4

Organic Substances in Bank filtration and Groundwater Recharge- Process Studies

“organics” group: Technische Universität Berlin

Responsible project leader: Prof. Dr. Martin Jekel

Contents

I List of Abbreviations

AOBr	Adsorbable Organic Bromine
AOC	Assimilable organic carbon
AOI	Adsorbable Organic Iodine
AOX	Adsorbable Organic Halogens
BDOC	Biodegradable dissolved organic carbon
BTS	Benzene- and Toluene sulfonamides
COD	Chemical oxygen demand
D	Dalton
d	Dispersion [m^2/d]
DC	Direct Current
DOC	Dissolved Organic Carbon
DWQC	Department of Water Quality Control
ELGA	Ultra Pure Deionized Water
FIA	Flow injection analysis
FLD	Fluorescence detection
HPLC	High Pressure (Performance) Liquid Chromatography
IC	Ion chromatography
LC-OCD	Liquid Chromatography – Organic Carbon Detection
LOD	Limit of detection
LOQ	Limit of quantification
MS	Mass spectroscopy, Mass spectrometer
MON	Mean Oxidation Number
NASRI	Natural and Artificial Systems for Recharge and Infiltration
NBDOC	Non-biodegradable DOC
NDSA	Naphthalenedisulfonic Acid
NSA	Naphthalenesulfonic Acid
OC	Organic Carbon
POC	Particulate Organic Carbon
POP	Persistent Organic Pollutants
R	Factor of retardation
SPE	Solid Phase Extraction
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TrBA	Tributylamine
UPW	Ultra Pure Water
UVA	UV-Absorption (254 nm)

II List of Figures

III List of Tables

1 Results

1.1 Lake Tegel bank filtration site

The monitoring of the bank filtration field site Berlin-Tegel by the „Organics"-subproject within NASRI started in May 2002. Previous research projects of the Department for Water Quality Control (DWQS) conducted research at this transect and several uncontinuous datasets are available. The monitoring of abstraction and monitoring wells ended in August 2004, but the sampling of surface water was continued until June 2005.

The monthly analytical program for all samples was comprised of DOC, UVA_{254}, UVA_{436}, LC-OCD, and differentiated AOX (adsorbable organic halogens e.g. AOI, AOBr)-analysis. Additionally, trace organic compounds were analyzed for a time period of 16 months. Trace compound analysis focused on three groups of target compounds. These groups were X-ray contrast media (Iopromide); bacteriostatica (Sulfamethoxazole), and Naphthalenedisulfonates (1,5-NDSA; 1,7-NDSA; 2,7-NDSA). Results of the field monitoring are reported in the following chapters.

1.1.1 Lake Tegel - Results bulk organics

1.1.1.1 Surface water Lake Tegel

In Lake Tegel the amount and character of bulk organics were characterized by measurements of dissolved organic carbon (DOC), UV-absorption at 254 nm, and color at 436 nm. The SUVA, a measure of aromaticity of the water, was calculated as a quotient of UVA_{254} and DOC. Table 1 provides the arithmetic mean, median and standard deviation of 36 monthly measurements.

Over these three years of monitoring, the DOC-concentration in Lake Tegel remained in a range between 6.5 mg/l and 8 mg/l. A variation between winter and summer of 0.5-1 mg/l was observed. Slightly higher DOC concentrations were found in the summer months March to September. Figure 1 confirms these results. A comparison of the recent concentrations with data obtained from 06/1998 – 06/2000 (Ziegler; 2001) shows that the DOC-level in Lake Tegel decreased by 1-1.5 mg/l. Ziegler (2001) reported a median DOC-concentration of 8.6 mg/l.

Table 1 Results bulk organic parameters in surface water Tegel 2002-2005 (n=36)

	DOC	UVA_{254}	UVA_{436}	SUVA
	[mg/l]	[1/m]	[1/m]	[l/m*mg]
Arithmetic mean	7.17	15.08	0.52	2.11
Median	7.10	15.02	0.48	2.09
Standard deviation	0.48	1.11	0.11	0.17

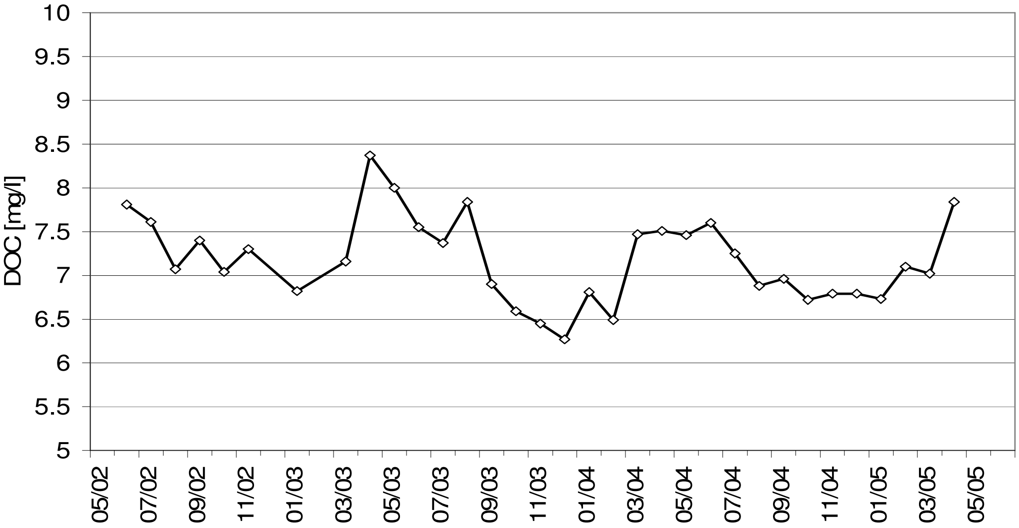


Figure 1 Time series of DOC concentration in Lake Tegel

UVA_{254} of the surface water was measured between 13 and 17 m^{-1}. A clear seasonal variation was revealed (Figure 2), which did not correspond with changes in DOC concentration. Generally, higher UVA_{254} were found in winter months November to May. This variation is a stable long term effect since it was already observed in the years 1998-2000 by Ziegler (2001).

The calculated SUVA ranged between 1.7 to 2.4 l/m*mg. Changes in aromaticity (SUVA) of the surface water resulted from the described changes of DOC and UVA_{254}. The share of aromatic structures on total DOC (expressed by SUVA) was high in periods of low DOC and high UVA_{254} (e.g. winter). With beginning of spring rising DOC concentrations generated a decrease of SUVA. It can be concluded that additional DOC during summer is mostly of aliphatic nature.

The UV absorption at 436 nm of water from Lake Tegel was relatively stable during the observation period at 0.5 m^{-1}. The water was not visibly colored and no seasonal or other changes were observed.

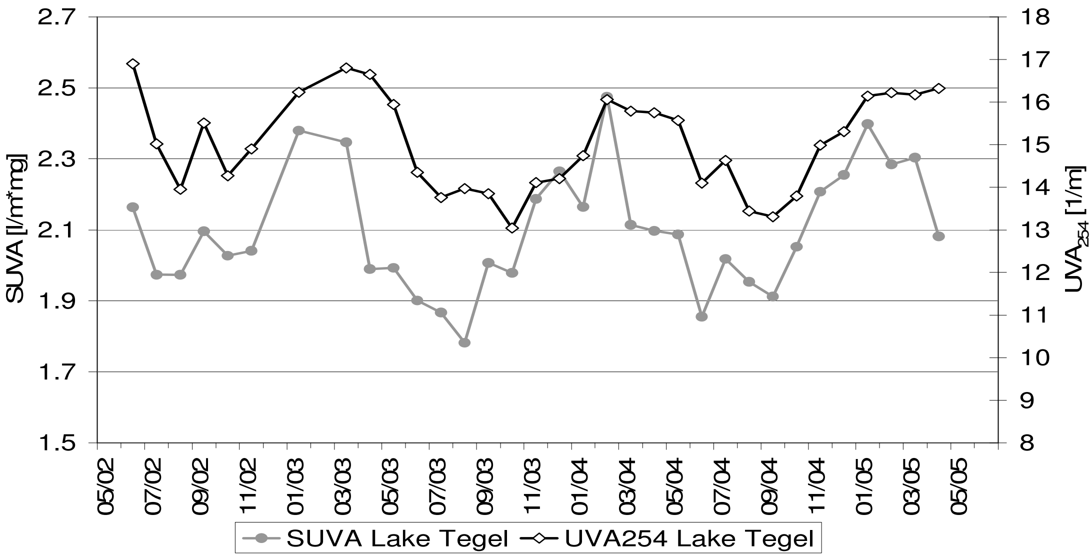


Figure 2 UVA_{254} and SUVA of Lake Tegel surface water

In three years of monitoring different potential factors of influence for bulk organic concentration and character in Lake Tegel were revealed.

- algae blooms in spring and summer
- seasonal variation of the discharge of the Lake Pipeline (water from upper Havel)
- changes in the discharge of sewage treatment plant (STP) Schoenerlinde
- seasonal differences in natural precipitation

The observed seasonal variations of bulk organic parameters in the lake are the sum of these different influences. By comparison of time frames a weighting of importance of the factors for the observed changes was possible.

- Algae blooms can occur in Lake Tegel between March and October because of preferential light and temperature conditions.
- The proportion of water from upper Havel, which is pumped through the lake pipeline, treated in the surface water treatment plant (OWA) and then discharged into the lake, varies highly with the seasons. During winter less than 10% of the total discharge of the OWA originates from the Havel-River. Between May and October the proportion rises to more than 60% (Figure 3).
- Natural precipitation might also affect the DOC concentration in Lake Tegel. A lack of precipitation could result in a reduced dilution of the effluents of the sewage treatment plant Schoenerlinde which discharges over the Nordgraben and the OWA into Lake Tegel. The sum of monthly precipitation since 2002 is presented in Figure 4.

- The discharge of the waste water treatment plant Schoenerlinde increased during the observation period. But the singular event did not significantly affect the character of the surface water DOC in Lake Tegel. Commonly, the effluent quality (regarding bulk organics) and quantity of STP`s are relatively constant over the seasons. Therefore, it is unlikely that seasonal variations in Lake Tegel originate from the STP Schoenerlinde.

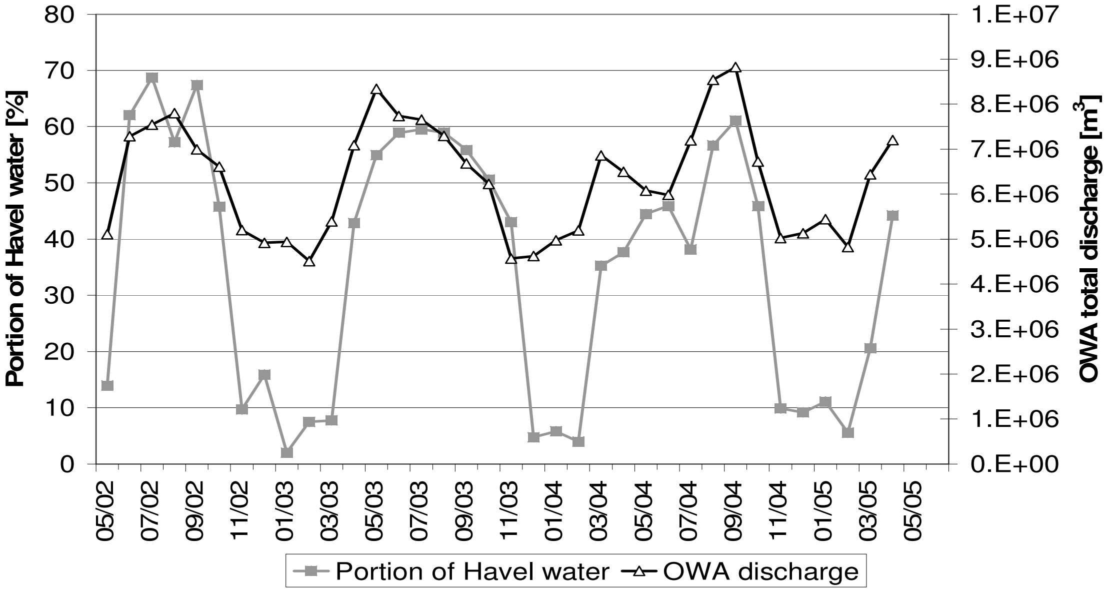


Figure 3 Total discharge into Lake Tegel and the portion of water from the Havel (lake pipeline)

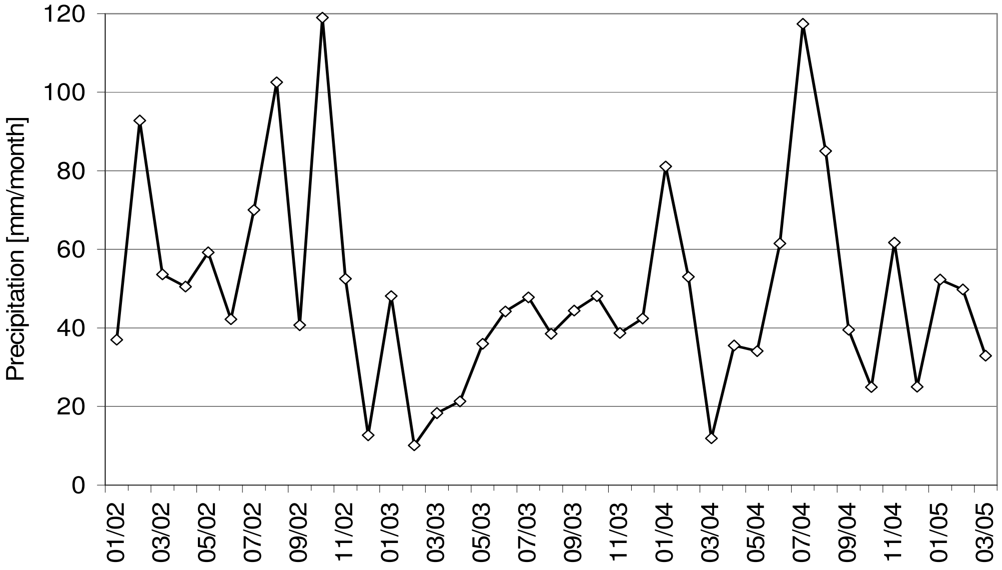


Figure 4 Natural precipitation in the area of Lake Tegel (data from BWB, WW Tegel)

An evaluation of the four different factors of influence was conducted by taking into account all available data. It was found, that seasonal variation of DOC in Lake Tegel seems to originate mostly from annual algae blooms. The time frame of elevated DOC concentration fits to the observed time for algae blooms. Furthermore, the additional DOC was found to be of aliphatic nature (SUVA results) what is characteristic for algae associated DOC.

The reversed seasonal variation of UVA_{254} in Lake Tegel can be explained by changing dilution of the effluent of the treatment plant Schoenerlinde by water from the upper Havel. Highest UVA_{254} results are observed in time periods of very few dilution of the treated effluent in winter. A minimal time shift between the peaks can be explained by the retention time of the lake. The transect is located approximately 2 km south of the point where the OWA effluent enters the lake.

Distribution of natural precipitation in the observation period is very irregular (Figure 4). Strong differences in total precipitation (2002: 733 mm; 2003: 438 mm; 2004: 630 mm) and distribution of the annual precipitation were recorded in the three years of the observation period for the region of Berlin. Therefore, it is unlikely, that any regular changes of bulk organic parameters in the lake originate primarily from changes in dilution by precipitation. But heavy or missing precipitation can be an additional effect which adds to other factors of influence. For instance, the highest DOC concentration in the lake (04/04: 8.4 mg/l) was measured after three subsequent months of very few precipitation.

However, concentration and character of bulk organics in Lake Tegel is relatively stable with some seasonal variations, which are mainly due to algae blooms and changing operation of the lake pipeline. Natural precipitation and the effluent of sewage treatment plants are only of minor importance.

Furthermore, the seasonal change in character of DOC can be accessed by LC-OCD. Chapter 1.1.2 provides more information on general composition of the DOC and changes during the observation period.

1.1.1.2 Bank filtration-DOC

The fate of bulk organics during infiltration was monitored for 2¼ years with a monthly sampling of monitoring wells which were located along the infiltration path of the surface water. The change in concentration and character of bulk organics during infiltration depended on various factors, like retention time, redox conditions, soil properties, and hydrogeological conditions. The minor seasonal changes that were described for the surface water could not be found in the time series of the monitoring wells, since they were superposed by an effective mineralization of organic material.

Results are presented in form of time series and box plots (Figure 5, Figure 6). Box plots are defined by the median (horizontal centre line), the 25%- and 75%-quartiles (box), and the minimum and maximum values (vertical lines). Extreme values and outliers are shown but not considered for quartile calculation. Removal rates are calculated from the medians, because for some wells the data pool is relatively small and the median is a more stable indication in the case of small data sets (Zöfel, 2002). The results are actual measured concentrations and were not adjusted for potential dilution.

Data illustration was simplified by a separation of the infiltration process in two stages. The more shallow monitoring wells located close to the bank area in the top aquifer represent mostly short term infiltration (retention time <3 months) under oxic conditions. Monitoring wells in the second aquifer have longer retention times and showed for most of the observation period anoxic and anaerobic redox conditions. However, the two groups are regarded as two different flow paths but have to be considered as two subsequent stages. Most of the lake water is initially infiltrating under oxic conditions at the water/sediment interface. The major flow path runs through 3310, 371OP, 371UP, 3302 towards 3303, and the production well 13. During infiltration oxygen is used up quickly because of mineralization of DOC and sedimentary bound particulate organic carbon (POC) (~0.5 % w/w) and most of the 4-5 months long infiltration (100 m) to the production well is usually taking place under anoxic and anaerobic conditions (iron and manganese reduction). The extension and position of the redox zones varies seasonally and is horizontally stratified. For a more detailed description of the hydrogeological setup of the field site read NASRI Report 1 (Chapter 1.3.).

An evaluation of the data pool 2002-2004 showed that the DOC concentration of the lake water is reduced considerably along the transect to a residual of around 4.7 mg/l, based on the last monitoring well (3303) in front of the production well 13. It was found that the initial infiltration under oxic conditions is very important for an efficient DOC removal. Figure 5 shows that a DOC removal of 25-30 % can be achieved under oxic conditions with retention times of some days or a few weeks. During summer the shallow monitoring wells (3310, 3311) could not be sampled because of lower surface water level, but the recorded data exhibit some indications that the efficiency of DOC degradation during initial oxic infiltration is temperature dependent. Higher DOC concentrations during colder months were found in monitoring well 3311, 3310 and 3308.

The low DOC levels in 372 might be explained by longer retention time under permanently oxic conditions. In the upper aquifer oxygen is continuously introduced into the ground water by variations of the water level, which is caused by the pumping schedule of BWB.

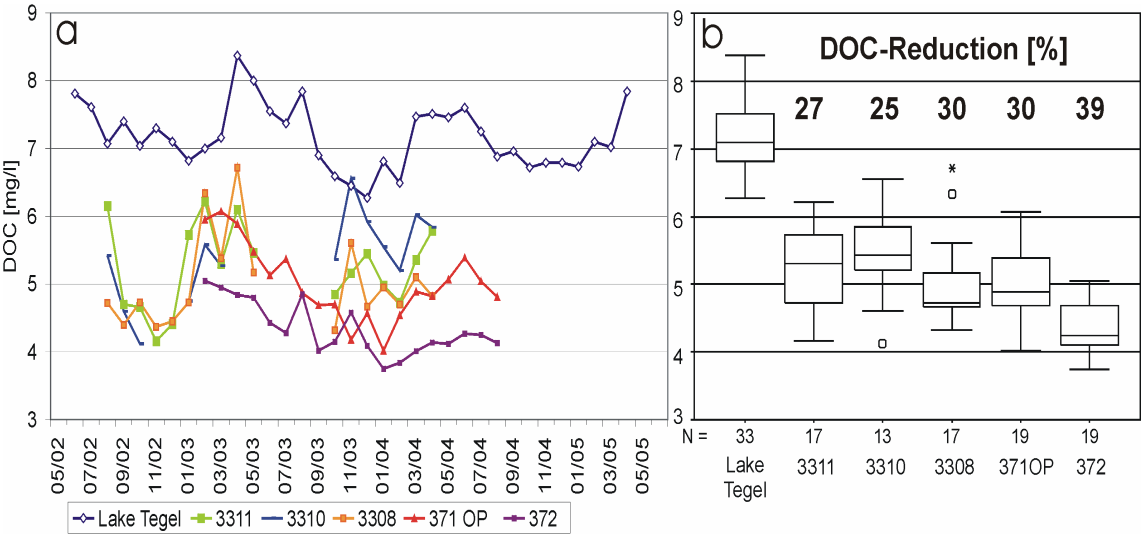


Figure 5a/b Fate of DOC during infiltration to the shallow monitoring wells (a: time series; b: box plots)

Bank filtrate in the second aquifer originates mainly from surface water that infiltrated under oxic conditions from the lake through the first aquifer. Besides by infiltration through the upper aquifer, minor portions of bank filtrate of different ages enter the transect from under the lake. Water composition of this fraction is not exactly clear, since no monitoring well is located under the lake. Without much doubt monitoring well 374 (only sampled eight times towards the end of the project) contains water that is representative for this fraction. The DOC of 374 was 4.6 mg/l (δ=0.3 mg/l). The results for 374 show that the water composition is similar to the actual young bank filtrate, but because of the higher age it does not directly depend on surface water quality. It is believed that the water in 374 represents a very old bank filtrate (~25 years).

Furthermore, a hydraulic model of the “Model” group (see NASRI Report 2) proposed that the influence of the older bank filtrate changed during the observation period. Therefore, it is difficult to access initial parameters for the infiltration path in the second aquifer. To provide results, the bulk organic data evaluation of the “Organic” group uses surface water concentration as reference instead, because for most monitoring wells the majority of water is young bank filtrate (retention time < 4.5 months) and the influence of older water is negligible. However, in some datasets slightly different characteristics of the samples, predominantly from 3301, are visible.

Reduction of DOC concentration during infiltration in the second aquifer is displayed in Figure 6. The average DOC mineralization ranges from 30-35% and is increasing with higher retention times. As mentioned, monitoring well 3301 is somehow influenced by older bank filtrate from under the lake and exhibits slightly elevated DOC levels. Presumably, well 3301 receives also portions of young bank filtrate that infiltrated with a short oxic zone under mostly anaerobic conditions. A slower DOC removal under anaerobic conditions explains higher average DOC concentration in well 3301.

Monitoring well 371UP, 3302 and 3303 are dominated by water infiltrating through the top aquifer with retention times of 2.8 to 4 months. During this time 32-34% of the initial surface water DOC is degraded. Water from production well 13 is a mixture of infiltrated water of different age and approximately 25-30% of background groundwater. The background well 3304 shows a relatively low DOC of 2-3 mg/l and dilution reduces the DOC concentration of the abstracted raw water to ~4 mg/l.

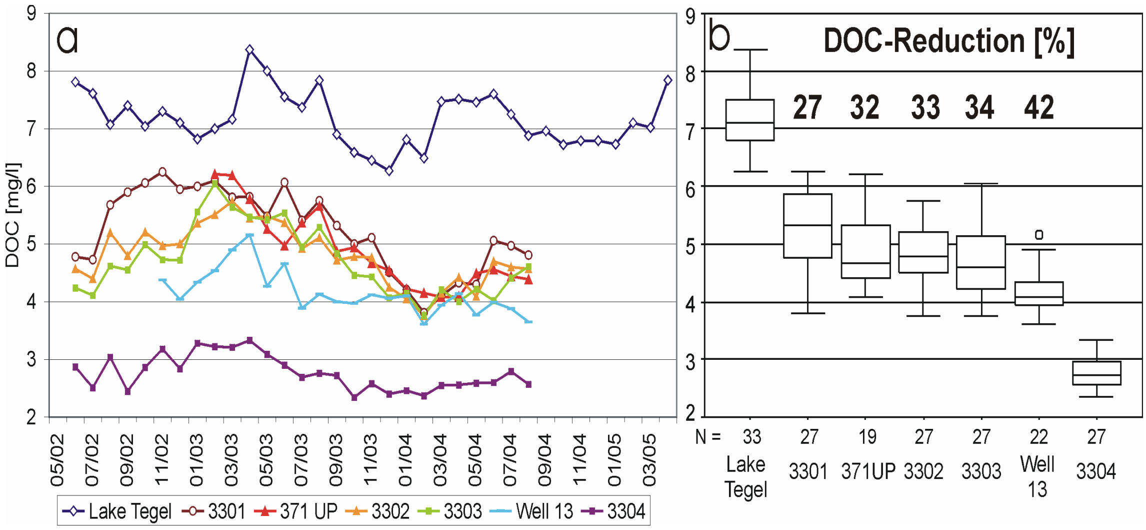


Figure 6a/b Fate of DOC during infiltration to the deep monitoring wells (a: time series; b: box plots)

However, DOC concentrations in the deep monitoring wells showed heavy variations over the observation period (more than 2 mg/l fluctuation). The changing DOC concentrations can not be ascribed to different DOC levels in the surface water. A factor of influence for DOC removal which was confirmed in pilot scale experiments are the dominant redox conditions. It is assumed that the variation in DOC levels in the second aquifer is motivated by changing redox conditions.

During the first sixteen months (05/02 – 09/03) of the observation period the redox conditions in the deeper aquifer were strongly anaerobic with occurring iron and manganese reduction. Nitrate levels were significantly reduced during infiltration (Average NO_3-N: 3302: 0.07 mg/l and 3303: <LOQ). The average nitrate concentration in the surface water was 1.83 mg/l NO_3-N. After summer 2003 the redox status of the transect changed. Summer 2003 was very dry in Berlin and the combination of low water level in Lake Tegel and heavy pumping of the production well pumps led to an expanded zone of unsaturated infiltration under the lake. After passaging the biologically very active water-sediment interface the bank filtrate was aerated again during an unsaturated infiltration. Beginning in October 2003 until June 2004, elevated oxygen and nitrate concentrations were observed in the deeper monitoring wells and the production well (∅-NO_3-N: 3302: 1.16 mg/l and 3303: 0.47 mg/l). During these nine

months the dominant redox conditions at the field site changed from anoxic/anaerobic with Fe/Mn-reduction to oxic. The time series of Figure 6 gives insight to the effect of changed redox conditions. The differences in fate of bulk organics between the two redox conditions are discussed below.

Comparing mineralization of DOC during the oxic and anoxic/anaerobic infiltration period reveals that under both conditions similarly ~3.0 mg/l DOC were removed between surface water and production well. Dilution in the production well is assumed to be constant (~30% background groundwater) and the background monitoring well 3304 shows low DOC-concentrations during the entire observation period (oxic: 2.5 mg/l; anoxic/anaerobic: 2.9 mg/l). Figure 7 proves that the degradation kinetics of DOC, which can be assessed by the monitoring wells between surface water and production well, is different under oxic or anoxic/anaerobic conditions. A more rapid removal of DOC under oxic conditions was observed, whereas anoxic/anaerobic conditions cause a slower but continuing removal. Under oxic conditions, 35% of DOC is degraded from surface water to the first deep monitoring well 3301.

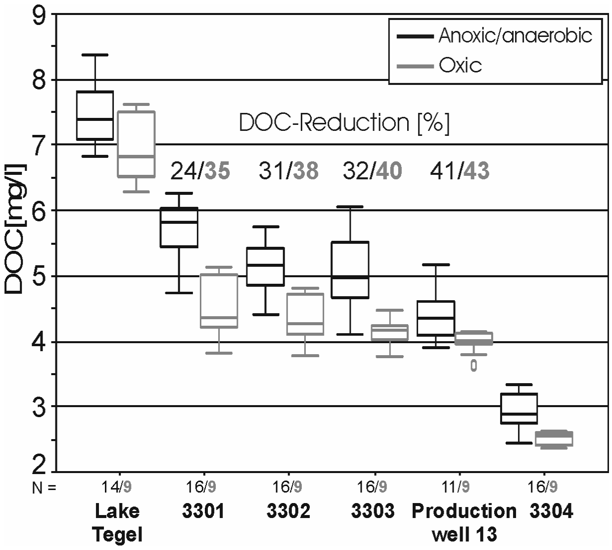


Figure 7 Fate of DOC during infiltration under different redox conditions

During further infiltration the fraction of degraded DOC is increasing by only 5 % (3303) or 8% (Well 13, includes some dilution). Under anoxic/anaerobic conditions only 24% of the initial DOC is degraded in monitoring well 3301. The continuing removal of DOC leads to reduction rates of 32% (3303) and 41% in the production well (Figure 7). In the extracted raw water, the residual DOC-concentrations are comparable.

However, under anoxic/anaerobic conditions the slower process of DOC-mineralization demands the entire retention time, whereas under oxic conditions the efficient removal during initial infiltration is followed by a plateauing of DOC levels and a slower removal. Under both conditions, a similar residual DOC concentration can be achieved, if sufficient retention time is allowed under anoxic/anaerobic conditions. Results demonstrate that regardless of dominant redox state a fraction of 4-4.5 mg/l of residual DOC is not degradable under Lake Tegel field conditions. This is consistent with DOC concentration of the very old bank filtrate in 374.

Based on all results, it is assumed that (sustainable) biodegradation controls the DOC removal and that (non-sustainable) adsorption of DOC to the sediment is minimal.

Evidence is given by the consistency of DOC removal for ~100 years of operation and the higher SUVA of the infiltrated water (see chapter 1.1.1.4). Additionally, Davis (1982) found that DOC is not adsorbed to quartz at neutral pH.

The biological stability of the residual DOC of 4-4.5 mg/l shows that the portion of BDOC in this residual is very small. This is advantageous for the drinking water supply. Despite of the relative high DOC concentration, the organic carbon is not available for biological growth in the public water supply. Furthermore, the results underline the necessity to control and monitor the system of bank filtration regularly, to avoid drastic changes in the subsoil conditions that affect DOC-removal efficiency.

1.1.1.3 Bank filtration-UVA$_{254}$

UV absorption at 254 nm decreases during infiltration along the transect because aromatic and double-bonded organic structures are degraded. Removal rates are slightly lower but comparable to DOC removal rates (Figure 8). In the shallow monitoring wells the UVA$_{254}$ reaches to 60-80% of the surface water. Monitoring well 3310 exhibits a considerably higher UVA$_{254}$ than well 3311, showing a stronger influence of surface water. The very low UVA$_{254}$ of 372 is consistent with low DOC concentrations of this well, which are assumed to be caused by long retention time for this well (Figure 8a).

The UVA$_{254}$ in the deeper wells is in a similar range. The mentioned change in redox conditions also affected the UVA$_{254}$-results. During the oxic period the UV-absorption was slightly lower. But for some wells this effect was superposed by a strong fluctuation of UVA$_{254}$. Particularly, well 3301 and 371UP showed strong seasonal variations of UV-absorption. From summer to late fall, a higher UVA$_{254}$ was measured than during the rest of the year. Contrary to Ziegler (2001), who hypothesized the variations as a time shifted response to the seasonal UVA-changes in the surface water, it is now believed that two different effects might be responsible for the variations.

First, monitoring well 374 (UVA$_{254}$=12.9 1/m; δ=0.3 1/m) proves that older bank filtrate from under the lake has a higher average UVA$_{254}$ than young bank filtrate. Due to heavier pumping of the abstraction well during summer the influence of older bank filtrate on the wells 3301 and 371 UP might be increased, leading to higher UV-absorptions in these samples during summer.

Secondly, due to higher water temperature during summer and fall, the transformation of particulate organic matter (POC) from sediment and the release of fractions of humic like material from the POC could be elevated. Or parts of the minimal fraction of hydrophobic DOC that adsorbed during infiltration to the sediments are released because of the smaller adsorption capacity of the sediments at higher temperatures. However, the small amounts are not detected by DOC-analysis but by UVA, because of the high UV activity of the released material. Schoenheinz et al. 2004 showed on examples from the Elbe river that during periods of elevated water temperatures sediments can release DOC fractions.

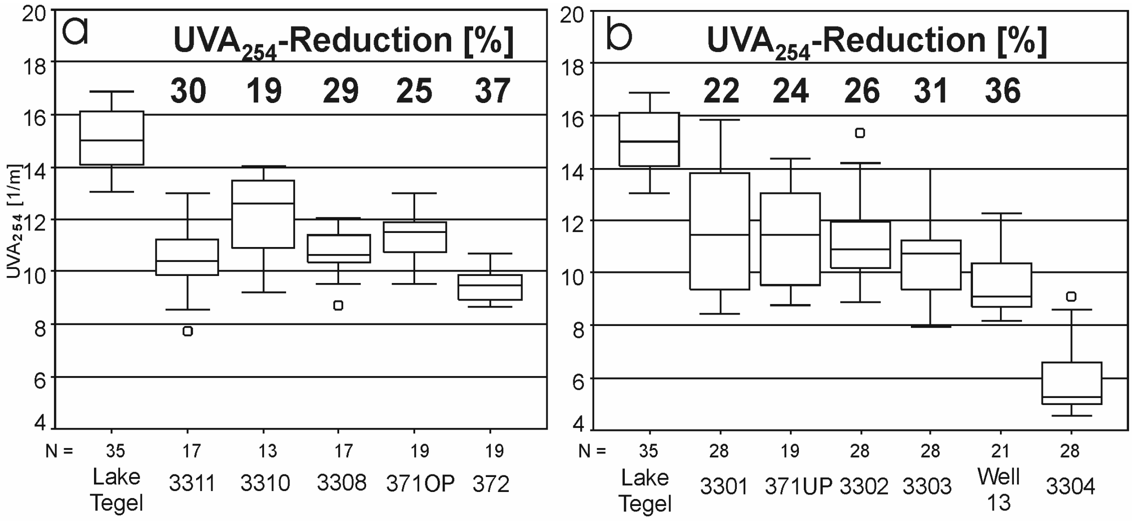


Figure 8 Change of UVA_{254} during infiltration to the monitoring wells (a: shallow wells; b: deep wells)

It remains unclear which effect is responsible for the seasonal variations of UV_{254} in the deeper monitoring wells, but because of results of the hydrogeology group the second explanation seems more likely. The hydrogeology group found out that the influence of older bank filtrate on the deep monitoring wells to be relatively small. The assumption of Ziegler (2002) that seasonal fluctuations in the second aquifer are shifted responses of the surface water quality is unlikely, because the time shift is 8 months (too long) and the variation in the deeper monitoring wells have higher amplitudes than the surface water variations. Therefore, it is assumed that the seasonal change in UVA in the deep wells is caused by temperature effects. Figure 8b displays the heavy variations and the relative low UVA_{254} reduction in 3301 and 371UP. The background groundwater has, consistently with DOC-results, a lower UVA_{254}, leading to some dilution effects in the production well.

The color measured at 436 nm decreased during infiltration from 0.5 1/m (surface water) to average values of 0.3-0.4 1/m in the individual monitoring wells. No seasonal changes or effects were observed.

1.1.1.4 Bank filtration-SUVA

DOC-results and UVA_{254}-measurements can be used to calculate the specific UV-absorbance (SUVA), which reveals more details about the mechanisms of DOC-mineralization because a change in SUVA during treatment or infiltration indicates a preferred removal of aliphatic (SUVA-increase) or aromatic (SUVA-decrease) carbon sources.

SUVA of surface water in Lake Tegel is around 2.1 l/m*mg. During infiltration at the bank filtration site an averaged increase of 5-10% was observed in the shallow monitoring wells. Unfortunately, the shallow monitoring wells fell dry during summer so that recorded SUVA results were mostly measured during winter. The results are often unstable and show high standard deviations. However, existing results indicate that during short aerobic soil passage aliphatic carbon sources are preferentially used. As an exception, well 3311 showed a slightly lower SUVA than the surface water. Monitoring well 3311 is located close to the lake but shows the lowest nitrate levels of all shallow wells. Potentially, more aromatic and double-bond structures are degraded during a partly anoxic infiltration to well 3311. The seasonal variation of SUVA which was reported for the surface water could not be found in the shallow monitoring wells.

The deep monitoring wells also exhibited an increase in SUVA (5-10%) (Figure 9). Very clearly, a seasonal variation of SUVA was found. But the variation did not originate from the time shifted variation in the surface water because in the lake the highest SUVA results were measured during January-March, whereas in the deep wells SUVA peaked during August-December. This time shift of 8 months can not be explained by 3-5 months retention time.

In fact, since SUVA is calculated from UVA_{254} (and DOC) the seasonal variation of SUVA in the deep wells most likely derives from the same effect that is responsible for the variation of the UVA_{254}. Similarly to the discussion of UVA_{254} for 3301 and 371UP, the deep monitoring wells could be influenced by small portions of organic material with a high aromaticity which were released from the sediments because of the higher temperature of the infiltrating water. This would explain the observed effects in SUVA. The assumption that heavier pumping during summer increased the influence of older bank filtrate from under the lake in the deep wells is unlikely for the already mentioned reasons (Chapter 1.1.1.3). However, SUVA of the older bank filtrate was found to be 25% higher than the actual SUVA of the surface water (374: SUVA=2.6 l/m*mg; δ=0.1 l/m*mg).

Because of these uncertainties it is difficult to discuss the SUVA results in the deep aquifer. But in column experiments (see soil column chapter 1.4) it was found that the SUVA decreases during longer anoxic/anaerobic infiltration pointing towards a better removal of aromatic compounds under low redox conditions.

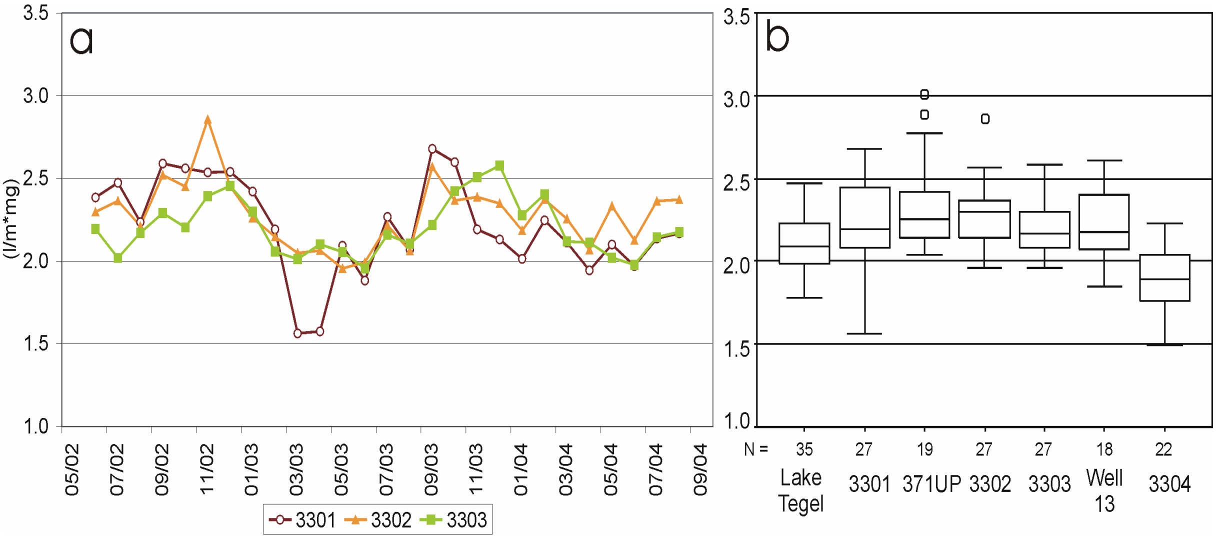


Figure 9 Fate of SUVA during infiltration to the deep monitoring wells (a: time series; b: box plots)

The SUVA of the extracted raw water from well 13 (median: 2.2 l/m*mg) is similar to the surface water. In background groundwater, SUVA was calculated to be 1.9 l/m*mg.

Results also indicate that permanent adsorption of DOC onto clay or particulate organic matter in the sediment is not important. In such a case, lower SUVA results could be expected because aromatic organic compounds tend to be more hydrophobic and prone to adsorption. Therefore, it is not likely that permanent adsorption of DOC to the subsoil occurs.

However, results also show that aliphatic carbon sources are preferentially used during initial aerobic soil passage. Aliphatic compounds are rapidly degraded under oxic conditions. Furthermore, some results point towards a better mineralization of aromatics under anaerobic conditions.

LC-OCD measurements revealed that the changes in SUVA result from the fast removal of the PS-fraction and from a change of aromaticity in the HS-fraction (see soil column chapter1.4). In the online measurement the HS-fraction showed major changes in SUVA, while HS-building blocks and LMA were constant. It is assumed that in the HS-fraction aliphatic side-chains are mineralized quickly, but aromatic and double-bond structures remain for a longer period unchanged. During further infiltration more aromatic structures in the HS-fraction are degraded and the SUVA decreases. In anoxic infiltration, the increase in SUVA is slower. LC-OCD measurements proved that under anoxic conditions the slower removal of PS is responsible for the slower rise of SUVA. In the HS-fraction no initial preferential removal of aliphatic-side chains was observed and the SUVA remained stable during the first 1.6 m of infiltration. Afterwards, the mineralization of aromatics from the HS-fraction leads to a decreasing SUVA.

Generally, it can be summarized that under oxic conditions the degradation of DOC follows more strictly a sequence, where aliphatic compounds are initially degraded and subsequently aromatics. Under anoxic/anaerobic conditions the fate of aromatics and aliphatics seems to be more balanced.

1.1.2 Lake Tegel - LC-OCD

1.1.2.1 Surface water-LC-OCD

Surface water of Lake Tegel was also analyzed regarding the character of dissolved organic carbon using the technique of liquid chromatography with online carbon detection (LC-OCD), also known as SEC-OC (size exclusion chromatography). This analysis allows differentiating between different fractions of DOC, which are mostly defined by size and hydrophobicity. More detailed information on LC-OCD analysis and on interpretation of the obtained chromatograms is described by Huber et al. (1996).

Chromatograms (e.g. Figure 10) are interpreted as follows: The first peak in the chromatogram corresponds to the largest molecular weight fraction, interpreted as polysaccharides (PS; elution time at 35-45 min), the second peak corresponds to humic substances (HS; elution time 52 min) and HS-building blocks (secondary peak; 57 min), and the third to low molecular weight acids (LMA; 62 min). Neutrals and hydrophobic compounds elute after 65 minutes.

Figure 10 displays a characteristic chromatogram of Lake Tegel surface water. Over the time of the project more than 20 monthly measurements of Tegel surface water were conducted. After exclusion of failed and unreliable analysis 16 high quality measurements were selected. To avoid a presentation of all chromatograms, the obtained data was adjusted for retention time and baseline and afterwards mediated.

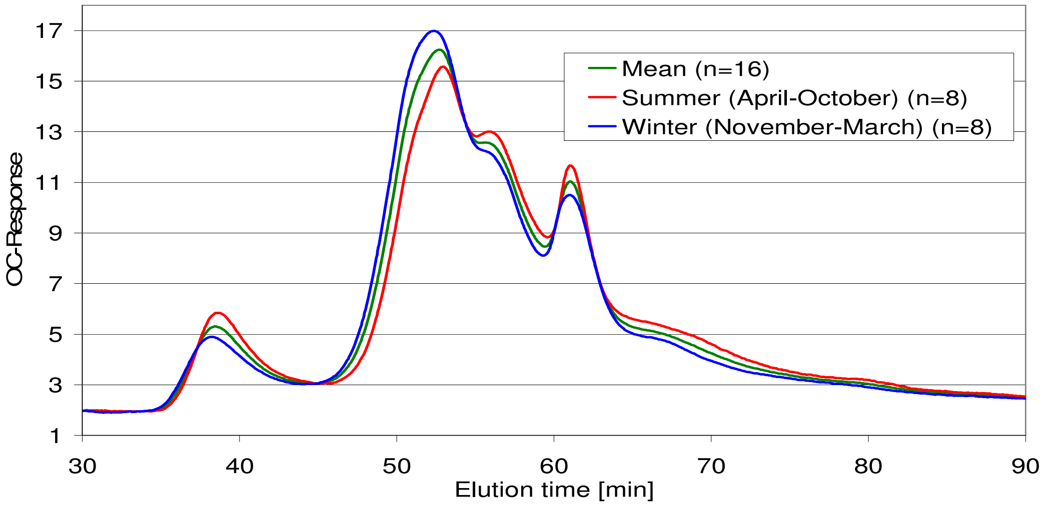


Figure 10 LC-OCD chromatogram of Lake Tegel surface water (seasonal changes)

The mean chromatogram in Figure 10 is the result of pooling all surface water chromatograms from Lake Tegel.

Table 2 gives results on portions of single DOC fractions averaged over the year. Humic substances are the most important fraction in surface water, accounting for ~46% (~3.3 mg/l) of surface water DOC. Other important fractions are humic substances-building blocks and neutrals and hydrophobics accounting for approximately 20-25% of total surface water DOC. Polysaccharides (9%) and low molecular acids (4%) are fractions of minor importance. All portions and equivalent concentrations are given in

Table 2 as a mean from sixteen measurements.

Table 2 Portions and concentrations of different fractions of DOC in Lake Tegel surface water – Differences between the seasons (Summer=April-October; Winter= November-March)

Share of	**Poly-saccharides**	**Humic substances**	**Humic substances-Building blocks**	**Low molecular acids**	**Neutrals and Hydrophobics**
Summer (n=8)	9.5 %	41.1 %	24.1 %	3.5 %	21.8 %
	0.70 mg/l	3.04 mg/l	1.78 mg/l	0.26 mg/l	1.61 mg/l
Winter (n=8)	7.8 %	50.1 %	20.1 %	4.2 %	17.8 %
	0.53 mg/l	3.41 mg/l	1.37 mg/l	0.29 mg/l	1.21 mg/l
Mean (n=16)	8.7 %	46 %	22.1%	3.7 %	19.7%
	0.62 mg/l	3.27 mg/l	1.57 mg/l	0.26 mg/l	1.40 mg/l

During evaluation of the chromatograms it became obvious that the proportions of DOC-fractions change slightly with the seasons. To capture the seasonal change, datasets were clustered into two groups; summer and winter. All chromatograms from April to October were pooled and characterized as summer state and data from November to March formed the winter state. The time periods were defined according to the data.

It was found that during summer, the fractions of polysaccharides, HS-building blocks and neutrals accounted for a higher percentage of the DOC, whereas the importance of humic substances decreased. The fraction of low molecular acids remained relatively stable during seasons at ~4%.

Table 2 and Figure 10 give more insight into seasonal effects on the DOC composition. It remains unclear, whether the decreased share of humic substances during summer derived from a more active biomass and more transformation into smaller molecules or from a higher portion of water from upper Havel in Lake Tegel (enforced operation of the lake pipeline during summer). Additionally, slightly higher DOC concentration during summer shifted the portions. Most probable the three effects (temperature, introduction of more algae associated DOC and a higher influence of Havel water) added up during summer and lead to a shift from humic like material to building blocks and neutrals. Unfortunately, it was not possible to isolate the influences of these effects on DOC composition.

However, there is a high probability that the higher portion of polysaccharides during summer was due to algae blooms. Different literature already described polysaccharide production during algae blooms and formation of extracellular polymer matter (EPM), which falls into the fraction of polysaccharides (Hoyer et al., 1985).

1.1.2.2 Bank filtration-LC-OCD

Figure 11 shows LC-OCD chromatograms of samples from the bank filtration site, and indicates that the character of DOC partly changed during infiltration. The final chromatogram derived from more than 12 measurements over one year by mediation. Under all conditions the fraction of polysaccharides (~0.6 mg/l, ~8.7% of surface water DOC) was most efficiently removed, whereas other fractions (HS, HS-building blocks, LMA and Neutrals) exhibited only partial removal. A seasonal effect (not shown) was observed for the PS concentration in 3310 and 3311. During warmer months a higher percentage of PS was removed. An annual mean of approximately 30% of PS of the infiltrating surface water was found in 3310 and only ~15% in 3311. The more distant monitoring wells did not contain measurable amounts of polysaccharides. LC-OCD results indicate that monitoring well 3310 is dominated by surface water, since the character of DOC corresponds highly to the surface water DOC. Monitoring well 3311 is located under the lake and differs already significantly from surface water regarding DOC-character. This indicates a more bioactive infiltration path or a longer retention time for 3311.

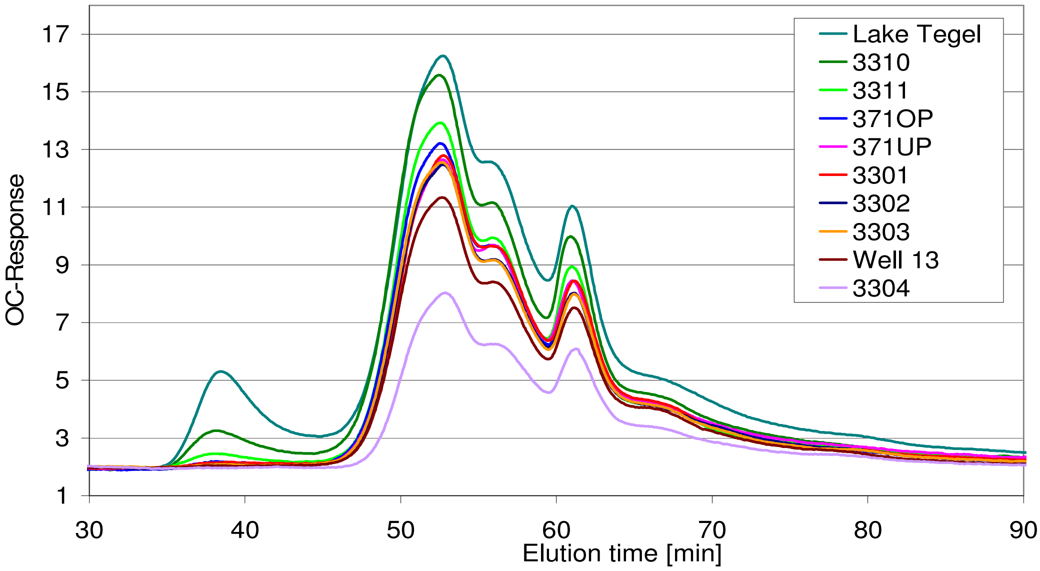


Figure 11 LC-OCD of transect at Lake Tegel (mean, n=12)

For all other fractions, which could be assessed by LC-OCD, decreasing concentrations, but no complete removal was observed during infiltration. The fractions of HS, HS-building blocks, LMA, and Neutrals showed removal rates ranging from 25% to 35% between surface water and monitoring well 3303. The similar removal lead to relatively constant proportions of the fractions regarding total DOC in the monitoring wells. The fraction of humic substances accounted for 46-51% of total DOC (HS-building blocks 22-26%; LMA 4-5%; Neutrals 17-22%). Table 3 gives proportions and concentrations of separate DOC-fractions for different wells. During the observation period, the proportions of DOC-fractions in the monitoring wells remained relatively stable. Potential effects of temporal changes in redox chemistry were not detected by the LC-OCD method because of lacking sensitivity. The fate of single fractions during infiltration is evaluated by comparison of concentrations in the monitoring wells along the infiltration path. Figure 12 displays the changing concentrations.

Plotting concentrations over retention time or infiltration distance did not lead to a clear presentation of the results and was rejected. The reasons for this decision will be discussed shortly. Retention time was not used, because for some wells it could not be determined (e.g. 3310, 3311). For some other wells retention time was strongly changing and was only specified with high standard deviations. The infiltration distance is no significant parameter since the flow velocity of the infiltrating water changes strongly along the transect. Furthermore, several monitoring wells are located on slightly different flow paths (e.g. 3301) which are influenced by small portions of other water types.

Table 3 Portions and concentrations of different fractions of DOC at transect Lake Tegel (n=12)

Share of	**Poly-saccharides**	**Humic substances**	**HS - Building blocks**	**Low molecular acids**	**Neutrals and Hydrophobics**
Lake Tegel	8.7 %	46 %	22.1 %	3.7 %	19.7 %
	0.6 mg/l	3.3 mg/l	1.6 mg/l	0.3 mg/l	1.4 mg/l
3310	4.2 %	50.5 %	23.4 %	4.8 %	17.2 %
	0.2 mg/l	2.7 mg/l	1.2 mg/l	0.3 mg/l	0.9 mg/l
3311	1.8 %	50.4 %	25.2 %	5 %	17.6 %
	0.1 mg/l	2.7 mg/l	1.4 mg/l	0.3 mg/l	1.0 mg/l
371OP	0.6 %	51.1 %	26.3 %	4.6 %	17.5 %
	0.0 mg/l	2.5 mg/l	1.3 mg/l	0.2 mg/l	0.9 mg/l
371UP	0.5 %	47.2 %	26.4 %	4.3 %	21.7 %
	0.0 mg/l	2.2 mg/l	1.2 mg/l	0.2 mg/l	1.0 mg/l
3301	0.8 %	49 %	26.7 %	4.6 %	18.9 %
	0.0 mg/l	2.6 mg/l	1.4 mg/l	0.2 mg/l	1.0 mg/l
3302	0.2 %	50.2 %	26.7 %	4.4 %	18.5 %
	0.0 mg/l	2.4 mg/l	1.3 mg/l	0.2 mg/l	0.9 mg/l
3303	0.4 %	49.9 %	25.2 %	4.4 %	20.1 %
	0.0 mg/l	2.3 mg/l	1.2 mg/l	0.2 mg/l	0.9 mg/l
Well 13	0 %	51.2 %	26.5 %	4.9 %	17.4 %
	0.0 mg/l	2.1 mg/l	1.1 mg/l	0.2 mg/l	0.7 mg/l
3304	0 %	45.6 %	29.6 %	5.8 %	19 %
	0.0 mg/l	1.2 mg/l	0.8 mg/l	0.2 mg/l	0.5 mg/l

However, Figure 12 shows that the decrease of total DOC is mostly due to a different behavior of separate DOC-fractions. 0.6 mg/l polysaccharides are removed very fast by instant mineralization in the oxic infiltration zone. The results of soil column experiments support the assumption of a rapid biodegradation for this DOC-fraction, because in an abiotic column only minor filtration effects were observed (see soil column chapter 1.4).

The fraction of humic substances is commonly regarded as mostly non-biodegradable, but results for the bank filtration transect Tegel show that 30% of this fraction was removed. Already during short term infiltration (3310) significant amounts of humic substances (0.6 mg/l) are attenuated. In the deeper aquifer the removal continues, but some portions of humic substances-rich water were introduced to the flow path from under the lake. This was obvious for monitoring well 3301, which shows considerably higher amounts of humic substances. Finally, 2.1 mg/l humic substances were found in abstraction well 13. The background groundwater concentration for humic substances was low with 1.2 mg/l.

The fraction of HS-building blocks remains relatively stable during infiltration after some removal close to the bank. Concentration level remained between 1.2 mg/l and 1.4 mg/l. A slight influence of older bank filtrate from under Lake Tegel may be indicated by a concentration increase in 3301. It is possible that fragments of partly mineralized humic substances add to this fraction. This would explain the constant concentration during further infiltration. Generally, all smaller DOC- fractions might be replenished by products of humic substances degradation. The background concentration of HS-building blocks is 0.8 mg/l. This means that HS-building blocks account for a slightly higher proportion of background DOC (~30%) compared to 22-26% in surface water and bank filtrate.

Low molecular acids are a very small fraction in Lake Tegel surface water, since only 4-5% of the DOC belongs to this fraction. LC-OCD results indicate that the importance of this fraction is not changing during infiltration. The concentrations remain at 0.2-0.3 mg/l. Despite of an apparent stability of this fraction the turn over might be high since LMA are classical mineralization intermediates and not known to be extremely persistent.

The fraction of neutrals and hydrophobics contains different organic molecules that migrate for different reasons slowly through the size exclusion chromatography column. Small sized molecules, hydrophobic and amphoteric organic compounds show up in this portion of total DOC. Therefore, this fraction is not very well defined. However, during infiltration a considerable amount of neutrals is removed instantly (0.5 mg/l). Afterwards the concentration remains stable at around 0.9 mg/l. Background concentration is low with 0.5 mg/l.

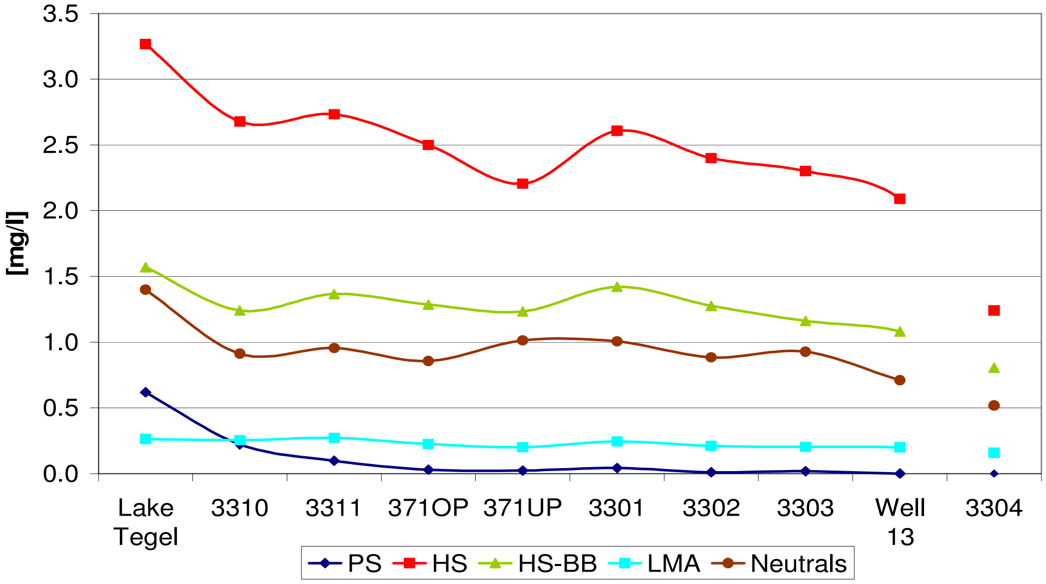


Figure 12 Concentrations of the different fractions of DOC at transect Lake Tegel

However, the LC-OCD analysis reveals that the changes in DOC-character during infiltration have not been dramatic but present. The most important difference between surface water and bank filtrate is the removal of the PS-fraction. For other portions of DOC more quantitative effects than qualitative changes were observed. Results are consistent with total DOC measurements. Furthermore, LC-OCD chromatograms of bank filtration site Tegel were comparable to the chromatograms obtained from other studied field sites and from soil column experiments. An evaluation of removal kinetics for DOC-fractions will be included in the soil column section (chapter 1.4), where exterior influences are minimized and retention times are definite.

1.1.3 Lake Tegel - AOI results

1.1.3.1 Surface water-AOI

Long term AOI-monitoring confirmed seasonal changes of AOI-concentration in Lake Tegel. Since 1998, the AOI in Lake Tegel surface water is measured in the Department for Water Quality Control of the TU Berlin. Figure 13 shows all measured data of the last seven years. Surface water AOI concentration was found to be highly variable over the year. During six of seven years, higher AOI concentrations were measured during late summer and fall. It is assumed that these seasonal changes derive from variations in dilution of sewage treatment plant effluents that are discharged into Lake Tegel.

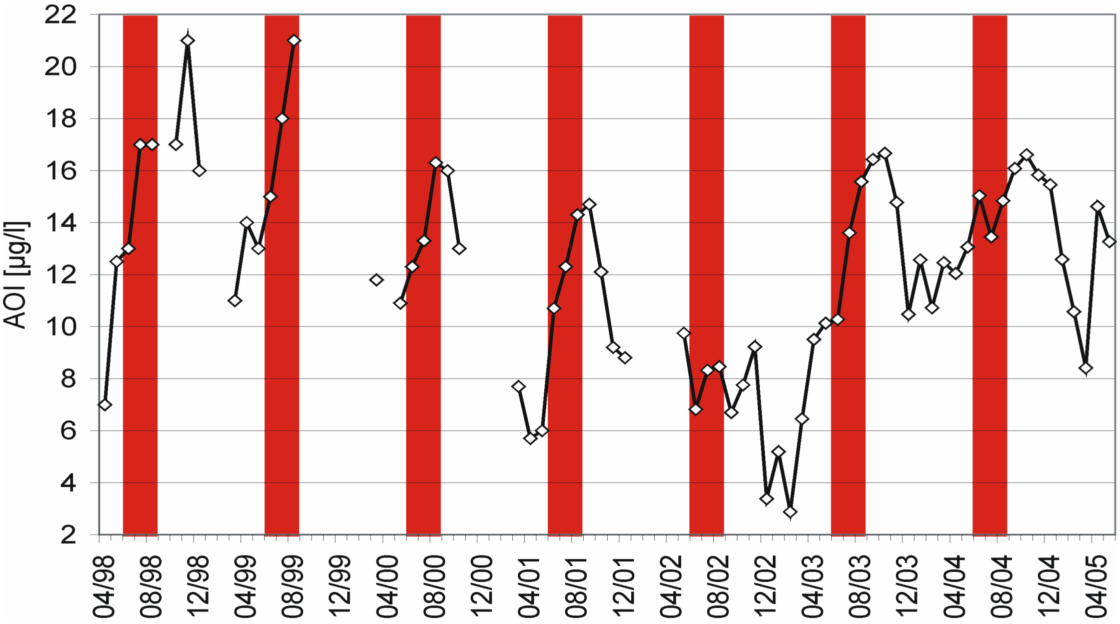


Figure 13 AOI concentration in Lake Tegel (1998-2005, summer months June, July, August marked)

From 1998 to 2001 the time series is incomplete, but available datasets show seasonal trends. During these four years, the average lake AOI concentration decreases and the peaks during summer show lower concentrations. In October 2001, the lake pipeline was reactivated and during the following year very low AOI concentrations were monitored. The dilution effect of the lake pipeline was enhanced by a very cold and wet summer in 2002. Here, no increased AOI levels during late summer and fall were found. With start of 2003 the AOI concentrations started to rise in Lake Tegel surface water. This increase corresponded well with higher concentrations of other waste-water borne contaminants (NASRI Report 1, section 1.4) and was caused by the extension of the sewage treatment plant (STP) Schoenerlinde. The effluent amount of STP Schoenerlinde increased considerably to more than 80.000 m^3/d. In 2003 and 2004, the known seasonal variations were observed despite of strong dilutions by the lake pipeline. Seven measurements in the upper Havel (01/2004-08/2004) confirmed that the AOI concentration of the diluting water is considerably lower than in Lake Tegel (Median=6.8 µg/l, δ=2.1 µg/l). Therefore, it can be concluded that the AOI-peaks are reduced by heavier dilution during summer. Without operation of the lake pipeline much higher concentrations during summer can be expected.

1.1.3.2 Bank filtration-AOI

Within the NASRI-project, AOI concentrations of samples from monitoring wells of transect Tegel were measured over 27 months. For a better presentation the transect was divided into shallow monitoring wells with mostly oxic conditions and deep monitoring wells with primarily lower redox potentials. Figure 14 presents AOI concentrations of the shallow wells, where fewer data is available because of dry periods during summer (3311; 3310) or late installation of the well (371OP). Therefore, this data needs to be interpreted carefully if no complete seasonal cycle was recorded.

For two of the shallow wells with retention times of less than a month (3310 and 3308) it was found that AOI concentrations corresponded closely to the surface water concentration. During some periods, the concentrations in the wells exceeded surface water AOI-concentrations. Overall, the available data for well 3310 and 3308 show, that AOI-levels were only reduced by 12% and 20%, respectively. Monitoring well 3311 displayed a relatively strong influence of surface water with comparable AOI levels during 2002 and early 2003. After the summer of 2003 AOI levels in 3311 were noticeably lower than in surface water. Monitoring well 3311 exhibited an AOI elimination of ~51%. This high elimination rate is caused by the predominant redox conditions in 3311. Contrary to 3310 and 3308, clear denitrification occurred in 3311. Despite of a short retention time and the presence of oxygen, nitrate concentrations in 3311 are significantly lower than in the other two wells and the surface water. Denitrification and AOI-mineralization probably occur in micro-anoxic compartments of the soil matrix in absence of oxygen.

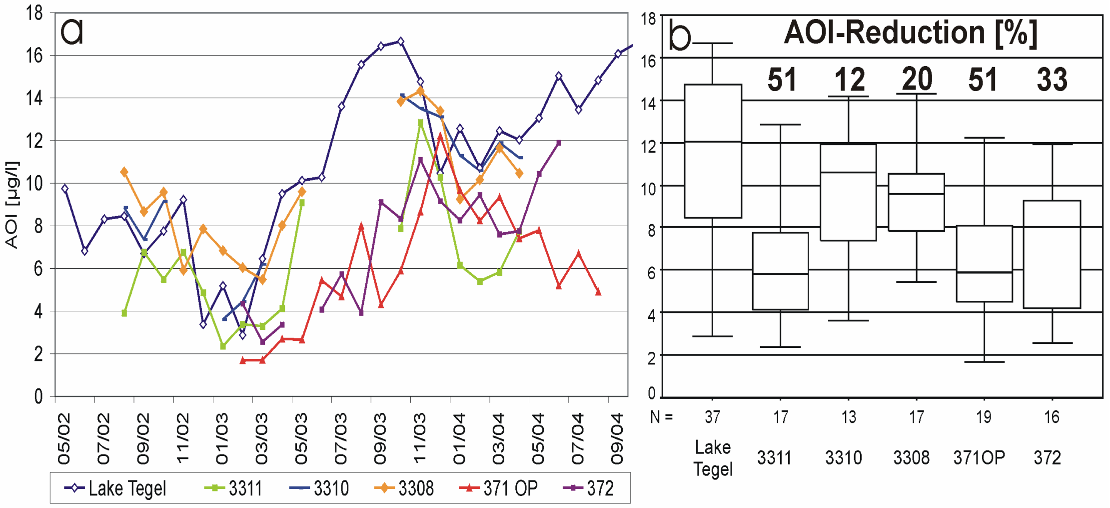


Figure 14 Fate of AOI during infiltration to the shallow monitoring wells (a: time series; b: box plots)

For shallow monitoring wells with longer retention times (371OP=> 1.1 months, 372=> 3.3 months), AOI-reduction rates of 51% and 33% were found (Figure 14). AOI-concentrations were highly variable, but did not follow necessarily the surface water concentration. It is unlikely that the increase of AOI-concentration in late summer 2003 was only caused by higher AOI-levels of Lake Tegel since spring 2003. In this case, retention times would propose an earlier peak. But the peak-period of AOI in 371OP and 372 occurs simultaneously with the already mentioned breakthrough of higher oxygen and nitrate levels to deeper and more distant wells from October 2003 - May 2004 (NASRI Report 1). Monitoring wells 371OP and 372 showed strong indications of occurring denitrification before and after this breakthrough. Until October 2003, no nitrate was found in 371OP and only low nitrate levels in 372 were observed. From October 2003, nitrate levels increased in both wells to surface water concentration before returning to the former low levels in June 2004. Fate of AOI in both wells indicates an association between these two parameters. During periods of high nitrate levels (missing denitrification), more AOI breaks through. The data also show that occurring denitrification seems to be more important for an effective AOI removal than longer retention times. Unfortunately, the effect of increased surface water concentration could not be quantified for the wells because it was superposed by the stronger effect of changing redox conditions.

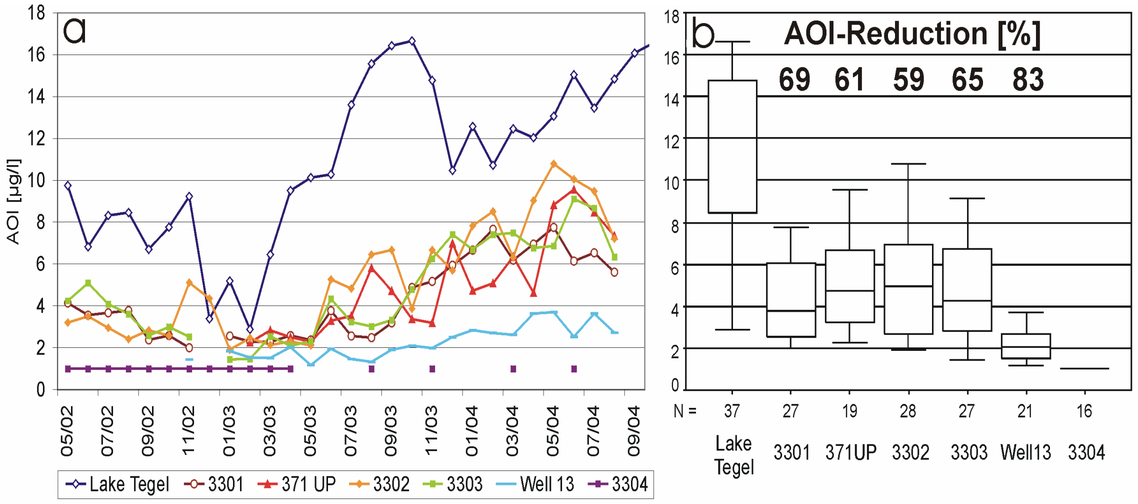


Figure 15 Fate of AOI during infiltration to the deep monitoring wells (a: time series; b: box plots)

Results for the deeper monitoring wells are depicted in Figure 15. In the deep aquifer at the bank filtration site Tegel, a relatively efficient degradation of AOI takes place under mostly anoxic/anaerobic conditions. Figure 15 shows that at low redox potentials, an AOI degradation of 60-70% is possible. AOI concentration of the background groundwater at the bank filtration site is very low (<1 µg/l) and the mixture leads to an AOI-concentration in the extracted raw water of 1-4 µg/l.

The time series of AOI measurements showed an increase in concentrations in the deep monitoring wells starting in June 2003. It is assumed that higher AOI levels are partly caused by changes of the surface water concentration. The deep wells (3301, 3302, and 3303) react approximately three months later with an increase in AOI-concentration. This retention time is similar to the one that was proposed by the hydrogeology group from FU Berlin (NASRI report 1). Furthermore, changed redox conditions allowed an easier break through of AOI. Hydrogeological effects which were explained earlier caused elevated nitrate levels in the deep wells (3301=>02/04-05/04; 3302=>11/03-06/04; 3303=>01/04-06/04). The two effects of rising surface water concentration and higher redox potentials could not be quantified separately, but it is believed that both effects add to the observed increase of AOI in the second aquifer. Measurements in abstraction well 13 confirm that changes also affect the raw water. A comparison of AOI levels in well 13 reveals an increase of 200-300% between the years 2002 and 2004. It is difficult to predict future AOI levels in the transect and abstracted water, but it can be summarized that degradation of AOI is more effective in soil passages with low redox potential. A general inverse correlation between AOI removal and redox potential seems to be valid. This inverse correlation most probably originates from the initial step of AOI-mineralization - reductive dehalogenation. It is known that degradation of halogen substituted organics is more effective in soil passages with low redox potential (Mohn&Tiedje, 1992). Therefore, low water level in

Lake Tegel and heavy pumping over longer periods should be avoided to guarantee low AOI concentrations in the bank filtrate.

1.1.4 Lake Tegel - AOBr results

1.1.4.1 Surface water-AOBr

AOBr concentration in Lake Tegel showed seasonal variations during the observation period (Figure 17). Higher concentration of AOBr during late summer and fall were observed and confirmed findings of earlier monitoring events (1998-2000). Contrary to AOI it is believed that the origin of AOBr in Lake Tegel is not mainly discharged waste water, but AOBr is also produced during algae blooms in the lake. Within the project, it was found that AOBr in Lake Tegel probably originates from three sources:

First, the AOBr load of the effluent of STP Schoenerlinde, which is relatively constant. Seven measurements (01/2004-08/2004) proved that the AOBr concentration of treated effluent, that is discharged via Nordgraben and Tegler Fließ into Lake Tegel, is relatively constant (Median=7.6 µg/l, δ=0.9 µg/l). The Nordgraben contains to a high percentage (65-90%) effluent of STP Schoenerlinde and is not prone to algae blooms (body of flowing water). It can be assumed that the share of AOBr which is introduced into Lake Tegel by the Nordgraben is constant and mainly of anthropogenic origin (disinfectants, flame retardants etc.).

During the same period (01/2004-08/2004) an increase of AOBr in the upper Havel was monitored (Median=9.4 µg/l, δ=1.7 µg/l, n=7). Water from the upper Havel is pumped to the northern end of Lake Tegel by the lake pipeline and represents more than 50% of the influent to Lake Tegel in the summer months. The upper Havel is a strongly eutrophic, slow flowing water body with algae blooms during summer. Therefore, it can be expected that the AOBr content of the upper Havel follows a seasonal pattern and that a share of AOBr is introduced by the lake pipeline to Lake Tegel. The origin of AOBr from the upper Havel is probably anthropogenic and algae associated with seasonally changing portions.

The third source for AOBr in Lake Tegel is production in the lake by algae. The build up of this fraction is strongly dependent on diverse factors that affect algae blooms (temperature, light, nutrients). It occurs predominantly during late summer.

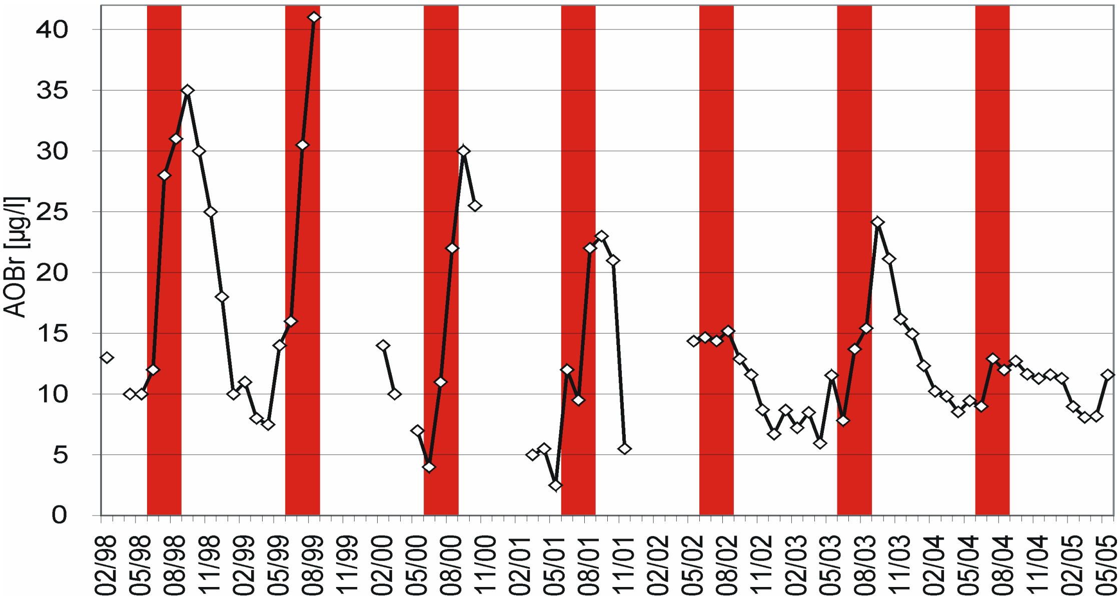


Figure 16 AOBr concentration in Lake Tegel (1998-2005, summer months June, July, August marked)

Figure 16 displays AOBr-concentrations of Lake Tegel which have been measured at the DWQC at TU Berlin since 1998. A clear seasonal variation can be recognized. Overall the peak concentrations measured in earlier projects (1998-2001) were not found during the NASRI-project. The highest concentrations in the observation period were measured during summer 2003. It is assumed that the measured peaks consisted to a high percentage of algae associated AOBr. During summer 2002 and 2004 no strong AOBr peaks in the surface water were observed, but the concentration increased slightly by 5-8 µg/l. During winter the AOBr concentration in the lake drops to 5-8 µg/l. This level is consistent with the AOBr concentration of the treated effluent. Therefore, the AOBr load of the lake during winter is probably of anthropogenic origin.

1.1.4.2 Bank filtration-AOBr

The fate of AOBr in the bank filtration process shows similarities to the behavior of AOI. Averaged for all monitoring wells removal rates were slightly lower. The observations revealed that AOBr concentrations in monitoring and abstraction wells are mainly dependent on surface water concentration and dominant redox conditions along the infiltration path. Overall, the AOBr-data set is difficult to interpret because some peaks in bank filtrate could not be linked to certain factors of influence. Furthermore, it is presently not clear whether anthropogenic and algae associated AOBr behave similar during infiltration.

Shallow monitoring wells with low retention times (<1 month) and oxic conditions showed very low removal rates (3310=> 9%, 3308=> 14%). For both wells, the data point towards a break through of the very high concentrations of the summer peak in fall 2003 (Figure 17). Unfortunately, data points for most summer months are missing. In well 3311, which has similar retention times but lower oxygen and nitrate levels, only 48% of surface water AOBr was found. This indicates a redox sensitivity of AOBr removal, similar to the process described for AOI.

For the more distant shallow monitoring wells 371UP and 372 removals of 45% and 24% were observed, respectively. The better reduction in 371UP is caused by a lower average redox potential of this well. In both wells no real break through of the surface water AOBr peak of 2003 was observed and the higher AOBr-concentrations during fall and winter of 2003/04 are assumed to be connected with the described change in redox conditions during this period.

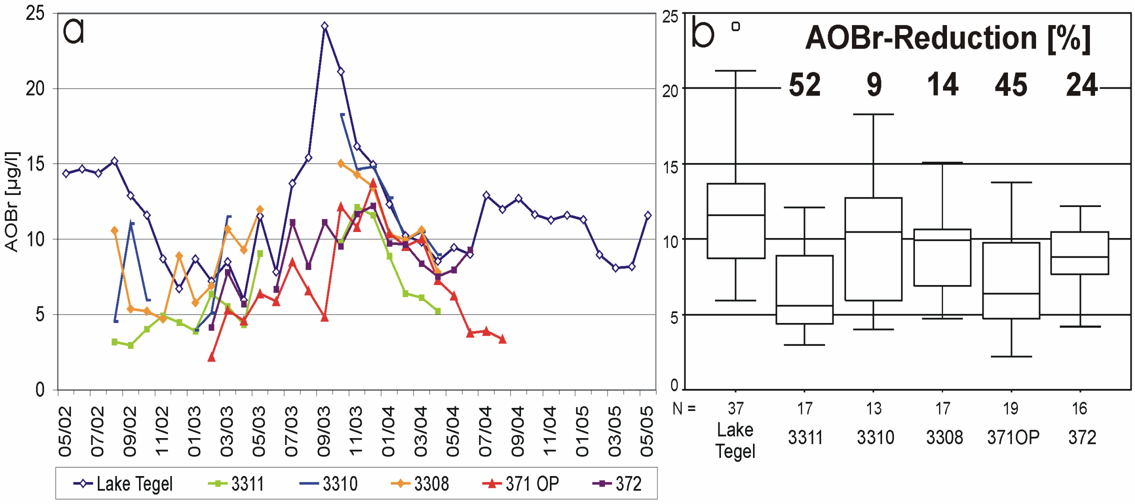


Figure 17 Fate of AOBr during infiltration to the shallow monitoring wells (a: time series; b: box plots)

Deeper monitoring well with mostly lower redox potentials showed reduction rates ranging from 50-70% (Figure 18). The abstracted raw water contained only 21% of surface water AOBr. Despite of an averaged high removal rate some of the deep wells exhibited a very low removal during certain periods. Particularly, during summer 2003 and summer 2004 the wells 3302 and 3303 showed AOBr concentrations that were comparable to surface water concentrations measured 3-4 months earlier. During these periods a considerably lower AOBr-removal took place. AOBr concentrations in monitoring well 3301 and 371UP increased only during the period of oxygen and nitrate break trough (09/03-06/04). This underlines the redox sensitivity of AOBr mineralization.

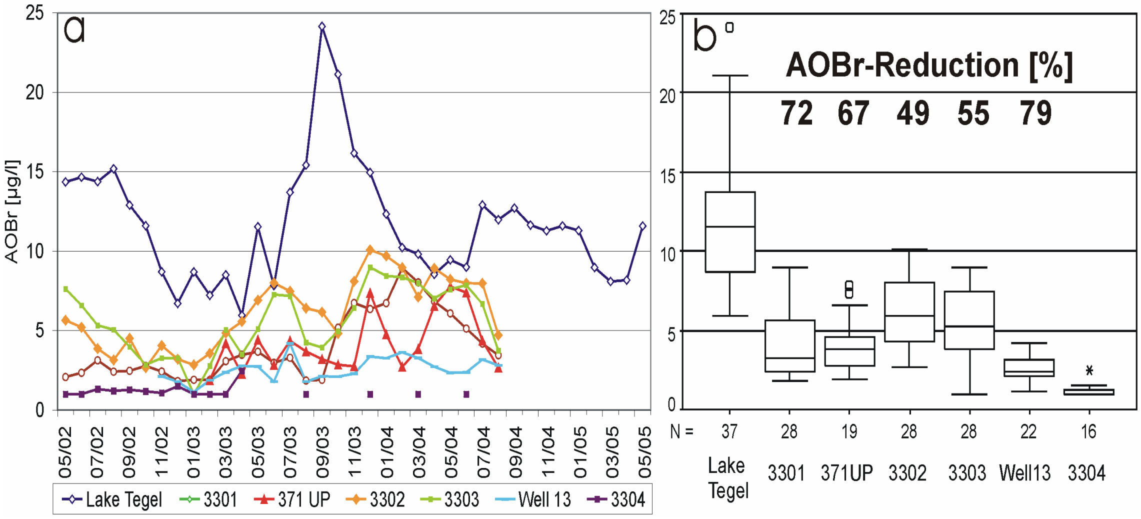


Figure 18 Fate of AOBr during infiltration to the deep monitoring wells (a: time series; b: box plots)

Data of the transect Tegel does not allow strong statements about the degradability of the two fractions of AOBr. But the strong summer peak of 2003 was only found in the shallow oxic monitoring wells. AOBr-concentrations in the deeper wells did not exceed the winter level of AOBr in Lake Tegel. In combination with data from other field sites the conclusion arises that the seasonal fraction of AOBr seems to be easier degradable than the anthropogenic fraction. Clearer results supporting this assumption were measured at transect Wannsee and the artificial groundwater recharge facility in Tegel (chapter Wannsee =>1.2, GWA =>1.3).

1.1.5 Lake Tegel – Trace pollutants results

1.1.5.1 Surface water-Trace organic compounds

Five different trace organic compounds were monitored in the surface water of Lake Tegel from May 2003 to June 2005. Iopromide, Sulfamethoxazole and three isomers of NDSA were selected. All five compounds are of anthropogenic origin and indicate an influence of treated waste water or a different type of contamination. Therefore, the pollutant level depends on the water quality of the discharging water bodies. The concentration in Lake Tegel is a function of the load discharged by Nordgraben (and Tegeler Fließ) and upper Havel (lake pipeline) since other sources for these compounds to Lake Tegel are not known. For the five compounds it is assumed that attenuation in surface water is of minor importance. All compounds are persistent and were not efficiently removed in sewage treatment plants. A photosensitivity is not described for one of the compounds.

Consistently, earlier studies found that the X-ray contrast agent Iopromide and the bacteriostatic Sulfamethoxazole originate mostly from the effluent of treatment plant Schönerlinde and enters the lake via Nordgraben and Tegler Fließ (Wischnack, 2000;

Hartig, 2000). Measured concentrations in the upper Havel were considerably below the contamination level of the Nordgraben. Isomers of the naphthalenedisulfonic acid were reported with highly variable concentrations in the effluent of STP Schönerlinde and in river Havel (Storm, 2002). The compounds are widely used and often found in the aqueous environment. However, Nordgraben and Tegeler Fließ showed generally higher concentrations than the Havel, pointing toward a higher pollutant load originating from the sewage treatment plant.

Figure 19 presents the concentrations of the target compounds in Lake Tegel during the observation period. All selected compounds were continuously detected in changing concentrations in surface water samples in front of the transect. Concentrations ranged from 50 ng/l to nearly 2000 ng/l for the different trace substances. A strong seasonal variation could not be determined, neither was a clear trend observed for one of the compounds. The results have to be interpreted with the knowledge that the concentration in Lake Tegel depend strongly on the quality of the effluent of the treatment plant Schönerlinde. Earlier studies demonstrated that the concentration of pollutants in the effluent varies highly, even on a daily basis (Storm, 2002; Hartig 2000). The level of pollution is smoothed during retention times in the receiving waters and in the surface water treatment plant Tegel. But nevertheless, it is possible that the pollution in front of the transect varies with a high frequency which can not be reproduced with monthly sampling events. The spatial variation of the substances in Lake Tegel was not determined in this study.

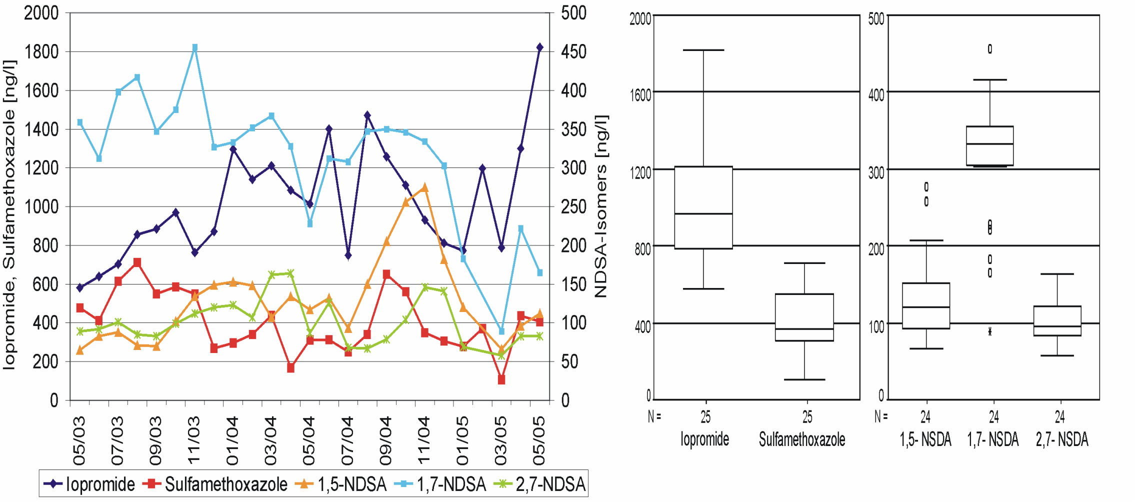


Figure 19 Trace pollutant concentration in Lake Tegel

The X-ray contrast agent Iopromide was detected in Lake Tegel with a median concentration of 969 ng/l (δ=297 ng/l, n=25). This is consistent with concentrations reported by Schittko (2004). Overall, concentrations were highly erratic with a slight trend to higher levels towards the end of the monitoring period.

The antibiotic drug Sulfamethoxazole showed median contamination levels of 371 ng/l (δ=153 ng/l, n=25). For this compound, slightly higher concentrations during the summers of 2003 and 2004 pointed toward a possible seasonality. The general contamination level in Lake Tegel did not change during the observation period.

Isomers of naphthalenedisulfonic acid were monitored for 26 months in surface water. Median concentrations were 96 ng/l (δ=30 ng/l, n=24) for 2,7-NDSA, 119 ng/l (δ=55 ng/l, n=24) for the 1,5-Isomer, and 334 ng/l (δ=83 ng/l, n=24) for 1,7-NDSA. These results differ considerably from monitoring results (n=7) obtained in 1999 and 2000 by Storm (2002). Compared with these results the concentrations of the 1,5- and the 2,7-Isomer were reduced by 40-50%, whereas concentrations of the 1,7-Isomer increased significantly to 150%. Time series of 2002-2005 demonstrated a decrease in contamination levels for the 1,7-Isomer toward the end of the monitoring, but it remains unclear whether this trend is going to continue. The 1,5-Isomer concentration peaks during summer and fall 2004 but returns to base level in winter.

Unfortunately, attempts to correlate trace compound concentrations in front of the transect to other waste-water indicators like Boron, Chloride, or electric conductivity failed on monthly basis. Presumably, the concentrations of the compounds in waste-water varies highly, so that the waste-water portion in front of the transect is no appropriate measure for trace pollutant concentration. But, on a more general long term basis the waste water portion and the pollution level for some single compounds behave similar. For instance, the NDSA-isomers concentrations increased in the surface water with the enlargement of STP Schoenerlinde in spring 2003.

1.1.5.2 Bank filtration-Trace organic compounds

Monitoring of infiltration behavior of the single compounds Iopromide, Sulfamethoxazole and different naphthalenedisulfonic acids had been started in spring 2003, providing data for the time period May 2003 to August 2004. The monitoring showed that these trace organic compounds which stand for different groups of persistent pollutants behave differently during infiltration. For some compounds, an influence of the redox conditions on the degradability could be revealed.

Iopromide occurred in the highest concentrations in surface water. Due to the fact that Iopromide as a triiodinated benzene derivate is part of the bulk parameter AOI (share in surface water ~5%), it was expected that the removal mechanisms for both parameters are similar. This was not confirmed. Contrary to the fate of AOI (see chapter AOI=>1.1.3) Iopromide showed a very good removal (99%) along the infiltration pass to the production well independently from redox conditions. At the bank filtration site Tegel Iopromide concentrations were reduced from the lake (969 ng/l, n=25, σ=297 ng/l) to the first observation well 3310 (80 ng/l, n=4, σ=75 ng/l) by 91%. In the last monitoring well in front of the production well (3303) sixteen measurements resulted in one measurement above limit of quantification (LOQ) and two detections under the limit of quantification. In the other 13 samples no Iopromide was detected. The limit of quantification for Iopromide was 20 ng/l. Detected traces below LOQ were entered into the data base with a concentration of half the LOQ (10 ng/l). Summarizing, more than 99% of surface water Iopromide was attenuated during soil passage at Tegel bank filtration site. Figure 20 displays the measured concentrations in the different monitoring wells. Only surface water results were included, that correspond to the measurements in the wells. These results did not point towards a difference in attenuation efficiency at different redox conditions. The break through of oxygen and nitrate in fall and winter 2003 did not affect removal performance. However, Iopromide is effectively removed during initial infiltration at the water- soil interface.

From the field data it remains unclear whether the attenuation of Iopromide is based on degradation or metabolization. Results from soil-column experiments (soil column chapter => 1.4) where the removal of Iopromide was compared with the reduction of AOI during infiltration showed that Iopromide and AOI behave different of during soil passage. It was found that a high percentage of the Iopromide molecule is altered (partially transformed) but not mineralized during the first part of soil passage. A complete mineralization is probably more efficient under anoxic/anaerobic conditions, as showed in the AOI-section (see chapter 1.1.3). Lopromide was not detected in background groundwater.

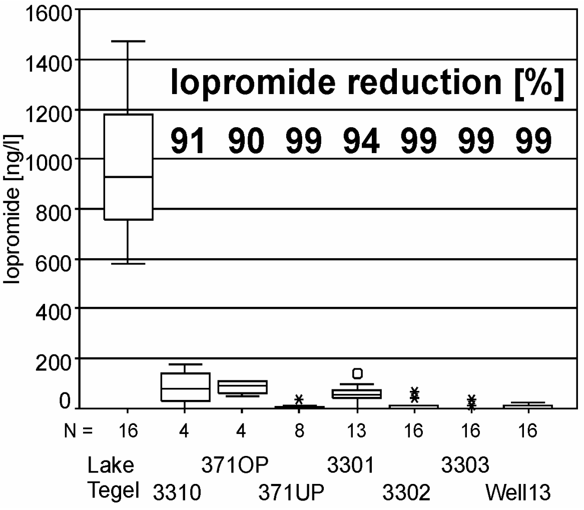


Figure 20 Fate of Iopromide during infiltration at the bank filtration site Tegel

The effluent concentration of the bactriostatic Sulfamethoxazole in Berlin treatment plants varies between 370-1200 ng/l. Because of its high stability it is also found in the surface waters at bank filtration sites. Sulfamethoxazole displayed an efficient removal during infiltration at bank filtration site Tegel, where it is degraded to approximately 25% of the initial concentration (monitoring well 3303). The concentration in the drinking water well is only 7% of the surface water concentration due to attenuation and dilution with non-polluted background groundwater (Figure 21). The compound was not found in background ground water. The degradation of Sulfamethoxazole seems to be redox dependent. Unfortunately, only 4 measurements of the oxic monitoring well 3310 (retention time <1 month) were conducted, because this well fell dry during summer. Higher concentrations of Sulfamethoxazole in 3310 compared to the surface water are most probably due to short term variations in surface water, which were not captured by monthly sampling events. However, data indicates no efficient removal during initial oxic infiltration. Consistently, with other field sites and column experiments, a removal is more efficient under anoxic/anaerobic conditions in the deeper monitoring wells (chapter Wannsee => 1.2 and soil columns =>1.4). The low concentrations in 371UP and 3301 are probably due to a cumulative effect, since these wells are characterized by very low redox potentials and some influence of older bank filtrate (NASRI Report 1, Chapter 1.4.5.). Figure 21a also shows higher Sulfamethoxazole concentrations in the monitoring well 3301, 3302 and 3303 from fall 2003 to spring 2004. It is assumed that the change in redox conditions (indicated by the break through of nitrate) during this period is responsible for the restricted attenuation and the higher concentrations. But it can not be ruled out that higher concentrations in surface water from 07/2003 to 11/2003 also play a role for the observed higher concentrations in the subsoil. Therefore, the consequences of a changed redox system for Sulfamethoxazole reduction can not be isolated. But the conducted research points towards a better removal of Sulfamethoxazole under anoxic/anaerobic conditions. This is furthermore consistent with findings of Schmidt et al. (2004) at other bank filtration sites in Germany.

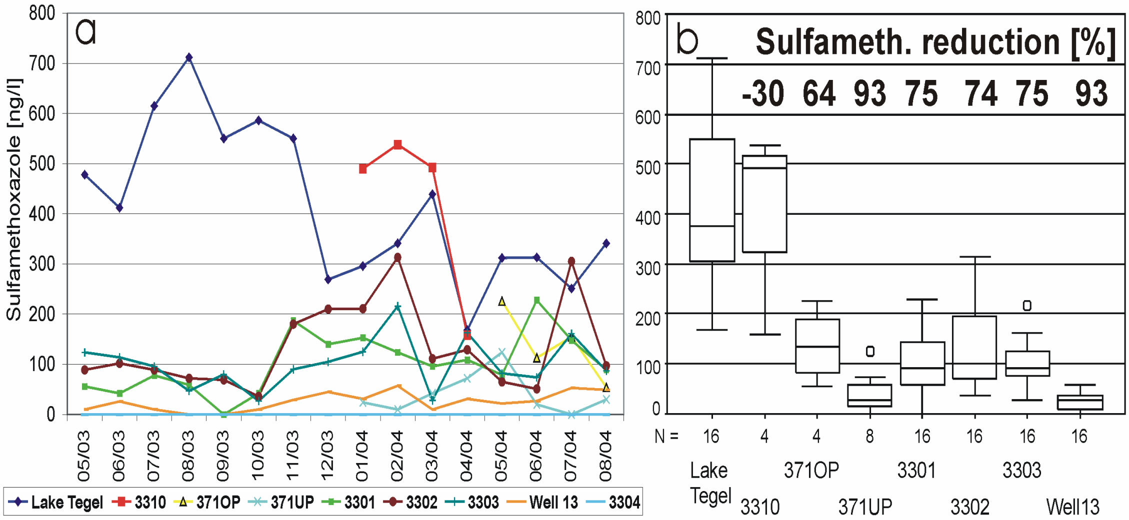


Figure 21 Fate of Sulfamethoxazole during infiltration at the bank filtration site Tegel (a: time series; b: box plots)

Naphthalenedisulfonates (NDSA) are well known polar contaminants of treated waste water and surface water. The different isomers have nearly similar chemical properties, but show a different degradation behavior. Within this study, the 1,5-, 1,7-, and the 2,7-NDSA isomers were monitored during infiltration process. It needs to be mentioned that all three isomers were present in the background groundwater in concentrations that were slightly lower or similar to the concentrations on the surface water influenced side of the well gallery. These pollutions most likely originate from Lake Flughafensee. Since the behavior of the isomers during infiltration differs, the results are presented subsequently.

In contrast to Iopromide and Sulfamethoxazole, the 1,5-naphthalenedisulfonic acid was not efficiently degraded at the bank filtration site Tegel. Concentrations of the very stable 1,5-naphthalenedisulfonic acid remained nearly constant throughout the infiltration process. The initial concentration only decreased by 15-20% during ~4 months of infiltration to the production well. One exception is the monitoring well 3301 which shows slightly lower concentrations of 1,5-NDSA. It is believed that this is partly due to some dilution with older bank filtrate. Furthermore, the data pool for this well is missing data sets for 02/2004-03/2004 which would probably increase the median concentration for this monitoring well. The time series show that during the observation period the concentration of 1,5-NDSA increased in surface water (Figure 22a). All monitoring wells reacted on the higher surface water concentration in order of their retention times. The time frames were consistent with the proposed retention times of the hydrogeological group (compare NASRI Report 1, Chapter 1.4.5.). This indicates that the retardation of NDSA is insignificant compared to an ideal tracer. The inefficient removal of 1,5-NDSA is consistent with findings of Stüber et al. (2002) who reported 1.5 NDSA as very stable and persistent in waste water treatment plants. These results proof that 1,5-NDSA is very poorly biodegradable and it can not be expected to eliminate high proportions of this compound during bank filtration.

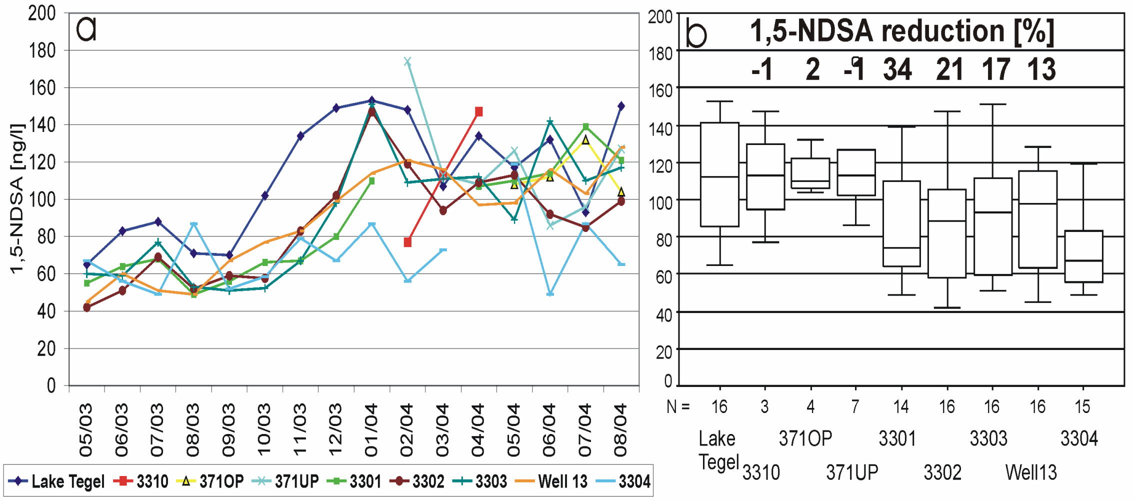


Figure 22 Fate of 1,5 - NDSA during infiltration at the bank filtration site Tegel (a: time series; b: box plots)

1,7-NDSA was present in the surface water of Lake Tegel in higher concentrations (334 ng/l; δ=83 ng/l; n=24) than the 1,5-isomer. Figure 23 displays results of monitoring wells and the corresponding surface water concentrations. Generally, a better removal was observed than for the 1,5-isomer, but the compound was also not attenuated easily in the first meters of infiltration. In the shallow monitoring wells 3310 and 371OP only 15% and 1% of the compound were removed, respectively. The abstracted raw water in production well 13 contained averaged 43% of the measured surface water concentration. The time series in Figure 23a is strongly dominated by an increase in concentration in the monitoring wells 3301, 3302, and 3303 during fall and winter 2003/04. This corresponds to the already mentioned temporary change in dominant redox conditions. However, at other field sites and in soil column experiments it was found that this isomer of NDSA is more efficiently degradable under oxic conditions. That is the reason why it was surprising to detect higher concentrations during a period of nitrate break through to the monitoring wells. The concentration increase might be explained by a die-off of a great portion of adapted biomass, which did not tolerate elevated nitrate and oxygen levels. A quick growth of an oxygen tolerant biomass, which was able to degrade this compound, might have been limited by low assimilable carbon concentrations in deeper parts of the aquifer. But in January/February 2004, the concentrations of 1,7-NDSA in the deeper monitoring wells decreased, despite of a presence of nitrate in both wells (3302 and 3303) until June 2004. It can be assumed that in the time period 11/2003 to 01/2004 the biomass slowly adapted to elevated nitrate levels. From 02/04 to 06/04 the adapted biomass provided an above average removal of 1,7-NDSA in the deep monitoring wells 3302 and 3303, which showed the highest nitrate concentrations. In Figure 23a, the very low 1,7-NDSA concentrations from 02/2004-06/2004 are visible, which are even below the pollution level in the production well and background groundwater during this period. These results are consistent with findings at other field sites that infiltration under more oxic conditions leads to a better removal of Naphthalenedisulfonates. After July 2004 the 1,7-NDSA concentration increased again in the deeper aquifer because of a return to anaerobic conditions after the depletion of the nitrate break through. The results show impressively that a change in redox chemistry at an infiltration site can cause dramatic changes in removal efficiency for trace compounds. The removal mechanisms in the system of bank filtration are usually robust, but can not be taken for granted since sometimes short term disturbances result in significant changes in pollutant removal.

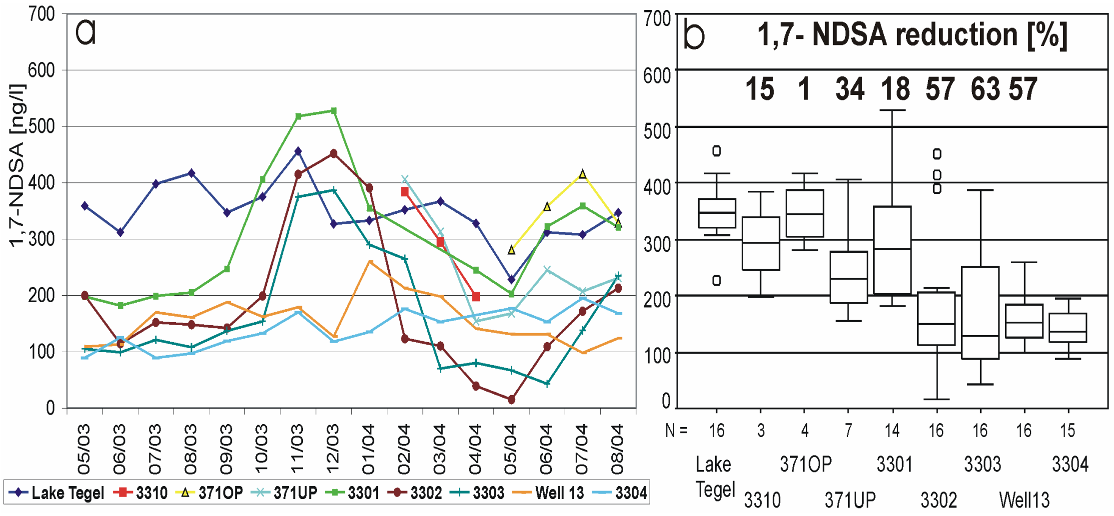


Figure 23 Fate of 1,7-NDSA during infiltration at the bank filtration site Tegel (a: time series; b: box plots)

Results for the 2,7-NDSA show the same trends that were observed for the 1,7-isomer. Generally, a partial removal took place during infiltration at the bank filtration site, and approximately 57% of surface water concentration was found in raw water. Because concentration levels for this compound were close to the limit of quantification in some monitoring wells, it has to be mentioned that detected traces below LOQ (30 ng/l) were set to ½ LOQ (15 ng/l). Figure 24 shows that the degradation performance in the deeper monitoring wells was dominated by redox conditions and kinetics of biomass adaptation. The shallow oxic wells did not exhibit an efficient removal. In the deep monitoring wells an increase in 2,7- NDSA was observed during fall 2003-winter 2003/04, which was followed by a period of very low concentrations in 3302 and 3303. Only traces below limit of quantification were detected in spring 2004 in these monitoring wells. The reasons for these concentration changes are assumed to be similar to the ones discussed for 1,7-NDSA (see above). In observation well 3301 a very low attenuation of the compound was found. In summer (06-08/2004) concentrations in 3301 rose to levels that were observed three months earlier in surface water (Figure 24). The weak attenuation of this partly degradable NDSA and the break through of temporarily higher surface water concentration into 3301 might be due to a higher portion of bank filtrate that infiltrated more distant from the bank under more anoxic/anaerobic conditions where an efficient removal is not feasible.

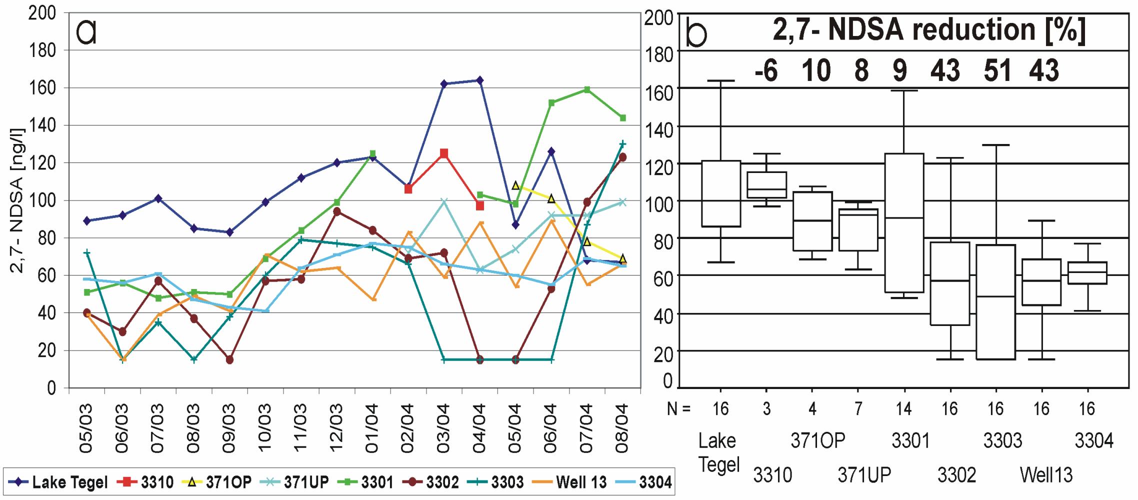


Figure 24 Fate of 2,7-NDSA during infiltration at the bank filtration site Tegel (a: time series; b: box plots)

Summarizing it was found that the X-ray contrast agent Iopromide was efficiently removed during bank filtration in Tegel. The other selected compounds, Sulfamethoxazole and the isomers of NDSA, were found in measurable concentrations in the production well. Concentrations ranged from 60-150 ng/l. Since raw water undergoes further treatment (aeration and rapid sand filtration for Iron and Manganese removal) and blending it is to be expected that the precaution value for anthropogenic organic contaminations in drinking water of the German Drinking Water Ordinance (100 ng/l) is not reached. Nevertheless, a further monitoring of the bank filtration field sites and the concentration in drinking water is advisable.

1.2 Lake Wannsee bank filtration site

The bank filtration field site Berlin-Wannsee was included in the monitoring program of the „Organics"-subproject within NASRI in May 2002. In the first part of monitoring the bank filtration transect Wannsee I at production well 4 was sampled. In February 2003 the drilling of transect Wannsee II was completed and the new transect provided a better insight into the processes at this field site because the distribution of monitoring wells allowed a better resolution of processes in the subsoil. From February 2005, the DWQC focused on the new transect at production well 3 and cancelled all measurements at the old transect. Therefore, the presented results refer mostly to the new transect Wannsee II as longer time series were measured here.

Investigations on the flow scheme of the bank filtrate at this field sites proved that only the upper part of the top aquifer is dominated by young bank filtrate. Monitoring wells with depth higher than ~15 m showed older bank filtrate with several years age which originates from distant infiltration areas (see NASRI Report 1). After a screening of the field site of half a year it became clear that all deeper monitoring wells do not show any response to the changes in surface water and all parameter were mostly stable over this period. Short measurement series of the deep monitoring wells characterized the water in this part of the aquifer and data were used for dilution calculation in the abstraction well. Afterwards, the samples of the deep wells were not analyzed for AOX and trace compounds since these methods were too time-consuming, and results were stable and predictable. Investigations of the DWQC focused instead on the shallow monitoring wells (205, 206, 202OP, 203, and abstraction well 3) which were influenced by recent surface water and which showed the fate of bulk and trace organics during infiltration with subsequent retention times. The monitoring of abstraction and monitoring wells ended in August 2004, but sampling of surface water was continued until June 2005. Additionally, spatial variation of surface water in front of the transect was investigated in two sampling campaigns (March and July 2004). The DWQC analyzed these samples for bulk organic parameters.

Generally, the monthly analytical program was comprised, as at the Tegel field site, of DOC, UVA_{254}, UVA_{436}, LC-OCD, and differentiated AOX (adsorbable organic halogens e.g. AOI, AOBr)-analysis. Additionally, trace organic compounds were analyzed for a time period of 16 months. Trace compound analysis focused on X-ray contrast media (Iopromide); bacteriostatica (Sulfamethoxazole), and Naphthalenedisulfonates (1,5-NDSA; 1,7-NDSA; 2,7-NDSA). Results of the field monitoring are reported in the following chapters.

1.2.1 Lake Wannsee - Results bulk organics

1.2.1.1 Surface water Lake Wannsee

The amount and character of bulk organics in Lake Wannsee was monitored over the period May 2002 to June 2005 using the described analytical methods (DOC, UVA_{254}, UVA_{436} and SUVA (calculated)). Table 4 provides the arithmetic mean, median and standard deviation of 36 measurements which were conducted monthly.

Table 4 Results bulk organic parameters in surface water Lake Wannsee 2002-2005 (n=36)

	DOC	**UVA_{254}**	**UVA_{436}**	**SUVA**
	[mg/l]	[m^{-1}]	[m^{-1}]	[l/m*mg]
Arithmetic mean	7.1	16.0	0.46	2.25
Median	7.2	16.1	0.52	2.27
Standard deviation	0.8 (11.2%)	1.3 (8.1%)	0.10 (20.4%)	0.14 (6.2%)

Average DOC levels of Lake Wannsee are similar to the ones observed at Lake Tegel, but the variation with seasons was found to be more pronounced. At Lake Tegel, the standard deviation of a similar DOC-data pool was only half as high as at Lake Wannsee. The observed range of DOC-concentrations was 5.5 – 9 mg/l with a maximum variation of 3.5 mg/l. Considerably higher DOC concentrations were found in the summer months April to September. The average difference between summer and winter DOC–levels can be quantified with ~2 mg/l, which is twice as high as the average variance in Lake Tegel. Figure 25 confirms these results.

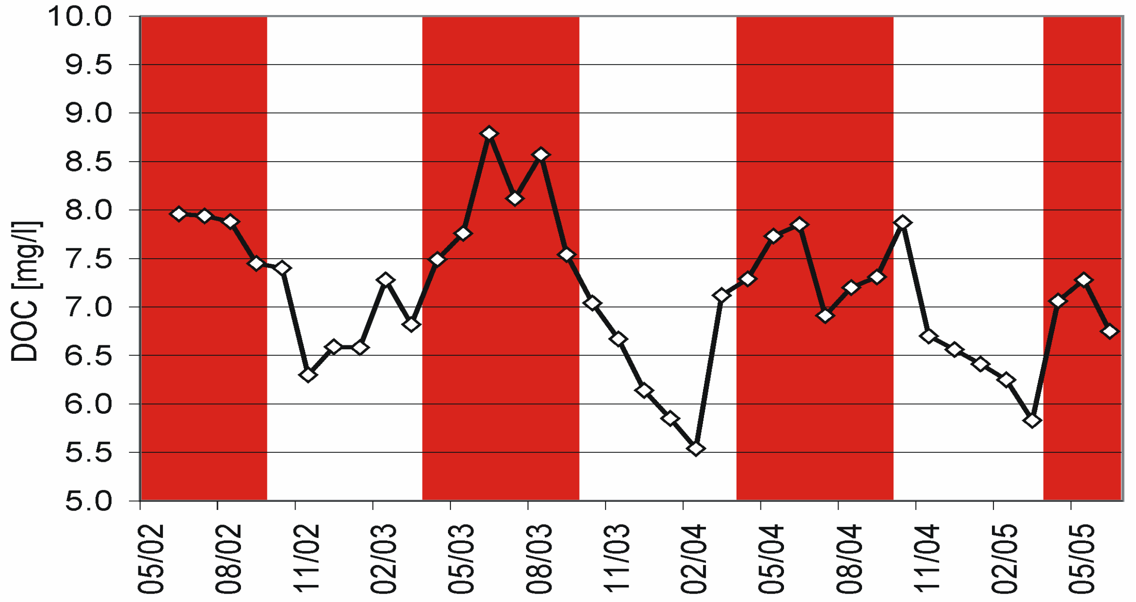


Figure 25 Time series of DOC concentration in Lake Wannsee

In Figure 25 the periods from April to September are marked, since during these times the WWTP Ruhleben discharges into the Teltow-Canal. During winter season, the treatment plant discharges into the Spree-River. Therefore, the waste water portion of the Havel water entering the lake from north is lower during summer. Earlier studies of the FU Berlin proposed that during summer water with a high portion of treated wastewater from the Teltow-Canal is entering Lake Wannsee from south through a chain of small lakes, influencing the water quality of Lake Wannsee. Until now it is unclear to which extend amount and character of organic water constituents in the lake change with this seasonal relocation of the point of discharge of WWTP Ruhleben. Of special importance is the changing waste water portion in front of the transect Wannsee. In order to quantify this effect and provide more insight into the seasonal distribution of the effluent organic matter in the lake, the DWQC took part twice in a surface water sampling campaign. The results of winter and summer campaign are shown in Figure 26 and Figure 27.

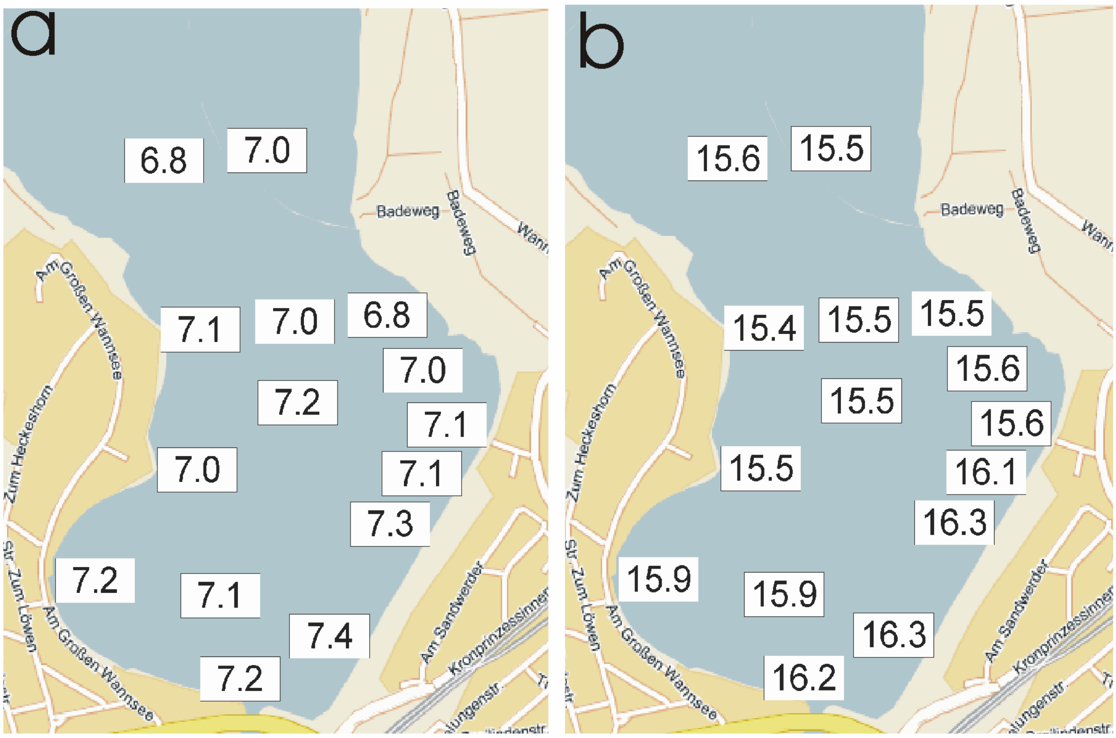


Figure 26 Distribution of DOC (a; mg/l) and UVA254 (b; m^{-1}) in Lake Wannsee in March 2004

Figure 26 provides results of the winter sampling. The DOC and UVA$_{254}$ results show higher concentrations of organics in the south east of the lake in agreement with results of the hydrogeology group (electrical conductivity, MTBE concentration). The elevated concentrations are probably due to an influence of treated wastewater from the Teltow-canal. Concentrations are only slightly higher (~0.3 mg/l DOC and ~0.5 m^{-1} UVA$_{254}$) in this area, but in combination with the inorganic parameters the results confirm the theory of an influence of Teltow-canal water on Lake Wannsee. In this case the bulk organics are not really an appropriate tracer for WW influence since the concentration difference between treated waste water and unaffected water is low. Unfortunately, trace organic analysis of this samples were not conducted at the DWQC. But the differentiated AOX-results (chapter 1.2.3.1) and NASRI Report 3 will give more insight into spatial distribution of trace organic substances in Lake Wannsee.

Figure 27 shows results of the summer sampling. During this campaign, the elevated concentration of treated wastewater on the south east bank of the lake could not be confirmed. Apart from one sampling point on the west bank of the lake (slightly elevated DOC and UVA$_{254}$) all sampling points showed comparable bulk organic results. Additionally, in both sampling campaigns a depth-profile (0; 2; 4; 6; and 7 m) in the middle of the lake was analyzed for bulk organic parameters. It was found that at this time no considerable variations occurred and that no pronounced depth-profile existed.

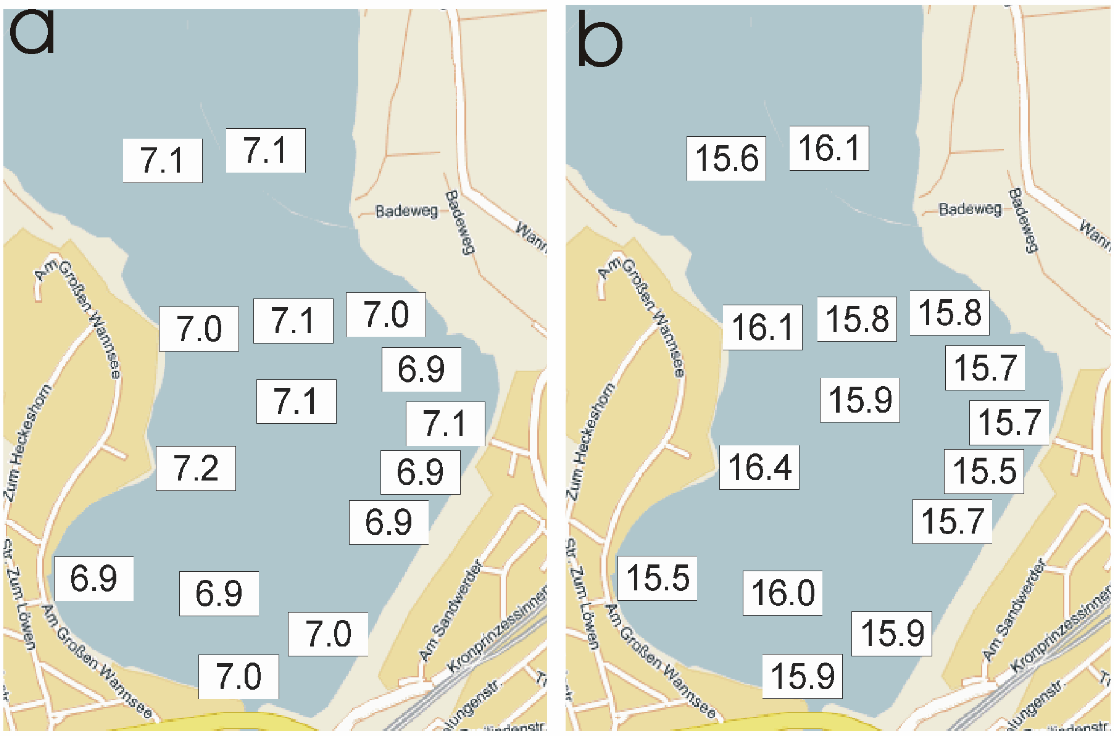


Figure 27 Distribution of DOC (a; mg/l) and UVA$_{254}$ (b; m^{-1}) in Lake Wannsee in July 2004

The limited output of the surface water sampling regarding the bulk organics is also reasoned by the fact that neither March 2004 nor July 2004 were characteristic months (based on bulk organics time series) for the winter or summer situation in the lake. This is evident after comparing the measured DOC concentrations of both sampling events, which are approximately the same. Figure 25 shows that a comparison of the situations in February 2004 and June 2004 would have resulted in more information output, since the characteristic seasonal changes of the bulk organics were more pronounced at this time. More details of this investigation on the spatial distribution of waste water influence are presented in NASRI Report 1. Summarizing, the hydrogeology group assumes a higher wastewater portion in front of the transect during summer because of a lower water flow in the main rivers entering Berlin (Spree, Havel). This leads to less dilution of the discharged treated effluent. Consistently, the DWQC observed higher DOC concentrations during summer (Figure 25).

However, the strong variations in DOC can not only be ascribed to the changing influence of the treated wastewater. It is unlikely that the seasonal variable point of discharge of WWTP Ruhleben cause a variation within surface water DOC concentration in front of the transect of 2 mg/l. It can be assumed that the major part of additional DOC during summer is associated with annual algae blooms. Since the phosphate concentration in Lake Wannsee is considerably higher than in Lake Tegel (phosphate elimination plant in operation), annual algae blooms are much stronger.

Another difference between Lake Wannsee and Lake Tegel is that the enforced operation of the lake pipeline during summer leads to an inverted situation in Lake Tegel. There, the proportion of treated wastewater is, directly opposed to Lake Wannsee, higher during winter.

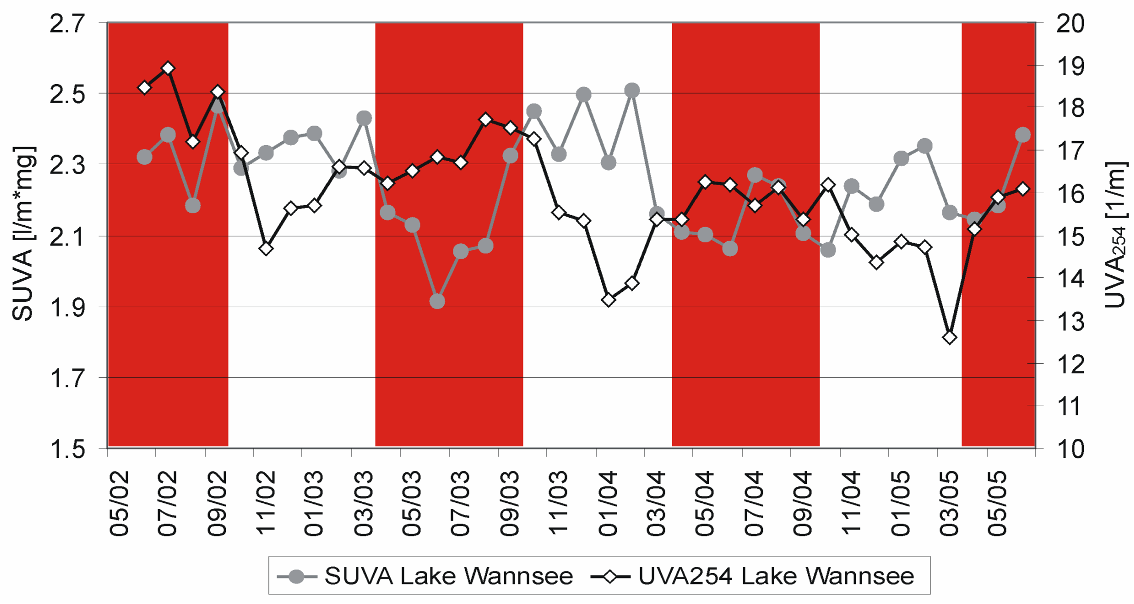


Figure 28 UVA_{254} and SUVA of Lake Wannsee surface water

UV-absorption at 254 nm of Lake Wannsee samples was only slightly higher than the UVA of Lake Tegel samples, with a similar range of variation (13 to 19 m^{-1}) (Figure 28). In Lake Wannsee, higher UV-absorption was observed during the summer months indicating a reversed schedule for seasonal changes of UVA_{254} compared to Lake Tegel. This is explained by the mentioned higher wastewater portion during summer and the artificially reversed situation at Lake Tegel. In Lake Wannsee, seasonal changes of UVA_{254} correspond to the DOC variations, whereas DOC variations are more pronounced. This is due to aliphatic DOC fractions which are produced during strong algae blooms which do not affect the UVA_{254}. This effect is visible by calculating the SUVA, a measure for aromaticity of DOC. Figure 28 shows that the SUVA is lower during summer, confirming a higher share of aliphatic carbon's during summer. Therefore, it can be assumed that a great share of additional DOC during summer is associated with algae organic matter.

Generally, the average SUVA in Lake Wannsee (2.27 l/m*mg) is slightly higher than in Lake Tegel (2.09 l/m*mg) proposing that aromatic DOC fractions are more important. It is unclear whether this is a sign of a higher average portion of treated wastewater in front of the transect or whether this is due to other unknown effects. Generally, treated wastewater in Berlin has an average SUVA of 2.4 l/m*mg (Bahr, 2005).

However, it can be summarized that the concentration and character of bulk organic matter in Lake Wannsee is more variable than in Lake Tegel with strong seasonal trends. This is mostly due to summery algae blooms and higher waste water portions during summer. The influence of seasonal relocation of the point of discharge of WWTP Ruhleben was not clearly visible in organic bulk parameter time series. Furthermore, the surface water sampling events gave no clear insight into spatial variation of organic water constituents. Due to the unclear spatial distribution of water quality in Lake Wannsee it needs to be clarified that all presented time series only reflect the conditions in front of the investigated bank filtration transect Wannsee II.

1.2.1.2 Bank filtration - DOC

Results from February 2003 to June 2004 are presented for the bulk organics at transect Wannsee II. The data is illustrated as time series and box plots, similar to the presentation in chapter 1.1 (Tegel bank filtration). It is essential to understand that only the top part of the aquifer is influenced by recent bank filtrate. The data evaluation will focus on this part of the aquifer, but will also include an overview of the concentration and character of bulk organics in deeper parts of the aquifer and the background groundwater. The most important flow path of actual bank filtrate considered at Wannsee II runs from surface water subsequently along the monitoring wells 205, 206, 202OP, and 203 towards the production well 3. Along this infiltration path it is assumed that nearly no dilution with deeper groundwater takes place. The proportion of older groundwater increases with depth in the deeper monitoring wells 202MP1, 202MP2, and 202UP. In 202MP1, a partial influence of actual surface water was observed, whereas 202MP2 and 202UP are exclusively dominated by older water (bank filtrate) that infiltrated years ago. Two monitoring wells on the landside of the production well, 204OP and UP, were also included within the monitoring. The production well 3 is a multilevel well which pumps only 20-25% young bank filtrate (retention time 3-4 months) because it abstracts water from different aquifers. Therefore, all information about amount and composition of organics in these aquifers will be included. More information of the hydrogeological situation at this field site is provided in NASRI Report 1.

An interesting feature of the field site Wannsee II is the comparison of the two monitoring wells 205 and 206. These wells are comparable regarding position and retention time (0.5-1 month) but belong to different redox zones. The dominant redox conditions depend on various factors of influence and affect the microbial activity. At the water-sediment interface of the bank region of Lake Wannsee water infiltrates under oxic conditions. Depending on the position in the lake, the infiltration takes place under more saturated conditions (monitoring well 205) or under unsaturated conditions (206). Under more saturated conditions, the mineralization of aqueous DOC and sedimentary bound POC during infiltration leads to a depletion of oxygen and nitrate (205) and a decreasing redox potential. Higher temperatures during summer intensify this process. Under unsaturated conditions, no depletion of O_2 and NO_3 occurs because of the close contact of the water to the interstitial air and the redox potential remains high. Therefore, a comparison of the two wells gives insight into the different effects of an oxic or anoxic/anaerobic infiltration. During further infiltration along the top of the upper aquifer oxygen is delivered to the bank filtrate continuously from the water - soil air interface since the water level varies depending on the pumping schedule of BWB. The infiltration along 202OP and 203 to production well 3 (70 m, 3-4 months) can be regarded as an oxic infiltration.

Contrary to the field site Tegel, strong seasonal surface water variations of organics influence the conditions in the subsoil. Especially, in the monitoring wells near the bank the seasonal variations of the surface water are visible. Figure 29 shows that monitoring well 205 and 206 follow the trend of surface water and show similar variations of DOC-concentration of more than 2 mg/l. In monitoring well 202OP and 203 the variations are observable as well, but with smaller amplitudes. DOC concentration in production well 3 is stable around 3.5 - 4 mg/l proving that only a small percentage originates from the flow path of the recent bank filtrate.

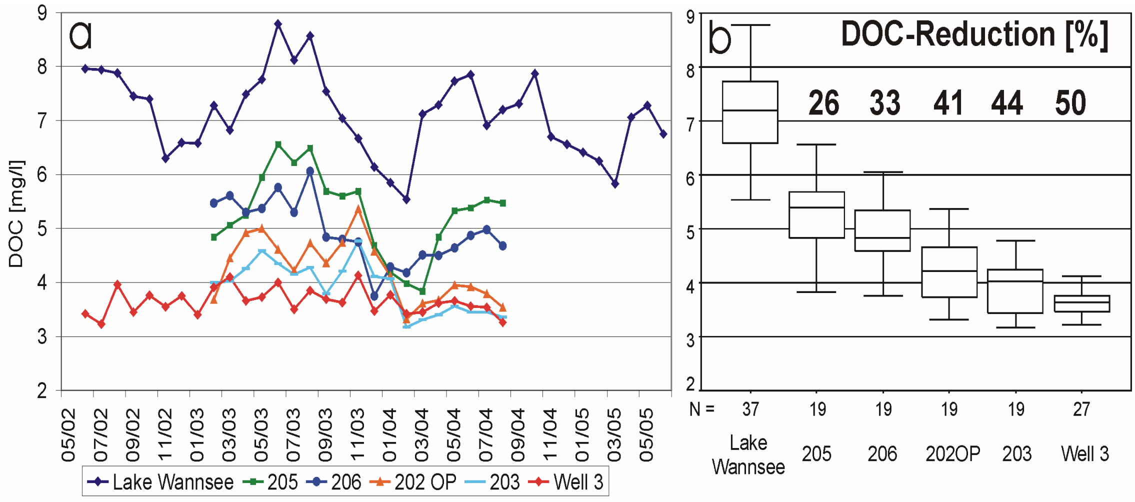


Figure 29 Fate of DOC during infiltration along transect Wannsee II (a: time series; b: box plots)

Figure 29 proves that along the infiltration path the concentration of organic compounds decreases considerably. Consistently with results from other field sites, the initial infiltration zone is very important and accounts for the largest step in DOC mineralization. Between 26 and 33 percent of the surface water DOC are removed within two to four weeks of infiltration to monitoring well 205 and 206. During the more oxic infiltration to well 205 seven percent more DOC are mineralized, supporting the theory of a faster DOC removal under oxic conditions. The further infiltration path constitutes a very long oxic infiltration of nearly 3-4 months. Such a long oxic infiltration was unique in the field sites selected by NASRI. At the bank filtration site in Tegel, the main infiltration path guides the water in the anoxic/anaerobic second aquifer and at the artificial groundwater recharge facility in Tegel retention times are only ~50 days.

Therefore, the long oxic infiltration provided interesting results on the long time behavior of organics under oxic conditions. It was found that after 2 - 4 months of infiltration (202OP and 203), 41 and 44 percent of the surface water DOC was degraded (Figure 29). The corresponding infiltration path was 23 m or 38 m long. Therefore, the infiltration velocity within the subsoil is relatively slow with 0.32-0.45 m/d (Tegel: ~0.75 m/d; GWR: ~2.2 m/d). The observed mineralization rate of 41-44% is higher than mineralization rates at the other field sites. In Tegel, it was found that 34-39% of the DOC was removed and ~40% at the groundwater recharge facility. The increased DOC removal might be due to two effects: first a different composition of the surface water DOC and secondly the long oxic soil passage. LC-OCD analysis and the high seasonal variance in the DOC time series showed that in Lake Wannsee algae associated organic compounds account for a higher percentage of total DOC than in Lake Tegel. It is known that these so called polysaccharides are easy degradable. Therefore, this could add to an increased mineralization rate and result in a difficult comparison of mineralization rates with the Tegel field sites. The effect of a very long oxic infiltration path is not investigated sufficiently. Results from the groundwater recharge facility and long term soil column experiments proposed that under oxic conditions a fast removal of degradable organic carbon is followed by stable conditions, where the non-degradable fraction of DOC remains in the water. But these results where obtained from field sites and experiments with retention times of 30-50 days. It might be possible that very slow transformation processes of this operationally-defined non-degradable DOC-fraction lead to a further mineralization under oxic conditions, which is only recognized during very long time frames.

In production well 3, the DOC concentration remained relatively stable between 3.5-4 mg/l during the monitoring period. This was expected because actual bank filtrate accounts only for a small portion of the abstracted water. Most of the water originates from the lower part of the top aquifer, from the second and third aquifer and from background groundwater. As part of the monitoring program, the organic composition of water from the lower part of the second aquifer (202MP2 and 202 UP) and background groundwater (204OP and 204 UP) were analyzed. Groundwaters from the second and third aquifer (second: 3334; third: 3332 and 3336) were sampled only once in March 2004 to obtain information which are necessary for calculation of the mixing proportions in the production well.

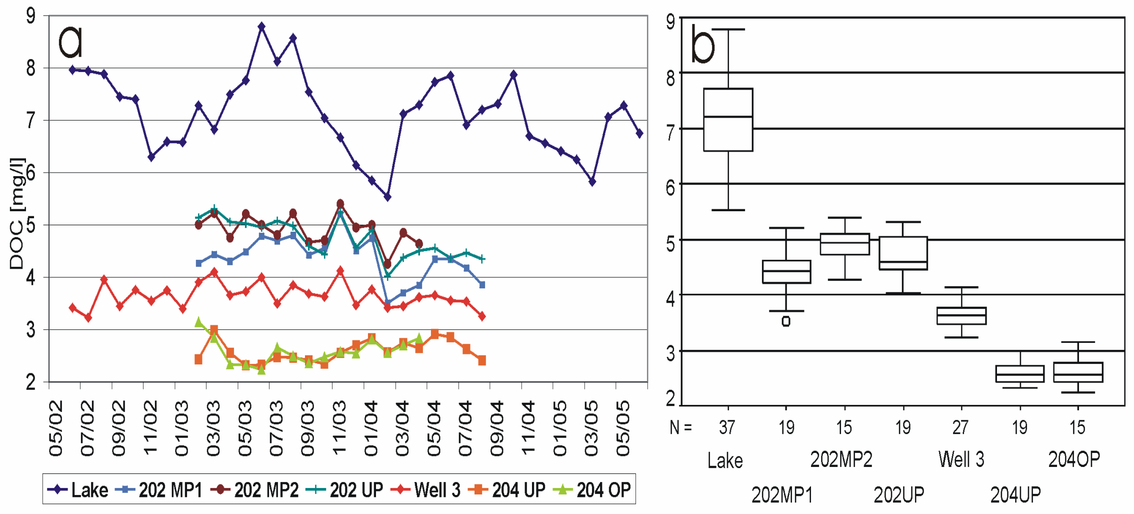


Figure 30 DOC concentration in deeper monitoring wells and background wells at transect Wannsee II (a: time series; b: box plots)

Figure 30 shows that in the deeper part of the top aquifer the influence of surface water declines with depth. No removal rates are given because for all water types the corresponding surface water concentration is not known. Monitoring well 202MP1 shows some of the variations of surface water. Furthermore, some other organic parameters indicated that this well is under certain circumstances under the influence of the surface water. The deeper wells 202MP2 and 202UP show relatively stable DOC concentrations of around 4.5-5.5 mg/l. These wells are representative for a stream of older bank filtrate with an age of ten years to some decades (NASRI Report 1, Chapter 1.5.7.). The fact that the DOC concentration in these wells is relatively high, compared with young bank filtrate after 3 months retention time, might indicate that the portion of non-degradable DOC in the surface water was higher at time of infiltration.

Stable DOC-concentrations of 2.3-3 mg/l were observed in the background groundwater. The more shallow well 204OP (8 m deep) behaved similarly to well 204UP (18 m). Therefore, the average concentration in background water can be quantified with ~2.6 mg/l.

Groundwater from deeper aquifers was only analyzed once by the DWQC. Table 5 gives results of the DOC quantification and proves that the concentration of organic water constituents is very low in the second and third aquifer. Since it can be assumed that the DOC concentration in the deep aquifer is stable and not prone to any variations, this screening can be included into the mixing calculations for the production well.

Table 5 Results DOC quantification in aquifer 2 and 3 at field site Wannsee

	3332	**3334**	**3336**
	[mg/l]	[mg/l]	[mg/l]
Aquifer	3	2	3
DOC	1.9	1.9	1.8

Altogether, the mixing calculations for production well 4 are based on four different fractions of water. These are young bank filtrate (203, Ø-DOC: 4.0 mg/l), older bank filtrate (202MP2, Ø-DOC: 4.9 mg/l), background groundwater (204UP, Ø-DOC: 2.6 mg/l), and very deep groundwater (3332, Ø-DOC: 1.9 mg/l). The ratio proposed by the hydrogeological group (23% young BF, 34% old BF and 43% deep and background groundwater) would lead to a theoretical DOC concentration in production well 3 of 3.55 mg/l, which is very close to the measured average DOC level of 3.6 mg/l. Therefore, the conducted DOC measurements support the results calculated by the hydrogeological group.

Compared with the bank filtration at Lake Tegel, DOC concentration within the raw water (3.6 mg/l) is slightly lower (Tegel: 4.2 mg/l). This derives mainly from the higher portion of deep groundwater, which is poor in organics. As in Tegel it is assumed that the portion of BDOC in the abstracted water is very small and regrowth potential is expected to be negligible.

1.2.1.3 Bank filtration - UVA$_{254}$

UV-absorption at 254 nm of the water samples was monitored during the same time period. It was found that during the infiltration of 3-4 months approximately 40-45% of UV-absorbing aromatic and double bond structures are removed. This is comparable to DOC removal rates but for certain monitoring wells strong differences between the removal of DOC and UVA have been observed.

Figure 31 shows that the different redox conditions in monitoring well 205 and 206 influence the removal efficiency for aromatic organic compounds. For the more oxic well 206, UVA$_{254}$ follows the trend in surface water and the removal is constant at three to five absorption units throughout the year. Overall, the average UV-absorption in 206 is 29% lower than in surface water. In monitoring well 205, the UVA$_{254}$ shows a very strong seasonal variation which might be connected to the redox system of this monitoring well. During summer, 205 is completely anaerobic with no oxygen and nitrate detectable. Figure 29 proves that during these periods still 2 mg/l DOC are removed during two to four weeks of infiltration to 205. Results of the UVA monitoring show that during summer nearly no removal of aromatic compounds in 205 takes place. This proposes that the 2 mg/l of removed DOC are of aliphatic nature. Since a preferred removal of aliphatic compounds under anaerobic conditions is not consistent with results from other field sites and literature, it is more likely that this strong seasonality in monitoring well 205 is due to an already mentioned temperature effect. Monitoring well 205 is located inside the lake, approximately 10 m farer from the bank as well 206. Investigations of the hydrogeology group on the character of the lake sediments revealed an irregular distribution of sediments with high organic contents (up to 10%) and sediments with lower organic matter content (NASRI Report 1, chapter 1.5). With increasing depth of the lake, a thicker organic layer developed. Therefore, it can be assumed, that the weak UVA removal during summer in 205 is due to desorption of organic material from lake sediment material. It is described in literature (Schoenheinz, 2004) that increased temperature leads to desorption of aromatic material which was part of sediment before or was sorbed to the inorganic material during periods of low temperature. Schoenheinz (2005) observed this effect at bank filtration sites at river Elbe. Monitoring well 205 is probably more effected than well 206 because the organic content of the sediments is higher in greater distances from the bank.

The decrease in UV-absorption potential in monitoring well 202OP and 203 complies with the observed DOC removal rates. A comparison of UVA and DOC removal rates for the production well (UVA: 42%; DOC: 50%) proposed an increased aromaticity of other water fractions that are abstracted by well 3.

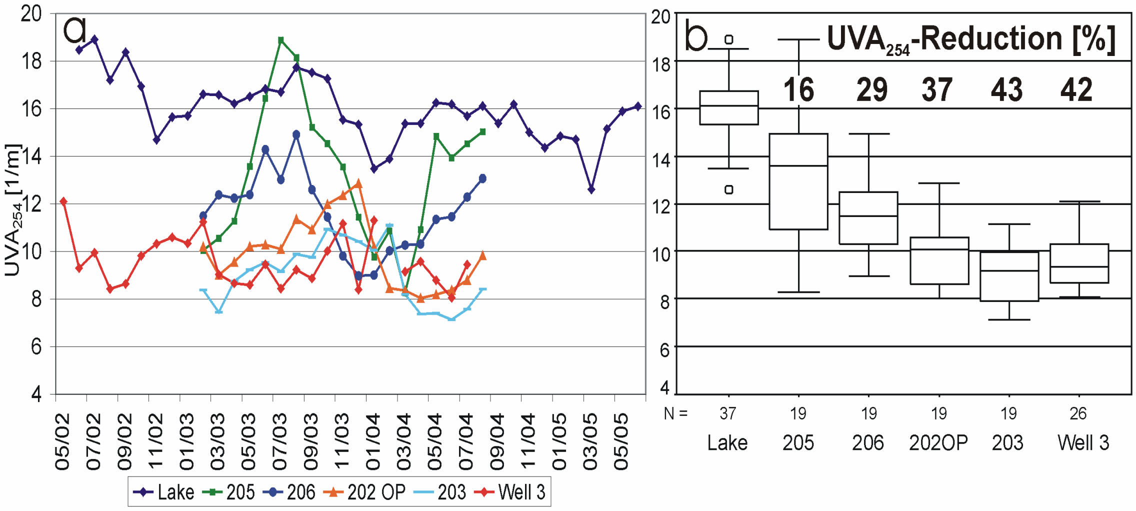


Figure 31 UVA$_{254}$ during infiltration along transect Wannsee II (a: time series; b: box plots)

UV-absorption results for the monitoring well cluster 202 (MP2, MP2 and UP) reveal consistent with the DOC results a decreasing seasonality with increasing depth (Figure 32). Only well 202MP1 shows a seasonal variance that can be compared with the trends in the shallow monitoring wells. Overall, the UV absorption of old bank filtrate is slightly higher than the UVA$_{254}$ of the young bank filtrate after infiltration. These results confirm the findings of DOC analysis. The increase of UVA$_{254}$ in monitoring well 202MP2 in winter 2003/04 could not be explained.

The background groundwater exhibits a very low UV-absorption with an average absorption of four to six absorption units (Figure 32). Some of the extremely high values of monitoring well 204UP might be due to analytical problems, which occur for strongly anaerobic iron containing samples. No seasonality was observed.

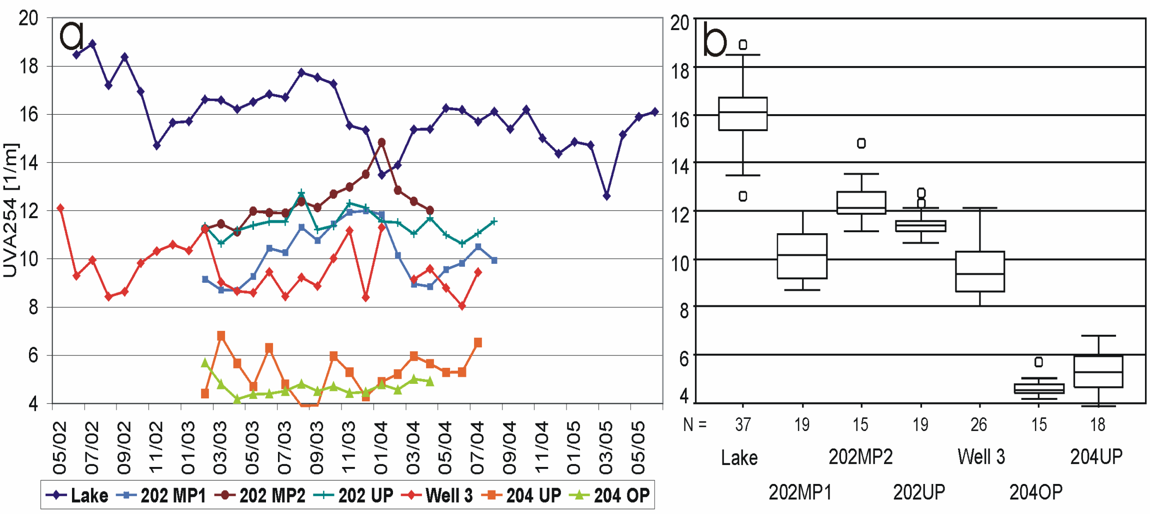


Figure 32 UVA$_{254}$ in deeper monitoring wells and background wells at transect Wannsee II (a: time series; b: box plots)

UVA$_{254}$ in the second and third aquifer was assessed with 4.5 to 6.5 absorption units. The calculation of UVA$_{254}$ of the production well based on the fractionation of the hydrogeological group would result in an absorption of 8.6 m^{-1}. This is similar to the measured average absorption of 9.4 m^{-1}.

Measurements of color at 436 nm were conducted. The low color of surface water (0.6 m^{-1}) was diminished during infiltration to values of 0.3-0.4 m^{-1}. Since these results are close to the detection limit no interpretation and conclusion arose from the conducted measurements.

1.2.1.4 Bank filtration - SUVA

The SUVA as a measure of aromaticity of organic carbon was calculated from the monitored DOC and UVA$_{254}$. It was found that, similarly to the effects observed in Tegel, the aromaticity increases shortly after infiltration and reduces during further infiltration. The average SUVA of the surface water of Lake Wannsee is ~2.3 l/m*mg (Figure 33). In the monitoring wells near the bank (205 and 206) the share of aromatic organic material on the total DOC rises and the average SUVA increases to 2.5 or 2.4, respectively. In 205, some of the high SUVA results were measured in summer when UVA results indicated a temperature driven desorption of aromatic carbon. However, after an initial increase the SUVA reduces along the flow path in monitoring well 202OP and 203. In well 203 the SUVA drops to 2.2 l/m*mg and is lower than in surface water.

This sequence is probably due to a preferred initial degradation of aliphatic compounds and a subsequent mineralization of degradable organics. It was similarly observed at bank filtration site Tegel.

The higher SUVA in the production well exhibits again that the abstracted water is a mixture of different fractions. Judging from the product water, the majority of source fractions is characterized by a higher aromaticity than the surface water. Since the SUVA of the source fractions is assumed to be relatively constant, the high variation of SUVA in the production well indicates variations in the composition of raw water (changing proportions of source fractions).

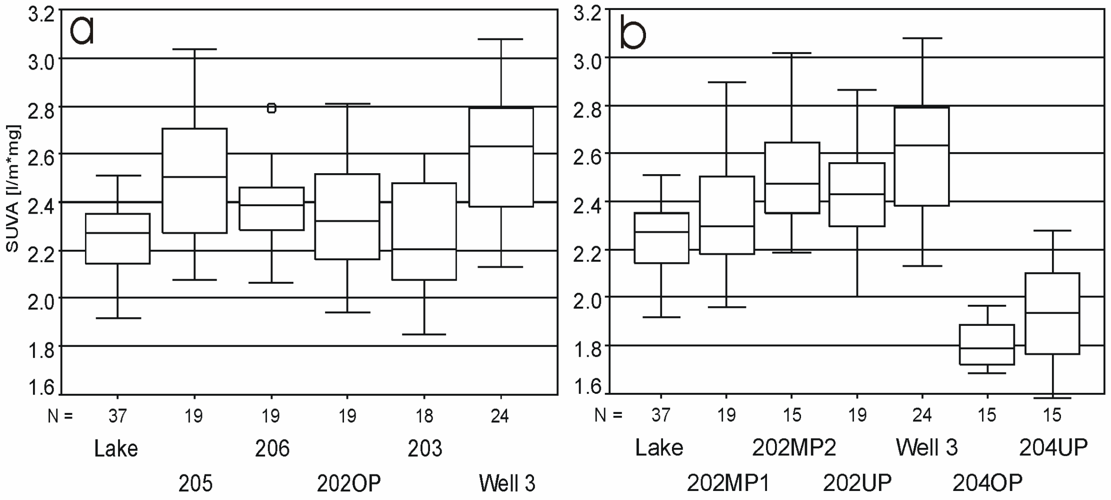


Figure 33 SUVA during infiltration to production well 3 (a: young bank filtrate; b: deeper wells and background groundwater)

Figure 33b shows that the fraction of older bank filtrate in the deeper part of the top aquifer is characterized by a high aromaticity and a SUVA of 2.4 to 2.5. Only for 202MP1, a lower SUVA was calculated because of an increased influence of young bank filtrate. However, observed results prove that the important fraction of long term bank filtrate from under the lake adds to the higher SUVA of the production water. The background groundwater is represented by monitoring well 204OP and UP, which exhibit a reduced importance of aromatic organics and a very low SUVA of 1.8 - 1.9 l/m*mg.

Investigations of the water from deeper aquifers resulted in SUVA calculations of 2.5 to 3.5 l/m*mg for the monitoring wells 3332, 3334, and 3336. Therefore, the aromatic character of carbon in the product water is mainly derived from the influence of old bank filtrate and very deep groundwater.

1.2.2 Lake Wannsee - LC-OCD

1.2.2.1 Surface water - LC-OCD

During the observation period, samples from Lake Wannsee were analyzed by the LC-OCD technique. The chromatograms give an insight into the composition of dissolved organic carbon. For evaluation purposes, the chromatograms were adjusted for retention time and baseline. The surface water was characterized by more than 20 monthly measurements of water samples from the lake in front of transect Wannsee II and two large scale surface water sampling events in March 04 and June 04. Monthly measurements give insight into any seasonal changes of the DOC-fractions and the surface water screening was conducted to reveal spatial differences across the lake.

Results of the monthly surface water sampling are presented in Figure 34. Unfortunately, some unreliable results had to be excluded from the evaluation process. Overall, thirteen measurements were mediated and pooled into groups that represent summer stage of Lake Wannsee or winter stage. The new results explain the findings of the DOC quantification and show consistently which seasonal changes of bulk organic composition occur in the lake.

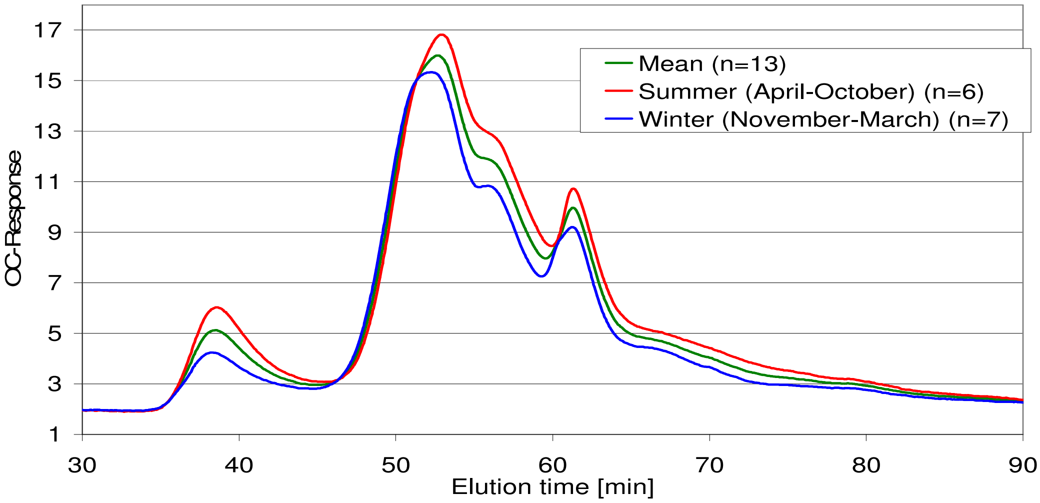


Figure 34 LC-OCD chromatogram of Lake Wannsee surface water (seasonal changes)

The general DOC composition, which is represented by the graph “Mean” in Figure 34, is similar to the bulk organics composition in Lake Tegel. The fractions were quantified by integration of the chromatograms and account for comparable proportions and absolute concentrations (Table 6). A slightly higher concentration of humic substances occurred in Lake Wannsee, whereas the fraction of neutrals and hydrophobics was less important. These variations are very close to the limits of the method and are therefore not interpreted. However, the most important fractions in Lake Wannsee surface water are humic substances (~48%), humic substances-building blocks (~22%) and neutrals (~18%).

The seasonal variations followed partly a different scheme as at Lake Tegel. Consistently with Lake Tegel surface water, the importance of polysaccharides increased during summer. In Lake Wannsee, the differences between summer and winter were even more pronounced. This can be explained by stronger algae blooms during summer that are not nutrient-limited as in Lake Tegel.

Regarding the other fractions, an increase in concentration of all fractions was observed. This is consistent with the strong seasonal variation of total DOC and proofs that not algae blooms alone are responsible for the changing DOC. Another very important factor of influence is the already mentioned dilution effect. During winter, precipitation and higher water levels lead to lower concentrations of all DOC-fractions. This was evidently shown by the presented results for Lake Wannsee. In Lake Tegel, this effect was not clearly visible because heavy pumping of the lake pipeline during summer leads to an artificial situation, which is not representative for Berlin surface water.

However, the evaluation of the changing proportions of DOC-fractions reveals similarities between the field sites Tegel and Wannsee. Although the concentration of humic substances increased slightly during summer (Table 6) the proportional share decreases from ~51% to ~44%, because of a considerably higher total DOC during summer. During summer the proportional share of polysaccharides, HS-building blocks, and neutrals are increased, which is most probably due to a more active biomass. A transformation of humic material into smaller molecules is boosted by higher temperatures.

A minor influence that could not be quantified could result from the seasonal change of the point of discharge of treatment plant Ruhleben. But a major influence is unlikely since these effects of changing proportional shares were similarly observed at field site Tegel.

Table 6 Portions and concentrations of different fractions of DOC in Lake Wannsee – Seasonal Differences (Summer= April-October; Winter= November-March)

Share of	**Poly-saccharides**	**Humic substances**	**Humic substances-Building blocks**	**Low-molecular acids**	**Neutrals and Hydrophobics**
Summer (n=6)	10.7 %	43.8 %	23.2 %	3.2 %	19.1 %
	0.82 mg/l	3.33 mg/l	1.76 mg/l	0.24 mg/l	1.45 mg/l
Winter (n=7)	7.2 %	50.5 %	22.0 %	4.3 %	15.9 %
	0.47 mg/l	3.25 mg/l	1.41 mg/l	0.28 mg/l	1.03 mg/l
Mean (n=13)	8.8 %	48.3 %	21.9%	3.5 %	17.6%
	0.63 mg/l	3.44 mg/l	1.56 mg/l	0.25 mg/l	1.26 mg/l

Investigations of the spatial variation of the DOC composition in Lake Wannsee at two different times in summer and winter exhibited that no measurable variation at a time was present. More than 20 LC-OCD chromatograms that were recorded in March 2004 and June 2004 showed exactly the same DOC composition which complied with the monthly measured sample in front of the transect. This would point towards a well mixed surface water and is consistent with the low variation of the total DOC-concentrations. However, in reality it shows that the LC-OCD technique is not qualified for tracing the influence of treated wastewater in Berlin surface water. Drewes and Fox (2000) showed that the DOC composition of a treated wastewater can be traced back to the DOC composition of the associated drinking water. Since in Berlin the drinking water source is mainly surface water with the intermediate step of bank filtration, no considerable differences between surface water and well treated waste water can be expected. Therefore, the LC-OCD technique is not appropriate to solve the quest of the spatial variation of wastewater influence. Nevertheless, the results confirmed the monthly measurements and show a spatial uniform organic composition in Lake Wannsee surface water.

1.2.2.2 Bank filtration - LC-OCD

Concentration and character of DOC changed during the process of bank filtration. LC-OCD analysis reveals the fate of different bulk organic fractions. At field site Wannsee, two problems influence the final organic composition of the abstracted water: First, the fate of organics during actual bank filtration along the upper part of the top aquifer and secondly, the mixing of different water types in the production well. Both issues were addressed during the observation period by characterizing organics on the flow path of young bank filtrate and determining the organic composition of the different sources of the final raw water.

Figure 35 presents the different LC-OCD chromatograms for the monitoring wells on the flow path of the recent bank filtrate. The results are comparable with the findings of the evaluations at field site Tegel. Similarly, the fraction of polysaccharides was removed most efficiently. The polysaccharides account in Lake Wannsee for ~9% of the surface water DOC, with higher portions during summer. At transect Wannsee II, a breakthrough of measurable amounts of polysaccharides was only found once (January 2004) in monitoring well 206. All other chromatograms indicated a complete removal of this fraction in all monitoring wells and no seasonal effects could be observed. In Tegel, the polysaccharides occurred during winter in the shallow wells close to the bank because the microbial activity was minimal due to low temperatures. At Transect Wannsee II, the infiltration path to monitoring well 205 and 206 is longer (5-6 m, Tegel 3310 and 3311: 2-3 m) and even at low temperatures nearly no polysaccharides break through to the monitoring wells.

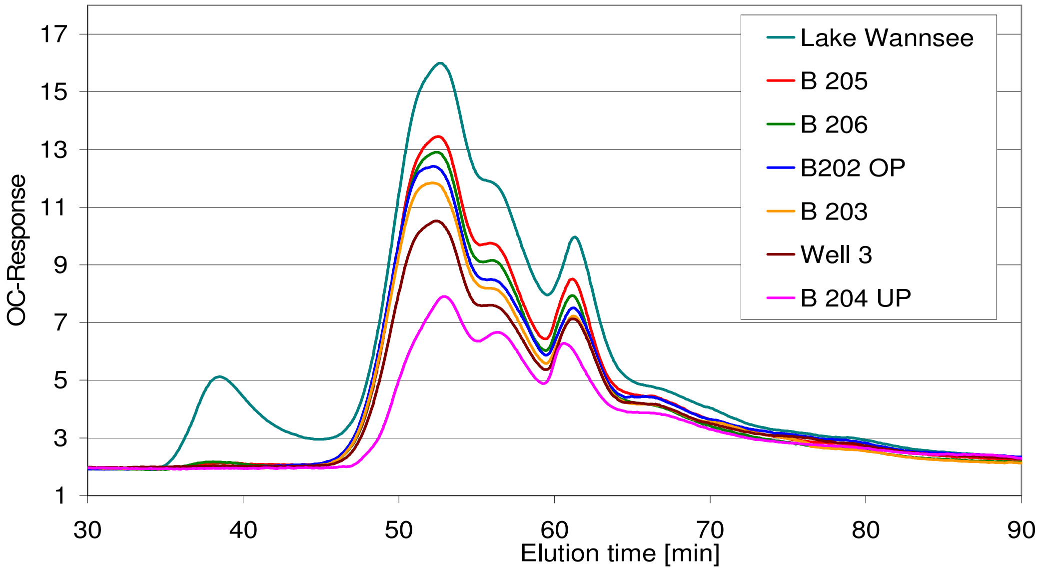


Figure 35 LC-OCD chromatograms of transect Wannsee II (mean, n=10)

All other fractions exhibited a partial removal similar to the observations at transect Tegel. Removal rates of humic substances, HS-building blocks, low molecular acids, and neutrals were found to range from 33-40%, which is slightly higher than in Tegel. This is consistent with results of the DOC analysis and most probably caused by the long oxic infiltration path. The calculation of removal rates is based on the comparison of the surface water and monitoring well 203 (Table 7). The proportions of the different fractions changed slightly because of the complete removal of the polysaccharide fraction. Table 7 shows that during mineralization of polysaccharides the importance of the fractions of HS-building blocks and neutrals increased considerably, whereas the proportion of the humic substances remained nearly stable. But the absolute concentration of all DOC-fractions declined along the infiltration path (Figure 36). However, a comparison of the monitoring wells 3303 in Tegel and 203 in Wannsee reveals that the DOC composition after soil passage is very similar and that only the absolute DOC concentration is slightly lower in monitoring well 203. Therefore, it can be concluded that the processes in the subsoil in Tegel and Wannsee are comparable. The difference in redox chemistry seems to influence mostly the quantity of DOC mineralized. Since all bank filtration processes that influence the DOC-composition and which can be assessed by LC-OCD were included in the discussion of the field site Tegel (Chapter 1.1.2.2. Tegel bank filtration) the following evaluation will focus on the effects of mixing in the production well.

Table 7 Portions and concentrations of different fractions of DOC at transect Lake Wannsee (n=10)

Share of	**Poly-saccharides**	**Humic substances**	**Humic substances-Building blocks**	**Low molecular acids**	**Neutrals and Hydrophobics**
Lake Wannsee	8.8 %	48.3 %	21.9%	3.5 %	17.6%
	0.6 mg/l	3.5 mg/l	1.6 mg/l	0.3 mg/l	1.3 mg/l
205	0.3 %	49.4 %	26.1 %	4.3 %	19.9 %
	0.0 mg/l	2.7 mg/l	1.4 mg/l	0.2 mg/l	1.1 mg/l
206	0.1 %	52.9 %	24.8 %	4.3 %	17.8 %
	0.0 mg/l	2.6 mg/l	1.2 mg/l	0.2 mg/l	0.9 mg/l
202OP	0.0 %	48.2 %	24.5 %	3.7 %	23.6 %
	0.0 mg/l	2.0 mg/l	1.0 mg/l	0.2 mg/l	1.0 mg/l
203	0.0 %	51.0 %	25.2 %	4.0 %	20.2 %
	0.0 mg/l	2.1 mg/l	1.0 mg/l	0.2 mg/l	0.8 mg/l
Well 3	0.0 %	45.8 %	24.7 %	4.5 %	24.9 %
	0.0 mg/l	1.7 mg/l	0.9 mg/l	0.2 mg/l	0.9 mg/l
204UP	0.0 %	39.5 %	28.4 %	4.4 %	28.6 %
	0.0 mg/l	1.0 mg/l	0.7 mg/l	0.1 mg/l	0.7 mg/l

Figure 37 gives an insight into the differences in DOC composition of the different source waters of production well 3. The previously discussed portion of young bank filtrate is comparable to the fraction of old bank filtrate in the deeper part of the top aquifer (202MP2 and 202UP). Both source waters are characterized by high DOC concentrations and a similar proportion of humic material (~50%). These similarities support the findings of the hydrogeology group that both water types are derived from Lake Wannsee surface water.

The background groundwater contains lower concentrations of DOC. In comparison with the surface water influenced bank filtrate, the proportions are shifted from the fraction of HS to HS-building blocks and neutrals. This effect is more dominant than in Tegel and is interesting since commonly the fraction of humic substances is regarded as mostly non-biodegradable and stable.

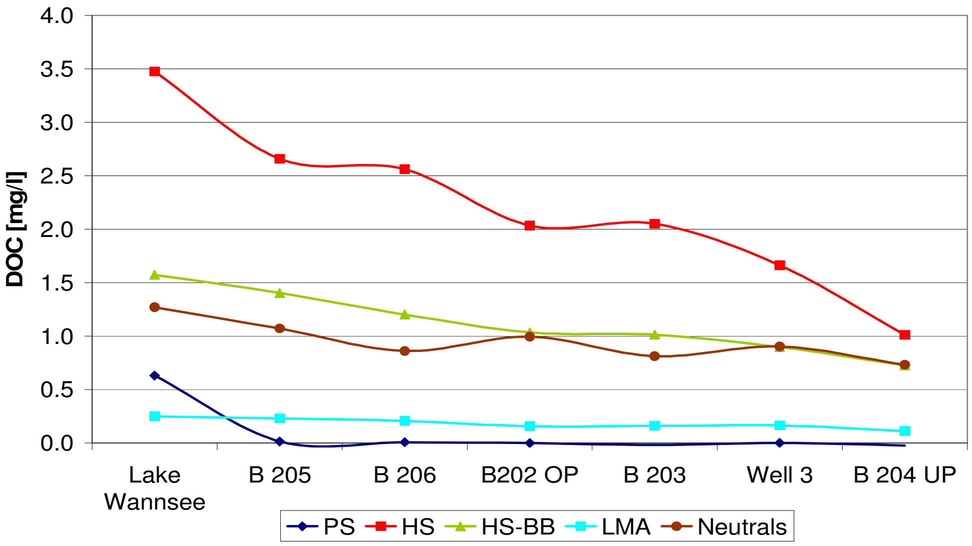


Figure 36 Concentration of different fractions of DOC along the infiltration path at transect Wannsee II

Unfortunately, sources and origin of the background groundwater were not investigated in this study. The deep groundwater from second and third aquifer was also characterized by low DOC concentrations and comparable low proportions of humic substances. Overall, the mixing of the different water types in the production well leads to a final organic composition of the raw water. The LC-OCD technique is not appropriate to discuss the relevant mixing proportions, but the proposed percentages (NASRI Report 1, chapter 1.5.8) fit to the presented results.

All results of the bulk organic characterization can be summarized as follows. During bank filtration, a fast removal of polysaccharides and only partial removal of all other DOC fractions was observed. None of the DOC fractions was persistent. The organics in the raw water of well 3 are a mixture of the bulk organics in the different abstracted water types.

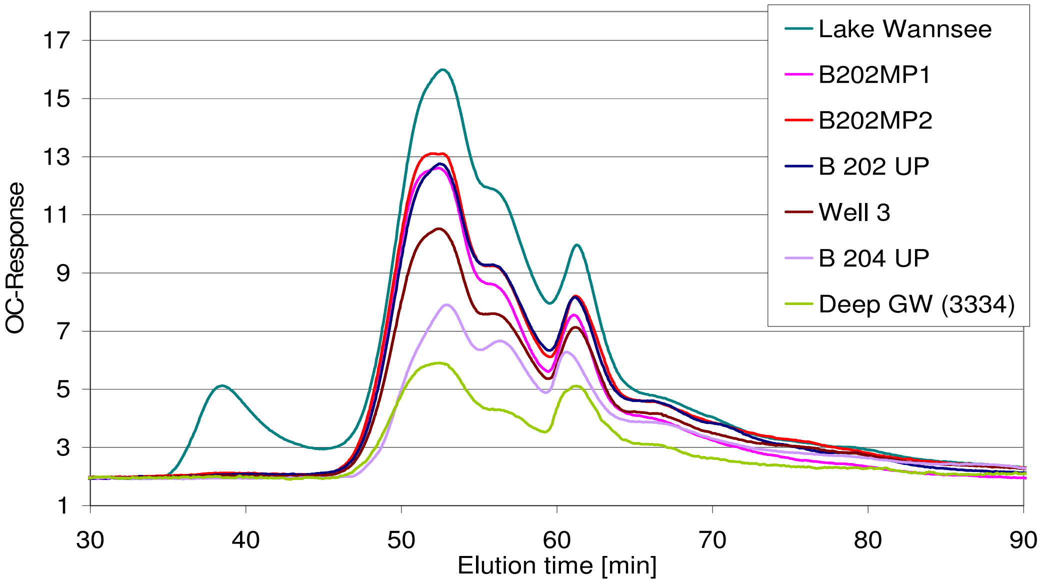


Figure 37 LC-OCD chromatograms of raw water sources at transect Wannsee II

1.2.3 Lake Wannsee - AOI Results

1.2.3.1 Surface water - AOI Results

The concentration of AOX (AOI and AOBr were measured) in the surface water followed a seasonal cycle with higher concentrations during summer. Throughout the observation period it was possible to monitor the influence of the climatic conditions on the AOI concentration in the surface water. Figure 38 shows that during the cold and wet year of 2002 the increase in AOI concentration during late summer and early fall is small compared to the years 2003 and 2004. Similar effects were observed in Lake Tegel. Furthermore, the lowest AOI concentration was measured in winter 2002/03 in both investigated surface waters. Since this was a high-precipitation period it can be assumed that the low concentrations are due to heavy dilution and that the seasonality is mostly derived from changes in dilution. The results indicate that the changing point of discharge of treatment plant Berlin Ruhleben has only a minor influence on the seasonality of AOI in Lake Wannsee.

However, the average AOI concentration in Lake Wannsee is 13.3 µg/l (δ=5.6 µg/l) which is slightly higher than in Lake Tegel (Average: 11.4 µg/l; δ=5.6 µg/l). The difference originates from more dominant summery peaks in front of transect Wannsee II. Here, concentrations of more than 24 µg/l were measured whereas in Tegel the maximum concentration in the years 2002-2005 was 17 µg/l. Since most of the AOI can be assigned to waste-water born contaminants it can be concluded that because of the operation of the lake pipeline in Tegel the influence of wastewater during summer is higher in Lake Wannsee. The AOI concentrations during winter are similar in both surface waters (6-12 µg/l) with some exceptions.

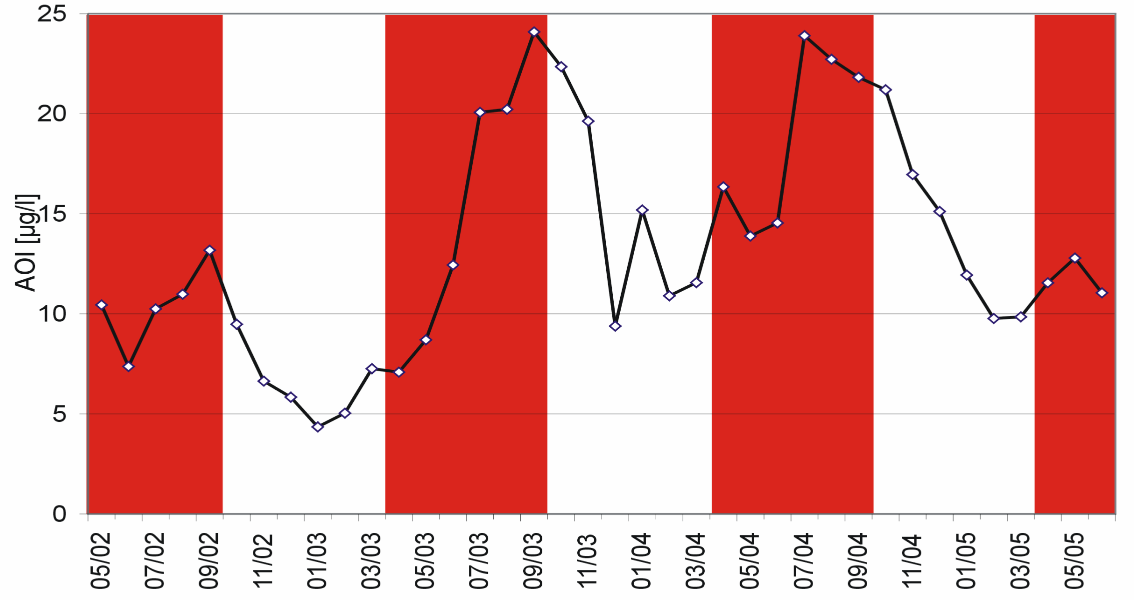


Figure 38 AOI concentration in Lake Wannsee (2002-2005, April-September marked)

Another point of interest was the influence of the treatment plant Ruhleben on the water quality in Lake Wannsee. Two already mentioned sampling campaigns were conducted to assess the spatial distribution of waste-water born contaminants in the surface water. AOI measurements were included into the analytical protocol. Results are presented in Figure 39. No statistically significant differences in the distribution of AOI in Lake Wannsee were found in the winter measurements in March 2004. In the southeast of Lake Wannsee the lowest concentrations were measured. This would implement a lower AOI concentration of the water entering Lake Wannsee from Teltow-canal through the small chain of lakes south of Wannsee. Water incoming from the north (containing WWTP Ruhleben effluent) has a higher AOI level. But the differences are very low and the circumstances of the sampling event (e.g. preceding precipitation) are unclear. Therefore, the results would point towards a nearly even distribution of the AOI concentration during winter in Lake Wannsee. The concentrations measured in the surface water campaign are approximately 4 µg/l lower than in the monthly scheduled sampling in front of the transect in March. This is probably due to a time difference between both sampling events.

The sampling campaign in July 2004 showed slightly higher concentrations of AOI on the east side of the lake compared with the west bank. During summer WWTP Ruhleben discharges into the Teltow-canal and could be responsible for increased AOI levels on the east bank of the lake. Electrical conductivity measurements of FU Berlin propose a preferential flow of the Teltow-canal water northwards along the east bank of Lake Wannsee. This would be consistent with the AOI results of the surface water sampling campaign. But the differences in concentration are again very low and close to the detection limit. Therefore, the results indicate that the changing point of discharge of treatment plant Berlin-Ruhleben has only minor influence on the seasonality of the AOI in the surface water. The spatial variation of AOI concentrations in the lake was found to be slightly influenced by Teltow-canal water. Unfortunately, the sampling campaigns did not capture peak concentrations of more than 20 µg/l. It remains unclear whether such high AOI concentrations occur only locally or in the whole lake. The depth profiles which were recorded in the middle of the lake as part of the surface water sampling showed AOI concentration similar to surface water in 2 m, 4 m, 6 m, and 7 m depth.

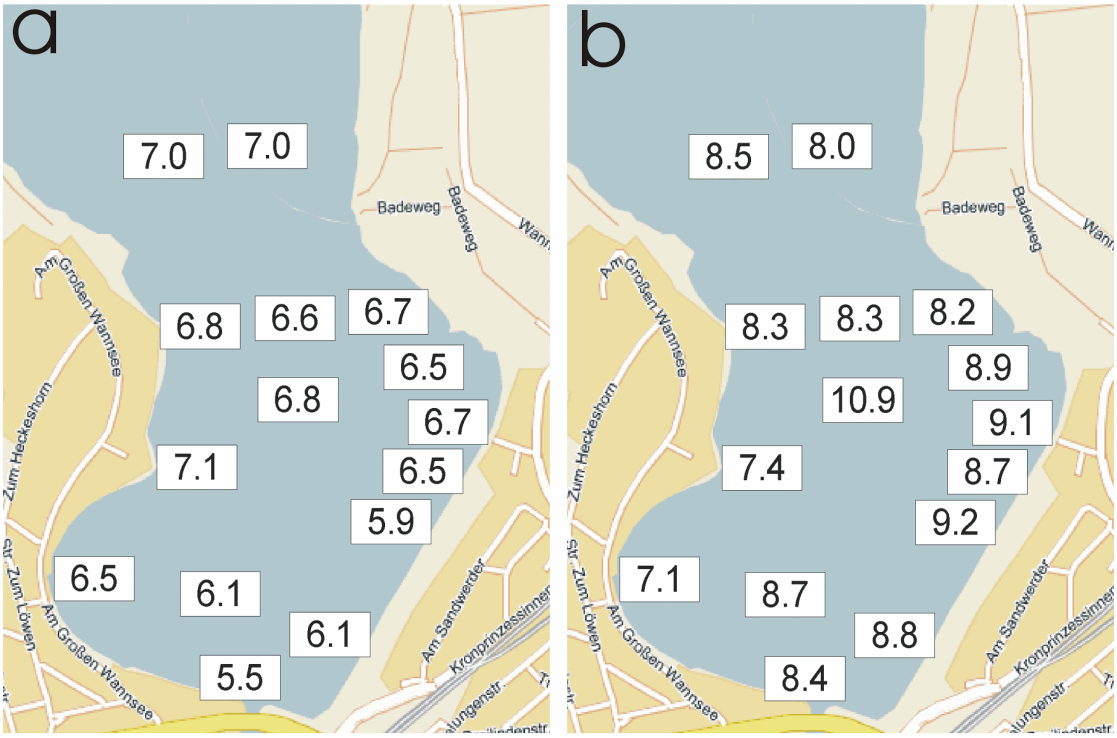


Figure 39 Distribution of AOI (µg/l) in Lake Wannsee in March 2004 (a) and July 2004 (b)

1.2.3.2 Bank filtration - AOI results

Besides the surface water investigations adsorbable organic iodine (AOI) of most of the samples from transect Wannsee II was measured as part of the monthly monitoring schedule. Since AOI is mostly of anthropogenic origin the removal rates were of special interest for the evaluation of the organic composition of the bank filtrate. All findings for the monitoring wells are based on 18 months measurements, whereas surface water and production well were sampled for a longer period.

Results show that the fate of AOI during infiltration is different under more aerobic (206, 202OP and 203) and anoxic/anaerobic (205) conditions. Any surface water variation of

AOI has a stronger effect on the aerobic monitoring wells, where the average AOI-reduction is only 20-35%. This seems not to be strongly dependent on retention times because the monitoring well with retention times of less than a month (206; 34%) shows better results than the monitoring well with retention times of more than 2 months (203; 22%). But all wells exhibited best removal efficiencies during summer season, which is probably due to temperature effects and the coupled changes in redox chemistry. In the shallow wells 206, 202OP, and 203 a shifted seasonal change in oxygen and nitrate concentration was observed. During winter, real oxic conditions dominated and during summer a depletion of oxygen and nitrate was observed. The combination of higher temperatures and lower redox potentials lead to a higher removal efficiency for AOI during summer months. Therefore, the summery surface water AOI-peaks did not occur in the monitoring wells. Highest concentrations in the wells were found during winter when the AOI mineralization was comparable low.

Monitoring well 205 has a slightly different redox chemistry. Due to saturated infiltration the bank filtrate remains anaerobic for nearly the whole year. The redox potential is considerably lower and nitrate reduction was observed in all seasons (NO_3-N: surface water: 1.0 mg/l; 205: 0.03 mg/l). The lower redox potential causes a more efficient reduction of AOI during the recharge process (63% during approximately one month retention time).

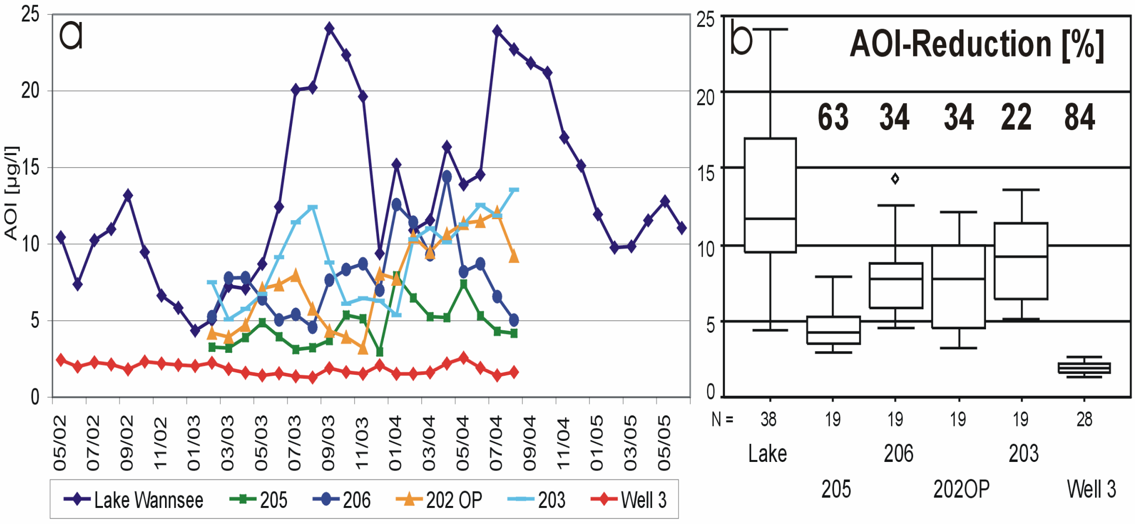


Figure 40 Fate of AOI during infiltration at transect Wannsee II (a: time series; b: box plots)

These results are consistent with findings at other field sites in Berlin. At the predominantly anoxic/anaerobic bank filtration site at Lake Tegel AOI reduction rates of app. 60-70% were observed during a 4-5 months infiltration (100 m infiltration distance). At the more oxic artificial recharge facility in Berlin-Tegel the measured average reduction rate was 30%. This inverse correlation between AOI-removal and redox potential is believed to originate from the initial step of AOI-mineralization -

reductive dehalogenation. The degradation of halogen substituted organics is more effective in soil passages with low redox potential (Mohn & Tiedje; 1992). Results from field site Wannsee evidently show that low redox potentials are essential for an efficient degradation of AOI and that even a duplication or triplication of retention times and infiltration distances can not compensate the absence of reducing conditions.

In Berlin-Wannsee the AOI of the other abstracted water fractions is very low (~2 µg/l) and the mixing in the production well (Well 3) leads to an AOI-concentration in the extracted raw water of 2-2.5 µg/l. The old bank filtrate is represented by the monitoring wells 202MP1, 202MP2 and 202UP. Figure 41 shows that this water fraction contains AOI concentrations of around 2 µg/l. Monitoring well 202MP1 is dominated by the old bank filtrate for most of the observation period but during winter and spring 2004 an influence of the young bank filtrate is visible. The AOI concentrations in 202MP1 increased considerably during this period. A comparison with the shallow wells (Figure 40) reveals that the increase of AOI level was also found in the young bank filtrate.

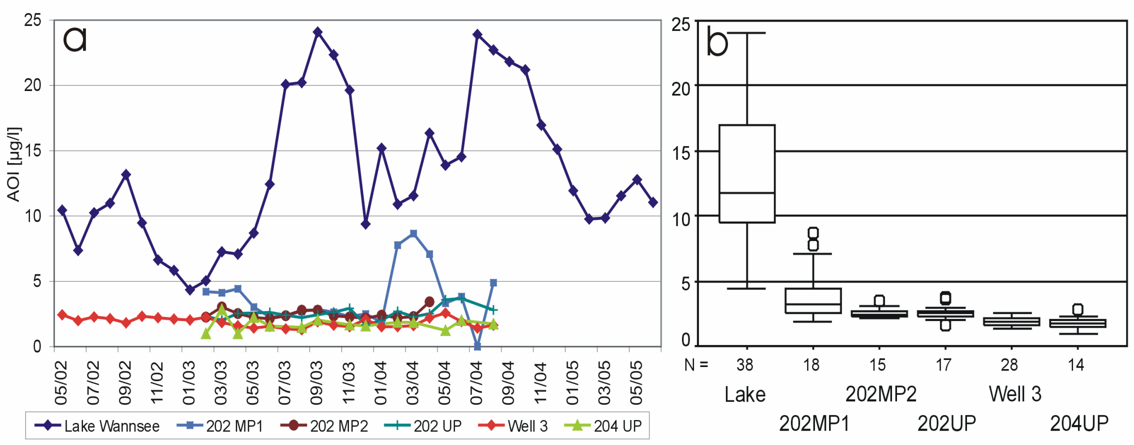


Figure 41 AOI in the multiple raw water sources at transect Wannsee II (a: time series; b: box plots)

Background groundwater (represented by 204UP) contains very low amounts of AOI. The average concentration was found to be 1.7 µg/l (δ=0.5 µg/l). For the deeper aquifers at field site Wannsee only one sampling was conducted. But taking in consideration the depth, it can be assumed that the water composition is very stable and no temporal variations occur. The sampling resulted in AOI levels below the limit of detection of 1 µg/l for the monitoring wells 3332, 3334, and 3336.

These findings explain the very low AOI concentration in the abstracted raw water. A calculation based on the mixing ratios proposed by the Free University Berlin would result in a AOI concentration of 3.3 µg/l in the abstracted raw water. Because of the low share of young bank filtrate, increasing AOI concentration are not expected to influence the product water quality at transect Wannsee II strongly.

1.2.4 Lake Wannsee - AOBr Results

1.2.4.1 Surface water - AOBr Results

The monitoring of adsorbable organic bromine (AOBr) concentration in Lake Wannsee for more than three years revealed a seasonal trend which is more dominant than in Lake Tegel (Figure 42). During winter and spring, AOBr concentration remains on a low level of about 6-8 µg/l. This fraction is believed to contain AOBr from anthropogenic sources (disinfectants, etc.). The concentration level is very similar to the one observed in Lake Tegel during winter. In summer and fall, AOBr concentration strongly increases (e.g. 2003: up to 500%; 2004: up to 400%) for a duration of 4-5 months. Putschew et al. (2003) found that the high AOBr concentrations are associated to algae blooms for two other Berlin lakes. Therefore, it seems consequential that the summery peaks in AOBr concentration are more dominant in Lake Wannsee than in Lake Tegel. Maximum concentration for Tegel were 25 µg/l during the observation period from 2002-2005. In Lake Wannsee, the AOBr level rose to more than 43 µg/l in summer 2003. Wannsee is more prone to algae blooms because of higher phosphorus concentrations (2004/2005: ∅=173 µg/l; δ=147 ng/l; n=10). Organobromines are formed by special types of algae, which bloom during late summer.

Altogether, the observed seasonality is known from literature and earlier studies of the DWQC. All results strongly support the theory of algae associated AOBr and the findings of Putschew et al. (2003).

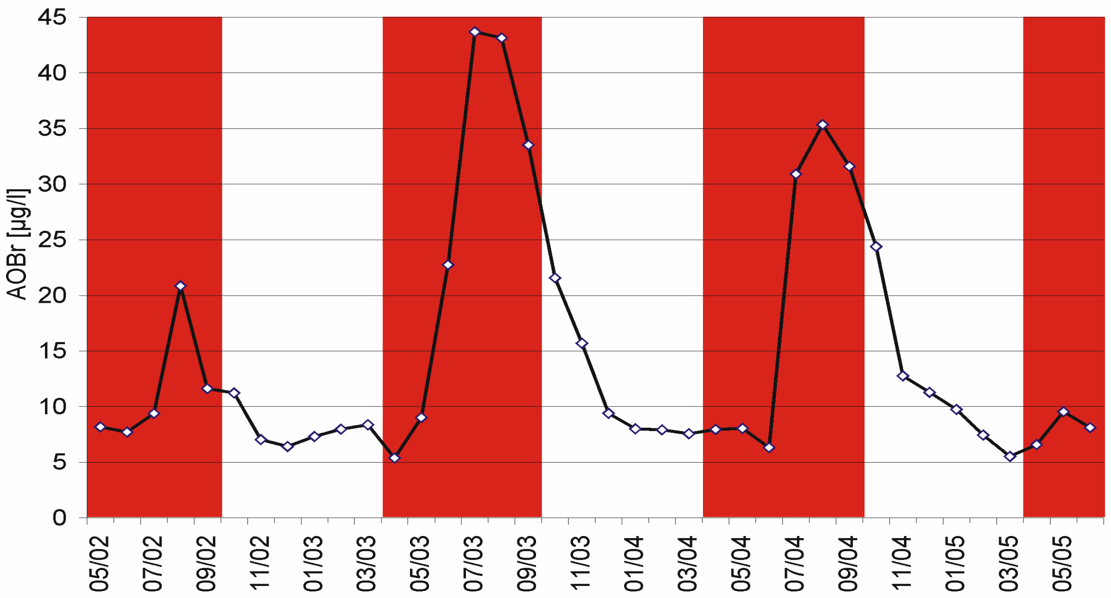


Figure 42 AOBr concentration in Lake Wannsee (2002-2005, April-September marked)

The spatial variation of AOBr concentration was investigated in the mentioned surface water sampling campaigns which is presented in Figure 43. In March 2004, slightly higher concentrations of AOBr in the north of Lake Wannsee were found. During winter, all AOBr is assumed to originate from anthropogenic sources. Therefore, higher concentrations in the north part of the lake indicate an influence of the treatment plant Ruhleben. No depth variation was found in winter.

At the time of the July campaign, the distribution of anthropogenic AOBr was superposed by algae associated organobromine. Areas with high AOBr concentrations would not specify waste water influence but regions of elevated algae activity. But in summer, AOBr concentrations seem to be evenly distributed in Lake Wannsee. The general concentration is considerably higher in summer compared to the winter sampling. A comparison with the time series (Figure 42) reveals some differences, which might be due to different sampling times (time of day) or sun activity. However, the results show that in July 2004, the activity of algae species which are responsible for the AOBr formation was evenly distributed over Lake Wannsee. It can be assumed that this is valid for all algae species. During summer, a slight depth variation was found in the middle of Lake Wannsee. On the surface, the AOBr concentration was approximately 2 µg/l higher than in the depths of 2, 4, 6, and 7 m. The observed -10% variation appears small since algae need light for growing. But Hütteroth et al. (2004) found that algae release AOBr during stress situations and during die-off. Therefore, higher AOBr levels in deeper waters could originate from descending dying algae.

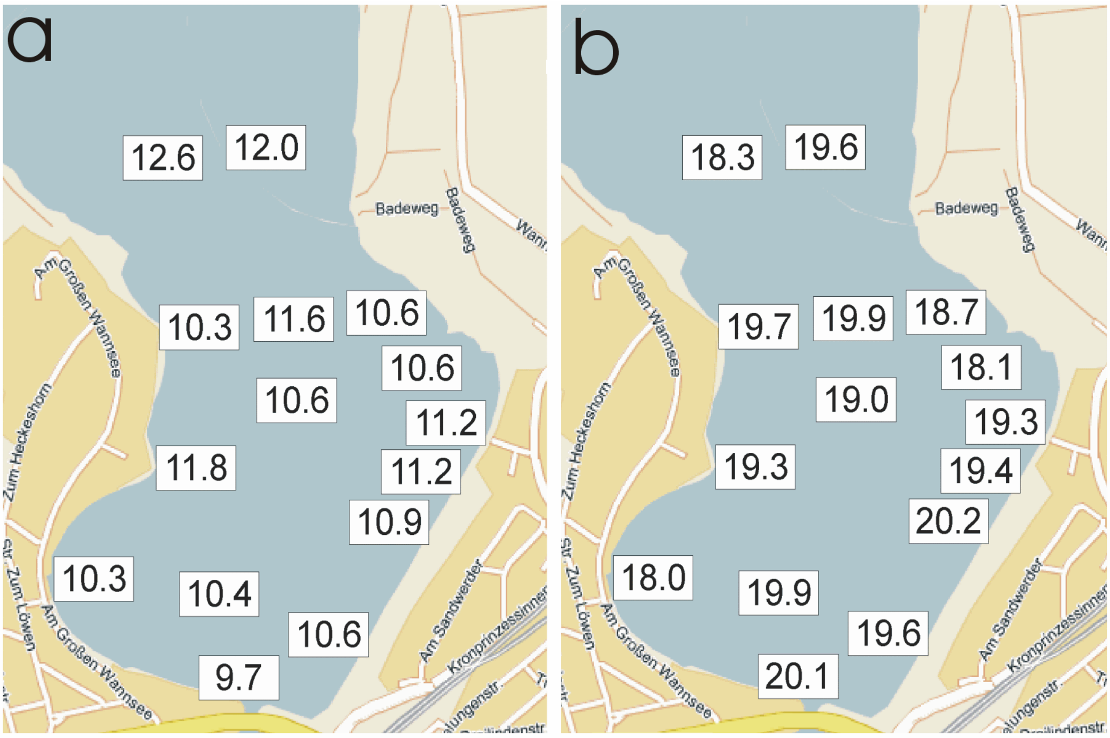


Figure 43 Distribution of AOBr (µg/l) in Lake Wannsee in March 2004 (a) and July 2004 (b)

1.2.4.2 Bank filtration - AOBr results

The fate of AOBr along the infiltration path at Wannsee II was investigated for 18 months. Observations pointed toward a similar removal mechanism for AOI and AOBr. Another important finding was that the strong surface water peaks during late summer did not influence the AOBr concentration in the subsoil.

Figure 44 shows that the monitoring well with the lowest redox potential (205) achieved a reduction of 68%. Under oxic conditions, average removal rates were clearly lower (206: 19%; 202OP: 30%; 203: 26%). These removal rates are based on median concentrations. In the median calculation, the summery surface water peaks are statistically regarded as extreme values and have less influence as in the calculation of the mean. A calculation on the basis of mean concentrations would result in higher removal rates. However, water of the production well contained only 22% of the surface water AOBr. Furthermore, it was proved that the anoxic/anaerobic well 205 is most efficient in removing AOBr, mineralizing more than 60% of the surface water AOBr. The more oxic monitoring wells 206, 202OP, and 203 exhibited only removal rates of 20-30%. It is believed that AOBr removal is influenced by redox potential and temperature, similar to the pattern observed for AOI.

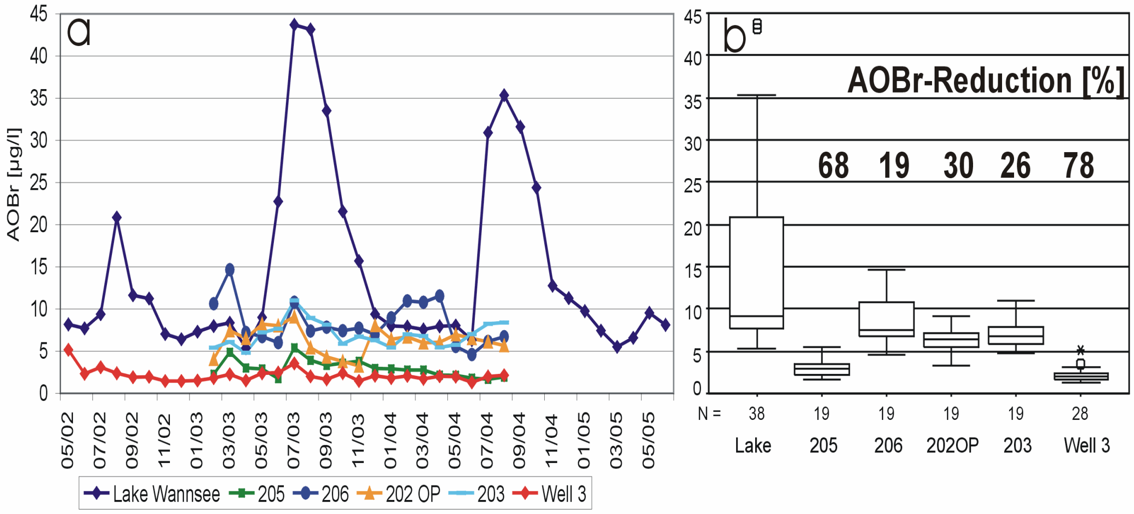


Figure 44 Fate of AOBr during infiltration at transect Wannsee II (a: time series; b: box plots)

For a complete evaluation of the AOBr results, a differentiation between the two fractions of AOBr seems to be necessary. Figure 44 shows that the summery peaks of AOBr in surface water are more dominant than the AOI peaks (Figure 40). It is unlikely that higher temperature and more reducing conditions during soil passage in summer increase the removal efficiency to an extend that a nearly 500% concentration increase is not visible in the monitoring wells. Therefore, the results can only be explained by a higher biodegradability of the algae associated AOBr fraction. Surface water investigations demonstrated that besides the algae associated AOBr fraction a fraction of adsorbable organic bromine exists which is present the year-round in surface water.

This fraction accounts for approximately 8 µg/l in the surface water. With respect to the monitored results, it can be assumed that this fraction behaves similar to AOI. An efficient removal under anaerobic conditions (205) and less mineralization under oxic conditions (206, 202OP etc.) was observed. On the contrary, a better biodegradability of algae associated AOBr was found. This seasonal occurring AOBr seems to be easily degradable under oxic and anoxic/anaerobic conditions, because the 500%-increase of AOBr-concentration during summer was not observed in any of the monitoring wells. A complete adsorption of this fraction onto soil matrix is unlikely, since the substances are very polar. Further research on the character and the behavior of algae associated AOBr are conducted by the DWQC (Hütteroth, 2004).

All other groundwater samples from monitoring wells that were not influenced by recent bank filtrate at Wannsee II contained very low concentrations of AOBr. Older bank filtrate in the lower part of the top aquifer was measured 38 times with concentrations between 1 µg/l and 3 µg/l (202MP2: 2.1 µg/l; δ=0.6 µg/l; 202UP: 1.8 µg/l; δ=0.3 µg/l). The background groundwater contained 1.3 µg/l (204UP; δ=0.3 µg/l) and no AOBr was found in the second and third aquifer (3332, 3334, and 3336).

Summarized, only the AOBr fraction which is present all year in the surface water shows the preferential removal under anoxic/anaerobic conditions that was observed for AOI. The heavy peak loads during summer seem to have no effect on the drinking water production and are therefore regarded as unproblematic.

1.2.5 Lake Wannsee - Trace pollutants results

1.2.5.1 Surface water - Trace organic compounds

It was explained earlier, that the surface water of Lake Wannsee is influenced by the discharge of river Havel entering the lake from north and water from Teltow-canal (through small Wannsee) incoming from south. The discharged volumes and the content of treated wastewater change over the seasons because of natural precipitation and the changing outlet of WWTP Ruhleben. Overall, the system was found to be very complicated. The electrical conductivity, chloride, and boron data indicate a higher waste water portion in front of the transect Wannsee II during summer (NASRI Report 1). This is consistent with the findings of DOC and AOI monitoring. Therefore, it was assumed that the monitoring of trace pollutants would show a similar seasonality. The investigated trace organic compounds were selected because they are present in surface water in detectable concentrations. Furthermore, the compounds can be easily assigned to treated wastewater because they are completely of anthropogenic origin.

Figure 45 presents the results of the surface water monitoring in front of Wannsee II from May 2003 to June 2005. Temporal changes of the concentrations of Iopromide (X-ray contrast agent), Sulfamethoxazole (Bacteriostatic), and three isomers of naphthalenedisulfonic acid (NDSA) were investigated. The results can not be compared with findings of earlier studies since no older data are available for this transect. However, Figure 45 shows that the concentration of most of the trace compounds varies highly in front of the transect. A comparison with surface water concentrations in Lake Tegel reveals that the average Iopromide concentration is very similar in both water bodies (Tegel: median= 969 ng/l; Wannsee: median= 936 ng/l). Sulfamethoxazole was found in considerably higher concentrations in Lake Tegel, where a median concentration level of 371 ng/l was found (Wannsee: median=195 ng/l). For the isomers of naphthalenedisulfonic acid Wannsee surface water concentrations were 50-100 ng/l higher than in Lake Tegel.

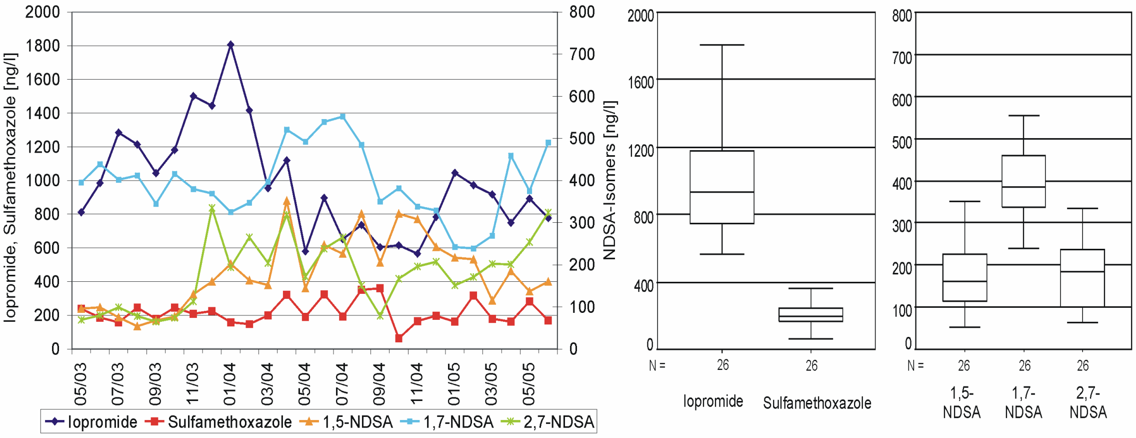


Figure 45 Trace pollutant concentration in Lake Wannsee (2003 - 2005, a: time series; b: box plots)

The selected trace compounds were found in all surface water samples of the monitoring period with concentrations above the limit of quantification. Because of the long time series it was of interest to detect eventual seasonal changes for the trace compounds. Figure 45 shows that the concentrations of the trace organics were highly variable but did not necessarily follow a seasonal scheme. This might be due to the fact that seasonal changes are superposed by strong short-term variations.

The X-ray contrast agent Iopromide was detected in the surface water with a median concentration of 936 ng/l (δ=318 ng/l, n=26). The concentrations were highly erratic with no general trend over the observation period. During summer of 2003, the concentration remained in a range between 800-1200 ng/l. In the following winter, an increase up to 1800 ng/l followed. Afterwards a decrease during spring and constant concentrations of about 700 ng/l during summer 2004 were observed. Another concentration increase during winter 2004/05 supports the trend of slightly higher concentrations during winter in front of the transect. This is contrary to the concentration of other waste water indicators. An explanation may arise from the different concentrations of X-Ray contrast agents in the effluent of the WWTP´s of Berlin. Studies of the DWQC showed that WWTP Schoenerlinde discharge contains incomparable high concentrations of X-Ray contrast agent because of the health complex Berlin-Buch, which discharges to treatment plant Schoenerlinde. Wischnack and Jekel (2000) found average Iopromide concentrations of more than 20 µg/l in 24h-mixed samples. Bahr et al. (2005) found concentrations of ~5 µg/l Iopromide in ten random samples of the effluent of WW treatment plant Ruhleben. Therefore, higher concentrations during winter could result from a higher portion of treated waste water from Schoenerlinde ending up in front of Wannsee II during winter. However, a comparison with the general waste water indicators like chloride and boron did not lead to satisfying results.

The antibiotic drug Sulfamethoxazole was found in Lake Wannsee with a median concentration of 195 ng/l (δ=72 ng/l, n=26). Figure 45 shows that no seasonality was observed for this pollutant and that the concentration level remained relatively constant. The fact that the average Sulfamethoxazole concentration is only half as high as in Lake Tegel points towards a different origin of the waste water share in Wannsee since all other waste water indicators show similar concentrations. Attenuation in the surface water is unlikely since Sulfamethoxazole is very stable and not photosensitive.

Results for the different NDSA-isomers show consistently with other field sites that the 1,7-NDSA is the most important isomer in Berlin surface waters. The median concentration of this compound was found to be 388 ng/l (δ=85 ng/l, n=26) in Lake Wannsee. The 26 months of monitoring resulted in median concentrations of 162 ng/l for 1,5-NDSA (δ=96 ng/l, n=84) and 183 ng/l for the 2,7-isomer (δ=96 ng/l, n=83). The time series for 1,7-NDSA shows that the pollution level for this compound remains relative stable over the monitoring period. A slight trend towards higher concentrations during summer can be recognized among the erratic concentration changes. This would be consistent with the proposed seasonal change in waste water influence. The time series of 1,7- and 2,7-NDSA show similarly low and stable concentration during summer 2003. With begin of winter 2003/04 the concentration of both isomers increases and shows irregular behavior. No seasonal dependency stands out for both compounds. The most characteristic indication of both time series is the strong increase in pollution level in November/December 2003 which remains high until the end of the observation period. Overall, the concentrations of NDSA are higher than at the other investigated field sites.

Because of strongly variable results for the trace compounds in Lake Wannsee any correlation attempts with other waste water indicators failed.

1.2.5.2 Bank filtration - Trace organic compounds

The single compound analysis for the trace pollutants Iopromide, Sulfamethoxazole, and different naphthalenedisulfonic acids was started in spring 2003, providing data for the time period May 2003 to August 2004. The monitoring was of special interest because transect Wannsee II provided the opportunity to observe very detailed the difference between oxic and anoxic/anaerobic infiltration. The monitoring wells 205 and 206 receive the same surface water. Both have similar retention times, but differ in the dominant redox conditions. Furthermore, the more distant shallow monitoring wells represent a comparable long oxic infiltration path. Therefore, the long time behavior of the analyzed trace compounds under oxic conditions could be studied.

The older bank filtrate in the deeper part of the top aquifer was sampled to obtain more information about the behavior of these compounds during decades of soil passage. It can be assumed that the trace compounds were present in the surface waters for at least 20 years. Naphthalenedisulfonic acids were used in industry since the second half of the 19th century. Sulfamethoxazole is widely used in medicine since World War II and Iopromide was introduced to the European medicine in 1985 under the product name Ultravist. Since the determination of age for the older bank filtrate proposed a time span of approximately ten years (202UP: 10.7 years) from infiltration to abstraction it is most probable that the analyzed trace compounds were present in the surface water at this time. No information exists about the average concentration ten to twenty years ago. Furthermore, the screening of the background groundwater and the deep groundwater revealed eventual anthropogenic influences on this groundwater streams.

Generally, it was found that these trace organic compounds which stand for different groups of persistent pollutants behave differently during infiltration. For most of the analyzed compounds, an influence of redox conditions on the degradability could be revealed. Furthermore, some temperature effects were observed.

Figure 46 presents data on the fate of Iopromide during infiltration. Surface water pollution level for Iopromide (~1000 ng/l) was considerably higher than for the other compounds. As mentioned, Iopromide is a triiodinated benzene derivate and part of the bulk parameter AOI. The results at Wannsee II confirm that the removal mechanisms under oxic conditions are completely different from the removal under anoxic/anaerobic conditions. This conclusion originates from a comparison of the AOI mineralization with the Iopromide removal. Of special interest was a comparison of the monitoring wells 205 and 206 which revealed more details on the degradation characteristics of Iopromide. Both monitoring wells are located under the lake and differ primarily in dominant redox conditions. During anoxic/anaerobic infiltration Iopromide concentration was reduced from the lake (1081 ng/l, n=16, σ=336 ng/l) to observation well 205 (363 ng/l, n=12, σ=118 ng/l) by 66%. This is consistent with the observed AOI reduction (205: 63%). Therefore, it could be assumed that a high portion of the removal of Iopromide was based on dehalogenation and mineralization. But during oxic infiltration Iopromide showed a clearly better removal of 96% (206: 41 ng/l, n=16, σ=35 ng/l) than AOI (206: 34%). This confirms that Iopromide and AOI behave differently during oxic infiltration. One assumption that arose from results of other field sites and soil column studies is that the Iopromide molecule is rapidly metabolized under oxic conditions, but not mineralized. The metabolite is not efficiently dehalogenated and remains detectable as AOI.

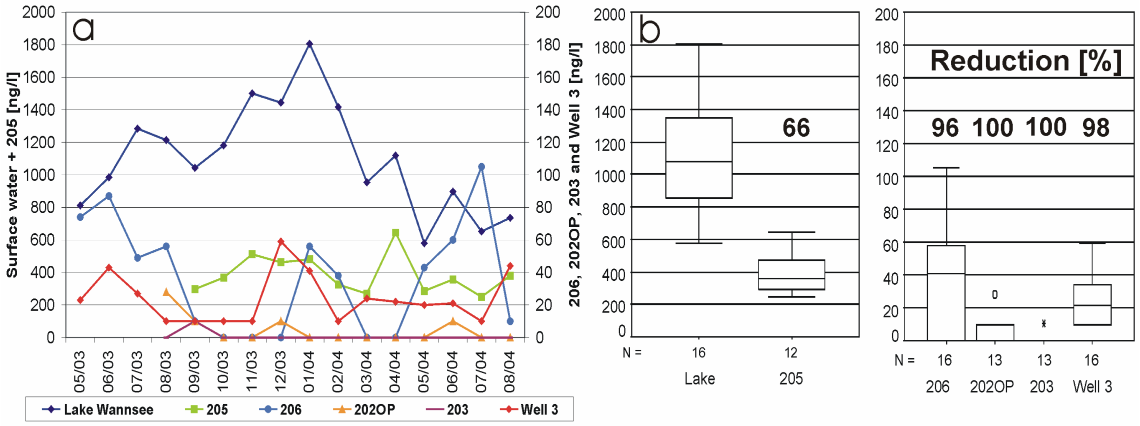


Figure 46 Fate of Iopromide during infiltration at transect Wannsee II (a: time series; b: box plots)

The time series of Iopromide measurements reveal more influences on the Iopromide removal. The contamination level in the anaerobic well 205 remains in the range of 300-500 ng/l over 12 months. For 206, the time series shows seasonal differences between concentrations under the limit of detection (5 ng/l) and concentrations of 60-100 ng/l. These effects can be explained by the influence of temperature and changing redox conditions. During summer, the redox potential in 206 decreases and a complete denitrification leads to anaerobic conditions. This was observed during the summer of 2003 and 2004. In this time, 206 resembles the conditions in 205 and a less efficient metabolization of Iopromide occurs. The higher concentrations during winter are due to reduced bioactivity because of low temperature. Overall, the most efficient Iopromide removal in 206 was observed during spring and fall.

However, along the further infiltration path towards the production well very low Iopromide concentrations were monitored. Contrary to the fate of AOI, Iopromide showed a very good removal along the oxic infiltration path to the production well. Only once a concentration above the limit of quantification (20 ng/l) was found in the monitoring wells 202OP and 203. Curiously, the concentration levels in the production well 3 are higher than in 203. The reason is unclear since all other abstracted water fractions (old bank filtrate, background groundwater, and deep groundwater) did not contain any measurable amounts of Iopromide. The time series of the production well also indicates higher concentrations during summer and winter months and lower concentrations during spring and winter. It must be assumed that these influences originate from a flow path which is not directly sampled by one of the monitoring wells and which also shows the shifted seasonal influences that were observed in 206. Overall, it can be summarized that the X-ray contrast agent Iopromide is efficiently attenuated at Wannsee II, but there were strong indications that one part of removal was based on an aerobic metabolization and not on dehalogenation and mineralization.

The bactriostatic Sulfamethoxazole was present in the surface water with concentrations of 150-350 ng/l. A comparison of monitoring well 205 and 206 showed clearly that the degradation of Sulfamethoxazole seems to be redox dependent as well. In Berlin-Wannsee, Sulfamethoxazole shows a better removal under anoxic/anaerobic conditions. Within approximately one month of infiltration to monitoring well 205 the surface water concentration (204 ng/l, n=16, σ=62 ng/l) was efficiently degraded (205: 3 measurements > LOQ; median: 0 ng/l, n=12, σ=12 ng/l). The oxic infiltration path along 206, 202OP, and 203 displayed smaller degradation rates ranging from 43% to 62%. A slight influence of a longer retention time was observed because the monitoring wells 202OP and 203 (retention times 2-4 months) showed higher removal rates than 206 (0.5 month). But even these very long aerobic soil passages did not eliminate the bacteriostatic compound completely. During the observation period, a trend towards higher concentrations in the shallow oxic monitoring wells was observed. Starting in winter 2003, the contamination levels of 202OP and 203 increased from less than 50 ng/l to more than 100 ng/l. The higher concentrations did not show influence on the abstracted water in well 3. However, the better removal of Sulfamethoxazole under anoxic/anaerobic conditions is consistent with the observations in Tegel and findings of Schmidt et al. (2004) at other bank filtration sites in Germany.

Background groundwater, old bank filtrate, and deep groundwater were found to be free of Sulfamethoxazole residues. Although Sulfamethoxazole was relative stable during oxic soil passage, the mixing with other groundwater fractions in production well 3 lead to very low concentrations, which are far below the precaution value for anthropogenic organic contaminants.

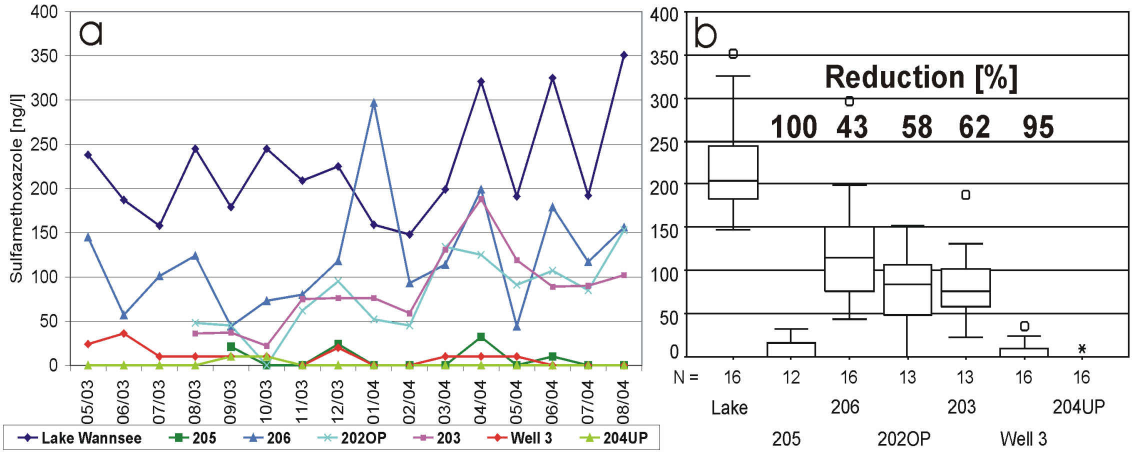


Figure 47 Fate of Sulfamethoxazole during infiltration at transect Wannsee II (a: time series; b: box plots)

The group of naphthalenedisulfonates was present in Lake Wannsee surface water with higher pollution levels than in Lake Tegel. Two of three monitored isomers showed a strong concentration increase during the observation period. Therefore, it was of interest to investigate the influence of the increased surface water concentration on the monitoring wells and the production well.

At other field sites and in soil column experiments, it was found that 1,5-NDSA is the most stable isomer from the group of the naphthalenedisulfonic acids. Figure 48 shows that surface water concentration increased during the period May 2003 – August 2005 from ~100 ng/l to a maximum concentration of ~300 ng/l. It was observed that the higher concentration in surface water leads to increasing 1,5-NDSA levels in the monitoring wells. Well 205 and 206 very closely follow the surface water concentration, supporting the findings of short retention times for these wells (0.5-1 month). The concentration of 1,5-naphthalenedisulfonic acid remained nearly constant during oxic (206) and anoxic/anaerobic (205) infiltration. The slightly higher median concentration in well 205 is due to short-term variations of the surface water which were not captured by monthly sampling. However, the compound did not show any removal within one month under either redox conditions. Along the further infiltration path only a time shift in the time series was observed. This time shift is consistent with results of tracer evaluations that were conducted by the workgroup from the Free University Berlin. The concentrations in 202OP and 203 increased to a similar pollution level approximately 4 months after the surface water rise. Therefore, it can be followed that no efficient removal of 1,5-NDSA takes place at Wannsee II. The removal rates stated in Figure 48 are strongly influenced by the time shift in the more distant monitoring wells and are therefore mostly too high. For consistency reasons they were calculated similarly to all other mentioned removal rates.

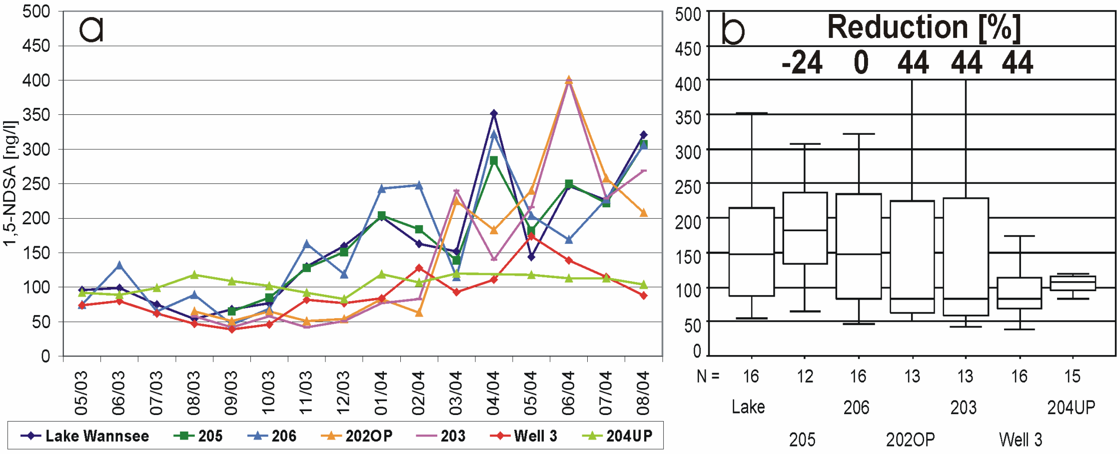


Figure 48 Fate of 1,5-NDSA during infiltration at transect Wannsee II (a: time series; b: box plots)

Figure 48 also shows that the contamination level in the background groundwater was stable over the monitoring period. The concentration of 1,5-NDSA in monitoring well 204UP was found to be 105 ng/l (n=15, σ=12 ng/l). This is similar to the concentrations found in 202MP2 and 202UP (Ø=106 ng/l, n=8, σ=25 ng/l). The sampling event in

March 2004 for the deep monitoring wells 3332, 3334, and 3336 resulted in NDSA concentrations below the limit of detection for the second and third aquifer. Therefore, the deep aquifers are most probable not influenced by anthropogenic substances.

These results show that 1,5-NDSA is very poorly biodegradable and elimination of this compound can not be expected during bank filtration. No influence of the redox conditions on the degradation was found. The final concentration of well 3 product water results from a mixture of non-polluted deep groundwater, 1,5-NDSA-containing old bank filtrate and background groundwater, and young bank filtrate. The calculated mixing proportions are consistent with the observed concentrations. A 300%-increase in 1,5-NDSA concentration in well 3 between fall 2003 and spring 2004 shows that young bank filtrate has a considerable influence on the product water composition. Overall, these results are consistent with findings of Stueber et al. (2002) who reported 1.5-NDSA as very stable in wastewater treatment plants.

1,7-Naphthalenedisulfonic acid was present in surface water of Lake Wannsee (Ø=381 ng/l, n=26, σ=96 ng/l) in slightly higher concentrations than observed at Lake Tegel (Ø=333 ng/l, n=25, σ=84 ng/l). It was found that the compound is partially degraded during oxic infiltration. This is consistent with findings at Tegel field sites and soil column experiments. In these studies it was proved that the degradable isomers of NDSA are more efficiently removed under oxic conditions. This is proved by a comparison of monitoring well 205 and 206. Both wells are receiving the same surface water but show different removal efficiencies in comparable time frames. In well 205, only 11% of the surface water concentration is removed during ~30 days of anoxic/anaerobic infiltration, whereas the oxic soil passage to well 206 removes 41% in less than a month. During further infiltration along the top part of the first aquifer, the concentrations of 1,7-NDSA decrease continuously and in monitoring well 203 75% of the substance is degraded. The time series in Figure 49 show that the measured concentration in monitoring well 205 follows closely the surface water concentration. For the other shallow monitoring wells a temperature effect was observed. The concentrations increased during winter 2003/2004 because of a temperature induced lower bioactivity. In 206, the 1,7-NDSA concentration in January and February 2004 were close to the surface water pollution level. This peak also occurred time shifted in the wells 202OP and 203.

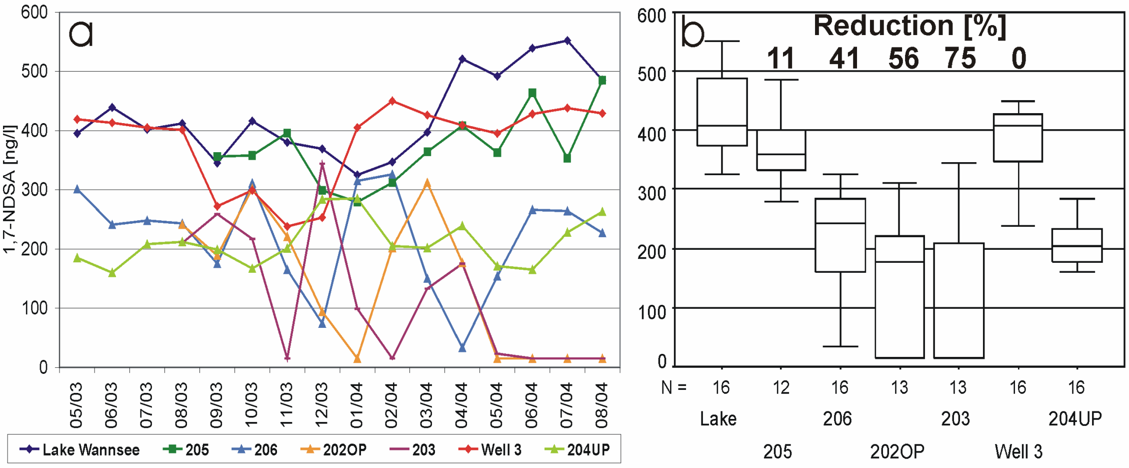


Figure 49 Fate of 1,7-NDSA during infiltration at transect Wannsee II (a: time series; b: box plots)

In production well 3, the 1,7-isomer concentration was measured to be similar to the surface water concentration. This is explained by a strong influence of old bank filtrate from deeper parts of the top aquifer. A screening of the monitoring wells 202MP2 and 202UP, which represent the old bank filtrate, confirmed median concentrations of 461 ng/l (n=8, σ=37 ng/l) for this groundwater stream. Background groundwater contains 1,7-NDSA at a level of 204 ng/l and the water from the second and third aquifer does not contain any measurable amounts of NDSA. This confirms the strong influence of the old bank filtrate on the product water. It can be assumed that the surface water concentration of NDSA was considerably higher during the times of infiltration of the old bank filtrate, or infiltration took place under more reducing conditions which inhibited a efficient removal of 1,7-NDSA (compare 205). The time series of production well 3 exhibits decreasing concentrations during summer and fall of 2003 and more or less stable concentrations during the rest of the observation period. It remains unclear whether an adapted pumping schedule during this hot and dry summer increased the influence of recent bank filtrate on the product water or whether higher temperatures lead to a more efficient degradation of 1,7-NDSA.

The 2,7-NDSA isomer monitoring showed results that were similar to the findings for 1,7-NDSA. Degradation of this compound is also more efficient under oxic conditions. The removal rates along the infiltration path of the recent bank filtrate were slightly higher than for the 1,7-isomer. Unlike 1,7-NDSA, the surface water concentration of 2,7-NDSA increased substantially during the observation period. The concentration increase occurred simultaneously with the already described rise of 1,5-NDSA pollution level during fall 2003. It remains unclear which effect was responsible for this significant change in concentration. The relocation of the discharge point for the WWTP Ruhleben seems to be no adequate explanation, since the contamination level did not drop in April 2004 back to former concentrations. The concentration in monitoring well 205 follows closely the surface water concentration and no efficient removal was found under anoxic/anaerobic conditions (Figure 50). In well 206, the temperature induced concentration increase in winter 2003/04 resembles the fate of 1,7-NDSA. This peak also occurs in the more distant shallow monitoring wells 202OP and 203 were the overall removal rate is 75% and 91%, respectively.

The average concentration in the production well increases during the observation period from ~50 ng/l to ~100 ng/l. This is most probably due to a cumulative effect, since the background water concentration also increases. The old bank filtrate (202MP2 and 202UP) was found to contain reproducible median concentrations of 80 ng/l (n=8, σ=18 ng/l). Therefore, it can be assumed that the 2,7-NDSA concentration increase in the product water is partly due to the strong concentration build up in surface water. Some uncertainties regarding the nearly simultaneous increase in the surface water and in the product water remain.

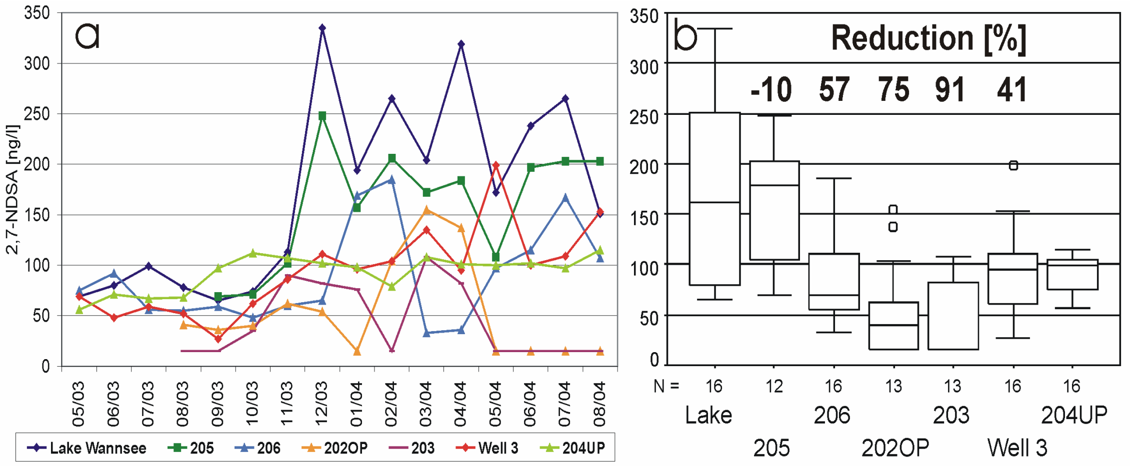


Figure 50 Fate of 2,7-NDSA during infiltration at transect Wannsee II (a: time series; b: box plots)

Summarizing, the results from the field monitoring at the bank filtration site Berlin-Wannsee provided insight into the degradation characteristics of the observed trace organic pollutants under field conditions. It was found that for most compounds the dominating redox conditions are an important parameter for the achievable reduction rates. In comparison with the field site Tegel the product water quality in Wannsee was less dependent from the surface water quality, since a larger portion of the product water derives from old bank filtrate or deep and background groundwater. Nevertheless, the concentrations of most of the investigated waste water born trace contaminants (Iopromide and the NDSA-isomers) were higher in Wannsee product water than in Tegel raw water. Sulfamethoxazole showed lower concentrations. This is reasoned by the strong influence of old bank filtrate at the Wannsee field sites which contains some of the pollutants in higher concentrations. The NDSA-isomers appear to be most problematic, since the mixing in well 3 leads partially to comparably high concentrations. E. g. the 1,7-NDSA isomer is present in well 3 raw water in average concentrations of ~400 ng/l, which is high above the precaution value of the German Drinking water Ordinance (100 ng/l). It appears to be necessary to investigate the effects of degradation and dilution during further treatment in the water works for these compounds. However, besides the strong influence of old bank filtrate the results for some compounds also display the influence of actual surface water quality on the abstracted raw water (e.g. 2,7-NDSA). Therefore, the protection of surface water and the monitoring of bank filtration processes remain necessary for high quality source water at the field site Wannsee.

1.3 Artificial groundwater recharge facility Tegel (GWR)

Surface water of Lake Tegel is used for groundwater augmentation at the artificial groundwater recharge site Tegel, which is located close to the bank filtration field site Berlin-Tegel. In three infiltration ponds with a total area of ~30.000 m^2 the Berlin Water works infiltrate 15 million cubic meter surface water annually. Since 2004 the amount of infiltrated water is decreasing due to restrictions of the Berlin government.

During summer months the surface water is micro-filtrated to remove suspended algae, which would minimize infiltration rates. The micro-filtration is not affecting any dissolved water constituents. Series of abstraction wells are located around the three infiltration ponds. The artificial groundwater recharge facility was selected as one of the field sites for the NASRI-project, because the conditions for infiltrating water differ considerably from conditions at the two selected bank filtration sites.

Despite of the fact that the distance between infiltration pond and abstraction well (107 m) is similar to the distance at bank filtration site Tegel, the infiltration velocity is higher. This leads to significantly shorter retention times of the filtrate in the subsoil. The average retention time of the in NASRI sampled production well 20 is ~50 days. Furthermore, the character of the sediments at the GWR differs from the naturally grown lake bank sediments. Generally, the sandy sediments are poorer in particulate organic matter than the sediments close to the bank of Lake Tegel and additionally, organic debris on the floor of the infiltration ponds is regularly scraped off to restore permeability. Due to these differences the conditions during infiltration vary from the conditions observed at Tegel bank filtration site.

The redox potential of the infiltrating water shows more often oxic conditions than the bank filtrate in Tegel. Only during summer months July to September measurable amounts of nitrate are removed by denitrification during the infiltration process. Mostly oxic conditions dominate the infiltration path at the GWR throughout the rest of the year. Beside the temperature dependency of the redox conditions an influence of the infiltration cycle was observed. The infiltration conditions at the GWR change significantly with the time schedule for the removal of the filtration cake layer on the bottom of the infiltration ponds. But the changes induced by this maintenance schedule occur in time frames of days or weeks and are not reproducible by a series of monthly measurements. Therefore, the discussion in this chapter will focus on the general situation at the groundwater recharge facility and will ignore short term variations. The twenty monthly measurements of bulk and trace organics capture a close summary of the important processes at the recharge facility. More detailed information on changes due to scheduled maintenance of the infiltration ponds is available in (NASRI Report 1, chapter 1.6).

Another important factor at the GWR is the short retention time, which is responsible for a very pronounced temperature profile in the abstracted water. Seasonal temperature variations of surface water of more than 20 K occur only slightly time shifted and nearly not attenuated in the production well. Therefore, the biomass which is responsible for degradation of bulk and trace organic compounds is more exposed to extreme temperatures at the GWR than at the bank filtration sites. This might lead to reduced removal and mineralization rates during long and cold winters.

However, the monitoring period of DWQC for the GWR started in October 2002 and ended in May 2004. A transect of monitoring wells and one production well at infiltration basin 3 was selected. The monthly analytical program consisted of DOC, UVA$_{254}$, UVA$_{436}$, LC-OCD, and differentiated AOX analysis. Over a time period of 13 months (May 2003-May 2004) the monitoring was extended by trace compound analysis. The behavior of five earlier mentioned trace compounds during infiltration at the GWR was investigated. Although the infiltrated water is pumped directly from Lake Tegel, samples from the infiltration pond were analyzed. A comparison of Lake Tegel samples and infiltration pond samples will identify eventual differences in organic composition, which might be derived from the micro-filtration process or photocatalytic effects. All results of field monitoring are reported in the following chapters.

1.3.1 Groundwater Recharge - Results bulk organics

Amount and character of bulk organics in the infiltration pond was monitored monthly over the period October 2002 to May 2004 using the described analytical methods (DOC, UVA$_{254}$, UVA$_{436}$ and SUVA (calculated)). Table 4 provides the arithmetic mean, median and standard deviation of all measurements and the corresponding data from Lake Tegel surface water.

Table 8 Results bulk organic parameters in GWR infiltration pond 3 and Lake Tegel surface water 2002-2004 (n=20)

		DOC	**UVA$_{254}$**	**UVA$_{436}$**	**SUVA**
		[mg/l]	[1/m]	[1/m]	[l/m*mg]
GWR Tegel	Arithmetic mean	7.4	15.3	0.47	2.08
	Median	7.5	15.3	0.47	2.05
	Standard deviation	0.8 (10.6%)	1.2 (8.0%)	0.14 (30.5%)	0.16 (7.7%)
Bank filtration Tegel	Arithmetic mean	7.2	15.1	0.52	2.11
	Median	7.1	15.2	0.48	2.09
	Standard deviation	0.5 (7.6%)	1.1 (7.3%)	0.11 (22.9%)	0.18 (8.8%)

It was found, that the average DOC level in infiltration pond 3 is similar to DOC concentrations observed in Lake Tegel. The median of 20 DOC measurements was 7.5 mg/l. Furthermore, a comparison of the parameters UVA$_{254}$, UVA$_{436}$ and SUVA pointed towards a very similar composition of bulk organic water constituents in both surface waters. This proves that the treatment by micro-filtration does not affect the dissolved organics. Additionally, it shows that the water composition at the pumping station (~1 km south of the bank filtration transect) is similar to the water quality in front of the transect.

Figure 51 proves that the observed changes over time for all three parameters (DOC, SAK_{254}, and SUVA) occur similarly in lake water and infiltration pond. This similarity confirms the results of the monitoring of the surface water in front of the bank filtration site. Any observed small differences are due to measurement mistakes and variations of time of sampling. During four months in winter 2002/03 the DOC level in the recharge pond is higher than in Lake Tegel. The reasons for this remain unclear, since DOC production by algae blooms in calm water bodies (recharge pond) was expected to occur during summer. Additionally, the comparison proves that no strong seasonal effects, which were not observed in Lake Tegel, influence the water quality in the recharge ponds. Judging from the heavy algae growth in the ponds during summer, an influence on the DOC-concentration and DOC-character could have been expected. This assumption was disproved by the presented results. More detailed information on the DOC-character of the recharge pond water will be provided with the LC-OCD analysis in chapter 1.3.3.

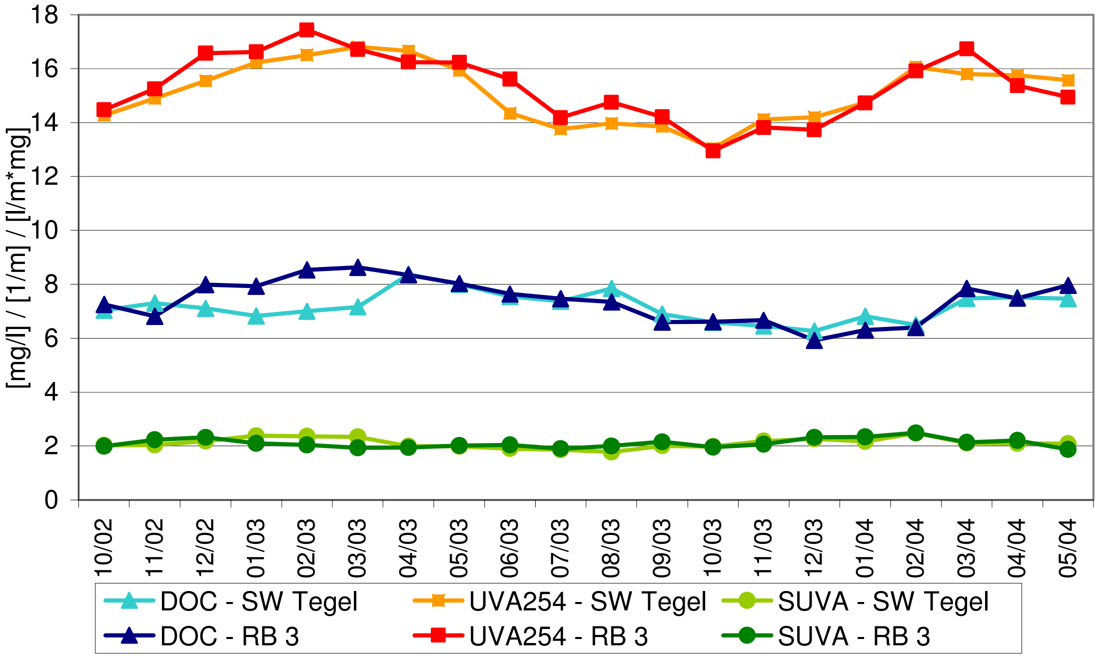


Figure 51 Comparison of bulk organics results for recharge pond 3 and Lake Tegel

Altogether, the study showed that the water quality of infiltrated water at the artificial groundwater recharge facility is similar to Lake Tegel surface water. Therefore, the discussion on seasonal influences on the organic water composition of the infiltrated water was included in the discussion of the bank filtration field site Tegel (Chapter 1.1).

1.3.1.1 Groundwater Recharge - DOC

During the time period from October 2002 to May 2004 20 monthly samples from the pond, eight monitoring wells and one production well were taken to describe the fate of bulk organics at the artificial ground water recharge facility Tegel. The monitoring wells were located in different distances and depths between recharge pond 3 and the production well 20. Additionally, the background ground water was monitored by separate monitoring wells. The hydrogeological setup of the field site and the exact positions of the monitoring wells were investigated by the hydrogeological group and are included in NASRI Report 1, chapter 1.3). Data evaluation of the Free University Berlin (NASRI Report 1) proposed that at this field site no dilution of infiltrating water on its way towards the production well occurs. The proposed mixing rations between infiltrating water and background groundwater in the production well are 80% recent infiltrate and 20% background water.

The two main effects that might influence the removal of bulk organic water constituents are the strong seasonal variations of temperature, which is nearly not attenuated during infiltration, and the changes in redox system. During winter the lowest measured water temperature in monitoring well 369UP (last monitoring well in front of production well) was 2.9°C. In next summer temperature in the same well reached 23.8°C. These temperature differences affect the whole infiltration path. As a consequence the redox system along the transect is dependent from seasons. During spring, fall, and winter oxygen and nitrate are present during infiltration. But during the extreme hot summer of 2003 oxygen and nitrate depleted from the system. It remains unclear, whether this effect occurs regularly or whether it was due to the extreme circumstances. However, compared to bank filtration at Lake Tegel the character of artificial infiltration is more oxic.

Figure 52 shows the fate of dissolved organic carbon during infiltration at the recharge facility. It stands out that after very short retention times of a few days and infiltration distances of 6-7 m (monitoring well 366 and 365) high shares of surface water DOC are mineralized. Compared to results of the mostly anoxic bank filtration site Tegel or monitoring well 205 in Wannsee the mineralization rates in the immediate infiltration zone of the GWR are high. This is most probably due to usually oxic conditions during infiltration. It is consistent with results from soil column experiments that under oxic conditions the mineralization of infiltrated BDOC takes place more rapidly. At GWR 70-80% of the overall DOC removal occurs before the infiltrate reaches the first observation well. During further infiltration the remainder of degradable organics is removed quickly and for most of the infiltration path stable DOC-concentrations were observed. Overall, approximately 40% of surface water DOC is removed during artificial recharge and the infiltrate DOC-concentration in front of the production well was assessed with 4-5.5 mg/l. Background groundwater was found to contain 4-5 mg/l DOC, similar to the final raw water.

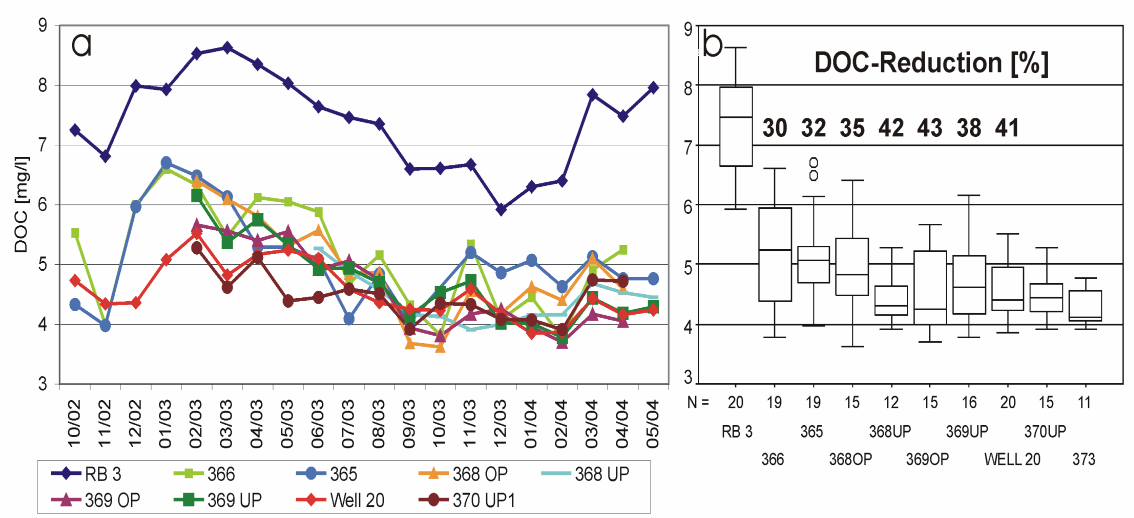


Figure 52 Fate of DOC during infiltration at GWR (a: time series; b: box plots)

The time series in Figure 52a shows that the DOC-concentration in the monitoring wells strongly depended on surface water DOC. Generally, the monitoring well-DOC followed the surface water concentration without a recognizable time shift. A slight seasonal variance of the degraded DOC in the wells near the pond was observed. During winter the efficiency of DOC mineralization in monitoring well 365 is slightly reduced because of the low temperatures. During these cold periods the concentration difference between pond water and well 365 is decreasing to 1 mg/l, whereas during rest of the year 2-3 mg/l are removed in this section of the infiltration path.

The change of redox conditions in summer 2003, which was proved by depletion of oxygen and nitrate from the system, did not affect the DOC removal efficiency. In this time period the temperature-effect which enhances the biodegradation balanced the slower DOC-removal under anoxic/anaerobic conditions.

However, DOC concentration in the abstracted water was found to be variable in a range between 4 mg/l and 5.5 mg/l. The most important factor of influence at the GWR was the surface water quality. A slight influence of the temperature was measurable in the pond-near monitoring wells. Changing redox potentials during warm summers were observed to have no measurable effect on DOC removal. Overall, it can be assumed that abstracted water contains only non-degradable DOC. The achieved DOC-residual is equal to the non-degradable fraction observed during bank filtration at Lake Tegel. Therefore, these results support the findings of the monitoring at the bank filtration site Tegel.

1.3.1.2 Groundwater Recharge - UVA$_{254}$

UV-absorption at 254 nm of the pond water samples was found to follow the seasonal variations of Lake Tegel surface water. Higher UV-absorptions were measured during winter, because the portion of treated waste water in Lake Tegel is higher in winter months. UVA$_{254}$ in pond water was measured between 13 and 17m^{-1}. Figure 53b proves that UVA$_{254}$ is reduced by ~25% in the immediate infiltration zone (monitoring well 366 and 365). During further infiltration the overall removal rates increase to 30-35%.

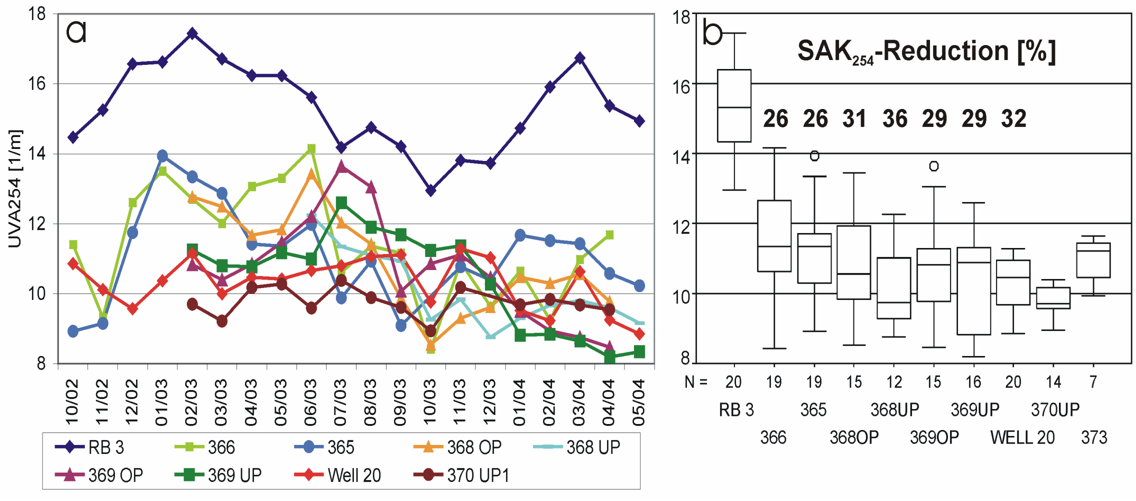


Figure 53 Fate of UVA$_{254}$ during infiltration at GWR (a: time series; b: box plots)

These results are comparable to the decrease of UV-absorption at the bank filtration site Tegel. At Wannsee field site more than 40% of the UVA$_{254}$ were removed during an infiltration of 2-4 months. But a plateauing of UV-absorption in the more distant monitoring wells at the GWR proposes that no additional removal of UVA$_{254}$ would be possible even with longer retention times. The land sided groundwater showed different UVA$_{254}$ in different depths. Average UV-absorption was ~10 m^{-1} in 370UP above the aquitard. Despite of a lower DOC-concentration in monitoring well 373 the UVA$_{254}$ was slightly higher. This indicates a different organic composition of groundwater above and under the aquitard.

The time series of UVA$_{254}$ of the monitoring wells samples at the GWR is difficult to interpret. For monitoring wells in the infiltration zone (366 and 365) a strong dependency of UV-absorption from pond water-UVA$_{254}$ was confirmed. More distant monitoring wells (368OP/UP and 369OP/UP) show a high variation and erratic changes in UV-absorption. Reasons for these changes in UV-absorption (range 8 to 12 m^{-1}) remain unclear. Figure 53 shows that during early summer 2003 water with a higher UV-Absorption dominated the infiltration path. Afterwards, UV-absorption in the mentioned monitoring wells decreased until spring 2004. No reference for this effect was visible in the pond water quality. Background groundwater and the raw water of the production well exhibited comparably stable UV-absorptions with no seasonal influences.

Overall, the observed UVA_{254} removal rates during artificial recharge are slightly lower than the measured DOC mineralization. This indicates an increased aromaticity in the final raw water compared to the infiltrated surface water.

The results for the color measurements at 436 nm were found to be close to the detection limit. Therefore, no interpretation and conclusion arose from these measurements.

1.3.1.3 Groundwater Recharge - SUVA

A better characterization of the organic carbon in the groundwater recharge system provided the parameter SUVA. SUVA is a measure of aromaticity of organic carbon and is calculated from DOC and UVA_{254}. Figure 54 proves that similarly to the bank filtration sites in Tegel and Wannsee the aromaticity of organic carbon increases shortly after infiltration. For the pond water median SUVA was calculated with 2.05 l/m*mg which is comparable to Lake Tegel SUVA. After infiltration aromaticity increases to a SUVA of ~2.2 l/m*mg in the infiltration zone (366 and 365) and up to 2.4 l/m*mg in more distant monitoring wells. Additionally, the variance and standard deviation of the measurements in the monitoring wells increases with distance from pond. Usually, longer infiltration stabilizes extreme values and smaller amplitudes of SUVA changes could have been expected.

However, Figure 54a provides explanation for the observed fate of SUVA. The time series points out two factors of influence for the SUVA:

First, during summer 2003 the SUVA of infiltrated water increases independently from surface water. It is assumed that the increased SUVA is due to a temperature effect that was similarly observed in the deep wells of bank filtration site Tegel. Organic material with a highly aromatic character is released from the sediment in times of warmer temperatures. It remains unclear whether this material is derived from POC degradation or adsorption processes. Despite of the sandy sediment structure a small percentage of hydrophobic and aromatic organics could adsorb to the material during cold season. If the material is released by higher temperatures, it would increase aromaticity of the infiltrate significantly. The fractions are very small and were not detected by DOC or UVA_{254} analysis. The peak during June to October 2003 can most probably be ascribed to this effect. Furthermore, this finding explains the higher variances of SUVA in more distant monitoring wells.

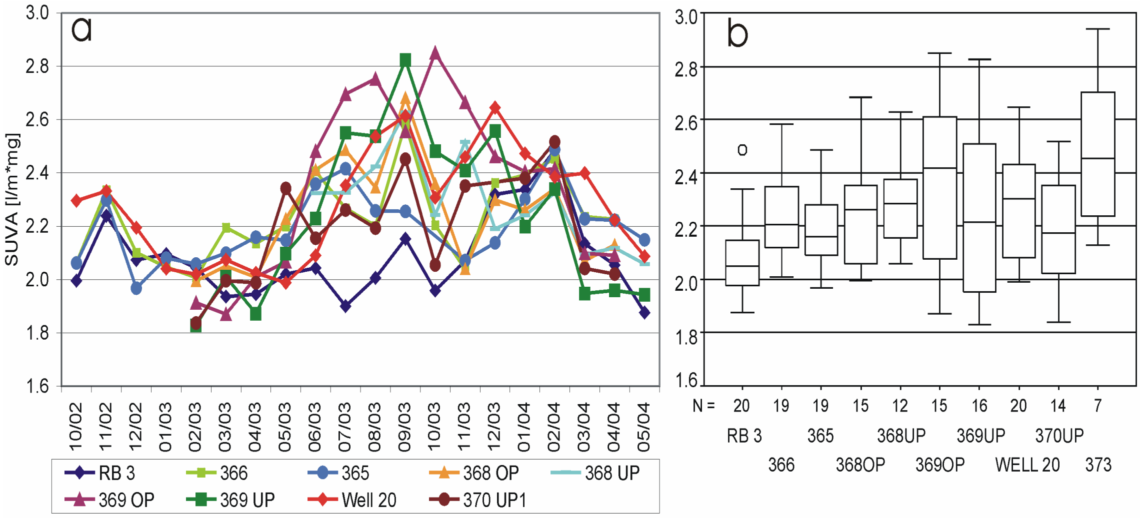


Figure 54 Fate of SUVA during infiltration at GWR (a: time series; b: box plots)

Second factor of influence on the SUVA of organic water constituents during infiltration is surface water quality. Starting in November 2003 until February 2004 the SUVA of the pond water increased to 2.4 l/m*mg. This change in water quality affected all monitoring wells nearly immediately. Because of short retention times the monthly sampling did not reproduce the time shift of the peak in the subsequent monitoring wells.

The background groundwater showed different aromaticities in the sampled depths. As signalized by the UVA results, the water in the deeper aquifer was characterized by a higher aromaticity of organics.

1.3.2 Groundwater Recharge - LC-OCD

The organic water constituents of the recharge pond water were characterized by 10 monthly measurements using LC-OCD technique. One point of interest was a comparison of the DOC character of Lake Tegel surface water and the water of the recharge pond. Table 3 shows that the integration of the LC-OCD chromatograms leads to similar results for both water types.

Table 9 Portions and concentrations of different fractions of DOC (Recharge pond 3, Lake Tegel)

	Poly-saccharides	Humic substances	Humic substances-Building blocks	Low molecular acids	Neutrals and Hydrophobics
Recharge pond	9.1 %	46.6 %	23.8 %	3.2 %	17.4 %
	0.7 mg/l	3.5 mg/l	1.8 mg/l	0.2 mg/l	1.3 mg/l
Lake Tegel (n=12)	8.7 %	46.0 %	22.1 %	3.7 %	19.7 %
	0.6 mg/l	3.3 mg/l	1.6 mg/l	0.3 mg/l	1.4 mg/l

It was found that the amounts and percentages for the five different DOC fractions corresponded closely within the limits of the method. Small variations occurred only in fractions, which were hard to quantify (HS-building blocks and Neutrals). Therefore, it is assumed that no strong influences on the character of organics in the recharge pond existed and that the water quality of the artificially infiltrated water complies with surface water quality of Lake Tegel. Seasonal changes observed for the polysaccharide fraction were found to be of the similar nature as in Lake Wannsee. Since these changes were not as pronounced, they were not evaluated more closely.

During infiltration the character of bulk organic compounds changed. Similar results were obtained at the two monitored bank filtration site. As quantitative DOC analysis indicated, most of the biodegradation of DOC and the changes within DOC-fractions occurred shortly after infiltration. Under mostly oxic conditions at the artificial recharge site BDOC removal was found to be a fast process. After the removal of BDOC the non-degradable DOC remained in the infiltrate and the DOC level plateaued at ~4.5 mg/l. However, Figure 55 shows that the LC-OCD chromatograms of pond water and the first monitoring well (366) are substantially different. Chromatograms of more distant monitoring wells have a similar shape as the 366. This is consistent with the mentioned results of DOC-quantification and proves that at the artificial recharge facility the qualitative and quantitative effects on the bulk organic composition occur concentrated near the water sediment interface close to the recharge pond. It can be assumed that biological activity in these sediment layers is considerably higher than in more distant layers.

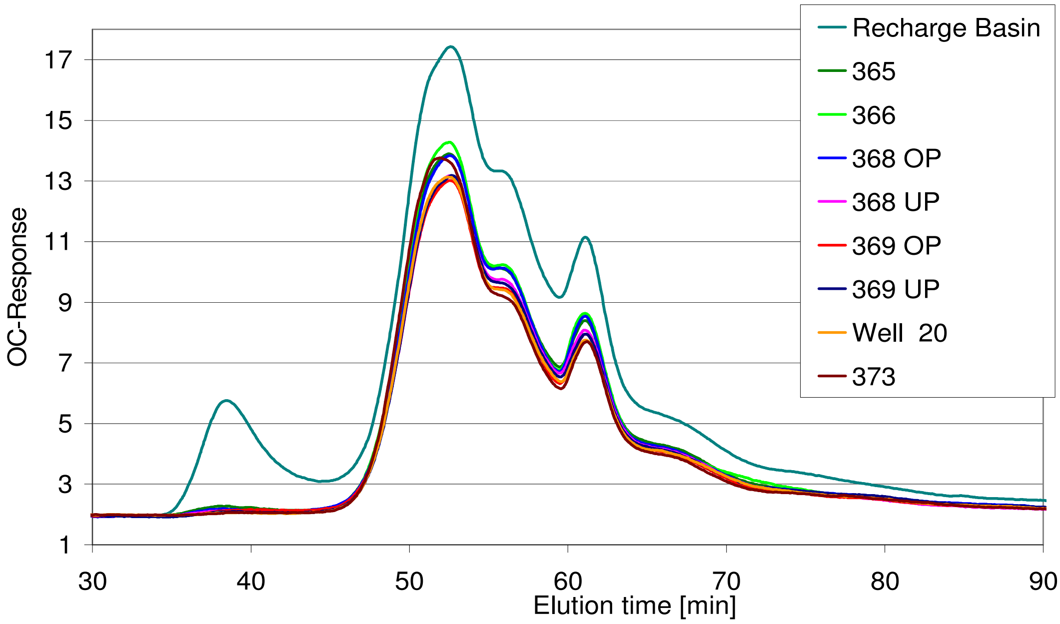


Figure 55 LC-OCD chromatogram of transect at the artificial recharge facility (mean, n=10)

Most important changes were observed within the fraction of polysaccharides, which were degraded very efficiently in the first infiltration step. Nearly no traces of polysaccharides were detected in all monitoring wells and the removal rate was close to 100%. All other fractions were only partially removed during infiltration. Figure 56 depicts in a summary of all ten LC-OCD measurements the monitored changes of DOC composition along the infiltration path. The highest change in concentration was found for the fraction of humic substances, which loose 1.1 mg/l from an initial concentration of 3.5 mg/l (30%). For all other fractions removal rates ranged from 30% to 40%. Together they resulted in an overall DOC mineralization of 38%. The character of bulk organics in background groundwater was found to be very close to the character of the organics in the infiltrated water.

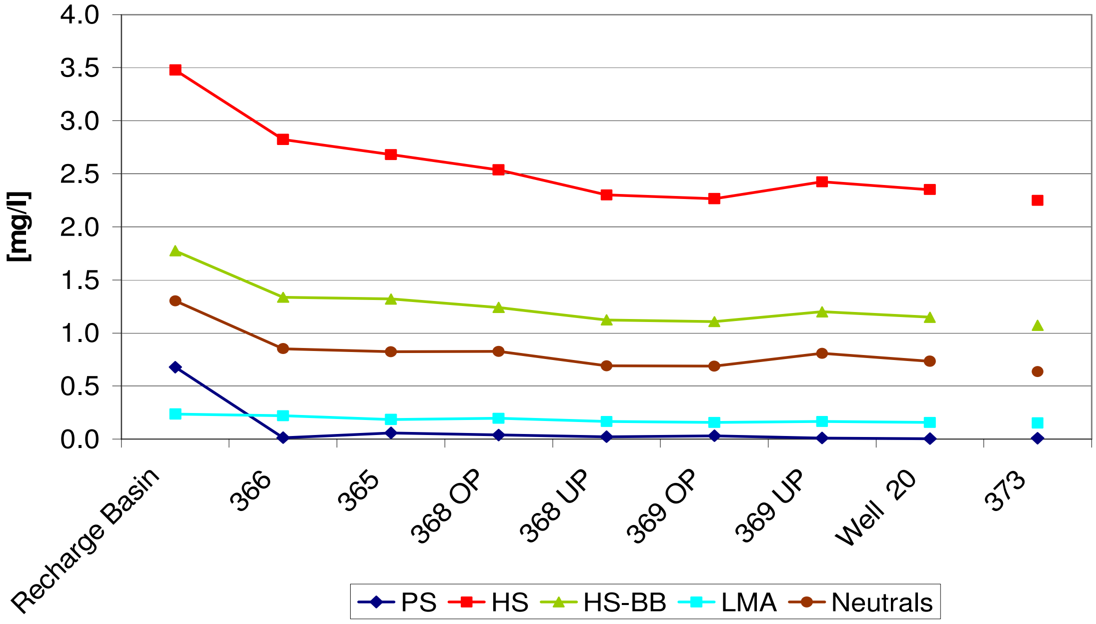


Figure 56 Concentrations of the different fractions of DOC at transect GWR

Table 10 provides the observed changes on concentration basis and the percentage variations. Since at the GWR no dilution with other groundwater within the circle of production wells occurs, all observed effects can be ascribed to biodegradation and transformation. Only in the production wells some dilution with background groundwater was present.

Table 10 Portions and concentrations of different fractions of DOC at transect GWR (n=10)

	Poly-saccharides	Humic substances	Humic substances-Building blocks	Low molecular acids	Neutrals and Hydrophobics
Recharge pond 3	9.1 %	46.6 %	23.8 %	3.2 %	17.4 %
	0.7 mg/l	3.5 mg/l	1.8 mg/l	0.2 mg/l	1.3 mg/l
366	0.3 %	53.8 %	25.5 %	4.2 %	16.2 %
	0.0 mg/l	2.8 mg/l	1.3 mg/l	0.2 mg/l	0.9 mg/l
365	1.2 %	52.9 %	26.0 %	3.7 %	16.2 %
	0.1 mg/l	2.7 mg/l	1.3 mg/l	0.2 mg/l	0.8 mg/l
368OP	0.8 %	52.4 %	25.6 %	4.1 %	17.1 %
	0.0 mg/l	2.5 mg/l	1.2 mg/l	0.2 mg/l	0.8 mg/l
368UP	0.5 %	53.5 %	26.1 %	3.9 %	16.0 %
	0.0 mg/l	2.3 mg/l	1.1 mg/l	0.2 mg/l	0.7 mg/l
369OP	0.7 %	53.3 %	26.1 %	3.7 %	16.2 %
	0.0 mg/l	2.3 mg/l	1.1 mg/l	0.2 mg/l	0.7 mg/l
369UP	0.2 %	52.6 %	26.0 %	3.6 %	17.5 %
	0.0 mg/l	2.4 mg/l	1.2 mg/l	0.2 mg/l	0.8 mg/l
Well 20	0.1 %	53.5 %	26.1 %	3.6 %	16.7 %
	0.0 mg/l	2.4 mg/l	1.1 mg/l	0.2 mg/l	0.7 mg/l
373	0.2 %	54.6 %	26.1 %	3.7 %	15.4 %
	0.0 mg/l	2.2 mg/l	1.1 mg/l	0.2 mg/l	0.6 mg/l

Overall, LC-OCD analysis proved that the same fractions of DOC are responsible for the depletion of total DOC during bank filtration and artificial recharge. In both systems the BDOC is part of all fractions of DOC, whereas the polysaccharide fraction contains only BDOC. It can be assumed that the biological effects in bank filtration and groundwater recharge are of the same nature. The described changes occurred within a maximum infiltration time of 50 days under the mostly oxic conditions of the groundwater recharge facility. Results from bank filtration site Tegel showed that under anoxic or anaerobic conditions this time frame would not be sufficient for a complete mineralization of BDOC.

1.3.3 Groundwater Recharge - AOI Results

The concentration of adsorbable organic Iodine in recharge pond 3 is comparable to concentrations in the surface water of Lake Tegel. Figure 57 compares the time series of both sampling points. The concentration in recharge pond 3 follows the surface water concentration with a slight time shift which is most probably due to the location of the pumping station farer south in Lake Tegel. The results are consistent with the assumption that a high portion of AOI is introduced to Lake Tegel with treated effluent which enters Lake Tegel at the north end. Therefore, it can be assumed that AOI concentration was neither depleted nor increased by additional retention time in Lake Tegel, micro-filtration treatment or additional retention time in the recharge pond.

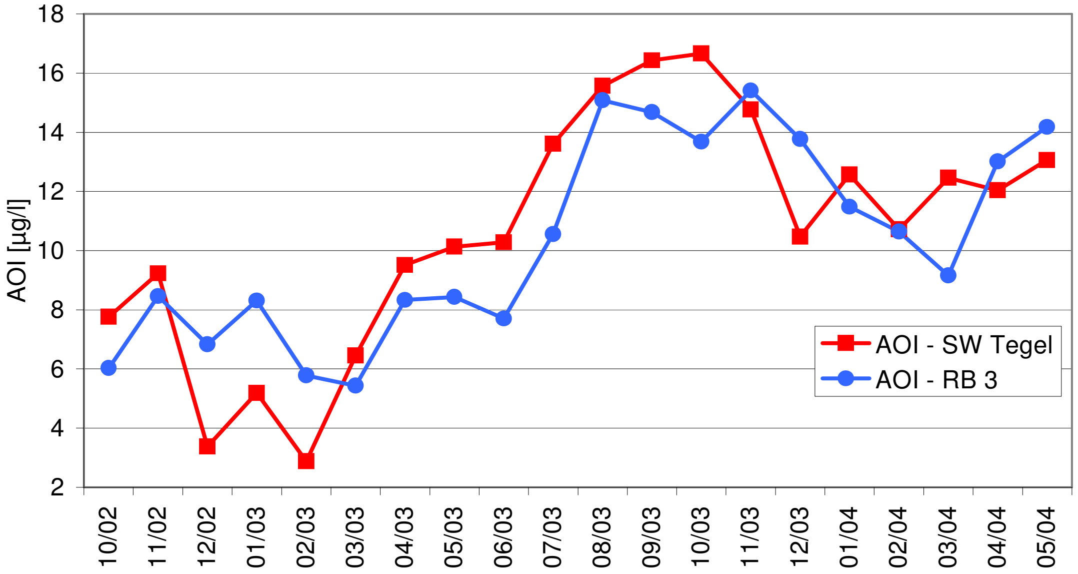


Figure 57 Comparison of AOI concentrations measured in recharge pond 3 and Lake Tegel

Fate of AOI during infiltration at the artificial groundwater recharge facility was monitored over a time period of 20 months from October 2002 to May 2004. Within the observation period a strong increase of AOI-levels from concentrations around 6-8 µg/l to more than 14 µg/l was found. The changes in the monitoring wells and the abstracted water after the strong surface water concentration increase revealed interesting details about the fate of halogenated organic compounds during artificial recharge.

Along the infiltration path towards the production well only very few remediation of the AOI occurred. Figure 58 shows that the monitoring wells close to the production well were found to contain most of the time nearly as much AOI as the surface water. Temporarily higher concentrations are due to short term variations of surface water. In well 365, 366 and 368OP removal was less than 10% and observed differences were often close to the limit of detection. Along the further infiltration path some remediation was present, but compared to the bank filtration field site in Tegel the removal rates of maximum 25% were very low. This is explained by very low retention times at the artificial recharge facility and mostly oxic conditions during infiltration. Only during hot summers redox conditions in the infiltration area switch to anoxic and slightly anaerobic. The effect of the changing redox system on the fate of AOI can be observed best in monitoring well 369OP and the production well. At both sampling points AOI concentrations start to rise in spring 2003 with the surface water. But in September 2003 the AOI-concentrations in 369UP and the production well drop although the surface water concentrations remain on a high level. From measurements of redox potential and nitrate concentration it was known that during summer the system switched to anoxic/anaerobic conditions for approximately 3 months. During this time a better remediation of AOI was found. Reductive dehalogenation was proved at other field sites to be the most effective removal mechanism for adsorbable halogenated compounds. This effect influenced the AOI removal rates during summer 2003 and lead for a limited time period to lower AOI concentrations in the production well.

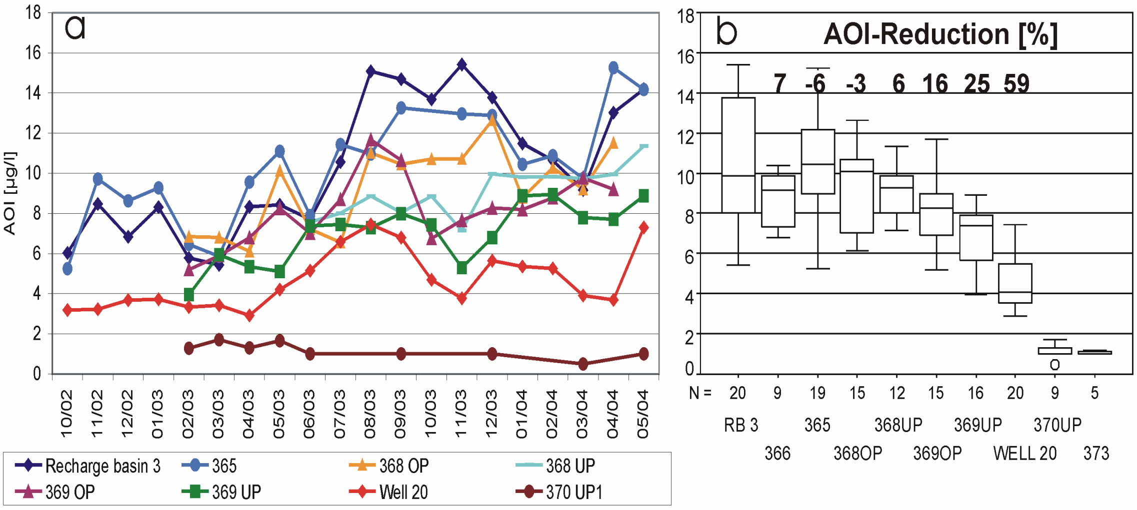


Figure 58 Fate of AOI during infiltration at GWR (a: time series; b: box plots)

However, Figure 58 exhibits clearly that the AOI concentration of the abstracted water is strongly dependent from surface water quality. Because of short retention times increased surface water AOI-concentrations break through nearly immediately to the production well. A 100% increase of AOI concentration in the surface water lead to more than 100% increase in the abstracted water, where AOI-levels rose from ~3 µg/l to more than 7 µg/l. Because of some dilution with background groundwater the overall removal rates for the production well add up to nearly 60%. Background groundwater was found to be very low in AOI with concentrations around the limit of detection (1 µg/l). However, the average AOI concentration of the abstracted water at the artificial recharge site is ~4 µg/l. This is approximately double as high as the AOI concentration of the product water at the bank filtration site (~2 µg/l). Furthermore, the AOI level of the product water at GWR was found to be highly variable. This finding was proved by the last measurement in May 2004.

Overall, it can be summarized that the conditions at the artificial recharge site Tegel are not favorable for an effective dehalogenation of AOI. Short retention times and mostly oxic conditions during infiltration allow high concentrations of AOI to pass through the soil to the production well.

1.3.4 Groundwater Recharge - AOBr Results

Adsorbable organic Bromine at the artificial recharge site was monitored in the same time period as the AOI. Figure 59 shows that for most of the monitoring time AOBr concentration in the recharge pond was equal to the AOBr levels in Lake Tegel. Only during summer of 2003 the recharge basin contained higher concentrations than the surface water of Lake Tegel. This can be explained by additional sun exposure and low water movement in the recharge ponds, which consequentially induced stronger algae blooms. Parts of the AOBr are known to be associated with algae and occur in surface waters in times of strong algae blooms or during die off times of these blooms. The strong AOBr peak in the recharge basin is most probably due to perfect conditions for algaes in the ponds. Contrary to the AOI peak no time shift was observed for the AOBr peak in summer 2003, indicating the origin of the increased AOBr level in the lake and not in discharged treated effluent. This is consistent with all results from the field sites Wannsee and Tegel. The AOBr levels of Lake Tegel and the recharge basin are identical during winter, when most of the AOBr is of anthropogenic origin and enters Lake Tegel with the treated effluent.

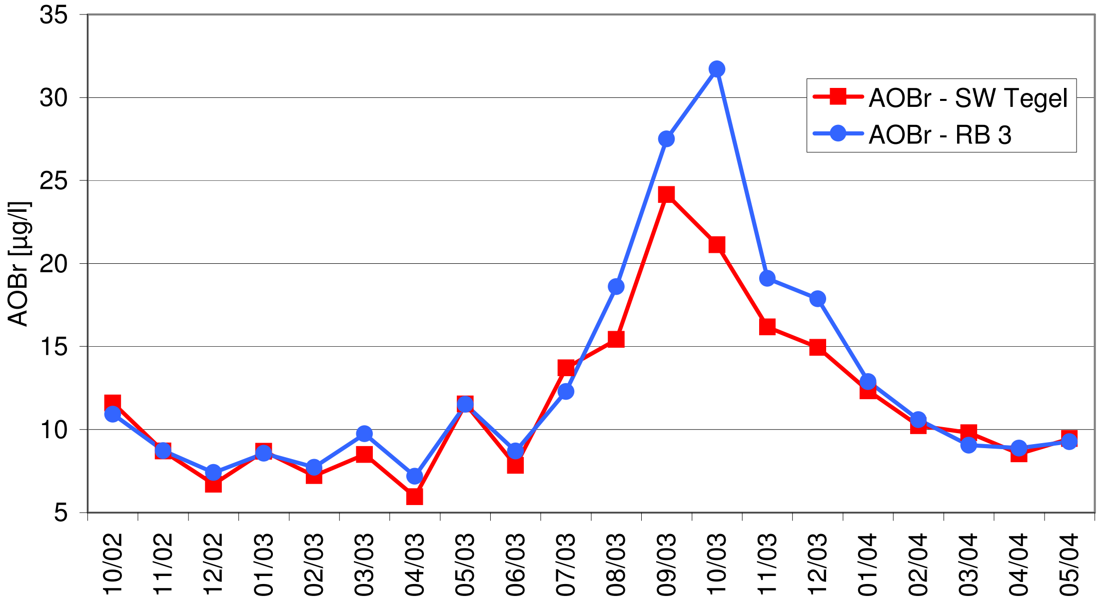


Figure 59 Comparison of AOBr concentrations measured in recharge pond 3 and Lake Tegel

During infiltration towards the production well the two different fractions of AOBr showed a completely different behavior. Anthropogenic AOBr which is present all year in surface water in concentrations between 6 µg/l and 10 µg/l was not removed during the 50 day infiltration time. The observed removals during these times were very often in the range of the accuracy of the method and the average removal rates for all monitoring wells were under 10%. Only in the production well, where dilution with the low AOBr-background groundwater occurs, a removal of 38% of AOBr was observed.

Contrary to this, the algae associated AOBr was removed completely in the first monitoring well 365. The peak in the surface water is statistically regarded as an extreme value (Figure 60b), but the time series in Figure 60a proves that no higher concentrations were measured in pond near monitoring wells during the period of elevated AOBr. Therefore, it can be concluded that algae associated AOBr is easy degradable under oxic conditions, whereas the other anthropogenic AOBr-fraction is not degradable under the conditions of the GWR. A slight indication of a better removal during the anoxic/anaerobic period in late summer 2003 is visible in monitoring well 369UP and the production well. In this time period the AOBr-levels in the mentioned wells decrease despite of high surface water concentrations. Consistently with results from all other field sites a dehalogenation of anthropogenic AOBr occurs only under anaerobic conditions.

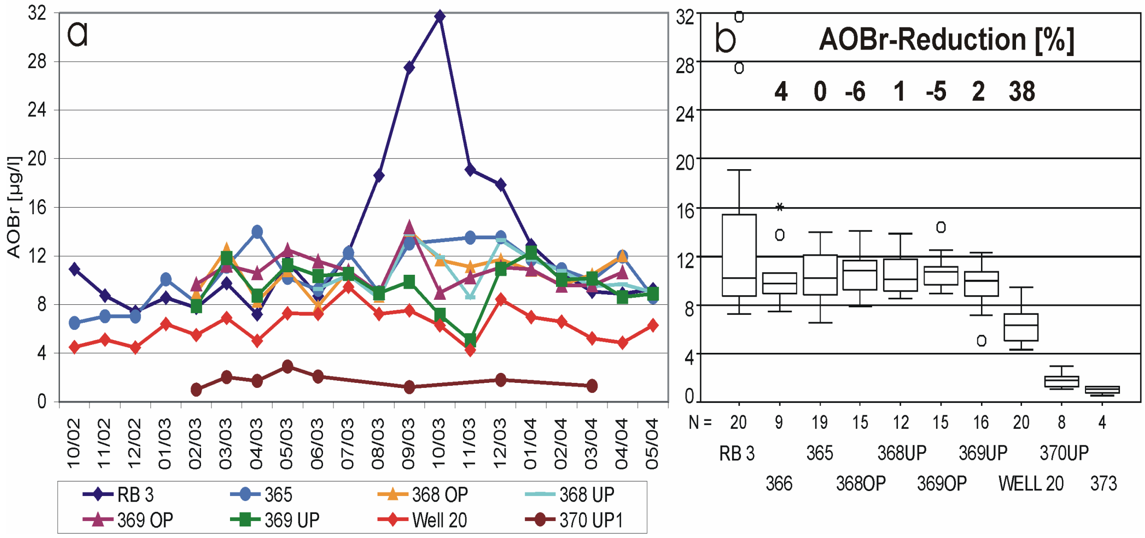


Figure 60 Fate of AOBr during infiltration at GWR (a: time series; b: box plots)

Overall, the results from the artificial recharge site confirm the findings of the two bank filtration field sites. No efficient dehalogenation was expected at the recharge site. A comparison of AOI and AOBr reveals that at all field sites the removal rates for anthropogenic AOBr are lower than for AOI. The summery peaks of AOI, which are due to less dilution of the treated effluent occur most probably also for anthropogenic AOBr. But in the surface waters these peaks are superposed by high algae associated AOBr concentrations that occur only during summer. These very high AOBr levels were found to be unproblematic for the drinking water production since they are easily mineralized during bank filtration and groundwater recharge.

1.3.5 Groundwater Recharge - Trace pollutant results

For a period of thirteen months the fate of trace pollutants along the infiltration path from the recharge pond to the production well 20 was investigated. Not all monitoring wells were included in this analytical program. The following chapter describes the behavior of the selected trace compounds (Iopromide, Sulfamethoxazole and three isomers of naphthalenedisulfonic acid) using datasets of the monitoring wells 365, 368UP, 369UP, 373 and the production well 20.

Infiltration at the artificial groundwater recharge facility is characterized by a high hydraulic loading rate of 1-2 m/d, short retention times and mostly oxic conditions. The fate of the trace compounds under these conditions is different from the behavior at the bank filtration field sites. Additionally, it was of interest to compare the concentration of trace pollutants in the recharge pond and in Lake Tegel. Since the water is pumped from Lake Tegel and seasonally (Summer) micro-filtrated, before it enters the recharge pond, a comparison of the measured concentrations would reveal any effects of this treatment on trace pollutants. Figure 61 shows the time series of Iopromide and Sulfamethoxazole concentrations in the recharge pond and Lake Tegel. It was found that the Iopromide concentration in the recharge pond was most of the time lower than in the lake. The average difference was ~ 100 ng/l. It is assumed that the difference is due to some bioremediation of Iopromide in surface water or in the biofilms of pumps and piping of the GWR facility. Iopromide was found at all field sites and in soil column experiments to be easily metabolized. The triiodinated benzene structure of the molecule remains most likely unaffected under oxic conditions. AOI results proved that no deiodination occurred on the way from the lake to the recharge pond.

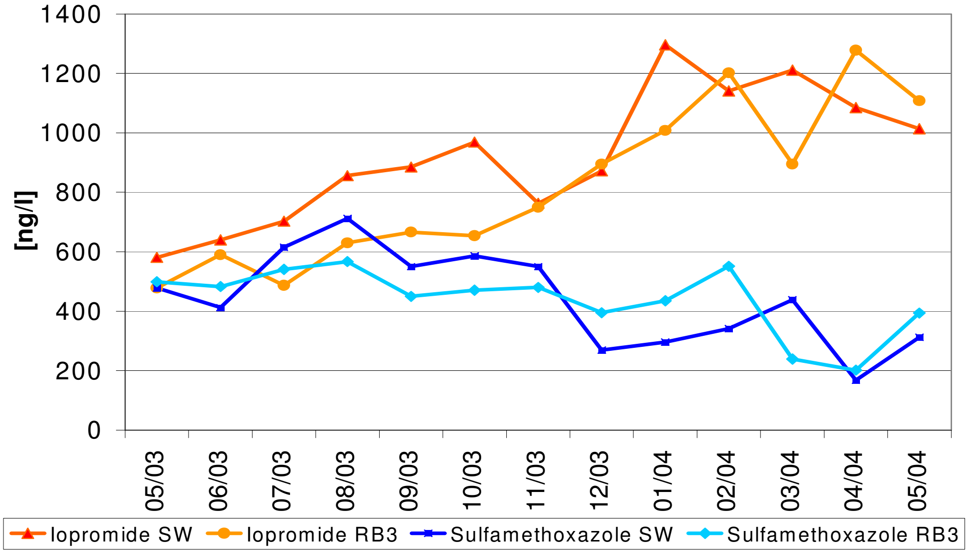


Figure 61 Comparison of Iopromide/Sulfamethoxazole concentration in recharge pond and surface water of Lake Tegel

For all other monitored compounds time series and mean concentrations in the recharge pond and the lake pointed towards no removal in surface water (Figure 62). Temporal variations of surface water concentration were responsible for slight variations. But a statistical evaluation of the datasets revealed no significant differences between lake concentration and recharge pond pollution level. Table 11 provides arithmetic mean, median concentration and standard deviation of all monitored trace compounds in recharge pond 3. All compounds were measured thirteen times during the time period May 2003 to May 2004.

Table 11 Monitoring results for trace pollutants in recharge pond

	Iopromide	Sulfameth.	1.5-NDSA	1.7-NDSA	2.7-NDSA
	[ng/l]	[ng/l]	[ng/l]	[ng/l]	[ng/l]
Arithmetic mean	819	439	104	327	105
Median	750	471	105	348	97
Standard deviation	267	111	30	59	38

The trends of the time series were present in both data sets. Figure 61 and Figure 62 indicated increasing surface water concentrations for Iopromid, 1,5-NDSA and 2,7-NDSA. For 1,7-NDSA the concentrations remained nearly stable during the observation period and for Sulfamethoxazole the pollution level decreased slightly.

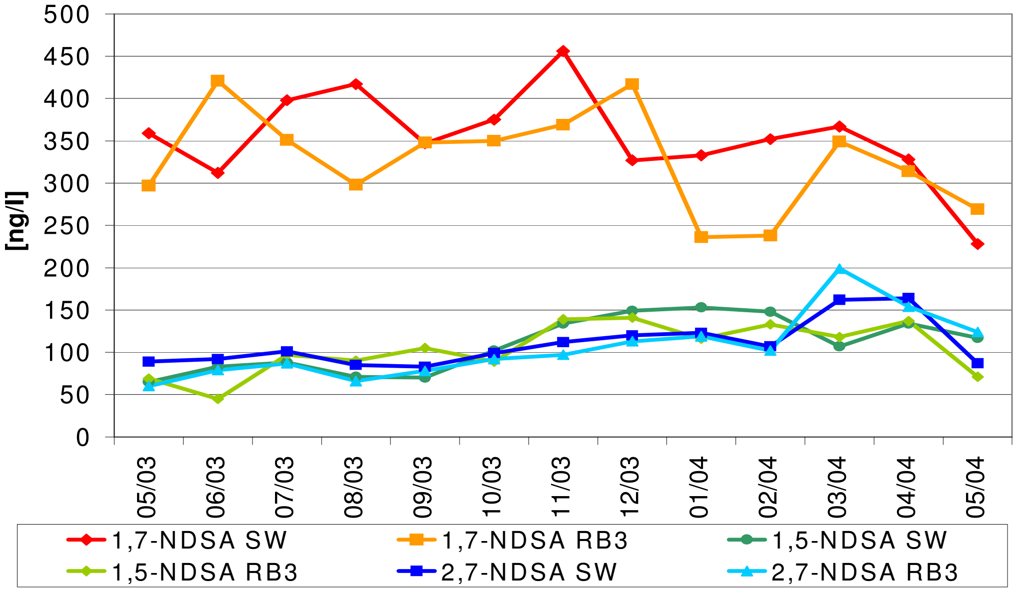


Figure 62 Comparison of NDSA concentrations in recharge pond and surface water of Lake Tegel

Figure 63 provides insight into the behavior of the X-ray contrast agent Iopromide at the artificial recharge facility. It was found that Iopromide is efficiently removed during recharge. Measurable concentrations were only found in monitoring wells close to the recharge pond. In the first monitoring well 365, Iopromide concentration was already depleted to an average of 6% of surface water concentration (removal rate: 94%). In more distant monitoring wells only traces of the Iopromide molecule were detected and removal rates were calculated with 100%. A similar efficient depletion of Iopromide was observed at all field sites and in soil column experiments.

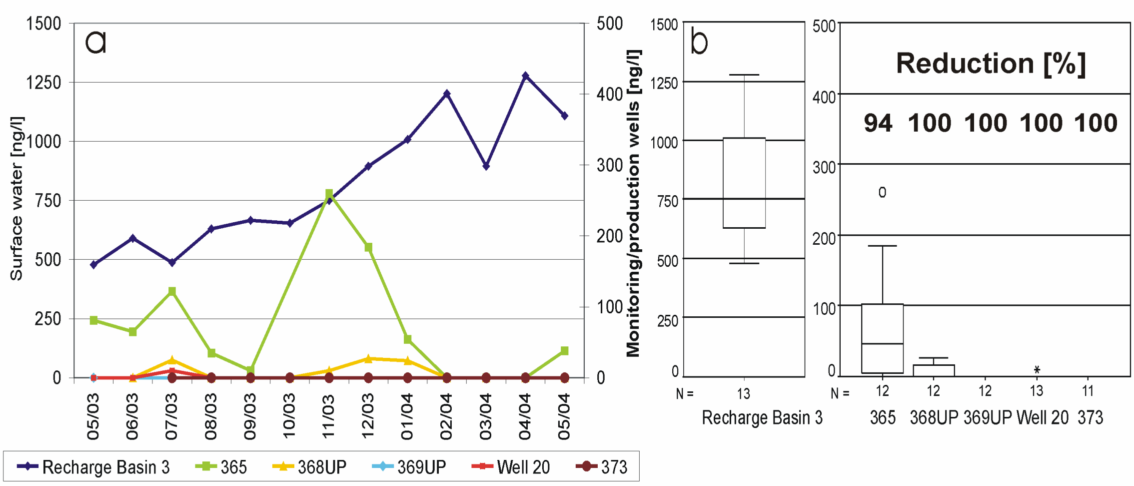


Figure 63 Fate of Iopromide during infiltration at GWR (a: time series; b: box plots)

But it was proved that no efficient mineralization of Iopromide is possible under oxic conditions. Therefore, it is concluded that the low concentrations of Iopromide, which were measured in the monitoring wells at the GWR, are due to a metabolization of the molecule. It was observed that metabolization occurred fastest under oxic conditions. A dehalogenation and mineralization of the Iopromide molecule can only be expected under strongly reducing conditions. Since redox potentials at the GWR are high for most of the year the dominating removal mechanism for this x-ray contrast agent is assumed to be metabolization. The time series of Iopromide in Figure 63a shows an increase of Iopromide concentration in monitoring wells during winter 2003. The significantly higher concentrations in monitoring well 365 and the slightly increased levels in 368UP were most probable due to temperature effects. Low water temperatures and lower biological activity in the infiltration area seem to inhibit the metabolization of Iopromide partly.

The antibiotic drug Sulfamethoxazole was present in recharge pond water in concentrations of 200 – 550 ng/l with a slight trend towards lower concentrations at the end of the monitoring period. From literature data (Schmidt et al. 2004), results of field monitorings and soil column experiments it was known that Sulfamethoxazole is preferably degraded under anaerobic conditions. Since redox conditions at the GWR are mostly oxic and retention times are short compared to the other field sites, no efficient removal of Sulfamethoxazole could be expected.

Figure 64 shows that the observed removal rates (40-55%) were lower than at the bank filtration site Tegel. There, a reduction of 75% of the antibiotic was achieved within 3-4 months of infiltration (monitoring well 3303) under mostly anoxic/anaerobic conditions. The average raw water concentration at the bank filtration site was 26 ng/l because of some dilution with background groundwater. At the artificial recharge site raw water concentration of Sulfamethoxazole in the production well is four times higher (110 ng/l). This is consistent with the mentioned literature data and indicates a preferred removal of Sulfamethoxazole under anaerobic conditions. Results of the field site Wannsee showed that under oxic conditions even a retention time of 3 months is not improving the removal rates for Sulfamethoxazole significantly. Therefore, it is clear that the less efficient removal of Sulfamethoxazole at the GWR is due to the dominant oxic redox conditions and not necessarily to short retention times.

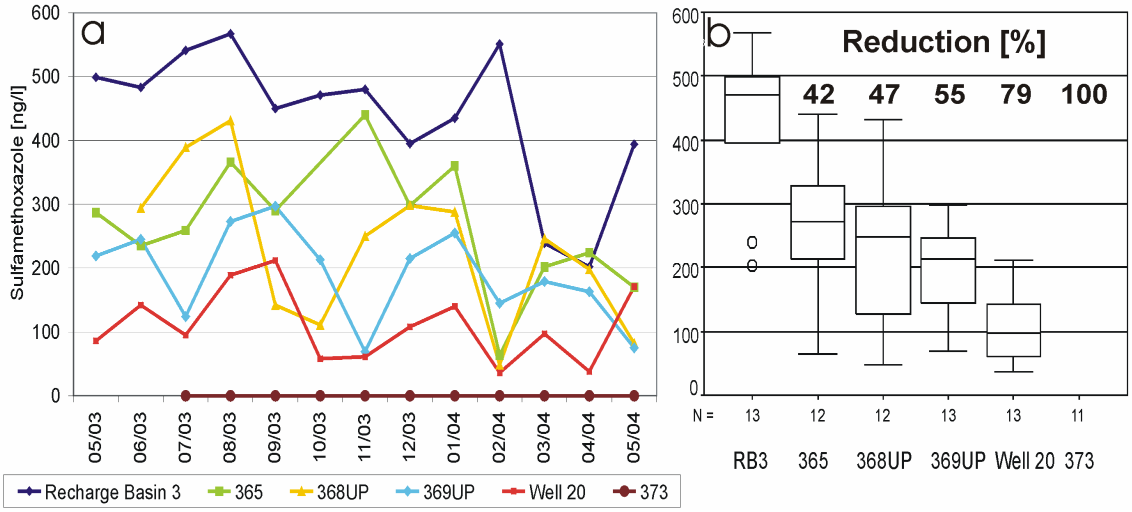


Figure 64 Fate of Sulfamethoxazole during infiltration at GWR (a: time series; b: box plots)

In Figure 64a, the time series of Sulfamethoxazole concentrations in the monitoring wells is presented. It was found that Sulfamethoxazole concentration in the monitoring wells is highly variable and not necessarily dependent on surface water concentration. Erratic changes in concentration indicate several factors of influence. Besides temperature the changing states of the recharge cycle might influence the removal efficiency. Unfortunately, a comparison of the results with recharge schedule (NASRI Report 2, chapter 2.2) did not lead to clarification. A detailed analysis was not possible with monthly measurements. However, Sulfamethoxazole concentration in the raw water was found to be relative stable in the range 50-200 ng/l. No Sulfamethoxazole was present in the background groundwater.

The monitored isomers of the naphthalenedisulfonic acid were found to be present in pond water at the artificial recharge facility. Despite of their nearly similar chemical structure, the observed removal rates differed substantially. 1,5-NDSA was found to be mostly persistent, whereas 1,7- and 2,7-NDSA showed removal rates of 60-80%. This discrepancy was also observed at two bank filtration field sites. Therefore, the results of the monitoring of the artificial recharge facility confirm the general findings on the biological removal of naphthalenedisulfonates.

1,5-NDSA isomer is the most persistent single compound in the monitoring program of the DWQC. Soil column experiments proved that oxic conditions are favorable for the mineralization of naphthalenesulfonates. Therefore, the infiltration path towards the monitoring well provided good conditions for the mineralization of naphthalenesulfonates. Figure 65 shows that even under these favorable conditions the 1,5-NDSA isomer is not efficiently mineralized and the pollution level decreases only by 10% during 50 days of infiltration towards monitoring well 369UP. The production well was found to contain slightly lower concentrations because of some dilution with background groundwater. All NDSA-isomers were found in the background groundwater in measurable concentrations.

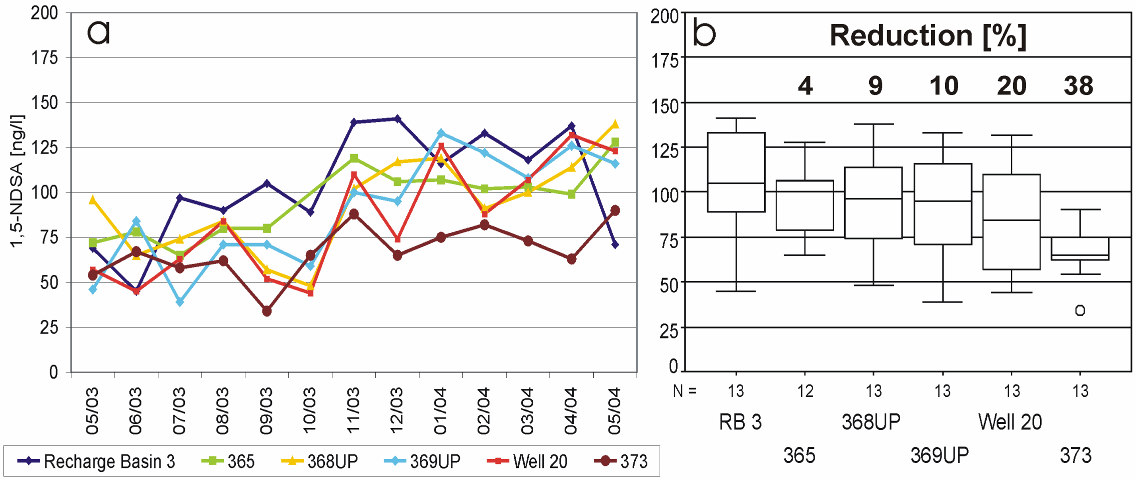


Figure 65 Fate of 1,5-Naphthalenedisulfonic acid during infiltration at GWR (a: time series; b: box plots)

The time series in Figure 65a show that the slight trend towards higher concentrations during the monitoring period originates from surface water. A comparison with results of the monitoring of Lake Tegel proves that the surface water concentration of 1,5-NDSA increased. Since the retention times are short and the compound is not mineralized during infiltration, higher concentrations reach the more distant monitoring wells in short time. The stability of the compound would allow an interpretation of the results as a tracer, but the monthly sampling does not provide enough data. However, in all monitoring wells 1,5-NDSA concentration was found to be in the range 50-150 ng/l. The background ground water contained 60-80 ng/l. Because of the stability of the compound a high share of the surface water load enters the raw water. Fate of

1,5-NDSA during drinking water treatment was not investigated but considering the stability of the compound it is likely to find 1,5-NDSA in lower concentrations (dilution) in drinking water.

The other two monitored NDSA-isomers were removed more efficiently during soil passage. Figure 66 shows that the observed removal rates for 1,7-NDSA were ~60% and for 2,7-NDSA up to 85% (Figure 67). These removals were higher than mineralization rates observed at the bank filtration site Tegel. The oxic infiltration path at field site Wannsee provided a similar efficient removal of these two isomers. Contrary to the results for the 1,5-isomer, which was not degradable under either redox conditions, the 1,7- an 2,7-isomer were more efficient degraded under oxic conditions. Results of the GWR show that even oxic soil passages with short retention times of only 50 days can act as a barrier against these degradable pollutants.

Figure 66 shows that the surface water pollution level for 1,7-NDSA was high with concentrations between 250-450 ng/l. Despite of a removal of ~60% of the compound the median concentration in the produced raw water was 148 ng/l. Most of the removal was found to occur within the first meter of infiltration. Along the further infiltration path the concentrations were found to remain nearly stable. The time series in Figure 66a proves that a seasonal influence on the removal efficiency for 1,7-NDSA is given. During colder winter months in 2003/04 the concentrations in the monitoring wells increased considerably, indicating a strong influence of temperature on biodegradation. This seasonal influence is leading to a high variability of 1,7-NDSA concentration in the monitoring wells. Background groundwater pollution level was relatively stable between 100-150 ng/l.

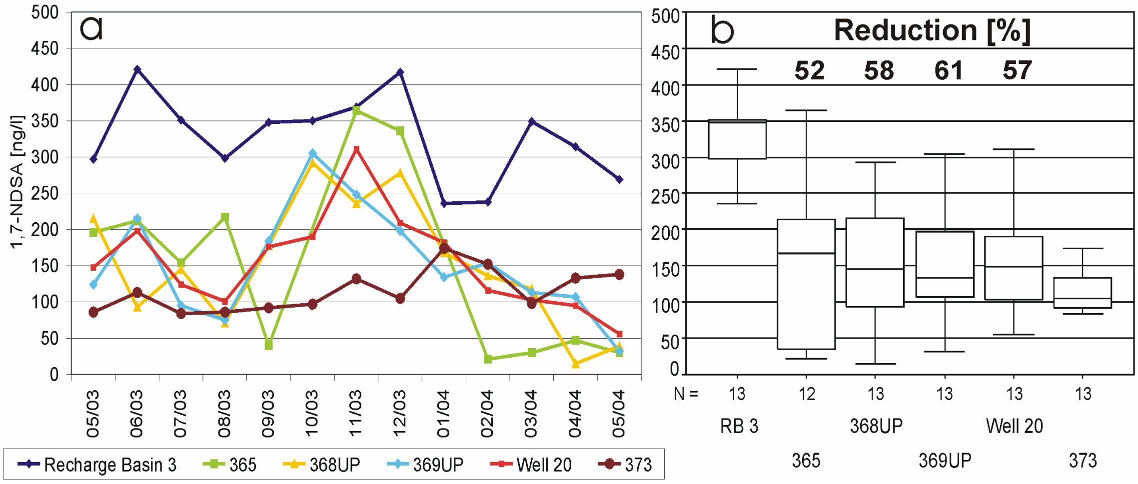


Figure 66 Fate of 1,7-Naphthalenedisulfonic acid during infiltration at GWR (a: time series; b: box plots)

Figure 67 provides results for the 2,7-NDSA isomer. For this compound the surface water concentrations were low in the range of 60-200 ng/l and the observed removal rates were high. Therefore, measured concentration in the monitoring wells were partly under the limit of quantification of 30 ng/l. Detected traces under the limit of quantification were entered into the database with half the limit of quantification (for 2,7-NDSA =>15 ng/l).

Figure 67 shows that 2,7-NDSA is efficiently removed during oxic soil passage. Most of the time only traces below the limit of quantification were found in the last monitoring well in front of the production well (369UP). During winter concentrations increased slightly because of the mentioned temperature effect, which is more apparent for the 1,7-NDSA. Because of some influence of polluted background groundwater the median concentration in the production well increased again to 42 ng/l. Overall, 2,7-NDSA was found to be the best degradable NDSA-isomer under the conditions of the groundwater recharge facility. Because of low surface water concentrations and the good degradability the raw water concentration is very low.

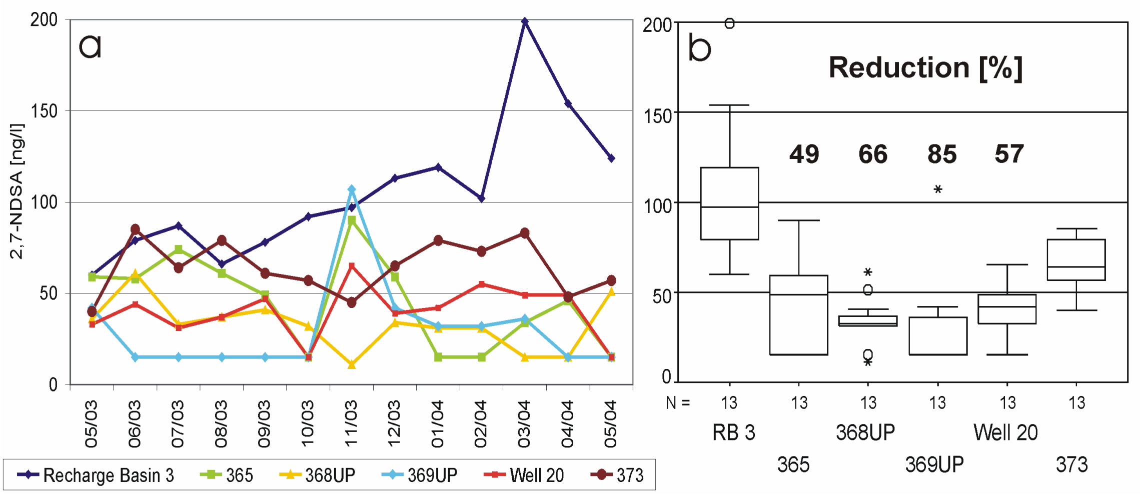


Figure 67 Fate of 2,7-Naphthalenedisulfonic acid during infiltration at GWR (a: time series; b: box plots)

Summarizing, all results of the monitoring of the artificial groundwater recharge facility support the findings of the other investigated field sites. Because of different conditions (retention time, redox potential) the behavior of trace compounds is not equal at all field sites. At the GWR the produced raw water contains the highest concentrations of Sulfamethoxazole. Similar to the other field sites Iopromide was metabolized quickly during infiltration and the 1,5-NDSA isomer remained persistent.

1.4 Soil column experiments

To complete the data basis obtained from the field monitoring, it was necessary to conduct soil column experiments. The experiments on soil columns were launched with the project start in 2002. Different soil column systems were installed, as simulations of one dimensional aquifers, to eliminate outside influences and to provide a closer insight into the kinetics of the degradation processes. The soil column experiments were used to isolate important factors of influence for the removal of the organic compounds (retention time, temperature, DOC-concentration, soil properties and hydrogeological conditions). The experiments without any disturbing outside influences produced results that helped to understand the degradation processes and kinetics of organics in the field.

Overall, four different soil column systems were utilized by the work group of the Department for Water Quality Control of the TU Berlin. The columns and the objectives of the research conducted on the systems are described more detailed in the following chapters.

1.4.1 Long retention soil column system (UBA Marienfelde)

The long retention soil column system was supervised by the work group of the Department of Water Quality Control at TU Berlin. The UBA Marienfelde provided work space and material for this unique opportunity to design a 30 m artificial infiltration path.

1.4.1.1 Set-up

The set-up of the long retention column system was one emphasis of the first phase of the project. The columns were operated in the drinking water treatment facility of the experimental field site at the UBA-Marienfelde. To start experiments it was necessary to combine the single columns to a soil column system and to install all piping and all peripheral equipment.

The columns were filled with natural middle/fine sand from the Berlin area for a preceding project. Precisely, the sand was derived from the sand pit “Horstfeld” near Zossen south of Berlin. Figure 68 shows the grading curve of the material, when it was analyzed for the first time during installation of the columns. The sand was filled to the columns as a disturbed sample and slightly compressed.

The following characteristics of the sand were measured at the time of column filling:

Water content:	2.3%
Loss on ignition:	0.3%
Carbonate-content:	0.3%
Uniformity coefficient:	2.87
k_f-value (from grain size distribution)	1.5-2.6 * 10-4 m/s
k_f-value (from lab experiments):	1.5-4.4 * 10-4 m/s
(in-stationary infiltration through 4 undisturbed samples)	
Density:	1.6 g/cm^3
Porosity (from grain size distribution):	31-40%
Porosity (from lab experiments):	40-44%
(calculated from the density of the soil in 4 undisturbed samples)	

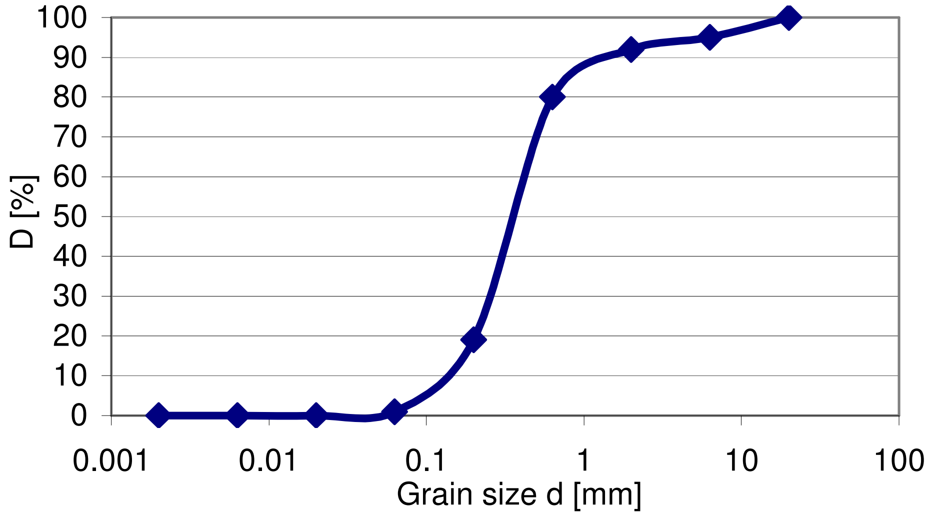


Figure 68 Grading curve of the used filling material

Previously, the columns were operated with a free water level without covers. Therefore, anoxic/anaerobic operating conditions and a reliable oxygen mass balance would have not been possible. To improve the design, covers for all columns were designed and manufactured by the machine shop of the TU Berlin. The covers had to fulfill the functions of keeping air (oxygen) out, to stabilize the redox system, and sealing the columns against leaking in case of a pressure build-up.

For all experiments the six single 5 m columns were connected in series to a 30 m soil column system. The system had a diameter of 0.4 m. The columns were made from 2 mm-stainless steel. At the bottom of each column was a 10 cm layer of coarser sand/gravel and at the top was a 15-20 cm water layer, before the water entered the tubing towards the next column. The columns were operated against gravity. The water entered the column at the bottom and flowed to the top. All six columns were connected with stainless steel tubing, because it was found that measurable amounts of oxygen diffuse through Teflon tubing (each connection is app. 6 m). For a real simulation of the flow path at the transects the system was operated under saturated conditions. A flow of 36 l/d accounted for a retention time of 30 days. Flow and hydraulic loading rate were selected to fit the conditions at the field site (Table 12).

Table 12 Characteristics of long retention soil column experiment

Total Length	Retention time	Effective Porosity	Total Flow	Hydraulic loading rate	Field-/Pore velocity
30 m	30 d	32 %	36 l/d	0.32 m/d	1.0 m/d

The columns were sampled at different depths to investigate the kinetics of bulk and trace organic degradation. Along the column system 21 sampling ports were sampled on a biweekly basis, to assure a regular monitoring of the fate of the target compounds. The sampling ports were made of stainless steel pipes, which were perforated at the middle of the column. The connection to the column wall was made of PVC. The water temperature in the columns and of the storage tanks was dependent from the temperature in the water work building in Marienfelde. The average temperature was 15℃, whereas during summer the temperature rose to 18-19℃ and during winter water temperature dropped to 12℃. Therefore, the average temperature is specified as 15℃ ± 4℃.

The water from Lake Tegel was spiked with the five target compounds. The spiking concentrations were selected to be approximately ten times higher than the background concentration in Lake Tegel. This assured stable concentrations in the column feed even when the concentration in the lake varied. An online dosage system for the five trace compounds was installed to assure a constant concentration of these five compounds in the influent. Table 13 gives an overview of the dosages of trace compounds to the lake water.

Table 13 Spiking concentrations for the long retention columns in Marienfelde

Trace compound	Iopromide	Sulfamethoxazole	1,5-NDSA	1,7-NDSA	2,7-NDSA
Spiking concentration	10 µg/l	2.5 µg/l	2.5 µg/l	2.5 µg/l	2.5 µg/l

Disturbances because of sampling were not problematic during experiments. Samples were taken starting at the end of the column system and a maximum of 8 x1 l samples on a sampling day. The sample amount was therefore 8 liter and significantly smaller than the daily flow through the columns (36 l). Sampling days had an interval of 2 weeks. On sampling days a pressure drop along the columns could be realized, but after 2-3 hours the conditions were back to normal. Figure 69 shows the soil column design schematic.

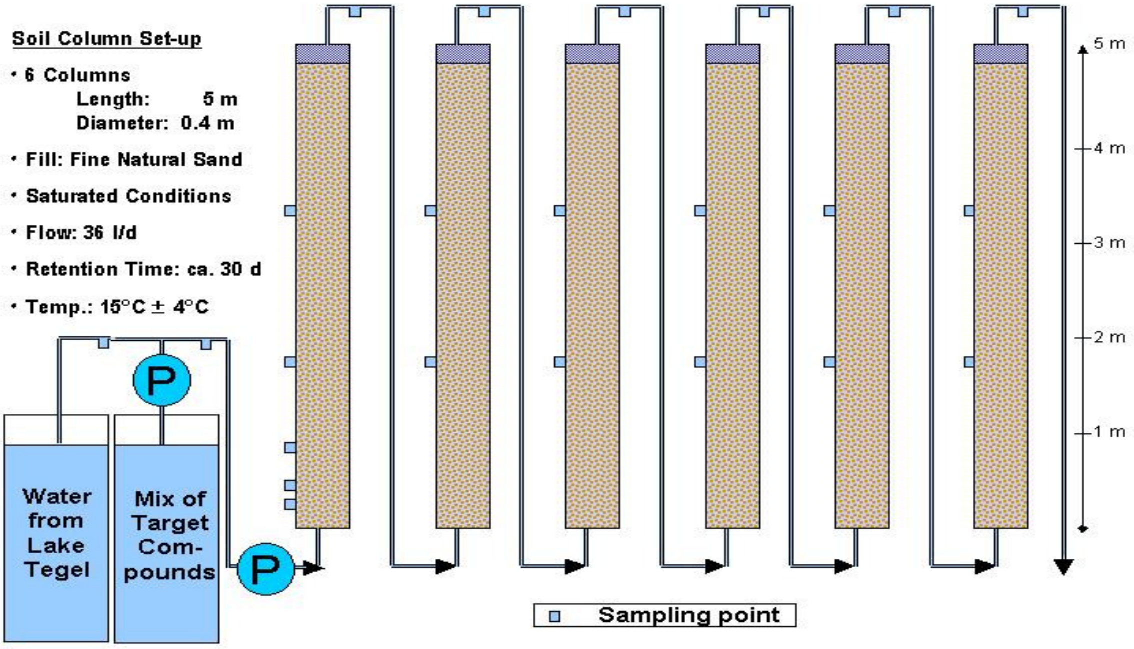


Figure 69 Experimental set-up of the long retention columns

By the end of August 2002 the final set-up of the six columns in series was completed and the operation started. First a rinsing cycle for each column was performed to remove any previous contaminants from the six aquifer columns. Over a time period of 6 weeks local drinking water was used for the rinsing process. The influent and the effluent were analyzed regarding UVA, DOC, Fe-Ions and Mn-Ions. Since the local drinking water is low in DOC (~2 mg/l) a leaching of organic compounds from the filling material would have been recognized. After 6 weeks of rinsing, the characteristics of the effluent were similar to the influent characteristics. However, towards the end of the rinsing the DOC-concentrations in the last sampling ports were approximately 20% lower than in the influent. This can be explained by an established microbial community, which degrades portions of the infiltrated DOC. The thorough rinsing and the detailed monitoring of the water quality during rinsing eliminated every doubt about the qualification of the soil column system (particularly the sand filling) for simulation experiments. The system was found to be free of contamination and perfectly suited for the planned experiments. The findings on the status of the long retention column system were consistent with the expertise of Schulz, 1998, who investigated the conditions of the soil columns in 1998.

Figure 70 Long retention soil columns Marienfelde (top part)

The adaptation period of the columns to the water supply from Lake Tegel was started middle of December 2002. After draining the drinking water, water from Lake Tegel was provided and fed to the columns. The water was pumped with 2 l/h (48 l/d) for nearly three weeks to fill the columns. Afterwards the flow was reduced to approximately 0.5 l/h (12 l/d) for 3 months to allow long term undisturbed development of biomass and an adaptation to the water quality of Lake Tegel. A monitoring of DOC and redox-conditions confirmed stable conditions at the end of the adaptation period. The spiking of the feed with the trace organic target compounds was started within the adaptation period.

In April 2003 the conditions of the columns were stable and the first part of the long term experiments with a flow rate of 36 l/d was started. During the first part of the experiment (04/2003 - 04/2004) oxic conditions were established in the soil columns to simulate the infiltration at the groundwater recharge facility. To assure oxic conditions the storage tank was mixed twice a day by a submergible pump and the infiltrating water was oxygen saturated. During this period oxygen was present in the whole column and no denitrification was observed. From May 2004 to May 2005 the redox status of the column system was switched to anoxic conditions (NO_3-reducing) by sparging the influent with nitrogen in a separate counter current column (O_2 in influent: ~1mg/l). Denitrification was observed but nitrate was not completely depleted from the system. No oxygen was detectable in the sampling ports. Monitoring of the DOC, UVA and redox-conditions ensured stable conditions over the time of these two experiments. Results from both phases will be presented in the following chapters.

As a service to other work groups in the project the soil column system was available at special times for other experiments. It was a good opportunity for all participants to check results of the monitoring at the transects in a nearly full-scale facility that eliminates all outside influences. The workgroups of Prof. Dr. Lopez-Pila, Dr. Heberer and Prof. Dr. Pekdeger used this possibility of the column system for separate experiments. The results of these studies are included in the respective reports.

1.4.1.2 Results

Tracer study

The tracer study was conducted to define the actual porosity, dispersivity and the affiliated characteristics (retention time etc.) of the soil column system. The tracer study was conducted from October 2002 until November 2002. A double tracer (Chloride/Bromide) was used in a pulse application and the flow rate was increased (60 – 80 l/d) to limit the duration of the study to 30-40 days. Drinking water was used as influent until the end of the experiment. During the study a daily sampling was used to describe the tracer movements through the columns as accurate as possible. The samples were analyzed at the TU Berlin for Chloride and Bromide using IC-technology. The background concentration of Chloride and Bromide in the used drinking water were determined in advance of the study with 100 mg/l Chloride und 1.2 mg/l Bromide.

The tracer study was completed by the end of November and determined the actual porosity, the individual travel time for each sampling point and the dispersion. This new knowledge reduced the analysis program, produced rapid results and improved the data basis for the aquifer simulation. The results were adapted to the lower flow during the aquifer simulation. The evaluation of the results was done in cooperation with the work group of Prof. Nützmann, who provided the program CXT FIT and a brief introduction into the program. The analysis of the data resulted in a model which is presented in Figure 71.

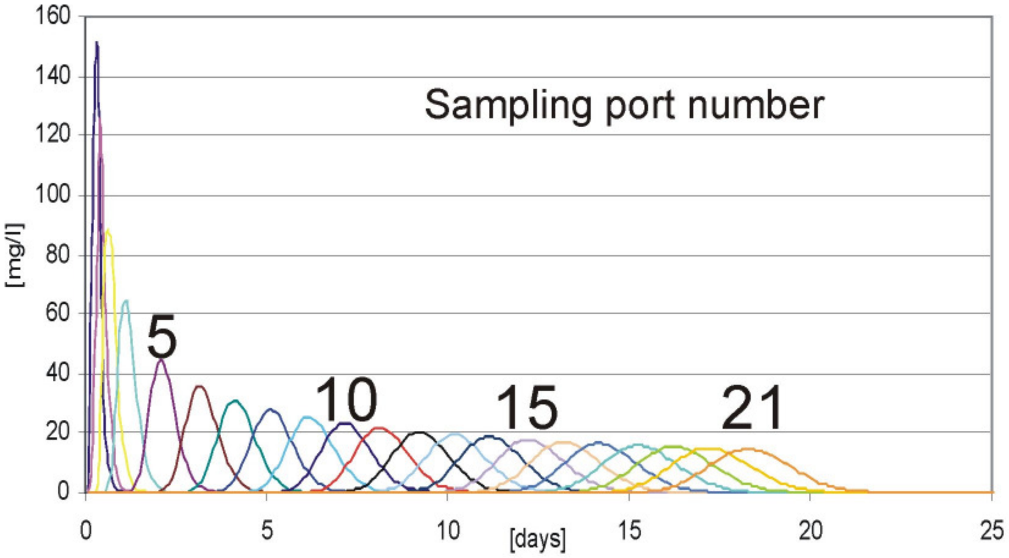


Figure 71 Model of Bromide-concentration at the 21 different sampling ports

The model was done in CXT FIT by calculating the average pore velocity and the dispersion from all bromide data. Afterwards, the findings where used to calculate the theoretical distribution of bromide in samples from the 21 sampling ports. The background concentration of bromide was below 0.15 mg/l in the used drinking water. The chloride background concentration was around 60 to 80 mg/l. Both data sets (chloride and bromide) showed the same results. But the bromide data could be analyzed more accurate because of the lower background concentration. At the last sampling point the results of the ion chromatography were checked by measurements of electrical conductivity, which confirmed the results by showing the same trends (data not presented). As a result of the tracer study it was found that the porosity of the filling sand is about 29% - 34% and the dispersion was approximately 0.1 m/d. The comparison of the model predicted and the measured bromide concentrations was difficult for the first sampling ports. Problems were:

- Short peak length (few hours to 1-2 days) combined with the unsuitable sampling rhythm (each port was sampled once a day except on the weekends).
- Unstable flow in the first five days of the experiment (pump was changed on day 6).

Nevertheless, the results for the sampling ports 9 to 21 were satisfying and fit into the predicted model. Figure 72 compares the measured and predicted concentration of bromide in port 16 and 21.

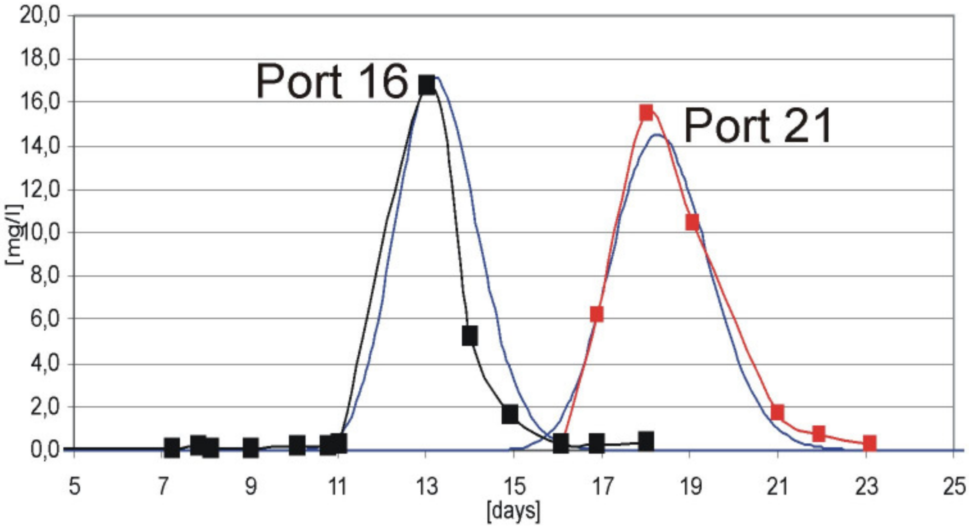


Figure 72 Predicted and measured bromide concentrations (port 16 and 21)

Inorganics - Results

During the experiments, the soil column system was also monitored for changes of inorganic parameters. Most important were the different electron acceptors, which controlled the redox potential (O_2, NO^{3-}, Fe-species). The redox potential itself and the oxygen saturation were measured biweekly. On a monthly basis the different redox sensitive water constituents (e.g. Nitrate, Fe^{2+}) were analyzed. Additionally, the FU Berlin measured monthly the major cations, anions and pH.

Figure 73 and Figure 74 provide the measured oxygen and nitrate content of the column system during both experiments. The following paragraphs describe the actual redox situation during both experiment parts more detailed:

Oxic phase: It was found that during the oxic stage oxygen was present along the whole column in decreasing concentrations. The water entered the column system oxygen saturated with O_2-levels between 8.5 mg/l - 11 mg/l depending on temperature. During the first 50 cm of infiltration or within 12 hours the oxygen concentration was cut by half. Afterwards a slower continuous depletion of oxygen was observed. The average O_{2}-concentration at the end of the column system was found to be ~1 mg/l. Along the column no reduction of the redox potential was measured. The redox potentials in the different sampling ports were found to range from 280-340 mV with no trend towards lower potentials at the end of the columns. Nitrate was present in all sampling ports in a comparable concentration. During the period May 2003-May 2004 the average surface water concentration of nitrate in Lake Tegel was 1.4 - 1.5 mg/l. Figure 74 does not provide error bars because most of the variation of the nitrate concentration is due to changes in the surface water that was used as influent. However, during the oxic stage the nitrate concentration remained stable along the infiltration path. The slight increase shortly after infiltration was most probably due to a nitrogen release from organic carbon structures. Overall, no denitrification was present in the oxic phase. This was consistent with the measured oxygen concentrations.

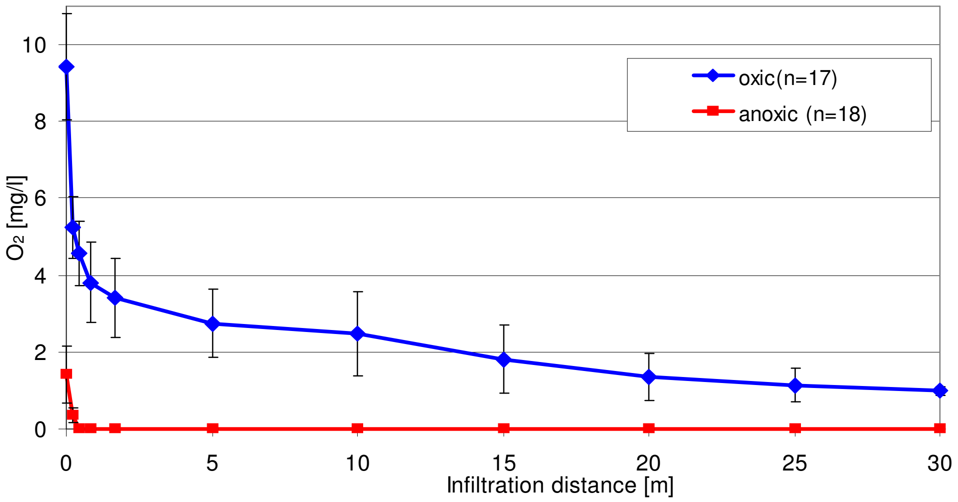


Figure 73 Oxygen concentrations during the both stages of the long retention soil column experiment

Anoxic phase: During the anoxic stage the water from Lake Tegel was sparged with Nitrogen before it was introduced to the column system. Furthermore, the submergible pump was removed to avoid high oxygen levels in the storage tank. Despite of all measures it was not possible to reduce the influent oxygen concentration under the level of 1.0 mg/l. Figure 73 shows that oxygen concentration of the infiltrating water was found to be in the range of 1 – 2 mg/l. But these small amounts of oxygen were rapidly used up by DOC-mineralization in the first centimeters of the column system. In the first sampling port after 0.2 m only traces of oxygen were found and after 0.4 m no oxygen was present in the infiltrate. All biweekly measurements during the anoxic phase confirmed no dissolved oxygen in the soil column system. Since oxygen was not present during this stage the biomass used nitrate as electron acceptor. The nitrate levels of the surface water rose to an average of 1.9 - 2.0 mg/l during the period May 2004 – May 2005. This slightly higher concentration guaranteed that nitrate was not completely depleted from the system. Figure 74 shows that along the column system the nitrate concentration was reduced but at no time of the anoxic stage nitrate was removed. Therefore, the second stage can be characterized as anoxic. The redox potential was not measured regularly during this stage since the monitoring of oxygen and nitrate delivered all necessary information on the redox status of the columns. However, the conducted measurements showed that the redox potential of the infiltrated water was in the range of 250 – 300 mV. Shortly after infiltration the redox potential decreased to 100 - 160 mV and remained nearly stable for the rest of the infiltration distance. The average redox potential of the soil column effluent was found to be 120 mV.

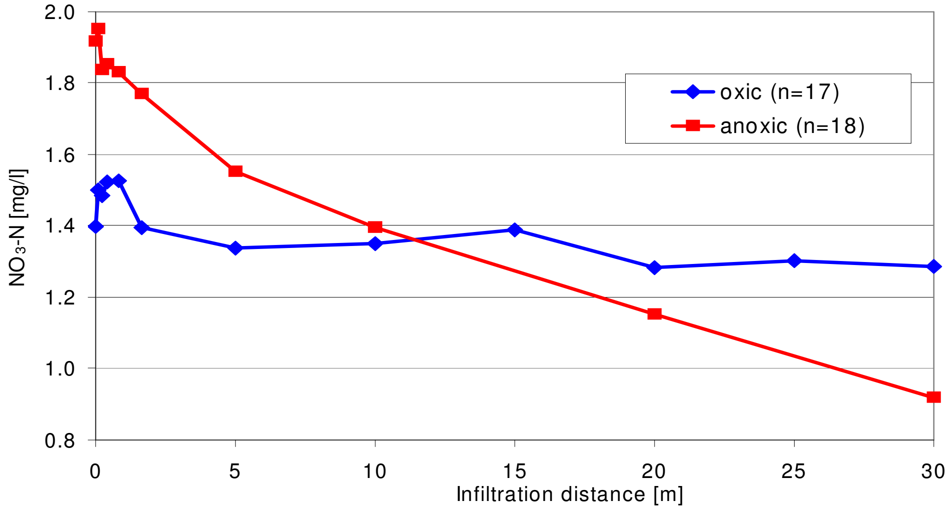


Figure 74 Nitrate concentrations during the both stages of the long retention soil column experiment

Additionally to the monitoring of the redox relevant parameters, the FU Berlin conducted a detailed analysis of the major cations/anions and the development of the pH-factor. It was found that during both stages the average pH decreased during infiltration. Figure 75 shows that during oxic infiltration the pH drops immediately after infiltration by 0.5 pH-units. This drop is explained by the release of CO_2 during mineralization of dissolved carbon, which forms carbonic acid. Furthermore, the oxic degradation pathway contains the formation of organic acids by introduction of oxygen into the molecule. Therefore, the pH-decrease is most probable due to the very fast degradation and mineralization of DOC during oxic conditions.

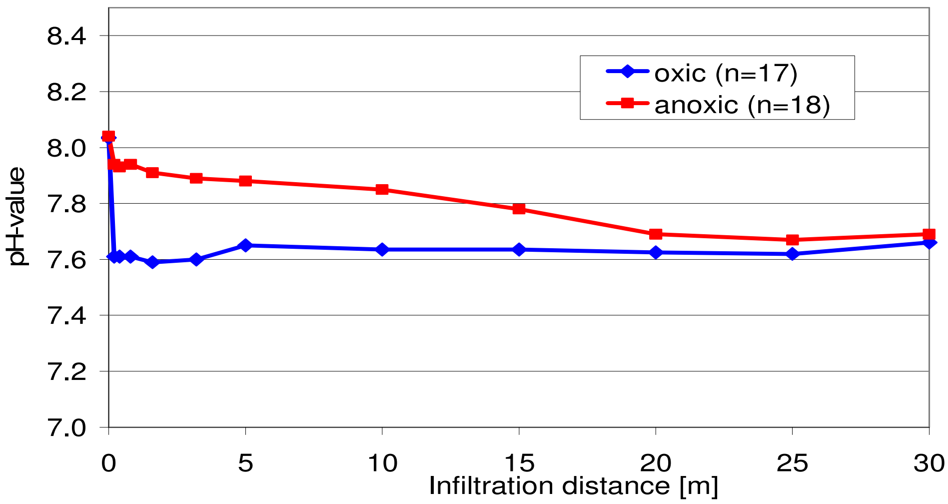


Figure 75 Development of pH during infiltration at both stages of the soil column experiment

During anoxic conditions the development of pH is a slower process. Corresponding to the slower DOC mineralization the pH decrease stretched over the entire infiltration distance. At the end the average pH of the effluent is similar in both phases.

The major cations were monitored to detect eventual changes in the ionic composition of the infiltrate.

Table 14 provides the average concentration of sodium, potassium, calcium and magnesium along the columns during the oxic and the anoxic phase. The table proves that no significant changes in the concentrations of the cations occurred during infiltration. From sediment properties it was known that the cationic exchange capacity of the filling material and the calcium carbonate content are very low. As a result no strong depletion of potassium (high CEC-selectivity) and no dissolution of calcium carbonate (caused by pH-decrease) were observed in the columns.

Table 14 Fate of major cations in soil columns (oxic and anoxic stage)

Sampling port	Infiltration distance [m]	Na+ [mg/l]	K+ [mg/l]	Ca+ [mg/l]	Mg+ [mg/l]
		oxic/anoxic	oxic/anoxic	oxic/anoxic	oxic/anoxic
Surface water	0.0	46.0 / 43.4	12.0 / 10.8	86.0 / 78.0	11.0 / 9.2
1	0.2	44.5 / 41.0	11.0 / 10.3	83.0 / 75.0	10.3 / 9.1
2	0.4	44.1 / 41.8	11.2 / 10.3	83.0 / 76.0	10.5 / 9.4
3	0.8	45.5 / 42.0	11.0 / 10.4	82.0 / 78.0	10.3 / 9.2
4	1.6	44.0 / 42.0	11.0 / 10.0	83.0 / 77.0	10.3 / 9.1
5	3.2	44.0 / 41.3	11.0 / 10.2	82.0 / 78.0	10.2 / 9.4
6	5	43.2 / 42.3	10.8 / 10.2	83.5 / 75.0	10.2 / 9.0
9	10	43.4 / 42.1	11.1 / 10.2	82.5 / 75.0	10.0 / 8.8

12	15	43.2 / 43.0	10.6 / 9.7	82.5 / 75.0	10.0 / 8.9
15	20	43.2 / 42.5	10.8 / 9.9	84.5 / 79.0	10.0 / 8.7
18	25	43.5 / 42.0	10.4 / 10.0	84.0 / 77.0	9.8 / 8.6
21	30	42.8 / 42.7	10.3 / 9.8	86.0 / 77.0	9.8 / 8.5

Additionally, the analytical program of the FU Berlin revealed that the electric conductivity (620 µS/cm ± 20 µS/cm) did not change during infiltration. Similarly, the anionic composition (Cl^- and SO_4^{2+}) remained constant. A slight increase in HCO_3^-, which was caused by CO_2 production during DOC mineralization, was observed for the oxic phase.

Bulk Organics - Results

During the two years of experiments on the columns a detailed monitoring of the fate of the bulk organics was conducted. The monitoring program consisted of DOC, UVA_{254}, UVA_{436}, adsorbable organic iodine and LC-OCD analysis. One focus of the investigations was the immediate infiltration zone. In the soil column system it was possible to achieve a high data resolution in this important stage of infiltration. The obtained data can supplement the field data, since no investigated field site provided a sufficient resolution of the bank area near the soil/water- interface. Along further infiltration samples were take every 5 m (equivalent to 5 days retention time).

DOC:

The DOC-results of the soil columns experiments are presented in Figure 76. It was found that in the oxic soil columns 47% of the DOC was removed during 30 days of infiltration. Most of the DOC-mineralization was observed within the first meter of the infiltration path. Overall, DOC-mineralization was a stable process and most of the variations of DOC-levels are due to changing surface water quality and analytical inaccuracies. The oxic stage of the experiment was planned as a simulation of the infiltration process at the artificial groundwater recharge facility. The results point out that the simulation was successful. Very similar to the fate of DOC at the artificial groundwater recharge facility a high portion of DOC was mineralized in the immediate infiltration zone. After 20 days of infiltration (20 m) the DOC-concentration remains constant at a level of 3.8 mg/l and no further reduction was observed. This concentration was found to be a very good estimation of the amount of non-degradable organic carbon in Lake Tegel surface water.

However, these results underline the importance of the soil layer close to the water/soil interface. It can be assumed that the biological activity in this area is significantly higher than in the deeper soil layers. At the GWR only 38% of DOC was removed in 50 days compared to 47% in the solid columns in 30 days. These differences are explained by the following factors of influence. At the GWR the redox system changes during summer to anoxic/anaerobic and the lower mineralization rates of this period are included in the average DOC-removal. Furthermore, the infiltration path at GWR is exposed to heavy temperature variations (±12°C) that forces the biomass to adaptation processes. The temperature of the soil column experiment changed in a considerably smaller range (±4°C).

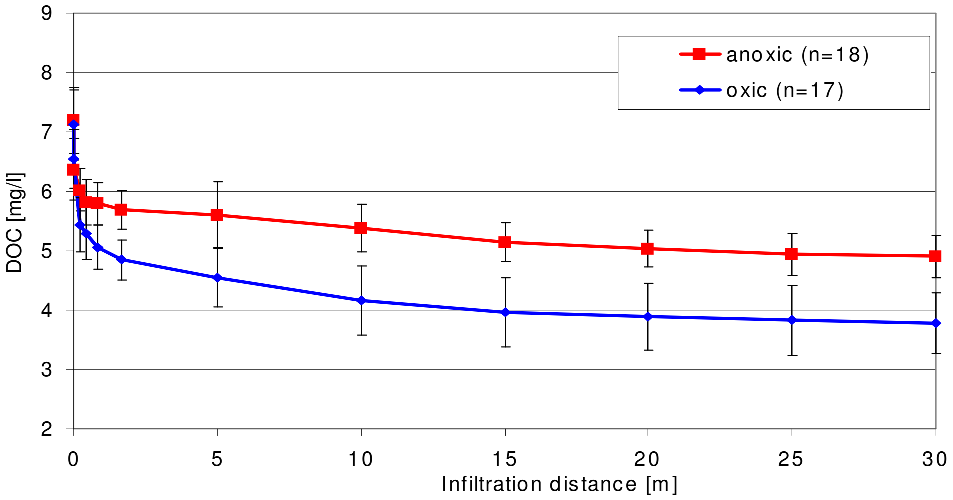


Figure 76 Fate of DOC during the two stages of the soil column experiment

For the simulation of anoxic conditions, the initial oxic phase, which occurs invariably in the field because of oxygen saturated surface water, was reduced to the lowest practicable dimensions (<0.21m). Under these conditions only 31% of the source water DOC was removed during 30 days of infiltration (Figure 76). Similar to the removal under oxic conditions a large portion of DOC is removed in the first infiltration layer. But compared to the oxic conditions the amount of mineralized DOC within the first 1.6 m is 1 mg/l smaller. After this rapid removal of easy degradable organic carbon a slower mineralization process starts. The results confirm that under anoxic conditions a smaller portion of DOC can be considered as easy degradable. The mineralization process in the anoxic column continues until the end of the column. After 30 days the average DOC-level was found to be 4.9 mg/l. Because of their limited retention time the column experiments could not clarify whether the residual non-degradable DOC-concentration is similar under oxic and anoxic/anaerobic conditions. The comparison of the final DOC residuals after infiltration at the bank filtration site Tegel and the GWR raised the explanation that an anoxic infiltration can reach after long retention times the same DOC-residual concentrations as a oxic infiltration.

However, the results supported the field results that the DOC removal under oxic conditions is considerably faster than under anoxic or anaerobic conditions. The simulation experiments allowed a more precise investigation of the fate of DOC during the first month of infiltration depending on the dominant redox conditions and showed that under both conditions the infiltration phase is of eminent importance. The overall removal rates are within the range of mineralization rates observed in the field. A slightly higher removal can be explained by a higher average water temperature in the soil columns (~15°C, field: ~12°C).

Since the data on DOC-mineralization were obtained in a closed system that rules out every outside influence, it was of special interest to model the fate of DOC. Different approaches on biodegradation of organic carbon are known. The most scientific model is based on a fractionation of DOC in groups of different degradability and a mineralization of the single groups after the rules of MONOD. This approach was originally introduced to water chemistry by Gimbel et al. (1992) and later used for similar modeling by Drewes, 1997 and Schoenheinz, 2004. The model used for the simulation of the soil column DOC-data was based on three different groups of DOC: an easy degradable fraction, a medium- and hardly-degradable fraction and the non-degradable fraction of organic carbon. The non-degradable fraction remained constant during infiltration, whereas the easy and medium-degradable fraction where depleted following the rules of exponential decay postulated by MONOD. Figure 77 shows the theory, which was the basis of the model.

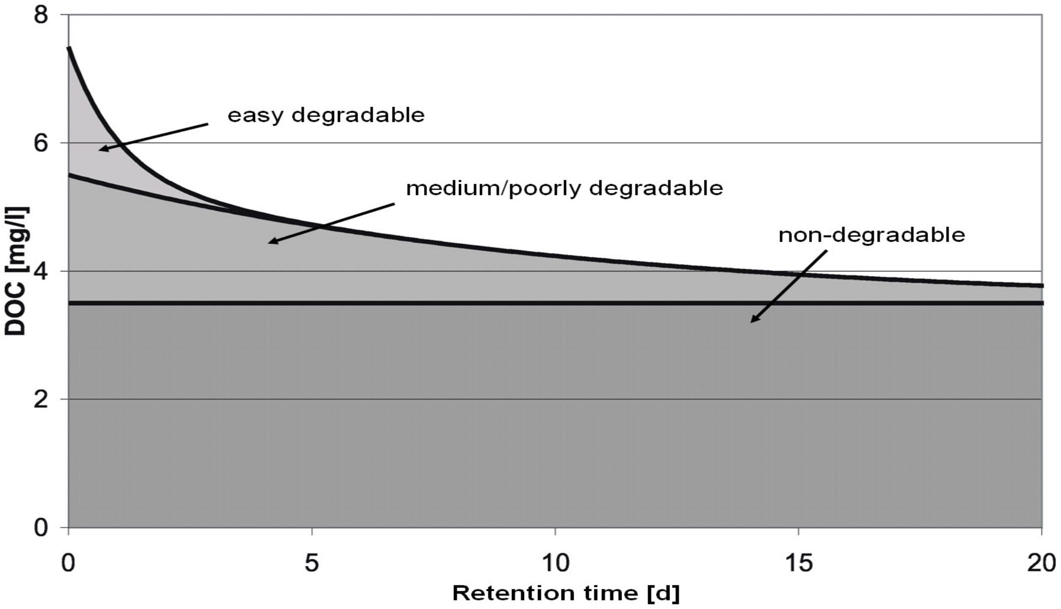


Figure 77 Theoretical basis of the DOC-degradation (adapted from Gimbel et al., 1992)

Based on the literature the DOC-mineralization in the long retention columns was modeled using Equation 1. The concentration of DOC at a certain time after infiltration (c_t) is dependent from the concentration of the three different fractions: easy degradable fraction (c_1), a medium- and hardly-degradable fraction (c_2) and the non-degradable fraction (c_3) and time (t). λ_1 and λ_2 are the degradation constants for the removal of the degradable fractions.

$$c_t = c_1 * e^{-\lambda_1 * t} + c_2 * e^{-\lambda_2 * t} + c_3$$

Equation 1 Model for the mineralization of DOC during infiltration (according to Gimbel et al., 1992)

Some postulations were necessary to receive good results from the model. First, the concentration of the non-degradable fraction was set to 53% of the surface water DOC, because under oxic conditions 47% of the source water DOC was degradable within 30 days. The plateauing of the DOC-concentration towards the end (Figure 76) indicated that all degradable DOC was mineralized. Therefore, under oxic conditions 3.8 mg/l were assigned to the non-degradable fraction. Under anoxic conditions the total DOC-concentration was slightly lower, resulting in 3.7 mg/l non-degradable DOC. Furthermore, the easy degradable fraction was quantified by DOC removal after ~20 h (0.8 m), following the example of Drewes, 1997. Herewith, a higher portion of the total DOC (2 mg/l) was regarded as easy degradable under oxic conditions (anoxic conditions 1.4 mg/l). The medium degradable fraction was calculated from the total DOC and the other two fractions. Table 15 provides the concentrations used in the model.

Table 15 Summary of modeling data for long retention soil column system

	C_1 [mg/l]	C_2 [mg/l]	C_3 [mg/l]	λ_1 [1/d]	λ_2 [1/d]
oxic	2	1.3	3.8	7.97	0.117
anoxic	1.4	1.8	3.7	7.31	0.019

The model used non-linear regression to fit the modeled decay curve to the observed DOC-concentrations. The calculation was conducted for the oxic and the anoxic stage and the results are presented in Figure 78. Overall, the model was able to depict the DOC decay under both conditions very detailed and the resulting R^2 (R^2>0.99) indicated a successful adaptation. Table 15 shows that despite of the different concentration of easy degradable carbon (c_1) the degradation constant (λ_1) was similar during both stages of the experiment. λ_2 as the degradation constant of the medium degradable DOC fraction pointed toward a faster degradation of this fraction under oxic conditions (factor~6). The calculation of the model showed that the concentration of the medium degradable fraction, which determines the fate of total DOC in the deeper filtration layers, fells under 0.1 mg/l (accuracy of the DOC measurement) after 23 days under oxic conditions. Contrary to this, it takes 155 days under anoxic conditions for the medium degradable fraction to remain under 0.1 mg/l. A comparison of these results with the experiences from the field exposes interesting similarities. At the GWR the DOC degradation process was completed after approximately 30 days and at the bank filtration site Tegel the DOC mineralization under anoxic/anaerobic conditions continued for 4.5 – 5.5 months (135 – 165 days).

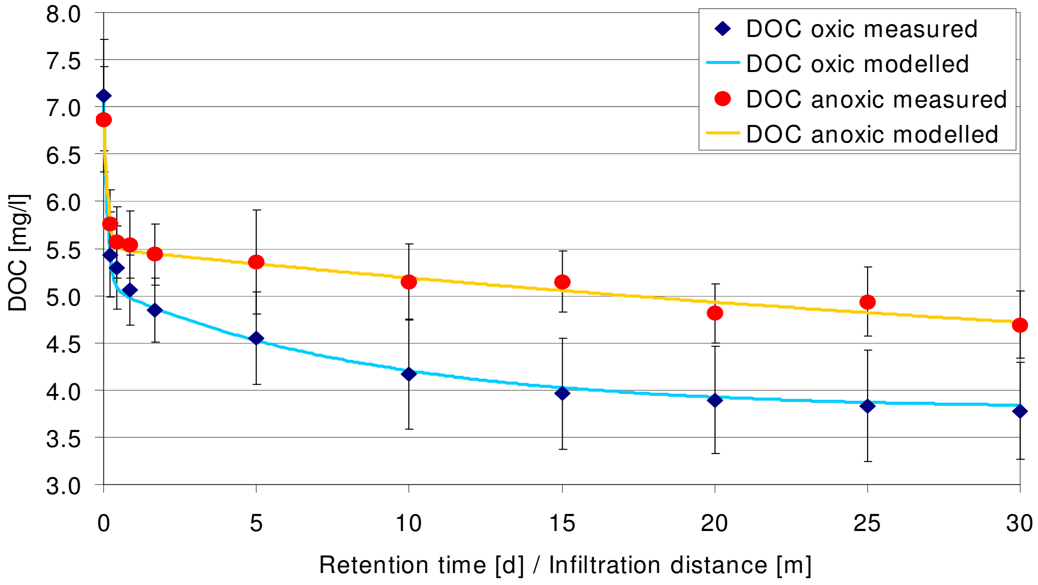


Figure 78 Results of the modeling of the DOC-degradation in the soil column system

To compare the results of the soil column experiments with the findings of the field monitoring Figure 79 depicts all results in one graph. Since most of the investigated field sites have no fine resolution near the bank, only a few data points, describing the fate of DOC during the first 30 days, were found for each transect. Most problematic was field site Wannsee, where only two data sets (monitoring well 205 and 206) are available for this time frame. Well 206 is representative for an oxic infiltration and well 205 has a more anaerobic character. The data sets of the GWR can be regarded as examples of an oxic infiltration and bank filtration site Tegel is a case of anoxic/anaerobic infiltration. Figure 79 shows that the model predicted DOC concentrations and the real DOC levels show similar trends. However, a comparison of the GWR data sets with the oxic model and the bank filtration Tegel data sets with the anoxic model proposes some methodical mistakes. The DOC levels in the reality are higher than the predicted DOC concentrations. This is most probably due to a large range of effects that influence the DOC degradation in the field, that were excluded in the soil columns (heavy temperature variations etc.).

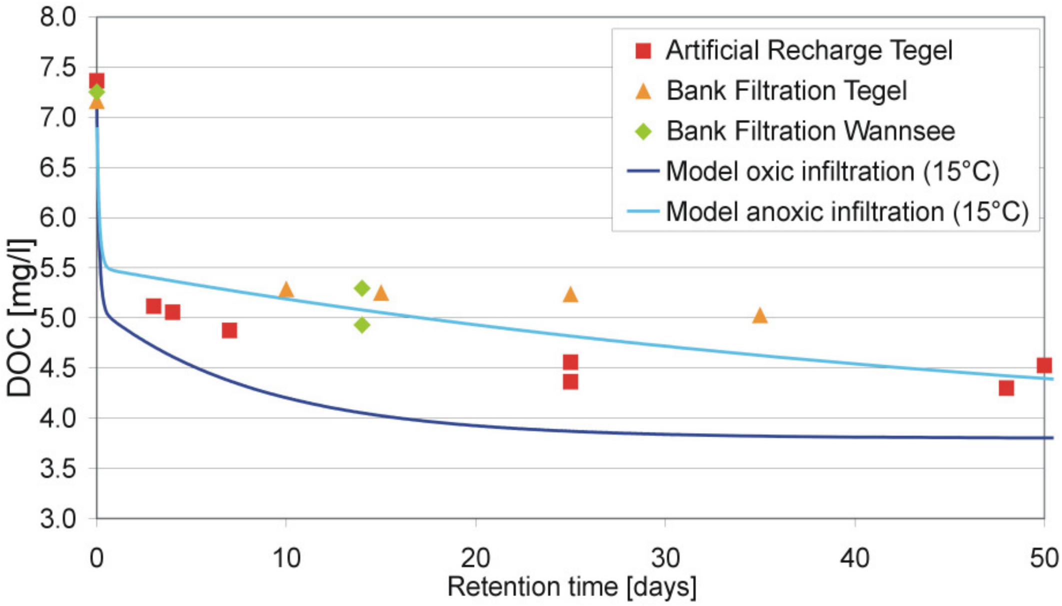


Figure 79 Comparison of model predicted DOC-concentrations with field-measured DOC levels

UVA:

The DOC-analysis was accompanied by a regular monitoring of the UV-absorption at 254 nm. It was found that UV-active organic carbons were removed during the infiltration process. The removal rates pointed towards a similar efficient mineralization of the aromatic and double bond structures and the total DOC. Under oxic conditions the UV-absorption at 254 nm decreased by 50%. A comparison of the actual UVA_{254}-removal with the removal of total DOC (47%) shows that the UV-active compounds were diminished slightly more efficient than DOC on the entire infiltration path. Under anoxic conditions the removal rates for UVA_{254} were 32% and therefore very similar to the rate for total DOC-mineralization (31%). Figure 80 shows the dynamic of UVA_{254}-removal. Most of the UV-active compounds were removed in the first part of the column system. Towards the end of infiltration a stabilization of the UVA_{254} was achieved under both conditions. More information on the behavior of aliphatic and aromatic carbons during infiltration is revealed by the combination of DOC and UVA_{254} results in the SUVA (following chapter).

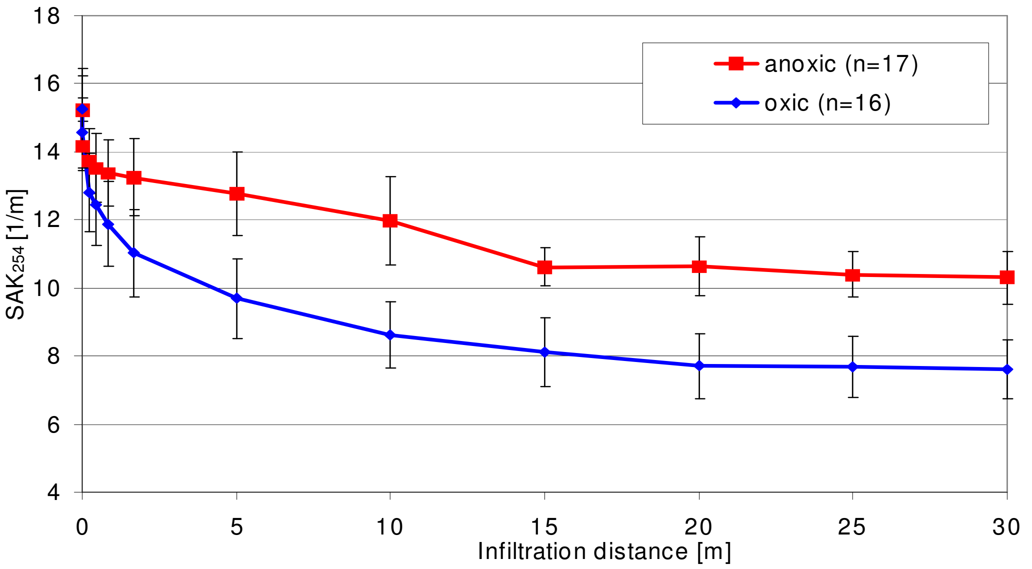


Figure 80 Fate of UVA_{254} during the two stages of the experiment

Measurements of the UVA_{436} (color) provided no additional results since the UVA_{436} level of the infiltrating water was very close to the detection limit. Therefore, no closer description of the parameter is provided.

SUVA:

The SUVA is the quotient of UVA_{254} and DOC-concentration and describes the character of the dissolved organic carbon more detailed. A high share of aromatic organic carbon on the total DOC leads to high SUVA-values. Therefore, the SUVA is a parameter, which is only dependent of the character of DOC but not of the amounts of organic carbon. The SUVA is very reliable in detecting changes in the aromaticity of DOC during infiltration.

The average SUVA of Lake Tegel surface water was 2.1 l/m*mg. During the oxic soil column experiment the SUVA increased very rapidly to 2.36 l/m*mg after 0.21 m infiltration (Figure 81). The results indicate that during initial aerobic soil passage aliphatic carbon sources are preferentially used. During further infiltration more aromatic structures are degraded and the SUVA decreases. After 5 days (5 m) of infiltration the SUVA of the infiltrate is equal to the SUVA of the surface water, which was used as feed water. Towards the end of infiltration the SUVA decreases under the initial SUVA, indicating a more efficient mineralization of aromatics.

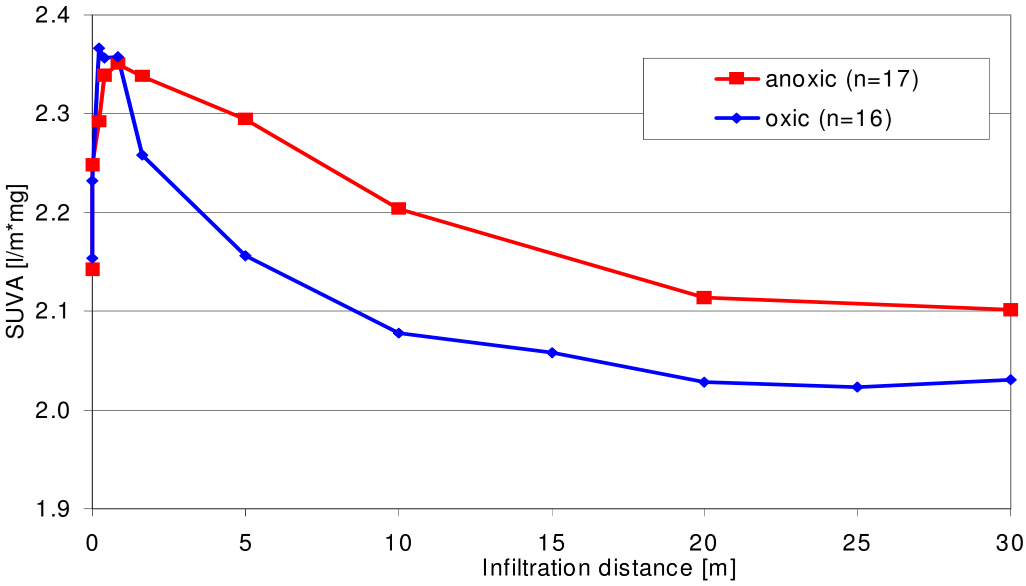


Figure 81 Fate of SUVA during the two stages of the soil column experiment

During anoxic infiltration the increase in SUVA is slightly slower reaching the maximum after 0.8 – 1.6 m of infiltration. Afterwards the SUVA is decreasing, but the aromatic part of the total DOC is mineralized considerably slower. Therefore, the decrease of SUVA continues slowly along the entire column. At the end of the infiltration the SUVA is similar to the initial SUVA.

However, the results indicate that under both redox conditions aliphatic compounds are initially degraded and subsequently aromatic structures. Under oxic conditions aliphatic carbon sources are preferentially degraded within the first 0.2 m. Under anoxic conditions the sequence of the degradation process is similar but significantly slower. Aliphatic carbon sources are preferentially degraded within the first 0.8 m. Therefore, the degradation process under anoxic conditions is slower by the factor of four. This is underlined by the fact that the final SUVA of the anoxic infiltration (2.1 l/m*mg after 30 days) is reached under oxic conditions after 8 days (8 m) of infiltration. Finally, the results indicate that the degradation processes are similar under both redox conditions and that the different SUVA results under oxic and anoxic conditions are mostly due to a stretched time frame.

LC-OCD:

A more detailed analysis of the changing character of the dissolved organic carbon was provided by LC-OCD. The LC-OCD technique allowed a fractionation of the organic water constituents in five fractions. The fate of the different DOC fractions was monitored by biweekly sampling. One important point of interest was the comparison of the DOC character of Lake Tegel surface water and the water infiltrated to the columns. It was necessary to detect potential differences in DOC-character, which were caused by the storage (maximum two weeks) of the surface water. Table 3 shows that the integration of the LC-OCD chromatograms leads to similar results for both water types. Therefore, it can be concluded that the storage did not influence the organic water composition and the results can be compared to the field results.

Table 16 Portions and concentrations of different fractions of DOC (Columns influent, Lake Tegel)

	Poly-saccharides	Humic substances	Humic substances-Building blocks	Low molecular acids	Neutrals and Hydrophobics
Column in-fluent (n=12)	8.7 %	44.1 %	24.6 %	3.7 %	18.9 %
	0.6 mg/l	3.1 mg/l	1.7 mg/l	0.3 mg/l	1.3 mg/l
Lake Tegel (n=12)	8.7 %	46.0 %	22.1 %	3.7 %	19.7 %
	0.6 mg/l	3.3 mg/l	1.6 mg/l	0.3 mg/l	1.4 mg/l

Generally, LC-OCD chromatograms of the oxic period of the long retention columns (Figure 82) were comparable to the chromatograms of the GWR field site. Both, in the field and in the columns the most fundamental change during infiltration was observed for the fraction of the polysaccharides. PS were efficiently removed in the first 0.21 m of oxic infiltration in the soil columns (Figure 82a). Furthermore, the fractions of HS, HS building blocks and LMA were only partially degraded. It is noteworthy that even a part of the HS peak was removed, generally assumed to be mostly non-degradable.

During the anoxic period of the column system (May 2004 - May 2005) the LC-OCD analysis proved a change in water quality of the surface water. The share of HS-building blocks and LMA on the total DOC of the source water decreased and the peak intensity of the corresponding peaks was reduced (Figure 82b). However, despite of this, a slower degradation of the polysaccharide fraction was observed under anoxic conditions. PS were still detectable after 30 days of anoxic infiltration (Figure 82b). The fractions of HS, HS building blocks and LMA showed a similar partial removal as under oxic conditions. Because of the generally slower DOC degradation kinetic, the chromatograms are more pooled together in the anoxic period. Despite of the PS-fraction, a difference in the general degradability of the single fractions under oxic or anoxic/anaerobic conditions was not observed.

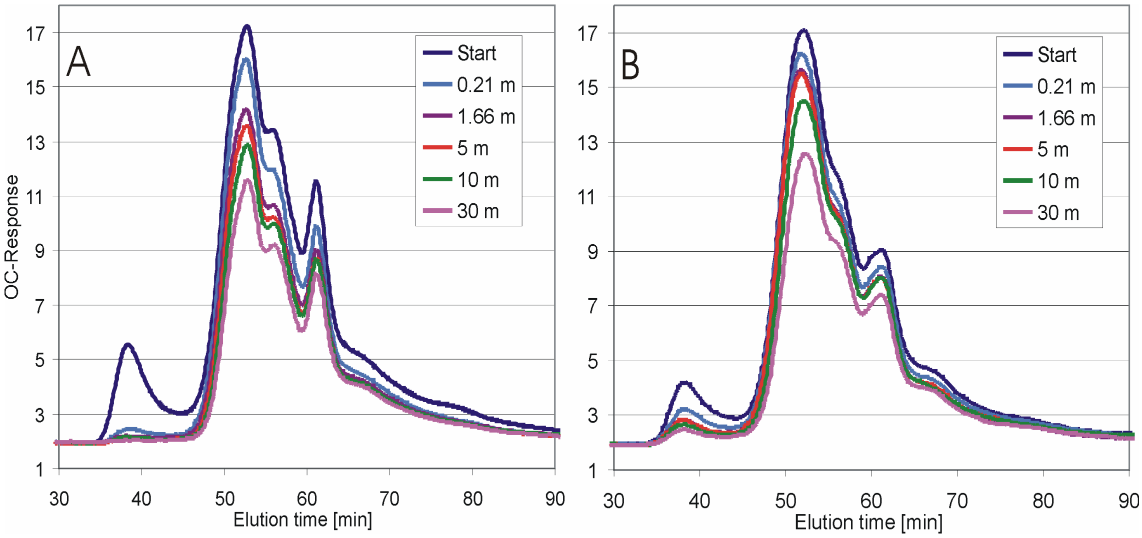


Figure 82 LC-OCD chromatogram of soil column experiment - oxic (A) / anoxic (B)

Furthermore, LC-OCD measurements revealed that the changes in SUVA result from the fast removal of the PS-fraction (elution time 35-45 min) and from a change of aromaticity in the HS-fraction (elution time 48-52 min). In the online measurement of the samples from the oxic stage the HS-fraction showed major changes in SUVA, while the SUVA of HS-building blocks and LMA were constant (Figure 83a). It is assumed that in the HS-fraction aliphatic side-chains are very fast mineralized, but aromatic and double-bond structures remain longer unchanged. LC-OCD measurements proved that under anoxic conditions the slower removal of PS is responsible for the slower rise of SUVA. In the HS-fraction no initial preferential removal of aliphatics was observed and the SUVA remained stable during the first 1.6 m of infiltration (Figure 83b). Afterwards, the mineralization of aromatics from the HS-fraction leads to a decreasing SUVA.

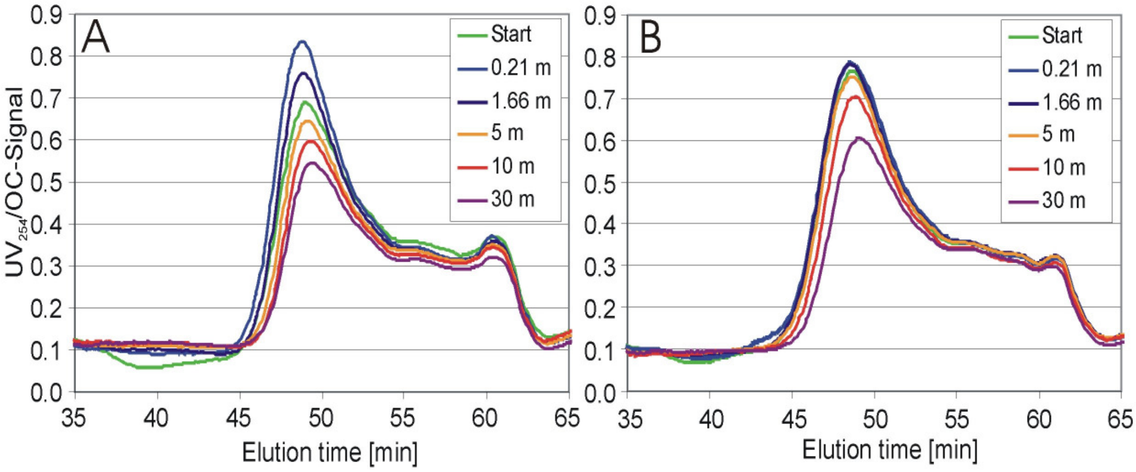


Figure 83 LC-OCD SUVA - chromatogram of soil column experiment - oxic (A) / anoxic (B)

Figure 84 provides more information on the behavior of the five different DOC-fractions along the oxic infiltration path. Most degradation processes in the single DOC fractions were completed after 2 days (2 m). Only, the concentration of the fraction of humic substances was found to change until day 10 after entering the column system. It was found that no significant changes in DOC composition occurred after ~10 days (10 m) of infiltration. The fraction of polysaccharides was completely removed within the first few centimeters. The most important fractions of DOC were the humic substances, followed by the HS-building blocks and the neutral fraction. The concentration of low molecular acids (LMA) remained constant along the infiltration path. It is assumed that this fraction is formed from biodegradation products of the other DOC-constituents. Therefore, no concentration changes were observed.

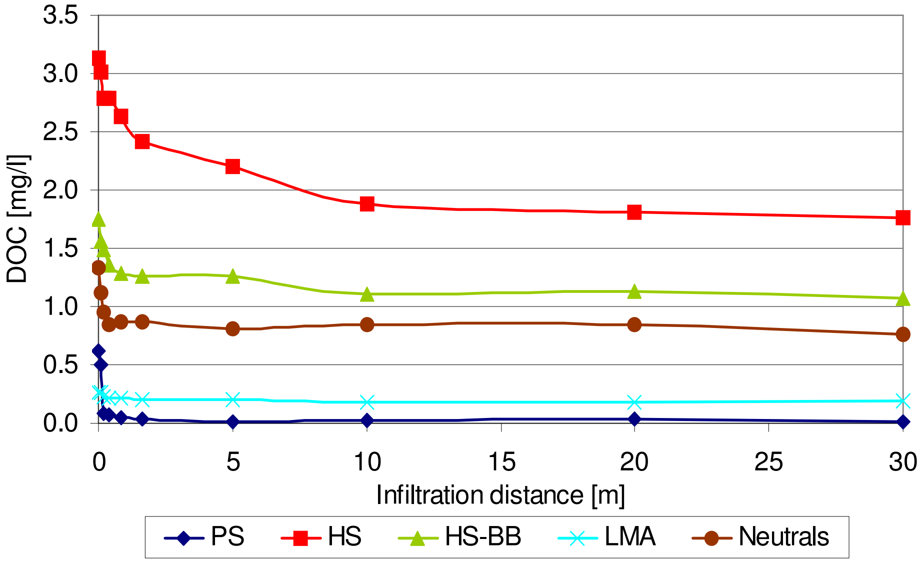


Figure 84 Fate of different DOC fractions along the infiltration path during the oxic stage

Figure 85 provides comparable results for the anoxic stage. It is obvious, that the degradation processes in the single DOC fractions are similar but considerably slower. The concentration of humic substances changes over the entire column. Furthermore, the concentration of neutrals is increasing slightly after 5 m of infiltration. Most probably the increase is due to mineralization fragments, which end up in this DOC-fraction. Figure 85 shows clearly that the fraction of polysaccharides is not completely mineralized.

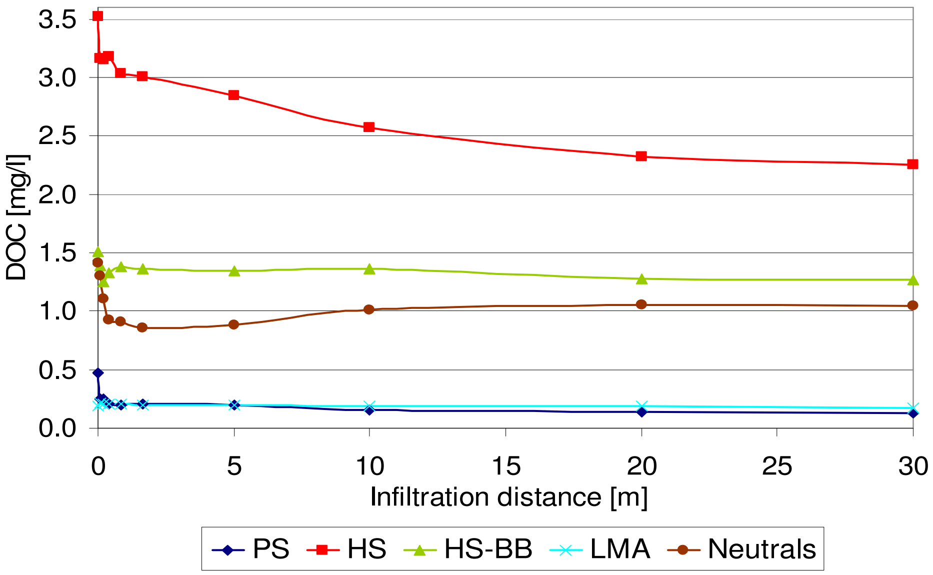


Figure 85 Fate of different DOC fractions along the infiltration path during the anoxic stage

Mass balances:

During infiltration the fate of oxygen or nitrate and organic carbon depend from each other. During mineralization of organic carbon oxygen and nitrate are used as electron acceptors. With the help of mass balances it is possible to assure that changes in oxygen or nitrate concentration are caused by DOC-mineralization. In special cases other factors (like mineralization of POC) influence the electron acceptor level. A mass balance reveals these hidden factors. Figure 86 shows the oxygen mass balance of the long retention column system under oxic conditions. The comparison of the measured oxygen concentration (red graph) with the oxygen concentration calculated on the basis of DOC mineralization (blue graph) proves that no important factors, which were not considered, influence the fate of oxygen.

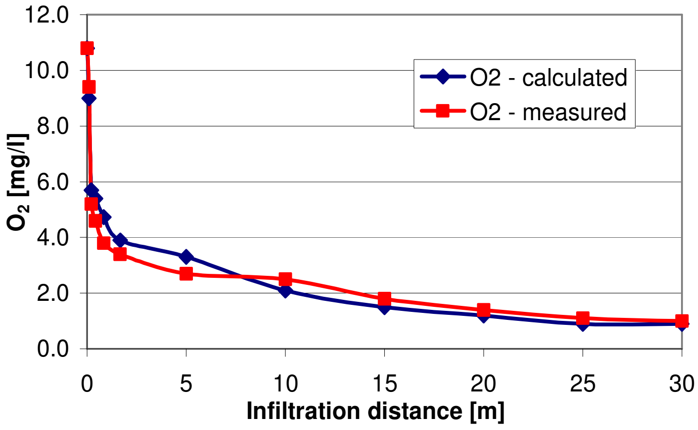


Figure 86 Oxygen mass balance of the long retention columns (oxic stage)

The so called mean oxidation number (MON) is necessary to set up an oxygen mass balance. The MON stands for the amount of oxygen (in mg) which is necessary to mineralize one milligram of organic carbon. The MON for natural surface waters is in the range of 2.5 – 3. In the calculation a MON of 3 was used. The mass balance showed that no significant mineralization of POC from the column sediment material took place. The measured and the calculated fate of oxygen correlate very well.
Figure 87 shows the nitrate balance of the anoxic stage of the long retention column experiment. The very low oxygen levels present in the influent were considered in the calculation. From the observed fate of DOC it was possible to calculate the nitrate consumption by the use of the MON and the oxygen content of NO_3^-. It was found that the calculated and the measured nitrate levels are similar at the different stages of infiltration. These results demonstrate that the objectives of the soil column experiments, to isolate biodegradation as an effect that controls the DOC-level, was successful.

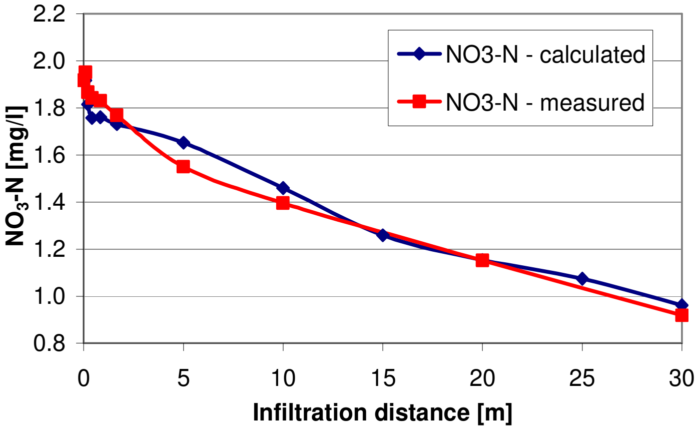


Figure 87 Nitrate mass balance of the long retention columns (anoxic stage)

The production of inorganic carbon is a parameter that could have been used for mass balancing. Unfortunately, the results of the TIC-measurements in the long retention columns are not satisfying and are therefore not used in the mass balance.
Figure 88 shows an overall picture of the bank filtration field site Berlin-Tegel with the most important processes. To simplify the approach a cube of one meter edge length was assumed and all important processes and in- and outputs were stated. The results from the experiment at the long retention column on the MON were transferred to the field. It was found that besides the mineralization of DOC a degradation of POC occurs, which is responsible for the anoxic/anaerobic conditions at the Tegel bank filtration site. A comparison of the effects in the field and at the soil columns showed that most effects that are important at the soil water interface in the field were not relevant in the column studies. The processes in the sediment were similar, whereas the degradation of POC and the dissolution of $CaCO_3$ were in the columns not as pronounced.

Furthermore, the influence of temperature on biodegradation was reduced since the columns were stored in conditions with lower temperature variations as in the field.

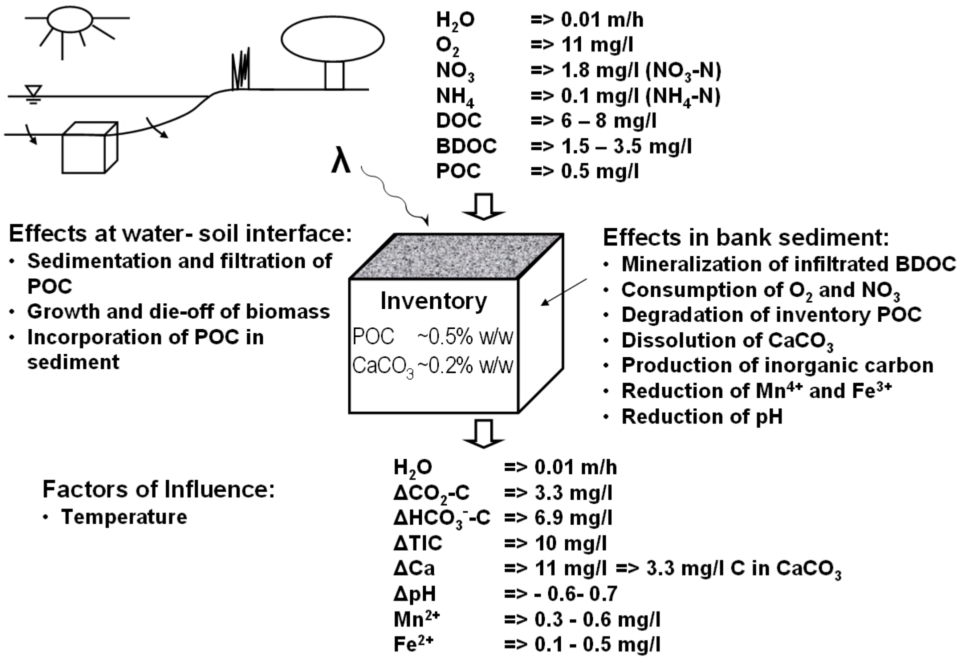
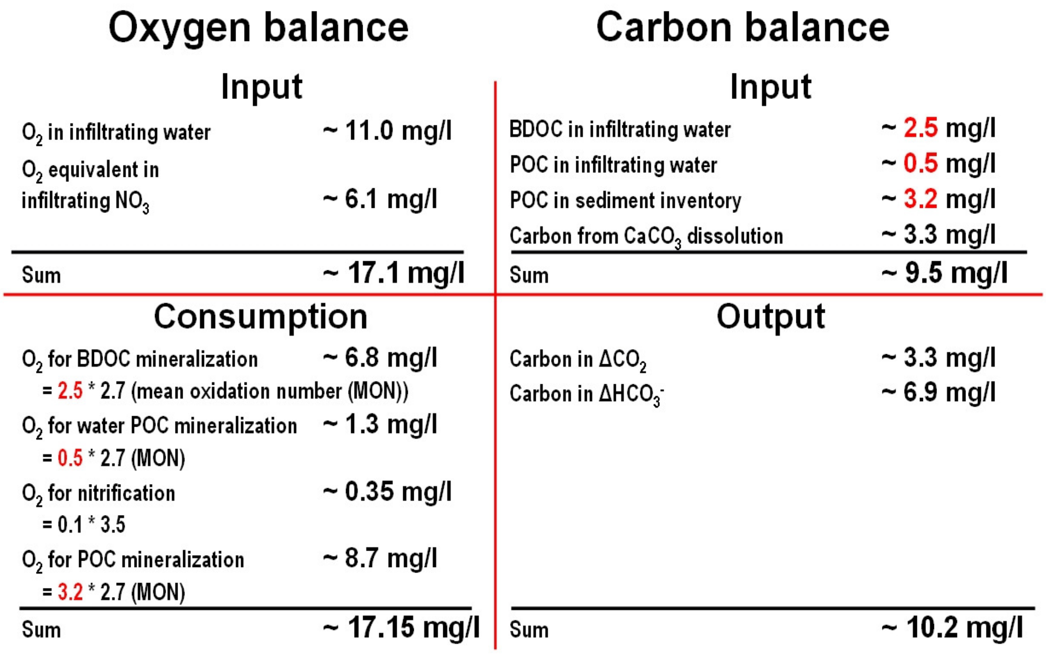


Figure 88 Simplified scheme of most important processes at the bank filtration site Berlin-Tegel

Figure 89 describes the mass balance complementing Figure 88. On the left side the oxygen mass balance is presented and on the right side the carbon balance. Input into the oxygen balance of the filtration process is provided by dissolved oxygen and nitrate. The processes consuming oxygen are BDOC- and POC mineralization and nitrification. Both balances work out nearly even, if the amounts of organic carbon used for oxygen consumption (marked red) are used as input values for the carbon balance.



Oxygen balance

Input

O_2 in infiltrating water	~ 11.0 mg/l
O_2 equivalent in infiltrating NO_3	~ 6.1 mg/l
Sum	~ 17.1 mg/l

Consumption

O_2 for BDOC mineralization = 2.5 * 2.7 (mean oxidation number (MON))	~ 6.8 mg/l
O_2 for water POC mineralization = 0.5 * 2.7 (MON)	~ 1.3 mg/l
O_2 for nitrification = 0.1 * 3.5	~ 0.35 mg/l
O_2 for POC mineralization = 3.2 * 2.7 (MON)	~ 8.7 mg/l
Sum	~ 17.15 mg/l

Carbon balance

Input

BDOC in infiltrating water	~ 2.5 mg/l
POC in infiltrating water	~ 0.5 mg/l
POC in sediment inventory	~ 3.2 mg/l
Carbon from $CaCO_3$ dissolution	~ 3.3 mg/l
Sum	~ 9.5 mg/l

Output

Carbon in ΔCO_2	~ 3.3 mg/l
Carbon in ΔHCO_3^-	~ 6.9 mg/l
Sum	~ 10.2 mg/l

Figure 89 Oxygen and carbon mass balance complementing Figure 88

The carbon mass balance compares the input concentration of organic carbon and calcium bound carbon with the inorganic species CO_2 and HCO_3^- standing at the end of the infiltration process. Overall, mass balances depict the most important processes during bank filtration and reveal eventual factors of influence, which were not considered earlier. The oxygen and carbon mass balances of the long retention columns confirmed the results presented in the bulk organics chapter.

AOI:

The AOI in the soil column system was composed of surface water AOI, which is present in Lake Tegel, and spiked AOI that was dosed into the influent. The X-ray contrast agent Iopromide was added to the influent at a concentration of 10 µg/l. Since Iopromide consist of nearly 50% iodine, this accounts for ~4.8 µg/l AOI. Therefore, the AOI measurements in the soil columns are ~5 µg/l higher than average surface water samples.

The AOI measurements at the long retention columns proved the assumption that there is nearly no AOI dehalogenation under aerobic conditions. Figure 90 shows that after an initial drop the AOI level remains constant along the column system during 30 days of oxic infiltration. Overall, only 9.1% of the initial AOI were mineralized under oxic conditions. This is consistent with the results of the GWR, where 6-16% of the AOI were removed during 25 days of infiltration (monitoring well 368 UP and 369OP). But at the GWR the redox conditions turned during summer months to anoxic/anaerobic.

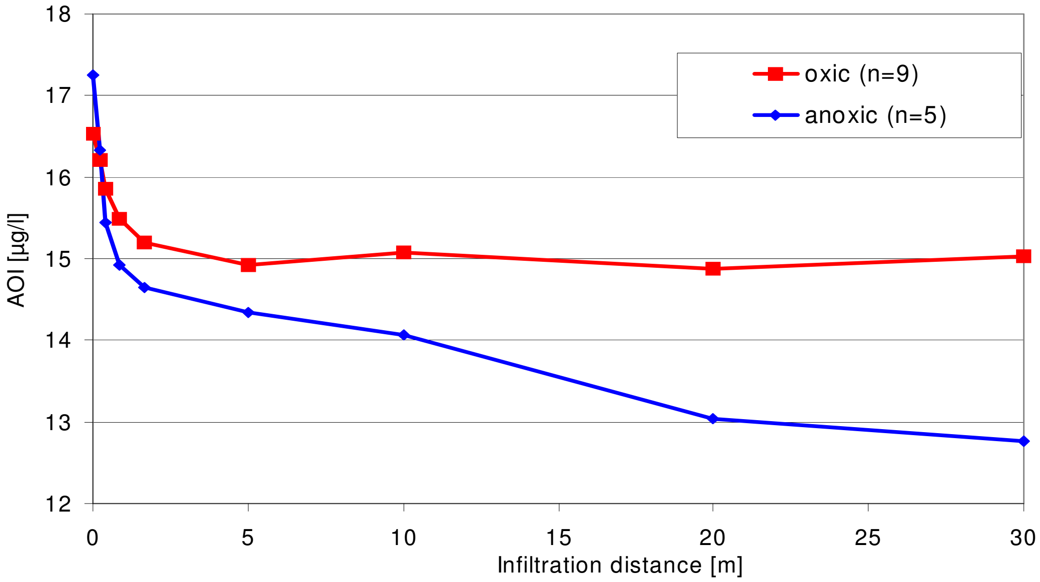


Figure 90 Fate of adsorbable organic iodine (AOI) during the two stages of the experiment

During a complete anoxic infiltration of 30 days 27% of the initial AOI were mineralized. The initial drop in AOI-concentration shortly after infiltration was more pronounced than under oxic conditions and during further infiltration the AOI-mineralization continues. A comparison with the monitoring well 205 (anaerobic, 63% AOI- removal within ~30 days) at the field site Wannsee demonstrates that under more reducing conditions the mineralization of AOI is even more enhanced. The soil column results support the hypothesis that an efficient AOI removal is only possible under reducing conditions by reductive dehalogenation. During the anoxic soil passage anaerobic micro-environments made the more efficient removal of AOI possible.

Trace Organics:

In the experiments on the long retention columns the same trace compounds were analyzed as in the field. Overall, five to six complete sets of samples were analyzed for each tested redox state. Therefore, all presented results are median concentrations of these measurements. A comparison of the results of the different sampling events of one redox state showed that general trend of all measurements was comparable and only small variations in the single sampling points occurred. This proves that over one year of operation in one redox state no significant variations of the removal efficiency for the investigated trace compound took place. Consequently, it can be assumed that the adaptation phase prior the experiments was sufficient and that the removal processes are sustainable over longer time periods.

A comparison of the results of both tested redox conditions showed that under oxic conditions the majority of the trace compounds showed significantly better removal rates. Only one isomer of the naphthalenedisulfonic acid was not degradable under both conditions. Figure 91 proves on a logarithmic scale that for most of the tested compounds an aerobic degradation was more efficient. But Figure 91 only shows the measured concentrations and does not consider whether the compound was removed by mineralization or metabolization. More information is given in the following pages.

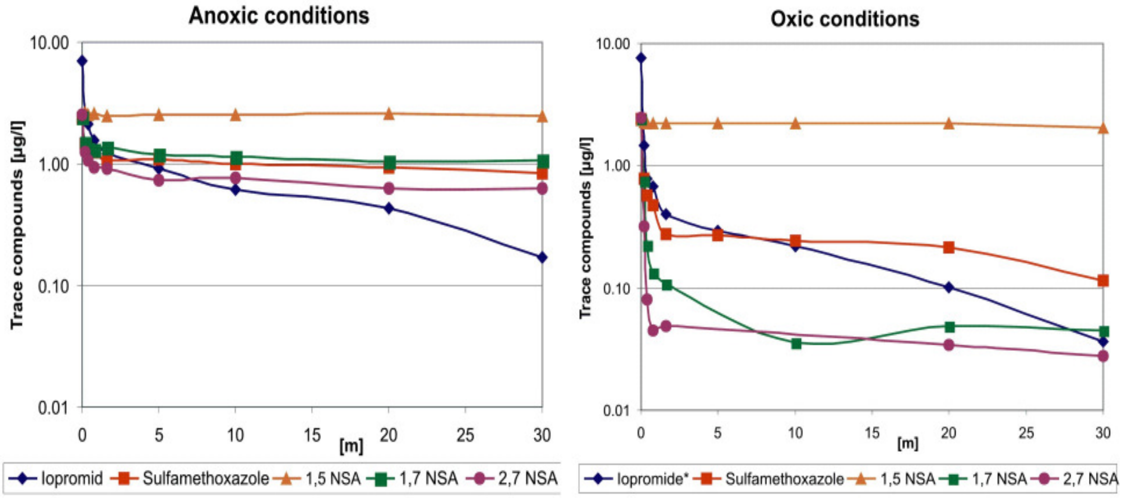


Figure 91 Fate of trace compounds under oxic and anoxic conditions in the long retention columns

Table 17 and Table 18 provide the average concentration of the trace compounds along the soil columns. Since water from Lake Tegel was used as influent, a certain amount of all trace compounds was present in the water before spiking. This concentration varied with the surface water concentration of Lake Tegel. The initial concentration is included in Table 17 and Table 18 under the heading “Lake Tegel”. The second heading “Influent” characterizes the water shortly before (20 cm tubing ID 4 mm) it enters the soil column and ~1.2 m tubing after the spiking. The spiking concentrations are included in Table 13. A detailed description of the setup is necessary, since even the short pathways of the water before entering the column system lead to some removal of trace compounds. Most affected was the X-ray contrast agent Iopromide, which was dosed to the influent water in a concentration of 10 µg/l. The measurements right in front of the soil columns showed a concentration increase of only 6-7 µg/l. Since this single compound was found to be easy removed it can be assumed that a mineralization/metabolization of ~30% of this compound took place in the biofilms of the inlet pipe. The real inlet concentrations of the other spiked compounds complied approximately with the calculated concentrations. Because of this fast depletion of Iopromide the spiking concentration of this compound was used instead of the measured inlet concentration for the calculation of the removal rates. All other removal rates were calculated with the measured concentrations.

The other columns of Table 17 and Table 18 show the fate of the trace compounds along the infiltration path in the column system. It is obvious that also for the removal of trace compounds the infiltration zone is of eminent importance. Particularly, under anoxic conditions the removal trace compounds was limited to the first meter infiltration path.

Table 17 Concentrations of target compounds in long retention columns / oxic conditions (n=6)

Means, n=6		Lake Tegel	LT + TC	BSM 1	BSM 2	BSM 3	BSM 4	BSM 6	BSM 9	BSM 15	BSM 21
Iopromide	**[µg/l]**	1.08	7.65	1.47	0.79	0.67	0.40	0.29	0.22	0.10	0.04
Sulfamethoxazole	**[µg/l]**	0.35	2.44	0.78	0.57	0.47	0.28	0.27	0.24	0.21	0.11
1,5-NDSA	**[µg/l]**	0.10	2.35	2.28	2.24	2.23	2.23	2.21	2.22	2.23	2.05
1,7-NDSA	**[µg/l]**	0.33	2.40	0.75	0.22	0.13	0.11	0.03	0.04	0.05	0.04
2,7-NDSA	**[µg/l]**	0.06	2.47	0.32	0.08	0.05	0.05	0.03	0.02	0.03	0.03

Table 18 Concentrations of target compounds in long retention columns / anoxic conditions (n=5)

Means, n=6		Lake Tegel	LT + TC	BSM 1	BSM 2	BSM 3	BSM 4	BSM 6	BSM 9	BSM 15	BSM 21
Iopromide	**[µg/l]**	0.65	7.02	2.61	2.11	1.56	1.22	0.92	0.61	0.44	0.17
Sulfamethoxazole	**[µg/l]**	0.39	2.39	1.47	1.31	1.26	1.07	1.10	1.00	0.93	0.83
1,5-NDSA	**[µg/l]**	0.13	2.56	2.64	2.53	2.61	2.50	2.55	2.52	2.59	2.46
1,7-NDSA	**[µg/l]**	0.23	2.42	1.49	1.33	1.30	1.35	1.20	1.14	1.05	1.07
2,7-NDSA	**[µg/l]**	0.08	2.51	1.25	1.07	0.94	0.92	0.74	0.77	0.63	0.63

Iopromide, the X-ray contrast agent was found at all field sites to be easy degradable. In the soil column experiment the concentration of Iopromide was found to decrease quickly under both redox conditions. A slightly faster removal was observed under oxic conditions. After 0.2 m of oxic infiltration the Iopromide concentration was 15% of the spiking concentration (10 µg/l). Under anoxic conditions 26% of the initial concentration was present after 0.2 m. At the end of the column system only traces of Iopromide were found under both redox conditions. (Figure 92)

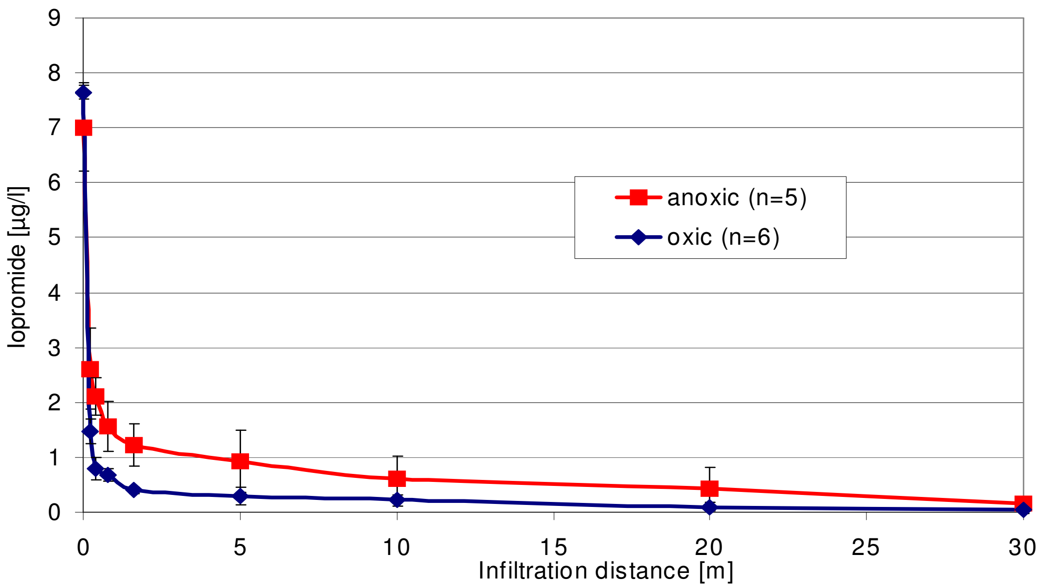


Figure 92 Fate of Iopromide under oxic and anoxic conditions in the long retention column system

A comparison with field results showed that the soil column experiment provides insight into the part of the infiltration path close to the bank. All of the investigated transects did not provide a sufficient resolution of this area. The removal rates of the soil column experiment were in the same order of magnitude as the field results. Most of the field sites were oxic near the bank area. Therefore, a comparison of the removal rates under oxic conditions with the removal rates of monitoring well 365 (GWR) and 3310 (Tegel) was conducted. The Iopromide removal in the GWR-well 365 was 96% after three days of infiltration (7 m infiltration path. The experiments at the soil columns showed exactly the same removal rates in a comparable time frame. At the field site Tegel Iopromide removal in well 3310 was 91% on an infiltration path of 3 m and a not really determinable retention time of less than 14 days. Altogether, the simulation of the Iopromide removal with the long retention soil columns was successful. The column simulations depicted the field results very closely.

To clarify the fate of the Iopromide molecule, it needs to be stressed that for the trace compound analysis a MS/MS-detector was used. This detector identifies the Iopromide molecule only if it is unaltered. A slight modification on the molecule would prevent detection by MS/MS since the exact mass of the molecule is essential for detection. The large molecule of Iopromide with several side chains is prone to metabolization. Therefore, another interesting aspect was to analyze Iopromide as a single compound and as a part of the general AOI. The spiking of 10 µg/l Iopromide increased the AOI concentration in the feed by 4.81 µg/l. The removal of the single compound Iopromide in the soil columns was as efficient as at the field sites. The measurement of AOI parallel to the single compound analysis revealed that Iopromide is not mineralized but only metabolized during infiltration. This was suspected at the field sites but was confirmed with the soil columns.

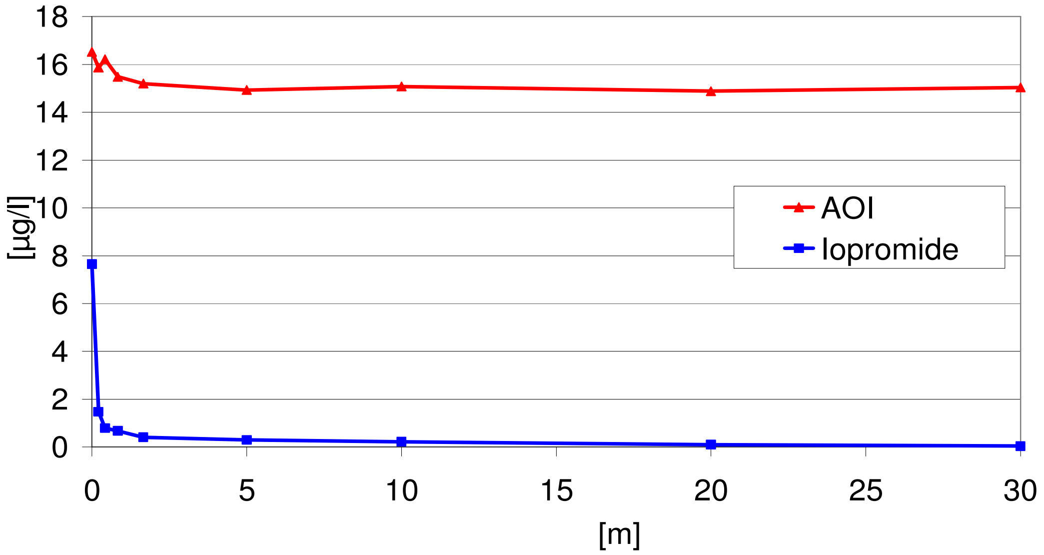


Figure 93 Concentrations of AOI and Iopromide in the columns under oxic conditions (means, n=6)

Figure 93 shows that the Iopromide concentration decreases very rapidly after infiltration. The AOI concentration remains relatively constant. This proves the assumption that the Iopromide molecule is aerobically metabolized during infiltration. But it still remains an iodinated organic molecule and is measurable as AOI. The chemical structure of the products of the metabolization is unclear.

Under anoxic conditions 27% of the AOI were removed during infiltration. A calculation reveals that a total mineralization of the Iopromide would reduce the AOI by 28%. The conformity is no proof of a total mineralization of Iopromide under anoxic conditions. It is believed that under anoxic conditions parts of the lake AOI and parts of the Iopromide derived AOI are mineralized.

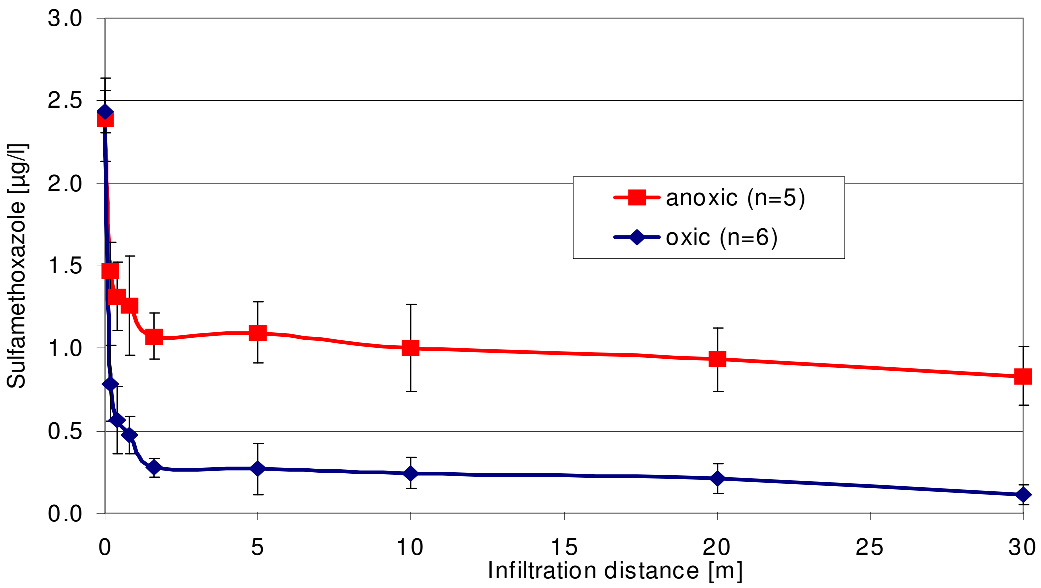


Figure 94 Fate of Sulfamethoxazole under oxic and anoxic conditions in the long retention columns

The bacteriostatic Sulfamethoxazole was spiked to the influent of the soil columns in a concentration of 2.5 µg/l. Figure 94 shows that degradation rates of 95% were reached under oxic conditions and approximately 60% under anoxic conditions. Most of the degradation took place in the infiltration zone. A comparison with other results reveals that in the field Sulfamethoxazole is more efficient degraded under anaerobic conditions. The example of the monitoring wells 205 and 206 at field site Wannsee showed very clear that Sulfamethoxazole is better degradable under anaerobic conditions. A summary of the field results shows, that under oxic conditions removal rates of 50-60 percent were observed within 30 days and 75-90% under anoxic/anaerobic conditions. Similar findings were reported by Schmidt et al. (2004).

Therefore, the results of the soil columns raised different questions. Why is the reduction of Sulfamethoxazole in the soil columns significantly better than at the field sites? An explanation could be derived from the higher spiking concentration and the higher temperature. In the soil columns a much higher (10x) influent concentration was used. It appears possible that higher concentrations of the pollutant are removed by another microbiological degradation step, which shows different redox dependencies. Another possibility could be an improved degradation of higher concentrations of the target compound and no biological effect on concentrations below a certain threshold concentration. Furthermore, the higher degradation rates in the soil columns might be due to the constant and often higher temperature (15°C±4°C).

However, there are different possibilities to explain the results of the soil column system, but the simulation of the Sulfamethoxazole degradation was not successful. Investigations on smaller soil column systems were set up to investigate the reasons for these misleading results.

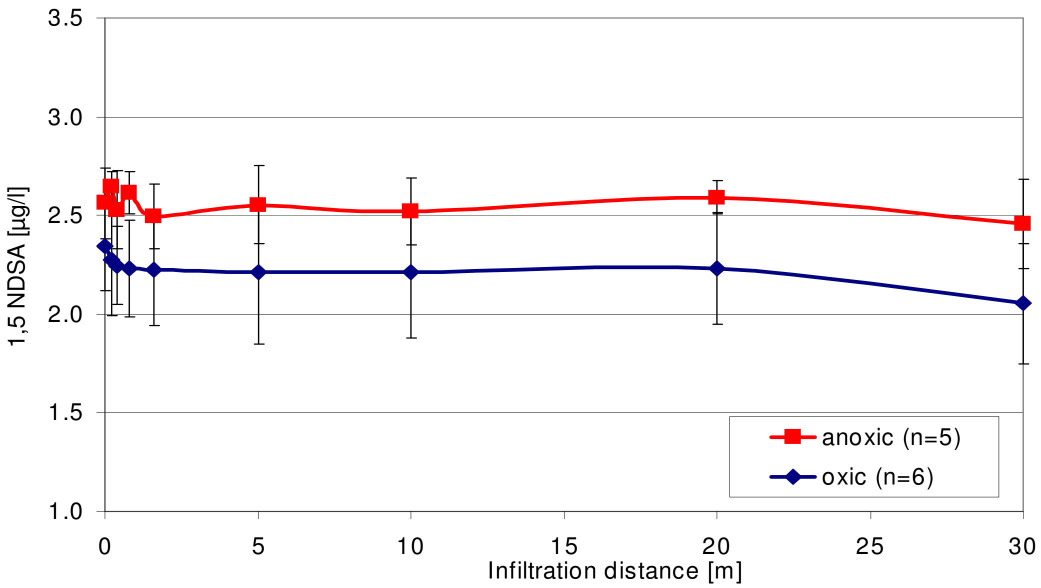


Figure 95 Fate of 1,5-NDSA under oxic and anoxic conditions in the long retention columns

The fate of the different isomers of the naphthalenedisulfonic acids were monitored in the soil column system. Field results showed that the very stable 1,5 –NDSA achieved degradation rates of ~10%. In the soil column system it could be confirmed that this isomer is nearly non-degradable. Under oxic conditions 12% of the initial concentration was degraded, whereas under anoxic conditions only 4% were removed.

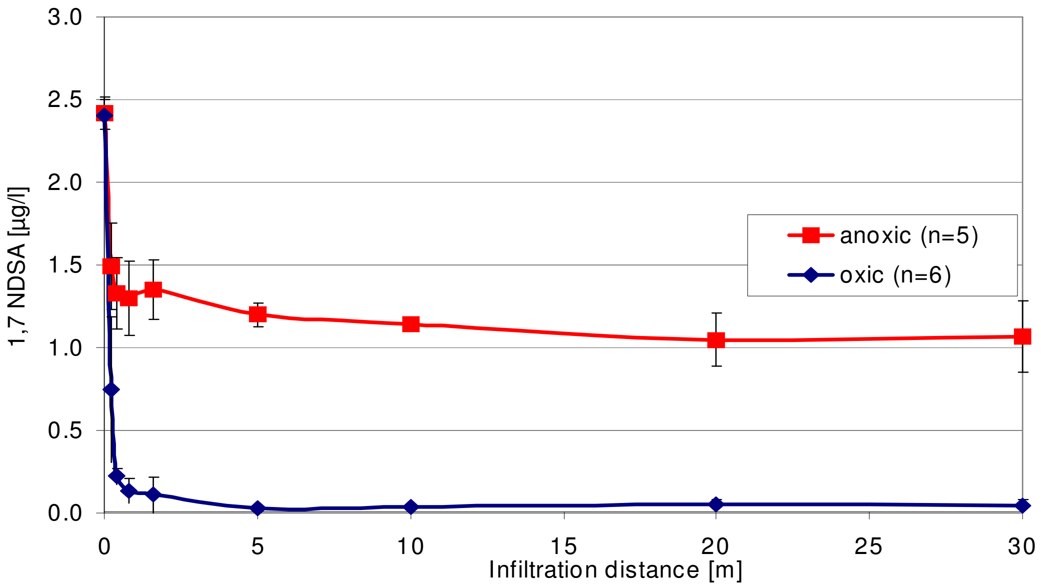


Figure 96 Fate of 1,7-NDSA under oxic and anoxic conditions in the long retention columns

All field results reported the 1,5-NDSA as very biostable and literature on NDSA removal in waste water treatment plants selected 1,5-NDSA as most persistent. The persistence of the 1,5-NDSA demonstrated clearly that the removal of the trace compounds is due to biodegradation and not adsorption. All monitored compounds are very polar and therefore not adsorbable to quartz sand.

The other two naphthalenedisulfonic acids were better degraded under oxic conditions. This is consistent with observations in the field. But the removal rates were considerably higher in the soil column experiment. For the 1,7- and the 2,7-NDSA, which are known as partly degradable, the calculation resulted in degradation rates of 99% or 100%, respectively. In the recharge facility only rates around 60% were measured. The reasons for the better degradation in the soil column system were most probably answered in the discussion on the behavior of Sulfamethoxazole. It is believed that the higher influent concentration and the elevated temperature are responsible for the better removal rates.

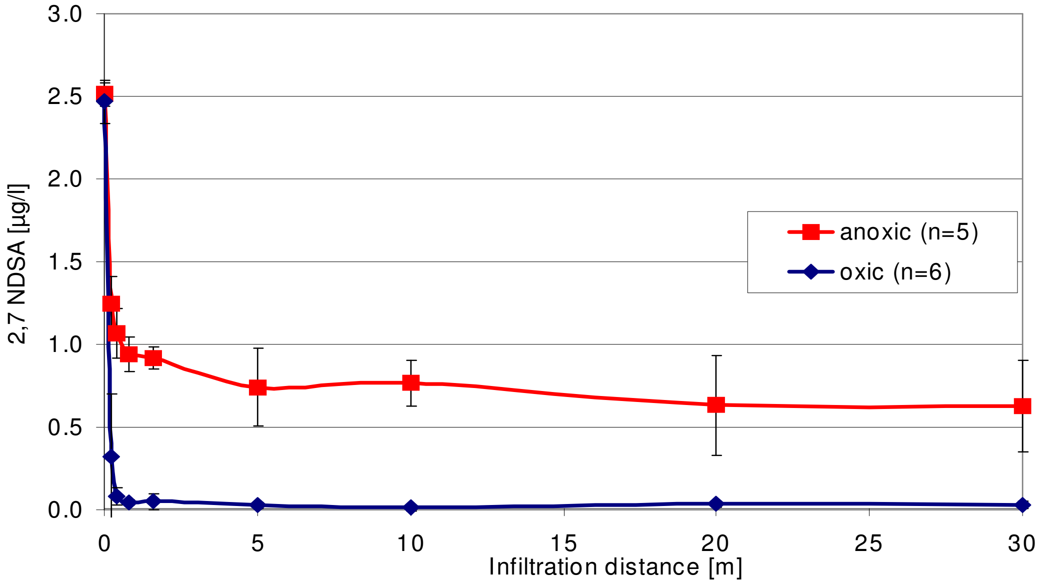


Figure 97 Fate of 2,7-NDSA under oxic and anoxic conditions in the long retention columns

However, the simulation of the fate of NDSA in the field by soil column experiments produced reliable results. The qualitative information on the influence of redox conditions agreed with the field observations. Only in the quantification of the removal rates the soil column experiments lead to an overestimation.

Sediment – Results: (mostly provided by FU Berlin)

Additionally to the characterization of the sediment material at the beginning of the experiments, the FU Berlin conducted sediment analysis of six sediment samples from the soil column system at oxic stage and six samples under anoxic conditions. The samples were taken from the top sediment layer of each column and represented sediment material after 5 m, 10 m, 15 m, 20 m, 25 m and 30 m infiltration. The samples were analyzed for grain size distribution and geochemical properties like C_{org}-content etc.. Furthermore, the distribution of biomass was assessed by a quantification of phospholipids in the different infiltration depths.

Table 19 Grain size distribution and hydraulic conductivities of sediments in the columns.

Parameter	**5 m**	**10 m**	**15 m**	**20 m**	**25 m**	**30 m**
Grain size [mm]	**fraction [%]**					
> 2	8.49	10.58	9.3	6.85	5.91	10.21
1-2	5.89	8.01	5.43	3.97	3.71	3.67
0.5-1	19.47	18.88	19.86	21.81	19.37	19.20
0.25-0.5	39.91	36.81	39.79	40.41	41.90	39.45
0.125-0.25	22.08	20.50	20.60	21.39	23.08	21.28
0.063-0.125	3.37	3.60	3.12	3.97	4.49	4.56
<0.063	1.78	1.63	1.89	1.61	1.54	1.63
k_f Hazen [m/s]	2.9E-04	3.0E-04	3.1E-04	2.8E-04	2.7E-04	2.7E-04
k_f Beyer [m/s]	2.4-2.6E-04	2.4-2.7E-04	2.5-2.8E-04	2.3-2.6E-04	2.2-2.4E-04	2.2-2.4E-04
U	2.8	3.0	2.8	2.8	2.7	2.9

As expected, the grading curves (Figure 98) of the column filling are remarkably similar and consistent with the grading curve recorded at time of the column filling (Figure 68). All 6 samples are medium sized sands with some fine and coarse grained sand and a minor fraction (< 5 %) of fine gravel. Hydraulic conductivities vary between 2.1 and $3.1*10^{-4}$ m/s. These values are similar to those obtained by core samples from the aquifers at the investigated field sites. Details are given in Table 19.

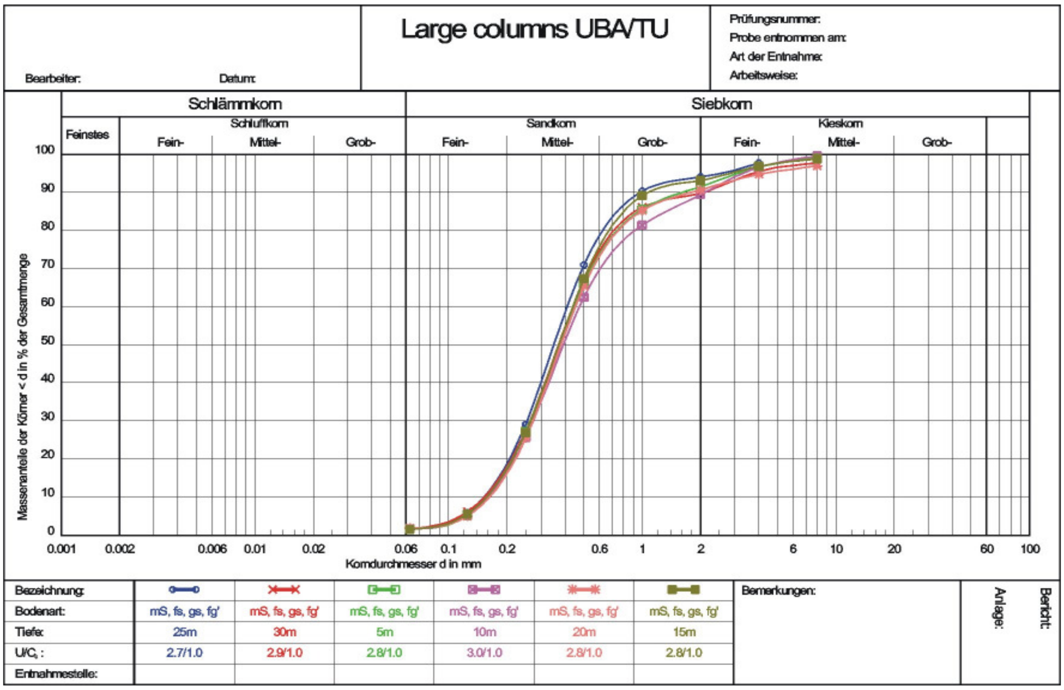


Figure 98 Sum curves of the column sediments.

The geochemical properties of the sediment are summarized in Table 20 and Table 21. The sands contain approximately 1.1-2.6 g/kg total iron, which is well within the range of iron contents encountered in the aquifer sediments from the field sites. Under oxic conditions the average iron content was 1.4 g/kg total iron and under anoxic conditions 1.9 g/kg total iron. At the first sampling (oxic conditions) roughly 46% of the iron is present as crystalline or amorphous Fe(III)Hydroxides- or Oxides, which is more Fe(III) than most field site aquifer samples contain. At the second sampling (representative for anoxic conditions) the share of oxidized iron species is reduced to ~37%.

Table 20 Geochemical properties of the column sediments (sampling after the oxic stage)

Parameter	5 m	10 m	15 m	20 m	25 m	30 m
Fe-ox [mg/kg]	605	660	715	715	550	660
Fe-red [mg/kg]	675	675	1150	725	575	700
Fe-total [mg/kg]	1280	1335	1865	1440	1125	1360
Mn-ox [mg/kg]	56.7	20.4	34.7	20.9	24.8	14.9
Mn-red [mg/kg]	18.3	17.0	16.3	9.8	9.5	10.3
Mn-total [mg/kg]	74.9	37.4	50.9	30.7	34.3	25.1
C-org [weight %]	0.047	0.035	0.034	0.040	0.043	0.027
C-inorg [weight %]	0.032	0.061	0.064	0.032	0.060	0.081
S-total [weight %]	0.001	0.002	0.003	0.003	0.003	0.003
CEC_{eff} [mmol(eq)/100g	0.406	0.343	0.302	0.374	0.324	0.337

The total manganese content of 25 to 75 mg/kg is similar to that of the aquifer. Under oxic conditions the total manganese content was slightly higher than under anoxic conditions (the difference is mostly due to changes in the first part of the column). Whereas the reduced Mn-species are relatively constant at both samplings, the amount of oxidized Mn-species is reduced under anoxic conditions. This is probably due to redox induced Mn-dissolution.

Table 21 Geochemical properties of the column sediments (sampling after the anoxic stage)

Parameter	5 m	10 m	15 m	20 m	25 m	30 m
Fe-ox [mg/kg]	472	629	532	544	841	1320
Fe-red [mg/kg]	1018	1265	2146	1173	775	991
Fe-total [mg/kg]	1490	1865	2678	1717	1616	2311
Mn-ox [mg/kg]	18.6	24.9	19.1	16.1	11.6	12.0
Mn-red [mg/kg]	13.7	11.2	30.8	21.8	15.4	17.2
Mn-total [mg/kg]	32.3	36.1	49.9	37.9	27.0	29.2
C-org [weight %]	0.032	0.048	0.039	0.032	0.036	0.032
C-inorg [weight %]	0.054	0.092	0.068	0.106	0.040	0.052
S-total [weight %]	0.000	0.001	0.000	0.000	0.000	0.000
CEC_{eff} [mmol(eq)/100g						

The sands contain between 0.03-0.08 weight % inorganic carbon, most likely to be calcite (Figure 99). The amount is equivalent to 2.5-6.7 g/kg Calcite and in good agreement with the 2-3 g/kg Ca^{2+} dissolved during pressure elution. No significant differences were observed under oxic or anoxic conditions. The inorganic carbon content is lower than in aquifer samples from the field sites which contain, with very few exceptions, >0.2 weight % C-inorg. The organic carbon content ranges under both conditions from 0.027 to 0.048 weight % organic C (0.27-0.48 g/kg). These values are well within the range of those encountered in the field. The Sulphur content (0.000-0.003 weight %) is rather low.

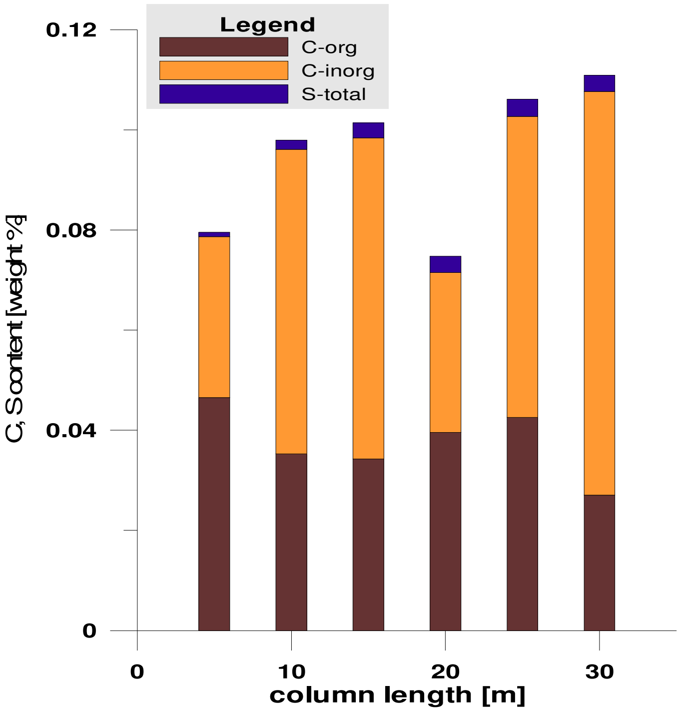


Figure 99 Carbon and sulphur contents of the column sediments under oxic conditions

At both sampling events the acid soluble cations were mainly Ca, Fe and Al with some Mg and K (with decreasing contents). Ca was less dominant than in the aquifer samples from the field sites. The total sum of acid soluble cations was roughly two times as high in the field, mainly due to the higher Ca (and Mg) contents. With 0.6-0.8 mmol (eq)/100g, the sum of the exchangeable cations was larger than the CEC_{eff} derived from the re-exchange with Ba (black crosses in Figure 100, right, 0.3-0.4 mmol (eq)/100g). Again, this may be explained with the dissolution of calcite (Kretschmar, 1991).

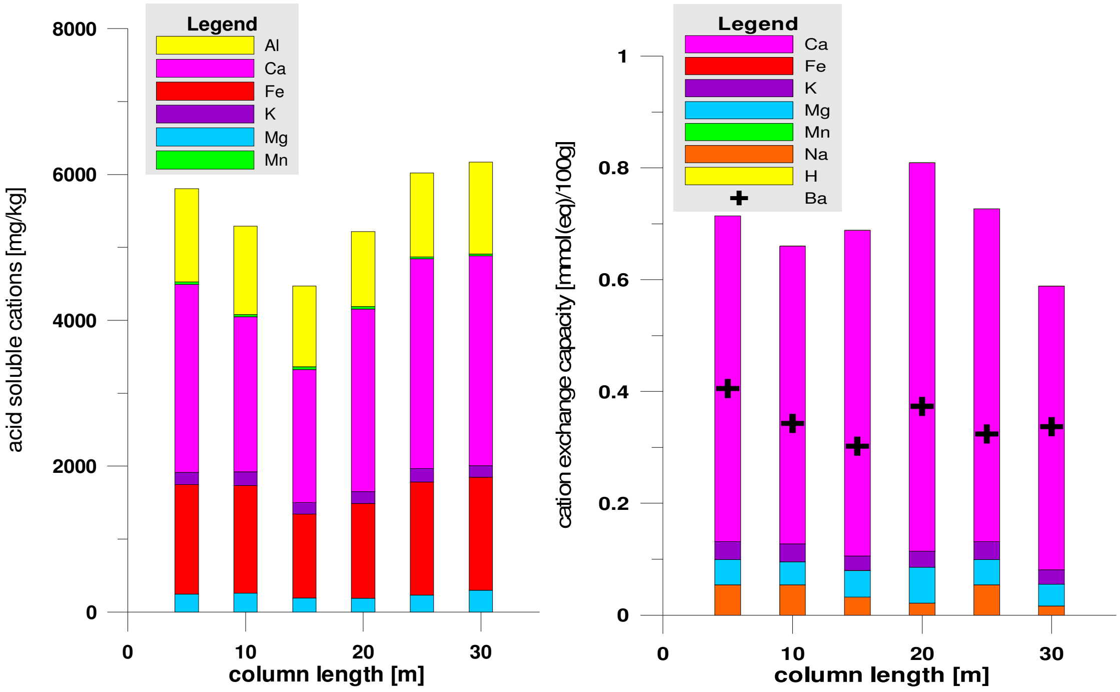


Figure 100 Acid soluble cations (left) and exchangeable cations (right) of the column sediments under oxic conditions

Additionally, the extractable amount of lipid bound phosphates was measured along the column after the oxic and the anoxic stage. The samples were sent to the University of New Hampshire/USA, where the work group of Prof. Collins conducted the phospholipid analysis. The quantification of lipid bound phosphates is a sensitive method for determining microbial biomass in sediments. The used method is described by detail in Findlay et al. (1989).

Since the content of lipid bound phosphates is a good estimate of active microbial biomass, the results give an overview on the distribution of microorganisms along the columns. Because of the laborious method and the expensive shipping only two sets of samples (each containing 6 samples) was sent to New Hampshire. The quantification of phospholipids in these sediments was performed as duplicates. In the analysis of the samples of the oxic stage the samples from 15 m, 20 m, 25 m and 30 m were found to be under the limit of quantification. Therefore, these samples were set to half the limit of quantification. For the quantification of the anoxic samples the sample volume was adapted and the limit of quantification was lower. Figure 101 shows the results of the phospholipid analysis.

The results indicate a considerably higher active biomass accumulation during oxic conditions at the first two sampling points. Unfortunately, no samples from the initial infiltration zone (at the bottom of column 1) and the first 5 m of the infiltration path could be analyzed. This is due to a lack of sediment sampling possibilities along the first column. The stainless steel cylinder only permitted a sampling after 5 m. Assuming an exponential decline of the biomass density with depth, the biomass profile of the first 5 m of infiltration could be modeled using the data points provided.

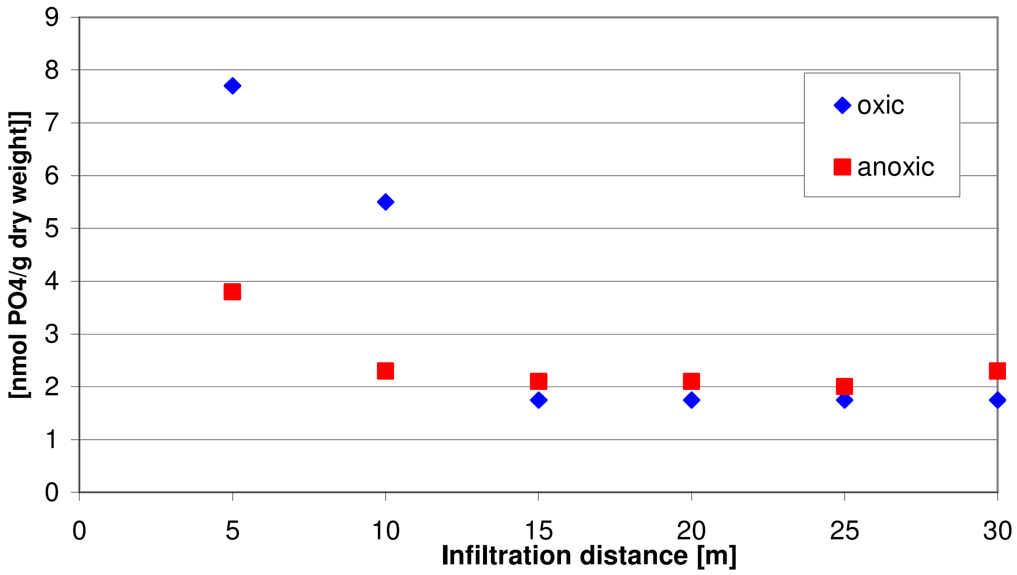


Figure 101 Results of phospholipid quantification along the columns after the oxic and anoxic stage

However, the results are consistent with the findings of the DOC- analysis. Under oxic conditions a larger amounts of DOC are mineralized in the first part of the column system (Figure 76). The phospholipid results show that the enhanced mineralization of DOC led to (is caused by) a higher biomass density in the first 10 m of infiltration. Furthermore, the results indicate that under oxic conditions the biomass density is lower and relatively stable between 15-30 m of infiltration. Under anoxic a higher biomass density at the sampling points at 5 m and 10 m was observed, which was considerably lower than under oxic conditions. Towards the end of the column system the biomass density under anoxic conditions was similar to the results under oxic conditions.

1.4.2 Short retention soil column system (TU Berlin)

Additionally to the soil column system in Marienfelde, soil column studies were conducted to study the fate of bulk and trace organic compounds under different redox conditions. Therefore, a set of short columns was installed at the department of water quality control at the TU Berlin. Furthermore, the column system was used to investigate the influence of the spiking concentration of the trace compounds on the elimination efficiency. A second experiment was designed to assess the importance of the initial amount of BDOC for the trace compound mineralization. These objectives were examined within the diploma project of Cornelia Mundt at the DWQC at TU Berlin.

1.4.2.1 Set-up

Altogether, 9 columns (length 1 m, retention time 6 days) were used to simulate the most important redox conditions and different successions of redox zones. The short retention columns were filled with silica sand and operated under controlled redox conditions with spiked Lake Tegel water. The columns had a retention time of 6 days and a flow of 0.8 l/d. Figure 102 shows a picture of the columns.

Figure 102 Short retention columns at the DWQC at the TU Berlin

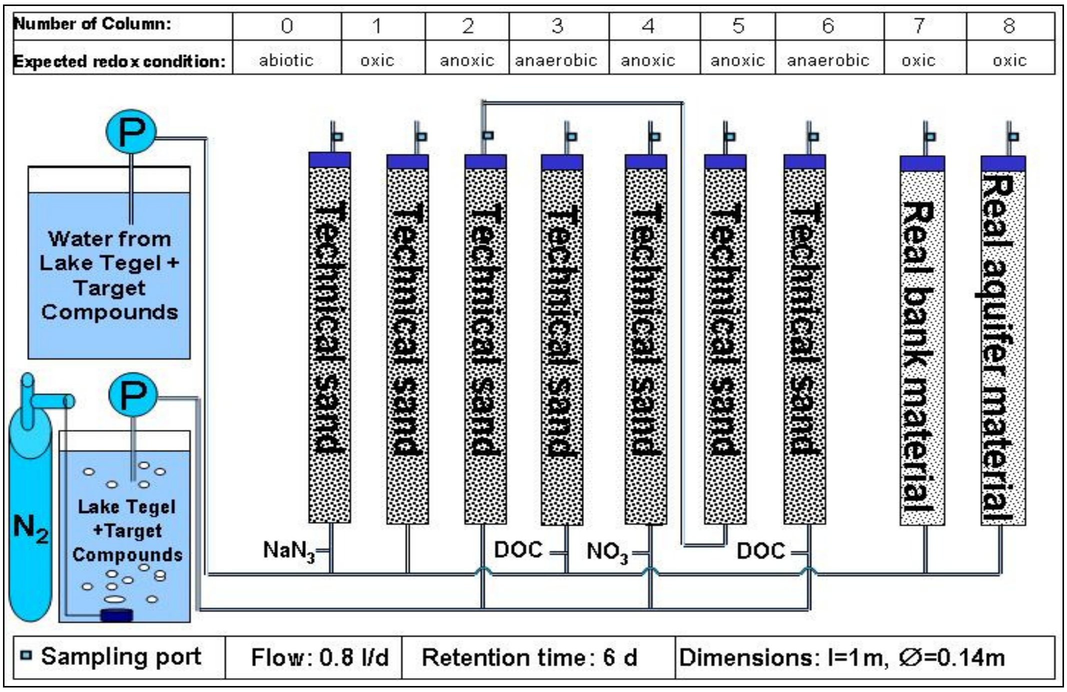
Five different combinations of redox conditions were represented in the column system. More short soil columns were utilized to quantify the role of adsorption and the differences between silica sand and original sediment material from a field site. Therefore, two additional columns were filled with sediment material from Lake Tegel; one should be representative for the instant bank region and another for the aquifer conditions. In contrast to the bank material, the aquifer material contains a smaller fraction of particulate organic carbon. The original material was taken as a disturbed sample and immediately after sampling introduced into the columns.

Additionally, one column was operated as an abiotic control to distinguish between biotic and abiotic processes. For this reason, the influent was spiked with sodium azide. Table 22 contains an overview of the materials used, the conditions of the columns and the concentrations of the spiked substances.

Table 22 Characteristics of the short retention soil columns

Column	Material	Influent (Lake Tegel water)	Concentrations of trace organics in the influent
0	technical sand	oxic + NaN_3 [8 g/l]	Iopromide [25 µg/l] Sulfamethoxazole [6.25 µg/L] 1,5-NDSA [6.25 µg/l] 1,7-NDSA [6.25 µg/l] 2,7-NDSA [6.25 µg/l]
1	technical sand	oxic	
2	technical sand	anoxic	
3	technical sand	oxic + DOC [4.5 mg/l]	
4	technical sand	anoxic + NO_3-N [5 mg/l]	
5	technical sand	effluent of *column* 2	
6	technical sand	anoxic + DOC [3 mg/l]	
7	bank material	oxic	
8	aquifer material	oxic	

The tank for the oxic columns was permanently aerated with air and had an average oxygen concentration of ~10 mg/l. For the elimination of oxygen, the anoxic tank was aerated with nitrogen gas. Figure 103 presents a schematic of the set-up of the short retention columns. The columns were operated in the basement of the DWQC at 19℃ ±3℃.



Number of Column:	0	1	2	3	4	5	6	7	8
Expected redox condition:	abiotic	oxic	anoxic	anaerobic	anoxic	anoxic	anaerobic	oxic	oxic

Figure 103 Experimental set-up of the short retention columns

The short columns were made of plexiglas and the tubing was PU (Polyurethane). Because of the considerably shorter distances compared to the long retention columns, oxygen diffusion through the tubing was not a problem. Adsorption tests with the investigated compounds and the used tubing proved no relevant loss due to adsorption onto the tube walls (compounds are very polar).

Columns 0 to *6* were filled with technical sand (Ø = 0.7-1.2 mm) and at the bottom and the top layers of 8 cm coarser gravel (Ø = 5 mm) provided stability and uniform flow conditions. The column system offered sampling ports only at the end of the column. A maximum of 800 ml of sample could be collected each day from one column. By adding organic carbon (starch) and nitrate to the influent different redox conditions were adjusted.

The adaptation period was selected to cover 6 months, to assure stable conditions in the columns and an adapted biomass for each of the enforced redox conditions.

In the first year of operation the main focus was to clarify the redox sensitivity of the bulk and trace compound degradation and the effects of different filling material. This time is referred in the following chapter as ***operation period 1 (OP1)***. Within the work of Cornelia Mundt on the column system two additional objectives were included into the work. The project focused on the influence of trace compound concentration and BDOC-concentration, two variable parameters that most probably influence the overall removal efficiency for trace pollutants. Both topics were addressed in separately designed experiments which are referred to as ***operation period 2*** (influence of trace compound concentration) and ***operation period 3*** (influence of BDOC-concentration).

Each of the additional experiments (**OP1** and **OP2**) was designed to investigate the trace- (and bulk-) organic removal under three artificially induced conditions, which were set up by variation of the investigated parameter. Thereby, the results of ***operational period 1*** were used as starting point and one of the three conditions.

However, in ***operation period 2*** the influence of the trace compound concentration on the removal efficiency (percentage) of the pollutants was investigated. In addition to the results of ***operational period 1*** two experiments with reduced spiking concentration were performed. The spiking concentration was reduced to one half of the initial concentration (LT 1/2) and one eighth of the initial spiking concentration (LT 1/8). The removal efficiencies on a percentage basis were compared to reveal differences. Eventual differences could have been caused by high threshold-concentrations or different removal mechanisms for diverse concentration levels.

In ***operational period 3*** the importance of the initial BDOC-concentration was investigated. It was of interest to assess eventual differences in trace compound removal under conditions of high BDOC levels and very low BDOC levels. Variations in the BDOC level affect the overall density of the biomass in the infiltration area. Furthermore, an effect on the variety of the microbial community is likely. Therefore, variations of BDOC are most likely to affect the efficiency of cometabolic mineralization processes. Specialized microorganisms that feed on the investigated trace pollutants are most likely not affected, since the trace compound spiking was not varied in this experiment. The different BDOC concentrations were realized by mixing Lake Tegel surface water with water from production well 13 at BF transect Tegel. It was assumed that well 13-water does not contain any BDOC after 4-5 months infiltration. Experiments were conducted with maximum BDOC (LT 1/2), 50% of the BDOC-concentration by a mixing of 50:50 (50-50 1/2) and 25% of the BDOC level (mixing 25:75=>25-75 1/2). The trace compound spiking was held constant during the experiments at half of the concentration of ***operational period 1***.

Table 23 Overview of conducted experiments on short retention columns

Operational period	Variation of	Time frame	Name of experiments
1	Redox conditions	07/03 – 09/04	LT 1/1
2	Trace compound concentration and redox conditions	10/04 – 12/04	LT 1/1 LT 1/2 LT 1/8
3	BDOC- concentration and redox conditions	12/04 – 02/05	LT 1/2 50-50 1/2 25-75 1/2

Each of the new experiments was commenced by a sufficient period of adaptation to the new conditions. Table 23 provides an overview of the different operational periods and time frames. The table also assigns the single experiments and their names to the operational periods. The actual concentrations of BDOC and spiked compounds are described in Table 24. The quantification of the BDOC resulted from the difference of measured DOC- concentration and share of non-degradable DOC.

Table 24 Names and characteristics of the conducted experiments

Experiment	Varied parameter	Spiking-concentration [µg/l]			Portions of Lake Tegel water [%]	Portions of well 13-water [%]	BDOC [mg/l]
		NDSA	Iopromide	Sulfamethoxazole			
Lake Tegel 1/1	Spiking concentration	6.25	25.0	6.250	100	0	2.3
Lake Tegel 1/2		3.125	12.5	3.125	100	0	2.3
Lake Tegel 1/8		0.781	3.12	0.781	100	0	2.3
Lake Tegel 1/2	BDOC-concentration	3.125	12.5	3.125	100	0	2.3
50-50 1/2		3.125	12.5	3.125	50	50	1.3
25-75 1/2		3.125	12.5	3.125	25	75	0.6

1.4.2.2 Results

After the adaptation period of the column system it was of importance to characterize the redox conditions in all columns separately. The redox zone analysis was based on measurements of oxygen and nitrate in the effluent of the columns. The state after 6 months of equilibration is pictured in Figure 104. The conditions remained constant during the time of the experiments.

- ***Column 0*** is the abiotic control, which is poisoned by NaN_3. The biological activity is very low and the oxygen is not depleted during infiltration.
- In ***column 1*** the water infiltrates under oxic conditions. In the effluent the oxygen concentration is low, but nitrate is not reduced.
- ***Column 2 and 5*** describe an anoxic infiltration in a connected system. ***Column 2*** receives oxygen free water with the nitrate level of Lake Tegel. The effluent of ***column 2*** is fed to ***column 5*** to allow longer retention times for the slower denitrifying biomass. Nitrate is still present in the effluent of ***column 5***.
- ***Column 3*** obtains oxic Lake Tegel water spiked with starch. The starch is converted rapidly, leading to short oxic and the anoxic redox zone. It is most likely that most of the filtration in ***column 3*** takes place under anaerobic conditions.
- ***Column 4*** is comparable to ***column 2***, but to enhance denitrification, nitrate is spiked overstoichiometricly.
- ***Column 6*** receives oxygen free water with starch, which promotes the fast reduction of nitrate.

It needs to be clear that the dimensions of the different redox zones are not measured, but the redox conditions in influent and effluent prove that these zones have developed during several months of equilibration time.

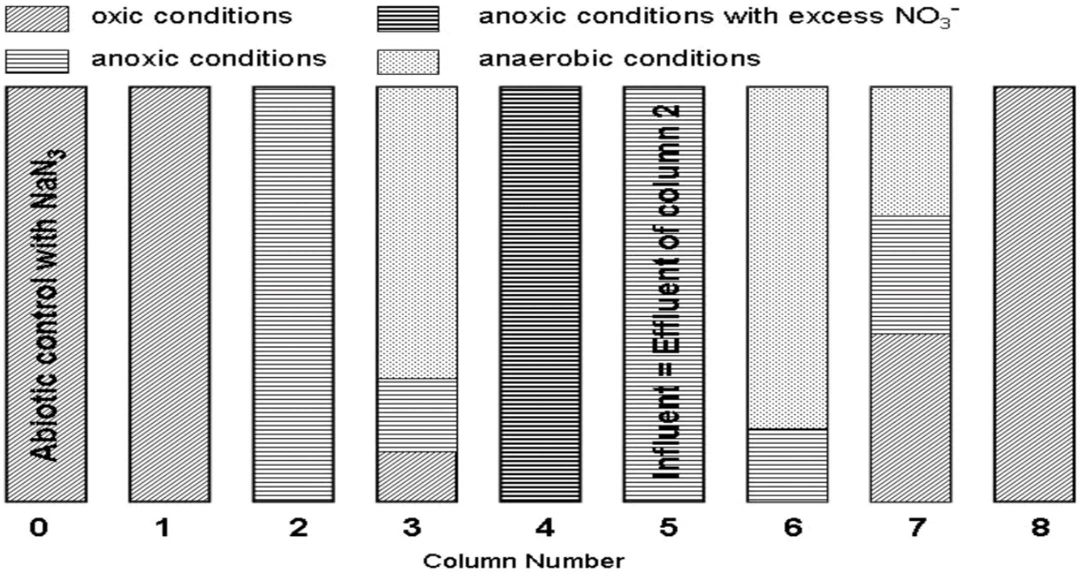


Figure 104 Developed redox zones in short retention columns (dimensions estimated)

In addition to these seven columns two columns with original material from the field site Tegel were operated. Because of high portions of POC in *column 7* organic carbon is still leaching from the soil because of the disturbance of the natural soil structure. Most leaching of DOC was observed in summer in periods of higher temperatures. The result was a high biological activity in the column due to the high amount of available dissolved carbon. Therefore, an oxic, an anoxic and an anaerobic zone are present in *column 7*. *Column 8* was filled with aquifer material and did not contain high portions of POC. Therefore, the redox conditions remained oxic along the infiltration path, comparable to *column 1*.

Table 25 provides the average oxygen and nitrate concentrations, measured during the entire operation of the short retention column system.

Table 25 Oxygen and nitrate levels in the column system

Column	Oxygen (n=34) [mg/l]	Nitrate (n=19) [mg/l]
Oxic influent	**10.0**	**1.6**
Effluent column 0	8.3	1.5
Effluent column 1	2.6	1.5
Effluent column 3	0.0	0.0
Effluent column 7	0.0	0.1
Effluent column 8	3.4	1.6
Anoxic influent	**0.0**	**1.5**
Effluent column 2	0.0	1.1
Effluent column 4	0.0	7.2 (spiked)
Effluent column 5	0.0	1.0
Effluent column 6	0.0	0.0

Operational period 1 (Influence of redox conditions):

The first operational phase focused on the quantification of the influence of the redox conditions on the bulk and trace organic compound removal. During the experiment conditions were held constant and an extensive monitoring program was conducted on the soil columns.

DOC: Regarding the behavior of the bulk organics it was found that the removal rates of the different columns varied. Figure 105 shows the results of the DOC monitoring. Please refer to Figure 104 to assign the actual redox conditions of the single column to the number of the column used in the description and the graphs. The analysis proved no efficient removal of bulk organics in the poisoned *column 0*. The average DOC effluent concentration of *column 0* is similar to the DOC level of the influent. The most efficient DOC removal was found during complete oxic infiltration in *column 1*. During six days of infiltration along a one meter infiltration path a removal of 18% of the initial DOC was achieved. Under anoxic conditions the DOC removal was not as efficient as under oxic conditions and much slower. *Column 2*, representing anoxic conditions only removed 2% of the DOC after 6 days of infiltration. After a prolonged infiltration period (*column 5*) the removal rate was increased to 17%. The results show evidently that bulk organic mineralization is considerably slower under anoxic conditions. The dosage of excessive nitrate (*column 4*) increased the removal rate of DOC within 6 days from 2% to 9%.

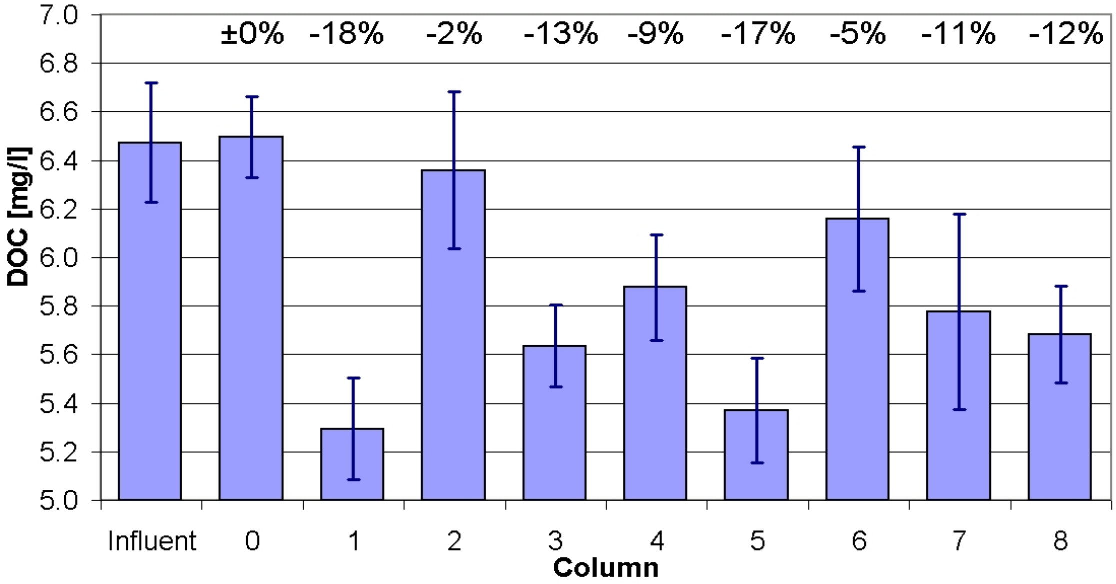


Figure 105 Fate of DOC under different redox conditions including standard deviation (n=25)

Two columns were operated under partly anaerobic conditions (*column 3* and *column 6*). The results of these columns have to be evaluated with care, since starch was added to the influent to achieve anaerobic conditions. It was found that starch dosage resulted in a sort of monoculture in the inlet pipe and in the immediate start of the column. This monoculture mineralized the starch efficiently and adjusted the redox conditions to the desired level, but it is unclear which amount of natural DOC was mineralized by this biomass. However, a comparison of both columns with anaerobic conditions (*column 3* and *column 6*) showed that the mineralization process was more complete in *column 3* which was fed with oxygen saturated water. The dosing of starch in *column 3* resulted in a high amount of available organic carbon for the microorganisms and increased the consumption of oxygen. Anoxic conditions were achieved rapidly, because about 2.7 mg oxygen is necessary for the mineralization of 1 mg DOC. Due to subsequent consumption of nitrate, which was confirmed by the analysis of nitrate, the conditions in *column 3* turned anaerobic. Thus, most of the degradation of BDOC took place under anaerobic conditions. Altogether, *column 3* provided a complete sequence of redox zones (oxic, anoxic and anaerobic) and achieved a mineralization rate of 13%. This is a higher removal than in *column 6*, where the redox situation consisted of anoxic and subsequently anaerobic conditions. In this column a removal rate of 5% was achieved (Figure 105).

Both columns with natural sediment fillings performed similar. Removal rates of 11% and 12% were achieved, respectively. Some influence on the removal rates was observed during summer, when parts of the POC leached from the sediment. This effect resulted in increased DOC levels in the effluent. *Column 7* was mostly affected by this process. Without the leaching the removal rates would have been considerably higher. *Column 7* showed a similar change of the redox conditions from oxic in the influent to anaerobic in the effluent. The reason was mineralization of POC from sediment filling. Contrary to the fast availability of starch, the mineralized POC is more complex. Therefore, it was assumed, that the anoxic and anaerobic zones begin more distant from the immediate infiltration zone. The oxic zone in *column 7* and the larger surface area available for the biomass (caused by smaller particle size) led to better degradation rates of DOC. The advantage of a larger surface area caused a higher biomass density. Altogether, *column 7* provided good conditions for DOC mineralization but the efficient mineralization is partly compensated by leaching POC. *Column 8* was filled with aquifer material containing less easily degradable POC. But the average particle size in the aquifer is larger than in the bank region. The average surface area combined with oxic conditions throughout the column provided above average removal potential for DOC.

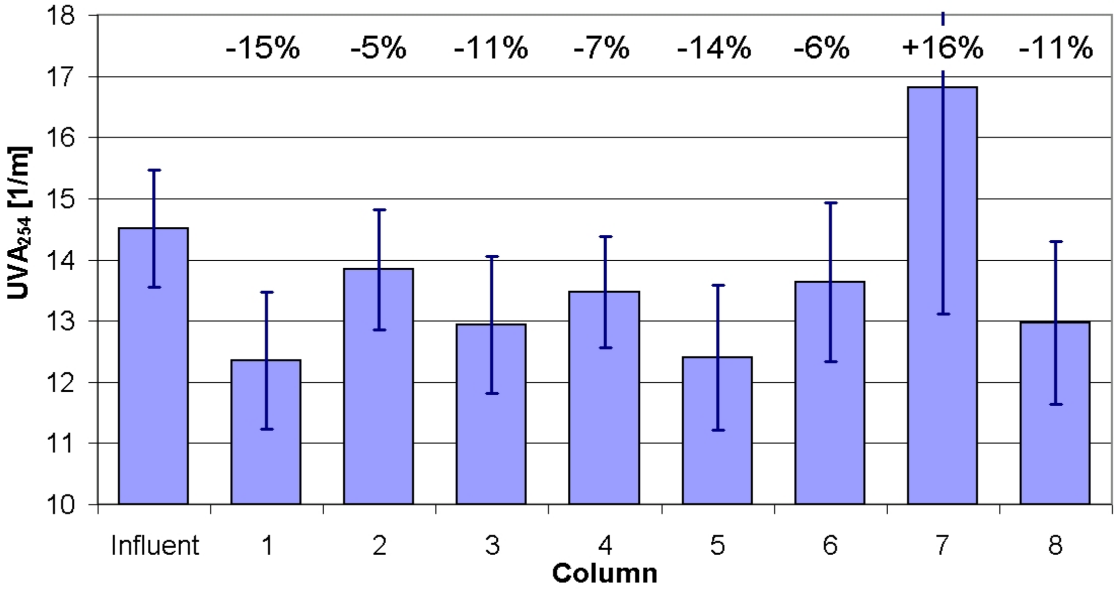


Figure 106 Fate of UVA$_{254}$ under different redox conditions including standard deviation (n=25)

UVA$_{254}$: Figure 106 shows that the UVA measurements were consistent with the DOC results. Because of the UV-absorption of sodium azide at the respective UV-wave length no measurements of the effluent of *column 0* were performed. Leaching of DOC from *column 7* during periods of elevated temperature resulted in an increase of the average UVA-absorption in *column 7* by 16%. The high standard deviation proves that leaching was limited to a few months in summer. Since this effect was not that strong for the parameter DOC, it can be concluded that the DOC that was leaching from the sediment has a very high aromaticity. All other results confirm the findings of the DOC analysis.

LC-OCD: The technique of LC-OCD was used to verify the fractions that were responsible for the decrease of the DOC-concentration during infiltration through the columns. It was of interest, whether different fractions of DOC were mineralized under certain redox conditions. A comparison of the pooled chromatograms of the experiment is presented in Figure 107 and Figure 108.

Because of a high salt content in the samples from *column 0*, the analysis of these samples with LC-OCD was difficult. The salt content lead to high ghost peaks towards the end of the elution time. Therefore, an evaluation of the fractions eluting lately was not possible. In spite of these problems, the measured chromatograms of *column 0* effluent proved, that the fraction of polysaccharides left the column without changes. Thus filtration effects, as a dominant factor influencing the fast removal of PS during infiltration, can be excluded. Because removal of this easily degradable fraction occurred only during passage through bioactive columns, the reduction of polysaccharides can be traced back to a biological degradation.

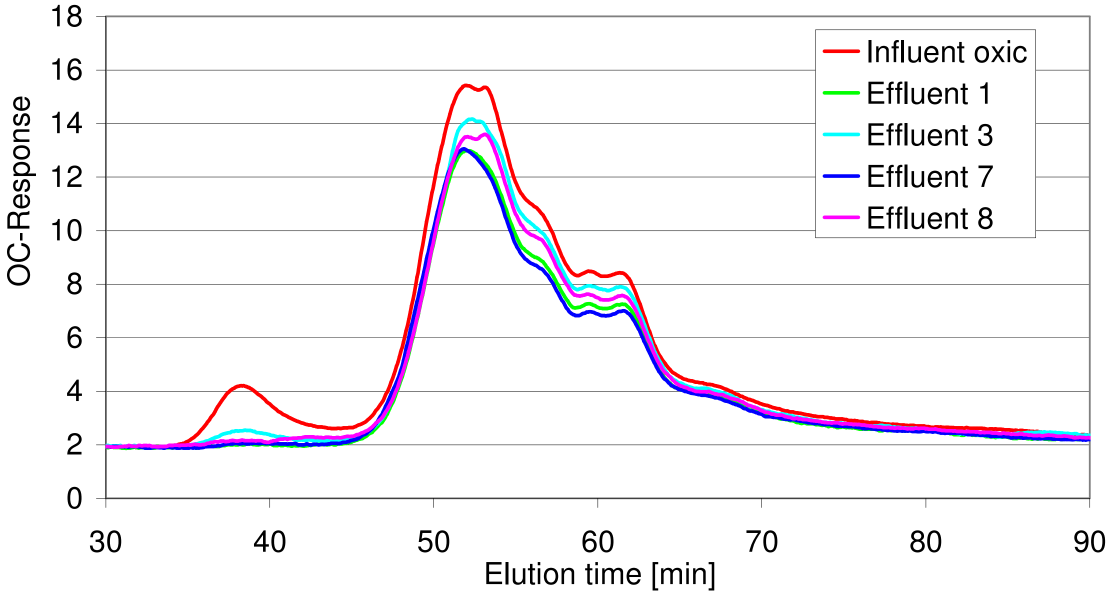


Figure 107 LC-OCD diagrams of the columns with oxic influent

Evaluation of the LC-OCD diagrams shows that the most affected DOC fractions in the columns are the polysaccharides and the humic acids. Low molecular weight acids are also reduced during soil passage.

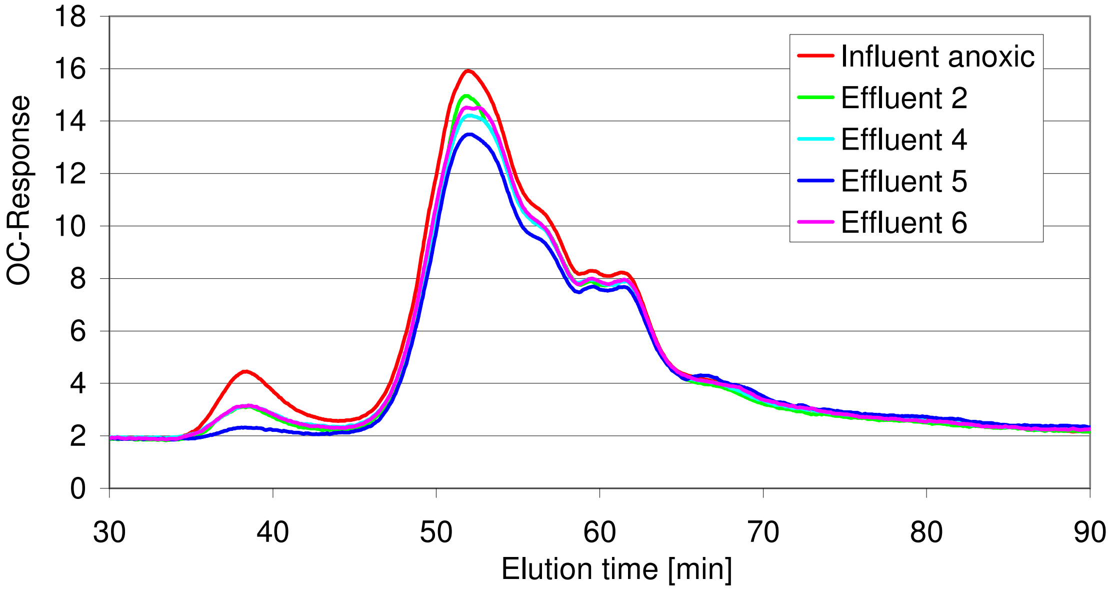


Figure 108 LC-OCD diagrams of the columns with anoxic influent

Figure 107 and Figure 108 show that the PS-fraction is removed completely under oxic conditions (*column 1, 7* and *8*). Columns operated under anoxic conditions show only ineffective degradation of PS (*column 2* and *4*). As an exception, polysaccharides are degraded almost completely in *column 5*, whereas in the other anoxic columns only half of the polysaccharide concentration was degraded. The redox conditions in *column 3* and *column 6*, which become anaerobic after a short distance, did not lead to a complete removal of polysaccharides. Overall, the anaerobic PS-elimination was comparable to the results of the anoxic columns. As polysaccharides are part of the BDOC and only ~50 % of the BDOC is mineralized in these columns, it can be concluded, that polysaccharides belong to the easily degradable fractions within the BDOC. Furthermore, the results in Figure 107 and Figure 108 show that the removal of the other assessable DOC-fractions complies with the results of the DOC-quantification. The investigation proved a comparable stability of the DOC fractions under the different tested redox conditions. The PS-fraction was found to be under all conditions easy degradable. Under anoxic/anaerobic conditions no complete removal of PS was observed but these redox conditions also lead to a minimized removal of the other DOC-fractions.

Summarizing the results of LC-OCD analysis it was found, that polysaccharides can be biodegraded completely during a period of 5 to 6 days under optimal conditions. Humic substances show a maximum degradation rate of 18 %. Only small parts of the humic building blocks and low molecular weight acids were degradable during soil passage under the tested conditions. The fraction of neutrals remained nearly constant under all conditions. This might indicate a balanced equilibrium between degradation and formation of these substances.

AOI: Additionally, the fate of AOI was investigated in the short retention column system. Figure 109 shows the results. Because of slightly different spiking concentrations in the oxic and anoxic influent the results are classified into columns with oxic influent and columns with anoxic influent.

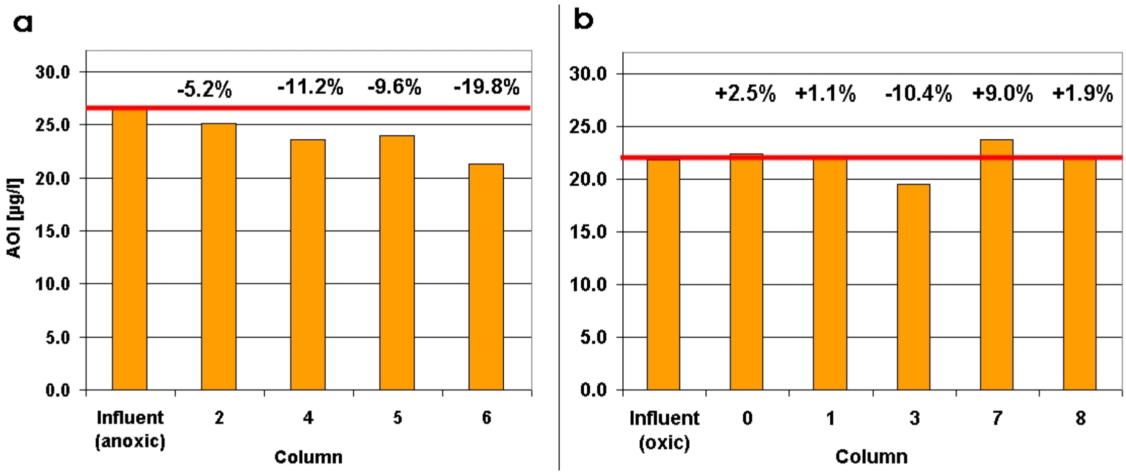


Figure 109 Fate of AOI under different redox conditions (a. anoxic influent/ b. oxic influent; n=6)

It was evident that the mineralization of AOI is more efficient under reducing conditions. Columns with oxic infiltration did not achieve considerable removal rates (*column 0, 1, 8*). Under anoxic conditions (*column 2, 4, 5*) between 5% and 11% of the AOI was mineralized. The highest removal rates were found for anaerobic columns. *Column 3* with an oxic influent but dominant anaerobic conditions achieved a removal rate of 10.4% and was only outperformed by *column 6*, which mineralized 20% of the initial AOI within 6 days of infiltration.

Table 26 Removal rates of AOI in short retention columns (sorted by dominant redox condition)

Oxic removal [%]	
Effluent 1	-1.06
Effluent 8	-1.90
Average oxic degradation	**-1.48**
Anoxic removal [%]	
Effluent 2	5.17
Effluent 4	11.23
Effluent 5	9.64
Average anoxic degradation	**8.68**
Anaerobic removal [%]	
Effluent 3	10.41
Effluent 6	19.78
Average anaerobic degradation	**15.10**

These results confirm the field results and the findings of the long retention column system. The reasons for the increase of AOI-concentration in *column 7* remained unclear. Since additional AOI might derive from AOI formation or AOI leaching from the sediment, the results are not included in the overall evaluation. Table 26 provides a summary of the removal rates and a calculation of the average removal rates. It is evident that the AOI-mineralization increases with decreasing redox potentials.

Trace compounds: The spiked trace organic compounds behave differently in the columns. Figure 110 illustrates the degradation performance of the individual columns. The spiking concentrations were 25 µg/l for Iopromide and 6.25 µg/l for Sulfamethoxazole and the NDSA-isomers. Figure 110 shows the measured concentration in the influent to the columns and the effluent concentrations.

In the abiotic *column 0* a slight decrease in the Iopromide concentration was observed, but the concentrations of the other trace compounds are nearly unchanged. Therefore, it can be concluded that adsorption does not play an important role in the short retention columns. Towards the end of the long term experiment some removal of 1,7- and 2,7-NDSA was observed. Together with the observed oxygen consumption in this column the results point toward a slowly growing azide-resistant biomass in *column 0*.

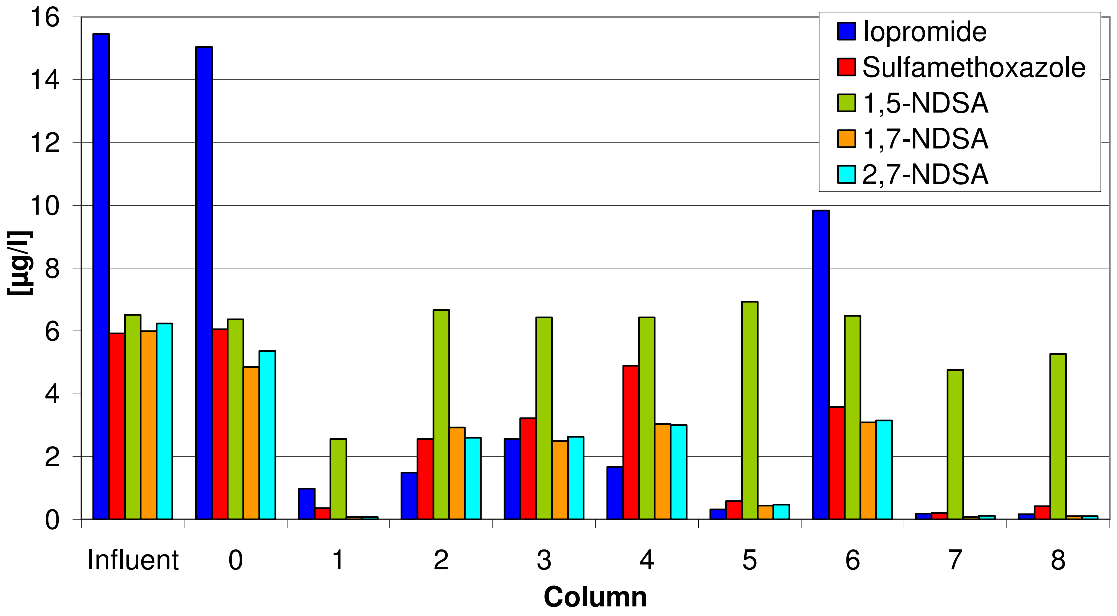


Figure 110 Trace organic compound concentrations in the effluent of the short columns (n=7)

In all technical sand columns (0-6) the 1,5-NDSA-isomer was observed to be very persistent. Only in *column 1* a removal of ~50% of the compound was observed. This removal was above average, since in the long retention columns and at the field sites the removal was considerably lower. The high removal might be ascribed to the higher temperature. The short retention columns were stored in the basement of the DWQC at 19℃ ±3℃.

The other trace compounds are most efficiently removed during oxic infiltration in *column 1*. Similar results can be observed after anoxic infiltration with the double retention time. After 6 days retention time (*column 2*) the removal is not as efficient as in *column 1*, but after additional six days of infiltration under anoxic conditions (*column 5*) the results are comparable to those of *column 1*. For the X-ray contrast agent Iopromide the final concentration is even lower than in *column 1*.

An inefficient removal of all compounds could be monitored in the columns, where most of the infiltration took place under anaerobic conditions (*column 3* and *6*). Furthermore, it was found that enhanced denitrification by adding nitrate is not necessarily beneficial for the removal of these trace compounds (*column 4*).

The best results were achieved with the original sediment in *column 7* and *8*. These results were probably due to the strong microbial activity in these columns. Adsorption onto the organic part of the soil matrix is not very likely because of the high polarity of the compounds.

Overall, the results confirmed the findings of the other experiments that oxic conditions are preferable for trace compound removal. The AOI results show that Iopromide is only metabolized under oxic conditions. AOI mineralization can only be achieved under anoxic/anaerobic conditions, whereas the efficiency increases with lower redox potentials. Similar to the results of the long retention columns the preferential removal of Sulfamethoxazole under anaerobic conditions, which is reported in literature, could not be reproduced. But since this anaerobic removal of Sulfamethoxazole was observed at the field site Wannsee, it is believed that the processes in the soil columns differ from the degradation pathways in the field. The reasons are most probably the different temperature and different concentration levels. This question is addressed more detailed in the discussion of the results of the long retention columns.

Operational period 2 (Influence of trace compound concentration):

Operational period 2 was conducted to test the influence of the trace pollutant concentration on the removal efficiency. The spiking concentration was varied, whereas all other conditions remained constant. The test simulated groundwater recharge or bank filtration at field sites with a different trace pollutant load or at one field site with a surface water of changing quality. It was of interest to confirm the achievable removal rates of the investigated trace compounds for different initial concentrations. To obtain relevant information the trace pollutant spiking was reduced first to ½ and afterwards to ⅛ of the initial spiking concentration.

Since all bulk organic parameters were held constant and the changing trace pollutant concentration did not affect the removal of the bulk organics, an evaluation of the bulk parameters was not included in the final NASRI Report. The fate of the bulk organics complied with the evaluation of the data in operational period 1.

AOI: Effluent concentrations of AOI of the different experiments were hard to interpret. Since the measured AOI consisted of surface water AOI and spiked Iopromide, the changed spiking level only reduced one fraction of the overall AOI. Furthermore, the inaccuracies of the method constricted a detailed data evaluation because the changes in AOI concentration during soil passage were very small. To assess the information, the effluents of oxic, anoxic and anaerobic columns were pooled. Afterwards, mean values of the effluent concentration of each experiment were calculated, in order to give a general statement. Table 27 shows the calculated degradation rates. The results reveal that there is no significant influence of the spiking concentration on the degradation of AOI. Under all redox conditions no general trend towards lower or higher removal rates was observed. Considering the error of measurement even the variations in the oxic removal rates are not very clear. The results only confirm the redox dependency of AOI mineralization.

Table 27 Influence of spiking concentration on AOI-mineralization

Variation of the spiking concentration	100% [1/1]	50% [1/2]	12.25% [1/8]
Average oxic degradation [%]	-1.5	4.3	-5.8
Average anoxic degradation [%]	8.7	6.6	8.6
Average anaerobic degradation [%]	15.1	14.0	16.5

The limited results were also due to fluctuations of the AOI-level in Lake Tegel surface water. A comparison with degradation rates from field experiments show that the field results (60 - 65% for anoxic infiltration and 30 - 35% for oxic infiltration) deviate clearly from the results of these column experiments. This can be attributed to longer retention times in the field experiments. Altogether, the spiking concentration of the trace organics does not seem to have an influence on the decrease of the AOI-concentration.

Trace organics: During variation of the spiking concentration the efficiency of the trace compound removal was quantified for each of the adjusted pollution levels. Each data point is the median of at least two sampling events (LT 1/1 => n=7) and each sample was run as duplicate.

Figure 111 presents the results of the Iopromide monitoring. It was found that the Iopromide removal was not dependent from the initial concentration of Iopromide. In all columns, with the exception of *column 6*, the removal rates ranged between 80% and 100%. In *column 6* the results of the last trace compound level could not be quantified. Although the removal rates of *column 6* were considerably lower (~40%), in general no influence of the varied spiking concentration was observed. These results on the redox dependency of the metabolization of Iopromide were already confirmed in the experiments during operational period 1.

Focusing on the varied spiking concentration, the results of operational period 2 strengthened the theory that Iopromide is metabolized cometabolically. In this case the unspecified biomass responsible for Iopromide metabolization depends not exclusively on Iopromide as organic carbon source, but mineralizes also other carbon from the BDOC pool. Since the BDOC concentration remained stable, the resources for the respective biomass did not change. This fact resulted in stable removal rates for Iopromide independent from the spiking concentrations. A threshold-concentration, which would point towards a metabolic mineralization of Iopromide, was not found.

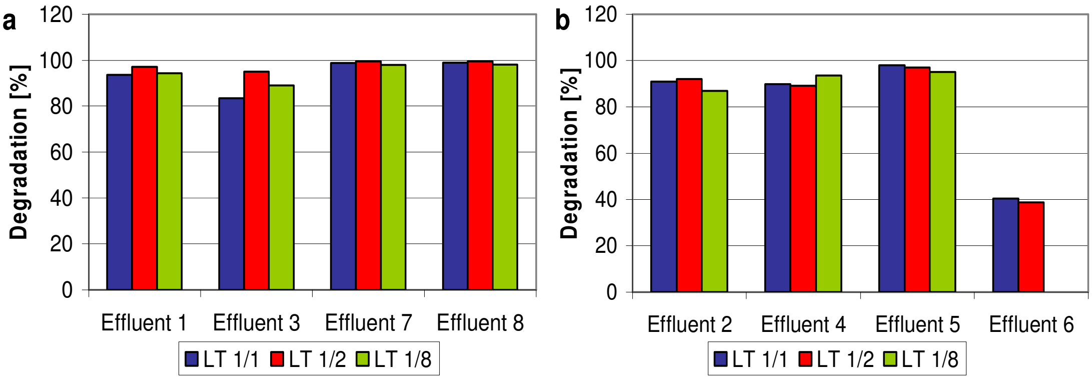


Figure 111 Iopromide degradation in the columns with oxic influent (a) and anoxic influent (b)

The results for the antibiotic Sulfamethoxazole are presented in Figure 112. It was found that the Sulfamethoxazole removal was dependent from the spiking concentration. In most columns the removal efficiency decreased when the initial concentration level was reduced (*Column 1, 2, 5, 7* and *8*). In *column 3, 4* and *6* the trend was not clear. However, the reduction of the removal efficiency at lower spiking concentrations points towards a metabolic mineralization process for Sulfamethoxazole. With decreasing concentration the specialized biomass, responsible for the removal of the antibiotic, does not receive sufficient organic carbon as electron donor. Therefore, the specialized biomass is reduced. If the initial concentration under-runs a so called threshold concentration, the enzymes necessary for Sulfamethoxazole mineralization are not induced any more and the Sulfamethoxazole removal stops. This leads in experiments with decreasing influent concentration to reduced removal efficiencies since these are calculated on percentage basis incorporating the influent and the effluent concentration. In *columns 2, 5, 7* and *8* the decrease in removal efficiency between LT 1/2 and LT 1/8 is above average, which could be interpreted as an approach to an eventual threshold concentration.

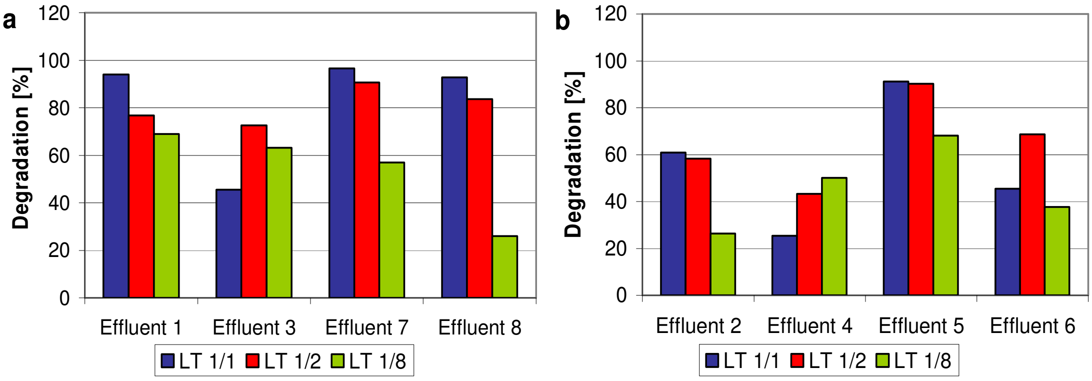


Figure 112 Sulfamethoxazole removal in the columns with oxic influent (a) and anoxic influent (b)

However, the spiking concentration at the lowest level (~780 ng/l) was approximately twice as high as the average concentration in Lake Tegel. This probably explains the overall higher removal rates in the short retention columns. At the artificial recharge site in Tegel the Sulfamethoxazole removal within 50 days of infiltration was 55%.

The monitoring of the NDSA-isomers indicated in some columns higher removal rates in experiments with low initial concentrations. All columns, except the columns with natural sediment filling, showed these tendencies for the degradable NDSA-isomers. In *columns 2, 3, 4* and *6* an increase of 10% to 30% of the degradation rate was observed in “low-spiking“-experiments. In *column 4* the NDSA-removal did not increase until the spiking concentration was reduced to 1/8.

However, this observed improved removal with decreasing initial concentration is contradictory to the expected behavior and the theory of threshold-concentrations. An explanation would be the adaptation of the biomass of the columns to NDSA removal. In case of a decrease of the NDSA concentration, the potential for NDSA removal would remain constant, if the biomass does not exclusively feed on NDSA. A constant removal potential combined with lower initial concentration would lead to increased proportional removal rate. The results might indicate, that the enzymes necessary for NDSA mineralization are present in average biomass (constitutive enzyme) and do not need to be induced.

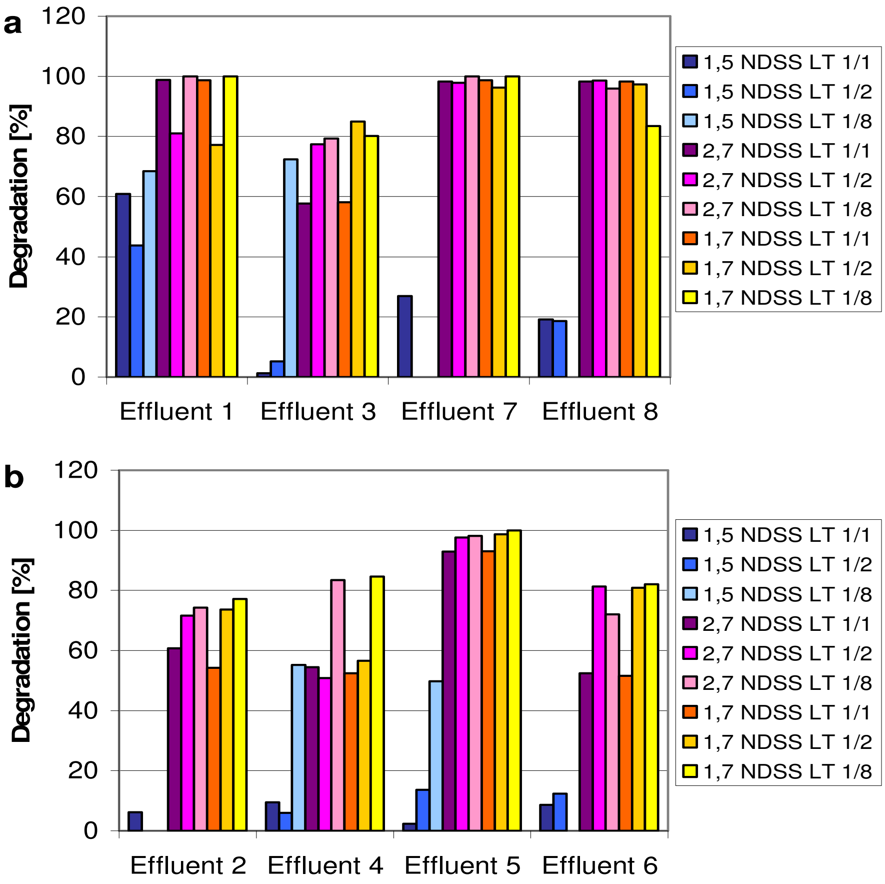


Figure 113 NDSA-removal in the columns with oxic influent (a) and anoxic influent (b)

However, the results of operational period 2 supplement the results of operational period 1. But the results are difficult to generalize, because of the special conditions in the columns. Altogether, these findings are a first approach to the topic. More detailed experiments towards the objectives of identifying the influencing parameters of trace compound removal are necessary.

Operational period 3 (Influence of BDOC-concentration):

Operational period 3 was designed to assess the influence of the initial BDOC concentration on the removal efficiencies for bulk and trace organic compounds. To obtain relevant information the BDOC content of the influent was varied, whereas the trace compound spiking remained stable. Water from Lake Tegel and production well 13 was used to mix the different influents. The DOC-concentration of Lake Tegel water was relatively constant during the experiments. Therefore, the different experiments were comparable. The average DOC-concentration was 6.8 mg/l with a standard deviation of 0.2 mg/l. Influent concentrations were about 6.0 mg/l. The difference between these two values can be explained with BDOC degradation during the storage of the water. Infiltration under optimal aerobic conditions over 30 days in the long retention columns proved that the residual DOC fraction was 3.8 mg/l in Lake Tegel water. This was defined as non-biodegradable DOC (NBDOC) and used for the calculations of the BDOC-fractions and the BDOC degradation rates. Moreover, it was assumed, that water from production well 13, which was used for the dilution of Lake Tegel water, did not contain any BDOC.

Bulk organics: Figure 114 shows the percentages of degraded BDOC during infiltration classified into columns with oxic and anoxic influent. Unfortunately, the last part of the experiment, using a 25:75 (Lake Tegel : Well 13) mixture could not be evaluated, because the BDOC-concentrations were too low. The differences between influent and effluent and among the effluents were within the accuracy of the DOC-quantification method.

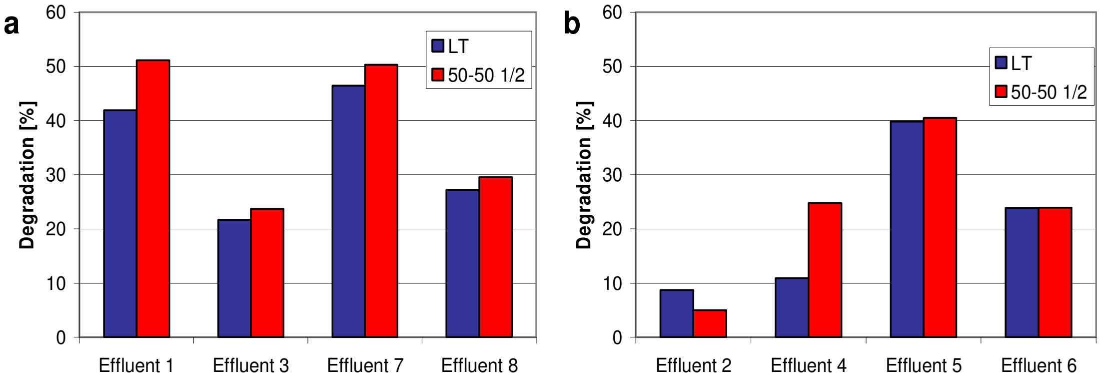


Figure 114 BDOC-degradation in the columns with oxic influent (a) and anoxic influent (b)

The results presented in Figure 114 confirm the results of operational period 1 (Figure 105). It was proved that the average BDOC degradation was higher under oxic conditions. A comparison of *column 1* and *column 2* shows, that the rate of degradation was also faster under oxic conditions. BDOC degradation under different redox conditions showed no significant dependency from the varying influent BDOC-concentrations. Despite of the reduction of available BDOC to one half, the same percentage of the initial BDOC was mineralized. It was concluded, that different BDOC concentrations do not have a fundamental influence on the conversion of BDOC.

LC-OCD: The influence of the reduction of BDOC was monitored via LC-OCD. Thereby, it was found that the decrease of the BDOC of the influent affected all fractions of DOC. The fraction of the polysaccharides showed the most significant decrease. It was concluded, that a relevant part of the polysaccharides can be characterized as BDOC. A comparison of the evaluation of the LC-OCD diagrams and the results of the BDOC-removal proved the already mentioned findings concerning the efficiency of the columns under the tested redox conditions.

AOI: To evaluate the influence of varying BDOC on the AOI-removal, the columns were classified by the dominant redox condition. *Column 1* and *8* were selected as oxic columns, *column 2* and *4* as anoxic column and *column 3* and *6* as anaerobic column. *Column 7* was not considered, because of AOI-formation in the column (discussed earlier). *Column 5* was not included because of the doubled retention time.

Table 28 shows the average AOI removal. The removal rates for the influent with the highest BDOC-concentration (Lake Tegel surface water) were comparable to the mineralization rates assessed during operational period one. During minimization of BDOC by adding water from production well 13 to the influent, the removal rates for AOI partly changed. Under oxic conditions the AOI removal was under all conditions very low and the variations are within the accuracy of the method. In the anoxic columns 8-10% of the initial AOI was mineralized, independently from the BDOC concentration. Only under anaerobic conditions the mineralization rate decreased considerably from 21% to 11% when the BDOC-concentration was cut by 75%.

Table 28 Influence of BDOC-variation on AOI mineralization

Variation of the BDOC-concentration	Lake Tegel	50-50	25-75
Average oxic degradation [%]	-2.5	0.8	3.8
Average anoxic degradation [%]	7.9	9.8	9.7
Average anaerobic degradation [%]	20.7	14.0	11.3

It can be followed that the amount of available BDOC does not directly influence the AOI mineralization under oxic and anoxic conditions. Under anaerobic conditions an influence was found and quantified. A decrease of AOI mineralization was observed when less BDOC was available.

Overall, the BDOC additionally affects the AOI removal, because of its importance for the development of the dominant redox conditions. High BDOC levels are favorable for AOI removal, because mineralization of BDOC leads to more reducing conditions. This effect was not investigated in this study.

Trace organics: The analytical program of the BDOC-variation test was completed by a monitoring of the trace compounds. The efficiency of the trace compound removal was quantified for each of the BDOC-levels. Since the columns represent different redox conditions, it was possible to assess the BDOC-dependency for each of the represented conditions. For some compounds the BDOC-concentration of the influent had an impact on the removal. Prior to the data evaluation the following theoretical considerations were summarized.

Scenarios:

1. If the trace organic removal remains constant during BDOC-reduction this would indicate an independent biomass, responsible for the pollutant removal. The specialized microorganisms are not influenced by the BDOC level, since the concentration of the pollutant (main energy source) does not change. This scenario would indicate a metabolic mineralization by specialized bacteria strains.
2. A decrease of the trace organic removal with BDOC-reduction would point toward a cometabolic mineralization of the trace compounds. In this case it can be assumed that the trace compounds are mineralized within the course of general BDOC-removal. In case of lower BDOC-concentrations the density of unspecialized biomass would decrease, reducing the amount of exo-enzymes and therewith the trace organic removal.
3. An increase of trace organic removal with BDOC-reduction could be explained by a modification of the present biomass. Since the BDOC-concentration decreases, parts of the biomass could induce enzymes that are necessary for the trace compound removal. When the easier degradable BDOC is not available, the focus shifts to more complex carbon structures. This could result in an increasing pollutant removal.

However, the evaluation of the data was found to be very complicated. The trace compound removal was tested for each BDOC-influent concentration and then compared. Figure 115 shows the behavior of Iopromide under different conditions. An evaluation of the sample •Column 6 / 25:75• was not possible and the missing column in the diagram does not indicate a removal of 0%. The removal rates of all samples are between 90% and 100%, with the exception of *column 3* and *6*. The lower removal rates in these columns are most probably caused by the anaerobic conditions in parts of the columns. It is known that mineralization of organic carbon is considerably slower under anaerobic conditions, but on the other side anaerobic conditions are favorable for dehalogenation. All experiments pointed clearly towards a metabolization as the dominant removal process for Iopromide. A comparison of AOI and Iopromide behavior proved this in all soil column experiments. The lower removal rate under anaerobic conditions proposes that the metabolization is an oxic process. Under anaerobic conditions this process was not as efficient. Furthermore, parts of the Iopromide are possibly dehalogenated during the short retention time.

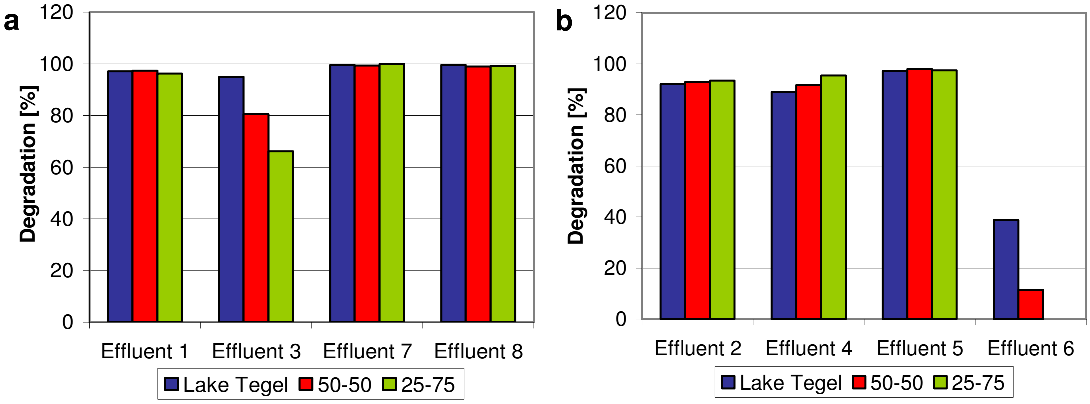


Figure 115 Iopromide degradation in the columns with oxic influent (a) and anoxic influent (b)

The decreasing BDOC-concentration has no influence on the Iopromide metabolization rates under oxic and anoxic conditions. Only in *column 3* and *6*, under anaerobic conditions, the Iopromide removal decreases with lower BDOC-concentrations. This indicates a cometabolic removal mechanism for Iopromide under anaerobic conditions. In oxic or anoxic conditions the decreasing BDOC did not show any effect. This might be explained by the fact that the reduction of BDOC from 2.2 mg/l to 0.6 mg/l did not affect the BDOC degrading biomass strong enough to reduce the metabolization of Iopromide. Since Iopromide is a huge molecule with several aliphatic side chains, a metabolization is a simple process. The biomass is obviously able to metabolize Iopromide under these conditions.

Overall, the Iopromide removal rates are consistent with field data and prove that Iopromide is not persistent during soil passage. But the persistence of the unknown metabolites formed from the Iopromide molecule is indefinite and was not investigated in detail in this project. The results of the AOI measurements propose a high stability of the Iopromide metabolites under oxic conditions.

The results of the comparison of the NDSA are presented in Figure 116. Since the 1,5-NDSA is very persistent, in some cases the effluent concentration was higher than the influent concentration. These negative removal rates, caused by measurement mistakes, were set to zero. Because of the completely different degradation characteristics of the 1,5-isomer and 1,7-and 2,7-NDSA, the isomers are evaluated separately.

The 1,7-and 2,7-NDSA isomer were found to be biodegradable in preceding experiments. In the experiments with varying BDOC-concentrations the removal rates were found to be in a range of 50-100% (Figure 116).

The highest removal rates (90-100%) were achieved in the columns with natural sediments from the field sites. In these columns no dependency of the NDSA-removal from the initial BDOC-level was found. Furthermore, the oxic *column 1* and *column 5* provided an efficient elimination of the 1,7- and 2,7-NDSA.

In the *columns 1, 2* and *4* the removal rates increased with lower BDOC-levels. This would point towards a situation as described in scenario 3. The decreasing BDOC-concentrations could force the active biomass to use alternative organic carbon sources. Within this process the biomass induces enzymes that are necessary for the NDSA-removal. This could explain the more efficient 1,7- and 2,7-NDSA removal under low BDOC conditions.

The anaerobic *columns 3* and *6* did not show a significant trend with changing BDOC concentrations. The removal rates were below average, most probably due to unfavorable redox conditions.

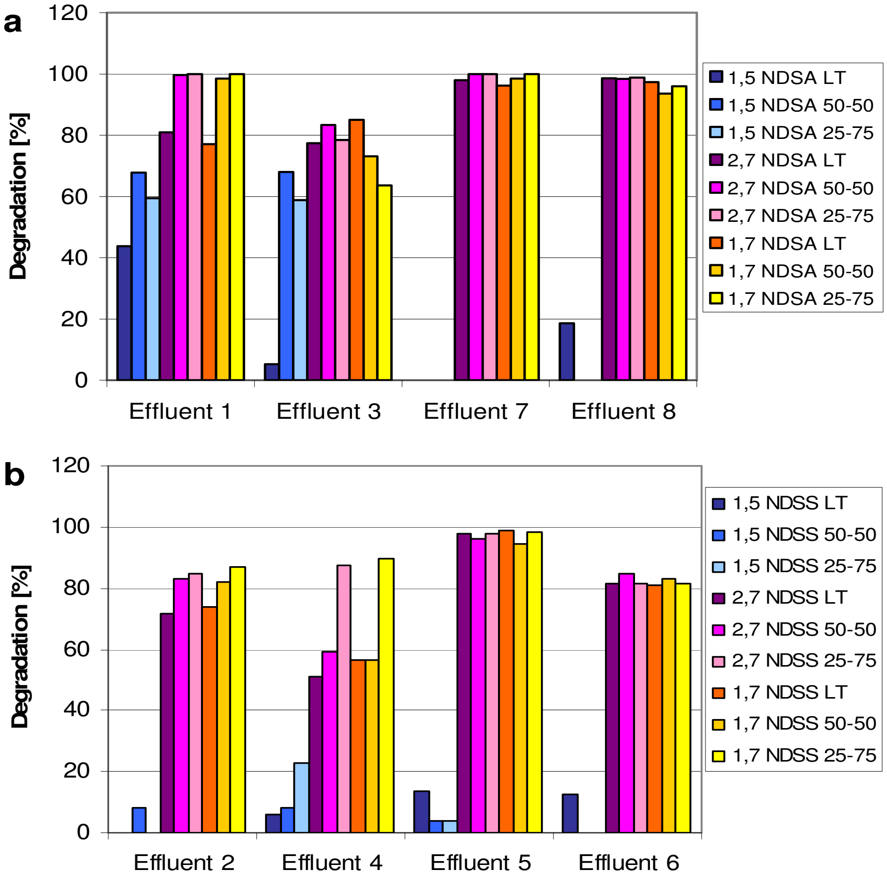


Figure 116 NDSA-degradation in the columns with oxic influent (a) and anoxic influent (b)

The 1,5-NDSA isomer was found to be considerably more persistent than the other investigated isomers. In most columns no removal of this compound was observed. A maximum of 20% mineralization was found in *column 2, 4, 5, 6, 7* and *8.* The results of *column 1* and *3* are contrary to the results of the field monitoring and the long retention columns. These experiments showed that the 1,5-NDSA is slightly better degradable under oxic conditions, but removal rates did not exceed 20% of the initial concentration. The only explanation might be the higher water temperature in the short retention columns.

However, in comparison to all other results of the project the NDSA-removal rates were found to be very high in the short retention columns. Under some redox conditions an influence of the BDOC concentration on the NDSA removal was found.

Unfortunately, an evaluation of the results of the Sulfamethoxazole screening was not possible, because a dilution mistake during the preparation of the stock solution lead to concentrations below the limit of quantification.

1.4.3 Temperature controlled soil column system (TU Berlin)

To assess the influence of different temperature on the degradation properties and kinetics of bulk and trace organic compounds an additional soil column system was installed at TU Berlin. The results of the investigations are mainly based on the project work of Uwe Huebner at the DWQC at TU Berlin.

The results of the field monitoring, especially the long term temperature monitoring by automatic probes revealed strong temperature variations along the flow path at bank filtration sites. Of even greater importance was the temperature variation at the artificial groundwater recharge site in Tegel. The measured temperature differences between summer and winter state in the last monitoring well in front of the production well were more than 20 K. At bank filtration field sites the temperature variation was lower due to longer retention times.

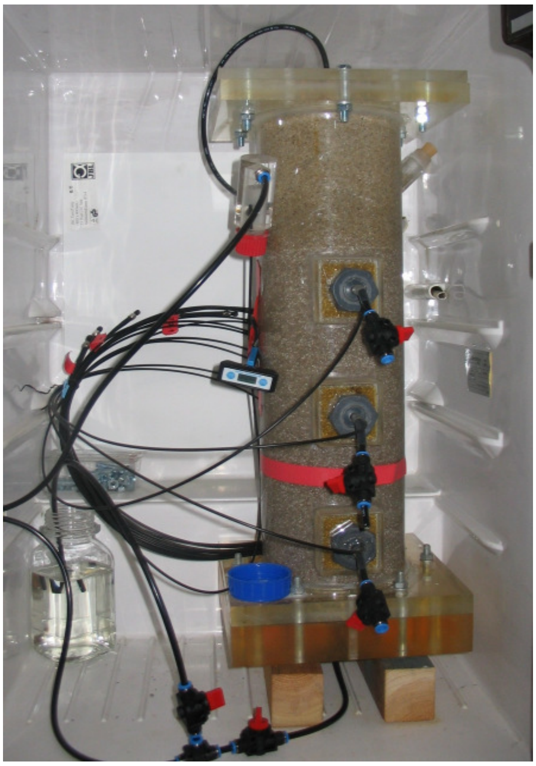


Figure 117 Picture of the set-up used for the investigations of temperature influence

However, since it is known for long that biological degradation processes are temperature dependent it was of interest to quantify this effect. For the objective of the project it was of special interest because the temperature variations occur naturally every year and have significant influence on the raw water quality of the abstracted water. This is most important for the GWR facility.

The objective of this part of the project work was investigating the temperature effect qualitatively and quantitatively. Furthermore, the degradation of the organic compounds at different temperatures was modeled using different approaches for bulk and trace organic compounds.

1.4.3.1 Set-up

The temperature controlled soil column system was installed to simulate conditions of artificial recharge facility in Berlin-Tegel at different times of the year using a soil column system. The set-up of the system is depicted in Figure 118. Three plexiglas columns with a length of 0.5 m and a diameter of 14 cm were operated with surface water from Lake Tegel at different temperatures. Two columns were cooled in standard fridges at 5℃ and 15℃. The third column was stored in a small incubator at constant 25℃. The columns were operated against gravity. To achieve constant concentrations of the investigated trace compounds an online-spiking system was installed. The spiking concentrations were selected to be similar to the spiking of the long retention soil column system (Table 13). Additionally to the sampling ports for column influent and effluent, three sampling opportunities along the columns at 5 cm, 18 cm and 30 cm were included. Each sampling point was combined with an optical oxygen probe.

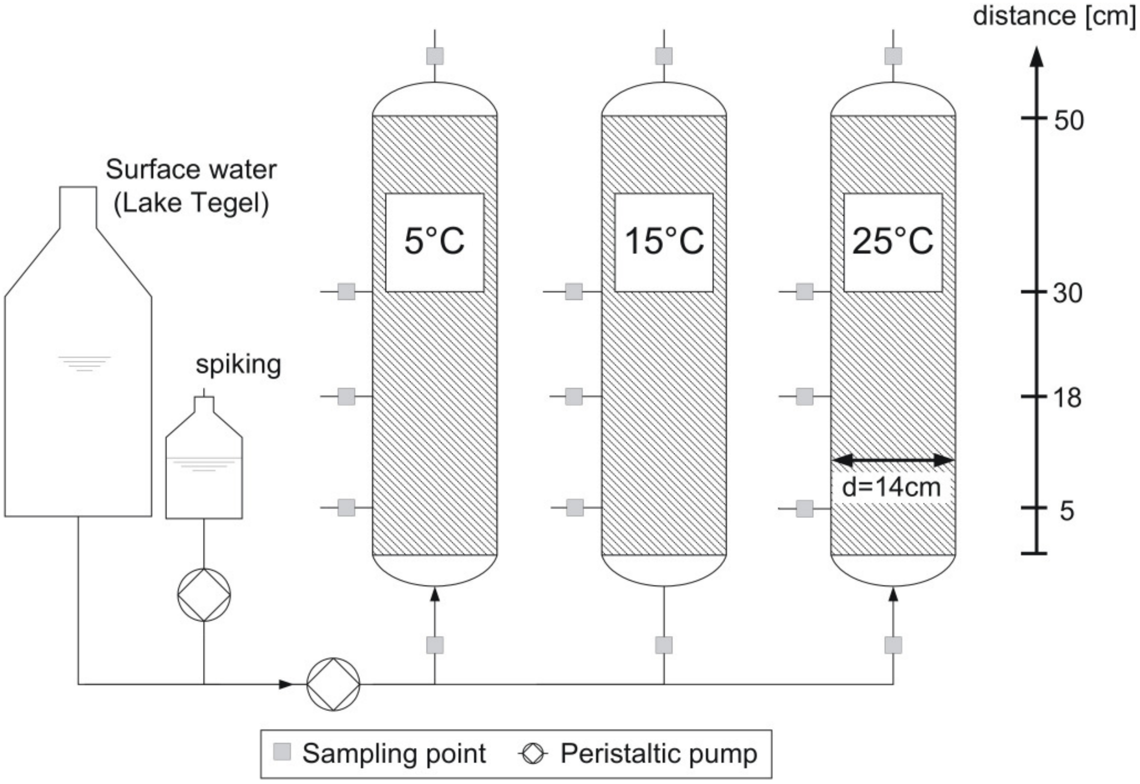


Figure 118 Schematic set-up of the temperature controlled soil column system

The time period which was assigned for adaptation was two months under room temperature and subsequently three months under operating conditions. Afterwards the monitoring proved an intact biomass in all columns and the experiments started.

To guarantee stable conditions the temperature was measured regularly and adjusted if necessary. All characteristics of soil columns are presented in Table 29.

Table 29 Operating conditions for the temperature controlled soil column system

	5°C	15°C	25°C	n
Temperature [°C]	5.9 +/-0.8	15.0 +/-0.7	25.0 +/-0.5	37
Flow [ml/column*d]	439 +/-18	452 +/-25	458 +/-24	14
Retention time [d]	6.3			
Pore velocity [cm/d]	8.3			

The columns were filled with industrial sand (0.7-1.2 mm) which was used already for the short retention soil columns. The characteristics of the sand are described more detailed in chapter 1.4.2.1. Because no fine sand fractions were used for the column filling and the surface of silica sand is particularly negative charged no significant sorption affects were expected.

As mentioned, the column system was operated with water from Lake Tegel, which was filtered with a micro filter to avoid an entry of coarse POC. Before the water entered the columns trace compounds were spiked by a peristaltic pump system. The concentration levels were: X-ray contrast media Iopromide (10 µg/l), antibiotic Sulfamethoxazole (2.5 µg/l) and each isomer of naphthalenedisulfonic acid (2.5 µg/l). Table 30 shows medians and standard deviations of characteristic parameters measured in column influent. Investigations were conducted in winter/spring with high oxygen concentrations in Lake Tegel.

Table 30 Characterization of the surface water used as influent

	Unit	Median	Standard deviation	n
pH-value	-	7.96	0.25	8
Oxygen	**[mg/l]**	11.12	0.49	29
Nitrate	**[mg/l]**	2.5	0.31	9
DOC	**[mg/l]**	7.32	0.43	10
UVA_{254}	**[m^{-1}]**	15.74	0.34	10
SUVA	**[l/mg*m]**	2.15	0.16	10

To achieve a better picture of the redox situation, the electron acceptors oxygen and nitrate were measured. A direct measurement of redox potentials was not conducted because the columns were completely oxic and the redox potential was similar at the start and the end of the columns.

Results of oxygen measurement are presented in Figure 119. High standard deviation of oxygen results at 25℃ is related to comparably high values in the beginning of analysis. In all columns a significant oxygen demand was observed, whereas at higher temperatures more oxygen was consumed. This is consistent with the results of the DOC analysis. A removal of nitrate during infiltration was not observed.

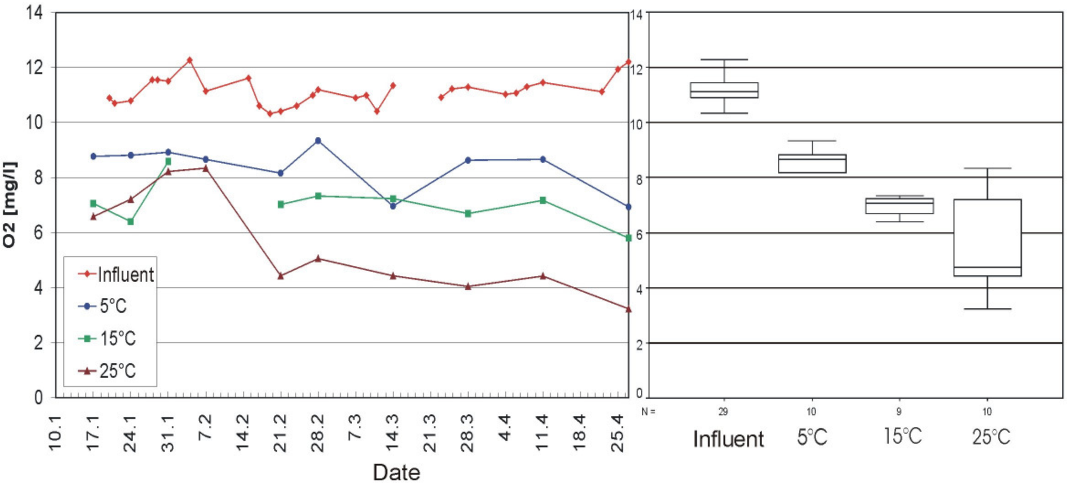


Figure 119 Oxygen concentration in the influent and the three different effluents

Table 31 shows the monitoring schedule of the first part of the experiment, where the pore velocity was adjusted to 8.3 cm/d and the retention time was 6.3 days. To analyze bulk organics and trace organics ten samples were taken on a weekly basis from the influent and the effluent of each column. At the sampling ports along the column the trace compounds were only analyzed three times.

Table 31 Monitoring schedule of the first part of the experiments at the column system (01-04.2005)

		17.1.	24.1.	31.1.	7.2.	21.2.	28.2.	14.3.	28.3.	11.4.	27.4.
Influent and Effluent	pH	x				x	x	x	x	x	x
	DOC	x	x	x	x	x	x	x	x	x	x
	UVA	x	x	x	x	x	x	x	x	x	x
	LC-OCD	x	x	x	x	x	x	x	x	x	x
	AOI	x	x	x	x	x	x	x	x	x	x
	HPLC-MS/MS	x	x	x	x	x	x	x	x	x	x
	HPLC-FLD	x	x	x	x	x	x	x	x	x	x
	FIA		x	x	x	x	x	x	x	x	x
Sampling ports at 5, 18 and 30 cm	pH	x				x	x	x	x	x	x
	DOC	x	x	x	x	x	x	x	x	x	x
	UVA	x	x	x	x	x	x	x	x	x	x
	LC-OCD	x	x	x	x	x	x	x	x	x	x
	HPLC-MS/MS							x		x	x
	HPLC-FLD						x		x		x
	FIA		x	x	x	x	x	x	x	x	x

Some trace compounds were removed that efficient that the data pool for the description of the degradation kinetics was not sufficient. Therefore, in an additional operating period with shorter retention times was started after the first part of the investigations was finished. The second experiment consisted of four weeks adaptation period and subsequently three sampling events in a time interval of two weeks. The experiments at the temperature controlled soil columns ended in July 2005.

1.4.3.2 Results

DOC and SAK$_{254}$

After an adaptation period of 4 months the column system was operated under a close monitoring schedule for the time period of six months. A sampling of the reservoir and the column effluents was performed on a weekly basis. The results of DOC and SAK$_{254}$–measurements are shown in Figure 120 and Figure 121 as medians from ten different measurements. Additionally, the standard deviations, which are mainly due to variations of the surface water quality, are depicted in the diagrams and provide a good impression on the stability of the results. Table 32 explains the dependency between distance and retention time in the columns.

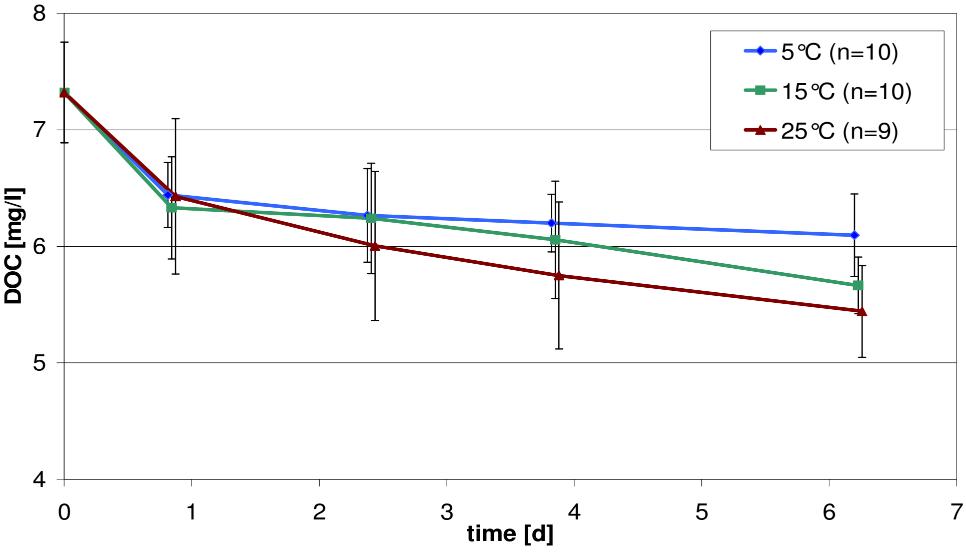


Figure 120 Degradation of DOC along the columns

The DOC-measurements show a fast mineralization of organic carbon in the first few centimeters of the columns, which does not seem to be dependent from temperature. All columns were found to perform similar efficient during the initial infiltration phase. The removal of UV-active organic compounds was also most efficient in the first part of the infiltration. Similar to the results of the DOC analysis no dependencies from temperature were observed. The fast removal can be explained by a mineralization of easy degradable portions of DOC, which are instantly available for biological degradation. The results indicate that the temperature has no significant influence on the DOC-mineralization in the instant infiltration zone.

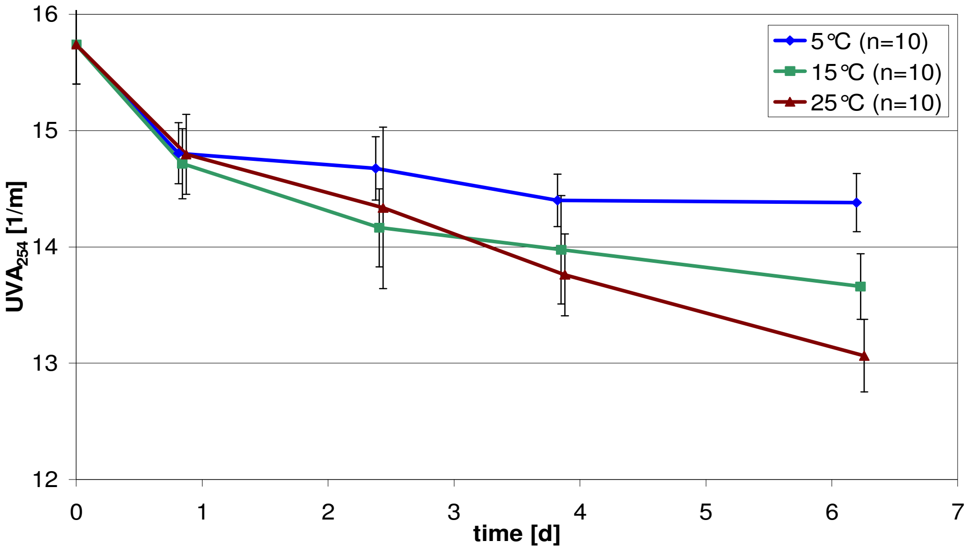


Figure 121 Fate of UVA_{254} along the columns

Along the further infiltration path an influence of the different temperature on the bioactivity was clearly visible. The results of the DOC-analysis and UVA_{254} show consistently that the removal of organic substances is more efficient at higher temperatures. Further degradation of organics in deeper parts of the filter beds is enhanced in the columns with higher temperatures, leading to higher removal rates for DOC and UVA_{254}.

Despite of similar trends for DOC and UVA, the more precise analytical method for UVA_{254}-measurements provide a clearer picture of the temperature dependency of the bulk organic degradation (Figure 121). The standard deviations of the UVA data pool is lower than for the DOC data pool, showing that differences in the fate of DOC under different temperatures is statistically relevant. The DOC measurements were problematic, since the concentration differences were low and sometime in the range of the accuracy of the quantification method. However, a significant increase of mineralization potential of bulk organic compounds with increasing temperature could be shown. But the temperature effect was of greater importance in the deeper parts of the infiltration path. During initial infiltration no significant effect of temperature was observed.

Table 32 Retention time at the different sampling points along the columns

Distance [cm]	**5**	**18**	**30**	**50**
Retention time [d]	0.8	2.4	3.9	6.3

A summary of the bulk organic results is provided by Table 33, which shows all removal rates of the different columns. The BDOC removal was calculated assuming a non-degradable DOC-portion of Lake Tegel surface water of 3.8 mg/l. This was a result of a long term infiltration experiment at ~15℃ in the long retention column system. Since the amount of BDOC might vary with the temperature, this calculation simplifies the problem and should be regarded as a trend.

At the end of the columns (after 50 cm / retention time: 6.3 d) 26% of the initial DOC and 53% of BDOC were removed at 25℃. In the same infiltration time and distance only 17% of DOC (35% BDOC) could be removed at 5℃. In all columns only a partly removal of BDOC was observed, so that longer retention times would most probably lead to higher removal rates.

Table 33 Degradation rates after 6.3 d (effluent)

	5℃	**15℃**	**25℃**
DOC	17%	23%	26%
BDOC	35%	47%	53%
SAK_{254}	9%	13%	17%

The fate of SUVA (ratio of medians from SAK_{254} and DOC) during infiltration along the different columns is shown in Figure 122. A strong increase of SUVA in the beginning of infiltration can be seen in all columns, which is due to the mineralization of aliphatic polysaccharides. In deeper infiltration beds no significant changes were measured. There microorganisms have to mineralize aromatic structures as well, leading to a balance in the ratio aromatic/aliphatic organic compounds. No significant temperature dependency of SUVA could be shown.

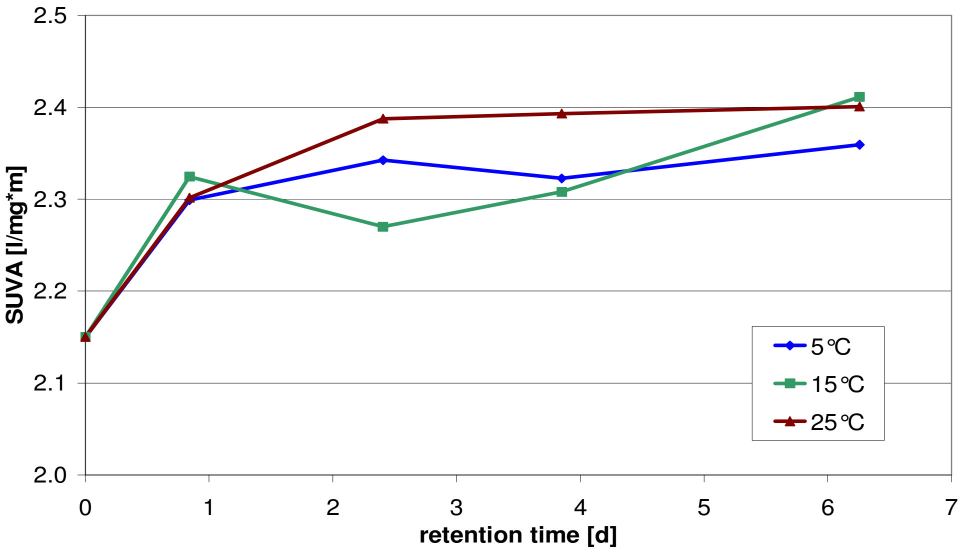


Figure 122 SUVA along the columns (median/ calculation from ten DOC and SAK measurements)

LC-OCD

To assess the fractions that were responsible for the observed changes in the bulk organic composition the LC-OCD technique was used to fractionate the DOC in five fractions. LC-OCD analysis was performed of every sample used for DOC measurement and the results are presented as averages from ten different chromatograms (Figure 123). The mediation of the chromatograms summarizes the obtained results into a presentable amount of data and allows to focus on the most important changes. Therefore, minor changes and single measurement mistakes are not misinterpreted.

Figure 123 shows the results of OC-detection after the fractionation by size exclusion chromatography. Comparing column effluents (Figure 123a) a good removal of polysaccharides at all temperatures was found. A nearly complete degradation of the PS-peak occurs at 15°C and 25°C. At 5°C about 75% of the polysaccharide-fraction was removed. At 25°C the polysaccharide removal accounts for ~16% of the total DOC removal.

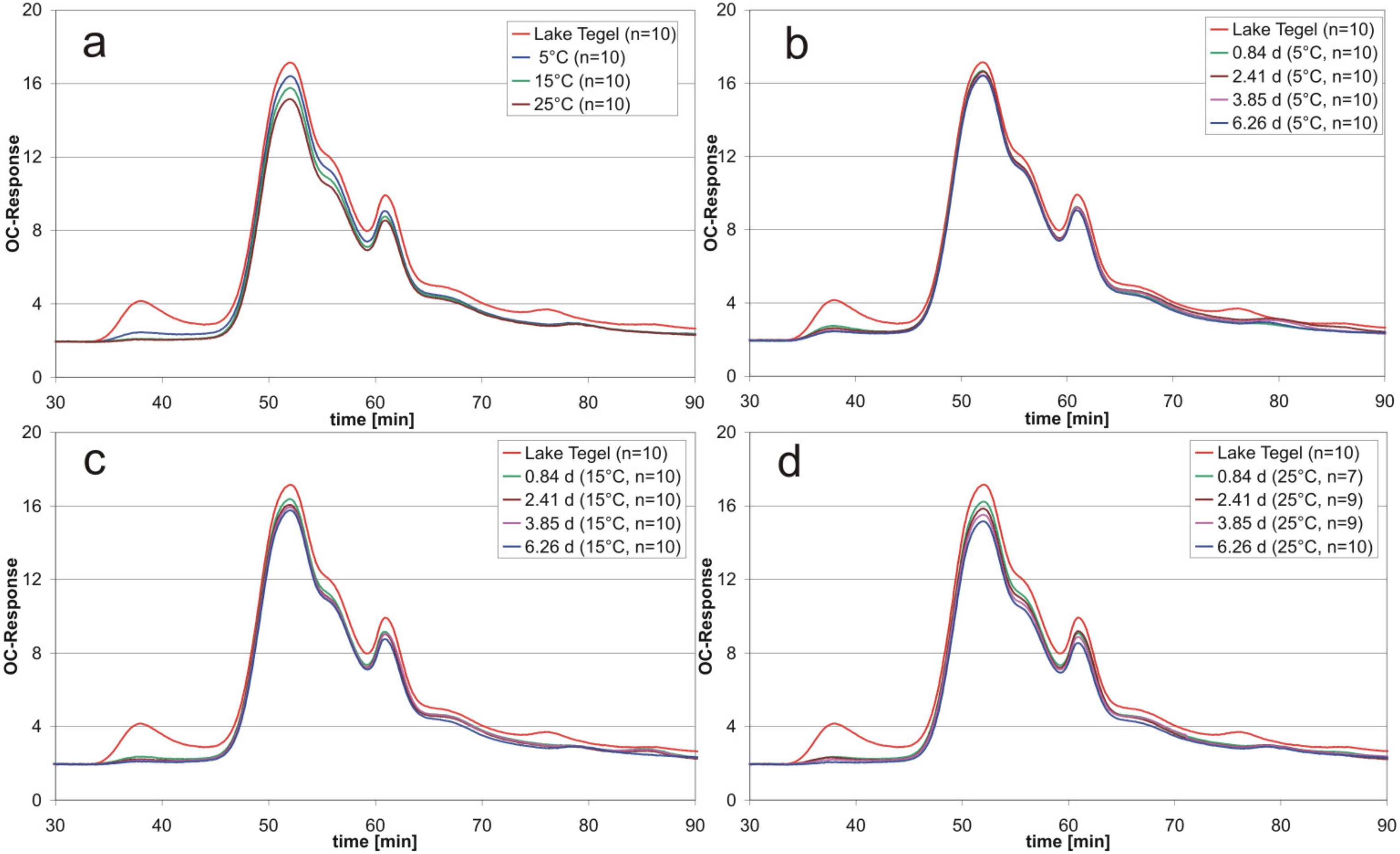


Figure 123 LC-OCD-chromatograms: a) column effluents; b) column at 5℃; c) column at 15℃; d) column at 25℃

For humics the degradation follows a definite temperature dependency. The degradation rates increase with higher temperatures. Whereas at 5°C only in the initial infiltration phase some removal of humic compounds was observed, the degradation of humics continues along the entire infiltration path at 25°C (Figure 123d). Overall, the maximum removal rate for humic substances during 6.3 d of infiltration is ~22% (in the 25°C column) accounting for 28% of the total DOC mineralization (Table 34).

No temperature dependency could be proved for the removal of humic building blocks, low molecular acids and neutrals. For buildings blocks and LMA no significant changes were observed, probably due to reformation during humic degradation. However, these fractions are not discussed more detailed, but Figure 123 shows that most changes in these fractions occurred during initial infiltration.

The measurements along the columns (Figure 123(b-d)) are consistent with the DOC results, showing the highest degradation rates at the beginning of infiltration. Especially degradation of aliphatic polysaccharides was very fast and mostly completed at the first sampling point at 5 cm. Humics were removed continuously at 25°C whereas at 5°C the removal rates decrease considerably after the first sampling point.

More detailed data provide the results presented in Table 34. The quantitative results are derived from an integration procedure for LC-OCD chromatograms, which was developed on the basis of the work of Huber (2001). The OC-response was used for quantification. Table 34 shows the results of integration.

Table 34 Results of LC-OCD integration

		Poly-saccharides		**Humics**		**Building Blocks**		**Low molecular acids**		**Neutrals**		**DOC**
		mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l	%	mg/l
feed		0.45	6.1	3.57	48.7	1.55	21.2	0.24	3.2	1.52	20.7	7.32
5°C	0.84 d	0.17	2.8	3.28	52.4	1.51	24.1	0.21	3.4	1.08	17.3	6.44
	2.41 d	0.15	2.4	3.25	50.6	1.53	23.7	0.21	3.2	1.29	20.0	6.27
	3.85 d	0.12	1.9	3.19	51.6	1.51	24.5	0.21	3.4	1.15	18.6	6.2
	6.26 d	0.11	1.9	3.18	52.7	1.48	24.5	0.20	3.3	1.06	17.6	6.1
15°C	0.84 d	0.08	1.4	3.14	51.3	1.51	24.6	0.22	3.5	1.17	19.2	6.33
	2.41 d	0.05	0.8	3.07	52.1	1.47	25.0	0.21	3.6	1.09	18.4	6.24
	3.85 d	0.04	0.6	3.02	51.0	1.49	25.1	0.22	3.8	1.15	19.5	6.06
	6.26 d	0.02	0.3	2.95	52.2	1.46	25.9	0.20	3.5	1.02	18.1	5.67
25°C	0.84 d	0.09	1.4	3.08	51.0	1.53	25.3	0.21	3.5	1.13	18.8	6.43
	2.41 d	0.07	1.1	3.00	51.4	1.49	25.5	0.24	4.1	1.05	17.9	6.00
	3.85 d	0.05	0.8	2.92	50.9	1.45	25.3	0.21	3.6	1.11	19.4	5.75
	6.26 d	0.01	0.1	2.77	51.4	1.43	26.5	0.19	3.6	0.99	18.4	5.44

Figure 124 shows the SUVA which was calculated as the quotient of UV-response and OC-response during LC-OCD fractionation. The maximum at 48 min is not identical with maximum of humics (52 min). This proves that the high molecular humics, eluting at 48 min, have the highest share of aromatic structures. This is consistent with the findings at the field sites and the long retention column experiments. The measured increase of SUVA (Figure 122) can primarily be ascribed to the degradation of aliphatic polysaccharides (36-44 min). For the SUVA of humics only little differences without any temperature dependency were detected.

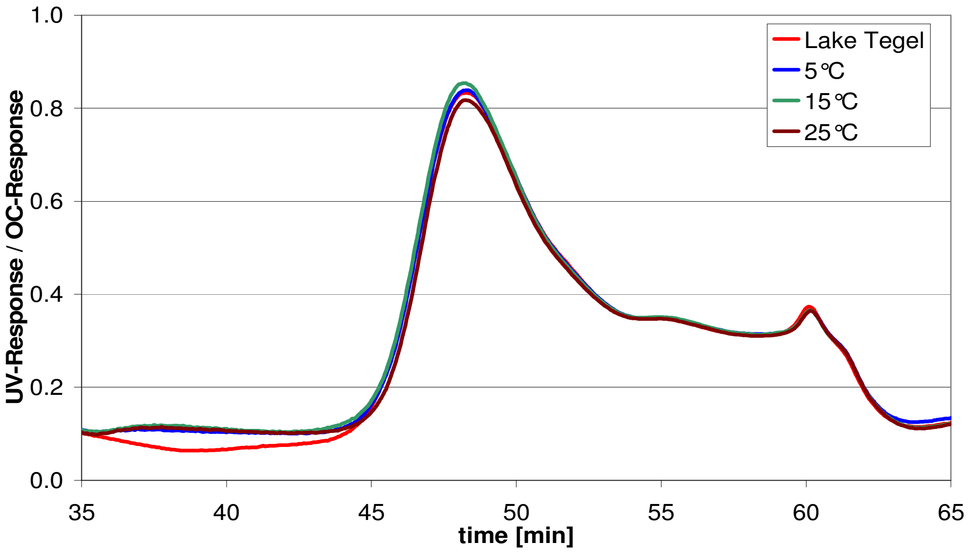


Figure 124 SUVA of column effluents at 5°C, 15°C and 25°C

Figure 125 provides more detailed information by describing the changes of SUVA along the column at 25°C. The graph proves that besides the strong influence of the polysaccharides on the SUVA, the humic substances also show some influence on the overall SUVA.

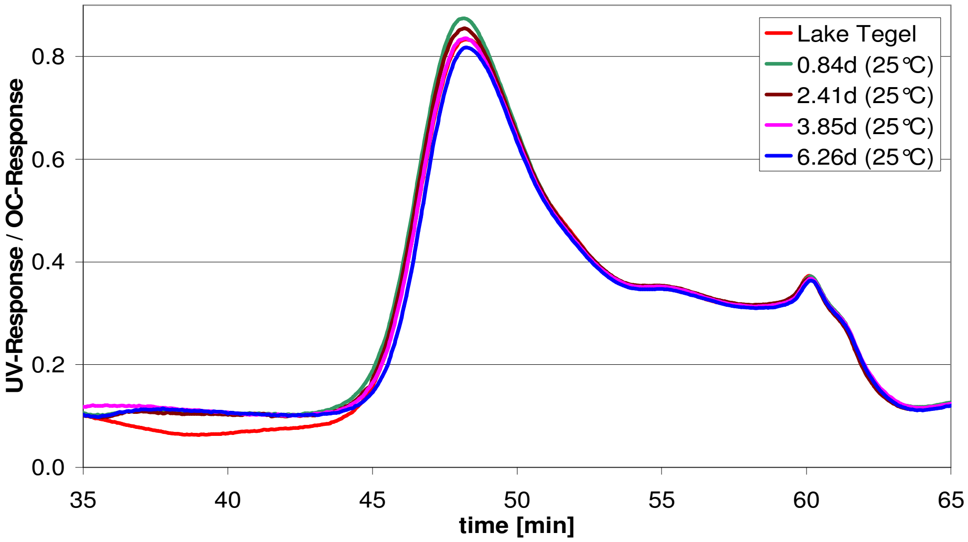


Figure 125 SUVA along the column with 25℃

In the beginning of the infiltration the SUVA of humic substances increases (peak at 48 min). It can be assumed that microorganisms start to crack aliphatic side chains of the humic molecules, causing an overall increase of the share of aromatic structures in this fraction. In the deeper layers of the filter bed the portion of aromatic carbons is decreasing, most probably because easy degradable aliphatic structures are exhausted and microorganisms have to use aromatics as well. Towards the end of infiltration the ratio of aromatic to aliphatic structures is again similar to the ratio in the feed water.

Adsorbable organic iodide (AOI)

Since the question of the temperature dependency of AOI-mineralization remained unclear, AOI was included into the monitoring program of the temperature regulated column system. Because of the oxic conditions in the column system, no significant mineralization of AOI was expected. However, AOI was measured as additional parameter to characterize the degradation process of Iopromide.

Table 35 shows the AOI results as medians.

The average AOI concentration in Lake Tegel during the operation of the column system was measured with 11.6 +/- 2.7 µg/l (n=4). Feed samples were taken after spiking so that the spiked Iopromide is included in the feed results. Knowing that 10 µg/l Iopromide-spiking would result in an AOI increase of 4.8 µg/l, the estimated feed concentration is about 16.4 µg/l. This corresponds well with the measured concentrations. However, the results implicate a slight increase of AOI-concentration of 1.5-2.9 µg/l at all temperatures during infiltration. This is most probable due to measurements mistakes, since these slight increases do not correspond with other results of the project. An unlikely explanation could be the formation of iodinated organic compounds from inorganic iodine species.

Table 35 AOI results of temperature regulated soil column system, n=9

	Feed	5°C	15°C	25°C
AOI [µg/l]	15.8 +/- 2.4	18.7 +/- 2.6	17.4 +/- 2.3	17.7 +/- 1.4

Modeling

Because a mathematical description of the biological degradation of heterogeneous bulk organics with a model using only one degradation constant is not possible, the three parametric description proposed by Gimbel et al. (1992) is used. This model was used earlier for the modeling of DOC mineralization in the long retention column.

To achieve representative results that describe the biodegradation sufficiently, a fractionation of the total DOC into three fractions (easy, medium/poorly and non-degradable) is necessary. The amount of non-degradable DOC needs to be quantified for the used feed water. For the modeling of the temperature regulated soil column system the amount of non-degradable DOC in Lake Tegel water was derived from results of the long retention soil column system. The fraction removed during infiltration to the first sampling point (after 0.84 d) was defined as easy-degradable DOC. The DOC-results were modeled two times using the software SPSS. Because of the fact that the removal of the easy degradable fraction seemed to be not temperature dependent, the degradation constant of the easy-degradable fraction was fixed as an average from all columns for second modeling (Table 36).

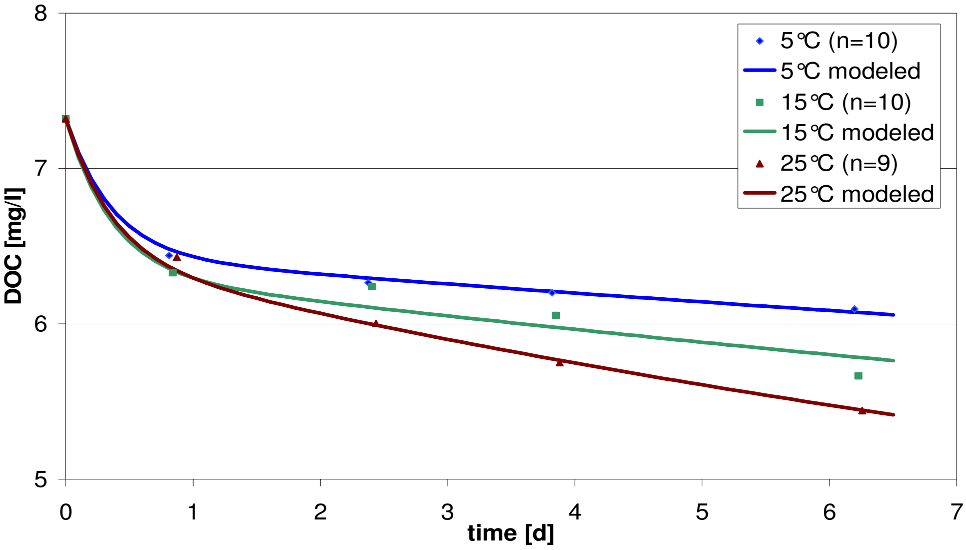


Figure 126 Models for the DOC degradation with the used soil column data

The results of the modeling of total DOC degradation using three fractions of different degradability are shown in Figure 126 and Table 36. It is evident that the kinetic of DOC degradation in the columns was described very well. The correlation coefficients of the models at all temperatures are sufficiently high with R^2 of more than 0.97 (Table 36).

Furthermore, Table 36 shows that the modeled degradation constant of the medium/poorly degradable fraction (λ_2) increases considerably with higher temperatures. The results indicate that a 10 K temperature rise caused an increase of the degradation constant by the average factor of ~1.8. Thereby the factor of λ_2 was slightly higher between 15°C and 25°C than between 5°C and 15°C.

Table 36 Model constants of the DOC-modeling using Equation 1

	C_1 [mg/l]	λ_1 [d^{-1}]	C_2 [mg/l]	λ_2 [d^{-1}]	C_3 [mg/l]	R^2
5°C	0.88	2.77	2.64	0.024	3.8	0.997
15°C	0.99		2.53	0.039		0.975
25°C	0.89		2.63	0.075		0.997

The description of the fate of DOC, using three fractions and different degradation constants, was tested earlier (e.g. in Drewes (1997) and Schoenheinz (2004)). Because of the use of many variable parameters for the model, time-consuming tests are necessary to assess the concentrations of the fractions. Furthermore, the model must be adapted for each water type separately.

Therefore, one objective of the work at the temperature controlled soil columns was to test the possibility to fractionate the DOC before modeling using LC-OCD and model the mineralization of some of the fractions with one degradation constant. Of special interest was the fraction of polysaccharides, which showed a behavior during infiltration that can be compared with a single compound. The fraction of humic substances was tested, but believed to be too heterogeneous to fit to a model for a single compound decay.

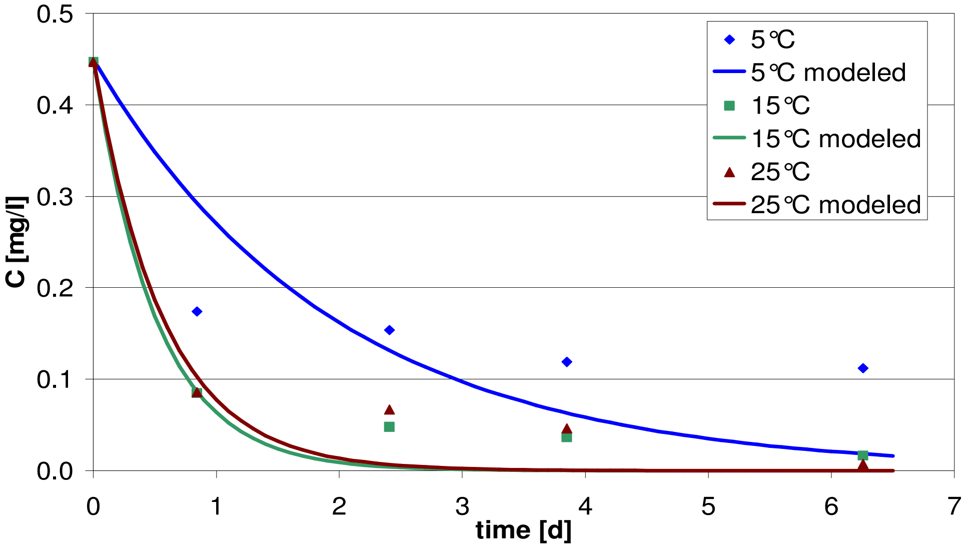


Figure 127 Modeling of polysaccharide removal with a one degradation constant model

Figure 127 and Figure 128 show the results of HS- and PS-modeling with one degradation constant. Analog to the total DOC modeling a non-degradable fraction, which is calculated from results of the long retention column system, was included into the model for humic substances. In Figure 128 the model for the decay of the humic fraction shows an insufficient correlation, proving the humics as a very heterogeneous fraction with easy degradable, poorly and non-degradable substances. Regarding the modeling of polysaccharides a higher correlation factor was achieved, but the description of this fraction is also not sufficient with only one degradation constant.

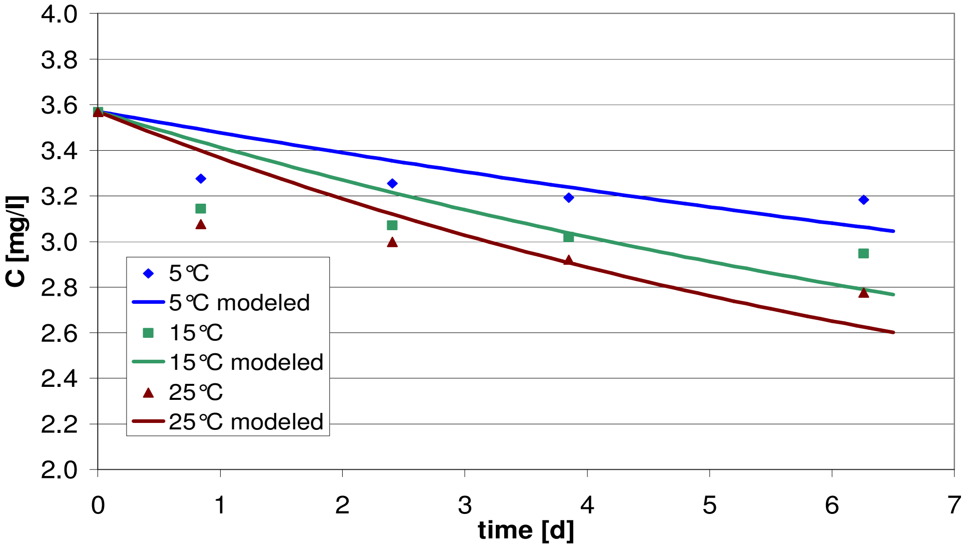


Figure 128 Modeling of the fraction of humic substances with a one degradation constant model

Table 37 proves that the DOC-fractions assessed by LC-OCD are still to heterogeneous to be modeled with a single compound decay model. The models include the temperature variation of the humics and polysaccharide decay but do not predict the kinetics of the real degradation process.

Table 37 Modeling constants of PS- and HS-removal with a one degradation constant model

		C_1 [mg/l]	λ_1 [d^{-1}]	C_2 [mg/l]	R^2
Polysaccharides	5°C	0.45	0.511	-	0,663
	15°C	0.45	1.96		0,968
	25°C	0.45	1.759		0,947
Humics	5°C	1.77	0.054	1.8	0.298
	15°C	1.77	0.093		0.435
	25°C	1.77	0.122		0.629

Results of HS- and PS-modeling with two degradation constants are presented in Figure 129, Figure 130 and Table 38. Modeling was conducted with a similar approach as the one used for DOC. It was found that the removal of humics as well as polysaccharides can be better described as a degradation process including at least two fractions.

An increase of the degradation constant λ_2 by the factor of 2.7 was observed for the medium degradable fraction of polysaccharides between 5°C and 15°C. Between 15°C and 25°C no differences in removal rates were measured. The polysaccharides are a well defined group of organic compounds, which do not contain a non-degradable portion. But since the ratio of easy degradable to medium degradable PS shifts with temperature, the prediction of the behavior of PS in a given situation remains complicated. The results provide some insight, but do not eliminate the need of degradation tests before modeling.

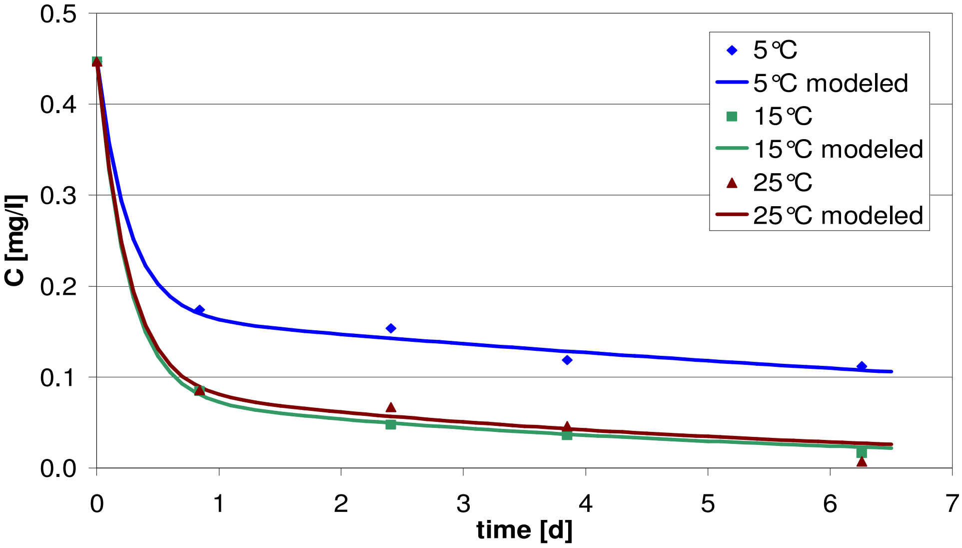


Figure 129 Modeling of polysaccharide mineralization with two degradation constants

The results for the even more heterogeneous humic fraction are presented in Figure 130. It was found that the degradation of the easy degradable fraction of humics was nearly temperature constant. Therefore, a uniform degradation constant for this fraction was used. A significant temperature dependency was measured for medium-degradable humic substances. Consistent with the total DOC results a temperature-rise of 10 K caused an increase of the degradation constant λ_2 by the factor 1.8. In contrast to the influence of temperature on DOC degradation, the effect of temperature rise on HS-degradation was little higher between 5°C and 15°C than between 15°C and 25°C.

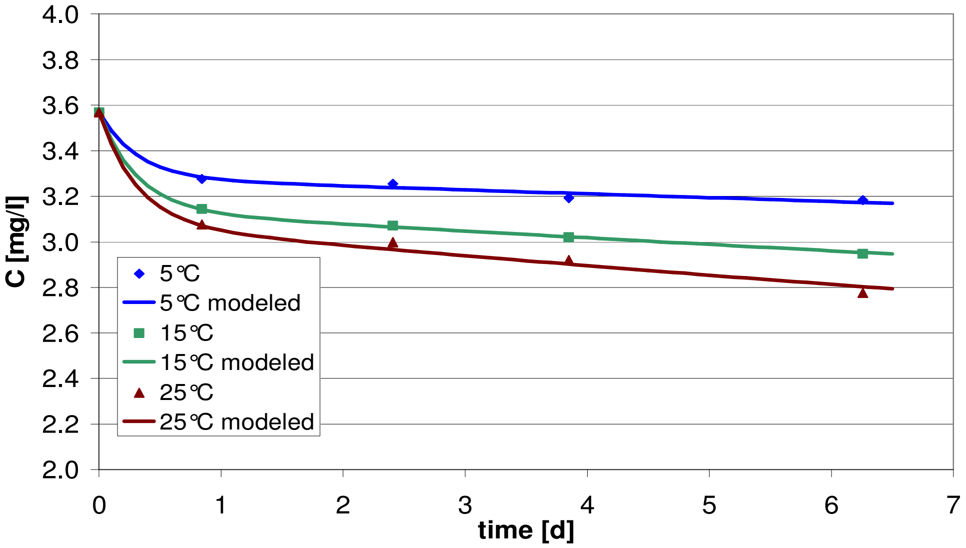


Figure 130 Modeling of HS-removal with two degradation constants

However, the results show that a prediction of the behavior of the LC-OCD assessed DOC fractions in soil columns is possible. The fractions can definitely not be modeled as single compounds. The temperature dependency that was found for the total DOC mineralization was also valid for the degradation of the single DOC-fractions. Overall, it can be summarized that the mineralization of easy degradable fractions of DOC is not significantly dependent from temperature (in the range 5°C –25°C). For medium-/poorly degradable fractions an increase of degradation efficiency by the factor of 1.8 was observed during a temperature increase of 10 K. This proves the often mentioned rule of the thumb, that biological processes are twice as efficient after a temperature increase of 10 K.

Table 38 Results of the HS- and PS-modeling with two degradation constants

		C_1 [mg/l]	λ_1 [d^{-1}]	C_2 [mg/l]	λ_2 [d^{-1}]	C_3 [mg/l]	R^2
Polysaccharides	5°C	0.28	3.973	0.17	0.073	-	0.998
	15°C	0.37		0.08	0.199		0.999
	25°C	0.36		0.09	0.191		0.996
Humics	5°C	0.29	3.234	1.48	0.012	1.8	0.993
	15°C	0.43		1.34	0.024		0.999
	25°C	0.49		1.28	0.039		0.993

Trace organic pollutants

Additionally to the bulk organic parameters, the behavior of selected trace organic compounds was investigated in the temperature controlled column system. The set-up of the columns allowed sampling along the infiltration path, which was beneficial for the assessment of the degradation kinetics of the trace compounds. The monitoring schedule is included in the set-up chapter. Because of the required higher sample volumes for trace compound analysis the influent and the effluent of the columns were sampled more often (10x), whereas the sampling ports along the columns were only used for three sampling events during the operation period. Therefore, the data pool for the sampling ports along the column is smaller than the data pool for the influent and effluent of the column.

The same selection of trace compounds that were used for the field monitoring and the other soil column experiments was used for the investigations at the temperature controlled soil columns. From the group of naphthalenedisulfonic acids the 1,5-, 1,7- and 2,7-isomer were analyzed. Figure 131 shows the concentration of 1,5-NDSA along the columns. Confirming other results no biodegradation was observed even in the column operated at 25°C. In all columns the concentration remained at the level of the influent concentration during the 6.3 d of infiltration. The results of 1,5-NDSA prove that no significant influence of sorption processes is present in the soil columns and that polar substances (as the tested trace compounds) do not tend to adsorb to the sand surface. Therefore, the removal of other substances must be mostly related to biodegradation. Results of additional experiments with shorter retention time confirm these conclusions.

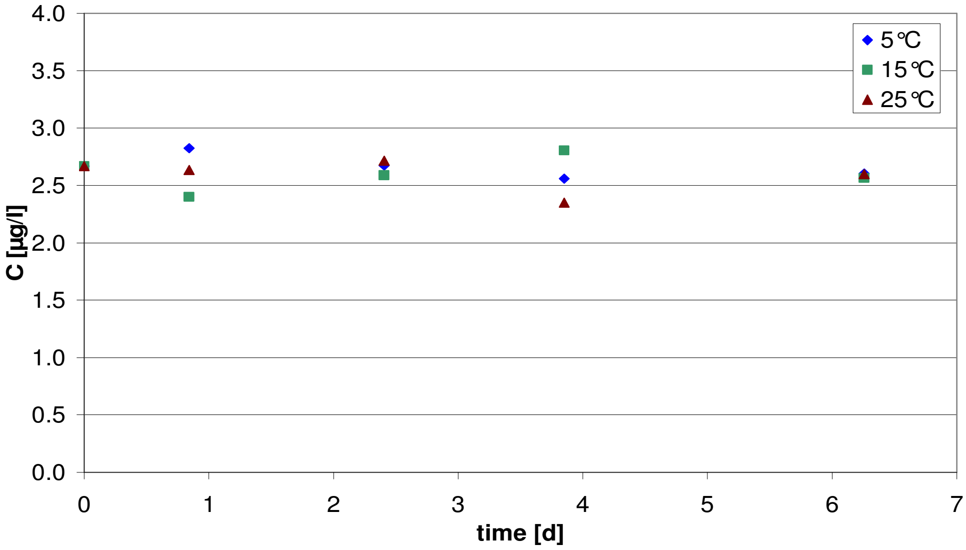


Figure 131 Behavior of 1,5-NDSA (v=8.31cm/d) along the different columns

The other isomers of NDSA were found to be degradable under favorable conditions. After the first test of the degradability with a pore velocity of 8.3 cm/d some of the trace compounds were already degraded in the first sampling port and differences between the efficiency at 15°C and 25°C were not clearly visible. Therefore, a second test with higher flow velocities was performed to emphasize the initial infiltration zone. The second set of experiments was conducted at a pore velocity 15.9 cm/d reducing the retention time of the columns from 6.3 days to 3.2 days. The results confirmed the findings of the first set of experiments and provided a better insight into the processes in the immediate infiltration zone. A better differentiation of the performance of the 15°C column and the 25°C column was possible.

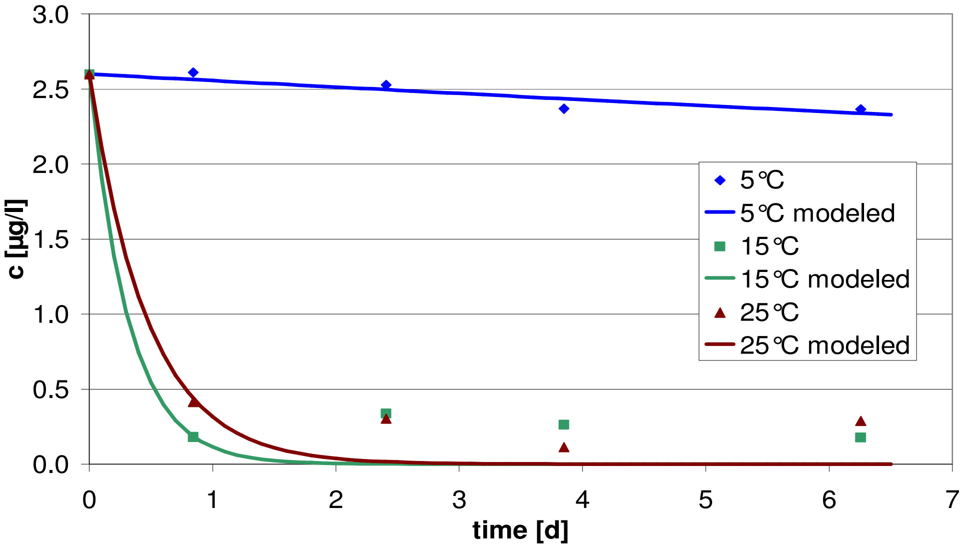


Figure 132 Degradation of 1,7-NDSA at different temperatures (v = 8.31 cm/d; n=3-10)

The behavior of 1,7- and 2,7-NDSA at different temperatures and retention times is presented in Figure 132, Figure 133, Figure 134 and Figure 135.

The data points represent the measured concentrations, whereas the drawn through lines show the results of modeling. Differences of measured start concentrations are related to variations in spiking.

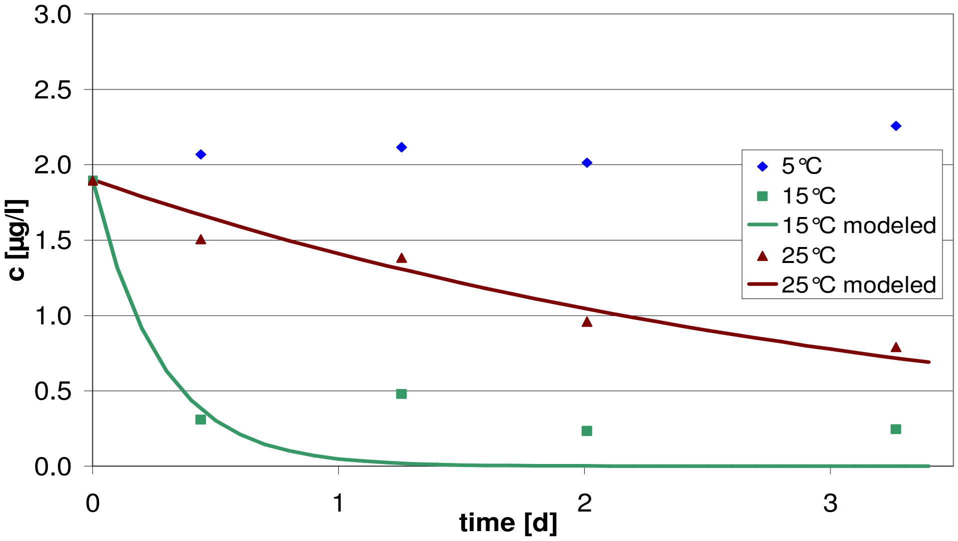


Figure 133 Degradation of 1,7-NDSA at different temperatures (v = 15.92 cm/d; n=3)

Figure 132 shows that at 5℃ a very slow removal of 1,7-NDSA was observed and even after more than 6 days of infiltration the removal rate was only around 10%. Under more favorable conditions, at 15℃ and 25℃, a considerably higher removal of 1,7-NDSA was found. After one day of infiltration approximately 90% of the initial concentration was removed (Figure 132). Unfortunately, no significant difference between the efficiency at 15℃ and 25℃ was observed at a pore velocity of 8.3 cm/d. Figure 133 confirms the stability of 1,7-NDSA at 5℃, but clarifies that 1,7-NDSA biodegradation at 15℃ was considerably faster than at 25℃. The degradation constant at 15℃ is similar during both experiments, but λ for the decay at 25℃ is smaller during the experiment with the higher pore velocity.

The complete stability of 1,7-NDSA at 5℃ might be explained by a threshold temperature between 5℃ and 15℃ under which a not-achievable activation energy limits biodegradation. The fact that such processes are of importance is confirmed by the rising fraction of non-degradable DOC with decreasing temperature that were found by Schoenheinz (2004). Similar to the results of the for 1,7-NDSA, Wesnigk et al. (2001) found a significant decrease of Nitrilotriacetat- mineralization under 7℃.

Table 39 Modeling results for 1,7-NDSA

	v = 8.31 cm/d			v = 15.92 cm/d		
	C_0 [mg/l]	λ [d^{-1}]	R^2	C_0 [mg/l]	λ [d^{-1}]	R^2
5°C	2.6	0.017	0.848	1.9	-	-
15°C		3.132	0.952		3.665	0.837
25°C		2.114	0.959		0.298	0.946

In both experiments the 1,7-NDSA was not mineralized completely, even under the most favorable conditions at 15°C. Therefore, the mathematical modeling of the 1,7-NDSA decay includes a systematic error. The degradation of 1,7-NDSA ceases after a concentration of about 0.3 µg/l is reached. This is maybe due to a threshold concentration. The existence of a threshold concentration would propose a metabolic degradation of 1,7-NDSA, since cometabolic degradations would not be affected by a threshold concentrations.

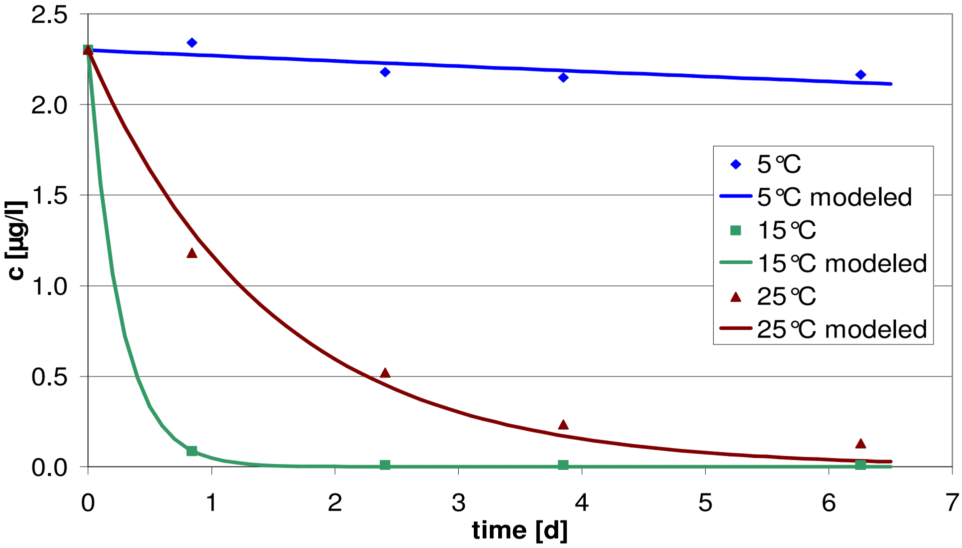


Figure 134 Degradation of 2,7-NDSA at different temperatures (v = 8.31 cm/d; n=3-10)

The results of the degradation experiments for 2,7-NDSA show a similar behavior of this NDSA-isomer. Nearly no removal of 2,7-NDSA was observed in the column at 5°C. At both pore velocities the removal at 15°C is more efficient than at 25°C. Furthermore, no or a much lower threshold concentration was observed during the mineralization of 2,7-NDSA.

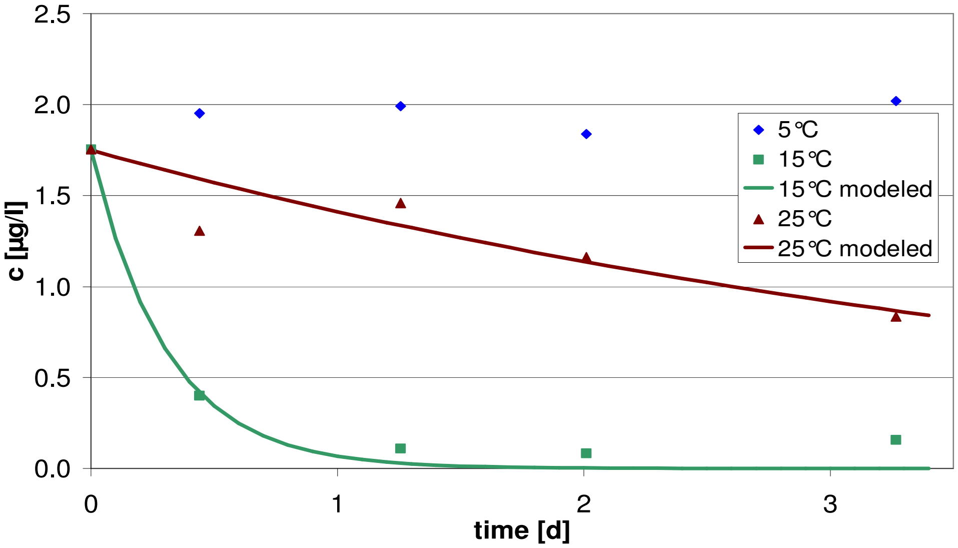


Figure 135 Degradation of 2,7-NDSA at different temperatures (v = 15.92 cm/d; n=3)

Between 15°C and 25°C a decreasing removal of both degradable NDSA-isomers with temperature was observed. This effect was actually clearer in the results of the experiment with shorter retention times. The temperature optimum for NDSA-degrading microorganisms is apparently around 15°C. Maybe this can be related to the adaptation processes. The population in the soil columns is comparable and adapted to conditions at the Lake Tegel bank filtration site. The mean annual water temperature of Lake Tegel is between 10°C and 15°C. Therefore, a more efficient NDSA-removal at 15°C might be due to the adaptation onto the conditions at Lake Tegel. Garing (2005) investigated at the same columns the removal of microcystin under different temperatures and found no improvement of mineralization rates between 15°C and 25°C.

Table 40 Modeling results for 2,7-NDSA

	v = 8.31 cm/d			v = 15.92 cm/d		
	C_0 [mg/l]	λ [d^{-1}]	R^2	C_0 [mg/l]	λ [d^{-1}]	R^2
5°C	2.3	0.013	0.687	1.75	-	-
15°C		3.857	0.999		3.252	0.98
25°C		0.676	0.999		0.215	0.79

Actually, for the experiment with higher pore velocity better degradation rates in a comparable time frame were expected due to a faster transport of nutrients to microorganisms. These expectations were not confirmed by the measurements. At 5°C and 25°C even a negative influence of increasing velocity was observed. However, most of the degradation took part in the first centimeters of the infiltration path.

Due to the higher pore velocity in the second experiment the contact time in the bioactive layer at the start of the columns was shorter and maybe not sufficient for an effective degradation. A longer adaptation period at higher velocities could have resulted in an extension of the bioactive layer in deeper parts of the filter bed. Eventually, this would lead to higher degradation rates in a similar time frame.

Additionally to the fate of NDSA in the soil column system the behavior of Iopromide and Sulfamethoxazole was investigated. The results of all measurements and the modeling of the fate of the X-ray contrast media Iopromide are presented in Figure 136 and Table 41. A good removal of Iopromide in soil passage was observed in all temperature controlled columns. Consistently, relatively high degradation constants of λ ~2 were found at all temperatures, proposing only very few influence of temperature onto the degradation efficiency of Iopromide. Comparing the Iopromide results with AOI findings it is proved that no dehalogenation of Iopromide occurred, because AOI was not degraded at all. It was already evident in other investigations that Iopromide is only metabolized by microorganisms.

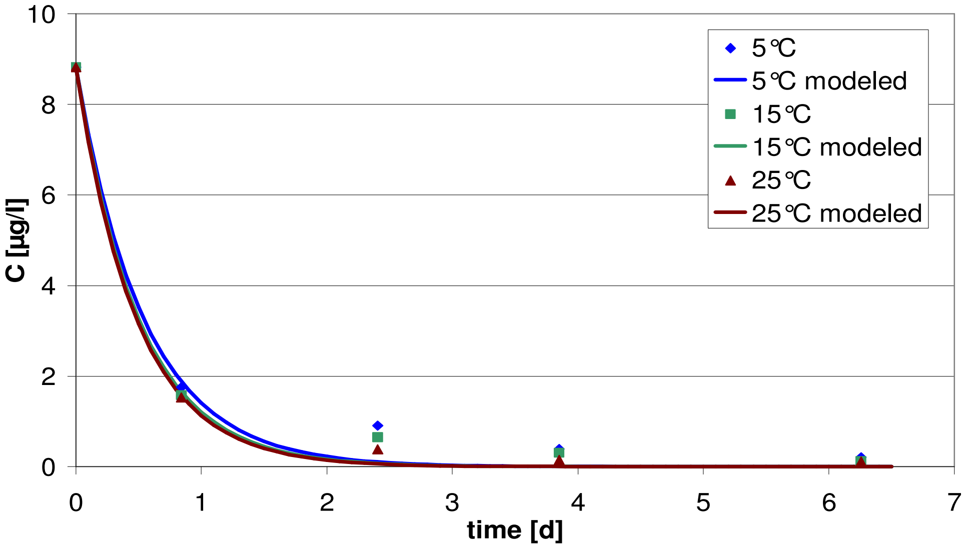


Figure 136 Degradation of Iopromide along the different columns (v=8.31 cm/d, n=3-10)

However, despite of the fact that Iopromid is only metabolized, it was found that Iopromide is apparently easy available for microorganism attack under all investigated temperature conditions. This implies a wide temperature optimum for the responsible microorganisms or a large variety of different microorganisms that are able to metabolize Iopromide. The results for Iopromide show no threshold concentration, which would point toward a metabolic biodegradation. This confirms results of short retention columns, which described a cometabolic degradation of Iopromide under anoxic conditions.

Table 41 Modeling results for Iopromide (v = 8.31 cm/d)

	C_0 [mg/l]	λ [d^{-1}]	R^2
5°C	8.82	1.836	0.984
15°C		1.991	0.992
25°C		2.056	0.997

Degradation of the antibiotic Sulfamethoxazole in the soil column system was monitored closely using the described sampling schedule. The results and the modeling are shown in Figure 137 and

Table 42. It was found that the removal significantly depends on temperature. At 5°C degradation of Sulfamethoxazole was considerably slower than in the 15°C and 25°C column. The degradation rate increased by the factor of 10 when the temperature rises to 15°C, whereas only little differences in λ were observed between 15°C and 25°C. Similar to 1,7-NDSA a threshold concentration of ~0.3 µg/l was found.

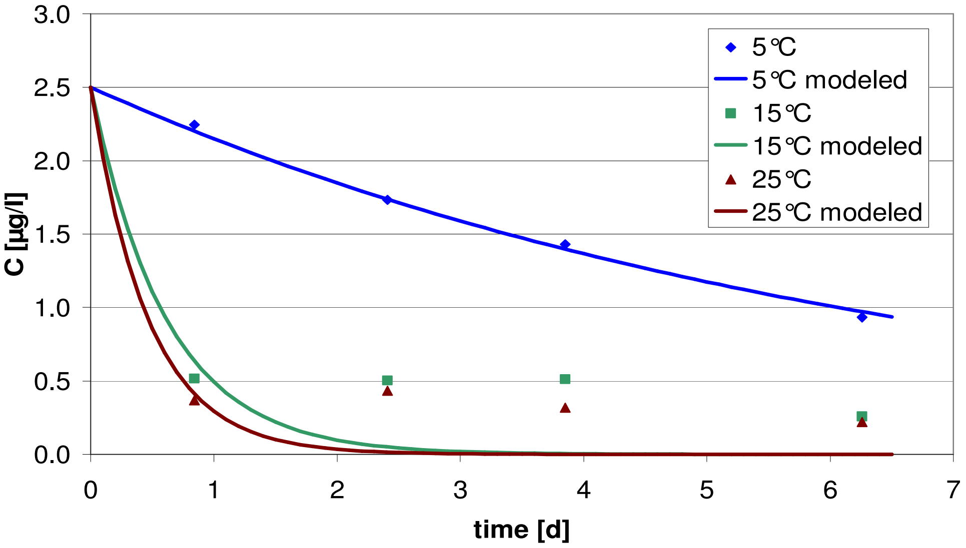


Figure 137 Degradation of Sulfamethoxazole along the different columns (8.31 cm/d, n=3-10)

Temperature optimum and spectrum of Sulfamethoxazole degradation differ from the results for the NDSA-degradation. Apparently, Sulfamethoxazole degrading organisms are more tolerant to temperature variations, because an efficient removal was observed at 15°C and 25°C. It might be possible that the optimal temperature for Sulfamethoxazole-decaying microorganisms is around 20°C and both experiments are similarly suboptimal. The threshold concentration points towards a metabolic process of specialized biomass, but it is also possible that several microbial strains with different temperature optima are able to utilize Sulfamethoxazole.

Table 42 Modeling results for Sulfamethoxazole (v = 8.31 cm/d)

	C_0 [mg/l]	λ [d^{-1}]	R^2
5°C	2.5	0.151	0.997
15°C		1.625	0.842
25°C		2.142	0.914

Results for Iopromide and Sulfamethoxazole behavior in the experiments with shorter retention times are not presented because the results were not representative. In the same period investigations with high spiking concentrations of microcystin were started, which possibly influenced the adapted biomass.

Overall, the degradation of Iopromide is more temperature tolerant than the degradation of the other investigated trace pollutants. This might be due to the fact that Iopromide is metabolized in a cometabolic process whereas the other trace organics are apparently removed by metabolic processes. Thus the temperature dependency can be explained as follows. Nonselective cometabolic enzymes are produced by many microbial strains with different temperature optima whereas metabolic degradation occurs by only few specialized strains with fixed temperature requirements.

1.4.4 Column experiments to assess the retardation coefficients

The column system for the determination of the retardation factor was installed at the TU Berlin. For the evaluation of the field data and the planning of the soil column experiments the retardation factor was of eminent importance. Low retardation factors were expected, because the investigated trace compounds were very polar. Since the particulate organic compound content of the sediment might influence the absorption processes of the organics during soil passage, the retardation tests were conducted with different sediments. Three different POC-contents were tested.

1.4.4.1 Set-up

The used column system consisted of three plexiglas-columns (Figure 138). Each column was 0.451 m long and had a diameter of 0.064 m (Volume: 1.45 l). Column I was filled with Lake Tegel bank material. The filling of column III was the industrial sand used for all column experiments (Ø = 0.7 – 1.2 mm). Column II was packed with a 50:50-mix (weight-based) of both materials. The columns were fed with drinking water (flow = 0.11 l/d), exchanging six pore volumes per day.

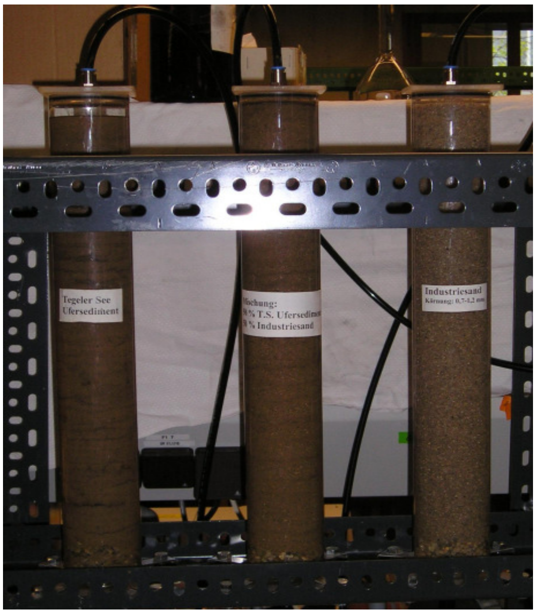


Figure 138 Soil columns for the determination of the retardation factor

To determine the retardation of Iopromide, Sulfamethoxazole and the NDSA-isomers 5 ml of a cocktail, containing the trace compounds and sodium chloride, was fed to the column in a pulse application. The cocktail consisted of a mixture of 40 g/l NaCl, 40 mg/l Iopromide and 40 mg/l 1,7-NDSA and 10 mg/l Sulfamethoxazole. The trace compound concentrations were selected in this range because very small sample volumes were taken from the columns and no concentration step was possible before analysis. Sodium chloride was used as an ideal tracer and a retardation factor of 1.0 was assumed. The behavior of the trace compounds was compared to the fate of electrical conductivity measured with a flow through-cell. The conductivity was logged in 5 minutes intervals. Sampling for the trace compound determination was conducted every 18 minutes. Therefore, the given concentrations are mean concentrations of this interval.

1.4.4.2 Results

Loss on ignition: Before the start of the experiments the loss on ignition was determined. The calculated values for the loss on ignition are shown in Table 43. As expected, bank material of Lake Tegel showed the highest loss on ignition (0.56 %), whereas the technical sand has the lowest loss on ignition (0.13 %). The value of the loss on ignition of the technical sand was above expectations, because it should not contain any organic material. As expected, the ignition lost of the mixture of both materials was near the mean of both materials, proofing the determination method.

Table 43 Loss on ignition of the different filter materials

Number of column	Loss on ignition [%]
I	0.56
II	0.34
III	0.13

Trace compounds: Results of the determination of the retardation coefficients are shown in Figure 139. The Iopromide as well as the Sulfamethoxazole peak reached the end of the columns in all experiments with no significant time differences (compared to the sodium chloride peak). Thus, it appears that neither Iopromide nor Sulfamethoxazole are retarded by the sediment. A difference between the materials with different POC-content was not observed. The results of the 1,7-NDSS were not shown because they were comparable to those of Iopromide and Sulfamethoxazole.

Conclusions concerning the dispersion can be drawn from the different shapes of the peaks. Column II generated a more expanded peak (decreased amplitude) in comparison with the other columns. This indicates a higher dispersion and is consistent with the mixing of the two sediment types. Furthermore, column II was found to have the lowest porosity of the tested columns.

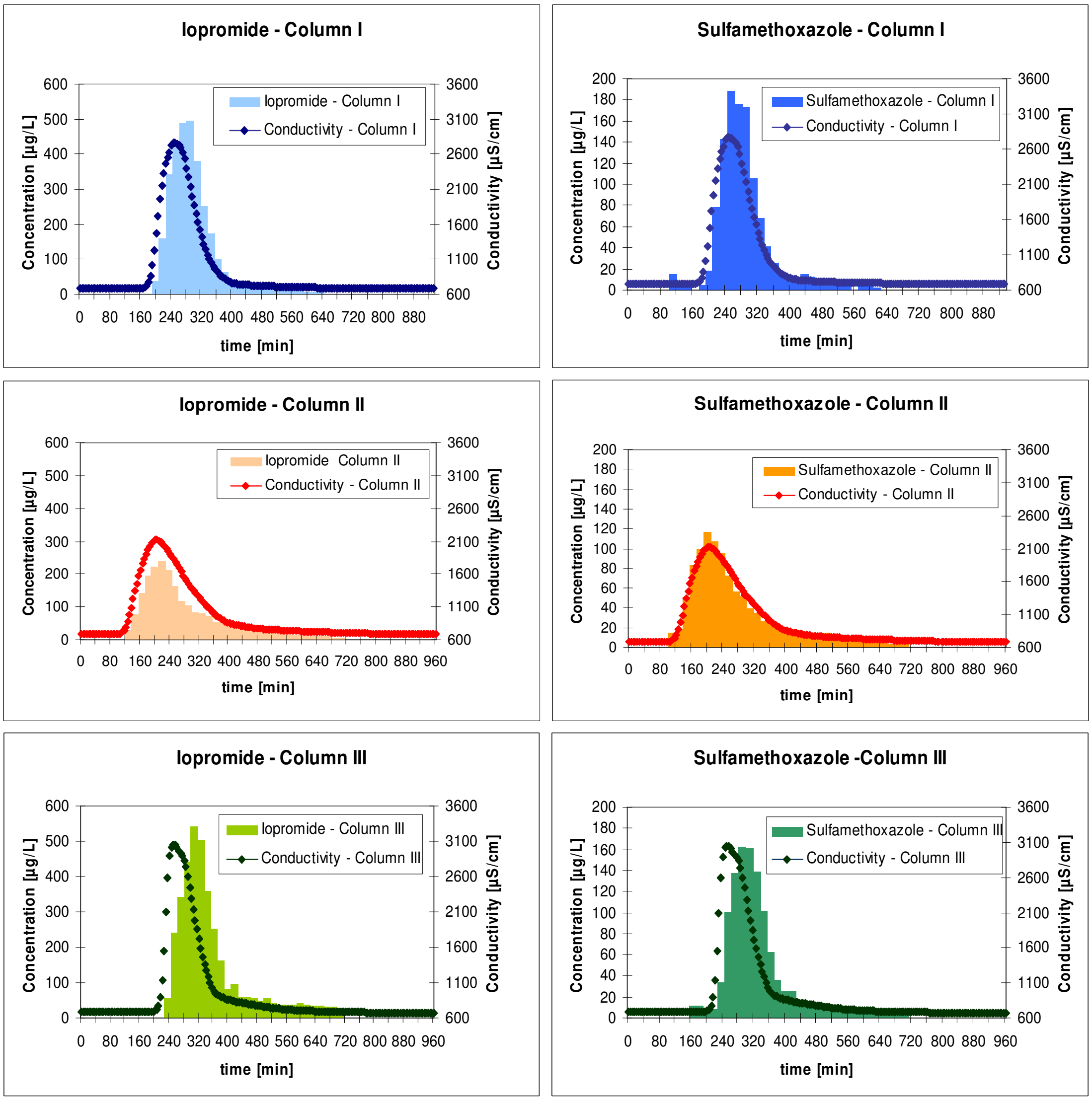


Figure 139 Retardation of Iopromide and Sulfamethoxazole in comparison with the electrical conductivity at different column materials

Calculation of the pore velocity (V), the dispersion (D) and the retardation coefficient (R) were carried out with the program CXT fit (Version 2, Free Software Foundation, Inc. Boston, USA). Determination of V and D was conducted by inverse modeling with the help of the measured conductivity and the assumption R=1 for sodium chloride. The next step was the inverse calculation of R and µ of the different trace organics for each column. Generated values are listed in Table 44. Additionally, the porosity was determined by the ratio of Darcy- and pore velocity.

Table 44 Retardation coefficients of the trace organics for different filter materials

	Porosity [%]	V [m/d]	D [m^2/d]	R		
				Iopromide	Sulfamethoxazole	1,7-NDSS
Column I	33.4	2.503	0.014700	1.076	1.029	1.004
Column II	29.5	2.833	0.050000	1.064	1.000	1.000
Column III	35.1	2.377	0.009513	1.136	1.092	1.094

The results of the CXT-fit modeling, shown in Table 44, confirm the conclusions. The results are shown in Figure 140. A mass balance proved that a partial degradation of all three trace organic substances took place in the columns. During modeling, this was taken into account by adjusting the parameter µ. The data showed that degradation of the compounds was comparable in column I and column III, whereas column II showed a slightly elevated degradation. The dispersion in column II was determined with 0.05 m^2/d, which is five times higher than the dispersion of the other columns (dispersion 0.01 – 0.015 m^2/d). The mixing of both materials with different grain sizes leads to differences in the lengths of the infiltration paths and thus to a higher dispersion. The porosity of column II was 29.5 %, whereas values for column I and column III show higher values of 33.4 % and 35.1 %. The pore velocity, which is linked to the porosity, was calculated for column II with 2.8 m/d. In contrast column I and column III show smaller pore velocities of only 2.5 m/d and 2.4 m/d.

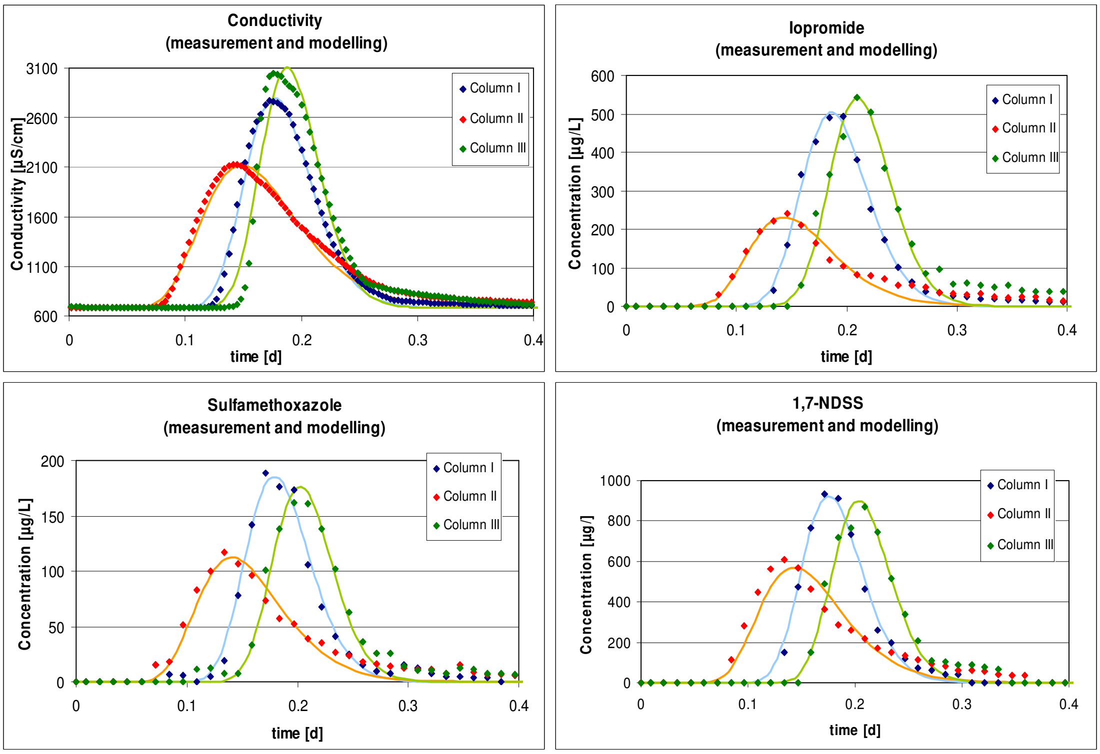


Figure 140 Conductivity and concentration of the trace organics (measured and modeled)

Independently from the material (POC-content) used for the column filling, the retardation coefficient reached values of 1.0-1.1. This proves that retardation does not play an important role for the behavior of the investigated compounds in the subsoil. Contrary to the expectations, different fractions of organic matter (see Table 43) showed no impact on the retardation. In Figure 140 color-coordinated graphs show the measured values (dots) and the modeled breakthrough (line). It is obvious, that the characteristic of the measured data comply with the results of the modeling.

Summarizing, it was confirmed that the polar and hydrophilic character of the investigated trace substances prevents an adsorption onto organic or inorganic parts of the sediment. Retardation was found of no importance for the tested trace compounds. It is assumed that the results can be transferred to the field to understand the behavior of these substances in the field better.

2 References

Bahr, C. (2002) Untersuchungen zur katalytischen Ozonung refraktärer Organik in Abwasser (Catalytic Ozonation of Refractory Organic Compounds in Waste Water) Diploma thesis at Department of Water Quality Control, Technical University of Berlin (in German)

Bahr and M. Jekel (2005) Final Report of "Pilotuntersuchungen zur kombinierten oxidativ-biologischen Behandlung von Klärwerksabläufen für die Entfernung von organischen Spuren- und Wirkstoffen und zur Desinfektion (PILOTOX)", Research Project of the Berlin Center for Competence for Water.

Berliner Wasser Betriebe (Berlin Water Works - BWB) (2003) http://www.bwb.de.

Cosovic B., D. Hrsak, V. Vojvodic and D. Krznaric (1996) Transformation of organic matter and bank filtration from a polluted stream. Water Res., 30(12), 2921-2928.

Davis J. A. (1982) Adsorption of natural dissolved organic matter at the oxide/ water interface. Geochim. Cosmochim. Acta 46 (1982), p. 2381-2393

Drewes J. and P. Fox (1999) Behaviour and Characterization of Residual Organic Compounds in Wastewater Used for Indirect Potable Reuse. Water Science and Technology, 40 (4-5) 391–398

Drewes J. E. (1997) Untersuchungen zum Verhalten organischer Abwasserinhaltsstoffe bei der Wiederverwendung kommunaler Kläranlagenabläufe zur künstlichen Grundwasseranreicherung. (Behavior of organic compounds in domestic effluents used for groundwater recharge). Fortschritt-Berichte VDI-Verlag No 174, Umwelttechnik, Düsseldorf (in German)

Findlay R. H., G.M. King, L. Watling (1989) Efficacy of Phospholipid Analysis in Determining Microbial Biomass in Sediments. Applied and Environmental Microbiology, 11/1989, 2888-2893

Fritz B., J. Sievers, S. Eichhorn and A. Pekdeger (2002) Geochemical and hydraulic investigations of river sediments in a bank filtration system. In: Dillon, P. (ed.): Management of Aquifer Recharge for Sustainability, Balkema, Adelaide, Australia 95-100.

Gimbel R., M. Gerlach, H.-J. Mälzer (1992) Die Testfiltermethode als Simulationsgrundlage des Störstoffverhaltens bei Untergrundpassagen. (A method using test filters as an approach to simulate underground passage of undesired compounds) Sechstes Mülheimer Wassertechnisches Seminar. Berichte aus dem

Rheinisch-Westfälischen Institut für Wasserchemie und Wassertechnologie. Bd. 6, 126-163, Mülheim

Hartig C. (2000) Analytik, Vorkommen und Verhalten aromatischer Sulfonamide in der aquatischen Umwelt. (Analysis and behavior of aromatic sulfonamides in the aquatic environment). Doctoral Dissertation accepted by: Technical University of Berlin, School of Process Sciences and Engineering, 2000-08-29, http://edocs.tu-berlin.de/diss/2000/hartig_claudia.htm

Heberer T., I.M. Verstraeten, M.T. Meyer, A. Mechlinski, and K. Reddersen (2001) Occurrence and fate of pharmaceuticals during bank filtration—Preliminary results from investigations in Germany and the United States. Water Resour. update, 120, 4–17

Hiemstra P., R. J. Kolpa, J. M. van Eekhout, A. L. van Kessel, E. D. Adamse and J. A. M. van Paassen. Natural recharge of groundwater: Bank filtration in the Netherlands. J. Water Supply: Res. T., 52(1), 37-47.

Hoyer O., B. Lüsse, H. Bernhard (1985): Isolation and characterization of extracellular organic matter from algae. Zeitschrift Wasser-Abwasser-Forschung (Journal of water and waste water research) 18, 76-90

Huber S. and A. Balz (2005) DOC-Labor Dr. Huber, What is LCOCD about, 07.01.2006, <http://www.doc-labor.de>

Huber S. and F. Frimmel (1996) Gelchromatographie mit Kohlenstoffdetektion (LC-OCD): Ein rasches und aussagekräftiges Verfahren zur Charakterisierung hydrophiler organischer Wasserinhaltsstoffe (Gelchromatography coupled with carbon detection: A fast and powerful method to characterize hydrophilic organic water constituents). Vom Wasser, Vol. 86,277-290.

Hütteroth A., A. Putschew, M. Mania and M. Jekel (2004) Cyanobakterien: Die Quelle für bromorganische substanzen in Oberflächenwässern? Proceedings of the annual Meeting of the Water Chemical Society Germany, 17.-19.05.2004, Bad Saarow, Germany.

Jekel M. and S. Wischnack (2000) Herkunft und Verhalten iodorganischer Verbindungen im Wasserkreislauf. (Origin and behavior of organic iodine compounds in water cycles). Chemische Streßfaktoren in aquatischen Systemen. Schriftenreihe Wasserforschung, Vol 6, B. Weigert, C. Steinberg and R. Brüggemann (eds.), Wasserforschung e.V., Berlin, 61-69.

Kretschmar, R.,1991. Kulturtechnisch-Bodenkundliches Praktikum, ausgewählte Laboratoriumsmethoden, eine Anleitung zum selbständigen Arbeiten an Böden. Christian-Albrechts-Universität Kiel, 7. Auflage.

Kuehn, W. (2003) Development of drinking water treatment along the Rhine River with special emphasis on riverbank filtration. 6th International Symposium on Water Supply Technology. Kobe, March 18 - 19, 399 - 412.

Miettinen I. T., P. J. Martikainen and T. Vartiainen (1994) Humus Transformation at the bank filtration water plant. Water Sci. Technol., 30(10), 179-187.

NASRI. 2003. http://www.kompetenz-wasser.de.

Oleksy-Frenzel J., S. Wischnack and M. Jekel (2000) Application of ion-chromatography for the determination of the organic-group parameters AOCl, AOBr and AOI in water. Fresen. J. Anal. Chem., 366, 89-94.

Pekdeger A., G. Massmann, B. Ohm. 2nd Periodic Report: Hydrogeological-hydrogeochemical processes during bank filtration and groundwater recharge using a multitracer tracer approach. NASRI-Projekt, (2004) 80 pages.

PreSens (2005) Precision Sensing GmbH, Support, How does a oxygen microsensor work?, 01.12.2005 <http://www.presens.de/html/start.html>

Putschew A., M. Mania and M. Jekel (2003) Occurrence and source of brominated organic compounds in surface waters. Chemosphere, 52, 399-407.

Putschew A., S. Schittko and M. Jekel (2001) Quantification of triiodinated benzene derivatives and X-ray contrast media in water samples by liquid chromatography-electrospray tandem mass spectrometry. J. Chromatogr. A, 930, 127-134.

Ray C., T. Grischek, J. Schubert, J. Wang and T. Speth (2002) A perspective of riverbank filtration. J. Am. Wat. Wks. Assoc., 94(4), 149-160.

Rittmann B.E. and V.L. Snoeyink (1984) Achieving biologically stable drinking water. J. Am. Wat. Wks. Assoc., 76(10), 106-114.

Schittko S., A. Putschew and M. Jekel (2004) Bank Filtration: a suitable process for the removal of iodinated X-ray contrast media? Wat. Sci. Tech., 50 (5), 261-268

Schmidt C.K., F.T. Lange; H.-J. Brauch. (2004) Assessing the impact of different redox conditions and residence times on the fate of organic micropollutants during riverbank filtration. Proceedings “4th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water”, 13.-15.10.2004, Minneapolis, Minnesota.

Schoenheinz D. (2004) DOC als Leitparameter zur Bewertung und Bewirtschaftung von Grundwasserleitern mit anthropogen beeinflusster Infiltration, Doctoral Dissertation accepted by: Technical University Dresden, School of Geohydrological Sciences, 2004-03-15.

Schoenheinz D., T. Grischek, E. Worch (2003) Investigations into Temperature effects on DOC degradation during riverbank filtration. Paper presented at the 11th Biennial Symposium on Groundwater Recharge, Phoenix, AZ, June 5-7.

Schulz H. J. (1998) Gutachten über die Nutzbarkeit einer Säulenanlage zur Durchführung von Simulationen des Abbauverhaltens von Schadstoffen in der Grundwasserpassage (Certificate on the usability of a soil column system for simulation experiments on the fate of pollutants during infiltration). Report of the German Federal Environmental Agency (8 pages).

Stan H. J. and M. Linkerhäger (1994) Vorkommen von Clofibrinsäure im aquatischen System – Führt die therapeutische Anwendung zu einer Belastung von Oberflächen-, Grund- und Trinkwasser? (Occurrence of clofibric acid in aquatic systems – Pollution of surface-, ground and drinking water by therapeutical use?). Vom Wasser, 83, 57 – 68.

Storm T. (2001) Aromatische Sulfonate - Untersuchungen zum Stoffverhalten in Industrieabwasser und aquatischer Umwelt mit HPLC-MS. (Aromatic sulfonates - Investigations into the behaviour in industrial wastewater and the aquatic environment with HPLC-MS), Doctoral Dissertation accepted by: Technical University of Berlin, School of Process Sciences and Engineering, 2002-05-27. http://edocs.tu-berlin.de/diss/2002/storm_ thomas.htm.

Storm T., T. Reemtsma, M. Jekel (1999) Use of volatile amines as ion-pairing agents for the high-performance liquid chromatographic-tandem mass spectrometric determination of aromatic sulfonates in industrial wastewater. J. Chromatogr. A, 854, 175-185.

Stüber, M., T. Reemtsma, M. Jekel (2002) Determination of naphthalene sulfonates in tannery wastewater and their behaviour in a membrane bioreactor. Vom Wasser, 98, 133-144.

Ternes T. A. and R. Hirsch (2000) Occurrence and behaviour of x-ray contrast media in sewage facilities and the aquatic environment. Environ. Sci. Technol., 34(13), 2741-2748.

Ternes T. A., M. Meisenheimer, D. McDowell, F. Sacher, H. Brauch, B. Haist-Gulde, G. Preuss, U. Wilme and N. Zulei-Seibert (2002) Removal of Pharmaceuticals during Drinking Water Treatment. Environ. Sci. Technol., 36(17), 3855-3863.

Tufenkji N., J. N. Ryan and M. Elimelech (2002) The promise of bank filtration. Environ. Sci. Technol. A-Pages, 36(21), 422A-428A.

Van der Kooij D. (2003) Managing regrowth in drinking water distribution systems, in WHO-Heterotrophic plate count and drinking water safety. eds. by J. Bartram, J. Cotruvo, M. Exner, C. Fricker and A. Glasmacher, IWA Publishing, London, UK.

Verstraeten I.M., Th. Heberer, and T. Scheytt (2002) Occurrence, characteristics, and transport and fate of pesticides, pharmaceutical active compounds, and industrial and personal care products at bank-filtration sites. In Riverbank Filtration—Improving Source-Water Quality, chapter 9, eds. C. Ray, G. Melin, and R.B. Linsky. Dordrecht, Netherlands: Kluwer Academic Publishers.

Weiss W. J., E. J. Bouwer, W. P. Ball, C. R. O´Melia, R. Aboyetes and T. F. Speth (2004) Riverbank filtration : Effect of ground passage on NOM character. J. Water Supply: Res. T., 53(2), 61-83.

Wesnigk, J.B., M. Keskin, W. Jonas, K. Figge, G. Rheinheimer (2001) Predictability of Biodegradation in the Environment: Limits of Prediction from Experimental Data. in Biodegradation and Persistence. ed. B. Beek, Springer-Publishing, Berlin-Heidelberg, Germany.

Wischnack S. and M. Jekel (2000) Untersuchungen zu iodierten organischen Stoffen im Tegeler See und im Wasserwerk Tegel. Final report of a research project founded by the Berlin Water Works, TU Berlin, Department of Water Quality Control, February 2000

Ziegler D. (2001) Untersuchungen zur Nachhaltigkeit der Uferfiltration und künstlichen Grundwasseranreicherung in Berlin. (Investigations on the sustainability of bank filtration in Berlin's water cycle), Doctoral Dissertation accepted by: Technical University of Berlin, School of Process Sciences and Engineering, 2001-04-24. http://edocs.tu-berlin.de/diss/2001/ziegler_doerte.htm

Ziegler D., C. Hartig, S. Wischnack and M. Jekel. 2002. Organic substances in partly closed water cycles. In Management of Aquifer Recharge for Sustainability. ed. P. Dillon. Sweets & Zeitlinger, Lisse.

Zöfel P. (2002) Statistik verstehen. (Comprehensive statistics), Addison-Wesley, Munich, Germany