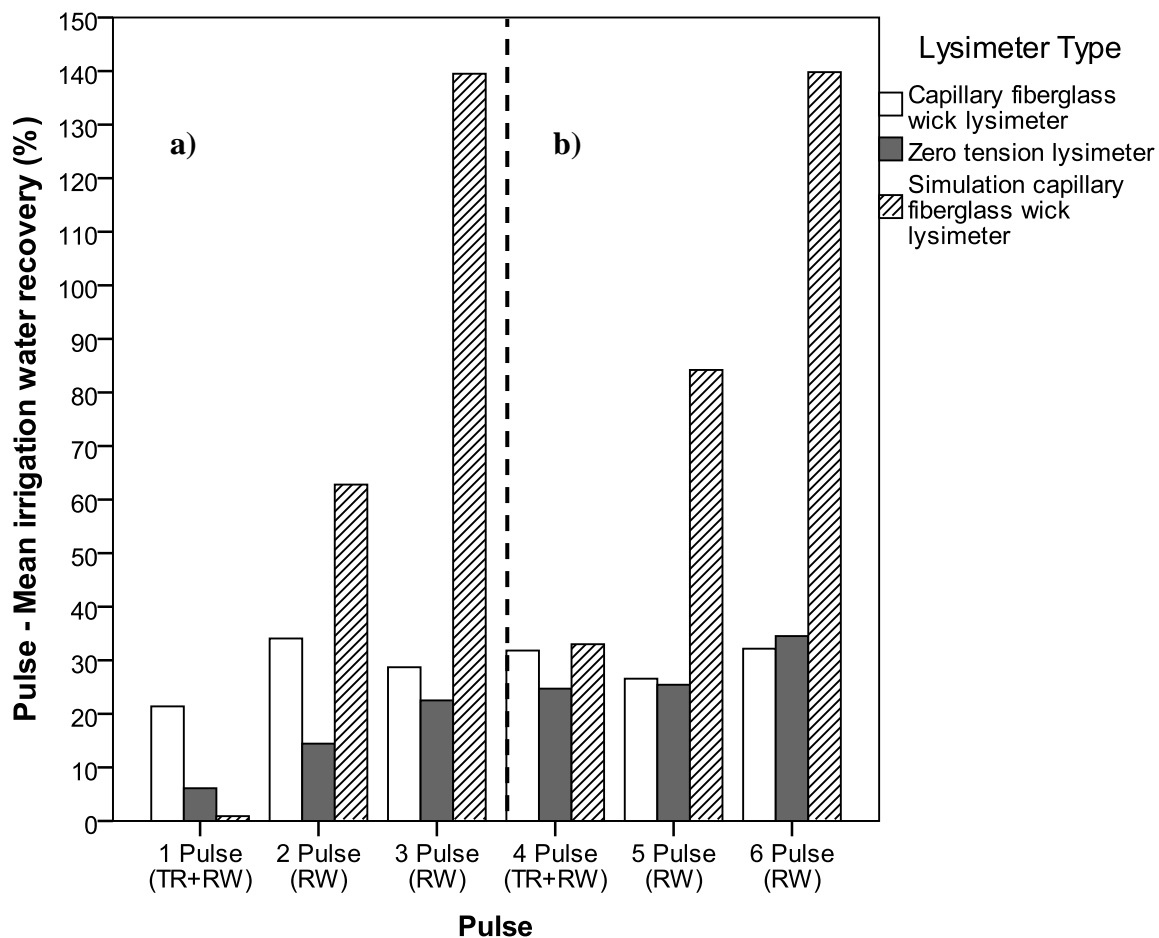

Fig. 3-1 Measured and simulated recovery of irrigation pulses by TL, ZT under initially dry a) and under initially moist b) soil conditions (TR = Tracer Pulse; RW = Rainwater Pulse)

Subsequent irrigation events did not significantly increase drainage rates. Thus, there are no indications for moisture-related changes of water repellency and hence preferential flow path pattern under our experimental conditions. However, the high irrigation intensities used in this example may have promoted by-passing of water repellent areas, while long, steady rains might rewet water repellent soil profiles more uniformly (Gjettermann et al., 1997; Legout et al., 2009; Taumer et al., 2006).

However, our findings are in agreement with former studies showing that preferential flow pathways were persistent over consecutive infiltration cycles, for weeks, months or even years (Buchter et al., 1995; Glass et al., 1988; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998). It is therefore likely that we were not able to eliminate the small scale heterogeneity of the water conductivity, with high evapotranspiration rates in order to induce initially dry soil conditions and with high irrigation rates in order to induce initially moist soil conditions.

Promoted water flow and finger formation through wetter soil parts has also been observed in other studies (Lennartz et al., 2008; Ohrstrom et al., 2004; Ritsema & Dekker, 1994; Kim et al., 2008). Because of hysteresis in the water retention curve, these previous created finger pathways recur and persist during following irrigation events as already described by Glass et al. (1989). The measured saturated hydraulic conductivity of the topsoil in this site is in the range 11.5 cm h^{-1} and decreases drastically under unsaturated conditions at pF 1.8 by about three orders of magnitude to approximately 0.1 mm h^{-1} (Taumer, 2007). As a result of the higher saturated hydraulic conductivity in flow fingers consecutively infiltrated water may be preferably transported through established flow pathways. The persistence of preferential flow pathways using high rainfall intensities (30 mm h^{-1}) and rates (260 mm) at our study site was further confirmed by a dye tracer experiment at these plots (chapter 4). Percentage of the stained soil areas and hence the cross section of flow pathways was only 64 % (SD 18).

Measured breakthrough curves (BTCs) of individual lysimeters showed a similar shape when plotted against time, although cumulative fluxes varied among lysimeters (Fig. 3-2). Lysimeters started to drain on average 1.9 hours (SD 0.8) in TL and 1.5 hours (SD 0.4) in ZT after the irrigation started. Except to one TL (TL1) total water was recovered under both initially dry and moist conditions within an average of 3.8 hours (SD 1.9) in TL and 2.1 hours (SD 1) in ZT after pulse application. The slightly later arrival times of the tracer in TL might be explained by the relatively low hydraulic conductivity of the capillary fiberglass wick of $\approx$ 200 cm d^{-1} at -50 cm pressure head (Knutson & Selker, 1994).

Measured breakthrough curves (as a function of time) differ considerably to the simulated (Fig. 3-2). Only the cumulative drainage recovered by one TL (TL 5) was in the range of that simulated (post-hoc multiple comparison test). In general, simulated water collection curves varied from the measured in that they gradually increase after each pulse of irrigation to peak fluxes.
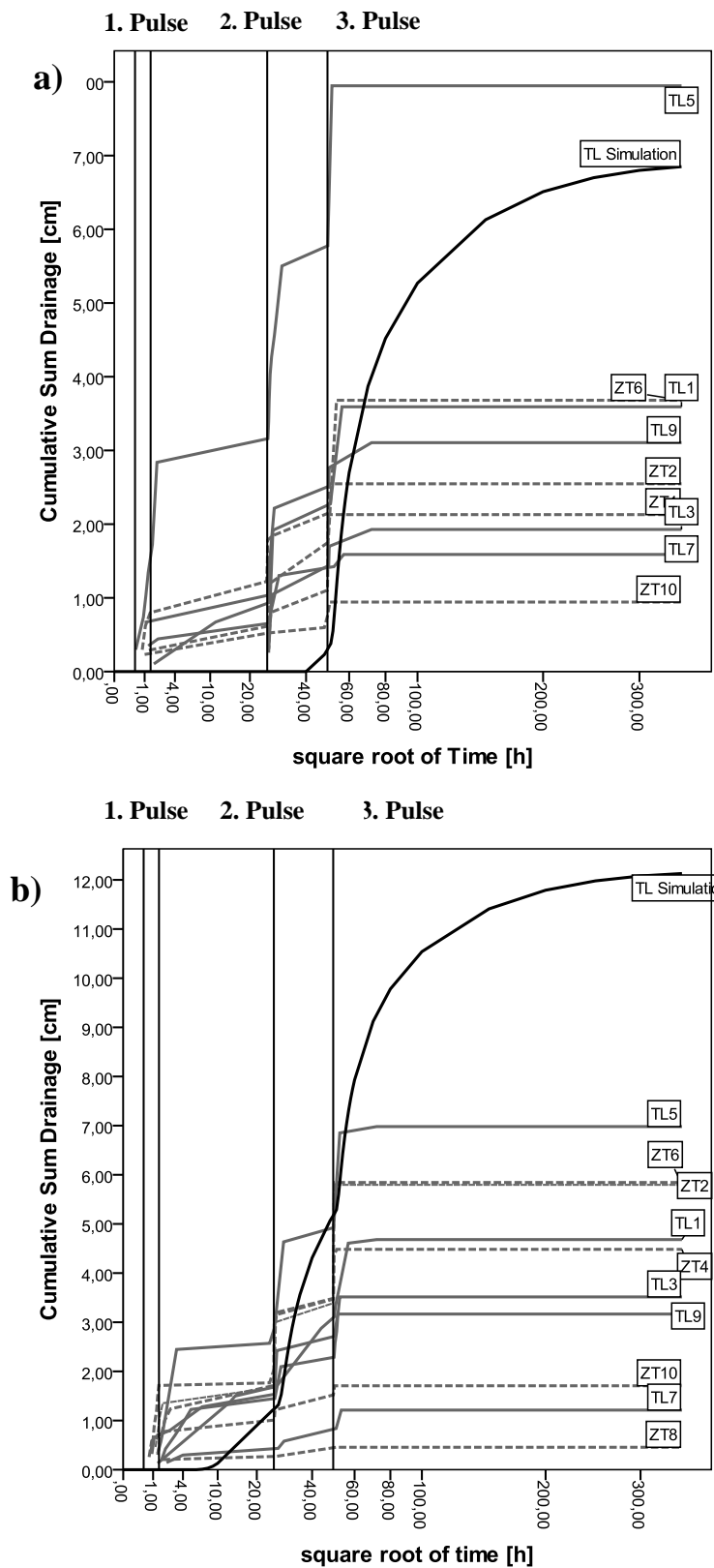
Fig. 3-2: Measured (TL and ZT) and simulated (TL Simulation) cum. drainage water breakthrough curves (cm) after each irrigation pulse as a function of time: under initially dry (a) and initially moist soil conditions (b)

Furthermore, simulated initial water collection assuming uniform matrix flow was highly delayed compared to the measured. Under initially dry and moist conditions first discharge in TL was simulated 48 hours and 7 hours after onset of irrigation, respectively. In contrast short drainage water breakthrough times over consecutive infiltration cycles and the fast increase in leachate volumes after each irrigation event under both initially moist and initially dry conditions again indicate that irrigation water in the field soil was mainly transported through preferential flow pathways at flow velocities comparable to the soil saturated hydraulic conductivity. Hence, a more realistic simulation of water recoveries would need to take the spatial variability of the soil hydraulic properties into account (Peters & Durner, 2009).

Average measured water recoveries of applied in TL under initially dry and initially moist soil conditions (28 % and 30 %) were smaller and statistical different than those predicted (53 % and 94 %) using the Richards equation. The fact that measured mean water fluxes in TL were smaller than predicted fluxes assuming matrix flow indicates that preferential flow bypasses the lysimeter pan surface. However, as a result of the seepage of -60 cm at the TL surface used in the model, higher outflow water fluxes were simulated in the TL compared to those simulated in the adjacent field soil without lysimeter when the soil pressure head increased above -60 hPa. For both ZT scenarios under initially dry and moist soil conditions no seepage fluxes were simulated. In contrast measured water fluxes collected by ZT in the field were almost comparable to those collected by TL. Consequently, an irrigation intensity of 3 cm h^{-1} and a total irrigation mass of 12.9 cm for this highly permeable sandy soil was not sufficient under uniform matrix flow conditions to saturate the soil matrix above the lysimeter pan. This again indicates that water fluxes sampled by ZT in the field were from saturated fingers. ZT may therefore be useful to detect water flow in saturated preferential flow paths in field soils as suggested by Legout et al. (2009) and Peters & Durner (2009).

3.4.2 Tracer - mass recovery

Average chloride mass of total applied chloride recovered by TL in the initially dry soil plots was three fold higher (67 %, SD 54) compared to that recovered by ZT (21 %, SD 16), although this differences were only weak statistical significant (p = 0.095). Average chloride masses recovered by TL (66 %, SD 39) and ZT (73 %, SD 45) in the initially field moist soil plots were comparable (Fig. 3-3).
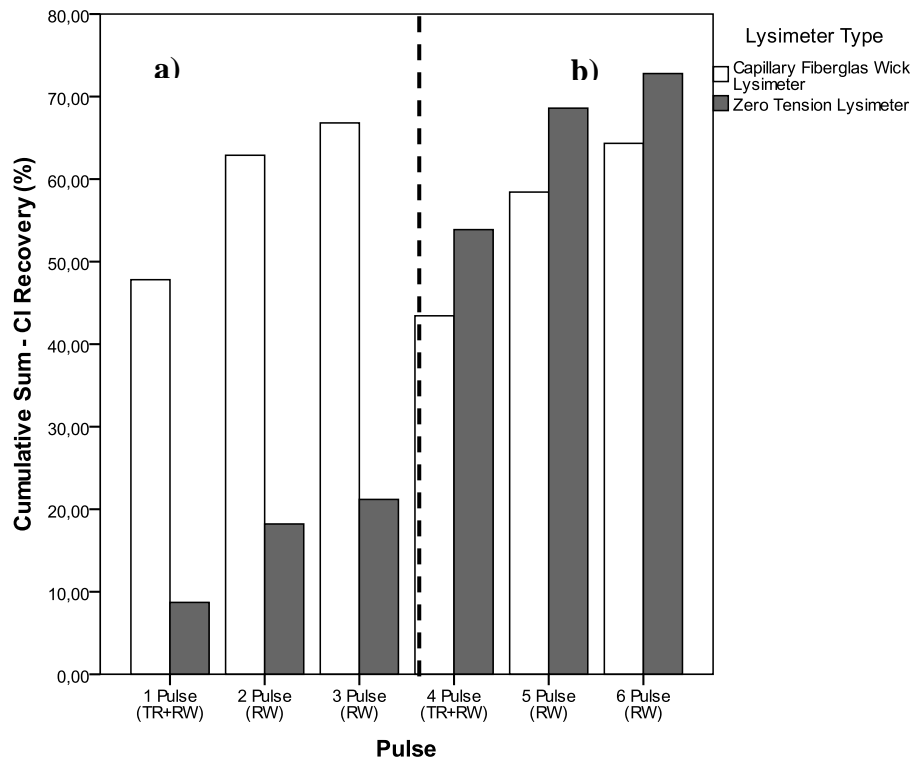
Fig. 3-3: Chloride recoveries with consecutive pulse application by TL and ZT under initially dry a) and initially moist soil b) conditions

While TL and ZT performed comparable well under initially moist soil conditions, ZT worked much better under initially moist conditions, which is in agreement with calculated recoveries of water fluxes and with results obtained by Peranginangin & Steenhuis (2009). We assume that under initially dry soil conditions the tracer pulse application rate (1.4 cm) was not sufficient to saturate the fingers above the ZT. This may cause a bypassing of the ZT pan. Under initially moist conditions increasing water saturation of flow fingers may explain the higher chloride recoveries.

Although chloride peak concentrations among lysimeters were varying, cumulative chloride BTCs showed a similar shape when plotted against time. Except to one TL (TL1) chloride breakthrough curves under both initially dry and moist conditions increased to peak concentrations within only an average of 2.5 h of application. The predominance of preferential transport under both moisture regimes is strengthened by the fact that TL recovered 70 % of total recovered chloride during the first irrigation pulse and that chloride recoveries in two subsequent irrigation cycles were low. Chloride recoveries in ZT under initially dry conditions were low and did not differ among individual leaching cycles. In contrast under initially moist conditions ZT recovered also 74 % of the total recovered chloride during the first pulse of irrigation (Fig. 3-3). Moreover, the first discharge in both

lysimeter types under initially moist conditions originated not from water that was stored in the soil, but from the new incoming chloride tracer solution.

Our findings are in agreement with results from previous studies, indicating that preferential flow accelerates transport of solutes, which are applied to the soil surface due to increased velocities in preferential pathways and may be therefore more dangerous to groundwater (Beven & Germann, 1982; Ciglasch et al., 2005; Hendricks et al., 1993; Jaynes et al., 2001; Ohrstrom et al., 2004; Peranginangin & Steenhuis, 2009; Peters & Durner, 2009; Reichenberger et al., 2002; Steenhuis et al., 1998). This is particularly the case when storm like rainfall events occur, representing a worst case scenario for accelerated contaminant transport (Kim et al., 2008). However, increasing solute transport under preferential flow conditions is only true if the solute (e.g. agrochemicals) enters the soil with the rain water. In contrast the transport of solutes originating from the soil matrix is decreased under preferential flow conditions, as seepage water bypasses a large part of the soil matrix (Kung et al. 2000; Lipsius & Mooney, 2006).

Even though mean Cl mass recoveries were strongly correlated to mean irrigation water recoveries (r^2 = 0.94 for TL, r^2 = 0.79 for ZT), irrigation water recoveries were lower than chloride recoveries (Table 3-4).

Table 3-4: Irrigation water and Cl mass recovery under initially dry and moist soil conditions

Lysimeter Type	Initially dry - Recovery Irrigation Water in %	Initially dry - Recovery Cl in %	Initially moist - Recovery Irrigation Water in %	Initially moist - Recovery Cl in %	Mean Recovery Irrigation Water in %	Mean Recovery Cl in %
TL	28	67	33	66	31	66
ZT	14	26	29	73	21	47
Total	21	49	31	69	26	57

While tracer mass recoveries were in the range of those reported in other studies (BrandiDohrn et al., 1996; Boll et al., 1991; Jemison & Fox, 1992; Siemens & Kaupenjohann, 2004), irrigation water recoveries were slightly lower compared to other studies. Similar discrepancies between water and tracer recoveries have been also reported in a field study realized by Peranginangin & Steenhuis (2009) in a silty clay loam soil. This discrepancy may be induced though lateral redistribution of irrigation water into drier, not mobile soil parts, while it is likely that two fold lower irrigation rates used to apply the tracer solution (1,4 cm) compared to those used to leach the tracer were only sufficient to fill up the macropores in the preferential flow pathways. With the new incoming irrigation water the tracer solution in the

macropores was drained and saturated flow conditions in preferential flow paths became predominant with a considerable amount of irrigation water not recovered due to lateral redistribution into not hydraulic active soil parts. The dominance of lateral redistribution was demonstrated in the dye tracer experiment conduced subsequently at these plots. Here we found that dye stained areas in the Ah horizon were not always vertically connected and that lateral redistribution of the dye tracer solution increased with depth due to a decrease in water repellency (chapter 4).

3.5 Conclusion

Water and Cl BTCs were measured on five organic rich water repellent sandy soil plots, each instrumented with one tension (TL) and one zero-tension lysimeter (ZT) at 0.35 cm soil depth under initially dry and moist soil conditions. Storm like rainfall events were used to leach the tracer. Water and solute recoveries in TL and ZT were highly variable although the experimental test site comprised only 7 m², suggesting that small scale spatial variable hydraulic properties and the soil surface microtopography contributed to a different share of preferential pathways above each lysimeter. We conclude from our results that both lysimeter types are generally well suited to collect water from partly saturated preferential flow pathways when strong rainfall events occur, representing worse case scenarios of accelerated fluxes through preferential flow pathways. However, under dry conditions, TL are favourable devices to collect water from unsaturated flow fingers.

4 Flow paths patterns in a dry and moist partially water repellent soil

4.1 Abstract

Water repellency has been shown to cause preferential transport of water and solutes in the soil. The extent and severity of water repellency is affected by the soil moisture content. Consequently relations between soil moisture contents and the flow path cross sectional area have to be expected.

We investigated the effect of soil moisture contents in a partially water repellent soil on the flow path cross sectional area. For this purpose we performed a dye tracer experiment using Brilliant Blue in three initially moist and two initially dry soil plots. An irrigation intensity of 30 mm h^{-1}, representing natural occurring strong rainfall events at our test site, was used to apply the dye tracer. The horizontal cross sectional area of dye stained areas were analysed using digital image processing.

Results show that regardless on the initial soil moisture condition preferential flow took place, but the flow path cross sectional area under initially moist conditions with 64 % (SD 18) was statistical significantly higher than under initially dry conditions with 40 % (SD 31). Regardless of the pre-moisture status dye coverage increased from the top to the bottom of the Ah horizon most likely due to a reduction in soil water repellency. The high correlation in irrigation water recoveries by lysimeters between the study presented here and that conducted previously indicate further that flow path patterns in partially water repellent sandy soils under high rainfall intensities and rates are persistent and independent on the pre-moisture status of the soil.

4.2 Introduction

Solute and water fluxes in soils and groundwater are greatly affected by spatial variable hydraulic properties of the subsurface. One of the main factors affecting heterogeneous solute transport and water flow in the contaminated organic rich sewage topsoil at our experimental test site has been found to be caused by water repellency and the soil surface microtopography leading to spatially and temporally variable preferential flow path patterns (Taumer, 2007; Wessolek et al., 2009). Water repellency and preferential flow has been found by Taumer et al., 2006) at the experimental test site and is well described in literature to follow a moisture related seasonal trend. Desiccation of the soil during the dry summer induced water repellency and the share of the water repellent spots was above 60 %. During the moist season

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in autumn or winter water repellency often diminished or disappeared and share of the water repellent spots decreased to approximately 10 % (Taumer et al., 2006). Further it was shown that the amount of preferential flow depends on the rainfall intensity. Short intensive rain showers in the desiccated soil tend to trigger preferential flow, while long, steady rains moisten the soil more uniformly (Kohne & Gerke, 2005; Taumer et al., 2006). Several authors reported that soil becomes water repellent when the water content decreases below a certain critical value, which was found to vary widely for different soils (Dekker & Ritsema, 1996; Dekker et al., 2001; Doerr & Thomas, 2000). In contrast various studies showed that preferential flow path pattern induced by water repellency persisted over weeks, months or years (Buchter et al., 1995; DiCarlo et al., 1999; Glass et al., 1988; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998; Wendroth et al., 1999). This was also demonstrated in field studies performed by Taumer et al. (2006) and Wessolek et al. (2009) at the experimental test site, reporting that flow fingers persisted at a particular location until the soil was either completely saturated or desiccated such that the soil water history was eliminated. Various researchers therefore suggested that intrinsic soil properties may be responsible for persistence of preferential flow pattern (Buchter et al., 1995; Ciglasch et al., 2005; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998). The stability of preferential flow pathways at the experimental site was supported by results obtained in two lysimeter studies performed previously (chapter 2 and chapter 3). In the first study under natural rainfall conditions we reported that the effectiveness of collection performance by TL followed a moisture-related trend, but leachate collection efficiencies were underestimated also in the moist season compared to those expected for homogeneous infiltration. In the following study it was further shown that six subsequent storm-like irrigation events did not significantly increase drainage rates sampled by lysimeters and that water fluxes were accelerated compared to matrix flow. Our previous results therefore suggest that water repellency and preferential flow under rainfed conditions and under storm like rainfall conditions persisted during the study time.

Various researchers have demonstrated that preferential flow pathways in the field can be visually accessed by dye tracers (Forrer et al., 2000; Flury et al., 1994; Ghodrati & Jury, 1990; Gjettermann et al., 1997; Hangen et al., 2004; Kramers et al., 2009; Lipsius & Mooney, 2006; Nektarios et al., 2007; Perillo et al., 1999; Yasuda et al., 2001). But in contrast to conservative tracers dye tracers give no information on temporal behaviour of preferential flow (Flury et al., 1994). Using image analysis dye coverage of stained areas in the soil profile can be easily assessed. The dye tracer Brilliant Blue FCF (Color Index 42090) has been

frequently used to visualize flow pathways in vadose zone and was selected in our study because of its low toxicity, good visibility and mobility with respect to other dye tracers (Flury et al., 1994). But because the food dye tracer Brilliant Blue (BB) is sorbed much stronger to the soil than conservative tracers, water flux velocities cannot be predicted (Flury & Fluhler, 1995; Kasteel et al., 2002; Morris et al., 2008). BB retardation was found by Perillo et al., 1998 to increase at slower application rates and at lower BB concentrations. Especially clay minerals were shown in soils to adsorb BB (Morris et al., 2008), while organic matter content was demonstrated to be negatively correlated with sorption (Ketelsen & Meyer-Windel, 1999). It was further reported that sorption of BB to soil material increased with increasing ionic strength and acidity of the background solution (German-Heins & Flury, 2000; Ketelsen & Meyer-Windel, 1999). Advantages and disadvantages of different dye tracers used in the vadose zone hydrology to visualise flow pattern have been reviewed by Allaire et al. (2009).

The objective of our study was to support the results obtained in our previously performed studies with respect to the persistence of preferential flow pathways. Furthermore we want to determinate the influence of the soil moisture regime on the flow path cross sectional area using a dye tracer experiment. Initially dry and initially moist soil conditions were used to evaluate the influence of the seasonal climate on the flow path cross sectional area at the experiment site, were prolonged dry periods in the summer are followed by a wet period. In order to simulate a worst case scenario of accelerated solute transport through preferential flow paths, an irrigation intensity of 30 mm h^{-1} representing natural occurring strong rainfall events was used to apply the tracer.

4.3 Material and Methods

4.3.1 Site description

Our study was performed in a 1 m by 7 m field plot located within a former sewage site in Berlin Buch, Germany. Sewage infiltration was practiced for almost 100 years and stopped in 1985. Because the sewage farm consisted of different sewage galleries and sewage basins the physico-chemical soil parameters had pronounced small scale heterogeneities, which were strongly linked to the organic matter contents (Hoffmann, 2002; Schlenther et al., 1996). The vegetation is dominated by dry grasslands (mainly couch grass; syn. Elytrigia repens). The slope at the lysimeter plots soil surface varied from 3 % to 5 %. The capillary fringe is situated at about 400 cm below the surface. The soil of the plots is classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (30 cm – 40 cm thick) over medium

sized homogenous sandy subsoil. Sand is the dominant textural fraction accounting for about 98 % by mass. Table 2-2 and Table 2-2 show basic physical and chemical soil properties at the experimental test site.

Table 4-1: Basic physical soil properties
(-) not determined, (*) based on Taumer (2007),(**) based on Hoffmann (2002)

Depth [m]	Soil horizon	Texture [%]			Bulk density [g cm^{-3}]	Conductivity [cm d^{-1}]		Air capacity [m^3 m^{-3}]	Porosity [m^3 m^{-3}]	Water content [m^3 m^{-3}]	
		Sand	Silt	Clay		k_s	at 63 hPa			at 63 hPa	15 000 hPa
0.35	Ah	98	1.4	0.6	1	275 **	0.1 *	0.26 **	0.45 **	0.25	0.05 *
> 0.35	C	97.3	2.3	0.4	1.5 *	694 **	-	0.33 **	0.40 **	0.10 *	0.01 *

Table 4-2: Basic chemical soil properties of the Ah horizon
(SD: standard deviation)

	pH (CaCl$_2$) [-]	pH (H$_2$O) [-]	Conductivity [µS cm^{-1}]	Organic Matter [g kg^{-1}]	C [g kg^{-1}]	N [g kg^{-1}]	S [g kg^{-1}]	C/N ratio [-]
Mean	4.4	5.0	197	86.0	44.38	4.40	1.24	10.18
SD	.4	.6	55	2.5	1.05	.12	.045	.65

4.3.2 Irrigation simulator

In order to simulate natural rainfall allowing high uniform water and solute application onto small areas an irrigation simulator was constructed. The irrigation simulator consisted of a PVC box (100 cm by 70 cm by 30 cm-deep) containing at the bottom disposable syringe needles (Ø = 0.6 mm and 30 mm long, Braun B, Melsungen AG) placed at a distance of 1 cm apart. The irrigation simulator was placed at about 0.1 m - 0.2 m above the soil surface. After artificial rainfall was filled in the box and air in the needles was removed with a pressure device in order to initiate drainage. The irrigation box operated at a rainfall intensity of approximately 30 mm h^{-1}, corresponding to measured strong rainfall events at the experimental test site. The chemical composition of the artificial rainwater was similar to the composition of unpolluted rainwater in Germany (51 µmol NH$_4$NO$_3$ l^{-1}, 9 µmol (NH$_4$)$_2$SO$_4$ l^{-1}, 11 µmol CaCl$_2$*2 H$_2$O l^{-1}, 1.5 µmol K$_2$S$_2$O$_7$ l^{-1}, 4µmol MgSO$_4$*7 H$_2$O l^{-1} and 12 µmol Na$_2$SO$_4$ l^{-1}) with an electrical conductivity of 23 µS cm^{-1}. The pH was adjusted to 5 with diluted HNO$_3$.

4.3.3 Brilliant Blue tracer experiment

The dye tracer Brilliant Blue FCF (Color Index 42090) in a concentration of 1 g l^{-1} was irrigated on 5 plots. Each of the plots had a surface area of 0.7 m² and was instrumented with two types of lysimeters, respectively one ZT and one TL, installed at about 35 cm beneath the litter and the Ah horizon. A detailed description of the installation procedure is given in chapter 3. A buffer area around each plot of 0.2 m was maintained. Initially dry and initially moist soil plots received six pulses of artificial rainwater (30 mm h^{-1}) during 11 days corresponding to a cumulative irrigation rate of approximately 260 mm. After pre-irrigation three plots representing initially moist conditions were immediately covered with plastic planes to prevent soil evaporation and rainfall infiltration. Because soil water contents close to field capacity (pF = log$_{10}$(h in cm) = 1.8) in the 0.3 m³ - 0.4 m³ topsoil ranged between 50.2 mm and 112.4 mm, the amount of pre-irrigation (260 mm) was supposed to be sufficient to achieve at least field capacity. In contrast initially dry soil conditions were obtained by roofing of two soil plots with plastic awning for 45 days during the late summer 2008 in order to prevent irrigation infiltration and to promote soil evaporation. During that period the daily reference evapotranspiration ETo according to the FAO Penman-Montheith method (Allen et al., 1998) was calculated by using daily values of air temperatures, relative humidities, wind speeds, atmospheric pressures, psychometric constants and solar radiations from the climate station Berlin Tegel situated at 25 km from the test site. The cumulative evapotranspiration ETo corresponded to about 150 mm, which was supposed to be sufficient to desiccate the topsoil to water contents close to 15000 hPa. The plot surface vegetation was reduced before the tracer application. After onset of the pre-irrigation, the three initially moist soil plots were immediately irrigated with each 14 mm pulse of the BB tracer solution. BB tracer pulse was subsequently leached with one pulse of artificial rainwater (29 mm). This procedure was repeated on the two initially dry plots. After irrigation the plots were immediately covered with plastic planes to prevent soil evaporation and rainfall infiltration. The day after tracer application each plot was excavated from the top into 10 cm deep horizontal sections until a depth of 30 cm to 40 cm using trowels and a ruler with water level. Each horizontal section was photographed with a digital camera (Fujifilm, FinePix S6500 fd). Photographs for each plot were taken within one day. Four reference points at each corner of the plot were used to correct the photographs for geometrical distortion. After photographs have been taken the volumetric water contents at corresponding soil depth from 6 uniformly distributed points were measured with small TDR probes (rod length 41 mm, rod spacing 10 mm, rod diameter 2 mm) and the locations were documented with a second photo. Subsequently soil samples

and undisturbed steel cylinder cores of 100 cm^3 volume at the corresponding points were taken at the same position in consecutive depths. The following described image processing was performed with ArcGIS 9.1 (ESRI Ltd., Redlands, USA). The reference points which had been photographed with the soil horizon were used to georeference the photographs and correct them for their geometrical distortion. Afterwards 10 cm of each site of the digital photos was clipped in order to eliminate random effects. Each pixel was subsequently transformed into polygons (5 mm * 5 mm) and grid values ranging from 0 to 255 for each RGB (red, green and blue) channel were assigned using nearest-neighbour-interpolation. Even though we used a gray scale for each photo we could not correct the photos for uneven illumination as a consequence of the microtopography and the roughness of the surface causing shadowy stains, which may have contributed to potential classification errors. The classification into stained and unstained pixels was realized defining a grid value threshold, yielding into dye coverage maps. Because of ineffective illumination corrections specific threshold values were selected for each photograph. In order to obtain a percentage of the flow path cross sectional areas, the sum of stained classified areas were divided by the total plot area.

4.3.4 Analysis of soil

During the profile excavation five uniformly distributed undisturbed steel cylinder cores of 100 cm^3 volume and soil samples were collected for each 0.1 m horizon layer to a depth of 0.4 m. All samples were sealed in plastic bags and stored at 4 °C. Volumetric water contents, bulk densities, and the water contents at 63 hPa were determined using undisturbed steel cylinder cores of 100 cm^3 volume. Soils samples at corresponding soil depths were analysed for gravimetric water contents, dry mass (at 105 °C), organic matter contents (by loss on ignition at 550 °C during 5 h), organic C, N, S contents with a CNS-Analyser (vario EL, Elementar Analysensysteme GmbH), pH and electrical conductivity.

4.3.5 Statistical analysis

Means, standard deviations (SD), analysis of variance and correlations of the normally distributed data (Kolmogorov-Smirnov statistic, Shapiro-Wilk statistic) were computed with the statistical analysis programme SPSS. Parametric (Independent-Samples T Test, Paired-Samples T-Test) statistical tests were performed in order to test for significant differences in the dye coverage between initially dry and initially moist soil conditions. The probability level (p) of all tests was 95 %.

4.4   Results and Discussion

Fig. 4 1 and Fig. 4 2 illustrate the dye coverage from the litter layer at 0 cm depth to the bottom of the Ah horizon at 30 cm to 40 cm depth in the initially moist (a, b, c) and initially dry soil plots (d, e). The horizons are classified in light (= dry) and bluish (= moist) areas. The image analyses of the stained soil areas evidently indicate that the tracer solution was preferentially transported through finger like structures induced by water repellency and the microtopography. Preferential flow was not a consequence of visible soil features such as root channels. No earthworm activity was recorded due to contaminants loads in the topsoil. Furthermore dye coverage maps show, that dye stained areas from horizontal section to horizontal section were not always vertically connected and indicate that water repellency stimulates the generation of distribution flow as suggested by Ritsema & Dekker (1995) into less water repellent areas. Dye coverage was more evenly distributed in bottom horizontal layers of soil plots (a, b and e), due to a mixture with the non-hydrophobic sandy subsoil.
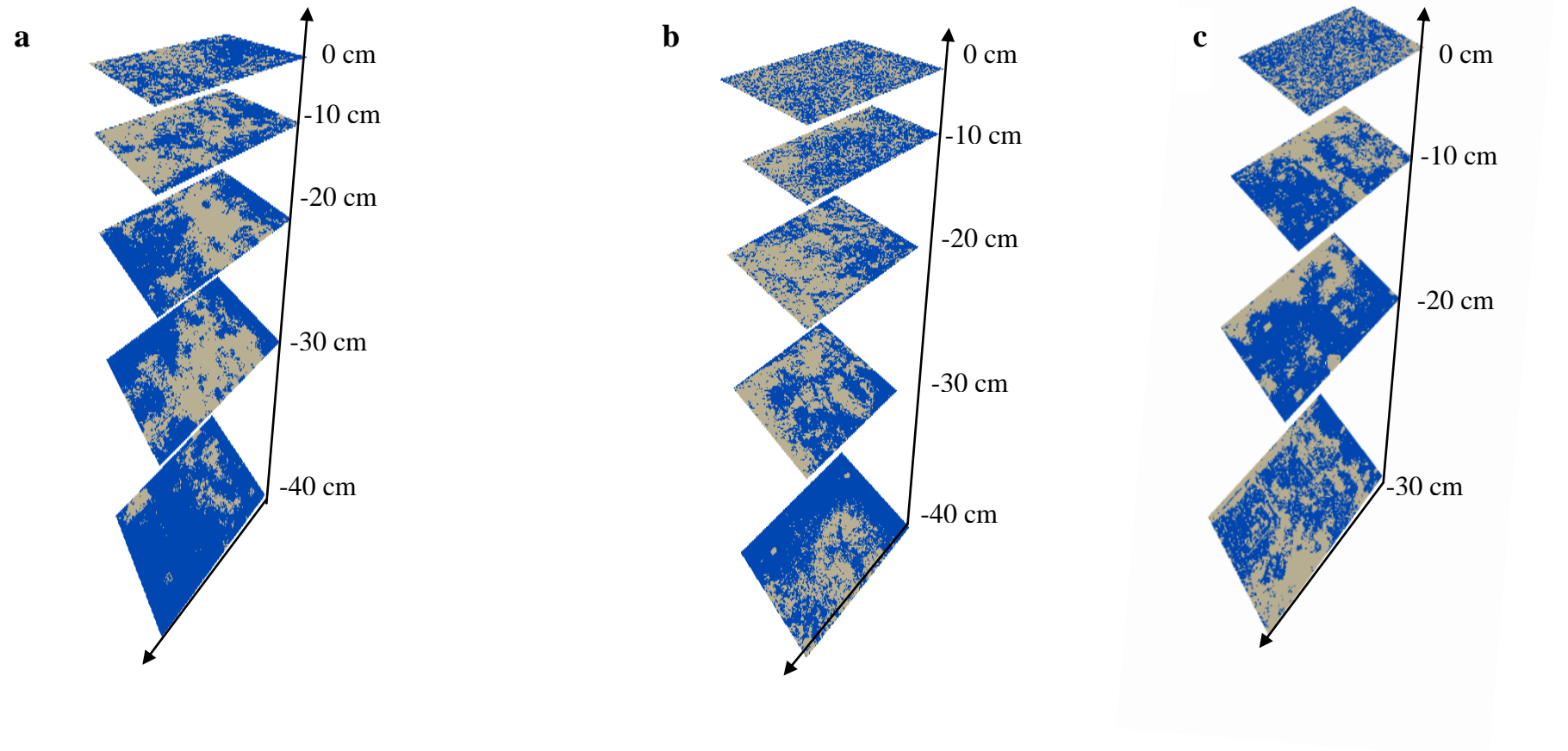
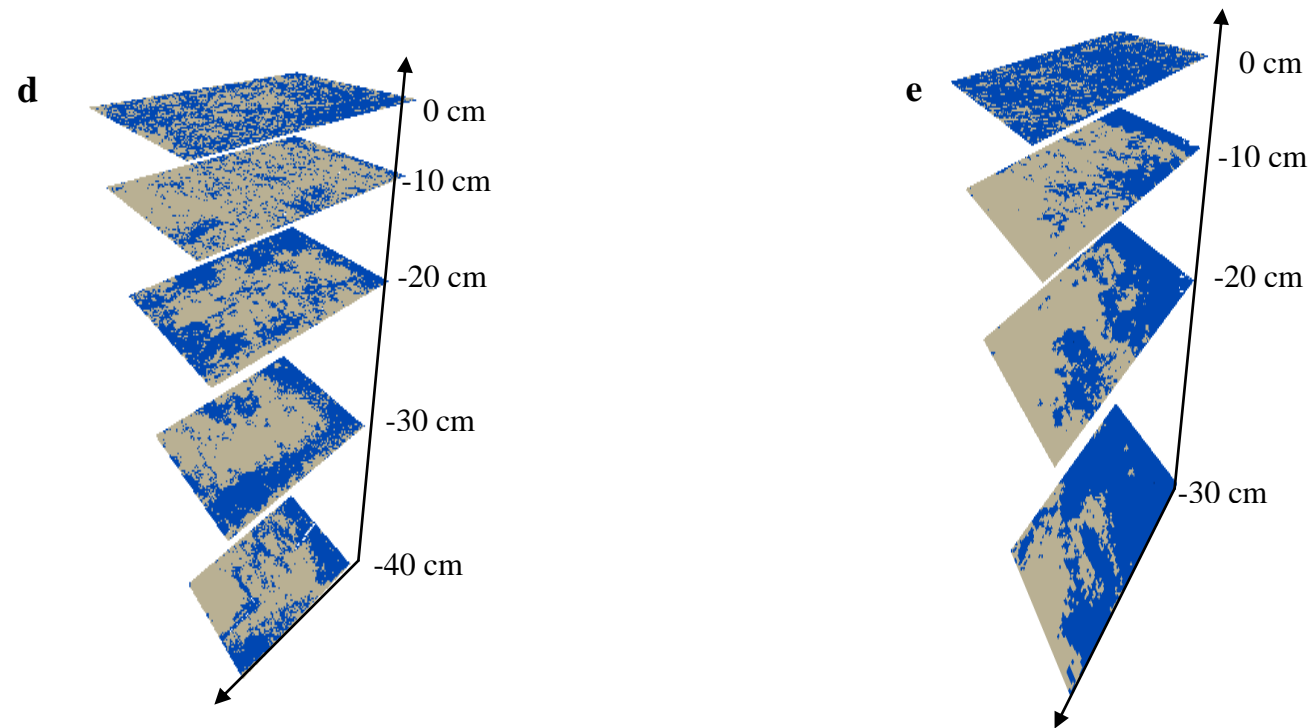Fig. 4-1: Dye coverage from the top to the bottom of the Ah horizon on initially moist soil plots (a, b, c)

Fig. 4-2 : Dye coverage from the top to the bottom of the Ah horizon on initially dry soil plots (d, e)
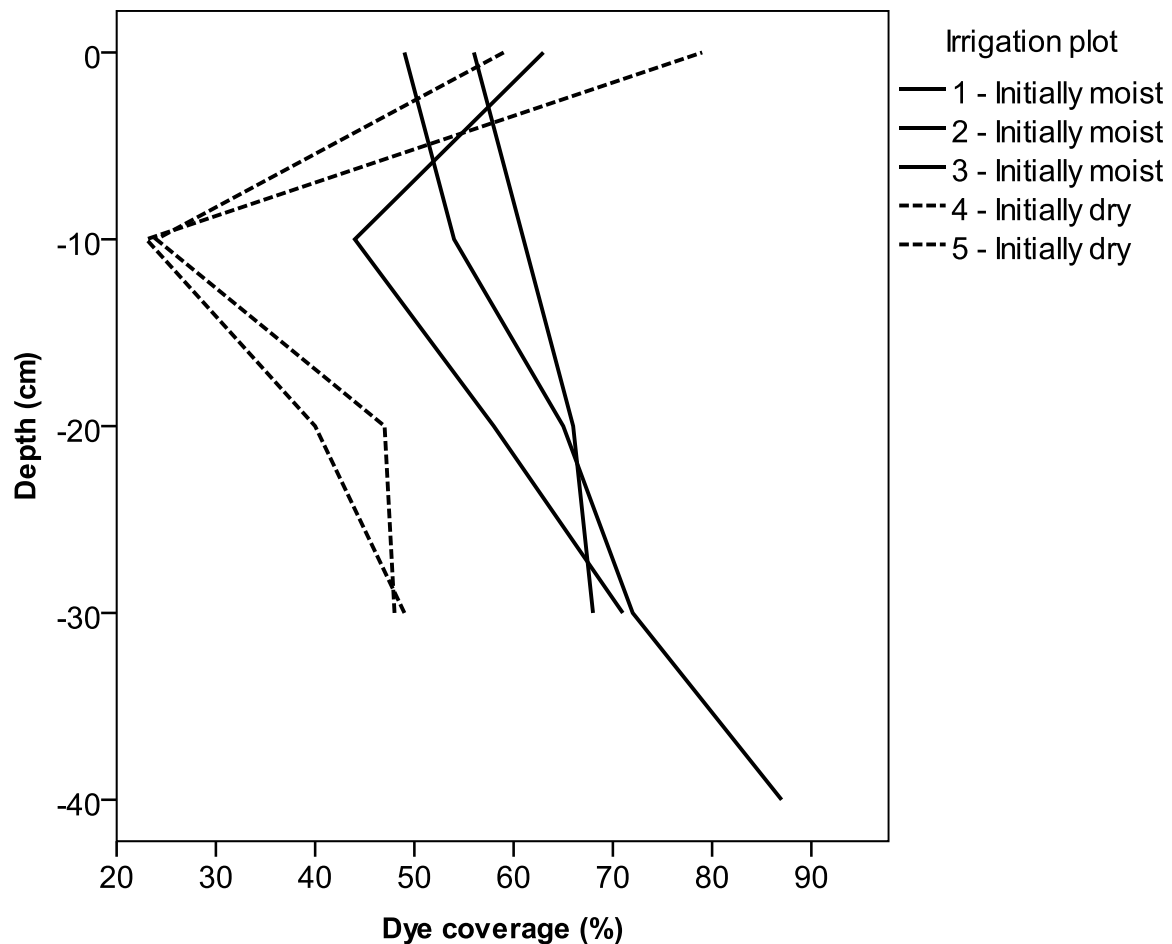
Fig. 4-3: Dye coverage (%) with depth in soil plots

Although the dye tracer solution was evenly irrigated on the soil surface and the vegetation was reduced prior to irrigation, the dye coverage on the litter surface was quite low with a mean of 56 % (SD 7) under initially moist and 69 % (SD 14) under initially dry conditions (Fig. 4-3). The hydrophobic litter layer and the microtopography caused that the tracer solution infiltrated from slightly elevated positions into sinks. Under initially dry conditions a minimum of dye coverage (24 %) was found in 10 cm depths beneath the litter horizon. Mean dye coverage under initially moist condition (64 % and SD 18) was significant higher than the mean dye coverage under initially dry condition (40 % and SD 31). This difference is likely related to dye tracer solution lost via surface run-off under initially dry conditions, which was observed but not quantified. Regardless of the pre-moisture status, the mean dye coverage increased significantly from the horizontal section at 10 cm depth below the soil surface (53 % in initially moist and 24 % in initially dry) to the bottom of the Ah horizon at 30 cm - 40 cm depth below the soil surface (70 % in initially moist and 49 % in initially dry) to 24 % in the initially moist and 51 % in the initially dry plots, respectively. Hence an increase of dye stained areas and finger diameter with depth indicates that the dye tracer was lateral

redistributed into less hydrophobic soil parts as suggested by Lipsius & Mooney (2006) and Ritsema & Dekker (1995). In general the hydrophobic litter-Ah horizon layer was shown to extend to a depth between 10 cm and 20 cm. Although differences in organic matter content between top and the bottom of the Ah horizon were not statistical significant, the organic matter of the hydrophobic litter-Ah horizon layer was mainly composed by partially decomposed plant residues that produce hydrophobic humic substances and waxy materials. Therefore the more widespread and higher cross section of stained areas below the hydrophobic top layer may be related to a reduction in organic matter hydrophobicity and hence in water repellency as suggested by Doerr et al. (2000). In addition the mean soil bulk density of the hydrophobic litter-Ah horizon layer (0.83 g cm³) was significant lower than that of the bottom of the Ah horizon (1.1 g cm³). An increase in bulk density with depth may have increased water holding capacities (Lennartz et al., 2008), although no correlation between water contents and bulk densities could be detected.
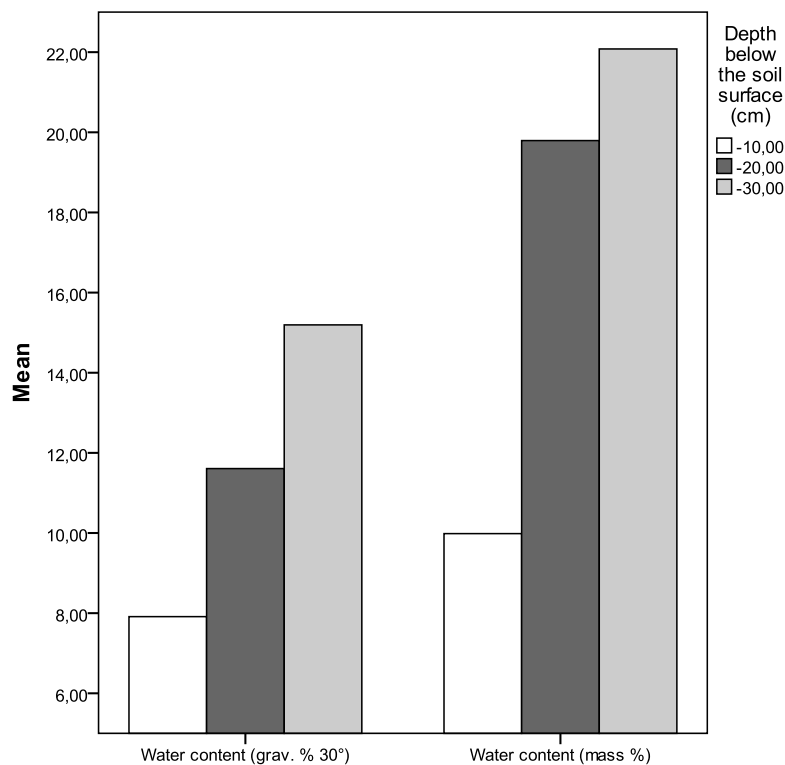

Fig. 4-4: Mean water contents within horizons under initially dry condition

Similar to the dye coverage, mean water contents (grav. % and mass %) of uniformly distributed soil samples under initially dry condition increased significantly with depth from the first horizontal layer at 10 cm depth below the soil surface to the bottom of the Ah horizon (Fig. 4-4), while no significant differences were found for the initially moist plots.

Water fluxes sampled by individual lysimeters were highly spatial variable and were not related to the mean effective transport volume determined from the dye coverage. These findings suggest that although dye tracer solution was lateral redistributed into less hydrophobic soil parts, these soil parts were not hydraulically active. The dye coverage may have therefore overestimated the flow path cross sectional area. The weak link between dye coverage and initial moisture content leads to the assumption that we were not able to induce a complete desiccation in the initially dry or a complete saturation in the initially moist soil plots in order to investigate the seasonal variability in water contents, water repellency and hence preferential flow path distribution sufficiently. Thus soil desiccation with a reference evapotranspiration ETo according to the FAO Penman-Montheith method (Allen et al., 1998) of 150 mm was not sufficient in order to induce initially dry soil conditions within the entire topsoil after the plots had been previously irrigated with approximately 260 mm. Soil water contents measurements revealed that only the litter and the hydrophobic Ah layer up to a depth of maximal 20 cm was desiccated under initially dry conditions. It is therefore likely that soil desiccation below a soil depth of 20 cm in order to induce initially dry conditions failed due to a reduction in soil water uptake by roots and plant transpiration during the end of the growing season (1st August to 15th September). In addition the 10 cm large litter layer may have acted as a buffer reducing potential evaporation from the soil. In contrast the failure in establishing initially moist conditions can be mainly attributed to the high irrigation intensity (30 mm h⁻) used to saturate the soil which may have promoted referential flow in this water repellent soil, while long, steady rains were demonstrated to rewet the soil profile more uniformly (Gjettermann et al., 1997; Kohne & Gerke, 2005; Legout et al., 2009; Taumer et al., 2006). These findings support therefore our results of our previously conduced irrigation water pulse study (chapter 3). Because we used comparable initial conditions with respect to the initial soil moisture contents and irrigation intensities at the same soil plots it allows us to compare these results. The high correlation in irrigation water recoveries by lysimeters between the lysimeter study performed previously and the experiment presented here (TL $r^2 = 0.64$ and ZT $r^2 = 0.55$) demonstrated that we were no able to eliminate the soil water history using high irrigation and evapotranspiration rates in order to induce a spatial shift of flow fingers as suggested by Wessolek et al. (2009), which indicate that flow patterns were stable over consecutive infiltration cycles in undisturbed and permanently vegetated partially water repellent sandy soil under high rainfall intensities and rates (Glass et al., 1989; Dekker & Ritsema, 1996; Lennartz et al., 2008; Ritsema et al., 1998b). The persistence of flow fingers cannot only be related to microtopography and the high irrigation intensity used

in this experiment, but may be also linked to intrinsic soil properties (Buchter et al., 1995; Ciglasch et al., 2005; Hagedorn & Bundt, 2002; Hendrickx et al., 1993; Lennartz & Kamra, 1998), causing small scale differences in the soil hydraulic conductivity. Hence water flow and finger formation was promoted through wetter soil parts as suggested by Lennartz et al. (2008), Ohrstrom et al. (2004) or Ritsema & Dekker (1994). Because of hysteresis in the water retention curve, these previous created finger pathways recurred and persisted during the present study (Taumer et al., 2006; Ritsema et al., 1998a).

4.5 Conclusion

The dye tracer experiment under initially moist and initially dry soil conditions was used to evaluate the moisture related extend and severity of water repellency on the cross sectional area of water flow in an organic rich and sandy topsoil. Results show that we were not able to eliminate the soil water history using high irrigation rates in the initially moist soil plots and high evapotranspiration rates in the initially dry soil plots in order to investigate the moisture related variability in water contents, water repellency and hence preferential flow path distribution sufficiently. Dye pattern of all horizontal sections indicated that preferential flow took place under both moisture regimes, but the flow path cross sectional area under initially moist condition (mean 64 %, SD 18) was significant higher than under initially dry condition (mean 40 %, SD 31). However the weak link between dye coverage and initial soil moisture content suggests that the high irrigation intensity used in this study, promoted referential flow along finger pathways already formed during former infiltration cycles. Dye coverage overestimated the cross sectional areas of water flow, indicating that not all stained areas were hydraulic active. Hence care should be taken when using dye coverage maps to visually access preferential flow pathways in partially water repellent soils.

5 Colloid mobility through capillary fiberglass wicks

5.1 Abstract

Various in situ monitoring techniques are available to collect soil solution from which plate lysimeters are mostly used. While sampling of colloids in soil solutions extracted by zero-tension lysimeter is expected to be unproblematic, capillary fiberglass wicks, which are frequently used in tension lysimeter, may retain colloids by filtration or due to physico-chemical deposition. The aim of our study was therefore to determinate colloid retention by fiberglass wicks in the lab using soil suspensions with high colloidal mass concentrations, representing therefore a worst case scenario of colloid mobility in the field. For this purpose we rinsed soil suspensions, containing various colloidal aggregate types, subsequently through fiberglass wicks.

Fiberglass wicks retained colloids during the first flush, while retention was neglected after repeated rinsing. Discarding the first soil solution sample extracted by fiberglass wicks in lysimeter field studies can therefore minimise the underestimation of colloidal fluxes through the vadose zone.

5.2 Introduction

Contaminant transport toward the groundwater has become a severe problem in the last century. Beside the mobility of truly dissolved contaminants much interest was recently attracted in evaluating colloid-bound contaminant transport in unsaturated soils. Especially the mobility of strongly sorbing contaminants such as low soluble heavy metals and PAHs can be enhanced when they are colloid-bound. In natural environments mobile subsurface colloids occur as a mixture of complex aggregates containing components like aluminosilicate minerals (especially clay minerals), oxides and oxyhydroxides of Fe, Al, and Mn, silica, carbonates, or natural organic matter (NOM). Inorganic colloids are often stabilized by adsorbed natural organic matter (mostly fulvic and humic acids) by both increasing electrostatic repulsion and steric repulsive forces (Kretzschmar et al., 1995; Kretzschmar et al., 1998; Liang & Morgan, 1990; Ryan & Gschwend, 1990; Tiller & Omelia, 1993).

Various in situ monitoring techniques are available to collect soil solution from which plate lysimeters are mostly used. In dependence of the way soil solution is extracted from the soil system two types of lysimeters are distinguished: the free-drainage system and the suction-controlled drainage system. Sampling of colloids, bacteria, and viruses with free-drainage lysimeters is expected to be unproblematic since colloids are not excluded by filtration

(Kaplan et al., 1993; Ilg et al., 2007; Thompson & Scharf, 1994). In contrast fiberglass wick which are frequently used tension lysimeters (Biddle et al., 1995; BrandiDohrn et al., 1996; Holder et al., 1991) may retain colloids by filtration or due to physico-chemical deposition which may lead to an underestimation of colloid-bound transport of contaminants through the vadose zone. Various researchers have analysed colloid retention by fiberglass wicks. Czigany et al. (2005) observed that decreasing flow rate under unsaturated conditions, resulted after bypassing fiberglass wicks in lower recoveries of various types of colloids (feldspathoids, ferrihydrite, montmorrillonite, kaolinite and mixture of colloids). They concluded that colloid retention in the wicks was due to physico-chemical deposition (electrostatic and van der Waals interactions) rather than physical straining in water films because the estimated water film thicknesses were much larger than the colloid diameters. Similarly Shira et al. (2006) reported a considerable retention of negatively charged silica microspheres and ferrihydrite in fiberglass wicks. In contrast Biddle et al. (1995) showed that capillary wick lysimeters have proven successful for collecting representative samples of colloids and do not retard migration of colloids in percolating soil solutions.

For our future lysimeter field study it was therefore of particular interest, if solutions sampled by capillary fiberglass wick lysimeters are representative for the analysis of colloids. In order to quantitatively determine the potential retention of colloids by fiberglass wicks a lab experiment was performed, in which soil suspensions were subsequently rinsed through fiberglass wicks. We used soil suspensions which were generated by mechanical shaking of organic rich sewage soil samples with water. Colloid mass concentrations in soil suspensions used for this experiment were higher than in drainage waters, representing therefore a worst case scenario of colloid retention by fiberglass wicks.

5.3 Material and Methods

5.3.1 Generation and characterisation of the soil suspensions

The soil samples used in our experiment originated from the Ah horizon of an acid hortic anthrosol at our future lysimeter installation site in Berlin Buch, Germany. Sand is the dominant textural fraction accounting for about 98 % by mass. The field-moist soils samples were homogenized and sieved (< 2 mm). Subsequently the soil samples were shaken with deionised water (1:20 dry soil weight to volume ratio) using an end-over-end shaker (GFL 3040) at approximately 12 rpm for 16 h. Colloid-bound plus truly dissolved soil suspension fractions (≤ 1 μm) were obtained by centrifugation (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) at 176 g for 7 min. An aliquot of the supernatants (≤ 1 μm)

were ultracentrifuged at 222194 g for 1.5 h in order to obtain almost truly dissolved suspensions ($\leq$ 10 nm). Colloid-bound plus truly dissolved soil suspensions ($\leq$ 1 µm) were analysed for the average colloid size by dynamic light scattering (HPPS – High Performance Particle Size, Malvern Instruments), zeta potential using a Zetasizer DTS 5200 photon correlation spectrometer (Malvern Instruments), turbidity using a turbidimeter (Hach 2100P ISO), pH and electrical conductivity. In addition both soil suspension fractions (<1 µm and <10 nm) were analysed for dissolved organic carbon concentrations by a total organic carbon analyser (TOC – 5050 A, Shimadzu), for Si, Fe, Al, Ca, Mg, K and Na concentrations by flame atomic absorption spectroscopy (Perkin Elmer 1100 B) and for Pb and Cu concentrations by a Graphite furnace-Atomic Absorption Spectrometer (Varian SpectrAA 880Z). The elemental composition of the colloids was obtained by calculating the difference between the concentrations of both fractions (<1 µm and < 10nm) (Fig. 5-1).

Table 5-1: Soil suspension properties
(-) not determined

	Unit	**Fraction**		
		Total ≤ 1 µm	Dissolved < 10 nm	Colloid-bound >10 nm $- 1$ µm
pH	[-]	5.2	-	-
Turbidity	[FNU]	200	-	
Conductivity	[µS cm^{-1}]	231.5	-	-
Mean Particle Size	[nm]	698.3	-	-
Zetapotential	[mV]	-20.8	-	-
TOC	[mg l^{-1}]	10.36	6.40	3.96
Si	[mg l^{-1}]	4.78	0.50	4.28
Fe	[mg l^{-1}]	3.06	0.04	3.02
Al	[mg l^{-1}]	3.13	2.93	0.09
Ca	[mg l^{-1}]	6.71	5.85	0.86
Mg	[mg l^{-1}]	0.60	0.43	0.18
K	[mg l^{-1}]	1.50	1.08	0.43
Na	[mg l^{-1}]	3.90	0.53	3.38
Pb	[µg l^{-1}]	73.0	2.0	70.5
Cu	[µg l^{-1}]	128.4	44.5	83.9

5.3.2 Testing colloid mobility through capillary fiberglass wicks

We used round braided fiberglass wicks (no. 1381 from Pepperell Braiding Company, Pepperell, MA), each having a diameter of 14.5 mm. Two fiberglass wicks of 1 m length were cleaned using the standard washing procedure by combustion at 400 °C for 4 h in order to remove glue and other organic materials and rinsed afterwards with 0,01 M HNO_3 and distilled–deionised water (Knutson et al., 1993). Soil suspensions (< 1 µm) were parallelly rinsed through two fiberglass wicks for three times (each with one litre per hour). Subsequently fiberglass wicks were rinsed twice with each one litre of distilled–deionised water. Aliquots of the soil suspensions after the flow through the fiberglass wicks were filtrated through a 1 µm glass microfiber filter (Whatman GF 6). Non-filtered soil suspensions before and after the flow through the fiberglass wicks and filtered soil suspensions were analysed for lead and copper by a Graphite furnace-Atomic Absorption Spectrometer (Varian SpectrAA 880Z) and for turbidity using a turbidimeter (Hach 2100P ISO).

5.4 Results and Discussion

5.4.1 Characterisation of the soil suspension

Elemental composition of colloids shows that colloids were mainly composed by organic carbon, Si, Fe and Na, while Ca, K, Mg and Al occurred at minor concentrations (Table 5-1). Colloids occurred as a mixture of complex aggregates containing most likely iron oxides and clay minerals coated by organic C. Although zeta potential was not extraordinarily large (-21 mV) organic coating of the colloids may have increased colloid stability (Kretzschmar et al., 1995; Kretzschmar et al., 1998; Tiller & Omelia, 1993). The moderately high negative surface charge of the colloid and the high turbidity (200 FNU) indicate that the colloids in the suspension were stable and mobile at the given moderately acid pH and at the fairly low salt concentrations (151 mg Salt l^{-1}). Pb in soil suspension occurred almost exclusively colloid-bound, while Cu was up to 65 % colloid-bound.

5.4.2 Colloid mobility through capillary fiberglass wicks

The retention of lead and copper in both fiberglass wicks declined from 20 % to 5 % and from 16 % to 3 % respectively from the first to the third flush with soil suspensions. All of the lead (34 %) and cupper (24 %) retained by the capillary wicks was remobilised after flushing with distilled–deionised water (Fig. 5-1). These results were also reflected by the differences in turbidity before and after the soils suspensions were passed through the fiberglass wicks. Initial turbidity declined to 86 % after the first flush and to 99 % after the third flush. The

reduction in the turbidity indicated that the colloid-bound fraction being mainly retained by fiberglass wicks. Rinsing with distilled–deionised water released almost all retained colloids, which was reflected by the turbidity values in water after bypassing the fiberglass wicks. In contrast Fig. 5-2 shows that filtration through the 1 µm glass microfiber filter caused a slight increase of the lead and cupper concentration up to 9 % ($6µg$ l^{-1} and $19µg$ l^{-1}, respectively) soil suspensions. We can conclude that fiberglass wicks caused retention of colloid-bound copper and lead during the first passage of the soil suspensions which could be neglected after repeated rinsing. Similar results were also obtained in a wick test study performed by Biddle et al. (1995). Discarding the primary soil solution sample collected by fiberglass wick lysimeters in field experiments helps therefore to minimise the risk of colloid retention. Generally there was no evidence of lead and cupper retention by filtration, rather a slight increase, indicating that chemical impurities of glass microfiber filters need to be removed by rinsing with distilled–deionised water before their usage. In addition we demonstrated that centrifugation is an adapted method for the generation of soil suspensions with a specific particle size, because filtration did not diminish Pb and Cu concentrations. However we have to acknowledge that the colloid-bound lead and cupper of the soil suspensions used for this experiment were much higher than they would occur in our field experiments, therefore representing a worst case scenario of colloid mobility. Our findings of colloid retention are in agreement with observations from other authors (Czigany et al., 2005; Shira et al., 2006), although chemical composition of colloids, pH values of solution and flow rates were different. Czigany et al. (2005) concluded that positive edge charges were likely responsible for strong particle deposition and that particles were unlikely removed by straining in water films, because film thicknesses were much larger than the particle diameters. Whether remobilization of colloids after rinsing with distilled–deionised water was consequence of physical perturbations induced by the kinetic energy of water movement or of chemical perturbations induced by a decrease of the ionic strength or an increase in pH of distilled–deionised water could not be determined.
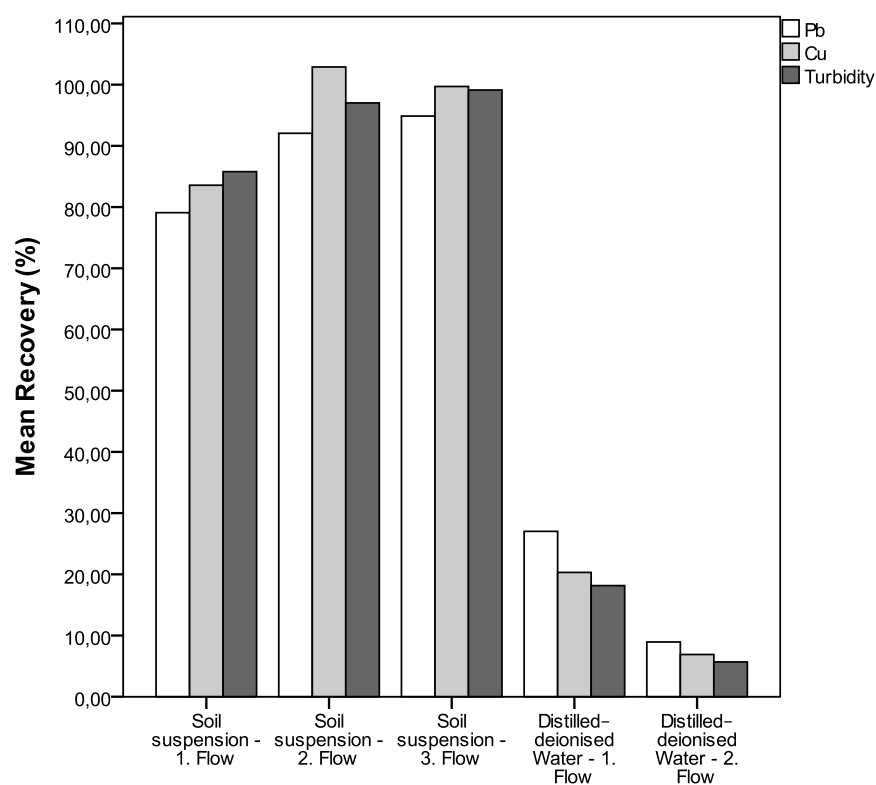
Fig. 5-1: Mean percentual recovery of Pb, Cu and turbidity after rinsing of soil suspensions and distilled–deionised water through the fiberglass wicks
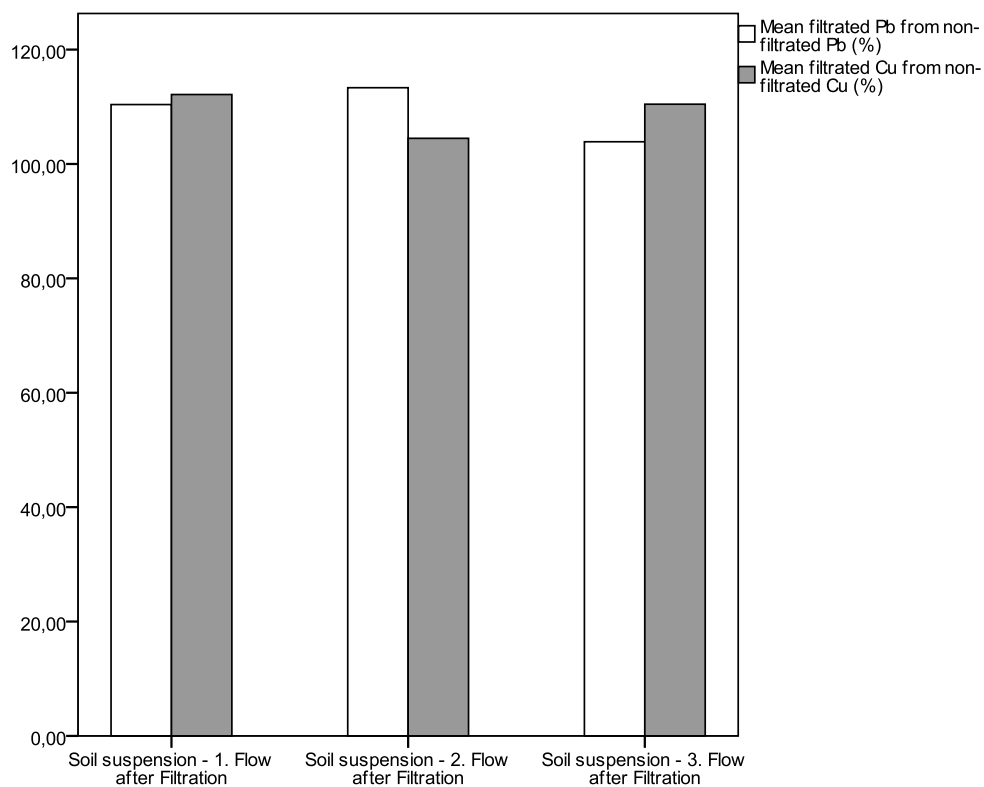

Fig. 5-2: Percentage of filtrated Pb and Cu from non-filtrated Pb and Cu contents in soil suspensions

5.5 Conclusion

For our future lysimeter field study using capillary fiberglass wicks in order to monitor solute fluxes it was of major interest, if sampled solutions after bypassing fiberglass wicks were representative for the analysis of colloids. In order to quantitatively determine the potential retention of colloids by fiberglass wicks a laboratory experiment was performed, in which soil suspensions, generated from organic rich sewage soil samples at our future lysimeter installation site, were subsequently rinsed through fiberglass wicks. Colloidal suspensions contained high colloidal mass concentrations compared to that in drainage water, representing therefore a worst case scenario of colloid retention by fiberglass wicks. Results indicate that fiberglass wicks retained colloids after the first flow of the soil suspensions through the fiberglass wick, while retention could be neglected after repeated rinsing. Discarding the first soil solution extracted by fiberglass wick lysimeters in field experiments helps therefore to minimise the underestimation of colloidal fluxes through the vadose zone. It can be therefore concluded that the capillary fiberglass wick lysimeter is an appropriate in situ monitoring technique to sample different types of colloidal fluxes at our experimental test side.

6 Mobility of colloid-bound and truly dissolved organic carbon, heavy metals and PAHs in a water repellent soil

6.1 Abstract

Heterogeneous preferential flow patterns in partially water repellent soils make the prediction of solute fluxes difficult. Preferential flow may decrease the risk of groundwater contamination, since water repellent and contaminated soil parts are bypassed, or increase it, since hydraulic shear forces may cause a rapid downward transport of colloid-bound contaminants through the vadose zone. The aim of our study was to identify environmental factors which control the transport of dissolved and colloid-bound contaminants in an undisturbed heterogeneous contaminated and water repellent sewage soil. Within the framework of our research we exemplarily analysed the mobility weakly sorbing heavy metals (Cd, Ni and Zn), strongly sorbing heavy metals (Cr, Cu and Pb) and of the hydrophobic organic contaminates (PAHs) in soil solutions collected by five zero-tension and five tension lysimeters at 30 cm - 40 cm depth beneath the litter-Ah horizon for 24 time intervals over a 16-month period.

Our study showed that annual contaminant mass fluxes in soil solutions were strongly positive related to the lysimeter mean collection efficiencies, whereas such a correlation did not exist for the measured contaminant concentrations in soil solutions. This indicates that the transport of contaminants is controlled by the total cross sectional area of water flow. Results hence confirm that temporally persistent preferential flow patterns decrease contaminant mobility, since seepage water bypasses a large part of the polluted soil matrix. Colloid-bound contaminant transport (< 10 %) did not play a major role in the organic rich acid soil (pH 4-5). Hydraulic shear forces through preferential flow pathways after strong rainfall events did not contribute to an increase in colloid-bound contaminant transport. It was further demonstrated that the mobility of the Zn, Ni and Cd was positively related to the soil solution's electrical conductivity. Dissolved organic matter (DOM) contributed significantly to the mobility of Cu and partly to the mobility of Cr. Due to the high sorption affinity to the organic matter no Pb and almost no PAHs were mobilised from the organic rich acid soil.

6.2 Introduction

Former sewage farming at our experimental test site in Berlin Buch, Germany, have resulted in non-uniform and simultaneous sedimentation of heavy metals and PAHs (polycyclic aromatic hydrocarbons) with the solid organic particles in the sewer causing a high spatial

variable distribution of contaminants and organic matter in the topsoil (Hoffmann, 2002; Schlenther et al., 1996) and hence a heterogeneous mobility of contaminants. The transport of water and solutes in this soil is expected to be further controlled by water repellency causing heterogeneous preferential flow path patterns (chapter 2 and chapter 3). Results from previously conduced tracer experiments at the experimental test site gave hints that preferential flow decreases the risk of groundwater contamination, since water repellent soil parts are bypassed.

Because heavy metals and PAHs are mainly bound to the organic matter in the sandy test site soil, their mobility and availability is moreover controlled by their specific distribution characteristic between immobile solid phases, mobile colloidal particles and dissolved species (Bruemmer et al., 1986; Kretzschmar et al., 1999), which in turn are depended on physico-chemical soil and soil solution properties. The main physico-chemical factors affecting heavy metal mobility are the chemical bonding form, pH-value, redox potential, conductivity and ionic strength. The pH value is one of the most important factors affecting heavy metal mobility (Dijkstra et al., 2004; Forstner & Haase, 1998; Yin et al., 2002). In contrast to heavy metals, the mobility of PAHs in the soil is influenced by their chemical structure. Commonly higher molecular weight PAHs (e.g. Benzo(a)pyren) have a higher hydrophobicity and toxicity, a lower solubility and a lower chemical or microbial degradation potential and persist therefore longer in the environment compared to lower molecular weight PAHs (e.g. Naphthalene). Several studies demonstrated that dissolved organic carbon (DOC) and suspended in situ mobilized colloids can facilitate the transport of strongly sorbing contaminants such as Cu, Cr, Pb or PAHS (Citeau et al., 2003; de Jonge et al., 2008; Grolimund et al., 1996; Guggenberger et al., 1994; Impellitteri et al., 2002; Lassen & Carlsen, 1997; Linde et al., 2007; Ponizovsky et al., 2006; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Temminghoff et al., 1997; Weng et al., 2002; Yin et al., 2002). Colloid-bound contaminant transport at the experimental test site is expected to be low due to soil acidity, while hydraulic shear forces through preferential flow pathways may cause colloid release and a rapid downward transport of colloids through the vadose zone, since no physical colloid filtration takes place (Jacobsen et al., 1997; McKay et al., 2000; Mishurov et al., 2008; Pilgrim & Huff, 1983; Ryan et al., 1998; Saiers et al., 1994).

To our knowledge, so far, no research has been conducted that attempts to quantify the impact of water repellency on contaminant fluxes in soil solutions collected by plate lysimeters in a organic rich sandy sewage soil. The aim of our research was to exemplarily analyse the mobility of the weakly sorbing heavy metals Cd, Ni and Zn and of the strong sorbing heavy

metals Cr, Cu and Pb and of PAHs in soil solutions collected by five zero-tension (ZT) and five capillary fiberglas wick (tension) lysimeters (TL) at 30 cm to 40 cm depth beneath the litter-Ah horizon for 24 time intervals over a 16-month period. It was therefore of particular interest if short-term changes of the soil moisture regime and hence in the cross sectional area of preferential flow influences contaminant mobility at the partially water repellent soil. The objective of this study was further to find out whether preferential flow decreases the risk of groundwater contamination, since water repellent soil parts are bypassed, or if it increases, since hydraulic shear forces may cause a rapid downward transport of contaminants through the vadose zone. Moreover we will identify physico-chemical factors which control the contaminant mobility, but also access the role of DOC and colloids in the vertical transfer of contaminants.

6.3 Material and Methods

6.3.1 Site description

Our study was performed between January 2007 and March 2008 in a 1m wide by 7 m long field plot located within a former sewage site in Berlin Buch, Germany. Sewage infiltration was practiced for almost 100 years and stopped in 1985. Because of non-uniform sedimentation of the solid organic particles in the sewer, the physico-chemical soil properties have a high small scale spatial variability. The vegetation is dominated by dry grasslands (mainly couch grass: Elytrigia repens). The soil surface slope at the study site varies from 3 % to 5 %. The first aquifer is situated at about 400 cm below the surface. The mean annual precipitation and temperature (1961 - 1990) for Berlin Buch are 564.3 mm and 8.8 °C (Germany's National Meteorological Service) respectively and the climate is characterised as semihumid to semiarid. The year 2007 can be described as relatively moist and warm, with a mean temperature at Berlin Buch of 10.2 °C and a precipitation of 804 mm. Based on the seasonal climatic characteristics described in chapter 2 and observations already made by Taumer (2007) at the experimental test site the sampling period can be divided into a growing (April 2007 – September 2007) and two non-growing seasons (November 2006 - March 2007 and October 2007 – March 2008).

6.3.2 Experimental setup

In the planning of our study it was not clear which type of lysimeter would be most suitable for monitoring contaminant fluxes at the highly heterogeneous contaminated and water repellent sewage soil. Therefore we installed during November 2006 and April 2008 two

types of lysimeters, respectively five capillary fiberglass wick (tension) lysimeters (TL) and five zero-tension lysimeters (ZT), alternately side by side at 30 cm to 40 cm beneath the litter and the Ah horizon. Here we monitored water flows and 12 chemical properties from 121 soil solution samples taken during 24 collection periods. We chose non-adsorbing materials (fiberglass, polycarbonate, stainless steel and teflon) for the construction of the lysimeters to ensure their suitability for PAHs and heavy metals sampling. In order to remove potential contaminations, lysimeter materials were cleaned with 0.01 M HNO_3 and rinsed after it with distilled-deionised water and air dried prior to their installation. Percolates from the lysimeter polycarbonate boxes (25 cm by 25 cm by 10 cm-deep) were drained through teflon tubes into acid-washed brown glass Duran bottles. A detailed description on the lysimeter construction and their installation is given elsewhere (chapter 3).

Sampling was performed between 2006-11-1 and 2007-8-13 every 1-2 weeks, with the shortest intervals occurring during periods of high precipitation and with the highest interval during dry periods with low or no precipitations. From 2007-8-14 sampling occurred monthly. Each sampling time brown glass bottles with soil solution samples were substituted by empty acid-washed, ultra-sonic cleaned and combusted (300 °C) bottles and the sampled soil solutions were stored (4 °C) in the laboratory prior to analysis. Due to bypass flow of the ZT soil solution volumes were often insufficient to quantify chemical parameters.

6.3.3 Analyses of soil

After the lysimeter study was completed soil samples were taken from three horizon depths (10 cm to 30 cm) above each lysimeter. Composite soils samples above each lysimeter at corresponding soil depths were analysed for organic matter contents (by loss on ignition at 550 °C during 5 h), organic C, N, S contents by a CNS-Analyser (vario EL, Elementar Analysensysteme GmbH), pH and electrical conductivity. Further total soil heavy metal concentrations (Cd, Cu, Pb, Zn, Cr and Ni) were determined on composite samples above each lysimeter after an aqua regia digestion (DIN 38406) by an Atomic Absorption Spectrometer (Perkin Elmer 1100B). A certified reference material (Federal Institute for Materials Research and Testing, BRM#06a, BRM#06b) for the total heavy metal analytic was used for quality control (mean recovery 98 %, standard deviation (SD) 8.4).

6.3.4 Analyses of lysimeter soil solutions

Soil solution samples were analysed for the zeta potential using a Zetasizer DTS 5200 photon correlation spectrometer (Malvern Instruments), average colloid size by dynamic light

scattering (HPPS – High Performance Particle Size, Malvern Instruments), electrical conductivity, pH and turbidity using a turbidimeter (Hach 2100P ISO). Prior to element analysis an aliquot of the stock soil solution samples was ultracentrifuged at 222200 g for 1.5 h at 20 °C (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) and the isolated supernatants were subsequently filtered through a 0.1 μm polycarbonate filter in order to separate the colloidal fraction from the truly dissolved fraction (≤ 10 nm). Acidified percolate samples at pH 4 were analysed for total (original soil solution) and truly dissolved Cd, Cu, Pb, Cr and Ni by a Graphite furnace-Atomic Absorption Spectrometer (Varian SpectrAA 880Z), for total and truly dissolved Zn by flame atomic absorption spectroscopy (Perkin Elmer 1100 B) and for total and truly dissolved organic carbon concentrations (DOC) by a total organic carbon analyser (TOC – 5050 A, Shimadzu).

Total and truly dissolved PAHs were extracted with cyclohexane (500 mL sample, 25 mL solvent each time). Subsequently the organic phase extracts were dried with anhydrous sodium sulphate and concentred to ca. 5 mL by evaporation. Samples were further cleaned with Alox-Silicagel and concentrated to ca.1 mL by evaporation. Total and truly dissolved PAHs were measured with a gaschromotograph (Agilent Technologies GC Model 6890N) which was in turn coupled to an Agilent mass selective detector (Agilent Technologies Model MSD 5973N). A capillary column (DB-5MS, J&W Scientific, Fa. Agilent) with a film thickness of 0.25 μm, an internal diameter of 0.25 mm, and a length of 30 m was used for the PAH analyses. The recovery was determined based on internal standards of 7 deuterium-labelled PAHs added to the samples prior to extraction. The deuterium-labelled internal standard Fluoranthene D10 was added into the vial in order to quantify the exact extract volume. The detection limit was 1 μg l^{-1}. A certified PAH reference material (RTC, No: CRM134-050) was used for quality control (mean recovery 100 %). For the appraisal of PAH contaminations we summarised 16 non-substituted PAH lead substances based on the Environmental Protection Agency (EPA) which are referred as 16 EPA PAH.

6.3.5 Statistical analysis

Determined soil solutions chemical parameters from the first 6 weeks were excluded from the statistical analyses. Means, medians, standard deviations (SD), analysis of variance and correlations were computed with the statistical analysis programme SPSS. Parametric (Independent-Samples T Test, Paired-Samples T Test) and nonparametric (Wilcoxon signed-rank Test, Mann-Whitney U-Test) statistical tests were used because the data were only partly normally distributed (Kolmogorov-Smirnov statistic, Shapiro-Wilk statistic). Statistical tests

were performed to determine temporal and spatial differences in solute concentrations and solute mass fluxes. Chemical and physical soil properties above lysimeter plots were further tested for statistical significant differences. The probability level (p) of all tests was 95 %.

6.4 Results and Discussion

6.4.1 Main soil properties

The soil is classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (20 cm – 35 cm thick) over medium sized homogenous sandy subsoil. Table 6-1 and Table 6-2 show basic physical and chemical soil properties of the experimental test site soil in Berlin, Buch. Organic matter contents were significantly positive correlated to the water contents (mass %) at 63 hPa ($r^2 = 0.543$), electrical conductivities ($r^2 = 0.63$) and the soil pH ($r^2 = 0.51$). The former sewage field was characterised by a strong soil acidification in the topsoil (mean pH = 4.4) and in the subsoil (mean pH = 3.8) as a result of proton release through mineralisation of organic matter in the humus-rich topsoil and reoxidation of metal sulphide in the subsoil, which causes the remobilisation of heavy metals (Hoffmann, 2002).

Table 6-1: Basic physical soil properties at the experimental test site.
(-) not determined, (*) source Taumer (2007), (**) source Hoffmann (2002)

Depth [m]	Soil horizon	Texture [%]			Bulk density [g cm^{-3}]	Conductivity [cm d^{-1}]		air volume [m³/m³]	Porosity [m³/m³]	Water content [m³/m³]	
		Sand	Silt	Clay		k_s	at 63 hPa			at 63 hPa	15 000 hPa
0.35	Ah	98.0	1.4	0.6	1.0	275 **	0.1 *	0.26 **	0.45 **	0.25	0.05 *
> 0.35	C	97.3	2.3	0.4	1.5 *	694 **	-	0.33 **	0.40 **	0.10 *	0.01*

Table 6-2: Basic chemical soil properties of the Ah horizon at the lysimeter plots
(SD: standard deviation)

	pH (CaCl$_2$) [-]	pH (H$_2$O) [-]	Conductivity [µS cm^{-1}]	Organic matter [g kg^{-1}]	C [g kg^{-1}]	N [g kg^{-1}]	S [g kg^{-1}]	C/N ratio [-]
Mean	4.4	5.0	197	86.0	44.38	4.40	1.24	10.18
SD	.4	.6	55	2.5	1.05	.12	.045	.65

6.4.2 Total heavy metals contents in lysimeter soil plots

Heavy metal concentrations and organic matter contents in the topsoil were highly spatial variable (Fig. 6-1), which Hoffmann (2002) and Schlenther et al. (1996) identified as a result

of the sewage farming with nonuniform and simultaneous sedimentation of the pollutants with the solid organic particles in the sewer. Hence total topsoil heavy metal concentrations were highly correlated to the soil organic matter, organic C and organic N contents (Table 6-3). Heavy metals in the sandy topsoil were mainly bounded to the organic matter and were mainly located in the Ah horizon (80 % - 90 %), while the subsoil was characterised by a small sorption capacity for heavy metals (Schlenther et al., 1996). As expected heavy metals concentrations were positive correlated to pH values (CaCl$_2$) due to a higher leachability of the heavy metals in more acid soil plots (Table 6-3).
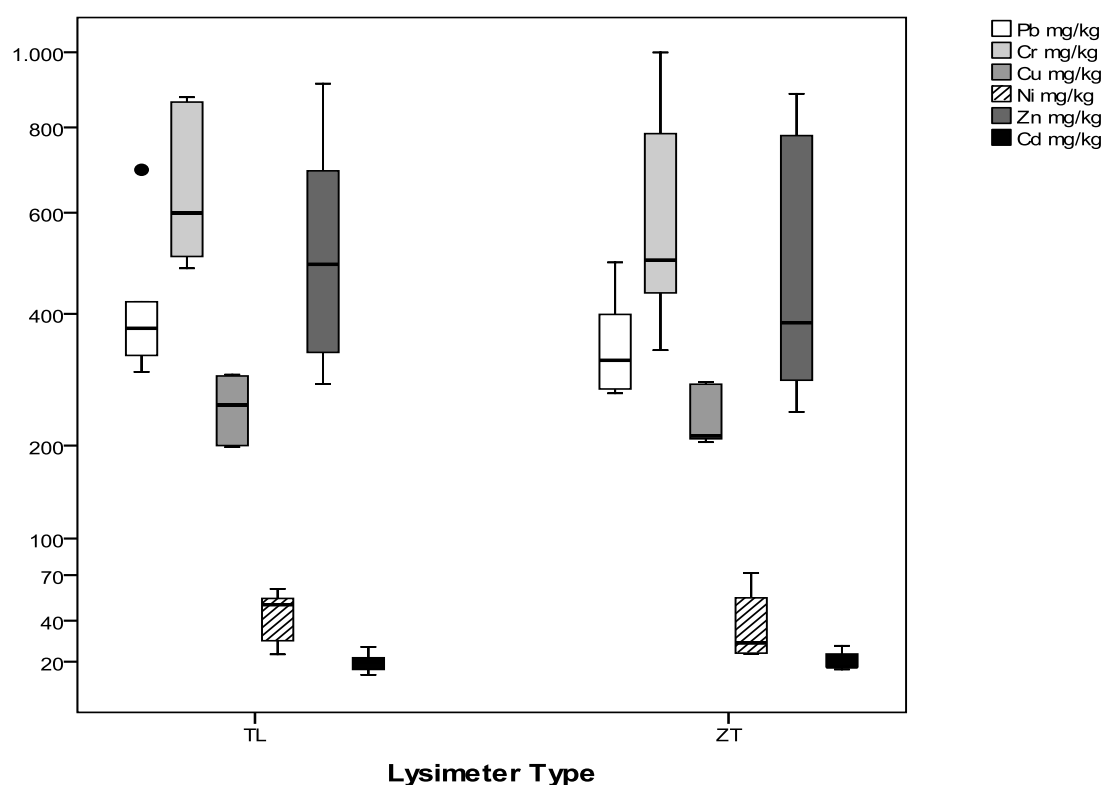
Fig. 6-1: Total heavy metals concentrations in the topsoil above lysimeters

Table 6-3: Pearson's correlation coefficient (r)

	Organic matter [g kg^{-1}]	C [g kg^{-1}]	N [g kg^{-1}]	pH (CaCl$_2$) [-]	Water content at 63 hPA [m³/m³]
Zn (mg kg^{-1})	0.935	0.909	0.872	0.799	0.848
Ni (mg kg^{-1})	0.818	0.893	0.942	0.787	0.860
Cd (mg kg^{-1})	0.380	0.464	0.551	0.704	0.683
Cr (mg kg^{-1})	0.800	0.759	0.725	0.646	0.927
Cu (mg kg^{-1})	0.565	0.632	0.714	0.651	0.767
Pb (mg kg^{-1})	0.818	0.711	0.641	0.504	0.667

6.4.3 Main leachate characteristics

In accordance with the seasonal trend in the climatic water balance and in cross sectional area of water flow at this side reported in chapter 2 and by Taumer (2007) we will examine if the analysed leachate parameters follow a seasonal trend.

Since soil solution samples in contact with the atmosphere releases CO_2, (Elberling & Jakobsen, 2000; Kaupenjohann & David, 1996; Suarez, 1987), the pH value of soil solutions were increased by minimal 0.5 pH units to maximal 2 pH units compared to pH measured in 1:2.5 soil : water suspensions (5, SD 0.6) (Fig. 6-2). Soil solutions pH values were hence not representative and could not be used for evaluation of chemical processes. Increases of almost 2 pH units during the growing season may indicate that high temperatures favoured microbial activity and hence CO_2 production. Due to the high soil porosity (40 %) it is most likely that no reduction reactions took place in the soil. Although seepage water may have accumulated in the bottom of the lysimeters the water saturation threshold values of 60 % for aeration to limit microbial respiration (Gupta & Larson, 1982; Hillel, 1982; Linn & Doran, 1984; Neilson & Pepper, 1990) was most likely not reached.
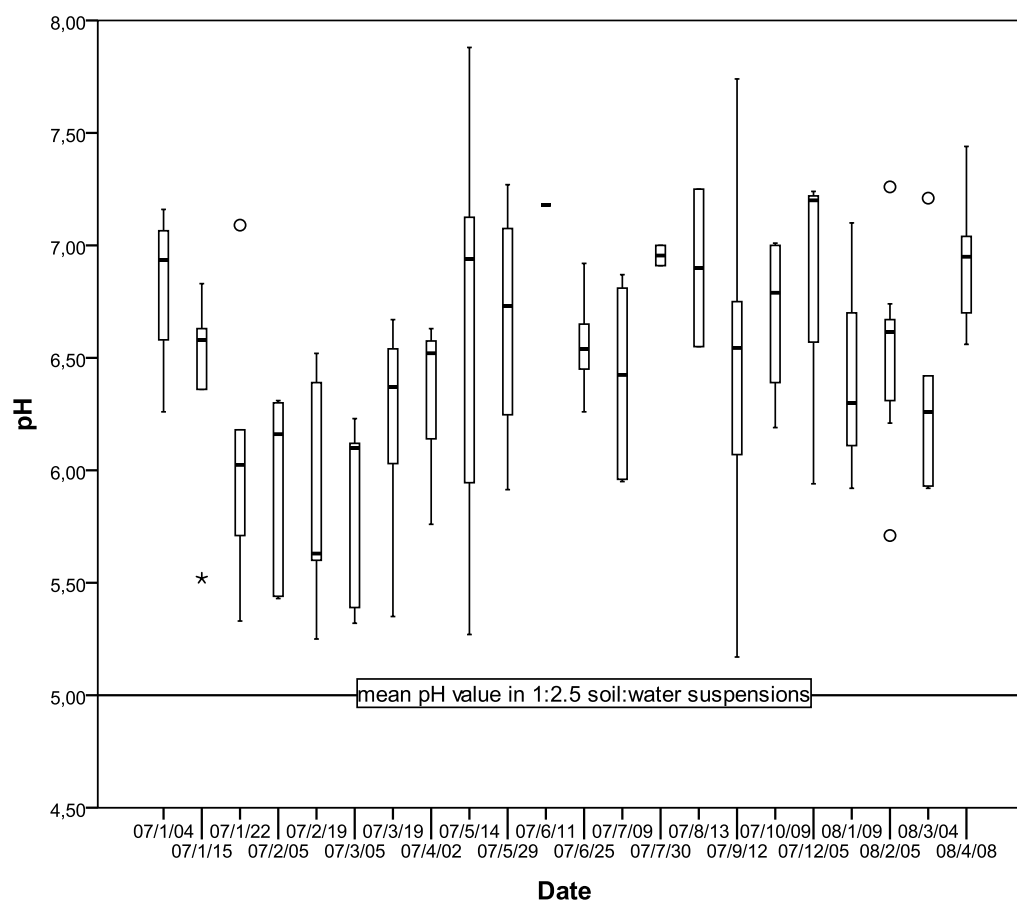
Fig. 6-2: Course of pH in soil solutions collected by TL and ZT

In consequence of higher pH values in soil solution during the growing season the zetapotential was significantly decreased during the growing season (-14.4 mV) compared to the non-growing seasons (-7.6 mV). No significant difference in soil solutions average zetapotential (-11.9 mV, SD 5.4), particle size (1182 nm) and turbidity (4.2 NTU, SD 2.8) between lysimeters were observed. Average electronical conductivities in soil solutions were highly temporal variability (SD 394) with a significant declining trend from beginning to the end of the study (Fig. 6-3).
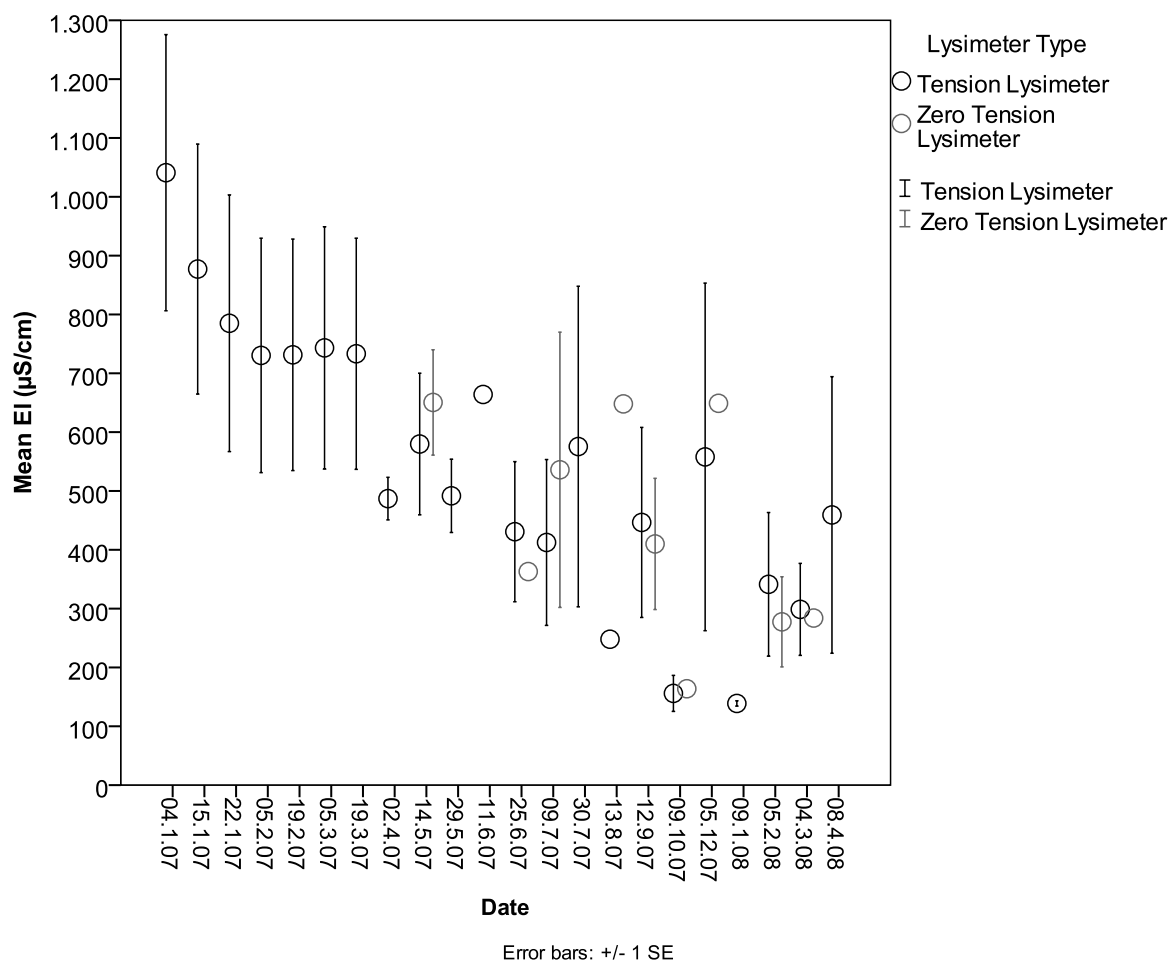
Fig. 6-3: Course of the electronical conductivity ($\mu S\ cm^{-1}$) in soil solutions collected by TL and ZT (error bars represent +/-1 standard error)

6.4.4 DOC mobility

DOC concentrations and mass fluxes were highly dynamic with time and space. Average DOC concentrations in soil solution differ significantly between the lysimeters (34 $\mu g\ l^{-1}$ to 86 mg l^{-1}). Only an average of 1.2 % of the total DOC was colloid-bound mobilised. DOC concentrations in soil solutions showed no significant differences between lysimeter types. ZT only collected soil water during strong rainfall events when water moved preferentially through saturated fingers (chapter 2). It is therefore likely that both lysimeter types during

strong rainfall events collected water fluxes through saturated preferential flow pathways, resulting in the collection of soil solutions with similar concentrations. Average DOC leachate concentrations in the growing season from April 2007 to September 2007 (73 mg l^{-1}) and in the non-growing season from October 2007 to March 2008 (70 mg l^{-1}) were significant higher compared to the non-growing season from January 2007 to March 2007 (45 mg l^{-1}) (Fig. 6-4).
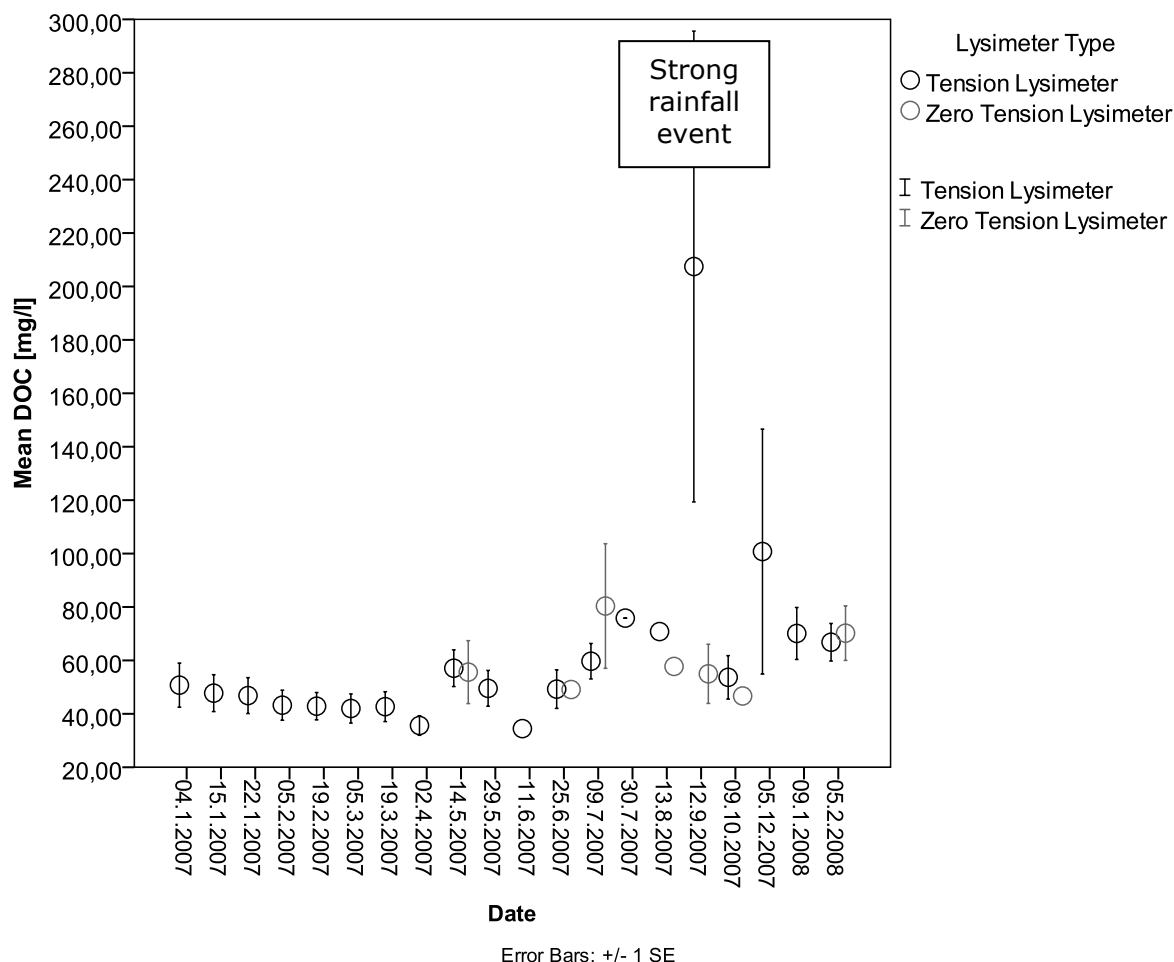
Fig. 6-4: Seasonal course of DOC concentrations (mg l^{-1}) in soil solutions collected by TL and ZT (error bars represent +/-1 standard error)

It is likely that the reduced DOC mobility recorded from January 2007 to March 2007 was caused by significant higher salt concentrations and lower pH values in soil solutions resulting in a increased contraction and precipitation of organic carbon (Andersson et al., 2000; Godde et al., 1996; Guggenberger et al., 1994; Hay et al., 1985; Impellitteri et al., 2002; Jozefaciuk et al., 1996; Karlik, 1995; Shen, 1999; You et al., 1999). It was evident that higher soil solution DOC concentrations during the growing season from April 2007 to September 2007 were caused by the accumulation of organic material followed by strong rainfall events after prolonged dry periods. .The highest DOC concentrations were recorded during a sampling period characterised by the highest recorded rainfall intensities (07/09/12). This

finding supports therefore results of numerous field studies, reporting higher DOC concentrations in soil solution with increasing temperatures due to a higher activity of microorganisms (Buckingham et al., 2008; Dalva & Moore, 1991; Federer & Sticher, 1994; Guggenberger & Zech, 1994; Kaiser et al., 2000; Mcdowell et al., 1998; Scott et al., 1998; Tegen & Dorr, 1996; Tipping et al., 1999) and increased DOC concentrations at the beginning of a rewetting period after dry periods as a result of microbial cell lysis (Chittleborough et al., 1992; Kalbitz & Knappe, 1997; Lundquist et al., 1999; Munch et al., 2002; Tipping et al., 1999; Totsche et al., 2007; Wehrer & Totsche, 2008; Wehrer & Totsche, 2009; Zsolnay et al., 1999).

As sampling time from October 2007 to March 2008 was not accurate enough (once the month), it was not evident if higher DOC concentrations were caused through high humification rates of accumulated litter in the fall (Godde et al., 1996).

Annual DOC mass fluxes during the entire sampling period were positively correlated to lysimeter collection efficiencies ($r^2 = 0.84$), indicating that the DOC fluxes are controlled by the total cross sectional area of water flow. It was shown that DOC annual mass fluxes between TL were not significant different, when they were corrected according to their collection efficiency.

Results indicate further that there was no dilution or increase of DOC concentration induced by high rainfall rates and were therefore in agreement with findings obtained by Mertens et al. (2007) and Reemtsma et al. (1999) demonstrating that release of DOC is independent on the flow rate.

6.4.5 Heavy metals mobility

While average heavy metal soil solution concentrations (Pb, Cr, Cu, Zn, Ni and Cd) between TL and ZT were comparable, annual heavy metal mass fluxes were manifold higher (5-11) in soil solutions collected by TL than by ZT (Fig. 6-5 and Fig. 6-6).

Table 6-4: Concentrations (Conc.) and annual mass fluxes in soil solutions collected by TL and ZT
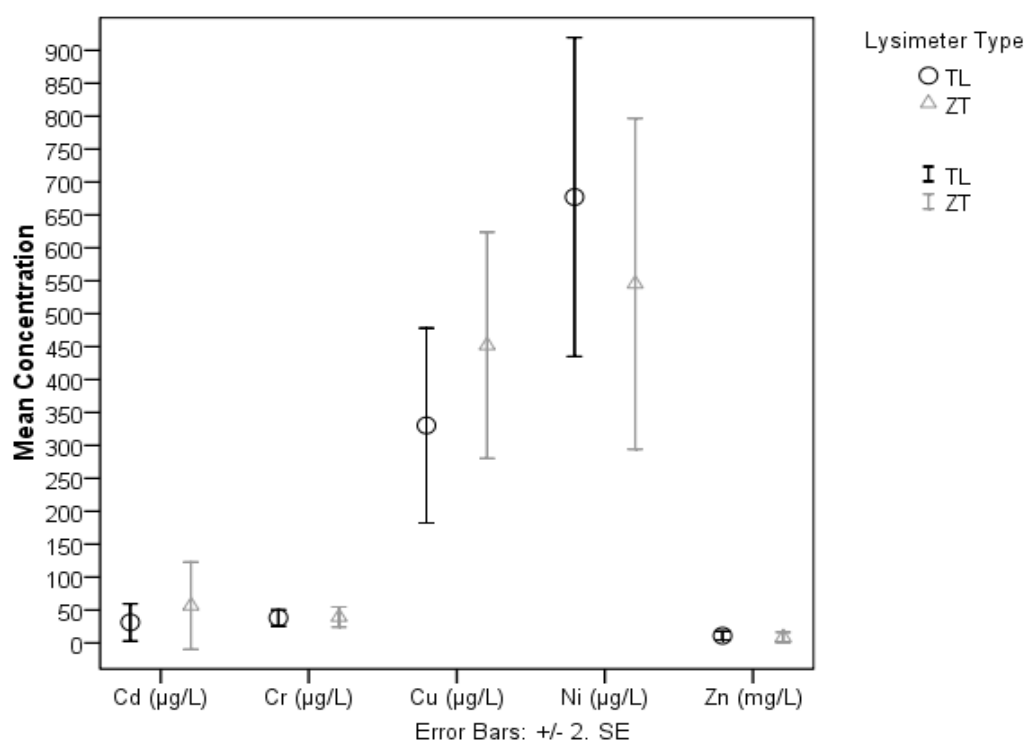
Fig. 6-5: Concentrations in soil solutions collected by tension lysimeter (TL) and zero tension lysimeter (ZT)
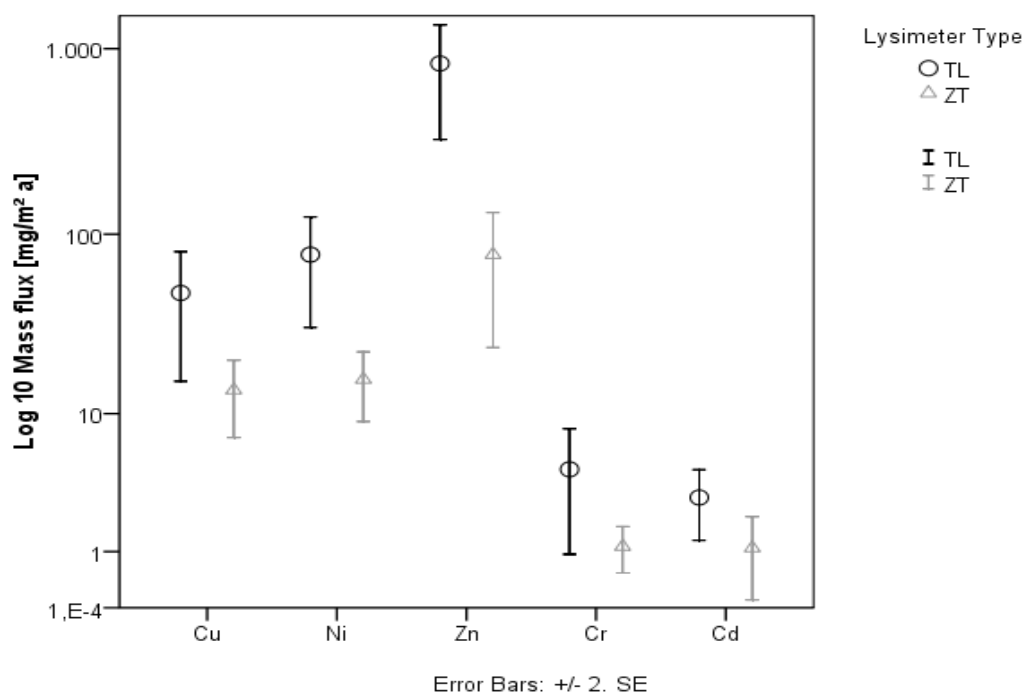

Fig. 6-6: Annual mass fluxes in soil solutions collected by tension lysimeter (TL) and zero tension lysimeter (ZT)

Similarities of heavy metal concentrations in soil solution between the lysimeter types can attributed to the fact that ZT operated only when strong rainfall events occurred, leading to the sampling of accelerated transported soil water through saturated preferential flow paths in both lysimeter types (chapter 2).

As sample volumes of ZT were mostly not sufficient to complete analyses, the following discussion refers to heavy metal mobility in soil solutions collected by TL. In consequence of the different mobility characteristics of sampled heavy metals we will discuss the mobility of the weakly sorbing heavy metals Cd, Ni and Zn and of the strong sorbing heavy metals Cr, Cu and Pb separately.

Mean leachate concentrations of Cd, Zn and Ni were highly temporal variable and declined significantly from the non-growing season January 2007 to March 2007 to the non-growing season October 2007 to March 2008 to 90 %, 80 % and to 50 % respectively (Fig. 6-7).
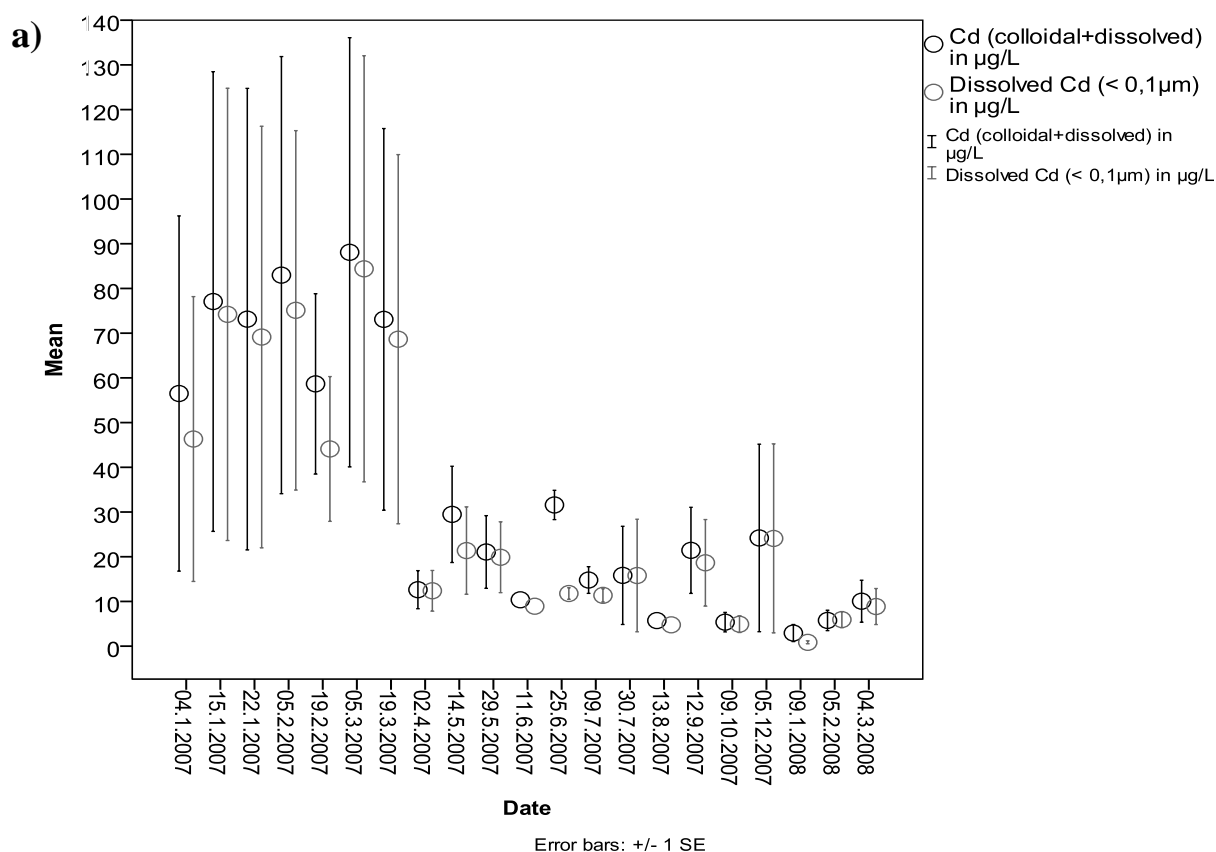
a)
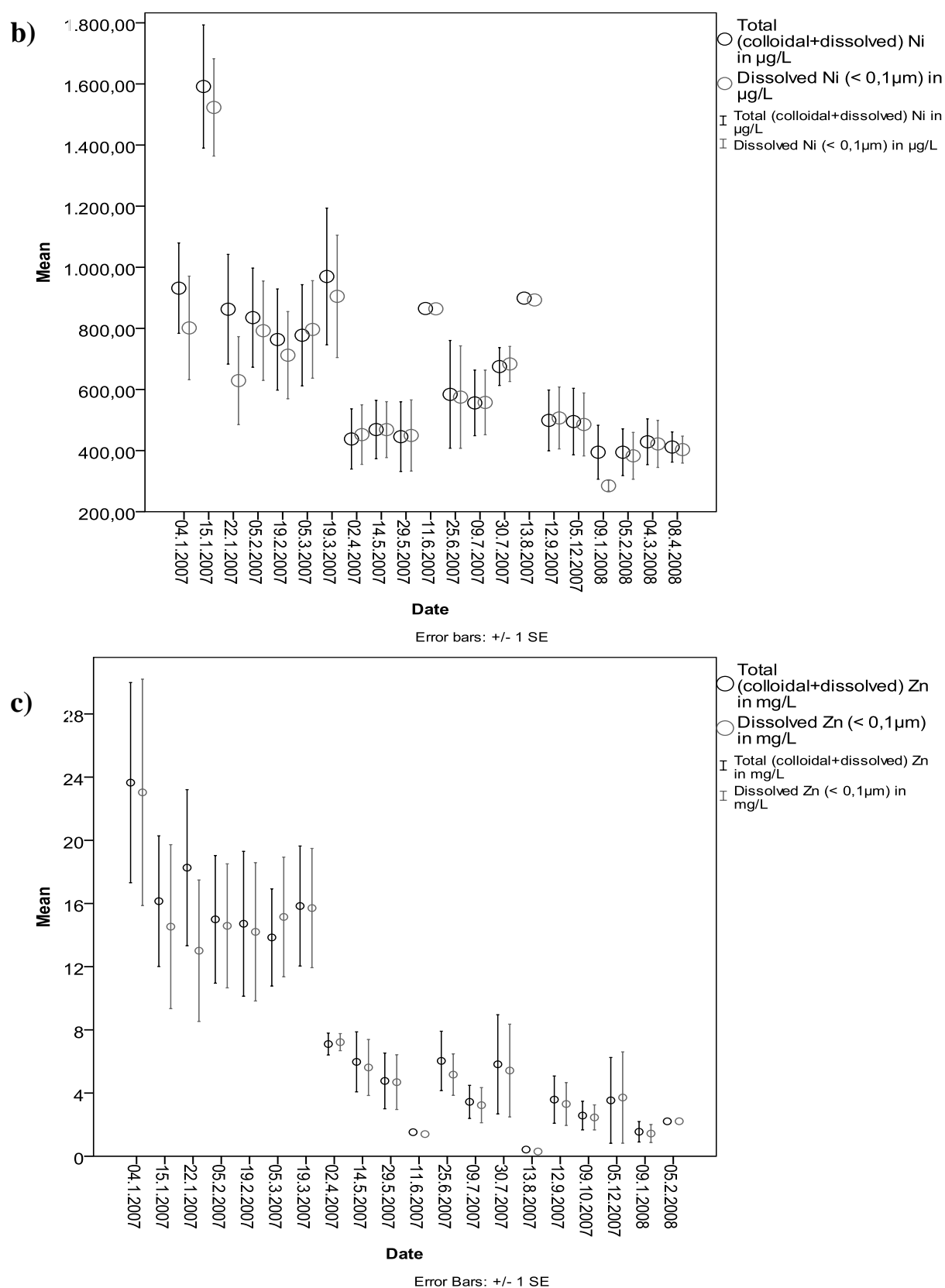
Error bars: +/- 1 SE

Fig. 6-7: Course of Cd (a), Ni (b) and Zn (c) concentrations in soil solutions collected by TL (error bars represent +/-1 standard error)

The similar release patterns for Zn, Ni and Cd were supported by their high correlations (Table 6-5) and were hence in agreement with other studies on heavy metal sorption and transport behaviour in acidic soils (Buchter et al., 1989; Hoffmann, 2002; Voegelin et al., 2001; Denaix et al., 2001).

Table 6-5: Pearson's correlation coefficient (r) between Cd, Ni and Zn concentrations in soil solutions (**the correlation is at the level of 0.01 (two-sided) significant)

	Ni Total [$\mu g \ l^{-1}$]	Zn Total [$mg \ l^{-1}$]
Cd Total [$\mu g \ l^{-1}$]	0.613**	0.786**
Ni Total [$\mu g \ l^{-1}$]		0.768**

Mass fluxes of Ni and Zn were positive related to leachate volumes ($r^2 = 0.605$ and $r^2 = 0.448$), indicating that no dilution effect of the concentrations due to higher infiltration rates was given. Zn, Ni and Cd have a low adsorption affinity to hydroxylated surfaces of Fe, Mn and Al-oxides and to the organic matter compared to the strong sorbing heavy metals and are therefore more influenced by pH and salt concentration alterations. Since the topsoil pH values (4 - 5) were below the element-specific threshold pH values (in brackets) of Cd (6.5), Zn (6.0 - 5.5) and Ni (5.5), they were desorbed from variably charged surfaces by proton competition and were therefore characterised to be very mobile (Scheffer & Schachtsschabel, 2002). The positive correlation between Cd, Ni and Zn concentrations and electrical conductivity ($r^2 = 0.60$, $r^2 = 0.41$ and $r^2 = 0.6$) in soil solutions, indicate that the decline in electrical conductivity from the beginning to the end of the sampling period was mainly responsible for the reduced mobility of the weakly sorbed metals Cd, Zn and Ni. Our results are consistent with other studies, reporting an increased mobility of weakly sorbed metals through high salt concentrations (Backstrom et al., 2004; Linde et al., 2007; Norrstrom & Jacks, 1998; Voegelin et al., 2003). Both non-growing periods were characterised by a similar net rainfall infiltration rates but rainfall was more homogeneous distributed from January to March 2007 (chapter 2). More homogeneous distributed water fluxes may have resulted in longer contact times between pore water and soil matrix and may have contributed to a higher desorption rates of salts and Cd, Zn and Ni. While it is likely that non homogeneous infiltration of low ionic strength rainwater characterised by shorter and stronger rainfalls intensities from October 2007 to March 2008 led to a shorter contact time between pore water and soil matrix resulting in lower desorption rates of Cd, Zn and Ni.

Since the topsoil pH value (4-5) was above the Pb-specific threshold pH value (< 4) almost no Pb (2.3 $\mu g \ l^{-1}$) was mobilised in soil solutions collected by lysimeters. Cr leachate

concentrations significantly varied between the lysimeters (13 µg l^{-1} to 71 µg l^{-1}), representing normal concentration in the slight acid soils and were moderate spatial and temporal variable. The average Cu leachate concentration differed significantly between the lysimeters (137 µg l^{-1} and 899 µg l^{-1}). Cr and Cu concentrations in soil solutions were less temporal variable compared to the more mobile heavy metals. Whereas Cu leachate concentrations showed no significant seasonal trend with a average concentration of 311 µg l^{-1} and a variation coefficient (VC) of 0.07, average Cr concentrations in the non-growing season from October 2007 to March 2008 (43 µg l^{-1}) were significantly increased by almost 50 % (Fig. 6-8). The similarity in Cr and Cu mobility behaviour was confirmed by their correlation ($r^2 = 0.5$). In addition the fairly high correlation between the leachate volume and the Cr ($r^2 = 0.83$) and Cu mass fluxes ($r^2 = 0.86$) indicated that no dilution effect of the chemical properties due to higher infiltration rates was given.

Cr, Cu and Pb have a high sorption affinity to the organic matter (both solid and dissolved). Their solubility and mobility can therefore either be reduced by binding to soil humic matter or increased by binding to soluble organic acids (Bergkvist et al., 1989). The high sorption affinity of Cu to organic matter is furthermore demonstrated by the positive correlation between the average Cu mass fluxes and the soil organic matter contents ($r^2=0.863$). Generally, it has been found that Cu and DOC concentrations were positive correlated (Fig. 6-9) and it is therefore likely that DOC contributed significantly to the mobility of Cu through complexation reactions, as indicated in other studies (Impellitteri et al., 2002; Linde et al., 2007; Olsson et al., 2007; Ponizovsky et al., 2006; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Temminghoff et al., 1997; Weng et al., 2002; Yin et al., 2002). An unexpected low correlation between Cr and DOC concentration was found ($r^2 = 32$), although many studies observed that that Cr is almost entirely complexed by DOC (Guggenberger et al., 1994; Linde et al., 2007).
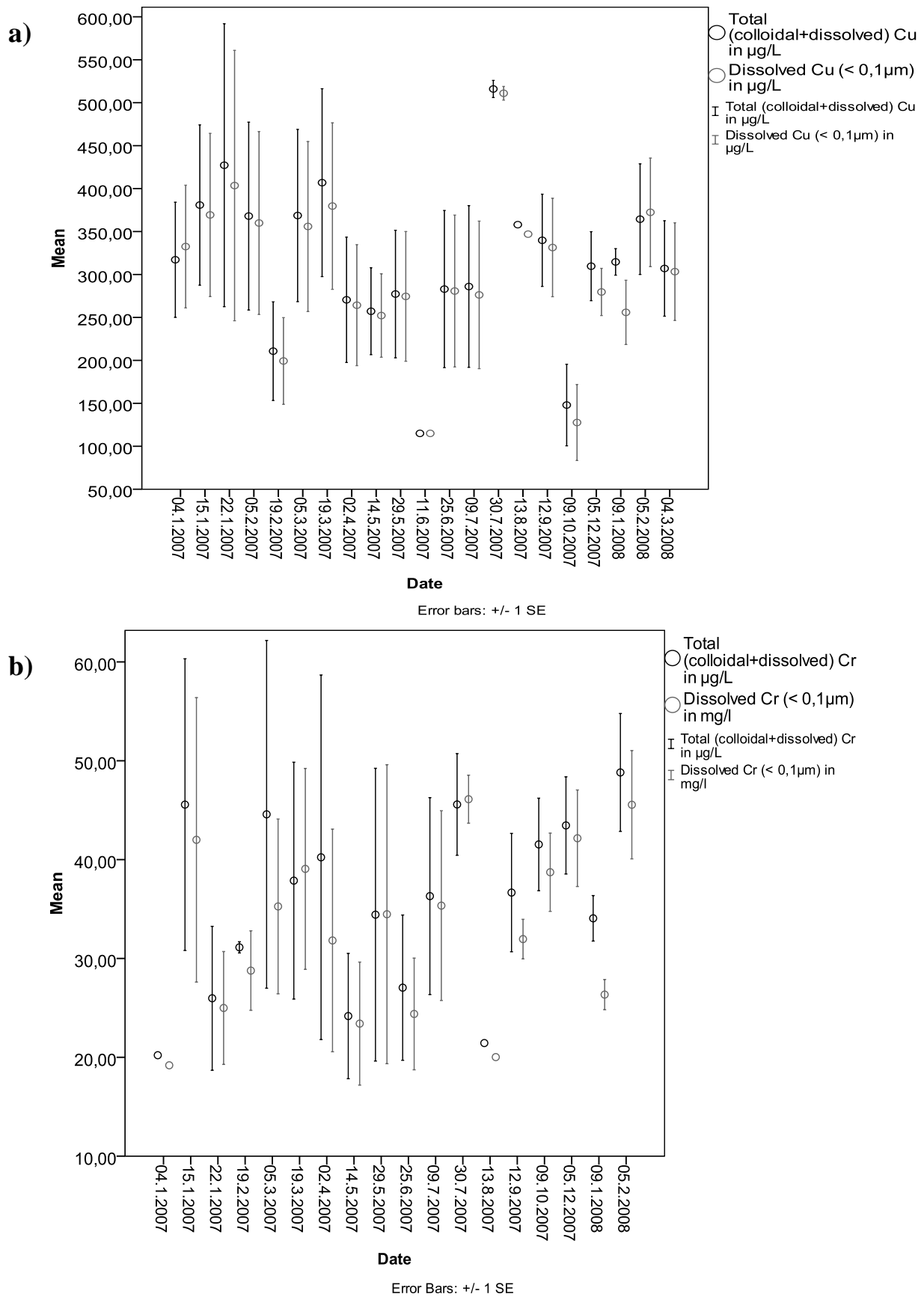
Fig. 6-8: Course of Cu (a) and Cr (b) concentrations in soil solutions collected by TL (error bars represent +/-1 standard error)
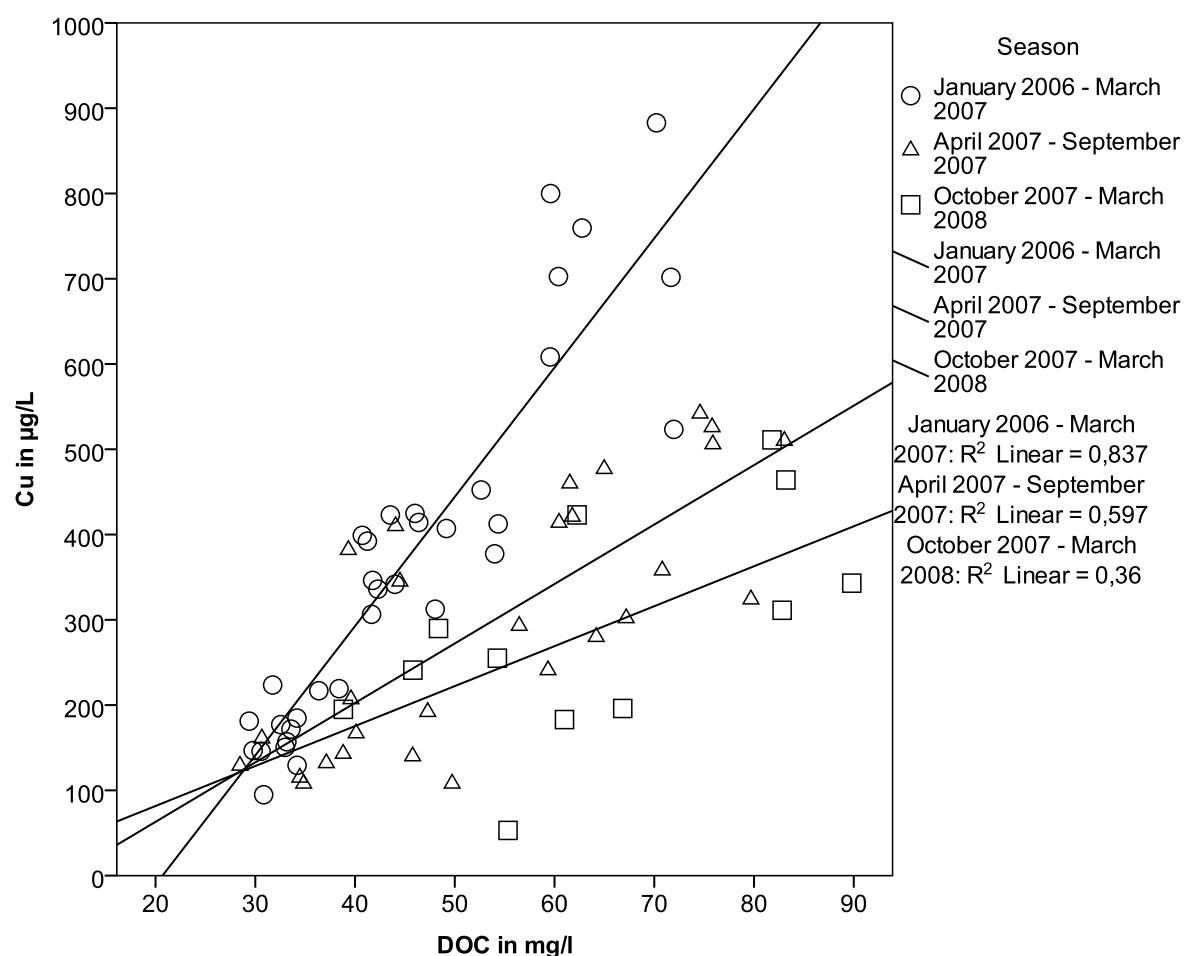
Fig. 6-9: Correlation between DOC (mg l^{-1}) and Cu (µg l^{-1}) in soil solutions collected by TL

6.4.6 Mobility of colloid-bound heavy metals

The mean percentage of the colloid-bound heavy metals in soil solutions collected by TL was relative low, amounting to 1.8 % (Ni), 3.7 % (Cu), 3.4% (Zn), 4.8 % (Cr) and 10 % (Cd), respectively. No colloid-bound Pb was detected in the soil solution, which is in agreement with results obtained from dispersion experiments with organic rich soil samples performed by Klitzke et al. (2008). These authors showed that colloid-bound Pb in aqueous soil suspensions increased at a pH value above 5.8. With exception to Ni, colloid-bound heavy metal mass fluxes (Cr, Cu, Zn and Cd) were positively related to total (colloidal + dissolved) mass fluxes. There was furthermore a high degree of correlation between average colloid-bound Cu concentrations in soil solutions sampled by TL and soil organic C (r² = 0.766) contents and total Cu concentrations in the soil (r² = 0.824), which is a result of high bond strength between Cu and the organic substances compared to other mobile heavy metals, where no correlations were found.

Several factors which we will discuss may have contributed to a low colloidal mobility from which the low soil pH values (4 - 5) may have been the most dominant. This assumption was

supported by the results obtained by Citeau et al. (2003), where the percentage of colloid-bound of Zn, Cd and Pb in a podzolic soil with pH ranges from 4 to 4.5 was less than 10 %. Further Hoffmann (2002) showed that Ca (60 % - 95 %) was the dominant cation in the soil solution at the experimental test site soil with a reported mean concentration of 50 mg l^{-1} (1997). Assuming that Ca concentration in soil solution did not decline, both the high solution ionic strength and low pH values (4-5) may have prevented colloid release (Grolimund et al., 1998; Kretzschmar et al., 1997; Vinten & Nye, 1985). Further several authors found that high amounts of sorbed Cu, Pb, Ni or Zn add positive charge to colloids and thus reduced their electrostatic repulsion leading to faster colloid aggregation and deposition (Heidmann et al., 2005; Karathanasis, 1999; Kretzschmar et al., 1997; Roy & Dzombak, 1997). It is likely that high amounts of these heavy metals in soil solutions collected by TL may have also reduced colloid mobility. Neither infiltration water intensity nor interplay of wetting–drying cycles followed by intensive precipitation was found to influence colloid mobility. Our results were therefore in good agreement with most studies in which no relationship between infiltration water velocity or intensity and mobilized particle concentrations was observed, concluding that hydraulic shear forces did not cause colloid release (Jacobsen et al., 1997; Ryan et al., 1998; Schelde et al., 2002; Villholth, 1999). Even though colloids may have been created at the soil surface by raindrop detachment (splash erosion), it is likely that low soil moisture contents in this partially water repellent sandy soil had prevented their mobility due to the creation of air-water interfaces to which particles adhere strongly (Crist et al., 2004; El-Farhan et al., 2000; Keller & Sirivithayapakorn, 2004; Lenhart & Saiers, 2002; Wan & Wilson, 1994a; Wan & Wilson, 1994b; Zevi et al., 2005). In addition soil water repellency caused by hydrophobic compounds of the soil organic matter may have enhanced the stability of soil aggregates, leading to a decreased breakdown (Chenu et al., 2000; Goebel et al., 2005; Piccolo & Mbagwu, 1999; Sullivan, 1990). This would also support our findings, because colloid mobility was (except for colloidal Cu) not depended on soil organic matter contents.

6.4.7 Mobility of PAHs

Soil solution samples were not always sufficient to conduct PAHs analysis. Therefore it was not possible to evaluate for seasonal trends. In addition it was not possible to compare PAH mobility between lysimeter types, because only three ZT soil solution samples were available for PAH analytic, compared to 21 TL soil solution samples. PAH are adsorbed due to their hydrophobicity especially to the soil organic matter (Chiou et al., 1988; Grathwohl, 1990; Karickhoff et al., 1979; Murphy et al., 1994; Petruzzelli et al., 2002). Hence mean PAH (16

EPA PAHs) concentrations in soil solution were positively related to topsoil organic matter contents ($r^2 = 0.834$) and organic C contents ($r^2 = 0.965$). No differences in mobility between low-condensed PAHs (2 - 4 fused rings) and high-condensed PAHs (5 - 6 fused rings) were observed, which may be caused by the predominance of high-condensed PAHs (90 %) in this soil (chapter 7). Various studies report that PAHs are mainly bound to high molecular weight and more hydrophobic DOM fractions (Chefetz et al., 2006; Guo & Ma, 2009; Ilani et al., 2005; Marschner et al., 2005; Polubesova et al., 2007; Raber & KogelKnabner, 1997; Schlautman & Morgan, 1993). No correlation between DOC and PAH concentrations in soil solutions collected by TL was found, which is in agreement with results of other studies (Totsche et al., 2007; Wehrer & Totsche, 2009; Weigand et al., 2002). Hence it is likely that more hydrophilic fulvic acids were predominant at pH < 5 (Reemtsma et al., 1999; You et al., 1999). Totsche et al. (2006) and Wehrer & Totsche (2008) found that PAHs were mainly associated with the colloids and particles size from 0.7 μm to 200 μm, which were mainly released under fast flow velocity driven by shear stress. In contrast we could not detect colloid- or particle-bound PAHs in soil solutions.

6.5 Conclusion

Our results are in agreement with previous studies (Impellitteri et al., 2002; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Yin et al., 2002; Weng et al., 2002) indicating that at low pH values, proton competition and/or proton promoted dissolution and at high salt concentrations, increased displacement (Backstrom et al., 2004; Linde et al., 2007; Norrstrom & Jacks, 1998; Voegelin et al., 2003), enhanced the mobility of Cd, Ni, and Zn in soil solutions. In contrast the mobility of the more strongly bound metals Pb, Cu and Cr was not affected by acidity and salt concentration alterations in the soil solutions as suggested by several researchers (Impellitteri et al., 2002; Impellitteri et al., 2003; Lair et al., 2007; Linde et al., 2007; Perez-Novo et al., 2008). Furthermore DOC contributed significantly to the mobility of Cu and partly to the mobility of Cr through complexation reactions, which is consistent with results of other studies (Impellitteri et al., 2002; Linde et al., 2007; Olsson et al., 2007; Ponizovsky et al., 2006; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Yin et al., 2002; Temminghoff et al., 1997; Temminghoff et al., 1998; Weng et al., 2002). PAH mobility was strongly positive related to the topsoil organic carbon contents.

Relatively low mean percentage of colloid-bound Cd, Ni, Zn, Cu and Cr (1.8 % - 10 %) indicates that both the high solution ionic strength and soil acidity (pH 4-5) may have prevented colloid release. Fast water fluxes through preferential flow paths during strong

rainfall events, was also not found to induce colloid mobility driven by shear stress as reported in previous studies (Jacobsen et al., 1997; McKay et al., 2000; Mishurov et al., 2008; Pilgrim & Huff, 1983; Ryan et al., 1998; Saiers et al., 1994). Colloids did not contribute to the mobility of strong sorbing contaminants such as PAH or Pb.

Soil solution concentrations did to not follow a clear seasonal moisture-related course. Strong precipitation intensities had no influence on heavy metals concentrations. Furthermore the positive correlation between mean water collection efficiencies and annual heavy metal mass fluxes ($r^2 = 0.5$ to $r^2 = 0.64$) indicate that contaminant fluxes were controlled by the cross sectional area of preferential flow above each lysimeter. Results hence confirm that temporally persistent preferential flow patterns decrease contaminant fluxes, since seepage water bypasses a large part of the polluted soil matrix. This assumption was supported by the fact that annual mass fluxes of Cd, Ni, Zn, Cu and Cr sampled by TL were less spatial variable, when they were corrected according to their collection efficiency (Fig. 6-10).
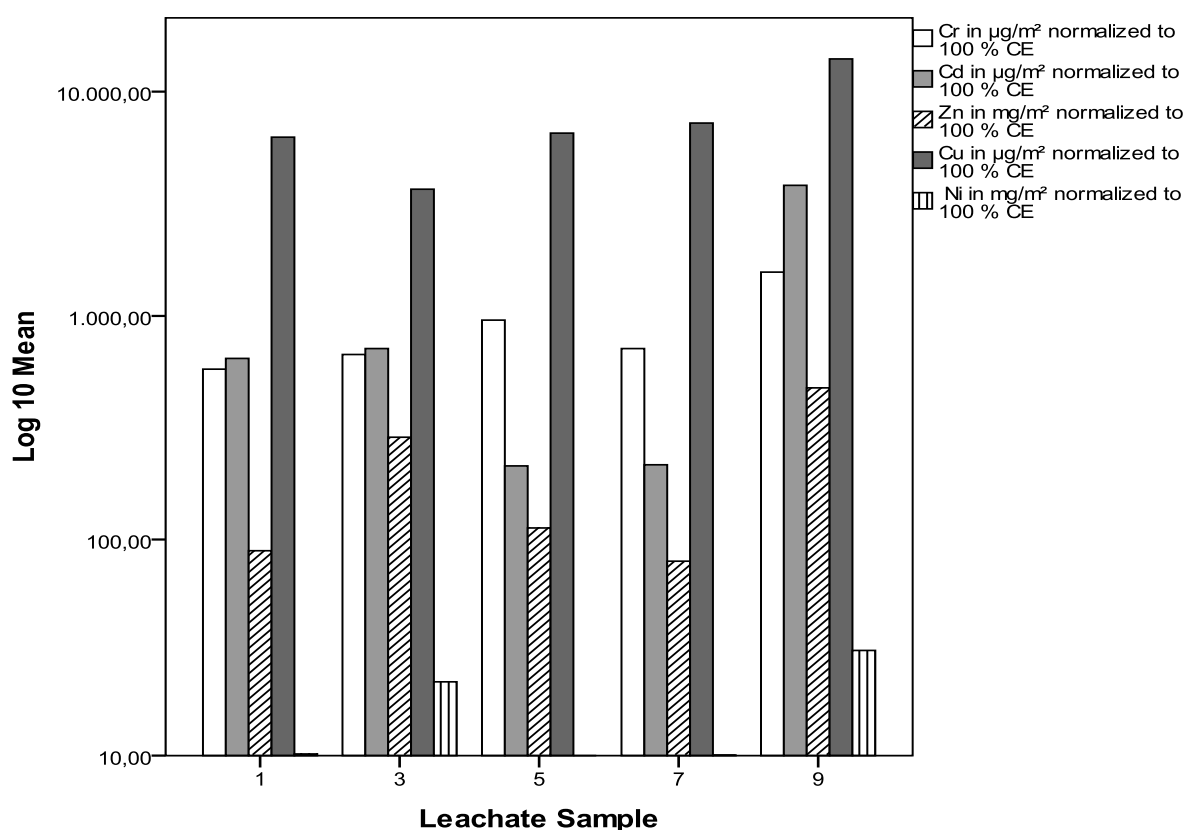
Fig. 6-10: Corrected mass fluxes of Cd, Ni and Zn to 100 percent collection efficiency in individual TL

The ratio of annual mobilised to total topsoil heavy metal contents showed that Ni and Zn were the most mobile elements (0.6 %), having minimum a 10 fold higher mobility compared to the other heavy metals (Zn>Ni>Cd>Cu>Cr>Pb), while the percentage of annual mobilised

Cd in soil solutions amounted to 0.05 %. Due to the low filter capacity of the sandy subsoil, the groundwater contamination risk by Cd, Ni and Zn is expected to be high with average concentrations exceeding the soil-groundwater exposure pathway guidance value according to the Federal Soil Protection Ordinance (BBodSchV, 1998) 4- (Cd), 10- (Ni) and 20-fold (Zn), respectively. No significant difference in average Zn, Cd and Cu concentrations in sampled soil solutions from 1998 (Hoffmann, 2002) and 2007/2008 could be observed, therefore the potential groundwater contamination risk in this soil will pose a continuous problem especially due to the high availability of these contaminants and due to minimal adsorption properties of the sandy and acid subsoil, resulting in a minimal retardation of heavy metals fluxes to the first aquifer.

Cu was considered as a moderate-mobility element in the contaminated sewage soil with soil pH values reaching the Cu-specific threshold pH value of 4.5 (Scheffer & Schachtsschabel, 2002). 0.05 % of the total topsoil Cu was annually mobilised with average soil solution concentrations exceeding 6 fold the soil-groundwater exposure pathway guidance value according to the Federal Soil Protection Ordinance (BBodSchV, 1998). Because Cr is low soluble and is mobilised at pH values below 4.5 (Scheffer & Schachtsschabel, 2002), only 0.002 % of the total topsoil Cr contents were annually mobilised, although the total topsoil Cr concentration was quite high. Cr concentrations did mostly not exceed the soil-groundwater exposure pathway guidance value of 50 µg l^{-1} according to the German Soil Protection Ordinance (BBodSchV, 1998). Hence the risk of groundwater contamination was expected to be negligible. No Pb was mobilised, indicating that Pb was adsorbed much more strongly to solid form of the organic matter compared to the other heavy metals at pH values between 4 and 5, presumably leading to the formation of stable insoluble Pb-organic complexes. Lead is one of the least mobile heavy metal in this soil. Therefore although total topsoil concentrations were fairly high, mobility from this organic rich and acid sewage soil is expected to be negligible (Kim et al., 2008; Scheffer & Schachtsschabel, 2002).

Mean PAH (EPA 16 PAHs) concentration in soil solutions sampled by TL did not exceed the soil-groundwater exposure pathway guidance value of 0.2 µg l^{-1}according to the German Soil Protection Ordinance (BBodSchV, 1998). Only an average of 0.003 % of the total topsoil PAH contents were annually mobilised. Diffusion of PAHs into internal binding sites (aging) may have also contributed to their low mobility. Furthermore soil acidity and availability of divalent cations may have resulted to the high sorption of PAHs and its low mobility as suggested by several authors (Murphy et al., 1994; Murphy & Zachara, 1995; Yang et al., 2001).

7 Mobilisation potential of colloid-bound and truly dissolved organic carbon, heavy metals and PAHs in water repellent and wettable urban soils

7.1 Abstract

Soil water repellency is assumed to control contaminant mobility and colloid retention of soils. Due to the low physico-chemical reactivity of the hydrophobic soil compounds we assume that the mobilisation potential in water repellent soils is lower than in wettable soils. In contrast water repellent areas in the field are often found to be persistent which may lead in the long term to a reduced leachability of contaminants. As a consequence mobilisation potential in water repellent soils may be higher than that in wettable soils. We tested these two contrasting hypothesis in a batch dispersion experiment, in particular if water repellency increases or decreases the contaminant mobilisation potential. For this purpose we analysed the mobilisation potential of dissolved and colloid-bound heavy metals (Pb, Cr, Cu, Cd, Ni, Zn) and PAHs from 12 adjacent actually water repellent and wettable soil pairs sampled from two urban locations, a municipal park and an undisturbed and permanently vegetated former sewage site, respectively.

Our study showed that total contaminant loads and physico-chemical soil properties between wettable and repellent samples did mainly not differ, concluding that sampled areas were not persistent water repellent or wettable. However our results indicate that the mobilisation potential of colloid-bound high molecular weight PAHs and colloid-bound Cu in the wettable sewage soil samples was higher than that in the adjacent water repellent soil samples, indicating that water repellency induced aggregation of the hydrophobic organic colloids. Furthermore organic carbon dissolution was increased in water repellent sewage samples, most likely due to microbial cell lysis and contributed to the mobility of Cu through complexation reactions. Minor differences in the mobilisation potential between water repellent and wettable samples were observed for the municipal park soil.

Results indicate that the accumulation of hydrophobic compounds at the former sewage site have partly contributed to a lower physico-chemical reactivity of the water repellent soil samples, but due to the long lasting leaching procedure only small differences between wettable and water repellent soil samples were found. In contrast the lack of accumulated plant residues at the municipal park suggests that water repellency was not generated by new input of hydrophobic substances at this site, but by low soil moisture contents.

7.2 Introduction

Soil water repellency or hydrophobicity is a common phenomenon in many dry soils and its occurrence and environmental implications (e.g. soil erosion, surface runoff, preferential flow) have been reviewed by several authors (DeBano, 2000; Doerr et al., 2007; Doerr et al., 2000). Water repellency is well described in literature to be particularly induced on permanently vegetated grasslands under dry conditions through the accumulation of hydrophobic organic compounds such as humic substances and waxy materials derived from partially decomposed plant residues (Mashum & Farmer, 1985; McHale et al., 2005; McKenna et al., 2002). These hydrophobic compounds cover the surfaces of soil particles and render them water repellent (Mashum & Farmer, 1985). The biological environment in the soil was further found to play a role in controlling soil water repellency. While soil fungi were found to increase soil water repellency (Chan, 1992; Dekker & Ritsema, 1996) several results indicate that in dependency of the bacterial strain encountered in soil samples, bacterial biofilms can hydrophilize or hydrophobize the soil surfaces (McKenna et al., 2002; Schaumann et al., 2007). Besides the impact of hydrophobic compounds, several authors reported that soil becomes water repellent when the water content decreases below a certain soil specific critical value (Dekker & Ritsema, 1996; Dekker et al., 2001; Doerr & Thomas, 2000).

Water repellency at our study site caused heterogeneities in the hydraulic status and thus led to preferential flow of water and solutes in the vadose zone (chapter 2 and chapter 6). Furthermore it was shown at our experimental test side (chapter 2 and chapter 3) and in various other studies that preferential flow patterns were persistent over consecutive infiltration cycles for weeks, months or years (Buchter et al., 1995; Glass et al., 1988; Hagedorn & Bundt, 2002; Lennartz & Kamra, 1998). It was therefore suggested that preferential flow patterns persists in water repellent sandy soils until the soils are either completely desiccated or saturated (Doerr & Thomas, 2000; Glass et al., 1988; Wessolek et al., 2009). We consequently assume that hydrophobic compounds are relatively physico-chemically inert and react very lowly on wetting. This was often related to slow conformational re-arrangements in the orientation of the hydrophilic and hydrophobic functional groups relative to the particle surface (Mashum & Farmer, 1985; Valat et al., 1991; Roy & McGill, 2000; Horne & McIntosh, 2000). Consequently leachability of contaminants from water repellent areas is expected to be decreased. This in turn may result in increased

total contaminant loads in the water repellent soil areas compared to adjacent wettable soil areas.

To determinate if contaminant mobilisation is dependent on soil hydrophobicity or other underlying physico-chemical soil properties several laboratory dispersion experiments have been performed. Although most studies did not found differences in major solid soil properties between moist and dry soil samples (Klitzke & Lang, 2007; Tack et al., 2006), several experimental results indicate that dried soil samples on rewetting released increased amounts of dissolved organic matter (Christ & David, 1996; Courchesne et al., 1995; Kaiser et al., 2001; Klitzke & Lang, 2007) and dissolved metals (Haynes & Swift, 1985; Fest et al., 2008; Tack et al., 2006).

Recent studies provided hints that water repellency of hydrophobic soil samples may even decrease upon drying (Bayer & Schaumann, 2007; Doerr & Thomas, 2000; Doerr et al., 2006; Hurraß & Schaumann, 2006). This was especially the case for studies realized in the laboratory, suggesting that re-establishment of soil hydrophobicity in the field after drying was additionally caused by new input of hydrophobic substances (Doerr & Thomas, 2000).

Due to these hints in literature in which potential differences in the state of hydrophobicity between laboratory dried and field moist water repellent soil are discussed, this study analyses the mobilisation potential of contaminants from adjacent actually water repellent and wettable soil sample pairs from the field in dispersion experiments. In this study two contrasting hypotheses are tested. The first hypothesis assumes that preferential flow bypasses large areas of the contaminated topsoil and leads to a decreased leachability of the contaminants in the water repellent areas. As a consequence total soil contaminant loads and potentially mobilisable amounts should be higher in the water repellent soil samples. The second hypothesis is based on the assumption that hydrophobic compounds are relatively chemically inert. Hence the mobilisation potential of contaminants in water repellent soil samples is expected to be smaller than in wettable soil samples. To test these two contrasting hypotheses the mobilisation potential of colloid-bound and of dissolved heavy metals and polycyclic aromatic hydrocarbons (PAHs) from adjacent actually water repellent and wettable soil sample pairs derived from two urban locations are compared.

7.3   Material and Methods

7.3.1   Study site and soil sampling

Our study was performed with adjacent wettable and water repellent soil samples taken from the Ah horizon at 10 to 20 cm depth beneath the litter horizon from two urban locations (Tiergarten and Buch) in Berlin, Germany.

At the former sewage site Berlin-Buch sewage infiltration was practiced for almost 100 years and stopped in 1985. Because the former sewage farm consisted of different sewage galleries, the small scale spatially variable physico-chemical soil were strongly linked to the organic matter contents (Hoffmann, 2002; Schlenther et al., 1996). The vegetation was dominated by dry grasslands (mainly couch grass; syn. Elytrigia repens). The soil was classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (30 cm – 40 cm thick) over medium sized homogenous sand subsoil (sand content 98 %). Berlin-Tiergarten (TG) is a municipal park built in the 18th century. After bomb damages during World War II and deforestation during the post-war period the park was reforested in the 1950s. The soil was classified as a deep, well drained Cambisol with medium sized homogenous loamy sand (sand content 86 %). The test site was situated on a lawn. These two urban locations were selected because of their contaminant loads and due to their pronounced small scale heterogeneous water repellent properties.

The Water Drop Penetration Time (WDPT) test as described by several authors (King, 1981; Dekker & Jungerius, 1990) was used to identify actually wettable and water repellent soil pairs on soil parts in the field. After the litter layer was removed and the surface was levelled potential adjacent water repellent (light and dry) and wettable (dark and moist) soil parts were visually assessed. The actual water repellency was then determined with three water drops of distilled water using a standard glass pipette which were placed on the adjacent potential water repellent and wettable soil pairs. Based on the mean time required for the three drops to enter the soil the actual water repellency was classified as wettable (< 1 s) and water repellent (> 180 s). In total 12 adjacent repellent and wettable soil pairs were sampled at 10 cm to 15 cm depth below the litter layer, respectively 7 from the former sewage site Buch and 5 from the municipal park Tiergarten. All soil samples were transferred directly after sampling into sealed brown glass flags and stored at 4°C. In the lab the actual water repellency of paired samples was remeasured on undisturbed steel cylinder cores of 100 cm^3 volume and the

persistence of soil water repellency was classified using the index as described by Dekker & Jungerius (1990). The measurement of the WDPT was stopped after 3 h.

Several authors reported that actually water repellent samples became less repellent when they were dried at 105 ºC (Bayer & Schaumann, 2007; Doerr et al., 2005; Hurraß & Schaumann, 2006); hence no potential water repellency at 105 °C was determined.

7.3.2 Analyses of soil

After field moist and dried soil samples were sieved (< 2 mm) they were analysed for gravimetric water contents, dry mass (at 105 °C), organic C, N, S contents with a CNS-Analyser (vario EL, Elementar Analysensysteme GmbH), pH and electrical conductivity. Total heavy metal (Cu, Pb, Cr, Cd, Zn, and Ni) soil contents were determined after an aqua regia digestion (DIN 38406) with an Atomic Absorption Spectrometer (Perkin Elmer 1100B). A certified reference material (BAM: BRM#06a, BRM#06b) for the total heavy metal analytic was used for quality control (average recovery 88 % - 112 %). To determine the total concentration of PAHs we extracted them from the soil samples by accelerated solvent extraction (ASE) with Hexan/Aceton (2 : 1). Subsequently the extracts were dried with anhydrous sodium sulphate and concentred to ca. 5 mL by evaporation. Further samples were cleaned with Alox-Silicagel and concentrated to ca.1 mL by evaporation. The concentrations of PAHs were measured with a gas chromotograph (Agilent Technologies GC Model 6890N) which was in turn coupled to an Agilent mass selective detector (Agilent Technologies Model MSD 5973N). A capillary column (DB-5MS, J&W Scientific, Fa. Agilent) with a film thickness of 0.25 µm, an internal diameter of 0.25 mm, and a length of 30 m was used for the PAH analyses. The recovery was determined based on internal standards of 7 deuterium-labelled PAHs added to the samples prior to extraction. The deuterium-labelled internal standard Fluoranthene D10 was added into the vial in order to quantify the exact extract volume. The detection limit was 1 µg l^{-1}. A certified PAH reference material (RTC, No: CRM134-050) was used for quality control (average recovery 100 %). For the appraisal of PAH contaminations we summarised 16 non-substituted PAH lead substances based on Environmental Protection Agency (EPA) which are referred as 16 EPA PAHs.

7.3.3 Dispersion experiments

We used the German batch leaching tests (DIN 38414 part 4, DEV S4-Test) with little modifications in order to determinate the mobilisation potential of contaminates. All

extractions on field-moist soil samples (< 2 mm) were performed with deionised water (1:10 weight to volume ratio) using an end-over-end shaker and the soil weight to volume ratios were adjusted for the initial gravimetric water contents. We used a shaking time of 16 h, instead of the proposed 24 h in the DEV S4-Test, on the basis of kinetic studies performed by Klitzke et al. (2008), who showed that Pb concentration equilibrium was reached after about 8 hours of shaking and Pb concentrations did not increase with shaking time. Prior to element analysis batch extracts were centrifuged at 176 g for 7 min (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) and then filtrated through a 1 µm glass microfiber filter (Whatman GF 6) in order to derive colloidal plus truly dissolved ($\leq$ 1 µm) suspensions. Afterwards aliquots of these suspensions were ultracentrifuged at 222194 g for 1.5 h (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) and the isolated supernatants ($\leq$ 10 nm) were subsequently filtered through a 0.1 µm polycarbonate filter in order to obtain almost truly dissolved suspensions. Acidified suspensions at pH 4 were analysed for total (colloid-bound plus truly dissolved) and truly dissolved Cu, Pb, Cr, Cd and Ni by a Graphite furnace-Atomic Absorption Spectrometer (Varian SpectrAA 880Z) and for total organic carbon (TOC) and truly dissolved organic carbon concentrations (DOC) by a total organic carbon analyser (TOC – 5050 A, Shimadzu). PAHs in suspensions were extracted with cyclohexane (500 mL sample, 25 mL solvent each time). Subsequently the organic phase extracts were dried with anhydrous sodium sulphate and concentred to ca. 5 mL by evaporation. Samples were further cleaned with Alox-Silica gel and concentrated to ca. 1 mL by evaporation. Measurement of the total and truly dissolved PAHs corresponded to the method described in chapter 7.3.2. Colloidal plus truly dissolved suspensions were additionally analysed for zeta potentials using a Zetasizer DTS 5200 photon correlation spectrometer (Malvern Instruments), average colloid sizes by dynamic light scattering (HPPS – High Performance Particle Size, Malvern Instruments) and turbidities using a turbidimeter (Hach 2100P ISO).

7.3.4 Statistical analysis

Means, standard deviations, analysis of variance and correlations were computed with the statistical analysis programme SPSS. Parametric (Independent-Samples T Test, Paired T Test, GLM Univariate Analysis) statistical tests were used because the data were normally distributed (Kolmogorov-Smirnov statistic, Shapiro-Wilk statistic). Paired T-Tests were used to test for significant differences in physico-chemical soil and suspension properties between

water repellent and wettable soil samples within each location (Tiergarten and Buch). The probability level (p) of all tests was 95 %.

7.3.5 Characterisation of the colloids

We used scanning electron microscopy (SEM; Hitachi S-2700) coupled with an energy-dispersive analysis of X-rays (EDX; SAMx, software 'IDFix' - acquisition parameter of the beam: accelerating voltage: 20 kV, beam current: 500 nA) in order to simultaneously acquire information on the size, shape, surface morphology and elemental composition of colloidal particles in soil suspensions. The colloidal plus truly dissolved suspension (< 1µm) of a wettable soil sample (Buch) was further diluted with deionised water (1:5 soil suspension to water ratio), and was subsequently applied to a glass plate, which was freeze-dried prior to the SEM/EDX analyses.

7.4 Results and Discussion

7.4.1 Colloid characterisation
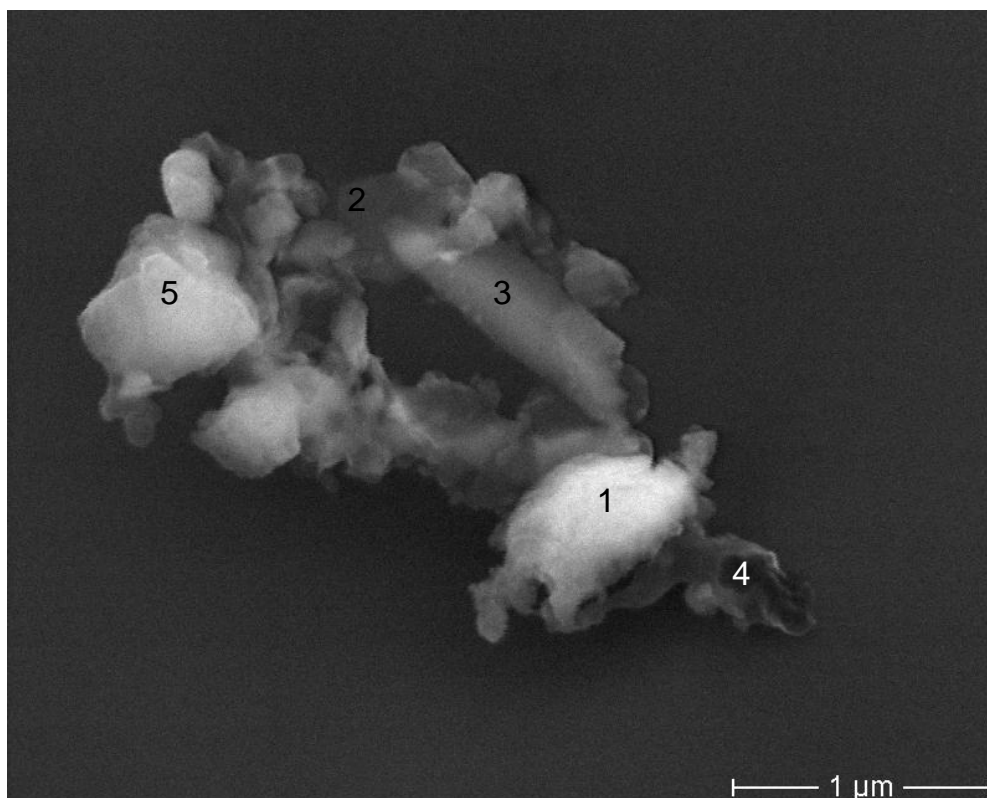
Fig. 7-1: Single colloidal particle viewed under the scanning electron microscope (SEM). The elemental composition of the five numbered parts within the colloid is derived through energy dispersive X-ray analysis (EDX)
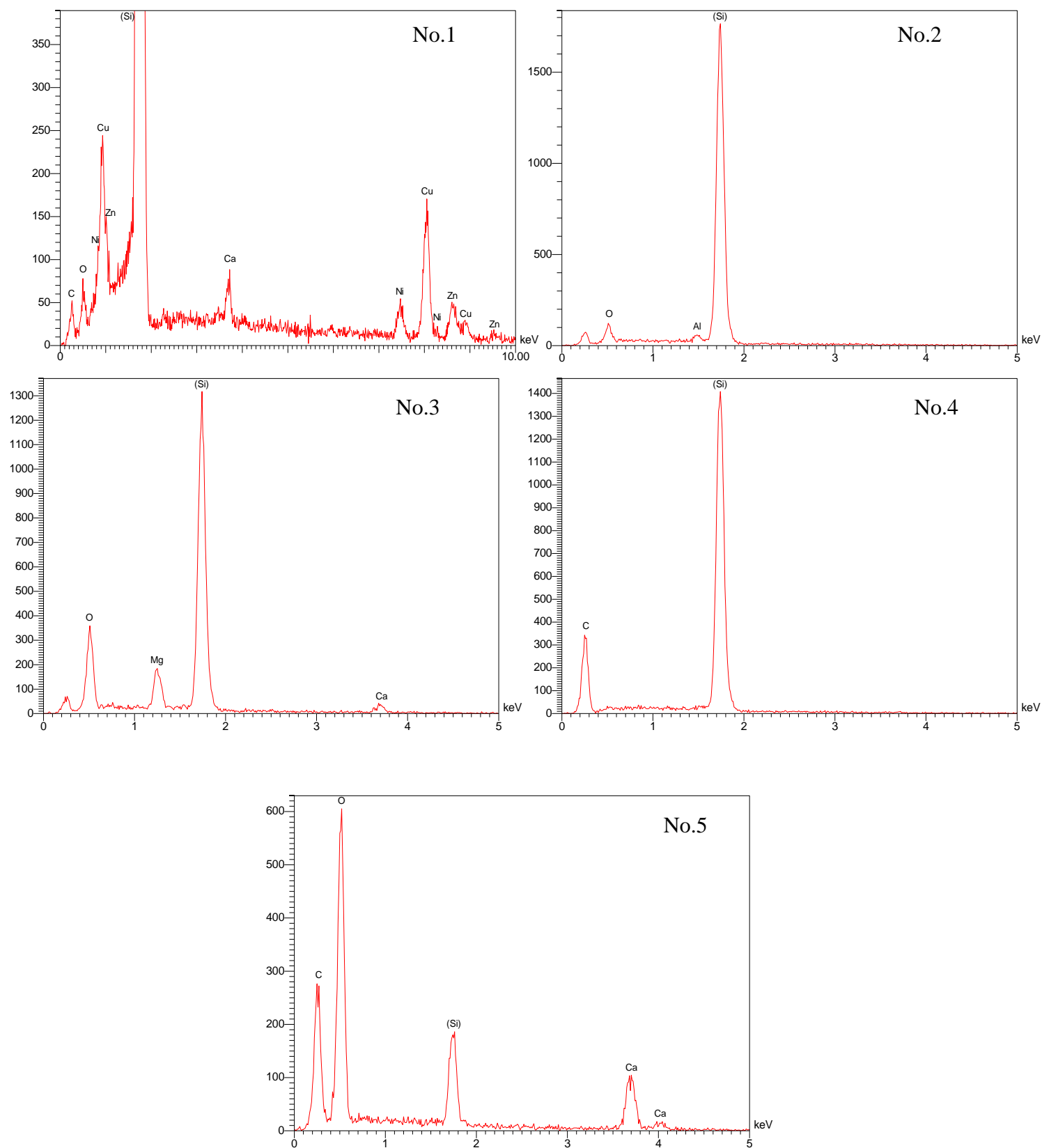
Fig. 7-2: Energy dispersive X-ray analysis (EDX) of five numbered parts (1-5) in the colloidal particle

Fig. 7-1 shows a representative example of the morphology and size of a single colloidal particle viewed under a scanning electron microscope (SEM). The X-ray analysis illustrate that colloids in the suspensions occurred as a mixture of complex aggregates (Fig. 7-2). The EDX spectra of the single colloidal particle detected Si and C as the main components. Humic substances, detected at part number 4 by the element C and morphological characterised by its amorphous structure, coats the different inorganic colloidal components of the colloid thereby altering the surface charge and increasing the colloid stability. Surprisingly all detected heavy metals (Cu, Ni, and Zn) were located at the same position (No 1) and seem to be adsorbed to negative charges of humic coated mineral compounds. The hexagonal structure of particle 2 and the predominance of the elements Si, Al and O points to a clay mineral. Particle 3 containing the elements Si, C, Mg and Ca may also present a clay mineral. Particle 5 with the predominant elements O, C, Si and Ca occurs further most likely in form of an organo-mineral particle.

7.4.2 Main soil properties

Total topsoil heavy metal concentrations at both locations were highly correlated to the soil organic matter (SOM) contents. In contrast the soil organic C contents were only correlated to the total Zn, Cd and Ni concentrations in the wettable samples. Even though water repellent and wettable soil pairs were located directly adjacent, water contents differed significantly (Table 7-1) which is an essential prerequisite for our experimental investigation. Wettable soil samples had significantly higher Pb contents at Buch and Cr and Ni contents at Tiergarten. Moreover pH values of wettable samples at Tiergarten were significantly increased, which is consistent with results of a study performed by Hurraß & Schaumann (2006) at the same site. These authors proposed that deprotonation of polar functional groups such as carboxylic and phenolic groups of the organic matter increases with increasing pH, which in turn increases wettability. However this small pH effect by approximately 0.3 pH units observed in this study is not likely to have a major influence. Soil organic C contents of Tiergarten samples were highly correlated to the water contents of wettable and water repellent soil samples. Therefore we suggest that organic C quantity may have influenced the state of water repellency at the Tiergarten location. Paired T-Tests (Table 7-1) indicated that most of the analysed soil solid properties did not differ significantly between wettable and water repellent soil samples. Similarity in contaminant loads between soil pairs may indicate that preferential flow path patterns were not persistent. On the other hand it is well documented that the cross section of preferential flow pathways may increase or decrease in dependence of the rainfall

rate. It is therefore likely that the immediate vicinity of sampled soil pairs does not reflect the spatial scale of persistent water repellent and wettable soil areas.

Table 7-1: Basic chemical soil properties, water contents and heavy metal contents of sampled soil pairs within each location
(SD: standard deviation; Paired T-Test: significant differences denoted as "Yes", no significant differences denoted as "No")

Soil Properties	Unit	Buch					Tiergarten				
		Wettable		Water repellent		T-Test Sig. Diff	Wettable		Water repellent		T-Test Sig. Diff
		Mean	SD	Mean	SD		Mean	SD	Mean	SD	
WDPT (laboratory)	[min]	2.7	2.4	143.0	64.0	Yes	1.0	0	114.0	73.0	Yes
Water content (105°C)	[g kg^{-1}]	186.3	36.0	117.9	47.2	Yes	211.0	26.6	97.9	30.2	Yes
Water content (30°C)	[g kg^{-1}]	158.3	35.6	78.7	13.2	Yes	201.3	25.5	88.7	29.9	Yes
pH (CaCl$_2$)	[-]	4.5	.4	4.5	.5	No	4.6	.5	4.4	.5	No
pH (H$_2$O)	[-]	5.0	.4	5.0	.3	No	5.5	.5	5.2	.6	Yes
Conductivity	[μScm^{-1}]	220.1	95.7	214.1	70.1	No	150.3	85.8	104.4	42.5	No
Organic matter	[g kg^{-1}]	90.1	15.2	88.2	7.2	No	330.1	52.1	202.3	60.7	Yes
Org. C	[g kg^{-1}]	49.7	9.3	50.6	5.2	No	51.3	9.4	46.5	11.9	No
Org. N	[g kg^{-1}]	4.9	1.0	4.9	0.6	No	3.1	.0.6	2.8	0.6	No
Org. S	[g kg^{-1}]	1.9	0.6	1.7	0.4	No	-	-	-	-	-
C/N ratio	[-]	10.3	.3	10.3	.4	No	16.5	1.1	16.6	1.5	No
Cu	[mgkg^{-1}]	213.0	35.3	199.0	34.4	No	28.9	12.4	24.3	11.1	No
Pb	[mgkg^{-1}]	281.8	50.2	257.1	47.3	Yes	59.6	15.3	54.9	17.3	No
Cd	[mgkg^{-1}]	18.9	5.6	17.9	5.5	No	.6	.2	.5	.1	No
Zn	[mgkg^{-1}]	481.4	110.6	447.9	138.9	No	-	-	49.0	13.4	No
Cr	[mgkg^{-1}]	422.6	43.4	396.8	39.7	No	20.6	2.7	14.9	2.7	Yes
Ni	[mgkg^{-1}]	33.6	9.2	33.7	8.0	No	11.1	1.1	8.9	1.3	Yes

7.4.3 Soil suspension properties

Almost all heavy metal concentrations in soil suspensions of wettable and repellent samples of both locations were correlated to the total topsoil heavy metal concentrations. As expected, the strongly sorbing heavy metals Cr, Cu and Pb were almost colloid-bound (Fig. 7-3), while the highly soluble heavy metals Zn, Ni and Cd occurred almost as dissolved species in soil suspensions. These results are consistent with several studies demonstrating that suspended in situ mobilized colloids can facilitate the transport of strongly sorbing contaminants such as Pb (Citeau et al., 2003; Grolimund et al., 1996), while Zn and Cd were mainly found in dissolved forms (Citeau et al., 2003; Denaix et al., 2001).

No differences in the percentage of mobilised heavy metals to total soil heavy metals were found between wettable and water repellent soil samples. Due to the stronger binding capacity of the low soluble heavy metals to the SOM, the percentage of mobilised heavy metals was lower than that of the highly soluble heavy metals (data not shown). Although mean heavy metal concentrations (Fig. 7-3) and other analysed properties of the suspensions (Table 7-2) between wettable and water repellent soil samples appear different in some cases, paired T-Test revealed only minor statistical significant differences, which are discussed in the following section.

Table 7-2: Basic soil suspension properties of sampled soil pairs within each location

Soil suspension properties		Buch					Tiergarten				
		Wettable		Water repellent		T-Test Sig. Diff.	Wettable		Water repellent		T-Test Sig. Diff.
	Unit	Mean	SD	Mean	SD		Mean	SD	Mean	SD	
TOC	[mg l^{-1}]	27,21	5,55	26,45	4,79	No	34,25	4,21	37,59	1,83	Yes
DOC	[mg l^{-1}]	11,40	1,27	13,79	0,99	Yes	20,88	6,87	19,41	4,41	No
POC	[mg l^{-1}]	15,81	5,31	12,67	4,15	Yes	13,37	5,23	18,17	5,08	No
POC	[%]	56,60	10,26	46,65	8,15	Yes	39,02	16,36	47,10	10,50	No
Turbidity	[NTU]	213,07	40,42	199,21	23,51	No	162,30	56,70	160,30	57,19	No
Particle Size	[nm]	437,57	35,99	416,01	105,78	No	470,20	133,97	403,60	92,59	No
Zetapotetial	[mV]	-28,50	7,08	-22,24	4,80	Yes	-22.68	8.20	-27.66	5.72	No
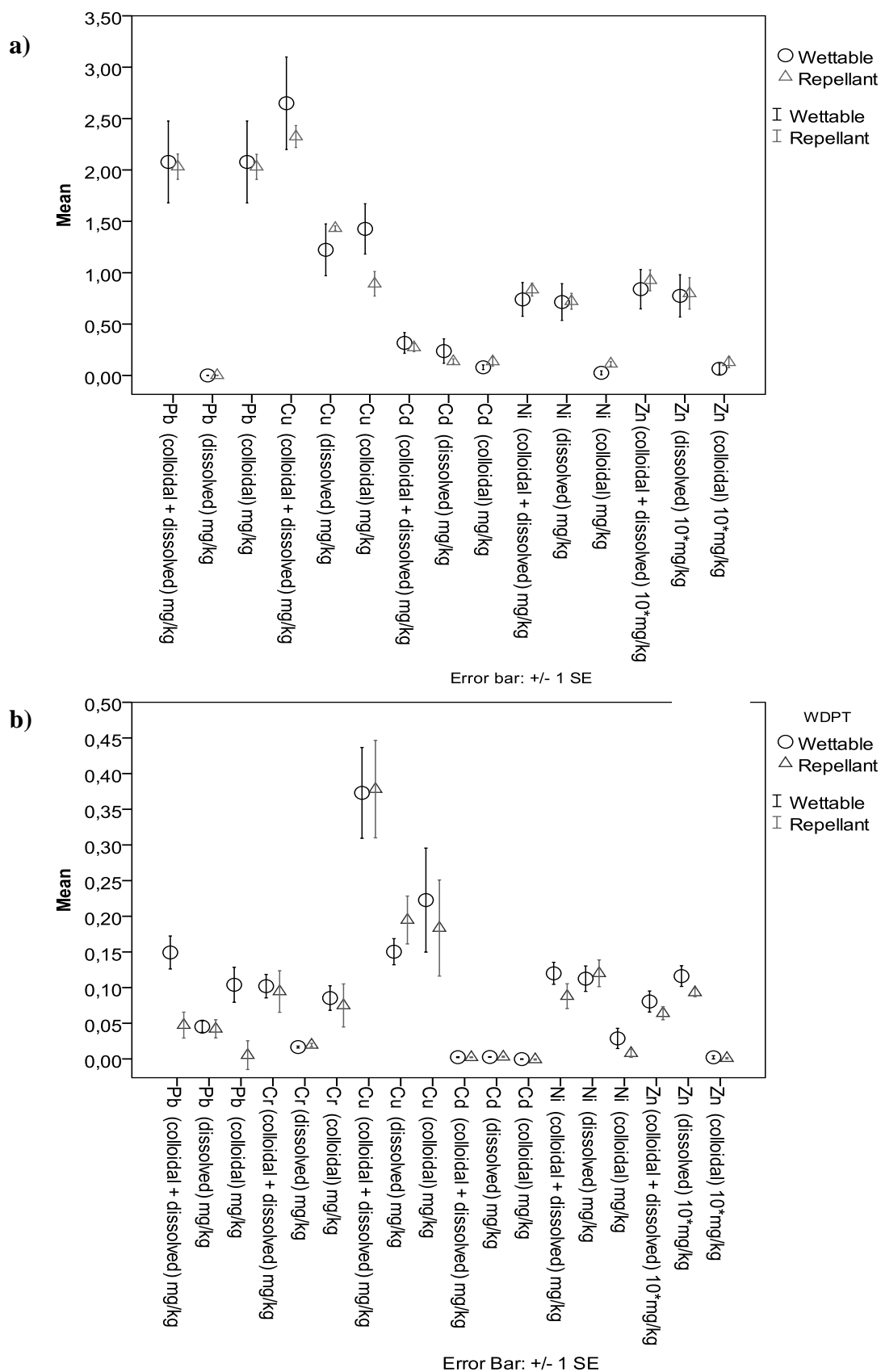
Fig. 7-3: Mean heavy metal concentration (Cr, Cu, Pb Zn, Ni and Cd) in soil suspensions of water repellent and wettable soil samples from the Buch location (a) and from the Tiergarten location (b) (error bars represent +/-1 standard error)

Even though total mobilised organic carbon in soil suspensions between water repellent and wettable samples did not differ, DOC concentrations in soil suspensions of water repellent samples at Buch location were significantly higher compared to those of adjacent wettable samples. These results are in accordance with findings for this site (Klitzke & Lang, 2007) and in the literature (Andersson et al., 2000; Christ & David, 1996; Courchesne et al., 1995; Godde et al., 1996; Kaiser et al., 2001) indicating that DOC concentrations are increased in dried soil samples upon rewetting. Many studies show that DOC concentrations in soil solution are higher in summer than in winter (Chittleborough et al., 1992; Dalva & Moore, 1991; Federer & Sticher, 1994; Guggenberger & Zech, 1994; Liechty et al., 1995; Mcdowell et al., 1998; Scott et al., 1998; Tegen & Dorr, 1996; Tipping et al., 1999) and increase at the beginning of a rewetting period after dry periods (Chittleborough et al., 1992; Kalbitz & Knappe, 1997; Lundquist et al., 1999; Merckx et al., 2001; Tipping et al., 1999; Totsche et al., 2007; Wehrer & Totsche, 2009; Zsolnay et al., 1999). Several researchers suggest therefore that during dry periods microbial activity which causes decomposition of DOC is reduced, while microbial cell lysis is enhanced, both contributing to an increased dissolution of organic carbon on wetting (Christ & David, 1996; Kalbitz & Knappe, 1997; Zsolnay et al., 1999). Soil suspensions of wettable samples from Buch had in turn significantly higher particulate organic carbon (POC) concentrations than those of adjacent water repellent samples. This finding suggests that water repellency increases attractive hydrophobic interaction forces between organic colloids, leading to higher aggregation and hence decreasing POC release. In addition it is likely that POC in water repellent samples was stronger sorbed to the hydrophobic SOM and therefore less mobile. Interparticle bonding or cementation of colloids from the initially dry soils as suggested by Kjaergaard et al. (2004) may have also decreased organic colloid mobilisation. Moreover zeta potential measurements indicated that surface charges of colloids and hence colloid stability and mobility are significantly higher in the soil suspensions of the wettable samples.

Water repellent samples at Buch location released furthermore significant more dissolved Cu and simultaneous less colloid-bound Cu than adjacent wettable samples, while total mobilised concentrations were similar. Our results are consistent with findings reported by Klitzke & Lang (2007) for aqueous concentrations of air dried and field moist samples at this site and by other researchers, indicating that DOC contributes significantly to the mobility of Cu through complexation reactions (Impellitteri et al., 2002; Linde et al., 2007; Olsson et al., 2007; Ponizovsky et al., 2006; Salam & Helmke, 1998; Shi et al., 2005; Strobel et al., 2005; Temminghoff et al., 1997; Weng et al., 2002; Yin et al., 2002). The higher concentrations of

colloidal Cu in soil suspensions of wettable soil samples may further indicate that Cu was mainly bound to organic colloidal particles. Klitzke & Lang (2007) suggested that equilibrium reactions between colloidal Cu and dissolved organically complexed Cu in the soil solutions of dried samples could lead to Cu desorption from the colloids, hereby increasing dissolved organically complexed concentrations.

Since the topsoil pH value (4.5 - 5) was above the Pb-specific threshold pH value (< 4) almost no dissolved Pb was mobilised in soil suspensions. Pb occurred almost colloid-bound (99 %), caused by the high affinity of Pb to the SOM. Due to the low affinity of the highly soluble heavy metals Cd, Ni and Zn to the soil organic C (McBride et al., 1997) no significant increases in organically complexed concentrations in water repellent samples on rewetting have been observed. These results are in accordance with findings obtained from soil solutions monitored at the Buch location (chapter 6) indicating that DOC contributed significantly mainly to the mobility of Cu. In contrast increased concentrations of colloid-bound Cd, Ni and Zn in the soil solutions of water repellent samples may indicate that these heavy metals were bound to inorganic colloids, which were dislodged from the SOM during the rewetting process. However due to the overall small colloid-bound fraction of these heavy metal these differences are only of minor importance.

Although heavy metals concentrations in the soil solutions of Tiergarten seem to be higher in the wettable samples than those in the repellent samples, these differences were only significant for Pb and Ni. Because Pb is one of last soluble heavy metal it is likely SOM was more disaggregated in the wettable samples which caused an increased Pb accessibility. In contrast a conceivable reason for the increased mobilisation potential of Ni was likely the higher total soil Ni concentrations in the wettable samples. Altogether we detected relatively few concentration differences of colloid-bound heavy metals between wettable and water repellent samples. The mean turbidity values in soil suspensions between repellent and wettable soil samples confirmed the similarity in colloid mobilisation characteristics, which is in agreement with former turbidity measurements in soil suspensions of dry and field moist soil samples at these sites (Klitzke & Lang, 2007).

EPA 16 PAH fingerprints (Fig. 7-4) show that soil and soil solution of Buch samples were mainly dominated by high molecular weight PAHs (5 - 6 fused rings). Due to the higher water solubility and the higher chemical or microbial degradation potential of low molecular weight PAHs (2 - 4 fused rings), it is likely that these compounds (Naphthalene to Phenanthrene) were already metabolised or mobilised in the Buch soil. In contrast high molecular weight

PAHs were adsorbed due to their higher hydrophobicity stronger to the organic matter (Karickhoff, 1981; Marschner, 1999; Wilcke, 2000) and resisted towards microbial transformation (Guerin, 1999; Reemtsma & Mehrtens, 1997). High molecular weight PAHs may have been also immobilised in this soil due to aging processed induced by PAH diffusion into less accessible internal binding sites of the soil organic matter (Weissenfels et al., 1992). It is also likely that the fingerprints reflect the kind of contamination of the former sewage farm. The 16 EPA PAH fingerprints of the Tiergarten soil were quite different and were mainly dominated by 3 and 4 fused rings PAHs (Fig. 7-5). PAHs at the municipal park soil may have originated from deposits of partly burnt rubble derived from bomb damages during World War II (Renger & Mekiffer, 1998) or from road traffic emissions.

Similar to the heavy metal concentrations, PAH concentrations were highly spatially variable among samples, reflecting the small scale heterogeneity of the SOM, to which the PAHs were likely bound. Almost all single PAH reference substances in the soil and in the suspension from both sites were highly correlated. In addition a correlation of almost all single reference substances between soil and suspension concentrations (16 EPA PAH r^2 = 0.691) in the Buch samples was observed. Hereby the statistical significance of correlation was higher for the high molecular weight PAHs. Total PAHs in soil samples from Tiergarten were negatively correlated to the electrical conductivity (16 EPA PAH r^2 = -0.632). At Buch location electrical conductivity correlated in contrast positively to the 5 and 6 fused rings PAHs. Generally it has been found that the sorption of hydrophobic organic compounds to mineral-associated humic substances increases as ionic strength and pH decreases, while divalent cations increase HOC sorption (Murphy et al., 1994; Murphy & Zachara, 1995; Murphy et al., 1992; Yang et al., 2001). It is therefore likely that divalent cations predominated in the Tiergarten soil and led to a decreased leachability of PAHs. In contrast the positive correlation found in the Buch soil suspensions reflects the increased PAH dispersibility with increasing sample ionic strength.

Dispersible PAHs in soil suspension were almost adsorbed to colloids. Hereby the colloid-bound fraction increased with increasing molecular weight of the PAHs (Table 7-3).

a)

Error bars: +/- 1 SE

b)
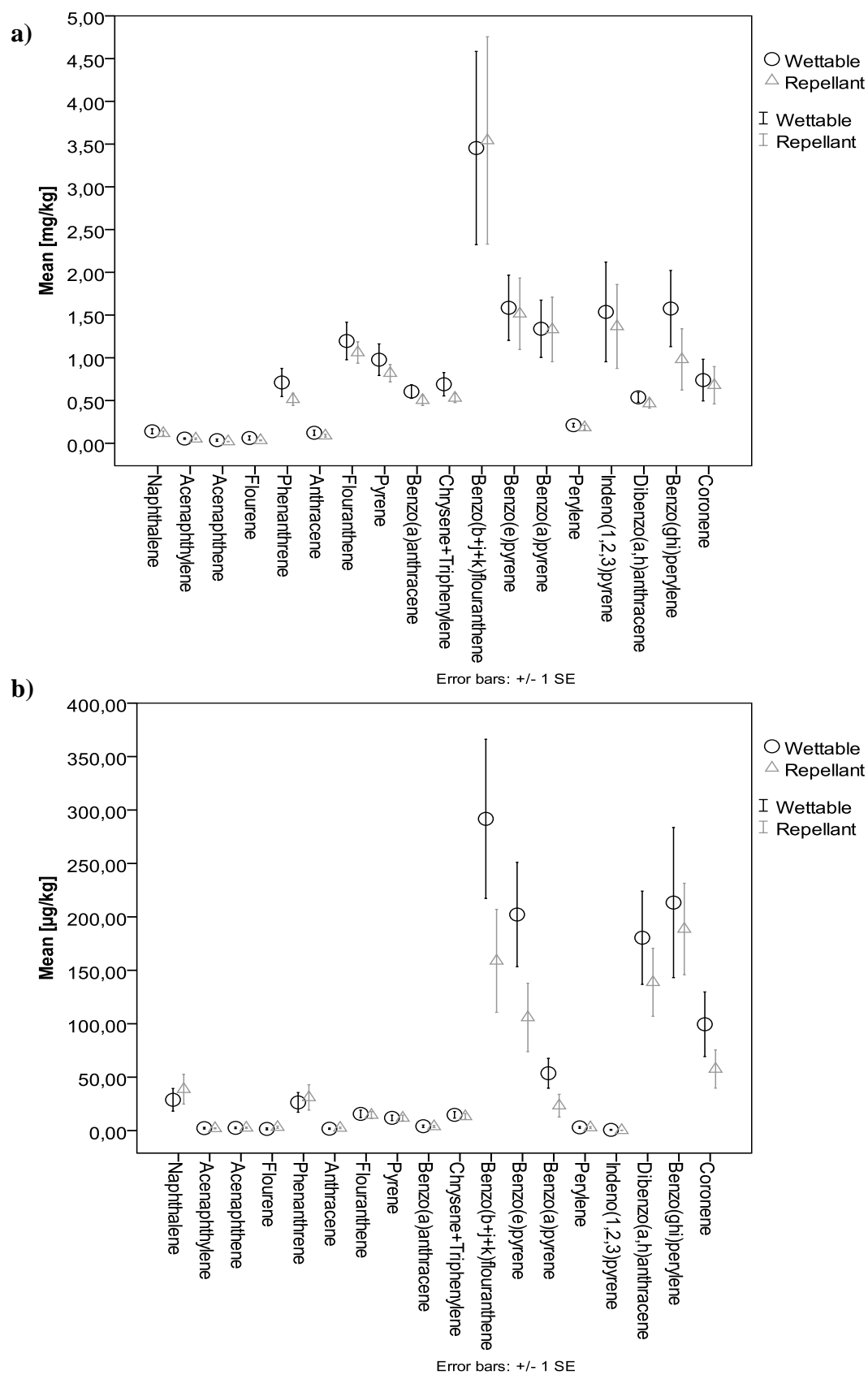
Error bars: +/- 1 SE

Fig. 7-4: 16 EPA PAH concentration in the soil (a) and in soil suspensions (b) of wettable and repellent samples at Buch location (error bars represents +/-1 standard error)
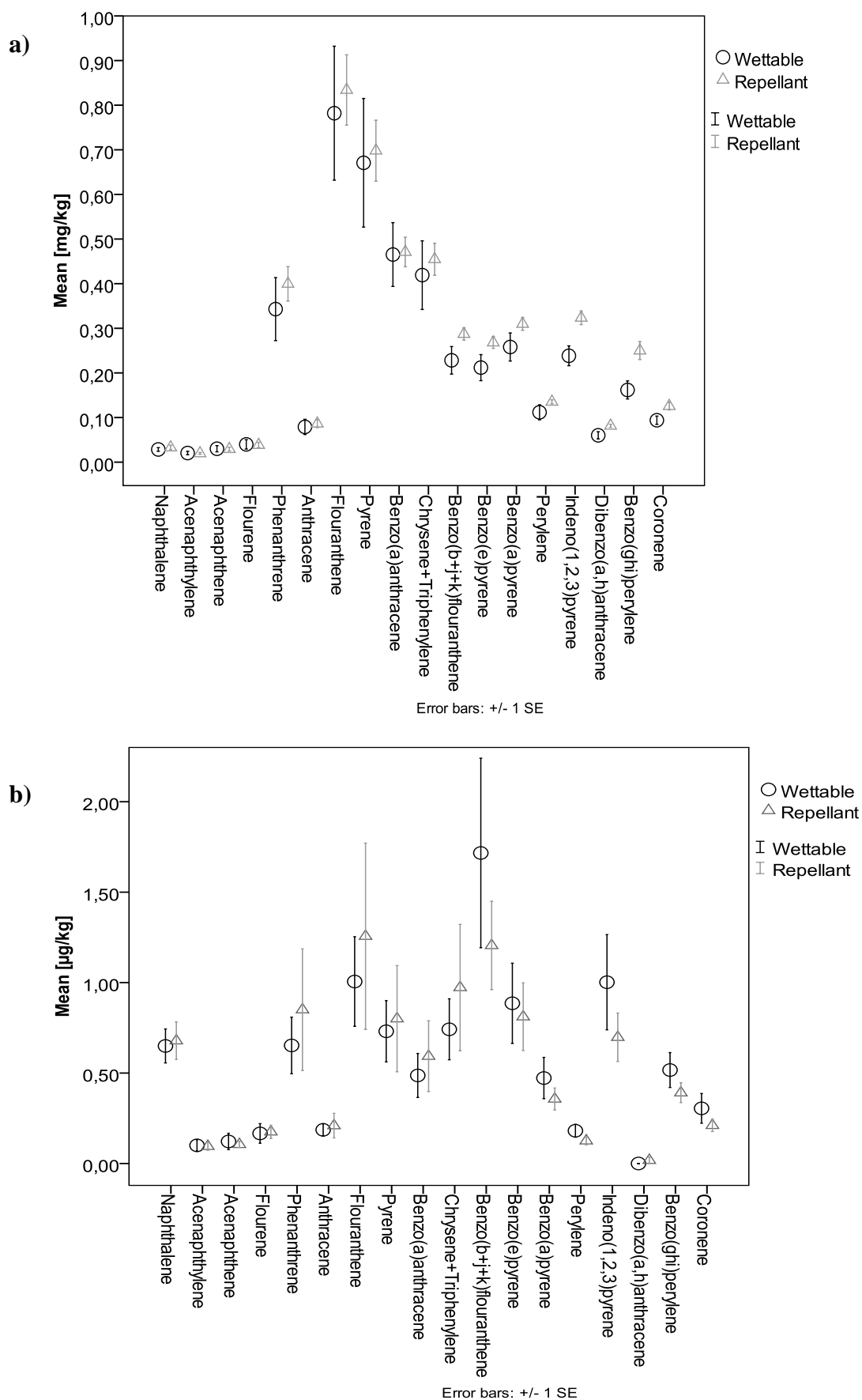
Fig. 7-5: 16 EPA PAH concentration in soil (a) and in soil suspensions (b) of wettable and repellent samples at Tiergarten location (error bars represents +/-1 standard error)

Table 7-3: Percentual share of colloidal PAH in soil suspension of Buch and Tiergarten samples

	3-ring PAH [%]	4-ring PAH [%]	5-ring PAH [%]	6-ring PAH [%]
Buch	52	79	91	98
Tiergarten	44	57	68	84

These findings are in agreement with previous studies suggesting that the affinity of hydrophobic organic contaminants such as PAH to colloids increases with increasing molecular weight and with the octanol/water partition coefficient of the PAH and with increasing organic carbon content of the colloids (Kretzschmar et al., 1999; Villholth, 1999). Similar to other earlier performed studies no correlation between DOC and PAH concentrations were found (Weigand et al., 2002; Wehrer & Totsche, 2009; Totsche et al., 2007). This may indicate that DOC in soil suspensions at pH values < 5 was mainly composed by a more mobile hydrophilic fraction (Reemtsma et al., 1999; You et al., 1999), while several studies have shown that PAHs were mainly bound to the hydrophobic DOM fraction (Chefetz et al., 2006; Guo & Ma, 2009; Ilani et al., 2005; Polubesova et al., 2007; Raber et al., 1998; Schlautman & Morgan, 1993), which is less mobile (Petruzzelli et al., 2002). Although total PAH concentrations in Tiergarten and Buch soils did not differ between water repellent and wettable samples, concentrations of almost all 5 and 6 fused rings PAH in soil suspensions of wettable samples from Buch were significant higher than those of water repellent samples. These differences were not found for the soil pairs from Tiergarten. These findings let us suggest that hydrophobic organic colloids in water repellent samples were aggregated due to attractive interaction forces, leading to a decrease in colloid mobilisation. Our results agree with that obtained by Wilcke et al. (2003), reporting that the mobilisation of high-molecular weight PAHs from air-dried samples are consistently lower than those in field-fresh extracted samples, which they attributed to the disaggregation or stretching of the SOM resulting in an increased PAH accessibility.

7.5 Conclusion

In summary we observed only small differences between wettable and water repellent soil samples with regard to the mobilisation potential of colloids and contaminants. At the former sewage site Buch it is likely that conformational changes occurred at the SOM surfaces of water repellent soil samples, but due to the long lasting leaching procedure only small differences between wettable and water repellent soil samples were found. The similarity in

release pattern of wettable and water repellent soil pairs let us suggest that physico-chemical dispersibility characteristic of wettable and water repellent soil samples become rather similar when they are subject to long lasting batch extraction procedures as these used here. Conformational changes occurring at the SOM surfaces of water repellent soil samples may influence the release properties only during the initial rewetting process. This leads to the assumption that strong mechanical shaking and the intense contact of soil particles with water in our dispersion experiments eliminated almost all potential existing dispersibility differences which may occur at lower and less intense contact times. This was also demonstrated by visible differences in turbidity obtained after manual shaking of water repellent and wettable soil samples for one minute. Aqueous solution of wettable soil sample was turbid, while that of the water repellent soil sample was clear. We therefore recommend for the future the investigation of dissolution mobilisation kinetics, in order to determinate the impact of soil water repellency on the mobilisation potential.

Total contaminant loads and physico-chemical solid soil properties between water repellent and wettable soil samples were almost identical. Also the percentage of mobilised contaminants to the total soil contents between wettable and water repellent samples revealed no differences. Hence our first initial hypothesis assuming that total contaminant loads and mobilisation potential of contaminants in water repellent areas are higher due to bypass flow of persistent water repellent areas in the field must be rejected. On the other hand it can be supposed that sampled soil pairs were not persistent water repellent or wettable due to their immediate vicinity. This is often found since the cross section of preferential flow pathways may increase or decrease in dependence of the rainfall rate. Our second initial hypothesis suggesting that the mobilisation potential of contaminants in water repellent soil samples may be decreased due to the low physico-chemical reactivity of hydrophobic organic compounds could be partly confirmed for the soil sample pairs from Buch location. Hereby it was shown that the mobilisation potential of colloid-bound Cu and colloid-bound high molecular weight PAHs was higher in the wettable samples. We assume therefore that organic colloids, to which these contaminants were likely bound, of water repellent samples are more aggregated and held by the hydrophobic organic surface due to attractive interaction forces. In contrast the mobilisation potential of dissolved Cu and DOC was increased in the water repellent areas, indicating that microbial cell lysis contributed to increased dissolution of organic carbon, which in turn increased the mobilisation potential of Cu-DOM complexes. These interrelations were not found for the Tiergarten soil samples. Contrary to the undisturbed grasslands at the former sewage site Buch, the municipal park Tiergarten is frequented by

people and the park is subject to maintenance operations, which prevent the accumulation of partly decomposed plant residues and hence hydrophobic substances. Our results lead therefore to the assumption that soil organic matter quantity rather than quality influenced the water repellency at the Tiergarten location. That is indicated by the correlation between water and organic c contents among wettable ($r^2 = 0.8$) and repellent soil samples ($r^2 = 0.5$), while no correlation was found for the soil samples from Buch.

8 Predicting the potential mobility of heavy metals in the field using batch elution experiments

8.1 Abstract

Groundwater risk assessment of contaminated sites using in situ monitoring techniques of soil solution is not always feasible. Various laboratory tests are available to evaluate solute concentrations in the field, from which batch dispersion experiments are frequently used. The aim of our study was to evaluate the applicability of the batch elution test DIN 38414 part 4 (DEV S4) to a seepage water prognosis. For this purpose heavy metals (Cr, Cu, Cd, Ni, and Zn) and DOC concentrations in soil solutions sampled by lysimeters were compared with soil suspensions extracted from composite topsoil samples above the lysimeter plots.

Our study results suggest that S4 batch leaching elution were able to predict mean field soil solution concentrations of DOC, Cu, Cr and Cd. The S4 batch leaching test failed to give an estimate of soil solution concentrations of the highly soluble heavy metals Zn and Ni.

8.2 Introduction

The groundwater contamination risk can be assessed through the evaluation of solute concentration and mass fluxes, using in situ monitoring techniques of soil solution and laboratory tests such as column leaching or batch leaching experiments. While in situ monitoring of the soil solution in the field is time-consuming and costly since seasonal and spatial variations have to be determined, batch leaching experiments are cheap and fast analysis methods, although they give only an estimation of the real in situ conditions. Column tests simulate better field conditions than batch tests too (e.g. more realistic L/S ratio), but are as well labour-intensive, time-consuming and costly compared to batch tests. Since direct monitoring of soil solution in the field is not always realisable, batch leaching tests for the quantification of solute fluxes and concentrations are needed. Various batch leaching tests exist which are categorized according the extractant and liquid-to-solid ratios (L/S ratios) used. These tests generally describe the maximal leachable solute concentration (mg l^{-1}) or the constituent release (mg kg^{-1} dry mass) in an aqueous solution under equilibrium conditions (Andres et al., 2002; van der Sloot, 1998). In this study the batch elution test DIN 38414 part 4 (DEV S4) is discussed which is mentioned besides three other leaching tests, in the German Soil Protection Ordinance for groundwater risk assessment. This leaching test closely resembles the one-stage European Standard batch leaching test (Draft European Standard prEN 12457, Procedure B). However, batch leaching tests can only give an estimation of the

real in situ conditions, since all particle surfaces are in intense contact with the eluting solution, and spatial and temporal variability of the flow field in the soil matrix is not considered (Buczko et al., 2004). In addition the high water soil (L/S) ratio 10:1 leads to dilution of weakly sorbed contaminants, while mechanical shaking may dislodge or create colloidal particles and thereby increasing concentrations of colloid-bound contaminants (Bergendahl, 2005). This may be especially true for strong sorbing heavy metals that have a tendency to associate with colloids such as Cu, Cr or Pb. In this context leachability of weakly and strongly bound contaminants are distinguished: If sorption is less pronounced, the leachability of a certain contaminant can be limited by its availability, hence the liquid phase concentration decreases with increasing L/S ratio. The constituent release (in mg kg^{-1} dry mass) is in this case is not affected by the L/S ratio. Otherwise, if the contaminant is very strongly sorbed, the leachability can be limited by reaching distribution equilibrium between the solid and the liquid phase. In this case the L/S ratio has no influence on the concentration (in mg L^{-1}), but on the release (in mg kg^{-1} dry mass) (Iden et al., 2008; Schuwirth & Hofmann, 2006).

Many factors may influence the release of heavy metals both in the field and in the batch elution test. Main factors are physical (particle size, particle homogeneity and porosity, or temperature), chemical (pH, redox conditions, complexation phenomena, binding form, reaction kinetics of individual heavy metals) and biological (Schuwirth & Hofmann, 2006; van der Sloot, 1996). However the most important parameter controlling leaching of metals and metalloids have been reported to be the pH value (Dijkstra et al., 2004; Sommerfeld & Schwedt, 1996; van der Sloot, 1998; Yin et al., 2002).

Discrepancies still exist in the applicability of leaching tests for groundwater risk assessment of contaminated sites. According to several studies S4 batch leaching concentrations are able to predict the mean or maximal field soil solution concentrations for some elements (Durner et al., 2004; Karnuth, 2003; Scheithauer et al., 2006a; Scheuering et al., 2005). This was especially true for Cu concentrations in which the S4 concentrations were able to predict the soil solution concentrations quite well (Durner et al., 2004; Scheithauer et al., 2006b; Scheuering et al., 2006).

Within this study we will identify therefore the suitability of the batch leaching test S4 as an alternative to field soil water sampling for the prediction of inorganic contaminant concentrations. For this purpose we compared S4 batch leaching concentrations with mean concentrations of soil solutions sampled by tension lysimeters in an annual field experiment.

8.3   Material and Methods

8.3.1 Site description

Soil solutions were monitored between January 2007 and March 2008 using five tension plate lysimeters installed in a 1 m by 7 m field plot located within a former sewage site in Berlin Buch, Germany. Sewage infiltration was practiced for almost 100 years and stopped in 1985. The soil is classified as a deep, well drained and acid hortic anthrosol with an Ah horizon (30 cm – 40 cm) over medium sized homogenous sandy subsoil. Sand is the dominant textural fraction accounting for about 98 % by mass.

8.3.2 Soil properties

After the lysimeter study was completed composite soil samples were taken from the Ah horizon (at 10 cm to 30 cm depths) above each lysimeter plate. Table 8-1 shows basic chemical soil properties at this site.

Table 8-1: Basic chemical soil properties
(SD: standard deviation)

	pH (CaCl$_2$) [-]	pH (H$_2$O) [-]	Conductivity [μS cm^{-1}]	organic matter [g kg^{-1}]	C [g kg^{-1}]	N [g kg^{-1}]	S [g kg^{-1}]	C/N ratio [-]
Mean	4.4	5.0	197.0	86.0	44.38	4.40	1.24	10.18
SD	.4	.6	55.0	2.5	1.05	.12	.045	.65

Total heavy metal topsoil concentrations between lysimeter plots were highly spatial variable (Fig. 8-1) and correlated, which Hoffmann (2002) and Schlenther et al. (1996) identified as a result of the sewage farming with nonuniform and simultaneous sedimentation of the pollutants with the solid organic particles in the sewer. Hence total topsoil heavy metal concentrations were highly correlated to the soil organic matter, organic C and organic N contents.
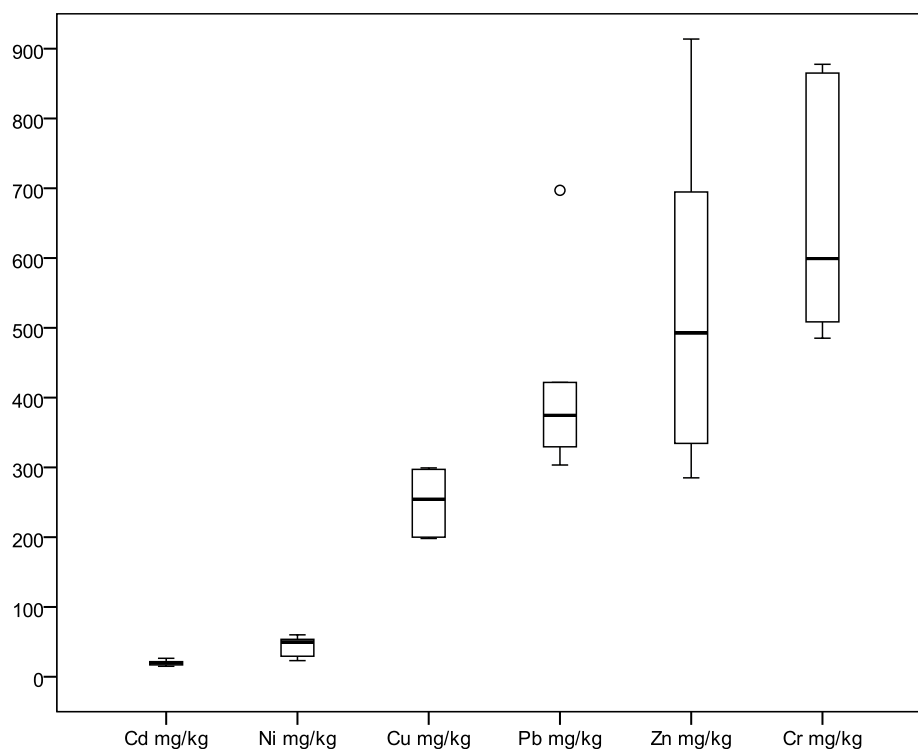
Fig. 8-1: Heavy metal topsoil concentrations (mg kg^{-1}) in the topsoil above lysimeter plates

8.3.3 Batch leaching test

We used the German batch leaching tests (DIN 38414 part 4, DEV S4-Test) with little modifications in order to determinate the mobilisation potential of contaminants. All extractions on field-moist soils (< 2 mm) were performed with deionised water (1:10 weight to volume ratio) using an end-over-end shaker at approximately 6 rpm for 16 h instead of 24 h according to kinetic studies realized by Klitzke et al. (2008). We assume that the composite soil samples used for the S4-Test average the soil properties over the surface area as well as over the horizon depth.

Prior to element analysis batch extracts were centrifuged at 176 g for 7 min (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) and then filtrated through a 1 μm glass microfiber filter (Whatman GF 6) in order to derive colloid-bound plus truly dissolved ($\leq$ 1μm) suspensions. Afterwards aliquots of these extracts were ultracentrifuged at 222194 g for 1.5 h (Beckman Coulter Preparative Ultracentrifuge Optima L-90 K) and the isolated supernatants were subsequently filtered through a 0.1 μm polycarbonate filter in order to obtain an almost truly dissolved fraction ($\leq$ 10 nm). Colloid-bound plus truly dissolved extracts were analysed for pH and electrical conductivity. Acidified suspensions at pH 4 were analyzed for total (colloid-bound plus truly dissolved) and truly dissolved Cu, Pb, Cr, Cd and Ni by a Graphite furnace-Atomic Absorption Spectrometer (Varian SpectrAA 880Z), for total

and truly dissolved Zn by flame atomic absorption spectroscopy (Perkin Elmer 1100 B) and for total (TOC) and truly dissolved organic carbon concentrations (DOC) by a total organic carbon analyser (TOC – 5050 A, Shimadzu).

8.3.4 Statistical analysis

Means, medians, standard deviations, analysis of variance and correlations were computed with the statistical analysis programme SPSS. Paired T-Tests were used to test for significant differences in chemical properties between batch extracts and soil solutions sampled by tension lysimeter. The probability level (p) of all tests was 95 %.

8.4 Results

Table 8-2: Average heavy metals (Pb, Cr, Cu, Cd, Ni and Zn) and DOC concentrations in S4-Batch soil suspensions and lysimeter soil solutions

	Lysimeter		Batch		Lysimeter		Batch		Lysimeter		Batch	
	colloidal + dissolved				dissolved				colloidal bound (%)			
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
DOC [mg l^{-1}]	49,3	14,8	34,6	20,1	47,6	12,4	15,5	3,2	1,2	,3	45,3	21,7
Cr [µg l^{-1}]	38,0	13,9	159,5	90,5	34,0	12,0	39,7	56,1	5,0	3,5	48,7	94,5
Cu [µg l^{-1}]	330,2	165,5	217,5	66,8	311,0	153,3	180,9	50,0	3,0	2,7	16,1	3,7
Cd [µg l^{-1}]	31,2	31,6	19,0	4,8	28,0	33,4	12,5	3,8	10,8	61,4	33,5	12,2
Ni [µg l^{-1}]	677,2	270,6	19,3	10,9	638,6	250,0	18,8	11,3	2,3	1,1	3,4	5,3
Zn [mg l^{-1}]	11,0	7,4	1,3	,8	9,7	5,6	1,2	,8	3,8	3,8	5,3	10,1

Cr

The average Cr concentration in S4 soil suspensions (160 µg l^{-1}) was about 4 times higher than that in the soil solutions (38 µg l^{-1}). The percentage of colloid-bound Cr (49 %) in S4 soil suspensions was about 10 times higher than that in lysimeter soil solutions (5 %). Paired T-Test showed no significance difference between truly dissolved Cr concentrations in S4 soil suspensions (mean 40 µg l^{-1}) and total Cr concentrations in soil solutions (mean 28 µg l^{-1}). Cr concentration in soil solutions and in S4 soil suspensions were highly correlated (r² = 0.824).

Cu

Paired T-Test showed no significance difference between the Cu concentrations in S4 soil suspensions (mean 218 µg l^{-1}) and soil solutions (mean 330 µg l^{-1}). However about 5 times more colloid-bound Cu (16 %) in S4 soil suspensions than in lysimeter soil solutions (3 %)

was mobilised. Cu concentrations in soil solutions and S4 soil suspensions were highly correlated ($r^2 = 0.716$)

Ni
Although the percentage of colloid-bound Ni in the S4 soil suspensions (3.4 %) and in lysimeter soil solutions (2.3 %) was almost comparable, the average Ni concentration in soil solutions (677 µg l^{-1}) was about 35 times higher than that in S4 soil suspensions (19 µg l^{-1}).

Zn
Although the percentage of colloid-bound Zn in the S4 soil suspensions (5.3 %) and in lysimeter soil solutions (3.8 %) was almost comparable, the average Zn concentration in soil solutions (11 mg l^{-1}) was about 8 times higher than that in the S4 soil suspensions (1.3 mg l^{-1}).

Cd
Paired T-Test showed no significance difference between the average Cd concentrations in S4 soil suspensions (19 µg l^{-1}) and that in the soil solutions (31 µg l^{-1}). However average colloid-bound Cd (33 %) in S4 soil suspensions was 3 times higher than in soil solutions (11 %).

DOC
Paired T-Test showed no significance difference between DOC concentrations in S4 soil suspensions (mean 35 mg l^{-1}) and that in soil solutions (mean 49 mg l^{-1}). However percentage of colloid-bound DOC in S4 soil suspensions (45 %) was 38 times higher than in lysimeter soil solutions (1.2 %).

8.5 Discussion

In order to evaluate the suitability of the S4 leaching test (DIN 38414 Part 4) to a seepage water prognosis, we compared concentrations of lysimeter soil solutions with those of S4 soil suspensions, prepared from composite topsoil samples above the lysimeter plots. It is evident that such a comparison has to be evaluated with caution, because S4 soil suspension concentrations do not consider seasonal variations of the soil solution concentrations. Soil particles are further in intense contact with the eluting solution in the dispersion experiments and therefore, the pore structure of the natural soil and the influence of the spatial variability of the flow field are not accounted for (Buczko et al., 2004).

Our study results suggest that S4 batch leaching tests are able to predict the mean field soil solution concentration of DOC, Cu, Cr and Cd. The batch extraction failed to give an estimate of the soil solution concentration of the highly soluble heavy metals Zn and Ni.

The high agreement in Cu, Cr, Cd and DOC concentrations between S4 soil suspensions and lysimeter soil solutions supports the hypothesis that Cd, Cu, Cr and DOC in soil suspensions and soil solutions were chemically equilibrated with the solid phase. Higher electrical

conductivities in the soil solutions (mean 632 μS cm^{-1}, SD 347) than those in the S4 soil suspensions (mean 197 μS cm^{-1}, SD 86) were likely responsible for the increased displacement and mobility of weakly sorbed metals such Ni and Zn (Backstrom et al., 2004; Linde et al., 2007; Norrstrom & Jacks, 1998; Voegelin et al., 2003). The highly soluble heavy metals Zn and Ni were almost mobilized as free ions in both S4 soil suspensions and lysimeter soil solutions, while the colloid-bound fraction of Cd, Cu and Cr was drastically elevated in the S4 soil suspensions. Lower salt concentrations in the S4 soil suspensions may have increased electrostatic repulsion between colloids, resulting in higher colloid release rates. It is also probably that mechanical breakdown of the aggregates during batch extraction procedure may have increased organic colloid dispersibility in the soil suspensions.

8.6 Conclusion

We conclude that the batch tests S4 can predict the potential mobility of low soluble heavy metals Cu and Cr, while it failed for highly soluble heavy metals Zn and Ni. For these heavy metals where sorption is less pronounced and the leaching process is availability controlled a lower L/S ratio would be needed in order to make concentration predictions. The high soluble elements show further a strong pH and conductivity dependency; therefore adjusting these leaching controlling parameters may result in a better match between concentrations in S4 soil suspensions and soil solutions.

9 Synthesis and general conclusion

9.1 Performance of tension and zero-tension lysimeter in a partially water repellent sandy soil at a former sewage site

Long term means of collection efficiencies (CE) indicate that TL (CE 32 %, SD 24) are the preferable devices in monitoring water fluxes in heterogeneous water repellent soils than ZT (CE 2 %, SD 2). Reduction in the cross sectional of water flow in the dry growing season decreases CE of TL when they are subject to bypass flow. However water repellency due to surface runoff from slightly elevated parts into sinks may also increase the performance of single TL if they are not bypassed by preferential flow. Unsaturated preferential flow is a common phenomenon under low to moderate rainfall rates in partially water repellent soil, which will not necessarily lead to accelerated water and solute fluxes through the vadose zone. ZT (CE 28 % SD 19) perform comparable well to TL (CE 31 % SD 19) under strong rainfall events. ZT are therefore the preferable devices for the detection of accelerated fluxes through saturate preferential flow pathways, what might be more dangerous for the groundwater contamination.

9.2 Persistence of preferential flow patterns in a partially water repellent sandy soil at a former sewage site

Heterogenic infiltration patterns are predominant under low to moderate rainfall rates and under strong rainfall intensities in partially water repellent soils. Although the cross section of preferential flow pathways varies depending on net infiltration amounts and the season, preferential flow pathways are persistent due to small scale spatially variable soil hydraulic properties, which promote water flow and finger formation through wetter soil parts. Because of hysteresis in the water retention curve, these previous created finger pathways recur and persist during following infiltration events. Lateral redistribution of infiltration water into less hydrophobic soil parts does not necessarily increase the cross section of water flow, when preferential flow pathways are not hydraulic active. Image analysis of dye coverages in the field may therefore overestimate the cross section of preferential flow pathways in partially water repellent soils.

9.3 Factors controlling the mobility of contaminants in a partially water repellent sandy soil at a former sewage site

The mobility of highly soluble heavy metals such as Cd, Ni, and Zn from organic rich acid soils is increased at low pH through proton competition and/or proton promoted dissolution and at high salt concentration through increased displacement. In contrast DOC contributes

through complexation reactions to the mobility of Cu and partly to the mobility of Cr. Pb and PAH are stronger sorbed to the organic matter and are hardly mobilised from organic rich acid soils. Colloid-bound contaminant transport (1.8 % - 10 %) does not play a major role in the partially water repellent and acid soil. High solution ionic strength, soil acidity (pH 4-5) and water repellency prevents colloid release. While inorganic or organo-mineral colloids may be disintegrated from the SOM and contribute partly to the mobility of some contaminants, organic colloids are held by hydrophobic interaction forces in the SOM and prevent the mobility of strong sorbing contaminants such as Pb and PAHs. Zn and Ni have a 10 fold higher mobility than the other heavy metals (Zn>Ni>Cd>Cu>Cr>Pb). High topsoil contamination loads and a low filter capacity of subsoil increases the potential groundwater contamination risk. Annual contaminant mass fluxes (Cd, Ni, Zn, Cu and Cr) are positively related to the lysimeter collection efficiencies; while contaminant concentrations in soil solutions are not related to the lysimeter collection efficiencies. This indicated that the transport of contaminants is controlled by the total cross sectional area of water flow. Under low to moderate rainfall rates unsaturated preferential flow predominates and decreases contaminant fluxes since great parts of the topsoil are bypassed. Only strong rainfall events accelerate contaminant fluxes through saturated preferential flow pathways which might be more dangerous for groundwater contamination.

9.4 Factors controlling the mobilisation potential of contaminants in water repellent and wettable soil samples in a batch dispersion experiment

The accumulation of hydrophobic compounds from partly decomposed plant residues can partly contribute to a lower physico-chemical reactivity of the SOM in water repellent soil samples. In contrast in soil with a deficit of accumulated plant residues, water repellency is not generated by new input of hydrophobic substances, but by low soil moisture contents.

Because total contaminant loads and physico-chemical properties between adjacent actually water repellent and wettable soil pairs sampled from the field are almost identical, it is assumed that adjacent soil samples are not persistent water repellent or wettable if they are sampled in the immediate vicinity. Periodical moisture-related alterations in the cross section of preferential flow pathways may mask the spatial pattern of persistent wettable and water repellent areas. On the other hand increased mobilisation potential of colloid-bound Cu and colloid-bound high molecular weight PAHs in the wettable samples indicate that SOM in water repellent soil is relatively chemically inert and decreases the release of organic colloids due to hydrophobic attractive interaction forces. In contrast microbial cell lysis contributes to

increased dissolution of organic carbon in water repellent soil samples, which in turn increase the mobilisation potential of Cu-DOM complexes.

The similarity in release patterns between actually wettable and repellent soil pairs suggests further that physico-chemical dispersibility characteristic become rather similar, when the soil sample pairs are subject to long lasting batch extraction procedures. Strong mechanical shaking and the intense contact of soil particles with water in dispersion experiments eliminates almost all potential existing leaching characteristics between actually wettable and water repellent soil samples which may occur at lower and less intense contact times. Conformational changes occurring at the SOM surfaces of water repellent soils may influence dispersibility characteristic therefore only during the initial wetting process.

9.5 Dispersion experiments to a seepage water prognosis

The S4 leaching test (DIN 38414 Part 4) has proven successfully in predicting the mean concentration of Cd, Cu, Cr and DOC of soil solutions sampled by lysimeters in an organic rich sandy soil, while it failed for the highly soluble heavy metals Zn and Ni. For these heavy metals where sorption is less pronounced and the leaching process is availability-controlled a lower L/S ratio is necessary in order to make concentration predictions. The highly soluble elements Zn and Ni show further a strong pH and conductivity dependency; therefore adjusting these leaching controlling parameters may result in a better match between concentrations in S4 soil suspensions and sampled soil solutions.

9.6 Outlook

Lysimeter size:

For future lysimeter studies in heterogeneous water repellent soils we recommend to increase sidewalls or pan sizes of plate lysimeters, in order to decrease bypass flow and increase lysimeter performance. However sidewalls may enhance the risk of preferential flow along the walls, while larger pan sizes may increase the risk of collapse of certain soil horizons during installation procedures. This is especially the case for soils with a low bulk density. We suggest therefore adapting the plate size to the flow finger diameter encountered in the field. Because of periodical flocculations in the cross section of water flow the plate size should be at least twice time greater than the mean flow finger size that is visually assed in the field.

Lysimeter type:

While TL are the favourable devices to monitor solute and water fluxes in the heterogeneous water repellent field soils, ZT can help to distinguish between saturated and unsaturated water fluxes.

Sampling interval:

Since soil solution samples in contact with the atmosphere releases CO_2, pH value in solutions are increased during long sampling intervals, which in turn may influence physico-chemical properties of the soil solutions. This is especially the case during wet and warm periods when CO_2 production is favoured by microbial activity. The sampling interval of soil solutions collected by lysimeter in the field should be kept to a minimum (maximal one week), when soil solutions physico-chemical parameters are of researcher's interest.

Sampling of potentially wettable and water repellent soil

Although the WDPT may help detecting of actually water repellent and wettable soil parts in the field, periodical moisture-related alterations in the cross section of preferential flow pathways may mask the spatial patterns of persistent wettable and water repellent soil areas. It is therefore recommended to complete sampling after a moist period, when dry soil parts are expected to be potential water repellent.

Dispersion kinetic studies of wettable and water repellent soil samples

In order to compare the release behaviour between water repellent and wettable soil pairs and to identify if the release in dependent on soil hydrophobicity or other underlying physico-chemical soil properties studies on dispersion kinetics are needed.

Dispersion kinetic studies should be less intense and short lasting, hereby resembling more accurate hydraulic shear forces encountered in the field soil than those used in the past.

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11 Annex

11.1 List of Figures

11.2 List of Tables

11.3 Abbreviations

AWI	air–water interface
BB	food dye tracer Brilliant Blue
BTC	breakthrough curve
CE	collection efficiency
CV	coefficient of variation
DEV S4	batch elution test DIN 38414 part 4
DOM	dissolved organic matter
EPA	Environmental Protection Agency
L/S ratios	liquid-to-solid ratios
MIR	minimal net infiltration rate
P	probability level
PAH	polycyclic aromatic hydrocarbons
PE	polyethylene
PET	potential evapotranspiration
PTFE	teflon
PVC	polyvinylchloride
RW	rainwater pulse
SD	standard deviation
SEM	scanning electron microscopy
TG	Berlin-Tiergarten
TL	tension lysimeter
TOC	total organic carbon
TR	tracer pulse
WDPT	Water Drop Penetration Test
ZT	zero-tension lysimeter

12 Acknowledgements