TECHNISCHE UNIVERSITÄT MÜNCHEN

Lehrstuhl für Bodenkunde

Polycyclic aromatic hydrocarbons released from a coal tar-contaminated gravelly soil under laboratory and natural conditions

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Vollständiger Abdruck der von der Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt der Technischen Universität München zur Erlangung des akademischen Grades eines

Doktors der Naturwissenschaften (Dr. rer. nat.)

genehmigten Dissertation.

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Die Dissertation wurde am 23.09.2005 bei der Technischen Universität München eingereicht und durch die Fakultät Wissenschaftszentrum Weihenstephan für Ernährung, Landnutzung und Umwelt am 03.02.2006 angenommen.

SUMMARY

The release of contaminants from non-aqueous phase liquids (NAPL) is a widespread problem at manufactured gas plant sites and associated industries. The evaluation of the release kinetics and transport behavior of NAPL-borne contaminants such as polycyclic aromatic hydrocarbons (PAH) is crucial for risk assessment and the selection of appropriate remediation strategies at NAPL-contaminated sites. The fate of PAH is often coupled to the release and redistribution of dissolved organic carbon (DOC) and colloids/particles.

This study investigates the release kinetics and the aqueous equilibrium concentrations of PAH in a dialysis experiment and the release mechanism of PAH, DOC, and particles up to a size of 200 μm from a NAPL-contaminated gravelly soil with a column outflow experiment in the laboratory and with free-drainage lysimeters under natural conditions.

For the first experiment, coal tar was enclosed in a dialysis tubing to exclude the effect of colloids/suspended particles on the aqueous equilibrium concentration. These tubings were placed in water for a period of 140 days at 20°C and 4°C. Samples were taken at several intervals to analyze the aqueous phase concentrations of PAH. The observed concentrations at the end of the experiment were then compared to the theoretical concentrations calculated according to Raoult's law. Mass transfer coefficients were determined for five selected compounds using a first-order nonlinear model. Soil material for the column experiment was collected at an abandoned industrial coal tar-contaminated site. The lysimeter experiment was conducted at the same location. To detect rate limited release, two columns were run at two different mean pore water velocities, and multiple flow-interrupts were imposed. Column effluent and seepage water samples were analyzed for DOC, pH, electrical conductivity, turbidity, and the content of particles larger than 0.7 μm. The 16 EPA-PAH were analyzed in two particle size fractions (filtrate: <0.7 μm; retentate: 0.7-200 μm).

In the dialysis experiment, maximum concentrations of total PAH reached 2250 μg l^{-1} at 20°C after 112 days and 1610 μg l^{-1} at 4°C after 140 days. The higher temperature resulted in higher concentrations and higher mass transfer coefficients. The determined mass transfer coefficients at 20°C for the five PAH were between 0.0015 h^{-1} and 0.025 h^{-1}. For the 20°C experiment, Acenaphthylene, Anthracene and Pyrene showed constant concentrations after 112 days whereas Benzo[a]pyrene and Benzo[ghi]perylene concentrations were still increasing. At 4°C, all five compounds showed increasing concentrations at the end of the experiment. The equilibration time of 140 days seemed to be not sufficient to reach equilibrium at 4°C. Comparison of the observed final concentrations with the aqueous equilibrium concentrations calculated according to Raoult showed the applicability of Raoult's law although the high molecular weight PAH had not reached equilibrium during the course of the experiment.

The column experiment revealed that the release of DOC and PAH in the filtrate was strongly rate limited. Measured PAH concentrations differed markedly from those calculated by Raoult's law. Equilibrium dissolution seems to be of minor importance for the studied materials and the applied flow conditions. Particle release as well as the release of particle-associated PAH were dependent on the flow velocity. For the slow flow velocity, 67% of the total PAH were found in the filtrate, while for the fast flow velocity the amount of particle-associated PAH decreased to 58%. The strong correlation of DOC with the PAH in the filtrate implies a marked influence of DOC on PAH transport. The similar PAH pattern in the filtrate, the retentate and the soil suggests that PAH transport took place predominantly in form of small NAPL droplets or fragments.

The results of the lysimeters showed that extended no-flow periods which were followed by high intensity rain events such as thunderstorms promoted the mobilization of particles in the size of 0.7-200 μm. The release of PAH in the fraction <0.7 μm is presumably coupled to the release of DOC. A transport of PAH in form of dissolved molecules seems to be negligible. In winter time, high particle concentrations were associated with freezing and thawing cycles followed either by rain or snowmelt. The overall export of PAH was dominated by particle-associated PAH in the fraction 0.7-200 μm. During the two-year monitoring period, a total of 135 μg PAH was mobilized in the filtrate (<0.7 μm) while the 8-fold mass, 1085 μg, was exported within the retentate. Extreme single release events occurred in January 2003 and 2004 when up to 340 μg PAH per seepage event were observed within the retentate. Freezing and thawing cycles seem to influence also the PAH source materials, i.e. the remnants of the NAPL phase. The high mechanical strain during the freezing resulted in the formation of particles. At the onset of the thawing and following rain or snowmelt events, PAH were exported from the lysimeter associated with these newly generated soil particles or within NAPL particles. The release and transport process of particle-associated PAH should be more thoroughly considered in risk assessment at contaminated sites.

ZUSAMMENFASSUNG

Die Freisetzung von Schadstoffen aus Teerölphasen ist ein weit verbreitetes Problem auf ehemaligen Gaswerkstandorten. Die Kenntnis der Schadstofffreisetzungsraten und –mengen aus solchen Quellen ist daher unabdinglich für die Risikobewertung und die Auswahl geeigneter Sanierungsverfahren. Die Freisetzung und der Transport solcher Schadstoffe, wie zum Beispiel der polyzyklischen aromatischen Kohlenwasserstoffe (PAK), werden durch mobile Sorbenten, wie z.B. gelöster organischer Kohlenstoff (DOC), anorganische Kolloide und suspendierte Partikel, beeinflusst. Die Mobilisierung und die Verlagerung von partikelgebundenen PAK an kontaminierten Standorten kann somit in einer Umverteilung der Schadstoffe innerhalb der ungesättigten Zone resultieren und diese können so auch das Grundwasser erreichen. Eine verlässliche Gefährdungsabschätzung setzt daher eine quantitative Beurteilung des Einflusses mobiler Sorbenten auf die Freisetzung und Verlagerung von Schadstoffen voraus.

Diese Studie befasst sich daher mit den Freisetzungskinetiken und den wässrigen Gleichgewichtskonzentrationen von PAK und den Freisetzungsmechanismen von PAK, DOC und mobiler Sorbenten bis zu einer Partikelgröße von 200 µm aus einem teerölkontaminierten, kiesigen Substrat anhand gesättigter Säulenexperimente im Labor und mit Lysimetern unter natürlichen Bedingungen.

Im ersten Experiment wurden Dialysemembrane benutzt, um die Konzentration der tatsächlich gelösten PAK zu erfassen und den Einfluss von Kolloiden und Teerölpartikeln auszuschließen. Dazu wurden die mit der Teerölphase befüllten Dialysemembrane in destilliertem Wasser bei 20°C und bei 4°C für 140 Tage equilibriert. Der Verlauf der wässrigen PAK-Konzentrationen wurde anhand mehrerer Probenahmezeitpunkte bestimmt. Daraus wurden für fünf ausgewählte PAK mit einem nichtlinearen Modell erster Ordnung die Freisetzungsraten ermittelt. Das Bodenmaterial für die Säulenexperimente wurde an einem teerölkontaminierten Altlastenstandort entnommen, an dem auch die Lysimeterexperimente durchgeführt wurden. Für die Säulenexperimente wurde ein spezielles experimentelles Design angewendet, welches zwei Säulen mit unterschiedlicher Fliessgeschwindigkeit und mehrere Flussunterbrechungen umfasst, um mögliche kinetische Limitierungen erfassen zu können. Die Analyse der Säulenperkolate, sowie der Sickerwasserproben der Lysimeter, umfasste die Bestimmung der 16 EPA-PAK in der flüssigen (<0,7 µm),

wie auch in der festen Phase (0,7-200 µm), den DOC-Gehalt, den pH, die elektrische Leitfähigkeit und die Trübe.

Im Dialyseexperiment erreichten die Konzentration der PAK-Summe Maximalwerte von 2250 µg l^{-1} nach 112 Tagen bei 20°C und 1610 µg l^{-1} nach 140 Tagen bei 4°C. Die höhere Temperatur führte zu höheren Gesamtkonzentrationen und zu höheren Freisetzungsraten. Die errechneten Freisetzungsraten bei 20°C lagen für die fünf PAK zwischen 0.0015 h^{-1} und 0.025 h^{-1}. Bei 20°C zeigten Acenaphthylen, Anthracen und Pyrene nach 112 Tagen konstante Konzentrationen, während die Konzentrationen von Benzo[a]pyren und Benzo[ghi]perylen nach 140 Tagen noch einen ansteigenden Trend aufwiesen. Für das 4°C Experiment war die Zeit von 140 Tagen anscheinend nicht ausreichend, um ein Gleichgewicht zu erreichen. Zur Überprüfung der Anwendbarkeit des Raoult`schen Gesetzes wurden die Gleichgewichtskonzentrationen nach Raoult berechnet und den beobachteten Endkonzentrationen gegenüber gestellt. Der Vergleich zeigte die generelle Anwendbarkeit des Raoult`schen Gesetzes unter Ausschluss kolloidaler Partikel, obgleich die höhermolekularen PAK die Gleichgewichtskonzentrationen während des Experiments nicht erreichten.

Die Säulenexperimente zeigten anhand des Einflusses von Fliessgeschwindigkeit und Dauer der Flussunterbrechungen eine stark ratenlimitierte Freisetzung von PAK in der Fraktion <0,7 µm und von DOC. Die beobachteten PAK-Konzentrationen in dieser Fraktion wichen stark von den nach dem Raoult`schen Gesetz errechneten Konzentrationen ab. Die Freisetzung von Partikeln und partikelgebundenen PAK in der Fraktion 0,7-200 µm war abhängig von der Fliessgeschwindigkeit. Der Gesamtaustrag von PAK aus den Bodensäulen wurde durch die Fraktion <0,7 µm dominiert. Bei der geringeren Fließgeschwindigkeit wurden zwei Drittel des Gesamtaustrages (67%) in dieser Fraktion ausgetragen. Für die höhere Fließgeschwindigkeit lag dieser Anteil nur noch bei 58%. Die starke Korrelation zwischen der Freisetzung von DOC und PAK in der Fraktion <0,7 µm deutet auf einen erheblichen Einfluss von DOC auf die Freisetzung von PAK hin. Die übereinstimmenden PAK-Muster der Fraktionen <0,7 µm, 0,7-200 µm und des Bodenmaterials legen den Schluss nahe, dass der Transport von PAK hauptsächlich in Form von kleinen Teeröltröpfchen oder -fragmenten stattfindet.

Die Ergebnisse der Lysimeter zeigten, dass lange Trockenperioden gefolgt von Starkregenereignissen oder Schneeschmelzen die Freisetzung von 0,7-200 µm großen Kolloiden und Partikeln begünstigen. Im Gegensatz zu den Säulenexperimenten

dominierte unter Feldbedingungen die Fraktion 0,7-200 µm den PAK-Austrag. In der Fraktion <0,7 µm ist die Freisetzung vermutlich an die Freisetzung von DOC gebunden. Der Transport in Form gelöster PAK-Moleküle scheint vernachlässigbar unter den beobachteten Bedingungen. Maximale PAK-Mengen wurden jeweils im Winter ausgetragen. Durch den Wechsel von Gefrieren und Auftauen und der damit verbundenen mechanischen Belastung des Bodenmaterials kam es zur Bildung und Freisetzung von Partikeln und partikelgebundenen PAK, die durch darauf folgende Regenereignisse oder Schmelzsickerwässer ausgewaschen wurden.

Der PAK-Austrag aus dem untersuchten Bodenmaterial ist stark an die Bildung und Mobilität von Kolloiden und suspendierten Partikeln gebunden und sollte daher bei der Bewertung des Stoffaustrages mit dem Sickerwasser innerhalb der Beurteilung kontaminierter Standorte in Betracht gezogen werden.

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GLOSSARY

Ace	Acenaphthene
Acy	Acenaphthylene
a	Parameter of the gamma distribution
Ant	Anthracene
BaA	Benz[a]anthracene
BaP	Benzo[a]pyrene
BbFlA	Benzo[b]fluoranthene
β	Parameter of the gamma distribution
$\beta*$	Variable for partitioning in non-equilibrium transport models
bgl	Below ground level
BkFlA	Benzo[k]fluoranthene
BghiP	Benzo[ghi]perylene
C_{act}	Concentration after the flow was resumed
C_{eq}	Equilibrium concentration
C_i	Concentration before the flow-interrupt
C_{meas}	Measured concentration
C_{org}	Organic carbon
C_t	Concentration within the coal tar
C_w	Aqueous equilibrium concentration
Chr	Chrysene
D	Coefficient of dispersion
ΔS_m	Entropy of fusion at melting temperature
Da	Damköhler number
Da'	R-dependent Damköhler number
DahA	Dibenz[a,h]anthracene
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
EC	Electrical conductivity
FAU	Formazine Attenuation Units
F_{ed}	Dithionite soluble iron manganese
F_{eo}	Oxalate soluble iron
FlA	Fluoranthene
Flr	Fluorene

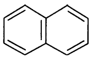
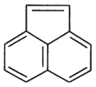
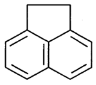
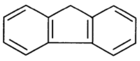
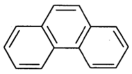
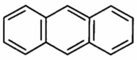
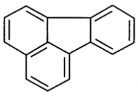
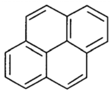
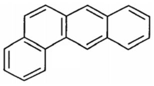
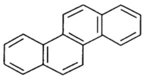
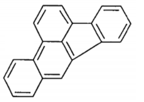
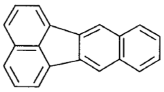
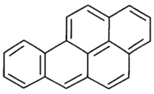
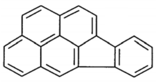
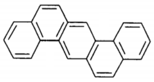
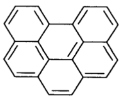
GC-MS	Gas chromatography - mass-spectrometry
k_{eff}	Effective mass transfer coefficient
IcdP	Indeno[1,2,3-c,d]pyrene
ICP-OES	Inductively coupled plasma - optical emission spectroscopy
ID	Inside diameter
K_{oc}	Partitioning coefficient soil organic carbon - water
L	Column length
λ	Dispersivity
LEA	Local equilibrium assumption
Mn_d	Dithionite soluble manganese
Mn_o	Oxalate soluble manganese
MW	Molecular weight
MW_t	Molecular weight of the coal tar
Nap	Naphthalene
NAPL	Non-aqueous phase liquids
ω	Dimensionless mass transfer coefficient
PAH	Polycyclic aromatic hydrocarbons
Phe	Phenanthrene
pv	Pore volume
Pyr	Pyrene
R_g	Universal gas constant
R	Retardation factor
r^2	Coefficient of determination
S_{max}	Concentration in the coal tar
S_{scl}	Subcooled liquid solubility
S_w	Aqueous solubility
$S_{w,\ m}$	Molecular aqueous solubility
SD	Standard deviation
T_m	Melting temperature
T	System temperature
t	Duration of the flow-interrupt
Θ	Volumetric water content
TSTR	Two-Site/Two-Region model
US-EPA	United States Environmental Protection Agency
v	Mean pore water velocity

1 INTRODUCTION

Polycyclic aromatic hydrocarbons (PAH) are a group of several hundred individual compounds containing at least two condensed benzene rings. They are formed ubiquitous by incomplete combustion of organic substances such as coal, oil, gas, wood, garbage, or tobacco. Once emitted, e.g. within soot particles, they are distributed atmospherically and therefore they are found throughout the environment in air, water and soil. PAH are an important environmental issue due to their persistence and their ecological toxicity. They exhibit carcinogenic, mutagenic and toxic effects (ATSDR, 1995). Their recalcitrance against microbial and chemical transformation in soils is high (Cerniglia, 1993; Ghoshal et al., 1996; Alexander, 1999; Weigand et al., 2002). PAH are considered immobile within the unsaturated zone because of their very low aqueous solubility, their high hydrophobicity, and their high affinity to the organic fraction of the soil matrix (Mackay & Shiu, 1977, Marschner, 1999). Table 1 show selected properties of the 16 PAH compounds from the priority list of the United States Environmental Protection Agency (US-EPA).

PAH are common pollutants on industrial sites contaminated by non-aqueous phase liquids (NAPL). NAPL are organic liquid or semi-liquid phases which represent a potential source of pollution in the subsurface of coke-oven, mineral oil and tar oil processing sites. Once NAPL are spilled on the ground, they migrate downwards to locations with abrupt textural changes or the capillary fringe. There they may spread laterally or accumulate resulting in the formation of secondary contaminant sources (Abriola and Bradford, 1998; Totsche et al., 2003a, b). PAH are major NAPL components and are therefore important NAPL-borne contaminants. The evaluation of the PAH release kinetics and transport behavior is therefore crucial for risk assessment and the selection of appropriate remediation strategies at NAPL-contaminated sites. The release of PAH from fresh NAPL has been shown to follow a dissolution process according to Raoult's law (Lane and Loehr, 1992; Lee et al., 1992; Eberhardt and Grathwohl, 2002): Here, the equilibrium concentration of an individual PAH compound in the aqueous phase is given by the product of the PAHs mole fraction in the NAPL phase and its aqueous solubility. However, possible rate limitations of the dissolution process may arise from diffusive limitations or from rate limited mass-transfer.

Table 1 Properties of the 16 US-EPA priority PAH

compound (formula)	structure	MW [g mol^{-1}][a]	S_w [mg l^{-1}][b]	log K_{oc}[c]
Naphthalene **($C_{10}H_8$)**		128	30	2.97
Acenaphthylene **($C_{12}H_8$)**		154	16.1	1.40
Acenaphthene **($C_{12}H_{10}$)**		154	3.47	3.66
Fluorene **($C_{13}H_{10}$)**		166	1.98	3.86
Phenanthrene **($C_{14}H_{10}$)**		178	1.29	4.15
Anthracene **($C_{14}H_{10}$)**		178	0.07	4.15
Fluoranthene **($C_{16}H_{10}$)**		202	0.26	4.58
Pyrene **($C_{16}H_{10}$)**		202	0.14	4.58
Benz[a]anthracene **($C_{18}H_{12}$)**		228	0.014	5.30
Chrysene **($C_{18}H_{12}$)**		228	0.002	5.30
Benzo[b]fluoranthene **($C_{20}H_{12}$)**		252	0.0012	5.74
Benzo[k]fluoranthene **($C_{20}H_{12}$)**		252	0.00055	5.74
Benzo[a]pyrene **($C_{20}H_{12}$)**		252	0.0038	6.74
Indeno[1,2,3-c,d]pyrene **($C_{22}H_{12}$)**		276	0.062	6.20
Dibenz[a,h]anthracene **($C_{22}H_{14}$)**		278	0.0005	6.52
Benzo[ghi]perylene **($C_{22}H_{12}$)**		276	0.00026	6.20

[a] molecular weight; [b] aqueous solubility (Mackay and Shiu, 1977; Walters and Luthy, 1984); [c] partitioning coefficient soil organic carbon-water (ATSDR, 1995)

For example, aging of NAPL, i.e. the depletion in soluble and volatile compounds and the biochemical transformation and polymerization of NAPL at the NAPL/air or NAPL/water interface, might result in the formation of high-viscous boundary layers. Such interfaces markedly limit dissolution and mass transfer kinetics of NAPL-borne compounds to the aqueous phase (Luthy et al., 1993; Nelson et al., 1996; Totsche et al., 2003a; Ghoshal et al., 2004), including the release of PAH (Mahjoub et al., 2000).

The presence of organic and inorganic colloids and suspended particles is known to substantially affect the mobility and transport of PAH. They act as mobile sorbents or carriers for PAH and other strongly sorbing solutes and thus facilitate their transport (Chiou et al., 1986; Grolimund et al., 1996; Villholth, 1999; MacKay and Gschwend, 2001; Kim and Corapcioglu, 2002; Totsche and Kögel-Knabner, 2004). Colloids are defined as suspended inorganic and organic particles of 1 nm to 1000 nm in size. Due to their characteristics, they provide surfaces, voids, and pores which may serve as sorption sites or sorption volume. Besides inorganic particles, such as clay minerals, metal hydroxides and oxides, organic (e.g. humic substances, soot particles) and bioparticles (bacteria, viruses, fungi) act as possible pollutant carriers (Chiou et al., 1986; Kögel-Knabner and Totsche, 1998; Kim and Corapcioglu, 2002; Totsche and Kögel-Knabner, 2004). Colloid mobilization is promoted by a change of pH, ionic strength or increased hydrodynamic forces caused by the infiltration of rain water (McDowell-Boyer, 1992; Ryan and Gschwend, 1994; Ryan and Elimelech, 1996; Bunn et al., 2002). Under natural conditions, such changes occur as a result of the variability of the climatic boundary conditions (precipitation, radiation, temperature) and the heterogeneity of the soils (McCarthy and McKay, 2004). A qualitative and quantitative understanding of the controls of soil-borne colloid/particle release and transport and the possible kinetic limitations is therefore an essential prerequisite for the understanding of the fate of PAH at contaminated sites.

The objectives of this study are (i) to determine the aqueous equilibrium concentration of PAH in contact with an aged coal tar, (ii) to quantify the release kinetics of PAH from an aged coal tar under laboratory and natural conditions, (iii) to test the applicability of Raoult's law to predict aqueous PAH concentrations, and (iv) to investigate the influence of colloids and suspended particles on the fate of PAH in laboratory and field experiments.

In the first experiment, the aqueous concentrations and the release kinetics of dissolved PAH at equilibrium with an aged NAPL phase were determined and the applicability of

Raoult's law was tested. To exclude the effect of colloids and particles on the aqueous phase concentration, release experiments were conducted using dialysis tubings (Woolgar and Jones, 1999). For this purpose, coal tar was enclosed in dialysis tubing and placed in water filled bottles for a period of 140 days at 20°C and 4°C. Samples were taken at several intervals to analyze the aqueous phase concentrations of the 16 EPA PAH. An aged coal tar taken from an abandoned industrial site was used to determine any discrepancies to the kinetics of "fresh" or synthetic coal tar described in the literature. The observed aqueous phase PAH concentrations after 140 days were then compared to concentrations predicted by Raoult's law.

The release and transport of PAH, dissolved organic carbon (DOC) as a possible carrier, and colloids/particles from contaminated gravelly soil material were studied in column experiments. The soil material contaminated with an aged coal tar originated from the same industrial site as in the dialysis experiment. Expecting the mobilization of large particles due to the high permeability of the gravelly material, particles up to size of 200 μm were investigated. To distinguish between PAH associated with large colloids or suspended particles on the one hand and PAH associated with small colloids or in dissolved form on the other hand, column effluent was filtered at 0.7 μm. As possible kinetic limitations of the release can only be detected within a small range of the ratio of the mass-transfer timescale to the transport timescale, an experimental design introduced by Wehrer and Totsche (2003, 2005) was applied. This design employs two different flow rates and at least two flow interrupts of different duration. The selected mean pore water velocities of 6.4 mm h^{-1} and 30 mm h^{-1} correspond to low and high rainfall intensities.

The third part of this work was to investigate the release of PAH, dissolved organic carbon (DOC), and colloids/particles under natural conditions. It focused on the effect of the climatic boundary conditions on the fate of PAH and colloids or particles. For this purpose, three free-drainage lysimeters were installed within gravelly soil material at the above mentioned industrial site. Again, particles up to a size of 200 μm were investigated because the eluviation of larger particles was expected due to the coarse texture and the high permeability of the gravelly material. The seepage water was filtered at 0.7 μm. In addition to the analysis of the seepage water, the amount of precipitation, the temperature in various depths and the soil moisture within one lysimeter was recorded. The applicability of Raoult's law was tested by comparison of calculated and observed PAH concentrations in the filtrate (<0.7 μm).

2 MATERIALS AND METHODS

2.1 Soil material and site history

The lysimeter experiment was conducted at an abandoned industrial site (area=0.03 km^2) located within the city of Munich, Germany. Soil material for the column experiment and samples of coal tar were collected at the same location. The site was used for high temperature distillation of tar, fuel production and mineral oil processing for about 110 years until it was put out of action in 1984. Spills occurred accidentally, through comparably slight damage in World War II and by improper depositing of residues (Guggenberger, 2002). The parent materials of the soils are quaternary glacial and postglacial gravelly sediments of limestone and dolomite (80%), with minor amounts of igneous and metamorphic rocks (Baumann et al., 2002). The amount of fine material (<2 mm) is generally less than 20% wt. Typical soils are Calcaric Regosols and Calcaric Luvisols. Due to construction activities, the natural soil profile is destroyed. Soils are contaminated with remnants of the fuel production, mineral and tar oils, in the following designated as non-aqueous phase liquids (NAPL). In 1988 the site was partly remediated by source zone excavation. Recent studies, however, established that still significant amounts of residual NAPL can be found heterogeneously spread throughout the unsaturated zone at various depths (Figure 1). Major NAPL compounds are PAH and petroleum-derived hydrocarbons.

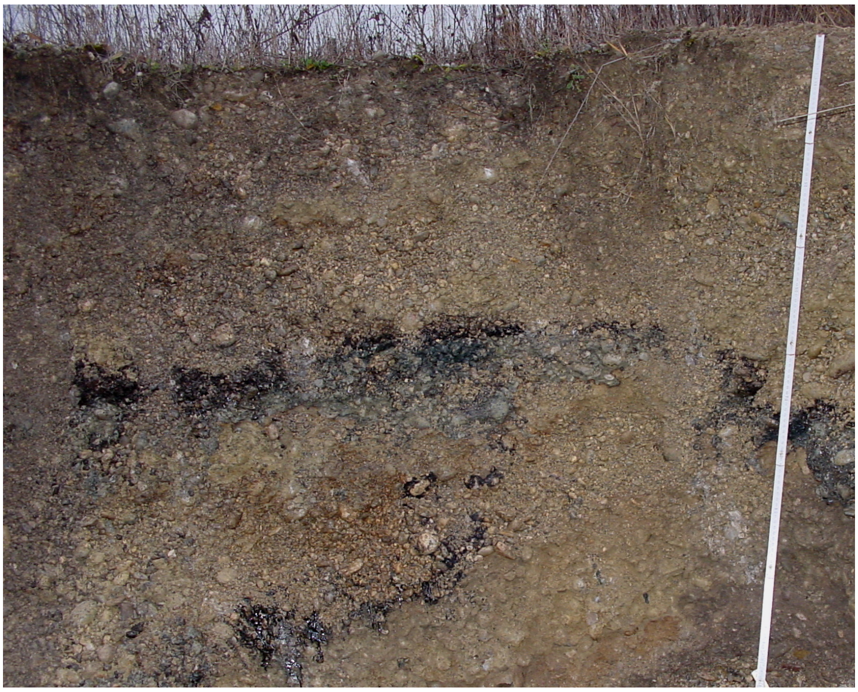


Figure 1 Soil profile with coal tar contamination.

2.2 Physical and chemical properties of the soil material

Particle size analysis was done by dry (>2mm) and wet sieving (sand fractions), and a sedimentation method with X-ray attenuation measurement (silt and clay fractions) [Sedigraph 5100, Micromeritics GmbH, Mönchengladbach, Germany]. The fraction <2 mm was analyzed for contents of organic carbon and carbonate in duplicate by dry combustion [CN-Analyzer Vario EL, Elementar, Hanau, Germany]. The contents of total and inorganic carbon were measured in air dried samples and after ignition at 550°C, respectively. The organic carbon concentration was calculated from the difference between total and inorganic carbon content. The pH values were determined in deionized water and in 0.01 M $CaCl_2$ solution using a soil to solution ratio of 1:2.5 (Avery and Bascomb, 1974). The oxalate and dithionite soluble iron and manganese were extracted according to Schwertmann (1964) and Mehra and Jackson (1960) and quantified by ICP-OES [Vista Pro CCD Simultaneous, Varian GmbH, Darmstadt, Germany]. Bulk densities were determined with an excavation method as described by Blake and Hartge (2002). The grain size distribution and physical and chemical properties of the soil material are given in Figure 2 and Table 2. The selected profiles 1 and 2 represent the locations of lysimeter 1 and lysimeter 2 and 3, respectively. The mineral phase is composed of limestone and dolomite gravels with small amounts of sand, silt and clay with embedded sand and silt lenses (profile 1, Figure 2).

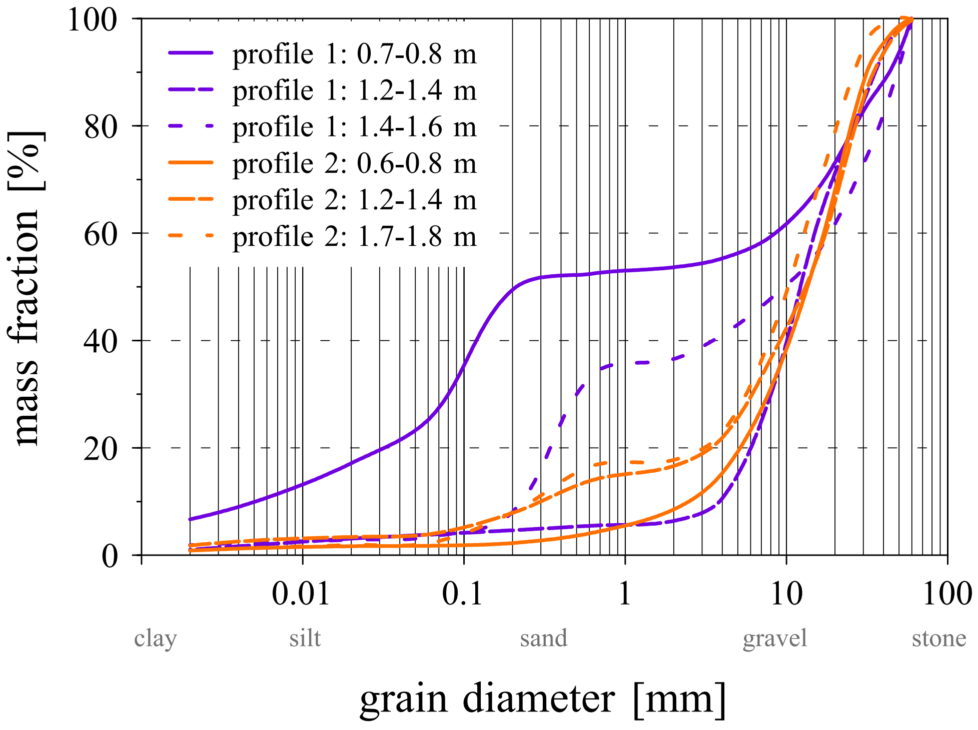


Figure 2 Grain size distribution of the soil material within the profiles.

Table 2 Properties of the soil material

profile	depth		gravel	sand	silt	clay	bulk density	pH		C_{org}	$CaCO_3$	Fe_o	Fe_d	Mn_o	Mn_d
	[m]		[% wt.]				[g cm^{-3}]	(H_2O)	($CaCl_2$)	[g kg^{-1}]		[mg kg^{-1}]			
1	0.7	0.8	46.6	27.7	19.1	6.6	2.5	9.1	7.9	1.3	187	3.0	123	1.4	2.7
1	1.2	1.4	93.7	2.5	2.8	1.0	2.5	8.8	7.9	2.4	752	3.4	40	0.9	2.6
1	1.4	1.6	63.4	33.1	1.6	1.9	1.9	9.2	8.0	1.1	548	2.1	31	0.7	1.4
2	0.6	0.8	91.5	6.7	0.9	0.9	2.3	9.2	7.9	0.9	723	1.4	33	0.7	2.0
2	1.2	1.4	83.0	12.8	2.3	1.9	2.3	9.0	7.9	1.0	535	1.9	47	0.9	3.0
2	1.7	1.8	82.0	15.5	1.6	0.9	2.2	9.4	8.0	1.0	524	2.1	40	1.7	2.8

The bulk density reaches values as high as 2.5 g cm^{-3}, a consequence of both, the high density of the minerals and compaction during construction activities (note that the site is an abandoned industrial site). The carbonate content reaches values up to 750 g kg^{-1}. Thus, the pH at the site is expected to be controlled predominantly by the dissolution of the carbonates: The pH (H_2O) and pH ($CaCl_2$) reach values up to 9.4 and 8.0. The content of organic carbon is between 0.9 and 2.4 g kg^{-1}. This represents predominantly the content of the NAPL in this material due to its minor extent of natural organic carbon. The natural organic carbon content is low because of the former industrial use of the site and the currently sparse vegetation.

2.3 Properties of the coal tar

The NAPL found within the unsaturated zone of this contaminated site is an aged coal tar (Figure 3). The properties of the coal tar are given in Table 3. It consists mainly of aromatic compounds (65%) and high molecular paraffins, naphthenes and asphaltenes. The properties are typical of many types of coal tars. Lee et al. (1992) report analytical data on eight coal tars which cover a wide range of density, viscosity, water content and molecular weight.

Figure 3 Coal tar at the field site. The integrity of the aged NAPL interfaces are destroyed during the excavation of the profile.

Table 3 Properties of the coal tar

density [a] [kg m^{-3}]	1.054 (65°C)
kinematic viscosity [b] [mm^2 s]	225 (20°C) / 48 (40°C)
molecular weight [c] [g mol^{-1}]	295
water content [d] [% wt.]	2.3
aromatic compounds [e] [% wt.]	64.7
boiling range [f] [°C]	200-560

[a] Test method EN ISO 12185, 1996; [b] Test method EN ISO 3104, 1994; [c] cryoscopic; [d] Test method EN ISO 12937, 2000; [e] Test method IP 346; [f] Test method DIN 51435, 1989

2.4 Dialysis experiment

This experiment was conducted to determine the temperature dependent release kinetics and aqueous phase equilibrium concentrations of PAH from the aged coal tar at 20°C and 4°C in a climatic chamber. Dialysis membrane tubings were used to exclude the effect of colloids and suspended particles on PAH dissolution. Thus, only the fraction of PAH passing the membrane will be measured in the exterior solution. Any other PAH associated with colloids and suspended particles or small NAPL particles will remain inside the tubing.

After carefully separating the coal tar from remains of the mineral phase, 10 g coal tar and 10 ml of degassed, distilled and deionized water were filled into a 20 cm regenerated cellulose membrane dialysis tubing with a molecular weight cut-off of 1000 Dalton (Spectra/Por 6, Spectrum Laboratories Inc., Los Angeles CA, USA). Each end of the tubing was sealed with a copper wire. The coal tar filled tubings were placed in 1 l borosilicate glass bottle coated with tin foil to exclude light and closed with Teflon-lined screw caps (Figure 4). The bottle was filled with 1000 ml of degassed, distilled and deionized water. Sodium azide (0.5 mmol l^{-1}) was added to prevent microbial activity. The solution had a neutral pH of 7.0 and an electrical conductivity of 60 µS cm^{-1}. The experiment was run in three replicates for each temperature. In addition, one blank bottle per temperature was included as reference, subject to the same preparation but without coal tar.

Samples were taken at intervals of 0.08, 2, 7, 28, 56, 112 and 140 days during the 20°C experiment. At 4°C, sampling intervals were 0.04, 7, 56 and 140 days.

Figure 4 Coal tar enclosed in dialysis tubing.

2.5 Column experiment

The release of PAH, dissolved organic carbon (DOC), and suspended matter was studied with a column system under water-saturated flow conditions (Figure 5). To minimize sorption of PAH, the columns (height: 15 cm; ID: 9.4 cm), the porous plates [200 µm mesh, emc GmbH, Erfurt, Germany], which were used as bottom and top capping, and all tubing were made of stainless steel. The supply vessels and the sample vials were made of glass. A peristaltic pump [Ismatec, Glattbrugg, Switzerland] was used to feed the solution. It was installed upflow of the columns to avoid sorption of PAH to the PVC pumping tube. Column effluent was collected with a fraction collector [CF-1, Spectrum Chromatography, Houston TX, USA]. The experiments were conducted at 20°C in a climatic chamber.

To minimize effects due to differences in the column filling and to guarantee for equal initial conditions, repacked soil columns were used. The soil materials were collected below a contaminant source area in a depth of 0.6-0.8 m, air-dried and homogenized (Table 4). Gravels >3 cm were removed. The sample preparation will result in the destruction of the integrity of aged NAPL interfaces (Figure 3). This, however, is in agreement with the way the site is used at present: Excavation, filling, leveling, and compaction of the site resulted indeed in the disintegration of the soil structure. Concomitantly new NAPL surfaces are exposed, while others are coated with mineral soil material. Thus, construction activities are supposed to affect the release of NAPL-borne contaminants in a comparable manner as the column pre-treatment.

The filling procedure resulted in homogeneously repacked columns with bulk densities of 2 g cm^{-3}. The columns were slowly saturated from bottom to top to prevent any air entrapment. All solutions were made with degassed, deionized, and bidistilled water. Consequently, the solutions were not buffered and the pH was 7.0 (removal of CO_2). To prevent microbial activity, 0.5 mmol l^{-1} sodium azide was added. Sodium perchlorate (0.01 mol l^{-1}) was used as an inert electrolyte to maintain a moderate ionic strength (1160 µS cm^{-1}). Except for the flow-interrupts, the mean volumetric flow rate was kept constant throughout the experiments at 11 ml h^{-1} (slow) and 50 ml h^{-1} (fast), i.e. 0.044 and 0.20 pore volumes per hour, resulting in mean pore water velocities of 6.4 mm h^{-1} for the slow and 30 mm h^{-1} for the fast column.

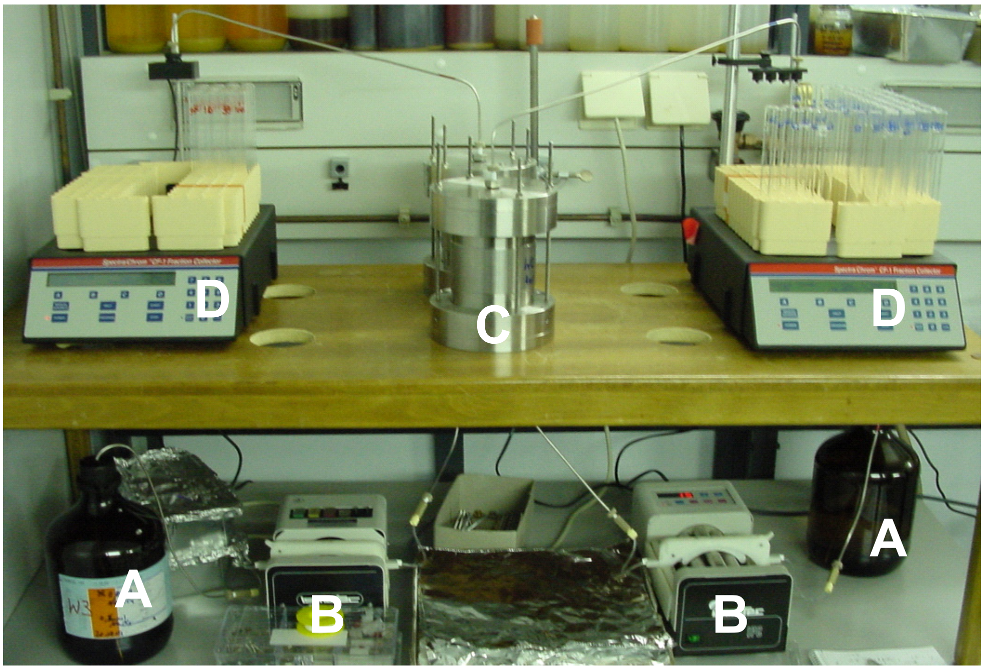


Figure 5 **Set-up of the column experiment with the supply vessels (A), the peristaltic pumps (B), the soil columns (C) and the fraction collectors (D).**

2.5.1 *Applied flow scheme and analysis of transport properties*

Mass transfer of PAH to the liquid phase may be kinetically limited and can be detected by flow-interrupts (Brusseau et al., 1997). In short term column experiments, however, flow-interrupts are only effective within a small range of the ratio of the mass-transfer timescale to the transport timescale. Wehrer and Totsche (2003), (2005) showed that the detectability of rate-limited mass transfer can be improved if two columns are used which are percolated at sufficiently different mean pore water velocities and if the flow is interrupted at least twice. In the presented experiments, one column, denoted as 'slow', was percolated at a mean pore water velocity of 1 pore-volume per day while the second column, denoted as 'fast', was percolated at approx. 5 pore volumes per day. Six pore-volumes were exchanged before the flow was interrupted for 1 day. Flow was resumed for another 5-6 pore volumes before it was interrupted a second time for 5 days. Finally, 6 pore volumes were exchanged again.

Analysis of the transport regime was done with chloride (10^{-2} M NaCl) as non-reactive tracer. To check the homogeneity and reproducibility of the filling procedure, a tracer transport experiment was conducted with an additional third column prepared in the same way as the two others. A flow-interrupt was also imposed on the breakthrough of the tracers to check whether physical or chemical processes are responsible for rate limitations. Column dispersivities $\lambda=D/v$ (D: coefficient of dispersion; v: mean pore water velocity) were obtained by inverse fitting of the chloride breakthrough curves using the local equilibrium assumption and the Two-Site/Two-Region models of the CXTFIT code in comparison (Parker and van Genuchten, 1984).

2.6 Lysimeter experiment

The effect of natural boundary conditions on the release of PAH, particles and DOC was studied with natural gradient/free drainage lysimeters [emc GmbH, Erfurt, Germany]. In a natural gradient or free-drainage lysimeter, water is allowed to drain freely through the soil under gravity alone. Free-drainage lysimeters were used to minimize sorption of PAH to suction devices. The monitoring was performed from September 2002 until October 2004 with a three month no-monitoring period due to vandalism at the site.

Lysimeter size was 0.5 m x 0.5 m with a total height of 0.35 m. The volume for soil material was 0.06 m^3. All lysimeters were made of stainless steel and were equipped with a stainless steel screen at the bottom [mesh size: 200 µm, emc GmbH, Erfurt, Germany] to allow export of particles up to 200 µm. Soil material was refilled without further compaction and covered by an undisturbed, 2-5 cm thick layer of vegetated topsoil. As described for the column experiments, the disturbed refilling of the lysimeters and the resulting destruction of the soil structure is usual at an industrial site, e.g. after the use of excavators. The filling procedure resulted in homogeneously refilled lysimeters with bulk densities which are similar to those found in the surrounding soil. Three lysimeters were used to study the mobilization of PAH, DOC and particles within very low (lysimeter 1), low (lysimeter 2) and high (lysimeter 3) contaminated soil material (Table 4). The contamination of lysimeter 1 reflects the background level within the soil material at this site.

Table 4 Properties of the soil material used for the lysimeter and column experiments

lysimeter	**depth**	**gravel**	**sand**	**silt**	**clay**	**bulk density**	**PAH**
	[m]		**[% wt.]**			**[g cm^{-3}]**	**[mg kg^{-1}]**
1	0.05 - 0.25	71.0	18.3	7.3	3.4	2.0	2
2	0.05 - 0.25	80.5	14.0	3.9	1.6	2.0	20
3	0.05 - 0.75	80.5	14.0	3.9	1.6	2.0	20-81
3	0.30 - 0.45	NAPL contaminated material				1.055[a]	46000[a]
column	0.60 - 0.80	80.5	14.0	3.9	1.6	2.0	81

[a] NAPL

Lysimeter 3 was installed in a contaminant source area. It was elongated to a total height of 0.85 m (0.18 m^3 volume) to refill a soil profile including NAPL-contaminated material and the subsequent soil passage (Figure 6). Two dielectric probes [ECH$_2$O, Decagon Devices Inc., Pullman WA, USA] were installed at a depth of 0.2 m and 0.5 m within lysimeter 3 to monitor soil moisture contents. Soil temperatures were determined at depths of 0.15, 0.40, 0.80 m and at ground level by a temperature probe. Due to the repeated vandalism at the field site, these parameters have been recorded only since December 2003.

The amount of precipitation was monitored with one rain gauge for each lysimeter. Amount of precipitation was determined and effluent samples were taken immediately after precipitation events high enough to result in a recharge of seepage water (event triggered sampling). The seepage water was collected in glass vessels. In general, the period of time between recharge and sample collection was smaller than 24 hours. Thus, PAH redistribution between the aqueous phase and the colloids/particles fraction can be neglected.

Figure 6 Installation of Lysimeter 3 at the field site.

2.7 Analytical methods

2.7.1 *Physicochemical parameters*

Analyses of all liquid phases comprised the determination of pH [ion-sensitive electrode, SenTix 41, WTW, Weilheim, Germany] and electrical conductivity [TetraCon 625 conductivity cell, WTW, Weilheim, Germany]. Dissolved organic carbon (DOC) was determined as non-purgeable organic carbon using a TOC-Analyzer [5050A, Shimadzu, Kyoto, Japan] after filtration <0.45 µm and acidification. Turbidity was determined by spectral absorption measurement at 860 nm [Cary 50 UV-Vis Spectrophotometer, Varian GmbH, Darmstadt, Germany] in samples shaken horizontally for 10 seconds after allowing one minute settling time. It is expressed as Formazine Attenuation Units (FAU). The adsorption at 254 nm was determined to calculate $SUVA_{254}$, which is defined as the UV absorbance divided by the DOC concentration. It is a relative measure for the aromaticity of DOC. The breakthrough curve of chloride within the column experiment was measured with an ion-selective electrode [Ionplus Chloride, Orion Research Inc., Beverly MA, USA].

2.7.2 PAH extraction

The extraction of PAH from coal tar was done with hexane. Three separate subsamples of approximately 0.3 g coal tar were sequentially extracted four times with each 40 ml hexane and ultrasonification for 15 minutes. The extracts were dried by passing through anhydrous sodium sulfate. After volume reduction in a rotary evaporator, the extracts were cleaned up by pre-conditioned silica gel/aluminum oxide columns. PAH were eluted with 30 ml hexane, 10 ml hexane/dichloromethane 9:1 and 40 ml hexane/dichloromethane 4:1 into a 100 ml volumetric flask and brought to volume. Before analysis, the extracts were diluted by a factor of 100.

Soil samples were extracted according to Hartmann (1996). Extraction was done by saponification with methanolic aqueous potassium hydroxide, exposed to ultrasonification for 1 hour at 65°C and allowed to equilibrate for at least 4 hours at 65°C. The liquid phase was then separated by centrifugation, extracted with hexane and dried over anhydrous sodium sulfate. The extracts volume were then reduced by means of a rotary evaporator and cleaned up by passing pre-conditioned silica gel/aluminum oxide columns. PAH were eluted with 3 ml hexane and 8 ml hexane/ether 20:1.

Prior to the extraction of PAH, the column effluents and the seepage of the lysimeters were filtered with fiber glass filters with a mesh size of 0.7 µm [GF 92, Schleicher & Schuell MicroScience GmbH, Dassel, Germany]. This pore size represents the smallest commercially available glass-fiber based filter. The extraction of the 16 EPA priority pollutants in the filtrate was done with solid-phase (Chladek and Marano, 1984). The filtrate (<0.7 µm) was mixed with methanol and added onto pre-conditioned solid phase cartridges containing octadecyl (C_{18}) bonded silica adsorbents. The columns were then freeze-dried. PAH were eluted five times with 1.5 ml hexane and three times with 1.5 ml of a 3:1 hexane/dichloromethane mixture. Each step was allowed to equilibrate for 10 minutes. All extracts were evaporated as required to enable detection.

The PAH in the retentate (particle fraction 0.7–200 µm) were determined by sequentially extracting the freeze-dried fiber glass filter three times with hexane/acetone 1:1 and ultrasonified for 15 minutes. The extracts were then dried over anhydrous sodium sulfate, cleaned up with pre-conditioned silica gel/aluminum oxide columns and eluted with 3 ml hexane and 8 ml hexane/ether 20:1. Prior to analysis, the extracts were evaporated as required to enable detection.

For the column experiments, the concentrations in the fraction 0.7-200 µm are given in µg l^{-1}: The detected PAH masses are based on the sample volume which passed the 0.7 µm filter.

2.7.3 PAH analysis

The determination of PAH was performed with capillary gas chromatography/mass-spectrometry (GC-MS) [GC 8000, MD 800, Fisons Instruments, Manchester, UK] supplied with a DB 5 MS column [internal diameter 0.25 mm, film thickness 0.25 µm; J. and W. Scientific, Folsom CA, USA]. Samples were injected splitless with an injector temperature of 280°C. He served as carrier gas at 1.0 ml per minute. The GC temperature program started at 85°C for 4 minutes, increased to 160°C with 15°C per minute, held for 2 minutes, increased to 300°C with 5°C per minute and held for 15 minutes.

PAH were quantified with a mixture of seven deuterated PAH [PAH surrogate cocktail, Cambridge Isotope Laboratories Inc., Andover MA, USA]. PAH recoveries of the internal standard were quantified by adding an external standard [Perylene D-12, Supelco, Bellefonte PA, USA].

All individual PAH analyses were done twice. Results are given as means of two individual analyses with error bars indicating maximum and minimum of the measured PAH concentrations. In general, the difference in between the two measurements is small.

2.8 Data evaluation

To further analyze the processes which control the PAH release behavior, we calculated PAH dissolution in order to test the applicability of Raoult's law. Aqueous equilibrium concentrations of the single PAH were calculated using Raoult's law and compared to the measured PAH concentrations of the dialysis experiment, in the filtrate of the column effluents and the seepage of lysimeter 3. According to Raoult's law the equilibrium concentration of a solute in the aqueous phase is controlled by its mole fraction in the NAPL and its aqueous solubility:

$$C_w = C_t \cdot MW_t \cdot S_{w,m} \qquad [1]$$

where C_w [mg l^{-1}] is the aqueous equilibrium concentration of the solute, C_t [mg g^{-1}] is its tar-oil concentration, MW_t [g mol^{-1}] is the molecular weight of the tar phase and $S_{w,m}$ [mol l^{-1}] is the compounds molecular aqueous solubility. For the column experiments, the molar fractions of PAH were calculated based on the determined concentrations in the soil material which were scaled to the mean coal tar content of the soil (1.0 g kg^{-1}). For the dialysis and lysimeter experiments, the determined PAH concentrations within the coal tar were used (Table 5). A mean molecular weight of 295 g mol^{-1} were adopted for the coal tar (Table 3). Additionally, single PAH concentrations assuming minimum and maximum molecular weights of 230 g mol^{-1} and 780 g mol^{-1} were calculated to cover a wider span of coal tar types (Lee et al., 1992).

As PAH are solid as pure compounds at ordinary temperatures and pressures but liquid in the NAPL phase, the subcooled liquid solubilities were used instead of the aqueous solubility. The subcooled liquid solubility (S_{scl}) for the 16 EPA PAH at each temperature were calculated using equation 2 (Peters et al., 1997):

$$S_{scl} = S_w \cdot e^{\left(\frac{\Delta S_m \cdot (T_m - T)}{R_g \cdot T}\right)} \qquad [2]$$

where S_w [mg l^{-1}] denotes the aqueous solubility of the solid compound, ΔS_m [J mol^{-1} K^{-1}] is the entropy of fusion at the compounds melting temperature (T_m [°K]), T [°K] is the system temperature and R_g [J K^{-1} mol^{-1}] is the universal gas constant. Aqueous solubilities were taken from Mackay and Shiu (1977) and Walters and Luthy (1984) (Table 1). For the entropy of fusion of PAH, a mean value of 56.1 J mol^{-1} K^{-1} was adopted (Yalkowsky and Banerjee, 1992).

The data of the dialysis experiment are presented as mean values of the three triplicates at each temperature with the standard deviation. Five compounds were selected from the 16 EPA PAH to observe the different behavior of the two- (Acenaphthylene), three- (Anthracene), four- (Pyrene), five- (Benzo[a]pyrene) and six-ring PAH (Benzo[ghi]perylene).

A first-order nonlinear model which uses a gamma distribution for the rate parameter was fit to the data (Gustafson and Holden, 1990):

$$\frac{\partial S}{\partial t} = S_{\max} \cdot (1 + \beta \cdot t)^{-\alpha} \qquad [3]$$

Here, S_{max} [mg kg^{-1}] represents the PAH concentration in the coal tar, β [h^{-1}] and a [-] are parameters of the gamma distribution. The mean of the effective mass transfer coefficient k_{eff} [h^{-1}] was obtained from the product of β and a. Assuming zero initial PAH concentration in the aqueous phase, i.e. all PAH are stored within the coal tar at the very beginning of the experiment, and equilibrium concentration for infinite time, equation 3 can be solved analytically for an effective mass transfer coefficient. For the 4°C experiment, it was not possible to fit a rate parameter for the release of Benzo[ghi]perylene due to very low concentrations, even below the limit of determination (two times).

For the column experiments, the parameters characterizing the rate-limited release of DOC and PAH were analyzed by data obtained from the breakthrough curves. The effective mass transfer coefficient k_{eff} [h^{-1}] was calculated according to Münch et al. (2002):

$$k_{eff} \cdot t = \theta \cdot \ln\left[\frac{C_{eq} - C_i}{C_{act} - C_i}\right] \qquad [4]$$

Here, t [h], Θ [cm^3 cm^{-3}], C_{eq} [mg l^{-3}], C_{act} [mg l^{-3}], and C_i [mg l^{-3}] denote the duration of the flow-interrupts, the volumetric water content, the equilibrium concentration, the concentration after the flow was resumed, and the effluent concentration before the flow-interrupt, respectively.

The parameters C_{eq} and k_{eff} were calculated using the concentration before and after the flow-interrupts by inverse simulations with Mathcad 2000 Professional [Mathsoft Inc., Cambridge MA, USA].

The ratio of the reaction-time scale to transport-time scale was described by the dimensionless Damköhler number Da [-]. It is used as a measure for the degree of non-equilibrium (Bahr and Rubin, 1987):

$$Da = \frac{L \cdot R \cdot k_{eff}}{v} \qquad [5]$$

Here, L [cm] is the column length, R [-] is the retardation factor of the observed substance, and v is the pore water velocity [cm h^{-1}]. The retardation factor R for the release process is unknown as the desorption isotherms of DOC and PAH were essentially unknown for this material. Therefore, a R-dependent Damköhler number was calculated:

$$Da' = \frac{Da}{R} = \frac{L \cdot k_{eff}}{v} \qquad [6]$$

Assuming the same release process for the material at the different flow velocities, the R-dependent Damköhler number Da' can be used as a relative measure for the time scale of the release to the time scale of the transport regime.

For the lysimeter experiment, Spearman’s rank correlation was used to analyze the dependencies between the set of parameters. It is a distribution-free analog of correlation analysis. It can be applied to compare two independent random variables, each at several levels. Spearman's rank correlation works on ranked data, rather than directly on the data itself. Additionally, F-values were calculated for the determined correlation coefficients and the associated significance levels of 0.1, 0.05, 0.025, 0.01 and 0.005 are presented.

3 RESULTS AND DISCUSSION

3.1 Dialysis experiment

3.1.1 PAH concentrations of the coal tar

Total and single PAH concentrations of the coal tar are given in Table 5 as mean of triplicate analyses with the standard deviation for each compound. The 16 EPA PAH represent approximately 5% wt. of the coal tar. Phenanthrene and Fluoranthene are the most abundant compounds. Two thirds of total PAH is composed of 2- and 3 –ring PAH compounds. These results fit to many typical coal tars as reported by Lee et al. (1992) and Mahjoub et al. (2000) who described PAH concentrations in coal tars to range between 7000 mg kg^{-1} and 220,000 mg kg^{-1} and 2- and 3 –ring PAH concentrations of 41,000 mg kg^{-1}.

Table 5 Concentrations of the 16 EPA PAH within the used coal tar (Ct)

compound (abbreviations)	rings	C_t [mg kg^{-1}] ± SD [%]
Naphthalene (Nap)	2	1325.3 ± 16.0
Acenaphthylene (Acy)	2	69.1 ± 16.2
Acenaphthene (Ace)	2	4604.9 ± 13.8
Fluorene (Flr)	2	4897.6 ± 14.7
Phenanthrene (Phe)	3	11351.3 ± 16.1
Anthracene (Ant)	3	2198.4 ± 15.2
Fluoranthene (FlA)	3	6797.2 ± 19.1
Pyrene (Pyr)	4	4457.7 ± 19.0
Benz[a]anthracene (BaA)	4	2581.7 ± 21.8
Chrysene (Chr)	4	2898.7 ± 20.7
Benzo[b]fluoranthene (BbFlA)	4	1634.0 ± 20.8
Benzo[k]fluoranthene (BkFlA)	4	598.2 ± 20.0
Benzo[a]pyrene (BaP)	5	1143.1 ± 21.5
Indeno[1,2,3-c,d]pyrene (IcdP)	5	747.1 ± 23.1
Dibenz[a,h]anthracene (DahA)	5	217.2 ± 23.1
Benzo[ghi]perylene (BghiP)	6	507.2 ± 23.6
total PAH		46028.7 ± 17.6

3.1.2 Total PAH release

The course of the total PAH concentration over time for the experiments at 20°C and 4°C are presented in Figure 7. After 140 days of equilibration time, total PAH concentration reached values of 2250 µg l^{-1} at 20°C and 1610 µg l^{-1} at 4°C. The lower temperature resulted in a significant lower final concentration. For 20°C, a time constant aqueous phase PAH concentration was found after 112 days of equilibration time, which points to the fact that equilibrium was reached in between 56-112 days. Whether the same holds true for the 4°C experiment has to stay open, as additional concentration measurements in the time interval between 56 days and 140 days are lacking. Based on the theoretical temperature dependence of rate parameters (Arrhenius equations), it is to be expected that equilibrium was not achieved for the 4°C experiment.

The observed equilibration times are much larger than those reported in previous studies (Lee et al., 1992; Priddle and MacQuarrie, 1994; Mukherji et al., 1997; Woolgar and Jones, 1999). The reason for this is the limited mass transfer of PAH to the aqueous phase. This limitation is caused by the polymerization of the used coal tar due to aging processes (Luthy et al., 1993; Mahjoub et al., 2000; Ghoshal et al., 2004).

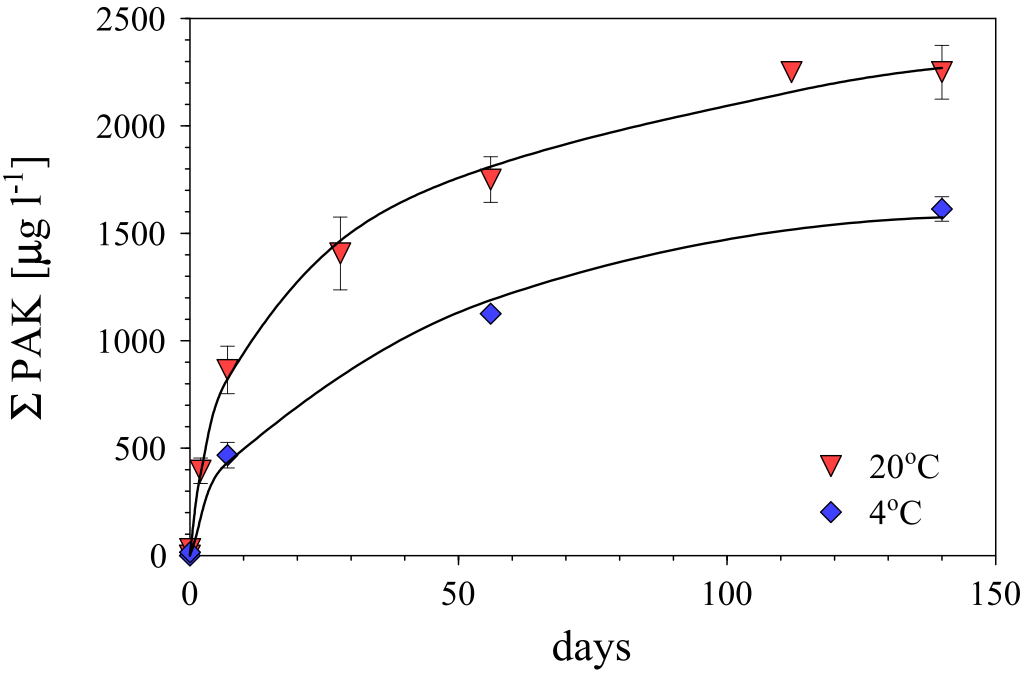


Figure 7 Total PAH concentrations over time for 20°C (a) and 4°C (b). Symbols indicate measurements, line the fit by the used nonlinear model.

In contrast, the reported equilibrium times of at most several days are caused by fresh or synthetic NAPL phases used in these studies.

A temperature dependence of the rate parameters can be seen in Table 6. The higher temperature lead to a mass transfer rate of the PAH sum twice as high as for the 4°C experiment. The activation energy of dissolution for the PAH calculated using the Arrhenius equations and the determined mass transfer rates for 20°C and 4°C was 31 KJ mol^{-1}. This seems to be a reasonable value as Ghosh et al. (2001) (and references therein) reported activation energies of desorption below 100 KJ mol^{-1} for PAH and PCB from soils and sediments. The obtained value for the PAH concentration in the coal tar (S_{max}) deviates from the concentration determined in the analysis of the tar (Table 5 and 6). This low value of S_{max} indicates that only a small fraction of the total coal tar mass is involved in the release process of PAH (Wehrer and Totsche, 2005).

Table 6 Determined mass transfer coefficients (k_{eff}), PAH concentrations in the coal tar (S_{max}), aqueous equilibrium concentrations (C_w) calculated according to Raoult (assuming molecular weights for the coal tar of 295 g mol^{-1}, 230 g mol^{-1} and 780 g mol^{-1}) and measured aqueous concentrations after 140 days ($C_{meas\ 140}$)

20°C	k_{eff} 10^{-3} [h^{-1}]	S_{max} [mg kg^{-1}]	$C_{w\ 295}$ [µg l^{-1}]	$C_{w\ 230}$ [µg l^{-1}]	$C_{w\ 780}$ [µg l^{-1}]	$C_{meas\ 140}$ [µg l^{-1}]
∑PAH	12.7	2142	933	727	2467	2249.5
Acy	4.90	3.47	11.3	8.84	30.0	7.2
Ant	3.12	81.4	23.3	18.1	61.5	55.3
Pyr	3.85	21.4	17.8	13.9	47.0	16.0
BaP	0.94	0.35	0.20	0.15	0.52	0.484
BghiP	0.08	1.38	0.01	0.01	0.04	0.113
4°C	k_{eff} 10^{-3} [h^{-1}]	S_{max} [mg kg^{-1}]	$C_{w\ 295}$ [µg l^{-1}]	$C_{w\ 230}$ [µg l^{-1}]	$C_{w\ 780}$ [µg l^{-1}]	$C_{meas\ 140}$ [µg l^{-1}]
∑PAH	6.07	1678	1531	1193	4047	1612.8
Acy	2.67	4.51	18.4	14.4	48.7	4.2
Ant	1.35	30.3	44.6	34.8	118	36.8
Pyr	1.55	18.9	31.2	24.3	82.4	6.3
BaP	0.61	1.81	0.36	0.28	0.95	0.116
BghiP	-	-	0.03	0.02	0.08	-

3.1.3 Release of selected PAH compounds at 20°C

The temporal course of the release of the selected single PAH compounds is given in Figure 8a. For Acenaphthylene (Acy), Anthracene (Ant) and Pyrene (Pyr) a curve with a plateau after 140 days was observed. Ant was most abundant with 55 µg l^{-1}. All compounds except BaP and BghiP showed a time constant concentration after 112 days indicating equilibrium was reached in between 56-112 days of equilibration time.

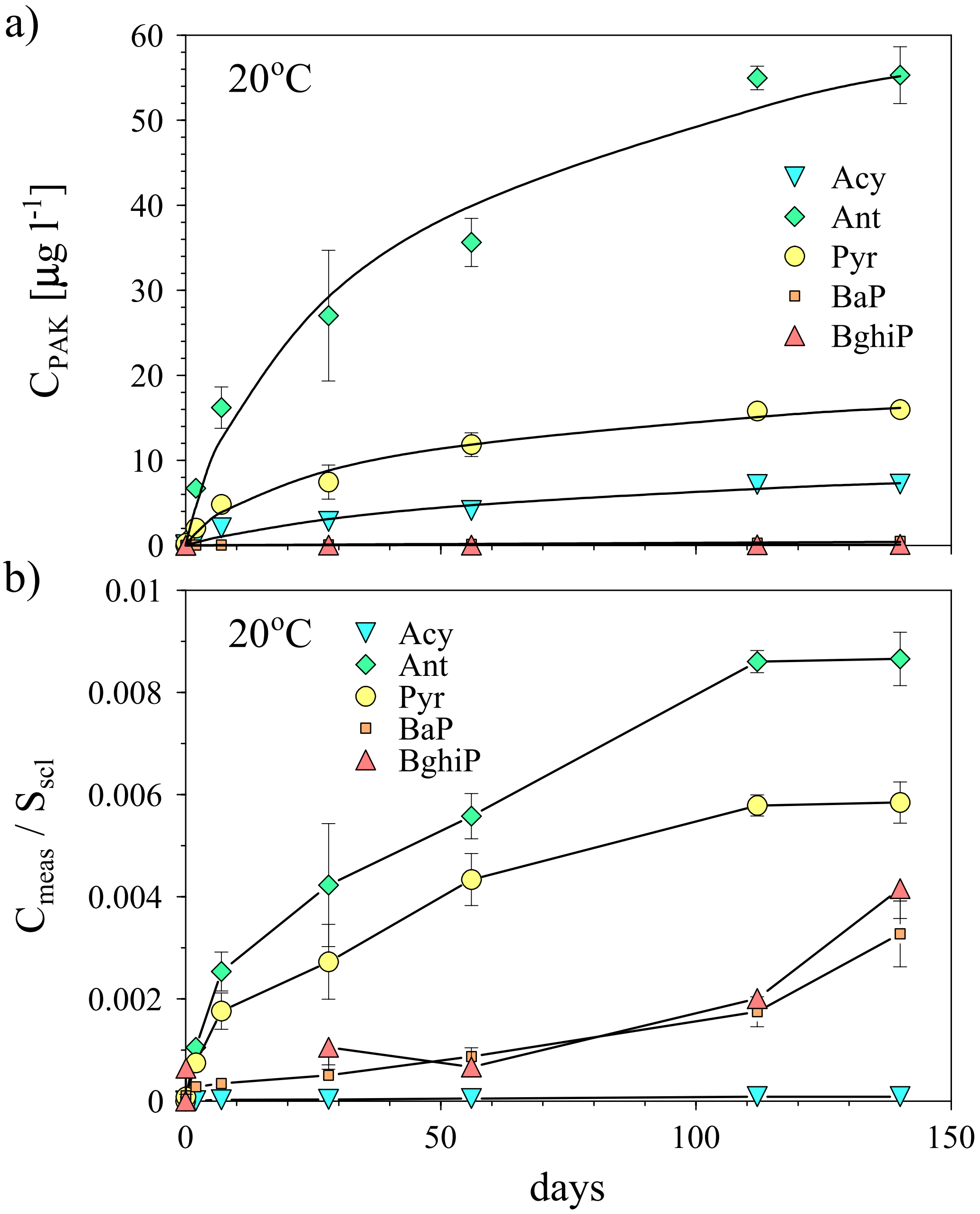


Figure 8 **Release of the selected PAH compounds at 20°C. Symbols indicate measurements, line the fit by the nonlinear model (a). Concentrations of the compounds normalized to their subcooled liquid solubility over time at 20°C (b).**

For the high molecular weight compounds BaP and BghiP the time period of 140 days seems not enough to reach equilibrium. Ant and Pyr reached higher concentrations than Acy despite its much higher water solubility. The aqueous solubility is therefore not the sole property which controls the release of the PAH from the coal tar.

To appraise the effect of the aqueous solubility, the found concentrations were normalized to their subcooled liquid solubility. Additionally, according to Raoult's law the coefficient of aqueous concentration to the component's solubility provides an approximate value for the mole fraction of the component in the organic phase. Figure 8b shows the concentrations of the selected single compounds over time normalized to their subcooled liquid solubility. All compounds achieved very low percentages of their solubilities at the end of the experiment. Ant shows the largest mole fraction within the chosen compounds, followed by Pyr, BghiP, BaP and Acy. This order fits well the one determined in the analysis of the coal tar (Table 5). This indicates that the mole fractions of the compounds are controlling factors for the release of PAH from coal tar besides their aqueous solubility.

3.1.4 Release of selected PAH compounds at 4°C

The release of the selected PAH at 4°C was almost linear and reached no constant level at the end of the experiment (Figure 9a). Ant was again the most abundant compound with 37 $\mu g\ l^{-1}$. As expected, aqueous equilibrium concentrations were not achieved after 140 days as a result of the low rate parameters and the limited mass transfer due to aging and the low temperature.

The course of the normalized concentrations of the five PAH is given in Figure 9b. The observed concentrations are again very low percentages of their theoretical solubilities. They only reach up to one third of the values found for the 20°C experiment. The observed mole fractions show the same proportions like the ones observed for 20°C and within the coal tar.

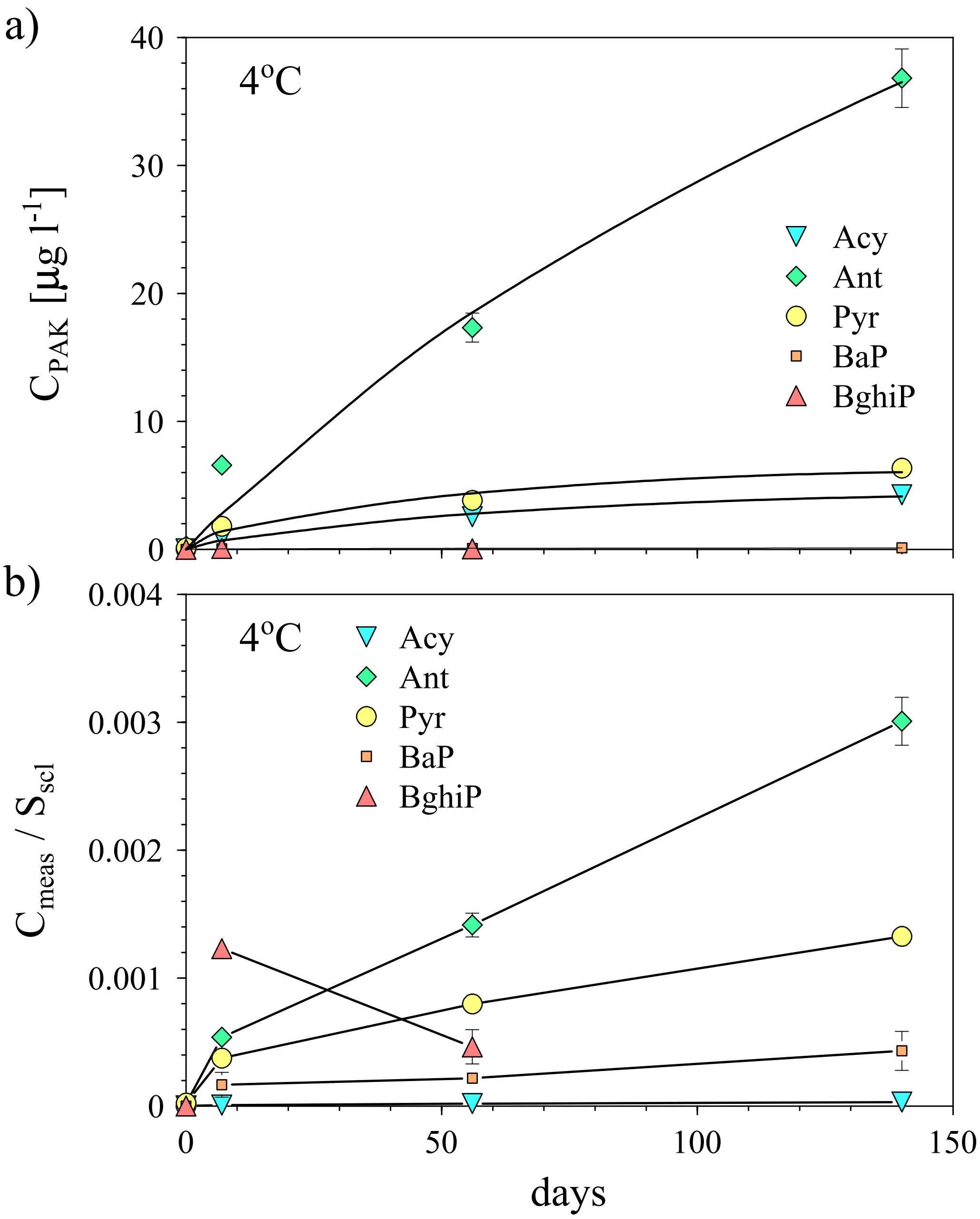


Figure 9 **Release of the five selected PAH compounds at 4°C. Symbols indicate measurements, line the fit by the used nonlinear model (a). Concentrations of the compounds normalized to their subcooled liquid solubility over time at 4°C (b).**

3.1.5 *Release kinetics*

The determined mass transfer coefficients (k_{eff}) and the calculated PAH concentrations in the coal tar for the total PAH and the five selected compounds (S_{max}) are presented in Table 6. For all compounds, the higher temperature lead to an increase of the mass transfer rates. This is probably caused by the lower viscosity of tar at the higher temperature which induced an increased diffusion coefficient of the different compounds in the organic phase (Mahjoub et al., 2000). The determined mass transfer coefficients are much lower than those found by Woolgar and Jones (1999). They calculated 0.19 h^{-1}, 0.03 h^{-1} and 0.04 h^{-1} for Acy, Ant and Pyr from NAPL using the dialysis tubing method.

The much higher values result from the fact that they used fresh NAPL material instead of an aged NAPL phase. Moreover, they employed a linear first-order model to fit their data. In the case of our data, the linear first-order model and a kinetically controlled mass transfer model were not able to describe the data as adequately as the one by Gustafson and Holden (1990). These two models yielded higher rate coefficients and unreasonable low values of S_{max}. (data not shown).

3.1.6 *Comparison with Raoult's law*

The aqueous equilibrium concentrations calculated after Raoult compared to the measured concentrations after 140 days are given in Figure 10a and 10b. For the 20°C experiment, the observed concentrations match well with the ones predicted by Raoult's law. At 4°C, only the observed concentrations after 140 days for 6 of the 16 studied compounds correspond with the predicted values. Generally, the high molecular weight PAH (>3 rings) have not reached their equilibrium concentrations during the course of the experiment. Thus, the duration of 140 days was not sufficient for these compounds. As discussed above, this is an effect of the low temperature.

These results show the applicability of Raoult's law for the investigated, although aged coal tar at lab scale if the influence of colloids and particles is excluded.

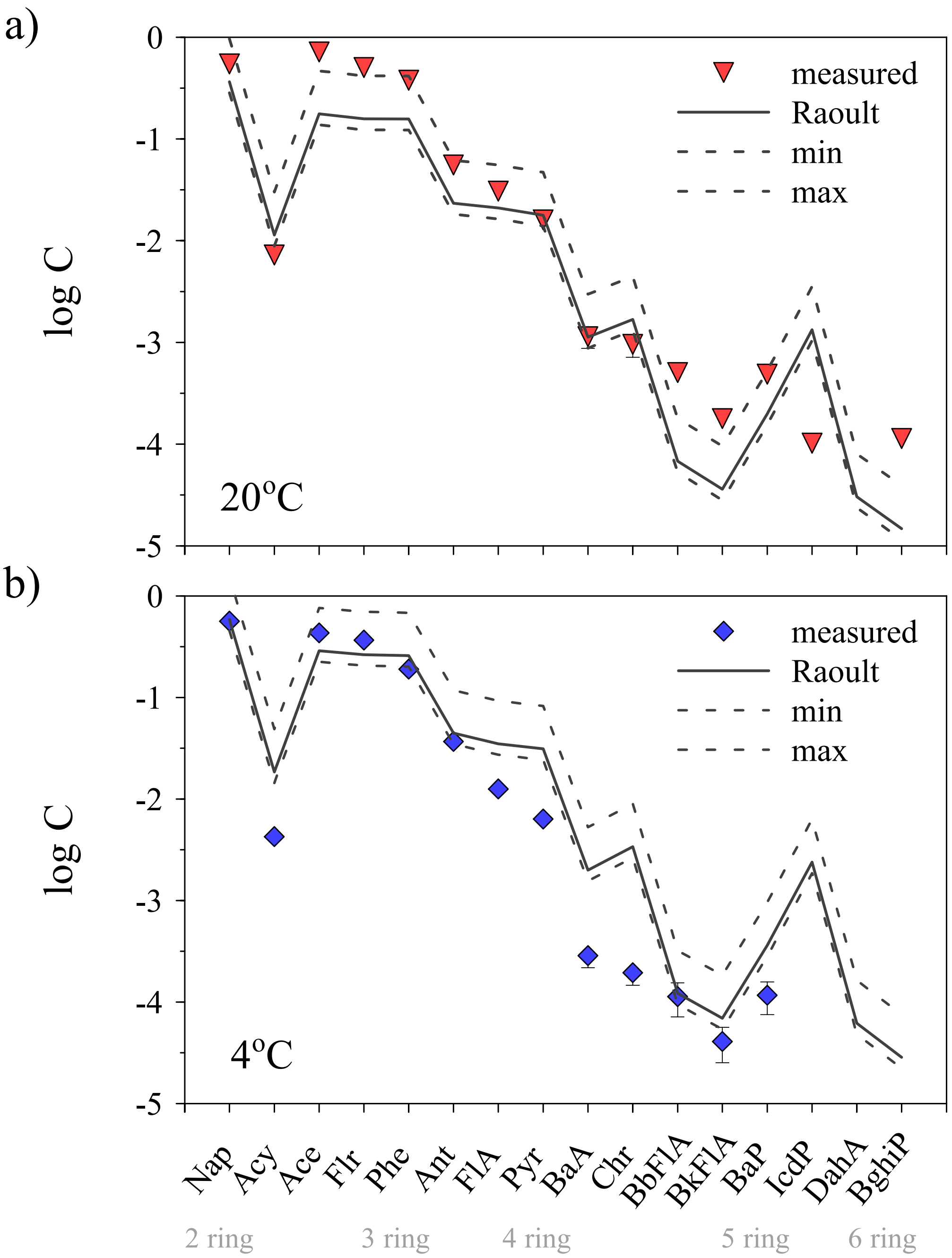


Figure 10 **Aqueous equilibrium concentrations calculated according to Raoult's law and measured concentrations of the single PAH at 20°C (a) and 4°C (b). Naphthalene (Nap), Acenaphthylene (Acy), Acenaphthene (Ace), Fluorene (Flr), Phenanthrene (Phe), Anthracene (Ant), Fluoranthene (FlA), Pyrene (Pyr), Benz[a]anthracene (BaA), Chrysene (Chr), Benzo[b]fluoranthene (BbFlA), Benzo[k]fluoranthene (BkFlA), Benzo[a]pyrene (BaP), Indeno[1,2,3-c,d]pyrene (IcdP), Dibenz[a,h]anthracene (DahA), Benzo[g,h,i]perylene (BghiP).**

3.1.7 Summary

Aqueous equilibrium concentrations and the release kinetics of the 16 EPA PAH were determined at 20°C and 4°C using a dialysis tubing to exclude the influence of colloids and suspended particles. The higher temperature resulted in higher concentrations and higher mass transfer coefficients. The experiments duration of 140 days seemed not enough to reach equilibrium at 4°C. Comparison of the observed final concentrations with the aqueous equilibrium concentrations calculated according to Raoult's law showed its applicability for the used aged coal tar at laboratory scale although the high molecular weight PAH had not reached equilibrium during the course of the experiment.

The observed mass transfer coefficients were lower and the equilibration times much longer than found in the literature. Mass transfer of PAH to the aqueous phase was limited due to aging of the coal tar. Thus, long time periods are necessary for equilibrium dissolution at contaminated sites, where NAPL phases have aged over several decades. As a consequence, aqueous equilibration concentrations might be achieved only under low lateral flow velocities in groundwater environments contaminated with aged NAPL phases. Furthermore, the process of equilibrium dissolution is likely to be of minor importance for the release of PAH within the unsaturated zone because of the high vertical flow velocities and therefore lower contact time of the seepage water with the NAPL phase. In addition, the influence of colloids and suspended particles or NAPL droplets on the aqueous concentrations as well as non-equilibrium conditions during the release of the contaminants must be considered.

3.2 Column experiment

3.2.1 Breakthrough of chloride

The breakthrough of chloride was used to determine the flow regime and to detect non-uniform macroscopic flow. Physical non-equilibrium as one source for rate-limited transport was also checked by superimposing a flow-interrupt to the chloride breakthrough. Figure 11 shows the breakthrough of chloride for the fast column, the slow column, and a third column, which was run as a repetition. All three breakthrough curves were symmetric. The arrival wave was of sigmoidal shape and completed after 4 pore volumes (pv) had been exchanged. Neither early breakthrough nor tailing was observed. The good agreement of the chloride breakthrough of the two slow-flow columns shows that the filling procedure indeed resulted in homogeneously and reproducible packed columns. Differences in the packing as a possible source for different breakthrough behavior between the slow and the fast column can therefore be excluded.

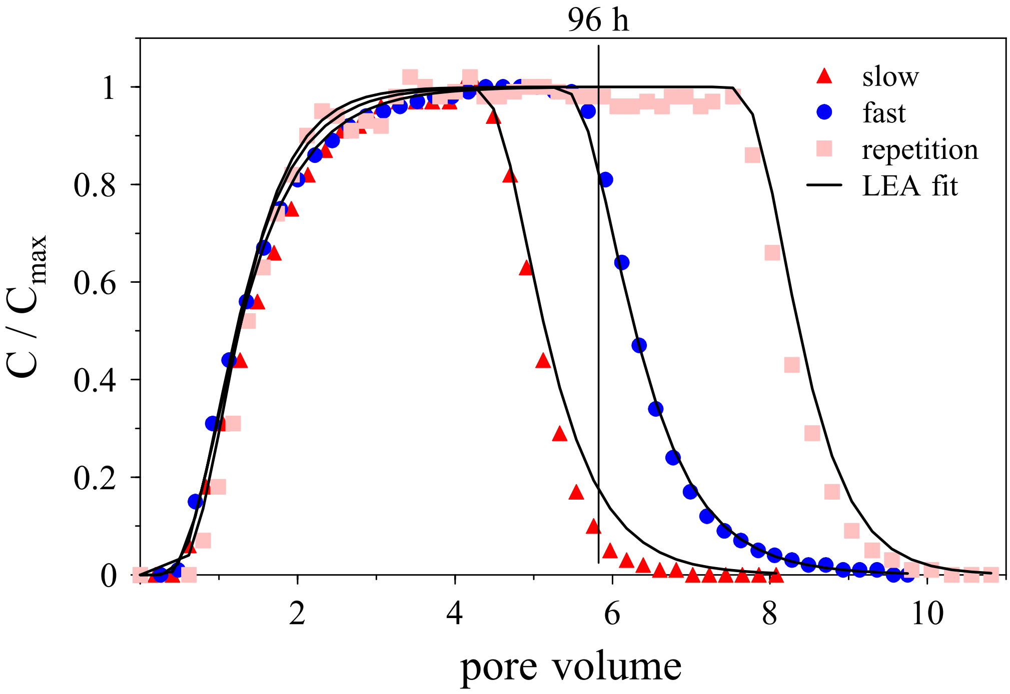


Figure 11 Results of the chloride breakthrough for the fast column, the slow column and its repetition. Symbols indicate measurements, line the fit. Results of the TSTR model are not included. The flow-interrupt is indicated by the vertical line.

Chloride effluent concentrations before and after the flow-interrupt did not differ. Thus, physical non-equilibrium due to mass transfer between mobile and immobile flow regions is negligible. Any rate limited transport is therefore due to other than physical non-equilibrium processes. This is also corroborated by the results of the inverse modeling using the CXTFIT code: Best fit results were obtained for chloride transport assuming the local equilibrium assumption (LEA) (Table 7), with the parameters D and R subject to fitting, while no improvement of the fit was obtained for the Two-Site/Two-Region model (TSTR) and the TSTR model parameters β^* and ω were insensitive to the data.

Table 7 **Results of the inverse modeling of the chloride breakthrough data. The 95% confidence limits for the fitted parameters are given in brackets**

Local Equilibrium Assumption	**Repetition**	**slow**	**fast**
pore water velocity [mm h^{-1}]	9.4	6.4	30
R[a] [-]	1.36 (+1.42; –1.31)	1.36 (+1.42; –1.30)	1.42 (+1.44; –1.40)
λ[b] [cm]	1.34 (+1.69; –0.99)	1.76 (+2.20; –1.31)	2.04 (+2.18; –1.89)
r^2 [c] [-]	0.984	0.984	0.999

Two Site / Two Region model	**Repetition**	**slow**	**fast**
pore water velocity [mm h^{-1}]	9.4	6.4	30
R[a] [-]	1.36 (+1.42; –1.31)	1.36 (+1.42; –1.30)	1.42 (+1.44; –1.40)
λ[b] [cm]	1.34 (+1.69; –0.99)	1.76 (+2.20; –1.31)	2.04 (+2.18; –1.89)
r^2 [c] [-]	0.984	0.984	0.999
β* [d] [-]	0.649 (+394; – -393)	0.977 (+22.5; – -20.6)	0.999 (+2.07; – -0.07)
ω[e] [-]	100 (+220100; – -219900)	100 (+311800; – -311600)	100 (+334600; – -334400)

[a] retardation factor; [b] dispersivity; [c] coefficient of determination; [d] dimensionless variable for partitioning in non-equilibrium transport models; [e] dimensionless mass transfer coefficient (Toride et al., 1999)

Slight retardation of chloride was observed due to anion exchange on the solid phase (Table 7). Anion exchange can occur because of the positively charged surfaces of calcite due to protonation reactions (Davranche et al., 2002). The large longitudinal dispersivities reflect the fact that coarse textured material was used within the columns. The larger dispersivities for the fast column might indicate the effect of the development of physical non-equilibrium (immobile water) at higher flow velocities. In an equilibrium model this would result in higher dispersivities (Koch and Flühler 1993). However, the TSTR-fit showed now improvement over the LEA.

3.2.2 Course of pH and electrical conductivity

Among others, the stability of colloids is controlled by their properties, such as surface charge and the ionic strength of the solution, which dictate the repulsive or attractive forces between colloidal particles (Ryan and Elimelech, 1996; Hofmann et al., 2003). The surface charge might be strongly dependent on the solution pH because the mineral surfaces functional groups exchange protons with the solution (Ryan and Elimelech, 1996). The ionic strength is also important for the stability of a colloidal system (Ryan and Gschwend, 1994; Bunn et al., 2002). The infiltration of low-ionic strength solutions, such as rain water, results in the expansion of the diffuse double layer and in an outbalancing of the repulsive forces over the attractive forces (Ryan and Elimelech, 1996). This prevents coagulation and leads to a mobilization of colloids. Consequently, the pH and the ionic strength of the soil solution are important factors in the mobilization process of colloids and should be measured to evaluate their possible effect on mobilization.

Figure 12 shows the course of pH and electrical conductivity (EC) of the slow and fast column. The pH values ranged from 7.1 to 7.8 for the slow column and from 6.6 to 7.4 for the fast column. Compared to the input pH of 7.0, the slow flow conditions resulted in an increased pH over the whole experiment. The fast column showed almost no difference to the input pH after 3 pv were exchanged.

No response of the electrical conductivity to the short flow-interrupt was observed for both columns, but the longer stop lead to increased values after flow was resumed. After onset of the flow, the effluent EC in the slow and fast column increased to a level of 1290 $\mu S\ cm^{-1}$ and 1270 $\mu S\ cm^{-1}$, respectively, both above the input EC level (1160 $\mu S\ cm^{-1}$). The slow column showed a generally higher EC than the fast column.

While the short flow-interrupt had little effect, both columns responded markedly to the longer flow-interrupt, with a slightly higher increase for the fast column. The higher EC, in comparison to the input solution, continued for 6 pv for the fast column and 10 pv for the slow column. Then, the effluent EC dropped to 1220 µS cm^{-1} (slow) and 1180 µS cm^{-1} (fast), respectively.

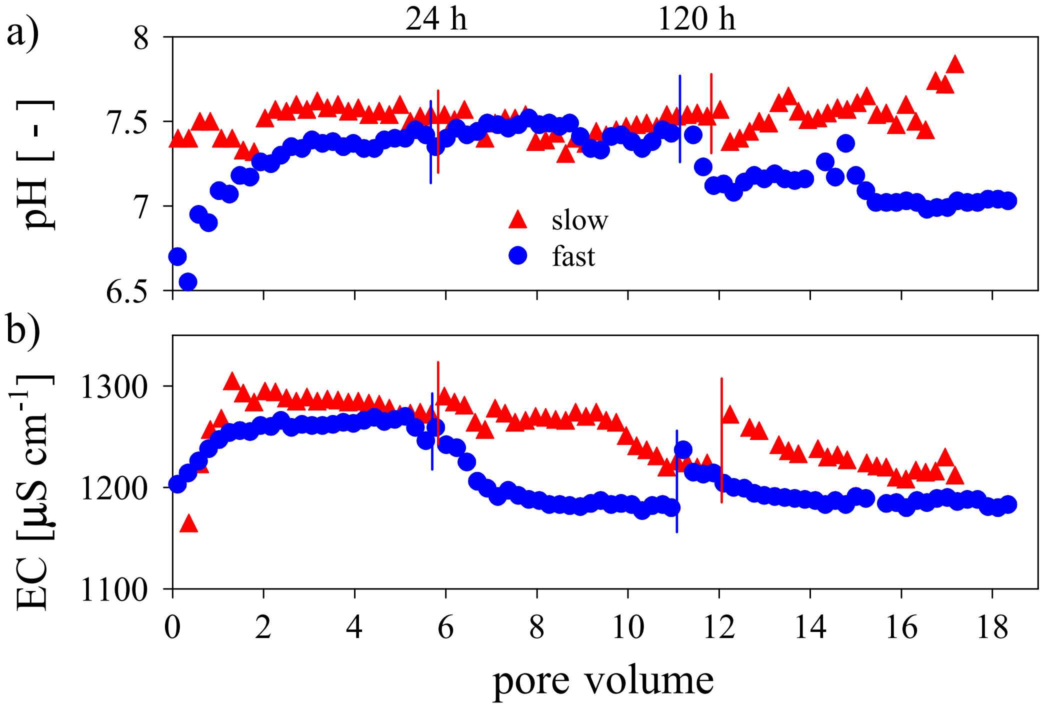


Figure 12 Course of pH (a) and the electrical conductivity (EC) (b). Flow-interrupts are indicated by the vertical lines.

The effluent pH of this material should be affected mainly by the dissolution of carbonates and by the release of organic matter which results in the formation of dissolved organic matter (DOM). While the first would result in a pH increase, compared with the unbuffered and neutral input solution, the release of organic matter should lower the pH due to a deprotonation of e.g. carboxyl functional groups. For both columns, effluent pH was higher than the input solution, indicating that the effect of the dissolution of carbonates outbalances the effect of DOM formation. The higher effluent pH of the slow flow column, in comparison to the fast column, points to the fact that the dissolution of carbonates und the development of the pH is rate limited. The longer residence time in the slow column results in a prolonged time for the dissolution process. However, the equilibrium pH of the material (pH_{H2O}=9.0, table 1) was never reached. The maximum pH to be reached under flow conditions seems to be much smaller than the batch-equilibrium pH for this carbonate material. A possible explanation for this discrepancy is the difference in the way the solutions for pH measurements are obtained. The preparation of a soil suspension, necessary to measure the pH of the soil, results in the destruction of aggregates and the formation of new carbonate surfaces which will increase the pH. Under flow conditions, the soil material is usually not that drastically disturbed. Another reason could be the bad wettability of the soil material as a water drop penetration time-test revealed. A bad wettability results in a reduced contact and thus reaction surface area of the solution to the soil material.

The electrical conductivity of the effluent was controlled by the level of the EC in the input solution and by possible interactions of the solution with the soil material. The release and dissolution of carbonates should result in an increase of the effluent EC. The formation of DOC, however, will not inevitably result in an increase of EC. It rather depends on the presence and amount of ionic functional groups and the protonation state of DOC. For both columns, the effluent EC was up to 130 µS cm^{-1} higher than that of the input solution (1160 µS cm^{-1}).

Together with the concomitant pH raise, it can be concluded that the dissolution of carbonates contributes most to the EC of the effluent. Dissolved organic matter, rich in ionic moieties, is of minor importance. The higher EC level of the slow column compared to the fast column is again the consequence of rate limited release, which affects the carbonates, the pH, and of course, also the EC. This is, again, supported by the marked response to the longer flow-interrupt. The fact that the EC declined for both, the fast and the slow column, after 6 pv and 10 pv have been exchanged, respectively, indicates that the pool of readily available carbonates is exhausted. From that on, the effluent EC is predominantly controlled by the level of the input solution.

3.2.3 Release of dissolved organic carbon

Figure 13 shows the release of dissolved organic carbon. Initially after the onset of the flow, maximum DOC concentrations of 20 mg l^{-1} and 16 mg l^{-1} were observed for the slow and the fast column, respectively, which were rapidly declining within the first two pv. Subsequently, a more constant and slightly declining DOC effluent level was observed which lasts for the rest of the experiment. In general, the slow flow column strayed in excess of the fast column. Again, the short flow-interrupt did not markedly affect DOC while the longer flow-interrupt resulted in strongly increased DOC effluent concentrations. At the end of the experiment, effluent concentrations were reduced to a constant level of about 12 mg l^{-1} for the slow and 4 mg l^{-1} for the fast column.

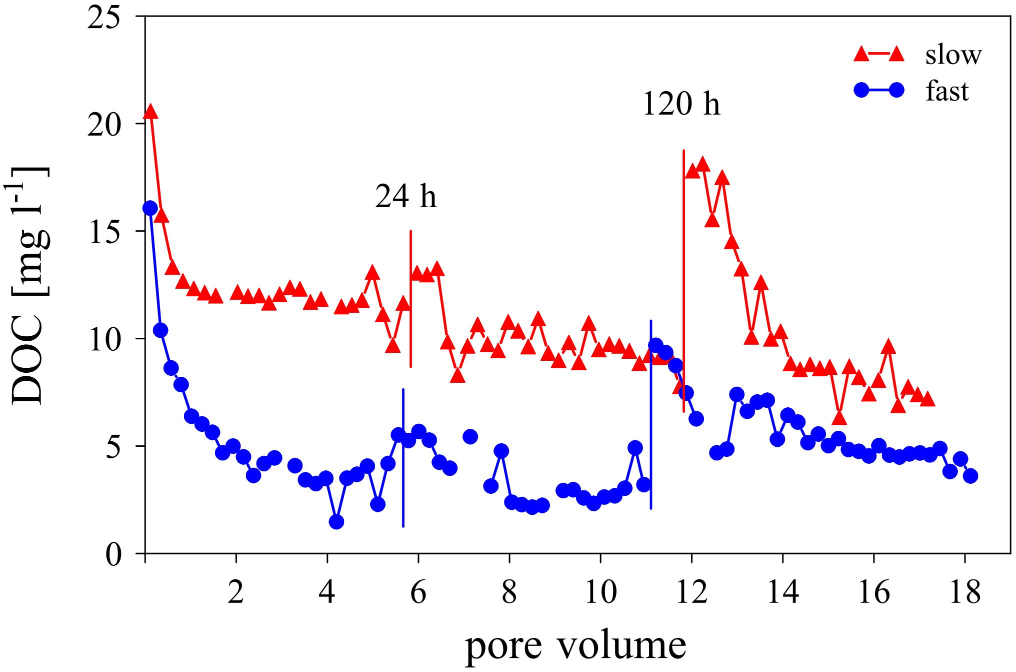


Figure 13 Dissolved organic carbon (DOC). Flow-interrupts are indicated by the vertical lines.

This two stage release behavior was already reported by others (Weigand and Totsche, 1998; Münch et al., 2002; Wehrer and Totsche, 2005) and seems to be quite unique for DOC. The initially high export, frequently called first flush, is explained by the export of readily available DOC produced during soil pre-treatment and mobilized during saturation prior to the experiment (Weigand and Totsche, 1998; Münch et al., 2002). Drying of soil material, for example, is known to produce water-soluble organic matter due to the lysis of microbial cells (Christ and David, 1994; Kaiser and Zech, 1998). This organic material dissolves rapidly upon rewetting and is washed out at the onset of the flow (Münch et al., 2002).

The first flush was followed by a constant stage of DOC export, which seems to be controlled by a fraction of DOC released under rate-limited conditions. The fact that this fraction shows slightly declining effluent concentrations reflects the situation that a finite pool of DOC is continuously exhausted.

Weigand and Totsche (1998) explained the two step release by the existence of at least two chemically different fractions of DOC in soils. One fraction is non-reactive with respect to the interactions with the soil matrix while the other is controlled by rate limited release characteristics. The assumption of at least two differently reactive DOC fractions is also supported by Wehrer and Totsche (2005) and our own measurements of $SUVA_{254}$. The UV radiation near 254 nm is absorbed by carbon-carbon double bonds. Any changes of UV absorbance are a measure for the relative change of the content of such moieties (Chin et al., 1994). The course of $SUVA_{254}$ showed initially increasing values and decreasing or constant values after the stop flows in each column (data not shown). The C=C double bond moiety was generally higher at the larger flow velocity. However, although the different moieties of DOC show different release behavior, $SUVA_{254}$ cannot be related to the reactivity of DOC (Weishaar et al., 2003).

Aside from the first flush, which seems to reflect a different and rapidly exhausted fraction of dissolved organic carbon, the response of DOC is the same as observed for pH and EC. Again, rate limited transport explains the observed release behavior which is supported by the higher yield at the slower flow velocity and the markedly increased effluent concentration after the longer flow-interrupt. The estimation of rate parameter k_{eff} and equilibrium concentration C_{eq} revealed the same k_{eff} values for the slow and the fast column within the found errors. The calculated values are given in Table 8. They are in a similar range as those published by Münch et al. (2002) (k_{eff}=1.6 x 10^{-3} h^{-1}, C_{eq}=94 mg l^{-1}). Due to higher total amount of C_{org} in their soils, they found a three times higher equilibrium concentration.

The calculated R-dependent Damköhler numbers *Da'* for the slow and the fast column are 0.021 and 0.005, respectively (Table 8). These low Damköhler numbers indicate non-equilibrium conditions, i.e. slow reactions, which are denoted by low rate parameters.

Table 8 Calculated rate parameter k_{eff}, equilibrium concentration C_{eq} and the Damköhler number *Da'* for DOC and PAH

k_{eff} (DOC) [h^{-1}]	0.9 x 10^{-3}
C_{eq} (DOC) [mg l^{-1}]	27.5
Da' (DOC) [-] slow / fast	0.021 / 0.005
k_{eff} (PAH) [h^{-1}]	1.0 x 10^{-3}
C_{eq} (PAH) [µg l^{-1}]	232
Da' (PAH) [-] slow / fast	0.022 / 0.005

3.2.4 *Course of turbidity*

Turbidity is the scattering effect of suspended solids on light and is a measure for suspended matter. The measurement is qualitative and cannot be directly correlated to micrograms per liter of suspended solids. Turbidity is time sensitive. Thus, if not determined immediately, results might be erroneous due to settling or aggregation of particles or co-precipitation of humic acids and minerals. To overcome such shortcomings, turbidity measurements should be done immediately after sample collection and follow a strict protocol.

The course of the effluent turbidity is given in Figure 14a. Turbidity showed maximum values of 100 FAU for the slow and 75 FAU for the fast column with generally higher turbidity for the slow column. Over the whole experiment, turbidity values continuously decreased until they reached values of 40 FAU for the slow and 20 FAU for the fast column. In both columns, the short flow-interrupt had no effect while the longer caused turbidity to decrease.

The observed turbidity values are high compared to, e.g. the European Standard which specifies values for solutions of high turbidity like sewages between 40 and 100 FAU (EN ISO 7027, 1999). Even at the end of the experiment, turbidity was still high.

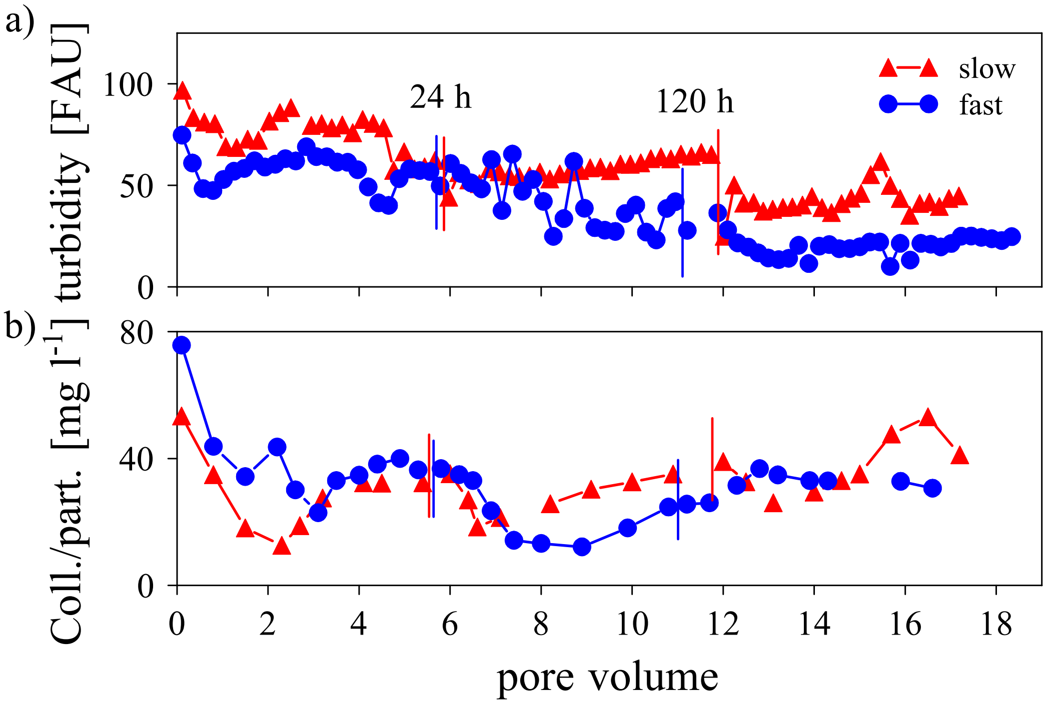


Figure 14 Turbidity expressed as Formazine Attenuation Units (FAU) (a) and concentrations of colloids and particles >0.7 µm (b). Flow-interrupts are indicated by the vertical lines.

Materials which contribute to turbidity are mineral colloids, suspended particles, biocolloids such as bacteria, and, of course, colloidal phase organic matter. The most important compounds are supposed to be colloids and particles of mineral provenience which are released when the cementing agents, the carbonates, are dissolved. Biocolloids seem to be of minor importance as sodium azide was added as biocide.

To a lesser extent particles of organic provenience contribute to turbidity because of the low content of natural organic carbon in this material. They seem to be particularly responsible for the initially increased turbidity values during the exchange of first two pore volumes. The first flush already discussed for the DOC can be found for turbidity, also. The observation that the slow column produced higher turbidity than the fast one was not expected. This rather implies that particles and colloids, which cause turbidity, are released under rate limited conditions as reported, for example by Lægdsmand et al. (1999) for undisturbed soil cores. The decrease of turbidity during the longer flow-interrupt, however, contradicts rate limited release. Other counterproductive processes seem to outbalance the rate limited release, e.g. the destabilization of the colloidal solution during the flow-interrupt. This might even be enforced by the increase of the EC which would result in a more efficient coagulation followed by sedimentation during no-flow conditions.

3.2.5 Course of particles in the retentate

At the onset of the flow, the release of particles in the size fraction 0.7-200 μm showed initially higher values (75 mg l^{-1}) for the fast column than for the slow column (53 mg l^{-1}) (Figure 14b). The initially high concentrations rapidly declined within the exchange of the first two pore volumes within both columns. Subsequently, effluent concentrations increased and reached values of 32 mg l^{-1} and 38 mg l^{-1} for the slow and the fast column, respectively. This wavelike raise and fall of the concentrations of the particles lasted until the very end of the experiment. Both the short and the longer flow-interrupt had no effect on the effluent concentration. Compared to the slow column, higher effluent concentrations were observed only for the first two pore volumes for the fast column. From that on, either equal or even smaller concentrations were found for the fast column than for the slow column.

As already discussed for the DOC, the initially high release is caused by the export of particles and larger colloids which were formed during pre-treatment of the soil. Drying and homogenization are known to be severe interventions which result in the formation of loosely attached materials. Upon onset of flow, these materials are exported to produce the first flush. Although this observation seems to be quite artificial at first sight, this situation is quite typical for soils at (abandoned) industrial and urban sites. Here, the ongoing disturbance due to construction activities including excavation, crushing, translocation, and backfilling of soil materials results in disintegration of profile build-up, structure and aggregates (Totsche et al., 2003a). It is to be expected that at such sites a large amount of particulate materials are relocated within the unsaturated zone and transported into deeper layers. The fact that the first flush wears off after two pore volumes have been exchanged suggests that these materials originate from a finite pool which is exhausted within a limited space of time.

The export of particles in the larger size fraction shows no clear dependence on flow velocity and no marked response to the flow-interrupts, indicating that the release is not that much dependent on the residence time. This contrasts the findings we have for EC and DOC which were found to be sensitive to both the flow velocity and the flow-interrupts. From these observations we have to conclude that release and mobility of particles in the large size fraction is predominantly independent of pH and EC. A weak correspondence of the large fraction with turbidity is found. Yet, turbidity measurement is most sensitive for colloids/particles in the size of a few micrometers (Gippel, 1995), and the suspended mass would be dominated by larger particles of the fraction 0.7-200 µm. A notable finding is that in the beginning the fast column produced more particles, while in the end the slow column had higher particle concentrations in the effluent. This can neither be observed for the turbidity nor for DOC. The effect of the different flow velocities, in particular the effect of the larger flow velocity, is supposed to be more effective and relevant for the larger size particles than for DOC, EC, and turbidity. This implies that for particles of the larger size fraction a third process has to be considered which controls their release behavior.

This is additionally supported by the observation that the mean pore velocity affects only the first flush, which is higher at the larger flow velocity. Besides first flush and rate limited transport, particle detachment and transport due to higher shear forces has to be taken into account. The pool of particles which can be hydraulically mobilized is thereby limited, which can be concluded from the fact that the slow column showed higher particle concentrations at the end of the experiment than the fast one.

3.2.6 Release of PAH in the filtrate and comparison with Raoult's law

The course of the polycyclic aromatic hydrocarbons in the filtrate is shown in Figure 15. Initial export of PAH was characterized by small but increasing concentrations for both columns with generally larger concentration for the slow column. Marked response of the PAH breakthrough was observed for both flow-interrupts with a more expressed reaction for the fast column. The observed maximum concentrations after flow has been resumed, i.e. 145 µg l^{-1} in the slow and 142 µg l^{-1} in the fast column, were almost independent of the duration of the flow-interrupt. At the end of the experiment PAH effluents showed constant concentrations of 80 µg l^{-1} (slow) and 20 µg l^{-1} (fast), respectively.

It should be noted that no first flush was observed for the PAH in the filtrate. Thus, the processes which cause first flush are not affecting the PAH in the small fraction. The export of PAH in the filtrate was in fact dependent on the residence time of the solution. The larger concentrations observed for the slow column along with the marked response to the flow-interrupts are clear indications for rate limited transport. The constant export of PAH at the end of the experiment is inversely correlated to the flow velocity: the 4.5 times higher flow rate resulted in four times lower concentrations. This, again, is a strong hint for rate limited transport.

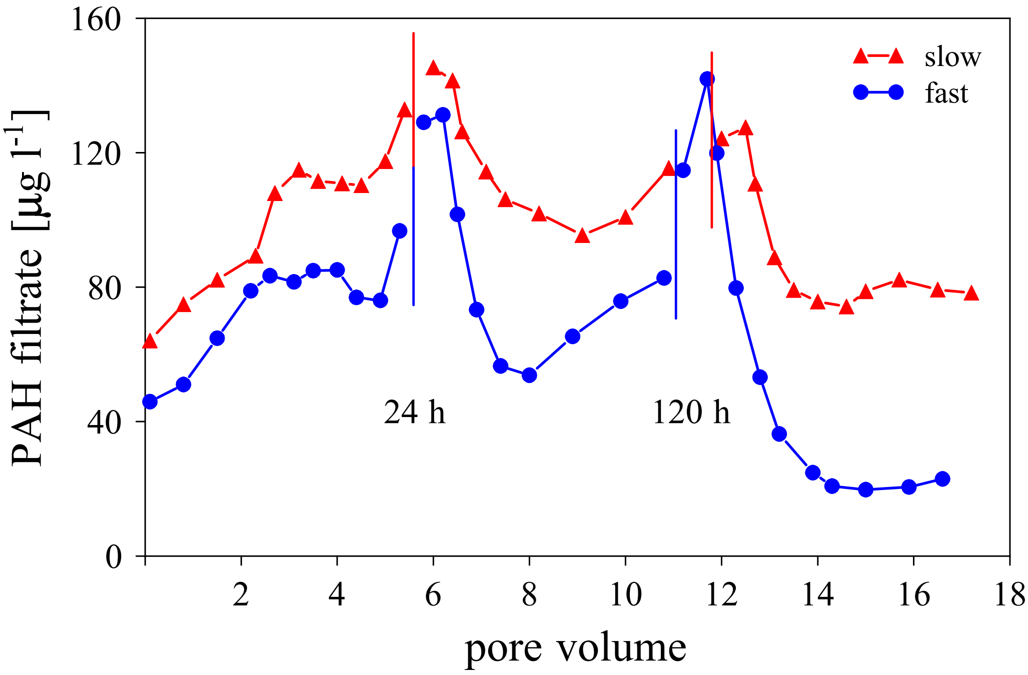


Figure 15 Concentrations of the sums of the 16 EPA PAH in the filtrate. Flow-interrupts are indicated by the vertical lines.

Another important observation is the fact that the maximum PAH concentrations reached after the flow-interrupt does neither depend on the duration of the flow interrupt nor on the flow velocity. In the fast column, the longer flow-interrupt resulted in almost the same effluent concentration than in the slow column. Moreover, during the longer flow-interrupt, the PAH concentration raise was small in the slow column and independent of the duration of the flow interrupt. This points to the fact that equilibrium concentration is almost accomplished in the slow column and that the flow-interrupts, even in the fast column, results in almost complete equilibration with the solution.

The fact that the effluent PAH concentration increased from the very beginning of the experiment until the first flow interrupt supports the interpretation that PAH release is governed by a rate limited mass transfer. Possible processes for the rate limited mass transfer are diffusion limited desorption from the solid phase or the rate limited dissolution from the aged NAPL phase. Rate or diffusion limited mass transfer from immobile to mobile regions, as the governing process, could be excluded as no such indications were observed in the conservative tracer breakthrough. Another explanation for the increasing concentrations at the beginning of the experiment might be the already mentioned bad wettability of the soil material.

A comparison of the release of DOC and EC on one hand and the PAH in the filtrate on the other hand reveals a strong correspondence for the remaining part of the breakthrough after the first flow-interrupt. Although PAH in the small fraction did not show a first flush, a mobilizing effect of DOC fractions might be assumed. While the readily available, non-reactive fraction of DOC, which caused the first flush, does not affect the transport of PAH, the DOC fraction characterized by rate limitation release might contribute or even control the rate limited export of PAH. A mobilization of PAH, which is facilitated by solubility enhancing co-solvents originating from the NAPL phase, i.e. benzene, could be excluded. Measurements of the surface tension of the seepage water collected from the investigated site showed no decreased values (70 mN m^{-1} in comparison to 72 mN m^{-1} for pure water).

The calculated rate parameter k_{eff} and the equilibrium concentration C_{eq} of PAH are the same for both flow velocities within the found errors (Table 8). The ratios of reaction time scale to transport time scale expressed as the *R*-dependent *Da'* are 0.022 for the slow and 0.005 for the fast column (Table 8). Again, the low Damköhler numbers indicate non-equilibrium conditions.

Figure 16 shows the calculated aqueous equilibrium concentrations according to Raoult and the measured concentrations in the filtrate. The comparison revealed no congruence of measured and calculated concentrations. For the identified 14 PAH (Naphthalene and Phenanthrene were below their detection limit), only the concentrations of Benz[a]anthracene, Chrysene and Dibenz[a,h]anthracene were in the range of the calculated values. Any uncertainties in this estimation affect only the absolute values and not the pattern of the PAH.

From these results it is concluded that Raoult's law does not help to explain the observed concentrations and that other processes aside dissolution control the release of PAH from the aged NAPL present in the used contaminated soil material. A possible explanation could be the rate limited formation and mobilization of small NAPL-"droplets" in the size of small colloids, which has been discussed, for example, by Pumphrey and Chrysikopoulos (2004) or the detachment of small fragments of the NAPL source material.

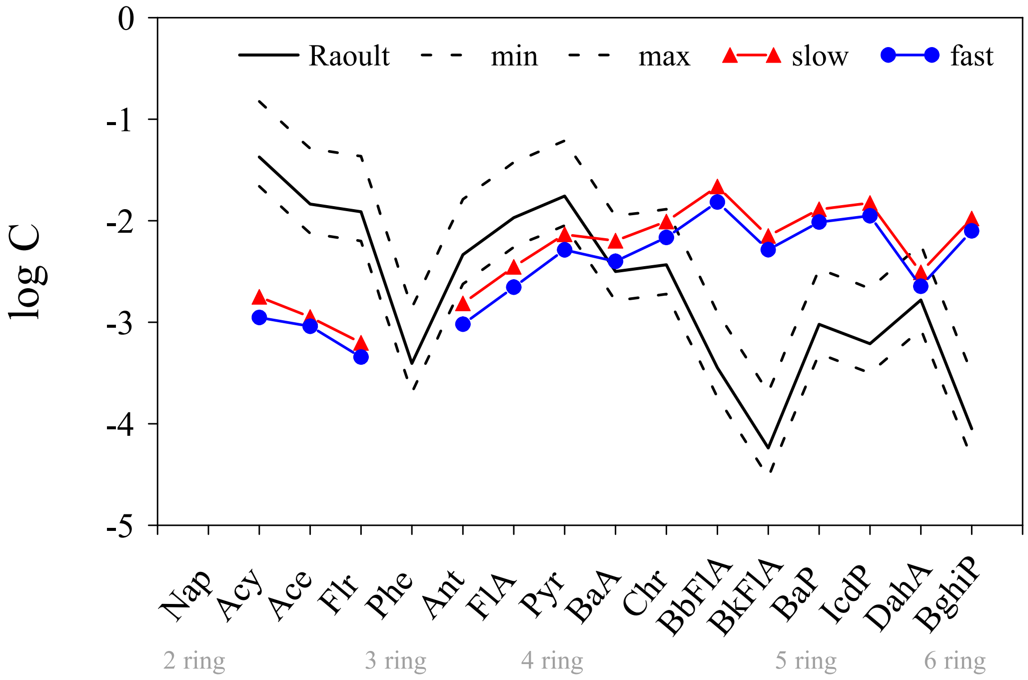


Figure 16 **Mean aqueous equilibrium concentrations estimated according to Raoult's law and mean measured concentrations of the single PAH in the filtrate.**

3.2.7 Release of particle-associated PAH (retentate)

The release of particle-associated PAH determined in the retentate is shown in Figure 17. The release is characterized by high initial concentrations of particle-associated PAH with maximum concentrations up to 87 µg l^{-1} for the slow column and 110 µg l^{-1} for the fast column. These high concentrations were followed by a steep decrease of the effluent concentrations. A clear dependence on the flow velocity was observed. From the beginning on to the first stop flow, the PAH concentration in the effluent of the fast column strayed in excess of the slow one, in between the first and the second interrupt the PAH concentration of the fast column dropped below the slow column, and from the second stop flow on until the end of the experiment the PAH concentration of the slow column strayed in excess of the fast one. A marked drop of the concentration of the particle-associated PAH was observed for the longer flow-interrupt for both columns, while the short flow interrupt resulted in reduced concentrations only for the fast column. In general, the breakthrough behavior of the particle-associated PAH followed the course of the breakthrough of the particles (Figure 14b). A clear first flush was observed. Even the same wavelike curvature can be identified within the breakthrough of the particle-associated PAH.

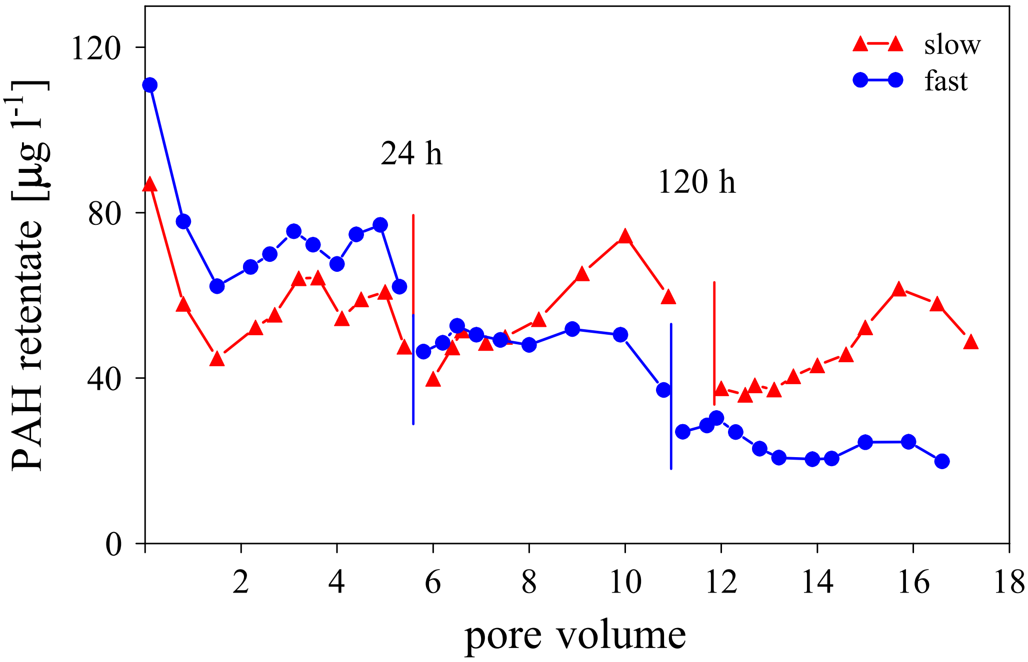


Figure 17 Concentrations of the sums of the 16 EPA PAH in the retentate. Flow-interrupts are indicated by the vertical lines.

The flow velocity has a significant effect on the export of particle associated PAH. Yet, the picture is more complicated and points to the fact, that different release processes are active within the column. At the onset of the flow, the overall effluent concentration was dominated by the first flush release. As already discussed for the particles, the larger amount of particle-associated PAH in the fast column has to be explained with a more effective and relevant export caused by higher hydraulic shear forces. This is also supported by the drop of particle-associated PAH as response to the flow interrupt. The larger particles are more susceptible to sedimentation and will deposit during no-flow conditions. The faster the flow velocity, the potentially larger are the transported particles. Thus, the effect of a concentration drop during no flow should be most expressed in the fast column, which indeed is seen in Figure 17 for the first flow-interrupt. With lasting flow, the first-flush wears off and so does the excess export of the particle-associated PAH in the fast column. The later stage of the experiment, in particular after eight pore volumes have been exchanged, is dominated by rate limited release of particle-associated PAH.

As already discussed, the effect of the larger flow velocity is more effective and relevant for the particles and such for the particle-associated PAH. The export of the particle-bound PAH is thus controlled by processes already discussed for the release of particles: First flush, particle detachment and transport due to higher shear forces on one hand and to a minor extent, also rate limited release of particle-associated PAH on the other. The dominance and duration of the individual process are thereby controlled by the size of the respective pools.

The comparative analysis of the pattern of the PAH in the soil, the filtrate, and the retentate should shed further light on the governing release and transport pathways. If PAH export would be controlled by the release and transport of the NAPL source material in form of droplets or fragments, the same fingerprint, i.e. the distribution pattern of the PAH, would be expected in the different fractions. PAH patterns of the soil material (sieved to 2 mm), the retentate (>0.7µm), and the filtrate (<0.7µm) were therefore analyzed and compared. The results of this comparison are given in Figure 18. Indeed, the PAH patterns were almost the same for the retentate and filtrate of both columns and for the soil material. All distributions show dominance of the higher molecular weight PAH (>3-rings), which account for about 90% of the total PAH. The fact that the PAH patterns are similar in all fractions, independent of flow velocity and particles size, imply that NAPL transport mainly occurs in form of particles of different sizes. Small NAPL droplets or fragments <0.7 µm are mobilized under a rate limited process as discussed above. The release of NAPL particles in the size of 0.7-200 µm is dominated by three alternating processes, i.e. the first flush, the hydraulic mobilization and, to a lesser extent, the rate-limited formation and release.

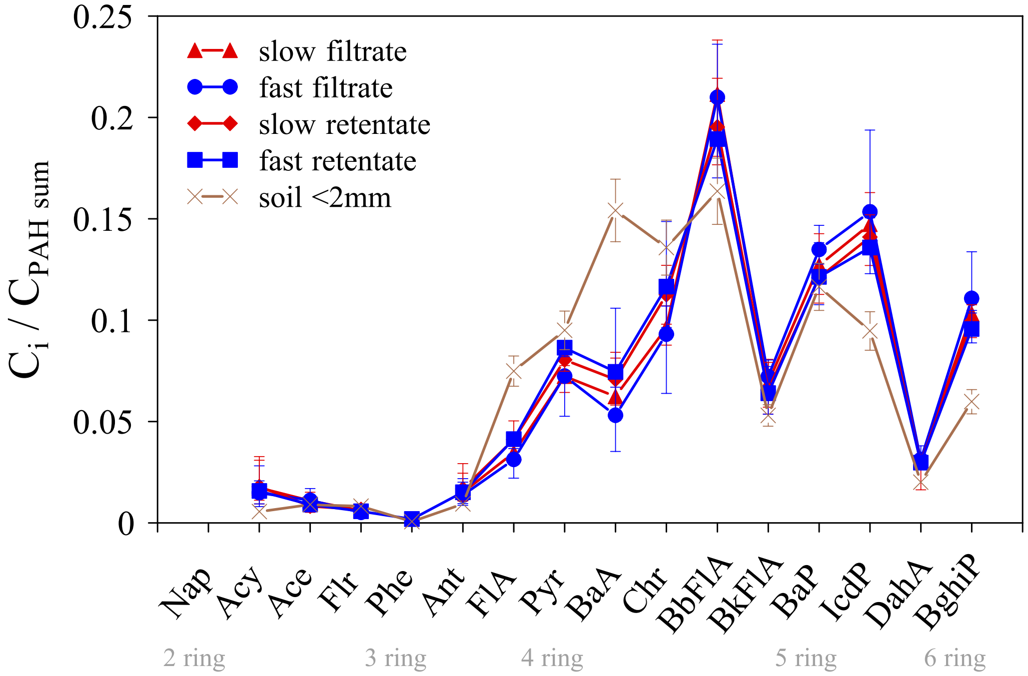


Figure 18 **PAH patterns in the soil material (sieved to 2mm), in the filtrate and in the retentate of the slow and the fast column.**

3.2.8 Mass balance: Mobilized masses of PAH, DOC, and particles

The overall masses of PAH, DOC and colloids/particles released from the columns are given in Table 9. Due to the rate limited release, the mobilized mass of DOC and PAH <0.7 µm were higher for the slow column. Overall PAH export was dominated by the smaller size fraction. The mobilized PAH mass in the filtrate of the slow column was almost twice as high as the mass exported within the retentate. For the fast column the export in the smaller size fraction was only 40% higher. The released mass of particle-associated PAH, as well as the exported mass of colloids/suspended particles in the >0.7µm fraction were almost the same for both flow velocities.

Table 9 Exported masses of DOC, colloids/particles >0.7 µm and PAH (in the two fractions) for the slow and fast column eluted within 16 pore volumes

	slow	*fast*
DOC [mg]	45	20
PAH mass, filtrate [µg]	400	270
colloids/particles >0.7 µm [mg]	117	119
PAH mass, retentate [µg]	210	194

3.2.9 Summary

With the applied experimental design it has been demonstrated that the release of DOC and PAH in the filtrate (fraction <0.7 µm) are rate dependent. DOC showed a significant first-flush release and a marked dependence on flow velocity and the flow interrupts. From this behavior it is concluded that DOC release is given by the superimposition of the breakthrough of at least two different DOC fractions: The export of the one fraction causes the first flush while the export of the other fraction is controlled by rate limited release. The pH, electrical conductivity and turbidity were also found to be affected by non-equilibrium. This suggests that processes which are affected on their part by pH and EC, e.g. the stability of colloidal solutions, should then be controlled by non-equilibrium. For prolonged no-flow conditions, it is to be expected that the increase of EC due to the dissolution of carbonates should result in the destabilization of colloids, thus affecting also any contaminants associated with these colloids. This was indeed found for turbidity and for the particle-associated PAH in the retentate. However, the release of particles (0.7-200 µm) was independent of pH and EC. It is suggested that the dominant particle release processes in this materials are the first-flush, the particle detachment due to hydraulic mobilization and to a lesser extent, the rate limited release.

For the slow flow velocity, 33% of the total PAH export was found in the retentate (2/3 in the filtrate), while for the fast flow velocity the amount of particle-associated PAH increased to 42% of the total PAH. The comparison of measured concentrations in the filtrate and aqueous equilibrium concentrations calculated according to Raoult's law has shown that dissolution of PAH from NAPL seems to be of minor importance.

This, however, might be different in groundwater environments with low lateral flow velocities, where the prolonged residence might be high enough to achieve the dissolution equilibrium more closely. The PAH in the filtrate are mobilized under rate limited conditions and showed strong correlation to the fraction of DOC released under rate limited conditions. This suggests that PAH in the filtrate seem to be closely connected with the DOC. One possible explanation would be that the DOC itself is part of the NAPL phase which was released as small fragment or droplet. This is also corroborated by the similarity of the PAH patterns of the filtrate and the retentate.

3.3 Lysimeter experiment

3.3.1 Temperature and soil moisture conditions

The mean annual air temperature of the study area is 8.9°C (1991-2000). The monthly mean air temperatures during the observation period reached their maximum value in August 2003 with 22.4°C and their minimum value in February 2003 with -4.4°C.

The temperature and soil moisture conditions within lysimeter 3 are given in Figure 19a and 19b. Soil temperatures indicate major soil freezing at the end of December 2003 down to about 0.3 m. The soil moisture content was generally low as a result of the high permeability and low water holding capacity of the coarse material. The very low water contents are due to a very hot and dry period in summer 2004.

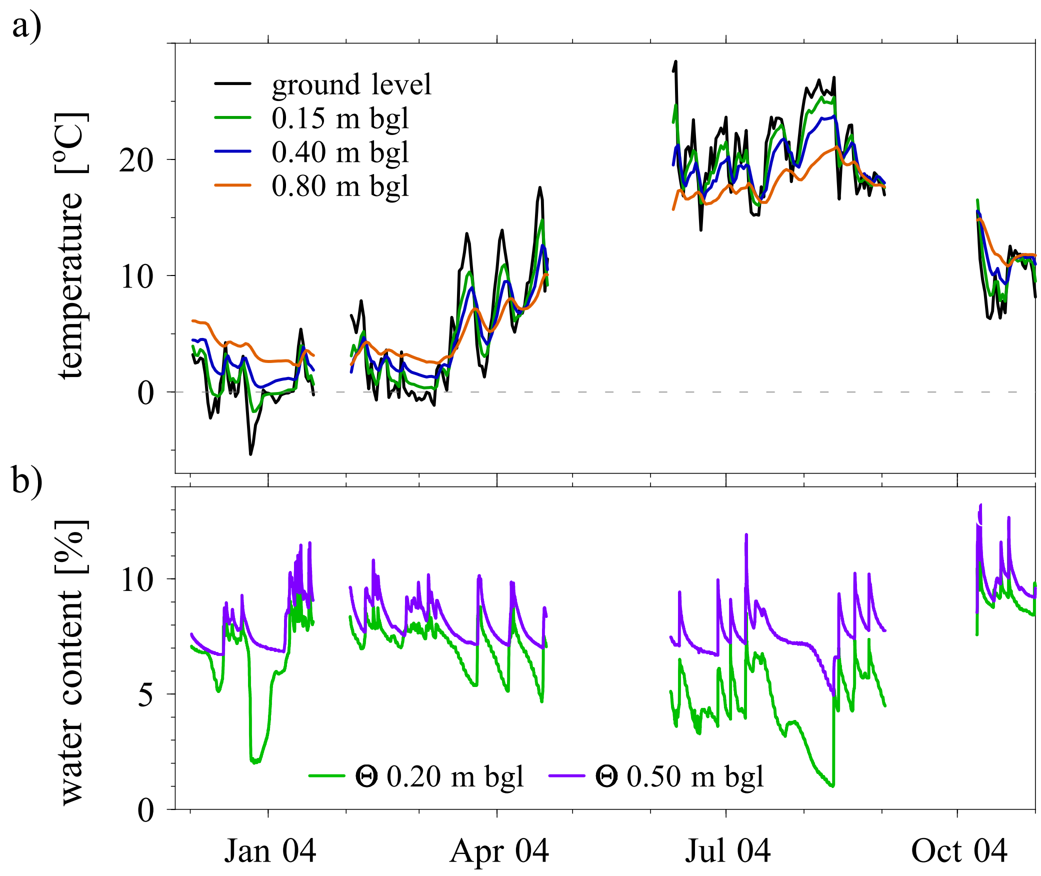


Figure 19 Temperatures at ground level and at three depths below ground level (bgl) (a) and soil moisture conditions at two depths (b) within lysimeter 3.

3.3.2 Precipitation vs. seepage

The mean annual precipitation is 815 mm (1991-2000). The precipitation amount of the entire sampling period (2 years) reached 1784 mm. The sums of precipitation together with the mean amount of seepage water of the three lysimeters are displayed in Figure 20. Peak values of the amount of precipitation and seepage water were 70 l m^{-2} and 60 l m^{-2}, respectively. In general, the amount of seepage correlated well with the precipitation. This was to be expected as evapotranspiration was low and the coarse material has a low water holding capacity and a high permeability. Deviations between the course of precipitation and seepage water result from (1) freezing and/or snow fall in December 2002, January, February, December 2003 and January 2004, (2) the corresponding snowmelt in December 2002, March 2003 and February 2004 and (3) increased evapotranspiration in summer 2004.

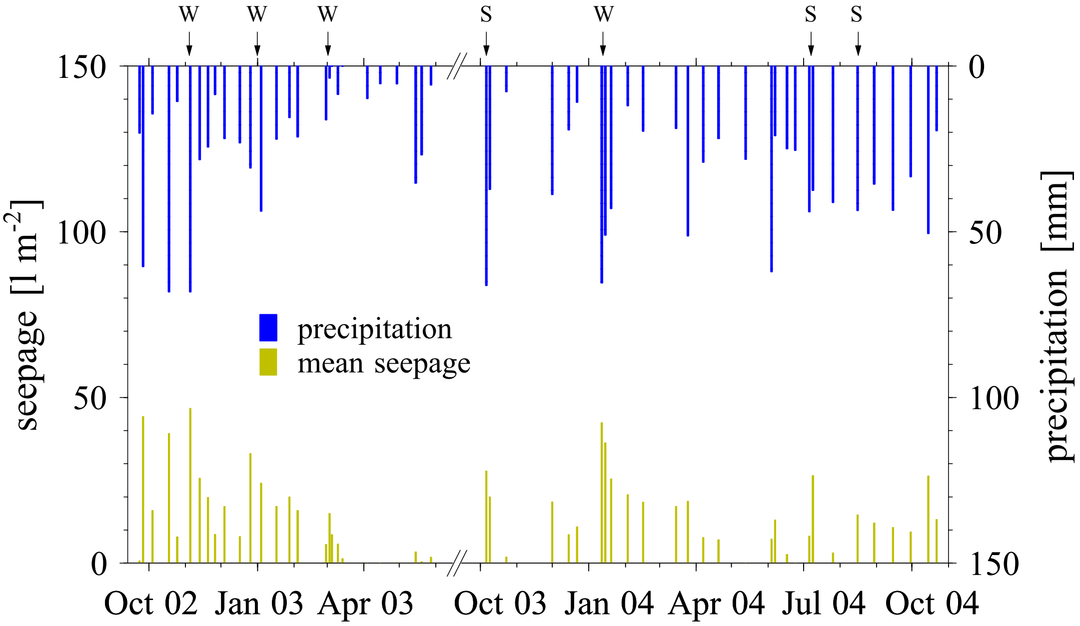


Figure 20 Mean precipitation and mean amount of seepage water during the two year monitoring period. Single events in summer are indicated by S, single events in winter by W.

3.3.3 Course of pH, EC and turbidity

The pH of the seepage water of all lysimeters varied from 7.1 to 8.4 (Figure 21a). pH values decreased after strong precipitation events and increased during dry periods. Lowest pH values, however, were observed in summer 2004.

Figure 21b shows the course of the electrical conductivity (EC) of the seepage water of the lysimeters. EC values of the lysimeters were between 200 µS cm^{-1} and 400 µS cm^{-1}.

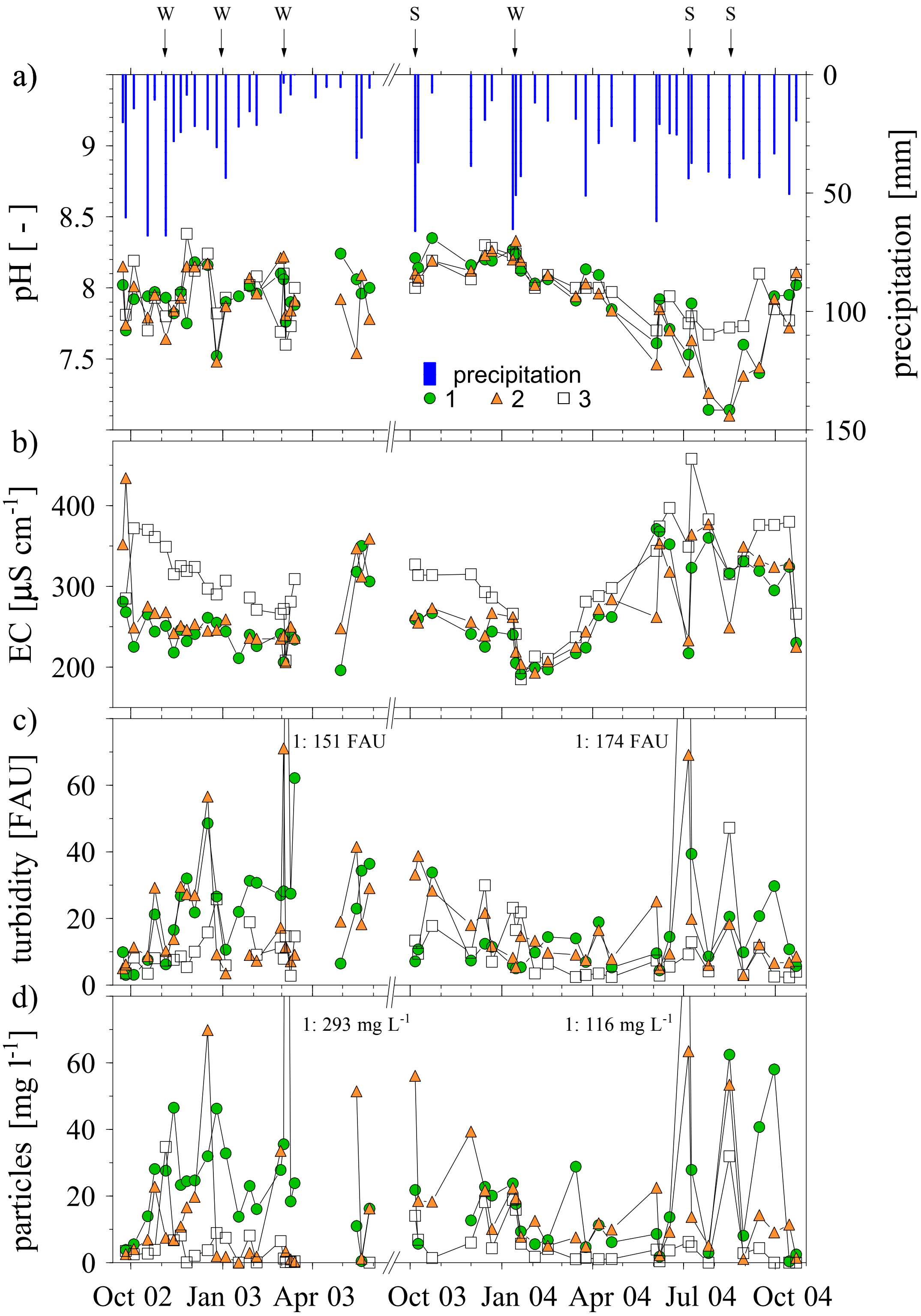


Figure 21 **Course of pH (a), electrical conductivity (b), turbidity (c) and colloids/particles (0.7-200µm) concentration (d) of the three lysimeters. Single events in summer are indicated by S, single events in winter by W.**

High EC values were observed at the start of the experiment and decreased in the following months. The EC of all lysimeters showed high values during summer periods and decreased in autumn and winter. Sharp declines are observed after a snowmelt in March 2003 and after high amounts of precipitation in January and July 2004.

The basic turbidity of the seepage of lysimeter 1 and 2 were about 20 FAU (Figure 21c). Lysimeter 3 showed generally lower values of turbidity. Increased turbidity values occurred after high amounts of precipitation. Extreme high values were observed for lysimeter 1 after the snowmelt in March 2003 and a thunderstorm in July 2004.

3.3.4 Course of colloids/particles, DOC and PAH

The concentrations of colloids and particles in the size of 0.7-200 µm showed levels of 15 mg l^{-1} for lysimeter 1 and 2 and about 3 mg l^{-1} for lysimeter 3 (Figure 21d). Increased particle concentrations were observed after strong precipitations events. As indicated by the turbidity data, the snowmelt in March 2003 and the thunderstorm in July 2004 resulted in extreme high exports of particles from lysimeter 1.

The course of DOC in the seepage water of the lysimeters are given in Figure 22.

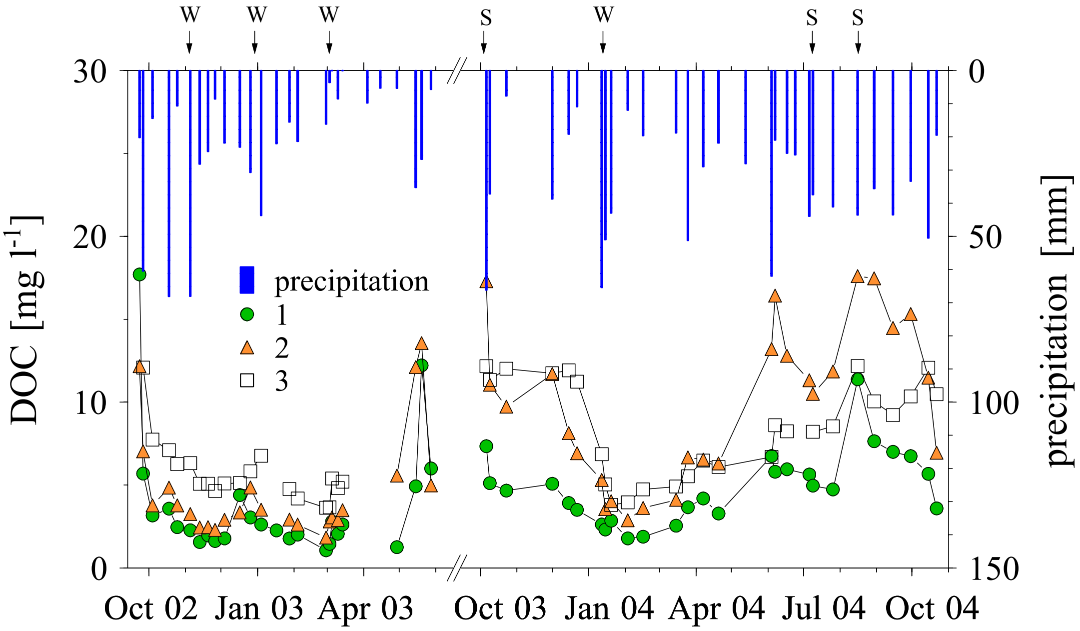


Figure 22 Dissolved organic carbon (DOC) of the three lysimeters. Single events in summer are indicated by S, single events in winter by W.

At the beginning of the experiment in October 2002 and with the restart in October 2003, the DOC showed high concentrations followed by a continuous decrease. In winter time, values generally below 6 mg l^{-1} were observed. During summer periods, DOC concentrations showed values up to 18 mg l^{-1}.

The amount of PAH exported from lysimeter 1 was very low in the filtrate (<0.5 µg per seepage event) as well as in the retentate (<3 µg per seepage event). For lysimeter 2, the PAH exported within the filtrate and the retentate were generally below 1 µg and 10 µg per seepage event, respectively. The mean amount of PAH released from lysimeter 3 was about 3 µg per seepage event in the filtrate and 23 µg per seepage event in the retentate (data not shown).

3.3.5 Mobilized amounts of colloids/particles, DOC and PAH

The total mobilized amounts of PAH in both fractions, DOC and colloids/particles (0.7-200 µm) released from the lysimeters during the monitoring period are given in Table 10.

Table 10 Total mobilized amounts of DOC, colloids/particles (0.7-200 µm) and PAH in both fractions eluted from the lysimeters during the two-year monitoring period, and the corresponding percentages mobilized via single release events

Total mobilized amounts during two years				
Lysimeter	**DOC [mg]**	**Colloids/particles [mg]**	**PAH filtrate [µg]**	**PAH retentate [µg]**
1	872	5083	8.7[a]	33[a]
2	1323	2556	15.7[a]	238[a]
3	1247	1382	135	1085

Percentage mobilized via single events				
Lysimeter	**DOC [%]**	**Colloids/particles [%]**	**PAH filtrate [%]**	**PAH retentate [%]**
1	37	60	34[a]	70[a]
2	34	47	30[a]	63[a]
3	37	72	39	85

[a] fewer data than lysimeter 3

Lysimeter 2 and 3 showed higher total amounts of DOC than lysimeter 1. The amount of mobilized colloids/particles increases from lysimeter 3 to lysimeter 2 to lysimeter 1. A remarkable fact is that 85 % of the total PAH amount were released from lysimeter 3 during several single events. The importance of single events for the release of PAH and colloids/particles in the size fraction 0.7-200 µm is observable for all lysimeters (Table 10).

3.3.6 pH and EC

The release of colloidal particles is strongly influenced by the physicochemical properties of the soil solution. The pH and the ionic strength dictate the repulsive or attractive forces between colloidal particles and are thus important for the stability of the colloidal system (Ryan and Gschwend, 1994; Ryan and Elimelech, 1996; Bunn et al., 2002). The infiltration of low-pH, low-ionic strength rain water leads to an expansion of the diffuse double layer and also the repulsive forces outbalance the attractive forces which result in a mobilization of colloidal particles (Ryan and Elimelech 1996).

The observed pH values for all lysimeters were lower than the equilibrium pH (H_2O) of the material (Table 2). This is due to the unsaturated conditions within the lysimeters and a too short contact time of the seepage water to the soil material to reach equilibrium. The pH of the seepage reacted inversely to the amount of precipitation. With high amounts of precipitation it decreased and increased at times with low precipitation (Figure 21a). The pH of the seepage water is controlled by the extent of dilution of the soil solution by low-pH infiltrating rain water and the mean residence time of the soil solution. Small amounts of precipitation with low intensities caused only low dilution of the resident soil solution. They resulted in prolonged residence times and low flow velocity and allow more time for the dissolution of carbonate minerals. In contrast, the infiltration of high amounts of rain water resulted in a marked dilution of the soil solution, increased flow velocities and therefore reduced contact time. Consequently, this results in a decrease of the pH. This effect resulted in pH drops of up to 0.6 units during snowmelts and after strong rain events in summer during the rapid infiltration of snowmelt/rainwater.

The EC of the seepage water from this material is mainly affected by the dissolution of carbonates and the release of organic substances. The dissolution of carbonates should result in an increase of the EC. The formation of DOC, however, will not inevitably result in an increase of EC. It rather depends on the presence and amount of ionic functional groups and the protonation state of DOC.

In general, the EC follow the course of the DOC concentrations (Figure 21b and 22). During summer months the EC of all lysimeters showed increased values as a result of increased DOC concentrations. The seepage water of lysimeter 3 showed generally higher values than lysimeter 1 and 2. This is explained by the release of NAPL compounds from the high contaminated soil material. The larger height of lysimeter 3 leads to a higher residence time of the soil solution and thus to a longer period of time for equilibration with the soil material.

3.3.7 Release of colloids/particles, DOC and PAH

The higher export of colloids/particles from lysimeter 1 compared to the other lysimeters is explained by the higher silt fraction of its material (Table 2). The lower total amount of colloids/particles for lysimeter 3 compared to lysimeter 2 is the result of its elongated seepage distance and higher filter capacity.

DOC concentrations in the seepage of the lysimeters showed constant levels of 3 mg l^{-1} (lysimeter 1 and 2) and 5 mg l^{-1} (lysimeter 3) (Figure 22). This constant release level (October 2002-March 2003 and January-April 2004) is specific for the respective material and the prevailing transport regime. The higher DOC concentrations for lysimeter 3 are partly due to the higher contamination and partly to the longer traveling distance in the elongated lysimeter which results in larger residence times of the seepage water. This points to the fact that the release of DOC is rate limited: The higher the residence time, the longer the period of time for equilibration and the higher the effluent DOC concentration. Rate limited release of DOC and material-dependent export levels have already been found for various natural and contaminated soils (Münch et al. 2002, Wehrer and Totsche 2005, Weigand and Totsche 1998). The different DOC levels of the three lysimeters are a result of their different contamination level. In addition to the natural organic matter, the NAPL phase serves as a source of DOC mainly in lysimeter 2 and 3. In spite of its lower contamination, lysimeter 2 showed higher DOC values than lysimeter 3 during spring and summer 2004. This might be explained on the one hand by the higher microbial activity during this time and on the other hand by the smaller height of lysimeter 2 which promoted the desiccation of the soil monolith and thus a larger production of water-soluble organic matter. Christ and David (1994) reported the production of water-soluble organic matter after drying of soil material due to the lysis of microbial cells.

The release of PAH has been shown to follow a dissolution process according to Raoult's law (Lane and Loehr 1992, Lee et al. 1992, Mukherji et al. 1997, Eberhardt and Grathwohl 2002). Aqueous equilibrium concentrations of the single PAH were calculated according to Raoult's law and compared to the mean PAH concentrations observed in the filtrate of lysimeter 3 to test the applicability of Raoult's law (Figure 23).

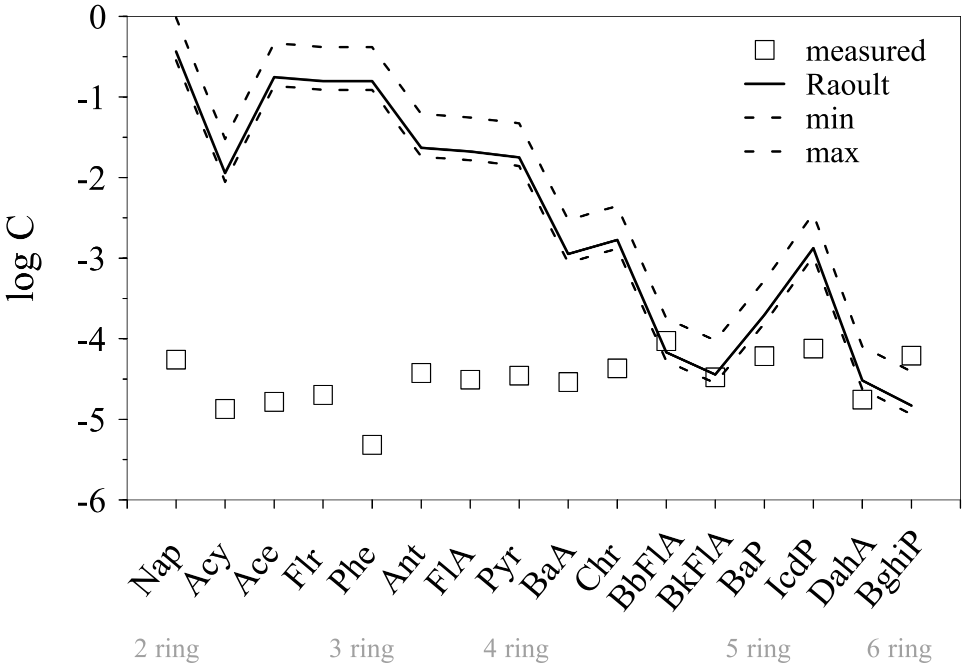


Figure 23 Mean aqueous equilibrium concentrations calculated according to Raoult with molecular weights for the coal tar of 295 g mol^{-1}, 230 g mol^{-1} (min) and 780 g mol^{-1} (max) and mean concentrations of the single PAH in the filtrate of lysimeter 3.

The comparison revealed that Raoult's law was not able to predict the observed concentrations. Only Benzo[b]fluoranthene and Benzo[k]fluoranthene were in the range of their calculated aqueous equilibrium concentrations. This demonstrates that the release of PAH in the fraction <0.7 μm is not solely controlled by dissolution according to Raoult's law. In fact, other processes, e.g. the formation and release of mobile sorbents such as DOC affect the mobility of PAH in the unsaturated zone.

The differences in the total exported amount of PAH between the lysimeters correspond to their level of contamination (Table 4). The overall PAH export from the lysimeters was dominated by the colloid/particle fraction in the size of 0.7-200 μm. For the whole monitoring period, 135 µg PAH were mobilized from lysimeter 3 in the filtrate (<0.7 µm) while the 8-fold mass, 1085 µg, was exported in the retentate. Similar distributions were observed for the lysimeters 1 and 2, although the total PAH export was much lower due to the lower contamination and the fact that the PAH data set is smaller for these two lysimeters. The PAH mass exported within the retentate from lysimeter 1 and 2 are 4-fold and 15-fold higher compared to the ones exported within the filtrate.

The general release of colloids and particles, DOC and PAH was superimposed by several single release events which seems to control the overall release situation (Table 10).

3.3.8 Single release events

Single release events were observed in November 2002, December/January 2002/2003, March 2003, October 2003, January 2004, July and August 2004. Single events in summer and autumn (October 2003, July and August 2004) were provoked by intensive precipitation such as thunderstorms after prolonged dry periods. During winter months (November 2002, December/January 2002/2003, March 2003, January 2004) they occurred after soil freezing followed by thawing and a high amount of melt or rain water infiltrating the soil material.

All single release events were characterized by high values of turbidity and high concentrations of colloids/particles in the size of 0.7-200 µm (Figure 21c and 21d). In summer, this was accompanied by high concentrations of DOC for all lysimeters and increased values of PAH released in the retentate of lysimeter 3 (Figure 22 and 24). Most striking was the extreme high export of PAH in the retentate of lysimeter 3 as a result of single release events in winter (Figure 24b).

Dry periods/thunderstorms in summer and autumn and freezing/thawing cycles in winter were most effective in the production of large colloids and particles (0.7-200 µm). A high mechanical strain due to the drying in summer and the freezing of the soil material in winter results in the formation of particles. The desiccation during summer 2004 and the freezing/thawing in winter 2003/2004 can be seen in Figure 19. These colloids and particles were then exported from the lysimeter with the following precipitation or snowmelt. The increased hydrodynamic forces as a consequence of the high amounts of water infiltrating within a short period of time lead to a mobilization of colloids and particles. This is supported by the highly significant correlation between the amount of seepage and the amount of colloids/particles (Table 11). In addition, decreased pH and EC values favored the release of colloids and particles (Figure 21a and 21b). Colloid and particle mobilization as a result of decreased pH and EC or increased flow velocity or rain intensities have already been shown by other authors (McDowell-Boyer, 1992; Kaplan et al., 1993; Ryan and Gschwend, 1994; Ryan and Elimelech, 1996; Bunn et al., 2002; Rousseau et al., 2004). This interplay of desiccation and intensive rain and freezing/thawing and snowmelt events, respectively, are therefore important triggers for the formation and redistribution of colloids and particles in the unsaturated soil zone.

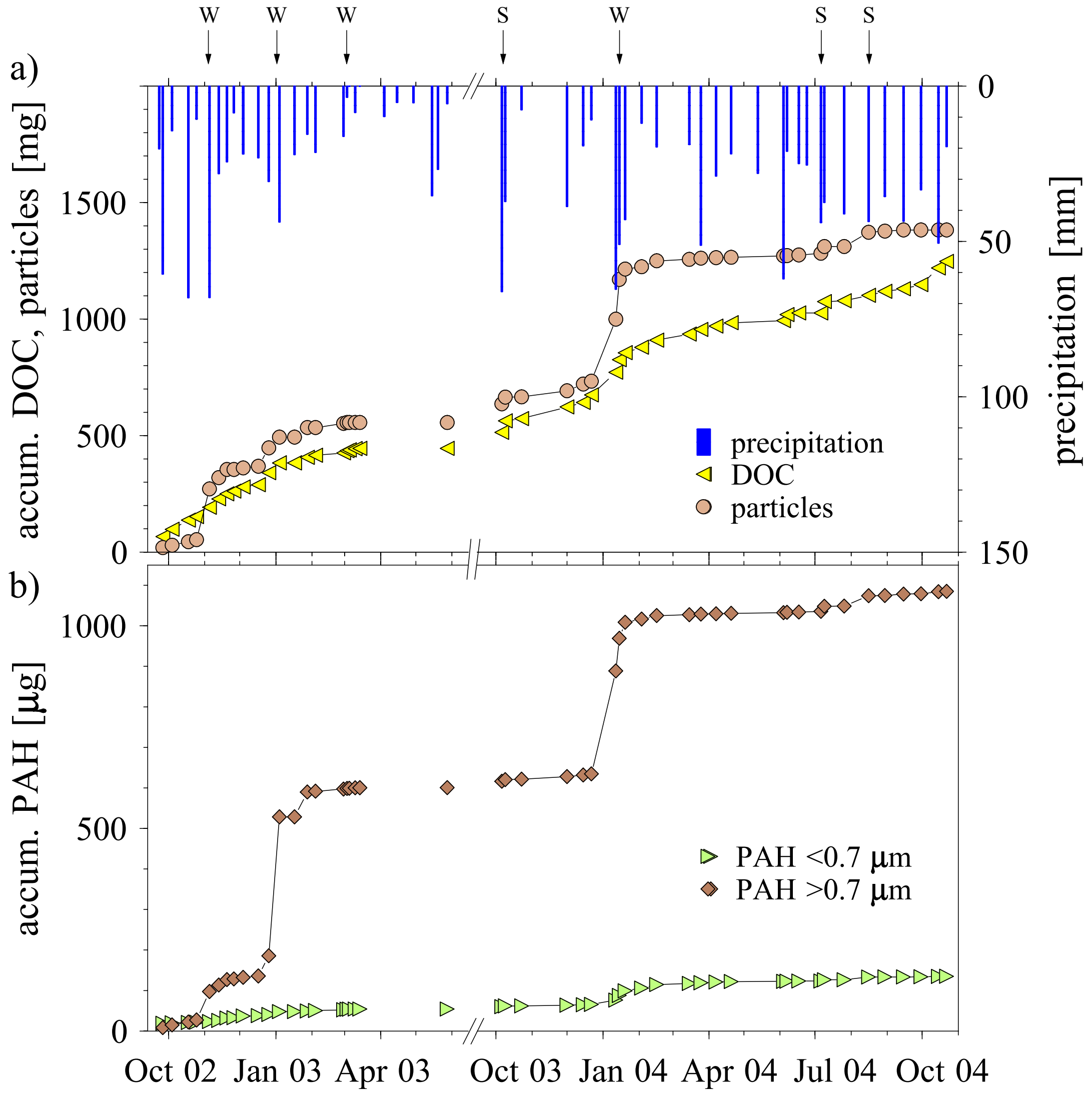


Figure 24 **Accumulated amount of DOC, colloids/particles (0.7-200µm) (a) and PAH in both fractions (b) exported from lysimeter 3. Single events in summer are indicated by S, single events in winter by W.**

Table 11 **Spearman's rank correlation coefficients calculated for selected bulk liquid parameters, PAH in both fractions and colloids/particles (0.7-200 µm). C denotes the concentration of the subscript parameter; M denotes the amount of the subscript parameter**

	precip	seep	pH	EC	C_{DOC}	M_{DOC}	turb	C_{par}	M_{par}
precipitation	1.000								
seepage	0.996	1.000							
pH		0.975	1.000						
EC		0.978		1.000					
C_{DOC}		0.994			1.000				
M_{DOC}		0.995	0.948	0.952		1.000			
turbidity		0.967				0.937	1.000		
$C_{particles}$		0.993		0.996	0.973		0.991	1.000	
$M_{particles}$		0.999		0.736		0.991	0.975		1.000
C_{PAH} filtrate		0.991			0.999			0.967	
C_{PAH} retentate		0.999			0.986			0.998	
M_{PAH} filtrate		0.989				0.999			0.984
M_{PAH} retentate		0.999				0.996			0.999

P=0.1	63	**P=0.05**	251	**P=0.025**	1007	**P=0.01**	6296	**P=0.005**	25000

The high DOC concentrations during the summer months were a result of dry periods and the decomposition/mineralization of plant material during the vegetation period (Figure 22). Drying of soil material is known to produce water-soluble organic matter due to the lysis of microbial cells (Christ and David 1994). This organic material dissolves rapidly upon rewetting (Kaiser and Zech 1998) and is washed out with the seepage water. Peak values of DOC in the seepage water after dry periods have been observed by Lamersdorf et al. (1998). In contrast to the rapid decreasing concentrations in September/October 2002, the high DOC concentrations after the summer 2003 lasted from October to December 2003. The reason for this delayed eluviation of DOC is the extreme dry summer 2003 followed by only a few precipitation events during autumn and early winter.

The DOC concentrations for the single events in winter showed slightly increased values. Only in January 2004, high amounts of infiltrating rain water lead to a high dilution and thus to decreased DOC concentrations. This behavior is explained on the one hand by the effect of freezing/thawing events which lead to a disruption of microbial tissues and an increase of the DOC values and on the other by the inverse relationship of DOC concentrations and the water flux (Kalbitz et al. 2000).

The cumulative amount of DOC, colloids/particles (0.7-200 µm) and PAH within the two fractions exported from lysimeter 3 are presented in Figure 24. The interplay of dry periods and thunderstorms during summer months resulted in a release of DOC and colloids/particles up to 69 mg and 80 mg per seepage event, respectively. Whereas up to 97 mg DOC and up to 266 mg colloids/particles per seepage event were exported from lysimeter 3 at release events in winter.

For the export of PAH in the filtrate, only slightly increased values were observed at the single release events. However, we found a highly significant correlation between DOC and PAH <0.7 µm (Table 11). The release of PAH in this fraction seems to be controlled by processes which act on the formation, release and mobility of DOC.

Remarkable were the extreme export of PAH in the retentate from lysimeter 3 at single events in winter (Figure 24b). Two single seepage events (January 2003 and 2004) resulted together in an export of 600 µg PAH in the fraction 0.7-200 µm. Freezing and thawing cycles seem to influence also the PAH source materials, i.e. the remnants of the NAPL phase. The freezing of water resulted in high mechanical strain, which lead not only to the formation of soil-borne particles but also very likely to the formation of NAPL particles. At the onset of the thawing and following rain or snowmelt events, PAH were exported from the lysimeter associated with these newly generated soil particles or within NAPL particles.

The importance of freezing of the source material is demonstrated at the release event in March 2003. Peak values of turbidity and particle concentration were found for lysimeter 1 and 2 as the result of a snow melt (Figure 21c and 21d). Again, this is caused by increased hydrodynamic forces due to the high amount of melt water infiltrating the soil. However, this event did not result neither in an increased release of particles in lysimeter 3 nor of PAH in any lysimeter. The freezing prior to this event seems to have not reached deeper soil horizons, i.e. the NAPL-contaminated soil material in lysimeter 3, to cause a release of particles-associated PAH or NAPL particles.

3.3.9 Summary

It was shown that the export of PAH from the studied contaminated soil is dominated by the release via the fraction of colloids and particles of 0.7-200 µm in size. Furthermore, the release of operationally defined dissolved PAH is strongly coupled to the release of DOC. Hence, the transport of PAH in the form of dissolved molecules is of minor importance within the unsaturated soil zone. This conclusion is supported by the results of the comparison with Raoult's law.

In contrast to the column experiment, we found that the overall PAH export from the lysimeters was dominated by the retentate (>0.7 µm). The reason for the different pathways of PAH export between the column and the lysimeter experiment is the difference between the conditions under which the PAH were mobilized. In contrast to the saturated steady-state conditions in the laboratory, preferential flow and accordingly high flow velocities during intense rain events are very likely to occur in the coarse soil material under field conditions. Consequently, colloids and particles in the size of 0.7-200 µm could be mobilized due to higher shear forces and transported more easily through the unsaturated zone. Additionally, the low ionic strength of the rain water in comparison to the percolation solution of the column experiments (EC: 1160 µS cm^{-1}) promotes the mobilization of colloids.

The occurrence of single and extreme release events resulted from freezing/thawing cycles or prolonged periods of non-flow during dry summer periods when potentially mobilizable particles are formed. These conditions followed by high intensity rain events, snow melts or thunderstorms lead to high loads of the seepage water with particles, DOC and PAH. In the laboratory, these conditions are difficult to reproduce in column experiments and therefore there is no evidence in the literature for the relevance of these processes for PAH mobilization either.

4 CONCLUSIONS

Laboratory column outflow experiments and lysimeter experiments under natural conditions are a useful tool to accurately assess the risk at NAPL-contaminated sites. Column experiments are important to identify and quantify the major release processes of contaminants under controlled and well-known conditions. They provide the necessary quantitative information that are needed for a prognosis and for the estimation of the propagation behavior of pollutants. In addition to column tests, the investigation of the release mechanisms and kinetics of NAPL compounds under natural conditions is inevitable to obtain a reliable prognosis of their potential hazard. Lysimeters are highly appropriate for this purpose. They allow to study the effects of preferential flow, variable soil moisture, and temperatures on the transport of water, solutes and colloids under field conditions.

The dialysis experiment showed the applicability of Raoult's law. Its ability to predict aqueous PAH concentrations at contaminated sites is, however, questionable. Whereas it should be possible to predict aqueous concentrations of PAH from NAPL source zones in groundwater environments with low flow velocities, this will be difficult under unsaturated conditions. Here, the contact time between NAPL phase and seepage water is not sufficient to reach equilibrium. Moreover, mass transfer of PAH to the aqueous phase is limited due to aging of the coal tar. The loss of soluble and volatile compounds, the biochemical transformation and polymerization of the NAPL lead to high-viscous or almost rigid skins which hinder the release of NAPL compounds. Thus, long time periods are necessary for equilibrium dissolution at contaminated sites where NAPL phases have aged over several decades.

The process of equilibrium dissolution according to Raoult's law is secondary for the release of PAH due to the influence of non-equilibrium conditions as well as mobile sorbents and NAPL droplets. This could be seen from the results of the column and the lysimeter experiments. The column experiment revealed that non-equilibrium controls the release of PAH in the filtrate and the release of DOC. It was shown for laboratory and field conditions that the release and transport of PAH in the filtrate is strongly coupled to the release of DOC. Hence, I conclude that transport of PAH in the form of dissolved molecules is of minor importance within the unsaturated soil zone of contaminated sites. This is supported by the comparison of the observed concentrations within the experiments with the ones predicted by Raoult's law.

An important pathway for the release of PAH is the transport associated to colloids and particles or in form of NAPL droplets. The particle-associated PAH accounted for up to 42% of the total PAH within the columns and up to 90% of the total PAH from the lysimeters. From the column experiment, it is concluded that the dominant release processes are the first flush, the hydraulic mobilization and, to a lesser extent, the rate-limited release of PAH-bearing NAPL-fragments or -droplets. Under natural conditions, the release of particle-associated PAH is controlled by single events. Mechanical strain, e.g. freezing and thawing cycles, results in the formation of particles within the PAH source materials, i.e. the remnants of the NAPL phase. At the onset of the thawing and following rain or snowmelt events, PAH were exported from the lysimeter associated with these newly generated soil particles or within NAPL particles.

These results emphasize the role of large colloids and particles, at least in gravelly soil materials, and single extreme events for the release, transport and redistribution of PAH under natural flow conditions in the unsaturated zone of contaminated sites. The study demonstrates that different meteorological and soil parameters such as the intensity, amount and duration of precipitation, soil moisture and soil temperature are important factors for the mobilization of PAH, DOC and colloidal particles. Without a profound understanding of the interaction of these parameters and the effect of their spatiotemporal variability on the unsaturated flow conditions, an estimation of the release and mobility of PAH at contaminated sites is not possible. The release and transport process of particle-associated PAH should be more thoroughly considered in risk assessment at contaminated sites.

For future research, the combination of laboratory experiments with a field monitoring based on lysimeters permits furthermore the evaluation and monitoring of the microbial degradation of pollutants and the transport of their metabolites within contaminated soil and groundwater environments. The occurrence of PAH metabolites has to be expected at NAPL-contaminated sites. The transport and relocation of PAH in form of small NAPL fragments or associated to colloids and particles increases the bioavailability and biodegradability of PAH compared to the bulk NAPL which is encapsulated by an interfacial skin. Hence, the investigation of the degradation products of different NAPL compounds and their ecotoxicity is also required to choose a successful remediation strategy.

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6 APPENDICES

Dialysis experiment at 20°C: PAH concentrations

time	**[d]**	**0.08**	**2**	**7**	**28**	**56**	**112**	**140**
Nap	**[µg l^{-1}]**	16.72	224.05	427.61	660.30	663.11	614.92	545.73
Acy	**[µg l^{-1}]**	0.07	0.67	2.06	3.00	4.09	7.16	7.20
Ace	**[µg l^{-1}]**	5.12	72.84	179.24	376.35	448.89	699.13	712.71
Flr	**[µg l^{-1}]**	3.74	49.98	138.75	294.36	379.53	519.68	502.39
Phe	**[µg l^{-1}]**	2.72	34.16	84.99	155.24	182.57	308.66	376.15
Ant	**[µg l^{-1}]**	0.54	6.70	16.19	29.94	35.62	54.96	55.29
FlA	**[µg l^{-1}]**	0.38	3.69	9.29	15.49	22.73	27.09	30.61
Pyr	**[µg l^{-1}]**	0.22	2.03	4.81	8.18	11.84	15.80	15.96
BaA	**[µg l^{-1}]**	0.02	0.19	0.33	0.58	0.72	1.05	1.13
Chr	**[µg l^{-1}]**	0.02	0.17	0.30	0.46	0.59	0.84	0.95
BbFlA	**[µg l^{-1}]**	0.02	0.05	0.09	0.08	0.11	0.28	0.50
BkFlA	**[µg l^{-1}]**	0.01	<0.001	0.04	0.03	0.04	0.10	0.18
BaP	**[µg l^{-1}]**	0.02	0.04	0.05	0.08	0.13	0.26	0.48
IcdP	**[µg l^{-1}]**	0.02	<0.001	<0.001	0.02	0.01	0.04	0.10
DahA	**[µg l^{-1}]**	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
BghiP	**[µg l^{-1}]**	0.02	<0.001	<0.001	0.03	0.02	0.05	0.11
PAK sum	**[µg l^{-1}]**	**29.63**	**394.58**	**863.75**	**1544.13**	**1750.01**	**2250.02**	**2249.49**

Dialysis experiment at 4°C: PAH concentrations

time	**[d]**	**0.04**	**7**	**56**	**140**
Nap	**[µg l^{-1}]**	8.95	281.62	549.65	563.43
Acy	**[µg l^{-1}]**	0.03	0.95	2.53	4.25
Ace	**[µg l^{-1}]**	2.30	80.43	241.32	431.79
Flr	**[µg l^{-1}]**	1.64	59.31	220.15	366.94
Phe	**[µg l^{-1}]**	1.25	32.41	82.78	190.00
Ant	**[µg l^{-1}]**	0.25	6.57	17.32	36.82
FlA	**[µg l^{-1}]**	0.19	3.42	7.27	12.52
Pyr	**[µg l^{-1}]**	0.11	1.79	3.82	6.34
BaA	**[µg l^{-1}]**	0.02	0.15	0.21	0.29
Chr	**[µg l^{-1}]**	0.02	0.13	0.17	0.19
BbFlA	**[µg l^{-1}]**	<0.001	0.07	0.05	0.11
BkFlA	**[µg l^{-1}]**	<0.001	0.03	0.02	0.04
BaP	**[µg l^{-1}]**	<0.001	0.04	0.06	0.12
IcdP	**[µg l^{-1}]**	<0.001	0.07	0.02	0.03
DahA	**[µg l^{-1}]**	<0.001	<0.001	0.01	0.00
BghiP	**[µg l^{-1}]**	<0.001	0.06	0.02	0.04
PAK sum	**[µg l^{-1}]**	**14.75**	**467.07**	**1125.41**	**1612.92**

Dialysis experiment: calculation of subcooled liquid solubilities

	molecular weight	***solubility (25°C)***	***melting point***	***subbcooled liquid solubility (20°C)***	***subbcooled liquid solubility (4°C)***
	[g mol^{-1}]	***[mg l^{-1}]***	***[°C]***	***[mg l^{-1}]***	***[mg l^{-1}]***
Nap	128	30	80	119.46	191.05
Acy	152	16.1	92	84.52	137.34
Ace	154	3.47	96	19.97	32.63
Flr	166	1.98	116	18.06	30.31
Phe	178	1.29	101	8.33	13.70
Ant	178	0.07	216	6.39	12.24
FlA	202	0.26	111	2.11	3.52
Pyr	202	0.14	149	2.73	4.79
BaA	228	0.014	158	0.34	0.60
Chr	228	0.002	255	0.45	0.90
BbFlA	252	0.0012	167	0.04	0.06
BkFlA	252	0.00055	217	0.05	0.10
BaP	252	0.0038	179	0.15	0.27
IcdP	276	0.062	163	1.67	2.98
DahA	278	0.0005	262	0.13	0.27
BghiP	276	0.00026	222	0.03	0.05

Column experiment: Breakthrough of chloride

	slow			fast			repetition	
time	**observed**	**fitted (LEA)**	**time**	**observed**	**fitted (LEA)**	**time**	**observed**	**fitted (LEA)**
[pv]	**[C / C_{max}]**	**[C / C_{max}]**	**[pv]**	**[C / C_{max}]**	**[C / C_{max}]**	**[pv]**	**[C / C_{max}]**	**[C / C_{max}]**
0.0	0.00	0.00	0.0	0.00	0.00	0.0	0.00	0.00
0.2	0.00	0.00	0.3	0.00	0.00	0.6	0.00	0.04
0.4	0.00	0.01	0.5	0.01	0.02	0.8	0.07	0.14
0.6	0.06	0.07	0.7	0.15	0.12	1.0	0.18	0.28
0.8	0.18	0.21	0.9	0.31	0.27	1.2	0.31	0.44
1.1	0.31	0.37	1.1	0.44	0.42	1.4	0.52	0.59
1.3	0.44	0.53	1.4	0.56	0.56	1.6	0.63	0.70
1.5	0.56	0.66	1.6	0.67	0.67	1.7	0.74	0.79
1.7	0.66	0.76	1.8	0.75	0.76	1.9	0.82	0.85
1.9	0.75	0.83	2.0	0.81	0.82	2.1	0.90	0.90
2.1	0.82	0.88	2.2	0.86	0.87	2.3	0.95	0.93
2.4	0.87	0.92	2.4	0.89	0.91	2.5	0.94	0.95
2.6	0.91	0.94	2.7	0.92	0.93	2.7	0.91	0.97
2.8	0.92	0.96	2.9	0.94	0.95	2.9	0.93	0.98
2.9	0.94	0.97	3.1	0.95	0.97	3.1	0.92	0.99
3.1	0.96	0.98	3.3	0.96	0.98	3.2	0.98	0.99
3.3	0.97	0.98	3.5	0.97	0.98	3.4	1.02	0.99
3.5	0.97	0.99	3.7	0.98	0.99	3.6	1.00	1.00
3.7	0.97	0.99	4.0	0.98	0.99	3.8	0.98	1.00
3.9	0.97	1.00	4.2	0.99	0.99	4.0	0.99	1.00
4.1	1.00	1.00	4.4	1.00	1.00	4.2	1.02	1.00
4.3	1.00	1.00	4.6	1.00	1.00	4.4	0.98	1.00
4.5	0.94	0.96	4.8	1.00	1.00	4.6	0.98	1.00
4.7	0.82	0.84	5.0	1.00	1.00	4.7	0.99	1.00
4.9	0.63	0.68	5.3	0.99	1.00	4.9	1.00	1.00
5.1	0.44	0.52	5.5	0.99	0.99	5.1	1.00	1.00
5.3	0.29	0.38	5.7	0.95	0.91	5.3	0.99	1.00
5.5	0.17	0.28	5.9	0.81	0.77	5.5	0.98	1.00
5.8	0.1	0.19	6.1	0.64	0.61	5.7	0.98	1.00
6.0	0.05	0.14	6.3	0.47	0.47	5.9	0.98	1.00
6.2	0.03	0.10	6.6	0.34	0.35	6.1	0.96	1.00
6.4	0.02	0.07	6.8	0.24	0.26	6.3	0.96	1.00
6.6	0.01	0.05	7.0	0.17	0.19	6.4	0.97	1.00
6.8	0.01	0.03	7.2	0.12	0.14	6.6	0.96	1.00
7.0	0.00	0.02	7.4	0.09	0.10	6.8	0.98	1.00
7.2	0.00	0.02	7.6	0.07	0.07	6.9	0.98	1.00
7.4	0.00	0.01	7.9	0.05	0.05	7.1	0.96	1.00
7.7	0.00	0.01	8.1	0.04	0.04	7.3	0.97	1.00
7.9	0.00	0.01	8.3	0.03	0.03	7.5	0.98	1.00
8.1	0.00	0.00	8.5	0.02	0.02	7.8	0.86	0.94
			8.7	0.02	0.01	8.0	0.66	0.78
			8.9	0.01	0.01	8.3	0.43	0.57
			9.1	0.01	0.01	8.5	0.29	0.38
			9.4	0.01	0.01	8.8	0.17	0.24
			9.6	0.00	0.00	9.0	0.09	0.15
			9.8	0.00	0.00	9.3	0.05	0.09
						9.5	0.03	0.05
						9.8	0.01	0.03
						10.1	0.01	0.02
						10.3	0.00	0.01
						10.6	0.00	0.01
						10.8	0.00	0.00

Column experiment: slow column

Time [pv]	pH [-]	EC [µS cm^{-1}]	DOC [mg l^{-1}]	turbidity [FAU]
0.1	7.4	-	20.6	96.7
0.4	7.4	1165	15.8	83.3
0.6	7.5	1223	13.3	81.1
0.8	7.5	1257	12.7	80.4
1.1	7.4	1268	12.3	69.0
1.3	7.4	1305	12.1	68.6
1.5	7.3	1293	12.0	72.7
1.8	7.3	1284	-	72.1
2.0	7.5	1295	12.2	81.6
2.3	7.6	1294	12.0	85.7
2.5	7.6	1288	12.0	88.2
2.7	7.6	1285	11.7	-
3.0	7.6	1289	12.1	79.4
3.2	7.6	1285	12.4	80.4
3.4	7.6	1287	12.3	78.3
3.6	7.6	1286	11.7	79.7
3.9	7.6	1284	11.8	75.8
4.1	7.6	1285	-	82.3
4.3	7.5	1283	11.5	80.5
4.5	7.6	1282	11.6	78.3
4.8	7.5	1278	11.8	57.3
5.0	7.6	1272	13.1	66.4
5.2	7.5	1273	11.1	58.0
5.4	7.5	1274	9.7	59.0
5.7	7.5	1272	11.6	62.2
1. Flow interrupt: 24 h				
6.0	7.5	1290	13.1	44.1
6.2	7.5	1284	13.0	56.2
6.4	7.6	1281	13.3	52.6
6.6	7.4	1264	9.9	50.8
6.9	7.4	1257	8.3	58.2
7.1	7.5	1278	9.7	56.6
7.3	7.5	1273	10.7	54.6
7.5	7.5	1264	9.7	54.2
7.7	7.5	1266	9.4	54.6
8.0	7.4	1270	10.8	56.4
8.2	7.4	1269	10.4	53.1
8.4	7.4	1267	9.6	55.6
8.6	7.3	1266	10.9	56.5
8.9	7.4	1274	9.3	57.3

Column experiment: slow column (continued)

Time [pv]	pH [-]	EC [µS cm^{-1}]	DOC [mg l^{-1}]	turbidity [FAU]
9.1	7.4	1270	9.0	58.6
9.3	7.4	1274	9.8	58.9
9.5	7.4	1266	8.9	57.1
9.7	7.5	1264	10.7	60.4
10.0	7.5	1251	9.5	60.4
10.2	7.5	1241	9.7	61.0
10.4	7.5	1237	9.7	63.0
10.6	7.5	1231	9.4	64.0
10.9	7.5	1220	8.8	63.0
11.1	7.5	1226	9.2	65.3
11.3	7.5	1224	9.1	64.3
11.5	7.6	1220	9.2	66.1
11.7	7.5	1224	7.8	65.1
2. Flow interrupt: 120 h				
12.0	7.6	-	17.8	24.9
12.2	7.4	1272	18.1	50.1
12.5	7.4	-	15.5	41.1
12.7	7.4	1259	17.5	41.4
12.9	7.5	1256	14.5	37.2
13.1	7.5	-	13.3	38.1
13.3	7.6	1242	10.1	39.0
13.5	7.7	1236	12.6	39.3
13.7	7.6	1233	10.0	40.2
14.0	7.5	-	10.3	44.4
14.2	7.5	1238	8.8	38.9
14.4	7.6	1230	8.6	36.5
14.6	7.6	1232	8.8	40.9
14.8	7.6	1227	8.6	43.6
15.0	7.6	-	8.7	46.0
15.2	7.7	1224	6.3	55.2
15.5	7.5	1221	8.7	61.7
15.7	7.6	1220	8.2	49.9
15.9	7.5	1210	7.4	43.4
16.1	7.6	1208	8.1	35.2
16.3	7.5	1217	9.7	41.0
16.5	7.5	1215	6.9	41.7
16.7	7.7	1216	7.8	39.6
17.0	7.7	1230	7.4	43.4
17.2	7.8	1212	7.2	44.7

Column experiment: slow column (continued)

Time [pv]	PAH (<0.7 μm) [μg l^{-1}]	PAH (>0.7 μm) [μg l^{-1}]	particles (>0.7 μm) [mg l^{-1}]
0.1	64.1	87.0	53.4
0.8	74.9	58.0	34.9
1.5	82.2	44.8	18.1
2.3	89.3	52.2	12.6
2.7	107.9	55.3	18.8
3.2	114.9	64.1	27.5
3.6	111.5	64.3	-
4.1	110.8	54.4	32.3
4.5	110.3	59.0	32.2
5.0	117.4	60.8	-
5.4	132.8	47.6	32.3
1. Flow interrupt: 24 h			
6.0	145.3	39.8	35.2
6.4	141.5	47.4	26.9
6.6	126.3	51.5	18.4
7.1	114.3	48.5	21.4
7.5	106.1	49.9	-
8.2	101.9	54.2	25.7
9.1	95.5	65.3	30.3
10.0	100.9	74.4	32.6
10.9	115.4	59.8	35.1
2. Flow interrupt: 120 h			
12.0	124.2	37.5	39.0
12.5	127.5	36.0	32.6
12.7	110.7	38.2	-
13.1	88.8	37.2	26.0
13.5	79.1	40.4	-
14.0	75.7	43.1	29.4
14.6	74.2	45.7	33.0
15.0	78.7	52.2	35.1
15.7	82.2	61.6	47.7
16.5	79.2	58.0	53.1
17.2	78.3	48.9	41.1

Column experiment: fast column

Time [pv]	pH [-]	EC [µS cm^{-1}]	DOC [mg l^{-1}]	turbidity [FAU]
0.1	6.7	1203	16.1	74.6
0.3	6.6	1214	10.4	60.9
0.6	7.0	1226	8.6	48.4
0.8	6.9	1238	7.9	47.4
1.0	7.1	1247	6.4	52.8
1.2	7.1	1254	6.0	56.9
1.5	7.2	1256	5.6	58.2
1.7	7.2	1255	4.7	62.0
1.9	7.3	1261	5.0	59.0
2.2	7.3	1260	4.5	60.4
2.4	7.3	1266	3.6	63.1
2.6	7.4	1259	4.2	62.0
2.8	7.3	1262	4.4	69.0
3.1	7.4	1261	-	64.1
3.3	7.4	1261	4.1	64.0
3.5	7.4	1262	3.4	61.4
3.7	7.4	1264	3.3	61.3
4.0	7.4	1263	3.5	57.6
4.2	7.3	1266	1.5	49.1
4.4	7.3	1269	3.5	41.3
4.7	7.4	1265	3.7	40.0
4.9	7.4	1267	4.1	53.2
5.1	7.4	1270	2.3	58.0
5.3	7.5	1259	4.2	57.3
5.6	7.4	1246	5.5	56.7
1. Flow interrupt: 24 h				
5.8	7.4	1259	5.2	49.7
6.0	7.4	1242	5.7	60.7
6.2	7.5	1239	5.3	55.8
6.5	7.4	1225	4.2	51.1
6.7	7.4	1206	4.0	48.2
6.9	7.5	1199	-	62.6
7.1	7.5	1191	5.4	37.6
7.4	7.5	1197	-	65.3
7.6	7.5	1192	3.1	47.0
7.8	7.5	1188	4.8	52.9
8.0	7.5	1187	2.4	42.1
8.3	7.5	1183	2.3	24.8
8.5	7.5	1183	2.1	33.6
8.7	7.5	1182	2.2	61.7
8.9	7.4	1181	-	38.6

Column experiment: fast column (continued)

Time [pv]	pH [-]	EC [µS cm^{-1}]	DOC [mg l^{-1}]	turbidity [FAU]
9.2	7.3	1184	2.9	29.1
9.4	7.3	1187	3.0	27.8
9.6	7.4	1183	2.6	27.3
9.9	7.4	1184	2.3	36.1
10.1	7.4	1183	2.6	40.2
10.3	7.3	1177	2.7	26.9
10.5	7.4	1182	3.0	23.0
10.8	7.5	1183	4.9	38.6
10.9	7.4	1180	3.2	41.9
2. Flow interrupt: 120 h				
11.2	-	1237	9.7	27.7
11.4	7.4	1215	9.3	-
11.7	7.2	1213	8.7	-
11.9	7.1	1214	7.5	36.4
12.1	7.1	1204	6.3	27.9
12.3	7.1	1200	-	21.6
12.5	7.1	1199	4.7	19.5
12.8	7.2	1194	4.8	16.7
13.0	7.2	1192	7.4	14.2
13.2	7.2	1191	6.6	13.4
13.4	7.2	1190	7.0	14.0
13.7	7.2	1189	7.1	20.4
13.9	7.2	1188	5.3	11.4
14.1	-	1187	6.4	20.0
14.3	7.3	1183	6.1	20.8
14.6	7.2	1187	5.2	18.7
14.8	7.4	1183	5.5	18.8
15.0	7.2	1191	5.0	19.7
15.2	7.1	1189	5.3	22.0
15.4	7.0	-	4.8	22.0
15.7	7.0	1184	4.7	10.0
15.9	7.0	1185	4.5	21.3
16.1	7.0	1180	5.0	13.1
16.3	7.0	1187	4.6	21.4
16.6	7.0	1185	4.5	20.9
16.8	7.0	1189	4.6	19.6
17.0	7.0	1190	4.7	21.3
17.2	7.0	1186	4.6	24.9
17.5	7.0	1188	4.9	25.0
17.7	7.0	1188	3.8	24.3
17.9	7.0	1181	4.4	23.7
18.1	7.0	1180	3.6	22.7
18.3	7.0	1183	-	24.7

Column experiment: fast column (continued)

Time **[pv]**	**PAH (<0.7 µm)** **[µg l^{-1}]**	**PAH (>0.7 µm)** **[µg l^{-1}]**	**particles (>0.7 µm)** **[mg l^{-1}]**
0.1	45.9	110.9	75.7
0.8	51.0	77.9	43.8
1.5	64.8	62.2	34.3
2.2	78.9	66.8	43.6
2.6	83.4	70.0	30.1
3.1	81.5	75.5	22.9
3.5	84.9	72.3	33.0
4.0	85.1	67.6	34.7
4.4	76.9	74.7	38.2
4.9	76.0	77.1	40.0
5.3	96.7	62.1	36.4
1. Flow interrupt: 24 h			
5.8	129.0	46.4	36.8
6.2	131.2	48.5	34.9
6.5	101.6	52.6	33.0
6.9	73.3	50.5	23.5
7.4	56.5	49.2	14.2
8.0	53.8	48.0	13.2
8.9	65.3	51.9	12.1
9.9	75.8	50.4	18.1
10.8	82.7	37.1	24.7
2. Flow interrupt: 120 h			
11.2	114.7	27.0	25.6
11.7	141.9	28.5	26.0
11.9	119.9	30.3	-
12.3	79.7	26.9	31.5
12.8	53.2	22.9	36.8
13.2	36.3	20.8	34.8
13.9	24.8	20.4	33.0
14.3	20.8	20.5	32.9
15.0	19.7	24.4	-
15.9	20.5	24.6	32.8
16.6	22.9	19.8	30.6

Lysimeter experiment: Soil temperature and moisture

date	temperature [°C]				water content [%]	
[DD.MM.YYYY]	**ground level**	**0.15 m**	**0.40 m**	**0.80 m**	**0.2 m**	**0.5 m**
01.12.2003	3.2	3.9	4.5	6.1	7.0	7.5
02.12.2003	2.5	3.2	4.4	6.1	6.9	7.3
03.12.2003	2.5	3.1	4.3	6.0	6.9	7.2
04.12.2003	2.9	3.7	4.5	5.9	6.8	7.1
05.12.2003	2.8	3.5	4.5	5.9	6.8	7.0
06.12.2003	1.5	3.2	4.5	5.9	6.8	7.0
07.12.2003	-0.9	1.4	3.8	5.8	6.8	6.9
08.12.2003	-2.3	0.3	2.9	5.4	6.5	6.9
09.12.2003	-1.7	-0.2	2.2	5.0	6.1	6.8
10.12.2003	-0.6	-0.3	1.8	4.6	5.6	6.8
11.12.2003	-1.8	-0.4	1.6	4.3	5.2	6.7
12.12.2003	0.7	-0.2	1.5	4.1	5.3	6.7
13.12.2003	1.7	0.2	1.6	4.0	6.0	6.7
14.12.2003	4.3	3.3	2.7	4.0	7.6	8.3
15.12.2003	1.1	1.9	3.1	4.3	7.7	8.3
16.12.2003	-0.1	1.0	2.5	4.3	7.6	8.2
17.12.2003	1.0	1.2	2.3	4.2	7.7	8.5
18.12.2003	-0.4	0.8	2.2	4.1	7.4	8.0
19.12.2003	0.0	0.9	2.1	4.0	7.4	7.8
20.12.2003	2.1	1.7	2.3	3.9	7.3	7.9
21.12.2003	3.1	2.6	2.9	4.0	7.8	8.6
22.12.2003	0.3	1.6	2.9	4.2	7.4	8.2
23.12.2003	-2.5	0.5	2.3	4.1	6.9	7.8
24.12.2003	-5.4	-0.9	1.7	3.8	3.0	7.5
25.12.2003	-4.5	-1.7	1.0	3.5	2.1	7.3
26.12.2003	-2.8	-1.7	0.6	3.2	2.1	7.2
27.12.2003	-2.3	-1.3	0.4	2.9	2.2	7.2
28.12.2003	-1.5	-1.0	0.4	2.8	2.2	7.1
29.12.2003	0.2	-0.4	0.4	2.7	2.6	7.0
30.12.2003	-0.1	-0.2	0.5	2.6	3.0	7.0
31.12.2003	-0.1	-0.2	0.6	2.6	3.4	7.0
01.01.2004	-0.2	-0.2	0.7	2.6	4.8	7.0
02.01.2004	-0.5	-0.2	0.8	2.6	5.6	6.9
03.01.2004	-0.9	-0.1	0.9	2.6	5.9	6.9
04.01.2004	-0.7	-0.1	1.0	2.7	5.9	6.9
05.01.2004	-0.3	-0.1	1.1	2.7	5.9	6.9
06.01.2004	-0.2	0.0	1.1	2.7	6.0	6.9
07.01.2004	-0.1	0.1	1.1	2.7	6.4	8.4
08.01.2004	-0.1	0.2	1.2	2.7	6.8	8.6
09.01.2004	0.0	0.2	1.1	2.6	8.5	9.8
10.01.2004	0.1	0.2	1.1	2.4	8.1	9.4
11.01.2004	1.5	0.3	1.1	2.3	8.6	10.0
12.01.2004	3.9	2.3	1.7	2.2	8.6	10.0
13.01.2004	5.4	4.0	2.9	2.6	9.9	11.5
14.01.2004	4.0	3.9	3.9	3.2	7.9	9.1
15.01.2004	1.3	2.2	3.2	3.6	8.2	9.3
16.01.2004	0.9	1.1	2.4	3.5	7.9	8.8
17.01.2004	1.2	1.4	2.2	3.3	8.5	9.9
18.01.2004	-0.3	0.7	1.9	3.1	8.1	9.1

Lysimeter experiment: Soil temperature and moisture (continued)

date	temperature [°C]				water content [%]	
[DD.MM.YYYY]	ground level	0.15 m	0.40 m	0.80 m	0.2 m	0.5 m
02.02.2004	6.6	3.1	1.7	2.4	8.0	9.4
03.02.2004	6.0	4.0	2.8	2.7	7.6	8.8
04.02.2004	5.1	3.4	3.2	3.1	7.4	8.4
05.02.2004	6.3	3.7	3.4	3.3	7.2	8.1
06.02.2004	7.8	4.8	4.0	3.7	7.0	7.9
07.02.2004	6.4	5.2	4.7	4.1	7.1	7.7
08.02.2004	2.2	3.0	4.2	4.3	8.5	9.5
09.02.2004	0.3	1.6	3.2	4.2	8.1	9.3
10.02.2004	2.4	1.9	2.7	3.9	7.9	9.0
11.02.2004	0.2	1.2	2.6	3.8	8.6	10.4
12.02.2004	-0.7	0.6	2.0	3.5	8.0	9.6
13.02.2004	1.8	1.1	1.8	3.3	8.3	9.7
14.02.2004	2.9	2.4	2.3	3.2	7.8	9.1
15.02.2004	2.7	2.6	2.8	3.4	7.7	8.7
16.02.2004	3.6	3.1	3.1	3.6	7.5	8.4
17.02.2004	-0.5	1.4	2.8	3.6	7.4	8.2
18.02.2004	0.0	1.0	2.2	3.5	7.5	8.0
19.02.2004	0.2	0.9	2.0	3.4	7.5	7.9
20.02.2004	0.8	0.7	1.9	3.2	7.3	7.9
21.02.2004	-0.5	0.4	1.8	3.1	7.0	7.8
22.02.2004	3.5	1.9	1.8	3.0	7.0	7.7
23.02.2004	0.4	1.7	2.5	3.2	7.7	7.5
24.02.2004	-0.1	1.0	2.1	3.2	8.0	9.1
25.02.2004	-0.3	0.7	1.8	3.2	7.8	8.7
26.02.2004	0.0	0.7	1.7	3.0	8.0	8.8
27.02.2004	-0.1	0.6	1.6	3.0	8.0	9.2
28.02.2004	-0.7	0.5	1.6	2.9	8.0	8.8
29.02.2004	-0.5	0.5	1.5	2.8	8.0	9.5
01.03.2004	-0.7	0.4	1.4	2.7	7.8	8.8
02.03.2004	-0.6	0.4	1.3	2.7	7.5	8.5
03.03.2004	0.0	0.4	1.3	2.6	8.0	8.2
04.03.2004	-0.1	0.4	1.3	2.6	8.3	9.6
05.03.2004	-0.8	0.4	1.3	2.6	8.1	9.3
06.03.2004	-1.2	0.2	1.3	2.6	7.5	8.6
07.03.2004	1.9	0.5	1.2	2.5	8.0	9.1
08.03.2004	2.4	1.7	1.7	2.5	7.8	8.8
09.03.2004	1.9	2.1	2.2	2.7	7.7	8.5
10.03.2004	0.9	1.9	2.3	2.9	7.5	8.3
11.03.2004	0.2	1.4	2.3	3.0	7.4	8.0
12.03.2004	2.8	2.0	2.2	3.0	7.2	7.9
13.03.2004	6.4	4.0	2.9	3.1	7.1	7.7
14.03.2004	5.5	5.0	4.1	3.5	7.0	7.6
15.03.2004	3.8	5.3	4.6	3.9	6.8	7.5
16.03.2004	10.4	7.0	5.4	4.3	6.5	7.4
17.03.2004	10.7	7.9	6.3	4.8	6.3	7.4
18.03.2004	12.0	8.7	7.0	5.3	6.0	7.3
19.03.2004	13.6	9.9	7.9	5.9	5.8	7.2
20.03.2004	12.8	10.3	8.7	6.5	5.7	7.2

Lysimeter experiment: Soil temperature and moisture (continued)

date	temperature [°C]				water content [%]	
[DD.MM.YYYY]	ground level	0.15 m	0.40 m	0.80 m	0.2 m	0.5 m
21.03.2004	10.3	9.9	9.0	6.9	5.5	7.2
22.03.2004	7.9	8.2	8.3	7.2	5.4	7.2
23.03.2004	4.1	6.2	7.4	7.1	5.4	7.2
24.03.2004	2.3	4.4	6.1	6.8	8.8	10.1
25.03.2004	2.2	3.3	4.8	6.2	7.9	9.2
26.03.2004	1.3	3.0	4.5	5.8	7.6	8.6
27.03.2004	2.6	3.3	4.1	5.4	7.3	8.3
28.03.2004	5.1	4.4	4.4	5.2	7.1	8.0
29.03.2004	6.4	5.4	5.0	5.3	6.8	7.8
30.03.2004	8.8	6.7	5.8	5.5	6.6	7.6
31.03.2004	10.6	7.9	6.6	5.8	6.3	7.5
01.04.2004	13.0	9.9	7.8	6.2	6.0	7.3
02.04.2004	13.9	10.7	8.8	6.8	5.7	7.3
03.04.2004	12.3	11.0	9.5	7.4	5.4	7.2
04.04.2004	10.9	10.2	9.5	7.8	5.2	7.2
05.04.2004	8.2	9.2	9.3	8.0	7.3	7.6
06.04.2004	5.7	7.5	8.4	8.0	7.8	9.1
07.04.2004	5.1	6.1	7.3	7.7	8.0	9.2
08.04.2004	6.1	6.4	6.9	7.4	7.5	8.7
09.04.2004	7.1	6.5	6.8	7.2	7.2	8.3
10.04.2004	6.8	6.9	7.1	7.1	7.0	8.0
11.04.2004	7.5	7.3	7.2	7.2	6.8	7.7
12.04.2004	9.3	8.1	7.4	7.2	6.6	7.5
13.04.2004	9.5	8.7	8.1	7.4	6.4	7.4
14.04.2004	11.1	9.7	8.5	7.6	6.1	7.3
15.04.2004	12.9	10.6	9.1	7.9	5.8	7.2
16.04.2004	16.4	13.1	10.4	8.3	5.4	7.2
17.04.2004	17.6	14.1	11.5	8.9	5.0	7.1
18.04.2004	16.5	14.8	12.6	9.6	4.8	7.0
19.04.2004	8.7	11.5	12.3	10.1	7.3	8.7
20.04.2004	11.4	9.2	10.5	10.1	7.0	8.4
09.06.2004	27.6	23.2	19.5	15.7	4.3	7.3
10.06.2004	28.5	24.7	21.0	16.5	3.7	7.1
11.06.2004	19.5	21.7	21.2	17.3	4.2	7.2
12.06.2004	18.0	19.0	19.4	17.4	6.2	8.6
13.06.2004	16.9	17.4	18.1	17.0	5.9	7.9
14.06.2004	20.8	18.8	17.7	16.6	5.4	7.6
15.06.2004	21.1	19.5	18.4	16.6	4.9	7.4
16.06.2004	20.2	19.9	18.8	16.7	4.4	7.2
17.06.2004	23.4	20.8	18.9	16.8	3.9	7.1
18.06.2004	20.2	20.5	19.7	17.1	3.6	7.0
19.06.2004	18.0	18.7	18.9	17.2	3.3	6.9
20.06.2004	13.9	16.2	17.6	17.0	3.9	7.0
21.06.2004	17.3	16.4	16.5	16.4	4.3	6.8
22.06.2004	18.8	17.9	17.2	16.1	4.2	6.8
23.06.2004	18.2	17.9	17.4	16.2	4.3	6.8
24.06.2004	21.0	18.9	17.6	16.2	4.2	6.8
25.06.2004	19.0	18.8	18.2	16.4	4.0	6.8

Lysimeter experiment: Soil temperature and moisture (continued)

date		temperature [°C]			water content [%]	
[DD.MM.YYYY]	ground level	0.15 m	0.40 m	0.80 m	0.2 m	0.5 m
26.06.2004	21.8	19.5	18.1	16.5	3.8	6.7
27.06.2004	22.2	20.5	19.0	16.7	6.0	9.4
28.06.2004	22.7	21.2	19.6	17.1	5.6	8.3
29.06.2004	22.2	20.9	19.7	17.4	5.0	7.7
30.06.2004	23.6	21.5	19.9	17.5	4.4	7.4
01.07.2004	18.6	20.2	20.2	17.8	4.1	7.3
02.07.2004	17.2	18.2	18.9	17.7	6.3	8.8
03.07.2004	19.0	18.0	18.0	17.3	5.6	8.0
04.07.2004	22.3	19.8	18.4	17.1	4.9	7.7
05.07.2004	21.8	20.5	19.4	17.3	4.3	7.5
06.07.2004	19.7	19.9	19.5	17.5	4.3	7.4
07.07.2004	20.5	19.8	19.2	17.5	4.2	7.3
08.07.2004	22.5	20.8	19.5	17.6	6.8	9.8
09.07.2004	17.9	19.1	19.4	17.9	6.3	8.9
10.07.2004	15.5	17.2	18.4	17.7	6.1	8.2
11.07.2004	15.2	16.4	17.4	17.3	6.4	7.9
12.07.2004	15.3	16.2	16.9	16.9	6.7	9.0
13.07.2004	15.2	16.0	16.6	16.6	6.6	8.8
14.07.2004	17.6	16.9	16.6	16.3	6.3	8.5
15.07.2004	16.8	17.1	17.1	16.3	6.5	8.6
16.07.2004	21.4	18.9	17.4	16.3	6.1	8.4
17.07.2004	22.2	20.5	18.7	16.6	5.6	8.0
18.07.2004	23.6	21.7	19.8	17.1	5.0	7.8
19.07.2004	22.6	22.1	20.6	17.6	4.5	7.7
20.07.2004	23.6	22.5	21.0	18.1	4.0	7.5
21.07.2004	23.6	22.6	21.3	18.4	3.7	7.4
22.07.2004	23.4	23.0	21.6	18.7	3.4	7.4
23.07.2004	22.5	22.5	21.8	19.0	3.2	7.3
24.07.2004	20.0	21.3	21.4	19.1	3.4	7.3
25.07.2004	21.5	21.1	20.7	19.0	3.7	7.3
26.07.2004	18.1	20.0	20.6	19.0	3.7	7.2
27.07.2004	19.8	19.6	19.6	18.7	3.8	7.2
28.07.2004	19.6	19.5	19.5	18.5	3.7	7.2
29.07.2004	21.6	20.0	19.3	18.3	3.6	7.2
30.07.2004	23.6	21.5	19.9	18.2	3.3	7.2
31.07.2004	25.0	22.8	20.8	18.4	3.1	7.2
01.08.2004	26.1	23.9	21.7	18.8	2.8	7.2
02.08.2004	25.7	24.2	22.2	19.2	2.5	7.1
03.08.2004	25.3	24.0	22.4	19.4	2.2	7.0
04.08.2004	25.8	24.3	22.6	19.7	1.9	6.9
05.08.2004	26.2	24.7	22.8	19.8	1.7	6.7
06.08.2004	26.8	25.0	23.2	20.1	1.6	6.4
07.08.2004	25.9	25.4	23.5	20.3	1.5	6.2
08.08.2004	25.6	24.9	23.5	20.5	1.4	5.9
09.08.2004	25.9	24.9	23.5	20.6	1.2	5.7
11.08.2004	25.5	24.8	23.6	20.8	1.0	5.2
12.08.2004	27.1	25.3	23.7	20.9	5.2	6.3
13.08.2004	20.5	22.1	23.1	21.1	4.5	6.6
14.08.2004	16.6	19.4	21.4	20.8	6.7	9.3
15.08.2004	20.6	19.8	20.0	20.0	5.9	8.4

Lysimeter experiment: Soil temperature and moisture (continued)

date	temperature [°C]				water content [%]	
[DD.MM.YYYY]	ground level	0.15 m	0.40 m	0.80 m	0.2 m	0.5 m
16.08.2004	20.4	20.2	20.3	19.7	5.5	7.9
17.08.2004	22.0	21.2	20.6	19.5	5.1	7.7
18.08.2004	22.9	21.8	21.0	19.6	4.7	7.6
19.08.2004	23.0	22.1	21.4	19.7	4.3	7.5
20.08.2004	19.2	20.7	21.2	19.8	5.3	7.4
21.08.2004	17.0	18.8	19.9	19.6	6.5	9.3
22.08.2004	17.5	18.1	19.0	19.1	6.0	8.8
23.08.2004	18.5	18.1	18.6	18.7	5.7	8.3
24.08.2004	17.5	18.3	18.8	18.5	5.8	8.1
25.08.2004	18.6	18.2	18.4	18.3	5.7	7.9
26.08.2004	16.9	17.9	18.5	18.1	6.9	10.0
27.08.2004	17.7	17.7	18.0	18.0	6.3	9.2
28.08.2004	18.9	18.2	18.1	17.8	5.9	8.6
29.08.2004	18.6	18.6	18.5	17.8	5.6	8.3
30.08.2004	17.9	18.3	18.5	17.8	5.3	8.0
31.08.2004	18.1	18.0	18.2	17.8	4.9	7.9
01.09.2004	17.0	17.5	18.0	17.6	4.6	7.8
08.10.2004	15.6	16.5	15.6	14.8	10.0	11.6
09.10.2004	11.4	14.1	15.3	14.9	9.5	10.9
10.10.2004	9.7	11.8	13.7	14.6	9.4	10.6
11.10.2004	8.5	10.5	12.5	14.0	9.1	10.0
12.10.2004	6.4	9.0	11.5	13.4	9.0	9.6
13.10.2004	6.3	8.3	10.5	12.8	8.9	9.3
14.10.2004	6.9	8.4	10.1	12.2	8.8	9.1
15.10.2004	10.3	9.5	10.1	11.9	9.3	9.6
16.10.2004	7.6	9.5	10.6	11.8	9.3	10.0
17.10.2004	6.3	7.8	9.8	11.6	9.2	9.8
18.10.2004	7.8	8.4	9.5	11.3	9.6	10.7
19.10.2004	6.8	7.8	9.3	11.0	9.4	10.2
20.10.2004	11.0	9.7	9.6	10.8	9.2	10.1
21.10.2004	12.5	11.3	10.7	11.0	9.5	10.9
22.10.2004	11.5	11.5	11.4	11.3	9.2	10.3
23.10.2004	12.2	11.4	11.5	11.5	9.0	10.0
24.10.2004	11.8	11.3	11.6	11.6	8.8	9.7
25.10.2004	11.9	11.3	11.6	11.7	8.7	9.6
26.10.2004	10.9	11.5	11.8	11.8	8.6	9.5
27.10.2004	10.6	11.0	11.6	11.8	8.6	9.4
28.10.2004	11.6	11.5	11.6	11.8	8.6	9.3
29.10.2004	11.4	11.2	11.6	11.8	8.5	9.3
30.10.2004	10.3	11.1	11.6	11.8	8.4	9.2
31.10.2004	8.2	9.5	11.0	11.7	9.7	9.5
01.11.2004	9.7	9.8	10.6	11.5	9.4	10.4
02.11.2004	10.5	10.4	10.7	11.4	9.2	10.2
03.11.2004	10.6	10.6	10.9	11.4	9.1	10.1
04.11.2004	10.5	10.8	11.1	11.4	9.0	10.0
05.11.2004	8.9	10.1	10.9	11.4	9.6	11.0
06.11.2004	7.5	8.8	10.2	11.3	9.4	10.8
07.11.2004	5.3	7.6	9.5	10.9	10.3	11.9

Lysimeter experiment: Soil temperature and moisture (continued)

date	temperature [°C]				water content [%]	
[DD.MM.YYYY]	ground level	0.15 m	0.40 m	0.80 m	0.2 m	0.5 m
08.11.2004	4.2	6.3	8.4	10.4	9.8	11.2
09.11.2004	2.1	4.8	7.5	9.9	10.4	12.1
10.11.2004	2.5	4.1	6.4	9.2	10.1	11.5
11.11.2004	3.5	4.6	6.2	8.7	10.0	11.2
12.11.2004	3.5	4.8	6.3	8.4	9.8	10.9
13.11.2004	3.0	4.5	6.1	8.2	10.3	11.8
14.11.2004	2.0	3.9	5.7	8.0	10.0	11.2
15.11.2004	0.0	2.2	4.9	7.6	9.7	10.8
16.11.2004	1.1	2.0	4.3	7.2	9.6	10.6
18.11.2004	5.9	5.8	5.7	6.9	-	-
19.11.2004	3.2	4.8	5.9	7.1	-	-
20.11.2004	0.3	2.7	5.0	7.1	-	-

Lysimeter experiment: Lysimeter 1

date [DD.MM.YYYY]	precip. [mm]	seepage [l m^{-2}]	pH [-]	EC [µS cm^{-1}]	turbidity [FAU]	particles [mg l^{-1}]	DOC [mg l^{-1}]	ΣPAK <0.7 [µg]	ΣPAK >0.7 [µg]
23.09.2002	20.2	0.5	8.0	281	9.8	-	17.7	-	-
26.09.2002	60.5	55.2	7.7	268	3.0	3.8	5.7	0.43	1.44
04.10.2002	14.4	16.7	7.9	225	3.1	5.5	3.2	0.15	0.43
18.10.2002	68.1	50.1	7.9	265	7.5	13.9	3.6	0.25	2.11
25.10.2002	10.7	7.8	8.0	244	21.2	28.1	2.5	-	-
05.11.2002	68.1	57.9	7.9	251	6.2	27.6	2.3	-	-
13.11.2002	28.2	25.4	7.8	218	16.5	46.5	1.6	-	-
20.11.2002	24.4	22.7	8.0	246	26.7	23.3	2.0	-	-
26.11.2002	8.6	10.0	7.8	232	32.0	24.4	1.6	-	-
04.12.2002	21.9	19.3	8.2	241	21.8	24.6	1.8	-	-
17.12.2002	23.2	10.2	8.2	261	48.5	31.9	4.4	-	-
26.12.2002	30.8	40.7	7.5	255	26.6	46.2	3.0	-	-
04.01.2003	43.8	24.7	7.9	244	10.6	32.8	2.6	-	-
17.01.2003	22.1	13.4	7.9	211	22.0	13.7	2.3	-	-
28.01.2003	15.6	25.8	8.0	240	31.3	23.0	1.8	0.14	2.34
04.02.2003	21.4	16.7	8.0	226	30.7	16.0	2.0	-	-
28.02.2003	16.2	4.2	8.1	241	27.0	27.8	1.1	0.08	0.36
03.03.2003	3.6	34.2	8.1	206	28.1	35.5	1.4	0.32	10.76
05.03.2003	0.0	0.6	7.8	237	151.3	292.6	2.8	0.01	0.22
10.03.2003	8.6	6.8	7.9	243	27.4	18.4	2.1	0.04	0.38
14.03.2003	0.0	0.7	7.9	234	62.1	23.8	2.6	0.01	0.02
04.04.2003	9.8	0.0	-	-	-	-	-	-	-
15.04.2003	5.3	0.0	-	-	-	-	-	-	-
29.04.2003	5.4	0.3	8.2	196	6.5	-	1.2	-	-
15.05.2003	35.3	6.5	8.1	318	22.9	10.9	4.9	0.42	0.37
20.05.2003	26.8	1.0	8.0	350	34.3	0.4	12.2	0.01	0.10
28.05.2003	5.7	3.2	8.0	306	36.4	16.2	6.0	0.01	0.22

Lysimeter experiment: Lysimeter 1 (continued)

date [DD.MM.YYYY]	precip. [mm]	seepage [l m^{-2}]	pH [-]	EC [µS cm^{-1}]	turbidity [FAU]	particles [mg l^{-1}]	DOC [mg l^{-1}]	ΣPAK <0.7 [µg]	ΣPAK >0.7 [µg]
06.10.2003	66.2	38.2	8.2	259	7.1	21.8	7.3	0.54	1.43
09.10.2003	37.2	21.6	8.1	260	10.7	5.6	5.1	0.26	0.24
23.10.2003	7.7	0.3	8.4	267	33.8	-	4.7	-	-
01.12.2003	38.8	19.2	8.2	241	60.4	12.7	5.1	0.15	0.31
15.12.2003	19.3	10.5	8.2	225	71.3	22.7	3.9	0.36	0.26
22.12.2003	10.9	10.5	8.2	244	64.0	20.1	3.5	0.05	0.71
12.01.2004	65.4	48.3	8.3	240	58.4	23.8	2.6	0.38	1.19
15.01.2004	51.0	42.0	8.2	205	58.0	17.6	2.3	0.27	0.93
20.01.2004	43.0	22.7	8.1	191	5.3	9.3	2.9	1.86	0.52
03.02.2004	12.0	20.1	8.0	199	9.8	5.5	1.8	0.17	0.20
16.02.2004	19.6	15.1	8.1	197	14.4	6.7	1.9	0.56	0.19
15.03.2004	18.8	16.5	7.9	217	14.0	28.8	2.6	0.15	0.26
25.03.2004	51.3	21.5	8.1	224	6.9	4.6	3.7	0.25	0.20
07.04.2004	29.0	7.3	8.1	264	18.8	11.2	4.2	-	-
20.04.2004	21.9	6.1	7.9	262	5.2	6.1	3.3	-	-
13.05.2004	28.1	0.0	-	-	-	-	-	-	-
04.06.2004	62.1	6.9	7.6	371	9.5	8.6	6.8	0.16	0.14
07.06.2004	21.0	13.5	7.9	368	4.4	1.7	5.8	-	-
17.06.2004	25.0	1.8	7.7	352	14.5	13.6	6.0	-	-
24.06.2004	25.5	0.0	-	-	-	-	-	-	-
06.07.2004	44.0	10.4	7.5	217	174.3	116.4	5.6	0.26	2.65
09.07.2004	37.5	31.5	7.9	323	39.4	27.8	5.0	0.77	1.53
26.07.2004	41.1	3.4	7.1	360	8.6	2.9	4.7	-	-
16.08.2004	43.6	16.2	7.1	316	20.5	62.4	11.4	0.24	1.97
30.08.2004	35.6	15.7	7.6	331	9.8	8.1	7.6	0.10	0.26
15.09.2004	43.5	15.9	7.4	319	20.7	40.7	7.0	-	-
30.09.2004	33.4	9.9	7.9	295	29.7	58.0	6.7	-	-
15.10.2004	50.5	31.2	8.0	324	10.7	0.3	5.7	0.28	1.20
22.10.2004	19.5	15.8	8.0	230	5.7	2.4	3.6	-	-

Lysimeter experiment: Lysimeter 2

date [DD.MM.YYYY]	precip. [mm]	seepage [l m^{-2}]	pH [-]	EC [µS cm^{-1}]	turbidity [FAU]	particles [mg l^{-1}]	DOC [mg l^{-1}]	ΣPAK <0.7 [µg]	ΣPAK >0.7 [µg]
23.09.2002	20.2	1.5	8.2	352	5.0	-	12.2	-	-
26.09.2002	60.5	55.5	7.7	434	6.2	2.5	7.0	3.93	4.02
04.10.2002	14.4	14.8	8.0	249	11.3	4.1	3.8	1.14	2.34
18.10.2002	68.1	45.1	7.8	275	8.7	6.8	4.8	2.41	8.92
25.10.2002	10.7	6.5	8.0	267	29.2	22.8	3.8	-	-
05.11.2002	68.1	57.2	7.6	268	10.2	7.4	3.2	-	-
13.11.2002	28.2	22.8	7.8	242	13.8	6.8	2.4	-	-
20.11.2002	24.4	19.6	7.9	251	29.5	10.8	2.5	-	-
26.11.2002	8.6	6.3	8.2	246	27.2	16.6	2.3	-	-
04.12.2002	21.9	18.1	8.2	253	27.0	19.7	2.9	-	-
17.12.2002	23.2	6.3	8.2	245	56.6	69.8	3.3	-	-
26.12.2002	30.8	22.8	7.5	246	9.2	1.9	4.8	-	-
04.01.2003	43.8	22.8	7.9	259	3.5	1.8	3.5	-	-
17.01.2003	22.1	22.0	-	-	-	-	-	-	-
28.01.2003	15.6	13.9	8.1	236	9.0	2.9	2.9	0.30	0.63
04.02.2003	21.4	22.5	8.0	235	7.3	1.8	2.6	-	-
28.02.2003	16.2	1.4	8.2	235	17.2	33.5	1.8	0.02	0.21

Lysimeter experiment: Lysimeter 2 (continued)

date	precip.	seepage	pH	EC	turbidity	particles	DOC	ΣPAK <0.7	ΣPAK >0.7
[DD.MM.YYYY]	[mm]	[l m^{-2}]	[-]	[µS cm^{-1}]	[FAU]	[mg l^{-1}]	[mg l^{-1}]	[µg]	[µg]
03.03.2003	3.6	0.2	8.2	239	71.0	-	2.8	-	-
05.03.2003	0.0	22.7	7.8	206	11.4	3.3	3.1	0.63	0.90
10.03.2003	8.6	6.2	7.8	250	7.1	1.0	2.9	0.10	0.12
14.03.2003	0.0	2.4	7.9	236	9.1	0.2	3.5	0.01	0.20
04.04.2003	9.8	0.0	-	-	-	-	-	-	-
15.04.2003	5.3	0.0	-	-	-	-	-	-	-
29.04.2003	5.4	0.2	7.9	248	19.0	-	5.6	-	-
15.05.2003	35.3	3.6	7.5	347	41.5	51.4	12.1	0.02	10.88
20.05.2003	26.8	0.3	8.1	312	18.2	1.2	13.6	0.00	0.36
28.05.2003	5.7	1.9	7.8	359	29.1	16.2	5.0	0.10	1.14
06.10.2003	66.2	22.4	8.1	264	33.1	56.1	17.3	0.45	17.34
09.10.2003	37.2	20.9	8.1	255	38.7	18.5	11.0	0.41	4.74
23.10.2003	7.7	2.0	8.2	273	28.3	18.3	9.7	0.03	0.38
01.12.2003	38.8	19.2	8.1	256	70.5	39.3	11.7	0.33	18.79
15.12.2003	19.3	8.9	8.2	239	83.3	21.7	8.1	0.32	5.64
22.12.2003	10.9	10.8	8.3	267	68.8	10.1	6.9	0.09	1.89
12.01.2004	65.4	22.2	8.2	262	64.5	22.4	5.3	0.24	10.86
15.01.2004	51.0	23.9	8.3	219	59.9	19.4	3.5	0.25	3.73
20.01.2004	43.0	22.5	8.2	204	14.7	7.7	4.0	0.29	2.40
03.02.2004	12.0	18.1	8.0	193	13.3	12.5	2.9	0.75	3.39
16.02.2004	19.6	14.1	8.1	207	9.7	5.0	3.6	0.20	0.76
15.03.2004	18.8	13.6	7.9	225	9.1	7.6	4.1	0.14	1.51
25.03.2004	51.3	20.1	8.0	244	7.5	4.8	6.7	0.22	1.16
07.04.2004	29.0	6.7	8.0	272	16.4	11.8	6.5	-	-
20.04.2004	21.9	6.2	7.8	284	7.8	9.9	6.3	-	-
13.05.2004	28.1	0.0	-	-	-	-	-	-	-
04.06.2004	62.1	9.1	7.5	262	25.1	22.4	13.2	0.14	0.84
07.06.2004	21.0	13.3	7.9	353	5.1	2.2	16.4	-	-
17.06.2004	25.0	2.7	7.7	318	9.4	9.2	12.8	-	-
24.06.2004	25.5	0.0	-	-	-	-	-	-	-
06.07.2004	44.0	9.7	7.4	233	69.1	63.5	11.3	0.16	73.63
09.07.2004	37.5	23.9	7.6	364	19.9	13.7	10.5	0.65	7.04
26.07.2004	41.1	4.3	7.3	377	6.0	5.1	11.9	-	-
16.08.2004	43.6	19.9	7.1	249	18.3	53.4	17.6	2.07	36.55
30.08.2004	35.6	13.8	7.4	349	3.0	1.1	17.5	0.09	0.27
15.09.2004	43.5	11.6	7.4	332	12.1	14.2	14.5	-	-
30.09.2004	33.4	11.5	7.9	324	6.6	9.1	15.3	-	-
15.10.2004	50.5	23.9	7.7	328	6.7	11.4	11.5	0.20	17.85
22.10.2004	19.5	13.1	8.1	225	8.6	1.4	6.9	-	-

Lysimeter experiment: Lysimeter 3

date	precip.	seepage	pH	EC	turbidity	particles	DOC	ΣPAK <0.7	ΣPAK >0.7
[DD.MM.YYYY]	[mm]	[l m^{-2}]	[-]	[µS cm^{-1}]	[FAU]	[mg l^{-1}]	[mg l^{-1}]	[µg]	[µg]
23.09.2002	20.2	0.0	-	-	-	-	-	-	-
26.09.2002	60.5	22.0	7.8	285	3.5	3.5	12.1	19.01	8.58
04.10.2002	14.4	16.1	8.2	372	8.2	2.5	7.7	1.16	6.67
18.10.2002	68.1	22.2	7.7	370	3.4	2.7	7.1	1.25	7.45
25.10.2002	10.7	9.5	7.9	361	8.0	3.8	6.3	0.46	4.55

Lysimeter experiment: Lysimeter 3 (continued)

date [DD.MM.YYYY]	precip. [mm]	seepage [l m^{-2}]	pH [-]	EC [µS cm^{-1}]	turbidity [FAU]	particles [mg l^{-1}]	DOC [mg l^{-1}]	ΣPAK <0.7 [µg]	ΣPAK >0.7 [µg]
05.11.2002	68.1	25.1	7.8	349	7.3	34.7	6.3	1.68	70.51
13.11.2002	28.2	28.7	7.9	315	7.6	6.7	5.1	2.94	15.93
20.11.2002	24.4	17.2	8.0	325	8.6	8.1	5.1	5.62	13.46
26.11.2002	8.6	9.7	8.4	319	5.3	0.0	4.6	0.99	1.44
04.12.2002	21.9	13.9	8.1	324	10.0	2.0	5.1	4.06	3.72
17.12.2002	23.2	7.5	8.2	297	15.8	3.7	5.1	0.91	3.74
26.12.2002	30.8	35.6	7.8	290	25.7	8.9	5.8	2.97	49.70
04.01.2003	43.8	24.8	7.9	307	5.9	7.4	6.8	6.95	342.75
17.01.2003	22.1	16.0	-	-	-	-	-	-	-
28.01.2003	15.6	20.3	8.0	286	18.9	8.1	4.8	1.68	61.42
04.02.2003	21.4	8.3	8.1	271	9.1	0.0	4.2	1.00	1.94
28.02.2003	16.2	11.3	7.7	266	11.2	6.5	3.6	1.88	5.26
03.03.2003	3.6	10.5	8.1	272	7.9	1.2	3.7	1.28	1.73
05.03.2003	0.0	2.4	7.6	208	14.7	0.2	5.4	0.21	0.43
10.03.2003	8.6	4.3	7.7	281	2.8	0.2	4.8	0.47	0.88
14.03.2003	0.0	1.1	8.0	309	14.6	0.4	5.2	0.03	0.35
04.04.2003	9.8	0.0	-	-	-	-	-	-	-
15.04.2003	5.3	0.0	-	-	-	-	-	-	-
29.04.2003	5.4	0.0	-	-	-	-	-	-	-
15.05.2003	35.3	0.0	-	-	-	-	-	-	-
20.05.2003	26.8	0.0	-	-	-	-	-	-	-
28.05.2003	5.7	0.2	-	-	-	0.0	-	0.00	0.32
06.10.2003	66.2	22.7	8.0	327	13.3	14.0	12.2	5.80	15.42
09.10.2003	37.2	17.3	8.1	314	9.3	6.9	11.3	1.73	4.21
23.10.2003	7.7	3.3	8.2	314	17.8	1.3	12.0	0.18	0.98
01.12.2003	38.8	17.0	8.1	315	65.7	6.0	11.7	1.85	6.29
15.12.2003	19.3	6.4	8.3	293	78.0	18.2	11.9	1.00	4.06
22.12.2003	10.9	11.6	8.3	286	60.4	4.3	11.2	0.91	2.64
12.01.2004	65.4	56.6	8.2	266	78.2	18.8	6.9	10.40	254.06
15.01.2004	51.0	43.0	8.2	241	71.6	15.9	5.0	11.71	80.71
20.01.2004	43.0	31.2	8.1	185	21.8	5.6	3.8	11.50	39.45
03.02.2004	12.0	23.8	8.0	213	3.5	1.7	4.0	6.48	8.12
16.02.2004	19.6	25.9	8.1	210	6.4	4.1	4.7	8.61	8.43
15.03.2004	18.8	21.2	8.0	237	2.4	1.0	4.9	2.57	1.85
25.03.2004	51.3	14.5	8.0	281	3.0	1.4	5.5	2.12	1.87
07.04.2004	29.0	9.1	8.0	288	3.5	1.0	6.5	1.93	0.97
20.04.2004	21.9	8.8	8.0	298	2.4	1.0	6.1	0.84	0.68
04.06.2004	62.1	5.8	7.7	344	7.4	3.9	6.7	0.53	1.70
07.06.2004	21.0	12.2	7.9	374	2.8	0.4	8.6	0.60	1.13
17.06.2004	25.0	3.2	7.9	397	5.5	3.6	8.2	0.10	0.41
06.07.2004	44.0	4.4	7.8	349	9.2	6.2	-	0.21	1.62
09.07.2004	37.5	23.8	7.8	458	12.8	4.8	8.2	2.90	12.81
26.07.2004	41.1	1.6	7.7	383	4.1	0.0	8.5	0.06	0.19
16.08.2004	43.6	7.7	7.7	315	47.2	31.9	12.2	6.82	25.61
30.08.2004	35.6	6.8	7.7	331	3.0	2.8	10.0	0.14	0.73
15.09.2004	43.5	4.7	8.1	376	11.2	4.3	9.2	0.28	3.64
30.09.2004	33.4	6.8	7.9	376	2.5	0.0	10.3	0.26	0.58
15.10.2004	50.5	23.8	7.8	380	2.3	0.0	12.1	0.90	4.90
22.10.2004	19.5	10.6	8.1	266	4.0	0.0	10.5	0.32	0.99

Lysimeter experiment: Lysimeter 1, PAH within the filtrate (<0.7 µm)

date	**Nap**	**Acy**	**Ace**	**Flr**	**Phe**	**Ant**	**FlA**	**Pyr**
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	<0.001	0.001	0.005	0.001	0.002	0.004	0.005	0.004
04.10.2002	<0.001	0.001	0.001	0.001	0.003	0.008	0.005	0.004
18.10.2002	<0.001	0.001	0.001	0.001	0.001	0.006	0.001	0.002
28.01.2003	<0.001	<0.001	<0.001	<0.001	0.002	0.003	0.001	0.001
28.02.2003	<0.001	<0.001	0.007	0.011	0.018	0.028	0.007	0.007
03.03.2003	<0.001	0.002	<0.001	0.001	0.002	0.004	0.002	0.002
05.03.2003	<0.001	<0.001	<0.001	0.015	0.024	<0.001	<0.001	<0.001
10.03.2003	<0.001	<0.001	<0.001	<0.001	0.002	0.018	0.001	0.001
14.03.2003	<0.001	<0.001	<0.001	<0.001	0.029	0.029	<0.001	<0.001
15.05.2003	<0.001	0.008	0.012	0.008	0.043	0.153	0.012	0.022
20.05.2003	<0.001	<0.001	<0.001	<0.001	0.021	0.013	0.004	0.007
28.05.2003	<0.001	<0.001	<0.001	<0.001	0.003	0.004	0.001	0.001
06.10.2003	0.010	0.001	0.001	0.001	0.001	0.038	0.001	0.001
09.10.2003	0.028	0.001	<0.001	<0.001	0.001	0.017	<0.001	<0.001
01.12.2003	0.012	0.001	0.001	0.001	0.002	0.012	0.001	0.001
15.12.2003	0.108	0.001	0.003	0.001	0.003	0.007	0.002	0.002
22.12.2003	0.011	0.000	0.001	0.001	0.002	0.003	0.001	0.001
12.01.2004	0.014	0.001	<0.001	0.001	0.001	0.008	0.001	0.003
15.01.2004	0.014	0.001	<0.001	0.001	0.001	0.005	<0.001	<0.001
20.01.2004	0.012	0.007	0.010	0.004	0.003	0.014	0.015	0.022
03.02.2004	0.012	0.001	0.001	0.001	0.002	0.012	0.001	0.001
16.02.2004	0.120	0.001	0.004	0.002	0.002	0.016	0.001	<0.001
15.03.2004	0.014	0.001	<0.001	0.002	0.002	0.017	0.001	0.001
25.03.2004	0.006	0.001	0.002	0.003	0.006	0.013	0.005	0.003
04.06.2004	0.046	0.001	<0.001	<0.001	0.002	0.040	0.001	0.001
06.07.2004	0.034	0.002	<0.001	<0.001	0.002	0.014	0.002	0.002
09.07.2004	0.032	0.002	<0.001	<0.001	0.002	0.041	0.002	0.002
16.08.2004	<0.001	0.005	0.002	0.002	0.005	0.003	0.004	0.003
30.08.2004	<0.001	0.001	<0.001	<0.001	0.001	0.018	0.001	0.001
15.10.2004	<0.001	0.001	<0.001	<0.001	0.001	0.025	0.001	0.002

date	**BaA**	**Chr**	**BbFlA**	**BkFlA**	**BaP**	**IcdP**	**DahA**	**BghiP**
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	0.001	0.002	0.002	0.001	0.001	0.001	<0.001	0.001
04.10.2002	0.001	0.003	0.003	0.001	0.001	0.001	<0.001	0.002
18.10.2002	<0.001	0.002	0.001	0.001	0.001	0.001	<0.001	0.001
28.01.2003	0.001	0.001	0.004	0.002	0.002	0.003	<0.001	0.003
28.02.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
03.03.2003	0.001	0.002	0.004	0.001	0.003	0.006	<0.001	0.007
05.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
10.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
14.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
20.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
28.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Lysimeter experiment: Lysimeter 1, PAH within the filtrate (<0.7 µm)(continued)

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				[µg l^{-1}]				
06.10.2003	<0.001	0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
09.10.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
01.12.2003	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15.12.2003	0.001	0.002	0.002	0.001	0.001	0.002	<0.001	0.002
22.12.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
12.01.2004	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.001
15.01.2004	<0.001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001	0.001
20.01.2004	0.017	0.034	0.056	0.017	0.034	0.037	0.009	0.040
03.02.2004	0.001	0.002	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
16.02.2004	<0.001	<0.001	0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15.03.2004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
25.03.2004	0.002	0.002	0.001	<0.001	0.001	0.001	<0.001	0.001
04.06.2004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
06.07.2004	0.001	0.002	0.004	0.001	0.003	0.015	0.003	0.013
09.07.2004	0.002	0.002	0.003	0.001	0.002	0.004	0.001	0.004
16.08.2004	0.001	0.003	0.006	0.002	0.002	0.004	<0.001	0.017
30.08.2004	<0.001	0.001	<0.001	<0.001	0.001	0.001	<0.001	0.001
15.10.2004	0.001	0.001	0.001	<0.001	0.001	0.001	<0.001	0.001

Lysimeter experiment: Lysimeter 2, PAH within the filtrate (<0.7 µm)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	<0.001	0.006	0.016	0.002	0.005	0.014	0.023	0.023
04.10.2002	<0.001	0.007	0.012	0.002	0.008	0.025	0.022	0.020
18.10.2002	<0.001	0.004	0.008	<0.001	0.007	0.019	0.013	0.012
28.01.2003	<0.001	0.003	0.004	<0.001	0.003	0.005	0.006	0.005
28.02.2003	<0.001	<0.001	<0.001	<0.001	0.005	0.006	0.006	0.005
05.03.2003	<0.001	0.002	0.001	0.001	0.002	0.006	0.007	0.006
10.03.2003	<0.001	0.002	0.002	<0.001	0.002	0.005	0.005	0.004
14.03.2003	<0.001	<0.001	<0.001	<0.001	0.008	0.007	0.005	<0.001
15.05.2003	<0.001	<0.001	<0.001	<0.001	0.004	0.003	0.002	0.002
20.05.2003	<0.001	<0.001	<0.001	<0.001	0.002	0.002	0.001	0.001
28.05.2003	<0.001	0.004	0.003	0.006	0.044	0.011	0.013	0.013
06.10.2003	0.012	0.006	<0.001	0.002	0.003	0.021	0.003	0.003
09.10.2003	0.030	0.002	<0.001	<0.001	0.001	0.013	0.003	0.003
23.10.2003	0.046	<0.001	<0.001	<0.001	0.003	0.010	0.002	0.002
01.12.2003	0.024	0.002	0.001	0.001	0.002	0.017	0.002	0.002
15.12.2003	0.106	0.002	0.004	0.001	0.002	0.010	0.002	0.002
22.12.2003	0.010	0.001	0.001	0.001	0.002	0.006	0.002	0.001
12.01.2004	0.012	0.001	0.000	0.001	0.001	0.011	0.002	0.004
15.01.2004	0.013	0.001	0.001	0.001	0.001	0.009	0.001	0.001
20.01.2004	0.021	0.001	0.001	0.001	0.001	0.008	0.001	0.001

Lysimeter experiment: Lysimeter 2, PAH within the filtrate (<0.7 µm)(continued)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				**[µg l^{-1}]**				
03.02.2004	0.128	0.002	0.004	0.002	0.002	0.011	0.001	0.001
16.02.2004	0.018	0.002	0.002	0.002	0.004	0.018	0.002	0.002
15.03.2004	0.009	0.002	0.001	0.001	0.002	0.017	0.001	0.001
25.03.2004	0.010	0.002	0.002	0.002	0.002	0.008	0.001	0.002
04.06.2004	<0.001	0.002	<0.001	<0.001	0.002	0.019	0.003	0.002
06.07.2004	<0.001	0.003	<0.001	<0.001	0.002	0.014	0.003	0.004
09.07.2004	<0.001	0.004	<0.001	<0.001	0.002	0.027	0.006	0.006
16.08.2004	<0.001	0.011	0.144	0.095	0.055	0.032	0.038	0.018
30.08.2004	<0.001	0.001	<0.001	<0.001	0.001	0.016	0.001	0.001
15.10.2004	<0.001	0.002	<0.001	<0.001	0.002	0.023	<0.001	0.002

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	0.014	0.020	0.038	0.013	0.031	0.039	0.007	0.032
04.10.2002	0.012	0.019	0.050	0.016	0.035	0.040	0.006	0.034
18.10.2002	0.007	0.011	0.039	0.014	0.024	0.028	<0.001	0.027
28.01.2003	0.002	0.005	0.016	0.006	0.009	0.011	<0.001	0.011
28.02.2003	<0.001	<0.001	0.008	<0.001	0.005	0.007	<0.001	0.007
05.03.2003	0.004	0.007	0.017	0.006	0.014	0.017	0.003	0.018
10.03.2003	<0.001	0.005	0.009	0.003	0.007	0.008	<0.001	0.009
14.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15.05.2003	<0.001	<0.001	0.003	0.001	<0.001	0.003	<0.001	0.003
20.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
28.05.2003	0.005	0.012	0.021	0.008	0.012	0.019	0.012	0.020
06.10.2003	0.002	0.004	0.006	0.002	0.004	0.006	<0.001	0.006
09.10.2003	0.002	0.003	0.005	0.002	0.004	0.005	<0.001	0.005
23.10.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
01.12.2003	0.002	0.003	0.003	0.001	0.002	0.004	0.001	0.003
15.12.2003	0.001	0.002	0.003	0.001	0.002	0.004	<0.001	0.005
22.12.2003	0.001	0.001	0.001	0.000	0.001	0.002	<0.001	0.002
12.01.2004	0.001	0.001	0.002	0.001	0.001	0.003	<0.001	0.003
15.01.2004	0.001	0.001	0.002	0.001	0.002	0.002	<0.001	0.003
20.01.2004	0.001	0.002	0.004	0.001	0.002	0.002	0.001	0.003
03.02.2004	0.001	0.002	0.004	0.001	0.002	0.002	<0.001	0.003
16.02.2004	<0.001	0.001	0.002	<0.001	0.001	0.001	<0.001	0.002
15.03.2004	<0.001	0.001	0.002	<0.001	0.001	0.002	<0.001	0.002
25.03.2004	0.001	0.002	0.003	0.001	0.002	0.003	<0.001	0.003
04.06.2004	0.001	0.003	0.005	0.002	0.003	0.010	0.001	0.009
06.07.2004	0.003	0.005	0.006	0.002	0.006	0.010	0.002	0.009
09.07.2004	0.006	0.008	0.010	0.003	0.009	0.014	0.002	0.011
16.08.2004	0.003	0.004	0.004	0.001	0.002	0.005	<0.001	0.004
30.08.2004	<0.001	0.001	<0.001	<0.001	0.001	0.002	<0.001	0.002
15.10.2004	<0.001	<0.001	0.001	<0.001	0.001	0.002	<0.001	0.002

Lysimeter experiment: Lysimeter 3, PAH within the filtrate (<0.7 µm)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	<0.001	0.070	<0.001	0.161	0.007	0.049	0.128	<0.001
04.10.2002	<0.001	0.009	0.010	0.021	0.011	0.081	0.013	0.010
18.10.2002	<0.001	0.008	0.006	<0.001	0.005	0.035	0.013	0.011
25.10.2002	<0.001	0.009	0.005	<0.001	0.004	0.026	0.014	0.011
05.11.2002	<0.001	0.007	0.010	<0.001	0.005	0.026	0.017	0.016
13.11.2002	<0.001	0.008	0.013	<0.001	0.006	0.030	0.024	0.025
20.11.2002	<0.001	0.011	0.019	0.010	0.010	0.043	0.040	0.050
26.11.2002	<0.001	0.008	0.010	0.005	0.009	0.047	0.023	0.027
04.12.2002	<0.001	0.012	0.015	0.007	0.006	0.035	0.033	0.040
17.12.2002	<0.001	0.010	0.017	<0.001	<0.001	0.023	0.027	0.032
26.12.2002	<0.001	0.008	0.010	<0.001	<0.001	0.018	0.020	0.023
04.01.2003	<0.001	0.011	0.014	0.007	0.006	0.023	0.032	0.039
28.01.2003	<0.001	0.007	0.009	0.005	0.003	0.014	0.020	0.024
04.02.2003	<0.001	0.010	0.012	0.007	0.004	0.020	0.028	0.034
28.02.2003	<0.001	0.009	0.021	0.011	0.007	0.021	0.041	0.047
03.03.2003	<0.001	0.008	0.013	0.006	0.004	0.020	0.029	0.035
05.03.2003	<0.001	0.008	0.010	0.006	0.006	0.017	0.023	0.027
10.03.2003	<0.001	0.011	0.012	0.006	0.005	0.028	0.025	0.032
14.03.2003	<0.001	<0.001	<0.001	<0.001	0.012	0.016	0.012	0.015
28.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
06.10.2003	0.037	0.017	0.051	0.300	0.007	0.115	0.038	0.040
09.10.2003	0.007	0.010	0.008	0.006	0.002	0.024	0.022	0.025
23.10.2003	0.043	<0.001	<0.001	0.002	0.003	0.020	0.011	0.014
01.12.2003	0.017	0.019	0.013	0.008	0.003	0.047	0.020	0.024
15.12.2003	0.219	0.010	0.012	0.004	0.004	0.041	0.037	0.034
22.12.2003	0.012	0.009	0.005	0.002	0.002	0.026	0.013	0.018
12.01.2004	0.114	0.013	0.030	0.013	0.003	0.037	0.037	0.051
15.01.2004	0.046	0.023	0.084	0.032	0.006	0.059	0.072	0.094
20.01.2004	0.017	0.022	0.033	0.013	0.005	0.045	0.064	0.094
03.02.2004	0.012	0.019	0.016	0.007	0.003	0.034	0.045	0.063
16.02.2004	0.152	0.021	0.024	0.008	0.004	0.047	0.056	0.082
15.03.2004	0.013	0.015	0.012	0.006	0.003	0.030	0.023	0.032
25.03.2004	0.009	0.017	0.009	0.004	0.003	0.029	0.032	0.041
07.04.2004	0.118	0.010	0.018	0.006	0.002	0.017	0.024	0.035
20.04.2004	0.105	0.009	0.014	0.006	0.002	0.020	0.013	0.019
04.06.2004	0.177	0.008	0.028	0.008	0.002	0.048	0.007	0.009
07.06.2004	0.009	0.009	0.003	0.002	0.002	0.054	0.008	0.011
17.06.2004	0.015	0.009	0.003	0.004	0.002	0.046	0.004	0.005
06.07.2004	0.007	0.011	0.005	0.003	0.002	0.027	0.009	0.012
09.07.2004	0.011	0.013	0.009	0.005	0.003	0.057	0.026	0.033
26.07.2004	0.014	0.009	<0.001	0.004	0.004	0.074	0.005	0.006
16.08.2004	<0.001	0.052	0.062	0.021	0.016	0.081	0.271	0.285
30.08.2004	<0.001	0.007	<0.001	<0.001	<0.001	0.021	0.004	0.005
15.09.2004	<0.001	0.013	0.008	<0.001	<0.001	0.032	0.008	0.010
30.09.2004	<0.001	0.011	<0.001	<0.001	<0.001	0.065	0.005	0.005
15.10.2004	<0.001	0.008	0.003	0.002	0.002	0.026	0.007	0.009
22.10.2004	<0.001	0.005	0.003	0.001	0.002	0.022	0.006	0.009

Lysimeter experiment: Lysimeter 3, PAH within the filtrate (<0.7 µm)(continued)

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	0.005	0.022	0.025	0.010	0.017	0.017	0.003	0.018
04.10.2002	0.005	0.020	0.026	0.010	0.021	0.025	0.005	0.023
18.10.2002	0.011	0.014	0.032	0.009	0.020	0.033	0.006	0.022
25.10.2002	0.010	0.013	0.028	0.008	0.017	0.027	0.005	0.018
05.11.2002	0.015	0.020	0.043	0.013	0.026	0.038	0.008	0.026
13.11.2002	0.028	0.032	0.062	0.017	0.039	0.070	0.014	0.043
20.11.2002	0.028	0.047	0.264	0.096	0.149	0.273	<0.001	0.265
26.11.2002	0.011	0.026	0.078	0.031	0.045	0.042	<0.001	0.044
04.12.2002	0.016	0.035	0.433	0.174	0.218	0.070	<0.001	0.077
17.12.2002	0.013	0.029	0.118	0.047	0.062	0.052	<0.001	0.056
26.12.2002	0.011	0.021	0.080	0.031	0.045	0.033	<0.001	0.034
04.01.2003	0.017	0.036	0.268	0.105	0.153	0.209	<0.001	0.203
28.01.2003	0.012	0.021	0.072	0.027	0.042	0.035	0.006	0.035
04.02.2003	0.021	0.033	0.102	0.036	0.062	0.059	0.003	0.053
28.02.2003	0.047	0.060	0.111	0.039	0.077	0.092	0.017	0.066
03.03.2003	0.029	0.041	0.087	0.031	0.060	0.062	0.011	0.051
05.03.2003	0.013	0.027	0.060	0.023	0.043	0.036	<0.001	0.039
10.03.2003	0.024	0.043	0.071	0.027	0.049	0.050	0.009	0.048
14.03.2003	<0.001	<0.001	0.027	<0.001	0.021	<0.001	<0.001	0.022
28.05.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
06.10.2003	0.031	0.041	0.091	0.029	0.063	0.082	0.016	0.066
09.10.2003	0.022	0.028	0.060	0.019	0.043	0.068	<0.001	0.055
23.10.2003	0.008	0.013	0.028	0.010	0.021	0.020	<0.001	0.023
01.12.2003	0.026	0.031	0.058	0.020	0.042	0.051	0.012	0.045
15.12.2003	0.028	0.034	0.050	0.017	0.039	0.045	0.010	0.040
22.12.2003	0.017	0.022	0.043	0.014	0.031	0.046	0.010	0.042
12.01.2004	0.053	0.049	0.085	0.026	0.065	0.085	0.015	0.059
15.01.2004	0.096	0.084	0.112	0.033	0.095	0.137	0.024	0.092
20.01.2004	0.083	0.172	0.298	0.094	0.173	0.162	0.038	0.162
03.02.2004	0.062	0.116	0.200	0.065	0.139	0.144	0.035	0.131
16.02.2004	0.094	0.161	0.184	0.060	0.144	0.139	0.035	0.117
15.03.2004	0.023	0.040	0.074	0.023	0.048	0.068	0.017	0.057
25.03.2004	0.034	0.057	0.084	0.026	0.059	0.087	0.023	0.071
07.04.2004	0.022	0.041	0.131	0.041	0.094	0.137	0.035	0.122
20.04.2004	0.014	0.024	0.038	0.012	0.027	0.036	0.009	0.033
04.06.2004	0.006	0.010	0.017	0.005	0.012	0.014	0.003	0.014
07.06.2004	0.008	0.014	0.021	0.007	0.015	0.017	0.004	0.015
17.06.2004	0.003	0.005	0.005	0.002	0.005	0.006	<0.001	0.007
06.07.2004	0.009	0.015	0.021	0.007	0.018	0.021	0.005	0.020
09.07.2004	0.029	0.041	0.057	0.018	0.050	0.072	0.015	0.050
26.07.2004	0.004	0.006	0.007	<0.001	0.007	<0.001	<0.001	0.010
16.08.2004	0.282	0.336	0.553	0.173	0.382	0.533	0.143	0.364
30.08.2004	0.004	0.007	0.009	0.003	0.006	0.009	<0.001	0.009
15.09.2004	0.006	0.010	0.027	0.009	0.017	0.048	<0.001	0.047
30.09.2004	0.004	0.006	0.012	0.004	0.007	0.020	<0.001	0.017
15.10.2004	0.008	0.012	0.018	0.005	0.012	0.018	0.005	0.015
22.10.2004	0.006	0.009	0.015	0.005	0.010	0.016	<0.001	0.013

Lysimeter experiment: Lysimeter 1, PAH within the retentate (<0.7 µm)

date	**Nap**	**Acy**	**Ace**	**Flr**	**Phe**	**Ant**	**FlA**	**Pyr**
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	<0.001	0.002	0.001	<0.001	0.003	0.003	0.013	0.010
04.10.2002	<0.001	0.002	0.001	0.001	0.004	0.003	0.012	0.010
18.10.2002	<0.001	0.004	<0.001	<0.001	0.006	0.005	0.019	0.017
28.01.2003	<0.001	0.009	<0.001	<0.001	0.006	0.009	0.030	0.031
28.02.2003	<0.001	0.009	<0.001	<0.001	0.012	0.007	0.037	0.034
03.03.2003	0.005	0.028	0.003	0.002	0.021	0.016	0.139	0.129
05.03.2003	0.045	0.037	0.008	0.015	0.055	0.049	0.121	0.124
10.03.2003	<0.001	0.007	<0.001	<0.001	0.008	0.008	0.022	0.022
14.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.053	0.049
15.05.2003	<0.001	0.009	<0.001	<0.001	0.010	0.009	0.023	0.023
20.05.2003	<0.001	0.012	0.003	0.018	0.041	0.016	0.027	0.033
28.05.2003	<0.001	0.010	0.007	0.004	0.012	0.009	0.028	0.028
06.10.2003	<0.001	0.005	<0.001	<0.001	0.006	0.004	0.022	0.018
09.10.2003	<0.001	0.002	<0.001	<0.001	0.002	0.002	0.005	0.005
01.12.2003	0.032	0.001	0.001	0.001	0.003	0.001	0.004	0.004
15.12.2003	0.027	0.002	0.001	0.001	0.004	0.002	0.008	0.008
22.12.2003	0.194	0.002	0.036	0.006	0.003	0.002	0.003	0.003
12.01.2004	0.006	0.002	<0.001	<0.001	0.004	0.003	0.012	0.011
15.01.2004	0.006	0.004	0.001	0.001	0.003	0.003	0.010	0.009
20.01.2004	0.010	0.004	<0.001	0.003	0.004	0.003	0.009	0.008
03.02.2004	<0.001	<0.001	<0.001	<0.001	0.002	0.003	0.004	0.004
16.02.2004	0.005	0.002	<0.001	<0.001	0.002	0.002	0.005	0.005
15.03.2004	0.004	0.002	<0.001	<0.001	0.003	0.002	0.006	0.006
25.03.2004	0.005	0.002	<0.001	0.002	0.002	0.001	0.003	0.003
04.06.2004	0.019	0.004	<0.001	0.004	0.004	0.003	0.006	0.006
06.07.2004	0.102	0.036	0.011	0.024	0.021	0.027	0.075	0.079
09.07.2004	<0.001	0.008	0.001	0.001	0.005	0.005	0.018	0.018
16.08.2004	<0.001	0.015	0.002	0.002	0.012	0.011	0.048	0.048
30.08.2004	<0.001	0.003	0.001	0.002	0.003	0.003	0.006	0.007
15.10.2004	<0.001	0.005	<0.001	0.002	0.005	0.005	0.017	0.017

date	**BaA**	**Chr**	**BbFlA**	**BkFlA**	**BaP**	**IcdP**	**DahA**	**BghiP**
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	0.014	0.014	0.012	0.005	0.008	0.010	0.002	0.008
04.10.2002	0.011	0.013	0.000	0.005	0.009	0.012	0.002	0.010
18.10.2002	0.020	0.017	0.021	0.007	0.013	0.022	0.004	0.014
28.01.2003	0.032	0.042	0.057	0.024	0.043	0.036	0.006	0.031
28.02.2003	0.025	0.031	0.042	0.016	0.034	0.032	0.007	0.032
03.03.2003	0.137	0.185	0.158	0.072	0.167	0.092	0.011	0.090
05.03.2003	0.099	0.129	0.189	0.068	0.132	0.135	0.073	0.123
10.03.2003	0.018	0.021	0.029	0.012	0.023	0.025	0.006	0.022
14.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
15.05.2003	0.023	0.026	0.027	0.012	0.023	0.024	<0.001	0.023
20.05.2003	0.025	0.031	0.039	0.013	0.027	0.035	0.025	0.033
28.05.2003	0.015	0.021	0.033	0.013	0.028	0.025	0.004	0.025
06.10.2003	0.014	0.015	0.019	0.006	0.014	0.015	<0.001	0.013
09.10.2003	0.003	0.004	0.006	0.002	0.004	0.005	<0.001	0.005
01.12.2003	0.002	0.002	0.004	0.002	0.003	0.003	0.001	0.003
15.12.2003	0.004	0.005	0.009	0.004	0.008	0.008	0.001	0.008
22.12.2003	0.002	0.002	0.004	0.001	0.003	0.003	0.001	0.004

Lysimeter experiment: Lysimeter 1, PAH within the retentate (<0.7 µm)(continued)

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				[µg l^{-1}]				
12.01.2004	0.009	0.008	0.010	0.004	0.009	0.010	0.002	0.007
15.01.2004	0.008	0.007	0.010	0.004	0.008	0.008	0.001	0.007
20.01.2004	0.009	0.011	0.009	0.003	0.007	0.007	<0.001	0.006
03.02.2004	0.005	0.006	0.005	<0.001	0.004	0.004	<0.001	0.004
16.02.2004	0.003	0.004	0.006	0.002	0.005	0.005	0.001	0.005
15.03.2004	0.005	0.007	0.007	0.002	0.006	0.006	0.001	0.006
25.03.2004	0.002	0.003	0.003	0.001	0.003	0.003	<0.001	0.003
04.06.2004	0.005	0.007	0.006	0.002	0.005	0.007	<0.001	0.006
06.07.2004	0.093	0.093	0.077	0.027	0.090	0.151	0.031	0.084
09.07.2004	0.014	0.022	0.022	0.008	0.021	0.027	0.005	0.019
16.08.2004	0.054	0.063	0.046	0.016	0.044	0.071	0.013	0.043
30.08.2004	0.005	0.007	0.006	0.002	0.006	0.008	0.001	0.006
15.10.2004	0.013	0.016	0.019	0.007	0.014	0.016	0.003	0.013

Lysimeter experiment: Lysimeter 2, PAH within the retentate (<0.7 µm)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	<0.001	0.006	0.001	0.001	0.005	0.008	0.028	0.025
04.10.2002	<0.001	0.007	0.003	0.002	0.011	0.010	0.058	0.048
18.10.2002	<0.001	0.015	0.003	0.003	0.018	0.018	0.093	0.076
28.01.2003	<0.001	0.003	<0.001	<0.001	0.003	0.004	0.011	0.010
28.02.2003	<0.001	0.002	<0.001	<0.001	0.003	0.002	0.012	0.010
05.03.2003	<0.001	0.004	0.001	0.001	0.002	0.002	0.013	0.013
10.03.2003	<0.001	<0.001	<0.001	<0.001	<0.001	0.005	0.011	0.010
14.03.2003	<0.001	0.002	<0.001	<0.001	0.004	0.003	0.015	0.014
15.05.2003	<0.001	0.094	0.008	0.010	0.056	0.039	0.456	0.446
20.05.2003	<0.001	0.004	0.001	0.002	0.005	0.003	0.020	0.019
28.05.2003	<0.001	0.083	0.013	0.033	0.068	0.060	0.335	0.310
06.10.2003	<0.001	0.041	<0.001	<0.001	0.057	0.047	0.318	0.292
09.10.2003	<0.001	0.038	<0.001	<0.001	0.032	0.038	0.141	0.132
23.10.2003	0.010	0.004	0.001	0.001	0.006	0.005	0.026	0.024
01.12.2003	0.052	0.050	0.012	0.014	0.146	0.157	1.030	0.939
15.12.2003	0.015	0.013	0.004	0.004	0.050	0.032	0.233	0.208
22.12.2003	0.329	0.014	0.044	0.009	0.025	0.022	0.120	0.100
12.01.2004	<0.001	0.027	<0.001	0.008	0.062	0.059	0.283	0.236
15.01.2004	0.011	0.018	0.003	0.003	0.018	0.027	0.124	0.107
20.01.2004	0.006	0.007	<0.001	<0.001	0.006	0.007	0.031	0.028
03.02.2004	<0.001	0.024	<0.001	<0.001	0.026	0.025	0.133	0.120
16.02.2004	0.003	0.004	<0.001	0.002	0.005	0.004	0.018	0.017
15.03.2004	0.010	0.015	0.004	0.007	0.021	0.015	0.089	0.083
25.03.2004	0.009	0.004	0.001	0.003	0.004	0.004	0.022	0.021
04.06.2004	0.006	0.005	0.001	0.003	0.005	0.004	0.030	0.029

Lysimeter experiment: Lysimeter 2, PAH within the retentate (<0.7 µm)(continued)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				**[µg l^{-1}]**				
06.07.2004	<0.001	0.202	0.014	0.073	1.095	1.591	2.968	2.863
09.07.2004	<0.001	0.035	0.004	0.006	0.037	0.045	0.260	0.245
16.08.2004	<0.001	0.076	0.007	0.017	0.162	0.160	1.001	0.873
30.08.2004	<0.001	0.002	<0.001	0.002	0.002	0.002	0.006	0.006
15.10.2004	<0.001	0.033	0.004	0.009	0.081	0.074	0.424	0.404

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				**[µg l^{-1}]**				
26.09.2002	0.021	0.026	0.031	0.011	0.025	0.028	0.006	0.022
04.10.2002	0.034	0.040	0.049	0.019	0.041	0.042	0.008	0.034
18.10.2002	0.080	0.067	0.069	0.022	0.051	0.071	0.014	0.044
28.01.2003	0.004	0.009	0.017	0.008	0.010	0.010	0.002	0.009
28.02.2003	0.004	0.005	0.008	0.003	0.007	0.005	0.001	0.005
05.03.2003	0.005	0.007	0.013	0.005	0.015	0.012	0.002	0.014
10.03.2003	<0.001	<0.001	0.015	<0.001	0.011	0.013	<0.001	0.013
14.03.2003	0.008	0.008	0.009	<0.001	<0.001	<0.001	<0.001	<0.001
15.05.2003	0.348	0.370	0.326	0.124	0.330	0.297	0.063	0.219
20.05.2003	0.011	0.014	0.014	0.006	0.014	0.009	0.003	0.010
28.05.2003	0.209	0.233	0.248	0.105	0.247	0.185	0.040	0.177
06.10.2003	0.243	0.211	0.244	0.078	0.202	0.212	0.040	0.149
09.10.2003	0.110	0.102	0.140	0.044	0.109	0.134	0.023	0.106
23.10.2003	0.012	0.013	0.014	0.006	0.015	0.012	0.002	0.014
01.12.2003	0.434	0.482	0.527	0.223	0.410	0.300	0.059	0.231
15.12.2003	0.213	0.152	0.117	0.042	0.119	0.110	0.016	0.077
22.12.2003	0.096	0.083	0.080	0.029	0.080	0.072	0.012	0.057
12.01.2004	0.145	0.127	0.146	0.056	0.139	0.100	0.019	0.073
15.01.2004	0.105	0.071	0.061	0.021	0.069	0.069	0.013	0.046
20.01.2004	0.032	0.037	0.021	0.007	0.022	0.018	0.003	0.015
03.02.2004	0.117	0.150	0.101	0.035	0.099	0.079	0.015	0.069
16.02.2004	0.013	0.017	0.014	0.005	0.014	0.013	0.003	0.012
15.03.2004	0.068	0.081	0.065	0.021	0.060	0.055	0.013	0.045
25.03.2004	0.016	0.019	0.013	0.005	0.014	0.019	0.003	0.012
04.06.2004	0.023	0.025	0.017	0.006	0.022	0.027	0.005	0.015
06.07.2004	1.670	2.436	1.196	0.476	1.198	0.914	0.173	0.643
09.07.2004	0.214	0.231	0.148	0.049	0.152	0.183	0.033	0.115
16.08.2004	0.822	0.744	0.424	0.136	0.481	0.437	0.096	0.245
30.08.2004	0.005	0.006	0.004	0.002	0.004	0.005	0.001	0.004
15.10.2004	0.256	0.268	0.234	0.080	0.200	0.162	0.038	0.128

Lysimeter experiment: Lysimeter 3, PAH within the retentate (<0.7 µm)

date	Nap	Acy	Ace	Flr	Phe	Ant	FlA	Pyr
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	0.004	0.020	0.021	0.015	0.020	0.041	0.163	0.156
04.10.2002	0.008	0.038	0.024	0.012	0.007	0.039	0.118	0.131
18.10.2002	0.008	0.019	0.031	0.012	0.007	0.024	0.097	0.108
25.10.2002	0.009	0.032	0.033	0.015	0.042	0.045	0.166	0.169
05.11.2002	0.013	0.143	0.054	0.090	0.222	0.424	2.010	1.590
13.11.2002	0.006	0.051	0.025	0.013	0.037	0.059	0.266	0.234
20.11.2002	0.015	0.080	0.052	0.023	0.023	0.066	0.304	0.299
26.11.2002	0.010	0.013	0.010	0.006	0.015	0.013	0.059	0.061
04.12.2002	0.007	0.019	0.019	0.007	0.006	0.021	0.090	0.101
17.12.2002	0.018	0.036	0.039	0.014	0.011	0.039	0.176	0.190
26.12.2002	0.012	0.059	0.069	0.028	0.035	0.109	0.749	0.645
04.01.2003	0.013	0.166	0.969	1.196	7.366	1.988	17.252	8.197
28.01.2003	0.015	0.092	0.221	0.386	1.913	0.591	2.940	2.052
04.02.2003	0.009	0.008	0.007	0.003	0.004	0.008	0.035	0.037
28.02.2003	0.021	0.041	0.027	0.012	0.014	0.028	0.252	0.259
03.03.2003	0.006	0.013	0.010	0.004	0.003	0.008	0.054	0.060
05.03.2003	0.005	0.006	0.003	0.002	0.002	0.003	0.015	0.016
10.03.2003	0.014	0.035	0.019	0.009	0.021	0.038	0.137	0.142
14.03.2003	0.012	0.009	0.006	0.003	0.006	0.009	0.028	0.031
28.05.2003	0.033	0.033	0.027	0.024	0.037	0.038	0.125	0.128
06.10.2003	<0.001	0.062	0.042	<0.001	0.031	0.073	0.267	0.268
09.10.2003	<0.001	0.032	0.017	<0.001	0.010	0.034	0.072	0.085
23.10.2003	0.035	0.026	0.016	0.006	0.008	0.039	0.098	0.118
01.12.2003	0.034	0.015	0.022	0.007	0.006	0.030	0.125	0.145
15.12.2003	0.055	0.026	0.034	0.011	0.015	0.044	0.272	0.257
22.12.2003	0.164	0.014	0.040	0.009	0.004	0.021	0.059	0.066
12.01.2004	<0.001	0.233	0.241	0.114	0.107	0.497	2.234	2.038
15.01.2004	0.011	0.098	0.079	0.038	0.057	0.218	0.965	0.897
20.01.2004	<0.001	0.072	0.045	0.018	0.016	0.082	0.520	0.507
03.02.2004	<0.001	0.039	0.019	0.009	<0.001	0.035	0.089	0.116
16.02.2004	0.003	0.019	0.017	0.007	0.006	0.021	0.135	0.130
15.03.2004	0.004	0.008	0.006	0.003	0.003	0.007	0.023	0.030
25.03.2004	0.002	0.011	0.008	0.006	0.003	0.010	0.037	0.044
07.04.2004	<0.001	0.010	0.008	0.009	0.010	0.010	0.033	0.038
20.04.2004	<0.001	0.008	0.006	0.008	0.003	0.007	0.021	0.027
04.06.2004	0.006	0.025	0.022	0.012	0.007	0.021	0.095	0.108
07.06.2004	0.008	0.009	0.024	0.015	0.003	0.007	0.026	0.030
17.06.2004	<0.001	0.015	0.012	0.014	0.008	0.012	0.047	0.049
06.07.2004	<0.001	0.030	0.030	0.017	0.010	0.029	0.127	0.137
09.07.2004	<0.001	0.045	0.029	0.011	0.008	0.052	0.200	0.213
26.07.2004	<0.001	0.019	0.018	0.054	0.013	0.021	0.029	0.038
16.08.2004	<0.001	0.251	0.187	0.066	0.050	0.260	1.271	1.337
30.08.2004	<0.001	0.014	0.008	0.009	0.003	0.011	0.034	0.039
15.09.2004	<0.001	0.089	0.045	0.044	0.019	0.082	0.307	0.323
30.09.2004	<0.001	0.009	0.011	0.036	0.003	0.007	0.024	0.030
15.10.2004	<0.001	0.019	0.012	0.007	0.003	0.017	0.080	0.088
22.10.2004	<0.001	0.009	0.007	0.018	0.002	0.009	0.031	0.036

Lysimeter experiment: Lysimeter 3, PAH within the retentate (<0.7 µm)(continued)

date	BaA	Chr	BbFlA	BkFlA	BaP	IcdP	DahA	BghiP
[DD.MM.YYYY]				[µg l^{-1}]				
26.09.2002	0.176	0.201	0.204	0.076	0.152	0.165	0.037	0.110
04.10.2002	0.134	0.190	0.240	0.087	0.176	0.239	0.054	0.164
18.10.2002	0.132	0.136	0.168	0.058	0.146	0.217	0.047	0.136
25.10.2002	0.208	0.192	0.270	0.071	0.154	0.313	0.060	0.153
05.11.2002	1.637	1.494	1.128	0.464	0.787	0.615	0.123	0.450
13.11.2002	0.289	0.260	0.272	0.091	0.178	0.240	0.051	0.153
20.11.2002	0.374	0.342	0.413	0.137	0.287	0.392	0.080	0.252
26.11.2002	0.042	0.063	0.077	0.029	0.056	0.079	0.011	0.057
04.12.2002	0.081	0.118	0.157	0.057	0.109	0.160	0.022	0.106
17.12.2002	0.144	0.206	0.315	0.119	0.224	0.261	0.040	0.182
26.12.2002	0.970	0.736	0.569	0.181	0.416	0.619	0.096	0.308
04.01.2003	4.137	4.508	3.056	1.334	2.317	1.423	0.350	1.094
28.01.2003	1.625	1.311	1.437	0.522	0.957	0.677	0.147	0.484
04.02.2003	0.021	0.034	0.071	0.030	0.048	0.034	0.007	0.036
28.02.2003	0.175	0.360	0.361	0.142	0.307	0.253	0.046	0.243
03.03.2003	0.042	0.068	0.086	0.035	0.084	0.065	0.013	0.068
05.03.2003	0.008	0.013	0.023	0.010	0.023	0.018	0.004	0.020
10.03.2003	0.119	0.167	0.202	0.073	0.176	0.164	0.038	0.156
14.03.2003	0.023	0.031	0.051	0.018	0.041	0.039	0.012	0.038
28.05.2003	0.076	0.125	0.147	0.059	0.142	0.102	0.038	0.112
06.10.2003	0.244	0.247	0.409	0.122	0.290	0.343	0.072	0.250
09.10.2003	0.071	0.089	0.150	0.052	0.107	0.126	0.026	0.101
23.10.2003	0.084	0.099	0.151	0.049	0.126	0.177	0.029	0.139
01.12.2003	0.135	0.124	0.188	0.061	0.164	0.230	0.041	0.150
15.12.2003	0.318	0.277	0.296	0.100	0.259	0.308	0.049	0.211
22.12.2003	0.077	0.073	0.088	0.029	0.080	0.097	0.017	0.072
12.01.2004	2.695	1.947	1.841	0.591	1.804	1.997	0.409	1.212
15.01.2004	1.098	0.782	0.810	0.274	0.770	0.763	0.155	0.487
20.01.2004	0.584	0.900	0.702	0.229	0.516	0.433	0.091	0.340
03.02.2004	0.117	0.225	0.182	0.059	0.154	0.152	0.031	0.140
16.02.2004	0.138	0.183	0.167	0.051	0.133	0.144	0.038	0.105
15.03.2004	0.022	0.039	0.052	0.016	0.039	0.046	0.012	0.042
25.03.2004	0.033	0.061	0.076	0.023	0.055	0.069	0.018	0.059
07.04.2004	0.026	0.048	0.060	0.019	0.045	0.051	0.013	0.048
20.04.2004	0.017	0.034	0.046	0.014	0.033	0.038	0.010	0.037
04.06.2004	0.088	0.137	0.172	0.053	0.134	0.135	0.036	0.122
07.06.2004	0.024	0.037	0.046	0.014	0.038	0.041	0.011	0.037
17.06.2004	0.044	0.060	0.064	0.020	0.053	0.050	0.014	0.050
06.07.2004	0.135	0.180	0.202	0.066	0.170	0.157	0.044	0.137
09.07.2004	0.252	0.259	0.233	0.064	0.210	0.319	0.075	0.182
26.07.2004	0.032	0.044	0.041	0.014	0.037	0.043	0.009	0.052
16.08.2004	1.567	1.726	1.467	0.420	1.273	1.914	0.430	1.118
30.08.2004	0.034	0.049	0.047	0.015	0.047	0.061	0.012	0.043
15.09.2004	0.249	0.346	0.446	0.143	0.294	0.338	0.096	0.274
30.09.2004	0.021	0.032	0.048	0.015	0.029	0.036	0.009	0.033
15.10.2004	0.064	0.088	0.121	0.039	0.086	0.095	0.027	0.080
22.10.2004	0.027	0.037	0.052	0.017	0.038	0.042	0.011	0.037

LEBENSLAUF

Name	Steffen Jann
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Ausbildung und Qualifikation

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DANKSAGUNG

Meinen Dank möchte ich meinem Doktorvater Dr. Kai Uwe Totsche für die hervorragende Betreuung dieser Dissertation, das gute Arbeitsklima und die stete Diskussionsbereitschaft und Hilfe aussprechen. Prof. Dr. Ingrid Kögel-Knabner danke ich für die Unterstützung dieser Arbeit mit vielen Tipps zur Verfassung wissenschaftlicher Texte.

Dr. Philipp Jaesche danke ich für die Hilfe bei allen technischen, wissenschaftlichen und sonstigen Fragen, sowie der tatkräftigen Mitarbeit im Gelände.

Bei Bärbel Angres bedanke ich mich für die unentbehrliche Unterstützung im Labor bei zahlreichen, arbeitsintensiven PAK-Analysen, ebenso bei Horst Fechter für die Hilfe bei den Versuchsaufbauten und den verschiedenen Analysen.

Den Kollegen Markus Wehrer und Dirk Hensel sei gedankt für den intensiven Meinungsaustausch, die gute Zusammenarbeit und die stetige Diskussionsbereitschaft.

Außerdem bedanke ich mich recht herzlich bei Claudia Guggenberger, Klaus-Holger Knorr und Michael Hügel für ihre Mitarbeit bei der Durchführung der Versuche im Rahmen ihrer Diplomarbeiten,

bei den studentischen Hilfskräften Gabi Kolb, Melanie Schmitt, Alex Dümig, Christoph Stöldt und Bernd Mazzolini für ihre tatkräftige Mithilfe bei Probenahmen, im Labor oder bei der Datenbearbeitung,

bei Josef Fischer für die Unterstützung bei allen technischen Fragen, der Mithilfe beim Einbau der Lysimeter und für die stete Versorgung mit allen wichtigen Informationen des Tages,

und bei meinen Kollegen Ingo Schöning, Thomas Caspari, Markus Steffens, Andreas Fritzsche, Carsten Müller, Britt Pagels, Nora Tyufekchieva, Josefine Beck und Dr. Karin Eusterhues und allen anderen am Lehrstuhl für Bodenkunde für die angenehme Atmosphäre während der Arbeit und für die netten, geselligen Runden in der gemeinsam verbrachten Freizeit.

Besonderer Dank gilt meiner Familie, allen voran meinen Eltern Annelie und Hans-Peter Jann für die liebevolle Unterstützung und fortwährende Bestätigung im Studium und bei der Promotion; ebenso meiner Freundin Bianca Wagenbach für ihre Unterstützung und fleißiges Korrekturlesen.