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INTERMEDIATE REPORT

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NASRI Natural and Artificial Systems for Recharge and Infiltration
Period 2001-2002
Project acronym: NASRI

by

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for

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2st periodic report

(Reporting period January to December 2003)

"Hydrogeological-hydrogeochemical processes during bank filtration and ground water recharge using a multi tracer approach"

Abstract:

The bank-filtration field sites Lake Tegel and Lake Wannsee as well as the artificial recharge site GWA Tegel are described qualitatively with regard to their clogging layer, sedimentary, hydraulic and hydrochemical properties to give a solid basis for the interpretation of specific compounds evaluated within NASRI and for subsequent modeling and quantification of the data.

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1 Extended Summary:

The present report characterizes the field sites Lake Tegel and Lake Wannsee as well as the artificial recharge site GWA Tegel in terms of their clogging layer, sedimentary, hydraulic and hydrochemical properties. As a result, a solid basis for the interpretation of specific compounds evaluated within NASRI and for subsequent modeling and quantification of the data is given. Major problems or difficulties where identified, in order to focus investigations on aspects not fully understood to date in the next project phase.

The combination of different tracers enables the interpretation of the flow regime. With the help of T/He analysis, ages of different water bodies can be estimated. The analysis of tracer showing distinct seasonal variations is used to estimate travel times while water constituents which are either mainly present in the bank filtrate or the background water are used for mixing calculations.

The proportions of treated wastewater in the surface water were estimated in front of the transects. The surface water composition varies largely both in time and space, which is a problem at Wannsee, where the surface water sampling point is not representative for the bank filtration input. Estimates for travel times of the bank filtrate to individual observation and production wells are given and vary between days and several months. The production wells are a mixture of bank filtrate and water from inland of the wells and deeper aquifers, proportions of bank filtrate are given where possible to differentiate between contaminant removal and dilution. They vary between < 20 and > 80 %. The new observation wells enable a vertical differentiation of the infiltrate. It becomes clear that at Tegel and Wannsee, there is a strong vertical succession towards larger proportions of considerably older bank filtrate with depth. At the Wannsee transect, the observation wells deeper than the lake do not reflect the surface water signal at all. It will be important to combine the new information with hydraulic information of existing flow models (mainly of the IGB “model” group).

The evaluation of the redox conditions shows that redox successions proceed with depth rather than (only) in flow direction. In addition, the redox zoning (as characterised by the appearance or disappearance of redox sensitive species) is very transient. The zones are much wider in winter than in summer, in particular at the artificial recharge site GWA Tegel, probably due to temperature effects. This poses a challenge for the desired modelling and the interpretation of data from redox-sensitive substances.

2 Objectives of this project:

The main objective of the project is the detailed hydrogeological analysis of the bank filtration system at the target transects at Lake Tegel, Lake Wannsee and the artificial recharge pond 3 in Tegel (GWA) as well as at the semi-technical facilities in Marienfelde. The investigations aim for the general description of the hydrogeological, hydraulic, hydrogeochemical and hydrochemical conditions at the surface water/sediment/groundwater interface as well as within the aquifer at all sites studied on the basis of knowledge gained during previous investigations. Altogether, this will help to improve the knowledge on chemical processes accompanying infiltration including the retention of inorganic and organic compounds in both the saturated and the unsaturated zone close to the surface water source.

A major focus of the study is on the evaluation of spatial and temporal changes in water chemistry and quality depending on water flow paths and velocities which are extremely transient due to continuously changing pumping regimes of the production wells at all sites. The use of a combination of different tracers will help to derive travel times from the surface water to the productions wells, validate flow models and enable the calculation of the fraction of treated sewage in the bank-filtrate. Correlation between tracers and chemical parameters will allow to estimate the retention and degradation of the (sewage bound) chemical compounds in the sediments.

The first project phase (NASRi report 1) focused on the installation of new observation wells to improve sampling facilities and gain a better spatial resolution at all sites studied. First hydraulic and geochemical sediment properties were determined, surface and groundwater levels were continuously monitored which lead to the creation of a solid basis to understand the hydraulics and the geology of the sites.

Besides others, the main objective of the second project phase (this report) was to get an overview on travel times, mixing proportions and the hydrochemical situation at the field-sites studied.

The key questions dealt with were:

- What are the travel times from the surface water to observation and production wells?
- What is the proportion of bank-filtrate (and likewise deeper and landside groundwater) in the production wells?
- What is the proportion of treated wastewater in the surface water and production wells?
- What are the hydrochemical conditions at the sites, in particular with regard to redox conditions?

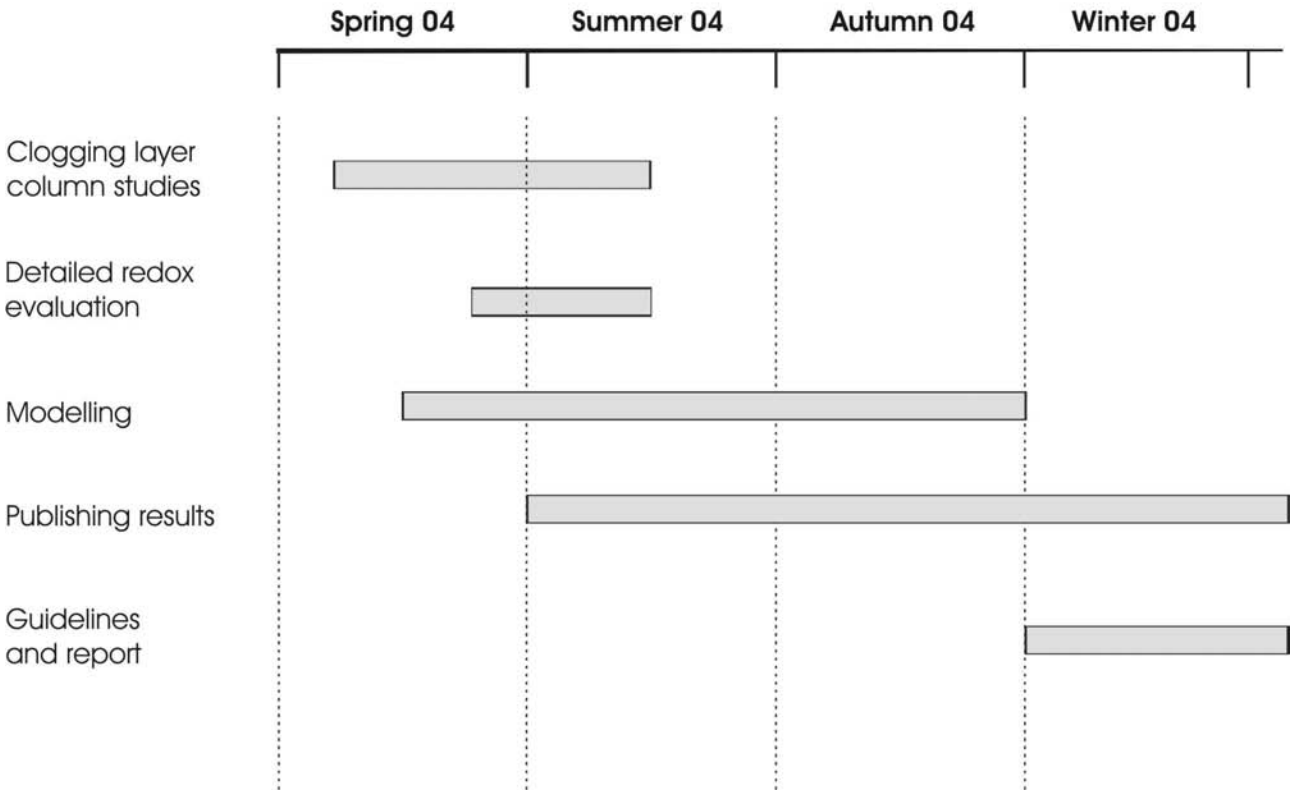
This is important because:

- Only with the knowledge of the time-scales of the processes studied, a definition of rates is possible.

- It is important to differentiate between dilution and real removal of potential contaminants during bank filtration.
- In order to understand the behaviour of specific substances studied by all working groups, the hydrochemistry, in particular the redox-state of the systems has to be known.

The aim of the last project phase will be the quantification of the processes described rather qualitative within this report. This will partly be done using models and in close cooperation to all other NASRI project partners.

Timetable



3 Intended and achieved tasks for the reporting period

Task	Achieved ?	Comments
Intended tasks (report 1):		
Monthly sampling / analysis of REE, $\delta^{18}O$ and δD	yes	
Evaluation of new REE and isotopic data collected since May 2002	yes	
Completion and publishing of the tracer test evaluation	yes	hydraulic model and results of analysis have been given to IGB for subsequent transport modeling; student thesis finished July 2003, paper is written mainly by B. Wiese (IGB), will be documented in IGB report
Completion of geological and geochemical description of sediments	yes	finished
Hydraulic simulation (2-D at transect) of a complete cycle of emptying and refilling of the artificial recharge pond Tegel	no	student project still being worked on
Completion of multi-tracer study of the surface water system of the Havel	yes	student project finished in July 2003 (within a DFG project but beneficial for NASRI
Sampling campaign of production wells near the artificial recharge pond Tegel	yes	galleries Saatwinkel and Hohenzollernkanal and surrounding observation wells were sampled together with BWB in summer 2003
Large-scale data evaluation (hydraulics and chemistry from well sampling campaign) in the surrounding of the artificial recharge pond Tegel	yes (almost)	to gain a better idea on the interaction between ponds, well galleries, lake, canal and the native groundwater influencing the transect, student project is almost finished
Sampling of all new observation wells at the 3 field-sites in January and February	yes	parallel to monthly sampling of BWB (old piezometers), the new wells were sampled by the FU in order to overcome capacity problems at BWB
Sampling of colloids for a first screening	yes	sampling campaign in summer 2003, analysis by Dr. Schäfer, Karlsruhe; due to problems with oxygen-free sampling no satisfactory results so far; will be repeated in spring
Investigations of clogging layer	started	cores were taken at Wannsee for geochemical and permeability analysis; some are currently prepared as columns
Evaluation of water quality data analyzed by BWB since May 2002	yes	hydrochemical system analysis with regard to standard parameters

Evaluation of the redox regimes	party	only with standard parameters, $\delta^{34}S$ and $\delta^{18}O$ of sulfate, δ-^{13}C of HCO_3 (and possibly more) will be done soon
Modification of existing flow model for bank filtration site Lake Tegel for transient conditions	no	is instead done by IGB, hydraulic data was therefore made available to IGB
Additional achieved tasks:		
Geochemical modeling of pore water data of the Lake Tegel mud	yes	visiting student project, with support of J. Greskowiak (IGB "model" group)
Temperature modeling of Lake Tegel data	yes	visiting student project using a modelmaker model developed by E. Holzbecher (IGB"model" group)
Conceptual modeling of well scenarios at the Tegel gallery	yes	combined student project supervised by IGB and FU (documented in IGB report)
Column experiments with large columns and Gd-DTPA	yes	finished in cooperation with DFG-project A. Knappe (results see Appendix 2)
Batch experiments with clogged Lake Wannsee sediments and drugs	yes	Joint experiments conducted at FU with substances applied and analysed by TU (drug group), experiments finished but still evaluated
Batch experiments with clogged Lake Wannsee sediments and Gd-EDPA	yes	Finished at FU within DFG project A. Knappe (see Appendix 2)
Analysis and interpretation of standard chemistry of large columns at UBA	yes	Sampling started in June 2003 and was first done every 2 weeks and is currently done monthly. Data was passed on to "organic" and "model" groups (~ 150 samples analyzed)
Analysis of standard chemistry during 2 slow sand filtration experiments and 4 enclosure experiments	yes	~ 15 samples each (~ 90 samples) were analysed, results were given to algae group (UBA) for interpretation of experiments
Supervision and planning of installation of deep observation well near well 13 in at transect Lake Tegel	yes	Well TEG374 is 37-39 m deep (filter screen above aquitard at depth of lowest well filter screen)
Analysis of standard cations and anions, δ18O and δD in unsaturated samples from GWA Tegel	yes	Cooperation IGB/FU, to support PhD thesis J. Greskowiak (IGB "model" group), ~ 200 samples were analysed
Drilling and analysis of sediment core within GWA storage pond 3	yes	Cooperation IGB/FU, to support PhD thesis J. Greskowiak (IGB "model" group)
Sampling for and evaluation of T/He for age dating	yes	Was done at observation and production wells at all three sites, analysis at Helis laboratory, University of Bremen, some newer wells still to be done

4 Methods

4.1 Tracer methods

The following pages give an overview on sediment properties, hydraulics, travel times, mixing proportions and hydrochemistry at all field-sites. The travel times and mixing proportions are based on the evaluation of available tracer data, mainly δD, $\delta^{18}O$, measured at the Alfred-Wegener-Institute in Potsdam and parameter measured routinely by BWB. Temperature is registered daily in most observation wells with automatic data logger.

Several tracers are useful to estimate either travel times from lake to production well or the proportion of bank-filtrate in the production wells. Some of these may behave like conservative, non-reactive tracers, useful to study the water movement; others may be particularly useful to identify effluent influence or the proportion of saline deeper groundwater. An overview on different tracers, their origin and difficulties associated with their use in Berlin is given in Table 1 (compare also Table 1, Appendix 1).

In case the abstracted water is a mixture of surface water and background groundwater only, the percentage of bank filtrate in the well (X) can be calculated as:

$$X[\%] = \frac{C_w - C_{GW}}{C_{SW} - C_{GW}} * 100$$

With C as the concentration of a suitable tracer in the groundwater (C_{GW}), well (C_w) or surface water (C_{SW}). The simple mixing formula can be used under the premise that the differences between ground and surface water are large and relatively stable and the well water is a mixture of 2 water components only. If several filter screens exist in different aquifers the calculation is more difficult (for example at Wannsee).

The boxplots were done with available data from May 2002 to October 2003. Because some of the observation wells have only been sampled since January 2003 or have fallen dry, the number of the samples varies and for some wells, only very few samples were analyzed. Therefore, the boxplots are only meant to give a first overview and time-series of the relevant wells have to be consulted.

Table 1:Overview on most important major tracer applicable in Berlin.

Tracer:	Origin:	Useful for the interpretation of:	Difficulties:
δD, $\delta^{18}O$	surface water with seasonal variations (precipitation)	water movement, proportion of bank filtrate in raw water	none, conservative tracer
Temperature	surface water with seasonal variations	water movement	retarding
Cl^-	surface water with seasonal variations (WWTP)	water movement	only if influence of saline groundwater can be excluded
Cl^-, Na^+, B	saline deeper groundwater	proportion of deeper saline groundwater	may vary strongly locally
SO_4^{2-}	dissolution of gypsum derived from building rubble in the shallow aquifer	proportion of shallow "native" groundwater	may vary strongly locally
B	surface water with seasonal variations (WWTP)	water movement, proportion of bank filtrate in raw water	only if influence of saline groundwater can be excluded
Gd-DTPA	surface water with seasonal variations (WWTP)	water movement, proportion of bank filtrate in raw water	possibly degradable
EDTA	surface water, effluent	water movement, proportion of bank filtrate in raw water	sometimes the background groundwater has also got very high concentrations
K	surface water with seasonal variations (WWTP)	water movement	Only if sorption on sediment can be excluded (e.g. Tegel), Generally not behaving conservative
T/He	Surface water, through atmospheric input	groundwater "age"	minimum age required is 2 months

4.2 Age dating

Samples were taken from selected wells T/^{3}He analysis. The method uses the ratio of the concentration of radioactive tritium (^{3}H or T) and its decay product ^{3}He in the groundwater to determine the groundwater age. The "age" τ is the time passed since the water had its last contact with the atmosphere, in the present case, since the water infiltrated into the aquifer. It is defined as (TOLSTIKHIN & KAMENSKIY, 1969):

$$t = \frac{t_{1/2}}{\ln 2} \ln\left(1 + \frac{^3He_{tri}}{^3H}\right)$$

with: τ = age [a]

$t_{1/2}$ = half-life of ^{3}H (12.43 years)

$^3He_{tri}$ = fraction of total ^{3}He produced by ^{3}H decay [TU]

^3H = tritium concentration [TU]

Tritium is expressed in tritium units [TU]. One TU corresponds to a T/^{3}H ratio of 10^{-18}. The natural ^{3}H concentration in the atmosphere is low (about 10 TU). In the 1950s and early 1960s the ^{3}H content in the atmosphere increased several orders of magnitude due to nuclear bomb testing. The concentrations have since been decreasing (Fig. 1). The method has been used in many groundwater studies but only in STUTE et al. (1997) and BEYERLE et al. (1999) did the groundwater originate from bank-filtration.

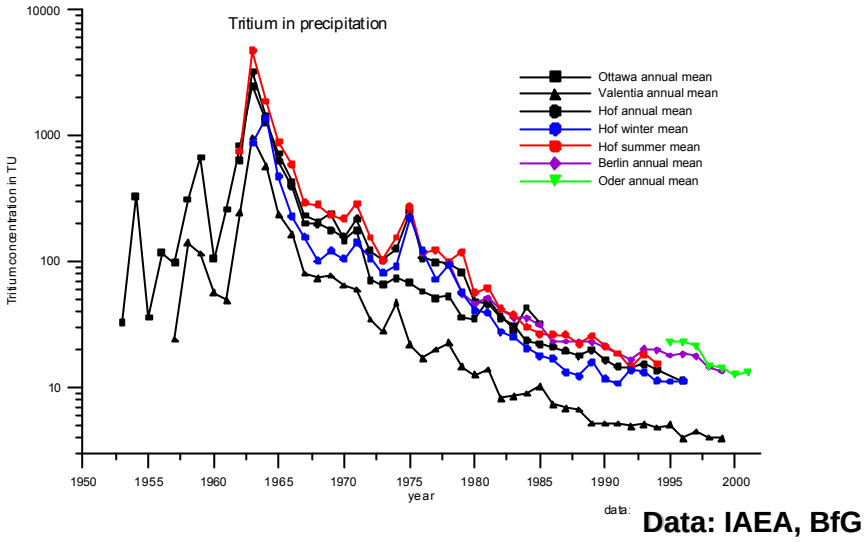


Figure 1: Tritium in the precipitation of several sites in the world (data source: IAEA, BfG).

5 Results

5.1 Surface Water Investigations

Surface water investigations were done within a student project (Doreen Richter, in cooperation with DFG project A. Knappe) in 2001 and 2002. The necessity to take the surface water into consideration when investigating the bank filtration system arises from the fact that it is the source of the bank filtrate and therefore, hydrochemical variations have a large impact on the quality of the bank filtrate.

Although the surface water is sampled within NASRI on a monthly basis, results only give very selective information for one particular point. Results of additional surface water investigations can help to understand the processes influencing the surface water quality and give an idea on its temporal and spatial variations. More detailed information on the Berlin Water Cycle is given in Appendix 1.

The surface water contains a considerable amount of treated wastewater, since the natural base flow is low and 6 wastewater treatment plants (WWTP) are in operation. Indications of wastewater influence in the surface water are high concentrations of wastewater indicators such as Cl^-, Na^+, SO_4^{2-}, B, DOC or Gd-DTPA, high temperatures (in winter) and more negative isotopic signatures, because of the groundwater share (more negative isotopic signature) in the drinking water.

Figure 2 shows the discharge of the 4 WWTP of interest (for locations refer to Fig.2, Appendix 1). The transect Wannsee lies within the influence of the WWTP's Stahnsdorf and Waßmannsdorf which are permanently releasing wastewater into the Teltowkanal, while Stahnsdorf discharges into the Nordgraben ditch north of Lake Tegel. Ruhleben, the largest WWTP discharges into the Spree during winter months (October-March) and into the Teltowkanal in summer. The discharge

varies on a daily basis but shows no seasonal fluctuations (Fig. 2). The concentrations of wastewater bound substances in the effluent, for example chloride, do generally not show clear seasonalities (this is not true for specific substances, for example drug residues, which may be prescribed more often during certain times of the year).

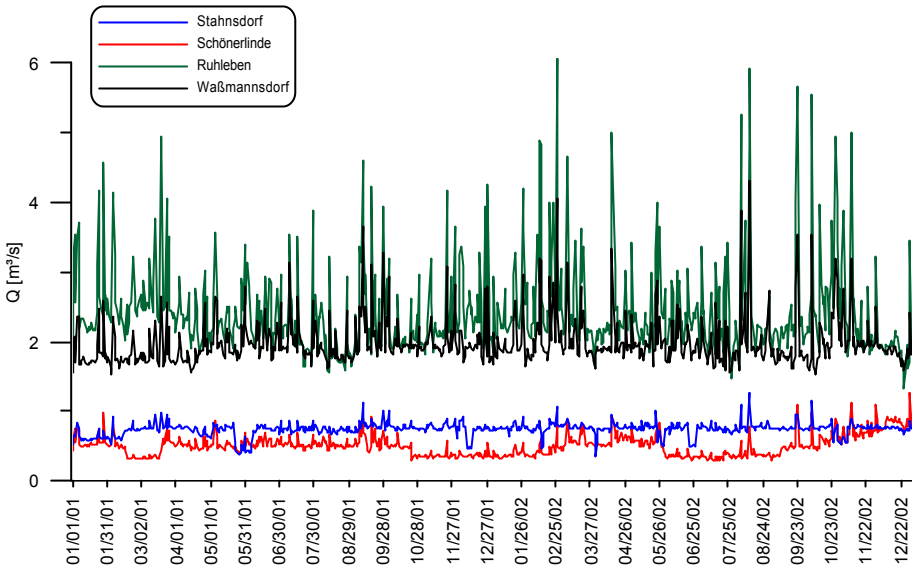


Figure 2: Discharge of wastewater treatment plants Stahnsdorf, Schönerlinde, Ruhleben and Waßmannsdorf in 2001 & 2002 (RICHTER 2003, data souce: BWB)

In contrast, the natural discharge is much higher in winter than it is in summer (Fig. 3), which results in a generally higher dilution of the wastewater and likewise lower concentrations of wastewater indicators in winter. 2002 was a very wet year, which is why most WW indicators did not show any clear peaks during summer and were therefore of no use for the interpretation of travel time. In contrast, 2003 was extremely dry and hot (Figures are currently extended for 2003).

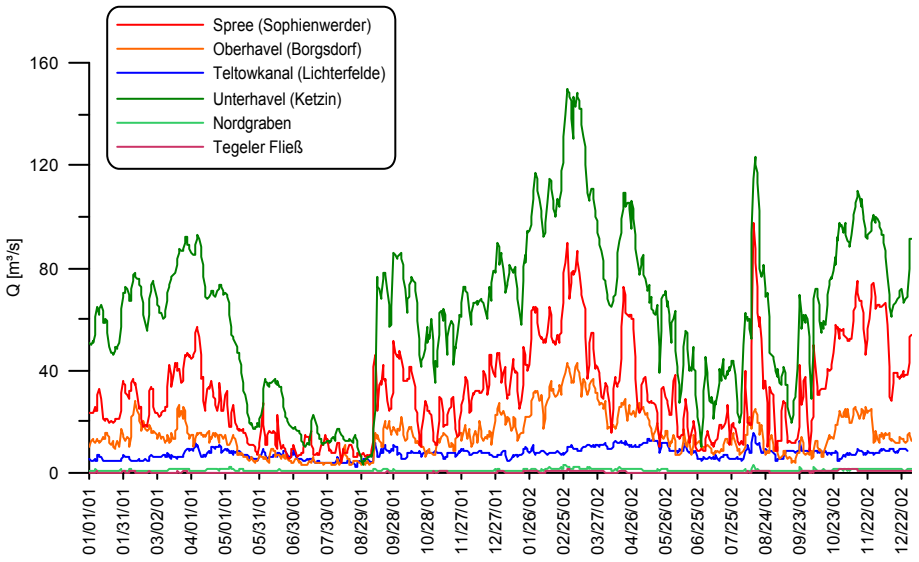
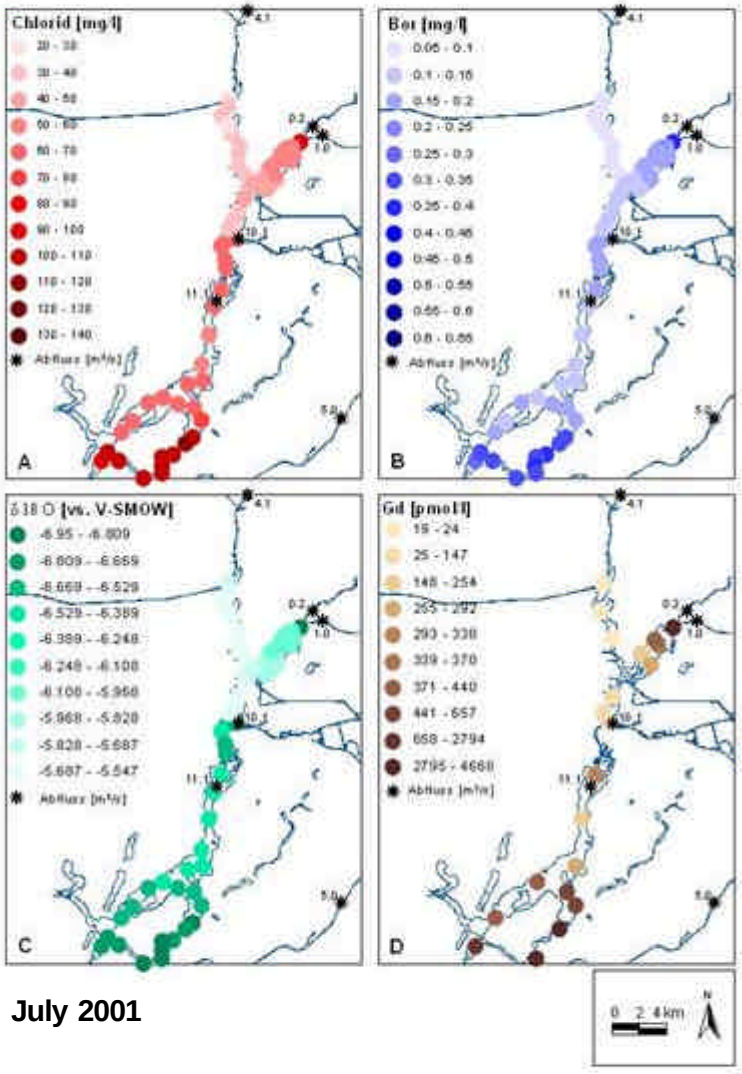
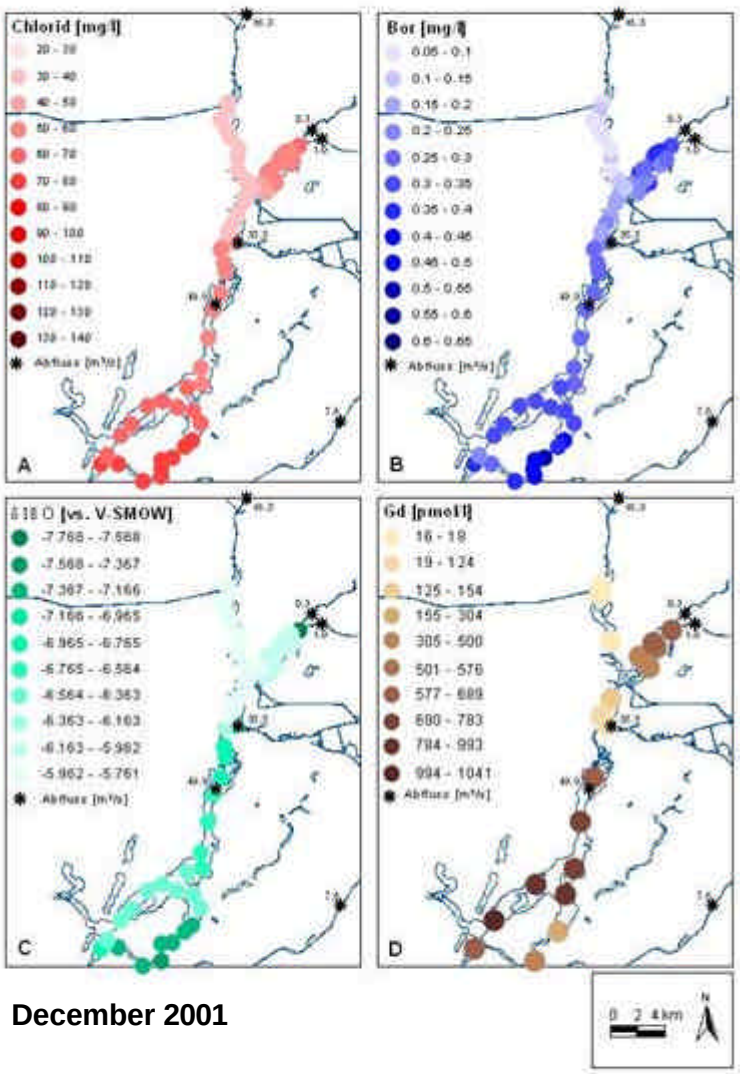


Figure 3: Discharge at several gauging stations throughout Berlin (RICHTER 2003, data source: Senstadt 2003).

Figure 4 shows maps of Cl^-, B and Gd concentrations and $\delta^{18}O$ values and in the surface water in July 2001 and December 2001. In July, the base flow was the lowest in 2001/2002. Therefore, the spatial differences and absolute concentrations of wastewater indicators are larger in July 2001 as compared to winter months. The concentrations are highest at the northern end of Lake Tegel, where the Nordgraben meets Lake Tegel and in the Teltowkanal, since they contain the highest proportions of treated wastewater. It becomes clear that the transect Lake Wannsee is located in an transition area between Teltowkanal water flowing northwards into Lake Wannsee and water of the Lower Havel, resembling the Spree water with lower proportions of treated wastewater. Figure 5 illustrates the approximate proportions of treated wastewater calculated as percentage of WWTP discharge of the total discharge (evaporation and abstraction disregarded). More detailed calculations for previous years were done by SCHUHMACHER & SKRIPALLE (1999).



July 2001



December 2001

Figure 4: Exemplary comparison of distribution of wastewater indicators in the surface water system in summer and winter (RICHTER, 2003).

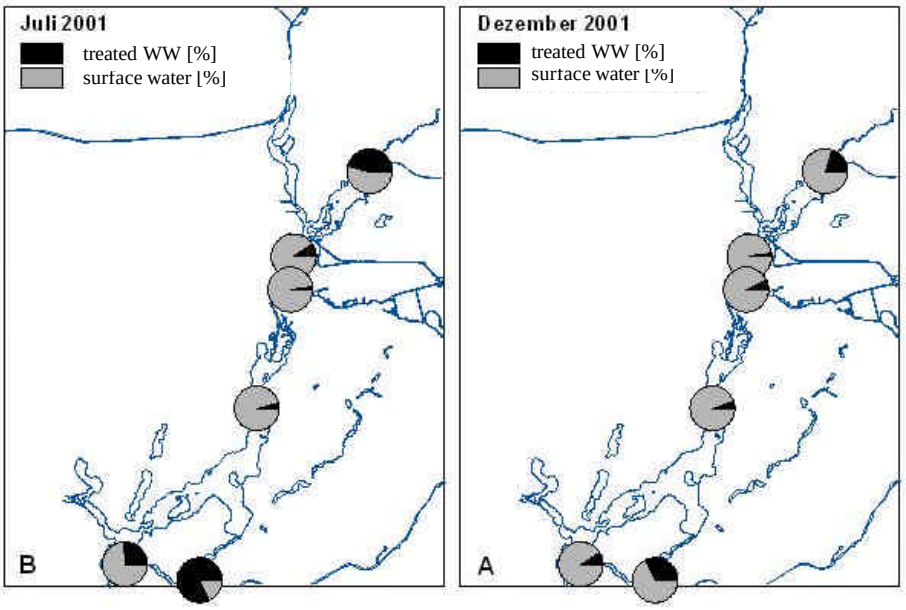


Figure 5: Exemplary proportion of treated wastewater in the surface water for summer and winter (RICHTER, 2003).

5.1.1 Lake Wannsee

Lake Wannsee is an area where water from the Lower Havel (Unterhavel) with a comparatively low percentage of treated WW and Teltowkanal water with a very high load of treated WW meet. The Teltowkanal water flows northwards through a chain of lakes ("Kleine Seenkette") into Lake Wannsee (Fig. 6). Because the concentrations of Cl^- and B vary strongly (Fig. 6) and samples were taken once in a month only, the calculation of the proportion of treated WW in front of the transect (point 351) is difficult (Fig. 7). However, it illustrates that values from a few % to > 50 % are possible. Highest proportions are encountered in summer, when the natural discharge is low and WWTP Ruhleben discharges into the canal.

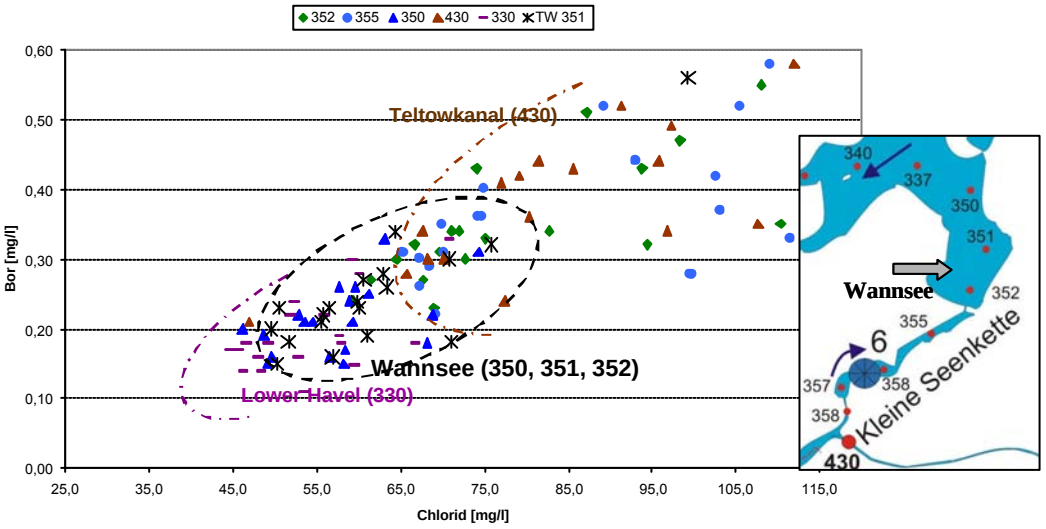


Figure 6: B versus Cl^- in the lower Havel, the Teltowkanal and Lake Wannsee (data from 2001-2002; RICHTER, 2003).

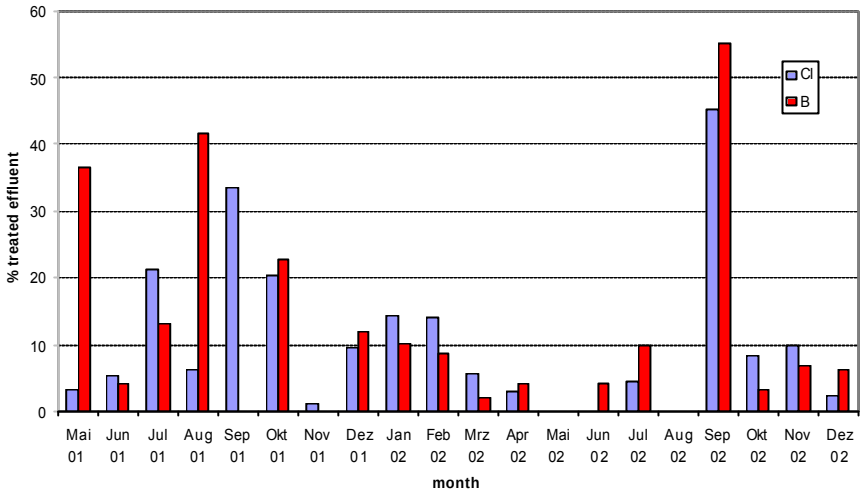


Figure 7: Proportion of treated WW in front of transect, calculated with B and Cl⁻ concentrations.

Apart from the seasonal fluctuations, the large differences in WW components throughout the lake (Fig. 4 and 8) constitutes a problem, because only one surface water sample is taken during NASRI sampling (in front of well 4), which is not necessarily representative for the bank-filtration source. The time-series of several potential tracer in the shallow observation wells within the lake show peaks appearing earlier than in the lake's time-series (3338, 3337, BEE205, Fig. 9). Because the transects are located in an area subject to large concentration gradients within the lake, 50 m further south concentrations may already be very different. In addition, transect 2 is not orientated perpendicular to the flow direction and it may receive water from 100 m further SE of the sampling point.

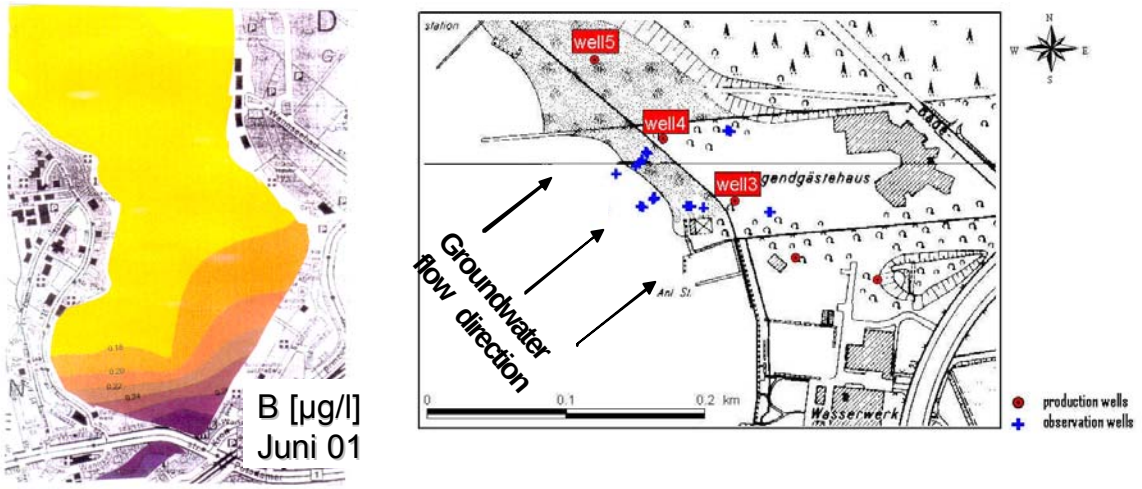


Figure 8: Left: B concentration sampled in a dense raster in Lake Wannsee in June 2001 (HINSPETER, 2002). Right: Locations of the Wannsee transects and approximate groundwater flow direction as shown in various groundwater head isoplans.

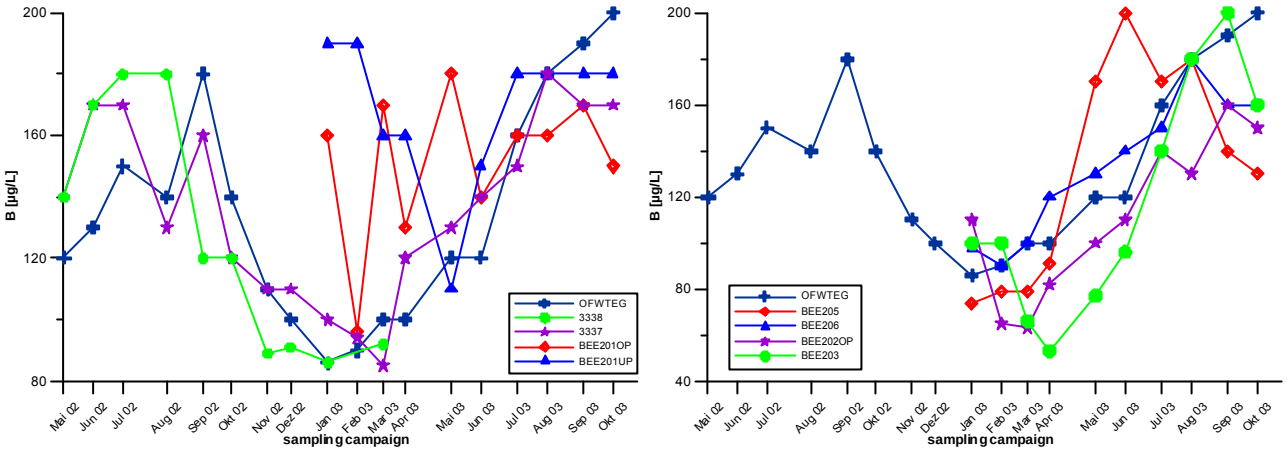


Figure 9: Time-series of B in shallow observation wells of transect 1 and 2. Dark-blue curve represents surface water sample (data source: BWB).

In addition, the behaviour of various surface water constituents differs from each other for unknown reasons (Fig. 10). Chloride, B, Na and electric conductivity are more or less constant before they rise to a clear peak in October 2003. Sulfate, Ca and Mg show a minimum in July/August 2002 and little variation in 2003. Only EDTA and B show the expected peaks in summer 2002 and 2003. In Lake Tegel, all parameters behave similar.

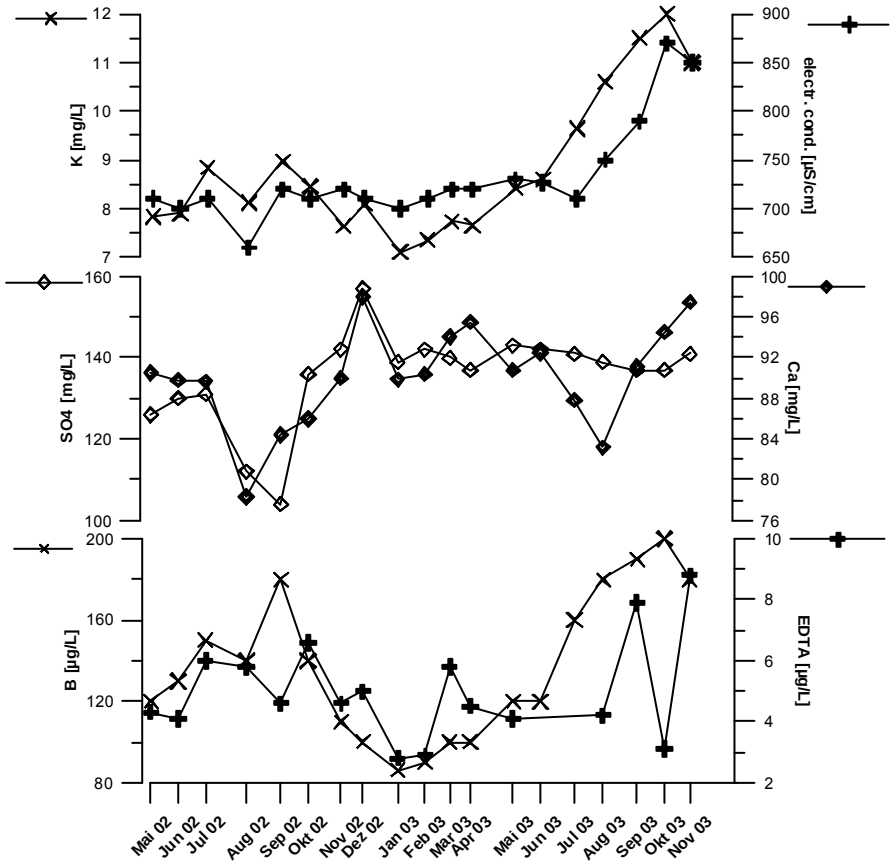


Figure 10: Electric conductivity, K, SO_4, Ca, B and EDTA in the surface water of Lake Wannsee (data source: BWB).

5.1.2 Lake Tegel

The Nordgraben and the Tegeler Fließ (both small ditches) discharge into Lake Tegel after passing through the OWA phosphate elimination plant, carrying a high load of treated WW from the WWTP Schönerlinde. A pumping device started operating in October 2001, pumping Upper Havel (Oberhavel) water into the OWA during summer months to dilute the treated WW when the base flow is low. The components of the discharge from the OWA (natural discharge Tegeler Fließ and Nordgraben, discharge WWTP Schönerlinde, Oberhavel water) are shown in Figure 11. The sum of these components is not always perfectly equal to the values given for the total OWA discharge (black line), probably due to measurement errors. The combination of the mixing with Oberhavel water and a very wet year has evened out the summer maximum of WW indicators in 2002, which was encountered in the past (FRITZ, 2002) and again in 2003, which was a hot and dry year. Therefore, the proportion of treated WW in front of the transect (point 310) was comparatively low (around 10 %) throughout 2002 (Fig. 13).

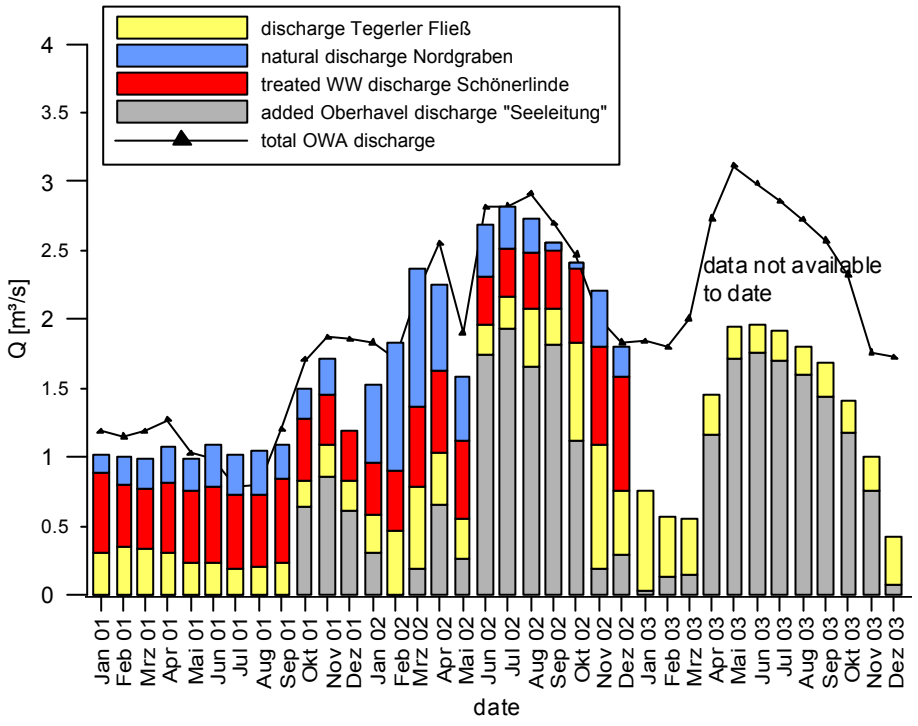


Figure 11: Total discharge of the OWA and components. Data source: SENSTADT, 2003 and BWB.

Compared to Lake Wannsee, the conditions within the lake are more stable in terms of spatial distribution of the WW. The WW influence diminished with increasing distance from the OWA outlet (Fig. 12) but around the transect, the spatial variation at a certain time is small.

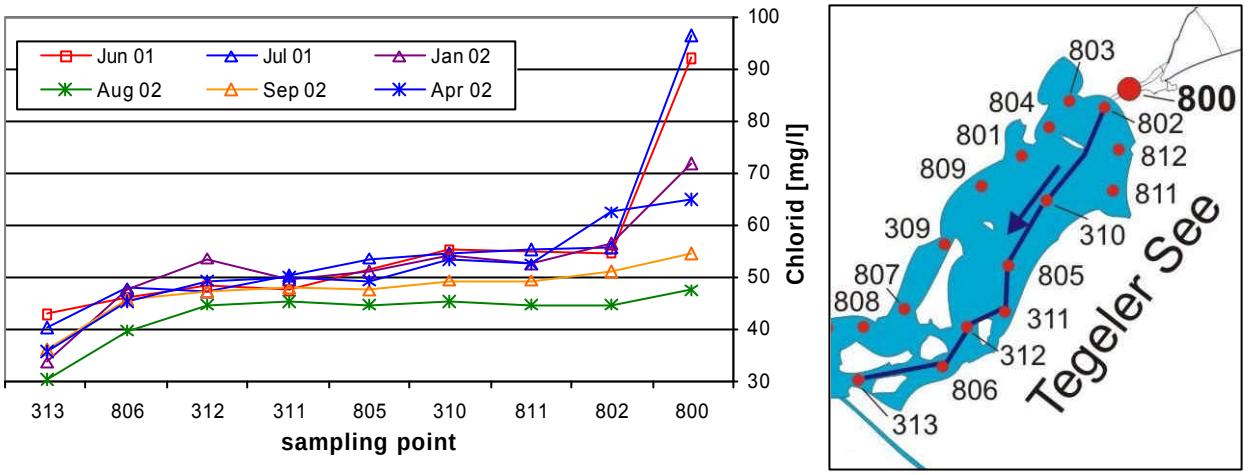


Figure 12: Chloride profile throughout Lake Tegel (RICHTER, 2001).

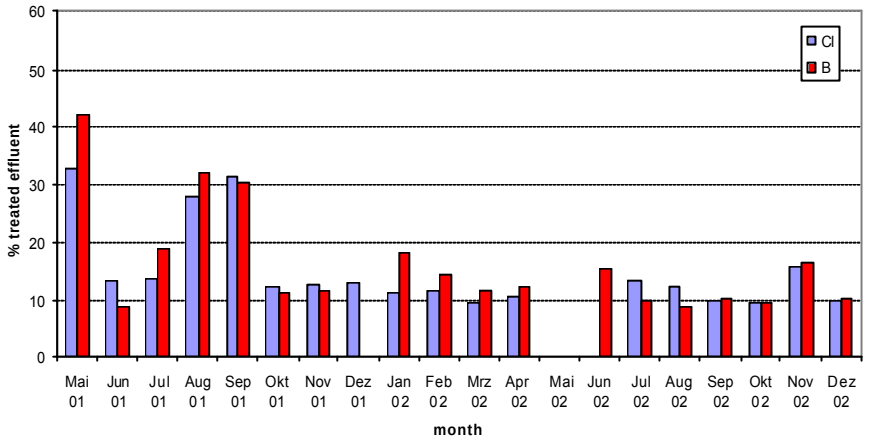


Figure 13: Percentage of treated WW in front of the transect calculated with Cl^- and B concentrations.

Fortunately for the bank-filtration study, a clear minimum in February 2003 could be seen for most WW indicators which enables to define travel times at the transect. Figure 14 illustrates the input concentrations for various water constituents in Lake Tegel, all showing a similar pattern.

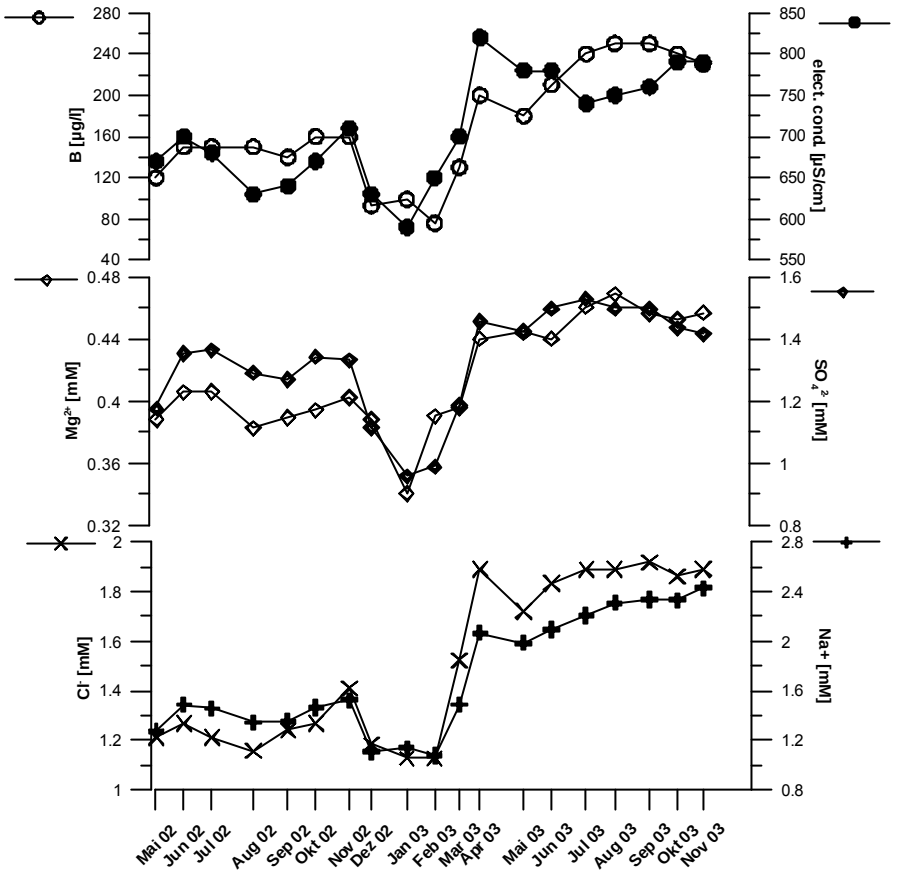


Figure 14: Electric conductivity, B, Mg^{2+}, SO_4^{2-}, C^{l-} and Na^{+} in Lake Tegel (data source: BWB).

5.2 Investigations at the field sites

5.2.1 Artificial recharge pond Tegel

Sediments

The Geology of the site as well as the geochemistry of core TEG367 was described in the previous report. The extent of the saalian glacial till (qsWA//gm) was evaluated with statistical methods, because cross-sections only existed for the production well galleries and few was known about the presence of the till below the recharge ponds. Available drilling data was made available by BWB. The till is rarely thinning out, it tends to be either present or not, usually with a thickness of a few meter. Because for the hydraulic and hydrochemical properties of the area, the presence, rather than the extent of the till, is of importance. The data was interpolated with the inverse distance method (5 m grid) using Surfer 7.02 (GOLDEN SOFTWARE, 2000) with the criteria present (1, green) or not present (0, red) only. The result is shown in figure 15 and it illustrates that the till, which was encountered in most cores in the north-east, is only present in a few patches in the south-west. The till is missing completely or in parts below the recharge ponds. Hence, the recharged water

can infiltrate into the deeper aquifer parts and reach all production wells of the galleries Hohenzollernkanal and Saatwinkel, which have filter screens below the till (compare Fig. 16).

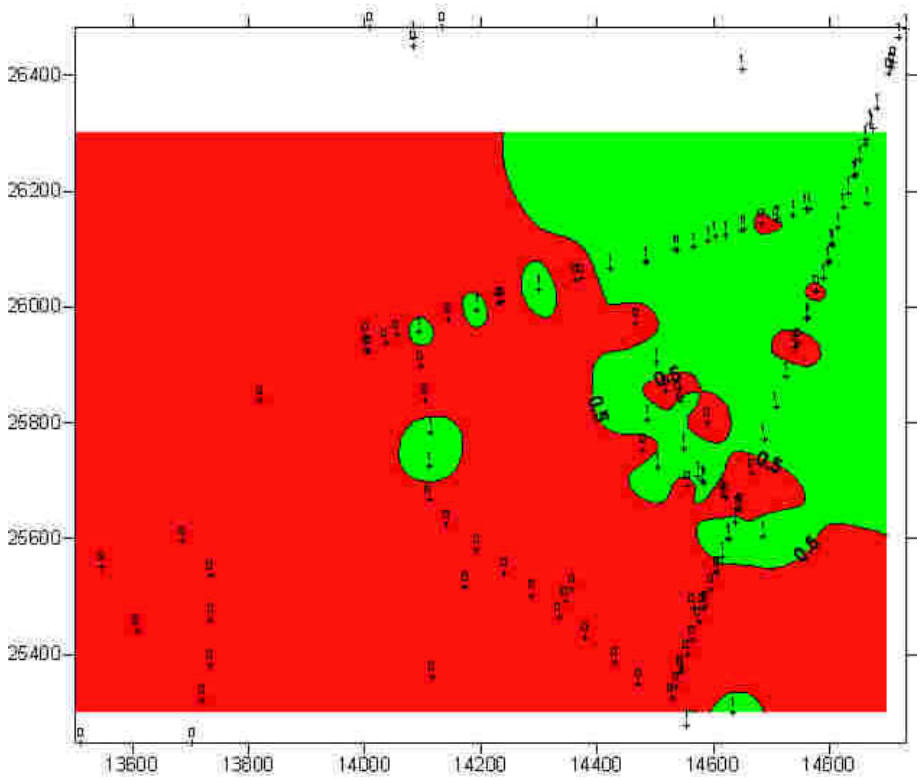


Figure 15: Glacial till distribution, inverse distance method (5 m Grid). 1= till present, 0 = no till. Areas where till is more likely to be present (>0.5) are shown green.

Figures from the second core analysed at the site (TEG369) are given in the following. The sands are fine to coarse grained with very little silt or clay. The k_f values derived from sieving of TEG367 and TEG369UP are fairly homogenous and vary over one order of magnitude from 1.5E-04 to 1.1E-03 m/s (Fig. 16). Similar to core TEG367, the most striking differences in terms of the geochemical characteristics of the sediment, are found between the unsaturated and saturated sediment zone (water-table depth: 6-9 m, depending on pond level). Carbonate (inorganic carbon) appears from a depth of around 6.4 m onwards (Fig. 18). The organic carbon content is low with 0.02-0.16 weight % (Fig 18). With a few exceptions, the total iron content is 1-2 g/kg Fe (Fig. 18). The share of reducible iron and manganese fractions (Fe & Mn(hydr)oxides) seems to be getting slightly less with depth. In terms of total ion concentrations (HNO_3 extraction, Fig. 17), aluminium and iron are the main minor cations in the unsaturated sands, while calcium (and magnesium) prevail within the saturated zone.

Two new deeper observation wells TEG368UP and TEG373 were drilled below the till in spring 2003 on both sides of well 20, in order to cover all water components mixing in the production well.

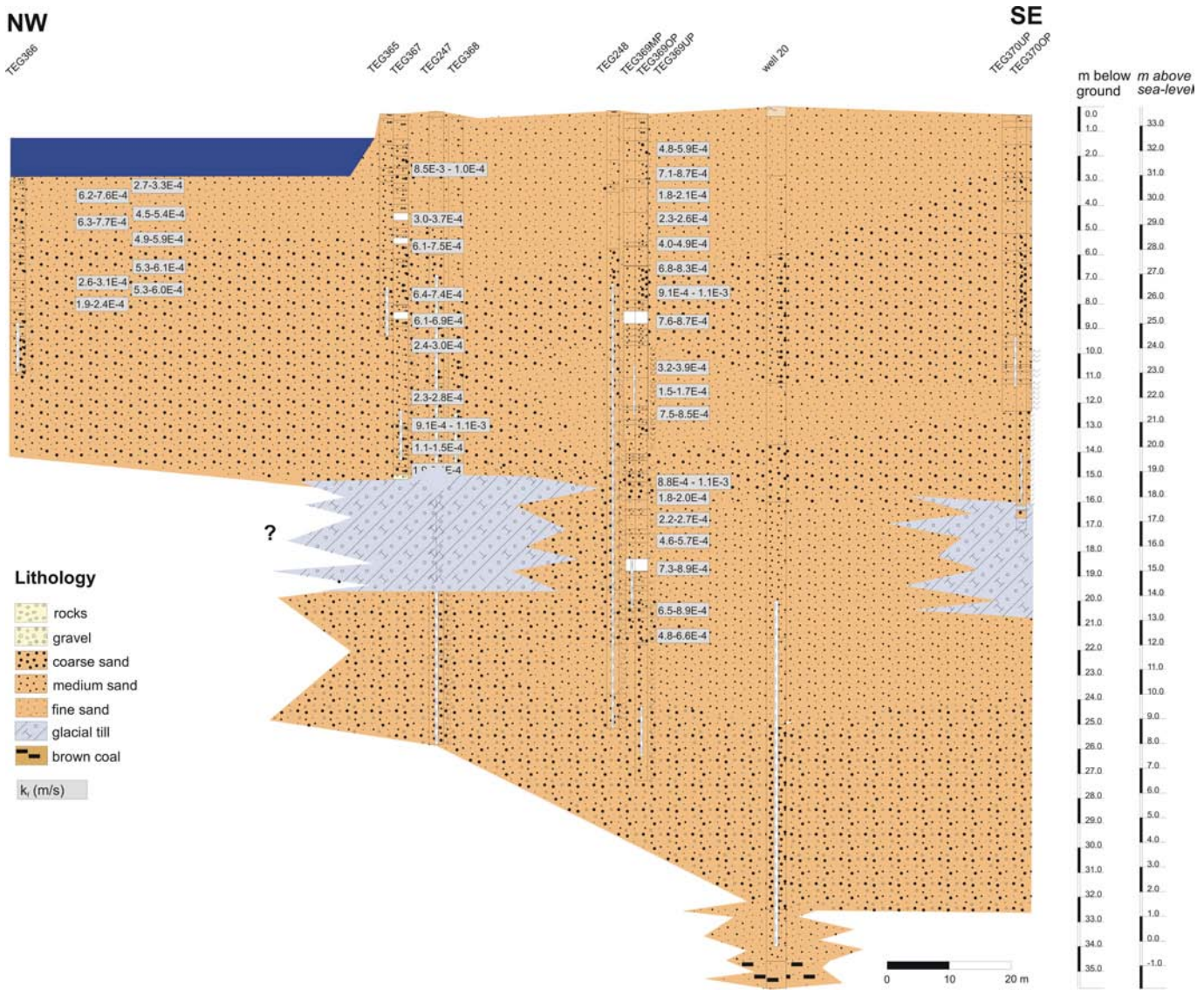


Figure 16: Lithological cross-section of the transect with k_f values obtained from sieving.

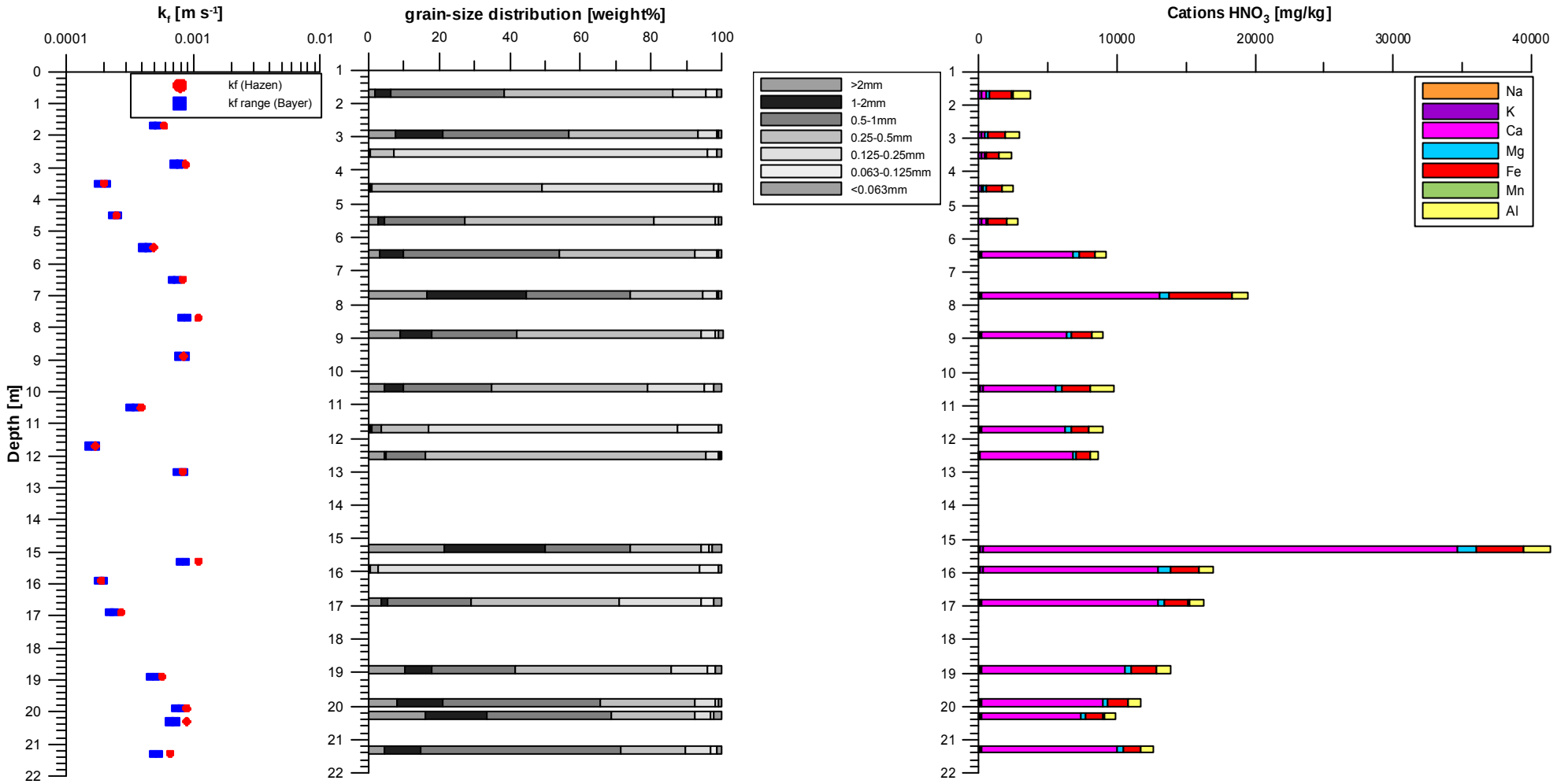


Figure 17: Hydraulic conductivities (k_f), grain-size distribution and cations from HNO3 extraction in core TEG369.

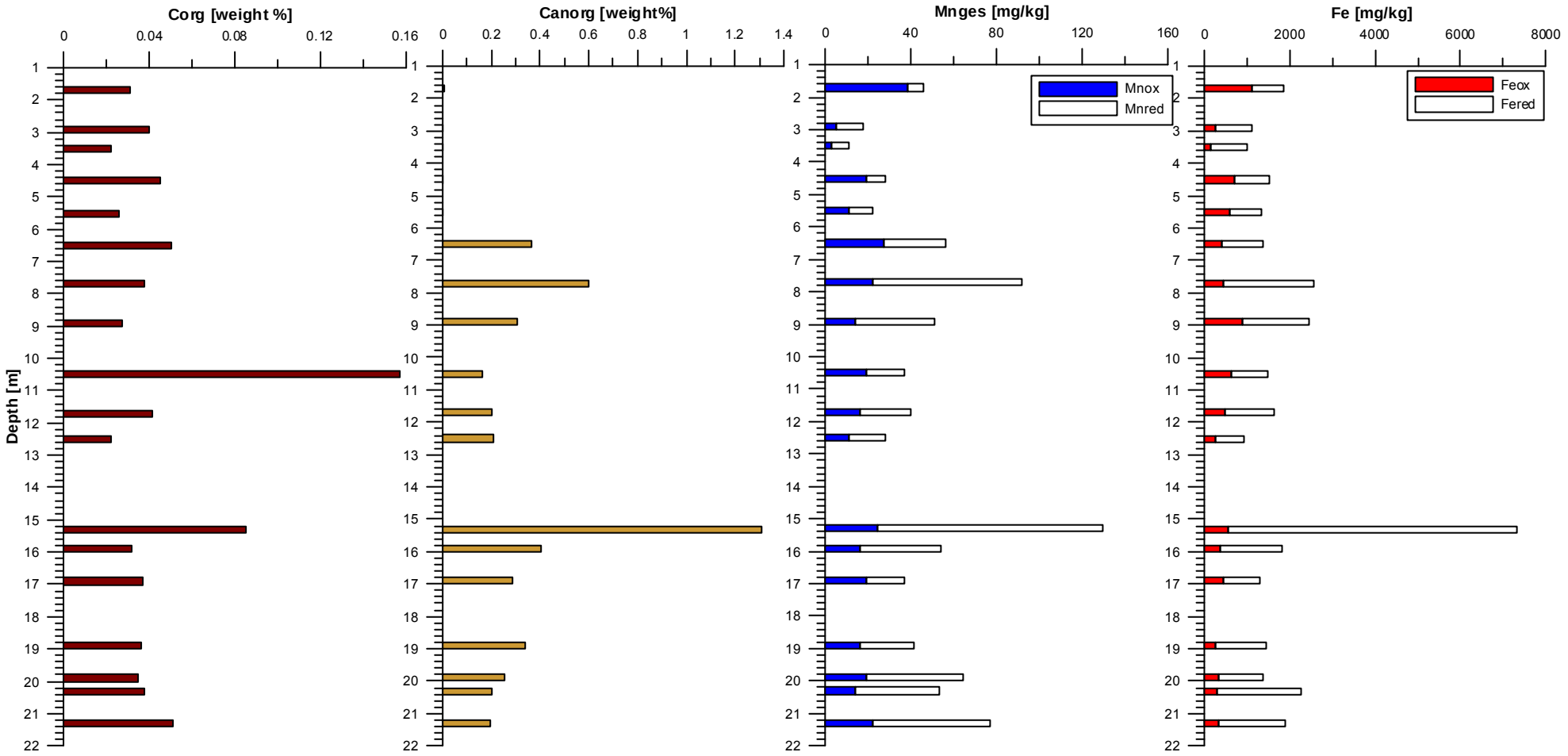


Figure 18: Organic and inorganic carbon content, Fe(III) and Fe(II), Mn(III) and Mn(II) content.

Hydraulic situation

The hydraulic situation has been described in more detail in the previous report. In addition, a hydraulic model exists at the IGB ("model" group). Figure 19 contains available water-level data from data loggers. It shows nicely how the groundwater-level drops as soon as the infiltration capacity is reduced due to clogging of the pond base, clearly before the pond is emptied (pond base 31 mNN).

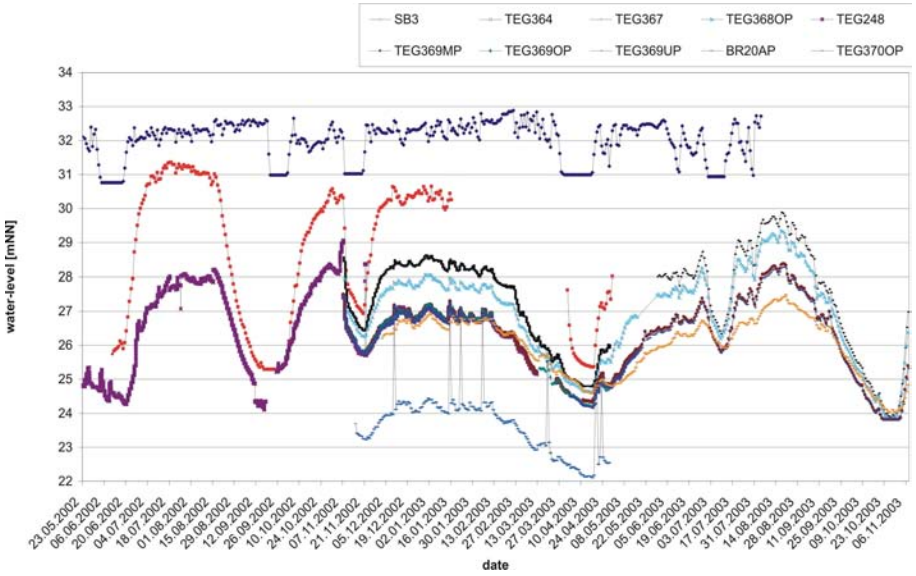


Figure 19: Available water level data of the recharge pond 3 (sb3), production well 20 and observation wells of the transect to date.

Tracer evaluation (travel times, groundwater age and mixing)

The travel times at the GWA transect are faster than at the bank filtration sites. The resolution of the time-series with a monthly sampling is to low to gain precise travel times. The tracer Cl, B and K would principally work, but apart from the production well, the fluctuations are a little too large to give nice shifts (Fig. 20). The isotopes really are the best tracer to give at least rough estimates for travel times, in particular, since they showed peaks in both 2002 and 2003. Examples for breakthrough curves of several conservative tracer are given in Figure 20. Best estimates from the isotopes are average travel times of 25 days to TEG368UP and TEG369OP and 50 days to TEG369UP and well 20. For the remaining observation wells, the graphs more or less lie on top of each other.

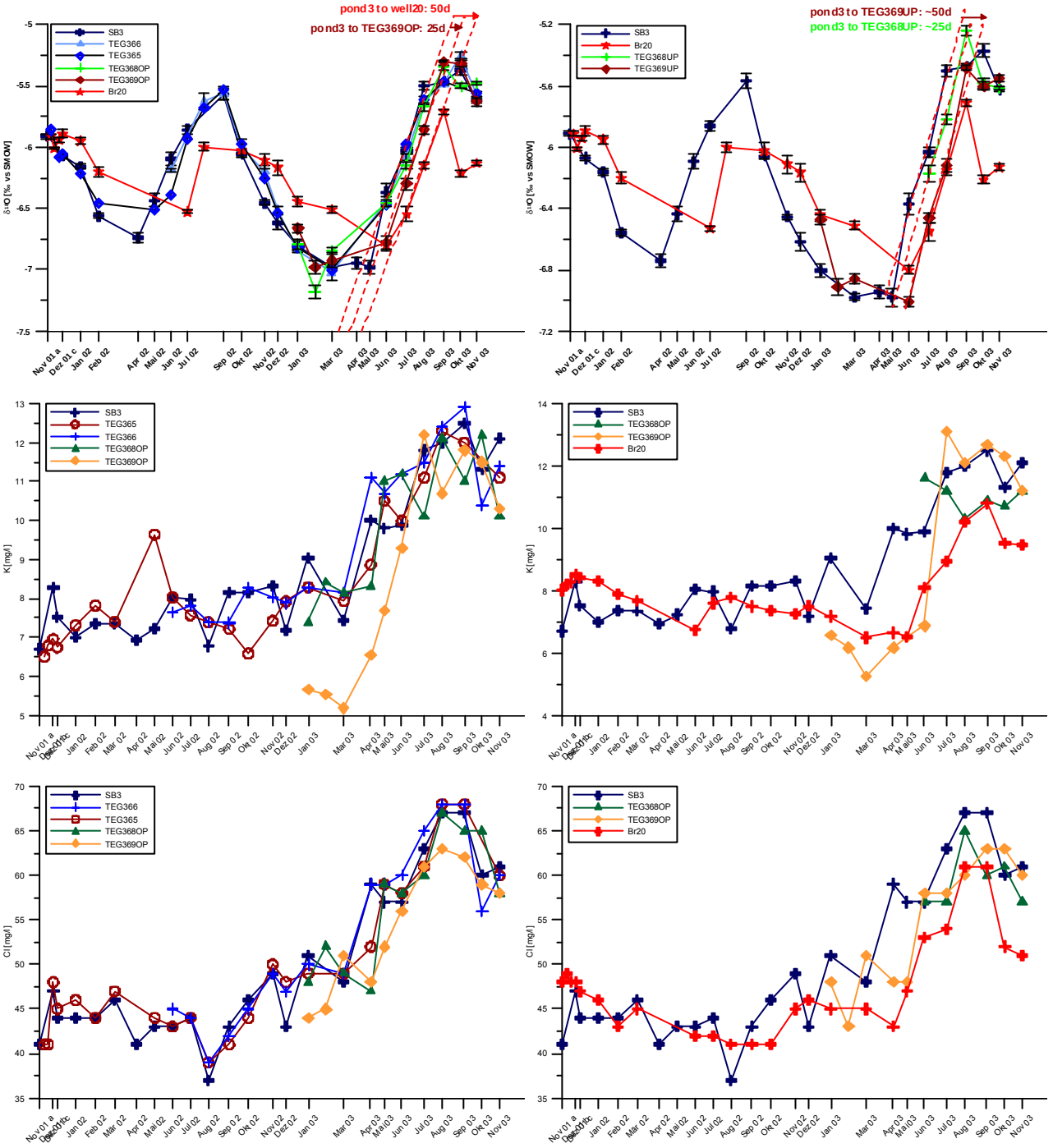


Figure 20: Concentration of $\delta^{18}O$, K and Cl in shallow (left) and deeper (right) observation wells.

The temperature data (Fig. 21) has a much better time resolution, because daily values exist. The temperature data can be used to estimate travel times clearly below 1 month. However, temperature is not a conservative tracer and the retardation factor has to be estimated from conservative tracer. The temperature shift from the pond to TEG364 is < 1 week, to TEG367 1 week, to TEG368OP 2 weeks, to TEG369OP 9 (2003) to 11 (2002) weeks. The logger temperature is representative for the depth of the logger in the well, rather than the filter screen depth which is why TEG369OP & UP are both representative for TEG369OP only. Judging from

the isotope shift to TEG369OP (~ 30 days), the temperature retardation factor is ~ 2.1. Hence, the approximate travel time to the wells close to the pond is < 3 days to TEG364, 3 days to TEG367 and 7 days to TEG368OP. The temperature varies between 0 and 25°C, which certainly has an effect on the behaviour of certain water constituents, which may be temperature sensitive. Figure 22 summarises the results of the travel time investigations and shows effective T/He ages, which are consistent with the travel times. The observation wells TEG369OP and UP give an effective age of 0. With a resolution of the method of half a year at the side, this could be expected and it proves, that 100% of the sampled water NW of well 20 really is originating from the pond only. The background water has an effective T/He age of 1.3 (shallow) and 4.3 (deeper) years. The production well, as a mixture of bank filtrate and native background water, lies in between with 2.3 years.

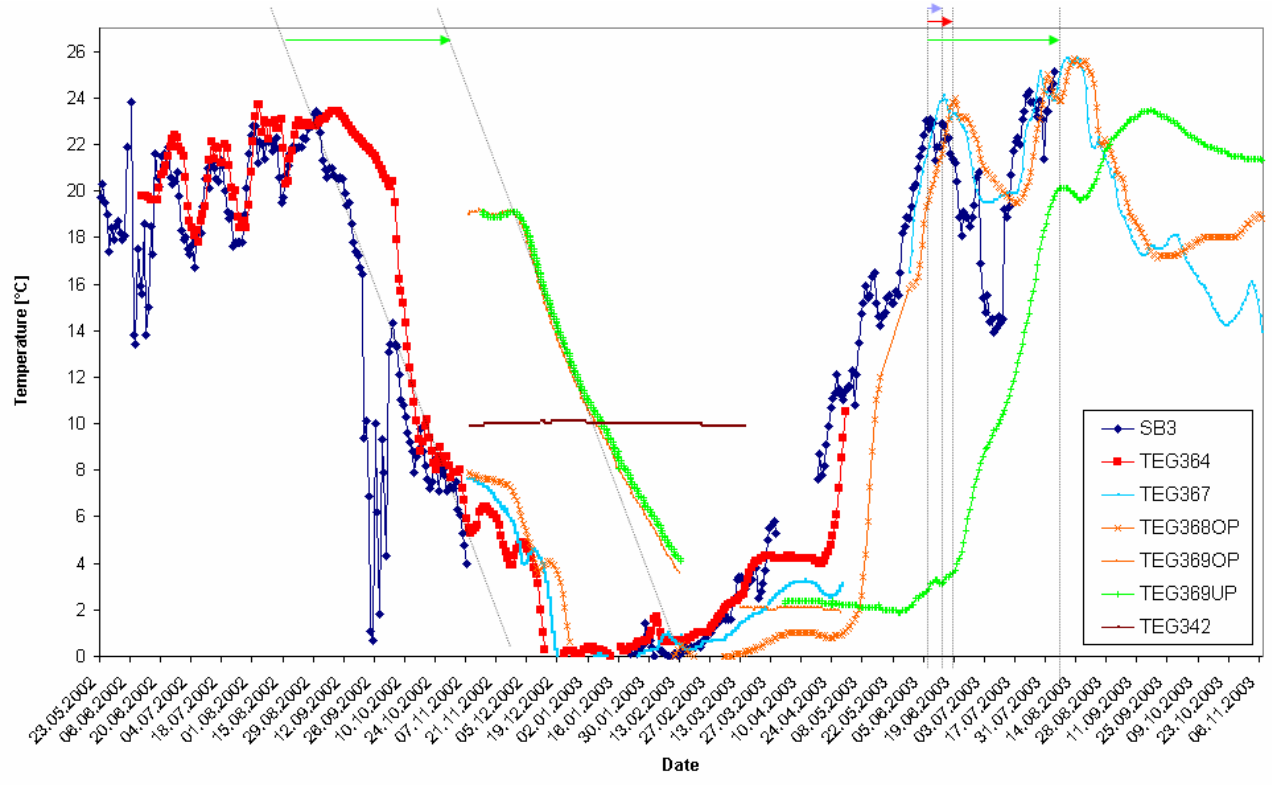


Figure 21: Daily temperature data from the GWA transect.

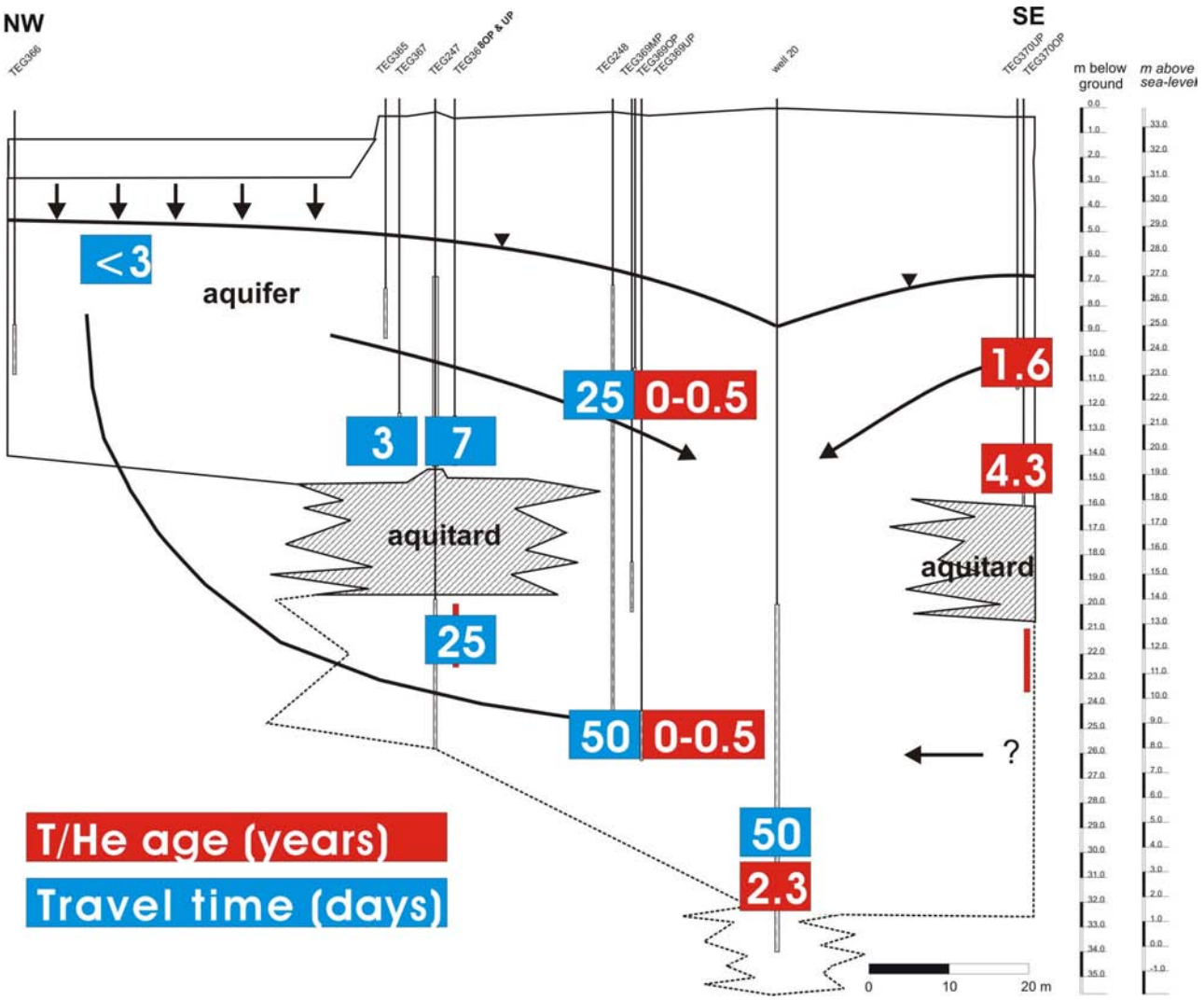


Figure 22: Estimates for average travel time and effective T/He age in observation and production well.

Plotting the $\delta^{18}O$ data versus δD data proves that the observation wells between pond and well 20 lie within the scatter field of the surface water (not shown). The production well 20, as already indicated by the time-series, fluctuates almost as widely as the surface water which is not the case in any of the other production wells at Wannsee or Tegel, where seasonal variations have been eliminated by mixing and dispersion. Interesting in figure 23 is that the vertical background groundwater variation is very large. The shallowest well (TEG370OP) plots in the same area as the production well 20, while the middle well TEG370UP (still above the till) resembles the former "background" well TEG342 (location Fig.29) at times. The deepest observation well TEG373, again, plots within the pond field.

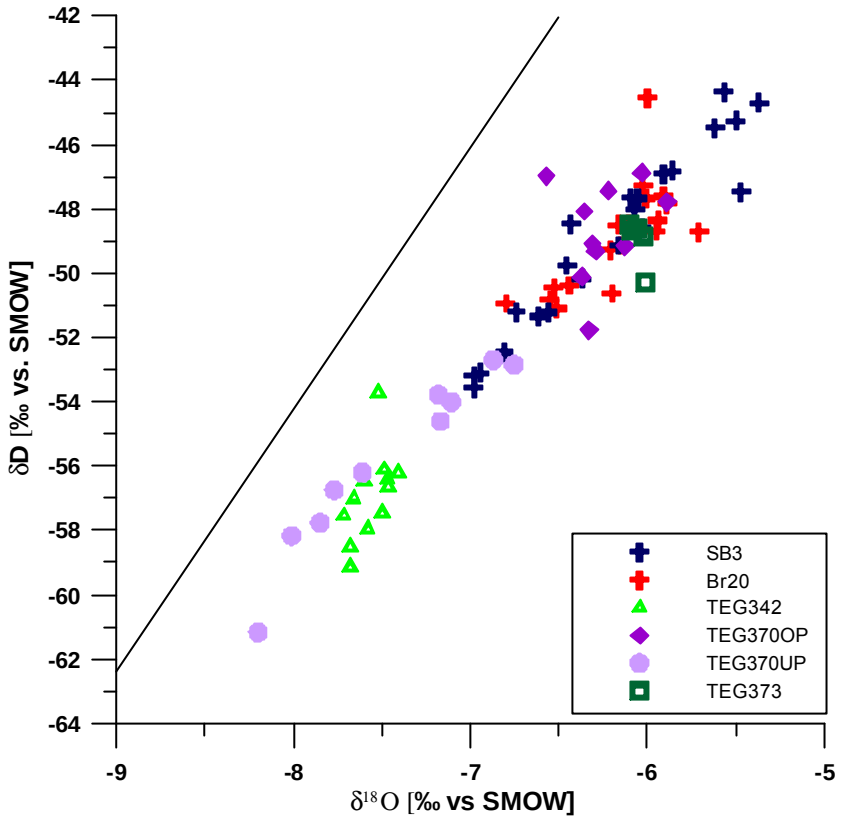


Figure 23: $d^{18}O$ versus dD [‰ vs SMOW] of pond water (SB3), production well and background groundwater. Data source: AWI Potsdam.

Selected boxplots of Na, Cl, B, EDTA, K and SO_4 are given in figure 24 and also illustrate, that the pond is the only source of the sampled water NW of well 20. They also show that it is not possible to calculate proportions of BF in the well with a simple 2 component mixing formula. In most cases, there is no clear difference between the water on both sides of the production well (EDTA or B). If there are clear differences, they are only found in one or two of the inland wells. For example, TEG370OP resembles the surface water in its $\delta^{18}O$, δD, B, EDTA, K and SO_4 content, but contains less Cl and Na. TEG370UP differs largely in its $\delta^{18}O$, δD and SO_4 content, but resembles the surface water in the remaining water constituents shown. These phenomena are currently not fully understood. However, it can be concluded that the variations in the background groundwater composition are much larger and far more complicated than expected, both in their vertical and horizontal (see below) extent. From the large scale investigations around the GWA and the flow model existing at the IGB is becomes clear that, depending on the pumping regime of the production well gallery, the background groundwater can flow towards the transect from further north or south, which would each result in a very different water quality (see below).

However, judging from the still strong seasonal variations, the proportion of BF in well 20 is probably rather large (> 80 %).

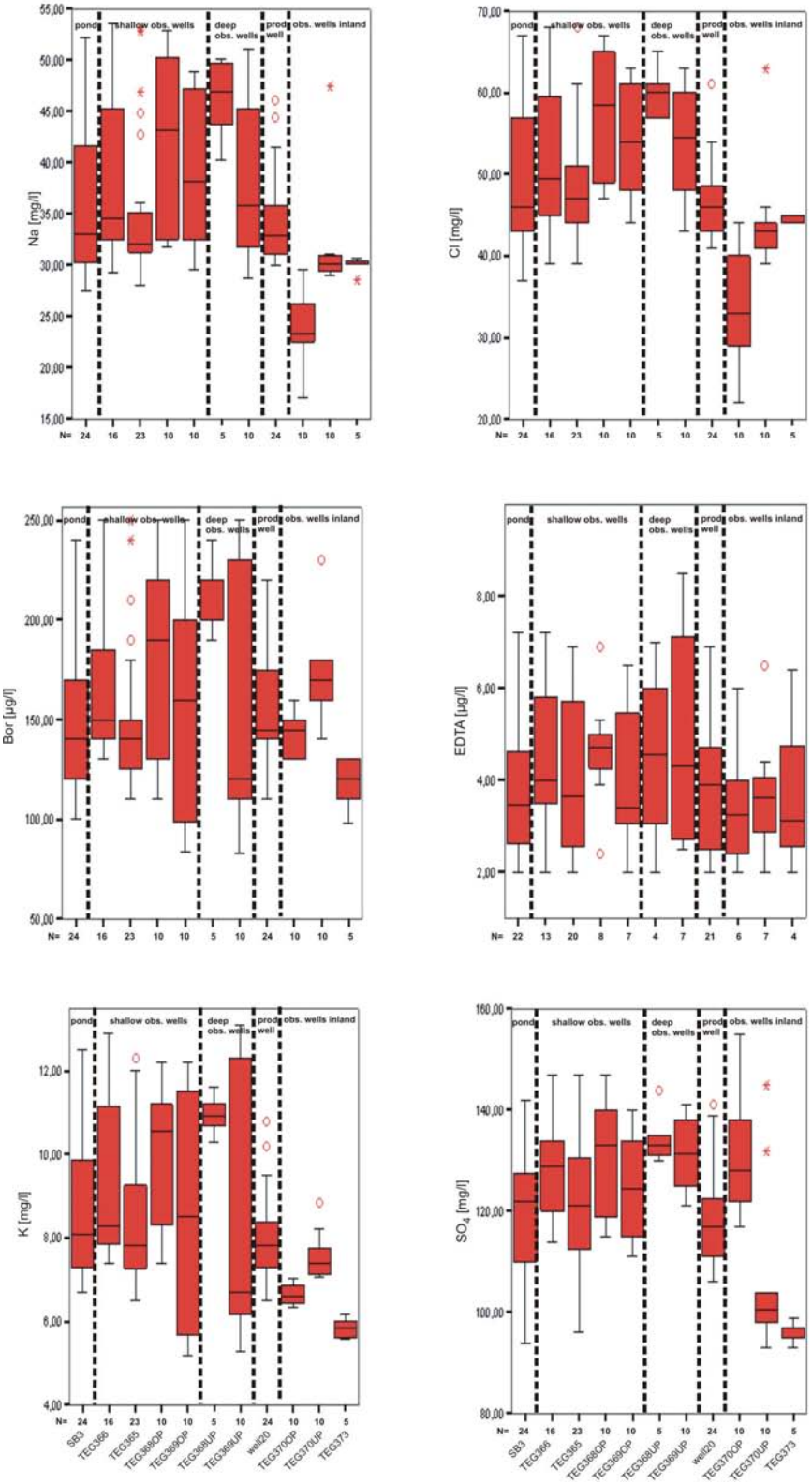


Figure 24: Boxplots for Na^+, C^-, B, EDTA, K & SO_4^{2-} at the GWA Tegel (data source: BWB.)

Hydrochemistry at the transect

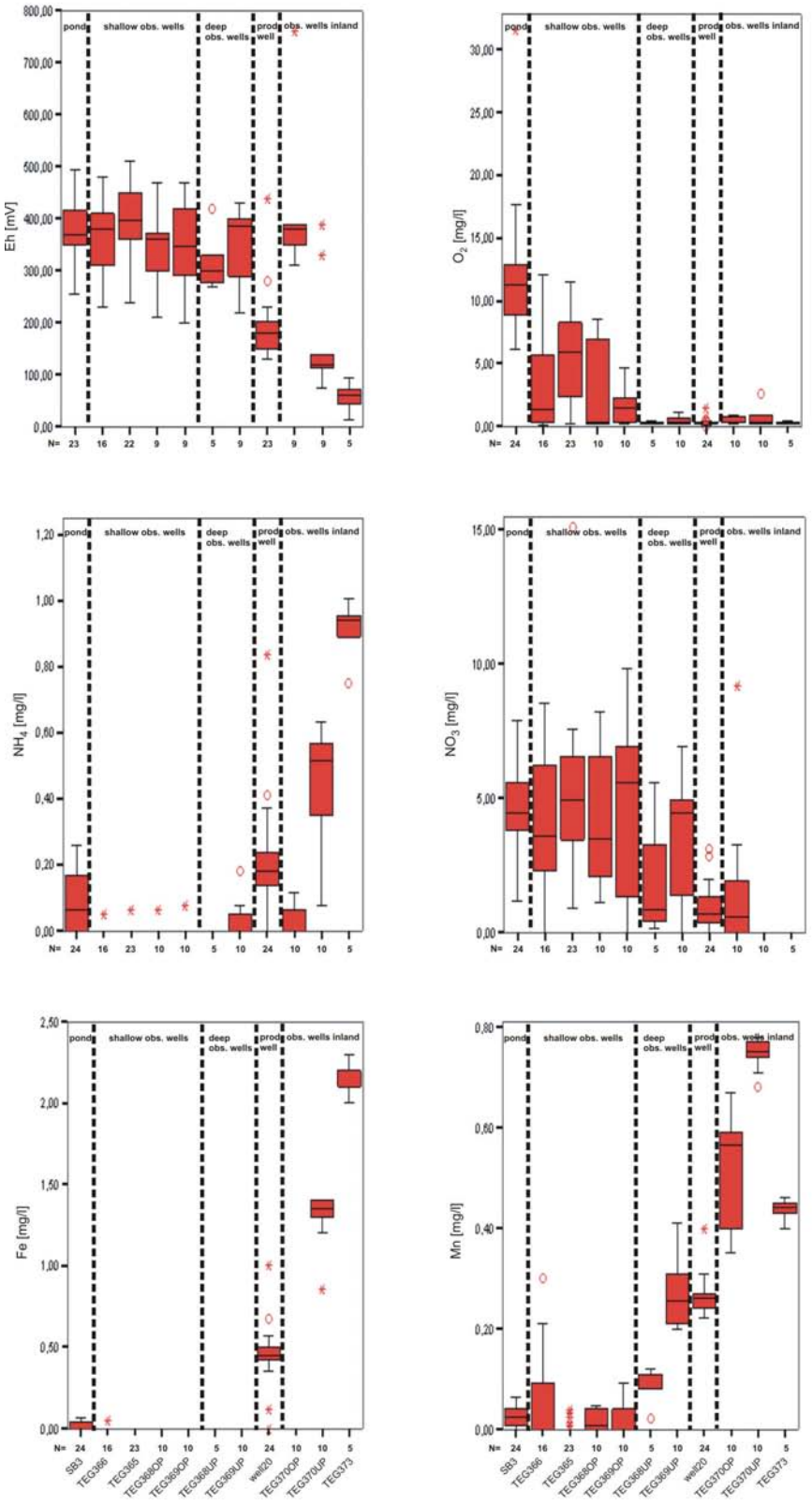


Figure 25: Boxplots of Eh, O_2, NH_4^+, NO_3^-, Fe^{2+}, Mn^{2+} of the GWA transect (data source: BWB).

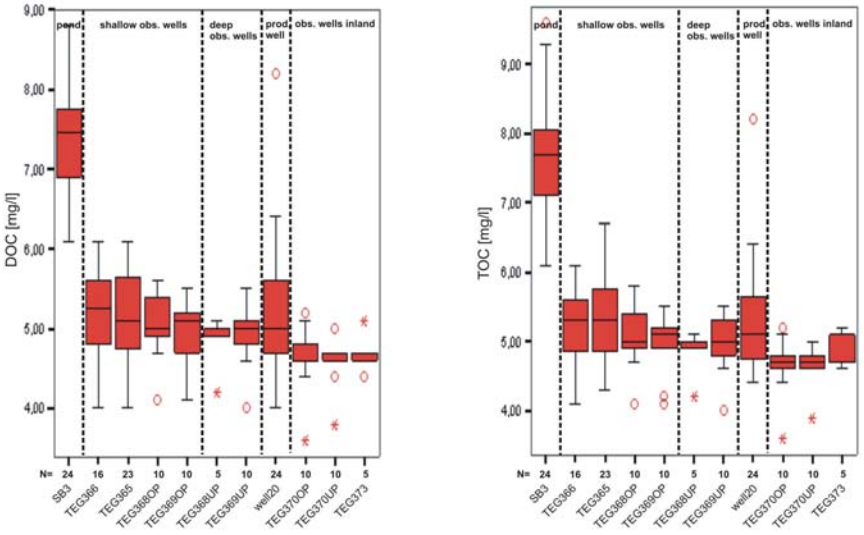


Figure 26: Boxplots for DOC and TOC (data source: BWB).

In terms of the redox conditions (Fig. 25 & 28), the evaluation of the box-plots shows that the shallow observation wells towards the pond still contain oxygen and nitrate. The deeper observation wells TEG368UP (below the till) and TEG369UP are free of O_2. Nitrate is still present, but in lower concentration than in the shallow wells and in the pond. Both observation wells and also TEG369MP in medium depth contain traces of Mn, in particular TEG369UP. The observation wells inland are O_2 free. In the shallowest well TEG370OP, NO_3 could still be detected, but Mn is also present. TEG370UP above the pond is NO_3 free and Mn and even Fe could already be sampled. TEG373 and also TEG370UP may even be slightly sulfate reducing, since SO_4 concentrations are comparatively low (Fig. 24) but sulfide is not analyzed in the project ($\delta^{34}S_{-SO4}$ analysis will be done(.

The boxplots demonstrate that the largest drop in DOC concentration occurs between pond and the first observation well, i.e. in the clogging layer, even though it is removed regularly. The DOC concentration drop is smaller than the O_2 reduction, which is why sedimentary bound organic carbon is likely to be an additional electron donator. The processes, both hydraulic and hydrochemical, are highly transient below the pond for various reasons including the pond operation, removal of the clogging layer, temperature effects, seasonal variations in the input of redox sensitive species (Fig. 27) etc. They are studied in great detail for the infiltration zone by the IGB “model” group (see IGB report).

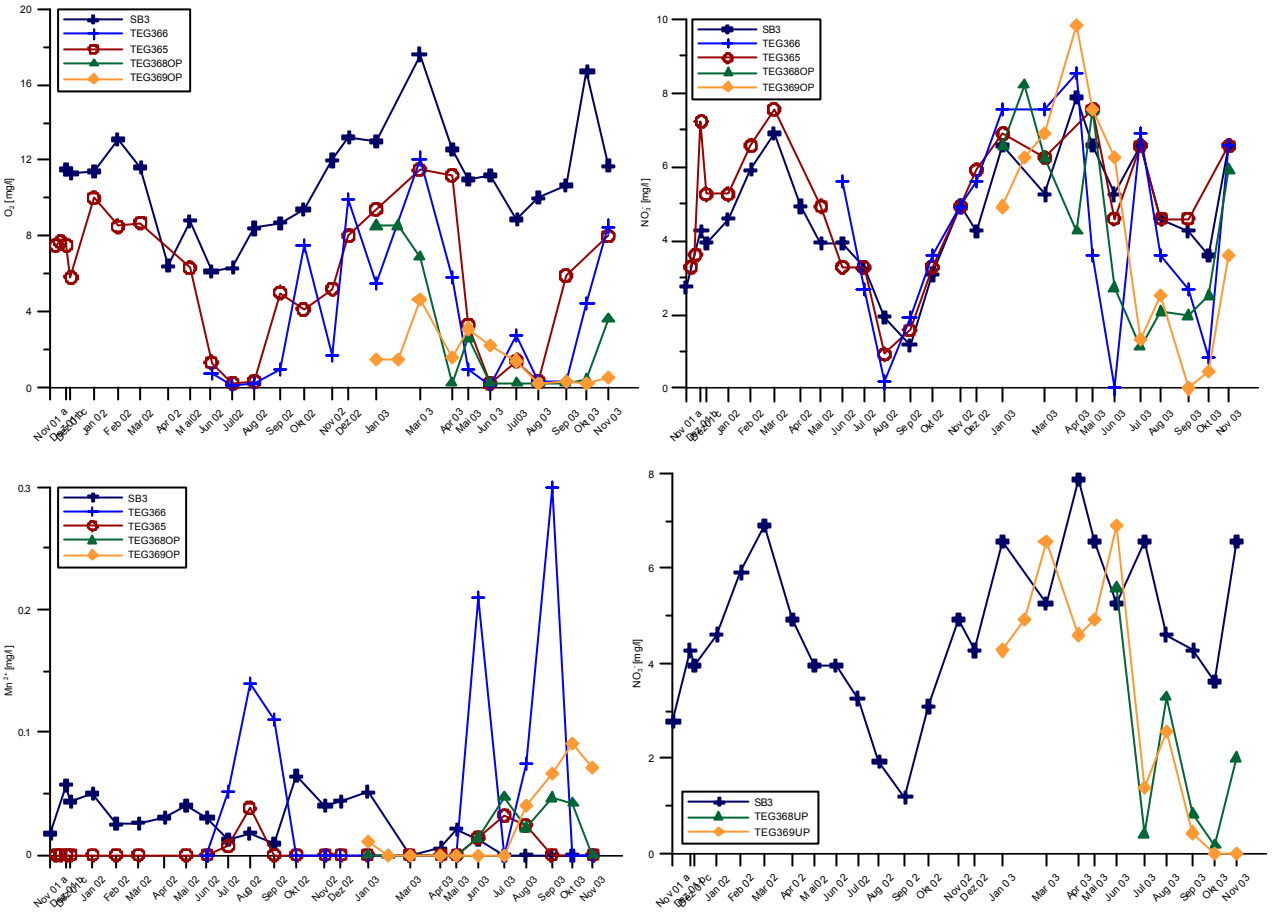


Figure 27: Seasonal variations in O_2, NO_3 and Mn in pond and shallow observation wells and NO_3 in deeper observation wells (data souce: BWB).

Figure 28 shows the approximate redox zoning in the groundwater in summer and winter. It exemplifies where O_2 and NO_3 are still present and where Mn and Fe already appear seasonally. The zoning is different NW and SE of the production wells. Rather than abrupt changes, the transition from one zone to the next is fluent and also moving with time. For example, the O_2/NO_3 as well as the NO_3/Mn boundary moved towards TEG368OP in summer 2003 (Fig. 28), when O_2 was fully reduced before reaching the first observation well and even traces of Mn were detected in the observation wells closest to the pond. Hence, the shallow wells of the GWA transect are not oxic at all times of the year as postulated before. The redox regime is highly transient and changes seasonally. Hence, the zoning does not primarily depend on the removal of the clogging layer but more on O_2 input variations and probably temperature effects (more bacterial activity at warmer temperatures).

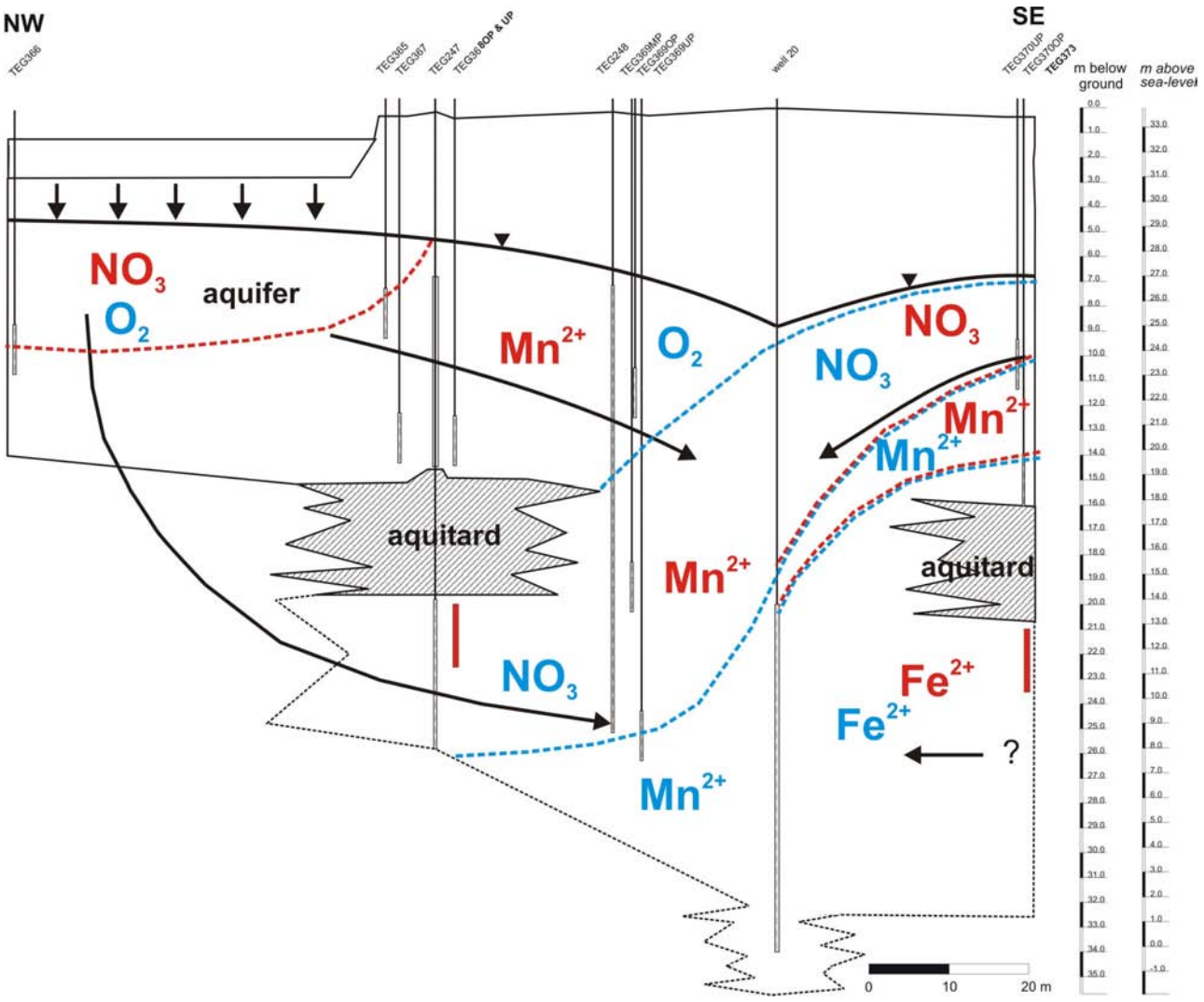


Figure 28: Redox regime at the GWA transect in summer (red) and winter (blue). Arrows indicate flow-direction but are only schematic.

Large Scale Hydrochemical Investigations

In order to get an idea of the variations in the groundwater and production well chemistry on a larger scale, a joint sampling campaign was conducted together in March and May 2003. The production wells operating at the time of the well galleries Hohenzollernkanal and Saatwinkel were sampled by BWB, while the surface water and observation wells in the area were sampled by the FU. All water samples were analysed by BWB with regard to parameters of the CREAM program. Stable isotopes were analysed by the AWI.

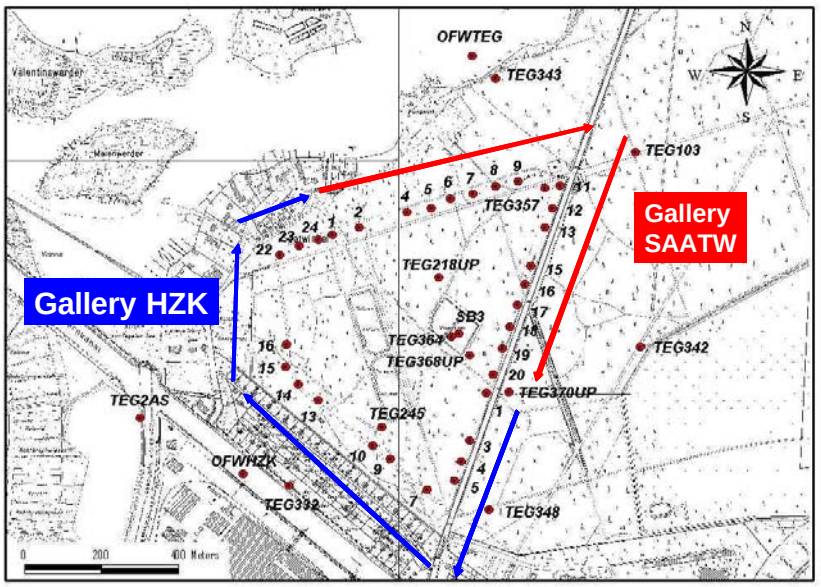


Figure 29: Production wells of the Hohenzollernkanal-Saatwinkel well triangle and surrounding observation wells sampled in summer 2003.

The following questions are of interest:

- What are the hydrochemical properties and the variability of the background groundwater?
- What are the effects of variations on single production wells of the two galleries?
- What is the share of artificially recharged groundwater in the individual wells?
- Did condition change since the last production well sampling campaign in the area in 1999?

The hydraulic situation in the area is highly transient, due to changing pumping regimes and the operation of the ponds which are regularly emptied and refilled. To give an idea on the flow directions, 2 snap-shots of the IGB flow-model (personal communication J. Greskowiak) are shown in figure 30.

The production wells near the airport (SAAT 11-20; HZK 1-5) are likely to be influenced by background groundwater and artificially recharged groundwater, while the production wells oriented towards lake Tegel (HZK 22-24; SAAT 1-9) should be a mixture of Lake Tegel and pond water, i.e. they should contain more or less 100 % of bank filtrate. The triangle side to the south-east may contain proportions of groundwater flowing below the Hohenzollernkanal.

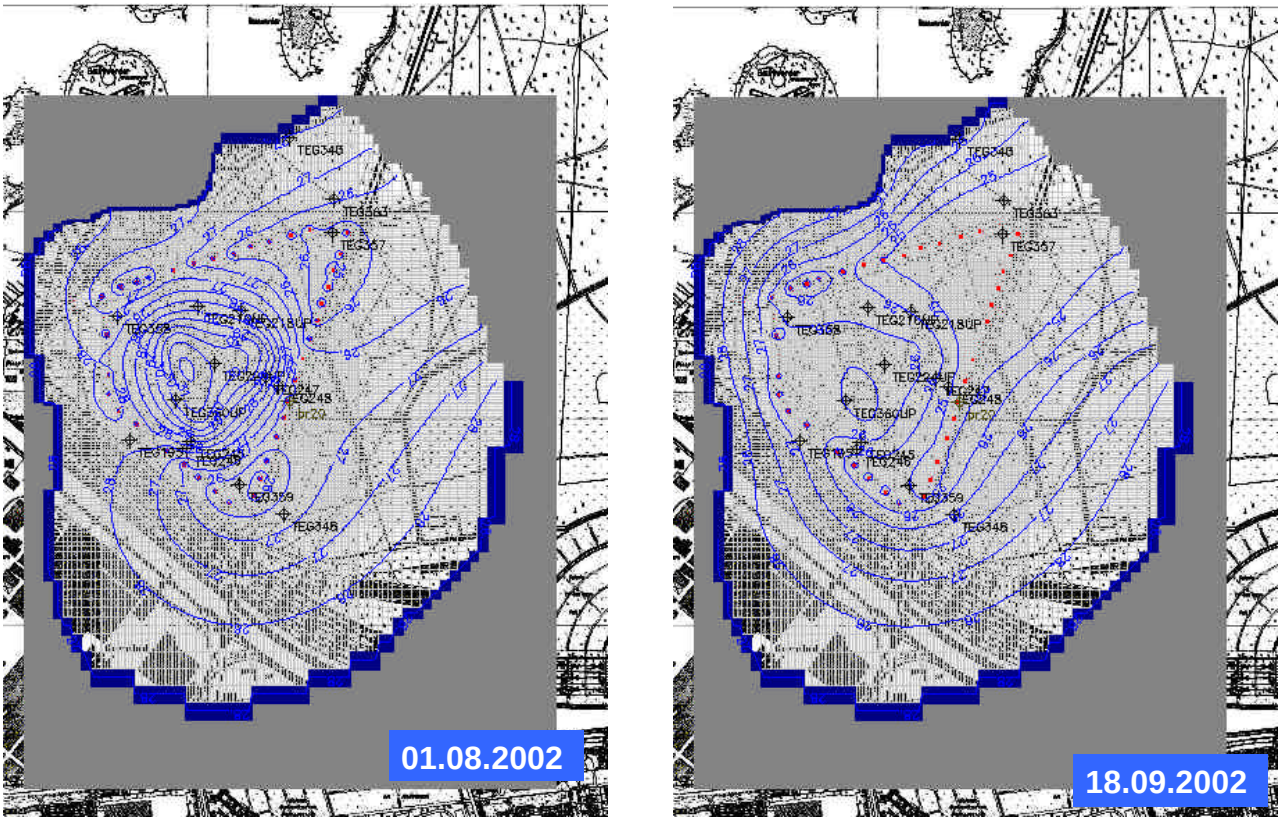
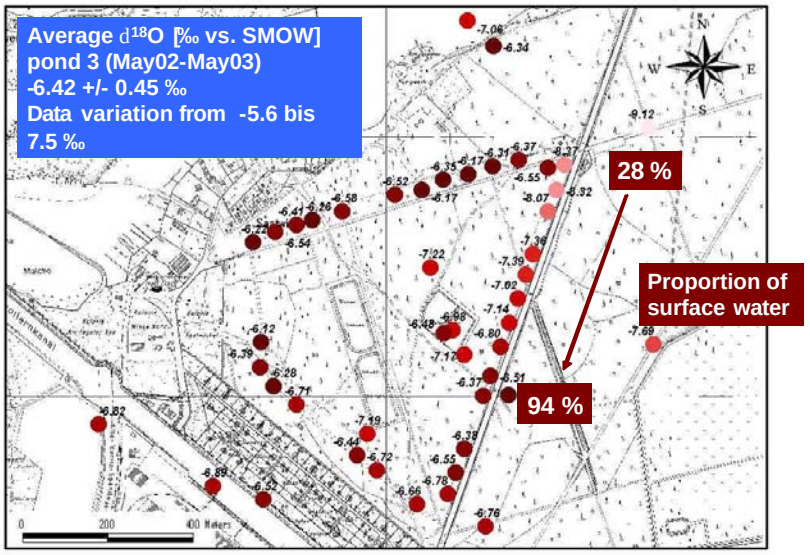
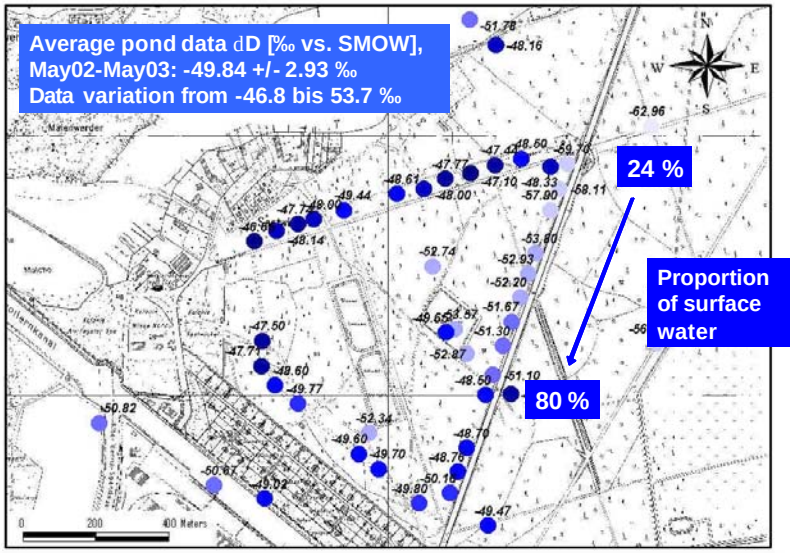


Figure 30: Groundwater head isolines of the hydraulic model of J. Greskowiak ("model" group, personal communication) for a situation where all 3 infiltration ponds are full (left) or empty (right).

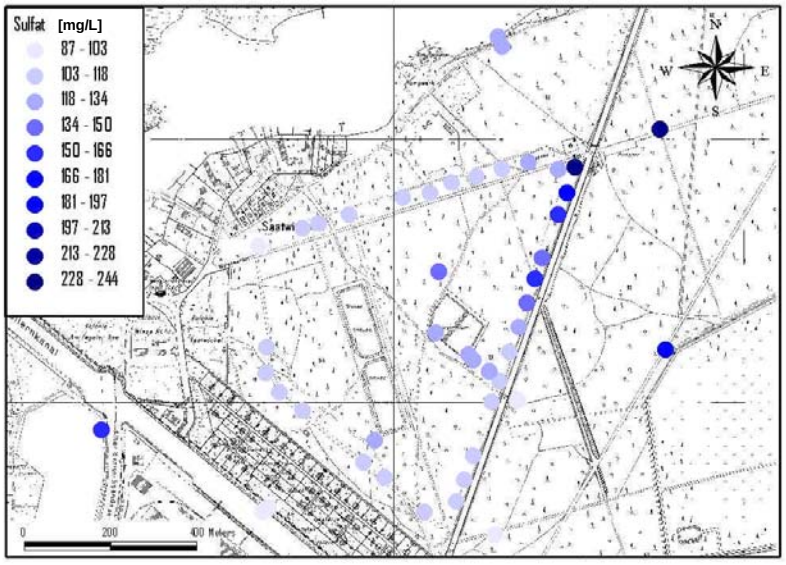
Figure 31 shows that the hydrochemistry of the "background" groundwater towards the airport, represented by TEG103, TEG342, TEG370UP & TEG348 is highly variable. While TEG103 and, to an extent, TEG342 represent the "typical" landside groundwater (e.g. low $\delta^{18}O$ & δD, high SO_4 & Ca, low Cl, Na, B), the $\delta^{18}O$ & δD and SO_4 values of TEG348 and TEG370UP lie within the range of those of the surface water (temporal variation of the surface water see previous chapters), indicating that there is a hydraulic connection between surface water (Hohenzollernkanal or even the Spree further south. Because there is hardly a difference between surface water and groundwater in the southern triangle, the proportion of BF can only be calculated for production wells SAAT 11-20 (Fig. 23, calculated with TEG103 only) and values are probably only accurate for well 11-13, which receive water from the TEG103 direction and differ strongly from the remaining wells (lower $\delta^{18}O$ & δD, higher SO_4 & Ca, lower Cl, Na, B).



a)



b)



c)

Figure 31: Influence from the NE: $d^{18}O$ (a) & dD (b) values [‰ vs. SMOW] and sulfate concentrations, March/May 2003.

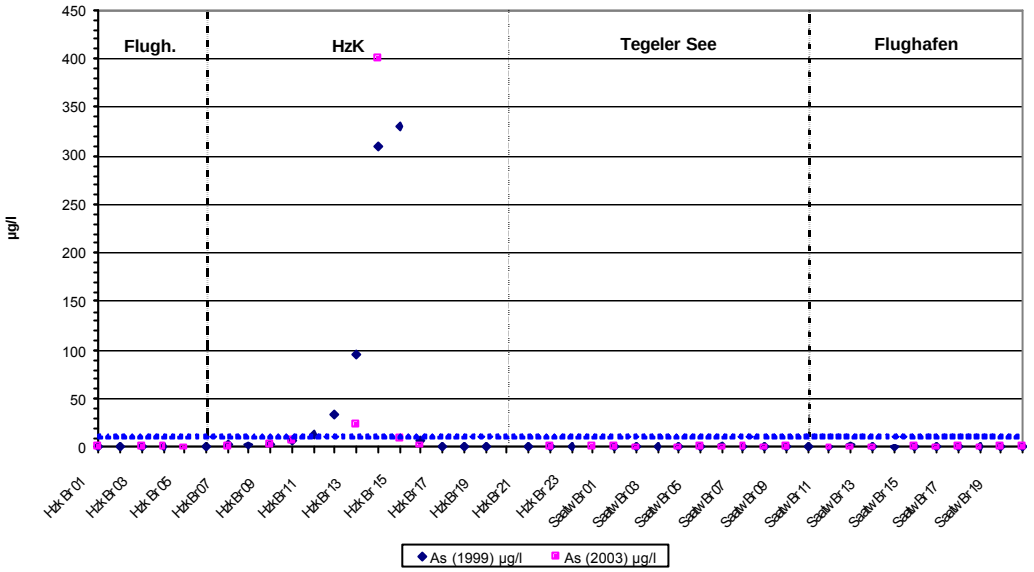


Figure 32: Arsenic concentrations in the production wells in 1999 and 2003. Blue-line: drinking water limit (data source: BWB).

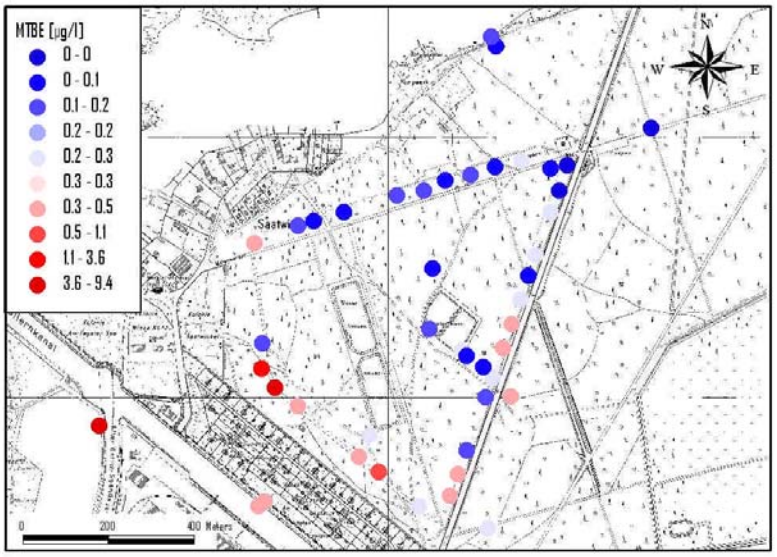
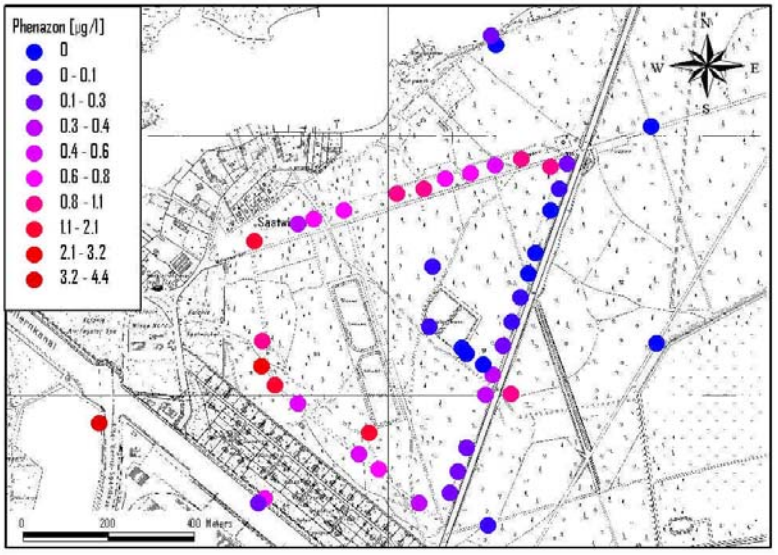


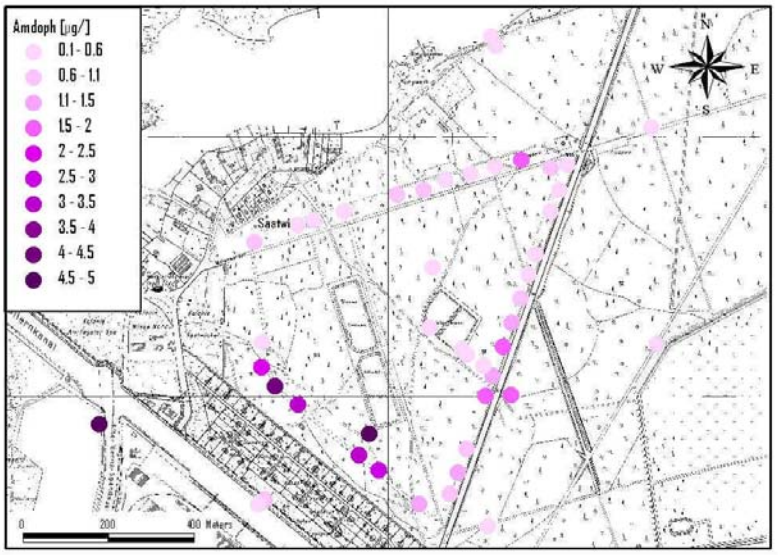
Figure 33: MTBE concentrations in samples wells in 2003 (data source: BWB).

The production wells in the south-west contain elevated concentrations of arsenic (Fig. 32, exceeding the drinking water limit), MTBE (Fig. 33), Phenazone (Fig. 34 a), AMDOPH (Fig. 34b) and EDTA, clearly originating from the other side of the Hohenzollernkanal, where highest concentrations are found in TEG2AS. As and MTBE originate from different contaminated industrial sites west of TEG2AS. The As pollution is known by BWB and As is removed during drinking water treatment (personal communication: U. Dünnbier).

While highest Phenazone (analgesic) and AMDOPH (oxidation product of of dimethylaminophenazone; REDDERSEN et al, 2002) concentrations are found in the south-west, highest propyphenazone (analgesic/anti-inflammatory) concentrations are found in the south-west and in the north, towards Lake Tegel. The phenazone-type pharmaceuticals and related substances originate from the surface water, where their presence is caused by their discharge from WWTP (HEBERER, 2002) or from former production spills of a pharmaceutical plant near Oranienburg on the Upper Havel, which produced phenazone-type pharmaceuticals. REDDERSEN et al. (2002) suspect that spills of the plant released into the environment in the past, when regulations were less strict, are the cause of some of today's findings of PhAC residues. Because of the pharmaceutical plant, phenazone and dimethylaminophenazone (not detected) concentrations in the surface water of the Upper Havel were probably considerably higher in the past decades than they are today (exact values are not known). In addition, the production of dimethylaminophenazone was stopped in 1978 (BRESSER, 1995). Therefore, the high concentrations of phenazone and AMDOPH as a persistent residue of dimethylaminophenazone (pers. comm. U. Dünnbier) in the south-west indicate, that the groundwater is probably older BF. It infiltrated from the Upper Havel 1-2 km further west, passed the industrial contamination sites (thereby accumulating As, MTBE etc.) and is now abstracted by the production wells with a considerable time lag of a few years to a few decades.



a)



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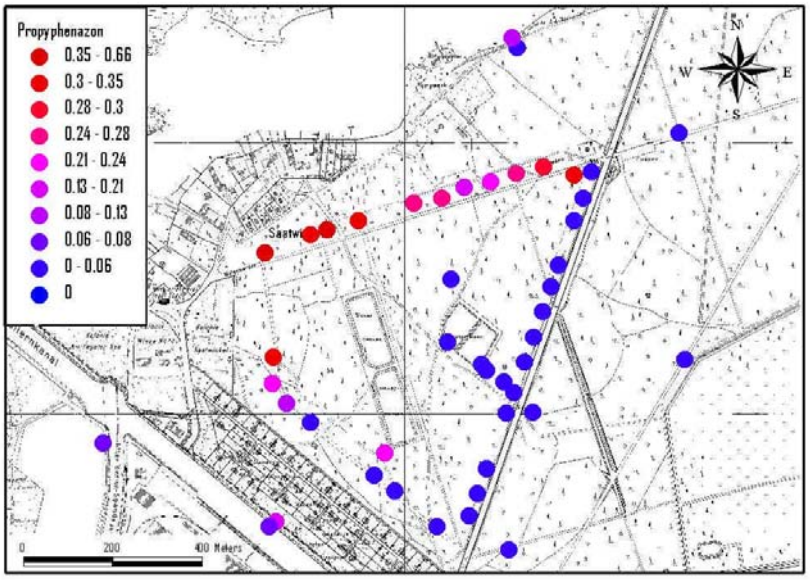


c)

Figure 34: Phenazone-type pharmaceuticals and residues phenazone (a), AMDOPH (b) & propyphenazone(c). Data source: BWB.

It seems that the share of “older” BF containing phenazone and, in particular, AMDOPH is getting larger with depth at all investigated sites (also at Wannsee and Tegel). In figure 34, the phenazone and AMDOPH concentration in the background groundwater of the GWA transect clearly increase from TEG370OP, TEG370UP to TEG373 to concentrations high above today’s findings in the surface water.

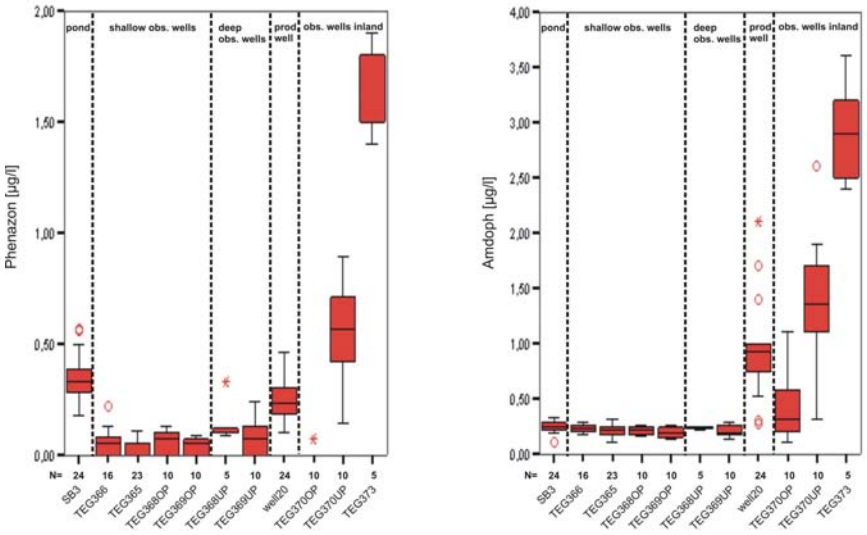


Figure 35: Boxplots for Phenazone and AMDOPH at GWA transect. Data source: BWB.

The higher propyphenazone concentrations towards Lake Tegel, where travel times should be in the order of magnitude of a few months suggest that it is presently brought in with the treated WW, thereby representing “younger” bank-filtrate.

Approximate input pathways in the area are shown in figure36

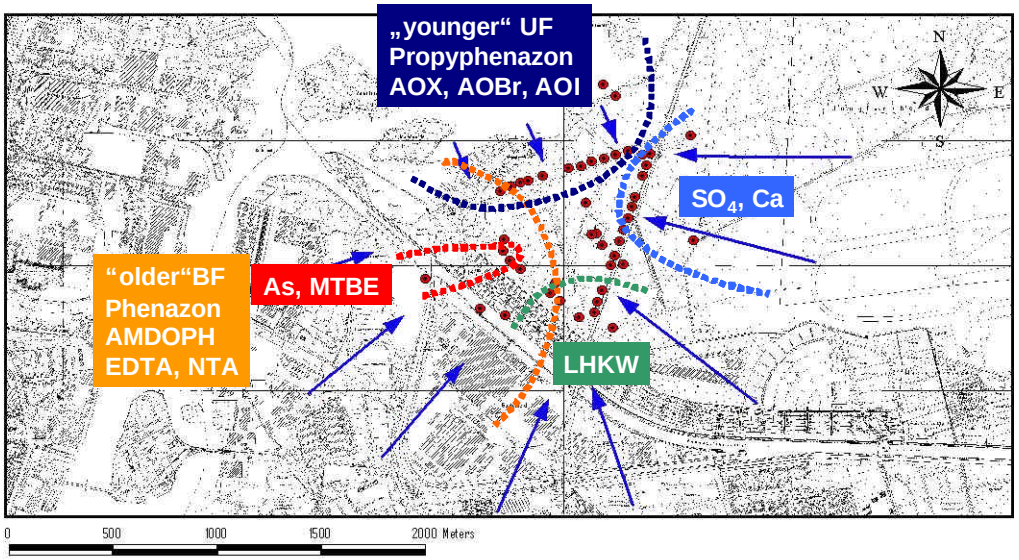


Figure 36: Summarising the major input paths for various water constituents.

Major conclusions & summary of GWA Tegel results:

- Travel times from the pond to the observation well at the transect are short and vary between a few days to observation wells below the pond to ~ 50 days to production well 20.
- The redox conditions are strongly transient (compare also "model" group). While most of the transect is oxic in winter, conditions become more reducing during summer, where Mn could already be detected in the observation wells directly below the pond. This has to be taken into consideration when interpreting the behaviour of redox sensitive species.
- The background groundwater variations are large, both in horizontal and in vertical direction.
- The influence of the background groundwater inland (airport) is greatest in the production wells with the lowest proportion of bank-filtrate (SAAT 11-19), manifested in low Cl & Na concentrations, low $\delta^{18}O$ & δD values as well as high Ca & SO4 concentrations.
- In the SW, the concentrations of As and MTBE are very high, because of several old contamination site SW of the Hohenzollernkanal.
- Pharmaceutically active compounds and AOX are originating from bank-filtration (compare "drug" and "organic" groups)
- The elevated concentrations of Phenazone & AMDOPH in the SW are originating from bank filtration at a time, when surface water concentrations were considerably higher ("older bank filtrate") due to spills from a pharmaceutical plant located at the Upper Havel in the past.
- Propyphenazone in particular seems to be present in higher concentrations today („younger BF")
- The concentrations of AOX, AOBr, AOCl & AOI of the production wells sampling campaign were lower in 2003, possibly only because 2003 was an extremely wet year (see chapter 5.1, compare "organic" group).

5.2.2 Bank filtration field site Lake Tegel

Clogging layer

The bottom of Lake Tegel is covered with very thick layers of mud sediments. These mud sediments are characterized by low hydraulic conductivity (2.1E-07 to 2.8E-09 m/s; FRITZ et al., 2002). At the lake borders, adjacent to the shores, the lake bottom is free of mud. However, the sands present in these areas are still heavily clogged, resulting in a hydraulic conductivity of 5.4E-06 m/s (FRITZ et al., 2002). Despite decreasing infiltration capacity, the presence of the low conductivity sediments has two positive effects. First, their relatively low permeability slows travel

times from the lake to the production wells. Second, they are far more effective in removing contaminants than unclogged aquifer sands, as the high proportions of organic matter and the finer grained material increase the adsorption and reduction capacities of the sediments. Analysis of mud sediment cores, taken from Lake Tegel, (SIEVERS, 2001) revealed that at the upper parts of the mud profile, the organic carbon content exceeds 22 % and at a depth of 80 cm below the mud surface, the organic carbon content exceeds 17 % (Fig. 37). This extremely high organic content is expected to have a positive influence on the removal of certain undesirable contaminants by microbial activity.

One species, undesired in high concentrations in the drinking water and detected in the water resources of Berlin, is sulfate. Relatively high concentrations of sulfate have been sampled in the surface water systems of Berlin in the past. A maximum concentration of 175 mg/l was detected during the period between February 1998 and October 1999 in the main pond of Lake Tegel, and a maximum concentration of 184 mg/l was detected during the period between May 1998 and June 1999 in Lake Müggelsee (FRITZ, 2002). There is also a big concern that sulfate concentrations in the river Spree may strongly increase in the future since open pit mining upstream of Berlin was largely abandoned after 1990. The former open mines are currently flooded and will be used as storage ponds for the Spree in order to discharge water into the Spree when the base flow is low. Sulfate concentrations within the ponds are extremely high with up to 60 meq/l in 2000 (KOFAHL, 2004) In the case of future Spree concentrations exceeding the drinking water limit, these cannot be diluted with groundwater because the groundwater itself (first and second aquifer) contains sulfate in concentrations higher than drinking water limits over large areas of Berlin (SOMMER VON-JARMERSTEDT et al. 1998; PEKDEGER et al. 1998).

Reduction of sulfate during bank filtration is a natural process with the positive effect of reducing sulfate concentrations. Therefore, the study of sulfate reduction during bank filtration in the lake sediments around Berlin is of great interest.

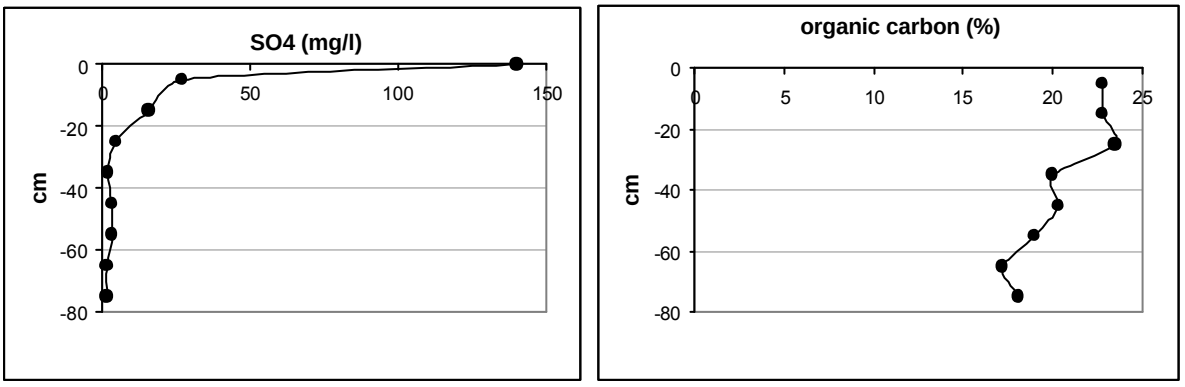


Figure 37: Sulfate in the pore water and organic carbon in the sediment of the mud sediment cores (SIEVERS, 2001).

Sulfate reduction kinetics through a mud profile in Lake Tegel (Anat Bernstein)

Sulfate concentrations were sampled along an 80 cm core of mud sediments, drilled in the bottom of Lake Tegel (Sievers, 2001, Fig. 38). Assuming that sulfate transport through the profile could be derived by diffusion and that the depletion in sulfate concentration was a consequence of redox reactions only, the geochemical computer program PHREEQC was used to fit first-order kinetic coefficients to the reduction process rates. The first-order coefficients obtained were 1.49×10^{-7} s^{-1} and 2.0×10^{-8} s^{-1} for the sections 0-10 and 10-40 cm below the mud surface, respectively. In the lowest 40 cm of the mud profile, 40-80 cm below the mud surface, steady-state concentrations were observed. The variation in the reduction rate constants in the upper 40 cm were suggested to be a consequence of the different types of organic compounds along the profile, rather than the total organic matter content. The steady-state concentrations at the lowest part of the profile were suggested to be the consequence of either competition with other microbial populations or sulfide toxicity, a product of the sulfate reduction.

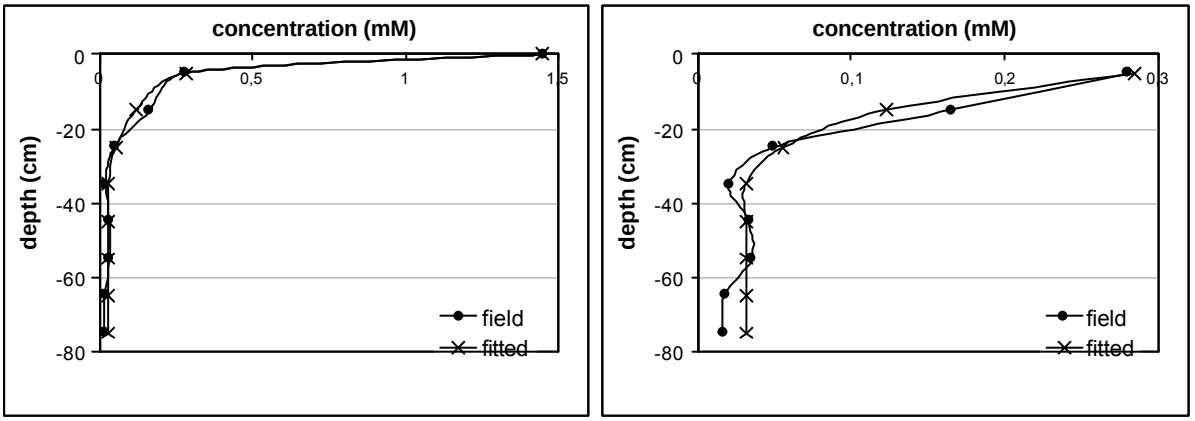


Figure 38: Sulfate concentration profile (full dots) and the fitted profile (crosses) using first-order kinetics. In the right figure the lake water concentrations were taken out in order to focus the scale.

Aquifer sediments

The sediments at the site are similar to those at the artificial recharge site Tegel. The *Saalian* till (qsWA//gm) was only encountered at TEG372 and ends between 3302 and TEG371UP. The lithological cross section of FRITZ (2002) has been complemented with the new information (Fig. 39). Results from sieving analysis of samples taken at each lithological change (or at least every metre) of core TEG371UP) were added to the cross-section for orientation. A relatively small variation from 1.5E-4 to 1.1E-03 m/s was observed, which is similar to hydraulic conductivities at the GWA Tegel.

Similar to core TEG367 and TEG369, the unsaturated sediment zone (or, more precisely what was the unsaturated zone over a long period of time) differs from the sands below. At present, the unsaturated zone is much larger than it would be without pumping, at a water-table depth of 7-12 m below ground, depending on the pumping regime. Carbonate (inorganic carbon) appears from a

depth of around 5.6 m onwards (Fig. 41) with a content of 0.16 to 1.3 weight %. The organic carbon content is low with 0.02-0.08 weight % (Fig. 41). With a few exceptions, the total iron content is 1-2 g/kg Fe (Fig. 41). The share of the reducible manganese fraction (Mn(hydr)oxides) seems to be getting slightly less with depth. In terms of total ion concentrations (HNO_3 extraction, Fig. 40), aluminium and iron are the main minor cations in the unsaturated sands, while calcium dominates within the saturated zone (Fig. 40).

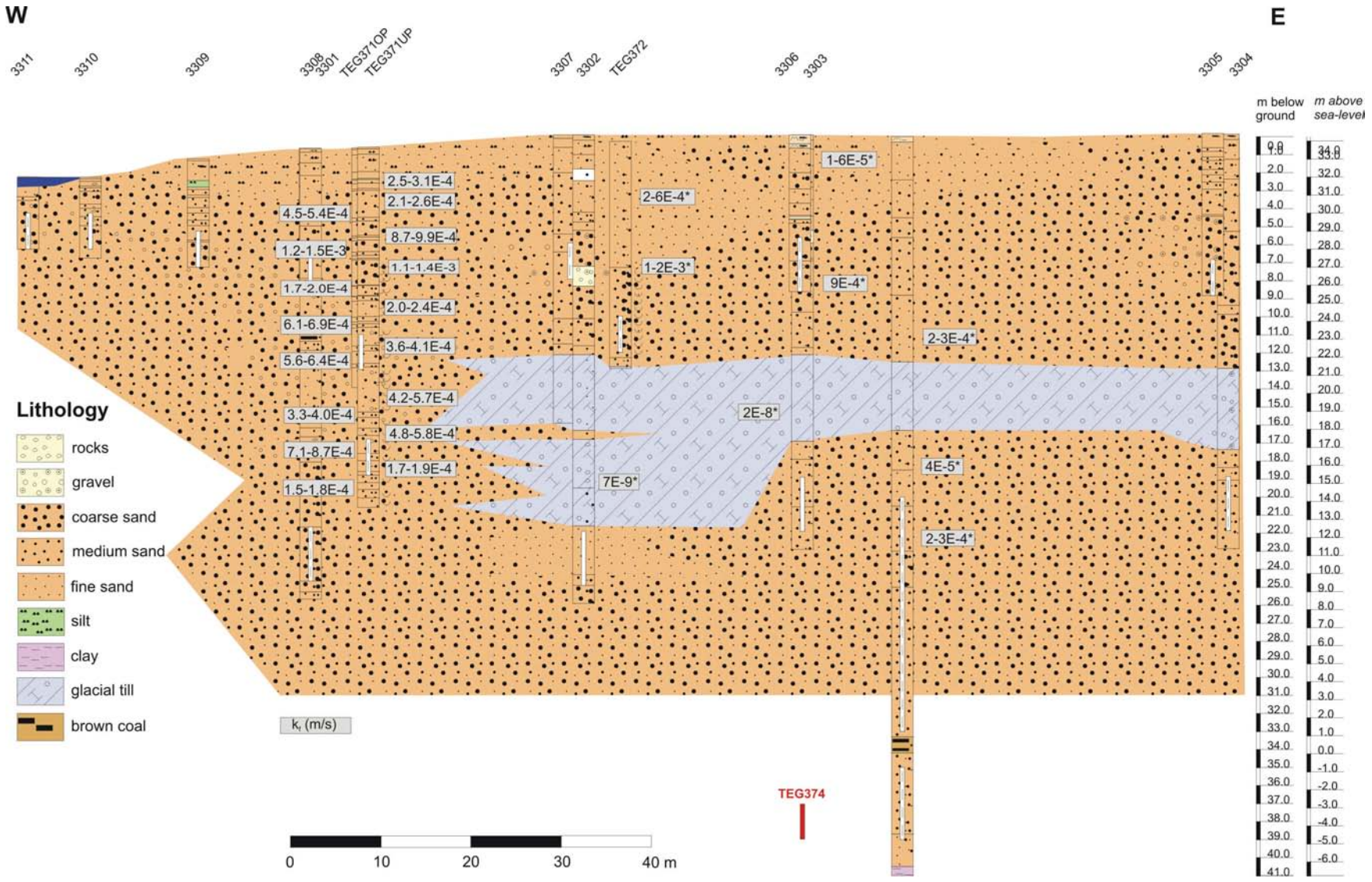


Figure 39: Geological cross-section of the transect Tegel with hydraulic conductivities from sieving of core TEG371UP. Values with from Fritz (2002).*

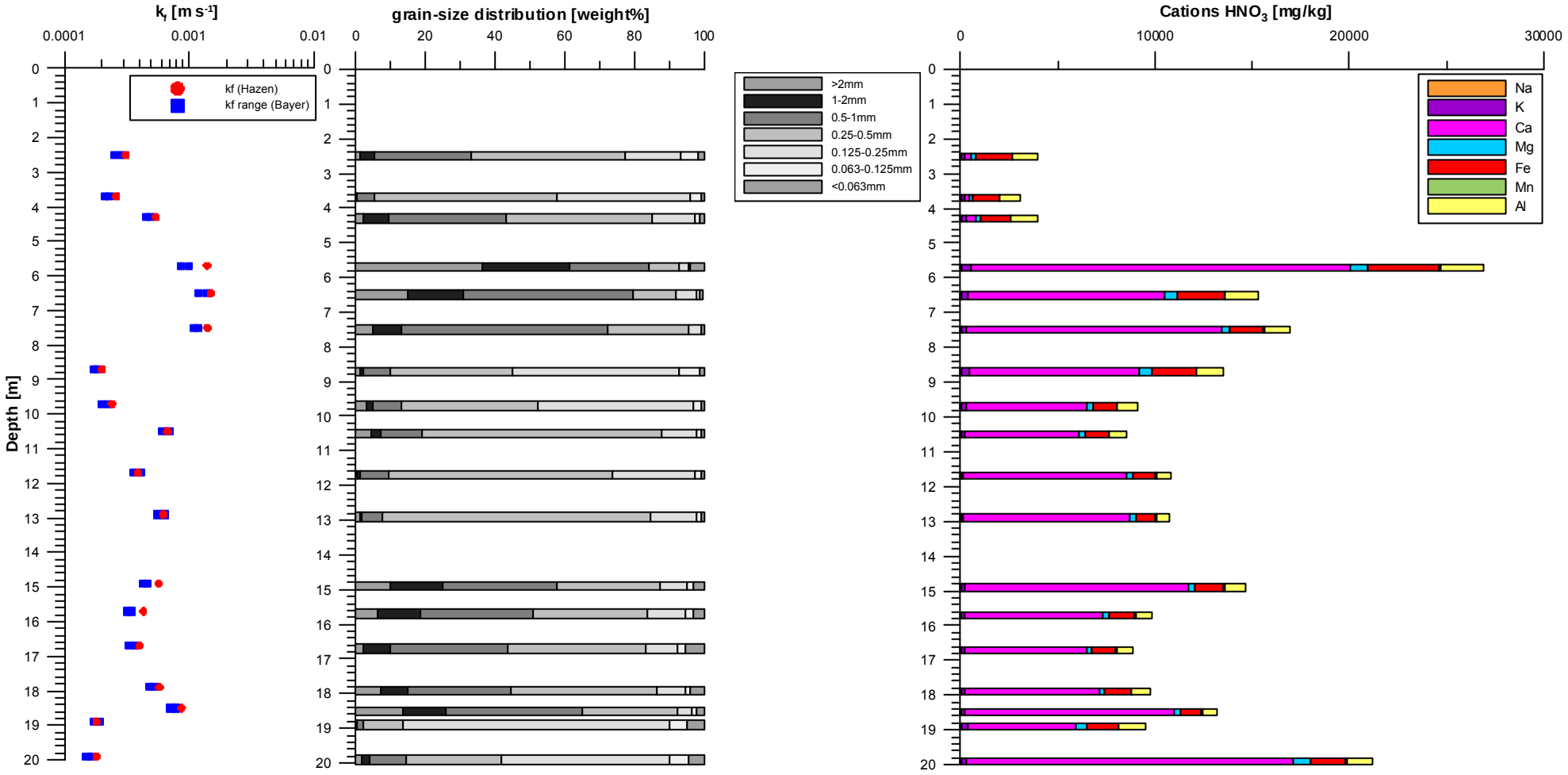


Figure 40: Hydraulic conductivities (k_f), grain-size distribution and cations from HNO_3 extraction in core TEG371UP.

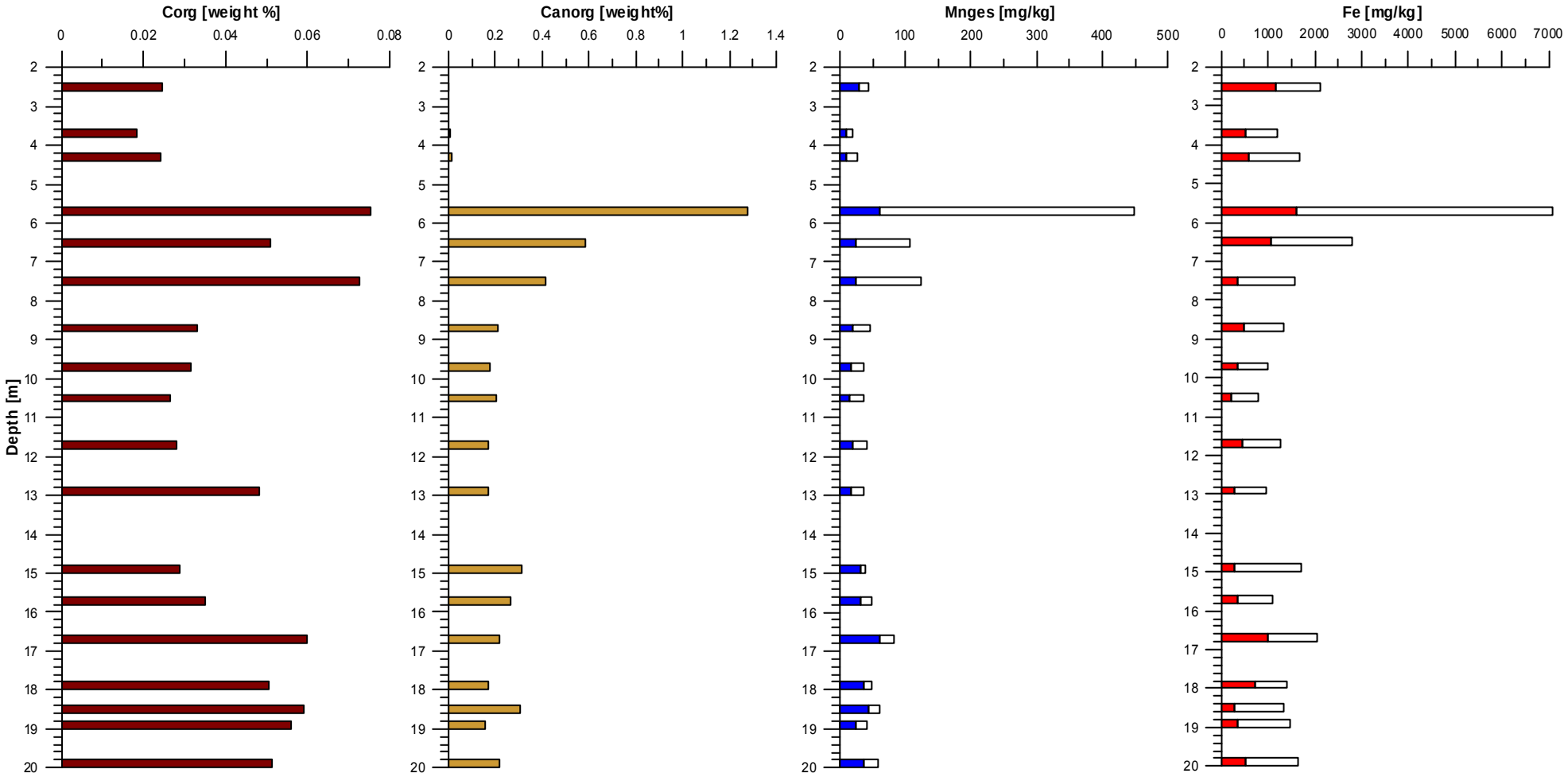


Figure 41: Organic and inorganic carbon content, Fe(III) and Fe(II), Mn(III) and Mn(II) content in core TEG371UP.

Hydraulic situation

A steady-state 3-dimensional model of the site was constructed in the previous projects (FRITZ, 2002) by EICHHORN (2000). A simplified transient 2-dimensional model, simulating a number of pumping scenarios was developed by RÜMMLER (2003) in joint co-operation between the IGB and the FU on the basis of pumping test data from EICHHORN (2000). The aim was to understand how flow-paths, travel times and proportions of bank-filtrate vary depending on pumping rates and well regimes. The thesis is described in detail in the IGB report ("model" group). Figure 42 shows the flow-paths of one scenario and is meant to give an idea on how flow-paths show a zigzag pattern due to alternating operation of the productions wells. In reality, the operation of the pumps does not show a clear pattern. But however strongly flow-paths may move, the following tracer evaluation still gives reasonable average values for residence times. But it has to be taken into account that the actual flow-path length may be much larger than expected. A 3-dimensional transient hydraulic model is currently developed at the IGB (see report "model" group).

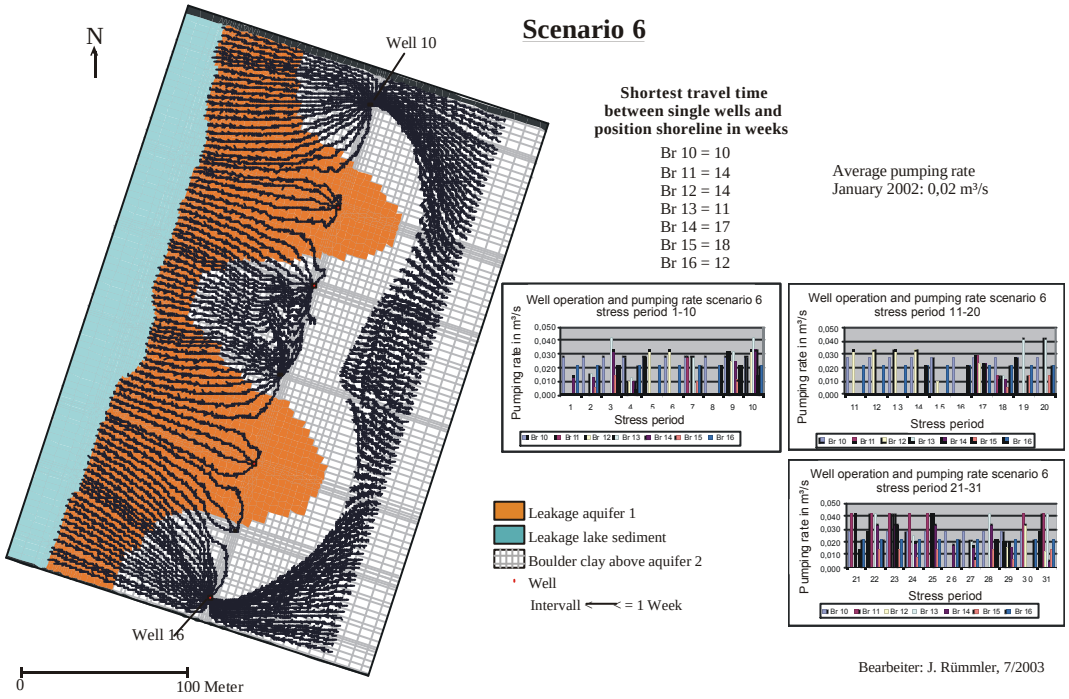


Figure 42: Flow-paths in a transient simulation with monthly alternation of wells 10, 12, 14, 16 and 10, 11, 15, 16 (RÜMMLER, 203).

Figure 43 shows water-level data available to date. It reflects that the summer 2002 was very wetwhile the summer 2003 was very dry and hot, resulting in an increase in water demand and therefore an increase in abstraction. In summer 2003, even the "deeper" shallow wells TEG372 and TEG371OP fell dry which means (since they have filter screens just above the till) that there was virtually almost no water above the till in the upper aquifer anymore.

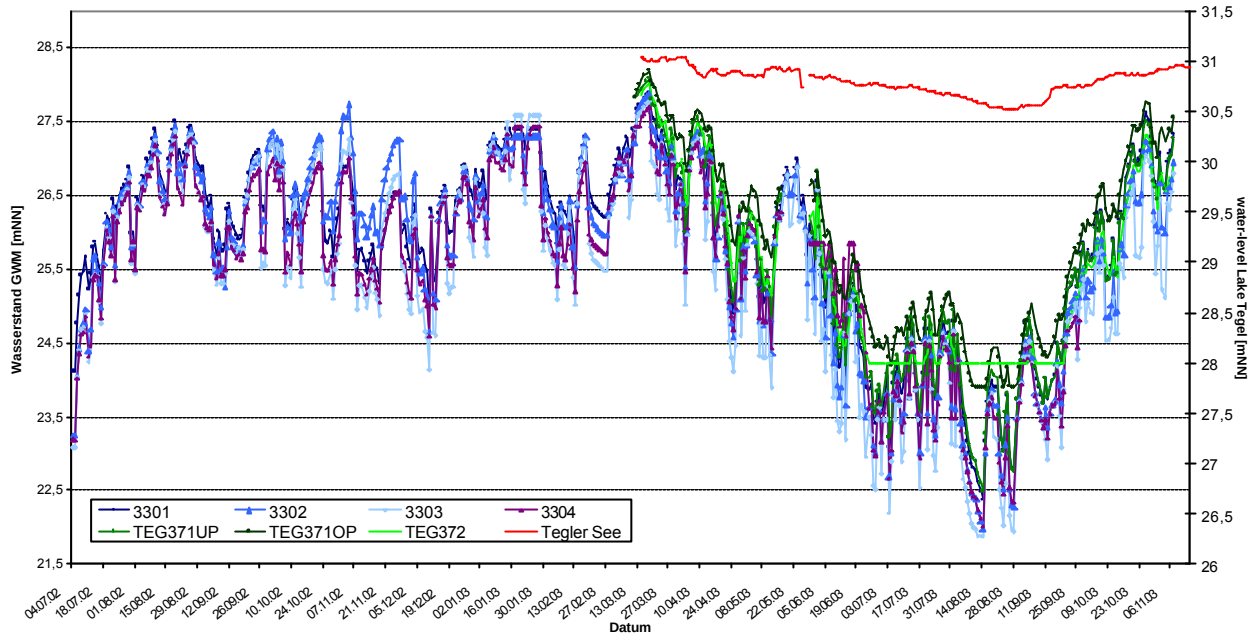
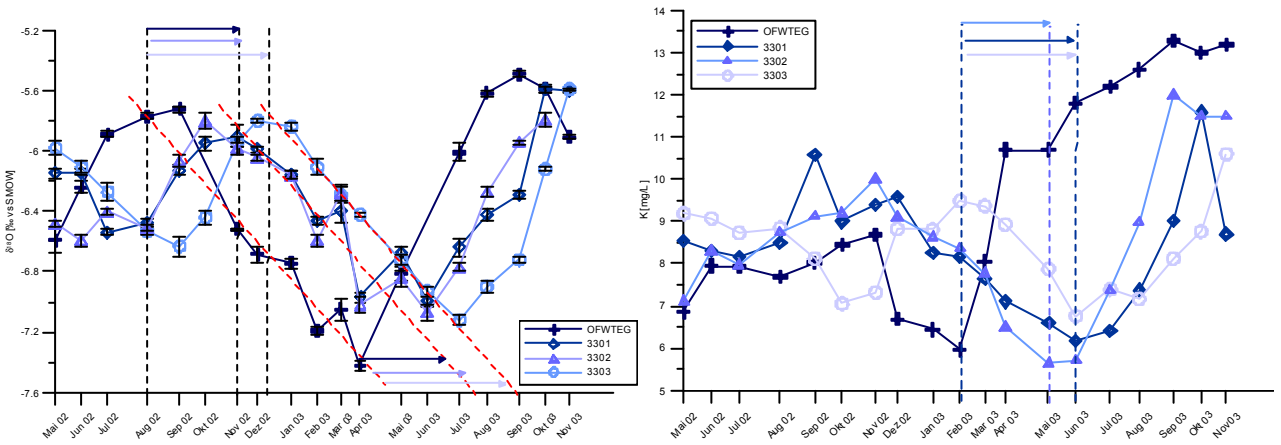


Figure 43: Available water-level data from data loggers at the transect Tegel.

Tracer evaluation (travel times, groundwater age and mixing)

Breakthrough curves of potential tracers were sighted and the suitable ones are shown below, divided into figures of the deeper (Fig. 44) and shallower (Fig. 45) observation wells. In 2002, only the stable isotopes developed a clear peak which changed with the minimum of WW indicators B, Cl^- and K in February 2003. Missing data is due to the fact that observation wells fell dry during summer months.



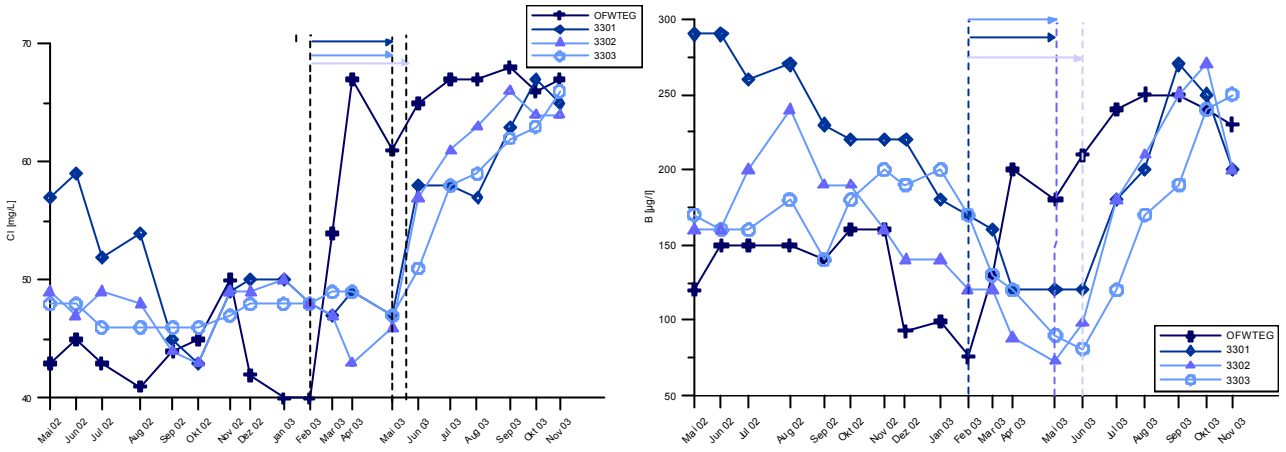


Figure 44: Figures of deep groundwater wells (3301-3303) to estimate travel times from shift of tracer breakthrough curves ($d^{18}O$, dD, Cl^- and B) indicated by arrows. Data source: AWI & BWB.

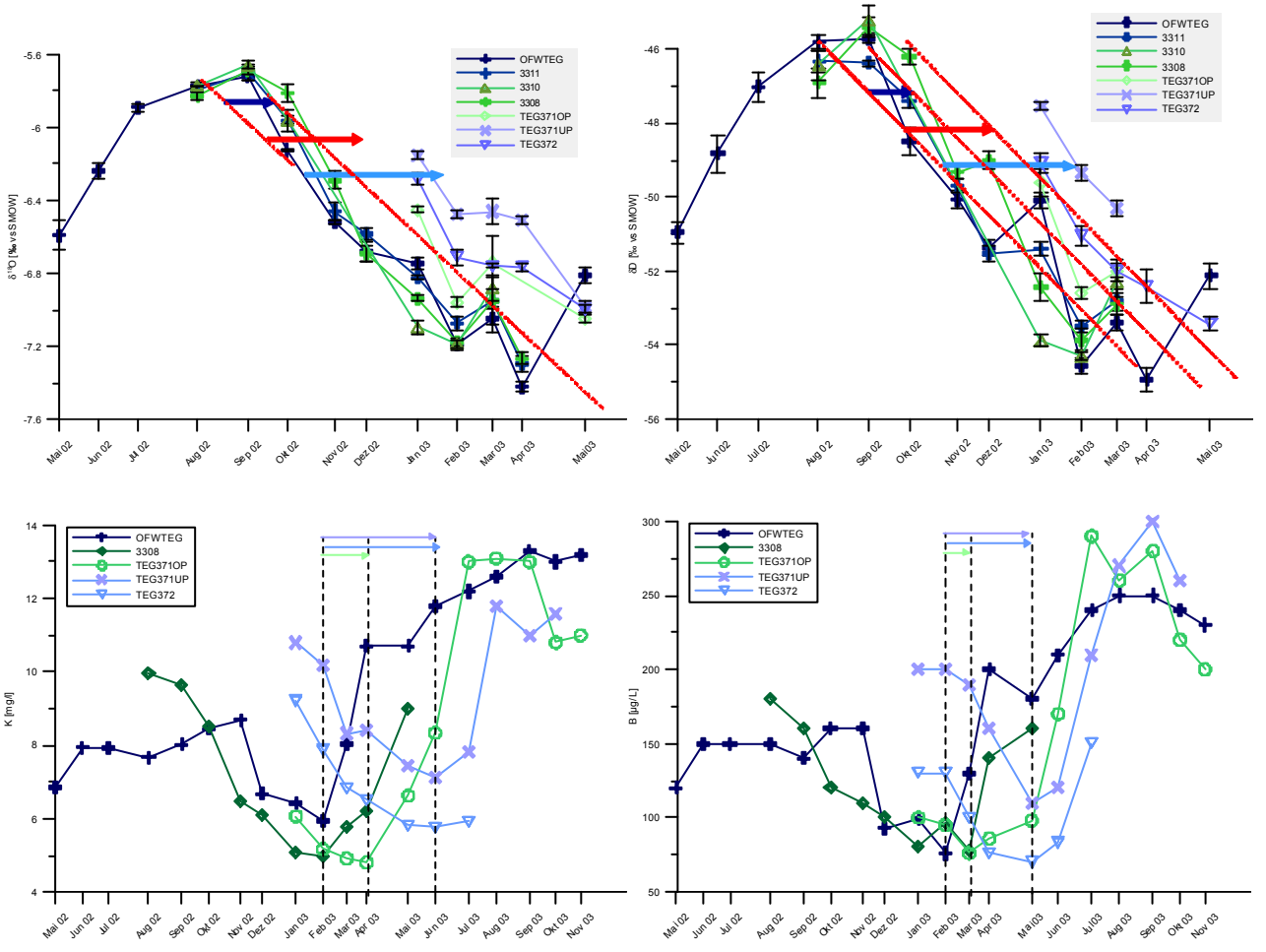


Figure 45: Figures of shallow groundwater wells (3308, TEG371OP, TEG371UP, TEG372) to estimate travel times from shift of tracer breakthrough curves ($d^{18}O$, dD, Cl^- and B) indicated by arrows. Data source: AWI & BWB.

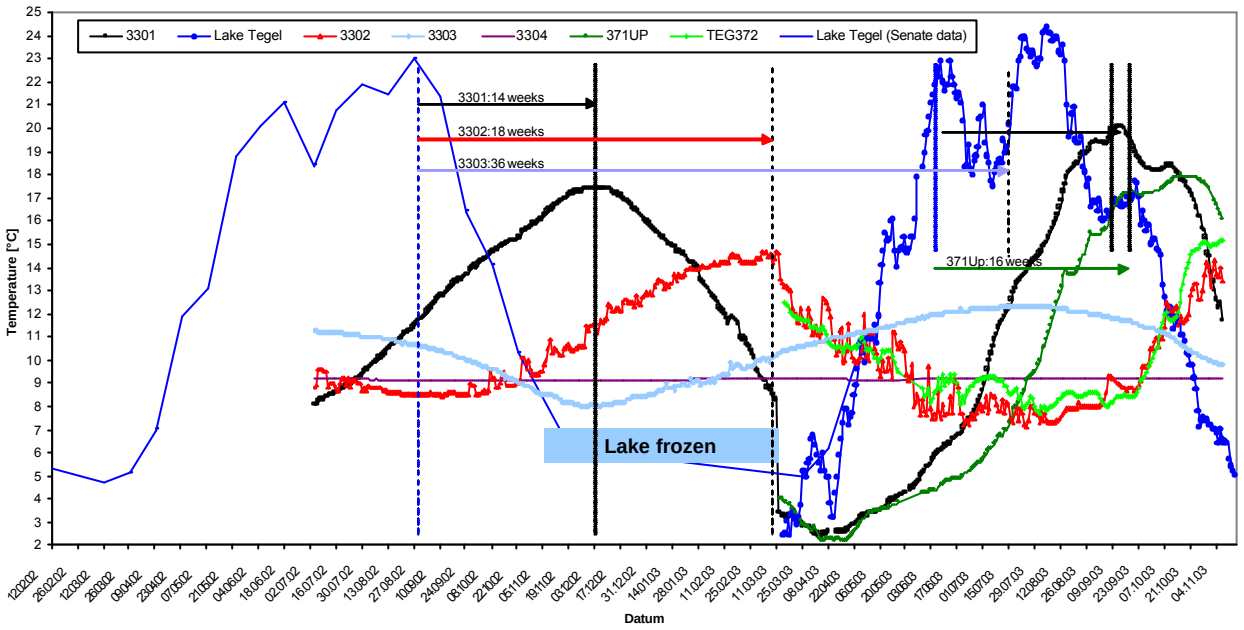


Figure 46: Temperature breakthrough curves registered with data loggers at the transect Tegel.

The temperature breakthrough curves have a better resolution than the monthly hydrochemical samplings, but they are not fully understood to date. From comparison with the conventional tracers, the retardation coefficient can be estimated, which would result in an R of 1 for 3301 (no retardation at all), 1.5 for 3302 and 2 for 3303. First attempts to model the heat flow were made by visiting student Virginia Robles Arenas with a modified version of HEATFLOW.MOD made by E. Holzbecher (IGB "model" group, pers. communication). At this stage, the temperature data interpretation still needs to be improved and cannot be used for travel times.

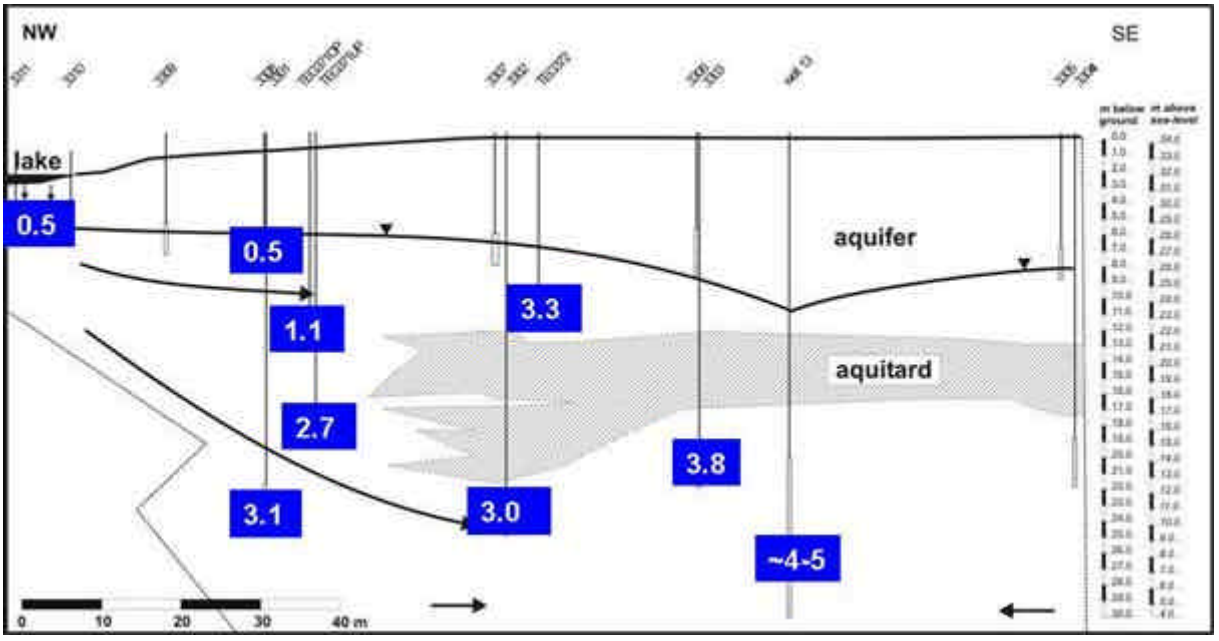


Figure 47: Summary of results from travel time estimation, best estimates for average values (details see Appendix ?).

Figure 47 summarises the results of the visual estimation of travel times from tracer breakthrough curves. The travel time from the surface water to well 13 on the shortest pathway is 5 months, which means that travel times have increased compared to 1999-2000, when Fritz (2002) observed travel times of 6-8 months. Well 3301, although closer to the lake than 3302, has a slightly larger travel time than 3302. 3301 and 3302 must be representing different flow paths from the lake. In addition, the shape of the breakthrough curves of 3301 sometimes differs from the lake input curves, for example for B (Fig. 44) with B concentrations much higher than in the lake sample. The effective T/He age of 3301 is 1.7 years. If 100 % of the water of 3301 was originating from the direct lake shore, the effective age should be 0-0.5 years (resolution of the method for this site), like it is for TEG371OP and 3303. The effective T/He age is not a "real" age but a mixture of the age of several water bodies. It does therefore not stand as a contradiction to the remaining tracer results. It only indicates that a (probably small) proportion of the water is considerably older than 6 months. It is not possible to say precisely how large this water volume is and what effective age it is composed of. Some water may be infiltrating at the other side and is flowing beneath Lake Tegel, especially since abstraction from the Tegel west gallery has increased.

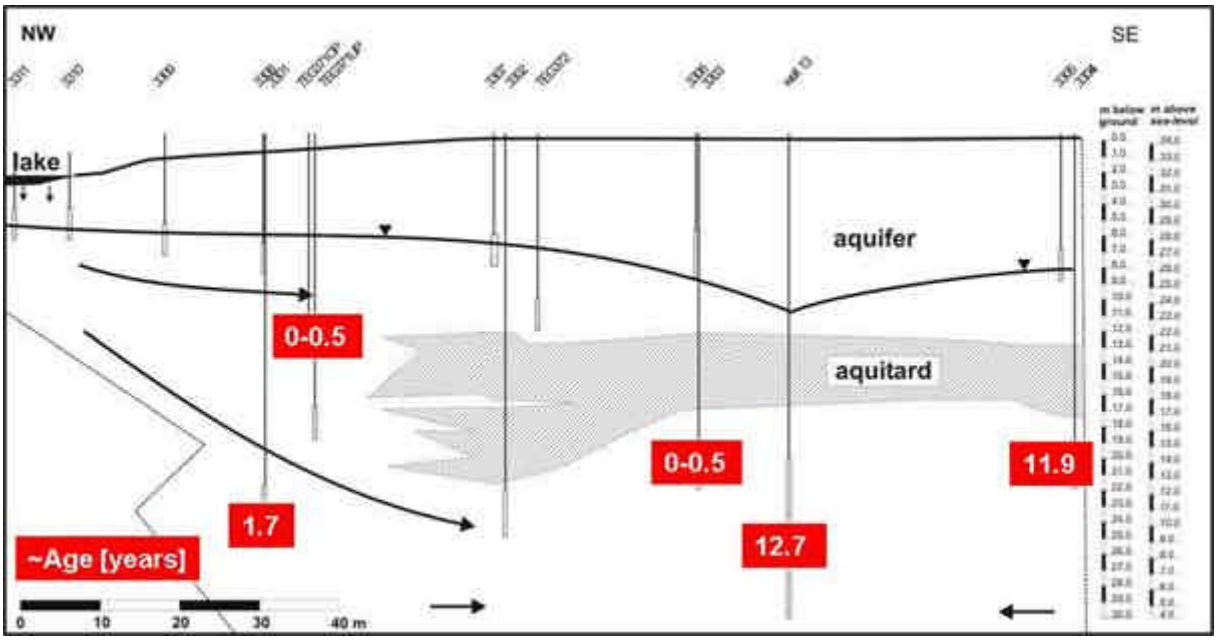


Figure 48: Results from T/He dating.

The production wells rarely show a seasonal variation similar to the observation wells. Only when extreme signals are found in the surface water, they can sometimes be seen with amplitudes that are considerably smaller. For example the B minimum of February 2003 prints though in well 13 with a time-lack of 5 months (Fig. 50).

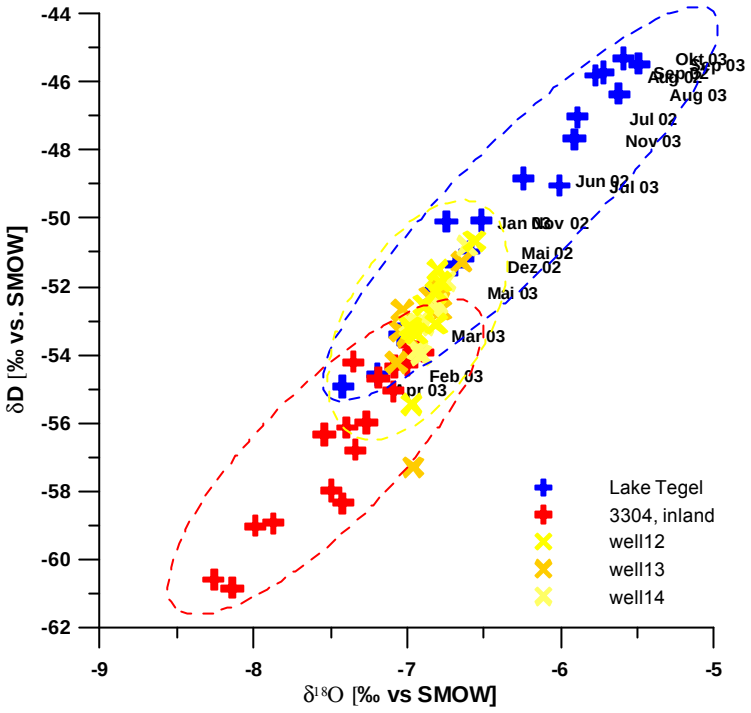


Figure 49: dD versus d18O in surface water, background groundwater and abstracted water in Tegel (May 2002-October 2003, data source: AWI).

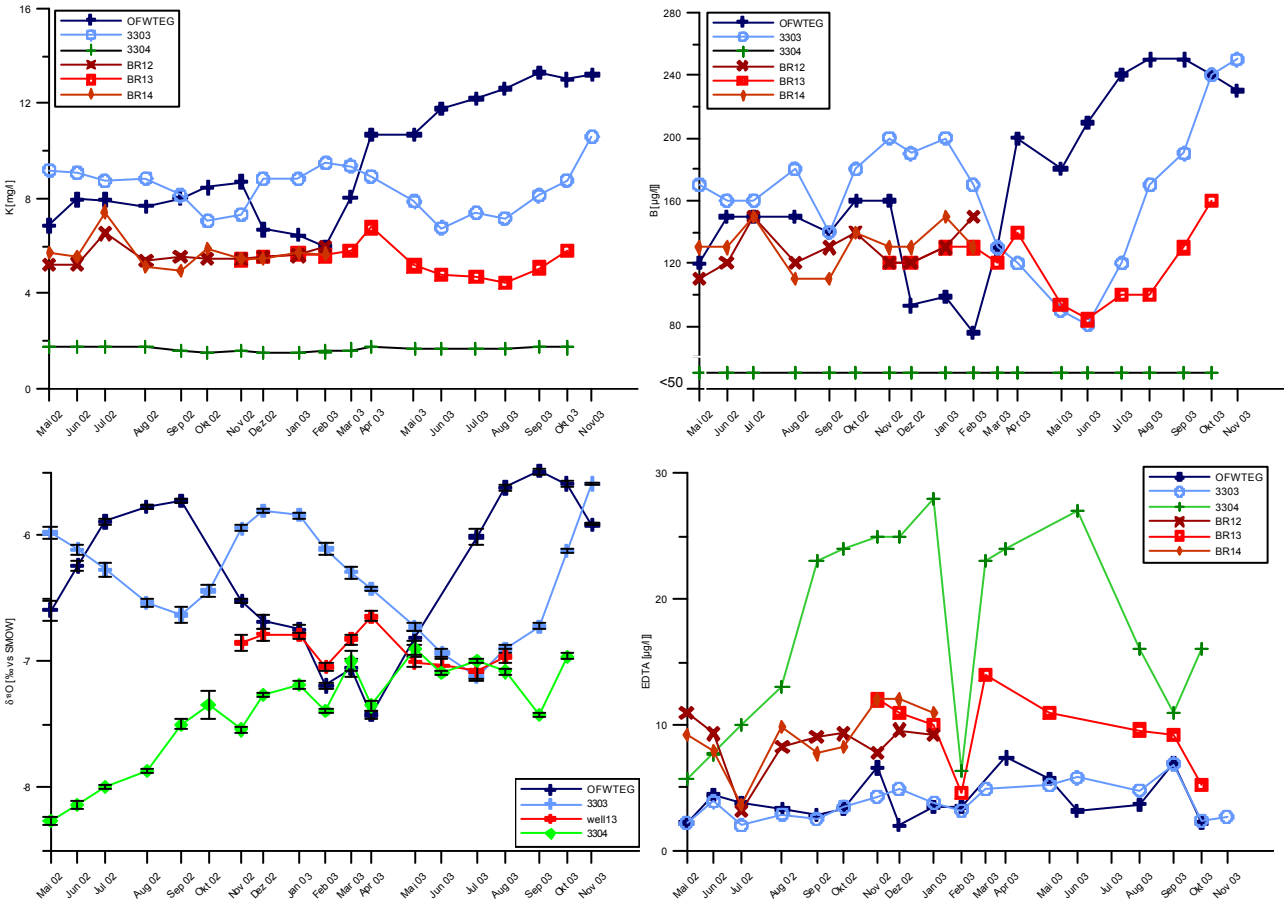


Figure 50: Time-series of K, B, d18O, EDTA in surface water, production wells and observation wells 3303 & 3304.

Figure (49) shows that on a stable isotope scatter plot, the production wells 12, 13 and 14 lie between surface water and background groundwater. To calculate the proportion of bank-filtrate in the production wells, conservative tracer with a clear difference in concentration between groundwater and surface water and fewer seasonal variations should be used. In Tegel, it is possible to use either average values or surface water concentrations from 4-5 months before or values of 3303 from the previous month. All three possibilities were tried with the stable isotopes, K, EDTA and B which show a sufficient difference between groundwater and surface water. Some difficulties arouse. For example, EDTA concentrations and isotope values in the background groundwater (3304) strongly changed in 2003, after having been more or less stable in the past (FRITZ, 2003). The isotope values increased to an extent, that they even resembled surface water values in February 2003. However, the fact that the production wells show no seasonal variations suggests that is may be more useful to use long-time averages only, rather then trying to calculate monthly percentages. Table ? gives an idea on the dimensions, but more precise proportions will be calculated, when 2 years data is available. All three production wells have a similar hydrochemistry, which is why well 12 and 14 are not sampled any longer.

Table 2: Proportions of bank-filtrate [%] in the production wells, calculated with average available data from May 2002-July 2003.

Tracer	Well 12	Well 13	Well 14
K	57	56	59
B	79	73	81
EDTA	66	62	63
δ^{18}**O**	67	67	68
δ**D**	63	66	62

Three facts indicate that the samples of the production wells are not only a mixture of bank-filtrate encountered in 3301-3303 and water from inland of the production wells (3304).

1. The average Cl^- and Na^- concentration of the wells is slightly higher than in the observation wells (Fig. 51)
2. Well 13 has an effective T/He age of 12.7 years, which is even older than the age of 3304 (11.9 years).
3. The seasonal variations of all tracers in the production wells are small.

Altogether, these phenomena indicate that a considerable proportion of the abstracted water originates from greater depth. The “deep” observation wells are only 20-25 m deep, while the aquifer base is encountered in 40.5 m below ground (Fig. 39). The lowest filter screen of well 13 is 35-39 m deep. It was therefore decided to install an additional deep observation well (37-39 m

below ground) which was completed in December 2003, in order to fully cover and understand all water components of the site. This deeper, older water may be older bank-filtrate coming from the other lake side or water from a different source, maybe from the next, more saline aquifer.

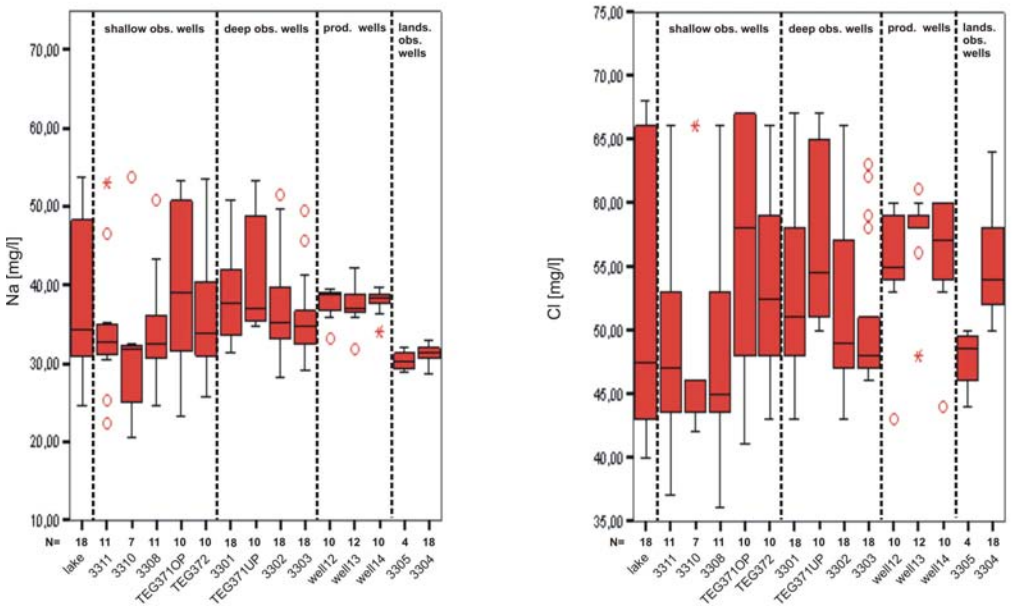


Figure 51: Boxplots of Na^+ and Cl^- at the Tegel transect (data source: BWB).

Hydrochemistry at the transect

The observation wells from the upper aquifer contain O2 throughout the year while the deep observation wells are anoxic or more precisely ferrous at all times. Fig. 53 gives an idea on the redox zoning. However, like at the GWA transect (but less extreme), the transition from one zone to another is fluent and slightly variable with time.

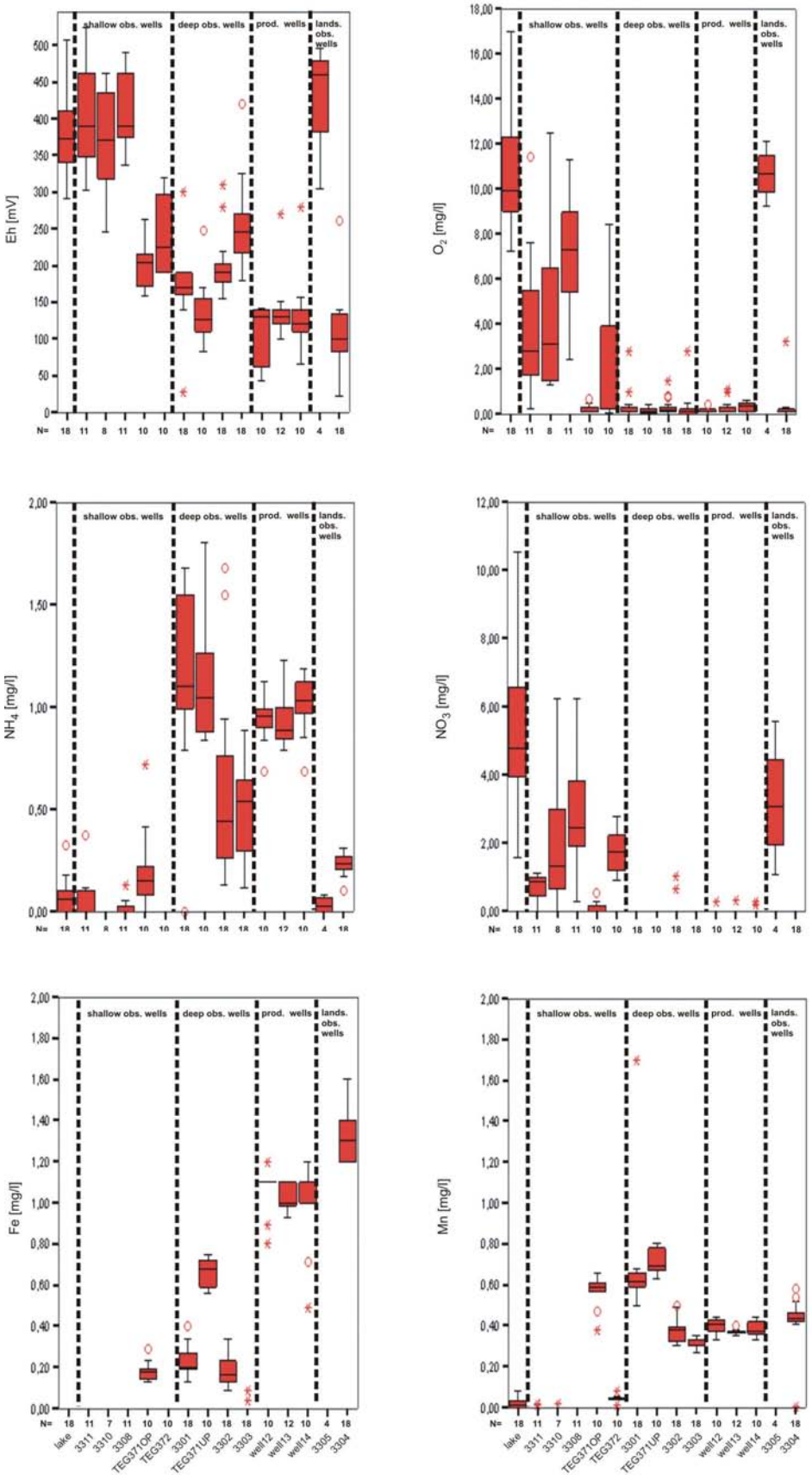


Figure 52: Boxplots of redox indicators Eh, O_2, NO_3^-, NH_4^+, Mn^{2+} & Fe^{2+} at the transect Lake Tegel. Data source: BWB.

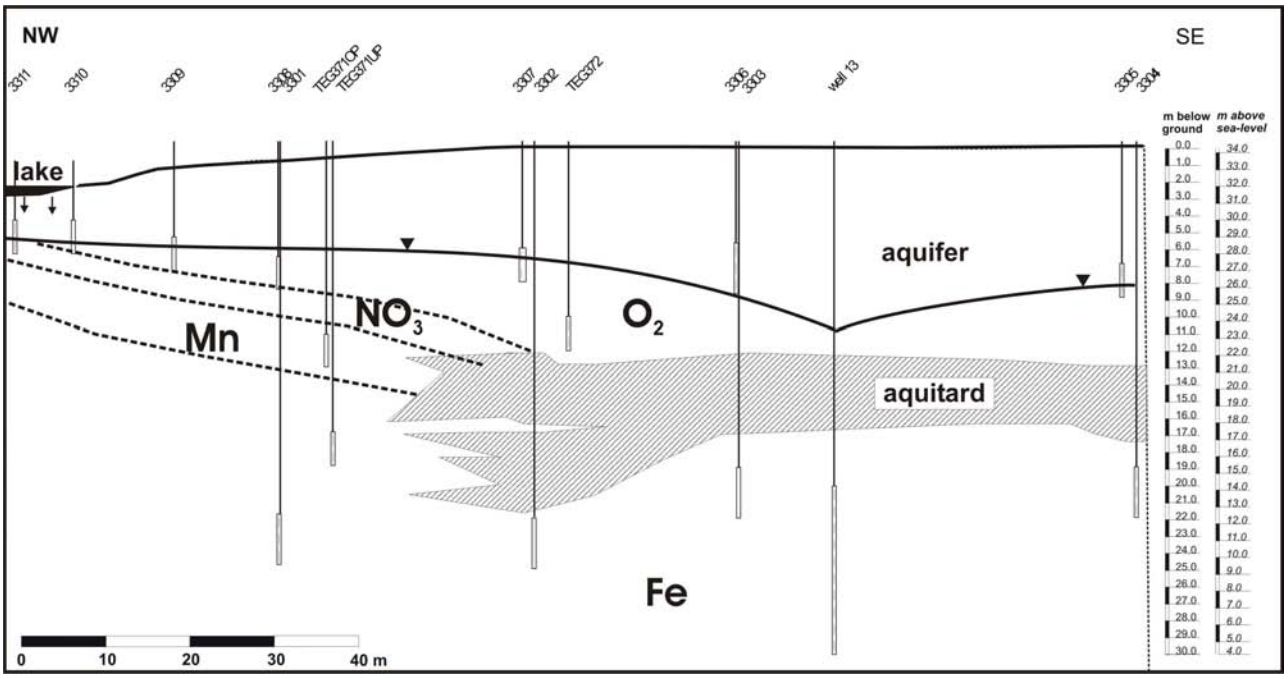


Figure 53: Approximate redox zoning as indicated by O_2, NO_3, Mn and Fe presence.

Major conclusions and summary Lake Tegel site:

- The fitted first-order constant for sulfate reduction in the uppermost 10 cm of the mud sediments profile is 1.49×10^{-7} s^{-1}. This value is 7.5 times higher than the fitted constant for the following section, 10-40 cm below the mud surface: 2.0×10^{-8} s^{-1}.
- When the first-order coefficients are expressed in terms of half-life, their values are 53 and 401 days in the upper 10 cm and the next 30 cm of mud, respectively. These values are consistent with the values found by MASSMANN et al. (2003).In the lowest 40 cm of the mud profile (40-80 cm below the mud surface), only slight variations in the sulfate concentration were observed. The reduction rate in this section was considered zero. The steady-state concentrations may be related to competition between the sulfate reducers and other microbial populations or to sulfide toxicity.
- Though an extremely high content of organic carbon is observed throughout the entire mud profile (22.8-17.2 weight %), it may be wrong to conclude that organic matter plays no role in the kinetics of sulfate reduction. However, any influence is expected to be a function of variations in the types of organic matter rather than variations in the total organic content.
- The most useful tracer for travel time evaluation are stable isotopes and (only for 2003), B & K.
- Although the temperature data has the highest time resolution, interpretation still needs to be worked on because of retardation.
- 3301 and 3302 have similar travel times. They must be representing different flow paths. In addition, 3301 contains a proportion of water that is older than 3 months.

- The age dating results, in combination with a lack in seasonality in the production wells, (and some chemical data) suggest that the production wells abstract a proportion of older bank-filtrate and/or deeper groundwater.
- The travel time of the bank-filtrate to well 13 on the shortest pathway is 4-5 months.
- The travel times seem to have increased in 2002/2003 compared to 1998/1999 (FRITZ, 2002) probably due to higher pumping rates.
- The most useful tracers for mixing calculations are stable isotopes, EDTA, B & K.
- The background groundwater characteristics changed in 2003 (rising EDTA, δD and δ^{18}O values). The changes probably have to do with greater strain on gallery West, but exact origin is not certain.
- Well 12-14 are very similar, the proportions of bank-filtrate in the wells are high, generally 60-80 % (depending on data used).
- All shallow wells contain oxygen, while the deeper observation wells are post-oxic or, more precisely, ferrous as classified by BERNER (1981).

5.2.3 Bank filtration field site Lake Wannsee

Clogging layer

FRITZ (2002) showed that the surface water infiltration takes place mainly at the lake shores, where the clogging layer is relatively thin compared to the thick mud layers generally present in the Lakes. This is obvious when considering the sulfate profile in figure 38 where sulfate is complete removed within 0.4 m. If a considerable part of the infiltrate would pass through the mud, the sulfate concentrations of the bank-filtrate would be lower than in the surface water which is not the case at any field-site. Therefore, the lake shores play a key role in the dynamics of the bank-filtration system. So far, the clogging layer at the Wannsee site had not been investigated. Therefore, 7 cores were taken drilled in January 2004. Two cores were taken in 1 m distance (water depth 0.1 m), 3 in 20 m distance (water depth 0.6 m) and 2 in 40 m distance (water depth 2.2 m) from the shoreline, all in the middle between the 2 piers and likewise in between the 2 transects. The cores from each location were drilled in 0.5 m distance from each other. One core from each location (1, 20 and 40 m) was cut open for a lithological description and geochemical analysis (cation exchange capacity, organic carbon, inorganic carbon, total sulfur, pyrite, Fe- and Mn(hydr)oxide content). The second core at each distance is used for DARCY flow experiments of the entire core and sections defined according to the lithology. Later, sieving analysis will be done to support the hydraulic conductivities derived from the experiments.

The 3rd core taken in 20 m distance from the shore, next to BEE205 will be used for a column experiment. The idea is to infiltrate Lake Wannsee water with a realistic velocity. When conditions

within the column have stabilized and steady-state conditions have been established, the pore water will be samples to evaluate the hydrochemistry of the infiltration zone. Later, a tracer test will be conducted and the column will be made available for other working groups which may be interested in the investigation of the surface-groundwater interface.

Figure 54: Taking cores from the clogging layer at Lake Wannsee in 1 m (left) and 40 m (right) distance from the shore.

Aquifer Sediments

The sediments at the Lake Wannsee transects are fairly homogenous. They mainly consist of fine- to medium sized sands of light greyish to brown colours. They are of glacial-fluvial origin (*Saalian* to *Weichselian* glacial period). Finer grained, organic rich sediments of the *Holstein* interglacial period (aquitard) were not encountered during the new drillings. From previous drilling campaigns it is known that they can be expected around sea-level, which is equivalent to 35 m below ground at the site. Three different aquifers are encountered. Note that in the following discussion, the aquifers are named upper, middle and lower aquifer, according to the division at the site and not according to the official numbering in Berlin by LIMACH & TIERBACH (1997). A lithological cross-sections of Wannsee 1 and Wannsee 2 with available k_f data are shown in figure 55 and 56. Figures of geochemical analysis of the new core BEE202UP are given below.

Again, the sands are fairly homogenous in terms of their hydraulic conductivity, which varies from 6.7*10E05 to 4.1E-04m/s. The organic carbon content is 0.04 to 0.26 weight %, with the exception of a sample containing 0.9 weight % organic C, because of small coal pieces. All samples contain carbonate which is probably due to the fact that the first analysed sample comes from a depth of 4.4 m below ground already.

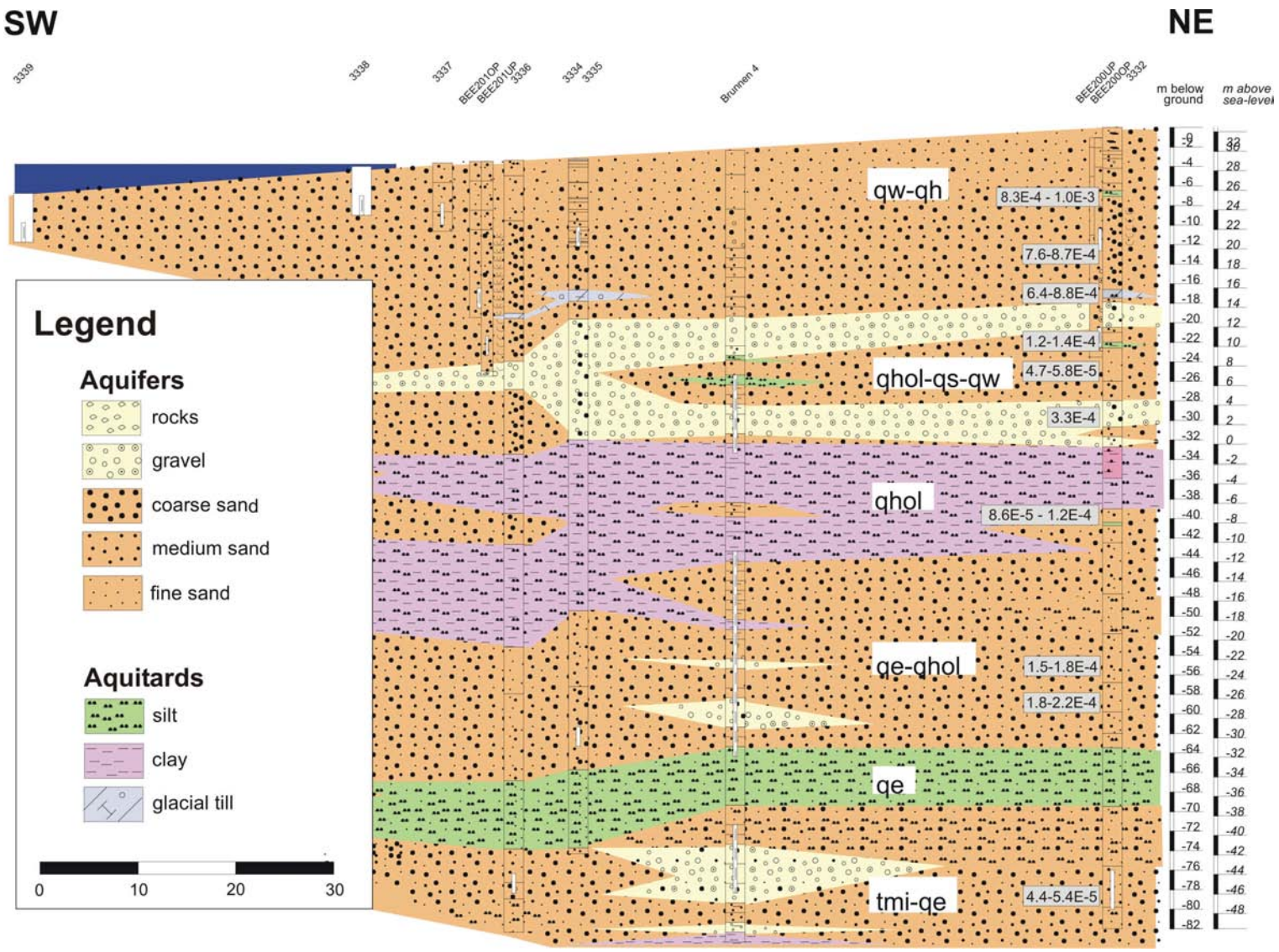


Figure 55: Lithological cross section of Wannsee 1 with k_f data of core 3332 (HINSPETER, 2002).

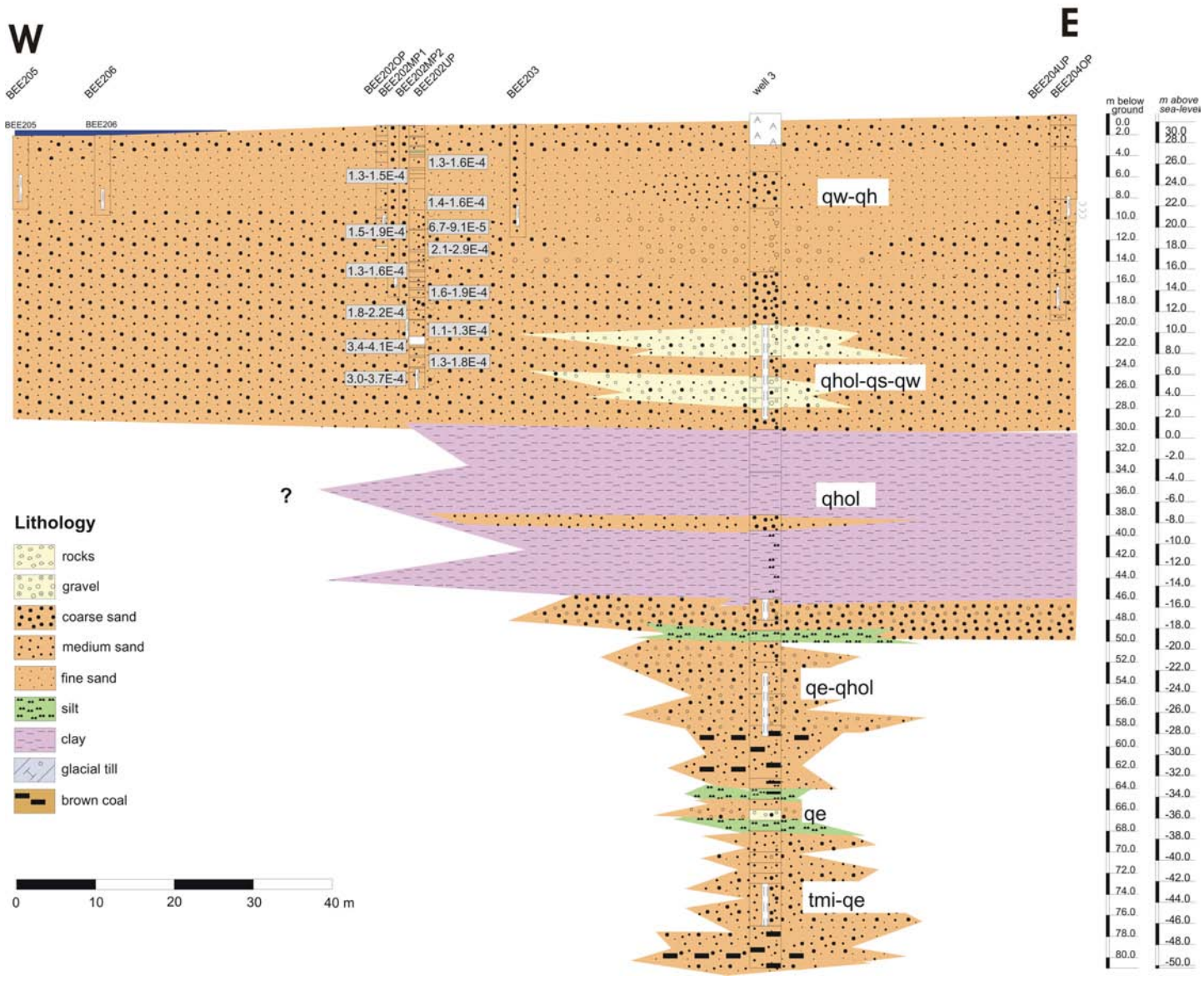


Figure 56: Lithological cross section of Wannsee 2 with k_f data of BEE202UP.

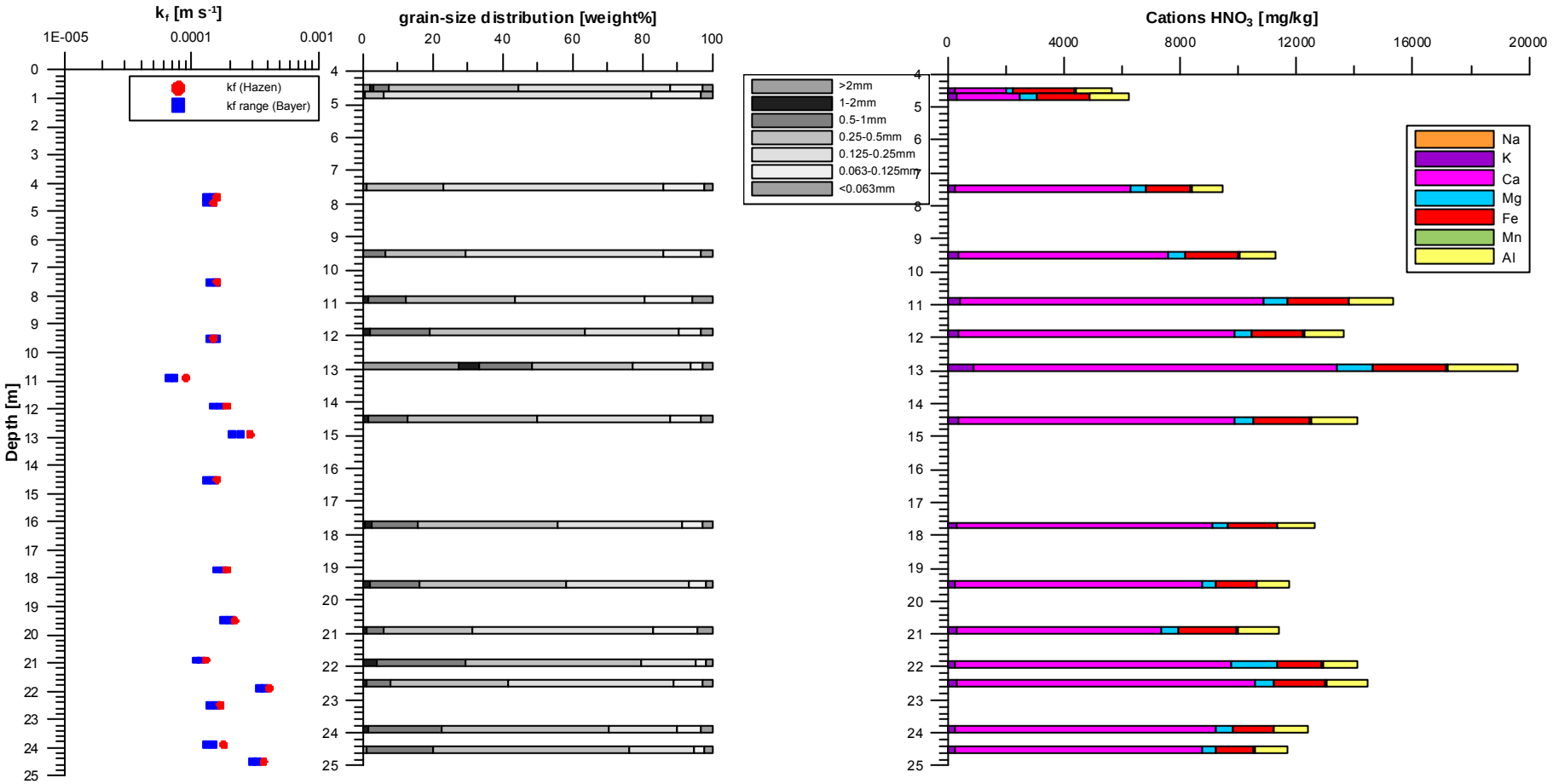


Figure 57: Hydraulic conductivities (k_f), grain-size distribution and cations from HNO_3 extraction in core BEE202UP.

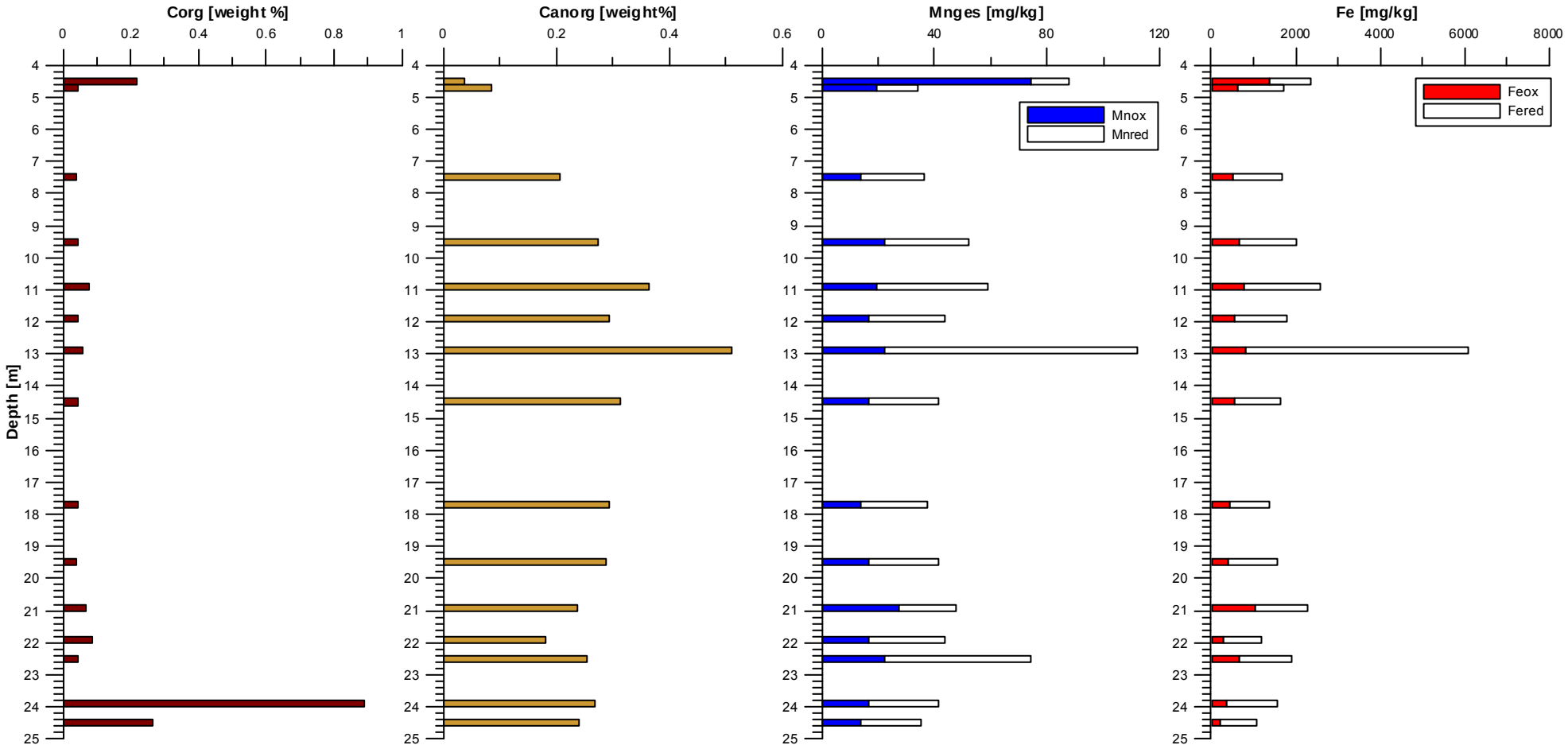


Figure 58: Organic and inorganic carbon content, Fe(III) and Fe(II), Mn(III) and Mn(II) content in core BEE202UP.

Tracer evaluation (travel times, groundwater age and mixing)

Figure 59 shows T and radiogenic ^{4}He concentrations originating from hydrogen bomb testing in the 1960s and the Uranium and Thorium decay within the aquifer respectively (transect Wannsee 1). If the U and Th contents of the sediment were known, one could use ^{4}He to date the deeper groundwater (BEYERLE et al., 1999). Because the U and Th contents are unknown, elevated concentrations of ^{4}He can only be used as an indicator for a relatively "old" groundwater. The concentration of $2.8*10^{-4}$ Nml/kg the deepest observation well 3336 suggests that the water is actually centuries old (pers. Communication J. SÜLTENFUß, 2003). In the two deeper aquifers, the groundwater is definitely considerably older than 50 years since T is already decayed and the ^{4}He values are high. Consequently, any "younger" substances (for example pharmaceutical residues or contrast agents) which were applied in the past decades only, should not be present in the 2 deeper aquifers. The deeper aquifers have not been sampled within NASRI because they do not belong to the bank-filtration system. However, to understand the mixing within the production wells, it would be recommendable to sample them at least once for all NASRI parameters. In contrast to the deeper T/He results, the shallow wells reflect the atmospheric concentrations of T at present, while ^{4}He and tritiogenic ^{3}He could not be detected. The resulting age is less than the resolution of the method of 3-6 months at the site. The production well is a mixture of all aquifers. Its T concentration of 2,4 TU can be used for a mixing calculation. The production well 4 abstracts ~ 22 % of bank-filtrate, provided that the shallow groundwater inland of well 4 contains no T too. According to BWB, the uppermost filter-screen of well 4 has been sealed. The well should abstract deeper groundwater only. However, results show that well 4 abstracts less bank-filtrate than the adjacent well 3, but is not completely seeled.

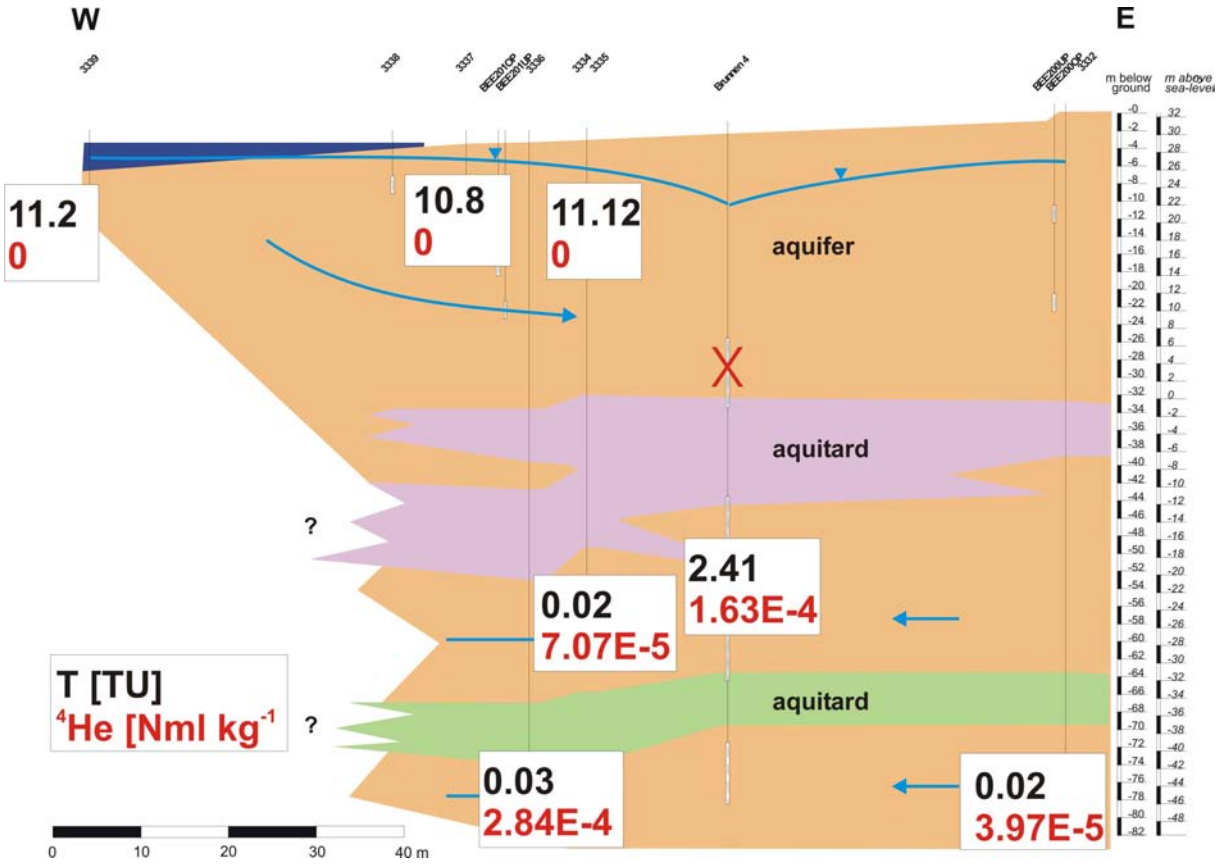


Figure 59: Tritium and radiogenic ^{4}He at Wannsee 2, sampling campaign summer 2002.

The tracer evaluation at the Wannsee transects turned out to be more complicated than expected. Isotope data of 2000/2001 and 2002/2003 shows that breakthrough curves of the shallow observation wells 3339, 3338, 3337 and 3335 reflect the surface water signal, the groundwater is made of BF only. Sampling of 3339, 3338 and 3335 stopped in February 2003 which is why data of 2000/2001 was added for reference. The curves illustrate that residence times for the shallowest wells are rather low at this particular site. Travel times are around 20 days from the Lake to 3337, ~ 30 days to 3338, < 30 days to 3335 and 65 days to 3339. The travel times are shorter to the wells at the shore than to those below the lake which is a consequence of the decreasing permeability of the sediments away from the shore. Observation well 3335 is at approximately 2/3 of the way to the production well. Therefore, on the shortest (shallowest) pathway, the BF takes roughly 1,5 months to reach well 4.

None of the remaining tracer (B, Cl, K or EDTA) are of much use at Wannsee 1. Potassium does not behave conservatively as it does in Tegel and EDTA fluctuates too much. The interpretation of Cl and B (Fig. 61) is difficult because of the lack of a clear peak in summer 2002, the same is true for transect Wannsee 2. The uncertainty of the input signal of the surface water of Lake Wannsee, caused by strong temporal and spatial variations was discussed earlier and causes problems, for example in 3338 (B, transect 1) or BEE205 & BEE203 (B, transect 2).

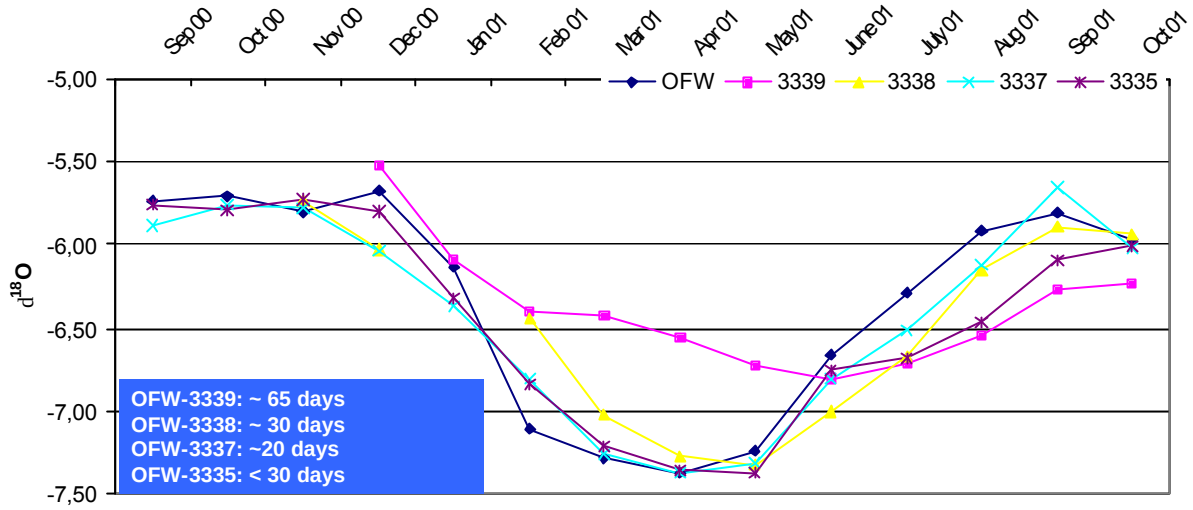


Figure 60: Isotope data from September 2000 to October 2001 (HINSPETER, 2002).

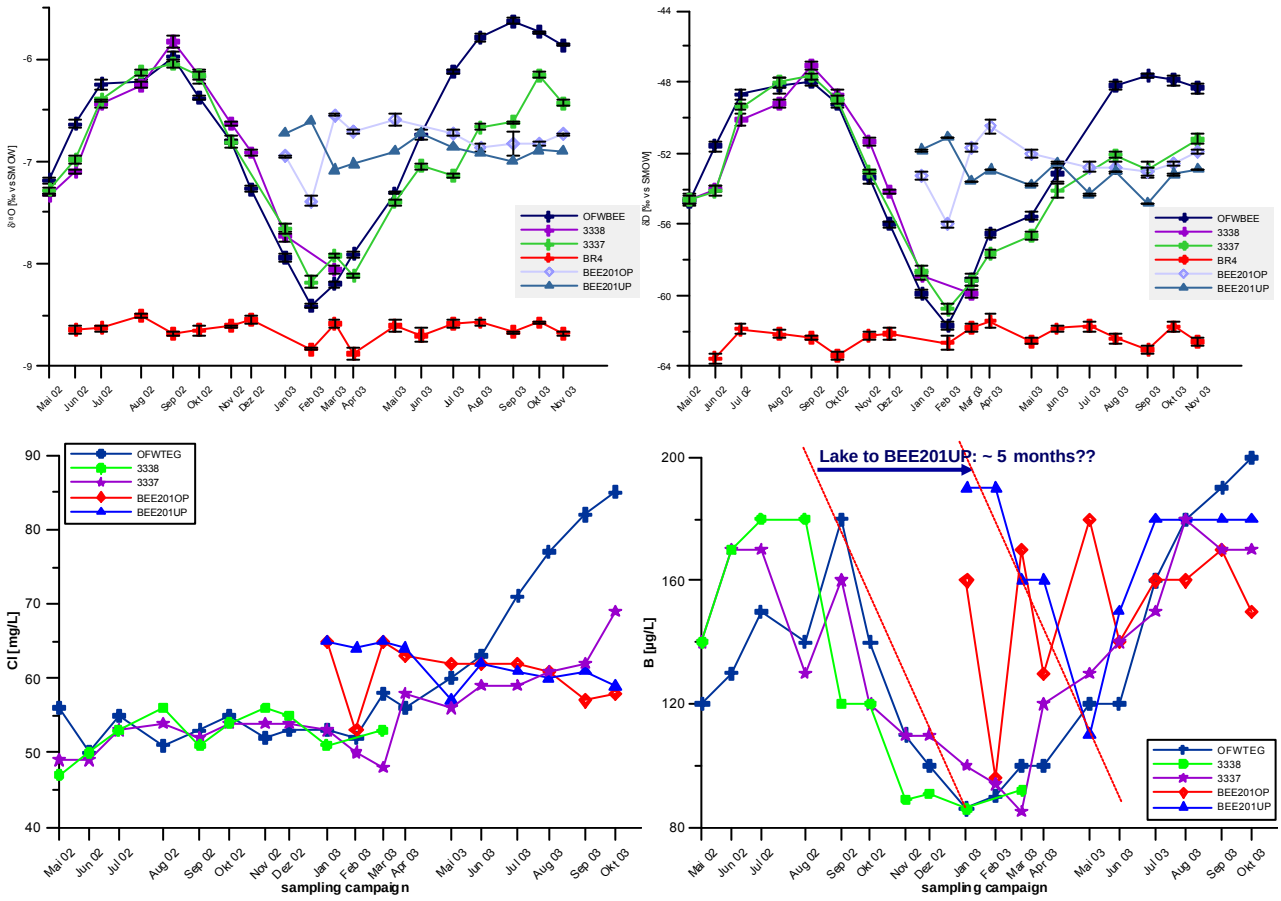


Figure 61: Time-series of Cl⁻, B, $d^{18}O$, dD in the shallow wells of transect 1 in Wannsee (Data source: BWB & AWI).

The best estimates for travel times of the shallowest wells at Wannsee 2 are 1 month to BEE205 and less to BEE206 closer to the shore (better hydraulic conductivity of the clogging layer).

Breakthrough curves of BEE202OP and BEE203 show an average time-lag of 2.4 and 2.6 months. Estimates vary depending on time and tracer (compare Fig. 62).

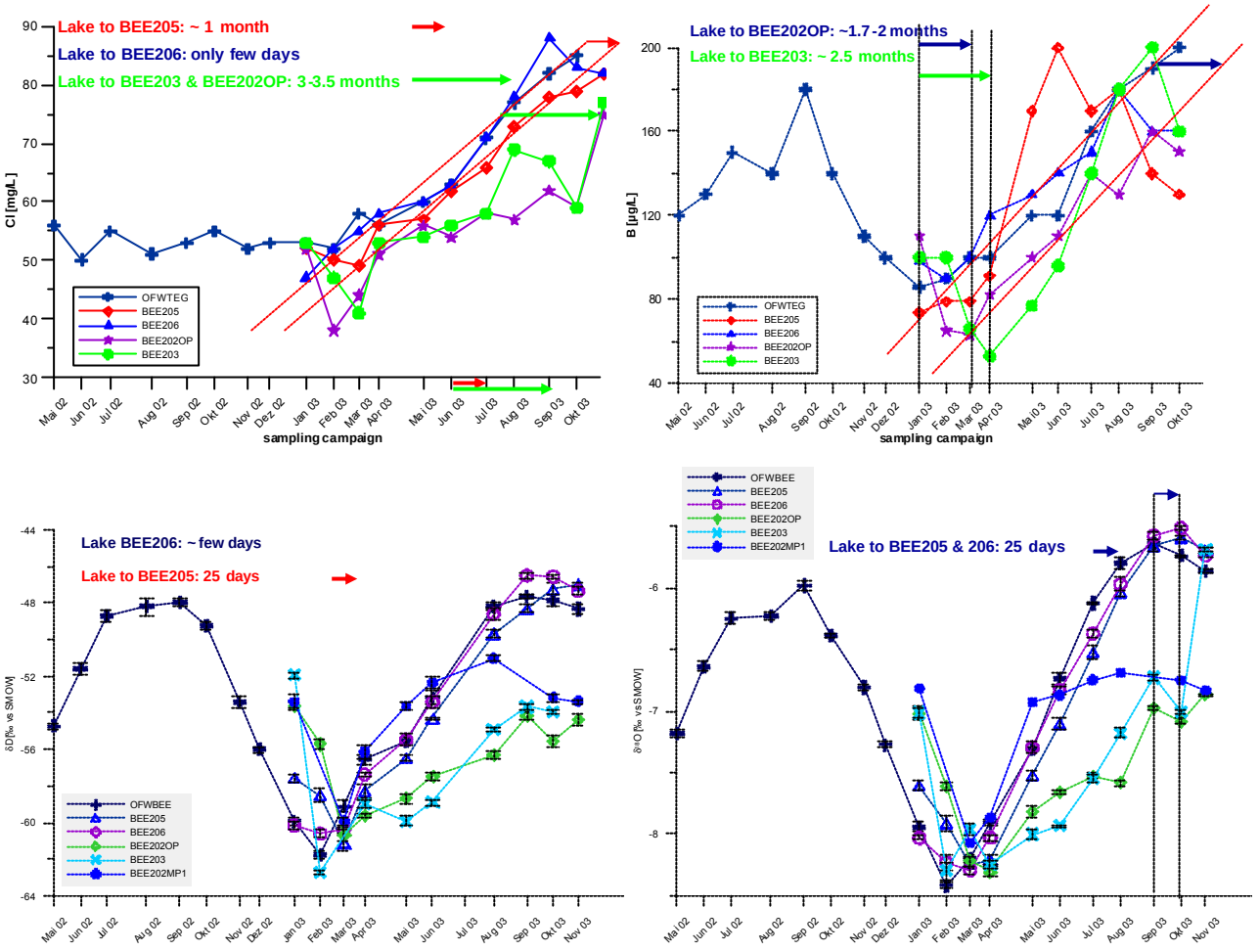


Figure 62: Time-series of Cl⁻, B, $d^{18}O$, dD in the shallow wells of transect 2 in Wannsee (Data source: BWB & AWI).

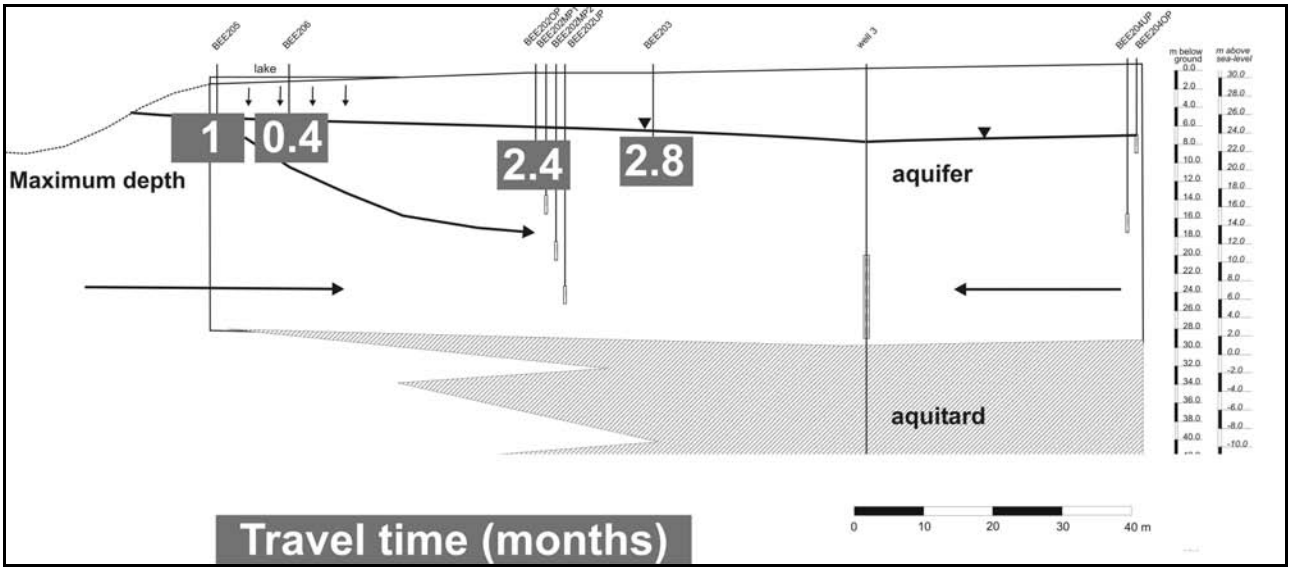


Figure 63: Summary of best estimates for average travel times of the lake Wannsee transect 2. Maxximum depth of Lake Wannsee indicated.

The new deeper observation wells BEE201OP (filter screen 13-15 m below ground) & BEE201UP (18-20 m below ground) at Wannsee 1 and BEE202MP2 (18.3-20.3 m below ground) and BEE202UP (23.1-25.1 m below ground) show no seasonal isotopic variation and resemble average surface water values (Fig. 64). The same is true to some extent for the shallower wells BEE202OP (8.5-10.5 m below ground) & BEE202MP1 (13.3-15.3 below ground) which already have a strongly damped signal. The succession of the 4 observation wells at BEE202 therefore does not reflect a chronological sequence (with increasing travel times with depth) but a decrease of the proportion of "young" BF (in terms of BF directly from the adjacent shore) with depth. The maximum depth of Lake Wannsee is ~ 9 m. The groundwater flow direction is from SW towards the well gallery. The elevated concentrations of wastewater indicators (B, EDTA, Fig. 65) in greater depth within the first aquifer and in particular elevated concentrations of substances such as phenazone and AMDOPH (Fig. 65) which presumably have been present in the surface water in higher concentrations in the past suggest that these wells contain bank filtrate which is at least partly originating from the past decades rather than from the past months. There is no well gallery on the other side of Lake Wannsee. Judging from groundwater head isolines, hydraulic conditions on the western side of Lake Wannsee are effluent, i.e. the water is exfiltrating from the aquifer into the lake. However, the surface water did somehow found a way to infiltrate into the aquifer. It is of great importance to focus more on the hydraulic situation in the next project year (a start has been made in "model" group with student thesis).

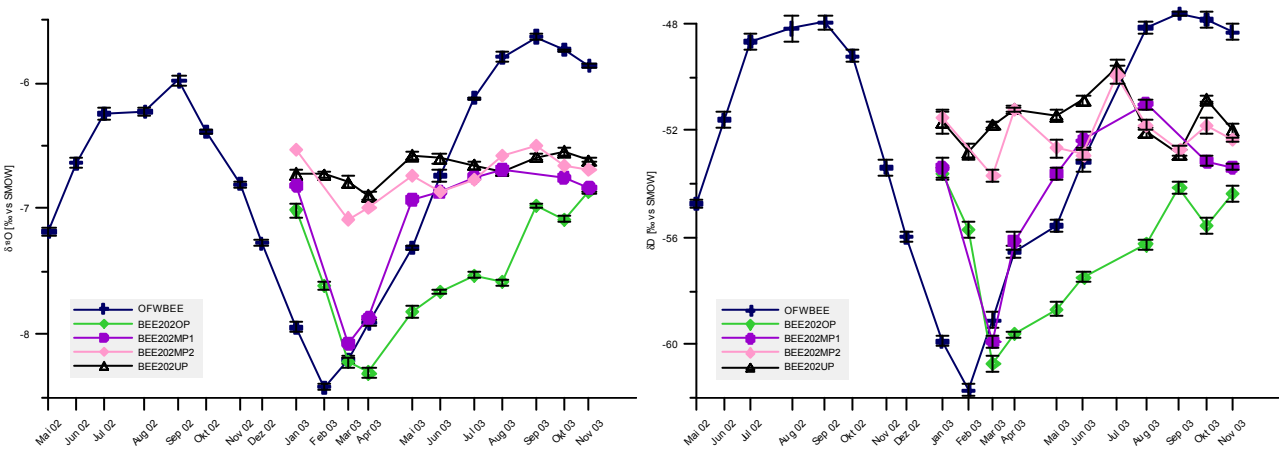


Figure 64: $d^{18}O$ & dD in the lake and observation wells BEE202OO-UP (Data source: AWI).

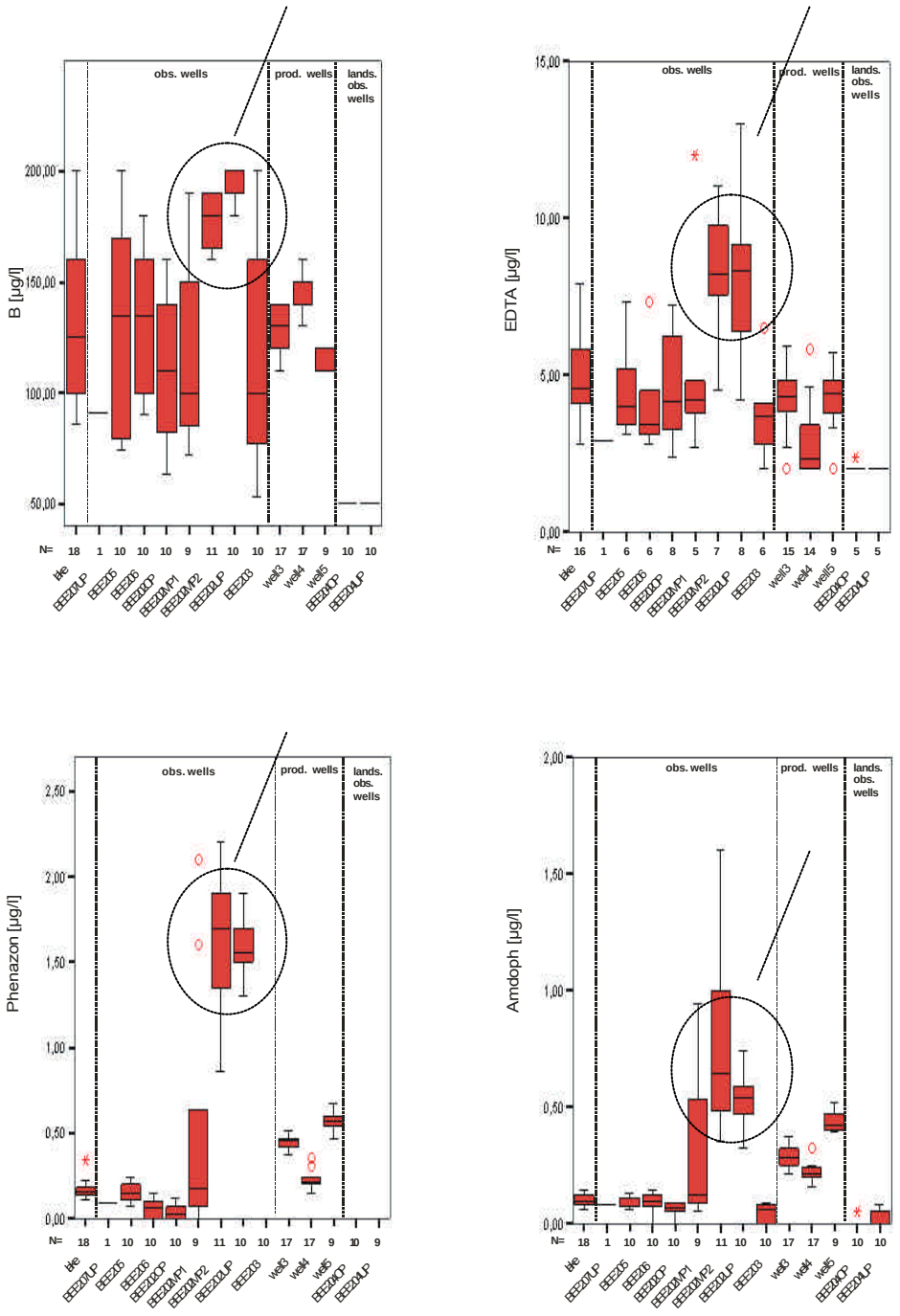


Figure 65: Boxplots of B, EDTA, Phenazone and AMDOPH in transect 2 at Wannsee (Data source: BWB).

Apart from the vertical graduation of water age and quality in the first aquifer, the production wells abstract water from 3 different aquifers. Figure 66 illustrates the differences of the groundwater which can best be seen in their EDTA, SO_4 and Cl concentrations. The groundwater from the uppermost aquifer towards the lake is bank filtrate (Ca-Na-SO_4-HCO_3-Cl water type). It contains elevated concentrations of Cl, SO_4 and EDTA (and other substances) as a result of the anthropogenic influence. The groundwater inland of the production wells is not influenced by bank filtration. EDTA, B and Phenazone concentrations are below the detection limit. It contains low Cl

but, typical for the shallow groundwater in Berlin, high SO_4 concentrations (Fig. 66 and 67). In addition, Ca, Mg, HCO_3 and CO_2 concentrations are higher and the pH is lower (around 6.9 instead of 7.5). The SO_4, Ca and Mg content are explainable with gypsum resolution from war debris as described by SOMMER VON JARMERSTEDT et al., 1998). Another possibility could be oxidation of sulfides due to the lowering of the groundwater table. The open questions will hopefully be solved within the next project phase with the help of $^{34}S_{SO4}$ analysis. The middle aquifer (3334) is a Ca-Na-HCO_3-Cl water. Sulfate has largely been reduced; EDTA (and presumably other "modern" substances) have not been detected. Towards the lake, the deepest groundwater well shows saline influence (3336), the Cl, Na and B concentrations are elevated (Na-Cl-HCO_3 water type). In addition, the groundwater is very old. According to WURL (1995), this is due to mixing with rising saline deeper groundwater. Inland of the production well (3332), the groundwater of the deepest aquifer has a low Cl and SO4 concentration (Ca-HCO_3 water type) and no EDTA. SOMMER VON JARMERSTEDT & FLECKENSTEIN (1997) called this groundwater type uninfluenced by any anthropogenic influence, i.e. pre-industrial.

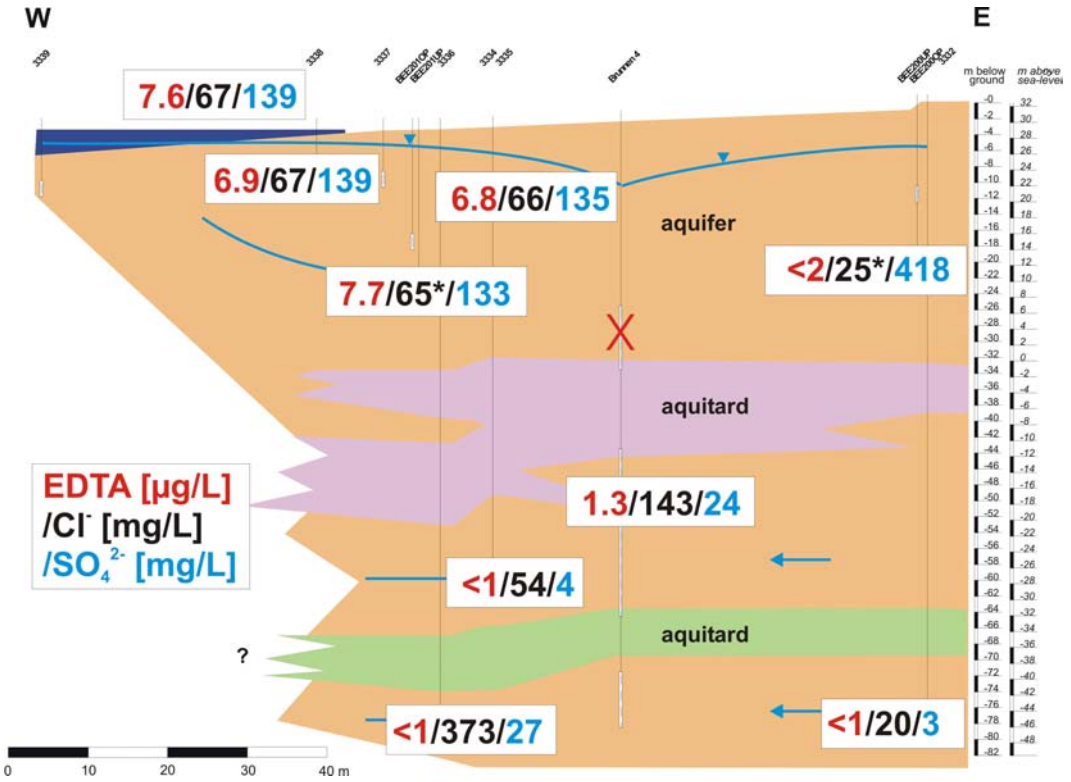


*Figure 66: EDTA, Cl and SO4 concentrations in transect Wannsee 1. Average data 10/2000 –11/2001 (HINSPETER, 2001) and, with *, BWB average 01/2003 – 04/2003.*

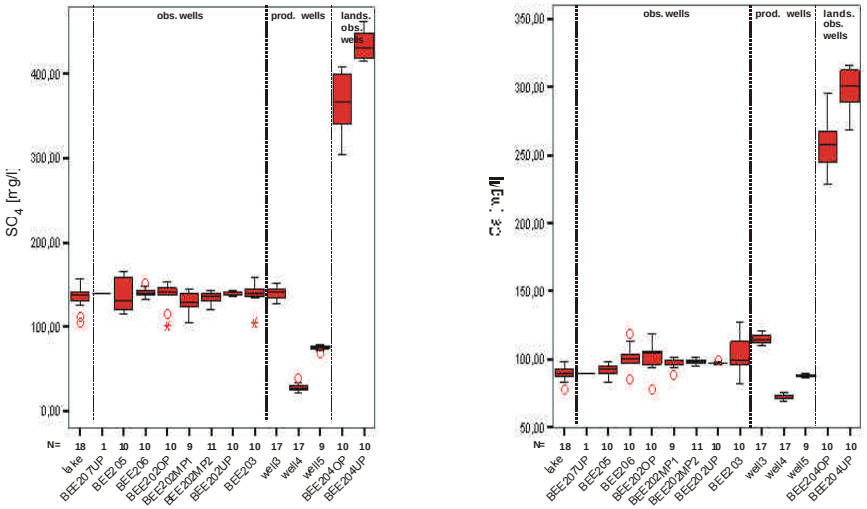


Figure 67: Boxplots for SO4 and Ca in transect 2 at Wannsee (Data source: BWB).

The scatter plot of δD versus $\delta^{18}O$ in surface water, production wells, deeper groundwater and background groundwater inland of the wells illustrates that well 4 has the lowest and well 3 the highest proportion of bank filtrate. To calculate mixing proportions is difficult, because 5 types of groundwater with different isotopic signatures and tracer concentrations are mixing in the wells.

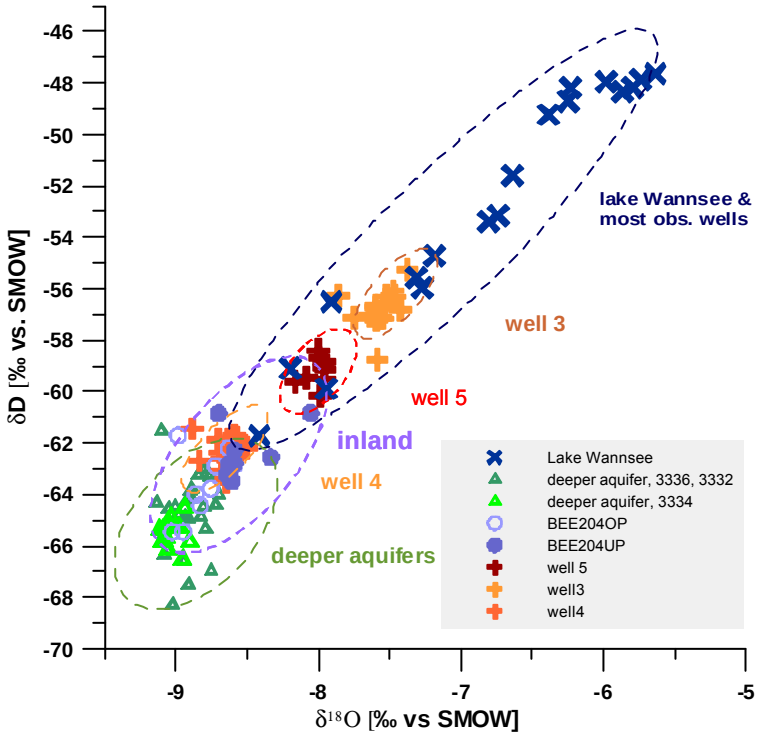


Figure 68: dD versus $d^{18}O$ in surface water, background and deeper groundwater and abstracted water in Wannsee. Deeper aquifers: Data 10/2000 –11/2001 (HINSPETER, 2001); remaining samples from May 2002-October 2003, data source: AWI.

The easiest possibility for mixing calculations is to use a tracer which is only present in the bank filtrate. Of the conservative tracer, only EDTA fulfills this premise. Depending on the background concentration assumed (detection limit is 2 µg/L), the proportion of BF is 80 % for well 3 and 30 % for well 4 (background concentration 2 µg/l, May 2002 – Oct. 2003) or 85 for well 3 and 49 % for well 4 (background concentration 1 µg/l, May 2002 – Oct. 2003) or 88 % for well 3 and 60 for well 4 (background concentration 0 µg/l, May 2002 – Oct. 2003). The difference is very large for well 4 but only marginal for well 3, because EDTA concentrations resemble the surface water concentrations. In figure 69 EDTA variations with time are shown which vary largely, probably also because of analytical problems. Boron cannot be used, because the deepest aquifer also contains elevated B concentrations.

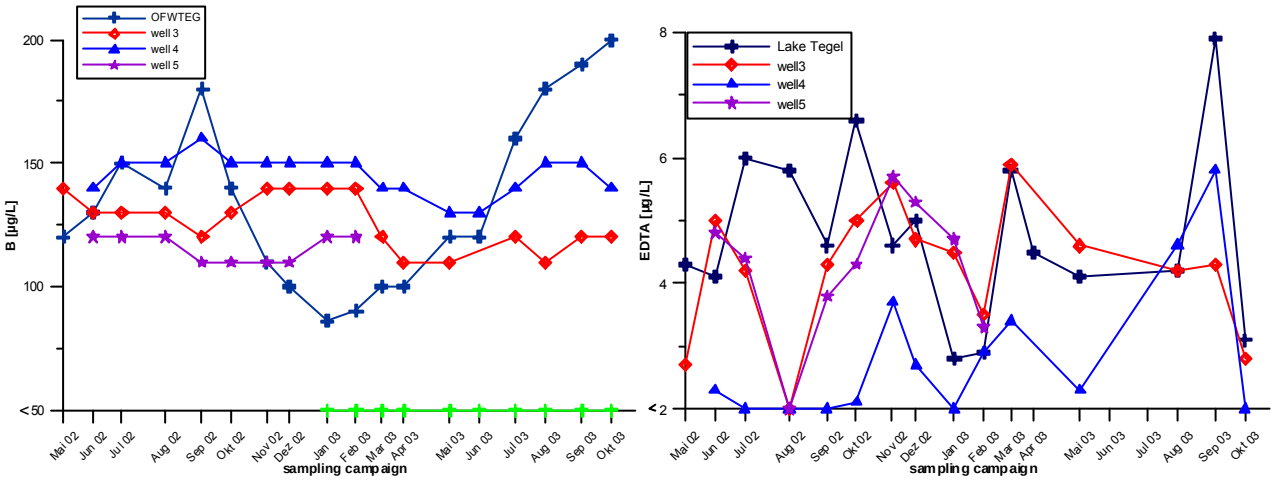


Figure 69: Time-series of B and EDTA in the production wells 3, 4 & 5 in Wannsee (Data source: BWB).

Hydrochemistry at the transect

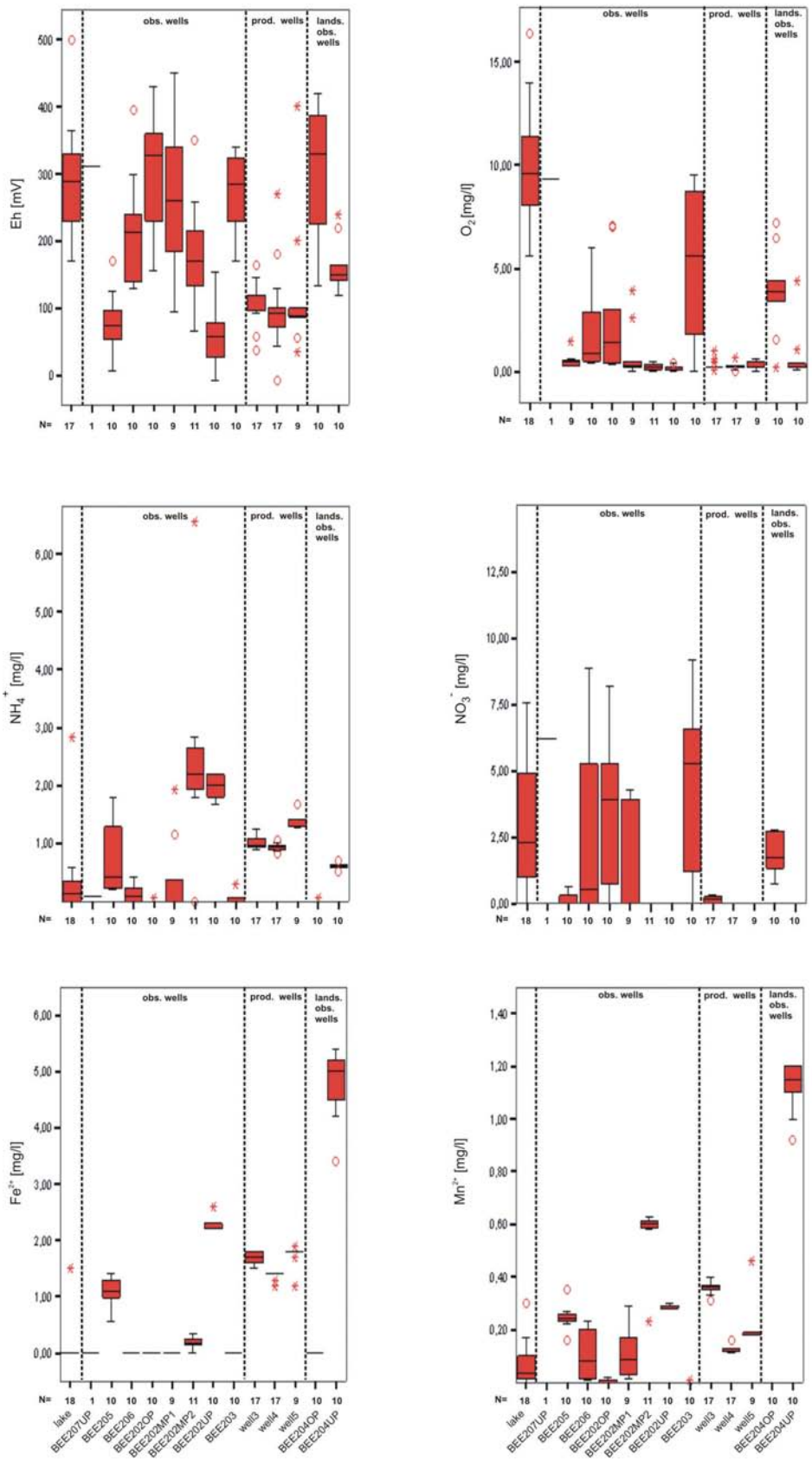


Figure 70: Boxplots of redox indicators Eh, O_2, NO_3^-, NH_4^+, Mn^{2+} & Fe^{2+} at the transect Lake Wannsee 2.

Similar to the other field-sites, the redox zones, as characterized by the presence of redox sensitive species such as O_2 and NO_3 (still present) or Fe^{2+} and Mn^{2+} (already present) are given in figure 70. Again, the boundaries between the zones are fluent and, similar to the GWA Tegel, they vary seasonally. In terms of the appearance of Fe^{2+} and Mn^{2+} the zones are fairly stable, but in terms of the O_2 and NO_3 concentration, they are highly variable. Examples are given in figure 72. In summer, the NO_3 concentration drops to zero even in the lake. Consequently, it drops below the detection limit in all shallow wells. The O_2 concentration of the shallow wells also decreases in summer, even though there is no change in the O_2 concentration within the lake. The redox processes seem to be strongly temperature dependant. Therefore, the zoning in figure 71 is representative for winter only and will be much smaller in summer/autumn.

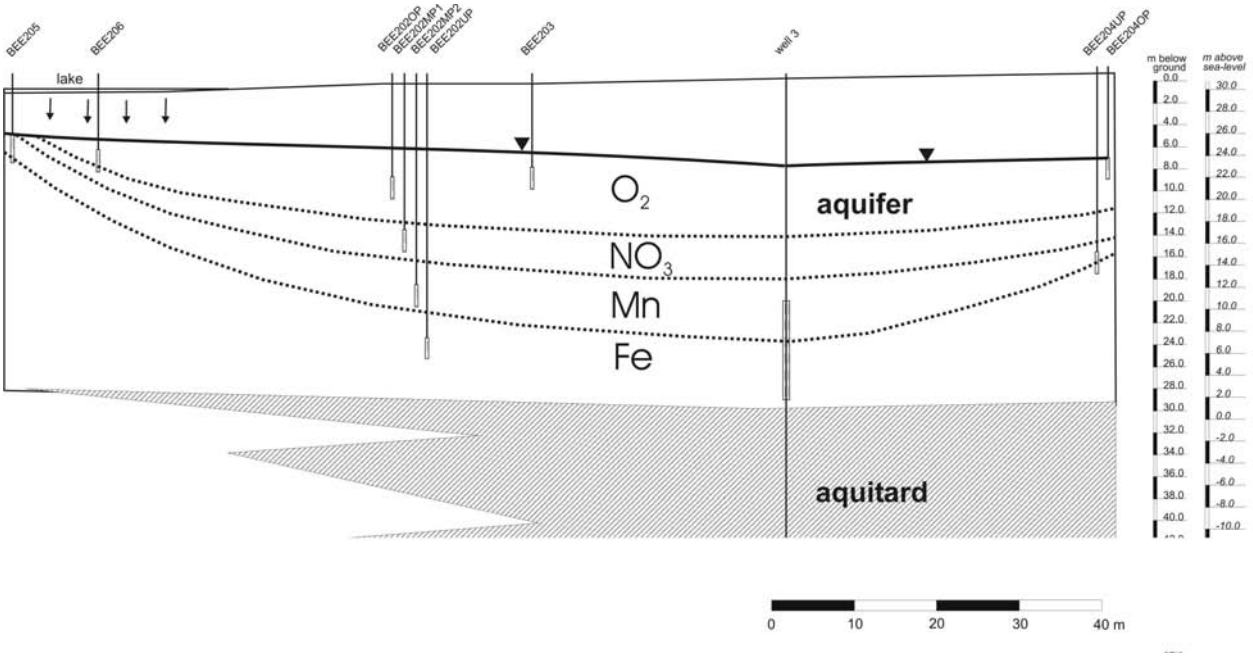


Figure 71: Approximate redox zoning as indicated by O_2, NO_3, Mn and Fe presence.

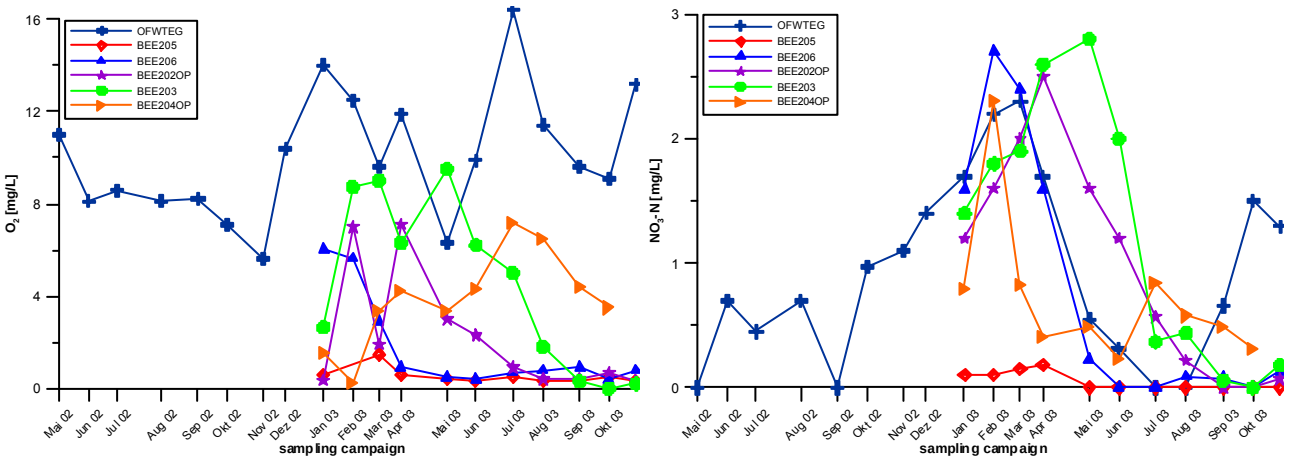


Figure 72: Seasonal variations in O_2 and NO_3 in shallow observation wells of the transect Wannsee 2 (data souce: BWB).

Major conclusions and summary Lake Wannsee site:

- The site interpretation is difficult and not fully understood to date.
- The surface water quality and conditions varies strongly within Lake Wannsee and also with time, in particular close to the transects. The sample taken each month in front of transect 1 is not sufficient to cover temporal and spatial variations in front of the transect. Surface water sampling in a dense raster within Lake Wannsee for all parameters would give an idea on the degree of variation.
- The travel time to the production well is ~ 1.5 months to well 4 and 3 months to well 3 on the shortest (shallowest) pathway.
- At least 5 different types of water from 3 different aquifers mix in the production wells, well 3 abstracts 80-90 % of BF and well 4 considerably less.
- For observation wells deeper than ~10 m, i.e. those deeper than the lake, the share of young BF (directly from the shore) decreases with depth. The remaining water is probably older and may originate from further south or other lake side.
- It is important to include link the chemistry with the hydraulics in the next project phase.
- Better values for mixing caclulations may be obtained when full years sampling available for all wells and with mixing calculations with several parameter (Cl, SO4, B, EDTA etc.) or modelling.

5.3 Semi-technical site (Marienfelde)

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5.4 Laboratory experiments

Samples from the large columns at UBA were analysed standard cations and anions from June 2002 to date, fortnightly in the beginning and monthly from October to now (~150 samples). The results were interpreted together with the groups “organics” and “model” and are discussed in the corresponding reports.

A column experiment with Gd-DTPA was carried out in the large columns in summer 2003 within a DFG project (PE 362/18-2). Because the results are relevant for NASRI, they are documented on in Appendix 2 for reference.

5.5 Overview on student projects

Student name	Thesis title	comments
Anat Bernstein	*Sulfate reduction kinetics through a mud profile in Lake Tegel*	Visiting student from Israel, project supported by C. Kofahl

		(FU) and J. Greskowiak ("model" group)
Nicole Engelmann	*Investigating the groundwater enrichment process at the Tegel infiltration pond 3 with the help of a two-dimensional flow model*	Not finished yet With support of J. Greskowiak ("model" group)
Silke Pühringer	*Preparation, evaluation and modelling of a tracer test conducted at the semi-technical bank filtration facilities of the UBA in Marienfelde"*	finished July 2003
Stephan Gruß	*Geological and Hydrochemical investigations in the vicinity of the Tegel infiltration ponds in Berlin*	Not finished yet In close cooperation with U. Dünnbier (BWB)
Alexander Nogeitzig	*Column study of an undisturbed core from the clogging layer at Lake Wannsee*	Started January 2004
Doreen Richter	*Evaluation of the surface water flow system of the river Havel and adjacent watercourses in Berlin with a multi-tracer approach*	Finished July 2003 Within DFG project A. Knappe (AWI)
Virginia Robles Arenas	*Temperature Modeling at the Transect Lake Tegel in Berlin*	Visiting student from Spain, project supported by C. Kofahl (FU) and E. Holzbecher ("model" group)

6 Discussion

A major conclusion of the present report is that the hydraulic and hydrochemical conditions are complicated and pose a great challenge for all working groups in the next project phase. The focus in 2004 will be the quantification and modeling of the processes identified and described quantitatively in this report.

All sites, in particular the bank filtration sites, show a strong vertical differentiation of the infiltrate in terms of age/travel time. The deeper the filter screen, the larger the proportion of water no originating directly from the shore. At Wannsee, the proportion of older BF with elevated concentrations of most WW indicators increases abruptly, as soon as the filter screens are deeper than the lake bottom. Hence, the water abstracted in the production well is always a combination

water of various travel times and consequently with different composition. In addition, the bank filtrate also mixes with groundwater from deeper aquifers and groundwater from inland of the wells.

The redox conditions are also highly transient, in particular at the GWA but also at the field sites. The redox zoning is spread out wider during winter while zones are smaller in summer, when the biological activity is larger, mainly due to temperature effect. In addition, the redox sequences are mainly a function of depth, rather than only on distance from the surface water. Oxygen diffusion through the unsaturated zone has to be considered under this perspective. Involving the transient redox condition into the data evaluation will help to explain the behavior of redox sensitive species.

The next project phase should aim for a close interaction and exchange between all working groups. With combined effort, the remaining problems identified may be solved. The information in this report is purely quantitative. In the next year rough estimates for travel times should be improved, mixing and dispersion has to be taken into account.

Rather than continuing sampling at the present site for much longer, certain aspects should be pursued. It would be recommendable to sample the surface water system at Lake Wannsee in a close raster. It would also be useful to sample the deeper aquifers at Wannsee and the Lieper Bucht transect where the groundwater is much older (> 50 and ~20 years respectively) to study long-term effects. Since the larger scale sampling at the GWA gave a feeling for the variations of the groundwater on a larger scale, it would help to sample the shallow groundwater at observation wells present in the surrounding of Lake Wannsee or Lake Tegel to support the hydraulic evaluations. In particular it would be useful to sample wells on the other side of the lakes in order to prove if the groundwater composition resembles the one in deeper aquifer layers.

7 Perspectives / Intended tasks for the upcoming project period (2004)

Task	comments
Analysis and evaluation of new isotopic data collected	To be continued until April 2004
Evaluation of water quality data analyzed by BWB	To be continued until April 2004
Analysis and interpretation of standard chemistry of large columns at UBA	To be continued for duration of experiments. In cooperation with "organics" and "model" groups.
Analysis of standard cations and anions in unsaturated samples from GWA Tegel	To be continued until summer 2004 to support "model" group
Surface water sampling and evaluation in a dense raster at Lake Wannsee.	Together with groups "algae", "organics", "bacteria" and "drugs"
Evaluation of the redox regimes at the field sites.	Use of standard parameters in combination with $\delta^{34}S$ and $\delta^{18}O$ of sulfate, $\delta^{13}C$ of HCO_3 and possibly more. In cooperation with University of Freiberg.
T/He age dating at new deeper observation wells	In spring 2004; age still missing for TEG368UP, TEG373, TEG374 and complete transect Wannsee 2. In cooperation with University of Bremen.
Repeating sampling of colloids	Due to problems with oxygen-free sampling no satisfactory results so far, together with
Sampling and analysis of transect Lieper Bucht (groundwater age ~ 20 years)	To have a comparison of a sight with a groundwater age of 20 years; in cooperation with other groups (if interested)
Quantification and modelling of selected aspects at the field-sites	Together with "model" group at IGB
Column study with undisturbed core(s) from Lake Wannsee clogging layer	To improve understanding of hydraulic and geochemical conditions in the infiltration zone (student project).
Publishing results obtained so far	!!!

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Massmann, G., Knappe, A., Pekdeger, A. (submitted). Investigating the influence of treated sewage in ground- and surface water using wastewater indicators in Berlin, Germany. Submitted to Acta Hydrochimica et Hydrobiologica

Appendix

1) Massmann, G., Knappe, A., Pekdeger, A. (submitted). Investigating the influence of treated sewage in ground- and surface water using wastewater indicators in Berlin, Germany.

2) Knappe, A., Dulski, P., Pekdeger, A. Möller, P. (submitted): Removal of gadolinium-DTPAcomplex during simulated bank filtration processes - A large-scale column experiment.

Integrated modeling concepts and bank filtration processes: coupled groundwater transport and biogeochemical reactions

Abstract:

At the previous project period the main research activities were investigated to carrying out and analysing a tracer experiment in the semi-technical test site Marienfelde and to develop modelling framework for simulation of reactive transport processes. The results of the meso-scale tracer experiment – flow velocities and dispersion coefficients - are of particularly interest for describing the hydraulic system of the test site as a basic for subsequent experiments using reactive substances. Reactive transport modelling was set up to model hydrogeochemistry at the bank-filtration test sites inside of the project. Based on the powerful software platforms ModelMaker and MathLab one-dimensional coupled reactive and transport models were developed and tested on benchmarks. Finally, measurement devices for sampling the unsaturated zone at the artificial recharge pond 3 nearby the Lake Tegel have been installed.

Project leader: Prof. Dr. Gunnar Nützmann

Working group: Dr. Christoph Horner, Dr. Ekkehard Holzbecher, Dipl. Ing. Bernd Wiese, Dipl. Geol. Janek Greskowiak

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Berlin, December 23, 2002

1. Extended summary

In the third period of the NASRI-project experimentally investigations and modeling studies achieve a new quality: on the one hand, field measurements at the transects and column studies allow a first estimation of flow, transport and degradation processes, and on the other hand, model applications and development allow to start with simulation and parameter identification. Here, the so-called soil-column group played an especially important role, i.e., for developing standards for column and enclosure experiments in order to identify the hydraulic and transport parameter with the help of models. Further, the review process during the summer workshop 2003 was helpful for the subsequent processing of the scientific destinations.

Beneath the recharge pond, geochemical and in situ oxygen measurements show the important role atmospheric oxygen plays both for the carbon cycle and inorganic chemistry at different stages of the operational recharge cycle. A preliminary conceptual view of the system has already been derived from these observations. In order to constrain these hypotheses, the sampling period will be continued until the end of summer 2004.

To simulate geochemical changes during bank filtration at Lake Tegel test site, the spatial distribution of hydraulic and conservative transport properties are necessary to be known. Thus, modelling studies have been carried out to investigate flow paths and travel times depending on pumping rates and/or regimes, and a 3-D model was developed to identify the hydrogeological matrix properties of the aquifer system. Final 3-D modeling works were done to estimate flow and dual tracer transport at test site Marienfelde as a basis for further bank filtration experiments.

In order to understand and to quantify non-conservative transport experiments in long soil columns different model approaches were continued. On the one hand, with the help of visualCXTFIT, ModelMaker and MATLAB solutions the behaviour of Gd-DTPA as an examplary biochemical component under quasi-natural conditions during bank filtration was modeled. It was found that Gd-DTPA is degraded in infiltrating surface water and this degradation does not occur with a constant rate. On the other hand, a sequential coupling of transport and reactive modeling tools was realized using MATLAB and PHREEQC. This model was applied to a long soil column experiment describing redox processes after infiltration with surface water from Lake Tegel. Comparison of modeled with measured data shows close agreement and an adequate description of transport and reactive processes taking place in the long retention column.

2. Objectives of this project period

The following objectives have been defined:

From measurements and conceptual model ideas the abrupt hydraulic change from fully saturation to unsaturated conditions during artificial groundwater recharge becomes important for the geochemical development. These processes must be examined based on collected field data from suction cup samples as well as from newly installed optical oxygen sensors in co-operation with the working group Hydrogeology from Free University (FU).

To study geochemical changes during bank filtration at Lake Tegel the spatial distribution of hydraulic and conservative transport properties are to be identified. Thus, a 3-D instationary flow model must build up to estimate these parameters as a first step on the way to set up a 3-D flow, transport and geochemical reaction model for this area. This works are strongly connected with the development of a hydrogeological structure model and geochemical investigations of the working group Hydrogeology (FU) and observed data, registered routinely from BWB.

In connection with these investigations, the question must be answered how do flow paths and travel times change depending on pumping rates and well regimes and how depends the amount of bank filtrate and pristine groundwater on pumping rates and/or well regimes? The intention of this last part is not to reproduce the hydrogeology in detail. The target is to find out general statements which are necessary for a conceptual water management model.

The testsite of Marienfelde has many prerequisites for performing bank filtration experiments of technical scale for other project groups (UBA, FU, TU). For that reason, at the beginning of the project a dual tracer experiment was carried out from UBA, FU, GFZ and IGB to estimate the hydrogeologic structure of the artificial aquifer and his dispersivity. With the help of a 3-D groundwater flow and transport model these matrix properties must be identified in order to built up a consistent parameter basis for further experiments.

One experiment at the large scale column facility at the UBA, lasting more than 30 days, with Gd-DTPA was performed by mainly by A. Knappe (GFZ – Geo-Research Center, Potsdam) within a project, funded by DFG (German Science Foundation). The aim of this experiment is to investigate the behaviour of the Gd-DTPA as an example biochemical component under quasi-natural conditions during bank filtration. With a length of 30 m the column has the same spatial dimension, as it is relevant for bank filtration systems. With approximately 1 m/d the flow velocity is also in the same range as it can be observed in several bank filtration systems. Moreover the infiltrated water for the experiment was taken from Lake Tegel. In focus of the work are modelling approaches, in particular of the steady state conditions, measured in the experiment.

In order to improve the performance and versatility of reactive modeling tools in the NASRI project, a coupling of well performed chemical speciation codes (such as PHREEQC, Parkhurst & Appelo, 1999) to hydrodynamic advection-dispersion codes is appropriate as suggested by

the NASRI Scientific Committee during its evaluation of the NASRI Workshop in June 2003. Here, the reactive sequential coupling approach via operator splitting is to be implemented within a MATLAB development environment. The model application should occur at a soil column experiment which was carried out by the Hydrogeology (FU) and Organics (TU) groups.

3. Intended and achieved tasks for the reporting period

Task	achieved?	comments
Understanding hydraulic and geochemical processes during artificial groundwater recharge (Lake Tegel)	Yes	Development of a conceptual model, expansion of measurements in the unsaturated zone (with working group Hydrogeology (FU))
2-D Model investigation about hydraulic effects (pumping regime of well galleries) on groundwater flow	Yes	To be extended to 3-D; basic information for a conceptual management model (with working group Hydrogeology (FU))
Literature study on bank filtration	Yes	to be continued
Determining of hydrogeological structure (3-D) of the Marienfelde test site aquifer & identification of conservative transport parameter	Yes	Results are important for all groups, which want to carry out experiments here (with UBA, GFZ, FU)
3-D instationary model of Lake Tegel test site: identification of hydraulic properties of the transect	Yes	Basis for modeling solute transport and chemical reactions (with working group Hydrogeology (FU))
Modeling transport and degradation of Gd-DTPA during soil column experiments	Yes	to be continued (with working group Hydrogeology (FU) and GFZ)
Coupling transport and chemical speciation with MATLAB	Yes	Simulation of soil column experiments; to be continued (with working groups Hydrogeology (FU) and Organics (TU))
Well gallery simulation MATLAB	Yes	Design of a conceptual management model; to be continued (with working group Hydrogeology (FU) and BWB)

4. Results

Field sites

Artificial recharge pond Tegel (J. Greskowiak)

As outlined in the previous NASRI Progress Report (January 2003 - June 2003), the abrupt change from Stage 3 (full saturated conditions) to Stage 4 (unsaturated conditions) forces air from the pond margins to flow beneath the recharge pond. The geochemical development during Stage 3 and its subsequent respond to the atmospheric oxygen impact after the abrupt transition to Stage 4 will be discussed based on collected field data from suction cup samples as well as from newly installed optical oxygen sensors.

Materials and Methods

From June 2003 until now sampling of the pond's surface water, groundwater and four suctions cups as well as oxygen measurements at four different depths has been undertaken weekly. To minimize pH increase due to degassing of carbon dioxide inside the suction cup (cp. Suarez, 1987), the water samples have been collected within one hour after applying vacuum to the cups. Alkalinity and pH were measured in the field immediately after sampling. Alkalinity has been determined by Gran Titration. All samples have been analyzed by the NASRI working group Hydrogeology (Free University of Berlin) on the major ions and Dissolved Organic Carbon (DOC).

Dissolved Oxygen (DO) concentrations of water samples collected with a suction cup do not represent the conditions in the adjacent soil due to prevailing aerobic conditions inside the cup. To circumvent this problem, oxygen probes have been directly installed next to the suction cups. The probes are based on an optical sensor that produces a fluorescence signal dependent on the present oxygen saturation (PreSens, 2001) and have been constructed in cooperation with the NASRI working group Hydrogeology. The technique for construction was developed by Hecht and Kölling (2001).

Furthermore, six cores of the pond's sediment have been taken on the 18 October 2003, shortly prior to the operational redevelopment of the pond's bottom. At that point of time, the developed clogging layer has reached its maximum thickness. The cores contained undisturbed pond sediment down a depth of approx. 15cm as well as the undisturbed clogging layer overlain by a surface water column of about 10cm. The thickness of the clogging layer in these samples

ranged from 1 to 5mm. In order to obtain quantitative information about the reduction potential of the clogging layer, three oxygen profiles have been measured in micrometer scale from the aerated water column into the clogging layer with a Clark-type microelectrode at the IGB. The water temperature during the three measurements was 17°C, 19.5°C and 21°C. To calculate the consumption rate of oxygen within the clogging layer, the effective diffusion coefficient was determined by measuring the total porosity of the clogging layer according to Lewandowski et al. (2002).

Results and Discussion

Oxygen

Once the pond has been flooded and saturated conditions have been established beneath the pond (around 23rd of July 2003, Fig. 1), oxygen saturations declined from about 65% to zero at all observed depths (Fig. 2). In the following 6 weeks they maintained at zero concentration until an abrupt change from saturated to unsaturated conditions occurred from 04–08 September 2003 (Fig. 1 and 2). During this change of hydraulic conditions, oxygen saturations increased up to 50%. Although the extent of the unsaturated zone grew very fast in Stage 4 (Fig. 3), oxygen saturations increased only to a minor amount (Fig. 2). No effect on oxygen concentration could be observed during the operational redevelopment from 17-28 October 2003. While saturated conditions had established within a short period of time after refilling the pond subsequent to redevelopment, oxygen saturations dropped very slowly and not as fast as in the previous operational cycle (Fig. 2). This can be well explained by decreasing microbial activity due to the difference of water temperature in summer and winter. The heightened oxygen concentrations at a depth of 200 cm compared to the lower depths are likely to be a result of preferential flow. Under homogeneous flow conditions oxygen concentrations are supposed to decrease with depth due to a longer flow path and therefore longer retention time within the sediment.

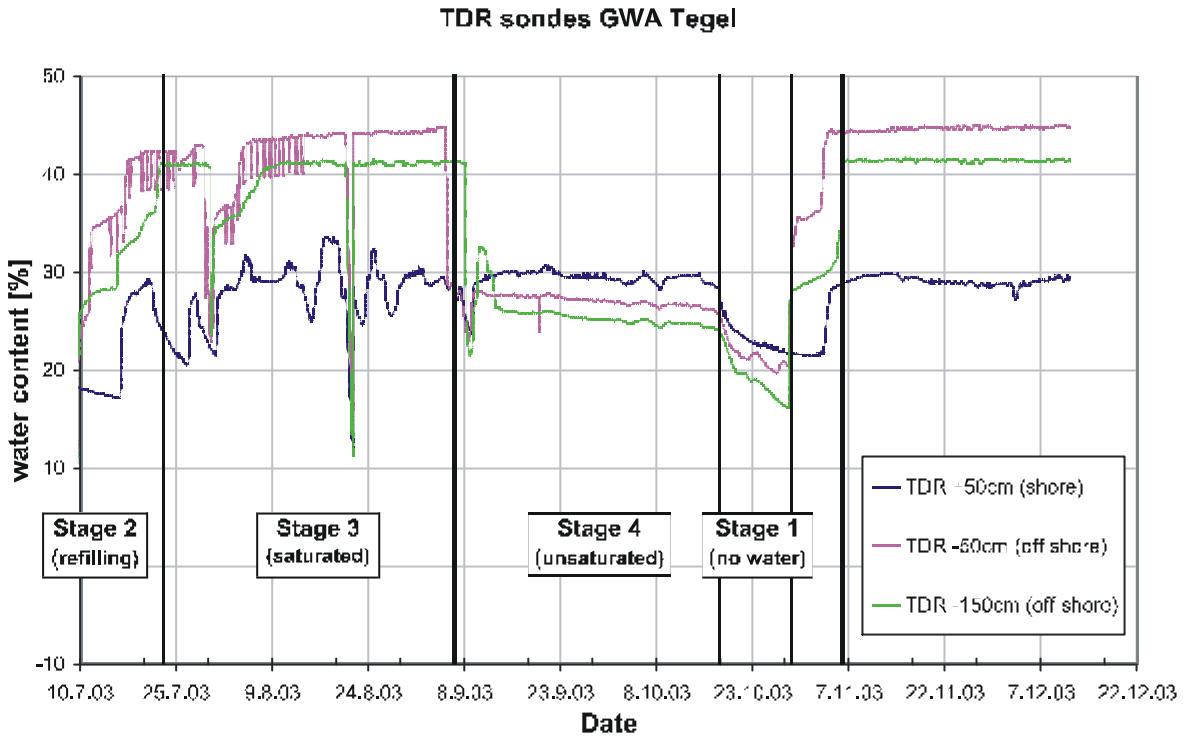

Fig.1: Measured water contents at 50cm and 150cm depths beneath the pond's bottom and at the shore, 50cm above the bottom.

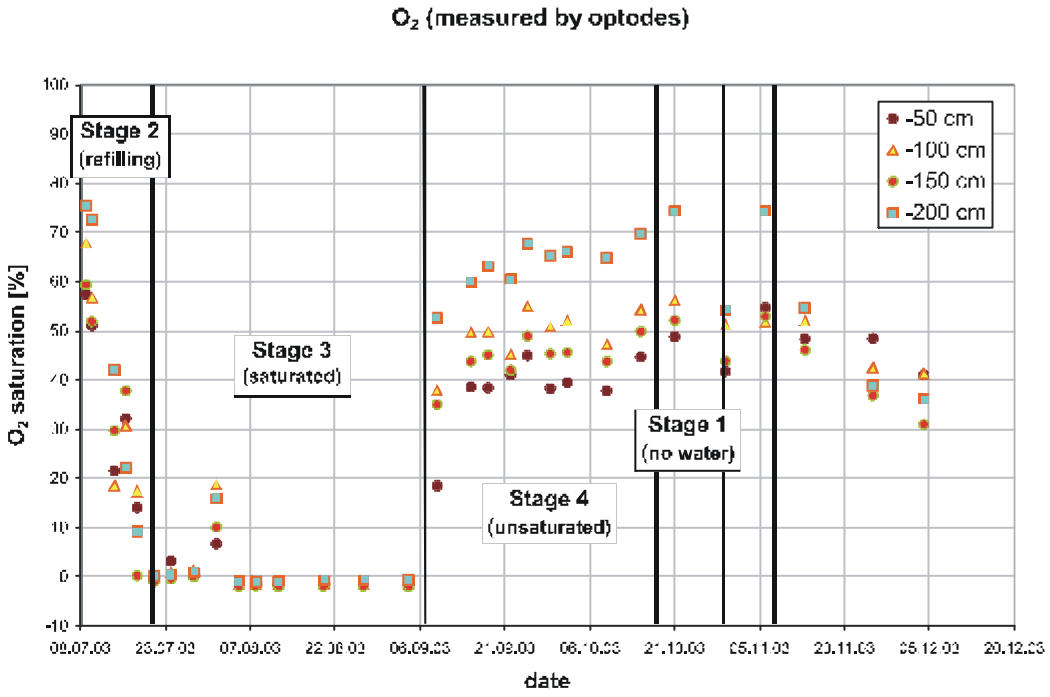

Fig. 2: Measured oxygen concentrations at 50cm, 100cm, 150cm and 200cm beneath the pond's bottom.

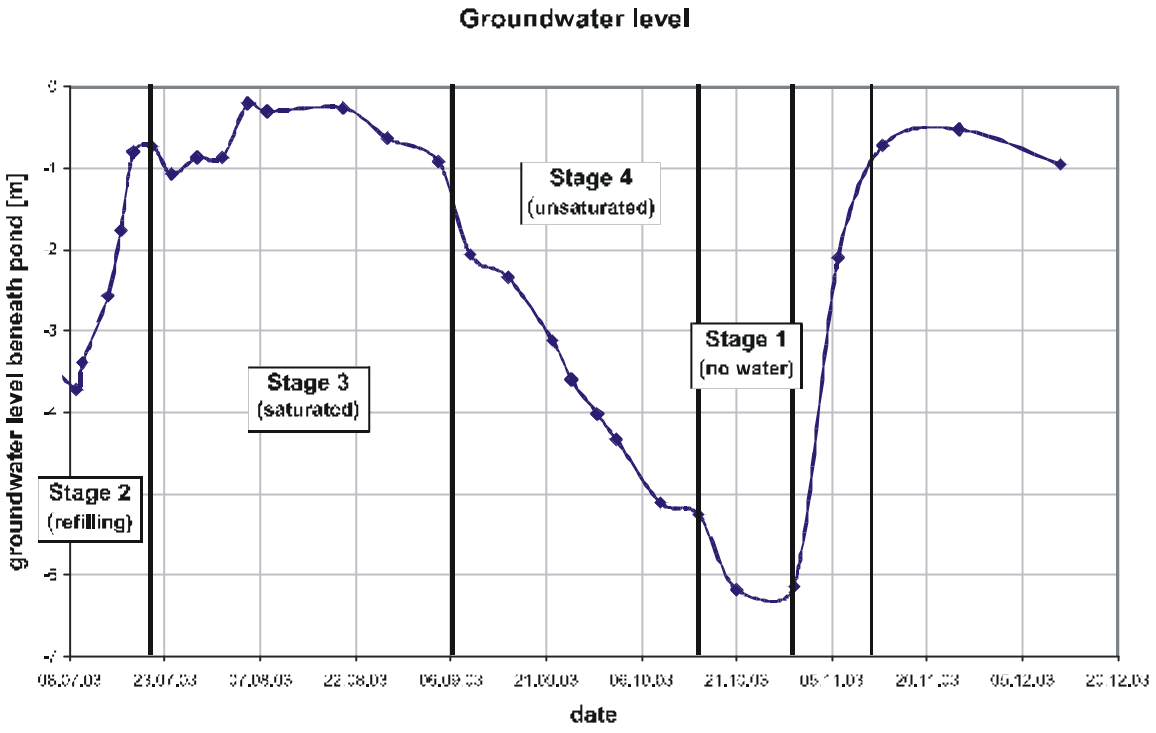

Fig. 3: Groundwater level beneath the pond. Measured at 8m depths beneath pond.

Major ions and organic carbon

Preferential flow is not only a phenomenon of the unsaturated zone affecting the composition of the extraction water, but also seems to have a considerable impact on geochemical measurements under saturated conditions beneath the recharge pond. Hence, the geochemical data gained from the different suction cups shows excessive scattering (Fig. 4), which indeed is not a result of analysis error (Fig. 4b). For that reason, a comprehensible trend of degradation related constituents versus depth could not be identified for the suction cups. Although the geochemical data of the extraction water does not allow a reliable quantification of the ongoing reactive transformations versus depth, trends versus time can give a general idea what kind of redox conditions are able to develop beneath the clogging layer.

A clearer trend versus depth can be found by comparing surface water and groundwater concentrations. In Stage 3, the increase in total inorganic carbon (TIC) is about 0.2-0.4 mmol/L (Fig. 4c). Because there is no observed increase in calcium concentration (Fig 4f), it can be assumed that TIC only is produced by mineralisation of organic carbon. The loss of DOC is about 0.16-0.33 mmol/L (0.2 - 0.4 mg/L, Fig. 4g). This suggests sediment bound organic carbon to be an additional carbon source for degradation. In Stage 4, where unsaturated conditions have been established and the extent of the unsaturated zone increases with time, sediment bound organic carbon becomes a more important factor in this context. It can be observed, that the degraded mass of DOC, while traveling to the observation well at 8m depths, cannot

account for the increased concentration of TIC (Fig. 4c). In the latter period of Stage 4, the concentration difference of TIC is approx. 1.2 mmol/L. According to

$$CH_2O + O_2 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^-,$$

it becomes clear that half of the inorganic carbon is derived from an organic carbon source, which means 0.6 mmol/L (= 7.2 mg/L) organic carbon must be degraded, while traveling to the observation well. It can be concluded that under aerobic conditions, the dominant electron donator must be sediment-bound organic carbon rather than DOC. The measured concentration difference of calcium of about 0.5 mmol/L (= 20mg/l, Fig. 4f) as well as the stable pH (Fig. 4a), which indicates buffering by calcite dissolution, underpins that hypothesis very well.

During Stage 4, the expanding thickness of the unsaturated zone versus time has an effect on the groundwater composition. While the unsaturated zone grows, increasing enrichment of total inorganic carbon and calcium can be observed. This can be well explained by the continuous expansion of the region, where atmospheric oxygen comes in contact with sediment-bound organic carbon, which is consequently degraded. Therefore, enrichment of degradation products within the seepage water must also increase with the expanding thickness of the unsaturated zone beneath the pond.

About 20-25 days after saturated conditions have been established in the first cycle (Stage 3), a significant drop of nitrate concentrations can be observed at all depths accompanied with a noticeable increase of manganese concentrations in two suction cups (Fig. 4d and 4i). Because manganese is not apparent in all suction cups and groundwater samples at this time, it can be presumed that reduction of manganese minerals only take place in so-called microenvironments, which commonly develop in stagnant water zones due to heterogeneous flow conditions. Manganese concentrations start to decrease when the redox-conditions are shifting back to nitrate reducing conditions. This shift could be explained by an overall decrease in microbial activity due to a rapid drop of temperature from over 25°C down to 18°C (not shown).

The drop of nitrate concentrations during Stage 4 allows two different hypotheses. In the first, decreasing concentrations at all observation depths are explained by decreasing concentrations in the surface water. This hypothesis is based only on one single surface water sample containing no nitrate. Another, more reasonable, explanation is the rising influence of the growing clogging layer on the ongoing degradation processes. High-resolution oxygen profiles of the clogging layer show a complete consumption of oxygen within the first 0.3 mm (Fig. 5). The linear decrease of oxygen saturation from about 2mm above the clogging layer is known as the Diffusive Boundary Layer (DBL), which is a stagnant water layer due to frictional forces between water and sediment. The thickness of the DBL can vary significantly dependent on different flow conditions (Larkum et al. 2002). No temperature dependence of the profiles

could be found. Although these profiles have been recorded under calm conditions where only diffusive transport took place, it is likely that oxygen does not break through the up to 5mm thick clogging layer under conditions where advection is the dominant transport mechanism. Once oxygen has already been depleted within the first part of the clogging layer, nitrate is the next expected electron acceptor to be consumed due to the degradation process. This results into low nitrate concentrations entering the unsaturated zone, which were indeed measured by the samplers.

Until now, the excessive sulphate and calcium peaks (Fig. 4e and 4f) observed at the transition from Stage 3 to 4 have not yet been clarified at all. The same holds for the noticeable iron concentrations at the beginning of the operational cycle (Fig. 4h).

Conclusions

Up to now, four main conclusions can be drawn from the observations presented above, i.e.:

- The switch from saturated to unsaturated conditions allows atmospheric oxygen to enter and to maintain in the pores until the new operational cycle begins.
- The continuous extending of the unsaturated zone exposes more and more sedimentary organic carbon for aerobic respiration and results in heightened inorganic carbon concentrations of the groundwater.
- Sediment-bound organic carbon is the most important electron donator during unsaturated conditions, whereas DOC contained in the surface water seems to be a less favorable substrate for biodegradation.
- During summer, redox conditions can develop temporarily down to manganese reducing conditions beneath the artificial recharge pond.

Further tasks

In order to constrain the proposed hypotheses, the further tasks are planned:

- The sampling period will continue until the end of summer 2004
- The consumption rate of oxygen in the clogging layer is to be determined by modeling
- Dialyses cells, so-called peeper, will be installed and analyzed
- PhreeqC batch-modeling will be done.
- The geochemical data and the proposed hypothesis will be discussed in detail with the NASRI working group Hydrogeology
- A one- or two-dimensional reactive transport model will be set up either PhreeqC2 (Parkhurts and Appelo, 1999) or with the simulators MODFLOW (McDonald and Harbaugh, 1988) and PHT3D (Prommer, 2002).

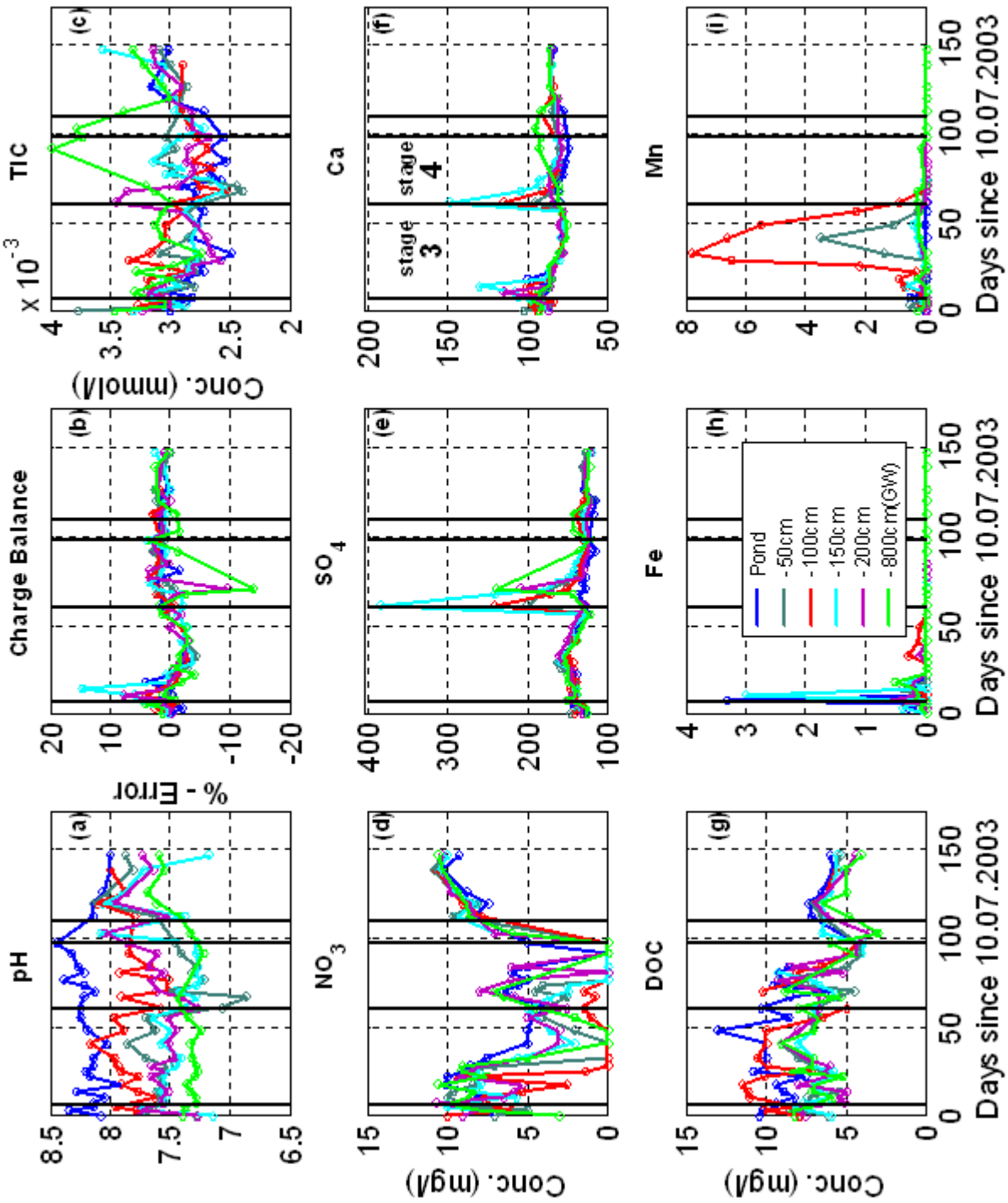

Fig. 4: Geochemical data of the surface water (Pond), groundwater (GW) and at 50cm, 100cm, 150cm, 200cm depths beneath the pond.

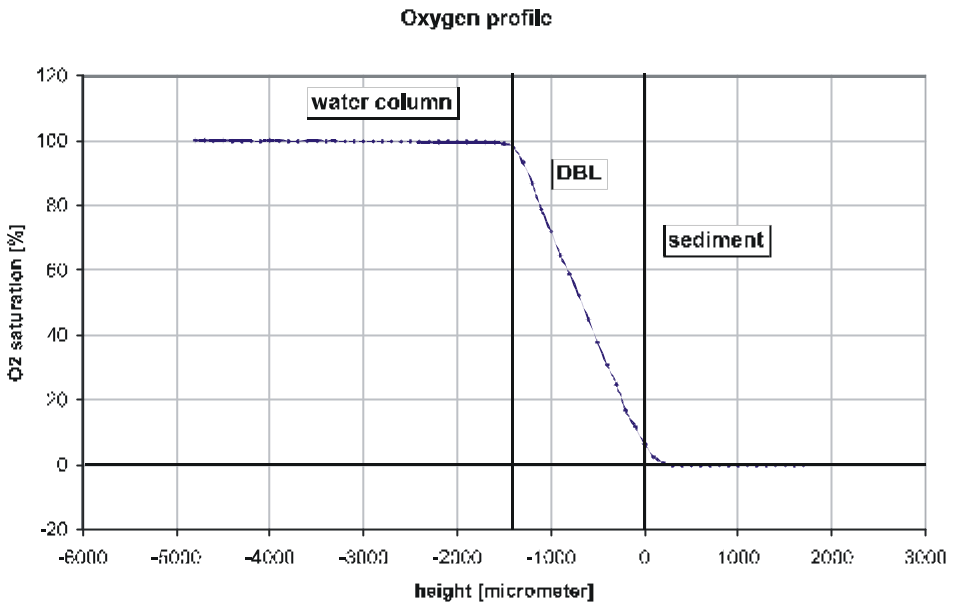

Fig. 5.: High-resolution profile of oxygen

4.1.2 Transient 2-D groundwater flow simulation (J. Rümmler, Diploma Student)

Former investigations of Pekdeger et al. (1999) on well galleries located adjacent to lake Müggelsee and lake Tegel leads to the following results: as an effect of small pumping rates and constant well regimes the hydraulic and chemical conditions of the bank filtrate near lake Müggelsee seems to be more 'consistent' than they are near lake Tegel, where higher pumping rates and irregularly well regimes takes place. It may be that the removal of specific substances is not ensured during bank filtration because of highly variable hydraulic and chemical conditions. In addition, this situation will become more critical in the future when some waterworks will be closed and, for example, if the well gallery Tegel West would produce more water then at present, increasing flow velocities could result in residence time that would not meet the "50-Day-Guideline". As a consequence, the following questions arise:

How do flow paths and travel times change depending on pumping rates and well regimes?

What is the correlation between the share of bank filtrate, pumping rates and/or well regimes?

To answer these questions, the hydraulic effects of different well regimes and pumping rates were simulated with the help of a numerical transient 2D-horizontal plane groundwater flow model, developed in PMWIN5.1 (Chiang & Kinzelbach 2001). The model area is located around the transect Tegel, which is examined within the NASRI project. The intention of this study was not to reproduce the hydrogeology in detail. The target was to find out general statements, which are useful for the development of management strategies. on well galleries located

adjacent to lake Müggelsee and lake Tegel The diploma thesis was carried out under the common supervision of the working groups Hydrogeology (FU) and Modeling (IGB).

Steady State Model

The model area was discretized by 10 000 cells. The lengths and widths of each cell ranges for ?x from 1.66 to 100 m, and for ?y from 1.66 to 5 m. The lower aquifer 2 has a thickness of 25 m and is modeled as porous, isotropic and confined/unconfined. The pumping rate per well is 0.0054 m³/s. It is the average of the pumping rate of the whole gallery (26 wells) for the period 12/98 - 05/99.

The boundary conditions are demonstrated in Figure 6. Because of the seepage of lake Tegels surface water through the lake sediments in aquifer 1 and 2 (marked light blue) and the leakage from aquifer 1 into aquifer 2 (marked orange), these areas are determined with a leakage-boundary of type 3. In the east it is assumed, that the water level of lake Flughafensee is fixing the groundwater level in aquifer 2, thus the eastern boundary (marked dark blue) is determined with the constant-head-boundary condition of type 1. The northern and southern borders of the model (marked dark gray) are located between two productions wells, whereby there is neither a flux into nor out of the model. They are determined as no-flow- boundary of type 2 in each case.

The sum of the squared residual is 0.18 (computed by PEST), reflecting a low deviation between measured and calculated heads. The absolute difference between measured and calculated data is given in Table 1.

Table 1: Absolute difference between measured and calculated groundwater heads

observation well	difference between measured and calculated heads [m]
3301	0.00
3302	0.02
3303	0.19
3304	0.09
6034	0.35

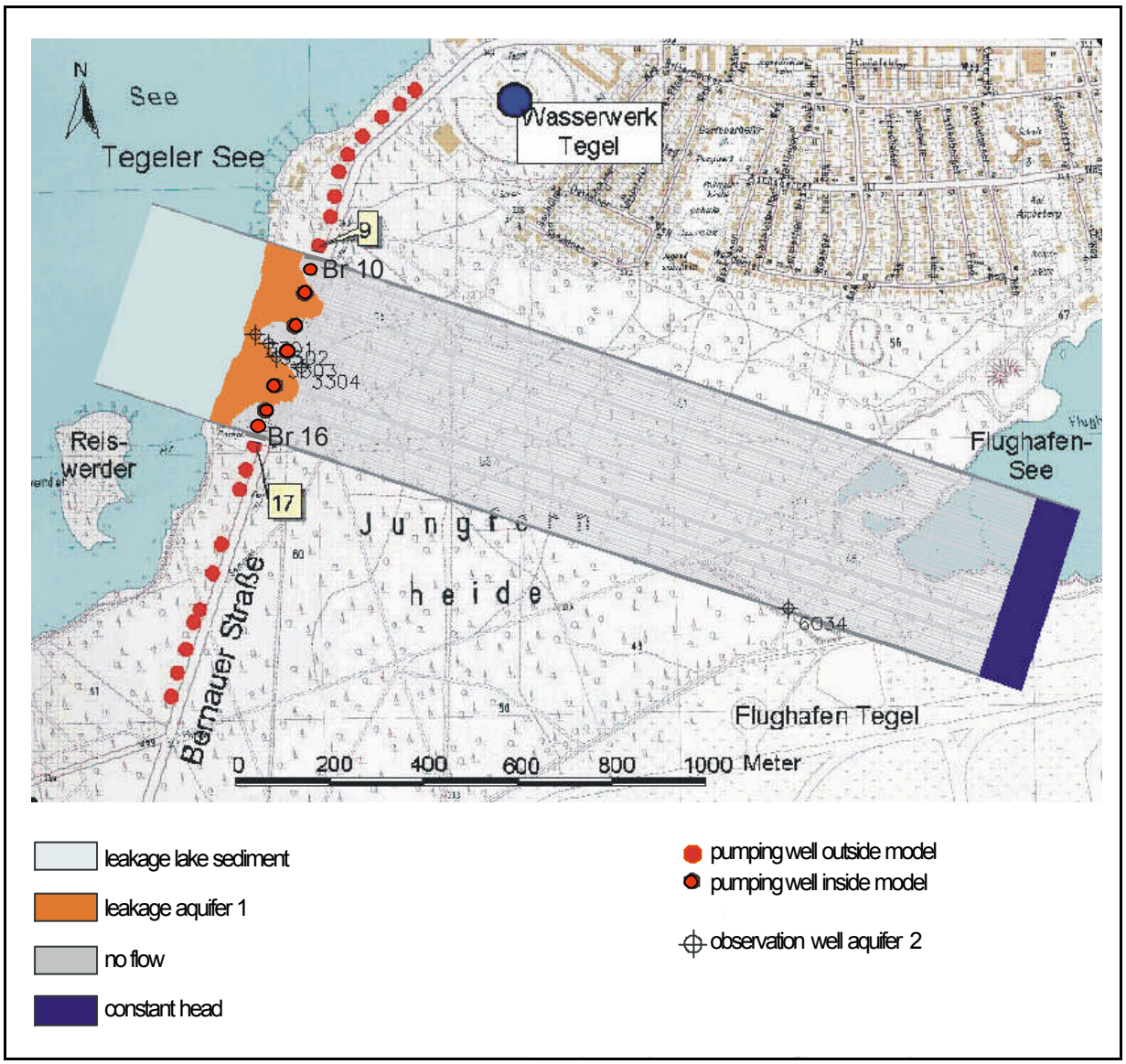

Fig. 6: Steady state model - boundary conditions

The highest difference is 0.35 m at observation well 6034, originally located outside of the model area. It was shifted along its groundwater contour inside of the model area. Thus observation well 6034 is weighted lower and the difference of 0.35 m is acceptable. The remaining deviations range between 0.00 and 0.19 m. These values are within limits allowed.

The hydraulic conductivity of the sediments and the width of the clogged sediment is documented in Table 2.

Table 2: Hydraulic conductivity of the mud, aquifer 1 and 2 as well as the width of the clogged sand

parameter	value before calibration	value after calibration
hydraulic conductivity mud	$4*10^{-8}$ [m/s]	$4*10^{-8}$ [m/s] and $4*10^{-7}$ [m/s]
hydraulic conductivity colmated sand	$5.5*10^{-6}$ [m/s]	$1.2*10^{-6}$ [m/s]
hydraulic conductivity aquifer 1	$1*10^{-4}$ [m/s	$5.2*10^{-5}$ [m/s]
hydraulic conductivity aquifer 2	$3*10^{-4}$ [m/s]	$5*10^{-4}$ [m/s]
width colmated sand	40 m	10 m

Transient Model

The simulation was done with pumping test data of a pumping test carried out at the transect Tegel in summer 1999 (Eichhorn 2000).
The model features are (in addition to the steady state model):

1) simulation length: 13 days
2) simulation periods: 13 (one for each changing of the well regime every 24 hours; well 10 and 16 are abstracting water at all times)
3) initial hydraulic head aquifer 1: between 27.20 m a.s.l. (period 1) and 26.17 m a.s.l. (period 13), (average of the heads of the observation wells in aquifer 1, measured during the pumping test)
4) storage coefficient for the unconfined aquifer: 0.25 (because the effective porosity is 0.3)
5) pumping rates of wells 11-15: similar to the real pumping test data
6) pumping rates of wells 10 and 16: They have to be higher than the real values to simulate the influence of the operating wells 1-10 and 16-26 at the beginning and during the pumping test

For the initial conditions the fivefold (0.15 m³/s) of the original pumping rate of well 10 and 16 is appropriate. To simulate the influence of wells 1-10 an 16-26 during the pumping test, the twice of the original pumping rate is suitable (well 10: 0.066 m³/s, well 16: 0.068 m³/s). Figure 7 shows the calculated and measured groundwater heads.
The variance is 0,11 with observation well 6034 and 0.093 without observation well 6034. The difference between measured and calculated groundwater heads is +/-0.6 m. These values are suitable, particularly for a 2D-model. The graphs of the calculated heads diverge from each other more than the graphs from the measured heads, because in reality, the hydraulic conductivity of aquifer 2 varies locally whereas in the model only one value was applied. The

concept to construct a general model requires the compromise of a general hydraulic conductivity, indeed within acceptable scopes, like here.

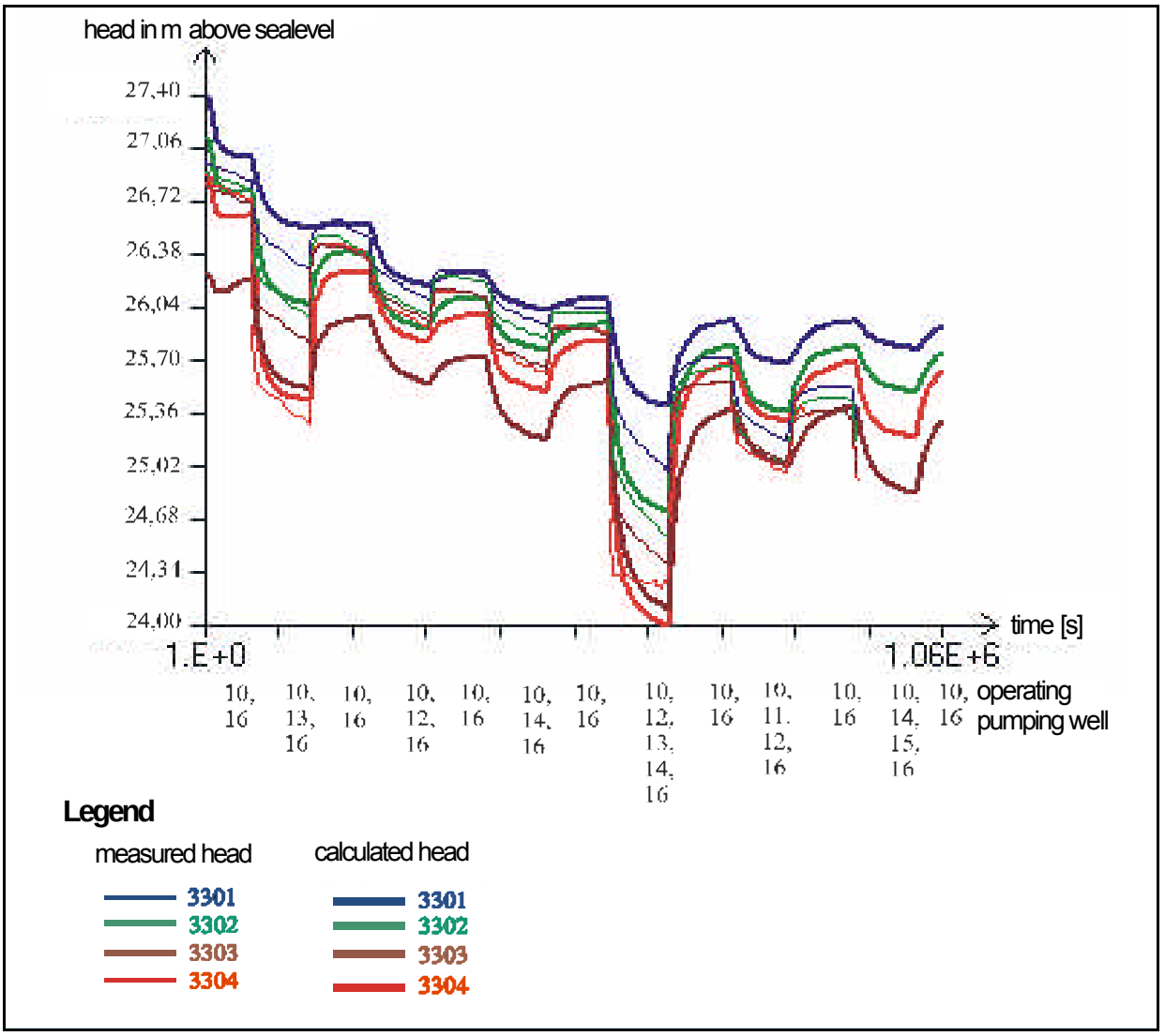

Fig. 7: Transient model - calculated and measured groundwater heads (Eichhorn 2000)

Well Scenarios

Following questions have to be answered:

1) How will the travel paths and travel times change depending on pumping rates and well regimes?
2) What is the correlation between the share of bankfiltrate and the pumping rates and/or well regimes?

In order to answer questions 1 and 2 well scenarios have to be construct, which provide general and practice-orientated statements. Figure 8 shows the chosen scenarios.

Scenarios 1-5 were assigned with a general pumping rate of 0.0054 m³/s per well (like in the steady state model), and scenarios 6-8 with a pumping rate of 0.02 m³/s per well, an average of the rates from January 2002. In order to keep the analysis simple and comparable, the combination of the operating wells has to be symmetric. The alternation interval between the well combinations is daily, weekly, and monthly. For practice-orientated conclusions it is useful to simulate a daily and monthly non-symmetric well regime.

To guarantee long travel times (28-34 weeks), the groundwater should be abstracted from all wells with a low pumping rate of about 0.0054 m³/s for each well.

If not all wells are supposed to operate at the same time it is recommended to arrange the wells in groups of 3 wells with a daily alternation interval and a pumping rate of about 0.0054 m³/s to ensure travel times between 32-35 weeks.

If a pumping rate of up to 0.02 m³/s per well is necessary, it seems that monthly alternations will be advantageous to reach travel times from 17-25 weeks. With regard to this the following assumption has to be checked in further thesis: The higher the pumping rate, the higher the alternation interval has to be to guarantee travel times of about 30 weeks. The catchment areas and hydrochemical conditions vary relatively strong.

If the pumping rates are higher than 0.02 m³/s per well, it might be possible that the “50-Day-Guideline” can not be guaranteed anymore. Further scenarios are needed to analyze whether there is a correlation between the increase of the pumping rate, the extension of the travel time, and the extension of the alternation interval.

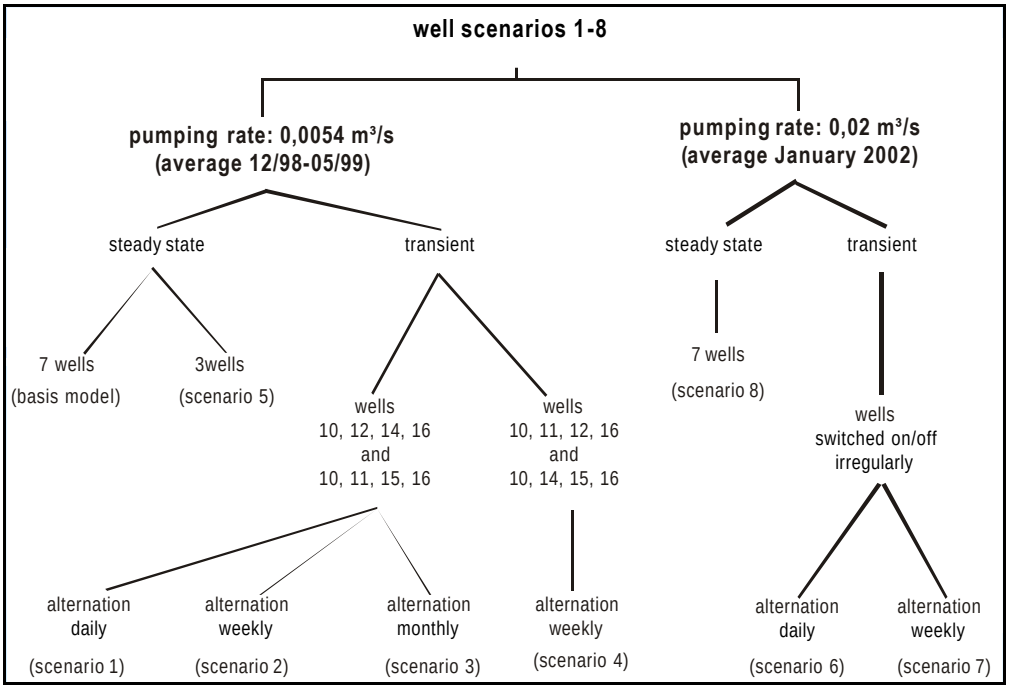

Fig. 8: Overview of well scenarios 1-8

To enhance the share of bank filtrate the pumping rate has to be higher than 0.02 m³/s. This is a contradiction to the recommendations named above. If an extension of the travel times is achieved according to the assumption mentioned above „the higher the pumping rate, the higher the alternation interval“, then a pumping rate over 0.02 m³/s might be possible.

The conclusions were:

Particularly the pumping rate has a significant influence on the travel time and the share of bank filtrate, but the alternation interval also has noticeable effects.
To guarantee long travel times, it will be the best to abstract groundwater from all wells with low pumping rates of about 0.0054 m³/s per well. If that is not possible, well grouping and a daily alternation interval is recommended to guarantee the conditions mentioned above.
If the pumping rate is supposed to increase up to the fourfold per well (0.02 m³/s) it was assumed that a monthly alternation interval is appropriate to ensure longer travel times. To check this in detail, more analyses should be made by numerical models. Consequently stable catchment areas and chemical conditions are not ensured, particular since aquifer 2 is semi confined.
If the pumping rate has to rise up to 0.04 m³/s the “50-Day-Guideline” may not be ensured any longer.
The leakage amount from aquifer 1 depends on the pumping rate. If the pumping rate increases to the fourfold, the leakage quantity arises about the fourfold too. The enhancement of the pumping rate also effects the origin of the bank filtrate: If the pumping rate is lower than 0.02 m³/s, the share of bank filtrate from aquifer 1 increases, while the share of bank filtrate from aquifer 2 and the share of ambient groundwater from the east decreases. The total share of bank filtrate persists. If the pumping rate is higher than 0.02 m³/s, the total share of bank filtrate rises from 88 to 94%. Because the increase is minimal, it was not recommended to enhance the pumping rate with regard to the negative effects mentioned above.

3-D groundwater and solute transport model (B. Wiese)

Testsite Marienfelde

Objective

The test site of Marienfelde has many prerequisites for performing bank filtration experiments in a semi- technical scale. Existing construction plans give a schematic overview of the subsurface sites construction. However, this knowledge must be verified and matrix properties must be calibrated. Therefore, a dual tracer experiment was carried out in 2002 by UBA, FU, GFZ and IGB, the model was discussed with the working group Hydrogeology (FU). The results

(breakthrough curves) should be integrated to a 3-D transport model describing the flow and transport properties. Then, this model can be used in order to decide which further bank filtration experiments are likely to produce significant results and act as basis for their set up.

Model Results

The hydraulic model for the test site was calibrated by spatial variation of the K_f-values (Fig. 9 and 9a). Calibration is focused on obtaining a good fit for the concentration maximum and travel time of the tracer breakthrough curves. Effective porosity was adjusted between 0.3 and 0.4 to a value corresponding with the K_f-value. These values are quite high but realistic taking into account the uniform distribution of the aquifer sediments.

- It has to be pointed out, that the calibrated K_f values are estimated values, and the real situation could be different.
- However, with this model it is possible to predict breakthrough curves for different pumping rates, which is relevant for planning of sampling.
- The calibrated K_f values can be used to re-estimate the grain size of the material the water of each sampling well flows through. This is of importance for describing matrix influences on geochemical reactions or filtration of phages.

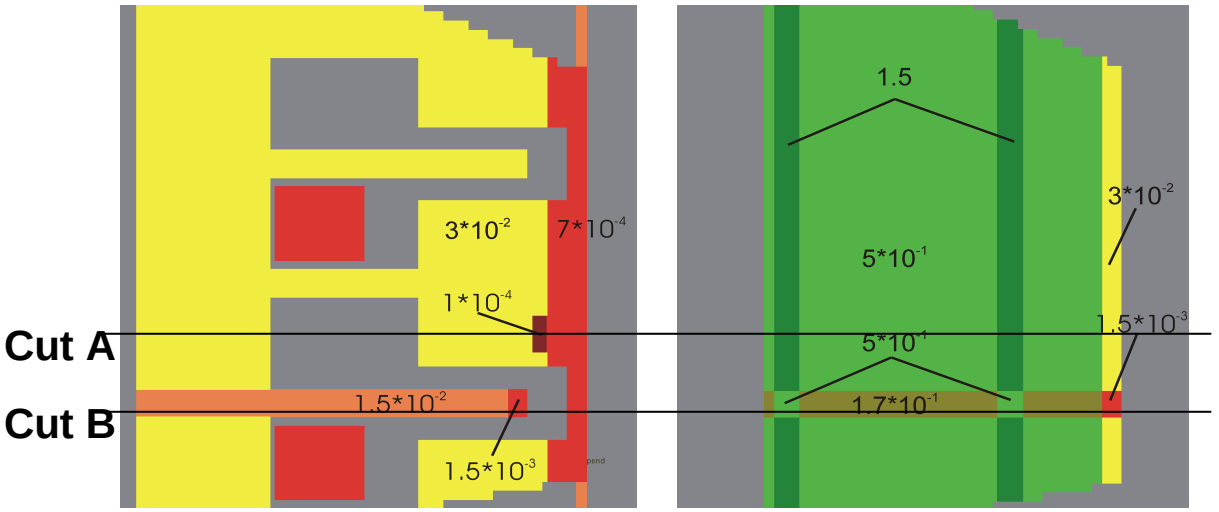

Fig. 9: Calibrated K_f values of the hydraulic model in horizontal layer 2 (left) and 15 (right).

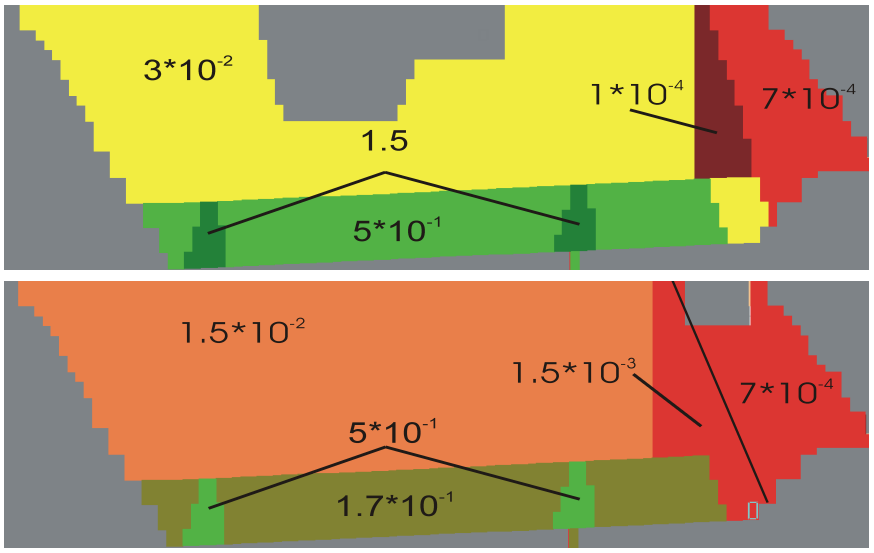

Fig. 9a: Cross sections A (top) and B (bottom) of hydraulic model (See Fig. 9)

Final conclusions for the test site are (some changes to the conclusions of the last report):

1. Uncritical boreholes for further experiments are 1, 3, 5, 7, 10, 12, 14 and the first drainage. These points can be described rather good by a 1-D and 3-D approach.
2. Rather uncritical points are 2, 4, 15. Aquifers material and probably shape locally differs from construction plans. The material is finer than according to the plans. However, this can be modeled well. Additionally finer material is closer to our field conditions. These points can be described rather good by a 1-D and 3-D approach.
3. The boreholes 6, 8, 13 and maybe 11 and the hind drainage are influenced by the upper and the lower layer. Under the present flow conditions the ratios can be estimated quite well, for other flow conditions these may change. These points can not be modeled by a simple 1-D but with a 3-D approach.
4. In well No. 9 bend streamlines create strong smeering. Transport properties can not be determined.
5. A clogging layer/Schmutzdecke is missing or only weakly developed (in March 2002).
6. The principal layer assemblage according to the construction plans is approved. Scenarios from the last report could not be approved. Differences from the expected breakthrough curves are based in local heterogeneities.

Outlook

Groups which intend to make experiments will be supported in planning and evaluation.
Modeling of the tracer experiment April/May 2002 can be considered as finished.

Transect Tegel

Objective

A 3-D instationary flow model is set up to identify the hydraulic properties of the transect and its surrounding area. It is the first step on the way to set up a 3-D flow, transport and geochemical reaction model for the transect. So the spatial focus of the model development is the transect, the interest of the surrounding areas is limited on their effect on the transect. In this report special focus is set on the spatial distribution of the glacial till layer.

Hydrogeological situation

To the bottom the model area is delimited by the Holstein aquiclude about 10m below sea level, ca. 45 m below land surface. This is documented by all boreholes of this area (see profiles (Voigt, Eichberg 2002). Above this follows the Saale glacial aquifer up to a level of about 18 m above sea level. On this a Saale glacial till-layer of about 4 m thickness is located. However, it is does not entirely cover the Saale aquifer but contains a number of windows. Above this the Weichsel aquifer is located from about 22m above sea level up to the land surface elevation of about 35 m above sea level. The lake Tegel is formed by the Weichsel glacial series. Its oldest sediments have an age of 13000 years (Pachur & Röper 1987), sedimentation started when the Weichsel ice age ended. Geologic profiles (Voigt & Eichberg 2002) indicate below and aside lake Tegel a fluivatile valley. Its extent is of importance for the extent of the till towards the lake. Geological profiles of the transect, investigated by the working group Hydrogeology are used for the model setup. The best estimation of the till extent until now was used by Rümmler 2003 (Fig.10)

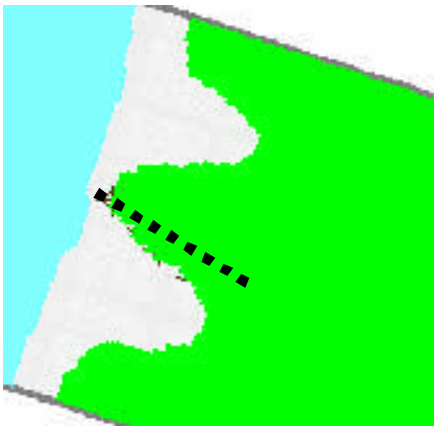

Fig. 10: Extent of the till layer (green) estimated on available geologic profiles. Blue color indicates lake Tegel, the dotted line represents the transect.

K_f values of the aquifers have typical values of $5*10^{-5}$ to $6*10^{-4}$. The glacial till layer has values of about $2*10^{-8}$ to $7*10^{-9}$. The extent of the glacial till is of high importance for the hydraulical situation. Due to numerous windows left open during its formation or formed by the subsequent glacial series, and the uncertainty if the marl is removed around the lake Tegel by fluviatile processes, much effort has to be put on determining its extension.

Lake Tegel

The bottom of lake Tegel is covered with mud of K_f values between $2.1*10^{-7}$ m/s und $2.8*10^{-9}$ m/s (Pachur & Röper 1987). This mud already has a thickness of about 1m at a water depth of 2 to 3 m (personal communication Judith Sievers 2003). This means most water infiltrates directly at the shore. This coincides with Eichhorn (2000) that only 15% of infiltration occur through mud near the shore, the rest at the part of the lake bottom which is not covered with mud. Water level varies between 31 and 31.6 m above sea level

Lake Flughafensee

The Lake Flughafensee is a former gravel-pit and has a depth of about 40 m. It is hydraulically well connected to both aquifers. Its water level varies between 30.6 and 29.6 m.

Model Structure

Precursor of the hydraulic model currently under development is the simulation of Jeanette Rümmler (Rümmler, 2003). Spatially it is slightly extended and includes now well 9 to 17 (Fig. 11). Vertically it is divided in 3 layers (Fig. 12). The upper layer represents the Weichsel aquifer, the middle layer the Saale till and the lower the Saale aquifer. Lake Tegel penetrates only the upper layer, to which it is hydraulically connected. The Lake Flughafensee penetrates all 3 layers and is well connected to both aquifers. In assumption of water table contours parallel to the well gallery, no flow from below the lake bottom and no flow through the Holstein aquitard below the model area these boundaries are set to no flow. Similar time averaged pumping rates of all wells of the gallery west (Fig. 11) and similar Water levels of TEG050 and TEG341 suggest water table contours parallel to the well gallery.

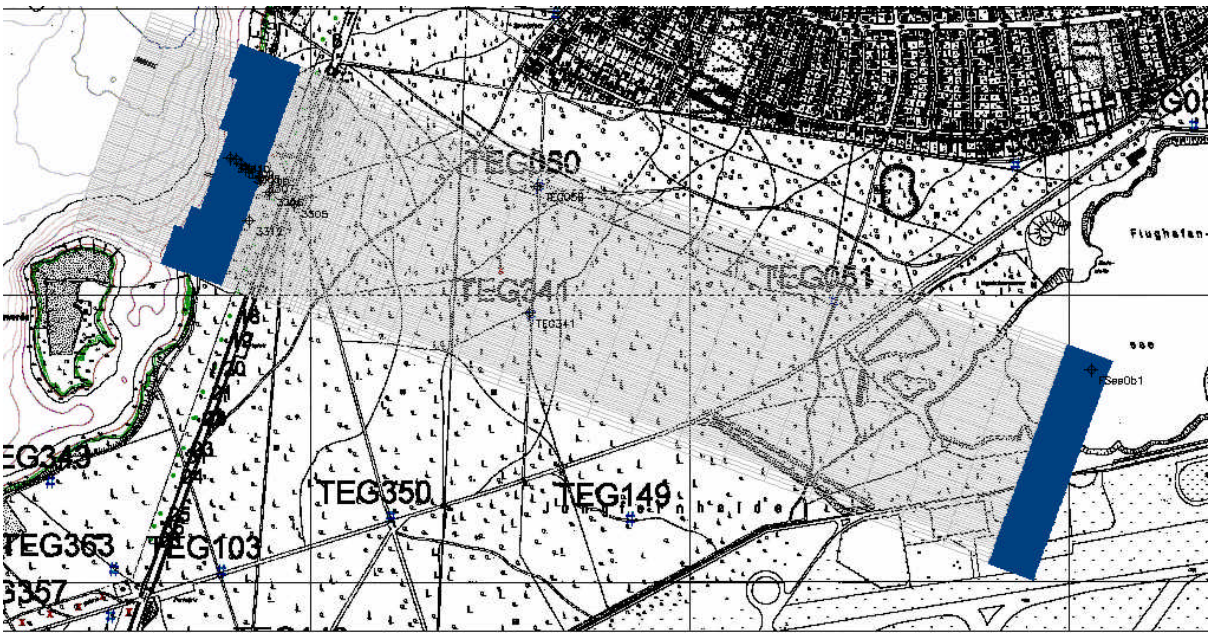

Fig. 11: Model extent and discretization. TEGXXX indicate observation wells monthly sampled. The blue areas indicate constant head and reservoir boundaries.

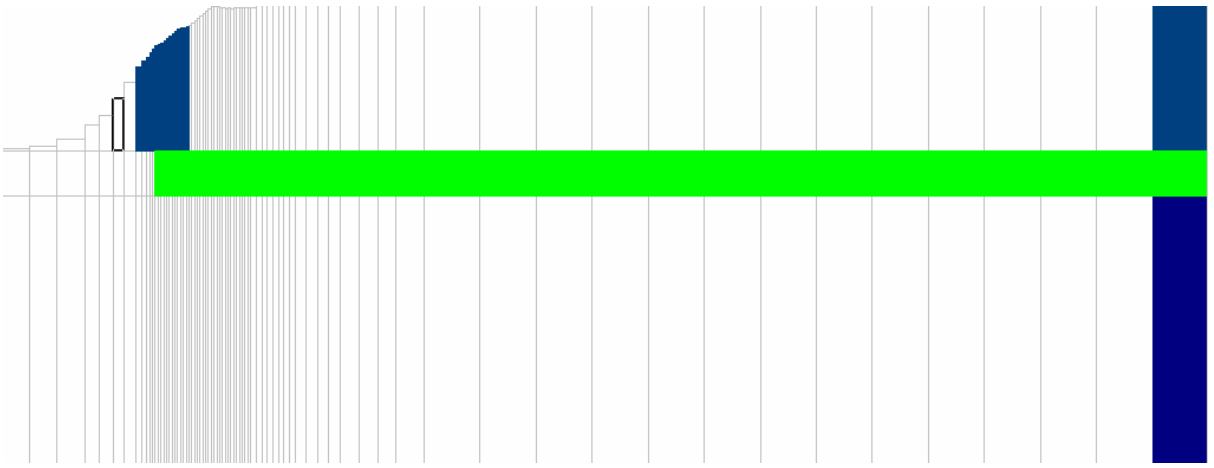

Fig. 12: Cross section of the model. Blue areas indicate constant head and reservoir boundary condition, the green area represents the glacial till.

Calibration

The main result intended to obtain by this model is the extent of the glacial till, which can be estimated much more reliable by evaluating the drawdown during pumping experiments. The advantage of this method is that a pumping experiment provides information of spatial distribution of hydraulic properties and reacts to very tiny confining layers which. However it has

to be taken into account that the shape of the till shown in all figures is an estimation of the real shape, which always remains unknown.

Vertical anisotropy seems to be less important for the confined reaction of the deep observation wells than the tills extent. Analyses of grain size distributions of observation wells 3301, 3302 and 3303 suggest horizontal K_f values of 1.8 to $3.4*10^{-4}$m/s. In vertical direction the variability of K_f values is not very high, anisotropy has a maximum value of only 2 in the lower layer.

An exemplary hydraulic calibration sequence with a constant horizontal K_f value of $5*10^{-4}$ m/s is depicted in Fig. 13, row 1. Data are taken from a pumping test carried out from 13th till 26th June 1999 (data from FU, Fritz & Pekdeger). During this test different wells or combinations of wells were run during 1 day, each combination followed by 1 day without pumping. It can be seen that observation well 3301 reacts confined, with a sudden drop of piezometric head as the extraction wells start pumping which means a low storage coefficient. In the model there is no sudden drop but more a constant decrease which means a high storage coefficient. So the confining layer between the extraction and observation wells has to be bigger than assumed in the model.

At well 14 the marl is not present, 3312 is not so deep as the marl would be penetrated. But taking into account the hydraulic reaction of 3312 to well 14 its obvious that there exists a confining layer, shielding the upper part of the aquifer to the lower part. The confining layer has also to be enlarged here.

In the second row of Fig. 13 the conduction of both wells is already better, however, the till still seems to be assumed not large enough.

The till extent of the third row of Fig. 13 represents a reasonable estimation for the aquifer structure regarding these two observation wells. However, the till is not present above 3301 and the sudden drop of the water table, which normally is characteristic for a confined situation, is caused by the combination of the vicinity of the till, the high vertical flux and a vertical anisotropy assumed with factor 5 for the aquifer above the till. The fact that the till does not extent to lake Tegel and a gap exists between the lake sediments and the till is documented in Voigt 2002. Productive discussion about the calibration was held with Gudrun Massmann (working group Hydrogeology).

Results

The actual result of calibration is shown in the first column and last row 3 of Fig. 13. However, this is only a current fit with different levels of certainty according to the state of calibration and the distribution of sampling and extraction wells. A final assessment will be given in the next report considering conservative transport.

Outlook

3312 enables us to estimate the lateral hydraulic influence on the transect from the south. At the north the next observation well is 3313, which has the double distance from the transect as 3312 and is not sampled yet. There will be modeled scenarios how the extent of the till influences the transect. As the calibration is performed with more than 12 observation wells, 7 pumping wells during several time periods, the calibrated shape of the till will change.

Simulation of flow and transport during the project duration will be performed using data and geochemical research results of the working group Hydrogeology (FU).

Subsequent transport modeling with different tracers will adjust K_f values and travel times. Based on the calibrated flow model the reactive transport model will be set up until June 2004 to identify measured geochemical evolution of infiltrated surface water.

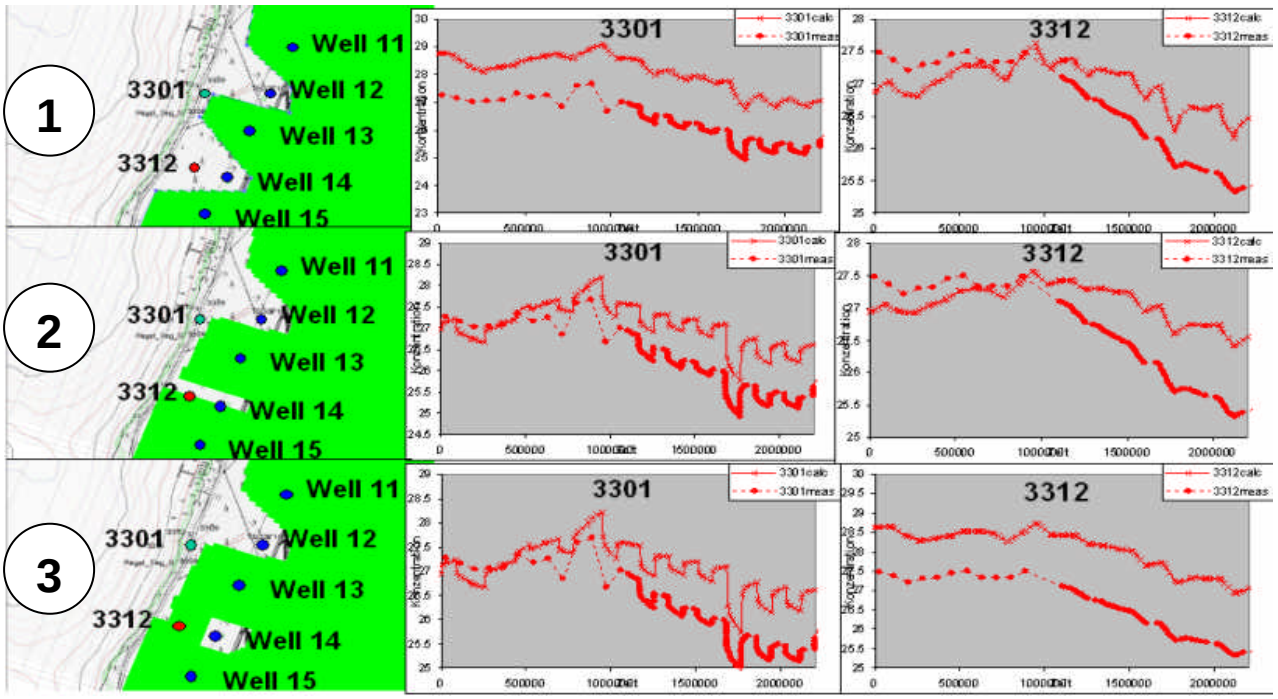

Fig. 13: Variation of the extent of the till (left column) and response of observation wells 3301 (middle column, deep aquifer) and 3312 (right column, shallow aquifer). The graphs show the simulated (crossed line) and measured (dotted line) piezometric head over the time. Observations and pumping rates from 13th to 26th June 1999.

4.2 Laboratory experiments

A model of degradation of Gd_DTPA in infiltration surface water (E. Holzbecher)

At the large scale column facility at the UBA several experiments were set-up (see NASRI working group at TUB (Jekel, Grünheid e.a.) for the general set-up of the columns and working groups at UBA and FUB for experiments). One experiment, lasting more than 30 days, with Gd-DTPA was performed by mainly by A. Knappe (GFZ – Geo-Research Center, Potsdam) within a project, funded by DFG (German Science Foundation). The outcome of this experiment is modeled at the IGB.

The aim of the experiment is to investigate the behaviour of the Gd-DTPA as an example biochemical component under near natural conditions during bank filtration. With a length of 30 m the column has the same spatial dimension, as it is relevant for bank filtration systems. With approximately 1 m/d the flow velocity is also in the same range as it can be observed in several bank filtration systems. Moreover the infiltrated water for the experiment was taken from Lake Tegel. In focus of the work are modeling approaches, in particular of the steady state conditions, measured in the experiment.

The steady states, observed in the experiment, are especially suited for a for detailed analysis as they not only present single observed values, but a series of 11 single measurements at each observation point. The higher reliability of these values is highlighted by the fact that fluctuations due to different difficulties at the beginning of the experiment show mean values which coincide with the plateaus observed in the later course of the experiment.

For a constant inflow concentration advection, dispersion and sorption without degradation would lead to the same constant plateau in all breakthrough curves. A spatially changing steady state can be tested by various mathematical approaches concerning the degradation process. Thus modeling focused on the steady-state concentrations, measured in the column, as these are the result of the degradation processes. Ordinary differential equations are derived from the general partial differential equations describing transient transport and degradation processes – those are presented in the introductory sub-chapter. The final sub-chapter concludes with an overview over numerical methods and tools applied in this study.

Model Equation

The first modeling approach follows from the assumption that, aside from advection and dispersion, degradation with a constant rate controls the behaviour of DTPA. Such a situation is described by a single partial differential equation for DTPA-concentration *C*:

$$j\,R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - j\,R\,l\,C \qquad (1)$$

with parameters: porosity j, retardation factor R, dispersivity D, Darcy-velocity v and degradation rate l. Aside from degradation the equation (1) includes storage, advection, diffusion, dispersion and fast sorption. In order to obtain a better description of the situation a more complex description can be chosen, in which the bacteria population X is introduced as a second variable.

$$j\,R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - a\,X\frac{C}{C+b}$$
$$\frac{\partial X}{\partial t} = g\,X\,\frac{C}{C+b} - d\,X^n \qquad (2)(A, B)$$

The degradation rate for the substrate is linearly dependent on X. For high concentrations C a maximum of degradation aX is reached. Half of that maximum is given for the substrate concentration C=b. Such a behaviour is described by the Monod-term, the last term in the first equation of (2). The same functional dependency is used to describe the growth of the bacteria population, where the coefficient g includes the relation between bacteria population and substrate concentration. The last term equation of (2)(B) accounts for the decline of the bacteria population or natural death of the bacteria, for which two additional parameters, d and n, are introduced.

Approaches as in eq. (2) are common in biogeochemical modeling. Many researchers use a linear term for the decline of X. For n=2 the approach coincides with the so called logistic equation, which is most popular in the biological / ecological sciences. As an alternative formulation of the same complexity another formulation is examined as first alternative. The substrate description (2)(A) is kept, while the bacteria equation (2)(B) is replaced by

$$\frac{\partial X}{\partial t} = g\,X\,\frac{C}{C+b} - d_1 X - d_2 X^2 \qquad (3)$$

In eq. (3) a linear and a quadratic decay term are included. In a discussion of various different mortality terms in ecological models Fulton *et al*. (2003) motivate such an approach, stating that the linear term represents ‘basal’ mortality, while the quadratic term is due to predators, which are not explicitly represented in the model. Some authors suggest to use an inhibition term for the bacteria population:

$$\frac{\partial X}{\partial t} = g\,X\,\frac{C}{C+b}\,\frac{e}{X+e} - d\,X \qquad (4)$$

where e denotes one additional parameter. The inhibition factor $e/(X+e)$ has also to be included in the decay term of the substrate equation.

Steady State Solution and Approximation

Steady states can be obtained in most cases for all presented approaches when the time-derivatives are set to zero. The most simple approach (1) for degradation without taking bacteria explicitly into account, leads to an ordinary differential equation for the steady-state curve $C(x)$:

$$\frac{D}{v}\frac{\partial^2 C}{\partial x^2} - \frac{\partial C}{\partial x} - VC = 0 \quad \text{with} \quad V = \frac{j\,l}{v} \tag{5}$$

for which analytical solutions can be given depending on the second boundary condition. With the condition of finite concentrations for all x-values one obtains the solution:

$$C(x) = c_{f0} \exp\left(-\frac{x}{2D}\left(\sqrt{v^2 + 4VDv} - v\right)\right) \tag{6}$$

For the steady state of the extended model, given by eq. (2), holds:

$$\begin{aligned} D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - a\,X\,\frac{C}{C+b} &= 0 \\ X\left(g\,\frac{C}{C+b} - d\,X^{n-1}\right) &= 0 \end{aligned} \tag{7}$$

The second equation of (7) has the trivial solution $X \equiv 0$, which can be of relevance only for the situation with no degradation, as the last term in the first equation vanishes under such circumstances. It can be seen easily for the term in the brackets that a non-zero steady state exists only for $n \neq 1$. For n=1 the term in the brackets vanishes for a single value of C (dependent on b, g and d), representing the only solution with non-zero X. This stands in contradiction to frequent observations of various different steady-state values for C, which depend on x. The case of a linear mortality term is thus special, as a non-trivial steady-state exists for constant C only. This characteristic disqualifies the exponent n for situations, in which a non-zero steady state is observed. For non-zero X the system of equations (7) can be re-written as

$$\begin{aligned} &D\frac{\partial C'}{\partial x} - vC' - a\,X\,\frac{C}{C+b} = 0 \\ &\text{for} \quad C' = \frac{\partial C}{\partial x} \qquad \text{and} \qquad X = \left(\frac{g}{d}\,\frac{C}{C+b}\right)^{1/(n-1)} \end{aligned} \tag{8}$$

The system (8) consists of two ordinary differential equations (for C and C'), which can be treated directly by appropriate software packages. For the solution inlet values C_{in} and C'_{in} are needed. As the sensitivity on the unknown additional parameter C'_{in} is extreme, the solution of (8) can be found for a limited parameter range only.

For advection dominated situations dispersion can be neglected in the differential equation. For the steady state and non-trivial bacteria population ($X \neq 0$) equation (2) can be simplified to

$$v\frac{\partial C}{\partial x} = -a\,X\,\frac{C}{C+b}$$
$$X = \left(\frac{g}{d}\frac{C}{C+b}\right)^{1/(n-1)} \tag{9}$$

Eq. (9) is not applicable for n=1. Replacing X in the first equation of (9) using the explicit expression in the second equation one obtains:

$$\frac{\partial C}{\partial x} = -\frac{a g^{1/(n-1)}}{v d^{1/(n-1)}}\left(\frac{C}{C+b}\right)^{1+1/(n-1)} \tag{10}$$

The steady state as solution of equation (10) is thus dependent on three parameters: n, b and $h := \frac{a g^{1/(n-1)}}{v d^{1/(n-1)}}$. Solving the first order differential equation (3), steady state concentrations can be simulated directly. For some given exponents equation (10) can be integrated directly, leading to a non-linear implicit relationship between C and x. In such a case it is even not necessary to solve a differential equation at all. For n=2 it can be integrated by separation of variables. Integration finally delivers a nonlinear relation between the steady-state concentration C and x:

$$x - x_0 = -\frac{1}{h}\left(C + 2b\,\log(C) - \frac{b^2}{C} - C_{in} - 2b\,\log(C_{in}) + \frac{b^2}{C_{in}}\right) \tag{11}$$

with $h = ag/vd$. For given initial conditions the value depends on the two parameters h and b only. For each x eq. (11) provides an implicit formula for the steady state concentration $C(x)$. Using an appropriate solution algorithm for the nonlinear eq. (11) the steady state can be obtained without having to solve any differential equation.

The described procedure to obtain the direct solution of the steady state can also be applied to the alternative formulation, including eq. (3). The non-trivial steady-state is then given by:

$$X = \frac{1}{d_2}\left(g\,\frac{C}{C+b} - d_1\right) \tag{12}$$

and the differential equation for the steady state is:

$$\frac{\partial C}{\partial x} = -\frac{ag}{vd_2}\left(\frac{C}{C+b}\right)^2 + \frac{ad_1}{vd_2}\frac{C}{C+b} \tag{13}$$

For the further examination the coefficients on the right side of eq. (13) are denoted by $h_1 = \frac{a}{v}\frac{d_1}{d_2}$ for the linear term and $h_2 = -\frac{a}{v}\frac{g}{d_2}$ for the quadratic term. Favoring equation (4) for bacteria population leads to the following differential equation for the steady state:

$$\frac{\partial C}{\partial x} = -h_1\left(h_2\,\frac{C}{C+b} - 1\right) \tag{14}$$

now with $h_1 = \frac{aed}{vg}$ and $h_2 = \frac{g}{d}$. In order to solve the steady state equations boundary conditions have to be specified additionally. It is generally assumed that there is an inflow concentration C_{in} for the substrate. An inflow concentration for the bacteria population, as well as initial conditions for substrate or bacteria are not of influence for the steady state. For the outlet the usual assumption of zero dispersive/diffusive flux is made. Eq. (8) requires the specification of a boundary condition $C'(0)$ or $\partial C / \partial x(0)$. In the simulations here this value is taken as an additional free parameter.

Numerical Modeling

At first parameter estimation runs were performed using CXT-FIT software, in order to estimate transport parameters (see last progress report, concerning the development of a user-friendly version at the IGB). CXT-FIT is based on analytical solutions for the transport equation (1). These simulations were performed by A Knappe at GFZ (Geo-Research Center Potsdam). Multiple step input was used with a constant input concentration based on the measured concentrations at the first observation point. The concentrations at the inlet were not used as boundary condition, as they were apparently not constant during the entire experiment. CXT-FIT was used for each breakthrough curve separately, to obtain optimal fits for parameters: velocity v/j , dispersion length $a_L=D/v$ and decay constant l. Models were set-up for the different steady state approximations using the ModelMaker software.

Flow velocity and dispersion length were taken from the CXT-FIT u=0.88 m/d, a_L=0.05 m. Biochemical parameters V, h, h_1, h_2 and b for the different approaches were obtained by a calibration run, using steady state concentrations during the constant inflow period of the experiment. Direct calculations of the steady state were performed for equations (5), (10), (13) and (14). Extended systems with two bacteria populations were also tested. Control calculations, including the optimization procedure, were made using Berkeley-Madonna. In addition the system (8), in which dispersion is also taken into account, was simulated also. Using the parameter h and the dispersion relation $D=a_L v$, the system (8) can be written also as:

$$\frac{\partial C'}{\partial x} = \frac{1}{a_L}\left[C' + h\left(\frac{C}{C+b} \right)^{1+1/n-1} \right] \qquad (15)$$

Some control calculations for the case n=2 were made using MATLAB™. The computations were performed with the available *fzero* command for the calculation of zeroes. MATLAB™ computations based on equation (11) were identical with ModelMaker results for the same parameter combinations. Moreover parameter fitting using MATLAB™ modules delivered the same results for the test-cases.

Results

The regularly measured Gd concentrations from the tracer (1500 ng/ml) remained sufficiently constant. Slight variations of matrix fluid volume resulted in concentration variations of about 2%. Each charge with a residence time of 10 days in the tracer vessel remained stable over at least ten days.

The initial desired concentration of 60 ng/ml Gd could not be continuously obtained at the beginning of the experiment. The measured Gd concentrations from the first sampling port (0.22 m) showed concentration variations between 61.8 ng/ml (+ 3%) and 46.7 ng/ml (- 22%). This is probably the result of an unstable inflow of tracer concentrate because of an insufficient pumping of the dosing pump. Chemical or biochemical reactions cannot explain a decrease of 22% in the first 0.22 m. The same varying concentration pattern could be observed in all following sampling ports. Nevertheless, after 20 days the Gd input was constant for the last eleven measurements with an average concentration of 54.5 ng/ml. This was comparable to the average input concentration of all measured values (54.7 ng/ml) at this point and 55 ng/ml were assumed as initial Gd input concentration into the column for further calculations.

Breakthrough curves (btc) for Gd have been obtained at all 11 observation points. Qualitatively all btcs show the same behaviour. With the advance of the front there is an initial steep rise, after which concentrations decline slightly. After a second rise to approximately the same level, which was reached before, the curves gradually decline to a steady state. As a function of distance or travel time from the inlet, a steady-state concentration can clearly be identified at all observation points. Steady state values decline with distance (see Figure 14). Finally btcs return to zero as response to the end of Gd-DTPA input at the end of the experiment.

The fluctuations with two peaks after the initial rise of the concentration can probably be attributed to a non-constant concentration at the inlet. As described above, due to mixing problems in the inlet water reservoir, which were not detected immediately, inflow concentrations declined in the beginning of the experiment.

Calculations with CXT-FIT provide values for velocity and dispersivity. Optimal fits are performed on basis of the breakthrough curve at each observation point. Mean values are u=0.88 m/d and a_L=0.05 m, where $u=v/j$ denotes the mean interstitial velocity and $a_L=D/u$ the dispersion length. Fitted degradation rates show a clear tendency towards lower values of m with increasing distance from the inlet.

The ModelMaker software was applied in order to model the steady-state directly based on eq. (10), and to perform a parameter estimation run for parameters n, b and h. Figure 14 shows results of for the best fit obtained with fixed n =2, for the best fit with variable n in comparison to the measured steady state concentrations. Allowing all three parameters to vary, values n =1.029, b =16.15, h =5425 were obtained as result of the parameter estimation procedure. Results are depicted in Figure 14. A control calculation was made using Berkeley Madonna

[27], which delivered: n =1.0295, b =16.38, h =5151 with a root mean square s =0.33, a result which differs from the ModelMaker result marginally. For comparison the approach without bacteria population (5) was also tested, which with s = 0.593 delivered a worse fit (with V = 0.00612).

The alternative model approach (3) with both a linear and a quadratic mortality term delivered a slightly worse fit. Using Berkeley-Madonna optimal values b=142, h_1=9.4, h_2=40 (defined in equation (13)) were obtained with a root mean square s=0.37. Additional calculations with a third approach using two bacteria populations with logistic growth produced a significantly worse fit (see Figure 15).

The formulation with inhibition term (4) was also tested. Best fit for the parameters of equation (14), was obtained using b=105, h_1=3 and h_2=3.4. With s=0.38 the mean root square is nearly the same as in the alternative approach (3), but higher than the approach with general exponent in the bacteria death description (see Figure 15).

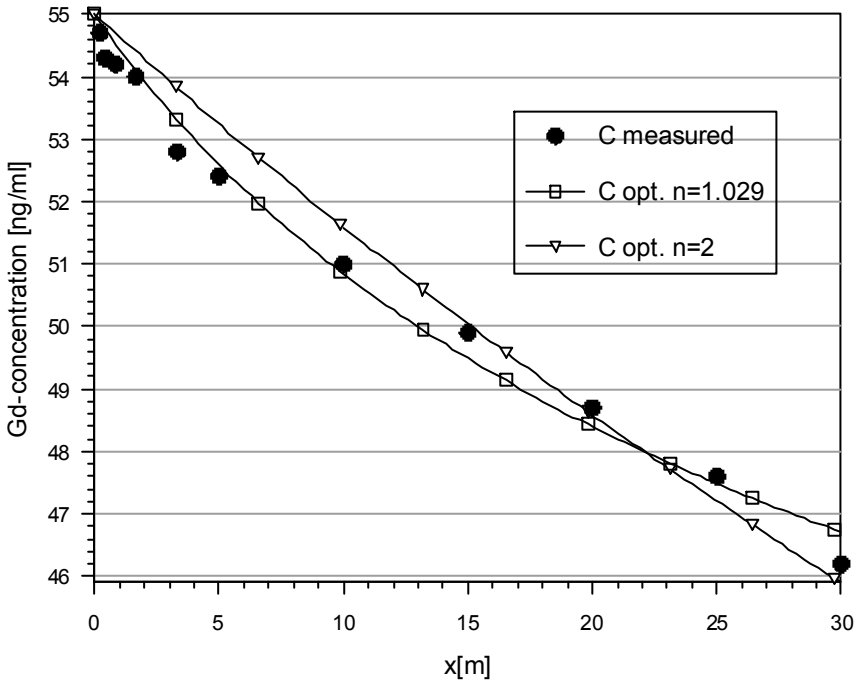

Fig. 14: Steady state Gd-concentrations, measured and modeled; model runs using ModelMaker with fixed parameter n=2 and free parameters b and h from eq. (10) (triangles); and free n, b and h from eq. (10) (squares); for parameter values see text

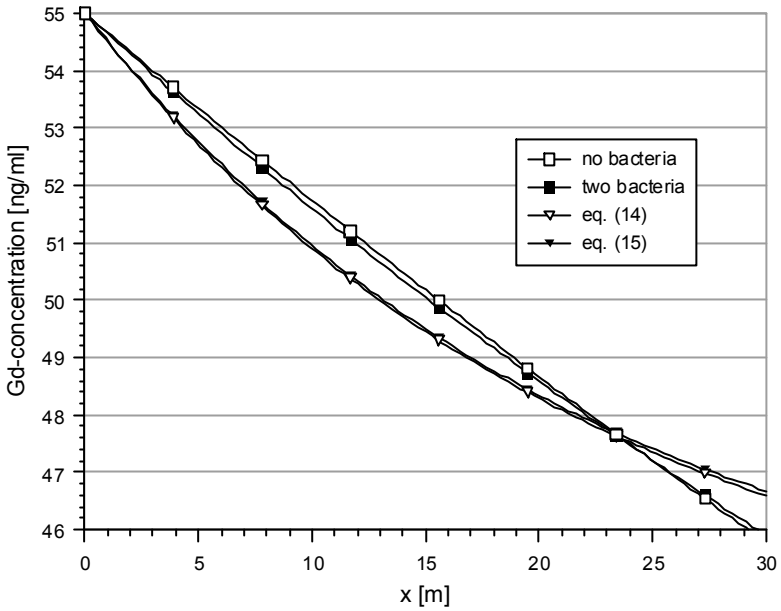

Fig. 15: Steady state Gd-concentrations under consideration of advection and degradation; results after parameter fitting on measured data for four different approaches for degradation: 'no bacteria' based on equation (5), 'two bacteria' based on an extension of equation (7) with *n*=2 for two bacteria populations, 'eq.(14)' on equation (13), 'eq. (15) on equation (14)

Note that best fits with approaches (13) and (14) with three adjustable parameters in the steady state model are only slightly worse than the best fit from equation (10) with also 3 free parameters. As could be expected all three results are much better than those for the simpler approaches with one or two parameters. However further extensions using two bacteria populations delivered only slightly better results, although the number of free parameters increased to six.

Discussion

Gd-DTPA is degraded in infiltrating surface water. It can thus be recognized as a tracer for smaller timescales only (compare tracer experiment Marienfelde as described in the 2002 report). Degradation of Gd-DTPA does not occur with a constant rate! Changing degradation along the column can be explained by a mathematical-analytical approach, which includes bacteria population. A procedure is outlined, from which steady-state concentrations can be obtained directly, i.e. without the simulation of the transient behavior. Under certain conditions it is even possible to simplify the mathematical problem to the solution of non-linear equations (see (11) derived for approach (2) with *n*=2 as an example).

It is shown that the existence of a steady state is not consistent with a linear mortality term for the biological component (approach (2) with *n*=1). Nevertheless, parameter estimation runs with the steady state calculations of the extended model show that with an exponent of *n*=1.027 the mortality term is close to the linear relationship. Alternative extended approaches with different

growth and mortality terms for the bacteria were examined additionally; two of those provided a similarly good fits.

Future field measurements have to show, whether Gd-DTPA behaves similarly in other environmental systems. The tracer experiment in Marienfelde shows that Gd may be more persistent under different conditions. However there are good reasons that the observed behavior in the column is near to field conditions.

The results can be used as a guideline for the study of other organic substances under similar conditions, concerning flow and boundary conditions. Such studies are currently prepared by other groups of the NASRI project (see groups at UBA concerning slow sand filters and enclosures). Additional experiments are also in preparation by the Hydrogeo group at the FUB.

The analytical method could also be suitable for field situations, provided steady state data are available. The study of the steady states can be suitable in degradation studies in general. Extended approaches can easily be tested using solutions for ordinary differential equations.

4.3 Model development

Coupling hydrodynamic transport to chemical speciation codes (Ch. Horner)

In order to improve the performance and versatility of reactive modeling in the NASRI project, a coupling of well performed chemical speciation codes (such as PHREEQC, Parkhurst & Appelo, 1999) to hydrodynamic advection-dispersion codes is appropriate as suggested by the NASRI Scientific Committee during its evaluation of the NASRI Workshop in June 2003.

PHREEQC is a very flexible chemical speciation code, which includes equilibrium, based aqueous chemical speciation, mineral precipitation/dissolution reactions (equilibrium based or kinetically controlled), ion exchange, reaction kinetics and hydrodynamic transport based on a uniform flow velocity. But Bank filtration test sites are characterized by a non uniform groundwater flow field between river bank and production well galleries due to the local aquifer lithology and (in general) time variable discharges on the production wells so that the options to calculate hydrodynamic transport within the PHREEQC package are not sufficient. Therefore an adequate coupling of hydrodynamic flow and (non reactive) transport to a chemical reaction module is a key task to assess the observed changes in pore water and soil matrix geochemistry and biogeochemistry along a bank filtration transect. As pointed out during the NASRI Workshop, a complete set up of a new additional reactive flow and reactive transport software is not the aim of the modeling group within the NASRI project (there are enough available complete software packages, see below), but a link of available transport and reactive software to global procedures to assess the hydro- and biogeochemical processes taking place

on the bank filtration test sites by reducing the spatial model dimension from three to one dimension (e. g. along a representative flow path line).

Examples of complete 2D and 3D flow and reactive transport software are

- TBC (Schäfer et al, 1998)
- PHAST (Parkhurst et al., 1999)
- PHT3D (Prommer, 2002)

TBC and PHT3D are available at the IGB. PHT3D is the reactive sub module of the newest version of the PMWIN series (Version 7.1), which includes MODFLOW as flow package and MT3DMS as multispecies transport package. From both software packages, PHT3D is the more adequate tool to model riverbank filtration tasks as provided by the NASRI project.

Features of PHEEQC and Coupling Chemistry to Transport

A detailed knowledge of the PHREEQC features (data management and modeling approach) is the precondition to use PHREEQC from external software tools. PHREEQC (Batch Version) is executed using the command

Phreeqc <Input file> <Output (protocol) file> <database file>.

The first issue is to generate the input file specifying the aqueous component concentrations and putting the different 'KEY WORD' options how to run PHREEQC and which data to write to the output file (Keywords 'SELECTED_OUTPUT, USER_PUNCH'. The data input is outlined in detail by the PHREEQC manual (Parkhurst & Appelo, 1999).

Coupling of PHREEQC to external programs (such as transport modules) is done by three steps

- Step 1: write the PHREEQC input file for each model node using the initial parameters and concentrations calculated by the hydrodynamic transport module,
- Step 2: call and run PHREEQC (batch version),
- Step 3: process the PHREQC results output and transfer them as updated node parameters and concentrations for the next time step,

Applying the sequential operator splitting technique concerning reaction and transport as the most suitable method to model reactive transport. An overview of coupling techniques is available by Barry et al. (2002). An additional important physical constraint to guarantee a correct coupling of chemical speciation and hydrodynamic transport is electro neutrality. Initial

composition sets as well as inflow concentration sets (transport boundary conditions) must result in electro neutrality. Because most inorganic components relevant for hydrochemistry are ionic species or charged complex species, a multispecies hydrodynamic transport generally will create a local charge imbalance. This electrical balance error has to be corrected in the chemical speciation module using the options offered by PHREEQC (see manual, Parkhurst & Appelo, 1999) . The PHREEQC module also can effectively process kinetics, due to its mathematical nature different from the advection-dispersion equation.

The reactive sequential coupling approach via operator splitting (see above) was realized within a MATLAB development environment. One reason to use the MATLAB environment is the fact that MATLAB is easily linked to external programs as PHREEQC so that all PHREEQC typical program options can be used for speciation calculation .The only thing to do is to supply the input data to PHREEQC and to extract the results to use for the next time step from the PHREEQC specific output.

Application: Simulation of the long retention soil column experiment

At the UBA site in Marienfelde, a long retention soil column experiment is ongoing since December 2003 as a semi technical simulation tool of bank filtration. The soil column has a length of 30 m and consists of original Pleistocene sandy aquifer material. The column is flushed by surface water from lake Tegel. Until February 2003, the column was flushed for adaptation. Values for chemical parameters (as Oxygen, DOC, pH, and inorganic chemical parameters) were measured, interpreted and received in form of a developed conceptual model from working groups Hydrogeology (FU) and Organics (FU) to IGB. A detailed description of this column and of its flow and transport parameters is given by the first NASRI report, part 5 (2003).

The chemical data sampled at different sampling location along the column reveal a nearly complete removal of inflowing and residual oxygen in the column in the major part of the large-scale soil column during the time interval from March 2003 to October 2003. At the beginning of the experiment, due to a vertical inhomogeneous distribution of the inlet oxygen concentration in the inlet tank, a significant lower oxygen concentration than expected (about 1mmol O_2/l) was flushed inducing a rapid nearly complete removal of oxygen near the inlet. Since August 2003, an additional pump was installed and provides a homogeneous oxygen concentration in whole the inlet vessel so that now the correct expected oxygen concentration is flushed. This is reflected by a proceeding oxygen front since September 2003, which probably has reached a nearly steady state until the end of October 2003.

Long retention column experiment: Model conceptualization

As shown above time variable boundary conditions must be applied to oxygen over whole the flushing period. For simplicity, only the time interval from April 2003 to the end of June 2003 showing the main changes of oxygen distribution over the column reach (100 d) was selected for a numerical simulation.

The observed distribution of oxygen can only be verified if several organic carbon species with different reactivity are assumed. While at the inlet a rapid consumption of oxygen and DOC can be stated, a significantly slower degradation of Oxygen is observed at the inner and outflow portion of the soil column. Therefore a more reactive Organic species e.g. representing polysaccharides and consumed first, and a less reactive organic carbon species has to be specified. As first runs using PHREEQC showed, the observed oxygen breakthrough could not be simulated using the pore velocity obtained from tracer experiments. Assuming an adsorption of the reactive organic carbon species, the oxygen breakthrough observed along the column was verified at least qualitatively. The adsorption source/sink term is formulated using a Freundlich isotherm

$C_{sorbed} = k \bullet C_{dissolved}^{y}$ With k as sorption constant and the exponent y ranging from 0 to 1.

First order decay was applied to organic carbon as a first (preliminary) approach.
Test runs have demonstrated a too fast reduction of oxygen if only the aqueous oxygen is modeled. Therefore additionally a double porosity approach for oxygen was set up. The algorithm to incorporate the double porosity approach was taken from the. Mobile and immobile Oxygen have to be specified as separated species interrelated by an exchange term (see the PHREEQC user's manual (Parkhurst & Appelo, 1999)). For immobile oxygen ($O_{2,\ immobile}$) , the exchange term is formulated as

$$\frac{dO_{2,immobile}}{dt} = a \bullet \left(O_{2,mobile} - O_{2,immobile}\right) / q_{immobil} \bullet R_{immobile}$$

With α as exchange factor (1/t), $\theta_{immobile}$ as porosity of the immobile zone (-) and $R_{immobile}$ as retardation (-) in the immobile zone.

NO_3^- and SO_4^{2-} (as indicated by the sampled chemical analyses) were included to the model as additional electron acceptors for biogeochemical reactions. To model possible half redox reactions, each possible valence state must be considered. Therefore N(0) representing elemental Nitrogen, N(-3) representing Ammonium species, S(-2) representing Sulfide species, and C(+4) and C(-4) representing Carbonate species and Methane were specified as additional species.

Besides the possible redox half reactions, chemical equilibrium subsumes mainly Calcite dissolution/precipitation including analytical Cl^-, Na, and $HCO3^-$ and Ca concentrations. Unless no solid matrix composition was known for the column a possible range of calcite concentration to reach approximately the observed solution pH can be estimated and was specified homogeneously to whole the column.

The reactive transport code is organized as follows: The hydrodynamic transport, the double porosity approach source/sink term for Oxygen and the adsorption term for the reactive Organic carbon are calculated by macros within the MATLAB environment outside of the PHREEQC module. These intermediate results are passed to the external PHREEQC module for the speciation calculation. The speciation values arising from the PHREEQC module are returned as input values for the next transport step.

In total, 19 species are included to the reactive transport model. 13 species are assigned as mobile species subjected to hydrodynamic transport. All assigned species are summarized in table 3, including their initial and inlet concentration. The concentrations were derived, if possible, from average analytic data.

Table 3: Modeled species and their initial and inlet concentrations

Species	Status	Initial concentration (mol/l)	Inlet concentration (mol/l)
Cl^-	mobile	0.001	0.002
$O(0)_{mobile}$	mobile	0.0006	0.0002
C(+4)	mobile	0.00336	0.0035
C(-4)	mobile	0	0
Ca	mobile	0.00136	0.002
Na	mobile	0.001	0.001
N(+5)	mobile	0.0002	0.0002
N(0)	mobile	0	0
N(-3)	mobile	0	0
S(+6)	mobile	0.0015	0.0015
S(-2)	mobile	0	0
$Orgc_{reactive}$	mobile	0	0.0005
$Orgc_{inert}$	mobile	0	0.0003
Temperature	immobile	20°C	20°C
PH	immobile	7.56	7.32
pE	immobile	13.49	14.84
Calcite	immobile	0.0096	0
$O(0)_{immobile}$	immobile	0.0006	0
$Orgc_{adsorbed}$	immobile	0	0

The column is discretized by 60 elements over its whole length. Table 4 figures the spatial and time increments and flow/transport parameters. The inflow is modeled using a constant concentration boundary condition.

Table 4: Space and time increments, flow and transport parameters

Parameter	Value
Number of elements	60
Element length	0.5 m
Number of time steps	400
Time step	0.25 d
Pore velocity	1 m/d
Dispersivity	0.2 m

As simulation starting time, April 9 2003 was taken. The simulation time was 100 d, so the simulation final time step results are to compare with the samples of July 3 2003. Choosing adequately both kinetic, exchange and adsorption parameters a verification of the measured oxygen profile is possible. All these parameters are at first numerical parameters with a physical background difficult to elucidate. In table 5 these parameters are indicated as specified (calibrated) for the column experiment verification by the simulation.

Table 5: Kinetic, exchange and adsorption parameters used to verify the large retention column experiment

Process	Parameter	Value
Exchange of O_2	R_{mobile}	1.0
Exchange of O_2	$R_{immobile}$	5.0
Exchange of O_2	θ_{mobile}	0.3
Exchange of O_2	$\theta_{immobile}$	0.1
Kinetics	1. Order decay constant	2e-3
Adsorption (Freundlich)	k	5.0
Adsorption (Freundlich)	y	0.99

Long Retention Column experiment: Model results

The model results are presented by figure 16-19 for O_2, DOC, HCO_3^- and pH as example parameters comparing simulation breakthrough to sampled values. From these figures showing a sufficient verification of the sample values for the simulation time interval between April 9 and July 3 2003, the specified conceptual model reveals adequate to describe the transport and reactive processes taking place in the long retention column. The next modeling step is to simulate the long retention column flushing over whole the sampling time interval, especially the change of the Oxygen inflow concentration due to a homogenization of the inlet solution. The present modeling demonstrates how the skills of the PHREEQC software can be adequately used also if more complicated reactive systems as familiar to the riverbank filtration issue are to simulate.

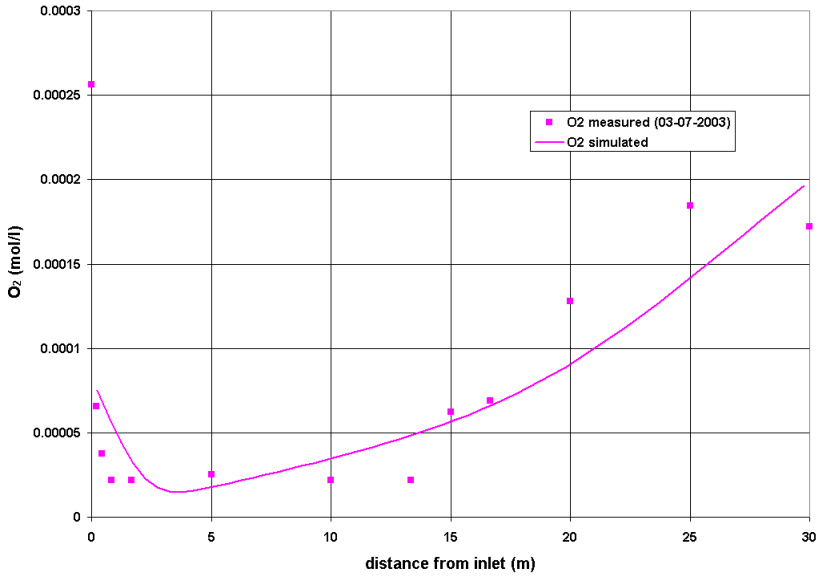

Fig. 16: Simulated and measured breakthrough of O_2

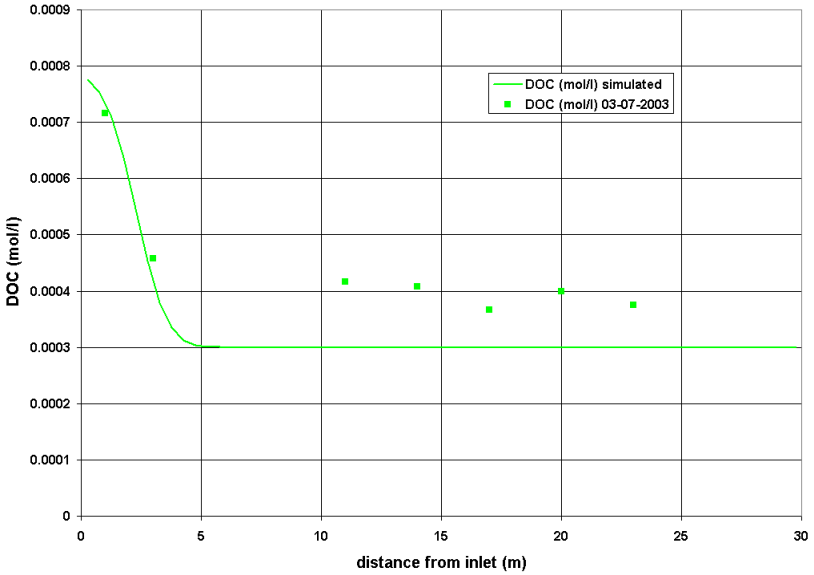

Fig. 17: Simulated and measured breakthrough of DOC

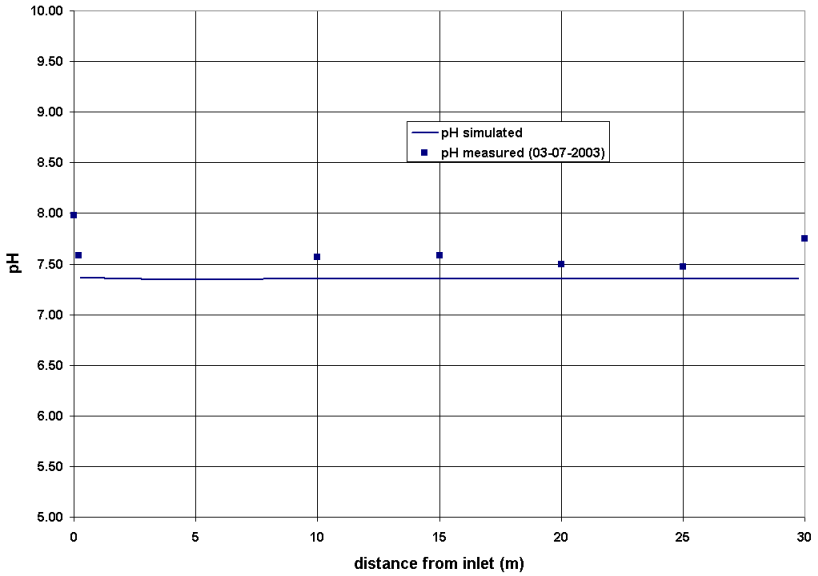

Fig. 18: Simulated and measured breakthrough of $HCO3^-$

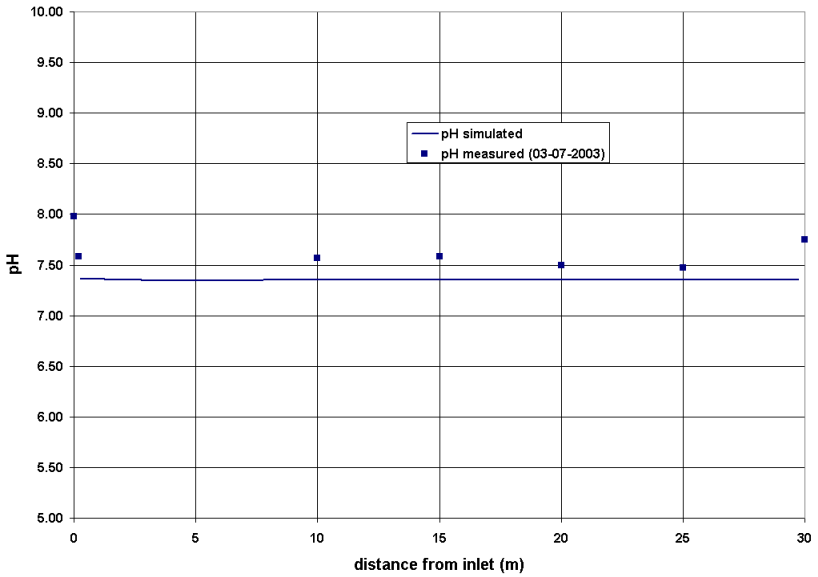

Fig. 19: Simulated and measured breakthrough of pH

5. Discussion

Experimental investigations of artificial recharge led to new findings about oxygen distribution and related redox processes during different stages of the operational cycle. Here, the concept for continuing the understanding of these mechanisms is clear: small scale measurements, especially with Dialyses cells, must be continued. Parallel, a transport and geochemical reaction model must be used in order to verify the observations, before in the next step more general conclusions for the ground water recharge can be derived.

Concerning soil column and enclosure experiments local models for local experiments at small scale were elaborated in order to identify the main mechanisms: In the case of Gd-DTPA new findings about degradation rates were achieved, which are of interest for the other working groups. Future field measurements have to show, whether Gd-DTPA behaves similarly in other environmental systems. The tracer experiment in Marienfelde shows that Gd may be more persistent under different conditions. However there are good reasons that the observed behavior in the column is near to field conditions. The results can be used as a guideline for the study of other organic substances under similar conditions, concerning flow and boundary conditions. Such studies are currently prepared by other groups of the NASRI project (see groups at UBA concerning slow sand filters and enclosures). Additional experiments are also in preparation by the working group Hydrogeology (FU). Further, coupled transport and geochemical reaction modeling of the same long column experiments allowed for the first time a sufficient simulation of measured breakthrough of O_2, DOC, HCO_3^- and pH as example

parameters. The so specified conceptual model reveals adequate to describe the transport and reactive processes taking place in the long retention column. Both models demonstrates how the skills of the available software (PHREEQC, ModelMaker, MATLAB…) can be adequately used, also if more complicated reactive systems during the riverbank filtration issue are to simulate. Here, the cooperation between modeling and other working groups must be continued and extended, i.e. for simulation of bacteriophages.

The first results on modeling bank filtration at test site Lake Tegel emphasize the role of hydraulic and hydrogeological parameters. On the one hand, simulated scenario results show how the pumping regime can influence the travel time and flow pathes from the shore line to the well galleries, and on the other hand, the hydrogelogical reconnaissance of sand and glacial till extent was confirmed by a 3-D non steady-state model. The first result plays an important role for the development of an management model, the second builts a basis for necessary transport and reaction modeling.

The development of a management model depends not only from hydraulic simulation results but also from simplifying strategies, which can be derived from fully 3-D models. Further, from the modeling side simple analytical solutions should be tested, and, economic and aspects of business management should be taken into consideration.

5. Perspectives / Intended tasks for the upcoming project period (January – June 2004)

Task	comments
Conceptual model for transport and geochemical reactions at GWA Tegel	Description of the four different stages / continuation of measurements until June 2004 / modeling (with working group Hydrogeology)
Setting up the 3-D Transport and reactive model of the Lake Tegel transect	Simulation of observed flow and reactive transport data / basis for a reduced conceptual management model (with working group Hydrogeology)
3-D modeling of groundwater flow at Lake Wannsee transect (PMWIN)	Basic information for interpreting observed data (with working group Hydrogeology)
Benchmark modeling with coupled transport and geochemical modeling tools TBC, PHT3D and MATLAB-PhreeqC	
Modeling and parameter identification of soil column experiments (non-conservative compounds)	Basic information for interpreting observed data, consequences for further experiments (TU, FU, UBA enclosures) (using visualCXTFIT or other quasi-analytical 1-D models) (with working groups Hydrogeology, Organics)
Reactive transport modeling (MATLAB-PhreeqC)	First redox simulations of column experiments and field data (TU, UBA enclosures, Lake Tegel transect)
Modeling particle-bound transport (colloid, bacteria)	Interpretation of column experiments (UBA working groups Bacteria, Algea)
Conceptual management model	Stepwise increase of complexity (well galleries, hydrogeological heterogeneities, transport behaviour) (with working groups Hydrogeology, BWB)

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“Occurrence and Fate of Drug Residues and Related Polar Contaminants During Bank Filtration”

Abstract:

In co-operation with several other project partners, this part of the NASRI project shall provide a quantitative data basis for the understanding and improvement of the removal of some PhACs and other polar compounds by carrying out detailed process studies. Previous studies and the investigations in 2002 have already shown a number of important factors influencing the rate and degree of degradation or adsorption of target compounds in such subsurface systems (Heberer at al., 2001 & 2004; Heberer & Mechlinski, 2003; Zühlke et al., 2004). At different field sites, including a novel transect at lake Wannsee and the lake Tegel transect, the occurrence of numerous pharmaceuticals (analgesics, antibiotics, anti-epileptic drugs, blood-lipid regulators, contraceptives…) and several other related, polar surface water contaminants was and will be monitored. At these field sites, their fate and behavior during bank filtration and artificial groundwater enrichment will be investigated. In parallel, the attenuation and fate of selected pharmaceuticals and other polar organics was and is also investigated in laboratory experiments and at semi-technical facilities. The compounds investigated in soil column experiments and at the semi-technical facilities are those identified in previous studies and during the above mentioned investigations as being most relevant for bank filtration. Additionally, the formation of metabolites was and shall be investigated. The results from these studies will be compared with the studies at the field sites to prove their transferability to natural, large-scale conditions. Final goal is to derive guidance recommendations for the optimum operation of bank filtration and groundwater enrichment sites achieving the best conditions for the removal of pharmaceuticals and related compounds.

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Berlin, February 12, 2004

1. Introduction / Background

The growing need for clean drinking water worldwide has increased the interest in natural surface-water treatment techniques such as bank filtration. Bank filtration has been used for more than a century in drinking-water production. Historically, it was recognized as an efficient natural attenuation process ensuring sustainability of drinking-water supply. If bank-filtration facilities are designed and constructed properly, the groundwater used for drinking-water supply can be protected efficiently from contamination with microbial organisms and inorganic or organic pollutants. Recently, however, several new types of organic contaminants, such as pharmaceuticals, have been found in the aquatic environment. Some of the polar pharmaceuticals also have been detected in groundwater and drinking-water samples, especially when water from induced recharge is used for drinking-water production (Verstraeten et al., 2002).

In the metropolitan area of Berlin, Germany, 100% of public-water supply originates from groundwater with approximately 70% from bank filtration and artificial recharge. At Lake Müggelsee in Berlin, bank filtration was used as a method of drinking-water treatment about 100 years ago. Currently, it is used at several locations in Berlin. Supply wells generally are drilled within short distances (as little as 600 m) from rivers, canals, and lakes (Pekdeger, 2001). The sewage treatment plants (STPs) often discharge their purified sewage water into the surface-water system upstream from well fields and their corresponding bank filtration or groundwater recharge facilities. Especially during low-flow conditions (primarily summer), the proportion of purified sewage in several waterways may be equal to or even greater than the natural surface-water discharge (SenSUT, 1999). Due to the progress in environmental analytical chemistry, increasing numbers of persistent organic compounds are being found in Berlin's surface water often released by municipal STPs (Heberer et al. 1998, 1999, 2002). Thus, monitoring of the quality of surface and bank-filtered water and understanding of local biochemical and hydraulic processes are needed to achieve and control a sustainable drinking-water supply.

2. Objectives of this project:

Bank filtration and artificial groundwater recharge are important, effective and cheap techniques for surface water treatment and removal of microbes, inorganic and some organic contaminants. In co-operation with the other project partners, this project shall provide a quantitative data basis for the understanding and improvement of the removal of some pharmaceutically active compounds and other polar compounds by

carrying out detailed process studies. Previous studies have already shown a number of important factors influencing the rate and degree of degradation or adsorption of target compounds in such subsurface systems. At different field sites, including a novel transect at lake Wannsee and the lake Tegel transect, the occurrence of numerous pharmaceuticals and several other related, polar surface water contaminants will be monitored and their fate and behavior during bank filtration and artificial groundwater enrichment will be investigated.

In parallel, the attenuation and fate of selected pharmaceuticals and other polar organics shall also be investigated in laboratory experiments and at semi-technical facilities. The compounds which will be investigated in soil column experiments and at the semi-technical facilities are those identified in previous studies and during the above mentioned investigations as being most relevant for bank filtration. Additionally, the formation of metabolites shall be investigated and conditions for their formation shall be identified. These results will then in return be applied to the studies at the field sites.

In combination with the other project partners, the ultimate goal of this project is the development of kinetic and equilibrium relations for implementation into hydrogeological models for validated descriptions of field sites and as tools for the optimal design and operation of bank filtration and groundwater recharge systems.

Intended work program:

Work package I:

Investigation of the fate of various pharmaceuticals and other polar contaminants at selected field sites in Berlin:

- Transect at lake Wannsee
- Transect at lake Tegel
- Artificial Recharge Pond (Groundwater Enrichment Site Tegel) : This part has been voluntarily added and was mainly carried out in terms of a diploma thesis (results are presented in section 5.5)

Contaminants under investigation: Many relevant compounds (approximately 80 substances) from various prescription classes such as analgesics, antibiotics, anti-epileptics, anti-rheumatics, beta blockers, blood lipid regulators, pharmaceutically active metabolites and several other polar compounds (pesticides, flame retardants, anti-corrosive).

Tasks:

- *Literature study*
- *Acquisition of data on the use of pharmaceuticals in human medical care in Germany/Berlin (prescriptions, over-the-counter, hospitals)*
- *Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites mainly by GC-MS, GC-MS/MS and LC-MS/MS,*
- *Interpretation of the results and modeling (in co-operation with project partners),*
- *Development and validation of multi-methods applying HPLC-MS/MS, GC-MS and GC-MS/MS,*
- *Interpretation of MS and MS/MS-spectra of unknown compounds,*
- *Identification of unknown compounds/metabolites*
- *Obtaining analytical standard compounds (together with work package II).*

Analytical Methods:

Analysis of more than 50 pharmaceuticals and other relevant compounds (pesticides, flame retardants, anti-corrosive) applying two validated multi-methods using solid-phase extraction (SPE), derivatization and gas-chromatography-mass spectrometry (GC-MS) detection with selected ion monitoring (SIM). Both methods have been elaborated, validated and published by Reddersen and Heberer (2003a,b). A method for the analysis of antibiotics and bacteriostatic compounds has been elaborated and validated within this project (section 5.2).

Work package II:

Investigation of transport, sorption and possible metabolism of selected pharmaceuticals and other polar contaminants in soil-column experiments and at semi-technical facilities (UBA-research facilities in Marienfelde). The compounds to be investigated in the laboratory experiments and at the semi-technical facilities are those identified in previous studies and during the above mentioned investigations as being most relevant for bank filtration and representative for similar future residues. In these studies, the formation of metabolites shall be investigated and conditions for their formation shall be identified. These results will then be applied to the studies at the field sites (work package I).

Preliminary list of compounds to be investigated: bezafibrate, carbamazepine, clofibric acid, diclofenac, ibuprofen, primidone and organophosphates (TCIPP, TCEPP). Metabolites resulting from the degradation of the original compounds during the experiments shall be identified, synthesized (if commercially not available) and quantified.

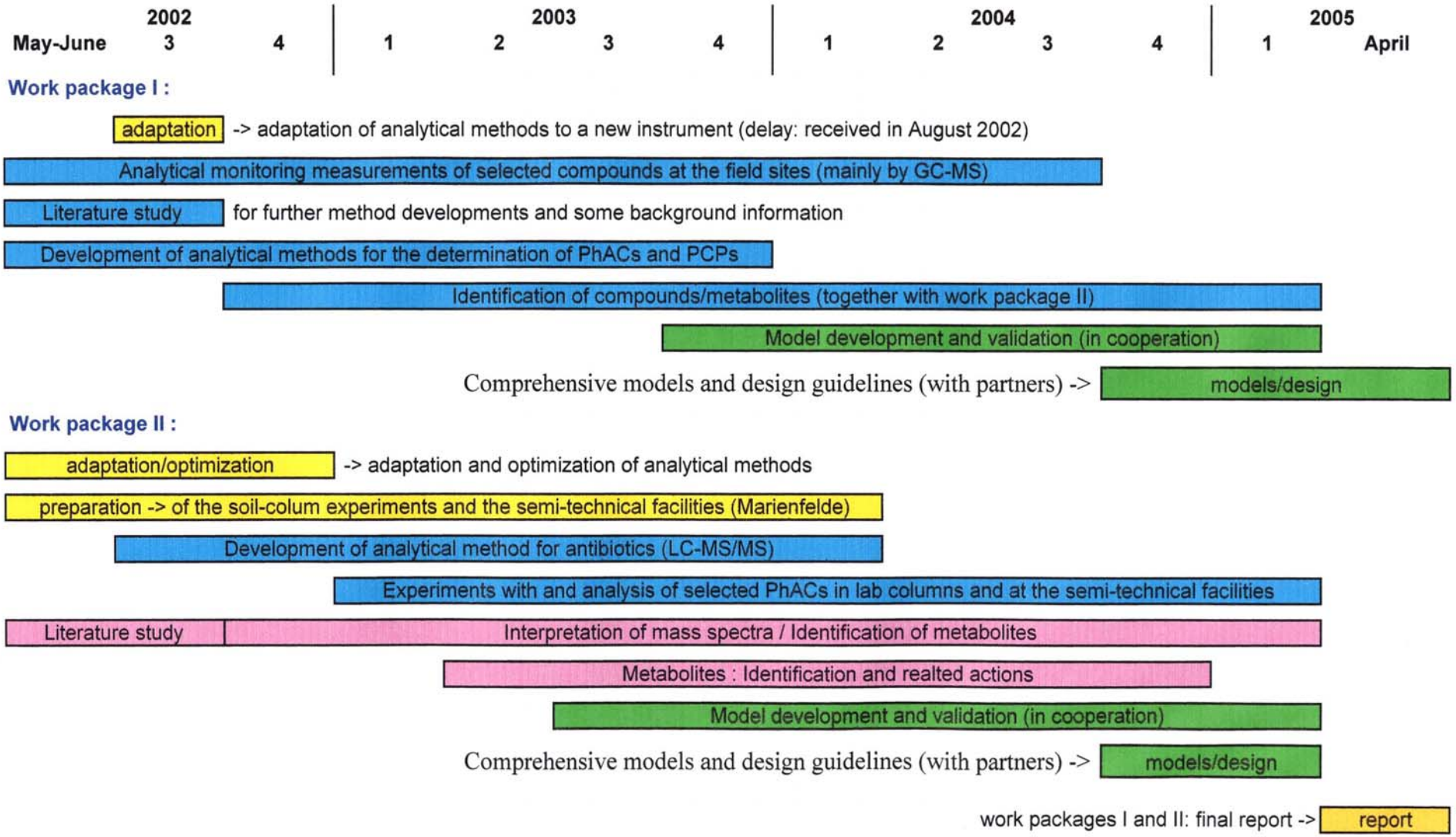
Methods/Tasks:

- *Literature study*
- *Analysis of the parent compounds mainly by GC-MS,*
- *Interpretation of the results and modeling (in co-operation with project partners).*
- *Method development and analysis of metabolites by GC-MS, GC-MS/MS, LC-MS/MS.*
- *Interpretation of MS and MS/MS-spectra.*
- *Chemical synthesis of metabolites as analytical standard compounds.*

Adjusted* time schedule:

* needed to be adjusted due to a delays and changes in total sampling periods

3. Timetable


2002
2003
2004
2005
May-June
3
4
1
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1
April
Work package I :
adaptation
-> adaptation of analytical methods to a new instrument (delay: received in August 2002)
Analytical monitoring measurements of selected compounds at the field sites (mainly by GC-MS)
Literature study
for further method developments and some background information
Development of analytical methods for the determination of PhACs and PCPs
Identification of compounds/metabolites (together with work package II)
Model development and validation (in cooperation)
Comprehensive models and design guidelines (with partners) ->
models/design
Work package II :
adaptation/optimization
-> adaptation and optimization of analytical methods
preparation -> of the soil-colum experiments and the semi-technical facilities (Marienfelde)
Development of analytical method for antibiotics (LC-MS/MS)
Experiments with and analysis of selected PhACs in lab columns and at the semi-technical facilities
Literature study
Interpretation of mass spectra / Identification of metabolites
Metabolites : Identification and realted actions
Model development and validation (in cooperation)
Comprehensive models and design guidelines (with partners) ->
models/design
work packages I and II: final report ->
report

4. Intended and achieved tasks for the reporting period from January to December 2003:

Task	achieved ?	comments
Literature study	✓	Up to date but will be continued throughout the whole project.
Acquisition of data on the use of pharmaceuticals in human medical care in Germany/Berlin (prescriptions, over-the-counter, hospitals)	✓	Has been achieved and will be continued in cooperation with another project (Army project). New and more precise Berlin data were obtained and evaluated and included into the calculations for the final report.
Obtaining analytical standard compounds (especially antibiotics)	✓	Finished but the search for radio-labeled standards for the analysis of antibiotics continues.
Development and validation of a multi-method for antibiotics applying HPLC-MS/MS.	✓	Finished: Evaluation of the limits of detection and quantitation (LODs and LOQs) of the instrument and the whole analytical method and application to “real” water samples. Introduction of the chemical-technical assistant (was hired later in October 2003 because of budget shortcuts) into the validated method. First field measurements in June 2003.
Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Tegel”.	✓	Analytical data recorded and reported (in section 5.1) from January to December 2003 for all “GC-MS” compounds (e.g. analgesics, antiepileptic drugs, blood lipid regulators) and from June to December also for the antibiotics (section 5.2). An extensive monitoring of all wells was be carried out in January and February. Wells for future research were selected after evaluation of the results from the extended monitoring.
Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Wannsee I”.	✓	Analytical data recorded and reported (in section 5.1) from January to December 2003 for all “GC-MS” compounds (e.g. analgesics, antiepileptic drugs, blood lipid regulators) and from June to December also for the antibiotics (section 5.2). An extensive monitoring of all wells was be carried out in January and February. To achieve an increased timely resolution of the transport study, nine monitoring wells of transects “Lake Wannsee I & II” and the lake in front of the field sites were sampled weekly.

Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Wannsee II”.	✓	Analytical data recorded and reported (in section 5.1) from January to December 2003 for all “GC-MS” compounds (e.g. analgesics, antiepileptic drugs, blood lipid regulators) and from June to December also for the antibiotics (section 5.2). An extensive monitoring of all wells was be carried out in January and February. To achieve an increased timely resolution of the transport study, nine monitoring wells of transects “Lake Wannsee I & II” and the lake in front of the field sites were sampled weekly.
Additional previously unintended task: Measurements at the groundwater enrichment plant in Tegel (GWA Tegel)	✓	Has been achieved in terms of a diploma thesis by Marc Adam in cooperation with the CREAM project. Full dataset from July 2002 to June 2003. Results presented in section 5.5.
Preparation and conduction of soil-column experiments: Measurements and interpretation of samples	✓	Practical experiments have been conducted in cooperation with NASRI working groups “organics” (Prof. Jekel) and “hydrogeology” (Prof. Pekdeger) in terms of a diploma thesis by Daniel Wicke. Results presented in section 5.3.
Preparation and conduction of experiments at the semi-technical facility of the UBA: Measurements and interpretation of data from slow sand filtration and enclosure study	✓	Practical experiments have been conducted in cooperation with NASRI working groups “algae” (Dr. Chorus), “bacteria” (Dr. Schewzyk) and “hydrogeology” (Prof. Pekdeger) in terms of a diploma thesis by Michael Voigt. Results presented in section 5.4.

In general, we are ahead of our intended program and additionally included several other unintended or valuable tasks (investigations at GWE Tegel, enclosure experiments). In 2003, special focus was laid on experimental (spiking) investigations and scientific co-operations with the other NASRI working groups, especially with groups “organics” (Prof. Jekel), “algae” (Dr. Chorus), “bacteria” (Dr. Schewzyk) and “hydrogeology” (Prof. Pekdeger). This work has currently been continued and intensified. Some details and the individual results compiled in the appendix to this report had to be deleted as requested by the project coordinator. The links to the appendix have been replaced by the term (details/results shown) “elsewhere”.

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List of publications and other presentations reporting results from the NASRI project:

Publications:

HEBERER, TH., MECHLINKSKI, A. (2003) Fate and transport of pharmaceutical residues during bank filtration. Hydroplus, 137 - Hydrosciences - October 2003, 53-60.

HEBERER, TH., MECHLINKSKI, A., FANCK, B., KNAPPE, A., MASSMANN, G., PEKDEGER, A., FRITZ, B. (2004) Field-Studies on the Fate and Transport of Pharmaceutical Residues in Bank Filtration. In: (HEBERER, TH. and VERSTRAETEN, I.M., eds.) Special Issue on the Fate and Transport of Pharmaceuticals and Endocrine Disrupting Compounds (EDCs) During Ground Water Recharge. J. Ground Water Monitoring & Remediation (GWMR) in press.

ZÜHLKE, S., DÜNNBIER, U., HEBERER, TH., FRITZ, B. (2004) Analysis of Endocrine Disrupting Steroids: Investigation of Their Release into the Environment and Their Behavior During Bank Filtration. In: (HEBERER, TH. and VERSTRAETEN, I.M., eds.) Special Issue on the Fate and Transport of Pharmaceuticals and Endocrine Disrupting Compounds (EDCs) During Ground Water Recharge. J. Ground Water Monitoring & Remediation (GWMR) in press.

Oral presentations:

HEBERER, TH.: Occurrence and fate of Pharmaceutical Residues at Bank Filtration Sites in Berlin. Presentation at the USGS bank filtration workshop, March 13-14, Lincoln, Nebraska, USA. and at the USGS headquarter in Reston, Virginia, USA.

HEBERER, TH., MECHLINKSKI, A., FANCK, B., KNAPPE, A., MASSMANN, G., PEKDEGER, A.: Fate and Transport of Pharmaceutical Residues in Bank Filtration. 3rd International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, March 18-21, 2003, Minneapolis, Minnesota, USA.

ZÜHLKE, S., DÜNNBIER, U., HEBERER, TH.: Analysis of Endocrine Disrupting Steroids and Investigation of Their Release into the Environment and Their Behavior During Bank Filtration. 3rd International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, March 18-21, 2003, Minneapolis, Minnesota, USA.

HEBERER, TH.: Impacts of Pharmaceuticals on the Environment: State of the Art and Identification of Sources in Urban Areas. Vivendi Environment workshop, April 1, 2003, Paris, France.

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HEBERER, TH., MECHLINKSKI, A., FANCK, B., ZÜHLKE, S., ADAM, M., VOIGT, M., WICKE, D., DÜNNBIER, U.: Occurrence and Fate of Drug Residues and Related Polar Contaminants during Bank Filtration. 1st International Bank filtration Workshop. June 10-12, 2003, Berlin, Germany.

HEBERER, TH.: Pharmaceutical Residues in the Berlin Water Cycle. EWRI World Water and Environmental Resources Congress, June 23-26, 2003, Philadelphia, Pennsylvania, USA.

HEBERER, TH. , MECHLINKSKI, A., FANCK, B.: Natural Attenuation and Transport of Pharmaceutical Residues during Bank Filtration - First results from an interdisciplinary research project entitled NASRI. Symposium at the EAWAG, August 25, 2003, Dübendorf, Switzerland.

HEBERER, TH.: Pharmaceutical Residues in the Aquatic Environment: Sources, Fate, and Natural Attenuation. 11th European Congress on Biotechnology, August 24-29, 2003, Basel, Switzerland.

MECHLINSKI, A. HEBERER, TH.: Transport and Attenuation of Pharmaceutical Residues During Riverbank Filtration. The Second International Riverbank Filtration Conference. September 16-19, 2003, Cincinnati, Ohio USA.

5. RESULTS

5.1. Results from the investigation of the transects at lake Wannsee and lake Tegel (analgesics, antiepileptic drugs, blood lipid regulators, metabolites, and related organic trace contaminants)

The investigations of pharmaceutical residues at transects “Lake Wannsee I” and “Lake Tegel” started in May 2002 were continued in 2003. Since January 2003, the new drilled monitoring wells at the transect “Lake Wannsee I” and the novel transect “Lake Wannsee II” were also included in this study. As described in the first periodic report, are eight drug residues, three herbicide residues, and three industrial residues were detected at the field sites. The mean concentrations of the detected compounds at the investigated transects are presented in the tables 1 to 4 .

Table 1. Compounds with positive findings and their mean concentrations [ng/L] at transect “Lake Wannsee I” (May 2002 to December 2003).

Transect Wannsee I between May 2002 – Dec. 2003	Surface water	3339	3338	3337	BEE201 OP	BEE201 UP	3335	Well 4	BEE200 UP	BEE200 OP
Diclofenac	75	38	42	40	46	38	22	23	8	n.d.
Clofibric acid	52	31	20	16	132	171	7	112	10	n.d.
Propyphenazone	109	104	86	81	312	320	47	26	95	25
AMDOPH	174	109	136	146	814	1211	133	274	170	175
Carbamazepine	415	265	318	340	151	69	311	23	23	48
Primidone	92	89	62	75	126	119	68	19	93	88
Indometacine	18	20	20	n.d.	n.d.	35	n.d.	n.d.	n.d.	n.d.
Bezafibrate	46	20	n.d.	15	23	33	n.d.	n.d.	n.d.	n.d.
Bentazone	21	29	25	19	12	15	18	16	5	5
Mecoprop	20	23	24	16	21	31	19	18	5	n.d.
p,p' –DDA	17	29	19	18	36	37	15	11	5	n.d.
o,p' –DDA	7	9	8	11	13	12	10	7	n.d.	n.d.
NPS	19	29	24	20	307	384	11	55	5	n.d.
TCEP	268	420	237	268	174	177	305	96	63	8
TCIPP	1466	1559	1576	927	684	343	830	91	98	30

Table 2. Compounds with positive findings and their mean concentrations [ng/L] at transect "Lake Wannsee II" (January to December 2003).

Transect Wannsee II Jan - Dec 2003	Surface water	BEE205	BEE206	BEE202 OP	BEE202 MP1	BEE202 MP2	BEE202 UP	BEE203	Well 3	BEE204 UP	BEE204 OP
Diclofenac	75	64	19	32	33	37	45	19	55	40	45
Clofibric acid	55	20	16	38	44	119	120	23	86	22	17
Propyphenazone	102	99	36	31	346	725	759	71	367	27	23
AMDOPH	220	168	200	94	728	1097	932	220	457	59	45
Carbamazepine	532	398	311	244	202	52	35	277	72	18	19
Primidone	118	92	86	79	98	118	118	106	64	12	13
Indometacine	16	5	10	n.d.	n.d.	n.d.	n.d.	n.d.	30	n.d.	n.d.
Bezafibrate	49	20	n.d.	n.d.	20	20	33	20	28	n.d.	n.d.
Bentazone	21	12	12	15	8	11	15	8	8	n.d.	n.d.
Mecoprop	22	21	15	10	16	19	20	9	14	15	12
p,p' -DDA	18	16	5	n.d.	28	33	38	40	19	n.d.	n.d.
o,p' -DDA	8	7	n.d.	n.d.	15	11	14	15	8	n.d.	n.d.
NPS	23	18	12	16	190	210	214	36	92	19	11
TCEP	292	235	213	81	177	174	281	90	205	114	81
TCIPP	1341	978	611	797	198	226	270	304	350	256	76

Table 3. Compounds with positive findings and their mean concentrations [ng/L] at the shallow wells and the water works well 13 of the transect "Lake Tegel" (May 2002 to December 2003).

Transect Tegel May 2002 to December 2003	Surface water	3311	3310	3309	3308	3307	TEG371 OP	TEG371 UP	TEG372	3306	Well 13	3305
Diclofenac	100	25	113	15	16	5	58	64	33	5	21	n.d.
Clofibric acid	48	23	55	10	16	n.d.	40	25	18	n.d.	35	n.d.
Propyphenazone	191	91	45	31	37	28	80	444	29	40	173	50
AMDOPH	365	345	273	223	211	140	324	613	223	84	1180	78
Carbamazepine	537	493	478	345	494	473	366	198	451	255	88	10
Primidone	100	108	78	44	67	58	104	151	86	39	67	8
Indometacine	15	18	18	n.d.	5	n.d.	65	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	41	n.d.	8	n.d.	30	n.d.	n.d.	35	n.d.	n.d.	10	n.d.
Bentazone	16	8	18	n.d.	5	n.d.	20	20	11	n.d.	15	n.d.
Mecoprop	18	23	28	n.d.	45	n.d.	33	23	27	n.d.	30	n.d.
p,p' –DDA	6	5	n.d.	5	5	5	5	8	n.d.	10	7	n.d.
o,p' –DDA	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	5	n.d.	n.d.	5	n.d.
NPS	67	18	20	20	14	38	149	99	167	35	36	n.d.
TCEP	494	222	574	116	197	90	295	329	184	23	108	74
TCIPP	3299	2508	2744	807	1110	468	2047	1338	1306	137	303	105

Table 4. Compounds with positive findings and their mean concentrations [ng/L] at the deeper monitoring wells and the water works well 13 of the transect "Lake Tegel" (May 2002 to December 2003).

Transect Tegel May 2002 to December 2003	Surface water	3301	3302	3303	Well 13	3304
Diclofenac	100	47	28	33	21	32
Clofibric acid	48	35	16	11	35	11
Propyphenazone	191	628	164	118	173	9
AMDOPH	365	663	407	383	1180	199
Carbamazepine	537	232	299	297	88	9
Primidone	100	114	98	98	67	13
Indometacine	15	35	n.d.	n.d.	n.d.	n.d.
Bezafibrate	41	33	10	n.d.	10	10
Bentazone	16	12	12	10	15	5
Mecoprop	18	21	15	8	30	21
p,p' -DDA	6	10	5	6	7	5
o,p' -DDA	n.d.	5	n.d.	n.d.	5	n.d.
NPS	67	67	22	12	36	107
TCEP	494	280	206	213	108	161
TCIPP	3299	1283	1289	982	303	77

A comparison of the three field sites revealed a similar behavior of the detected compounds during the riverbank filtration. Thus, the blood lipid regulator bezafibrate and the analgesic indometacine were significantly removed during the infiltration process and only traces of them could sporadically be detected in the water works wells. The analgesics diclofenac and propyphenazone were less efficiently removed during the ground passage and were found in the water works wells at concentrations up to more than 100 ng/L. To achieve an increased timely resolution of the transport study, nine monitoring wells of transects "Lake Wannsee I & II" and the lake in front of the field sites were sampled weekly. The results from this intensified sampling campaign are compiled in tables 5 to 8.

Table 5. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee II" (15.Sept.2003)*

Transect Wannsee II 15.09.2003	Surface water	BEE205	BEE206	BEE202OP	BEE202MP1	BEE203
Diclofenac	40	50	<5	15	15	n.d.
Clofibric Acid	35	15	5	10	35	5
Propyphenazone	55	60	20	15	400	5
AMDOPH	110	105	130	75	1000	60
Carbamazepine	735	775	875	470	265	490
Primidone	140	145	195	135	165	130
Indometacin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	n.d.	<5	n.d.	n.d.	5	n.d.
Bentazone	20	20	15	20	15	15
Mecoprop	15	10	n.d.	n.d.	5	n.d.
p,p' -DDA	25	30	5	10	50	5
o,p' -DDA	10	10	n.d.	n.d.	15	n.d.
NPS	10	20	10	10	300	5
TCEP	175	95	45	25	30	n.d.
TCIPP	620	460	290	235	95	125

Table 6. Compounds with positive findings and their concentrations [ng/L] the intensified sampling campaign *at transect "Lake Wannsee II" (29.Sept.2003)*

Transect Wannsee II 29.09.2003	Surface water	BEE205	BEE206	BEE202OP	BEE202MP1	BEE203
Diclofenac	25	25	n.q.	n.q.	15	n.d.
Clofibric Acid	45	10	5	5	50	5
Propyphenazone	50	50	15	15	260	n.d.
AMDOPH	180	180	145	150	950	110
Carbamazepine	515	415	385	270	130	345
Primidone	120	110	230	100	165	110
Indometacin	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	20	n.d.	n.d.	n.d.	n.d.	n.d.
Bentazone	15	10	15	20	20	10
Mecoprop	15	10	n.d.	n.d.	15	n.d.
p,p' -DDA	15	15	n.d.	n.d.	40	n.d.
o,p' -DDA	5	5	n.d.	n.d.	15	n.d.
NPS	5	10	10	10	300	<5
TCEP	195	100	45	40	55	n.d.
TCIPP	645	410	280	270	95	130

Table 7. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee II" (06. Oct.2003)*

Transect Wannsee II 06.Oct. 03	Surface water	BEE205	BEE206	BEE202OP	BEE202MP1	BEE203
Diclofenac	15	40	n.d.	n.d.	n.d.	n.d.
Clofibric Acid	40	n.d.	n.d.	n.d.	50	n.d.
Propyphenazone	130	70	35	40	565	n.d.
AMDOPH	215	130	200	165	945	125
Carbamazepine	620	n.d.	380	335	220	395
Primidone	185	n.d.	305	110	205	125
Indometacin	5	n.d.	5	n.d.	n.d.	n.d.
Bezafibrate	30	5	n.d.	n.d.	20	n.d.
Bentazone	n.d.	n.d.	n.d.	n.d.	<5	<5
Mecoprop	5	n.d.	n.d.	n.d.	n.d.	n.d.
p,p' –DDA	20	15	n.d.	n.d.	40	n.d.
o,p' –DDA	5	5	n.d.	n.d.	15	n.d.
NPS	10	10	n.d.	n.d.	190	n.d.
TCEP	520	255	60	45	90	n.d.
TCIPP	10645	6510	3915	3760	1650	1955

Table 8. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee II" (13.Oct.2003)*

Transect Wannsee II 13.Oct.03	Surface water	BEE205	BEE206	BEE202OP	BEE202MP1	BEE203
Diclofenac	50	40	15	n.d.	45	n.q.
Clofibric Acid	50	5	n.d.	n.d.	50	n.d.
Propyphenazone	115	75	40	55	410	30
AMDOPH	190	160	210	125	695	120
Carbamazepine	760	530	n.d.	n.d.	190	385
Primidone	245	140	n.d.	n.d.	160	100
Indometacin	<5	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	30	20	5	n.d.	30	5
Bentazone	n.d.	n.d.	n.d.	<5	<5	<5
Mecoprop	15	10	n.d.	n.d.	5	n.d.
p,p' –DDA	n.d.	<5	n.d.	n.d.	20	n.d.
o,p' –DDA	n.d.	n.d.	n.d.	n.d.	5	n.d.
NPS	10	15	n.d.	n.d.	245	n.d.
TCEP	185	70	25	30	60	n.d.
TCIPP	1515	780	435	570	300	320

Table 9. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee I" (15. Sept.2003)*

Transect Wannsee I 15.09.2003	BEESW	BEE201OP	3337	3335
Diclofenac	40	n.q.	40	15
Clofibric Acid	35	135	10	10
Propyphenazone	55	280	100	25
AMDOPH	110	960	105	65
Carbamazepine	735	90	460	380
Primidone	140	145	145	125
Indometacin	n.d.	n.d.	n.d.	n.d.
Bezafibrate	n.d.	5	5	n.d.
Bentazone	20	15	20	20
Mecoprop	15	10	10	5
p,p' -DDA	25	55	25	15
o,p' -DDA	10	20	10	5
NPS	10	455	15	10
TCEP	175	45	75	130
TCIPP	620	105	375	250

Table 10. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee I" (29. Sept. 2003)*

Transect Wannsee I 29.09.2003	BEESW	BEE201OP	3337	3335
Diclofenac	25	20	40	30
Clofibric Acid	45	180	10	10
Propyphenazone	50	215	180	125
AMDOPH	180	1080	70	190
Carbamazepine	515	30	270	265
Primidone	120	155	175	120
Indometacin	n.d.	n.d.	n.d.	n.d.
Bezafibrate	20	n.d.	n.d.	n.d.
Bentazone	15	15	n.d.	15
Mecoprop	15	10	n.d.	5
p,p' -DDA	15	45	25	15
o,p' -DDA	5	15	n.d.	5
NPS	5	630	n.d.	15
TCEP	195	60	n.d.	100
TCIPP	645	125	n.d.	185

Table 11. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee I" (06.Oct.2003)*

Transect Wannsee I 06.Oct. 03	BEESW	BEE201OP	3337	3335
Diclofenac	15	n.q.	65	n.q.
Clofibric Acid	40	200	n.d.	n.d.
Propyphenazone	130	510	280	35
AMDOPH	215	1315	175	95
Carbamazepine	620	175	465	315
Primidone	185	205	280	305
Indometacin	5	n.d.	n.d.	n.d.
Bezafibrate	30	20	5	n.d.
Bentazone	n.d.	<5	<5	n.d.
Mecoprop	5	n.d.	n.d.	n.d.
p,p' -DDA	20	45	25	5
o,p' -DDA	5	15	n.d.	n.d.
NPS	10	410	20	n.d.
TCEP	520	110	210	60
TCIPP	10645	1905	5700	3470

Table 12. Compounds with positive findings and their concentrations [ng/L] from the intensified sampling campaign *at transect "Lake Wannsee I" (06.Oct.2003)*

Transect Wannsee I 13.Oct.03	BEESW	BEE201OP	3337	3335
Diclofenac	50	50	65	30
Clofibric Acid	50	170	15	-5
Propyphenazone	115	375	125	55
AMDOPH	190	1070	200	145
Carbamazepine	760	170	340	310
Primidone	245	210	155	140
Indometacin	-5	n.d.	n.d.	n.d.
Bezafibrate	30	25	<20	<20
Bentazone	n.d.	<5	<5	n.d.
Mecoprop	15	25	<5	n.d.
p,p' -DDA	n.d.	15	5	n.d.
o,p' -DDA	n.d.	5	n.d.	n.d.
NPS	10	440	15	-5
TCEP	185	45	75	35
TCIPP	1515	370	715	505

5.2 ANTIBIOTICS

Adaptation, validation and application of a new analytical method for the analysis of antibiotics applying SPE and HPLC-MS/MS detection and first results from the project period between June and October 2003.

Experimental Section

Chemicals and Materials:

All pharmaceutical compounds under investigation were of analytical grade (>90%) purchased from Sigma–Aldrich (Steinheim, Germany), Promochem (Wesel, Germany), ICN Biomedicals (Meckenheim, Germany), Synopharm (Barsbüttel, Germany), and Salutas (Barleben, Germany). For dehydro-erythromycin, a decomposition product of the macrolide antibiotic erythromycin, no reference material is currently available. Therefore, it was prepared by ageing of an erythromycin solution. Solvents used for sample preparation and as mobile HPLC phase were of analytical grade obtained from Riedel de Haën (Darmstadt, Germany). Formic acid and EDTA disodium salt were purchased from Merck (Darmstadt, Germany).

Sampling:

Since May 2003, the transects at lake Wannsee and at lake Tegel were investigated monthly. All samples were filled into brown glass bottles and stored at 4°C in the dark prior to analysis.

Sample extraction:

A 500ml aliquot of sample was (as far as necessary) filtered and spiked with 500 mg of EDTA disodium salt to complex calcium and magnesium ions. The pH was adjusted to pH 4 using H_2SO_4 or NaOH. Then 5ml methanol and 50ng of fenuron-D6 and sulfamethizole (1mg/L solution in acetonitrile: water (70:30, v/v)) was added, which were used as internal standards for the overall procedure. Solid phase extraction was performed on 6 ml cartridges filled with 200mg of OASIS HLB (Waters, Milford, MC, USA). The cartridges were conditioned with 7ml of methanol and 3x7ml of purest water (pH 4.0). The samples were percolated through the cartridges at a flow rate of ~8ml/min using a vacuum manifold. Washing was performed by percolation of 7ml of highly purified water at pH 4. After the enrichment step the solid-phase material was dried with a gentle stream of nitrogen until no moisture was visible (ca. 1-2 hour). Elution was done with two times 1 ml

of acetonitrile and 4x1 ml of a mixture of acetonitrile:water:triethylamine, (90:9.5:0.5, v/v/v). The eluate was evaporated to dryness under a gentle stream of nitrogen at 35°C and the residue was dissolved in 0.5 mL of a mixture of water:acetonitrile (90:10, v/v) and then stirred for ~10sec.

HPLC conditions:

HPLC analyses were performed on a Waters Alliance System (Waters)

Antibiotics were separated using a 150x2.0 mm SYNERGIE^{TM} Hydro RP, 4.0µm column (Phenomenex, Aschaffenburg, Germany) operated with a security guard containing C18 Polar RP sorbent. Solvent A was acetonitrile and solvent B was water with 0.05% of formic acid. The flow rate of the eluent was 200µl/min. The applied gradient is shown in Table 13. Samples volumes of 10µL were injected. The approximate retention times of the analytes are shown in Table 14.

Table 13: *HPLC solvent gradient for the separation of 23 antibiotics*

Time [min]	solvent A (%)	solvent B (%)
0	10	90
2	15	85
5	15	85
7	24	76
10	24	76
17,5	40	60
20,5	60	40
20,5	95	5
28	95	5
28	10	90
55	10	90

MS-MS parameters:

Mass spectra were acquired in positive ion electrospray (ESI+) mode on a Micromass triple-quadrupole mass spectrometer (Manchester, UK). Nitrogen was used for drying and as nebulizing gas. The operating gas flow was set to 450 L/h for the cone gas and 50 L/h for the desolvation gas, respectively. The source temperature was heated to 100 °C and the ESI interface to 300°C. Capillary voltage was adjusted to 2.75 kV and extractor voltage to 3V. Low and high-mass resolution of the quadrupole were set to 14.0, and the ion

energy was set to 1.0. Details on the optimum setting of parameters for MS–MS detection are given in Table 2. Most substance were identified via their protonated molecular ion $[M+H]^+$ (precursor mass) and two corresponding ions used for confirmation (Table 14).

Table 14: *Compounds, retention time (t_R); molecular weight; MS-MS parameters and limits of quantification in surface water (LOQs).*

No	Substance	t_R [min]	MW	Precursor mass mostly (M+H)+	Cone Volt. [V]	Product Ions	Col. Energy [eV]	Dwell time [s]	LOQ_s [ng/L]
1.	Ceftazidime	5.2	547.6	274.5	18	**80.1** 126.1	**10** 25	**0.15** 0.05	10
2.	Ciprofloxacin	12.1	331.3	332.5	37	**288.4** 245.5	17 25	**0.15** 0.05	
3.	Clarithromycin	23.3	748.0	749.1	30	**158.3** 116.3	30 40	**0.15** 0.05	0.2
4.	Clindamycin	16.0	424.9	425.5	37	**126.4** 377.5	27 20	**0.15** 0.05	0.1
5.	Dehydro-Erythromycin	22.1	716	716.8	30	**158.4** 558.8	33 15	**0.15** 0.05	0.3
6.	Doxycycline	17.3	444.4	445.5	30	**428.5** 154.2	15 30	**0.15** 0.05	50
7.	Erythromycin	20.1	733.9	734.8	30	**158.5** 576.9	33 20	**0.15** 0.05	
8.	Enoxacin	10.8	320.3	321.5	40	**206.3** 234.4	27 20	**0.15** 0.05	50
9.	Metronidazole	5.7	171.2	172.5	25	**128.3** 82.2	15 20	**0.15** 0.05	2
10.	Moxifloxacin	15.3	401.4	402.6	40	**358.5** 261.4	18 23	**0.15** 0.05	2
11.	Norfloxacin	11.7	319.3	320.5	35	**276.4** 233.4	17 23	**0.15** 0.05	
12.	Ofloxacin	11.7	361.4	326.5	35	**318.5** 261.4	18 28	**0.15** 0.05	2
13.	Oxytetracycline	10.8	460.4	461.6	25	**154.4** 426.6	30 15-20	**0.15** 0.05	25
14.	Benzylpenicillin	21.8	334.4	160.2	35	**113.9** 86.8	13 20	**0.15** 0.05	2

15.	Phenoxymethyl-penicillin	23.5	350.4	160.2	35	**113.9** 86.8	13 20	**0.15** 0.05	2
16.	Piperacillin	20.6	517.6	518.6	30	**143.3** 160.4	15 10	**0.15** 0.05	2
17.	Roxithromycin	23.3	837.1	837.9	35	**158.4** 680.2	35 25	**0.15** 0.05	0.2
18.	Acetyl-Sulfamethoxazole	18.5	295.3	296.1	35	**134.0** 198.0	25 17	**0.15** 0.05	
19.	Sulfamethazine	12.1	278.3	279.5	20	**108.2** 124.3	27 25	**0.15** 0.05	3
20.	Sulfamethoxazole	17.7	253.3	254.4	30	**156.2** 92.2	16 28	**0.15** 0.05	1
21.	Tetracycline	12.4	444.4	445.6	25	**154.2** 410.3	25 17	**0.15** 0.05	5
22.	Trimethoprim	9.9	290.3	291.5	45	**123.2** 230.4	25 22	**0.15** 0.05	2
23.	Tylosin	21.0	916.1	917.3	35	**174.3** 772.9	35 30	**0.15** 0.05	2

Method Validation:

A comparison of the recoveries for the pure water samples and the tap water samples provided some information on the impact of the matrix on the analytical procedure (Table 3 (not all data shown)). The observed ‘‘matrix effects’’ include extraction effects (recoveries) and ion suppression or enhancement effects. Matrix interferences were of concern for most antibiotics and especially for sulfamethoxazole. Therefore, standard addition was used for quantification. Thus, low recoveries observed for some antibiotics were no drawback for their reliable determination because the reproducibility (standard deviation of a fivefold analysis < 10%) was excellent.

Limits of quantitation (LOQs) were calculated as the lowest standard concentration with signal to noise ratios equal to or larger than 10 (LODs are compiled in Table 14). The detection limits for the pharmaceuticals are between 0.1 and 50 ng/L in surface water, depending on the individual compounds.

Table 15: Comparison between recovery in pure water (Rpure) and drinking water (Rtap) (standard deviation in % are given in parentheses)

	R_{pure} [%]	R_{tap} [%]
Clindamycin	96 (3)	93 (6)
Trimethoprim	86 (4)	70 (5)
Sulfadimidine	85 (7)	64 (7)
Sulfamethoxazole	91 (6)	45 (7)
Dehydro-Erythromycin	125 (8)	82 (5)
Clarithromycin	86 (7)	64 (7)
Roxithromycin	76 (8)	50 (9)
Piperacillin	108 (4)	78 (7)
Benzylpenicillin	83 (3)	64 (6)
Phenoxymethylpenicillin	81 (2)	49 (5)

Results from the transect investigations

Since May 2003, the transects at lake Wannsee and at lake Tegel were investigated monthly. At transect “Tegel” the shallow wells 3311, 3310 and 3308 could not be sampled during June and September, because the groundwater level was beyond the screen of the wells. At transects “Wannsee 1” the well 3335 only sampled during the “Intensive sampling” in September/ October. At the beginning of July some wells of the transects at lake Wannsee were specially sampled. Tables 16-18 present the results measured at transects between May and October 2003. Only five of the 23 investigated compounds were detected at both transects including the macrolides clarithromycin and roxithomycin, the sulfonamide sulfamethoxazole, the sulfonamide synergist trimethoprim and the lincosamide clindamycin. Additionally, the macrolide metabolite dehydro-erythromycin was found. Trimethoprim, clarithromycin and roxithomycin are efficiently removed by bank filtration. They were found in the lakes and sometimes in the wells near the bank, but always below their LOQ. The concentrations of clindamycin and dehydro-erythromycin are reduced during the soil passage. In general, sulfamethoxazole was found at higher concentrations than the other compounds. It is the only antibiotic that was also detected in water-supply wells 3 and 13 (average concentration: 3 ng/L). Surprisingly, sulfadimidine was observed in some of the wells, e.g. in BEE202MP1, MP2, and UP. In Germany, this compound is not used in human medicine but for veterinary purposes. A more detailed

interpretation of the results will be given in the following progress report after consulting some public autorities and the other project partners from the NASRI project and when more data from the following sampling series are available. Tetracyclines and penicillines were not detected in a single sample. This is in agreement with the results of other studies [1-7]. Tetracyclines have been shown to be strong chelators and can sorb strongly to soil organic matter and mineral particles. Therefore, they should only sporadically or incidentially be found in as non-chelated compounds in surface waters [2-5]. Additionally, the ß-lactam ring of penicillines has a poor stability. It can be opened by ß-lactamase, a widespread enzyme found in bacteria, or by chemical hydrolysis. Therefore, intact penicillins are unlikely to not occur in the environment [1].

Table 16: Compounds with positive findings and their concentrations [ng/L] at transect "Tegel"; N.D.: not detected; N.A.: not analysed; >LOQ: > limits of quantification

ng/L	month	Trimetho-prim	Clarithro-mycin	Roxithro-mycin	Dehydro-Erythro-mycin	Clindamycin	Sulfa-methoxa-zole	Sulfa-metha-zine
surface water	May	40	43	71	345	55	490	N.D.
	June	45	43	78	460	61	277	N.D.
	July	16	17	21	112	44	276	N.D.
	Aug	12	13	19	113	41	390	N.D.
	Sep	10	14	21	143	55	533	N.D.
	Oct	11	20	31	83	62	411	N.D.
3311	May	< LOQ	1.8	1.8	2.2	2.2	10	< LOQ
	Oct	N.D.	N.D.	N.D.	4.1	3.1	220	N.D.
3310	Oct	N.D.	N.D.	N.D.	5	< LOQ	288	N.D.
3301	May	N.D.	< LOQ	N.D.	3.6	1.9	4	< LOQ
	June	N.D.	< LOQ	N.D.	3.2	2.1	11	< LOQ
	July	N.D.	N.D.	N.D.	2.9	2.1	2	< LOQ
	Aug	N.D.	N.D.	N.D.	1.6	1.4	N.D.	< LOQ
	Sep	N.D.	N.D.	N.D.	1.7	1.7	N.D.	3
	Oct	N.D.	N.D.	N.D.	1.6	2.2	35	4
3308	May	N.D.	< LOQ	< LOQ	< LOQ	< LOQ	69	N.D.
	Oct	N.D.	N.D.	N.D.	< LOQ	N.D.	N.A.	N.D.
TEG 371OP	May	N.D.	<LOQ	N.D.	8.4	4.4	34	N.D.
	June	N.D.	N.D.	N.D.	3.7	3.7	143	< LOQ
	July	N.D.	N.D.	N.D.	5.7	4.5	24	< LOQ
	Aug	N.D.	N.D.	N.D.	5.8	6.6	105	< LOQ
	Sep	N.D.	N.D.	N.D.	N.D.	3.6	25	3
	Oct	N.D.	N.D.	N.D.	3.1	3.7	200	< LOQ
TEG 371UP	May	N.D.	N.D.	N.D.	2.5	1.1	4	< LOQ
	June	N.D.	N.D.	N.D.	2.0	0.9	N.D.	< LOQ
	July	N.D.	N.D.	N.D.	3.0	1.3	5	4
	Aug	N.D.	N.D.	N.D.	1.9	1.4	5	6
	Sep	N.D.	N.D.	N.D.	N.D.	1.0	5	7
	Oct	N.D.	N.D.	N.D.	1.1	1.8	N.D.	6

Table 16 (continued): Compounds with positive findings and their concentrations [ng/L] at transect “Tegel”; N.D.: not detected; N.A.: not analysed; >LOQ: > limits of quantification

3302	May	N.D.	N.D.	N.D.	**2.8**	**< LOQ**	**29**	**< LOQ**
	June	N.D.	N.D.	N.D.	**2.9**	N.D.	**60**	**< LOQ**
	July	N.D.	N.D.	N.D.	**2.2**	**< LOQ**	**56**	N.D.
	Aug	N.D.	N.D.	N.D.	**1.5**	**< LOQ**	**67**	**< LOQ**
	Sep	N.D.	N.D.	N.D.	**1.7**	N.D.	**35**	**< LOQ**
	Oct	N.D.	N.D.	N.D.	**1.0**	N.D.	**20**	**< LOQ**
TEG 372	May	N.D.	N.D.	N.D.	**5.0**	**< LOQ**	**48**	**< LOQ**
	June	N.D.	N.D.	N.D.	**< LOQ**	N.D.	**45**	N.D.
	July	N.D.	N.D.	N.D.	**< LOQ**	N.D.	**29**	**< LOQ**
	Aug	N.D.	N.D.	N.D.	N.D.	**< LOQ**	**26**	**< LOQ**
	Sep	N.D.	N.D.	N.D.	N.D.	**< LOQ**	**26**	N.D.
	Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**52**	N.D.
well 13	May	N.D.	N.D.	N.D.	N.D.	**< LOQ**	**3**	**< LOQ**
	June	N.D.	N.D.	N.D.	**< LOQ**	N.D.	**4**	N.D.
	July	N.D.	N.D.	N.D.	N.D.	**< LOQ**	**5**	N.D.
	Aug	N.D.	N.D.	N.D.	N.D.	**0.2**	**5**	**< LOQ**
	Sep	N.D.	N.D.	N.D.	N.D.	**< LOQ**	**3**	**< LOQ**
	Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**3**	**< LOQ**
3304	May	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	June	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	July	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Aug	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Sep	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	Oct	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Table 17: Compounds with positive findings and their concentrations [ng/L] at transect “Wannsee1”; N.D.: not detected; N.A.: not analysed; >LOQ: > limits of quantification; MV: mean value; blue: extra sampling

ng/L	month	Trimetho-prim	Clarithro-mycin	Roxithro-mycin	Dehydro-Erythro-mycin	Clinda-mycin	Sulfa-methoxa-zole	Sulfa-metha-zine
surface water	20. May	**22**	**15**	**22**	**60**	**22**	**126**	N.D.
	17. June	**17**	**10**	**20**	**73**	**30**	N.A.	N.D.
	MV 02./03. July	**9**	**5.4**	**10**	**2.2**	**18**	**100**	N.D.
	22. July	**7**	**8.1**	**10**	**65**	**19**	**152**	N.D.
	19. Aug	**7**	**1.8**	**4.7**	**30**	**15**	**150**	N.D.
	15.Sep	**8**	**2.3**	**6.3**	**53**	**21**	**245**	N.D.
	22.Sep	**9**	**8.9**	**13**	**56**	**23**	**112**	N.D.
	29.Sep	**12**	**3.9**	**9.4**	**47**	**32**	**326**	N.D.
	06.Oct	**11**	**3.3**	**7.2**	**33**	**31**	**223**	N.D.
	13.Oct	**9**	**3.4**	**7.8**	**42**	**31**	**148**	N.D.
	21.Oct	**17**	**6.5**	**14**	**46**	**34**	**230**	N.D.

Table 17 (continued) : Compounds with positive findings and their concentrations [ng/L] at transect “Wannsee1”; N.D.: not detected; N.A.: not analysed; >LOQ: > limits of quantification; MV: mean value; blue: extra sampling

3337	17. June	N.D.	N.D.	N.D.	1.0	2.1	20	<LOQ
	03. July	N.D.	N.D.	N.D.	2.0	2.4	5	<LOQ
	22. July	N.D.	N.D.	N.D.	3.9	3.8	6	4
	19. Aug	N.D.	N.D.	N.D.	4.5	4.6	3	4
	15.Sep	N.D.	N.D.	< LOQ	5.4	5.9	2	N.D.
	24.Sep	N.D.	N.D.	< LOQ	4.9	5.6	1	4
	29.Sep	N.D.	< LOQ	< LOQ	4.9	6.3	3	<LOQ
	06.Oct	N.D.	< LOQ	N.D.	2.1	7.1	1	3
	13.Oct	N.D.	< LOQ	N.D.	2.7	6.9	3	4
	21.Oct	N.D.	N.D.	N.D.	3.4	7.2	7	4
BEE 201OP	17. June	N.D.	N.D.	N.D.	8.3	1.3	1	3
	22. July	N.D.	N.D.	N.D.	6.0	1.1	1	4
	19. Aug	N.D.	N.D.	N.D.	3.9	1.0	1	<LOQ
	15.Sep	N.D.	N.D.	N.D.	5.3	1.5	1	5
	24.Sep	N.D.	N.D.	< LOQ	3.5	1.3	2	5
	29.Sep	N.D.	N.D.	N.D.	4.4	1.4	1	N.D.
	06.Oct	N.D.	N.D.	< LOQ	1.6	1.5	2	5
	13.Oct	N.D.	N.D.	N.D.	2.3	1.5	2	4
	21.Oct	N.D.	N.D.	N.D.	1.6	0.4	< LOQ	4
BEE 201UP	17. June	N.D.	N.D.	N.D.	N.D.	N.D.	1	3
	03. July	N.D.	N.D.	N.D.	< LOQ	N.D.	< LOQ	4
	22. July	N.D.	N.D.	N.D.	1.6	0.2	N.D.	4
	19. Aug	N.D.	N.D.	N.D.	1.8	0.2	N.D.	4
	22.Sep	N.D.	N.D.	N.D.	1.1	N.D.	N.D.	8
	21.Oct	N.D.	N.D.	N.D.	3.4	1.5	6	6
3335	15.Sep	N.D.	N.D.	N.D.	1.2	0.4	22	N.D.
	24.Sep	N.D.	N.D.	N.D.	0.7	< LOQ	19	<LOQ
	29.Sep	N.D.	0.8	N.D.	1.3	1.5	26	4
	06.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	18	N.D.
	13.Oct	N.D.	N.D.	N.D.	< LOQ	N.D.	21	<LOQ
well 4	17. June	N.D.	N.D.	N.D.	N.D.	N.D.	< LOQ	N.D.
	22. July	N.D.	N.D.	N.D.	0.8	< LOQ	N.D.	N.D.
	19. Aug	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	24.Sep	N.D.	N.D.	< LOQ	2.9	N.D.	1	N.D.
	21.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

Table 18: Compounds with positive findings and their concentrations [ng/L] at transect "Wannsee2"; N.D.: not detected; N.A.: not analyzed; >LOQ: > limits of quantification; MV: mean value; blue: extra sampling

ng/L	month	Trimetho-prim	Clarithro-mycin	Roxithro-mycin	Dehydro-Erythro-mycin	Clinda-mycin	Sulfa-methoxa-zole	Sulfa-metha-zine
surface water	20. May	22	15	22	60	22	126	N.D.
	17. June	17	10	20	73	30	N.A.	N.D.
	MV 02./03. July	9	5.4	10	2.2	18	100	N.D.
	22. July	7	8.1	10	65	19	152	N.D.
	19. Aug	7	1.8	4.7	30	15	150	N.D.
	15.Sep	8	2.3	6.3	53	21	245	N.D.
	22.Sep	9	8.9	13	56	23	112	N.D.
	29.Sep	12	3.9	9.4	47	32	326	N.D.
	06.Oct	11	3.3	7.2	33	31	223	N.D.
	13.Oct	9	3.4	7.8	42	31	148	N.D.
	21.Oct	17	6.5	14	46	34	230	N.D.
BEE205	19. June	N.D.	1.2	3.0	3.0	27	2	< LOD
	03. July	N.D.	N.D.	< LOD	N.D.	20	2	N.D.
	24. July	N.D.	< LOD	0.8	1.3	22	< LOD	3
	21. Aug	N.D.	< LOD	< LOD	1	23	< LOD	< LOD
	15.Sep	N.D.	N.D.	< LOD	1.4	29	3	6
	22.Sep	N.D.	N.D.	N.D.	0.8	21	2	< LOD
	29.Sep	N.D.	N.D.	< LOD	0.8	20	2	< LOD
	06.Oct	N.D.	N.D.	< LOD	N.D.	16	2	< LOD
	13.Oct	N.D.	N.D.	< LOD	0.6	29	2	4
	23.Oct	N.D.	N.D.	0.6	0.6	26	9	N.D.
BEE206	19. June	N.D.	N.D.	N.D.	3.0	2.0	142	< LOD
	03. July	N.D.	N.D.	N.D.	3.0	2.0	72	< LOD
	24. July	N.D.	N.D.	N.D.	5.2	2.2	80	< LOD
	21. Aug	N.D.	N.D.	N.D.	6.7	2.6	41	< LOD
	15.Sep	N.D.	N.D.	N.D.	8.6	2.9	34	< LOD
	22.Sep	N.D.	N.D.	N.D.	12	3.2	41	< LOD
	29.Sep	N.D.	N.D.	N.D.	9.3	3.1	52	< LOD
	06.Oct	N.D.	N.D.	N.D.	4.7	2.9	44	N.D.
	13.Oct	N.D.	N.D.	N.D.	5.6	2.9	43	4
	23.Oct	N.D.	N.D.	N.D.	5.4	2.4	38	< LOD
BEE 202OP	19. June	N.D.	N.D.	N.D.	< LOD	< LOD	34	N.D.
	02. July	N.D.	N.D.	N.D.	N.D.	N.D.	29	N.D.
	24. July	N.D.	N.D.	N.D.	< LOD	< LOD	36	N.D.
	21. Aug	N.D.	N.D.	N.D.	< LOD	N.D.	43	< LOD
	15.Sep	N.D.	N.D.	N.D.	< LOD	0.2	32	< LOD
	22.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	16	< LOD
	29.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	24	N.D.
	06.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	23	< LOD
	13.Oct	N.D.	N.D.	N.D.	N.D.	< LOD	28	< LOD
	23.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	38	< LOD

Table 18 (continued): Compounds with positive findings and their concentrations [ng/L] at transect "Wannsee2"; N.D.: not detected; N.A.: not analyzed; >LOQ: > limits of quantification; MV: mean value; blue: extra sampling

BEE 202MP1	24. July	N.D.	N.D.	N.D.	N.D.	N.D.	**8**	**<LOD**
	21. Aug	N.D.	N.D.	N.D.	**< LOD**	N.D.	**5**	**4**
	15.Sep	N.D.	N.D.	N.D.	N.D.	**0.2**	**6**	**3**
	22.Sep	N.D.	N.D.	**< LOD**	N.D.	N.D.	**6**	**4**
	29.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	**6**	**4**
	06.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**6**	**5**
	13.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**5**	**4**
	23.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**6**	**5**
BEE 202MP2	19. June	N.D.	N.D.	N.D.	**1.9**	N.D.	N.D.	**4**
	24. July	N.D.	N.D.	N.D.	**3.5**	**< LOD**	N.D.	**4**
	21. Aug	N.D.	N.D.	N.D.	**3.7**	**< LOD**	N.D.	**9**
	24.Sep	N.D.	N.D.	N.D.	**< LOD**	**0.2**	N.D.	**4**
	23.Oct	N.D.	N.D.	N.D.	**1.8**	N.D.	N.D.	**6**
BEE 202UP	19. June	N.D.	N.D.	N.D.	**2.0**	**< LOD**	N.D.	**8**
	24. July	N.D.	N.D.	N.D.	**1.7**	**< LOD**	N.D.	**4**
	21.Aug	N.D.	N.D.	N.D.	**1.6**	**< LOD**	N.D.	**6**
	24.Sep	N.D.	N.D.	N.D.	**< LOD**	N.D.	N.D.	**7**
	23.Oct	N.D.	N.D.	N.D.	**0.9**	N.D.	N.D.	**4**
BEE203	19. June	N.D.	N.D.	N.D.	**< LOD**	**< LOD**	**64**	N.D.
	24. July	N.D.	N.D.	N.D.	**< LOD**	**< LOD**	**22**	N.D.
	21. Aug	N.D.	N.D.	N.D.	N.D.	N.D.	**21**	N.D.
	15.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	**39**	N.D.
	22.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	**60**	N.D.
	29.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	**47**	N.D.
	06.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**43**	N.D.
	13.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**37**	N.D.
	23.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**42**	**<LOD**
well 3	19. June	N.D.	N.D.	N.D.	**1.1**	**< LOD**	**3**	**<LOD**
	02. July	N.D.	N.D.	N.D.	**0.6**	N.D.	**3**	**<LOD**
	24. July	N.D.	N.D.	N.D.	**0.9**	**< LOD**	**3**	**<LOD**
	21. Aug	N.D.	N.D.	N.D.	**0.8**	N.D.	**3**	**<LOD**
	24.Sep	N.D.	N.D.	N.D.	N.A.	N.D.	**4**	**<LOD**
	23.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**3**	N.D.
BEE 204UP	17. June	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	22. July	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	19. Aug	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	24.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	21.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
BEE 204OP	17. June	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	22. July	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	19. Aug	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	24.Sep	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.
	21.Oct	N.D.	N.D.	N.D.	N.D.	N.D.	**3**	N.D.

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4) **Kolpin, D.W.; Furlong, E.T.; Meyer, M.T.; Thurman; E.M.; Zaugg, S.D.; Barber, L.B.; Buxton, H.T.:** Pharmaceuticals, Hormones, and Other Organic Wastewater Contaminantes in U.S. Streams, 1999-2000: A National Reconnaissance. Environmental Science & Technology, 2002, Vol 36, Iss 6, pp 1202-1211

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6) **Sacher, F.; Lange, F.T.; Brauch, H.-J.; Blankenhorn, I.:** Pharmaceuticals in groundwaters- Analytical methods and results of a monitoring program in Baden-Wurttemberg, Germany. Journal of Chromatography A, 2001, Vol 938, Iss 1, pp 199-210

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5.3 Investigation of the mobility of pharmaceutical residues using a soil column system

Introduction

In the course of a diploma thesis by Daniel Wicke, the behavior of four widely used pharmaceuticals (clofibric acid, diclofenac, ibuprofen and bezafibrate) as well as the drug metabolite AMDOPH was investigated using a 30m long soil column system. This study was carried out in cooperation with the working group of Prof. Jekel (NASRI – organics). Parameters were chosen for best possible simulation of natural conditions of groundwater recharge or bank filtration. The inflow of the soil column (water from Lake Tegel) was spiked with the four pharmaceuticals at a concentration of approximately 1.5 µg/l for one and two weeks, whereas AMDOPH was already present at concentrations of around 0.5 µg/l.

Materials and Methods

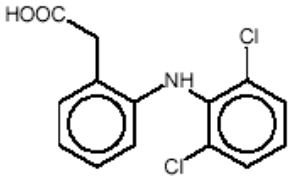
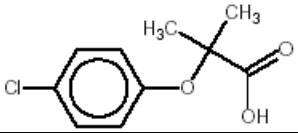
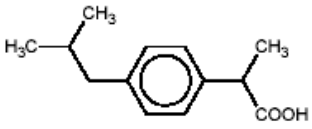
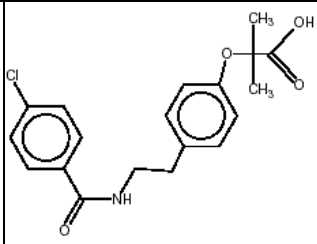
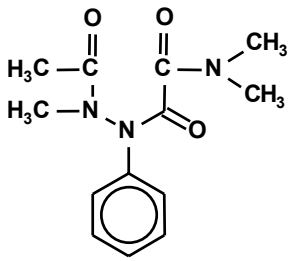
Selection of the examined compounds

Due to the immense number of pharmaceuticals, a selection of a few model compounds was made according to using the following criteria:

- Relevance of the compounds in the aquatic environment
- Selected compounds that have shown a different removal and transport behavior in previous studies
- All compounds should be analyzed with one analytical method (GC-MS) to save labor, time, and expenses

The compounds selected for this study are shown in table 1 (the metabolite AMDOPH was not added to the influent but it was already present in the used surface water used as influent/feed water).

Table 1: Chemical properties of the selected pharmaceuticals [29]

Compound	Structure	Mol. weight and formula	Log K_{ow}	solubility	Indication group
Diclofenac		296.2 $C_{14}H_{11}Cl_2NO_2$	4.51	2.37 mg/l	Antiphlogistic/ Antirheumatic
Clofibric Acid		214.7 $C_{10}H_{11}ClO_3$	2.57	582.5 mg/l	Blood lipid regulator (Metabolite)
Ibuprofen		203.3 $C_{13}H_{18}O_2$	3.97	21.0 mg/l	Antiphlogistic/ Antirheumatic
Bezafibrate		361.8 $C_{19}H_{20}ClNO_4$	4.25	k.A.	Blood lipid regulator
AMDOPH		263.2 $C_{13}H_{17}N_3O_3$	k.A.	k.A.	Metabolite of the antiphlogistic Dimethylamino-phenazone (no longer produced since 1978)

Soil Column Set up

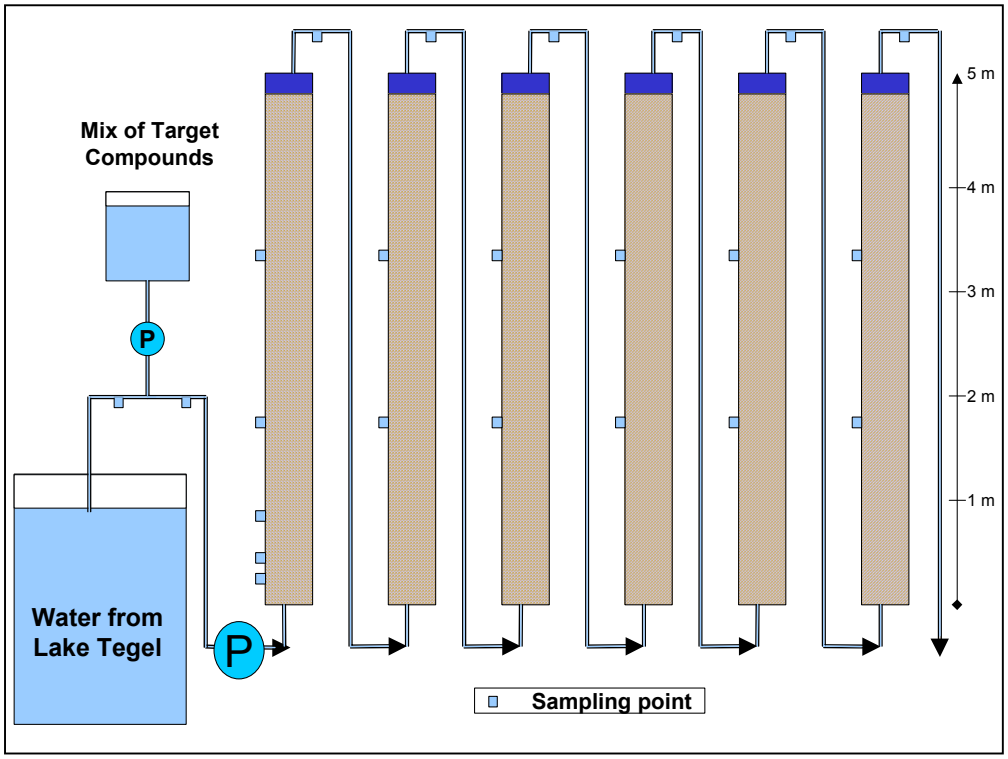


Figure 1: Upper part of the soil column

Experiments were carried out using a soil column system located at a test-field site of the UBA (Umweltbundesamt) in Berlin Marienfelde. A schematic view of the soil column system is shown in Figure 1. Six columns with an individual length of 5m and a diameter of 0.4m are connected with stainless steel tubes resulting in a 30m-long soil column. The system was installed as a simulation of a one-dimensional aquifer to eliminate outside influences. A flow of 36 l/day (Q=0.036 m³/d) results in a retention time of 30 days, which was confirmed by tracer experiments. The influent/feed water, surface water from Lake Tegel, was stored in a 500 l tank that had to be refilled every 12 to 14 days. The influent water was spiked with a mix of target compounds using a peristaltic pump (dilution factor 1:25). The compounds were stored in a refrigerated tank with a volume of 20 liters. The column could be sampled at 22 sampling points (see Figures 1 and 2), three in each column (at 166 cm,

333 cm, and 500 cm) with three additional sampling points in the first column (at distances of 21 cm, 42 cm, and 84 cm). These additional sampling points have been implemented assuming that degradation and adsorption processes will especially take place during the first meters of the soil column. The total distances to a specific sampling point and the individual description of the samples are listed in table 2.

Table 2: sampling points : ->

Labeling	Length [m]
1-0	0.0
1-1	0.2
1-2	0.4
1-3	0.8
1-4	1.7
1-5	3.3
1-6	5.0
2-7	6.7
2-8	8.3
2-9	10.0
3-10	11.7
3-11	13.3
3-12	15.0
4-13	16.7
4-14	18.3
4-15	20.0
5-16	21.7
5-17	23.3
5-18	25.0
6-19	26.7
6-20	28.3
6-21	30.0

Due to the construction of the sampling points, an extra (dead) volume of approximately 20 ml had to be considered during every sampling occasion. The connection between the columns is carried out using stainless steel tubes (diameter: 5 mm) to avoid growth of algae and adsorption. Prior start of the experiment in May, 2003, the column system has been conditioned (since December, 2002) using surface water from Lake Tegel. The initial retention time (3 months - 12 l/d) was reduced to 30 days (36 l/d) beginning in April, 2003. The photos in figures 2 to 5 shall be giving a visual impression of the system.

The soil column system is maintained by Steffen Grünheid, PhD student at the Department of Water Quality Control at the Technical University Berlin (working group of Prof. Jekel).

Soil Column Material

The columns used are filled with fine natural sand, a typical soil inside and around Berlin. It was obtained from the gravel pit „Horstfeld“ south of Berlin near Zossen. The known characteristics of the material are summarized in Table 3. The curve showing the size distribution of the grains can be found elsewhere.

Original water content	2.3 %
Content of humic substances	0.3 %
HCl-soluble carbonate content	0.3 %
„Ungleichförmigkeitsfaktor“	2.87
k_f-value	$1 \cdot 10^{-4}$ m/s
Porosity	31.9 %
Dispersion	0.04 m/d

Table 3: Known parameters of the soil-column material

Figure 2. Upper part of the soil column

Figure 3. sampling point

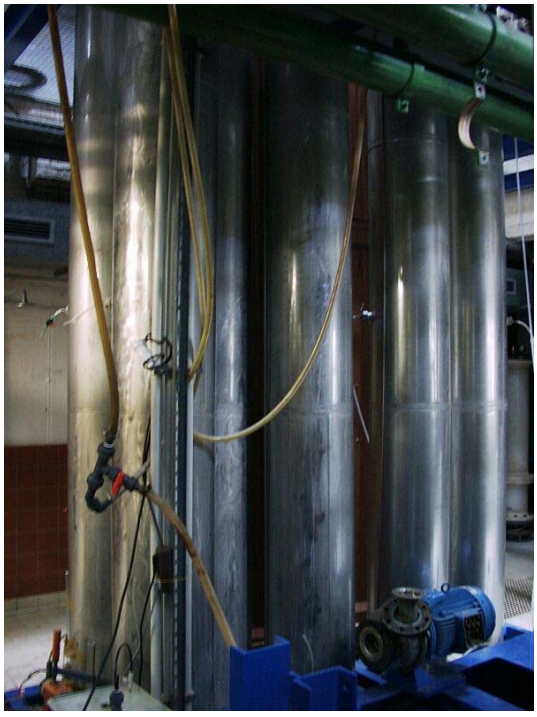
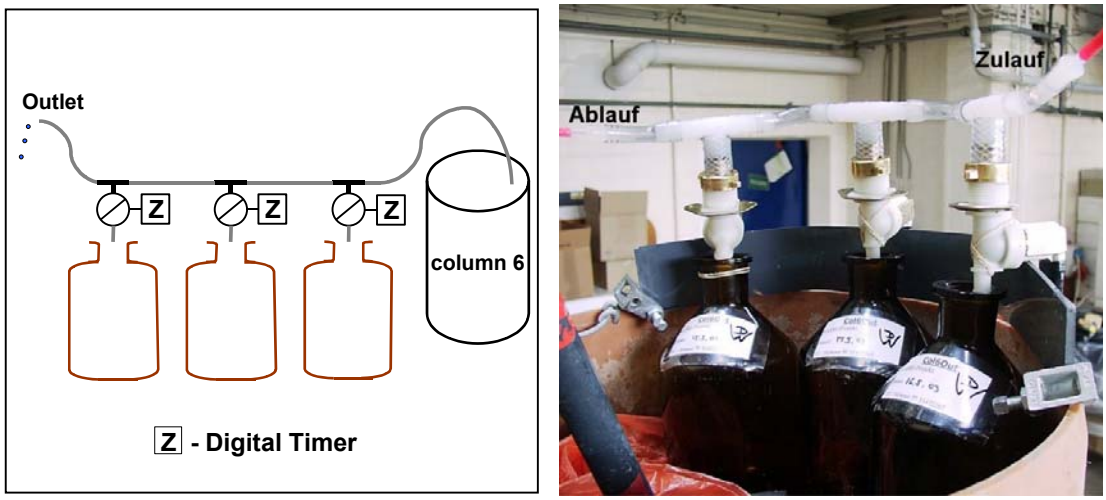


Figure 4. Soil column at the bottom

Figure 5. View upwards

Autosampler

Since it was only possible to access the test field site during weekdays, it was necessary to build a simple autosampler. This enabled us to take samples even during the weekend. The sampler was build by using a combination of digital clock timers and magnet valves. Appropriate programming of the timers made it possible to take samples (approximately 125 ml) automatically every three hours, which were combined every day. A scheme and a photo of the autosampler are shown in Figures 6 and 7.



Figures 6+7. Scheme and photo of the self-made automated sampling unit

Details about the experiments

The study on the mobility of pharmaceutical residues was divided into two experiments. At first, the selected compounds were added for two weeks (May 12th – May 26th) at a concentration of around 1.5 µg/l (also shown in Table 7). Samples were only taken at the end of the soil column using the autosampler for 13 weeks (until August 11th). In addition, samples from sampling point 1-0 were taken twice to measure the actual influent/feed concentration of the pharmaceuticals.

In the second experiment, the inflow/feed water was spiked at the same concentration for one week (June 23rd – June 30th) to investigate the behavior of the added compounds within the first few decimeters of the

column. Assuming that degradation and adsorption take place especially in the first meter of the column, samples have been taken manually once a day at sampling points 1-1 (21 cm), 1-3 (84 cm) and 1-4 (166 cm – see also table 2). A list of all collected samples is shown in table 4.

Table 4: Overview of all samples collected during this study

Description	Volume*	Dates of Sampling	Details
Lake Tegel	100 ml	May: 12., 23.; June: 3., 12., 24. July: 7., 21.; August: 4.	Taken from the storage tank after each filling
Col 1-0 (ColIn)	50 ml	May: 12., 23.; June: 26., 30.	
Col 1-1 (21 cm)	50 ml	June: 20., 23.-30. July: 1.-5., 7., 8.	No samples on 21./22. 6. and 6.7. (weekend)
Col 1-3 (84 cm)	50 ml	June: 20., 23.-30. July: 1.-5., 7., 8.	No samples on 21./22. 6. and 6.7. (weekend)
Col 1-4 (166 cm)	50 ml	June: 20., 23.-30. July: 1.-5., 7., 8.	No samples on 21./22. 6. and 6.7. (weekend)
Col6Out (column outlet)	100 ml	May: 16.-26. June: 3.-30. July: 1.-31. August: 1.-11.	

* volume used for one analysis

Instrumental Analysis

A multi-compound method has been used for analysis of the selected pharmaceuticals [18]. This method has been developed and validated by this working group. The four main parts of the laboratory analysis using this method are solid phase extraction (SPE), derivatization, quantification using GC/MS and data processing. The extraction of the pharmaceutical residues was done by using SPE-cartridges which were filled with 1 g of RP-C18 adsorbent. The eluate was then derivatized with PFBBr (pentafluorobenzyl bromide) and injected into the GC-MS system (Agilent Technologies) using selected ion monitoring. Details of the chemical analysis can be looked up in [18].

Figure 8: Derivatized sample

For processing the data the software HP Chemstation was used. For quantification, the following standard solutions were prepared: S5 (10 pg/µl), S4 (100 pg/µl), 5S4 (500 pg/µl), S3 (1 ng/µl) und 2S3 (2ng/µl). The correlation coefficient (r^2) for all calibration curves was always better than 0.95. To ensure the quality of the chemical analysis, 100 ng of the internal standard 2-(m-chlorophenoxy)-propionic acid were added to all samples prior to SPE. Recovery rates, calculated using the measured concentration of the internal standard are listed elsewhere. For quantitative measurement of diclofenac in surface waters it had to be taken into account that up to 40% might be converted into an artefact [17]. In consideration of this effect, the concentration of the diclofenac artefact detected in the samples was added to that of diclofenac. Limits of detection and determination for the analyzed compounds and volumes are summarized in table 5.

Figure 9. Solid Phase Extraction

Table 5. Limits of detection/determination for analyzed compounds (according to [32])

Compound	NG für V=50 ml (Col 1.1 – 1.4) [ng/l]	NG für V=100 ml (column outlet) [ng/l]	BG für V=50 ml (Col 1.1 – 1.4) [ng/l]	BG für V=100 ml (column outlet) [ng/l]
AMDOPH*	10	5	40	20
Bezafibrate**	150	75	600	300
Clofibric Acid	50	25	200	100
Diclofenac	10	5	40	20
Diclofenac Art.	50	25	200	100
Ibuprofen	20	10	70	35

NG – limit of detection BG – limit of determination

* for ground water ** own estimation for maintained GC/MS

Results

Chemical and physical parameters

To characterize the chemical and physical conditions of the soil column system, a number of parameters were routinely measured. These measurements were carried out by the Department of Hydrogeology (FU Berlin) and by Steffen Grünheid (Department of Water Quality Control of the TU Berlin). The results of these measurements are summarized in table 6. Graphs of these results can be found elsewhere.

Table 6 Summary of measured parameters

Parameter	Changes along column	Changes during experiment	Details
PH	x	-	Slowly decreasing from **8** to **7.5**
DOC-concentration	xx	-	Rapid decrease from **8** to **4 mg/l**
SAK_{254}	xx	-	Rapid decrease from **16** to **8 1/m**
DOC/SAK_{254}	x	-	Around **2**, little increase at the beginning, then slight decrease
Oxygen	xx	xx	Between **1** and **10 mg/l**, first completely saturated, later on decrease of O_2-concentration
Redox potential	xx	xx	Between **50** and **300 mV**, correlating with development of oxygen concentration
Conductivity	-	-	Stable around **680 µS/cm**
Kations			
Manganese, Iron	-	-	Not present
Sodium	-	-	Around **41 mg/l**
Magnesium	-	-	Around **10 mg/l**
Potassium	x	-	Around **10 mg/l**, slight decrease towards end
Calcium	x	-	Little increase from **90** to **98 mg/l**
Anions			
HCO_3^-	-	-	Around **170 mg/l**
Sulfate	-	-	Around **130 mg/l**
Chloride	x	-	Little increase from **60** to **68 mg/l**
Nitrate	x	x	Between **7** and **13 mg/l**, first slight increase, later on drop within the first meters (oxygen!)

- - not present **x** – minor changes **xx** – big changes

Pharmaceutical residues

All samples have been analyzed for clofibric acid, diclofenac, diclofenac-artefact, ibuprofen, bezafibrate, AMDOPH and the internal standard (to determine and control the individual recovery rates and to adjust the analytical results). Results off all measurements are listed elsewhere.

Preliminary experiments were carried out prior to analysis of samples taken from the soil column system to determine recovery data and to ensure that adsorption at the self-constructed autosampler can be neglected. Results of the recovery experiments are listed elsewhere. Recovery rates of the analyzed compounds varied between 93% and 120% with standard

deviations between 1.8% – 12.1%. According to another experiment with purified water spiked with the target compounds (comparison of autosampler-influent and effluent), no indication of adsorption to materials of the auto-sampler was determined. Analysis of the influent/feed water from Lake Tegel revealed the presence of AMDOPH at concentrations between 430 and 530ng/l (median value: 500 ng/l – see also box plot in figure 10). Background concentrations of the four added compounds have usually been below limits of determination (elsewhere).

Table 7. Concentrations of the pharmaceuticals at sample point 1-0

Sample name	Diclofenac [µg/l]	Clofibric acid [µg/l]	Ibuprofen [µg/l]	Bezafibrate [µg/l]
Col 1-0 13.5.	1.4	1.2	1.3	2.1
Col 1-0 23.5.	1.3	1.6	1.0	1.9
Col 1-0 26.6.	1.1	1.3	1.4	1.4
Col 1-0 30.6.	1.2	1.4	1.4	1.5

Influent concentrations of added pharmaceuticals

The influent concentration of all four added compounds was determined to be 2 µg/l. To achieve this concentration, a stock solution (10 mg/l) was prepared using S0-solutions (1 mg/ml in ethyl acetate). The stock solution was used for both experiments. To avoid an increase of the natural DOC in the influent water, organic solvents had to be evaporated and compounds were then re-dissolved in purified water.

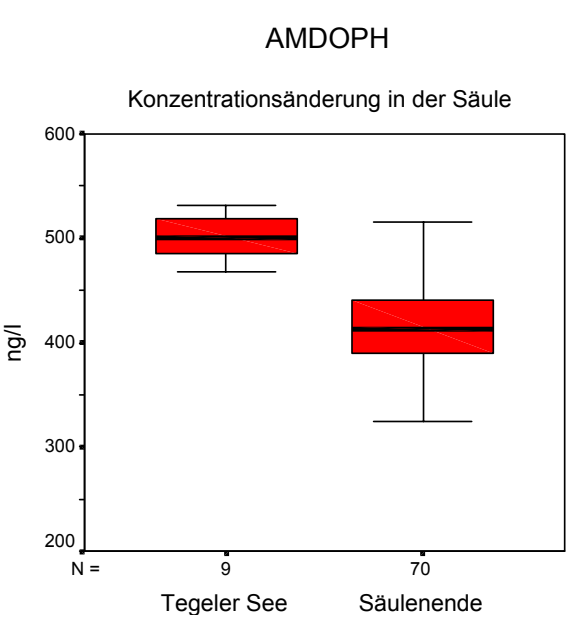


Figure 10. Concentration of AMDOPH before (feed water) and after soil passage (column effluent).

During this step, losses of non-dissolved residues sticking to the glass could not fully be avoided. Final influent concentrations of all added compounds (sampled at the beginning of the column) varied between 1 and 2 µg/l and are listed in table 7 and elsewhere. Comparison of the results showed slightly smaller concentrations of diclofenac and bezafibrate during the second experiment (24th to 30th of June). A probable explanation could be adsorption effects of these compounds to the glass.

First experiment

During the first experiment (influent spiked from 5/12/03 to 5/26/03), only the effluent concentrations of the pharmaceutical residues have been measured (Col 6.21). It has been expected that at least clofibric acid (that has been characterized in the literature as hardly degradable and very mobile) can be measured at the end of the column. Instead, the effluent concentrations of all four added compounds (clofibric acid, diclofenac, ibuprofen and bezafibrate) were below limit of detection. Only AMDOPH that was already detected in the surface water from Lake Tegel was also detected in the effluent of the column. Statistical calculations show a little decrease – median concentrations were reduced from 500 ng/l to 420 ng/l (see box plot in figure 10). Results of all samples from the end of the column including recovery rates can be found elsewhere.

Tracer experiment of the FU Berlin

The application of tracers is useful to compare the mobility of compounds in soil column experiments with unretarded behaviour. Since clofibric acid has been described in the literature as being a tracerlike compound (e.g. [7][13]) it was planned to use this compound as an internal tracer. Due to the unexpected elimination of clofibric acid, results of a tracer experiment conducted by the department of hydrology (FU Berlin) were used [12] as reference data. In these experiments a Gadolinium-tracer (Gd-tracer) was used that was added to the column from June 3rd through July 7th, 2003. A

breakthrough occurred after 33 days. The results of this tracer experiment were also used to calculate hydro-geological parameters such as porosity and dispersion (table 9).

Table 9. Parameters of the soil column derived from the Gd-tracer experiment

Mean velocity	0.91 m/d
Porosity	31.9 %
Dispersion	0.04 m
Dispersion coefficient	0.036 m²/d
Average residence time	33 days

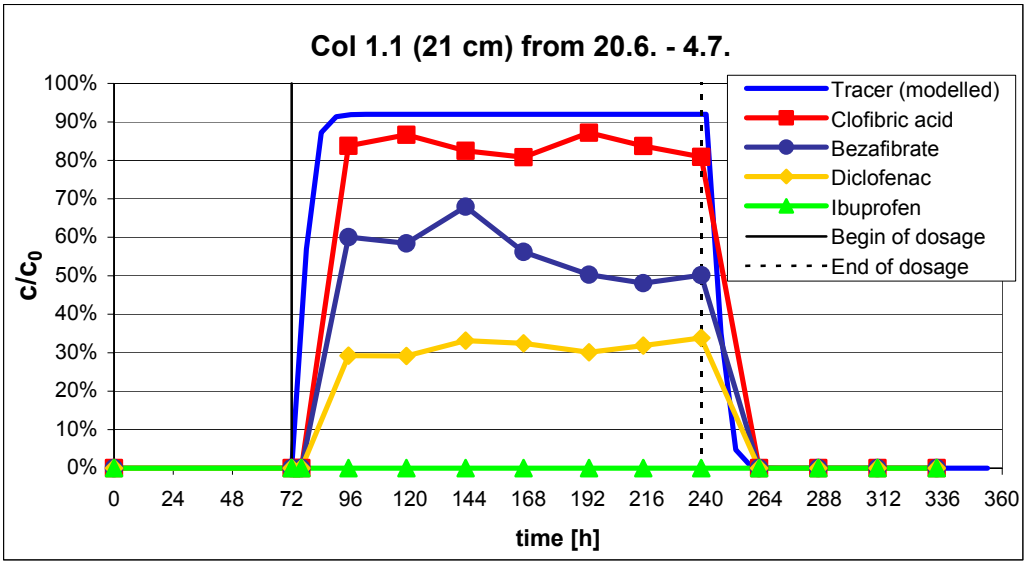
Second experiment

During the second experiment (pharmaceuticals added from 23rd to 30th of June), samples were taken only from the first few sampling points to investigate if the elimination process takes place within the first decimeters of the soil column. Samples were taken daily (see Table) from sample points Col 1.1 (21 cm), Col 1.3 (84 cm), and Col 1.4 (166 cm). The breakthrough-curves are compared with a modeled tracer breakthrough curve that was generated using the parameters gained from the Gd-tracer experiment (table 9). The modeled curve simulates the behavior of the Gd-tracer added together with the pharmaceuticals over the same time period. All results are listed elsewhere.

Breakthrough Curves

Breakthrough curves of the four added pharmaceutical residues at the three analyzed sampling points are shown in figures 11 to 13.

Figure 11. Breakthrough curves for the spiked pharmaceuticals at Col 1.1 (21 cm)



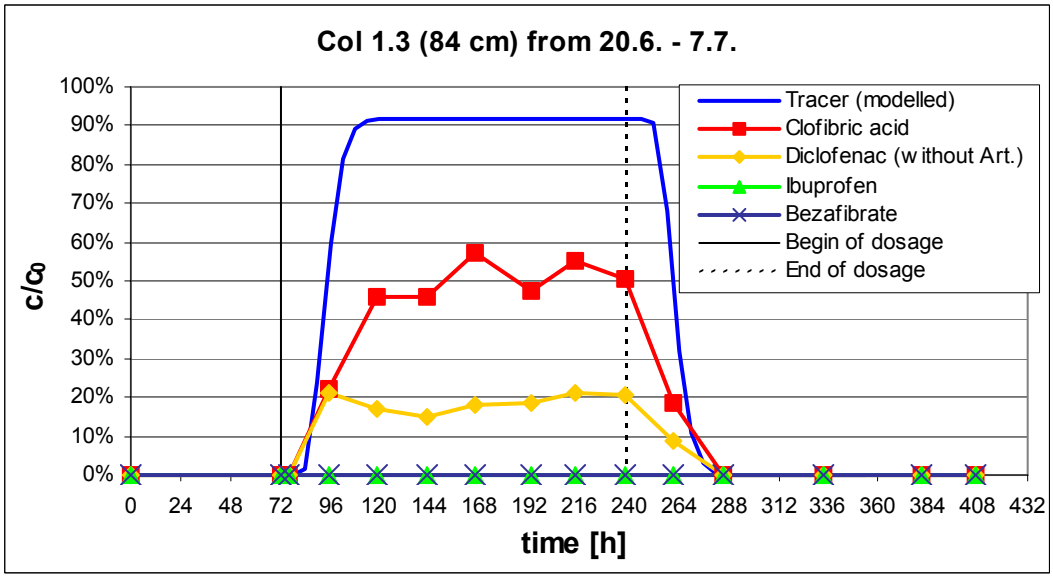


Figure 12. Breakthrough curves for the spiked pharmaceuticals at Col 1.3 (84 cm)

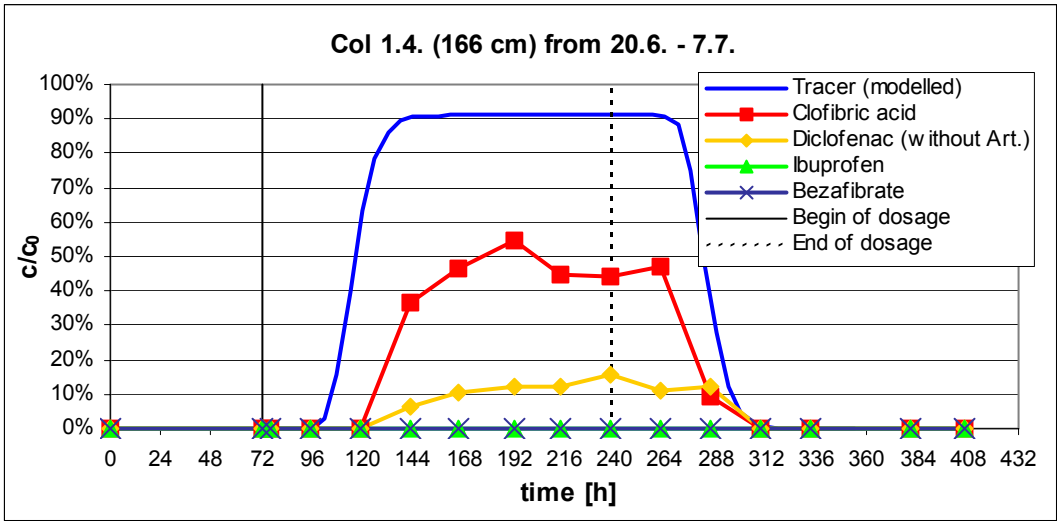


Figure 13. Breakthrough curves for the spiked pharmaceuticals at Col 1.4 (166 cm)

As shown in figure 11, the concentrations of the four added pharmaceuticals considerably changed already after a soil passage of only **21 cm**. The concentration of ibuprofen was already below the detection limit of 20 ng/l. After **84 cm** (Col 1.3), also bezafibrate was not detected any longer. The concentration of clofibric acid had also decreased to approximately 50% of the initial concentration. At **166 cm** (Col 1.4), the concentrations of the

remaining two compounds (clofibric acid and diclofenac) only decreased slightly compared to sample point Col 1.3. It has to be considered that due to the low resolution in time (one sample per day), the real start or ending of a peak may differ by several hours.

Summary of the results and interpretation

Comparing the results of the sample points Col 1.0 (influent), Col 1.1, Col 1.3, Col 1.4 und Col 6.21 (effluent), the following points can be summarized:

- all four compounds (clofibric acid, diclofenac, ibuprofen, bezafibrate) added to the feed water were removed within the soil column system,
- the concentration of AMDOPH was reduced by 15-20%,
- ibuprofen was eliminated within the first 21 cm of the soil column,
- bezafibrate was eliminated within the first 84 cm of the soil column
- the concentration of diclofenac was reduced by around 70% within the first 21 cm, and thereafter it continued to decrease slowly,
- the concentration of clofibric acid was reduced by approximately 50% within the first 84 cm, and thereafter it continued to decrease slowly.

It can be seen that the greatest decrease in concentrations takes place within the first decimeters of the soil column. This zone is also characterized by an extended microbial degradation, as confirmed by the DOC-graph (elsewhere). Because of this correlation, the pharmaceutical residues might be degraded co-metabolically during the degradation of the DOC. Due to the chemical structure of the examined compounds (see table 1) a complete microbial breakdown is not very likely. Instead, the pharmaceutical residues could be modified to more or less active but most probably polar compounds that might not be detectable with the applied analytical methods. The occurrence and effects of such metabolites have to be investigated in further experiments. It might also be possible that diclofenac and bezafibrate in particular are to a certain extent adsorbed to soil particles, since these two compounds have a log K_{OW} greater than four. However, when considering

this possibility, it must be taken in account that at the predominant pH, the compounds are partly ionized. In this respect, the given log K_{OW} is not a definite parameter for the adsorption of these compounds.

Exact degradation pathways of the analyzed pharmaceuticals cannot be derived from the recorded data. Through comparison of the results with earlier studies, further indications regarding the elimination process might be obtained. In order to demonstrate detailed degradation pathways of the analyzed pharmaceuticals, more experiments (especially to assess the adsorption potential) should and are currently conducted.

Conclusions final discussion

The experiments at the soil column system in Marienfelde revealed some unexpected results. A complete removal of **clofibric acid** has not been reported in the literature until now. In fact, some studies even described clofibric acid as an almost persistent and tracer-like compound [7,13,28,31, 33,34]. Only Preuß et al. [15] reported a reduction of clofibric acid concentrations by 40-60% in a soil column experiment.

The concentration of **diclofenac** was reduced comparably quickly. Already at the first sampling point (after 21 cm), only 30% of the initial concentration could be measured. Reported degradation of diclofenac in batch experiments ranged from only a few percent, to a maximum of 50% [14][34]. In a soil column experiment conducted by Mersmann et al. [13], no removal of diclofenac could be observed after passage through a 35 cm long column. On the contrary, Preuß et al. [15] reported a reduction of diclofenac concentrations by 60-80% after 80 cm.

The easy degradability of **ibuprofen**, as described in the literature [3,25,31,34] was confirmed in this study. After passing 21 cm through the soil column, it was already completely removed (concentration below limit of detection). Supposed modification to the metabolites carboxy-ibuprofen and hydroxy-ibuprofen, as described for example by Winkler et al. [31] and

Stumpf et al. [25], could not be confirmed due to the unavailability of the pure substances (can not be purchased).

Bezafibrate is predominantly described in the literature as a compound that can be easily eliminated [2,11,15]. The good adsorbability to GAC, as reported by Sacher et al. 2000 [19] and Ternes et al. 2002 [28], indicates that adsorption of bezafibrate to soil particles and organic material might be one possible way for its removal. Further experiments are necessary to confirm this assumption.

Comparison with other soil column studies

Comparing this study with other investigations on degradation of the selected pharmaceutical residues in soil columns, the results are quite different. But it has to be taken into account that the experimental conditions were quite different, too. While Preuß et al. 2001 [15] also observed a removal of all four compounds in a soil column (by 40% to 80%), Mersmann et al. 2002 [13] could not achieve a reduction of the concentrations of clofibric acid. A comparison of all three studies regarding results and experimental conditions is summarized in table 9.

A comparison of the different experimental settings and parameters indicates that the usage of aerobic surface water and a long conditioning time for development of stable hydrogeochemical and biological conditions are requirements for the degradation of clofibric acid and diclofenac during the soil passage. Under these conditions present in this study as well as in the study by Preuß et al., the concentration of clofibric acid and diclofenac were decreased after 80 cm of soil passage by at least 40% and 60%, respectively. In contrast, Mersemann et al. could measure almost no elimination of these compounds. Due to the indications of microbial breakdown reported by Preuß et al. it is possible that microbial degradation plays a significant role regarding the elimination pathways of the examined pharmaceuticals. However, Due to the chemical structure of the investigated compounds (see table 1) a complete microbial breakdown is not very likely.

Further investigations including a specific search for metabolites of the four added pharmaceuticals (mass spectrum interpretation of analysed samples) could reveal further details of elimination pathways.

Table 9. Comparison of experimental conditions of several studies investigating the degradation of pharmaceuticals in column experiments

Parameter	Preuß et al.	Mersmann et al.	This study
Column length	80 cm	35 cm	3000 cm
Water	Aerobic surface water	Anaerobic ground water	Aerobic surface water
Velocity	360 cm/d	36 cm/d	91 cm/d
Period of conditioning	1.5 months	5 days	4.5 months
Examples of investigated pharmaceuticals	Clofibric acid, Diclofenac, Ibuprofen, Bezafibrate	Clofibric acid, Diclofenac, Ibuprofen,	Clofibric acid, Diclofenac, Ibuprofen, Bezafibrate
Period of dosage	4 weeks	10 days	14 and 7 days
Concentration	100 µg/l	10 µg/l	1.5 µg/l
Results (elimination rates)	Clofibric acid: 40-60% Diclofenac: 60-80% Ibuprofen: 60-80% Bezafibrate: 60-80%	Clofibric acid: 0% Diclofenac: 3% Ibuprofen: 54%	Clofibric acid: >98% Diclofenac: >98% Ibuprofen: >99% Bezafibrate: >95%

Conclusions for groundwater recharge/bank filtration

It has been shown in this study that it is possible to eliminate the four examined pharmaceuticals by infiltration through a sufficient long soil passage. Elimination was predominately observed during the first meters of the soil column – ibuprofen, bezafibrate, and diclofenac were rapidly eliminated during the first centimetres, whereas the concentration of clofibric acid decreased more slowly (45-50% of the initial concentration after passing through 166 cm of soil). After 30 m of soil passage, none of the added pharmaceuticals could be detected anymore. Only AMDOPH (already present in the water of Lake Tegel) could be measured in the column effluent. The concentration at the column outlet after 30 m of soil passage was only 15-20% below the initial concentration.

It has to be emphasized that the results of this study are only valid for the chemical, physical, and hydrogeological conditions of the soil column in Marienfelde, and therefore cannot be generalized. It might be possible that elimination of these compounds is also achievable under real conditions of ground water recharge or bank filtration. To answer these questions comprehensive knowledge of hydrogeological conditions is necessary to rule out the possibility of e.g. dilution effects as a reason for concentration decrease. Furthermore, the contribution of microbial degradation in the elimination pathways and the importance of aerobic conditions and high concentrations of DOC and bacteria is of particular interest. In order to give general rules regarding elimination of pharmaceuticals further experiments are necessary, especially to investigate differences between the conditions in the soil column system and conditions predominant in real infiltration systems.

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5.4 Investigation of the behavior of selected pharmaceuticals during sand filtration

1. Introduction

In his diploma thesis, Michael Voigt investigated the behavior of four selected pharmaceuticals during sand filtration. Four experiments were carried out at the test-field site of the *Umweltbundesamt* (UBA, German federal environmental agency) in Berlin-Marienfelde[1]. Part of this field site are a large storage pond and four slow sand filters that can either be connected with or separated from the storage pond (Fig. 1). Within one of these filters three so-called enclosures, cylindrical pipes of about 1m height and an area of 1m^2, were installed. At the original sand filter samples could be taken only from the supernatant water layer and from the outlet, whereas at the enclosures it was also possible to collect samples from different depths beneath the sediment surface. Figure 1 shows a schematic illustration of the storage pond facility and of enclosure No. 3, which was used in the experiments presented here. Photos of the enclosures are shown in figure 2.

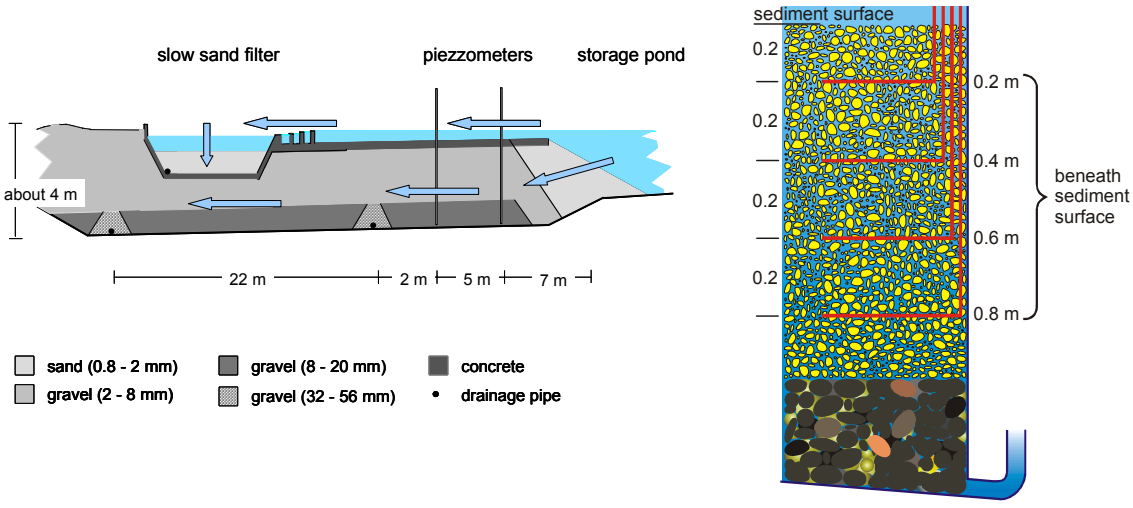


Fig. 1: Schematic illustration of storage pond with slow sand filter and build-in enclosure (UBA)

[1] UBA-Versuchsfeld Marienfelde, Schichauweg 58, 12307 Berlin

All experiments at the enclosures were conducted in cooperation with the working group (algae) of Dr. Chorus from the UBA.

Fig. 2: Photos of the enclosures during their construction and during experimental use (Photos by courtesy of UBA)

The first attempt to run the enclosure by a hydraulic gradient failed, therefore the outlet had to be connected to a pump. Pumps were also used to collect the samples from the sampling points.

Contaminant-free groundwater from the area underneath this filed-site was used to fill the storage pond and to carry out the experiments at the sand filtration facility. Before use, iron and manganese were removed from the groundwater by acreation and filtration before it was directed into the storage pond. Some parameters measured for this water are shown in table 1.

Tab. 1: Physico-chemical parameters measured for the groundwater used for the experiments (after iron and manganese removal)

Cations			
Na^+	**K^+**	**Ca^{2+}**	**Mg^{2+}**
46,4	4,3	125	17,7
Anions			
SO_4^{2-}	**NO_3^-**	**PO_4^{3-}**	**SO_4^{2-}**
236	0,3	<0,1	236
Other parameters			
DOC[2]	**pH**		**conductivity**
5,5 mg/L	7,8		963 µS/cm

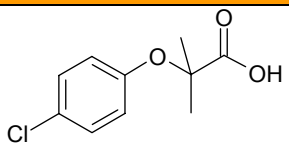
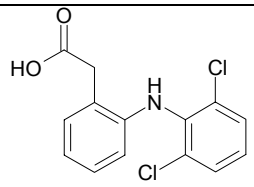
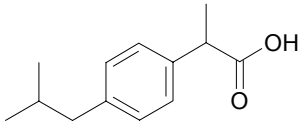
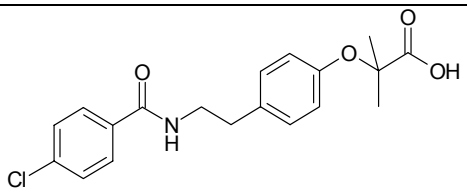
ion concentrations in mg/L

- Selected compounds for the spiking experiments

Four pharmaceuticals, namely clofibric acid, diclofenac, ibuprofen, and bezafibrate were chosen for this study. All four substances have already been found in the aquatic environment and have been selected as model-substances due to their different physico-chemical properties and their expected or reported different behaviour during groundwater recharge.

[2] *dissolved organic carbon*

Tab. 2: Selected pharmaceuticals

Name	Structure	Molecular weight totals formula	Group of prescription/use
Clofibric acid		296,2 $C_{14}H_{11}Cl_2NO_2$	blood lipid lowering agent (metabolite)
Diclofenac		214,7 $C_{10}H_{11}ClO_3$	non-steroidal antiphlogistic
Ibuprofen		203,3 $C_{13}H_{18}O_2$	non-steroidal antiphlogistic
Bezafibrate		361,8 $C_{19}H_{20}ClNO_4$	blood lipid lowering agent

- Instrumental Analysis

The pharmaceuticals were determined using a multi-method developed by our working group (Reddersen and Heberer, 2003) applying solid phase extraction (SPE), chemical derivatization and gas chromatography with mass spectrometric detection (GC-MS).

2. Results

A first experiment (slow sand filter experiment #1) with clofibric acid and diclofenac alone was carried out with one of the slow sand filters, where only samples from surface water and outlet could be taken.

Tab. 3: Experimental conditions for slow sand filter experiment #1

Slow sand filter experiment #1	
Date	23.– 25.04.2003
Flow rate	6,4 m^3/h
Filtration velocity	2,1 m/d
Filter bed thickness	0,8 m
Initial concentration of pharmaceuticals	1 µg/L
Condition of the sediment suface	large algae growth

In addition, sodium chloride was added as a tracer and conductivity was measured by the working group of Dr. Chorus from the *Umweltbundesamt*. The results from this preliminary experiment are shown in Fig. 3 and Fig. 4.

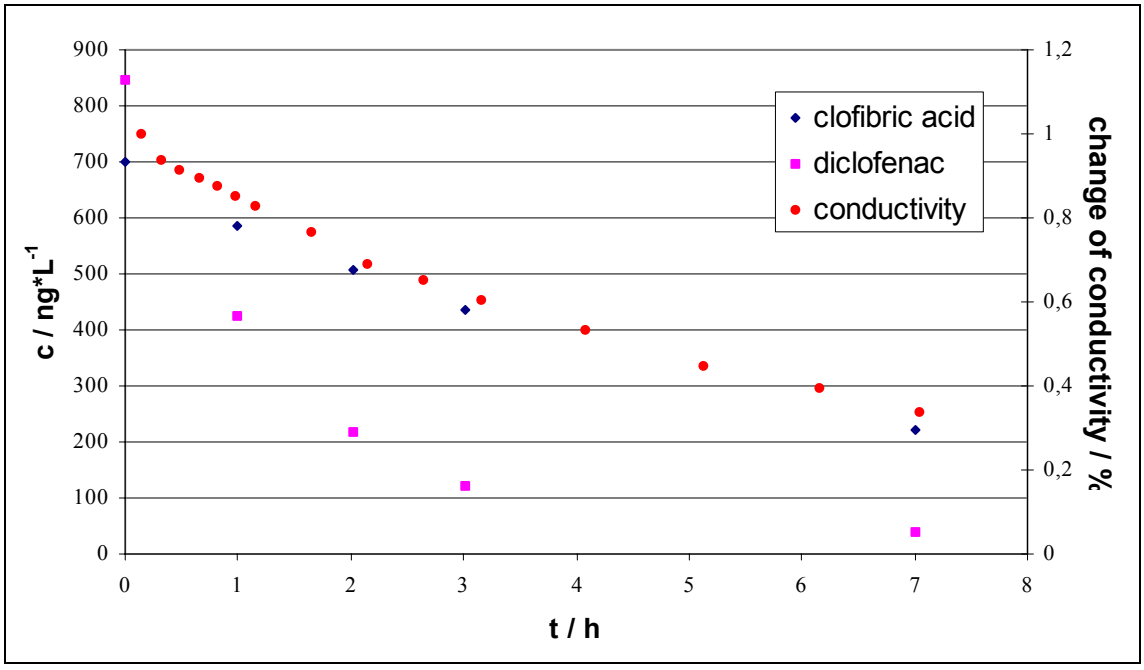


Fig. 3: Concentrations of pharmaceuticals and temporal change of conductivity measured in the spiked surface water during slow sand filter experiment #1 (23.-25.4.03)

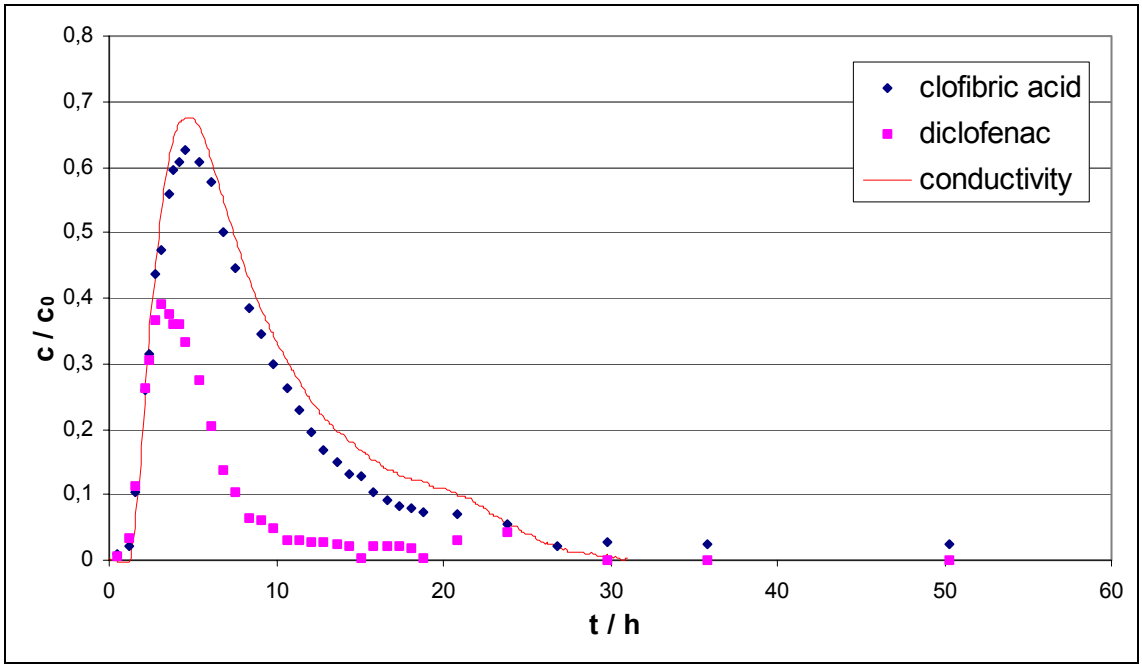


Fig. 4: Concentrations of pharmaceuticals and temporal change of conductivity measured in the outlet during slow sand filter experiment #1 (23.-25.4.03)

As can be seen from the results of this experiment, the concentration of clofibric acid changed similar to the concentration of sodium chloride that was observed by measuring the conductivity. Thus, clofibric acid showed the tracer-like behavior that has already been described for this substance in various references for this substance (e.g. Mersmann et al., 2002; Verstraeten et al., 2002). In contrast to that, there is a distinct decrease of the diclofenac concentration was observed in the surface water and it was assumed that this was caused by photolytical degradation, which has been for diclofenac in the literature (Buser et al., 1998, Tixier et. al., 2003). A mass balance was calculated which showed that 70% of the infiltrated amount of clofibric acid was detected at the outlet, while only 30% of the spiked amount of diclofenac was recovered (for diclofenac photolytical degradation has to be taken into account resulting in an unknown amount of diclofenac that was removed from the surface water without being infiltrated into the sand filter).

The experiment was repeated two month later (slow sand filter experiment #2) under different conditions and with all four substances (clofibric acid, diclofenac,

ibuprofen, bezafibrate). Again sodium chloride was used as a tracer. Additionally, microcystines (algae toxins) and bacteriophages (viruses) were added by the two working groups from the UBA (Chorus/Lopez-Pila).

Tab. 4: Experimental conditions for slow sand filter experiment #2

Slow sand filter experiment #2	
Date	17.– 19.06.2003
Flow rate	3,6 m^3/h
Filtration velocity	1,2 m/d
Filter bed thickness	0,8 m
Initial concentration of pharmaceuticals	1 µg/L
Condition of the sediment surface	cleared

The results for clofibric acid and diclofenac were comparable to those of slow sand filter experiment #1. However, the two additional substances ibuprofen and bezafibrate were fully attenuated during slow sand filtration and could not be detected in the outlet.

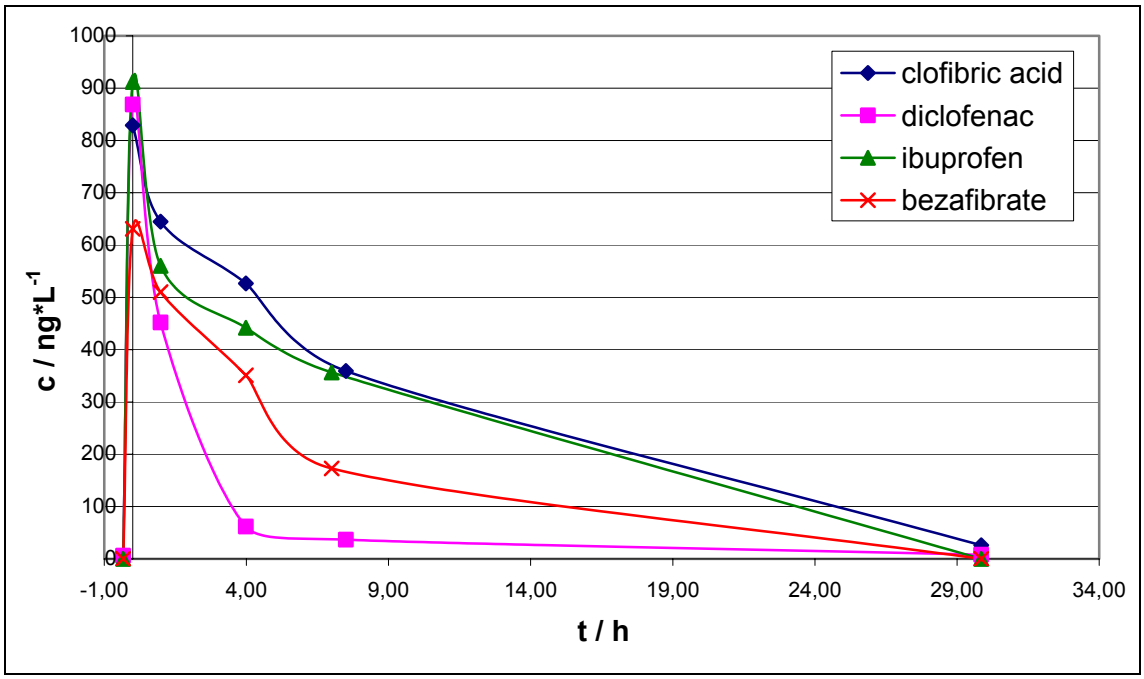


Fig. 5: Concentrations of pharmaceuticals measured in the surface water during slow sand filter experiment #2 17.-19.06.03)

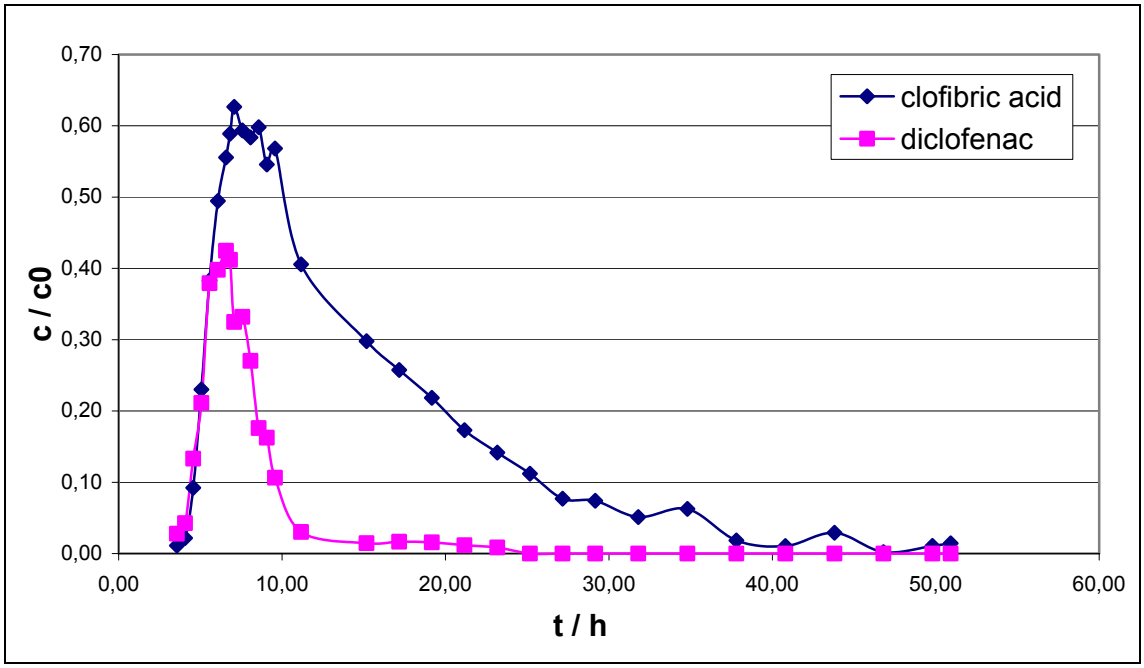


Fig. 6: Concentrations of pharmaceuticals measured in the surface water during slow sand filter experiment #2 17.-19.06.03)

Enclosure experiments

The first enclosure experiment was carried out in August 2003. The joined experiments were carried out together with several other groups of the NASRI-project. Besides PhACs some other compounds (microcystines, viruses, Gadolinium and again sodium chloride as a tracer) were also spiked to the feed water of the enclosures. Therefore, and because a sample-volume of only 25ml/min could be collected at the four sampling-points the initial concentrations of our pharmaceuticals had to be increased. The enclosure was covered to protect the UV-sensitive bacteriophages and to avoid photochemical reactions.

Tab. 5: Experimental conditions for enclosure experiment #1

Enclosure experiment #1		
Date	**05.– 06.08.2003**	
Flow rate	**0,05 m^3/h**	
Filtration velocity	**1,3 m/d**	
Initial concentration of pharmaceuticals	**clofibric acid diclofenac**	**ibuprofen bezafibrate**
	2µg/L	**5µg/l**
Condition of the sediment surface	**cleared**	

Figure 7 shows the temporal changes of concentrations for the four spiked pharmaceuticals in the supernatant water layer.

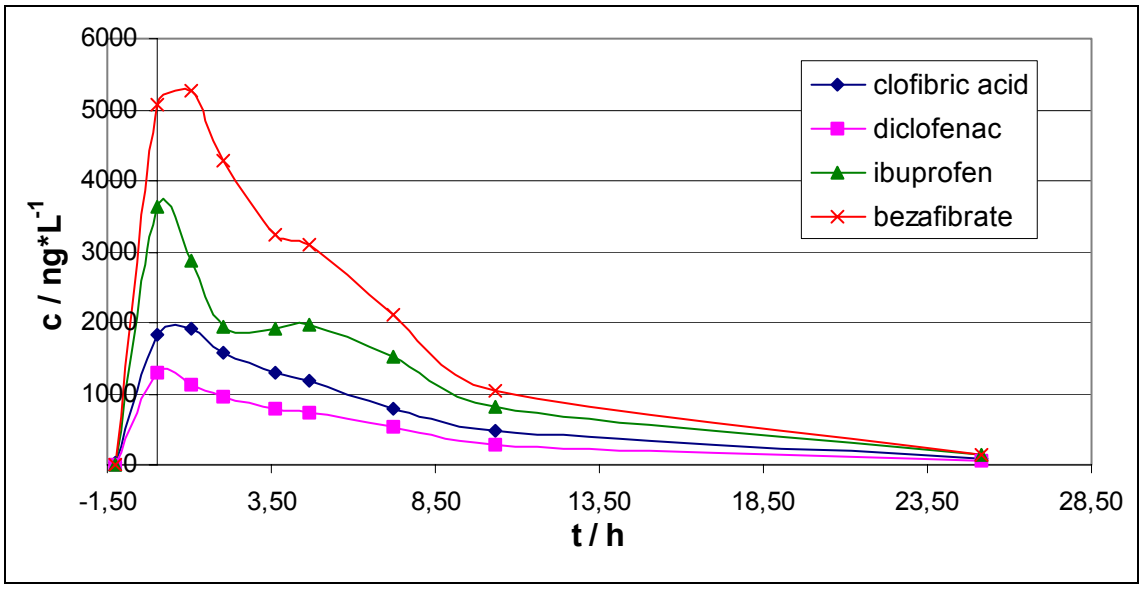


Fig. 7: Concentrations of pharmaceuticals measured in the spiked surface water during enclosure experiment #1 (05.-06.08.03)

Apart from their different initial concentrations the change of concentration was quite similar for all four substances. The rapid decrease of the diclofenac concentration that was observed in the first experiments did not occur because the enclosure was covered. This result also confirmed the assumption of a photolytical degradation of diclofenac in the supernatant water layer in both experiments with slow sand filtration. Therefore, adsorption at the top of the

sand filtration facilities can be excluded being an important cause for the decrease of the diclofenac concentration.

Fig. 8 shows the results measured for all four pharmaceuticals in the column of the enclosure at a depth of 20cm.

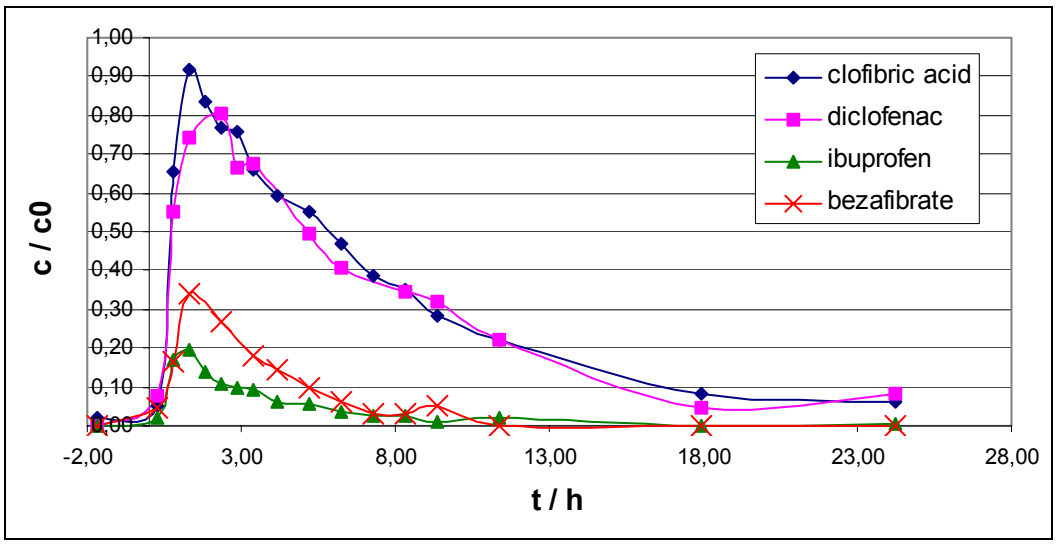


Fig. 8: breakthrough curves of pharmaceuticals measured at a depth of 20cm in the enclosure during enclosure experiment #1 (05.-06.08.03)

Ibuprofen and bezafibrate were already strongly attenuated resulting in rather low maximum c/c0 values of <0.4 and <0.2 respectively. From the mass balance it was calculated that only 10% and 20% of the infiltrated amount of ibuprofen and bezafibrate were found at sampling-point #1, respectively. In contrast to that clofibric acid was found at about 80% and diclofenac at about 85% of the initial amount.

After a passage of 40cm ibuprofen was not be detected anylonger. Only about 2% of the initial quantity of bezafibrate was recovered at sampling-point #2, while the mass balance resulted in 70% and 65% of the initial amount for clofibric acid and diclofenac, respectively.

The decrease of the recovered quantities continued at sampling-point #3 (60cm). 50% and 40% of the initial amounts of clofibric acid and diclofenac were

found here, respectively. Bezafibrate was not detected in any sample from this sampling-point.

Figure 9 shows the breakthrough curves for clofibric acid and diclofenac after 80cm (sampling-point #4), which is comparable to the thickness of the filter bed of the slow sand filtration units, described before.

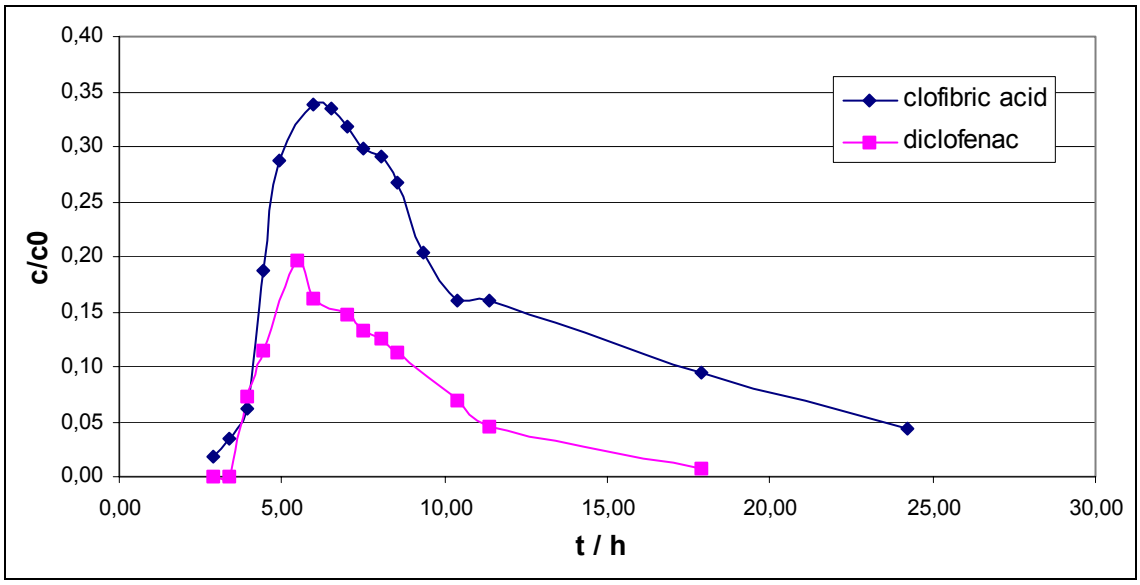


Fig. 9: Breakthrough curves of pharmaceuticals measured at a depth of 80cm in the enclosure during enclosure experiment #1 (05.-06.08.03)

In contrast to both experiments at the slow sand filter, a significant decrease of the clofibric acid concentration was observed in enclosure experiment #1. After 80cm only 35% of the initial amount was detected. Results for clofibric acid are summarised in figure 10. Similarly, the amount of diclofenac recovered at this sampling point were also much lower (15%) than in the slow sand filtration experiments (~30%), although photolytic degradation was inhibited by covering the enclosures (figure 11).

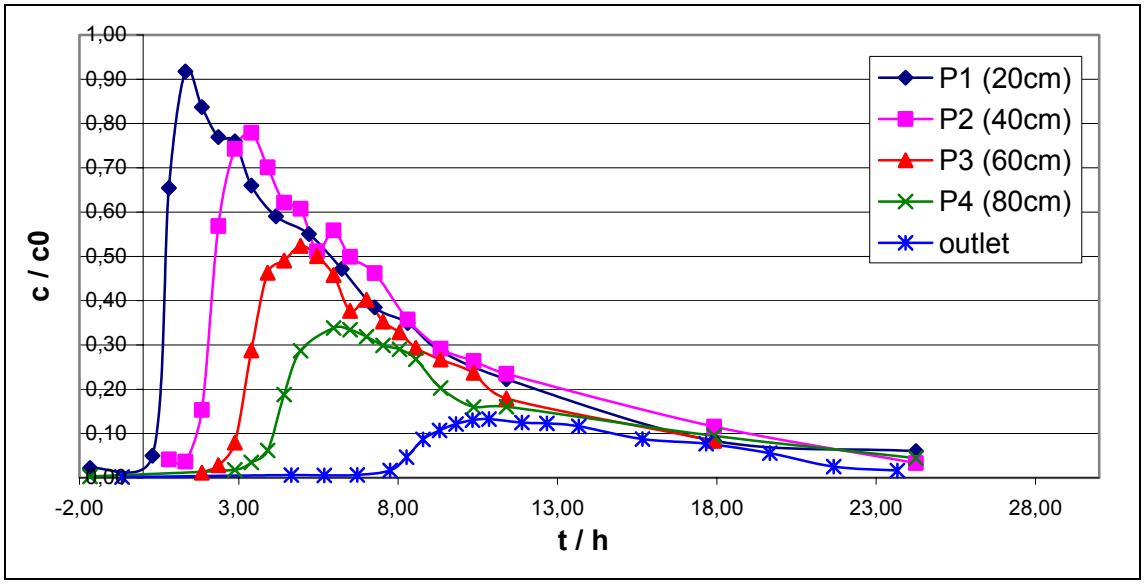


Fig. 10: breakthrough curves of clofibric acid measured during enclosure experiment #1 (05.-06.08.03)

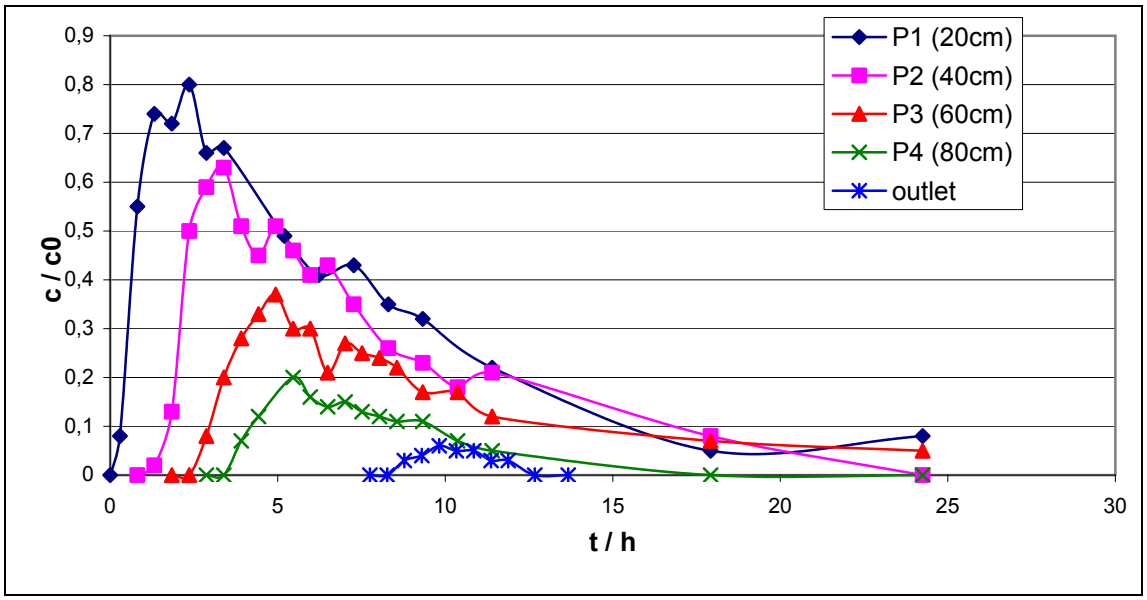


Fig. 11: breakthrough curves of diclofenac measured during enclosure experiment #1 (05.-06.08.03)

In contrast to that, the data of the conductivity measurement was nearly identical to those of the first two slow sand filtration experiments resulting in the breakthrough curves shown in figure 12.

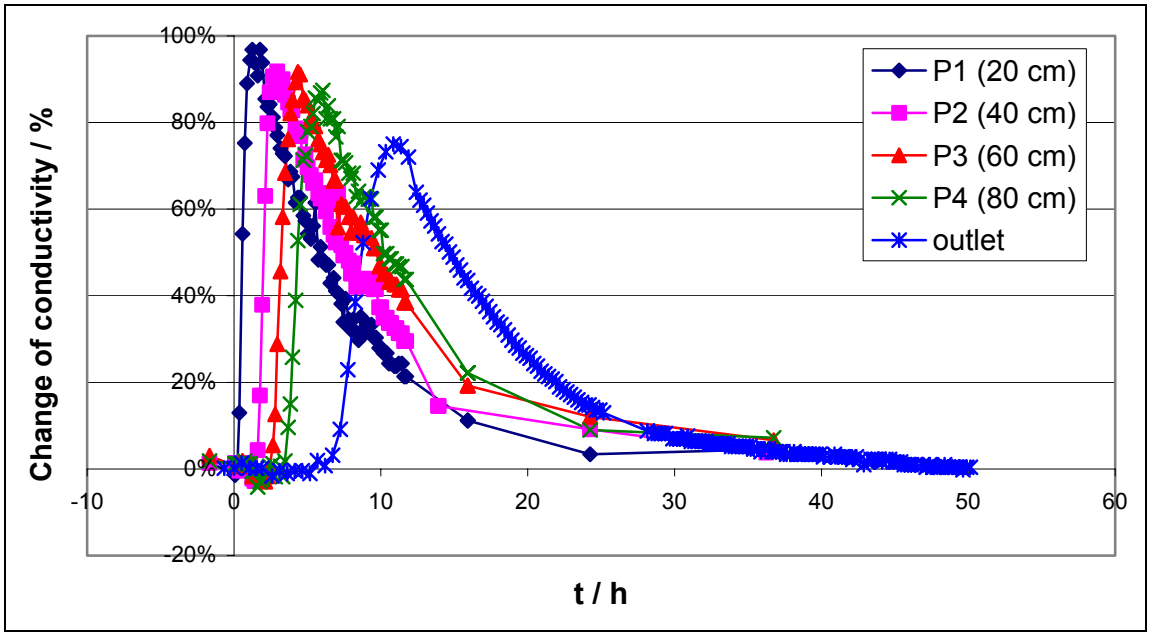


Fig. 12: temporal change of conductivity measured during enclosure experiment #1 (05.-06.08.03)

These curves showed only the typical decrease of the maximum conductivity after breakthrough caused by dispersion. Thus, a distinct difference between the conductivity data and the results for clofibric acid was observed in this experiment.

The second experiment at the enclosures was carried out one month later.

Tab. 6: Experimental conditions for enclosure experiment #2

Enclosure experiment #2		
Date	**09.– 10.09.2003**	
Flow rate	**0,05 m^3/h**	
Filtration velocity	**1,1 m/d**	
Initial concentration of pharmaceuticals	**clofibric acid diclofenac**	**ibuprofen bezafibrate**
	2µg/L	**5µg/l**
Condition of the sediment surface	**slightly developed clogging layer**	

For ibuprofen and bezafibrate the results of the first enclosure experiment were also confirmed in this experiment. However, both substances appeared to be

removed even more efficiently in this experiment with a slightly developed clogging layer. After 20cm (fig. 13) only about 3% of bezafibrate and 1% of ibuprofen were recovered, respectively.

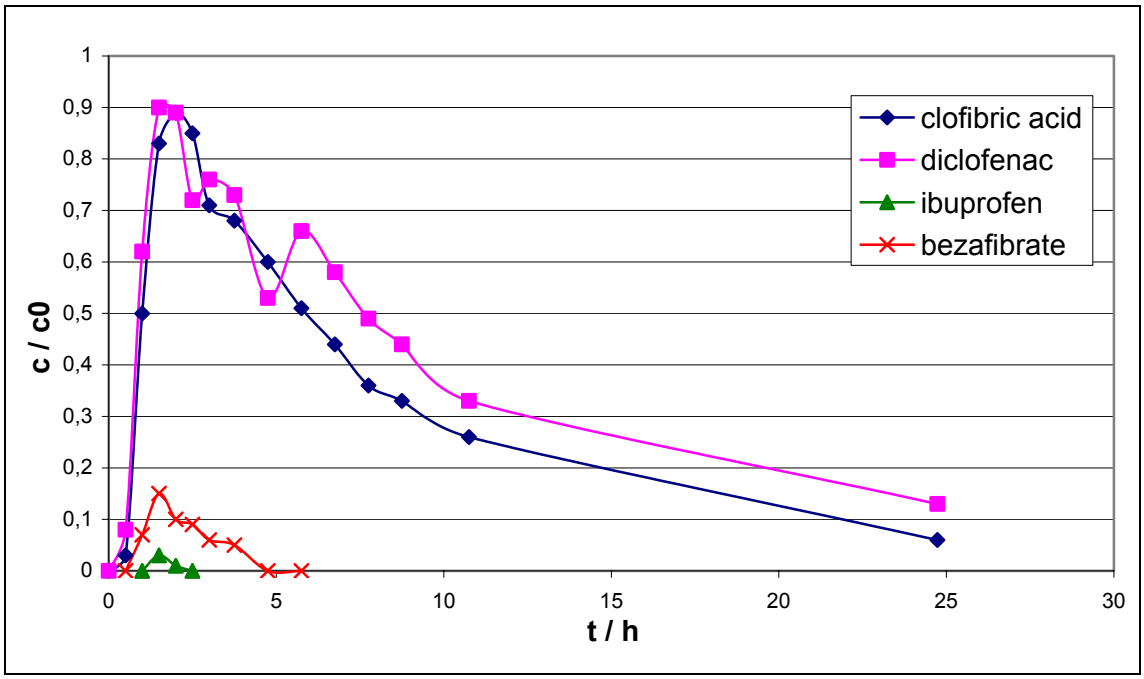


Fig. 13: Breakthrough curves of pharmaceuticals measured at a depth of 20cm in the enclosure during enclosure experiment #2 (09.-10.09.03)

Diclofenac again was found to be significantly attenuated, but was still detectable at distinct concentrations after 80cm (fig. 14).

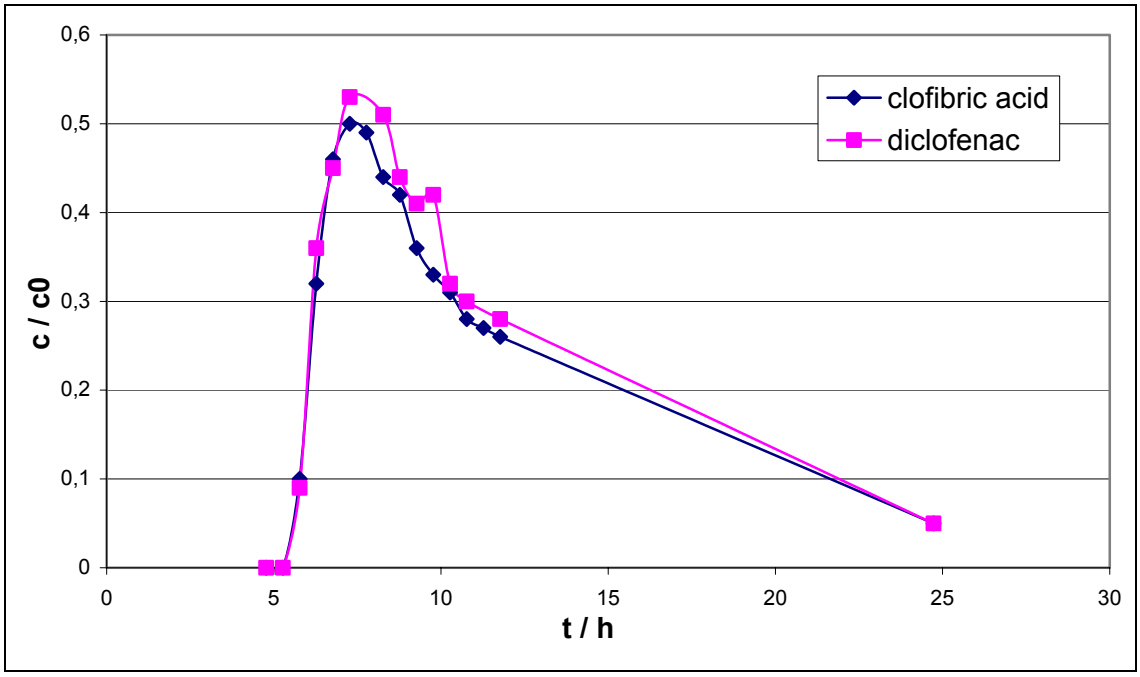


Fig. 14: Breakthrough curves of pharmaceuticals measured at a depth of 20cm in the enclosure during enclosure experiment #2 (09.-10.09.03)

The mass balance resulted in a recovery of 60% of the initial amount of diclofenac at sampling-point #4.

For clofibric acid the results of enclosure experiment #2 did not confirm those of experiment #1. 55% of the initial quantity of clofibric acid was detected at sampling-point 4. This is still less than the amount that was recovered in the first two slow sand filtration experiments, but the dramatic decrease of the total amount of clofibric acid that was observed in the first enclosure experiment (35%) was not observed again.

3. Discussion

The results from the experiments at the UBA facilities show that sand filtration is an efficient method to remove residues of pharmaceuticals such as ibuprofen and bezafibrate. This was confirmed by the slow sand filter experiments where both substances could not be detected in the outlet. This result was also confirmed in both enclosure experiments where the calculated mass balance

showed that both substances are already significantly attenuated in the first cm of the sand passage.

In enclosure experiment #2 with a slightly developed clogging layer the removal seemed to be even more efficient. This may indicate, that ibuprofen and bezafibrate are subject to a microbial degradation and that their removal is not only a result of an adsorption to the sediment. This would also be in accordance with other studies about these substances, which describe bezafibrate as a substance with little sorption properties (Ternes et al., 2002) and ibuprofen to be well degradable by microorganisms under aerobic conditions (Zwiener et al., 2000).

For diclofenac the enclosure experiments approved the assumption of a photolytical degradation. Thus, the rapid decrease of the diclofenac concentration that was observed in the first two experiments with slow sand filtration did not occur in the covered enclosure experiments carried out in the dark. All experiments show that diclofenac can be significantly attenuated but not completely removed by sand filtration.

Clofibric acid showed a different and varying attenuation behavior in these experiments. Especially, the results of enclosure experiment #1 and the first two experiments with slow sand filtration are contradictory. A recovered amount of only 35% of the initial quantity after 80cm sand passage (in enclosure experiment #1) was not exspected for this substance, which has been described as being rather persistent (Zwiener and Frimmel, 2000; Ternes et al., 2002, Andreozzi et al., 2003) and mobile (Mersmann et al., 2002) during groundwater recharge. As described above the first two experiments seemed to confirm this behavior during sand filtration, too. Nevertheless it was also reported that sand filtration has a certain ability to remove clofibric acid (Sacher et al., 2000; Preuß et al., 2001).

Several suggestions were considered about the differences between the experiments, that could possibly give an explanation for the observed differences. For example, it was suggested that there was an increased microbial activity caused by the high temperatures during enclosure experiment #1 in August 2003. On the other hand results of the first two experiments were comparable, although data showed that at least air temperatures varied stronger between these experiments than for example between slow sand filter experiment #2 and enclosure experiment 1.

Other considerations were made concerning a possible adaption of microorganisms at the filtration facility after the first two experiments or experimental errors like the usage of methanol helping to dissolve the pharmaceuticals for the experiments at the slow sand filter, but finally the observed differences could not be explained satisfactorily.

4. Summary

The behavior of four pharmaceuticals, namely clofibric acid, diclofenac, ibuprofen, and bezafibrate during sand filtration was investigated in four experiments carried out in co-operation with several other working groups of the NASRI-project at the facilities of the UBA in Berlin-Marienfelde.

Part of this field is a large storage pond with four slow sand filter units included in this facility. Within one of these filters three so-called enclosures, cylindrical pipes of about 1m height, were installed. Two experiments were carried out at one of the slow sand filters and at one of the enclosures, respectively. At the slow sand filters, samples could only be taken from the supernatant water layer and from the outlet. At the enclosure samples could also be taken also from four different depths (20cm, 40cm, 60cm, and 80cm) beneath the surface of the sediment.

The four selected pharmaceuticals showed distinct differences in their attenuation behavior. The results showed and confirmed that residues of less polar or less persistent pharmaceuticals such as bezafibrate and ibuprofen can efficiently be removed during sand filtration. Both substances were significantly attenuated within the first 20cm of the sand passage and were not detected in the outlet of the slow sand filters or the enclosure column.

For diclofenac a significant but no complete removal was observed. At the same time the experiments confirmed that this substance undergoes a photolytical degradation in the surface water of the slow sand filter caused by natural sunlight radiation.

Clofibric acid showed a inconsistent behavior in the experiments. In the slow sand filter experiments the concentration changes measured for clofibric acid were almost identical to those of sodium chloride, used as a tracer compound. However, in one of the enclosure experiments clofibric acid was found to be attenuated and the initial amount decreased to a quantity of only 35% of the infiltrated quantity after 80cm. The cause for this observed difference could not yet be explained satisfactorily.

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5.5 Occurrence and fate of pharmaceutical residues at the artificial groundwater enrichment plant in Berlin-Tegel

Description of the field site

The artificial groundwater enrichment plant Berlin-Tegel (GWA) is located in the north-western districts of Berlin at the eastern shore of Lake Tegel. Heart of this plant, belonging to the water work Tegel, is the recharge pond 3 (RP 3), which is used for infiltration of surface water, and the water work supply well 20. RP 3 is continuous filled with prefiltrated surface water from Lake Tegel. This surface water is under the influence of municipal sewage effluents from the sewage water treatment plant Schönerlinde located in northeast of Berlin and by surface water from the Havel River. Former investigations of this river detected PhACs at individual concentrations up to the µg per liter level [Heberer et al., 1998, 2002]. Each year about 15 mio. m^3 surface water infiltrate into the subsoil. The hydraulic conductivity in every samplepoint is similar and ranges from 1^{-3} - 1^{-4} (m/s). The hydraulic conductivity depends on the composition of the clogging layer at the bottom of the recharge pond. In progress of a continuous sedimentation of suspended matter and algae growth the hydraulic conductivity is decreasing. Therefore, it is necessary to remove the first centimeters of the ground to ensure a constant water flow. In general, the flow retention time of the infiltrated water from RP 3 to water work supply well 20 is less than two month.

Figure 1: Artificial groundwater enrichment plant Berlin-Tegel

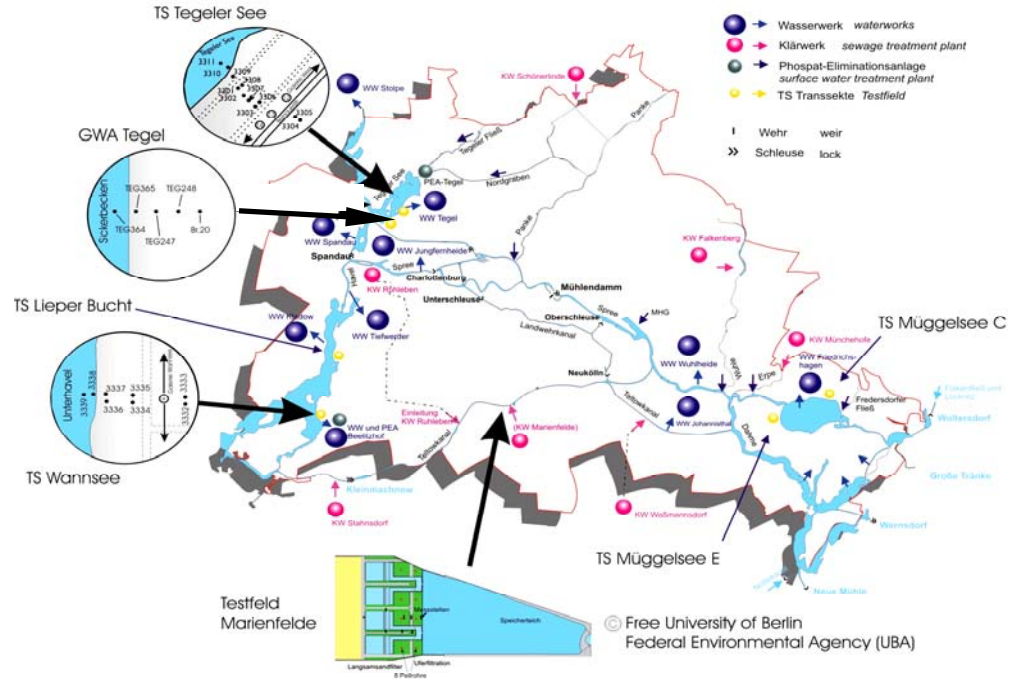

Figure 2: Location of the artificial groundwater enrichment plant Berlin-Tegel (GWA)

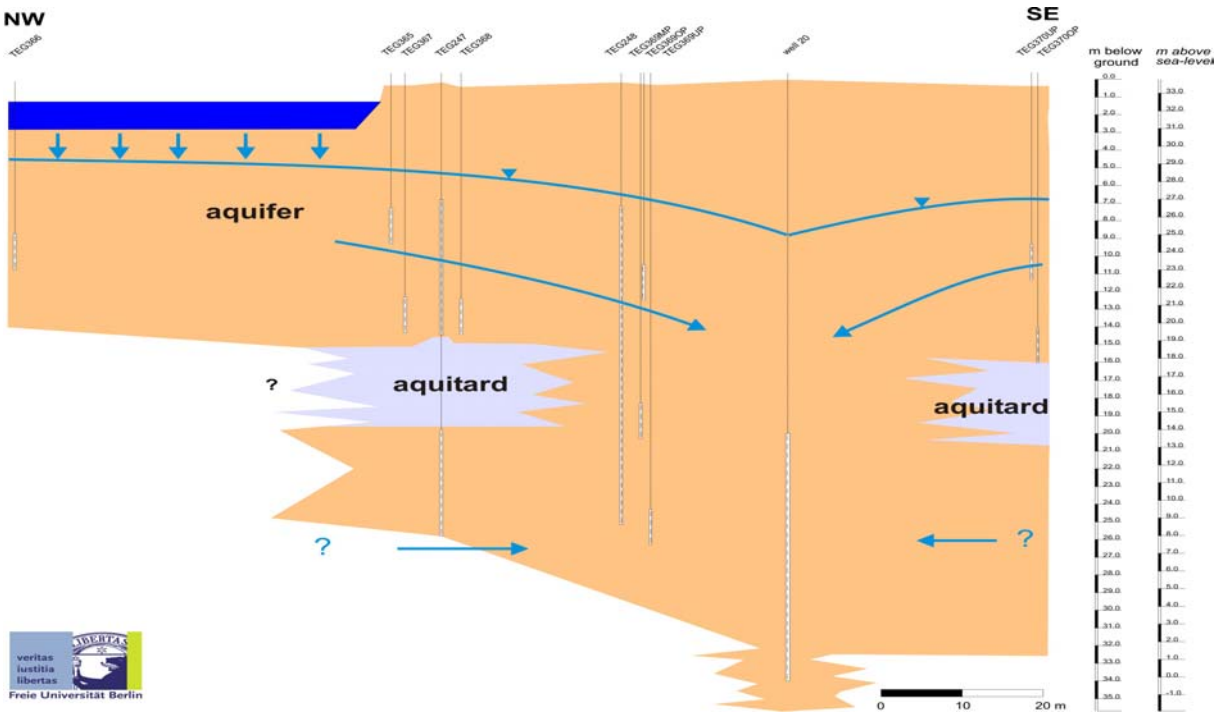

Figure 3: Hydrogeological cross section of the transect GWA Tegel with the recharge pond 3 and the water works well 20

The field site is equipped with different types of monitoring wells screened at various depths and drilled between the recharge pond, the water supply well and also at the landward side behind the water-supply well. A hydrogeological cross section of the transect is shown in figure 3.

The measurements at the GWA Tegel started in July 2002 and were carried out over a 12 month period. This transect sampled monthly allows to monitor the fate and transport of PhACs during groundwater recharge. Sampling points Teg 366 and Teg 365 and the water supply well 20 were sampled for 12 months, whereas sampling points Teg 247, Teg 248 and Teg 342 were analysed for 8 months (July 2002 to February 2003) and sampling points Teg 368, Teg 369 OP, Teg 369 UP, Teg 370 OP und Teg 370 UP for 6 months (January 2003 to June 2003). The analysis of the samples was carried out by a solid phase extraction (SPE), chemical derivatization and detection by gas chromatography mass spectrometry (GC/MS) applying selected ion monitoring (SIM). Two novel analytical methods allow the trace-level detection of the PhACs even in complex environmental samples [Reddersen and Heberer, 2003].

Results from the GWA investigations (July 2002 to June 2003)

In the monthly measurements at the transect GWA-Tegel 8 PhACs and 5 other contaminants were detected. The drug residues were bezafibrate, carbamazepine, diclofenac, indometacine, primidone, propyphenazone and the drug metabolites clofibric acid and AMDOPH. Furthermore, the pesticides 2,4-D, dichlorprop, MCPA and mecoprop as well as NPS (metabolite of a corrosion inhibitor) were also found in these samples. Figure 4 shows a MID-chromatogramm of the PFBBr-derivatized extract of sample RP 3 collected in November 2002. The antiepileptic drugs Carbamazepine and Primidone were derivatized with MTBSTF and do not appear in this chromatogramm.

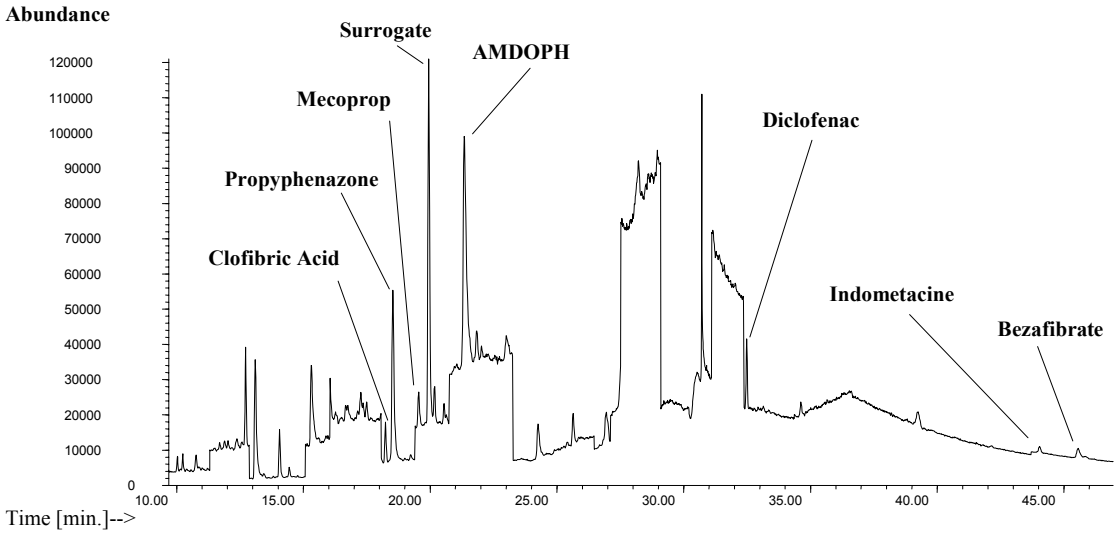

Figure 4: MID-chromatogramm of the derivatized extract of sample RP 3 collected in November 2002

A summary of all results is shown in table 1. It compiles the mean concentrations (n=12/8/6) of drugs and drug metabolites detected at the individual sampling points throughout the entire sampling period. Results from the other contaminants are shown elsewhere.

Table I: Mean concentrations [ng/l] of target PhACs throughout July 2002 to June 2003

PhAC	RP 3	Teg 366	Teg 365	Teg 247	Teg 368	Teg 248	Teg 369 OP	Teg 369 UP	Well 20	Teg 370 OP	Teg 370 UP	Teg 342
	n=12	n=12	n=12	n=8	n=6	n=8	n=6	n=6	n=11	n=6	n=6	n=8
Flowdirection:	→	→	→	→	→	→	→	→	←	←	←	←
AMDOPH	455	440	395	425	390	315	300	330	1570	1085	3915	160
Carbamazepine	470	545	430	385	460	430	220	230	210	20	20	15
Primidone	135	140	125	115	170	95	80	90	100	30	70	15
Propyphenazone	120	20	20	30	15	20	10	10	40	10	55	20
Clofibric Acid	20	5	5	10	10	5	5	5	5	15	n.d.	10
Diclofenac	135	15	45	5	15	10	n.q.	n.q.	10	n.d.	n.d.	n.d.
Indometacine	n.q.	n.q.	n.q.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Bezafibrate	30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

n.d.: not detected n.q.: not quantitated

The individual PhACs show a very different removal behaviour on their way on the soil passage to water-supply well 20. On the basis of PhAC removal rates calculated between RP 3 and well 20 these PhACs could been classified into three groups.

Table 2: Classification of target PhACs according to their removal rates

Group	PhACs	Mean removal rate up to Teg 248 [%]	Mean removal rate up to well 20 [%]
1 removal rate 0-50 %	AMDOPH	28	exceptional case
	Carbamazepine	9	(55)
	Primidone	30	26
2 removal rate 51-99 %	Propyphenazone	83	67
	Clofibric Acid	75	75
	Diclofenac	93	93
3 removal rate 100 %	Indometacine	100	100
	Bezafibrate	100	100

- Group 1 includes AMDOPH, carbamazepine and primidone and is characterized by modest removal rates of ≤ 30 % up to well 20. The higher removal rate (55%) for carbamazepine observed in well 20 is mainly caused by dilution with landward groundwater (Teg 370 OP to Teg 342), which shows only very low concentrations of carbamazepine. This assumption is also supported by the results obtained for sampling point Teg 248, which almost exclusively consists of water recharged from RP 3. In this case only a minor removal rate of 9 % was observed for carbamazepine. The drug metabolite AMDOPH represents an exceptional case. AMDOPH was detected in ground water samples from well 20 at average concentrations 240 % higher, than those in RP 3. This observation can be explained by the production spills of a former pharmaceutical production plant north of Berlin, which led to high concentrations of AMDOPH and the original drug dimethylaminophenazone in the Havel river and in the groundwater of northwestern districts of Berlin [Reddersen et al., 2002]. For sampling point Teg 248, only

influenced by the surface water of RP 3, a mean removal rate of 28 % was observed for AMDOPH.

- Group 2 includes clofibric acid, diclofenac and propyphenazone. These drugs are characterized by high removal rates of more than 70%. The elevated concentrations of propyphenazone in well 20 can be explained by the shares of contaminated landward groundwater (Teg 370 UP). Despite their good removal rates, portions of all three drugs arrived in the water of well 20.

- Group 3 includes bezafibrate and indometacine. These drugs were removed completely during the soil passage and could not even be quantified at sampling point Teg 366 (underneath RP 3) and near the bank at sampling point Teg 365.

Annual variations of the concentrations of the target PhACs

AMDOPH:

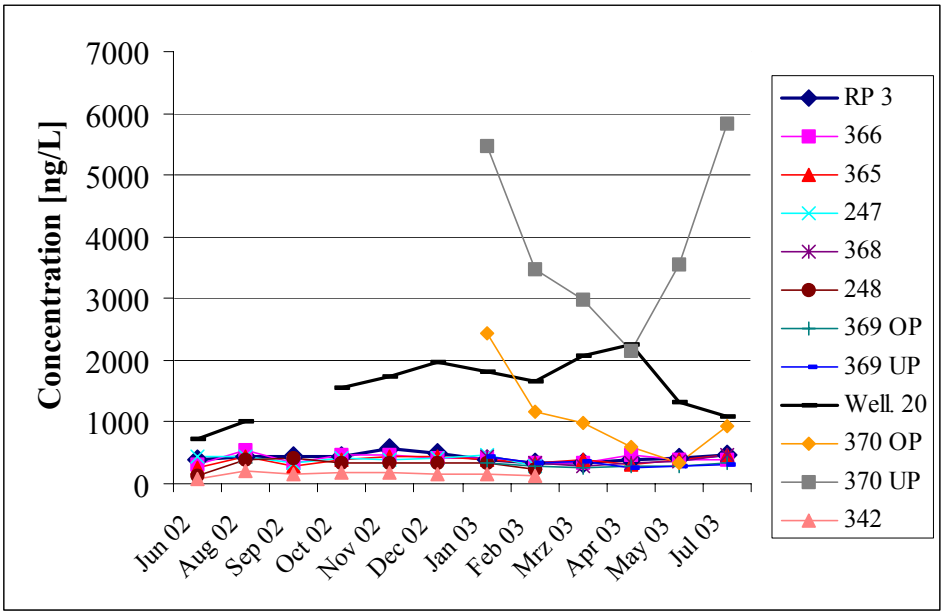

Figure 5: Concentration profiles of AMDOPH at the sampling points/wells (July 02 - June 03)

AMDOPH was detected with relatively constant concentrations in the surface water and in all wells that were only influenced by recent surface water recharge. In contrast to well 20 and the landward sampling wells they are not affected by contaminated landward groundwater, containing AMDOPH at concentrations between 225 and 570 ng/l. On the other hand, concentrations between 350 and 5845

ng/l of AMDOPH were found in the landward wells. The strong fluctuations of the concentrations in the monitoring wells Teg 370 OP and Teg 370 UP have to be attributed to the not yet completely clarified hydraulic conditions in the deeper groundwater aquifer. For the complete clarification of the hydraulic conditions in the deeper groundwater aquifers further hydro geological investigations are required. During the soil passage a mean removal rate for AMDOPH of 28 % in comparison to the surface water concentration was observed. This implies that under the prevailing recharge conditions, a majority of the AMDOPH (approx. 70%) was not adsorbed at soil particles or biodegraded by the microbial soil flora and reached almost unaffected the groundwater aquifer. Thus, the GWA is only less suitable for the removal of AMDOPH from surface water. Figure 6 shows a statistical evaluation of the AMDOPH concentrations at the individual sampling points as box plots graph. This figure also demonstrates the high mobility of AMDOPH as well as the low removal during the infiltration process. In addition it shows the high load of AMDOPH at the landward monitoring wells Teg 370 OP and Teg 370 UP and the water-supply well 20.

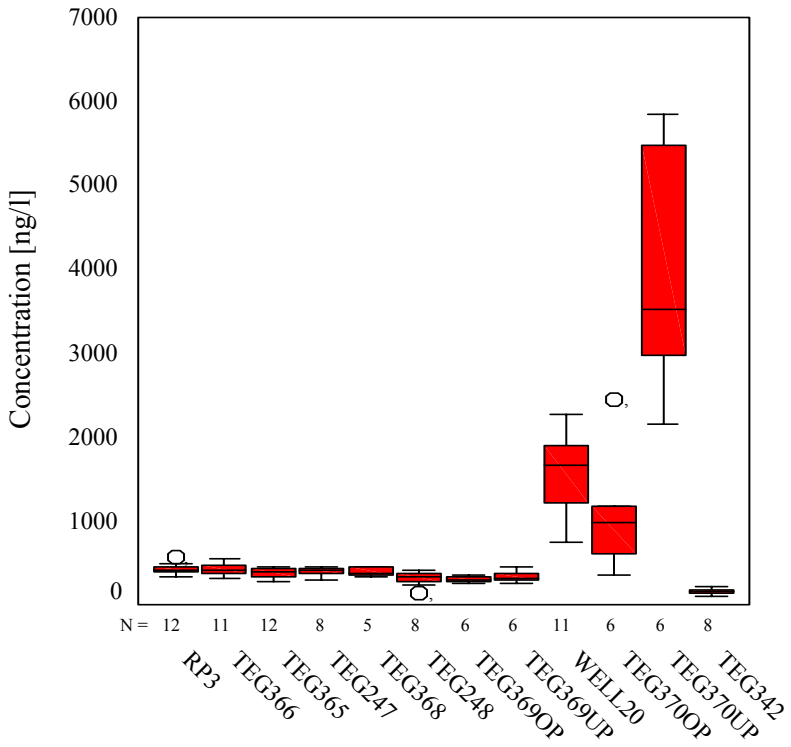

Figure 6: Boxplots of AMDOPH concentrations [ng/l] at the individual monitoring wells and the water-supply well 20

Carbamazepine:

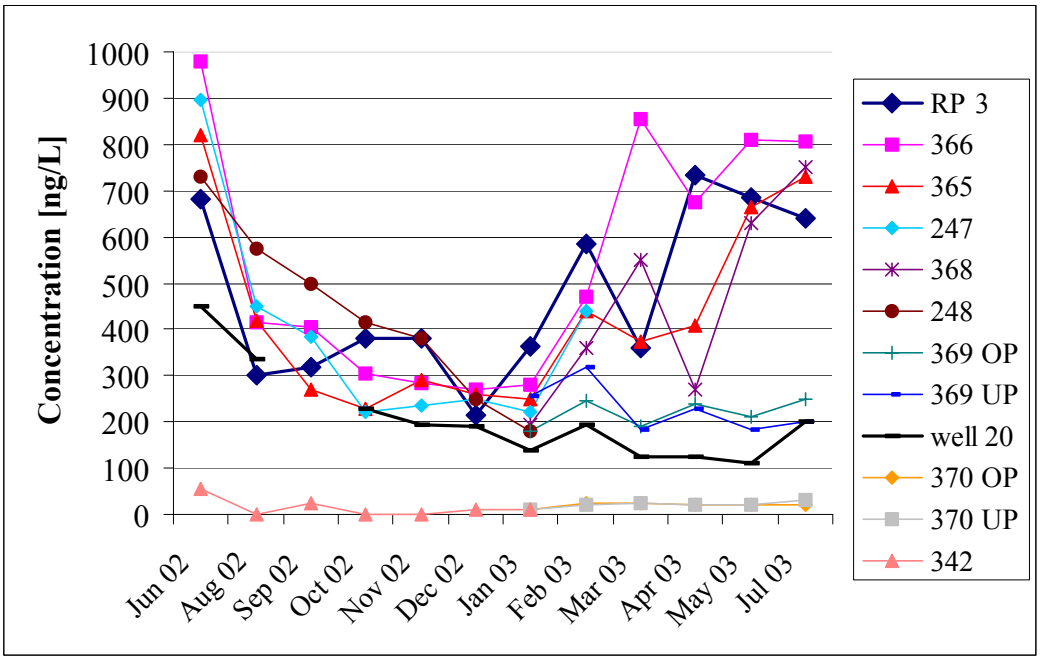

Figure 7: Concentration profiles of carbamazepine at the sampling points/wells (July 02 - June 03)

Carbamazepine was found with very variable concentrations in the surface water (RP 3) and in all wells except for the landward monitoring wells. It was detected in the surface water at concentrations up to 1 µg/l. The strong increase of the concentrations of carbamazepine starting in March 2003 might be explained by the phasing out of the sewage water treatment plant in Falkenberg located in the east districts of Berlin. Since March 27, 2003 its waste water was directed to the sewage water treatment plant in Waßmannsdorf (2/3) located in the south of Berlin and to the sewage water treatment plant in Schönerlinde (1/3) north of Berlin. The treated waste water from the sewage water treatment plant in Schönerlinde is discharged into the Nordgraben, which flows into Lake Tegel and causes an increase of the drug concentrations in the surface water. In tendency, the concentration profiles at the monitoring wells up to the water-supply well 20 follow the temporal changes of the concentration measured in the surface water. There is no significant removal of carbamazepine along the transect. Thus, up to monitoring well Teg 248, a mean removal rate of only 9 % was observed for carbamazepine. Carbamazepine, similar to AMDOPH, represents a very mobile drug residue, only attenuated to small degree under the prevailing recharge conditions. Thus, the GWA is less suitable for the

removal of carbamazepine from surface water. Figure 8 shows a statistical evaluation of the carbamazepine concentrations detected in the individual monitoring wells and in water-supply well 20. It shows the high mobility of Carbamazepine as well as the small removal during the infiltration process.

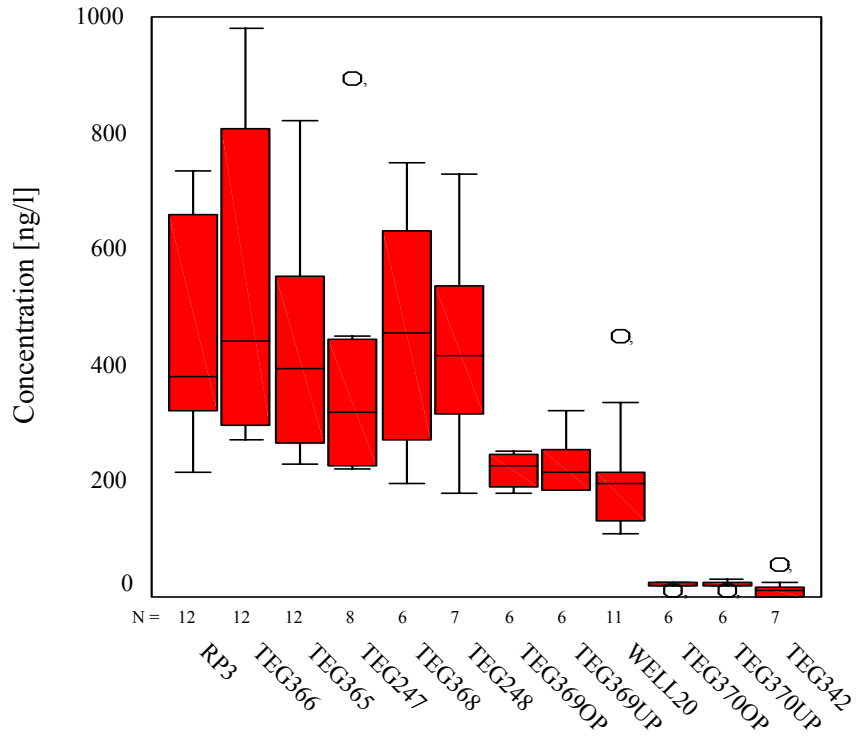

Figure 8: Boxplots for the carbamazepine concentrations [ng/l] measured at the individual sampling wells

Primidone:

Exactly like carbamazepine, primidone was detected with very variable concentrations in the surface water and in all monitoring wells. The increase of the concentrations, due to the distribution of the sewage treatment plant in Schönerlinde, starting in March 2003 could been recognized. In tendency, the concentration profiles of the monitoring wells up to the water-supply well 20 follow the temporal changes of the concentrations measured in the surface water. There is no significant removal of primidone along the transect. Thus, up to monitoring well Teg 248, a mean removal rate of 30 % was observed for primidone. The removal rate of primidone up to well 20 is not substantially improved (26 %), because Primidon was also detected in the landward sampling points at average concentrations of 70 ng/l. Primidone, similar to AMDOPH and Carbamazepine, is characterised by a very high mobility, and is only

attenuated to small degree under the prevailing recharge conditions. Figure 6 shows a statistical evaluation of the primidone concentrations at the individual sampling points as boxplots graph. This figure also demonstrates the high mobility of primidone as well as the low removal during the infiltration process.

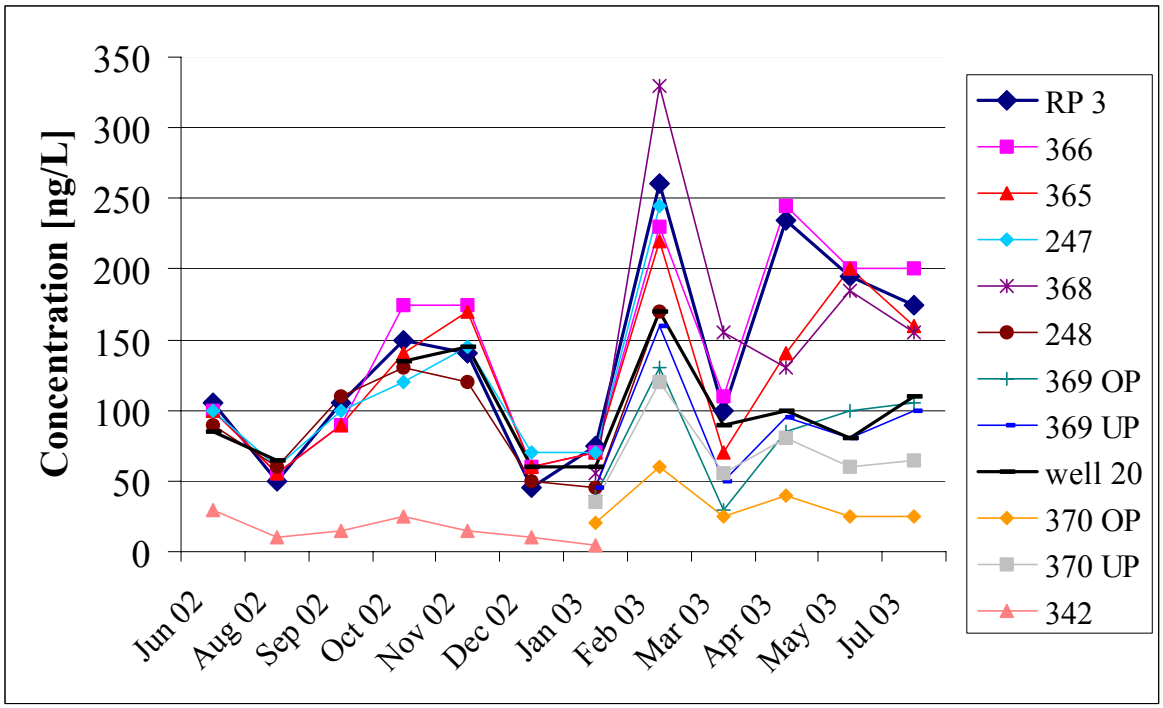

Figure 9: Concentration profiles of primidone at the sampling points/wells (July 02 - June 03)

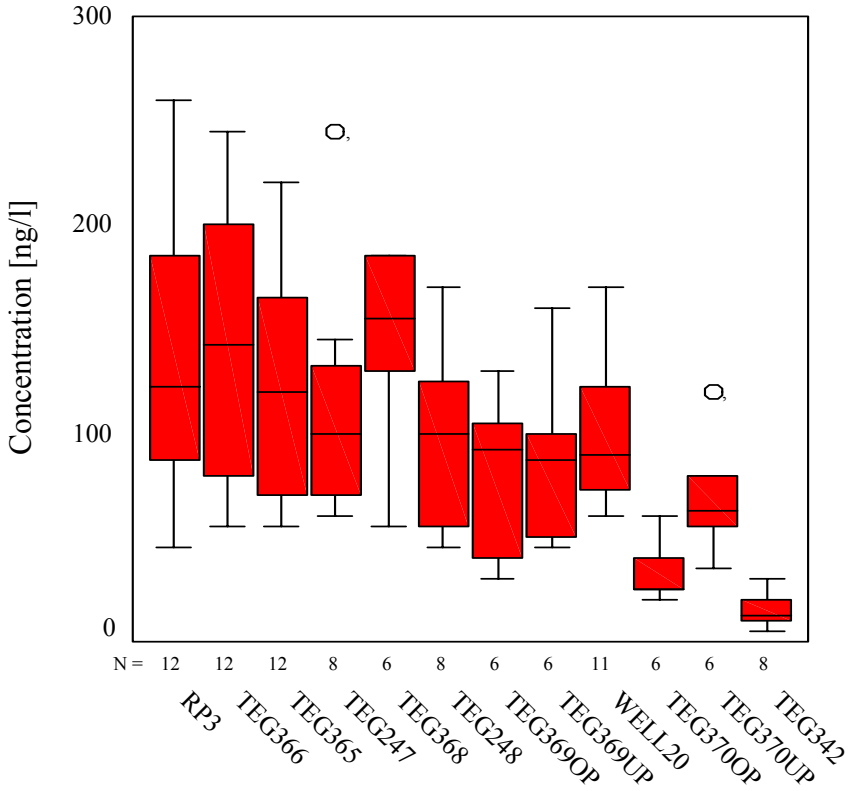

Figure 10: Boxplots of primidone concentrations [ng/l] at the individual monitoring wells and the water-supply well 20

Propyphenazone:

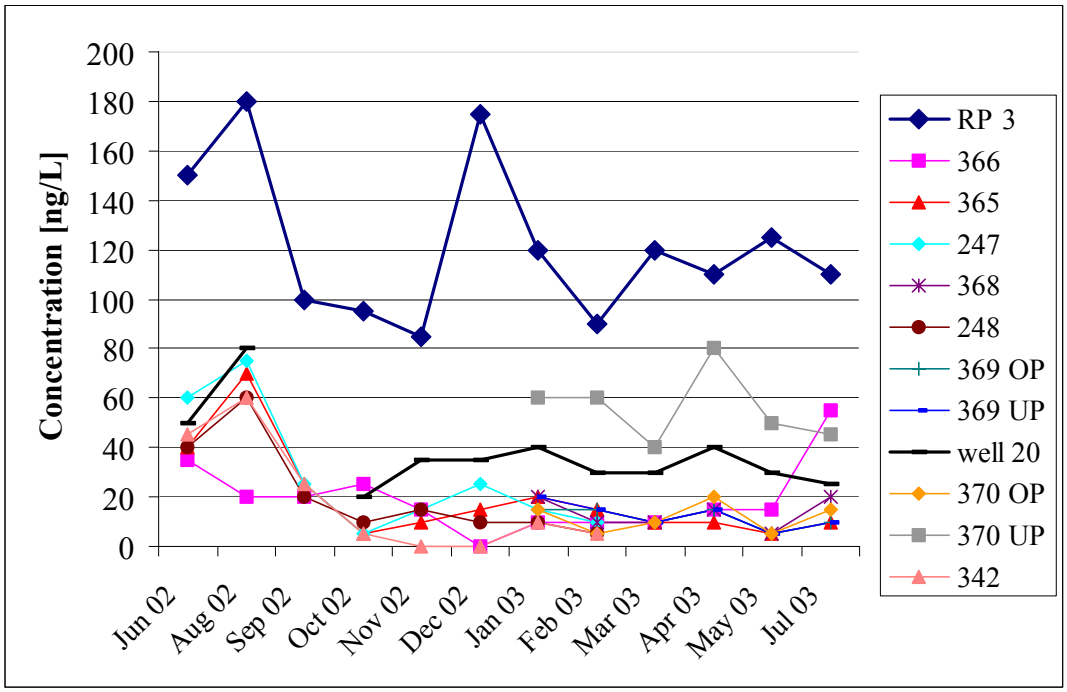

Figure 11: Concentration profiles of propyphenazone at the sampling points/wells (July 02 - June 03)

Propyphenazone was detected with relatively constant concentrations in the surface water (Fig. 11). The discharge of the sewage treatment plant Schönerlinde starting from March 2003 did not caused a significant increase of propyphenazone concentration in the surface water of Lake Tegel. This is supported by the constant decline in the prescription of propyphenazone as part of analgesic formulations. The main source for propyphenazone in the surface water of Lake Tegel are residues from the Havel river, which is contaminated by production spills of a former pharmaceutical production plant [Reddersen et the al., 2002]. In contrast to the group 1 PhACs, a much higher removal rate is reached for propyphenazone. A removal rate of 83 % was observed up to the monitoring well Teg 248. Propyphenazone loaded, landward groundwater (Teg 370 UP) caused an alleged lowering of the removal rate to 67 % at well 20. In general, the GWA is suitable for the pretreatment of propyphenazone loaded surface water lowering its concentration. Figure 6 shows a statistical evaluation of the propyphenazone concentrations at the individual sampling points as box plots graph. This figure also demonstrates the attenuation of propyphenazone during the soil passage.

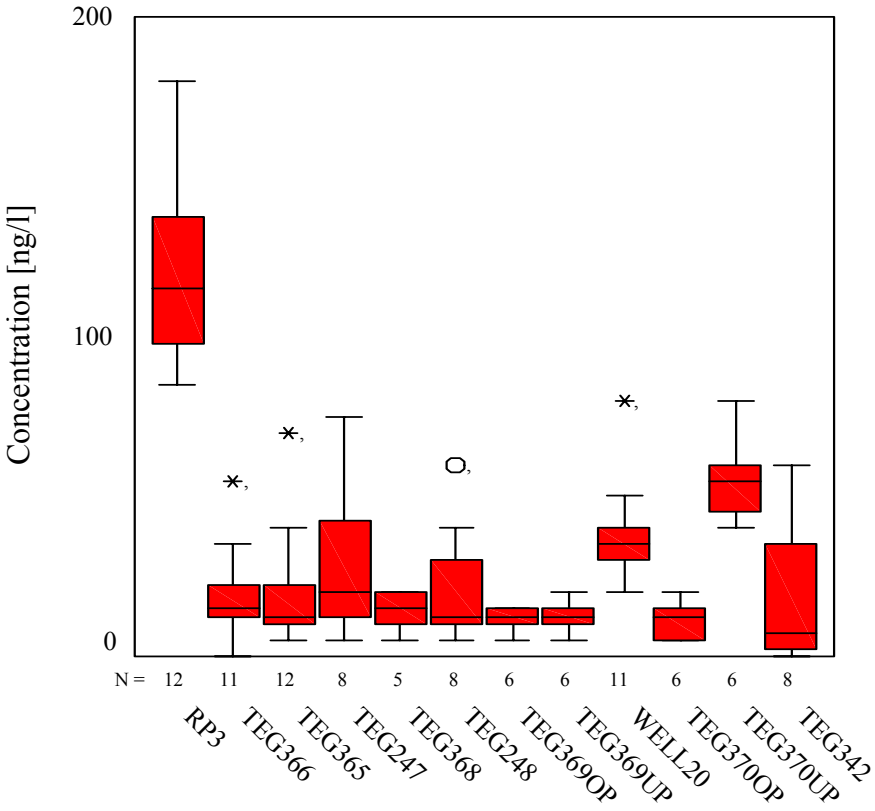

Figure 12: **Boxplots of propyphenazone concentrations [ng/l] at the individual monitoring wells and the water-supply well 20**

Diclofenac:

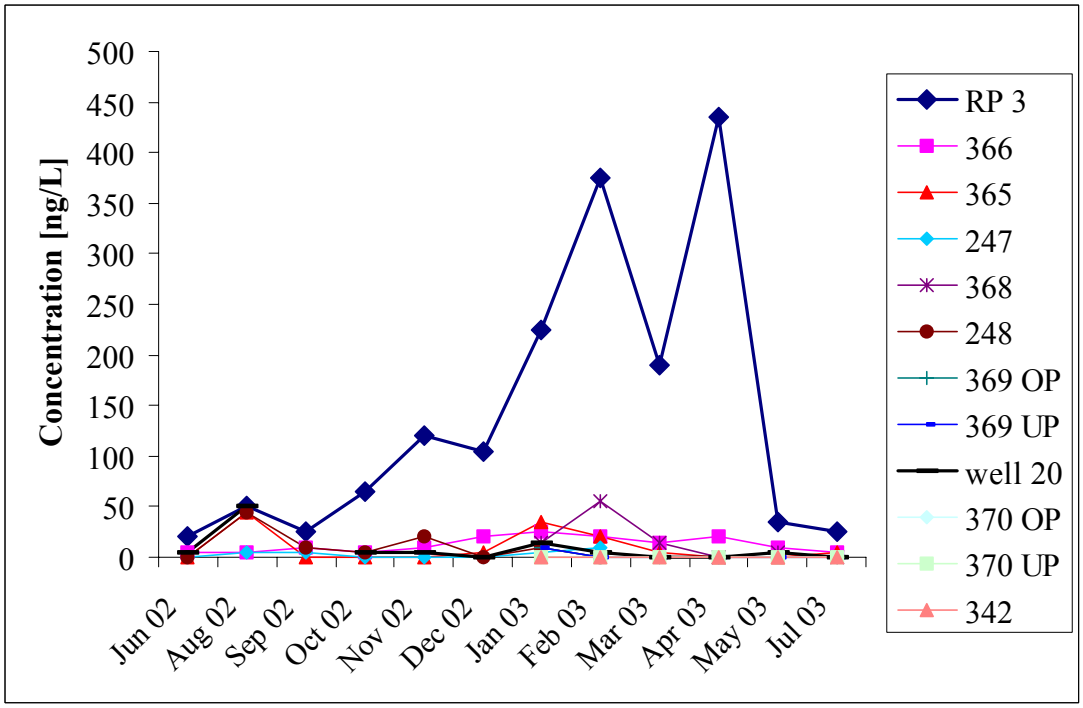

Figure 13: Concentration profiles of diclofenac at the sampling points/wells (July 02 - June 03)

The concentration profile of diclofenac in surface water shows pronounced temporal variations (Fig. 13). Higher concentrations between 65 and 435 ng/l during the winter and spring months decreased to values below 50 ng/l in the summer months. This is most likely caused by the photochemical degradation of diclofenac, as already described by Buser et al. (1998) and Tixier et al. (2003). Diclofenac was measured at relatively constant concentrations clearly below 50 ng/l in all monitoring wells up to water-supply well 20. This also demonstrates the ability of the GWA for the attenuation of diclofenac even with high concentrations in the winter months. At monitoring well Teg 248 and at water-supply well 20 a mean removal rate of 93% was determined. Thus, the GWA was found as being suitable for the pretreatment of diclofenac loaded surface water. Nevertheless, the removal is not complete and still small portions of diclofenac infiltrate into the groundwater aquifer and reach water-supply well 20. Figure 13 shows a statistical evaluation of diclofenac concentrations at the individual sampling points as boxplots graph. This figure also demonstrates the attenuation of diclofenac during the soil passage.

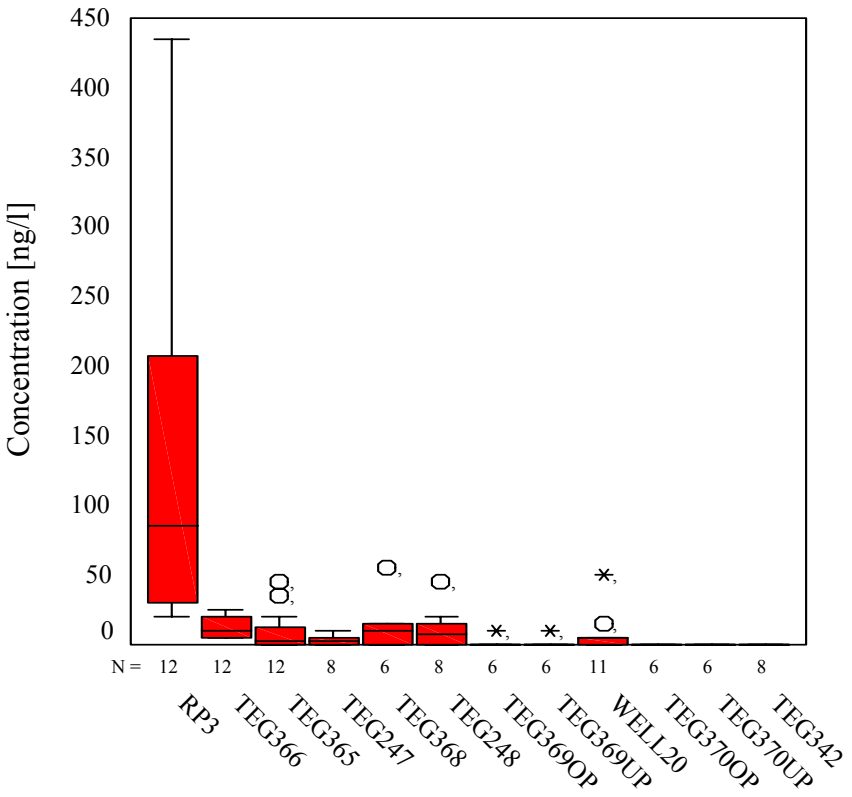

Figure 14: Boxplots of diclofenac concentrations [ng/l] at the individual monitoring wells and the water-supply well 20

Clofibric Acid:

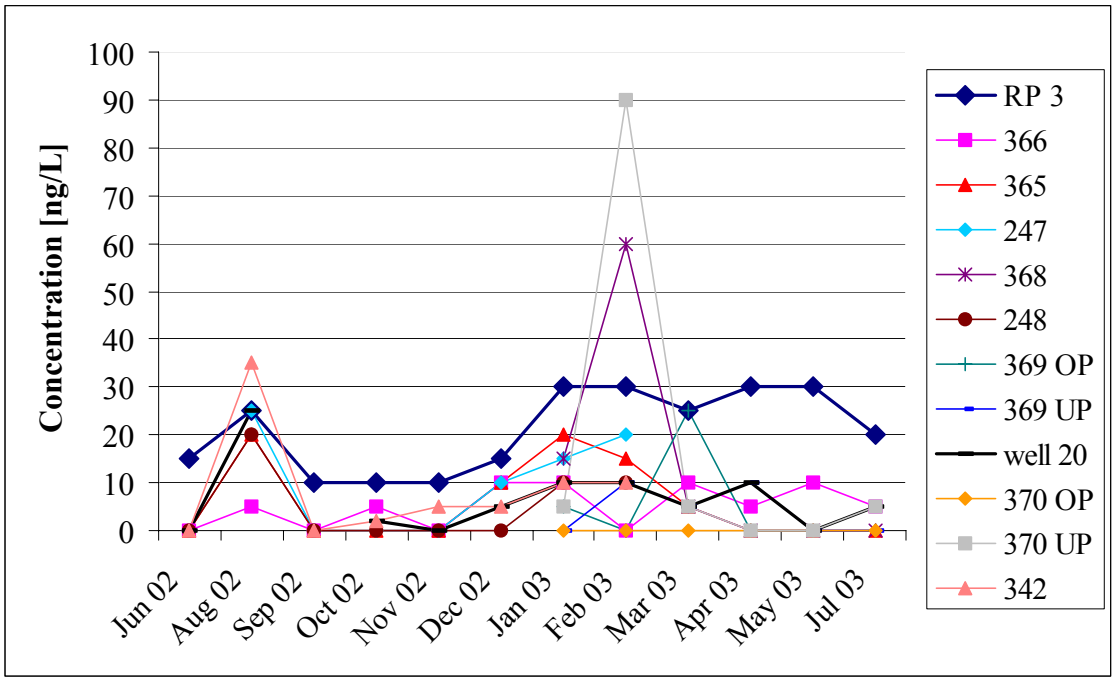

Figure 15: Concentration profiles of clofibric acid at the sampling points/wells (July 02 - June 03)

The drug metabolite clofibric acid was found with relatively constant concentrations in the surface water and in all monitoring wells. It was detected in the surface water at concentrations between 10 and 30 ng/l. Exactly like propyphenazone much higher removal rates result. Thus, up to both sampling points Teg 248 and water-supply well 20 an average removal rate of 75 % is observed. The clofibric acid based active substances were used more frequently in the past decades, thus, this persistente metabolite could adsorb already longer at the soil particles of the groundwater aquifer. The decreasing trend of the medication with derivatives of the clofibric acid is illustrated in the small concentrations in the surface water. However, thereby also the high persistence of the clofibric acid is demonstrated. Nevertheless, a relatively good decrease of the concentration could be observed. Thus, the GWA was found as being suitable for pre-treatment of clofibric acid loaded surface water. Figure 15 shows a statistical evaluation of clofibric acid concentrations at the individual sampling points as boxplots graph. This figure also demonstrates the attenuation of clofibric acid during the soil passage.

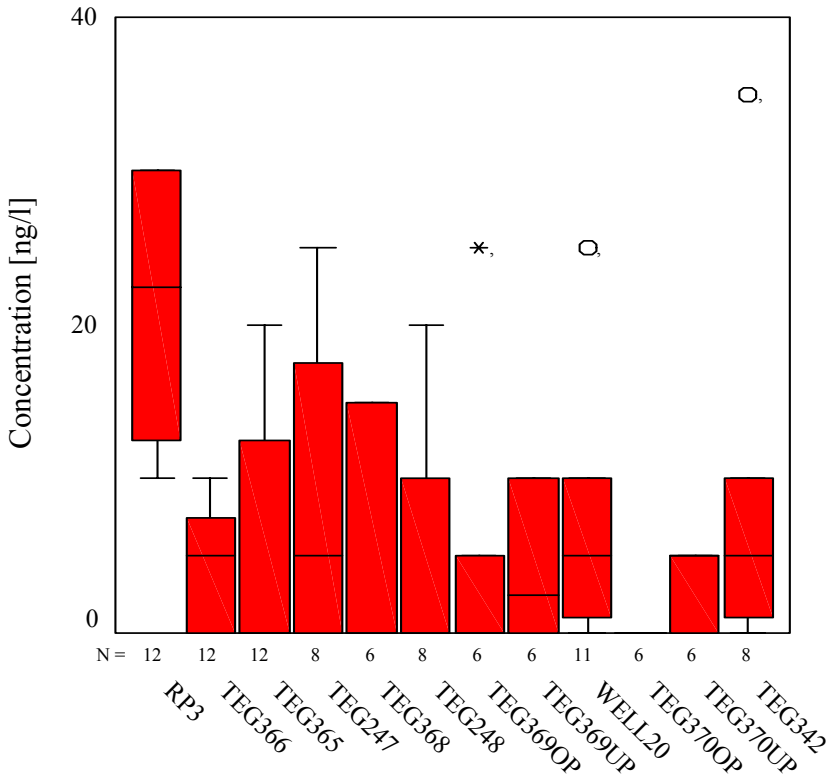

Figure 15: Boxplots of clofibric acid concentrations [ng/l] at the individual monitoring wells and the water-supply well 20

Bezafibrate and indometacine:

Bezafibrate and indometacine only occur in very small concentrations close to the limit of determination in the surface water. The remaining residues of both compounds were completely attenuated during ground water recharge, which was also observed by Brauch et al., 2000 and Heberer et al., 2002.

Conclusions

The results of this investigations show that there is a breakthrough of six of the eight detected drug residues during the artificial groundwater recharge into the water-supply well 20. Thus, the GWA can serve, due to the small cleaning achievement, at best for the pretreatment of contaminated surface water and is not sufficient for a complete removal of these residues.

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6. CONCLUSIONS AND PERSPECTIVES

The results from the field-sites, the semi-technical facilities (slow sand filters and enclosures) and the laboratory column experiments proved the ability of different groundwater recharge techniques for the removal of pharmaceutical residues and related contaminants. Non-polar or readily biodegradable compounds such as beza-fibrate or ibuprofen were easily removed at the field sites and in the different spiking experiments in the lab or at the semi-technical facilities. In contrast, very polar and persistent contaminants such as AMDOPH passed almost non-retarded all test systems and its concentration was only decreased by dilution. For other compounds and especially for clofibric acid the results were inconsistent. Clofibric acid was identified as mobile contaminant in the field-site investigations also present at considerable concentrations in the water-supply wells. On the other hand, a full removal of spiked clofibric acid was observed in the column experiments and a partial removal was also measured for the slow sand filter and enclosure experiments. Similar controversial results were also obtained for other compounds and give rise to the question of the applicability of the experiments carried out in the laboratory or at the semi-technical facilities to the natural/large-scale conditions at the field sites. Further experiments shall be clarifying this decisive question.

Perspectives / Intended tasks for the upcoming project period (January – December 2004)

Task	comments
Literature study	will be continued
Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Tegel”.	Will be continued until August 2004.
Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Wannsee I”.	Will be continued until August 2004.

Instrumental analysis of pharmaceutically active compounds, related polar contaminants and metabolites in samples from transect “Lake Wannsee II”.	Will be continued until August 2004.
Preparation and conduction of experiments at the semi-technical facility of the UBA: Measurements and interpretation of data from a second enclosure study with other pharma-ceuticals.	New practical experiments are currently conducted in cooperation with NASRI working groups “algae” (Dr. Chorus), “bacteria” (Dr. Schewzyk) and “hydrogeology” (Prof. Pekdeger) in terms of a master thesis by Eberhard Licht.
Preparation and conduction of batch sorption experiments for selected pharmaceuticals.	Practical experiments are currently conducted in cooperation with NASRI working group “hydrogeology” (Prof. Pekdeger) by Georges Pigoue.
Preparation and conduction of experiments at the semi-technical facility of the UBA: Measurements and interpretation of data from a third enclosure study with antibiotics.	New practical experiments are currently conducted in cooperation with NASRI working groups “algae” (Dr. Chorus), “bacteria” (Dr. Lopez-Pila) and “hydrogeology” (Prof. Pek-deger) in terms of a master thesis by a diploma student (beginning in 08/09 2004).
Additional unintended task:	
Measurement of antibiotics at the groundwater enrichment plant in Tegel (GWA Tegel)	Practical experiments will soon be started in terms of a diploma thesis by Stefanie Rögler.
Intensified interpretation of the scientific results and preparation of several scientific papers to be submitted to renown journals.	
Co-sponsoring of the 4th International Conference on Pharmaceuticals and Endocrine Disrupting Chemicals in Water, October 13-15, 2004, Minneapolis, Minnesota, USA. Preparation a special session on PhACs and EDCs during bank filtration.	

NASRI – Part 5

“Organic Substances in Bank filtration and Groundwater Recharge-Process”

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Content

Abbreviations

AOBr	Adsorbable Organic Bromine
AOI	Adsorbable Organic Iodine
AOX	Adsorbable Organic Halogens
BTS	Benzene- and Toluenesulfonamides
DOC	Dissolved Organic Carbon
DWQC	Department of Water Quality Control
EfOM	Effluent Organic Matter
HPLC	High Pressure Liquid Chromatography
NASRI	Natural and Artificial Systems for Recharge and Infiltration
NSA	Naphthalenesulfonic Acid
POP	Persistent Organic Pollutants
TIC	Total Inorganic Carbon
UVA	UV Absorption

1 Introduction

Bank filtration provides an important drinking water source to the city of Berlin. 56% of the drinking water is derived from bank filtration (the remainder is 14% replenished groundwater and 30% natural groundwater) (BWB, 2003). At most bank filtration sites, the surface water contain portions of sewage treatment plant effluent (Lake Tegel 10-30%) (Ziegler 2001). Due to water recycling, the introduction of effluent organic matter (EfOM) and persistent trace pollutants in the drinking water may be a concern.

The project "Organic Substances in Bank filtration and Groundwater Recharge - Process Studies" at the Department for Water Quality Control (DWQC) at the Technical University of Berlin is part of the "Natural and Artificial Systems for Recharge and Infiltration (NASRI)"-project of the Berlin Centre of Competence for Water (NASRI, 2003).

The research objectives of this part of the project are to study the removal of bulk organics (dissolved organic carbon (DOC) and EfOM) and trace organics at three field sites with different characteristics. Since the processes during bank filtration are very complex, it is difficult to predict bulk organic composition in the bank filtrate or to estimate important factors of influence for the degradation of trace compounds. For instance, it was shown in previous studies, that iodinated x-ray contrast medias are deiodinated under reductive conditions. Therefore, a bank filtration under anoxic or even anaerobic conditions would provide the removal of these trace pollutants. In addition to the redox state, factors such as retention time, initial degradable carbon concentration, soil properties and hydrogeological conditions may affect the final concentration.

In order to be able to prevent the intrusion of persistent pollutants into the drinking water, the factors of influence are studied for a few model compounds that represent groups of trace pollutants. This will provide a tool that can be merged with hydrogeological models and soil properties to predict the removal efficiency of a given field site.

2 Objectives of this project

The portion of the project of the Department of Water Quality Control at the Technical University of Berlin has the following objectives:

- Development of a quantitative knowledge for the removal of natural and anthropogenic organic substances in bank filtration and groundwater recharge.
- Compilation of kinetic and equilibrium equation for the degradation of organic compounds.
- Validation of the data from the transects in Tegel and Wannsee.
- Optimization of existing or future bank filtration sites.
- Continuation of previous research that was done at the transect in Tegel (Ziegler, 2001; Hartig, 2000; Storm et al, 1999) to detect long term changes and effects that help to understand the process of bank filtration.

- Differentiation between the effects of dilution and degradation of organic contaminants.
- Identification of upcoming problems for bank filtration sites.

3 Summary of the work in 2002

The project started in May 2002. The objectives for the first seven months were to start the monthly sampling of the three field sites in Tegel and Wannsee and to set up an analytical program for these samples. For the field sites, the monthly analytical program is comprised of DOC, UVA, LC-OCD and differentiated AOX (absorbable organic halogens e.g. AOI, AOBr)-analysis (Huber and Frimmel, 1996; Oleksy-Frenzel, 2000). Additionally, a set of long retention columns was set up and after a tracer study in November 2002 the aquifer simulation started in December 2002. Another objective was the adaptation of the single compound analysis. In November 2002, the work group started with the development of a suitable HPLC-method to analyze the selected target compounds.

In the first seven months of the project it was found that the DOC concentration decreases along the transects. The relatively high surface water DOC concentrations of 7.5-8.5 mg/l were degraded to app. 4-5 mg/l. This level is similar to the DOC of the background groundwater. The statistical trends of the data indicated a faster DOC-removal under aerobic conditions, while the data for anoxic wells shows a slower decrease. The faster aerobic DOC-removal was also apparent in the aerobic recharge transect. The final DOC achieved is virtually identical in groundwater recharge and bank filtration. The results for UVA at 254 nm proved these findings.

The lake concentrations of AOI and AOBr did not show the typical peak during the summer of 2002. It was assumed that the relatively wet and cold summer was responsible for the absence of these peaks. Regarding the behavior of the AOI and AOBr during the infiltration process different observations were made at the distinct field sites. A clear degradation of AOI and AOBr was found at the two field sites where the bank filtration takes place under low redox potentials. This is likely due to reductive dehalogenation. Only slight degradation of AOI and AOBr was observed at the oxic groundwater recharge site.

The set-up of the aquifer simulation experiment in Marienfelde was successfully finished in October 2002. The data from the following tracer experiments were interpreted regarding pore volume, retention time and dispersion. It was found that the material in the long retention columns provides a pore volume of app. 29% and a dispersion of 0.1m/d.

The feeding of the long retention columns with spiked water from Lake Tegel was started in December 2002. The retention time for the aquifer simulation experiment was set to 30 days.

4 Summary of work in 2003

In 2003 the workgroup “Organics” focused on the continuation of the monthly field site monitoring, the development and application of the single compound analysis and the simulation experiments utilizing soil columns. Progresses was made in all three work areas.

The monthly monitoring of the three field sites consists of DOC, $UVA_{254/436}$, AOI, AOBr and LC-OCD measurements. It was found that distinct peaks of the wastewater contaminants occurred during summer of 2003. This was likely due to the hot summer and little precipitation. Different boundary conditions also played a major role, such as the expansion of the sewage treatment plant Schönerlinde that discharges into Lake Tegel. The AOI concentration in Lake Tegel increased during summer to 16 µg/l, despite dilution by the lake pipeline. This concentration is similar to concentrations that have been observed in former years without dilution with Havel water. The influences of these higher surface water concentrations on the bank filtration and recharge systems could be monitored and are going to be evaluated. It was proven that the higher surface water AOI-concentrations affect the AOI level of the extracted drinking water at the recharge facility Tegel. The development of a method for the analysis of the trace compounds Sulfamethoxazole, Iopromide and Naphthalenesulfonic acids was completed in May 2003. This trace compound analysis was implemented into the monthly sampling program in May 2003. The trace compounds, Sulfamethoxazole and Iopromide, are analyzed by HPLC-MS/MS and the Naphthalenesulfonic acids by HPLC-FLD. The different behavior of the trace compounds during infiltration was tested with these methods.

The third important objective for 2003 was the continuation of the simulation experiments. Most simulation experiments were conducted at a set of long retention columns that was constructed in 2002. A 30 meter aquifer was simulated with a retention time of 30 days. In the first phase the columns were adjusted to aerobic conditions to replicate the infiltration conditions at the groundwater recharge facility. After the adaptation phase the columns were monitored regarding character and amount of DOC, AOI, UVA and trace compounds at the different sampling points. It was found that the simulation was successful and the removal efficiency was sometimes higher than the original field system. As a service to other work groups there was the possibility to use this simulated aquifer for experiments. The hydrogeology and the drug group used this opportunity. In April 2003 a second set of columns was installed at the DWQC at the TU Berlin. The short retention columns will be used to conduct experiments on the influence of changing redox conditions on the degradation of organics. Additionally, soil columns with original material from Lake Tegel were set up. These will clarify the role of particulate organic carbon for the redox system at the bank filtration sites.

As part of a study work, two experiments at the enclosures in Marienfelde were conducted to examine the importance of the “Schmutzdecke” for the removal of bulk organics and trace compounds.

5 Timetable

Table 1 summarizes the planned and completed tasks in the “Organics”-group of the TU Berlin. The timetable and the working program cover the period from 01/01/2003 until 04/30/2005.

Table 1 Project schedule

Year	2002						2003												2004												2005			
Month	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A
General soil column setup and tracer study																																		
Adaptation of 30 m-soil columns																																		
Simulation of aquifer in long retention columns																																		
Set-up and adaptation of short soil columns																																		
Experiments with short soil columns																																		
Enclosure tests at Marienfelde																																		
Adaptation of single compound analysis																																		
Single compound monitoring at field sites																																		
Development of biodegradation kinetics																																		
Adsorption studies for POP´s																																		
Model development and validation																																		
On-Site Monitoring																																		

Intended and achieved tasks for the reporting period 2003

Table 2 Tasks in reporting period 2003

Task	Achieved?	Comments
Continuous monitoring of the transects at Lake Tegel and Lake Wannsee and the groundwater recharge facility	Yes	Analysis of monthly sets of 40 samples regarding DOC, UVA_{254},UVA_{436} 27 samples regarding AOI and AOBr 30 samples regarding LC-OCD
Adaptation of single compound analysis for Iopromide, Sulfamethoxazole and Naphthalenesulfonic acids	Yes	Development of a suitable HPLC-method to analyze the selected target compounds was finished in May 2003
Monitoring of the field sites regarding single compounds	Yes	Analysis of monthly sets of 18 samples regarding Sulfamethoxazole, Iopromide and 8 Naphthalenesulfonic acids started in May 2003
Simulation of aerobic soil passage in the long retention column system	Yes	After the adaptation period the simulation started in June 2003 with Lake Tegel water
Monitoring of the performance of the long retention columns	Yes	Biweekly monitoring of DOC, UVA, O_2, redox conditions (monthly AOX and main cations and anions and single compounds)
Pharmaceutical tests at the long retention columns (Collaboration with the “drug” group of NASRI)	Yes	Spiking of clofibric acid, diclofenac, ibuprofen and bezafibrate to the feed of the columns and monitoring of different sampling points during summer 2003
Set-up of different short column systems	Yes	Installation of altogether 8 short retention columns (1m x 0.14 m) with a retention time of 3.5 days to evaluate influences on biodegradation processes, additionally set up of 2 columns with original Tegel material
Adaptation period for short retention columns	Yes	Columns were adapted to different redox potentials by spiking of nitrate, DOC and sparging with N_2
Continuous monitoring of short retention columns	Yes	Analysis of biweekly sets of 15 samples regarding DOC, UVA_{254},UVA_{436}, (monthly AOI and AOBr and single compounds)
Tests of behavior of single compounds in enclosures at Marienfelde (slow sand filtration)	Yes	Two experiments with monitoring of single compound concentrations (additionally monitoring of DOC, UVA_{254},UVA_{436}, AOX and LC-OCD)

6 Results in 2003

6.1 Investigations at the field sites

The monthly sampling of the transects at Lake Tegel and Lake Wannsee and the groundwater recharge facility in Tegel was continued in 2003. The samples were taken by a team of the BWB. The TU Berlin provided the sampling containers and was responsible for the pick-up of the samples from the drinking water plant Jungfernheide. In October 2003 the sampling team was assisted by the TU Berlin. The analysis program at the DWQC/TU Berlin contains $UVA_{254/436}$, DOC, LC-OCD, AOBr and AOI and since May 2003 the single compounds Iopromide (x-ray contrast agent), Sulfamethoxazole (antibiotic drug) and different naphthalenesulfonic acids (Intermediates for different industrial processes).
The results of the long term monitoring are presented.

6.1.1 Artificial recharge pond Tegel

The monitoring of the transect at the artificial recharge site in Tegel started in October 2002. By the end of 2003, the monitoring period for most parameters covered more than a year. A cross section of the transect is presented in the appendix.
The DOC-data are plotted in Fig. 1 as box plots with the 50%-quartile (horizontal centre line), the 25%- and 75%-quartiles (box). The error bars denote the 5th and 95th percentile values and the stars show the minimum and maximum values. The relatively high DOC of the surface water is reduced considerably along the transect to a level that is comparable to the background groundwater. The removal of DOC is obviously very efficient under the oxic conditions.

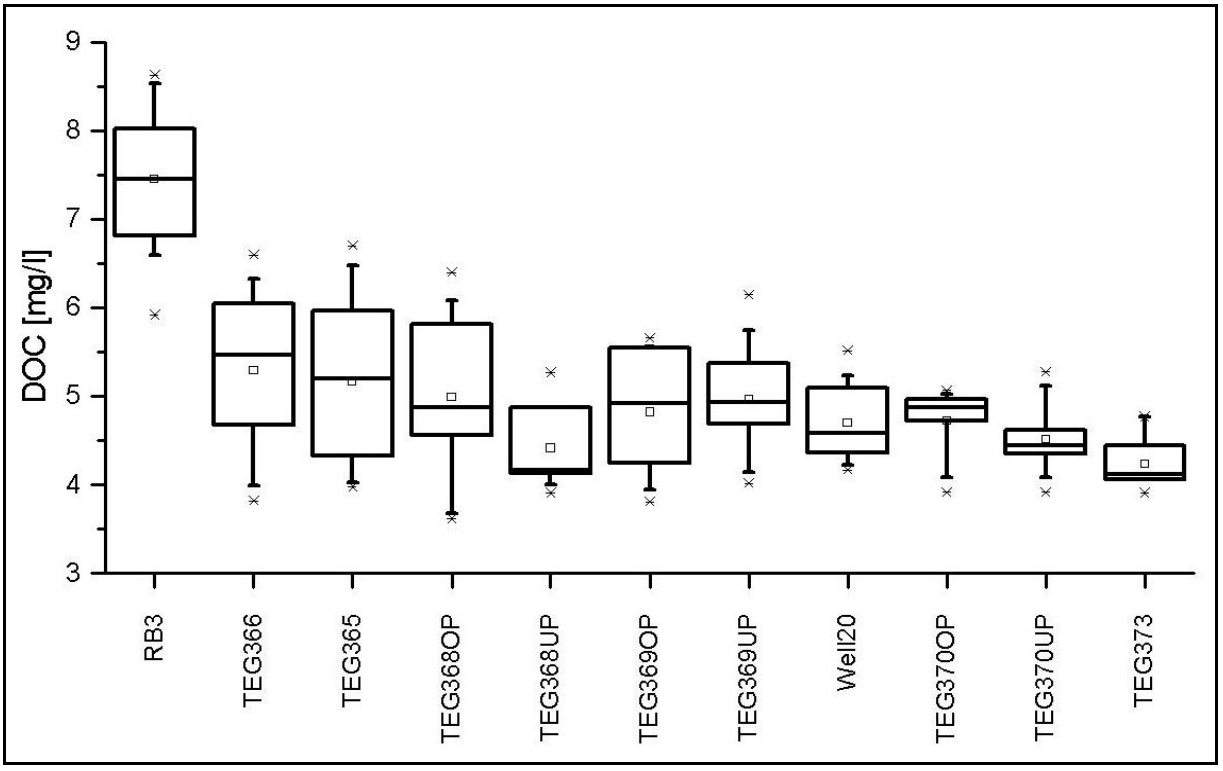


Figure 1 Box plots of DOC concentrations at the groundwater recharge facility (n=7-15)

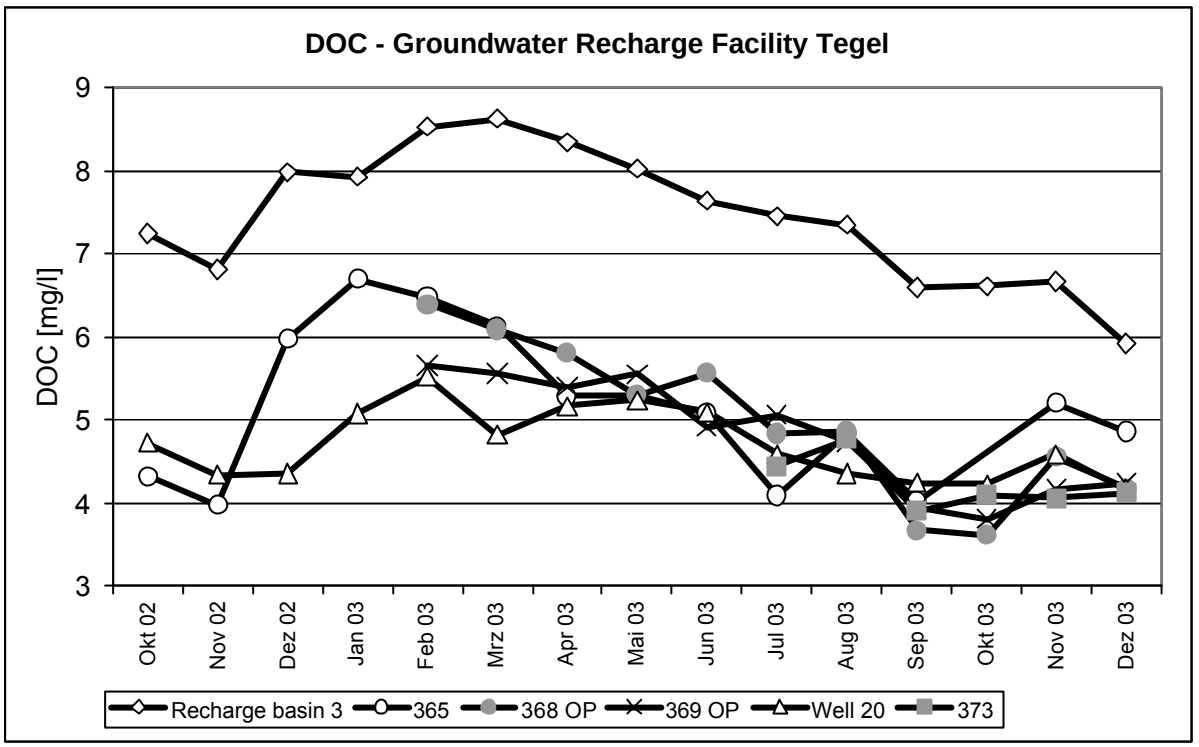


Figure 2 Time series of DOC at the recharge facility Tegel

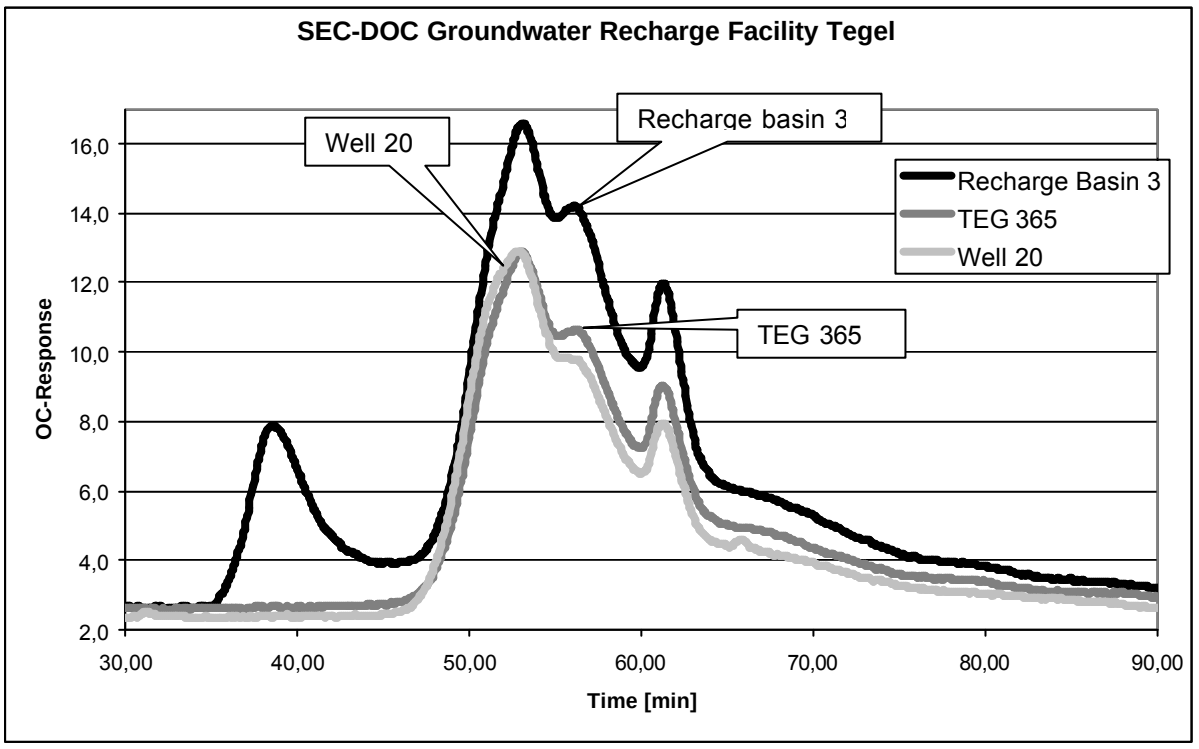


Figure 3 LC-OCD chromatogram of three groundwater recharge facility samples in August 2003

The time series in Figure 2 indicates that the DOC removal efficiency for the first few meters of soil passage varies with the seasons. Figure 2 shows that during winter the DOC concentration is higher near the recharge basin (observation well TEG365) than in the drinking water well 20. During summer, the DOC concentration is reduced in the first meter of soil passage to the level of the drinking water well. This might be due to a temperature dependent DOC removal

efficiency. In the winter season the slower DOC-degradation leads to relatively higher concentrations in the observation wells near the recharge pond. This effect is also visible in the UVA-data (not presented here).

The LC-OCD measurements confirmed this assumption that during summer most of the DOC degradation takes place during the first meter of infiltration. Figure 3 shows in a LC-OCD chromatogram that in August 2003 the character of the DOC in observation well TEG 365 was very similar to the DOC-character in the drinking water well. Only two meters from the edge of the recharge basin (TEG 365) the character of the DOC clearly changed. It can be seen that the fraction polysaccharides (elutes at 35-45 min) is degraded very efficiently. The fractions of humics (elution time 52 min), humic building blocks (57 min) and low molecular acids (62min) are partially degraded. During the further infiltration process the character of the DOC does not change significantly.

The higher DOC concentrations in the recharge pond during winter of 2002/2003 (Figure 2) are likely due to strong rainfall events or snow melt that flushed organic material from the surrounding forests into the recharge basin. This effect was not that strong in Lake Tegel.

Regarding the AOI and AOBr-data the findings of the last year could be confirmed. It is evidently shown that there is not a very efficient reduction of these compound groups during the recharge process (Figure 4 and 6). This could be due to higher infiltration velocities or due to the redox conditions in the field. It is known that the degradation of AOI and AOBr is more effective in soil passages with low redox potential. At the recharge facility the monthly drying cycles inhibit the establishment of low redox potentials.

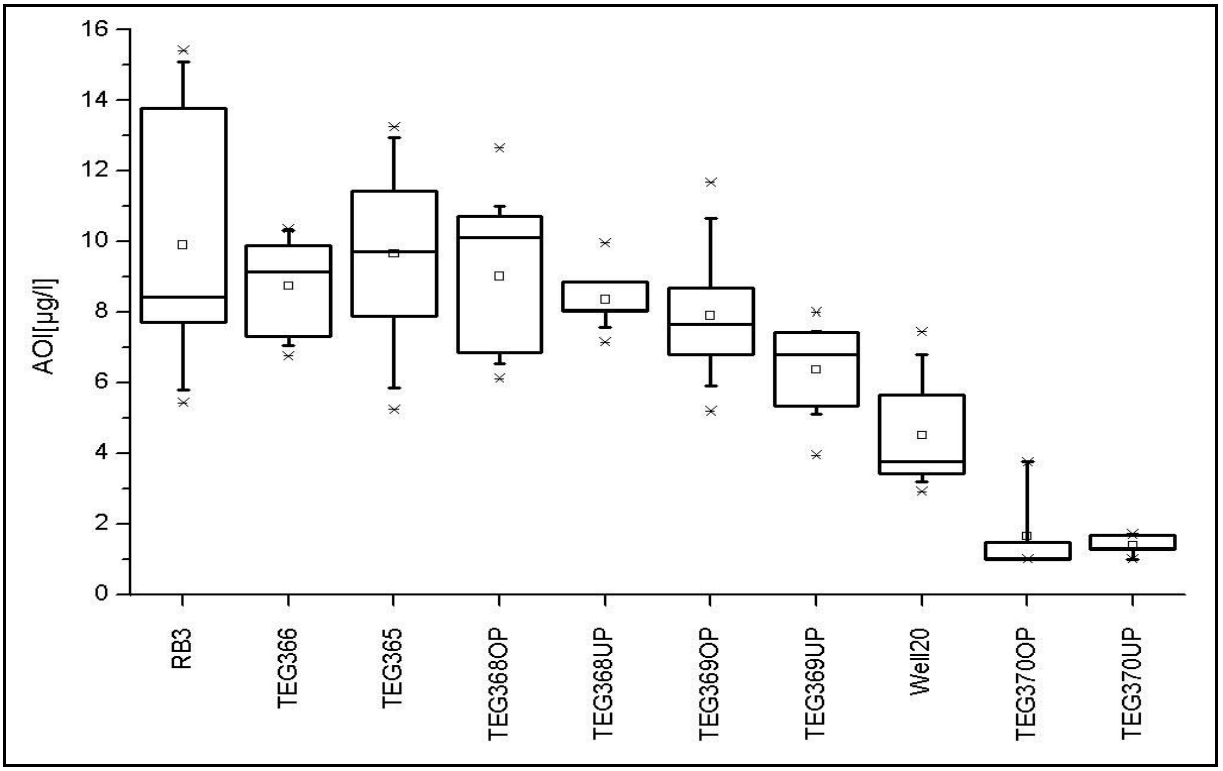


Figure 4 Box plots of AOI concentrations at the groundwater recharge facility (n=7-15)

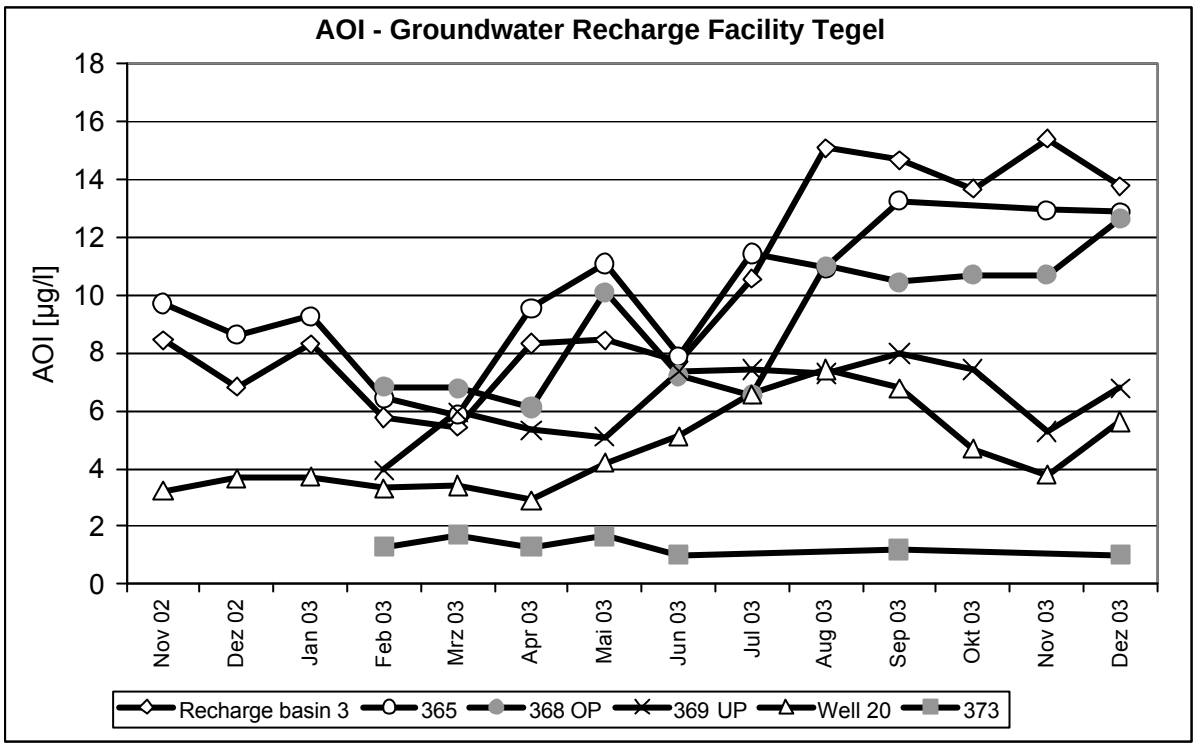


Figure 5 Time series of AOI concentrations at the groundwater recharge facility

Figure 5 shows that the AOI concentration in the recharge basin varied between 6 and 10 µg/l from November 2002 until June 2003. This surface water concentration resulted in a relatively stable AOI-level in the drinking water well of 3-4 µg/l. In summer 2003 the increase to 15 µg/l of the AOI-level in Lake Tegel and the recharge basin caused an immediate increase to 8 µg/l AOI in the drinking water well 20. This means that despite dilution by background groundwater a seasonal change in surface water quality can lead to considerably higher AOI concentration in the extracted drinking water.

Regarding the AOBr data, it can be assumed that there are two different fractions of AOBr. One fraction is present year round. Figure 7 shows that at Lake Tegel and the recharge site this fraction accounts for approximately 8-10 µg/l AOBr. The second fraction is only present in late summer and is probably linked with algae blooms. It can account for 20 µg/l AOBr and more.

The box plots of the AOBr data in Figure 6 reveal that there is nearly no reduction of the year round fraction of AOBr. The AOBr-concentrations are not decreasing along the transect. This AOBr fraction and the AOI show comparably low removal efficiency during soil passage. The water of the drinking water well 20 has lower concentrations because of the mixture of recharged water and background groundwater.

The second fraction that is linked with algae blooms also seems to be degraded under the oxic conditions of the recharge facility. Figure 7 shows no significant increase of AOBr concentrations in the monitoring wells after the increase in the surface water. This effect was not visible in 2002 because the wet and relatively cold summer did not contribute to a strong

algae bloom. The reasons for the degradation or adsorption of this second fraction of AOBr are unclear.

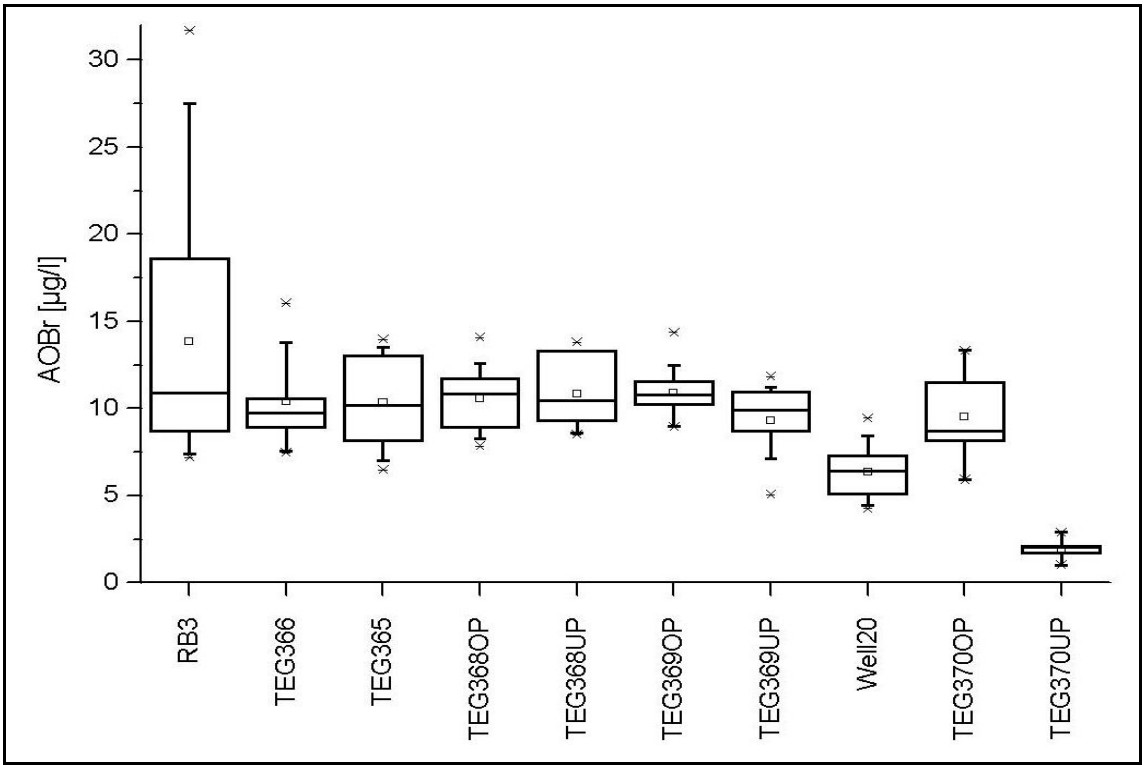


Figure 6 Box plots of AOBr concentrations at the groundwater recharge facility (n=7-15)

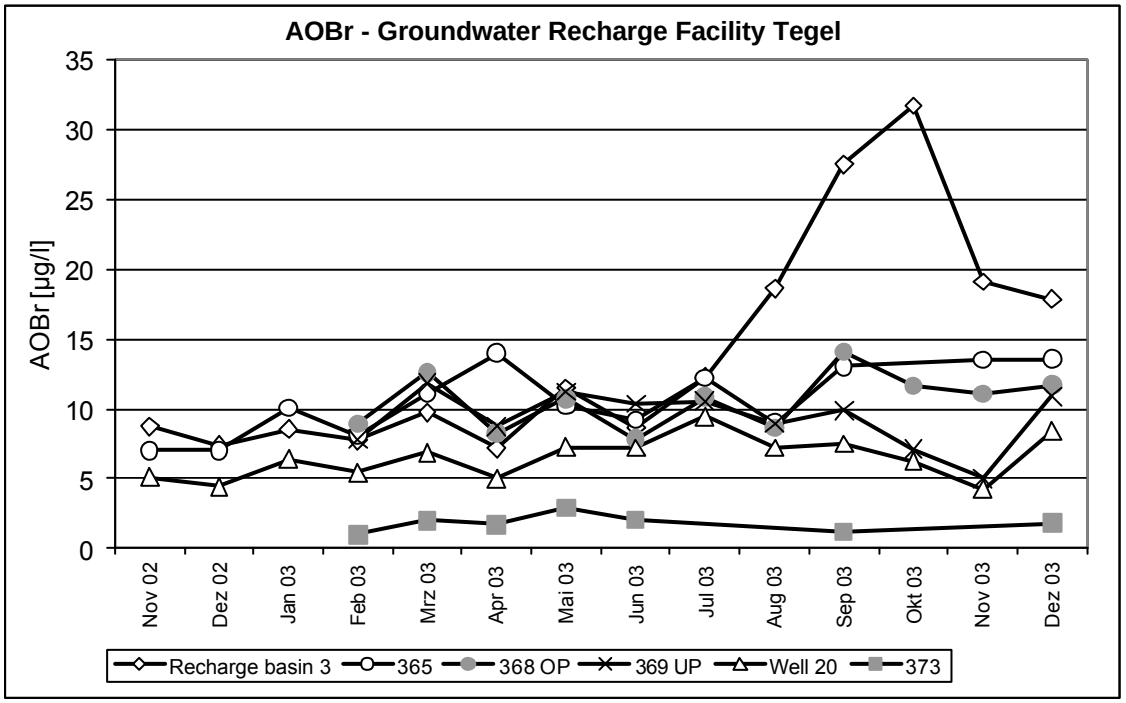


Figure 7 Time series of AOBr concentrations at the groundwater recharge facility

Additionally, single compound analysis was conducted for the trace pollutants Iopromide, Sulfamethoxazole and different naphthalenesulfonic acids. Figure 8 presents data from the trace compound analysis for the time period May 2003 to October 2003. The trace compounds

behave differently during the oxic infiltration process. The x-ray contrast agent Iopromide is degraded or metabolized very quickly. In the first observation well only approximately 10 % of the initial concentration is found and in the following observation wells the Iopromide concentrations are close to the detection limit. In contrast to that, the 1,5-naphthalenesulfonic acid is not degraded at all. All naphthalenesulfonic acids are present in the background groundwater. For the 1,7- and the 2,7 NSA degradation rates of approximately 60 percent were observed.

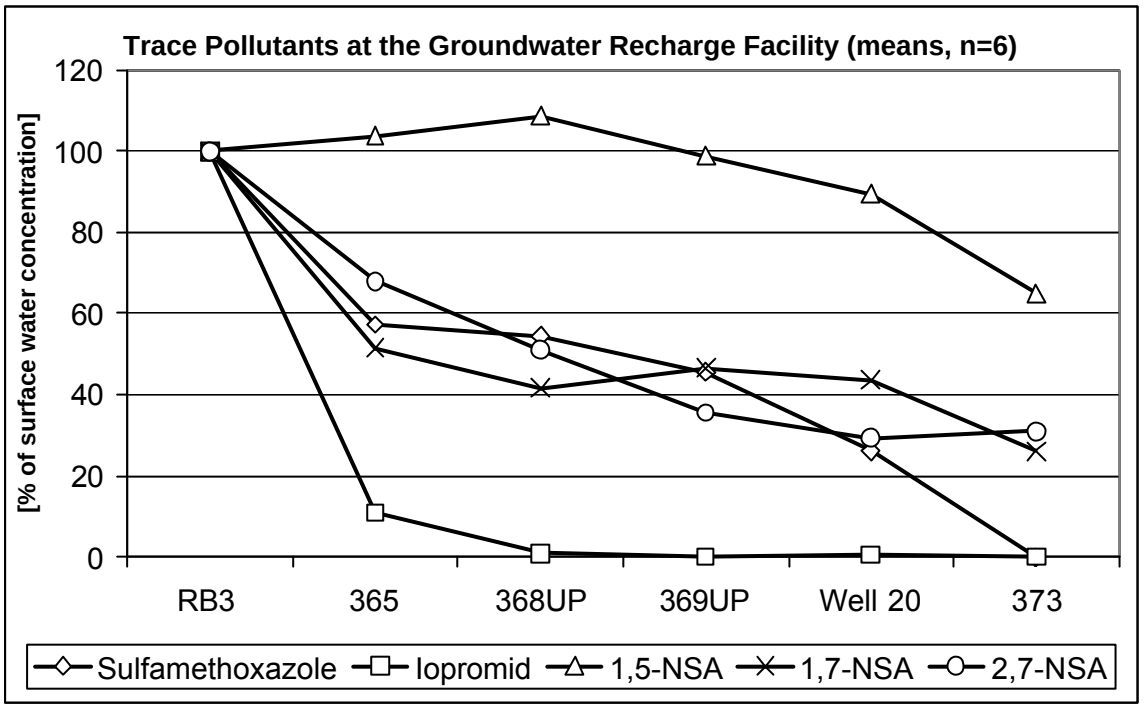


Figure 8 Fate of 5 different trace pollutants at the aerobic groundwater recharge facility

The absolute concentrations in ng/l are presented in Table 3. The persistent 1,5 NSA is present in the surface water in relatively low concentrations. From these selected compounds Sulfamethoxazole and 1,7 NSA are found in the highest concentrations in the drinking water well. Since there are only six measurements, it is not possible to determine a trend or a year profile for these trace compounds. The measurements will continue in order to receive at least one year of data.

Table 3 Absolute concentrations of the trace pollutants at the groundwater recharge facility

Means (n=6)	Sulfamethoxazole		Iopromid		1,5-NSA		1,7-NSA		2,7-NSA	
	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s
Recharge basin 3	502	40	584	76	72	27	357	80	79	9
TEG365	287	44	63	37	75	6	184	99	53	18
TEG368UP	273	128	5	10	79	15	149	47	40	11
TEG369UP	229	55	0	0	72	26	166	84	28	4
Well 20	130	56	3	6	65	16	156	38	23	7
TEG373	0	0	0	0	47	19	93	10	24	3

As an example Figure 9 displays the statistical data as box plots with the median value, the 25%- and 75%-quartiles and the minimum and maximum values of the six measurements for Sulfamethoxazole.

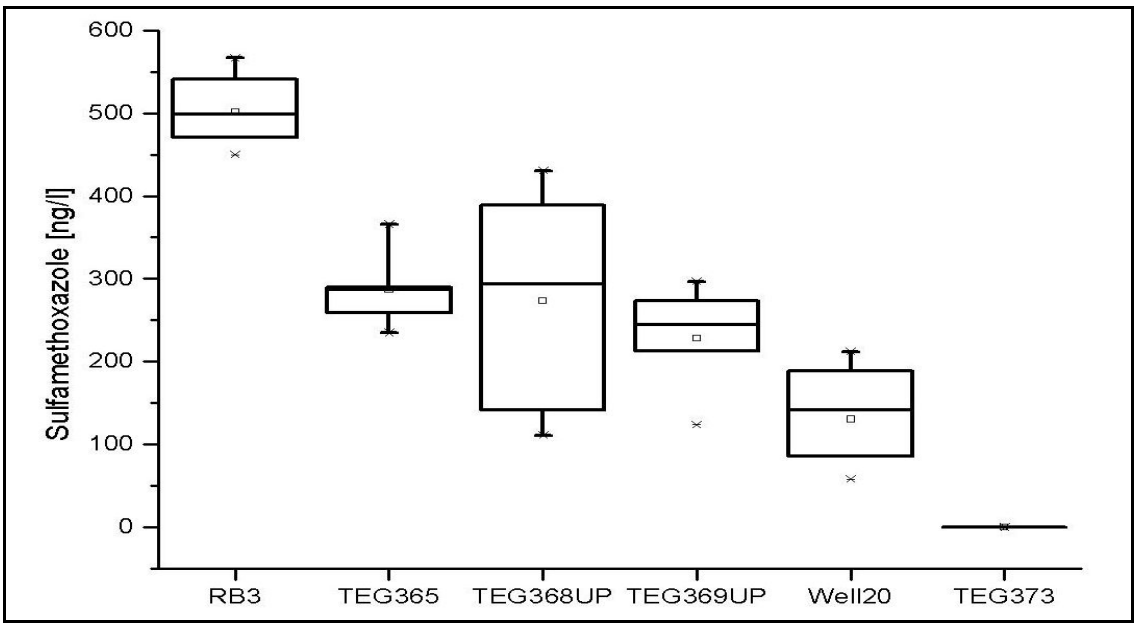


Figure 9 Sulfamethoxazole concentrations at the groundwater recharge facility (n=6)

6.1.2 Bank filtration field site Lake Tegel

The long term monitoring of the bank filtration transect at Lake Tegel started in May 2002. Samples are taken monthly by the Berlin Water Works. At the DWQC at TU Berlin they are analyzed regarding DOC, UVA_{254}, UVA_{436}, LC-OCD, AOI and AOBr. Monitoring the trace pollutants started in May 2003. For the bulk parameter the time series covers more than 18 months and for the single compounds six months. For some observation wells the data does not cover the entire time period, because they where either dry during summer or drilled in the last 18 months. The recent lay-out of the transect is presented in a cross section plan in the appendix. The monitoring results are shown in the following figures.

Figure 10 shows the behavior of the dissolved organic carbon in the bank filtration transect Tegel. The high DOC of the surface water (7-8 mg/l) is reduced to approximately 4-5 mg/l during infiltration and soil passage (reduction rate of 35%). The background DOC (approximately 3mg/l) is lower than the background DOC of the groundwater recharge site. In the drinking water well the bank filtrate and the background groundwater is mixed to an average DOC of 4.5 mg/l.

The difference between the DOC degradation in the oxic shallow wells and the anaerobic deeper wells can be seen in Figure 10. The two shallow wells 3310 and 3308 display a low DOC compared to the relatively short retention time of only days or weeks. In the deeper

anaerobic wells (3301, 3302, 3303) the DOC degradation is slower but reaches a comparable final concentration.

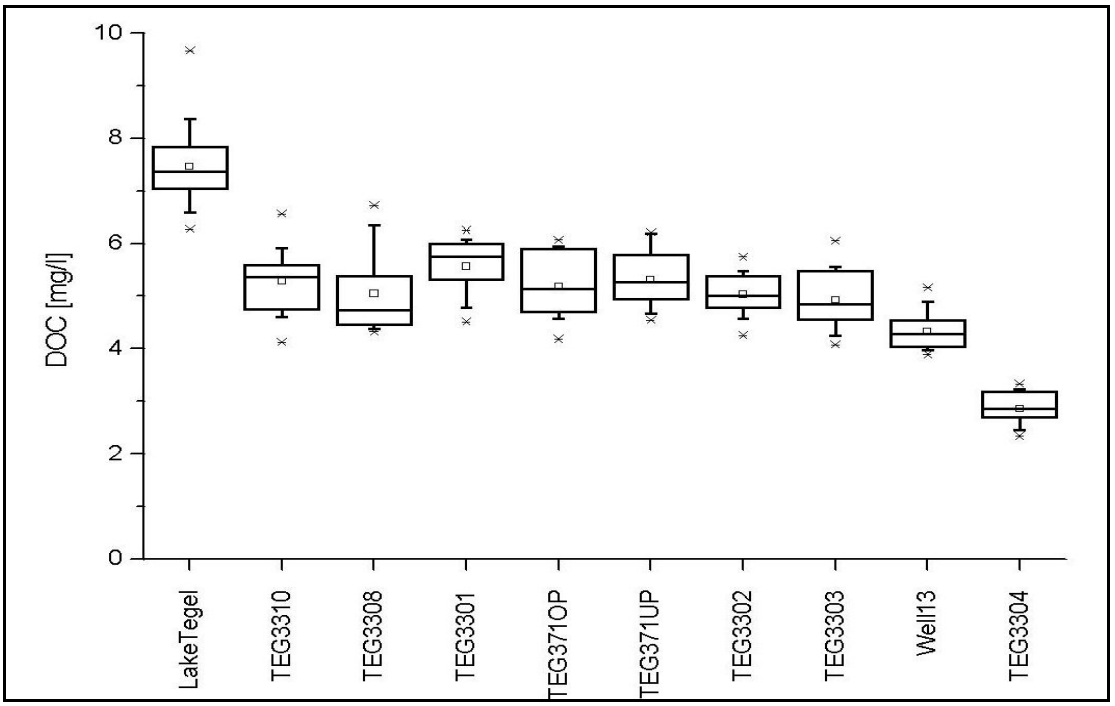


Figure 10 Box plots of DOC concentrations at the bank filtration site Tegel (n=11-18)

The time series of DOC measurements reveals that the DOC in Lake Tegel is relative constant between 6.5 and 8 mg/l. The high values in December 2002 and January 2003 are probably due to storm events, strong rainfall or snow melt that flushed organic material into the lake. It can be seen that the performance of the DOC degradation is relatively stable in the bank filtration transect.

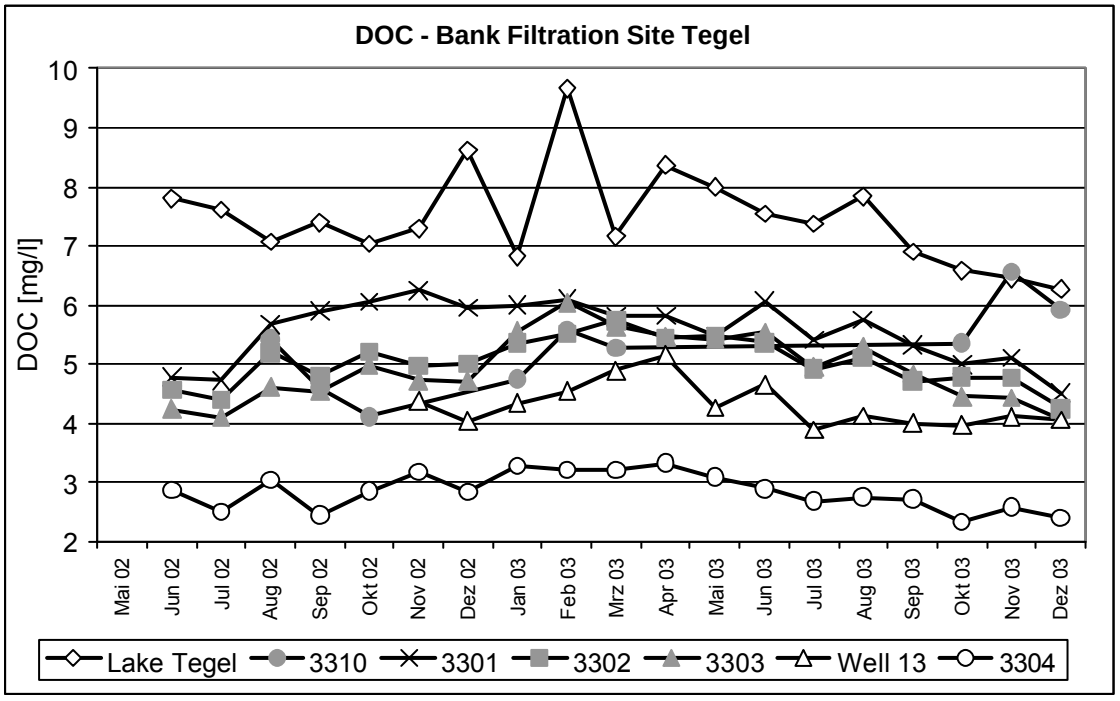


Figure 11 Time series of DOC at the bank filtration site Tegel

Despite these short term fluctuations the shallow and the deep monitoring wells show a constant removal for DOC. These results are proved by the LC-OCD measurements. As an example the LC-OCD-chromatograms of four May 2003-samples are displayed in Figure 12. The effects of the anaerobic infiltration on the character of the DOC are comparable to the results at the groundwater recharge facility. The fraction of polysaccharides is removed completely and the humics, humic building blocks and low molecular acids are partially removed.

The evaluation of the redox processes at the bank filtration site Tegel indicates that for the anoxic bank filtration, a significant degradation of particulate organic carbon (POC) is responsible for oxygen and nitrate reduction and for an increase in inorganic carbon.

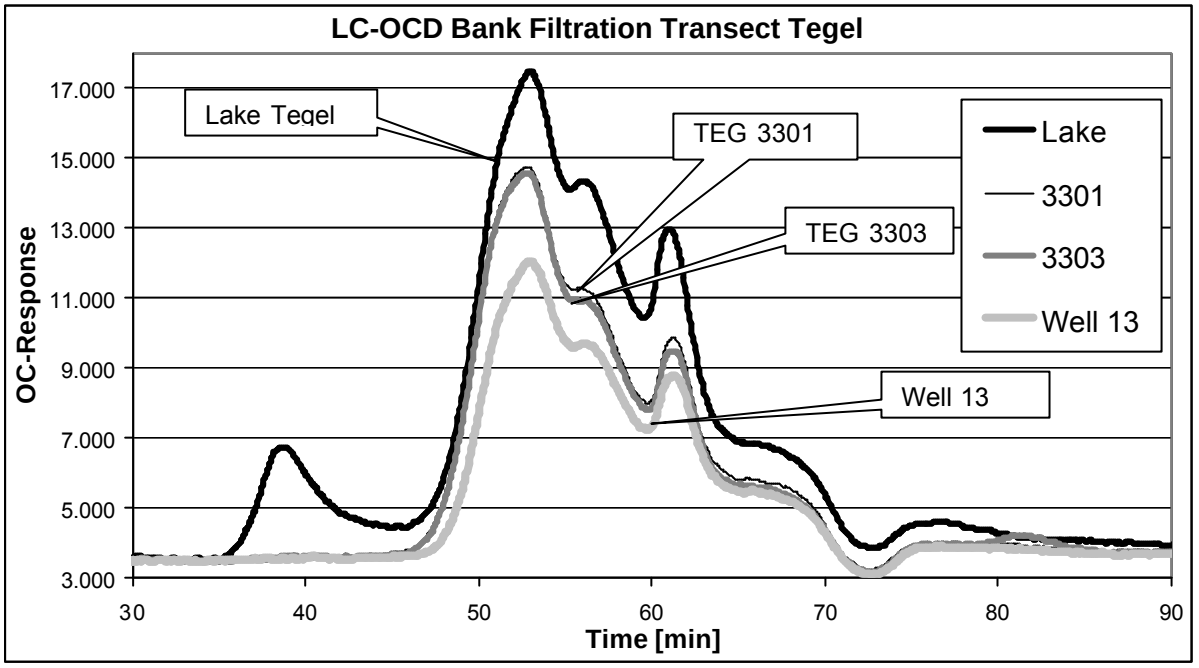


Figure 12 LC-OCD chromatogram of four bank filtration samples in Tegel in May 2003

The measurements of AOI reveal that a relative efficient degradation of AOI takes place during bank filtration at Lake Tegel (Figure 13). Contrary to the groundwater recharge facility a reduction of AOI in the deeper wells can be observed. It is obvious that the very shallow wells with short retention times (3310, 3308, 371OP) show no reduction of AOI. Oxic conditions and short retention times seem to prevent an efficient AOI degradation. The results of the deeper anaerobic wells (3301, 3302 and 3303) confirmed the findings of last year, that a AOI degradation is possible at low redox potentials. The medium shallow well (371UP) shows low AOI concentrations. Further monitoring will clarify which redox zone dominates at these observation wells and what the average retention times are. This information should explain the relatively high removal of AOI during infiltration to this well.

The AOI of the background groundwater is very low (1µg/l). The mixture leads to a AOI-concentration in the extracted drinking water of 1-2µg/l.

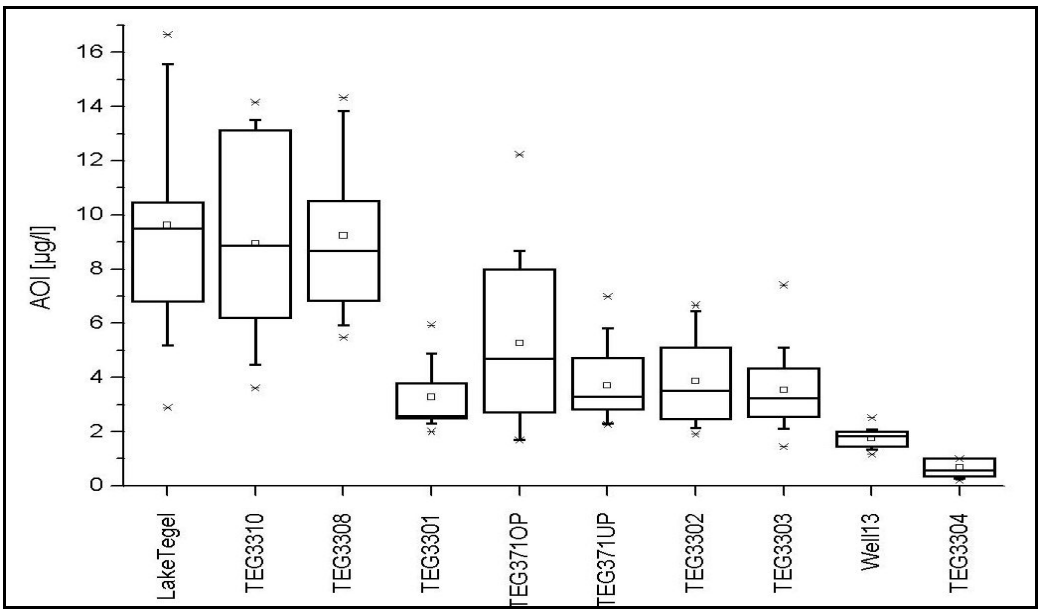


Figure 13 Box plots of AOI concentrations at the bank filtration site Tegel (n=11-18)

The time series of the AOI measurements show the reaction of the monitoring wells to the increase in AOI concentration of the surface water. No distinct AOI-peak was measurable during summer 2002. Therefore, this was the first opportunity to clarify the reaction of the bank filtration system in Tegel to a seasonal increase of AOI.

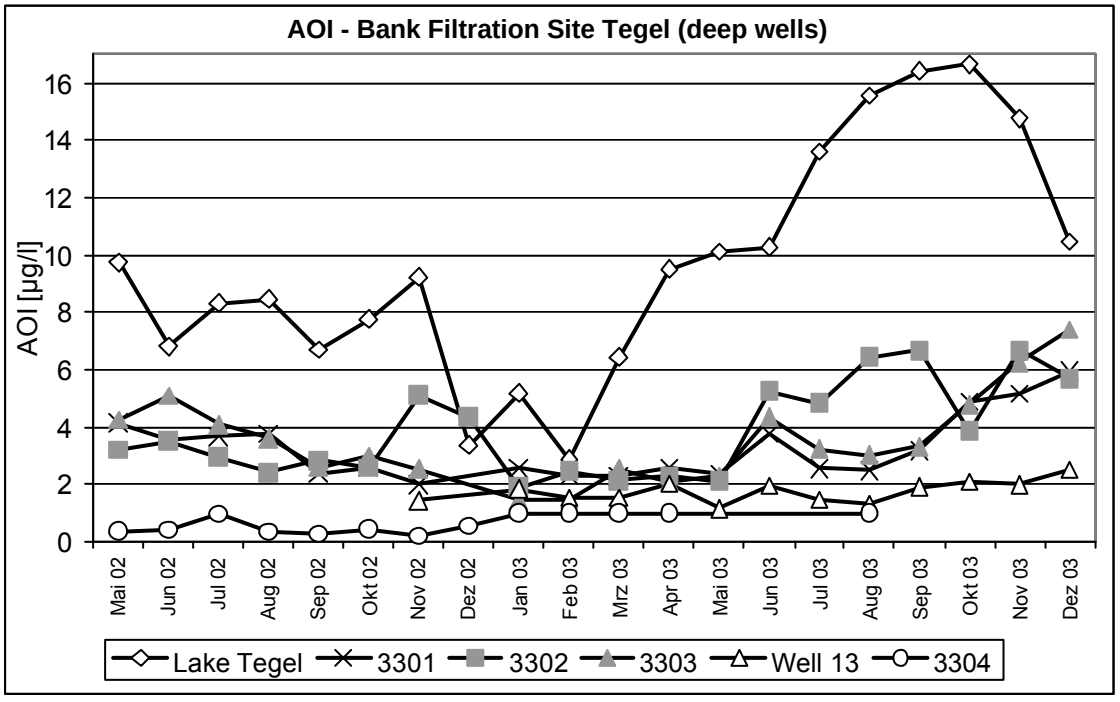


Figure 14 Time series of AOI in the deep wells at the bank filtration site Tegel

Figure 14 shows that the AOI of Lake Tegel increased in the time period February 2003 to October 2003 from 3 µg/l to 17 µg/l. The deep wells (3301, 3302, 3303) react three months later with an increases in AOI-concentration. This retention time is similar to the retention time that

was proposed for 3301 and 3302 by the hydrogeology group from the FU Berlin. The strongest reaction can be observed for monitoring well 3302.

The AOI concentration in this well triples from 2 µg/l to 6-7 µg/l during August and September 2003. Monitoring well 3301 reacts differently to the increase in surface water AOI. The first increase in June 2003 is smaller than for 3302 but later in September TEG3301 starts to rise to similar concentrations than 3302. The hydrogeological background of this process remains unclear. Monitoring well 3303 did respond to the AOI increase in the surface water too. But the increase was more comparable to 3301. However, it can be concluded that the deep monitoring wells are affected by the increase of the AOI concentration in Lake Tegel. Until now the drinking water well does not show an acute signal. The concentrations are still approximately 2 µg/l. But considering a retention time of 4-5 months for the drinking water well, the AOI-analysis of January- March 2004 might be of interest.

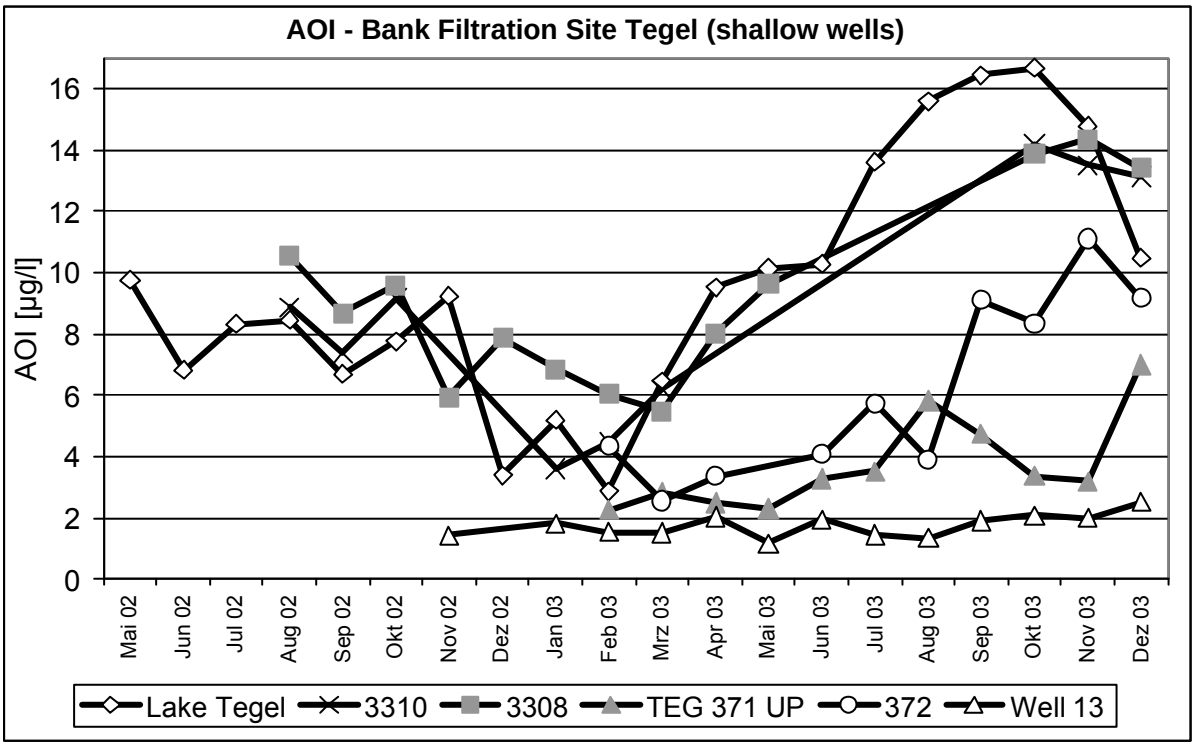


Figure 15 Time series of AOI in the shallow wells at the bank filtration site Tegel

The monthly monitoring of the shallow wells at Lake Tegel reveals that the AOI concentrations in the wells 3310 and 3308 are very dependent from the AOI of the Lake. The other medium depth monitoring wells (TEG371UP, TEG 372) show an increase in AOI as well, but with different retention times. It can be concluded that the bank filtration system at Lake Tegel seems to reduce the seasonal increase in AOI more effectively than the recharge facility. But until now it is not clear whether it can prevent an effect on the extracted drinking water.

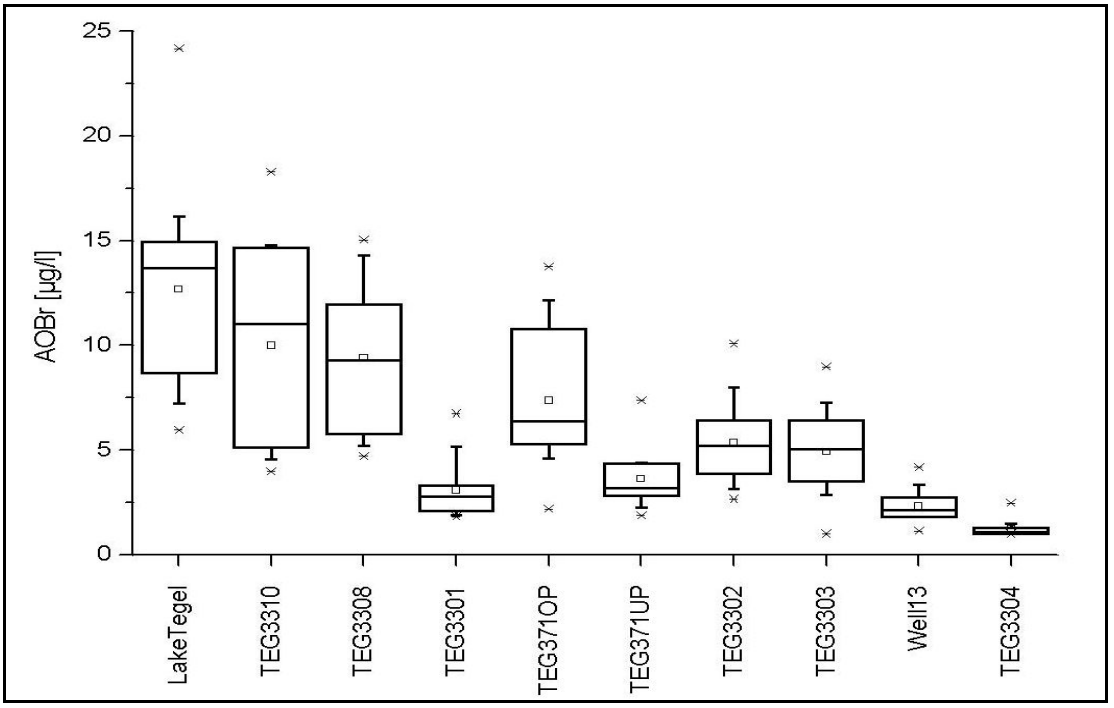


Figure 16 Box plots of AOBr concentrations at the bank filtration site Tegel (n=11-18)

The time series of the AOBr concentrations at the bank filtration site are similar to the AOI results. Figure 16 shows that AOBr is effectively degraded in the deep anaerobic monitoring wells. The shallow monitoring wells do not show a good removal of AOBr.

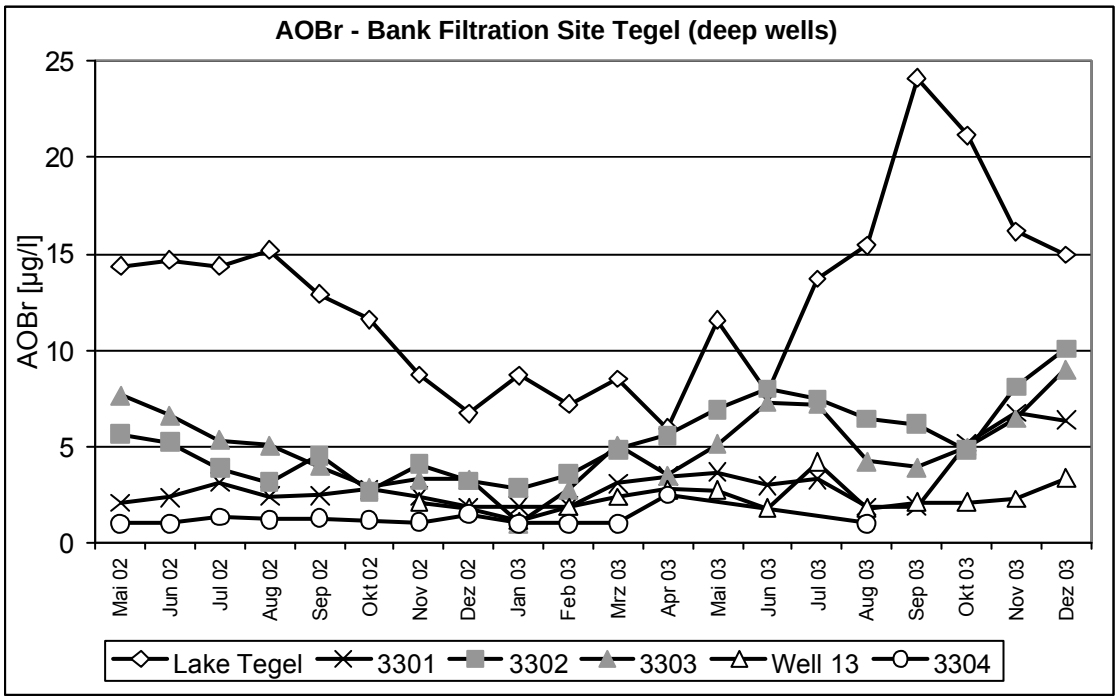


Figure 17 Time series of AOBr in the deep wells at the bank filtration site Tegel

However, Figure 17 proves that the high surface water concentrations (starting in July 2003) impact the concentrations in the deep monitoring wells. In November and December 2003, the

concentrations in TEG 3301, 3302, 3303 rise. The continued monitoring in 2004 will clarify the effect on the deep wells and the drinking water well.

The single compound analysis for the trace pollutants Iopromide, Sulfamethoxazole and different naphthalenesulfonic acids was started in spring 2003, providing data for the time period May 2003 to October 2003. In Figure 18 it is apparent that the trace compounds have a different degradability during the infiltration process. Similar to the oxic soil passage at the recharge facility, the x-ray contrast agent Iopromide is degraded or metabolized instantly. The antibiotic drug Sulfamethoxazole is also degraded in the first observation well to only approximately 10 % of the initial concentration. During the further infiltration process concentrations of Iopromide and Sulfamethoxazole are very low.

The trace organic analysis for Iopromide exhibited that the Iopromide concentration is reduced from the lake (772 ng/l, n=6, s=140 ng/l) to the first observation well 3301 (46 ng/l, n=6, s=24 ng/l) by 94%. The reduction rate between the groundwater recharge pond and the respective first observation well is similar (90%). Comparing these results with the inefficient reduction of AOI in the recharge facility, it can be concluded, that Iopromide and AOI behave differently during soil passage. Iopromide accounts for approximately 3-5% of the measured AOI in surface water. However, in the observation wells this ratio is greatly reduced (3302 => ~0.1%). This leads to the assumption that the Iopromide molecule is altered but not mineralized during the first part of the soil passage. This metabolism probably occurs under aerobic conditions because bank filtration and recharge facility show similar results.

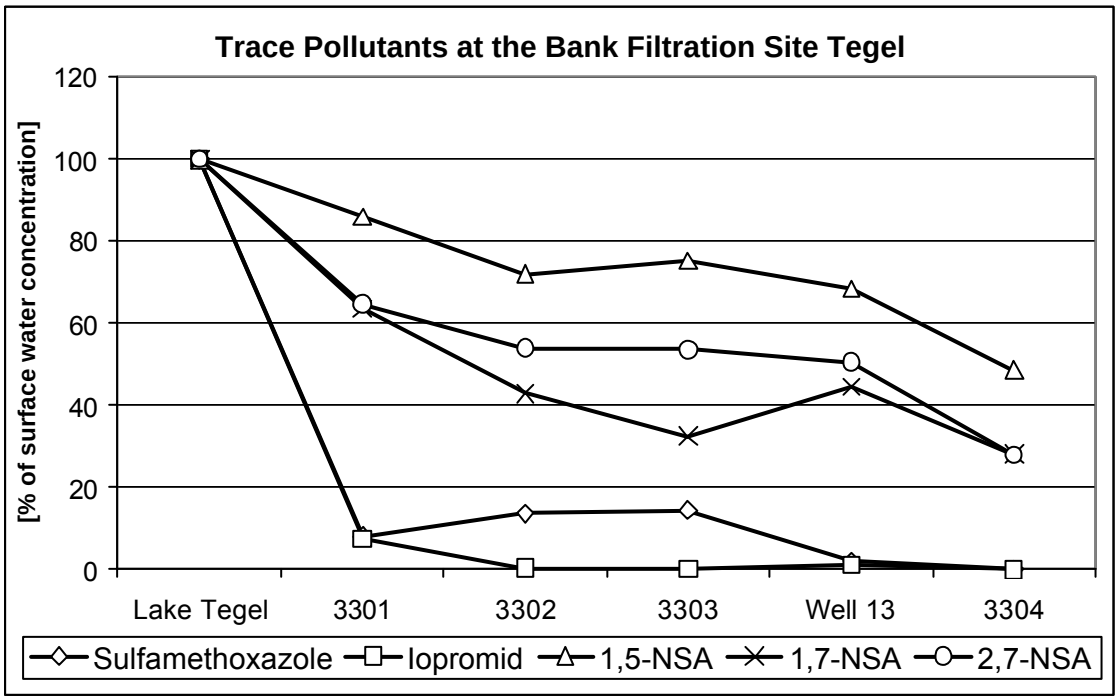


Figure 18 Fate of 5 different trace pollutants at the bank filtration site Tegel

Table 4 Absolute concentrations of the trace pollutants at the bank filtration site

Means (n=6)	Sulfamethoxazole		Iopromid		1,5-NSA		1,7-NSA		2,7-NSA	
	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s
Lake Tegel	559	96	772	140	66	9	356	46	84	17
TEG 3301	46	24	58	32	57	7	226	51	54	8
TEG 3302	76	21	3	4	48	7	153	16	45	21
TEG 3303	81	35	2	3	50	8	116	13	45	21
Well 13	12	10	9	8	45	9	159	32	42	16
TEG 3304	0	0	0	0	32	7	100	11	23	11

The concentration of the very stable 1,5-naphthalenesulfonic acid remains nearly constant. The initial concentration only decreases by 20%. This might be due to dilution with deeper groundwater (hydrogeology group FU Berlin). All naphthalenesulfonic acids are present in the background groundwater. For the 1,7- and the 2,7 NSA degradation rates of 50 to 60 percent were observed. Figure 19 presents the data for the 1,7-naphthalenesulfonic acid.

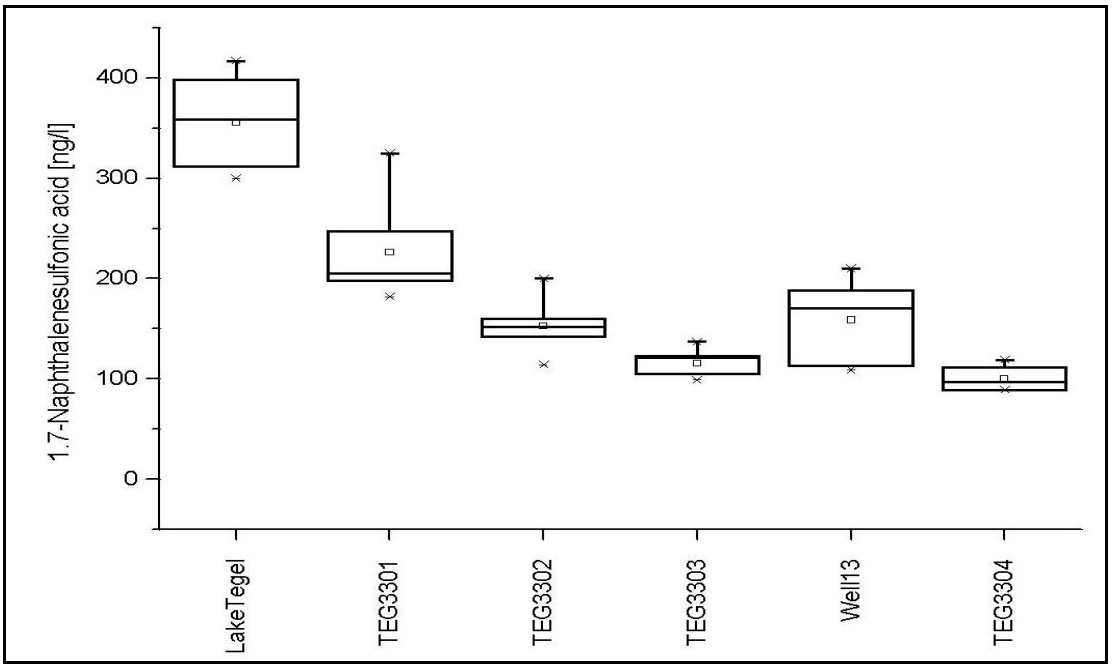


Figure 19 1,7-naphthalenesulfonic acid concentrations at the bank filtration site Tegel (n=6)

6.1.3 Bank filtration field site Lake Wannsee

The monitoring program for the bank filtration site Wannsee started in May 2002. During winter 2002/03 a new transect near drinking water well 3 was build because the old transect did not comply with the demands of the project. The sampling of the new transect started in February 2003. The samples from this new transect were included in the monthly analysis program. Only data from the new transect are presented in Figures 20 to 26.

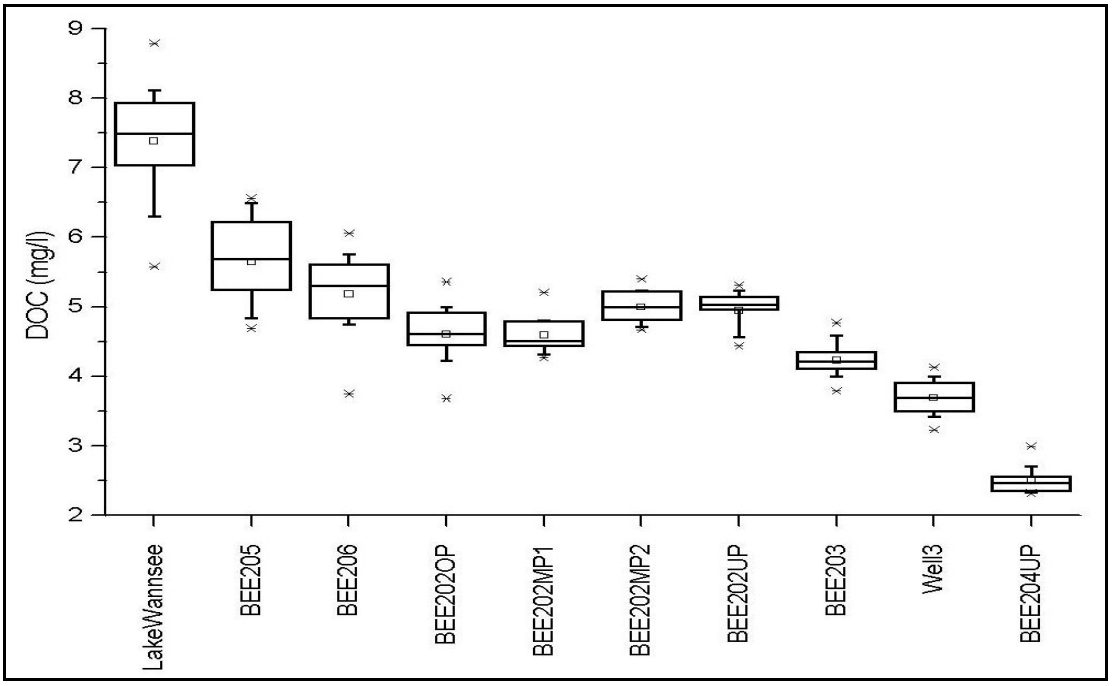


Figure 20 Box plots of DOC concentrations at the bank filtration site Wannsee (n=11-18)

The DOC-profile of the new transect at Lake Wannsee is comparable to the profile at the Tegel site. It is apparent that the high surface water DOC (7-8 mg/l) is reduced during infiltration to approximately 4.5 mg/l in BEE203. The wells BEE202MP2 and BEE202UP do not receive actual bank filtrate. The origin of this water is more or less unclear. It might be older bank filtrate that infiltrated through the lake bed or groundwater from the other side of the lake. Other parameters indicate that this water differs from the new bank filtrate in the other monitoring wells.

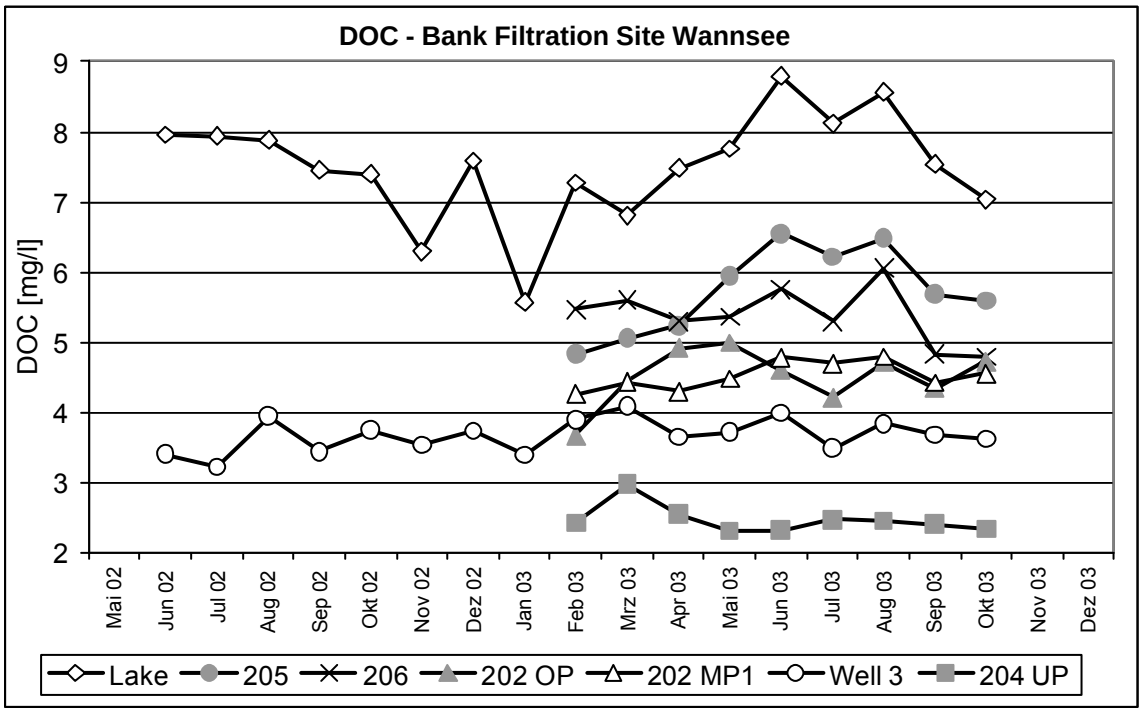


Figure 21 Time series of DOC concentrations at the bank filtration site Wannsee

The time series of DOC measurements show a fluctuation of the surface water DOC with the seasons. During the project it was found that algae blooms affect Lake Wannsee stronger than Lake Tegel. The higher DOC during summer might be due to algal cellular products. This fluctuation is also visible in the first observation well BEE205. The other monitoring wells and the background groundwater remain more or less at a constant DOC level. Because of the late construction of these transect the data base is not as strong as for the Tegel site.

The AOI monitoring shows that the AOI concentrations are decreasing towards the drinking water well, but the relatively shallow wells (BEE206, 202OP, 203) still contain considerable amounts of AOI (Figure 22). The deeper wells and the well BEE205 contain less AOI. BEE202MP2/UP contain less AOI because they are not probing the actual bank filtrate. For the monitoring wells BEE205 and BE202MP1 no final conclusion can be made because of the uncertain hydraulic situation. Currently, it is not clear whether the low AOI concentrations result from degradation of the AOI under anaerobic conditions or whether these wells probe different water. In collaboration with the hydrogeological group of the FU Berlin this question will be answered.

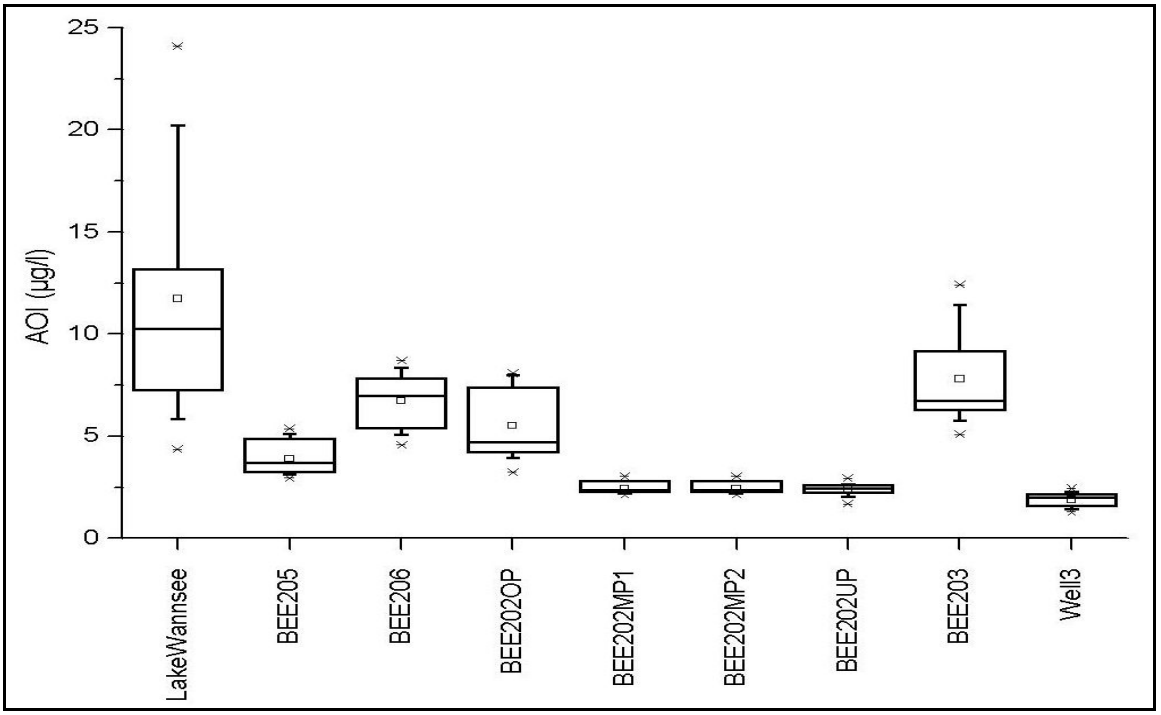


Figure 22 Box plots of AOI concentrations at the bank filtration site Wannsee (n=11-18)

In the time series of the AOI measurements the strong seasonal variations in the surface water is apparent (Figure 23). During the hot summer of 2003 the maximum AOI concentration is approximately 25 µg/l. But the rising of the AOI-concentration in the lake starts later than at Lake Tegel. A reaction of the monitoring wells is not really visible until now. Data for 2004 will clarify whether the seasonal variations of AOI affect the bank filtration system.

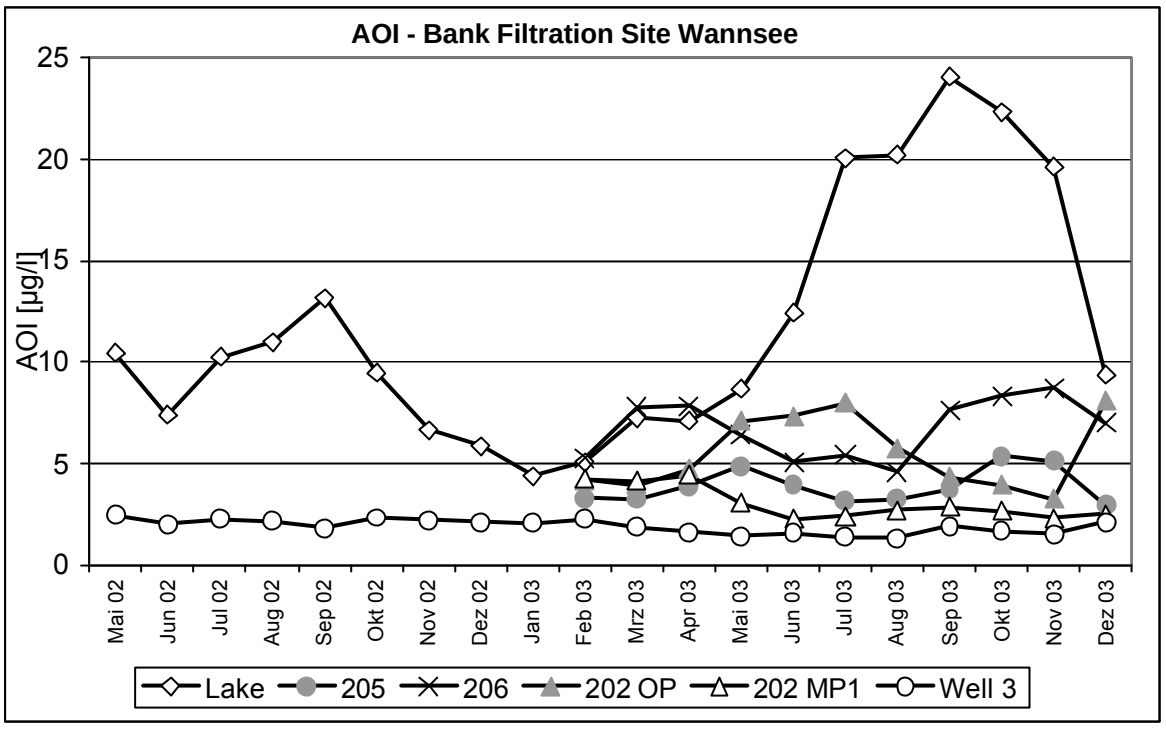


Figure 23 Time series of AOI in the monitoring wells at the bank filtration site Wannsee

The AOBr concentrations along the transect at Lake Wannsee follow a similar pattern as the AOI concentrations (Figure 24). For the interpretation of the data the hydraulic situation needs to be reliable. Figure 25 shows that the highest concentrations for AOBr (approximately 40-45 µg/l) are measured in July/August 2003. Compared to Lake Tegel the concentrations are higher (Tegel => 24 µg/l) and they are rising earlier. An alignment of the AOBr data with the algae blooms in the two different lakes will be part of the work in 2004.

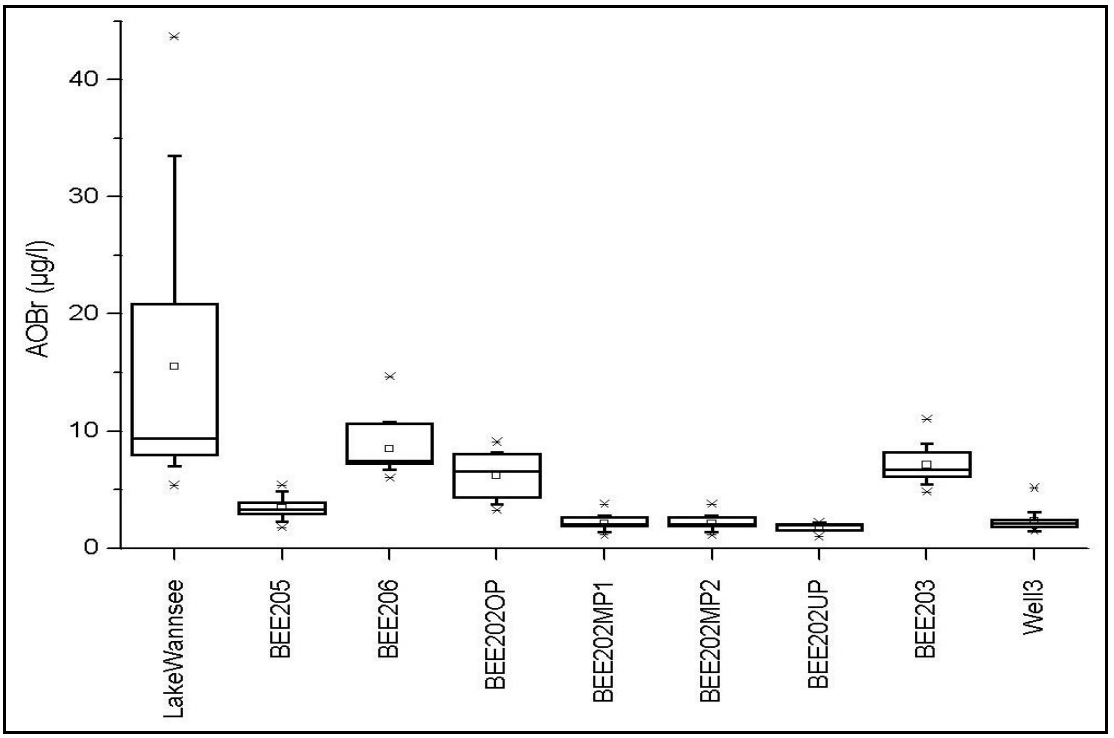


Figure 24 Box plots of AOBr concentrations at the bank filtration site Wannsee (n=11-18)

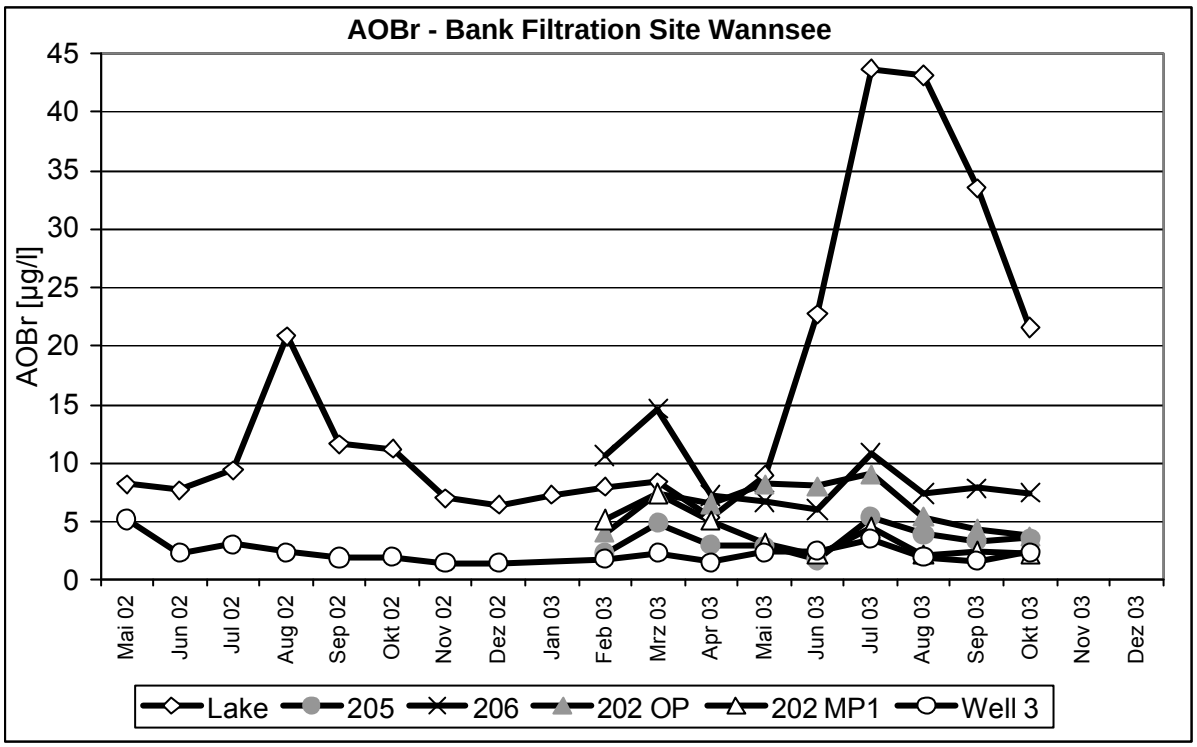


Figure 25 Time series of AOBr at the bank filtration site Wannsee

The trace pollutants analysis at Lake Wannsee shows that Iopromide and Sulfamethoxazole are degraded or metabolized during infiltration (Figure 26). The results are comparable to the findings at Lake Tegel. The concentrations of the Naphthalenesulfonic acids in the background groundwater are higher than in Tegel, but the levels in the drinking water well are comparable. Sulfamethoxazole and Iopromide are undetectable in the background groundwater.

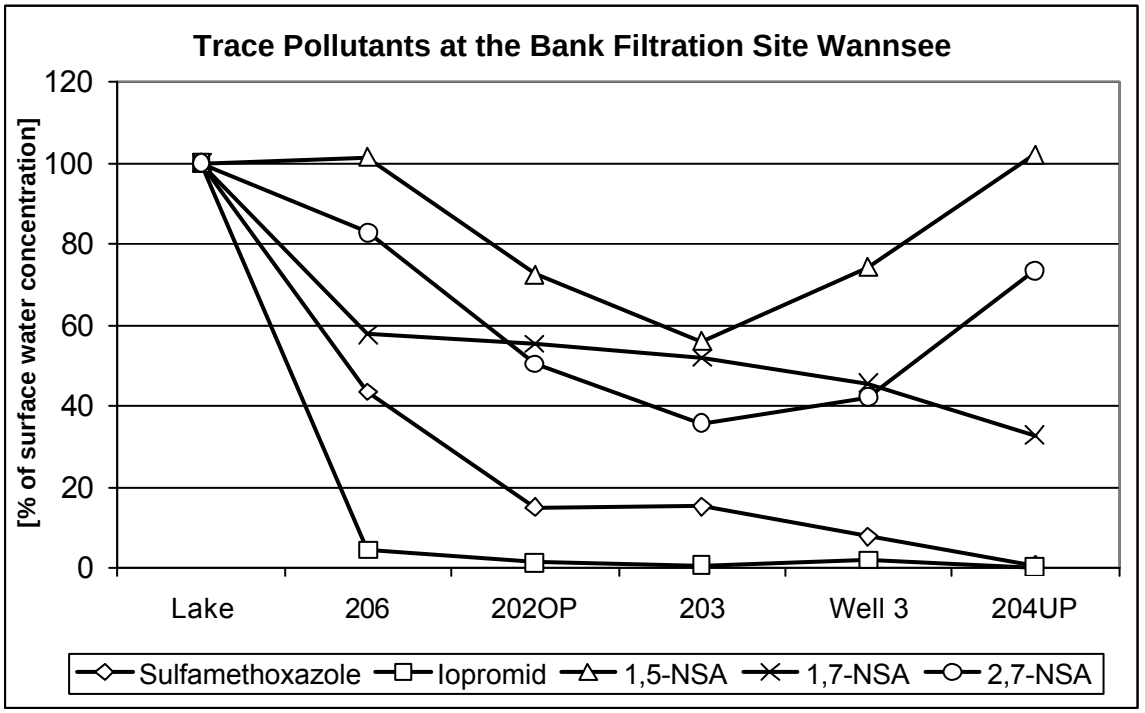


Figure 26 Fate of 5 different trace pollutants at the bank filtration site Wannsee

Table 5 Absolute concentrations of the trace pollutants at the bank filtration site

Means (n=6)	Sulfamethoxazole		Iopromid		1,5-NSA		1,7-NSA		2,7-NSA	
	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s	[ng/l]	s
Lake Wannsee	209	35	1087	159	78	16	441	100	78	11
206	91	36	47	31	79	27	254	48	64	15
202OP	31	22	14	11	57	6	244	46	39	2
202MP2	3	0	6	0	111	21	436	5	66	17
202UP	0	7	0	8	107	29	483	46	91	20
203	32	12	6	12	44	11	229	22	28	7
BBr3	16	2	21	0	58	15	201	15	33	9
204UP	1	0	0	0	80	15	145	29	57	11

6.2 Simulation experiments

6.2.1 Long-retention columns at the semi-technical site (Marienfelde)

The long retention soil column system was installed as a simulation of a one dimensional aquifer to eliminate outside influences and to provide a closer insight into the kinetics of the degradation processes. In 2002 the set-up of the columns and a tracer experiment were completed. The tracer experiment helped to characterize the filling of the columns regarding pore size and dispersion. In December 2002 the acclimation period of the columns was started. Water from Lake Tegel was provided and fed to the columns with a pumping rate of 1.5 l/h. This pumping rate results in a retention time of 30 days. An online dosage of the five trace compounds was installed to assure a constant concentration of these five compounds in the influent. The spiking concentrations were selected to be approximately ten times higher than the concentration in Lake Tegel. Table 6 gives an overview of the dosages of trace compounds to the lake water.

Table 6 Spiking concentrations for the long retention columns in Marienfelde

Trace Compound	Spiking Concentration
Iopromide	10 µg/l
Sulfamethoxazole	2,5 µg/l
1,5-NSA	2,5 µg/l
1,7-NSA	2,5 µg/l
2,7-NSA	2,5 µg/l

During this first part of the experiment it was planned to establish oxic conditions in the soil columns to simulate the infiltration at the groundwater recharge facility. The acclimation period for the columns lasted until May 2003. Monitoring of the DOC, UVA and redox-conditions was started to detect the stabling conditions. In May 2003 the profiles of DOC and UVA were nearly constant. Measurements of AOI, LC-OCD and trace compounds were started.

Additionally a collaboration with the “drug” group of the Department of food chemistry of the TU Berlin started at the end of May 2003. As part of this collaboration four pharmaceuticals (clofibric acid, diclofenac, ibuprofen and bezafibrate) were spiked to the column influent for two weeks and the effluent after 30 meter was analyzed. At the same time an experiment of the FU Berlin examined the stability of the Gadolinium-DTPA complex as a tracer. The results of these experiments verified the findings of the tracer experiment in 2002 regarding retention time, pore

volume and dispersion. The degradation of the pharmaceuticals was more complete than expected. Therefore, it can be concluded that a capable biological community was developed during the adaptation phase. The detailed findings of these collaborations will be available in the periodical reports by the hydrogeology group and the drug group.

Figure 27 shows the soil column design schematic.

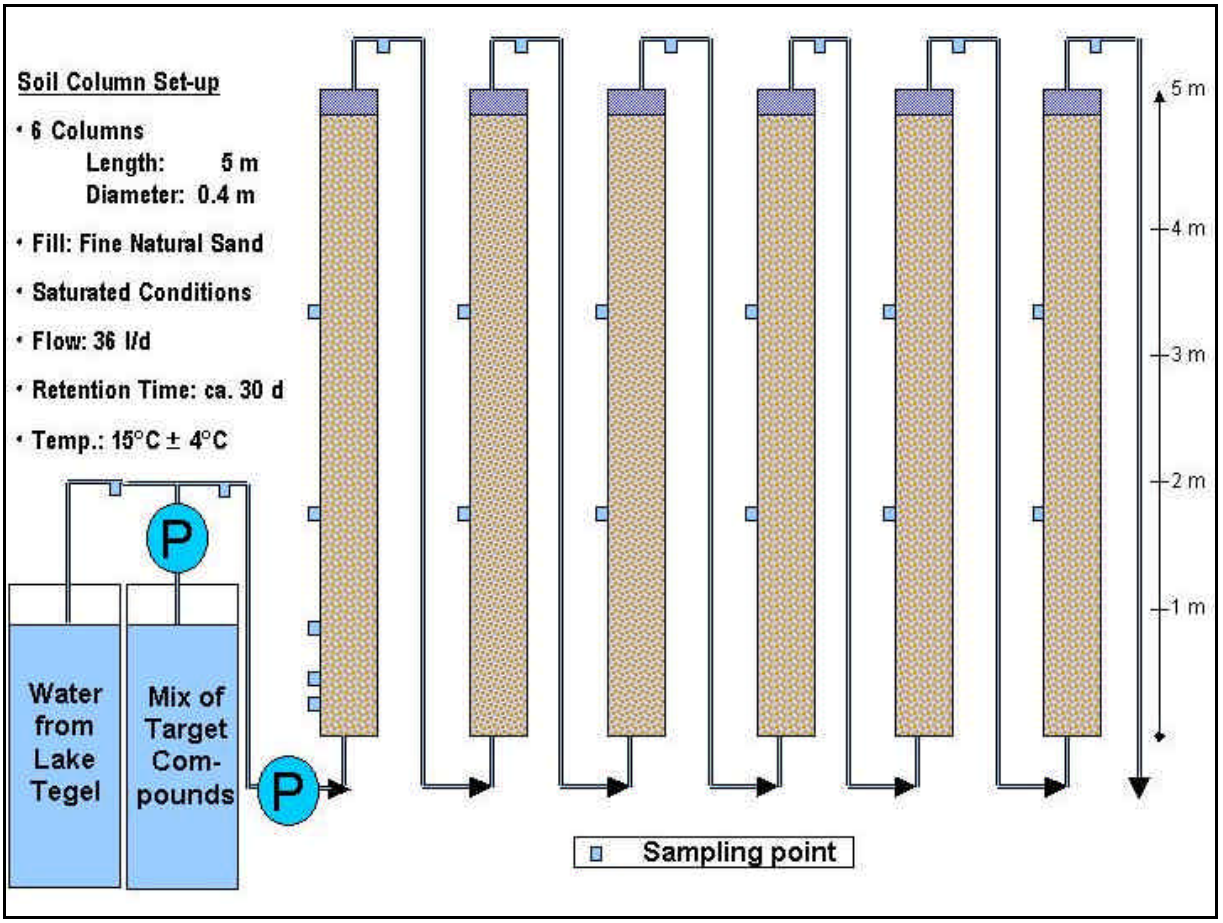


Figure 27 Experimental set-up of the long retention columns

The research of the DWQC at the long retention columns focused on the fate of dissolved organic carbon, the bulk parameters UVA and AOI and some trace compounds. The results are presented in the following figures.

Figure 28 shows that the profile of dissolved organic carbon in the long retention columns is comparable to the groundwater recharge facility. During the first five meters an efficient reduction of DOC takes place and after 10 meters the final concentration of 3.5-4 mg/l is achieved. This kinetic of DOC degradation is characteristic for an aerobic infiltration process. After a problem with the 600 l storage tank, which led to a depletion of oxygen out of the columns, the system is nearly back to complete oxic conditions since September 2003. Comparing the DOC profile, UVA data and the character of DOC in the product water it can be concluded that the long retention columns are a good simulation of the real recharge process at the facility in Tegel. Figure 29 demonstrates the efficiency of the degradation process. In the first 0.20 m of infiltration the character of the DOC is changed remarkably. The fraction of the

polysaccharides is completely degraded and the other fractions partially. This was observed at the field sites as well. The better resolution of the soil columns demonstrated how rapid this process is. The first meters of the infiltration medium seem to be very efficient. As a consequence it can be assumed that the microbial density is very high in this area.

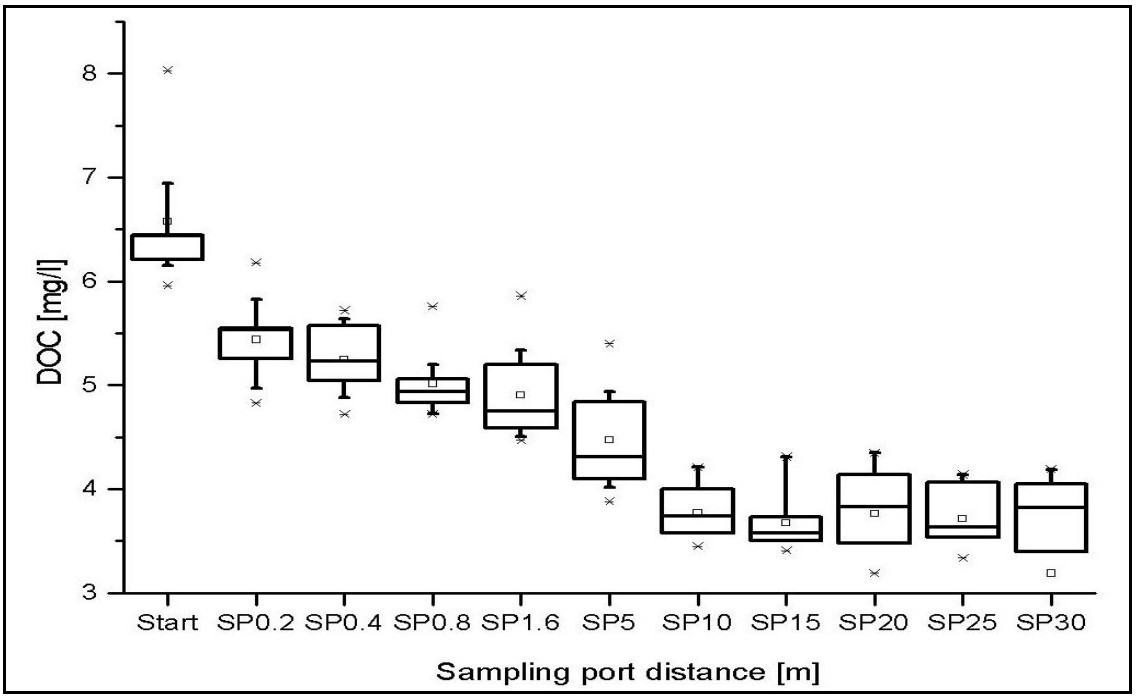


Figure 28 Box plots of DOC concentrations in the long retention columns (n=11)

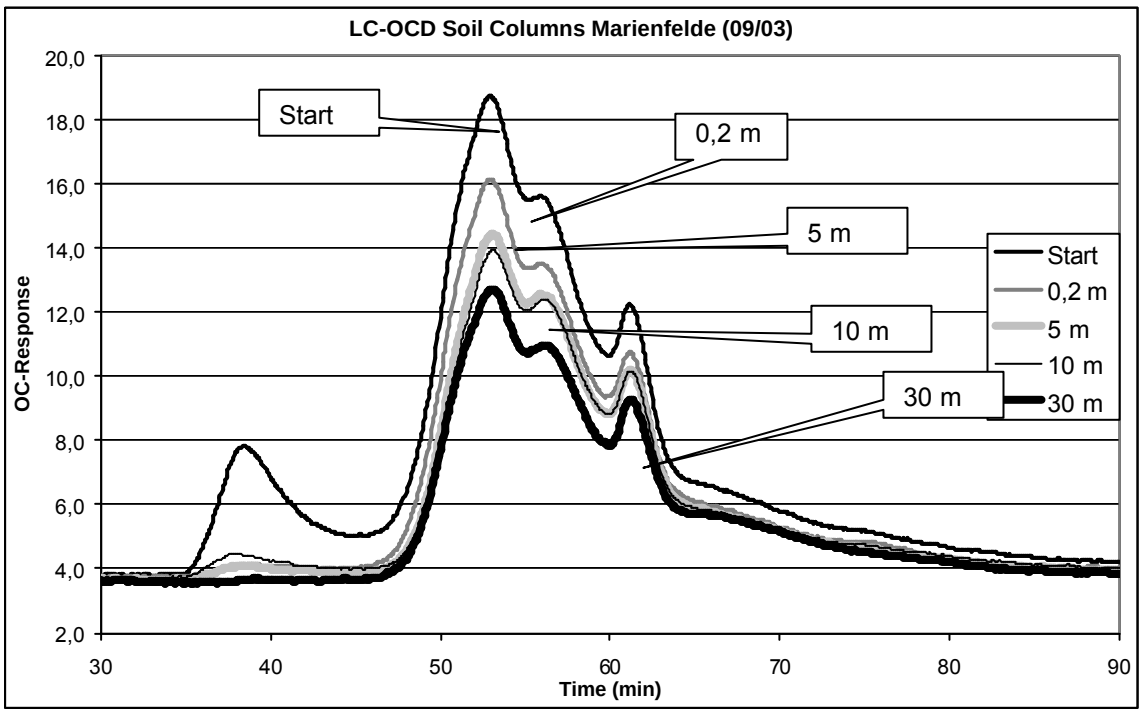


Figure 29 LC-OCD chromatogram of samples from the long retention columns (September 2003)

The AOI measurements proved the assumption that there is nearly no AOI reduction under aerobic conditions. Figure 30 shows that the AOI level remains nearly constant along the columns. The variation in the influent and the first sampling points is due to fluctuation of Lake Tegel AOI. The higher AOI concentrations will likely reach the sampling points at the end of the columns in January 2004. The spiking of 10 µg/l Iopromide increases the AOI concentration in the feed by 4.81 µg/l. The evidence that this AOI is not efficiently degraded was supplied by comparing time shifted samples.

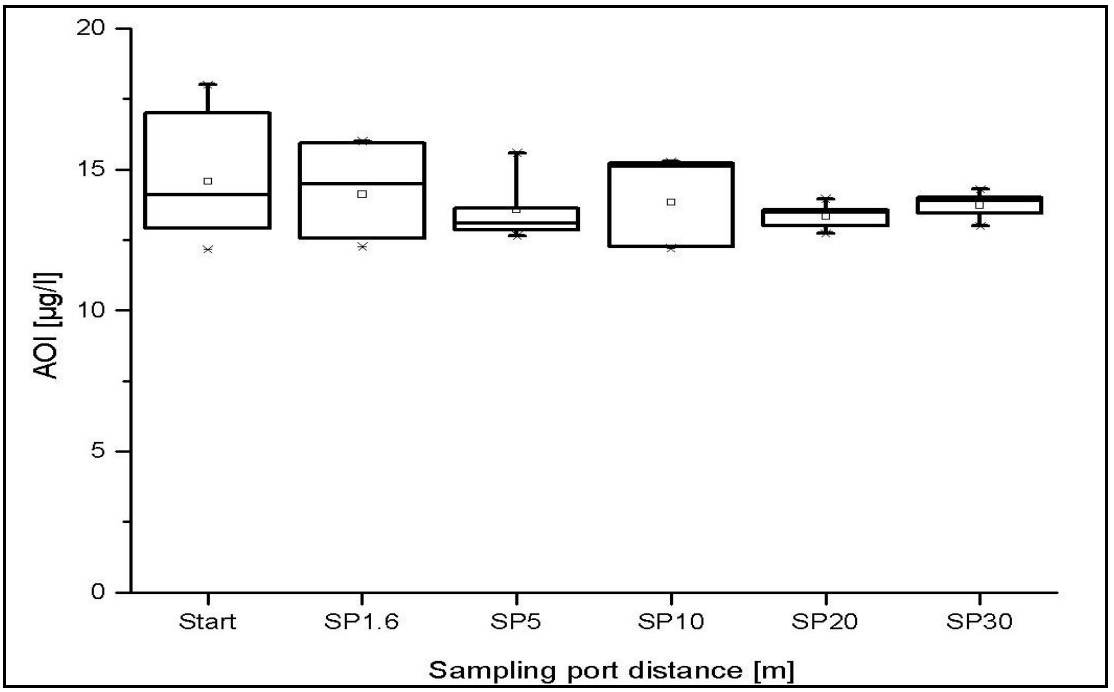
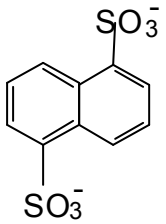
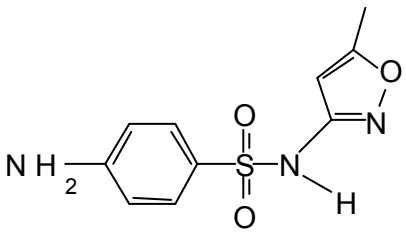
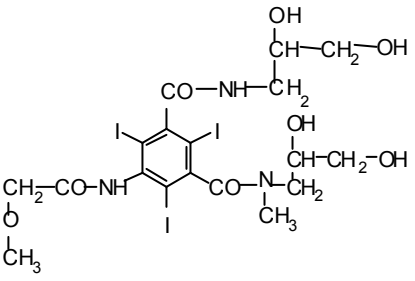


Figure 30 Box plots of AOI concentrations in the long retention columns (n=6)

At the long retention columns the same trace compounds were analyzed as in the field. Therefore, a comparison of the results was possible. Table 7 shows the chemical structure of the single compounds. One interesting aspect was to analyze Iopromide as a single compound and as a part of the AOI.

Table 7 Chemical structure of analyzed trace compounds

Naphthalenesulfonic acid	Sulfamethoxazole	Iopromide
		

In the monitoring of the soil columns it was found that the reduction of the trace compounds was often better than at the groundwater recharge site. For Sulfamethoxazole degradation rates of 50 to 60 % were measured at the recharge facility. In the soil columns with a much higher (10x) influent concentration, a reduction rate of 95% was reached. The retention rates of both systems are comparable around 30 days. The reason for a better degradation of Sulfamethoxazole in the soil columns is unknown. But two of the naphthalenesulfonic acids are better degraded as well. The 1,7- and the 2,7-NSA, known as partly degradable, were efficiently removed. The degradation rates were 99% or 100%, respectively. In the recharge facility only rates around 60% were measured. The very stable 1,5 –NSA achieved a degradation rate of 10%. This reiterates the assumption that adsorption does not play a major role for these compound groups in the soil columns.

Table 8 Concentrations of the target compounds in the long retention columns

Means, n=6		Lake Tegel	LT + Spiking	BSM 4	BSM 6	BSM 15	BSM 21
Iopromide	**[ng/l]**	**821**	**11100**	**857**	**967**	**48**	**83**
Sulfamethoxazole	**[ng/l]**	**430**	**2403**	**787**	**574**	**315**	**123**
1,5-NSA	**[ng/l]**	**124**	**2219**	**2436**	**2253**	**2119**	**2040**
1,7-NSA	**[ng/l]**	**255**	**2482**	**292**	**28**	**14**	**15**
2,7-NSA	**[ng/l]**	**124**	**2445**	**0**	**0**	**0**	**0**

The removal of 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 metabolized during infiltration. This was only suspected at the field sites but was confirmed with the soil columns. Iopromide is spiked to the lake water and accounts for approximately one third of the AOI (5 µg/l). Figure 31 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.

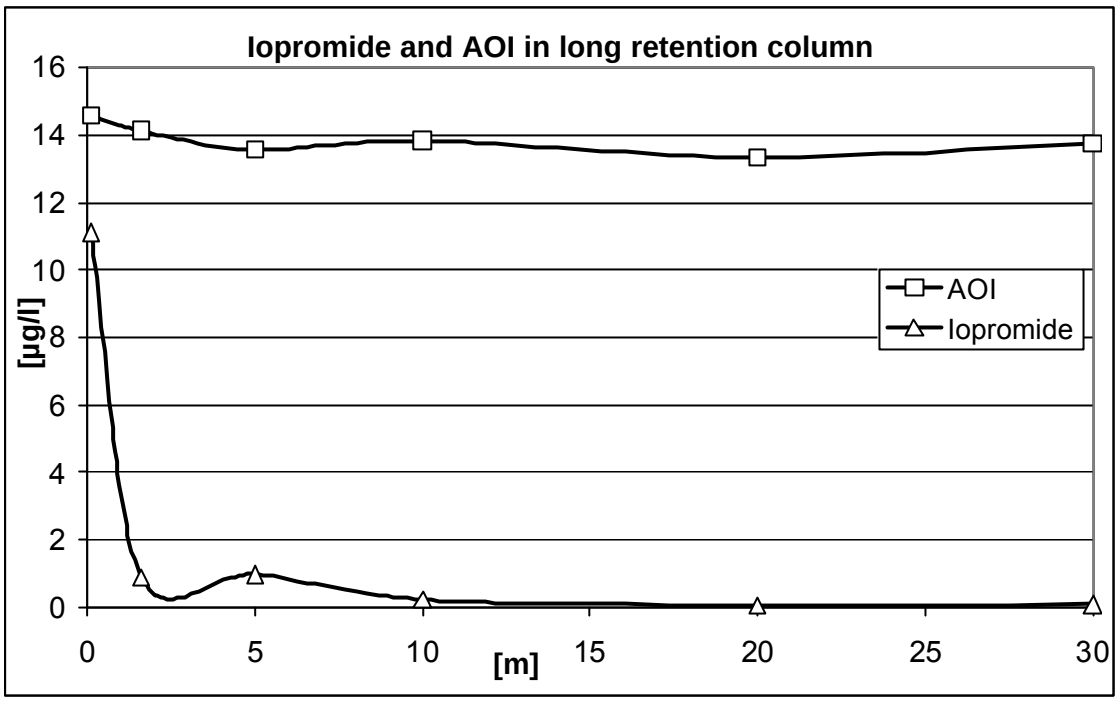


Figure 31 Concentrations of AOI and Iopromide in the soil columns (means, n=6)

The work at the soil columns will continue with an anaerobic phase. It is planned to deplete the oxygen from the system and to achieve anaerobic conditions. The monitoring of DOC, AOI, UVA, LC-OCD and trace components will continue to detect eventual changes in the removal efficiency.

6.2.2 Short retention columns at TU Berlin

In April 2003 a set of short columns was installed at the department of water quality control. These columns were used to examine additional influences on the degradation of organic carbon. The 1m short retention columns are filled with silica sand and operated under forced redox conditions with spiked Lake Tegel water. The columns have a retention time of 3.3 days and a flow of 1.5 l/d. Four different soil passage conditions are represented.

- Column 1 Aerobic soil passage
- Column 2 Anoxic soil passage (feed sparged with N_2)
- Column 3 Anaerobic soil passage (addition of starch)
- Column 4 Anoxic soil passage with enforced denitrification (N_2-sparged, NO_3^--addition)
- Column 5 Longer anoxic retention time (effluent of column 2)

The acclimation period started in April 2003. In July 2003 the DOC degradation rates and the UVA adsorption of the effluent were relatively stable. Samples for the monitoring were taken two times a month. Figure 32 presents a schematic of the set up of the short retention columns.

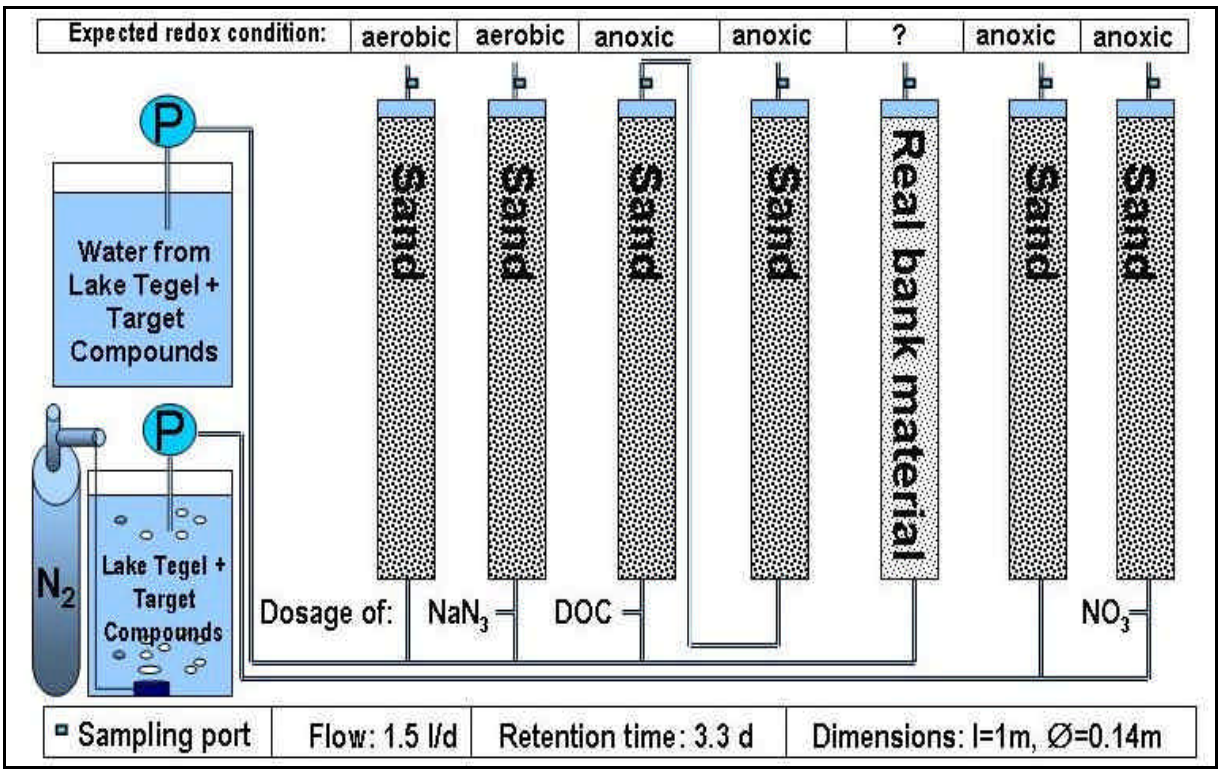


Figure 32 Experimental set-up of the short retention columns

Differences in the efficiency of DOC removal were visible under different redox conditions in the columns. Figure 33 shows the results for columns 1-5. Column 1 is representative for an aerobic soil passage. It is obvious that column 1 is performing best in DOC degradation. During 3.3 days of retention time approximately 18 percent of the DOC is degraded. A lower efficiency was observed under anaerobic conditions. Column 2 with an oxygen free influent only reaches 5 percent DOC removal after 3.3 days. But after an extension of the retention time under anaerobic conditions to 6.6 days (column 5) a removal rate of 14 percent was achieved. The anaerobic column with enhanced denitrification (column 4) performs more effective than column 2 without NO_3^--dosage. Column 4 removes approximately 12 percent of the DOC.

Since there are detectable differences regarding the degradation of DOC under different redox potentials, the short retention columns will be used to conduct research on the degradability of the different fractions of DOC under the given redox conditions. LC-OCD analysis will be used to quantify these variations. Additionally the trace compound analysis will continue. Until now the data base of the trace compound analysis at the short retention columns is not strong enough to draw final conclusions.

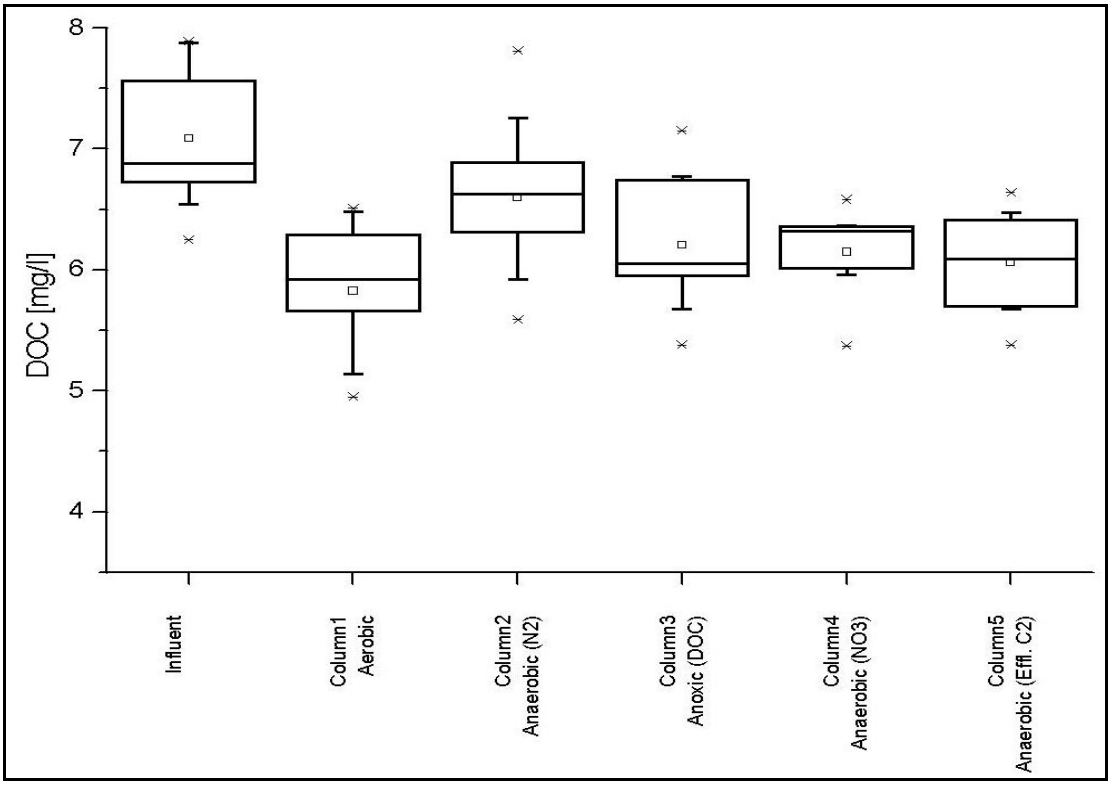


Figure 33 Box plots of DOC concentrations in the short retention columns (n=12)

More short soil columns are utilized to quantify the role of adsorption and the differences between silica sand and original soil material from a field site. Two additional columns are filled with material from Lake Tegel one should be representative for the bank region and one for the aquifer situation. The original material was taken as a disturbed sample and immediately after sampling introduced into the columns. Nevertheless, because of the disturbance of the natural soil structure DOC is leaching out of the columns. Momentarily a high biological activity is present in the columns due to the available dissolved carbon. But the monitoring shows that the leaching process declines and soon experiments should start to quantify the role of adsorption.

6.2.3 Enclosure experiments in Marienfelde

Two enclosure experiments in Marienfelde were conducted to examine the role of the "Schmutzdecke" in the degradation process for bulk and trace organics. This work was a collaboration with the algae group of the UBA. They were run as a part of a study work of Juliane Mohaupt at the DWQC. Therefore, two experiments were performed at the slow sand filters called enclosures, one with "Schmutzdecke" and one without. The influent was spiked with trace compounds and hourly monitoring assured that the effects of the infiltration were documented. Prior to these tests, the hydraulics of the enclosures were examined with tracer studies. Additionally, the "Schmutzdecke" was characterized with microbiological methods. The results of this study work will be available in April 2004.

7 Perspectives / Intended tasks for the upcoming project period (January – June 2004)

Task	Comments
Continue monitoring of field sites until June 2004	Monitoring will provide deeper insight in the processes at the filed sites. Especially, effects of changing boundary conditions for the bank filtration can be examined. Trace compound analysis is continuing until June 2004 to achieve one full year of data.
Examine the actual situation at Lake Tegel	Examination of the actual removal rates of the surface water treatment plant Tegel, Clarification of the influences on the composition of the organic bulk parameter in front of the bank filtration transect Tegel
Work out of mass balances	Mass balances for DOC, TIC and redox parameter will clarify the actual reactions during the infiltration process
Continue aerobic aquifer simulation in long retention columns	Aerobic simulation with spiked water from Lake Tegel will probably end by April 2004. Sample and analysis program on a biweekly basis.
Start of anaerobic aquifer simulation in long retention columns	Anaerobic simulation of bank filtration site Lake Tegel will probably start in April 2004. Sample and analysis program on a biweekly basis. Data for aerobic and anaerobic infiltration will allow the comparison of the fate of DOC, AOI, UVA and trace compounds.
Continue experiments with short retention columns	Build up of a database for the effects of the different redox conditions on the analyzed parameters. Parameter list: DOC, UVA, AOI, AOBr, LC-OCD, Trace compounds
Install database for data from previous research	Summarizing the data from previous research will help to validate and discuss the new data. Revealing long term effects.
Start of Adsorption studies	Adsorption studies for the trace compounds, batch tests of soil column test will be conducted
Start of the development of biodegradation kinetics	With the end of the monitoring of the field sites it is planned to develop kinetic equations for the removal of the bulk and trace compounds. Data from field measurements and Soil column data will be used.
Start of the model development	In collaboration with the model group it is planned to develop models for the fate of organic bulk parameters and trace compounds. These models should be applicable to other bank filtration sites and would add to the transferability of the NASRI results.

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4th periodic report

(Reporting period July to December 2003)

"Retention and Elimination of Cyanobacterial Toxins (Microcystins) through Artificial Recharge and Bank Filtration" ("Algae")

Abstract:

During the second year of the project the field observations were continued and a first series of technical scale experiments was conducted on the UBA's experimental field.
In spite of a very warm and dry summer the microcystin concentrations at Lake Wannsee did not exceed those measured in the last few years. In Groundwater samples analysed by ELISA microcystins were detectable at low concentrations sporadically in shallow observation wells.
On the UBA's experimental field a total of ten experiments were conducted on the slow sand filters and enclosures in cooperation with the working groups UBA-bacteria, TU-drugs, TU-organics and FU-hydrogeo.

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Berlin, January 30th, 2004

1. Extended Summary

During the second year of the project the field observations were continued and a first series of technical scale experiments was conducted on the sealed infiltration pond and enclosures on the UBA's experimental field.

The results of Lake and AR pond Tegel surface water sampling showed low microcystin (MCYST) concentration similar to those that had been observed during the last few years. This is due to only small cyanobacterial biovolumes resulting from low nutrient levels. As preliminary investigations did not show any detectable MCYST in the groundwater at these surface water concentrations no groundwater samples were analysed in 2003.

In spite of a very warm and dry summer the microcystin concentrations at Lake Wannsee did not exceed those measured in the last few years. The highest values for cell-bound MCYST measured resulted from a bloom of *Planktothrix agardhii* (as in the years before) and reached 20 µg/L. Extracellular MCYST was detected sporadically only with a maximum of 1 µg/L. In groundwater samples analysed by ELISA microcystins were sometimes detectable at concentrations lower than 0.5 µg/L in shallow observation wells. We have not been able to confirm these results by HPLC-PDA and are using HPLC-MS/MS for lower detection limits in 2004.

On the UBA's experimental field a total of ten experiments were conducted on the slow sand filters and enclosures in cooperation with the working groups UBA-bacteria, TU-drugs, TU-organics and FU-hydrogeo. Organic trace substances as well as viruses and bacteria were used.

The aim of the experiments conducted in 2003 was to quantify the elimination of the different substances in the first meter of sediment passage under aerobic conditions, with fairly high filtration rates and intact or missing schmutzdecke.

From the data available so far, a substantial reduction of extracellular MCYST (maximum concentration after 80 cm sediment passage: 15 % of input concentration) was observed even under unfavorable conditions (high filtration velocity, missing schmutzdecke, virgin sand). The observation of MCYST variants in the effluent samples that had not been detected in the water reservoir presented at the NASRI workshop was confirmed in all experiments that have been analysed so far. Additional efforts will be made in 2004 (e.g. external analyses by HPLC-MS/MS and MALDI-TOF, dilution experiments) to be sure that this is not an effect caused by analytical problems.

Our main focus until summer 2004 will be on the introduction of anoxic conditions in the enclosures with subsequent experiments using extracellular MCYST. Later in 2004 experiments with cell-bound toxins will be conducted focussing on the relation between cell-bound and extracellular MCYST in the water reservoir and in/on the sediment.

2. Objectives

The Objectives of this project are to

- **Determine the range of conditions under which microbial degradation of cyanobacterial toxins (microcystins, MC) in artificial recharge (AR) and river-bank filtration (BF) is reliable**.

  The investigations conducted so far have shown that AR and BF generally lead to an efficient elimination of cell-bound microcystins by filtration and of dissolved microcystins by biodegradation. Because of their human health relevance, the elimination of microcystins has to be secured for extreme conditions:

  - Missing schmutzdecke (AR) or lake sediments (BF),
  - Virgin sand (AR),
  - High filtration rates (AR),
  - Anoxic conditions (AR and BF).

- **Assess whether cyanobacterial cells accumulated at the sediment/water interface or in the filter body are a relevant source of toxins in filtered water**.

  Most of the microcystins in healthy populations are cell-bound. The high elimination rates during AR and BF are primarily due to physical filtration of the cells. However, investigations are lacking to show viability of cells retained on filters, whether they continue to produce MC, if and how fast they release MC and if there are degradation products which can be identified in the sediment. Investigations on the fate of the cyanobacterial cells retained on filters and in water-body sediments and their toxin content are therefore needed.

- **Determine the conditions under which lysis of cyanobacterial cells accumulated on filters and sediments may cause pulsed release.**

  As shown above high concentrations of lysing cyanobacterial cells, as would potentially be accumulated on a filter or sediment surface, can lead to high amounts of – potentially pulsed – release of dissolved MC. The cells filtered during AR or BF are a potential source of high MC-concentrations. It is therefore important to assess whether conditions occurring in practice may induce lysis and toxin release of cells accumulated on the upper layer of infiltration ponds or in lake sediments.

3. Timetable

The timetable as originally planned had to be changed due to delay in the construction of the enclosures (see 2nd report, Dec. 02). For this reason the first series of experiments on the enclosures could not be commenced until summer 2003 (rather than autumn 2002). Yet all experiments originally planned can be carried out until autumn 2004 (figure 0).

In the beginning of the project three large-scale experiments were planned for UBA's experimental field. In cooperation with the project partners UBA-bacteria and TU-drugs it turned out to be better to conduct more experiments with only slightly changed conditions shortly after each other in order to distinguish the effect of the changed conditions on substance removal. Due to these considerations a series of five experiments was carried out on the sealed infiltration pond in 2003. A second series is planned for summer 2004.

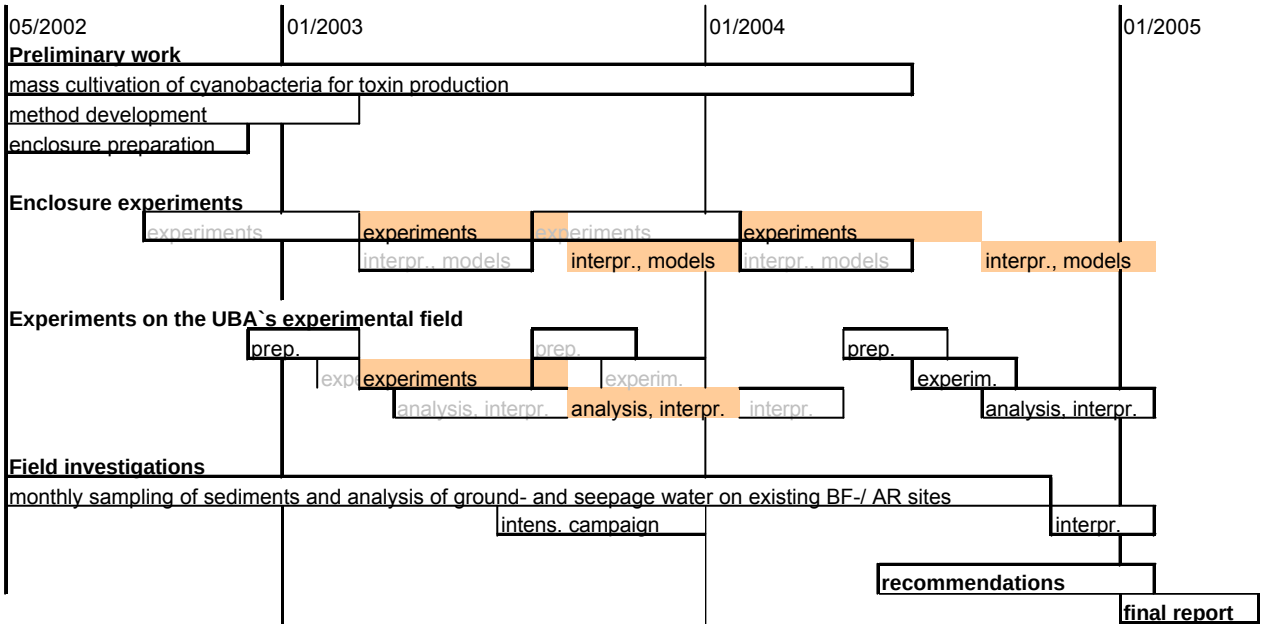

Figure 0: Adjusted timetable for the UBA-algae working group.

4. Intended and achieved tasks for the reporting period

Task	achieved ?	comments
Preliminary work		
mass cultivation of cyanobacteria	✓	
method development: microbiology and degradation products	(✓)	delay due to not granted cooperation with the microbiology working group at Flinders University, Adelaide, Australia. preliminary batch experiment will be conducted in 2004 by UBA-bacteria group
Field investigations		
monthly sampling and analysis of surface and groundwater (BF field sites Wannsee and Tegel)	✓	cooperation with BWB
weekly sampling and analysis of surface water (Lake Wannsee) during summer and autumn	✓	
sampling of lake sediment (Lake Wannsee)	✓	
monthly observation of phytoplankton development at AR pond Tegel (until may 2003)	✓	
Semi-technical site Marienfelde		
tracer experiments in enclosures, 1st series of experiments with dissolved MCYST	✓	6 months delay due to extremely cold weather until march and technical difficulties
2nd series of experiments with cell-bound MCYST and high DOC	-	see above, to be carried out in 2004
1st series of experiments on sealed infiltration pond	✓	conduction of five experiments instead of two planned for 2003

5. Results

5.1. Investigations at the field sites

With exception of the weekly samples for phytoplankton observation and the two cores of lake sediment at Lake Wannsee, all sampling was done by BWB.

5.1.1. Artificial recharge pond Tegel

Monthly samples of the surface water were first analyzed by microscope according to Lawton et al. (1999) to determine if cyanobacteria were present. In presence of cyanobacteria HPLC-PDA (High Pressure Liquid Chromatography – Diode Array) analyses for cell-bound microcystins were carried out after filtration and extraction according to Fastner et al. (1998). The results are shown in Table 1.

Table 1: Results of microscopic and HPLC-analysis of surface water at the artificial recharge pond in Tegel (GWA Tegel).

Date	Cyanobacteria detected by microscopic analysis	Biovolume (mm³/L)	Date of HPLC-DA analysis	cell-bound Microcystins variants (HPLC-DA) in µg/L
5/24/02	none	not determined	no analysis	
7/18/02	none	not determined	10/24/02	< 0.01*
8/15/02	few (*Microcystis* sp.)	0.06	10/23/02	< 0.01*
9/17/02	few (*Microcystis* sp.)	0.05	10/24/02	< 0.01*
10/18/02	very few (*Planktothrix agardhii*)	< determination limit	10/24/02	< 0.01*
11/21/02	very few (*Microcystis* sp., *Planktothrix agardhii* , *Limnothrix* sp. (?))	< determination limit	no analysis	
12/12/02	very few (*Planktothrix agardhii, Limnothrix redeckii*)	0.35	1/20/03	0.05
1/16/03	some (*Planktothrix agardhii, Limnothrix sp., Limnothrix redeckei, Pseudoanabaena sp.*)	0.27	1/29/03	0.14
2/13/03	some (*Planktothrix agardhii, Limnothrix sp., Limnothrix redeckei, Pseudoanabaena sp.*)	0.07	3/4/03	< 0.01*
3/13/03	very few	< determination limit	4/1/03	< 0.01*
4/24/03	very few (*Limnothrix redeckei*)	< determination limit	5/7/03	< 0.01*

* detection limit for individual MCYST variants

Only few cyanobacteria were found in the surface water of the AR pond. The highest biovolumes were observed during winter in December and January. During this time cyanobacterial biovolume reached values around 0.3 mm³/L. These are normal background concentrations for Lake Tegel and may be due to the fact that the microfiltration unit was shut off during winter.

Cell-bound Microcystins of 0.05 and 0.14 µg/L were detected in the December and January samples, respectively. However, extracellular Microcystin could be detected in none of these samples.

During a dry phase in July 2003 three cores (10 cm) were taken from the infiltration pond. One core was examined by microscope. The surface layer (1 mm) showed a high content of green algae (*Cladophora sp.*) and diatoms (*Navicula sp.*). Cyanobacteria were not present. Beneath the surface layer the amount of live organisms decreased rapidly.

Due to these low concentrations no groundwater samples were taken for toxin analysis and the investigations for cyanobacteria and microcystins in the surface water were not continued after April 2003.

5.1.2. Bank filtration field site Lake Tegel

As we know from investigations during the last few years (unpublished data by our own working group) cyanobacterial blooms have no longer been occurring in Lake Tegel (though minor populations have been present every summer, and temporarily increased concentrations of total P in 2001 provided a carrying capacity sufficient to sustain major populations). Therefore only surface water samples were taken for analysis of microcystin by ELISA.

The MCYST values measured are shown in figure 1. The bars indicating values lower than the limit of determination differ because this limit is specific to each ELISA series. Samples taken after June 2003 have not been analysed yet.

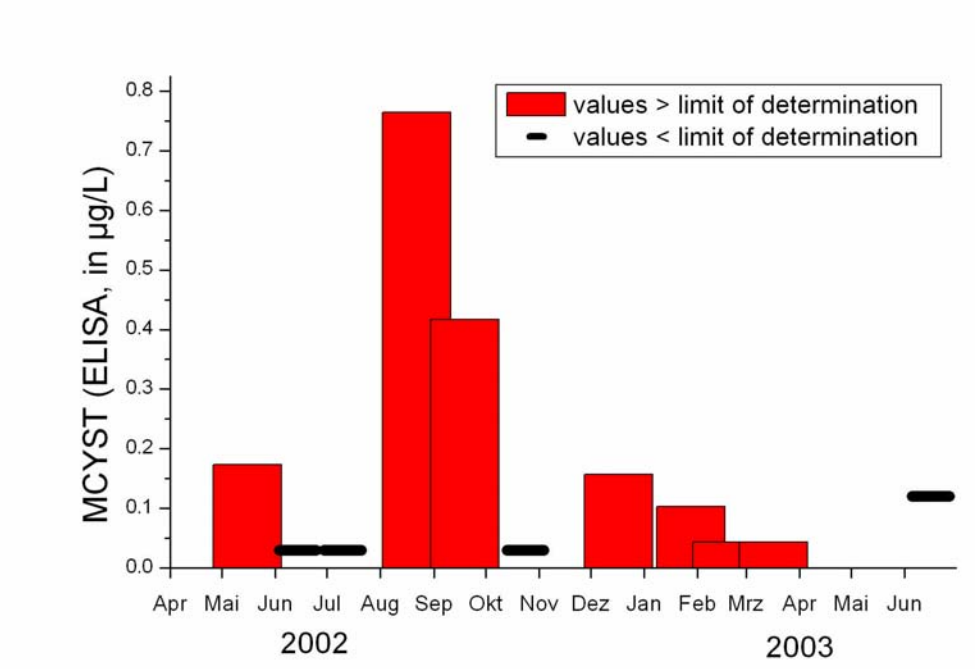

Figure 1: Total (cell-bound and extracellular) MCYST measured by ELISA in Lake Tegel.

Time patterns are similar to lake Wannsee, though at much lower concentrations, with the maximum values of microcystins (0.76 µg/L) being observed during late summer and autumn due

to a slight elevation in cyanobacterial biovolume (0.83 mm³/L in August, 14 % of total biovolume; unpublished data by our own working group). Qualitative microscopic observations show a similar development in biovolume for 2003.

5.1.3. Bank filtration field site Lake Wannsee

In addition to the monthly samples of surface and shallow groundwater for microcystin analysis that were taken by BWB surface water was sampled weekly in 0 m and 1 m depth. The aim was to obtain an accurate picture of the phytoplankton development which can sometimes vary in short terms in order to determine the optimal time for the intensive sampling campaign in autumn.

Surface water

During sampling a probe (FluoroProbe by bbe Moldaenke) which roughly reflects the biomass of major phytoplankton groups by prompt fluorescence response (see 2nd report, Dec. 02) was applied at about 1 m depth. Unfortunately, the values measured until July are not reliable, as the FluoroProbe had to be repaired in August, so that the first reliable fluorometric data in 2003 are from September.

The samples were additionally analysed by microscope for cyanobacterial biovolume according to Lawton et al. (1999) and by HPLC-PDA for cell-bound microcystins according to Fastner et al. (1998). The results are shown in Figure 2 and the values can be taken from appendix 1 and 2.

The microscopic analysis showed a massive cyanobacterial bloom of *Microcystis sp.* and *Aphanozomenon flos-aqae* in June and July. The maximum biovolume reached nearly 50 mm³/L, which is 4 times more than during the same time in 2002. The toxin concentrations, however, were similar to the year before, with a maximum of 5 µg/L. This is in part due to the unusual dominance of *Aphanozominon* , which so far has never been unambiguously shown to produce microcystins.

Similar to 2002 a second cyanobacterial bloom was observed from August to October. The pattern of MCYST variants changed distinctively compared to early summer, probably reflecting the development of *Planktothrix agardhii*. The samples for biovolume have however not been analysed yet.

Each sample with detectable cell-bound MCYST is subsequently analysed for extracellular MCYST after solid phase extraction according to Lawton et al. (1994). The results obtained so far are given in appendix 3. On three occasions values above the limit of determination were obtained (not all samples have however been analysed so far). The first time extracellular MCYSTs were determined was in the samples taken on 7th August. At this time the *Microcystis sp.* bloom was declining and extracellular MCYST concentrations reached 0.54 µg/L MCYST-LR in 1 m depth which approximately equals the concentration for cell-bound MCYST-LR (compare appendix 1). The samples taken the following 2 weeks have not been analysed yet, so we do not know for how long this unusual situation persisted.

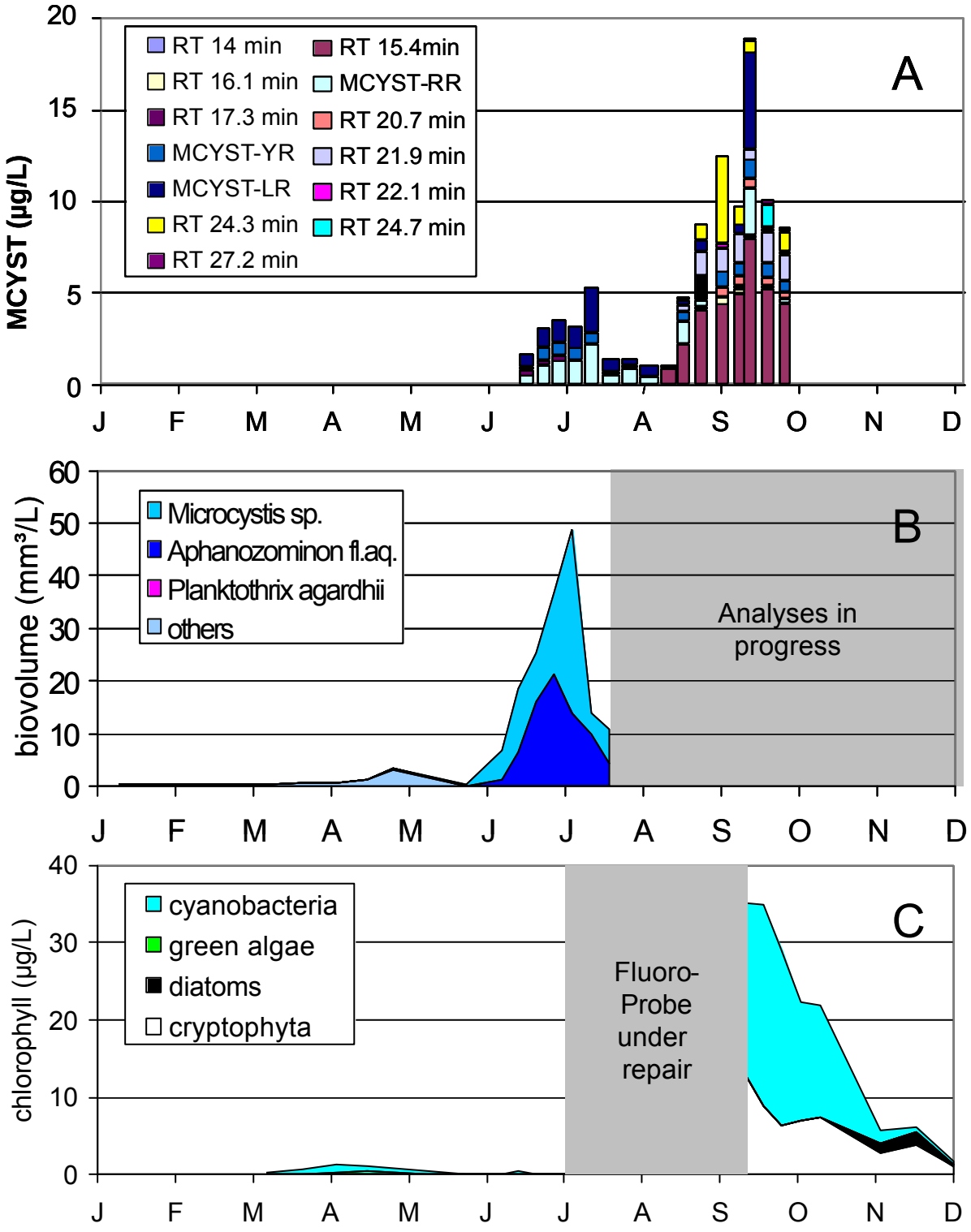

Figure 2:
A: Variants of cell-bound microcystin in Lake Wannsee during 2003 (RT = retention time).
B: Biovolume of cyanobacteria.
C: Cyanobacterial phyla, measured by the FluoroProbe (bbe Moldaenke), shaded areas: missing data.

In the sample taken on the 4th of September another extracellular MCYST variant was detected (retention time15.4 min), this one typical for *Planktothrix agardhii* (see figure 2). As the *Planktothrix* bloom was only just beginning there is no plausible reason for these values. The week before no

extracellular MCYSTs were detected. The samples taken one week later have, however not been analysed yet.
The third occasion on which extracellular MCYSTs were determined was in a sample collected from a slight surface scum that had accumulated in the wave zone. Cell-bound MCYSTs als analysed by HPLC reached nearly 20 µg/L. Two of the three extracellular variants detected were, however, not present in the cell-bound fraction.

Groundwater

A summary of the ELISA results of the ground- and surface water samples at Lake Wannsee is given in table 2. The values in detail can be taken from appendix 4. Samples taken before March 2003 were analysed using an ELISA that responds to the specific structure of the microcystin molecule (antibody MC10E7, Zeck et al. 2001a). After March 2003 a different antibody responding to the characteristic Adda-group of the MCYSTs was used (antibody AD4G2, Zeck et al. 2001b). The reason for this change in analytical method was that the Adda-ELISA, that usually shows a lower detection limit was not available earlier. The Adda-ELISA can include degradation products of MCYST whose ring structure has broken up but that still feature the Adda group (Zeck et al. 2001b). Not all samples taken in 2003 have been completely analysed so the values shown in table 2 give a first impression only.
The results show that regular positive ELISA response in groundwater is limited to the shallow observation wells 3339, 3338, 3337 and 3335 in transsect 1 as well as BEE205 and BEE206 in transsect 2. Values higher than 0.1 µg/L were only obtained when using the Adda-specific ELISA (see appendix 4).
Starting with the intensive sampling campaign in September 2003 samples from the shallow wells (3335, 3337, 3338, BEE201OP, BEE202OP, BEE202MP1, BEE203, BEE205 and BEE206) were additionaly analysed by HPLC. The results as completed so far (samples taken in November and December have not been analysed yet) show a single finding of 0.01 µg/L cell-bound MCYST in BEE202OP. This was not confirmed by the ELISA so that contamination during sample preparation can not be ruled out.

Table 2: Results of ELISA determination of total MCYSTs in ground- and surface water at Lake Wannsee transsects.

Observation point	Number of samples	Percentage > limit of determination	Maximum (µg/L)	Average (µg/L)
Surface water	40	98	50,8**	7.8
Transsect 1 (Well 4)				
3339	7	71	0.05	0.03
3338	14	14	0.25	*
3337	18	28	0.32	0.15
BEE201OP	10	10	0.17	*
BEE201UP	8	0	< 0.1	
3335	12	25	0.16	0.11
BEE200OP	2	0	< 0.1	
BEE200UP	2	0	< 0.1	
Transsect 2 (Well 3)				
BEE205	11	27	0.29	0.16
BEE206	12	17	0.37	0.21
BEE207OP	1	100	0.04	*
BEE207MP1	1	100	0.23	*
BEE207UP	2	0	< 0.1	
BEE202OP	10	10	0.14	*
BEE202MP1	10	10	0.2	*
BEE202MP2	7	14	0.02	*
BEE202UP	6	0	< 0.1	
BEE203	9	0	< 0.1	
well 3	1	0	< 0.1	
BEE204OP	6	0	< 0.1	
BEE204UP	6	0	< 0.1	

* only one sample above limit of determination
** surface scum

Lake sediment

On 20th August 2003 an international workshop was organised at the UBA with the topic: "Cyanobacteria in Sediments". Two experts on this field (Dr. Ihle, TU Dresden and Dr. Marsalek, Academy of Science of Czech Republic) as well as guests from different universities and research institutes were invited to join our team during sediment sampling, sample preparation and microscopic analysis. Following this practical section presentations were held in the afternoon. As a result sediment sampling, sample preparation as well as the microscopic method were optimised, and 6 cores taken during the workshop as well as 3 cores taken subsequently on other occations were analysed according to this method.

A first qualitative interpretation of the microscopic analysis show intact colonies of *Microcystis sp.* in the first few centimeters of the sediment, with autofluorescence indicating viability. In 20 cm depth however no colonies could be found. The microcystin analysis by ELISA are in progress.

5.2. Semi-technical site (Marienfelde)

Mass cultivation of cyanobacteria for toxin production

The cultivation of cyanobacteria (*Planktothrix agardhii* HUB 076) was continued in order to obtain enough toxin material for the large scale experiments. A concentrate of cyanobacterial cells was extracted in regular intervalls and new media was replenished. In May and June 2003 the culture was moved to and divided into two seperate basins, one for storage and one for cultivation. One reason was to have a second large culture in reserve, if one happened to deteriorate (as this happened in November when the temperature was accidently raised above 25 °C). The turbidity in the storage basin now has a relatively constant level of 250 mV and MCYST concentrations measured in Jaunary 2004 show high values around 200 µg/L for the main MCYST variant.

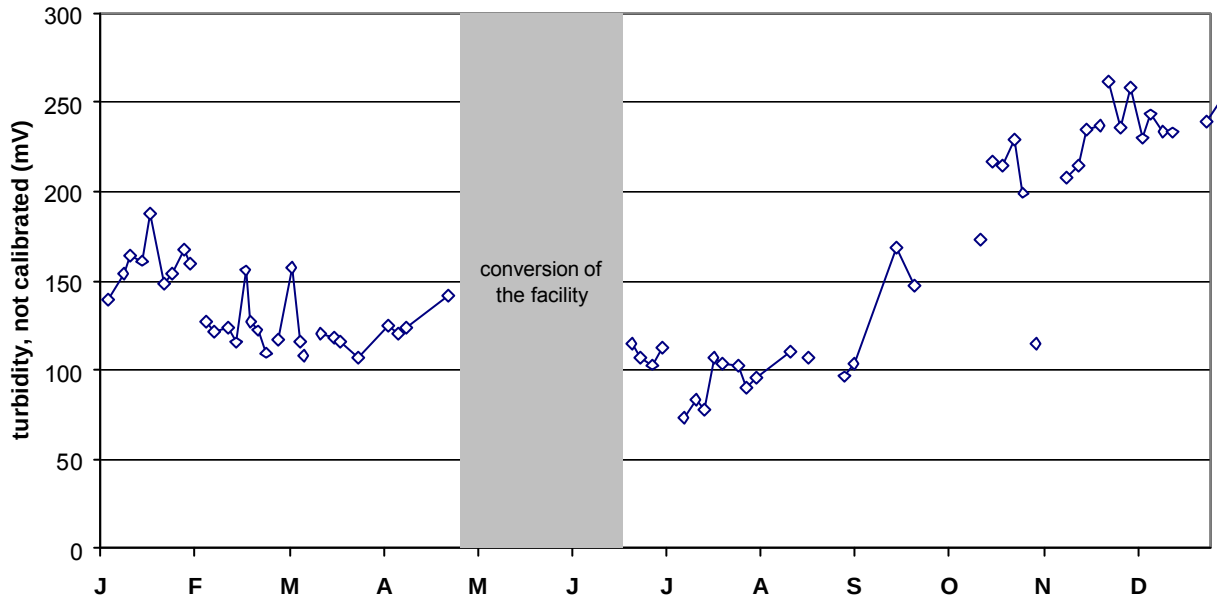

Figure 3: Turbidity (not calibrated) and microcystin concentrations of the cyanobacterial mass culture.

Experiments on the Sealed Infiltration Pond (Slow Sand Filter, SSF)

Several experiments under participation of different NASRI working groups were conducted on the sealed infiltration ponds or slow sand filters (SSF) at the UBA's experimental field in Marienfelde. Table 3 gives an overview over the substances applied and the adjusted conditions. The first set of experiments was conducted before a mutual recovery experiment had verified that there was no interference of the different substances applied. After this had taken place and the results showed that no interferences occured there was no reason for carrying out separate experiments, and subsequently all substances were applied together. The status of work for the different experiments is shown in table 4 and the results obtained so far are discussed separately below.

Table 3: Summary of the experiments conducted on the slow sand filter (SSF).

Identification	Date of application	working groups involved	substances applied	filtration velocity	status of the schmutzdecke
TV 5, Tracer 1	3/19/03	UBA algae, UBA bacteria	NaCl, viruses	2.4 m/d	little
TV 5, MC	4/15/03	UBA algae	MCYST		
TV 5, Tracer2	4/23/03	UBA algae, TU drugs	NaCl, drugs		
TV 6	6/17/03	UBA algae, UBA bacteria, TU drugs, TU organics, FU hydrogeo	NaCl, drugs, MCYST, viruses	1.2 m/d	developed
TV 7	11/19/03	UBA algae, UBA bacteria, TU drugs, TU organics, FU hydrogeo	NaCl, MCYST, bacteria	0.6 m/d	developed

Table 4: Status of work on the SSF experiments TV 5 – TV 7 (see above)

	TV 5	TV 6	TV 7
experiment completed?	Yes	yes	Yes
analyses completed for:			
- main anions and kations (by FU Berlin)?	no samples taken	yes	No
- tracer (EC, Chloride, by UBA)?	Yes	yes	No
- DOC (LC-OCD, SAK, by TU organics)?	no samples taken	yes	No
- trace substances (viruses, bacteria, MCYST, drugs, Gadolinium by participating working groups)?	Yes	in part	in part
mutual interpretation and modelling completed?	No	no	No

Conduction of the experiments

In preparation of the experiments the inflow to the SSF was adjusted to the desired amount. By vertical variation of the goose neck situated at the outflow the water level inside the water reservoir was then lowered so that none of the jagged edges used for aeration before the water flows into the water reservoir were covered with water. This had to be done to limit the mixed water body to the water reservoir directly above the filter. For optimal mixing a pump was installed in one corner of the water reservoir pumping about 15 m³/h horizontally in the direction of the basin center. The interpretation of the EC values directly after application of NaCl as a tracer showed complete mixing within five minutes after application.

The tracers and the trace substances were applied by spraying them evenly across the water reservoir with a hose from a barrel containing the concentrated substances diluted with 100 L of

tap water. The tracer applied was usually NaCl so that the sampling intensity in the different sampling points could be adjusted by observing the electerical conductivity.
The MCYST applied was extracted from the *Planktothrix agardhii* mass culture by centrifugation and freeze thawing in order to release the mainly cell-bound microcystins. The freeze thawed extract was homogenated and then centrifugated to remove the cell debris and stored frozen.
The SSF had been reconstructed in 2002 in order to achieve a better vertical flow (see report December 2002). To test this sampling ports were installed at the beginning of all 6 drainage pipes. These sampling ports were in use during the first tracer experiment (TV 5, Tracer 1 see 3rd report, June 2003). During the other experiments samples were taken from the water reservoir and the effluent only.
The aim of the experiments conducted in 2003 was to test MCYST elimination under a combination of 3 worst-case conditions (TV 5: virgin sand that had had no contact to MCYST, missing schmutzdecke and with 2.4 m/d high flow velocities) and then to see whether lower flow velocities (TV 6: 1.2 m/d and TV 7: 0.6 m/d) and development of the schmutzdecke can lead to better removal rates. Those results already available will be presented and discussed briefly in the following chapters. As mutual interpretation together with the other working groups involved and modelling has not taken place so far a final interpretation can not be presented for any of the experiments conducted in 2003.

Results and first interpretation of TV 5

The relative concentrations of the main MCYST variant (demethylated MCYST-RR) applied related to the initial maximum of 10.5 µg/L as well as the calculated dilution curve (confirmed by the tracer tests 1 and 2) are shown in figure 4. Other variants detected were an unidentified variant with a retention time of 14.2 minutes in the HPLC (one measurement in the sample taken 0.8 h after application with 0.22 µg/L) and another variant with a retention time of 21.7 minutes (detected in the first three samples taken after application with a maximum of 0.08 µg/L). This data was already presented at the NASRI-workshop 2003. The parallel ELISA analysis had to be repeated due to high errors and are not complete yet.
In the effluent the maximum concentration of the main MCYST variant was reached 13.5 h after application (figure 5). This is a distinctive retardation compared to the maximum of the tracer chloride that was measured 6 h after application in the preliminary tracer test (figure 6). The maximum reaches 1 µg/L which is a substantial reduction of 90 % compared to the input concentrations.
In additions four MCYST variants appear in the chromatograms of effluent samples that are not detected in the water reservoir (figure 5). These results have in part already been shown at the NASRI-workshop 2003 (samples taken after 10.5 h after application had not been analysed until then). Ongoing investigations will have to show if the occurence of new variants is an effect of the

partial degradation in the slow sand filter or caused by different detection limits in water reservoir and effluent.

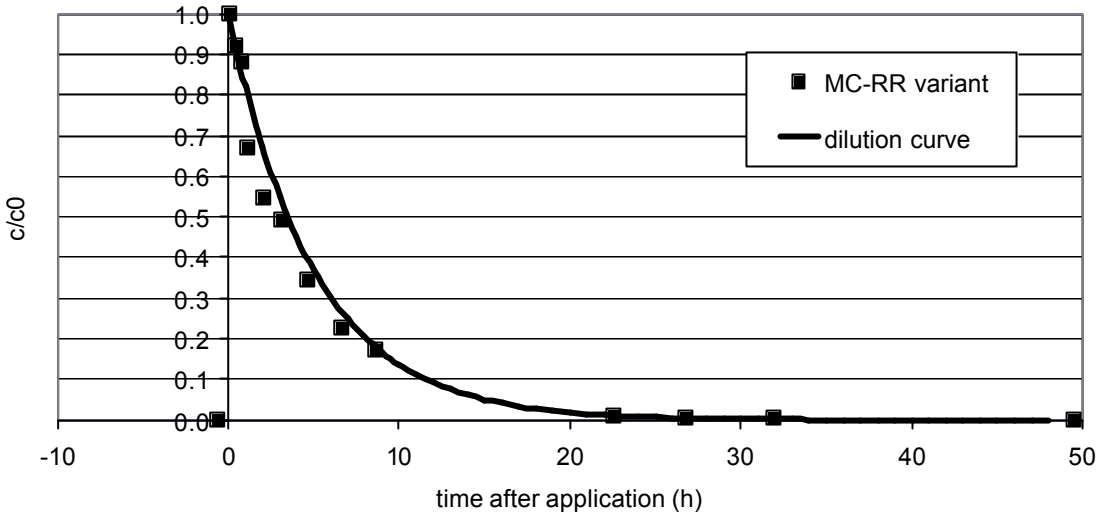

Figure 4: MCYST concentrations in the water reservoir during TV 5 as measured by HPLC.

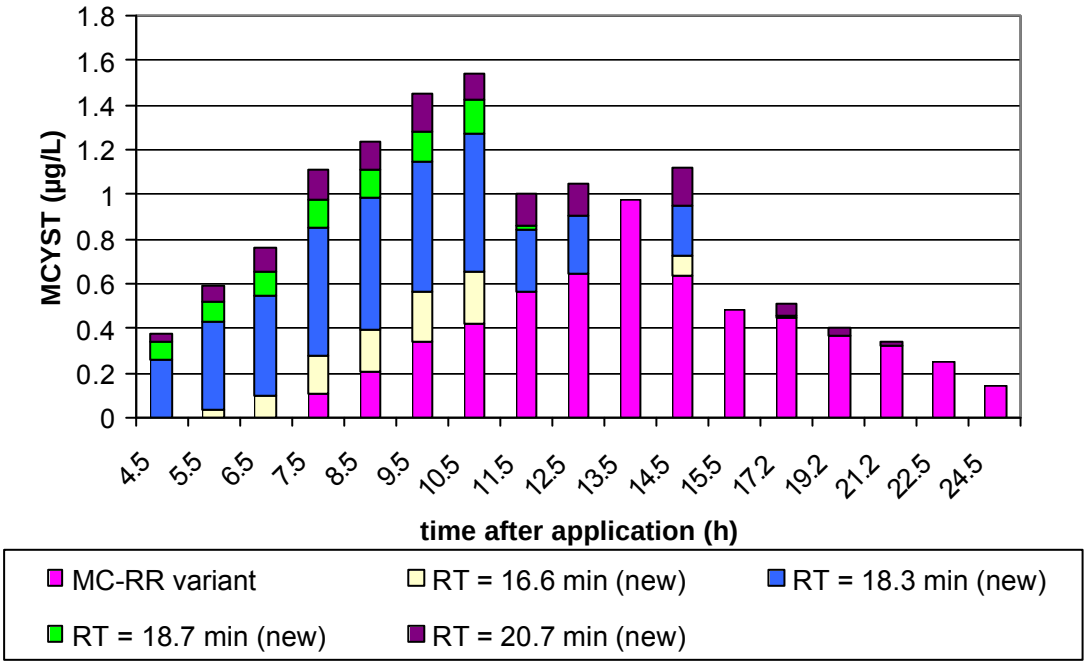

Figure 5: MCYST variants determined in the effluent during TV 5.

As subsequent analysis by MALDI-TOF carried out by Dr. Fastner at the TU Berlin showed that the variant with a retention time of 20.7 min was a demethylated MCYST-LR variant ([Asp3]MC-LR), sometimes present in traces the mass culture planktothrix agardnii strain. The other variants could not be identified due to insufficient amounts.

The mutual interpretation with the UBA bacteria and TU drugs group as well as the modelling is planned to be carried out in the beginning of 2004.

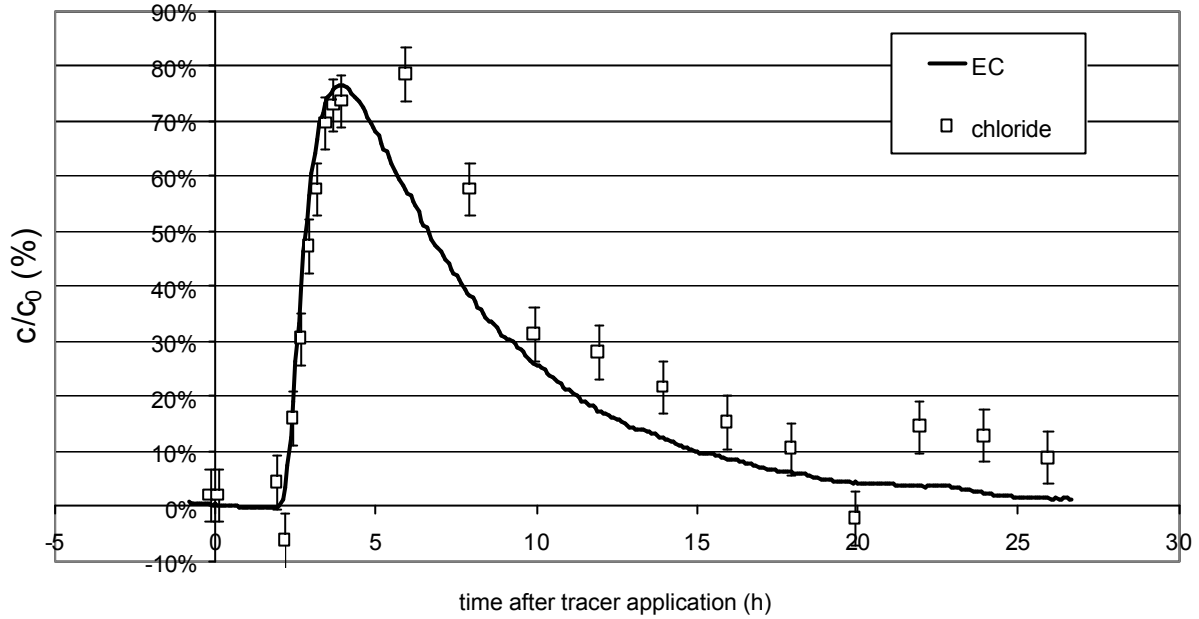

Figure 6: Relative values of electrical conductivity (EC) and chloride in the effluent during the tracer test before TV 5.

Results and first interpretation of TV 6

The microcystin analysis by HPLC and ELISA of the samples taken during TV 6 have not yet been completely analysed. During this experiment that was conducted using a moderate flow velocity, the main anions (with exception of HCO_3^-) and cations were measured in samples from the water reservoir and the effluent to check if any changes in hydrochemistry take place during the experiment. The analyses were carried out by the FU Berlin working group.

Table 5: Main anions and cations during TV 6 (data by FU Berlin).

	time after application	sodium	potassium	calcium	magnesium	chloride	sulfate	nitrate	phosphate
	h	mmol/L							
water reservoir	-0.6	2.02	0.11	3.13	0.74	2.82	2.46	0.005	< 0.001
	0.1	4.67	0.12	3.25	0.75	5.61	2.50	0.005	< 0.001
	5.1	3.61	0.12	3.20	0.74	4.51	2.35	0.006	< 0.001
	25.1	2.22	0.11	3.25	0.74	3.05	2.38	0.006	< 0.001
effluent	0.7	2.02	0.11	3.30	0.77	2.82	2.36	0.006	< 0.001
	6.1	2.94	0.12	3.40	0.81	4.09	2.35	0.006	< 0.001
	34.9	2.27	0.10	3.15	0.74	3.07	2.43	0.006	0.003

In the course of the experiment no relevant change in anorganic hydrochemistry can be seen with exception of sodium and chloride that were added for tracer reasons together with the trace

substances. The slight increase in calcium and magnesium in the effluent compared to the water reservoir before the experiment can indicate calcite solution in the filter bed. This has to be verified together with alkalinity measurements that were carried out during the later experiments. Simultaneously, DOC was analysed in a few representative samples. The results are shown in figure 7. They indicate an increase in DOC removal during the experiment that may be due to the addition of highly biodegradable saccharides together with the algal extract.

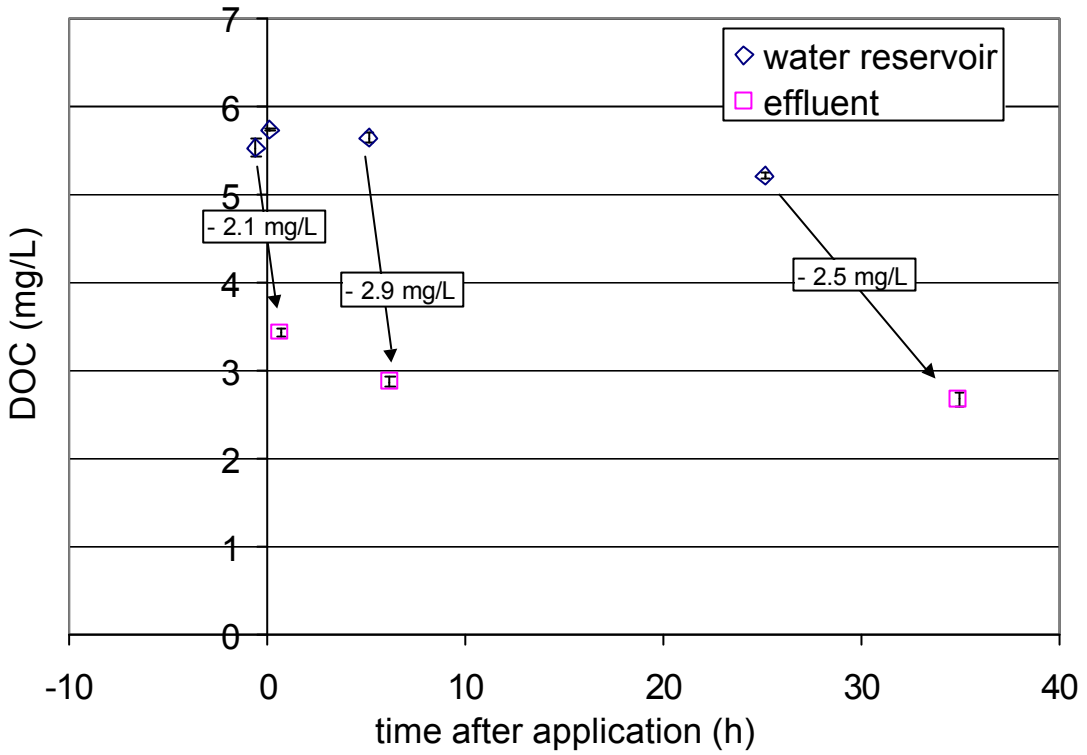

Figure 7: DOC values during TV 6.

In 2004 the remaining samples for MCYST analysis will be measured by ELISA and HPLC with a focus on the identification of new MCYST variants in the effuent by MALDI-TOF/MS (if present). Subsequently mutual interpretation and modelling will be carried out together with the other working groups involved (mainly UBA bacteria and TU drugs).

Development of the schmutzdecke

In order to quantify the development of the schmutzdecke on the SSF a core from the upper 5 cm of the filter bed was taken each weak starting from May 2003. After describing the macroscopic features of the core it was divided into 3 or 4 samples of which the working group UBA bacteria obtained 1 or 2 subsamples for determination of the total cell number and other microbiological parameters. The rest was again divided into 2 subsamples, of which one was used to determine water content and loss on ignition (LOI) and the other was used for microscopic analysis.

The results (figure 8) show high variations (minimum: 0.26 %; maximum: 4.4 %) in time and depth. The variations in depth increase over time. In the beginning of 2003 when the measurements started the differences in LOI between the layers sampled did not exceed 0,5 %. In autumn 2003 the difference on some occasions reached 2 %. The highest values of LOI were measured in the uppermost mm of the filter in some samples taken during summer and autumn 2003. On other samples of this layer taken during that time, however no relevant increase compared to the values measured in March 2003 was observed. This fact may be due to a high spatial inhomogenity. In order to test this 6 samples from different places distributed over the filter surface were taken on one occasion and analysed by the same method. The analyses are still in progress.

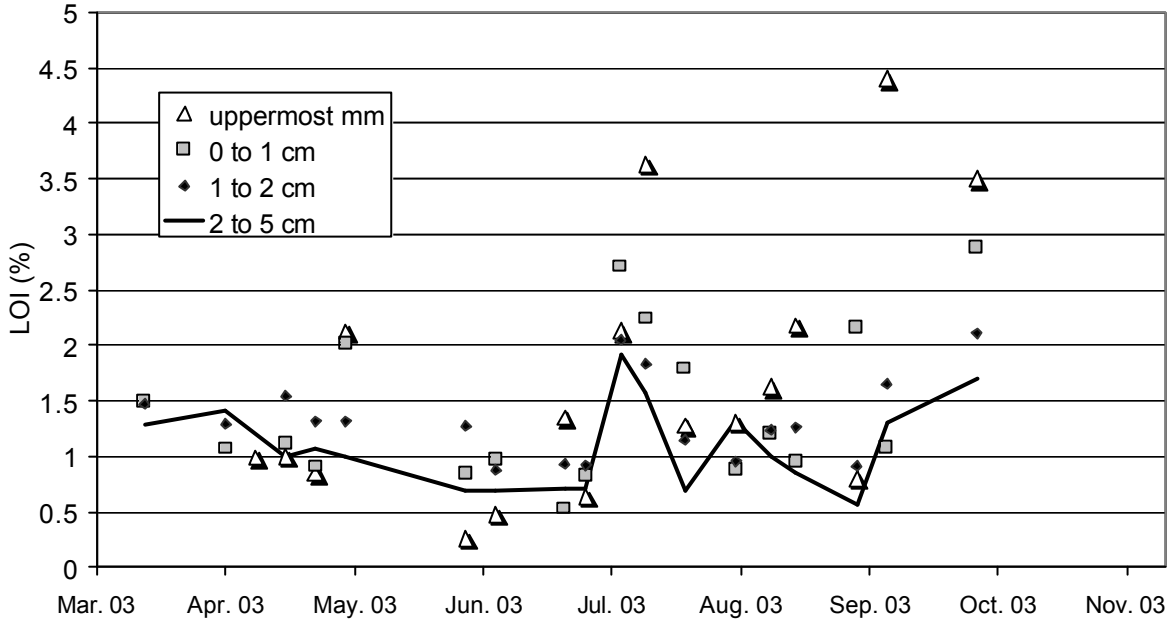

Figure 8: Loss on ignition (LOI) as measure for organic substanc in the filter bed of the sealed infiltration pond used for TV 5 to TV 7.

The third way of determining the development schmutzdecke was to measure the water table of the pond's water reservoir and the height of the goose neck at the effluent and to calculate the hydraulik resistance. It turned out, however, that during circular flow mode the goose neck did not allow a free spill. As the adjustment of the system was changed to flow through mode only during experiments most of the values obtained in 2003 could not be used for calculation of the hydrualic resistance. Reconstructions have been carried out in order to solve this problem in 2004.

Enclosure experiments

In 2003 four experiments with MCYST were carried out in the Enclosures. The details are given in table 6. The processing status can be taken from table 7.

Table 6: Summary of the experiments conducted on the enclosures (flow velocity was 1.2 m/d in all cases).

Identification	Date of application	Enclosure #	working groups involved	substances applied	schmutz-decke
E0	07/28/03	3	IGB model UBA algae	NaCl, KBr	no
E1	8/5/03	3	UBA algae, UBA bacteria TU drugs TU organics FU hydrogeo	NaCl, MCYST, viruses, drugs, Gadolinium	no
E2	9/9/03	3	UBA algae, UBA bacteria TU drugs TU organics FU hydrogeo	NaCl, KBr MCYST, viruses, drugs	yes
E3	11/11/03	2	UBA algae, UBA bacteria TU drugs TU organics FU hydrogeo	NaCl, MCYST, viruses, drugs, trace organics	yes
E4	25/11/03	2	UBA algae, UBA bacteria, TU drugs, TU organics, FU hydrogeo	NaCl, MCYST, viruses, drugs, trace organics	no

Table 7: Status of work on the SSF experiments.

	E1	E2	E3	E4
experiment completed?	yes	yes	yes	yes
analyses completed for:				
- main anions and kations (by FU Berlin)	yes	yes	no	no
- tracer (EC, Chloride, Bromide by UBA)	analyses in progress	analyses in progress	analyses in progress	analyses in progress
- DOC (LC-OCD, SAK, by TU organics)	yes	yes	analyses in progress	analyses in progress
- trace substances (viruses, bacteria, MCYST, drugs, Gd by participating working groups)	analyses in progress	analyses in progress	analyses in progress	analyses in progress
mutual interpretation and modelling	no	no	no	no

Experimental setting

The experimental setting was similar for all experiment carried out in 2003. The trace substances as well as the tracer were applied with a watering can in which the concentrates had been dissolved in 10 L of pond water. The water reservoir containing between 300 and 400 L was stirred using a stirring aparatus or pump for even distribution (this was tested in the experiment E0 with Cl^- and Br^- as tracers). Before the beginning of the experiment and then starting with the increase of electrical conductivity (that was used as an on-site tracer) samples for trace substance analysis were taken from the water reservoir, from the 4 (Enclosure 3, figure 9) or 2 (Enclosure 2) measuring ports inside the sediment and from the effluent. The sampling ports were connected to a peristaltic pump that delivered 50 ml/min (the amount extracted had to be limited in order not to disturb the hydraulic flow inside the enclosure). In order to achieve best comparablitiy all samples for individual analysis with exception of the samples for virus detection (UBA bacteria- working group) were collected in the same vessel and subsequently divided into several subsamples.

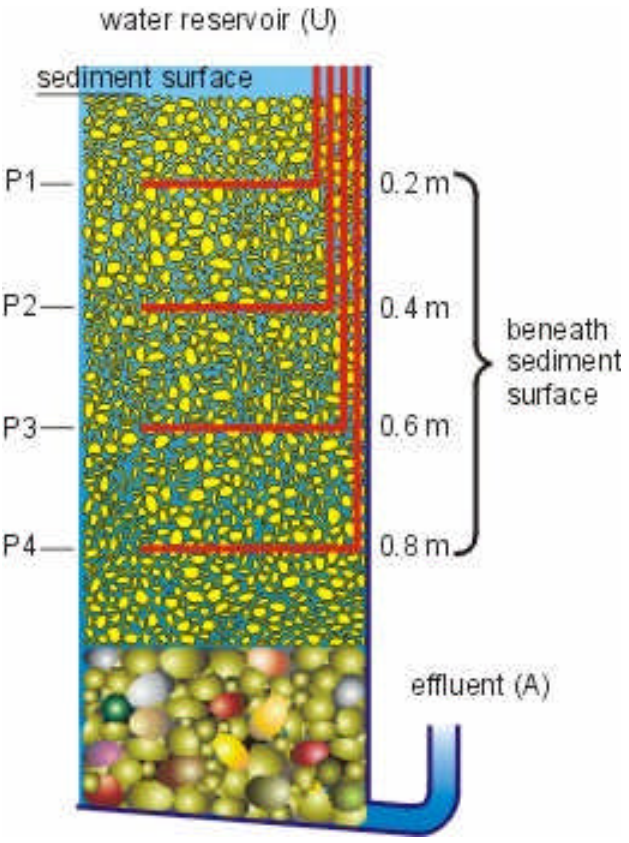

Figure 9: Cross section of Enclosure 3 (4 sampling ports) with courtesy of IGB.

Enclosure experiment #1

The first enclosure experiment (E1) was performed without schmutzdecke which was removed 5 days before the beginning of the experiment. Oxygen saturation was reached in the effluent before during and after the experiment so that we can presume aerobic conditions throughout the

experiment. The results of the on-site “tracer”, electrical conductivity (EC) are given in figure 10. Choride analyses are not complete yet, so detailed flow modelling has not been carried out so far.

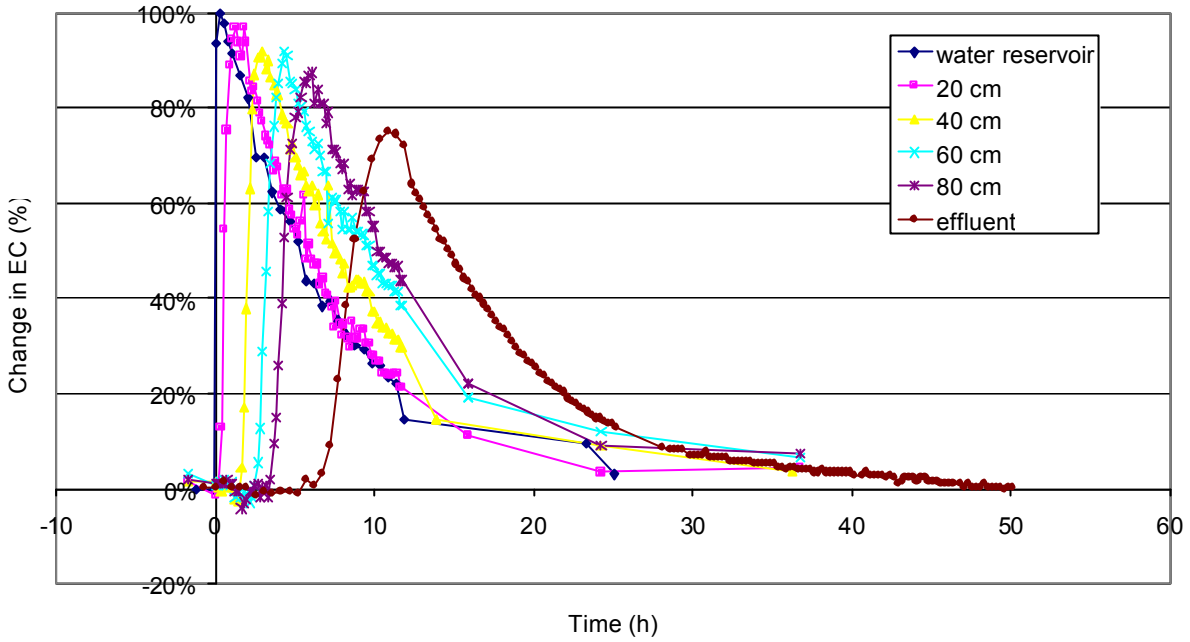

Figure 10: Changes in EC (percent of maximum change, 167 µS/cm) during E1.

As observed in TV 6 no significant changes in hydrochemistry concerning the main kations and anions were observed, with exception of the Na and Cl elevation due to tracer addition. Alkalinity was measured this time. The variations, however lie within the mean analytical error. For the next experiments the sensitivity was reduced by raising the titrated volume from 100 ml to 200 ml. Figure 11 gives the MCYST variants measured by HPLC in a few selected samples from the water reservoir (Ü2, Ü6), from the sampling ports (P1-X to P4-X) and from the effluent (AX). As observed in the first experiment on the sealed infiltration pond (TV5, figure 5) the MCYST variants found inside the filter bed differ distinctively from those found in the water reservoir. In addition to the variants found in TV5 four variants were found in the sampling port located 20 cm beneath the sediment surface that had not been detected before. The next step will be to identify the variants by MALDI-TOF/MS after separation by HPLC.
As soon as the results of the tracer analyses are available, flow modelling and mutual interpretation together with the other working groups will be carried out.

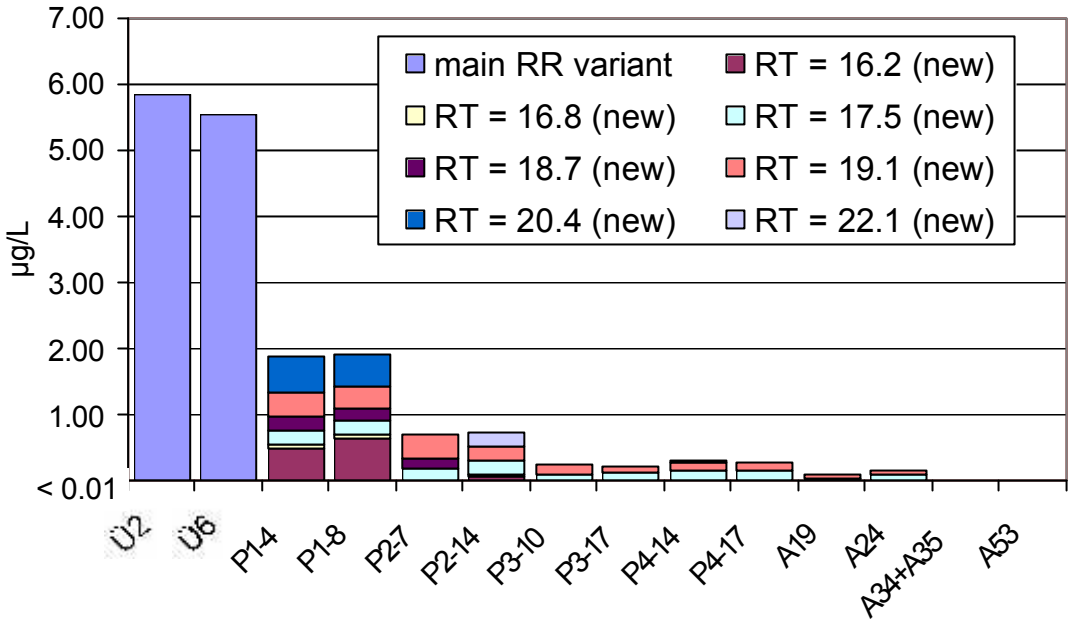

Figure 11: Microcystin variants characterised by their retention time in the HPLC (RT) as measured in enclosure experiment 1 (Ü: water reservoir; P1 to P4: observation points in 20 to 80 cm depth; A: effluent).

Enclosure experiment #2

The second enclosure experiment (E2) was conducted on the same enclosure as E1, after a schmutzdecke was allowed to develop for 4 weeks. The values of EC as the on-site “tracer” are given in figure 12. They show a slightly reduced flow velocity compared to the first tracer experiment (compare figure 10). This is due to a lower pumping rate (about 10 %), probably induced by higher hydraulic resistance of the “schmutzdecke”. Flow modelling will be carried out as soon as the chloride analyses are complete.

For the MCYSTs qualitative ELISAs in preparation of the HPLC analyses were conducted. Examples of the results are shown in figure 11. For quantitative interpretation some measurements have to be repeated so detailed interpretation has not been carried out so far. The results already show, however, a distinct retardation and reduction of the maximum compared with the EC values.

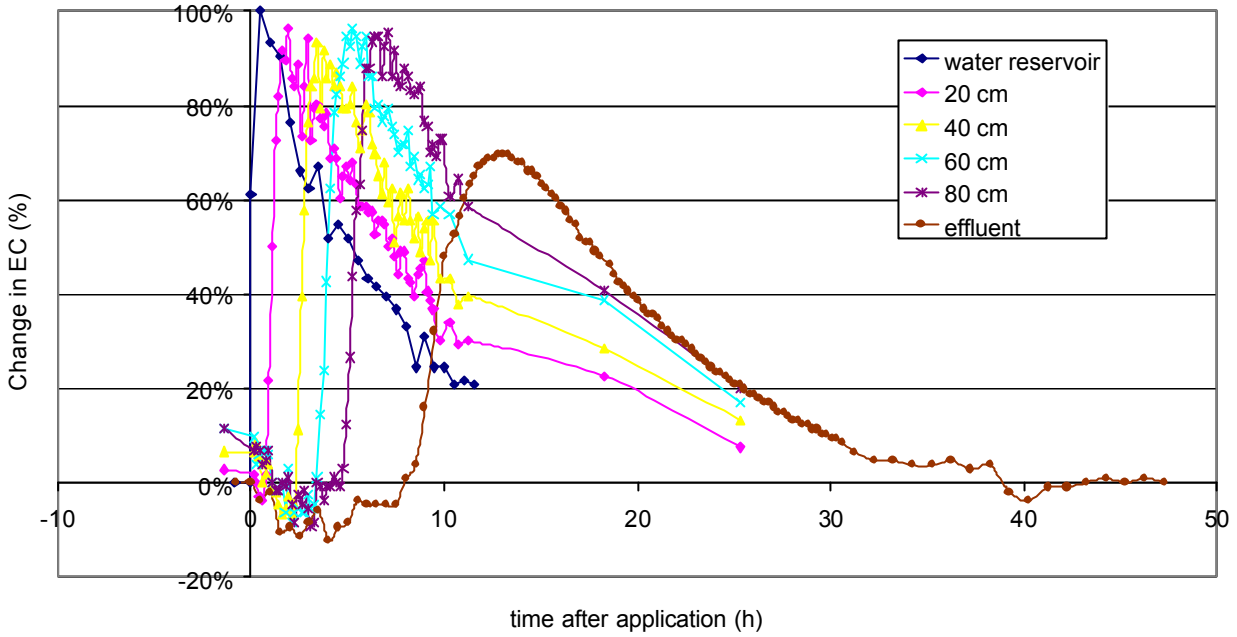

Figure 12: Changes in EC (percent of maximum change, 106 µS/cm) during E2.

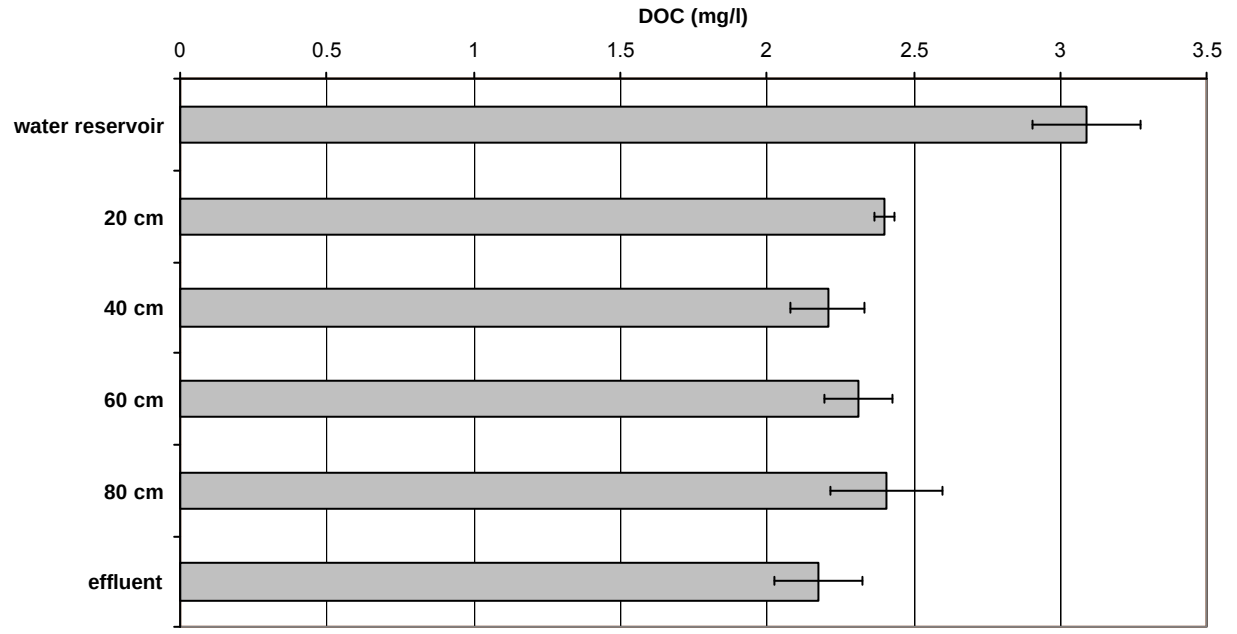

Figure 13: DOC values measured during E2 in the effluent (each bar represents the average of 3 samples taken before, during and after the tracer breakthrough, respectively; error bars show the minimum and maximum values, data by TU organics).

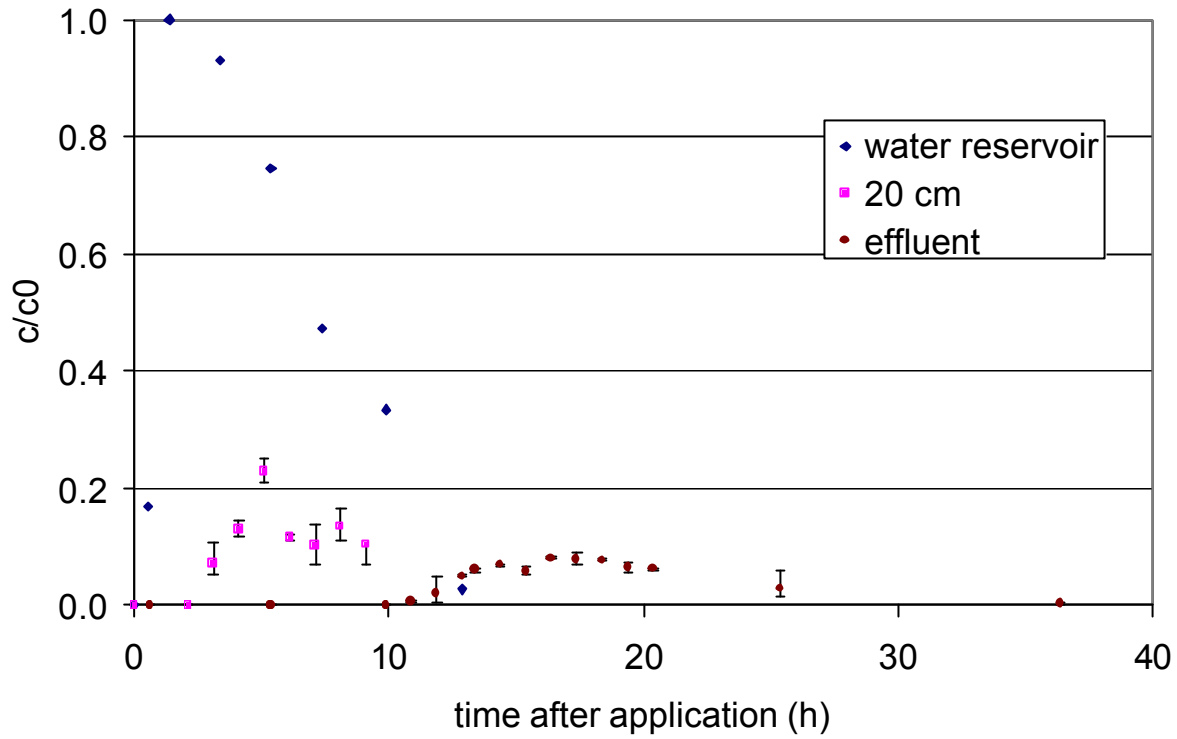

Figure 14: Results of an ELISA screening shown for samples from the sampling port at 20 cm and the effluent during E2.

6. Discussion

Artificial recharge pond Tegel

Concerning cyanobacteria and their toxins the water quality in the AR pond Tegel is closely linked to the one in Lake Tegel. Especially in winter when the microfiltration unit is shut off the amount of cyanobacteria as well as the MCYST concentrations are very similar. Our investigations have shown that during summer only very little cyanobacteria reach the artificial recharge pond, as levels in the lake are low and those present are probably mostly filtered out of the water passing through the microfiltration unit; further, due to suboptimal conditions (high light), cyanobacterial populations do not establish themselves in the pond.
Therefore, in 2004 no more regular investigations on cyanobacterial toxins will be carried out at the AR pond Tegel. The results of the new KWB funded project (monthly monitoring of nutrients, phytoplankton and MCYST concentration in Lake Tegel) will be observed closely and sampling at the AR pond will be recommenced only in case of a cyanobacterial bloom in Lake Tegel.

Bank filtration field site Lake Tegel

As in the last few years cyanobacterial population density in Lake Tegel was low in 2003 and the maximum concentrations of total microcystins (measured by Adda-specific Elisa) reached 0.76 µg/L. These concentrations are not sufficient to lead to detectable amounts in the bank filtered water, as earlier investigations have shown (Grützmacher et al. in prep.).
The nutrient levels in the lake, however, are in the threshold range in which cyanobacterial blooms can occur. A careful monitoring of the nutrient levels and the phytoplankton development is therefore neccessary and currently being carried out by our working group funded by KWB. In 2004 results will be observed closely so that sampling may recommence in case of a cyanobacterial bloom.

Bank filtration field site Lake Wannsee

In spite of the warm and dry summer in 2003 the results of the surface water sampling for this year showed a similar develepment of phytoplankton and MCYST as in 2002 with resulting MCYST concentrations around 5 µg/L (see 2nd report, Dec. 2002). During early summer *Microcystis sp.* dominated, although unlike 2002, together with *Aphanozomenon flos-aquae*. From the middle of August on until October a bloom of *Planktothrix agardhii* was observed in both years with the maximum MCYST concentrations in the water body reaching 10 µg/L. In 2003 additional samples were taken from the shoreline, where some surface scums had accumulated. However, the concentrations attained here were still quite low, with < 20 µg/L (sum of cell-bound microcystins

measured by HPLC), whereas in previous years in bloom situations scum concentrations in the range of mg/L were observed along other parts of the shoreline.
Extracellular MCYSTs were found sporadically in concentrations of up to 1 µg/L. These measurements will have to be verified by additional analyses (not all samples taken in 2003 have been analysed yet by HPLC and ELISA). The extracellular MCYST fraction poses the greatest threat to drinking water quality, as physical filtration, the main retention process for the cell-bound MCYSTs, will not contribute to its elimination.
In groundwater samples, however, MCYSTs were found only in very low concentrations. The HPLC analyses did not show any detectable MCYST variants (< 0.01 µg/L for the individual variants). By ELISA, however, distinct positive results were repeatedly found in those observation wells with the shortest residence time (table 8).

Table 8: Average ELISA results (cell-bound plus extracellular) and residence times (1st estimation by G. Massmann, FU hydrogeo) of shallow observation wells at Lake Wannsee Transsect.

observation well	residence time (d)	average ELISA result (µg/L MCYST)	number of samples	standard error (µg/L)
3339	65 (?)	0.03	5	0.01
3337	20	0.15	5	0.16
3335	< 30 (?)	0.11	3	0.08
BEE205	30	0.16	3	0.12
BEE206	13	0.21	2	0.23

Maximum values in both transsects lie around 0.3 µg/L, measured by Adda-ELISA. These samples will be also analysed by MC-ELISA shortly in order to find out which portion can be attributed to MCYSTs and which potentially are from degradation products. Additionally samples from three observation wells with the highest concentrations will by analysed by HPLC-MS/MS in 2004 for detection of lower concentrations of the individual MCYST-variants.
In addition to some analyses of samples taken 2003 (see above) that are still in progress, weekly surface water and monthly groundwater monitoring will be continued until August 2004. Samples taken from the observation wells 3337, 3338, BEE205 and BEE206 will be analysed by HPLC-MS/MS by the Centre for Water Quality (TZW) in Dresden (working group of Dr. Schmidt). After that surface water monitoring that is being carried out by ourselves will carry on after August and in the likely case of a cyanobacterial bloom in September additional groundwater samples from the shallow wells 3337, BEE 205 and BEE206 will be taken and analysed for toxins by HPLC-MS/MS.

Technical scale experiments on the UBA's experimental field

As many analyses of the experiments carried out on the UBA's experimental field are not completed yet, mutual interpretation and modelling together with all the working groups involved have not taken place. For this reason the following discussion will be limited to some practical points concerning the conduction of the experiments

a) Tracer: Chloride (added as NaCl) was used for tracer purposes during all experiments conducted in 2003. The main reason for using this tracer was the possiblity of using the EC as a value available on-site for selection of samples for further processing. During tracer breakthrouth, e.g. subsamples for Cl^- analysis could be taken in shorter intervalls from the sampling ports in the enclosures so that the increase could be verified by at least 3 individual measurements. As soon as the maximum EC values had been reached the sampling intervalls were expanded so that there was sufficient sample volume for all the different working groups for their individual analyses. In order to reduce any effects of the increase in ionic strength e.g. on the sorption capacity of the sediment, the rise in EC was limited to 10 % of the background. This proceedure will be continued in the experiments planned for 2004.

b) Anorganic chemistry: During the experiments carried out in 2003 (all aerobic) no relevant change in anorganic hydrochemistry (with exception of the elevation in NaCl induced by the tracer) was observed so far. This might change when anaerobic conditions are induced, as planned for 2004. Therefore these analyses will be continued and titrimetric measurement of CO2 (?) will be additionally carried out on-site.

c) DOC (LC-OCD and SAK): In contrast to the anorganic hydrochemistry changes in dissolved organic matter between water reservoir and effluent were observed in all the experiments so far. In cooperation with the TU organics group we would like to expand the measurements to regular samples taken inbetween the experiments, especially for the phase when DOC is added in order to achieve anaerobic conditions.

d) Determination of biomass: The biomass inside the sediment seems to be a crucial parameter for quantifying the effectiveness of the "schmutzdecke". Whether the parameter LOI (loss on ignition) is sensitive enough will have to be discussed together with the results from the core samples analysed by the group UBA bacteria.

e) MCYST analyses: During summer 2003 ELISA analyses could not be carried out due to very high temperatures that lead to quicker enzymatic reactions and insufficient detection limits. Therefore subsequent HPLC analyses were delayed so that some

samples have still not been analysed yet. For 2004 we are looking for an air-conditioned laboratory that we can use to speed up the analyses.

7. Perspectives / Intended tasks for the upcoming project period (January – June 2004)

Task	comments
Preliminary work	
mass cultivation of cyanobacteria	
method development: degradation products and microbiology	batch experiment will be carried out by the UBA bacteria working group to identify MCYST-degrading bactgeria; potentially quantification could be targeted.
Field investigations	
monthly sampling and analysis of surface and groundwater (BF field sites Wannsee and Tegel)	cooperation with BWB; Tegel only if cyanobacteria present in surface water
weekly sampling and analysis of surface water (Lake Wannsee) starting from May	Continuation of present programme
sampling of lake sediment (Lake Wannsee)	2 cores in March (to assess if cyanobacteria survive over winter) and 2 in November 2004 (to assess end-of-season population on the sediments)
Semi-technical site Marienfelde	
Mutual interpretation and modelling of 2003 experiments	In cooperation with the other working groups
anaerobic enclosure experiments with extracellular microcystins	anaerobic conditions will be induced by adding DOC and / or reducing flow velocities
observation of the “schmutzdecken”-development in enclosures and sealed infiltration pond	Continuation of present program with chemical, hydraulic and / or microbiological methods

8. References

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Grützmacher, G., Bartel, H., Böttcher, G. & Chorus, I. (in prep.): Teilprojekt „Wirksamkeit der Infiltration/Bodenpassage für die Retention von Algen- und Cyanobakterienmetaboliten“, Abschlußbericht des BMBF-Forschungsvorhaben: Stragtegien zur Vermeidung des Vorkommens ausgewählter Algen- und Cyanobakterienmetabo-lite im Rohwasser (Final report of the BMBF research project: strategies to avoid the occurence of selected metabolites of algae and cyanobacteria, subproject: efficacy of infiltration / soilpassage for the retention of algae and cyanobacteria metabolites).

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Zeck, A., Weller, M.G., Bursill, D. & Niessner, R. (2001b): Generic microcystin immunoassay based on monoclonal antibodies against Adda. Analyst **126**: 2002 – 2007.

9. Publications / Presentations

G. Grützmacher, G. Böttcher, I. Chorus & H. Bartel: Removal of cyanobacterial toxins by sediment passage. Presentation held at the conference “Wasser Berlin 2003”, March 2003.

G. Grützmacher, G. Böttcher, I. Chorus & H. Bartel: Removal of cyanobacterial toxins by sediment passage. Presentation at the EGS-AGU-EUG Joint Assembly, 06.-11. April 2003.

G. Böttcher, A. H. Ferreira Ferreira, R. Kurmayer: Chlorophyll a and Biovolume -TWO Parameters with ONE Factor? Correlation to Microcystin?. Presentation held at BBE Moldeanke workshop in June 2003.

G. Grützmacher, G. Wessel, I. Chorus & H. Bartel: Elimination of microcystins through slow sand and bank filtration. Presentation at the workshop “Cyanobacteria in Sediments”, 20. August 2003.

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We wish to thank I. Flieger for the HPLC analyses, K. Laskus for the microscopic analyses, H. Althoff, T. Starzetz, T. Köhler and C. Hensel for the technical assistance on the experimental field and I. Klinkmüller and M. Kock for supporting the field work.

Appendix 1a: Field data of cell-bound Microcystins in AR pond Tegel.

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (cell-bound) in µg/L											
			[D-Asp³]MC-RR	[D-Asp³,Dhb⁷]MC-RR	MC-RR	RT 17,35	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 22,1	RT 24,7	[D-Asp³]MC-YR	RT 27,6
AR pond Tegel	1/16/03	1/29/03	0.06	0.04	< d.l.	< d.l.	< d.l.	< d.l.	0.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
AR pond Tegel	2/13/03	¾/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
AR pond Tegel	3/13/03	4/1/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
AR pond Tegel	4/24/03	5/7/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 1b: Field data of cell-bound Microcystins in Lake Wannsee.

Observation point	Date	Date of A nalysis	Results of HPLC-PDA Analysis (cell-bound) in µg/L											
			[D-Asp³]MC-RR	[D-Asp³,Dhb⁷]MC-RR	MC-RR	RT 17,35	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 22,1	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water	2/20/03	3/3/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.02	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	3/21/03	4/1/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	4/4/03	4/15/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	4/4/03	4/15/03	< d.l.	0.09	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	4/17/03	5/7/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	4/17/03	5/7/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	4/29/03	8/13/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	4/29/03	8/13/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	5/9/03	5/16/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	5/9/03	5/16/03	0.21	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	6/6/03	6/19/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	6/6/03	6/19/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	6/20/03	7/2/03	< d.l.	< d.l.	0.42	0.28	< d.l.	< d.l.	< d.l.	0.66	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	6/20/03	7/2/03	< d.l.	< d.l.	0.50	0.32	< d.l.	0.37	< d.l.	0.68	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	6/26/03	7/2/03	< d.l.	< d.l.	1.15	0.22	< d.l.	0.82	< d.l.	1.17	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	6/26/03	7/2/03	< d.l.	< d.l.	0.92	0.27	< d.l.	0.62	< d.l.	0.99	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0-1m	6/26/03	9/19/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.79	< d.l.	1.11	0.34	< d.l.	< d.l.	< d.l.
surface water 0m	7/3/03	7/17/03	< d.l.	< d.l.	1.20	0.34	< d.l.	0.66	< d.l.	1.27	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	7/3/03	7/17/03	< d.l.	< d.l.	1.32	0.28	< d.l.	0.70	< d.l.	1.30	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	7/10/03	7/31/03	< d.l.	< d.l.	1.29	< d.l.	< d.l.	0.68	< d.l.	1.25	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	7/10/03	7/31/03	< d.l.	< d.l.	1.29	< d.l.	< d.l.	0.66	< d.l.	1.24	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	7/17/03	8/1/03	< d.l.	< d.l.	3.19	< d.l.	< d.l.	0.83	< d.l.	3.71	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	7/17/03	8/1/03	< d.l.	< d.l.	1.15	< d.l.	< d.l.	0.44	< d.l.	1.20	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	7/24/03	8/13/03	< d.l.	< d.l.	0.47	< d.l.	< d.l.	0.30	< d.l.	0.70	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	7/24/03	8/13/03	< d.l.	< d.l.	0.54	< d.l.	< d.l.	< d.l.	< d.l.	0.79	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	7/31/03	8/14/03	< d.l.	< d.l.	1.22	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	7/31/03	8/13/03	< d.l.	< d.l.	0.52	< d.l.	< d.l.	0.30	< d.l.	0.78	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	8/7/03	8/13/03	< d.l.	< d.l.	0.34	< d.l.	< d.l.	< d.l.	< d.l.	0.55	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	8/7/03	8/13/03	< d.l.	< d.l.	0.54	< d.l.	< d.l.	< d.l.	< d.l.	0.60	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	8/14/03	8/26/03	0.96	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	8/14/03	8/26/03	< d.l.	0.86	< d.l.	0.33	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 1b: Field data of cell-bound Microcystins in Lake Wannsee (continued).

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (cell-bound) in µg/L											
			[D-Asp³]MC-RR	[D-Asp³,Dhb⁷]MC-RR	MC-RR	RT 17,35	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 22,1	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water 0m	8/21/03	9/3/03	2.32	< d.l.	2.04	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	8/21/03	9/3/03	2.10	< d.l.	0.46	< d.l.	< d.l.	1.02	0.67	0.50	< d.l.	< d.l.	0.37	< d.l.
surface water 0m	8/28/03	9/3/03	4.08	< d.l.	< d.l.	< d.l.	< d.l.	1.43	1.31	0.67	< d.l.	< d.l.	0.89	< d.l.
surface water 1m	8/28/03	9/3/03	4.03	0.37	0.67	< d.l.	< d.l.	1.37	1.24	0.55	< d.l.	< d.l.	0.84	< d.l.
surface water 0m	9/4/03	9/8/03	4.50	0.35	0.21	< d.l.	0.45	0.93	1.30	< d.l.	0.30	< d.l.	1.09	< d.l.
surface water 1m	9/4/03	9/8/03	4.24	0.35	< d.l.	< d.l.	0.47	0.79	1.23	< d.l.	0.23	< d.l.	0.90	< d.l.
surface water 0m	9/11/03	9/15/03	4.67	0.28	< d.l.	< d.l.	0.45	0.74	1.50	0.58	< d.l.	< d.l.	0.88	< d.l.
surface water 1m	9/11/03	9/15/03	5.19	0.33	0.38	< d.l.	0.48	0.74	1.67	0.42	< d.l.	< d.l.	1.12	< d.l.
3335	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	9/15/03	11/5/03	0.01	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	9/15/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	9/15/03	9/23/03	10.47	< d.l.	5.12	< d.l.	1.69	< d.l.	< d.l.	10.48	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	9/15/03	11/5/03	4.46	0.23	< d.l.	< d.l.	0.32	0.47	1.47	0.13	< d.l.	< d.l.	0.98	0.25
surface water 0m	9/15/03	9/23/03	5.45	0.31	< d.l.	< d.l.	< d.l.	1.88	0.50	< d.l.	< d.l.	< d.l.	1.40	< d.l.
surface water 1m	9/15/03	9/23/03	5.48	0.36	< d.l.	< d.l.	0.40	0.62	1.71	0.28	< d.l.	0.10	1.23	0.25
surface water scum	9/15/03	9/23/03	10.50	< d.l.	5.12	< d.l.	< d.l.	1.69	< d.l.	10.48	< d.l.	< d.l.	< d.l.	< d.l.
3335	9/22/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	9/22/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	9/22/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	9/22/03	10/23/03	4.56	0.31	< d.l.	< d.l.	0.29	0.83	1.39	0.20	< d.l.	< d.l.	1.05	0.20
surface water 0m	9/22/03	10/23/03	5.32	< d.l.	< d.l.	< d.l.	0.41	0.74	1.64	0.25	< d.l.	1.20	0.16	0.29
surface water 1m	9/22/03	10/23/03	5.13	0.33	< d.l.	< d.l.	0.40	0.94	1.62	0.25	< d.l.	1.20	< d.l.	0.26
3335	9/29/03	11/5/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	9/29/03	10/23/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.			< d.l.	< d.l.
3338	9/29/03													
BEE201OP	9/29/03	1/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	9/29/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	9/29/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	9/29/03													
BEE205	9/29/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	9/29/03	11/6/03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	9/29/03	12/8/03	4.36	< d.l.	< d.l.	< d.l.	0.35	0.74	1.41	0.22	< d.l.	0.10	1.38	0.22

Appendix 1b: Field data of cell-bound Microcystins in Lake Wannsee (continued).

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (cell-bound) in µg/L											
			[D-Asp³]MC-RR	[D-Asp³,Dhb⁷]MC-RR	MC-RR	RT 17,35	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 22,1	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water 0m	9/29/03	11/6/03	4.43	0.36	< d.l.	< d.l.	0.40	0.60	1.47	0.20	< d.l.	0.10	0.99	0.19
surface water 1m	9/29/03	12/8/03	4.38	< d.l.	< d.l.	< d.l.	0.36	0.66	1.38	0.18	< d.l.	0.09	1.13	0.19
surface water scum	9/29/03	1/14/04	10.20	< d.l.	< d.l.	< d.l.	3.51	< d.l.	< d.l.	2.49	< d.l.	< d.l.	3.26	< d.l.
3335	10/6/03													
3337	10/6/03													
3338	10/6/03													
BEE201OP	10/6/03													
BEE202MP1	10/6/03													
BEE202OP	10/6/03													
BEE203	10/6/03													
BEE205	10/6/03													
BEE206	10/6/03													
surface water	10/6/03	1/14/04	3.55	0.33	< d.l.	< d.l.	0.34	0.49	1.18	0.16	< d.l.	0.08	0.79	0.17
surface water 0m	10/6/03													
surface water 1m	10/6/03													
3337	10/13/03													
3338	10/13/03													
BEE201OP	10/13/03													
BEE202MP1	10/13/03													
BEE202OP	10/13/03													
BEE203	10/13/03													
BEE205	10/13/03													
BEE206	10/13/03													
surface water	10/13/03	1/14/04	3.16	0.44	< d.l.	< d.l.	0.36	0.43	1.11	0.12	< d.l.	0.11	0.73	0.15
surface water 0m	10/13/03	1/14/04	4.59	< d.l.	< d.l.	< d.l.	0.50	0.85	1.69	0.30	< d.l.	< d.l.	1.32	0.27
surface water 1m	10/13/03	1/14/04	3.34	< d.l.	< d.l.	< d.l.	0.35	0.45	1.22	0.14	< d.l.	0.09	0.76	0.17
3337	10/21/03													
BEE201OP	10/21/03													
surface water	10/21/03													
surface water 0m	10/21/03													
surface water 1m	10/21/03													
BEE202MP1	10/23/03													
BEE202OP	10/23/03													
BEE203	10/23/03													
BEE205	10/23/03													
BEE206	10/23/03													
surface water 0m	11/13/03													
surface water 1m	11/13/03													
surface water 0m	11/27/03													
surface water 1m	11/27/03													

Appendix 2a: Cyanobacterial biovolume in Lake Wannsee surface water.

Date	Depth (m)	Biovolume (mm^3/L)				
		Microcystis sp.	Aphanozominon flos-aq.	Aphanozominon grazile	Planktothrix agardhii	other cyanobacteria
23. Jan 03	0	< 0.1	< 0.1	< 0.1	< 0.1	0.23
19. Feb 03	0	< 0.1	< 0.1	< 0.1	< 0.1	0.37
21. Mar 03	0	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
21. Mar 03	1	< 0.1	< 0.1	< 0.1	< 0.1	0.43
4. Apr 03	0	< 0.1	< 0.1	< 0.1	< 0.1	0.55
4. Apr 03	1	< 0.1	< 0.1	< 0.1	< 0.1	0.86
17. Apr 03	0	< 0.1	< 0.1	< 0.1	< 0.1	0.62
17. Apr 03	1	< 0.1	< 0.1	< 0.1	< 0.1	0.78
29. Apr 03	0	< 0.1	< 0.1	< 0.1	< 0.1	1.45
29. Apr 03	1	< 0.1	< 0.1	< 0.1	< 0.1	0.79
9. May 03	0	< 0.1	< 0.1	0.45	0.26	3.37
9. May 03	1	< 0.1	< 0.1	0.44	0.16	2.70
6. Jun 03	0	0.17	< 0.1	< 0.1	< 0.1	< 0.1
6. Jun 03	1	0.17	< 0.1	< 0.1	< 0.1	< 0.1
20. Jun 03	0	9.95	1.45	< 0.1	< 0.1	< 0.1
20. Jun 03	1	1.38	1.13	< 0.1	< 0.1	< 0.1
26. Jun 03	0	13.83	8.39	< 0.1	< 0.1	< 0.1
26. Jun 03	1	9.89	4.69	< 0.1	< 0.1	< 0.1
3. Jul 03	0	10.03	17.46	< 0.1	< 0.1	< 0.1
3. Jul 03	1	8.96	14.43	< 0.1	< 0.1	< 0.1
10. Jul 03	0	15.45	20.34	< 0.1	< 0.1	< 0.1
10. Jul 03	1	15.19	22.18	< 0.1	< 0.1	< 0.1
17. Jul 03	0	60.43	19.59	< 0.1	< 0.1	< 0.1
17. Jul 03	1	9.15	8.46	< 0.1	< 0.1	< 0.1
24. Jul 03	0	3.43	9.36	< 0.1	< 0.1	< 0.1
24. Jul 03	1	5.03	10.16	< 0.1	< 0.1	< 0.1
31. Jul 03	0	6.21	3.63	< 0.1	< 0.1	< 0.1
31. Jul 03	1	6.58	5.27	< 0.1	< 0.1	< 0.1

Appendix 2b: Results of the fluorometric measurements of surface water at Lake Wannsee.

Date	Number of Measurements	Depth [m]	Avarages (µg/L Chlorophyll)				
			Green algae	Cyanobacteria	Diatoms	Cryptophyta	Total
21. Mar 03	37	1.05	0.00	0.20	0.00	0.00	0.20
04. Apr 03	87	1.00	0.02	0.62	0.00	0.00	0.64
17. Apr 03	63	1.05	0.32	1.06	0.00	0.00	1.38
29. Apr 03	43	0.64	0.38	0.71	0.00	0.00	1.08
22. May 03	39	1.01	0.05	0.51	0.00	0.00	0.56
06. Jun 03	83	0.91	0.00	0.00	0.00	0.00	0.00
20. Jun 03	176	0.88	0.00	0.12	0.00	0.00	0.12
26. Jun 03	96	0.94	0.00	0.39	0.00	0.00	0.39
03. Jul 03	56	1.07	0.07	0.08	0.00	0.00	0.15
10. Jul 03	343	1.18	0.00	0.01	0.00	0.00	0.01
17. Jul 03	41	1.16	0.00	0.07	0.00	0.00	0.07
24. Jul 03	no measurement						
31. Jul 03	no measurement						
07. Aug 03	no measurement						
14. Aug 03	no measurement						
21. Aug 03	no measurement						
28. Aug 03	no measurement						
04. Sep 03	no measurement						
11. Sep 03	no measurement						
18. Sep 03	no measurement						
22. Sep 03	19	1.05	0.00	22.23	0.00	12.91	35.14
29. Sep 03	51	1.02	0.00	26.02	0.00	8.88	34.89
06. Oct 03	13	0.96	0.00	22.65	0.00	6.39	29.03
13. Oct 03	16	1.08	0.00	15.37	0.00	6.90	22.27
21. Oct 03	8	0.93	0.00	14.49	0.00	7.44	21.94
13. Nov 03	16	1.01	0.00	1.74	1.12	2.85	5.71
27. Nov 03	10	1.05	0.00	0.58	1.70	3.84	6.11
11. Dec 03	18	1.04	0.00	0.46	0.31	1.01	1.78

Appendix 3a: Field data of extracellular Microcystins in AR pond Tegel.

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (extracellular) in µg/L										
			[D-Asp³]MC-RR	[D-Asp³,Dhb7] MC-RR	RT 17,35	MC-RR	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 24,7	[D-Asp³]MC-YR	RT 27,6
AR pond Tegel	16-Jan-03	24-Apr-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.		< d.l.	< d.l.
AR pond Tegel	13-Feb-03												
AR pond Tegel	13-Mar-03												
AR pond Tegel	24-Apr-03												

Appendix 3b: Field data of extracellular Microcystins at Lake Wannsee Transsects.

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (extracellular) in µg/L										
			[D-Asp³]MC-RR	[D-Asp³,Dhb7] MC-RR	RT 17,35	MC-RR	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water	20-Feb-03												
surface water	21-Mar-03												
surface water 0m	4-Apr-03												
surface water 1m	4-Apr-03												
surface water 0m	17-Apr-03												
surface water 1m	17-Apr-03												
surface water 0m	29-Apr-03												
surface water 1m	29-Apr-03												
surface water 0m	9-May-03												
surface water 1m	9-May-03												
surface water 0m	6-Jun-03												
surface water 1m	6-Jun-03												
surface water 0m	20-Jun-03												
surface water 1m	20-Jun-03												
surface water 0m	26-Jun-03												
surface water 1m	26-Jun-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0-1m	26-Jun-03	23-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	3-Jul-03												
surface water 1m	3-Jul-03												
surface water 0m	10-Jul-03												
surface water 1m	10-Jul-03												
surface water 0m	17-Jul-03												

Appendix 3b: Field data of extracellular Microcystins at Lake Wannsee Transsects (continued).

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (extracellular) in µg/L										
			[D-Asp³]MC-RR	[D-Asp³,Dhb7] MC-RR	RT 17,35	MC-RR	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water 1m	17-Jul-03												
surface water 0m	24-Jul-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	24-Jul-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	31-Jul-03												
surface water 1m	31-Jul-03												
surface water 0m	7-Aug-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.47	0.21	< d.l.	< d.l.
surface water 1m	7-Aug-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	0.54	< d.l.	< d.l.	< d.l.
surface water 0m	14-Aug-03												
surface water 1m	14-Aug-03												
surface water 0m	21-Aug-03												
surface water 1m	21-Aug-03												
surface water 0m	28-Aug-03												
surface water 1m	28-Aug-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	4-Sep-03	19-Sep-03	0.17	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	4-Sep-03	19-Sep-03	0.31	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	11-Sep-03												
surface water 1m	11-Sep-03												
3335	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	15-Sep-03												
surface water 0m	15-Sep-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	15-Sep-03	19-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water scum	15-Sep-03	18-Sep-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3335	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	22-Sep-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 3b: Field data of extracellular Microcystins at Lake Wannsee Transsects (continued).

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (extracellular) in µg/L										
			[D-Asp³]MC-RR	[D-Asp³,Dhb7] MC-RR	RT 17,35	MC-RR	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 24,7	[D-Asp³]MC-YR	RT 27,6
BEE201OP	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	22-Sep-03	24-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	22-Sep-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	22-Sep-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	22-Sep-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3335	29-Sep-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	29-Sep-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3338	29-Sep-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	29-Sep-03	8-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	29-Sep-03	8-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	29-Sep-03	8-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	29-Sep-03	8-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	29-Sep-03	8-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	29-Sep-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	29-Sep-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	29-Sep-03	6-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	29-Sep-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water scum	29-Sep-03	7-Nov-03	< d.l.	< d.l.	< d.l.	0.32	< d.l.	0.11	< d.l.	1.07	< d.l.	< d.l.	< d.l.
3335	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	6-Oct-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3338	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	6-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	6-Oct-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 3b: Field data of extracellular Microcystins at Lake Wannsee Transsects (continued).

Observation point	Date	Date of Analysis	Results of HPLC-PDA Analysis (extracellular) in µg/L										
			[D-Asp³]MC-RR	[D-Asp³,Dhb7] MC-RR	RT 17,35	MC-RR	RT 21,16	MC-YR	[D-Asp³]MC-LR	MC-LR	RT 24,7	[D-Asp³]MC-YR	RT 27,6
surface water 0m	6-Oct-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	6-Oct-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3337	13-Oct-03	23-Oct-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
3338	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	13-Oct-03	10-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	13-Oct-03												
surface water 1m	13-Oct-03												
3337	21-Oct-03	6-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE201OP	21-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water	21-Oct-03	9-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	21-Oct-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	21-Oct-03	7-Nov-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202MP1	23-Oct-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE202OP	23-Oct-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE203	23-Oct-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE205	23-Oct-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
BEE206	23-Oct-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	13-Nov-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	13-Nov-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 0m	27-Nov-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.
surface water 1m	27-Nov-03	16-Dec-03	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.	< d.l.

Appendix 4: Field data of total Microcystins (by ELISA) at Lake Wannsee Transsects (shaded areas: Adda-ELISA).

Observation point	Date	MCYST (ELISA, in µg/L)
3335	12. Jun 02	0.01
3335	09. Jul 02	< 0.012
3335	20. Aug 02	< 0.012
3335	22. Oct 02	< 0.02
3335	26. Nov 02	< 0.01
3335	19. Dec 02	< 0.02
3335	23. Jan 03	< 0.02
3335	20. Feb 03	< 0.19
3335	15. Sep 03	< 0.002
3335	22. Sep 03	< 0.127
3335	29. Sep 03	0.16
3335	06. Oct 03	0.16
3337	15. May 02	< 0.012
3337	12. Jun 02	< 0.012
3337	09. Jul 02	< 0.012
3337	20. Aug 02	< 0.012
3337	17. Sep 02	0.01
3337	22. Oct 02	< 0.02
3337	26. Nov 02	< 0.01
3337	19. Dec 02	< 0.02
3337	23. Jan 03	< 0.02
3337	20. Feb 03	< 0.19
3337	18. Mar 03	< 0.19
3337	08. Apr 03	< 0.027
3337	20. May 03	< 0.115
3337	03. Jul 03	
3337	15. Sep 03	< 0.002
3337	22. Sep 03	0.10
3337	29. Sep 03	0.32
3337	18. Nov 03	< 0.11
3338	15. May 02	< 0.012
3338	12. Jun 02	< 0.012
3338	09. Jul 02	< 0.012
3338	20. Aug 02	< 0.012
3338	17. Sep 02	< 0.012
3338	22. Oct 02	< 0.02
3338	26. Nov 02	< 0.01
3338	19. Dec 02	< 0.02
3338	23. Jan 03	< 0.02
3338	20. Feb 03	< 0.19
3338	18. Mar 03	< 0.19
3338	20. May 03	< 0.115
3338	03. Jul 03	< 0.172
3338	29. Sep 03	0.25
3339	15. May 02	0.02
3339	12. Jun 02	0.02
3339	09. Jul 02	< 0.012
3339	17. Sep 02	0.04
3339	22. Oct 02	0.05
3339	26. Nov 02	0.02
3339	19. Dec 02	< 0.02
BEE200OP	23. Jan 03	< 0.02
BEE200OP	20. Feb 03	< 0.19
BEE200UP	23. Jan 03	< 0.02
BEE200UP	20. Feb 03	< 0.19
BEE201OP	23. Jan 03	< 0.02
BEE201OP	20. Feb 03	< 0.19
BEE201OP	18. Mar 03	< 0.19
BEE201OP	08. Apr 03	< 0.027
BEE201OP	20. May 03	< 0.115
BEE201OP	17. Jun 03	< 0.115
BEE201OP	15. Sep 03	< 0.002
BEE201OP	22. Sep 03	< 0.127
BEE201OP	29. Sep 03	0.17
BEE201OP	18. Nov 03	< 0.11
BEE201UP	23. Jan 03	< 0.02
BEE201UP	20. Feb 03	< 0.19
BEE201UP	18. Mar 03	< 0.19
BEE201UP	08. Apr 03	< 0.214
BEE201UP	20. May 03	< 0.115
BEE201UP	17. Jun 03	< 0.115
BEE201UP	03. Jul 03	< 0.172
BEE201UP	24. Sep 03	< 0.127
BEE202MP1	23. Jan 03	< 0.02
BEE202MP1	20. Feb 03	< 0.19
BEE202MP1	20. Mar 03	< 0.19
BEE202MP1	10. Apr 03	< 0.115
BEE202MP1	22. May 03	< 0.115
BEE202MP1	18. Jun 03	< 0.214
BEE202MP1	24. Jul 03	< 0.172
BEE202MP1	15. Sep 03	< 0.002
BEE202MP1	22. Sep 03	< 0.127
BEE202MP1	29. Sep 03	0.20
BEE202MP2	23. Jan 03	0.02
BEE202MP2	20. Feb 03	< 0.19
BEE202MP2	20. Mar 03	< 0.19
BEE202MP2	10. Apr 03	< 0.115
BEE202MP2	22. May 03	< 0.115
BEE202MP2	18. Jun 03	< 0.214
BEE202MP2	24. Sep 03	< 0.127
BEE202OP	23. Jan 03	< 0.02
BEE202OP	20. Feb 03	< 0.19
BEE202OP	20. Mar 03	< 0.19
BEE202OP	10. Apr 03	< 0.115
BEE202OP	22. May 03	< 0.115
BEE202OP	18. Jun 03	< 0.214
BEE202OP	02. Jul 03	< 0.172
BEE202OP	15. Sep 03	< 0.002
BEE202OP	22. Sep 03	< 0.127
BEE202OP	29. Sep 03	0.14
BEE202UP	19. Feb 03	< 0.02
BEE202UP	20. Mar 03	< 0.19

Appendix 4: Field data of total Microcystins (by ELISA) at Lake Wannsee Transsects (shaded areas: Adda-ELISA, continued).

Observation point	Date	MCYST (ELISA, in µg/L)
BEE202UP	10. Apr 03	< 0.115
BEE202UP	22. May 03	< 0.115
BEE202UP	18. Jun 03	< 0.214
BEE202UP	24. Sep 03	< 0.127
BEE203	22. Jan 03	< 0.02
BEE203	19. Feb 03	< 0.02
BEE203	20. Mar 03	< 0.19
BEE203	10. Apr 03	< 0.115
BEE203	22. May 03	< 0.115
BEE203	18. Jun 03	< 0.214
BEE203	24. Jul 03	< 0.172
BEE203	15. Sep 03	< 0.002
BEE203	22. Sep 03	< 0.127
BEE204OP	19. Feb 03	< 0.02
BEE204OP	21. Mar 03	< 0.19
BEE204OP	10. Apr 03	< 0.115
BEE204OP	20. May 03	< 0.115
BEE204OP	17. Jun 03	< 0.214
BEE204OP	24. Sep 03	< 0.127
BEE204UP	19. Feb 03	< 0.19
BEE204UP	10. Apr 03	< 0.115
BEE204UP	20. May 03	< 0.115
BEE204UP	17. Jun 03	< 0.214
BEE204UP	22. Jul 03	< 0.172
BEE204UP	24. Sep 03	< 0.127
BEE205	23. Jan 03	< 0.02
BEE205	20. Feb 03	< 0.19
BEE205	20. Mar 03	< 0.19
BEE205	08. Apr 03	0.04
BEE205	22. May 03	< 0.115
BEE205	18. Jun 03	< 0.214
BEE205	03. Jul 03	< 0.172
BEE205	24. Jul 03	< 0.172
BEE205	15. Sep 03	0.16
BEE205	22. Sep 03	< 0.127
BEE205	29. Sep 03	0.29
BEE206	23. Jan 03	< 0.02
BEE206	20. Feb 03	< 0.19
BEE206	20. Mar 03	< 0.19
BEE206	08. Apr 03	0.04
BEE206	22. May 03	< 0.115
BEE206	18. Jun 03	< 0.172
BEE206	03. Jul 03	< 0.172
BEE206	24. Jul 03	< 0.172
BEE206	21. Aug 03	< 0.11
BEE206	15. Sep 03	< 0.002
BEE206	22. Sep 03	< 0.127
BEE206	29. Sep 03	0.37
BEE207MP1	23. Jan 03	0.23
BEE207OP	23. Jan 03	0.04
BEE207UP	23. Jan 03	< 0.02
BEE207UP	20. Mar 03	< 0.19
Br. 3	24. Sep 03	< 0.127
Sickerbecken 3	15. May 02	0.06
Sickerbecken 3	16. Jan 03	0.10
TTS-OFW	16. May 02	0.17
TTS-OFW	14. Jun 02	< 0.034
TTS-OFW	10. Jul 02	< 0.034
TTS-OFW	22. Aug 02	0.76
TTS-OFW	19. Sep 02	0.42
TTS-OFW	24. Oct 02	< 0.034
TTS-OFW	17. Dec 02	0.16
TTS-OFW	28. Jan 03	0.10
TTS-OFW	18. Feb 03	0.04
TTS-OFW	17. Mar 03	0.04
TTS-OFW	16. Jun 03	< 0.115
TW-OFW	15. May 02	0.51
TW-OFW	12. Jun 02	0.44
TW-OFW	09. Jul 02	0.12
TW-OFW	09. Aug 02	1.34
TW-OFW	17. Aug 02	4.38
TW-OFW	20. Aug 02	1.61
TW-OFW	13. Sep 02	3.26
TW-OFW	27. Sep 02	1.47
TW-OFW	22. Oct 02	0.07
TW-OFW	25. Oct 02	0.05
TW-OFW	26. Nov 02	0.06
TW-OFW	19. Dec 02	0.04
TW-OFW	23. Jan 03	0.05
TW-OFW	20. Feb 03	0.06
TW-OFW	18. Mar 03	0.05
TW-OFW	08. Apr 03	0.24
TW-OFW	02. Jul 03	10.21
TW-OFW	03. Jul 03	6.52
TW-OFW	22. Jul 03	5.06
TW-OFW	15. Sep 03	8.80
TW-OFW	22. Sep 03	12.80
TW-OFW	23. Sep 03	1.55
TW-OFW	29. Sep 03	15.65
TW-OFW	06. Oct 03	10.92
TW-OFW	18. Nov 03	0.44
TW-OFW 0m	15. May 02	< 0.012
TW-OFW 0m	17. Jun 03	18.42
TW-OFW 0m	03. Jul 03	13.05
TW-OFW 0m	10. Jul 03	13.05
TW-OFW 0m	15. Sep 03	12.87
TW-OFW 0m	22. Sep 03	25.38
TW-OFW 0m	29. Sep 03	14.28
TW-OFW 0m	06. Oct 03	15.74
TW-OFW 0m	13. Nov 03	1.51
TW-OFW 1m	03. Jul 03	9.30
TW-OFW 1m	10. Jul 03	11.12

Appendix 4: Field data of total Microcystins (by ELISA) at Lake Wannsee Transsects (shaded areas: Adda-ELISA, continued).

Observation point	Date	MCYST (ELISA, in µg/L)
TW-OFW 0m	15. Sep 03	12.87
TW-OFW 0m	22. Sep 03	25.38
TW-OFW 0m	29. Sep 03	14.28
TW-OFW 0m	06. Oct 03	15.74
TW-OFW 0m	13. Nov 03	1.51
TW-OFW 1m	03. Jul 03	9.30
TW-OFW 1m	10. Jul 03	11.12
TW-OFW 1m	22. Sep 03	10.57
TW-OFW 1m	29. Sep 03	12.90
TW-OFW 1m	06. Oct 03	14.75
TW-OFW 1m	13. Nov 03	2.63
TW-OFW Ufer	15. Sep 03	50.85

Using bacteriophages, indicator bacteria, and viral pathogens for assessing the health risk of drinking water obtained by bank filtration

Project leader: Dr. J. M. Lopez-Pila, Dr. R. Szewzyk
Working group: Dr. H. Dizer, M. Fischer, H. Bohn

Abstract:

Investigations of *E. coli*, intestinal enterococci, and coliphages as indicator for human pathogenic bacteria and viruses in surface water and in the transect wells confirmed the high hygienic microbiological quality of the Lake Wannsee and Lake Tegel. Microorganisms in lake water ranged from 3 to 276 pfu/100 ml for coliphages, from detection limit up to 7 or 160 cfu/100 ml for intestinal enterococci and *E. coli*, respectively. The well water contained sporadically bacteria or phages. These findings did not allow a quantitative approach for the elimination of microorganisms in the Tegel and Wannsee sites.

Therefore, further investigations focused on the three model filtration plants of Marienfelde: the sandy soil column of 5 m length, the enclosure and the slow sand filtration pond with a filtration path of 100 or 80 cm, respectively. High virus retention was observed in all model filtration plants albeit the elimination rate had the tendency to decrease with increasing distance from the inoculation site. At the worst the elimination rate achieved was of one log in ca. 350 cm filter path.

Increasing the percolation velocity dramatically increased the mobility of the coliphages, pointing to the significance of an adequate water velocity for optimal elimination. Both, bacteria and coliphages remained entrapped in the filter sand for extended periods of time. Coliphages are still detectable in the column effluent after more than one year after being inoculated.

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Berlin, December 31, 2002

1. Extended Summary

E. coli, intestinal enterococci, and coliphages as indicator for human pathogen bacteria and viruses, as well as general heterotrophic bacteria were investigated in the surface water of Lake Wannsee and in water samples from 11 shallow observation wells as well as 2 regularly pumping sites of the Water Works Berlin along the transects 1 and 2 of Wannsee. Concentrations of the indicator microorganisms ranged from 3 to 276 pfu/100 ml for coliphages, from detection limit up to 7 or 160 cfu/100 ml for intestinal enterococci and *E. coli*, respectively, have confirmed high hygienic microbiological quality of the Lake Wannsee and Lake Tegel

The shallow observation wells and regularly pumping sites of the Water Works Berlin along the transects Wannsee were also probed for microorganisms. Only 4 or 7 of totally 99 water samples from 8 shallow observation wells contained coliphages or intestinal enterococci, respectively. Twenty two % of the samples were positive for *E. coli*. The cause for these postiive findings is not clear. In spite of using sterilised instruments, a secondary contamination of the well water can not be excluded. The new observation wells at the see basin, 207OP, MP1,MP2 and 207 UP were directly contaminated with see water and could not be incorporated into the study.

Therefore, for further assessment of the bank filtration process, further investigations focused on three model filtration plants of Marienfelde: the sandy soil column in a length of 5 m, the enclosure and the slow sand filtration pond with a filtration path of 100 or 80 cm, respectively.

Both phages, the somatic phage 241 and the F+-phage 138 were eliminated very efficiently in the first 100 cm of the column. Beyond the first 100 cm of the column the reduction performance decreased dramatically. For phage 138 distance necessary for reducing the phage concentration by one log (“one-log distance”) between the bottom of the column (the column was operated from bottom to top) and the 20 cm point was 13 cm. However, between the 80th and the 160th cm the estimate for the one-log distance was 133 cm.

With the phage 241, two estimates were carried out: the first one, using the concentrations obtained during the first 4 weeks of the experiment, the second taking the compounded results of 10 months

As was the case with phage 138, the one-log distances of the phage 241 increased with increasing column depth. From a one-log distance of 23 cm after 20 cm filter path to 346 cm after 320 cm filter path.

Several causes that might be responsible for the decreasing performance of the column are discussed, the heterogeinity of the viral suspension (monodispersed, aggregated) being the most suspected one. The results obtained in he enclosure and in the infiltration pond point to the same direction. The one-log distances have the tendency of become larger with increasing filtration distance.

Increasing the percolation rate from 1 to 8 m/d highly enhanced the mobility of the virus 241. At 160 cm column height and beyond the mobilization was very pronounced and the concentrations of free viruses reached at this level might be one thousand times higher than before the percolation rate was increased. At lower column heights the mobilisation was less manifest but the concentrations became still at least one order of magnitude higher. Another further increase of the water velocity from 8 to 24 m/day had as a consequence a further increase in mobility.

Aiming at establishing a relationship of the filtration properties of *E.coli*, intestinal enterococci and coliphages between themselves, we present results of filtration experiments carried out with these three microorganisms simultaneously. Furthermore, sand cores were analysed for the presence of bacteria and phage predators that might play a role in clearing the surface water from pathogens.

2. Objectives of this project:

The scope of the study should extend for at least three years. The program below aims at three years duration.

The investigations will be carried out in close collaboration with the other participant laboratories in order to share information on flow rates, quality of the water etc. Following a preliminary agreement of the participants the research will take place in the following sites:

- Semi-technical facilities of the UBA in Marienfelde; large pond for bank filtration and small pond or enclosure for sand filtration
- Observation wells along the transects of the Lakes Wannsee and Tegel

Other sites might be chosen at the discretion of the investigators if the results obtained so far considered appropriate.

Part of the project to be carried out in the experimental infiltration ponds of Marienfelde:

1) Cultivation and purification of a sufficiently large quantity of bacteria and f2-coliphages.
2) Spiking the large pond for river bank filtration with the bacteria and f2-coliphages. Collecting samples, determination of the concentrations of microorganisms in the surface water and in the filtrate.
3) Spiking the sand filtration units (enclosure) with the bacteria and f2-coliphages. Collecting samples, determination of the concentrations of microorganisms in the surface water and in the filtrate.

3a) as 2a) with at least another water filtration velocity.

A) First report on the infiltration results from the experimental field sites in Marienfelde, small and large ponds. First results from the surface waters and the transects.

4) Inoculation of filtrated raw wastewater (high content of natural phages!) into the enclosure. Collecting samples, determination of coliphages and human pathogenic viruses by molecular amplification methods in the infiltrated wastewater and in different steps of the filtration process. Concomitant investigation of the indicator bacteria in water and soil samples.
5) as 4) under different conditions.

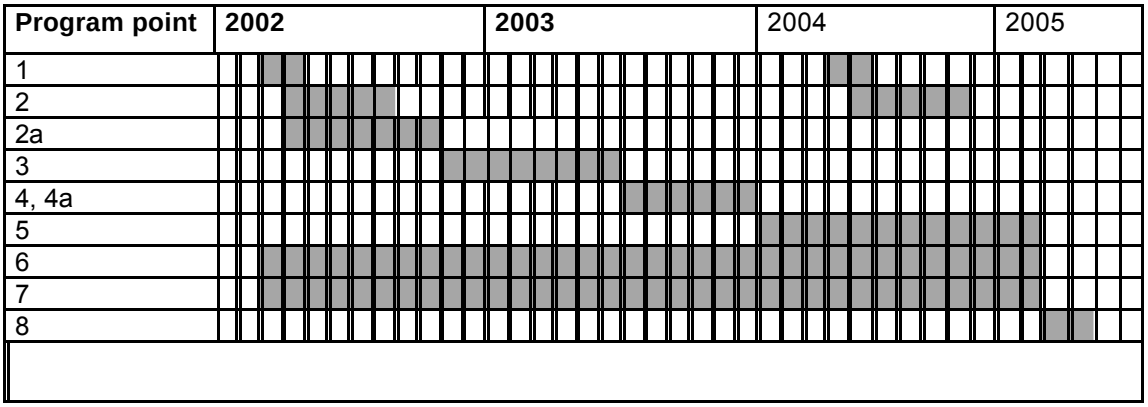
B) Second report. Infiltration results from the experimental field sites in Marienfelde. Results from the surface waters and the transects. Advance of a model by Nützmann et al. constructed on the basis of the experimental findings

Part of the project to be carried out in the field sites:

6) Representative determinations of total coliphages in the river water. Same for enteroviruses with molecular methods. Concomitant investigation of the indicator bacteria.
7) as 6) for appropriate sampling points in the transects. Investigation of indicator bacteria in water and soil samples with conventional as well as molecular methods.
8) Writing the final report.

3. Timetable

Table 1. Time table for program points and deliverables



4. Intended and achieved tasks for the reporting period

Table 2. Tasks for the first year of the project

Task	achieved ?	comments
Measuring indicator bacteria and coliphages in surface water and selected shallow wells along the transects 1 and 2 of the Lake Wannsee	Yes	Unfortunately, the new shallow observation wells along the transect 2 of the Lake Wannsee could not start operation.
Investigation in the long sandy soil column of Marienfelde: Inoculation of influent with Coliphage 138 and 241, sampling at 6 sites of the first column in regularly intervals, determination of coliphages in filtrate samples.	Yes	The hydrodynamic conditions in the sandy soil column were determined by working group “organic” TU-Berlin.
Investigation on the enclosure: Spiking with the selected culture suspensions of coliphages 138 and 241, and indicator bacteria. Collecting samples, determination of the concentrations of microorganisms in influent and in filtrates.	Yes	Due to the sensitivity of the applied reference compounds for microbial degradation, spiking of enclosure with bacteria cultures could not be carried out intensively.
Investigation on the slow sand filtration pond in Marienfelde: Inoculation of pond water with Coliphage 138 and 241, Collecting samples in regularly intervals, detection of coliphages in water samples.	Yes	
Batch experiences: Detection of adsorption capacity of the sandy soil applied by filling the filtration plants of Marienfelde	Yes	
Spiking the large bank filtration pond in Marienfelde with phages, tracing the phages along the drains and filtration paths	No	Because of some technical problems, investigation on the bank filtration pond will be carried out in 2004

5. Results.

5.1 Indicator bacteria and coliphages in water samples from the transects of Lake Wannsee

Water samples from the lake water and the transects Lake Wannsee 1 and 2 were taken monthly using sterilised pump modules and silicon tubing separately for each pumping station. Sampling was concentrated on the shallower and less distant wells because no positive samples had been found after long filtration paths during the previous sampling period. At the transect 1, the observation wells 3337 and 201OP were sampled at all sampling surveys. During some sampling times the flat observation well 3338 was dry. Sampling at the observation well 3335 of transect 1 was carried out only four times during the intensive sampling period from 15.9.03 to 15.10.03.

Four additional wells had been build in 2002 along transect 2 close to the shore of Lake Wannsee to allow for shorter filtration paths. Unfortunately, these new observation wells (207OP, 207 MP1, 207 MP 2 and 207UP) did not work during the sampling period in 2003. Well 207 MP2 was permanently dry. From the other wells water could be obtained only at three sampling times. Additionally, water samples of these wells were highly contaminated with indicator bacteria and coliphages probably due to direct lake water intrusion.

All samples were transferred in cooling boxes at (8 ± 2) °C, and immediately analysed in the laboratory. The indicator bacteria, *E. coli* and intestinal enterococci as well as coliphages were analysed in water volumes of up to 100 ml using standardized methods:
E. coli (DIN EN ISO 9308-1 or DIN EN ISO 9308-3 or Chromocult-agar); intestinal enterococci (DIN EN ISO 7899-1 or DIN EN ISO 7899-2), Colony count of heterotrophic bacteria (DIN EN ISO 6222 and DIN 38411 T.5, 1979), Coliphages (DIN EN ISO, 10705-2).

The concentration of indicator bacteria and coliphages in surface water samples from Lake Wannsee was very low (Fig 1). The concentration of coliphages varied between 2 pfu and 276 pfu/ 100 ml. The densities of indicator bacteria ranged from detection limit up to 7 cfu/100 ml for intestinal enterococci, and up to 160 cfu/100 ml for *E. coli*, respectively. Concentrations of indicator bacteria and especially of coliphages were higher during winter than during summer.

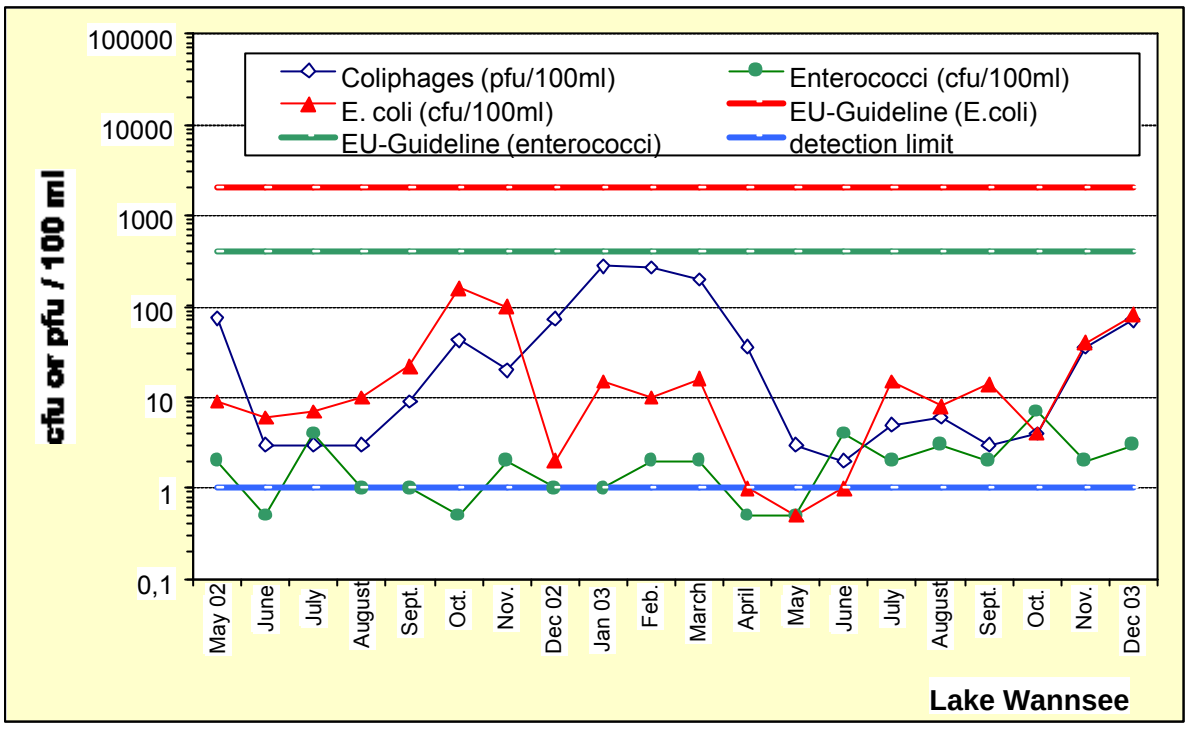


Fig 1: Concentration of indicator bacteria and coliphages in water samples from Lake Wannsee (EU-Guideline for E. coli: 2000 cfu/100 ml, for enterococci 400 cfu/100 ml)

Non of the regularly sampled wells along transect Lake Wannsee 1 (3337, 3338 and 201OP) contained coliphages in 100 ml. Only one out of four samples was positive for coliphages from well 3335. In contrast, six or 14 out of 38 samples from the observation wells were contaminated by *E. coli* or intestinal enterococci, respectively (Table 1). All water samples from the pumping well 4 were free from intestinal enterococci and coliphages but two samples contained *E. coli*.

Table 1: Occurrence frequency of indicator bacteria and coliphages in the water samples from transect Lake Wannsee 1 in the year 2003

Trasnsect Wannsee 1	**CPHG (+ / wells)**	**Intestinal enterococci (+ / wells)**	**E coli (+/ wells)**
surface water	13 / 13	8 / 13	10 / 13
3338	0 / 9	2 / 9	5 / 9
3337	0 / 12	1 / 12	3 / 12
3335	1 / 4	3 / 4	3 / 4
201 OP	0 / 13	0 / 13	3 / 13
total observation wells	**1 / 38**	**6 / 38**	**14 / 38**
pumping well 4	0 / 9	0 / 9	2 / 9

In the samples from transect Lake Wannsee 2 – apart from the newly built and contaminated wells - intestinal enterococci and coliphages were detected only in 1 or 3 out of 55 samples, respectively. *E. coli* was found in 8 out of 55 samples. No indicator microorganisms were detected in the water samples from pumping well 3.

Table 2: Occurrence frequency of indicator bacteria and coliphages in the water samples from transect Lake Wannsee 2 in the year 2003

Trasnsect Wannsee 2	**CPHG (+ / wells)**	**Intestinal enterococci (+ / wells)**	**E coli (+/ wells)**
surface water	15 / 15	12 / 15	14 / 15
BEE205	1 / 15	0 / 15	3 / 15
BEE206	0 / 15	0 / 15	0 / 15
BEE207OP (new)	3 / 3	0 / 2	2 / 2
BEE207MP1 (new)	3 / 3	0 / 2	2 / 2
BEE207UP (new)	3 / 3	0 / 2	2 / 2
BEE202OP	1 / 15	1 / 15	3 / 15
BEE203	1 / 10	0 / 10	2 / 10
total observation wells except new wells	**3** / **55**	**1** / **61**	**8** / **55**
pumping well 3	0 / 13	0 / 13	0 / 13

Extra care was taken to avoid contamination during sampling. Sterilised pumping modules and silicon tubing were used separately for each observation well. Nevertheless, secondary contamination of the water samples cannot completely be excluded since other partners in the project did not use sterile sampling equipment. Another possible source of contamination are biofilms on the surface of wires and instruments in the water column of the wells. Therefore, biofilm samples were taken with swabs and analysed for the indicator bacteria and coliphages. No *E. coli*, enterococci or coliphages were detected in these biofilm samples.

A deduction of retention ratios of the indicator microorganisms is not possible from the results of the transects due to the low concentrations of indicator microorganisms in Lake Wannsee and their sporadic occurrence in the observation wells.

5.2 Adsorption and transport behaviour of coliphages

No general deduction of transport behaviour can be achieved from the transects due to low concentrations of indicator microorganisms. To obtain more information about the adsorption and transport behaviour of coliphages in sandy soil under controlled conditions a series of experiments were conducted using long columns (5.1.1), enclosures (5.1.2), and filtration ponds (5.1.3) in Marienfelde.

Simultaneous addition of coliphages and bacteria was not possible in these experiment due to concerns about possible interactions between the bacteria and the trace chemical added by the “chemical group”.

5.2.1 Investigations in the sandy soil column.

The sandy soil columns - for simulation of ground water stream in an aquifer for 50 d - were inoculated with both coliphages and percolated continuously with water from Lake Tegel.

Percolation rate of lake water was adjusted to 0.5 L/h (100 cm/d) corresponding to a filtration speed of 100 cm/d for about 4 weeks (see 5.2.1.1). After four weeks the flow rate was increased to 4 L/h (800 cm/d) for two weeks and to about 12 L/h for 3 weeks (24 m/d, see chapter 5.3). Subsequently, percolation of the column was continued at a flow rate of 100 cm/day for further 8 months (see 5.1.1.2).

5.2.1.1 Short term experiments during 35 days

Coliphage 241 was added as a peak whereas coliphage 138 was continuously added to the column. To achieve this, a suspension (500 ml) of coliphage 241 was directly inoculated into the inlet of the column within 30 minutes. A suspension of coliphage 138 was added into the lake water reservoir of 500 L. Sampling was carried out daily from all drain tubes of the first column (20 cm, 40 cm, 80 cm, 160 cm, 340 cm and 500 cm).

Inoculation of the lake water reservoir with a suspension of coliphage 138 resulted in an initial density of 2 $x10^5$ pfu/ml which decreased to 550 pfu/ml after 35 d percolation time (Fig. 2). At 20 cm and 40 cm, coliphage 138 was found in relatively high concentrations of about 300 pfu/ml already at day 2. The first breakthrough of coliphage 138 at 80 cm and 160 cm, was observed at day 3 and 7, respectively. After 35 d, the concentration of coliphage 138 was about 10 at 20 cm and less than 1 pfu/ml at 40 cm. At 80 cm and 160 cm coliphage 138 was no longer detected in 100 ml of samples collected after 30 d (Fig.2). No coliphage 138 was found at 340 cm during the entire experiment.

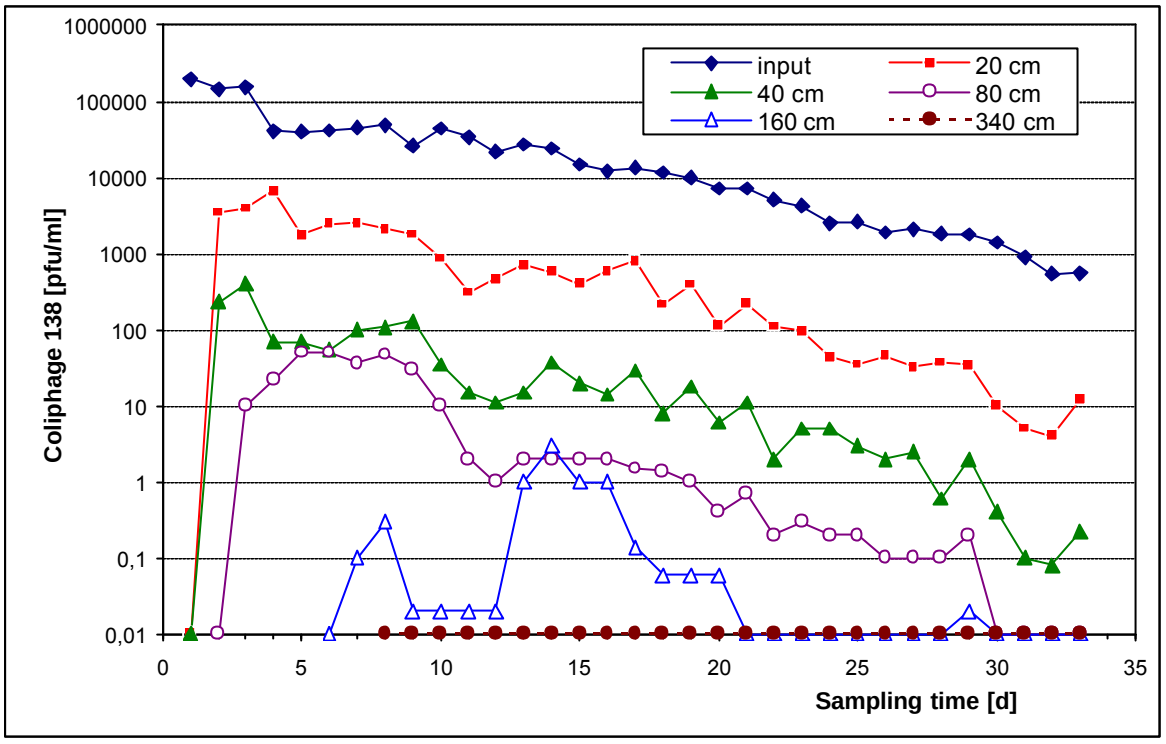


Fig. 2. Concentration of coliphage 138 in different levels of the sandy soil column at a flow rate of 100 cm/d; detection limit = 0.01 pfu/ml

The data were given to the “model group” for detailed analysis. For preliminary analysis, a best fit straight line was fitted manually to every curve to be able to estimate the breakthrough of phage 138 (Fig.3, Fig. 4).

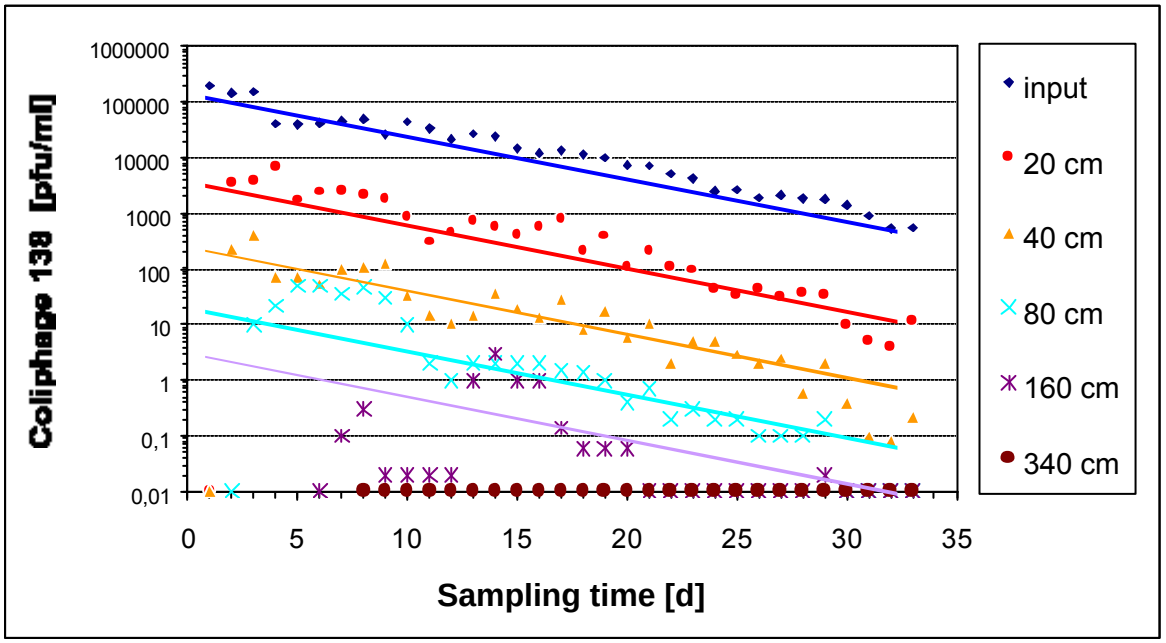


Fig. 3: Coliphage 138 – best fit straight lines

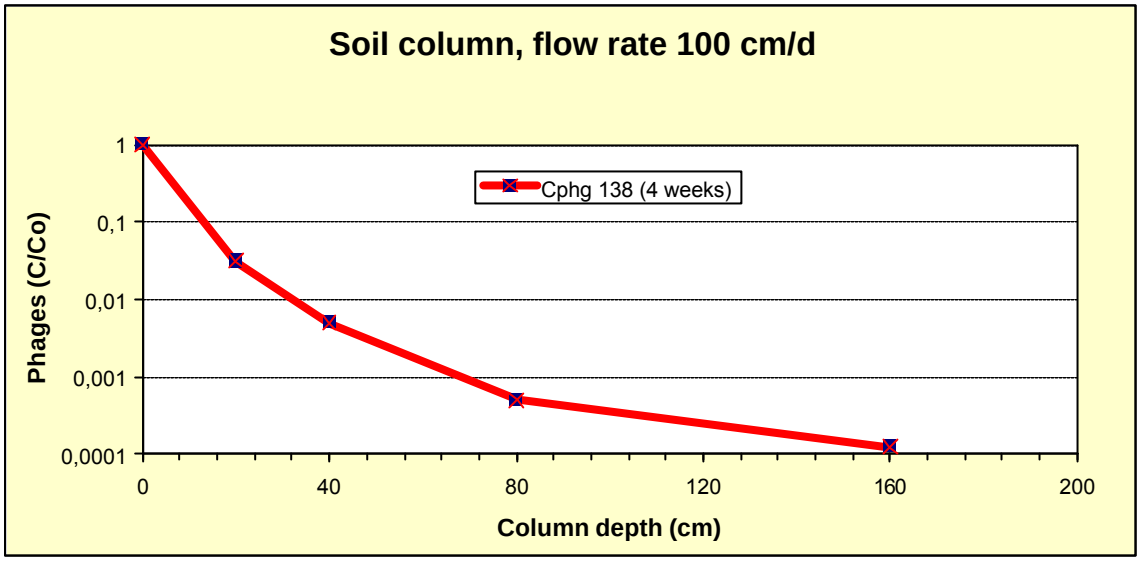


Fig. 4: Breakthrough of coliphage 138 in different levels of the sandy soil column at a flow rate of 100 cm/d. The numbers given are the concentrations C of phages detected at the respective level in correlation to the input concentration C_0.

At 20 cm, 40 cm, 80 cm, and 160 cm 3.2 %, 0.5 %, 0.05 % or 0.01 % of the input concentration of coliphage 138 were detected, respectively. This means that the relative breakthrough of coliphage 138 increased with increasing filtration path.

The concentration of coliphage 241 in the suspension was 5,8 x 10^7 pfu/ml corresponding to a total peak inoculum of 2.9 x 10^9 pfu (500 ml). First water samples were taken after one day. Coliphage 241 was detected at 20 cm and 40 cm at a concentration of 6,9 x 10^4 and 5.4 x 10^4 pfu/ml, respectively (Fig. 5). Breakthrough of coliphage 241 at 80 cm, 160 cm, and 340 cm was observed after 2, 5, and 8 days, respectively. The concentrations of coliphage 241 reached highest levels one or two days after breakthrough and declined subsequently one to two log units. Coliphage 241 was detected in all water samples up to 340 cm in slowly decreasing concentrations during further percolation for up to 35 d (Fig. 5). Very low concentrations of coliphage 241 were found in water samples from 500 cm during day 23-29. No positive samples were obtained at 660 cm.

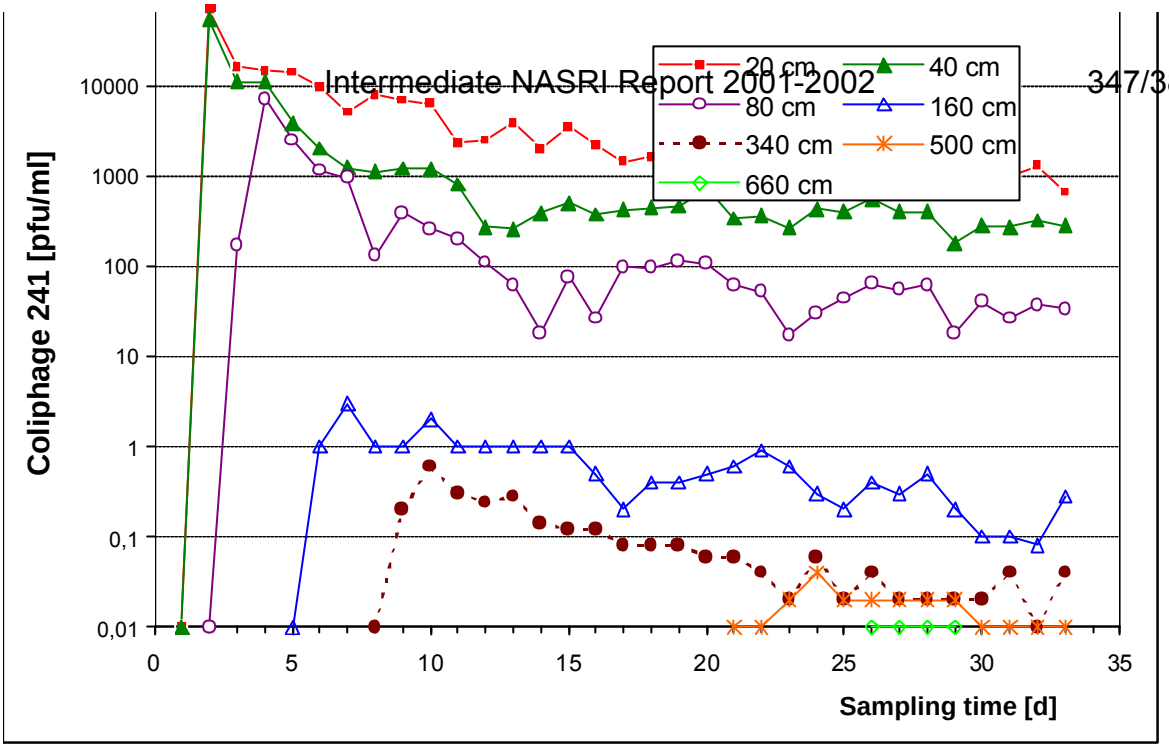


Fig. 5.: Concentration of Coliphage 241 in different levels of the sandy soil column at a flow rate of 100 cm/d; detection limit = 0.01 pfu/ml

The data were given to the "model group" for detailed analysis. For preliminary analysis, a best fit straight line was fitted manually to every curve to be able to estimate the breakthrough of coliphage 241 (Fig.6, Fig. 7).

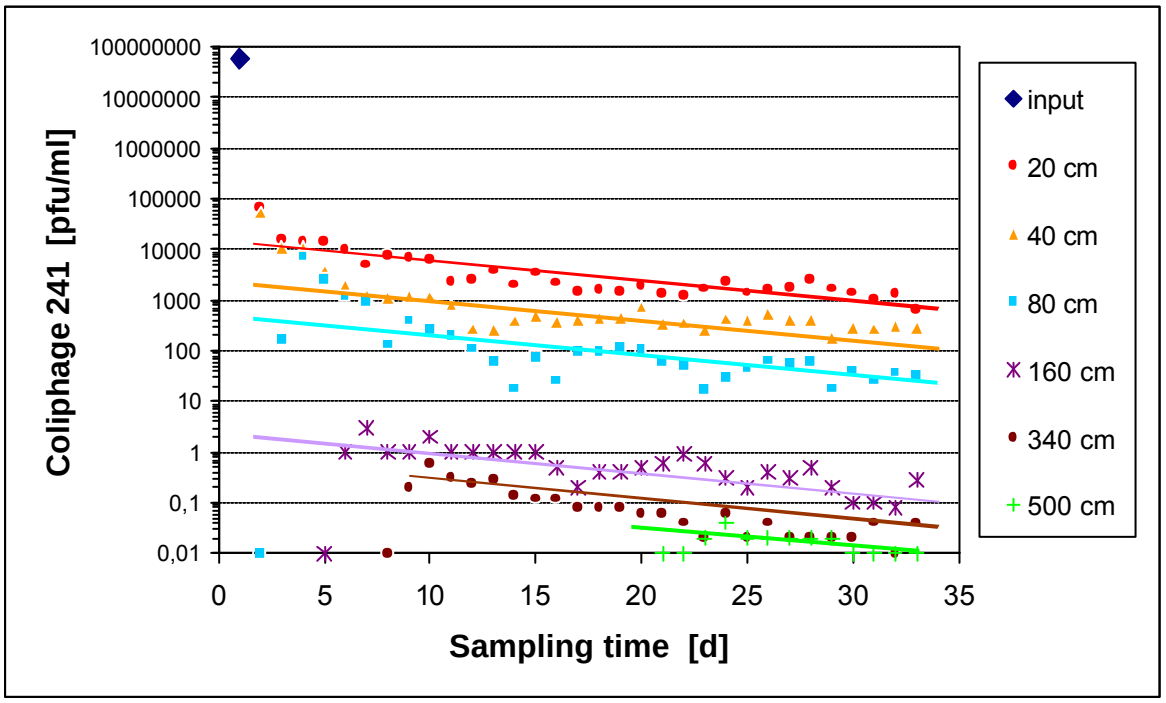


Fig. 6: Coliphage 241 – best fit straight lines

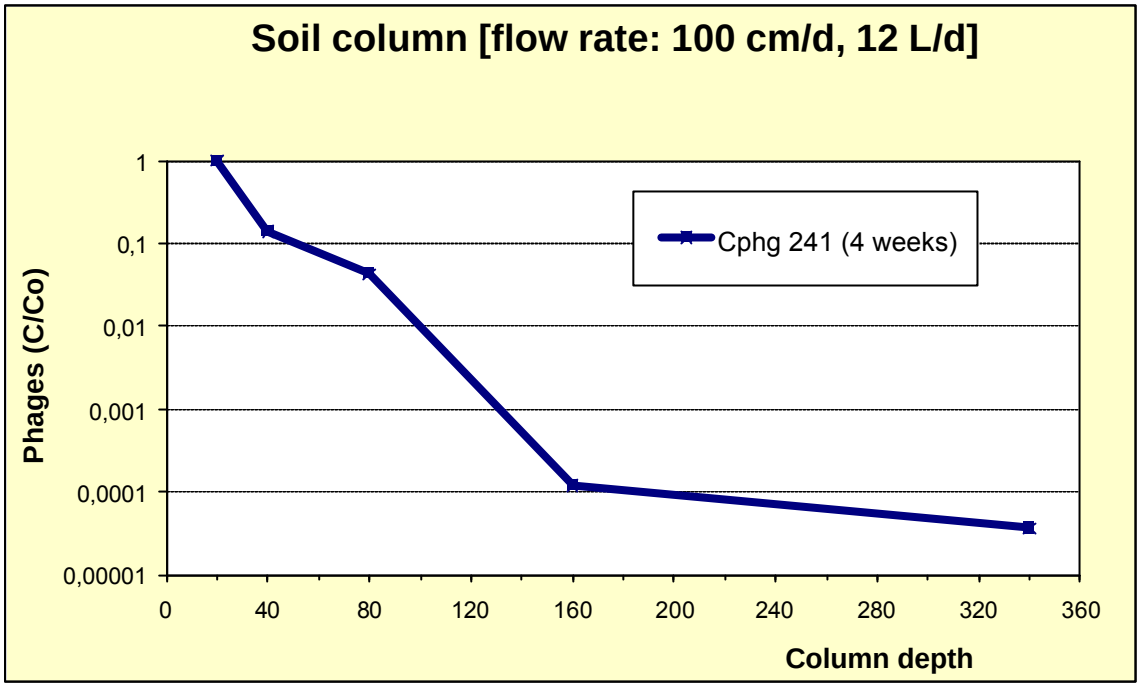


Fig. 7: Breakthrough of coliphage 421 in different levels of the sandy soil column at a flow rate of 100 cm/d. The numbers given are the concentrations C of phages detected at the respective level in correlation to the concentration C_0 at 20 cm.

As observed with coliphage 138, the relative breakthrough of coliphage 241 increased with increasing filtration path. At 40 cm, 80 cm, 160 cm, and 320 cm 14.1 %, 4.2 %, 0.01 %, or 0.003 % of the concentration at 20 cm were detected, respectively.

5.2.1.2 Effect of long term percolation on the migration of coliphage 241

Percolation of the sandy soil column with lake water was continued at a flow rate of 100 cm/d for 8 months. Sampling was carried out weekly from 7.4.03 up to 7.12.03 from all drain tubes of the first column (20 cm, 40 cm, 80 cm, 160 cm, 340 cm and 500 cm).

Coliphage 138 was only sporadically or no more detected in the water samples from different sampling sites of the column during this long term experiment.

Coliphage 241 was detected in all water samples during the 8 months of investigation. Concentrations of coliphage 241 were in the range of 10^4 to 10^3 pfu/ml in water samples from 20 and 40 cm within the first months, and declined about one log unit during the experiment (Fig. 8). Similar behaviour at a lower concentration levels was observed for the other sampling sites of 80, 160, and 340 cm of the column. At 500 cm coliphage 241 was only sporadically detected in low concentrations.

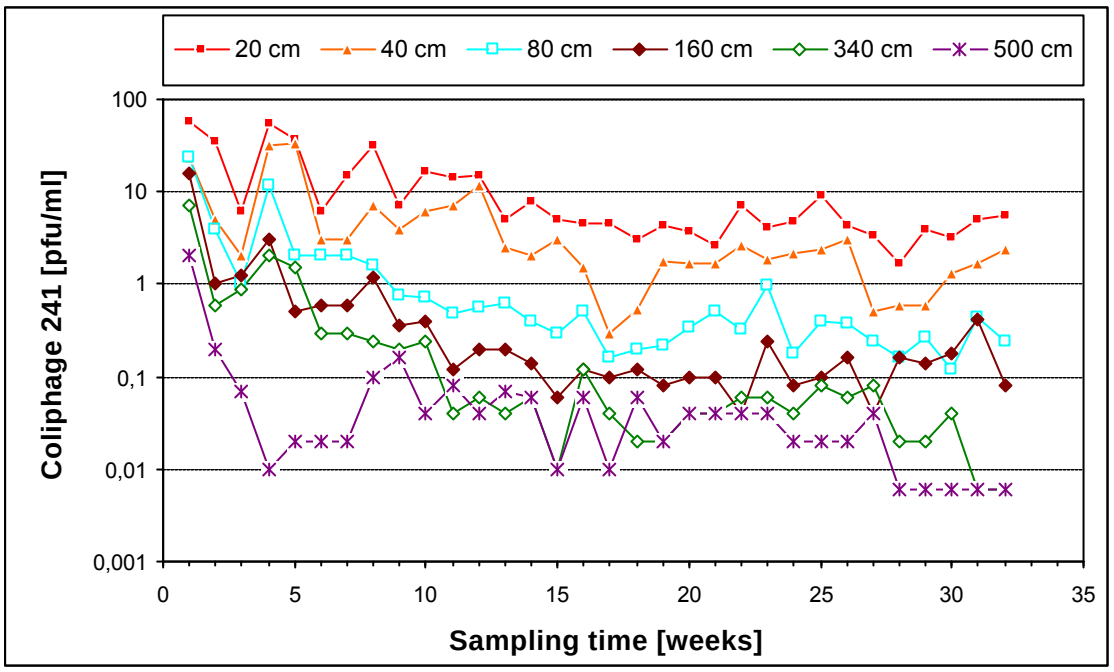


Fig. 8. Concentration of coliphage 241 in the sandy soil column during 8 month at a flow rate of 100 cm/d; detection limit: 0.01 pfu/ml

The data were given to the “model group” for detailed analysis. For preliminary analysis, a best fit straight line was fitted manually to every curve to be able to estimate the breakthrough of coliphage 241 (Fig.9, Fig. 10).

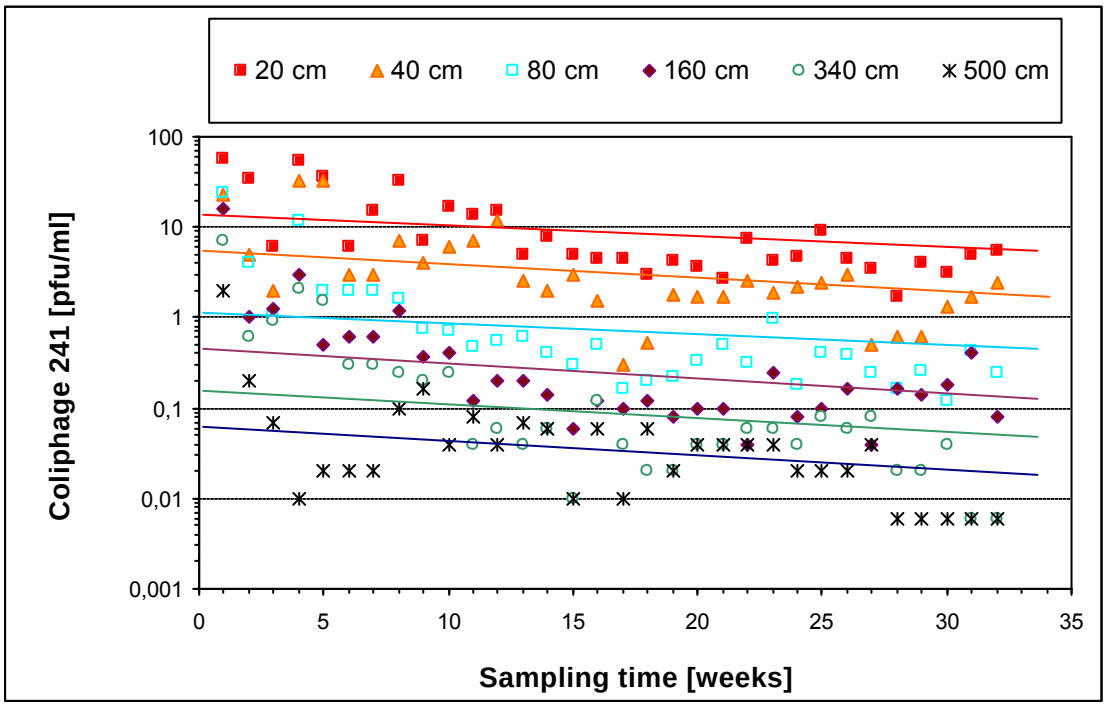


Fig. 9: Coliphage 241, 8 month – best fit straight lines

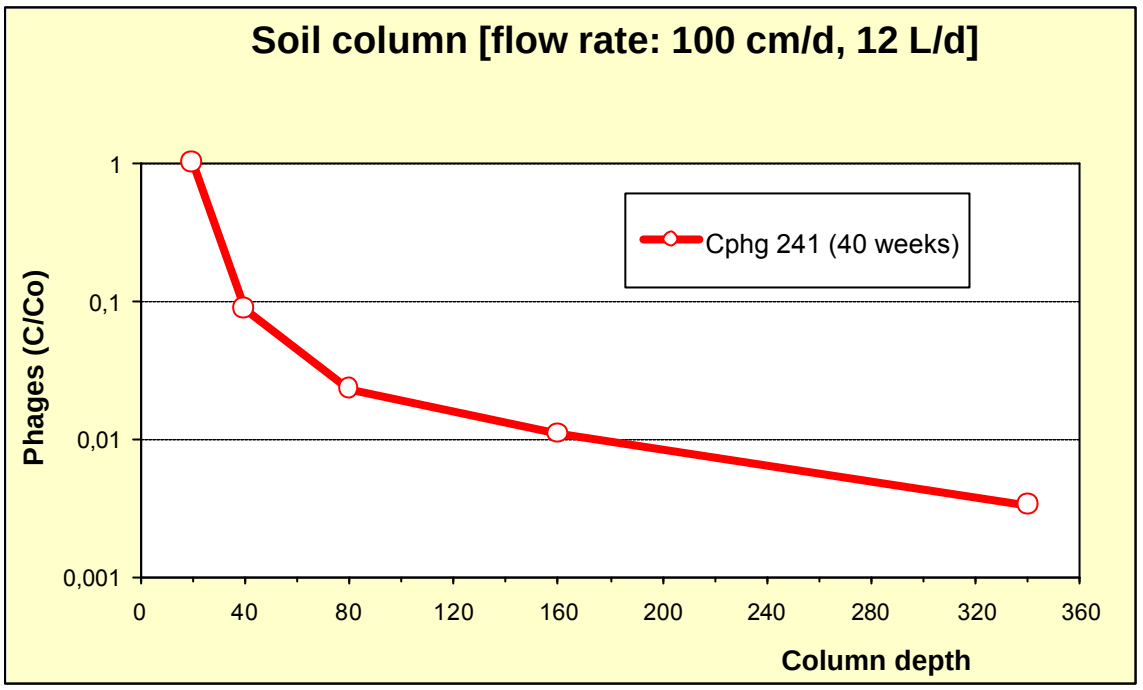


Fig. 10: Breakthrough of coliphage 421 in different levels of the sandy soil column at a flow rate of 100 cm/d. The numbers given are the concentrations C of phages detected at the respective level in correlation to the concentration C_0 at 20 cm.

In this experiment, the relative breakthrough again increased with increasing filtration path. This effect was especially pronounced after 160 cm and 340 cm. At 40 cm, 80 cm, 160 cm, and 320 cm 8.7 %, 2.3 %, 1.1 %, or 0.3 % of the concentration at 20 cm were detected, respectively.

5.2.2 Investigations in the enclosure

Enclosures filled with a defined type of sandy soil were applied for investigating adsorption and transport behaviour of both coliphages. The hydro dynamic conditions were adjusted to a constant flow rate of 50L/h corresponding to 120 cm/d. Sampling sites were located at the drain tubes from 20, 40, 60, and 80 cm depth as well as at the outlet at 100 cm depth.

Experiments with chemicals and coliphages were performed simultaneously. Reference compounds of all working groups were mixed in a stock solution of 10 L volume and added into the surface water reservoir of the enclosure containing 500 L of ground water pumped out from the aquifer in Marienfelde. Suspensions of coliphages 138 and 241 were inoculated directly into the water reservoir.

Sampling from the drain tubes was carried out in sterile flasks separately from the other groups in intervals ranging from 30 to 60 min within 12 h. An auto sampler was used for sampling the outlet over night. Furthermore, samples from the four drain tubes were collected daily during the first 1-2 weeks of operation.

Experiments were performed with clean, non contaminated soil of the enclosure as well as after the formation of a relatively thick clogging layer. No consistent differences in the behaviour of coliphages was detected and the experiments are, therefore, analysed together.

5.2.2.1 Experiment I (05.08.03, without clogging layer)

Coliphage 138 and coliphage 241 were added simultaneously to the water reservoir above the filter .

The concentration of coliphage 138 in the reservoir after inoculation ranged from 2×10^5 to 8×10^5 pfu/ml during the first 5 h of the experiment. Concentration decreased to 4.7×10^4 pfu/ml after a percolation time of 12 h (Fig 11).

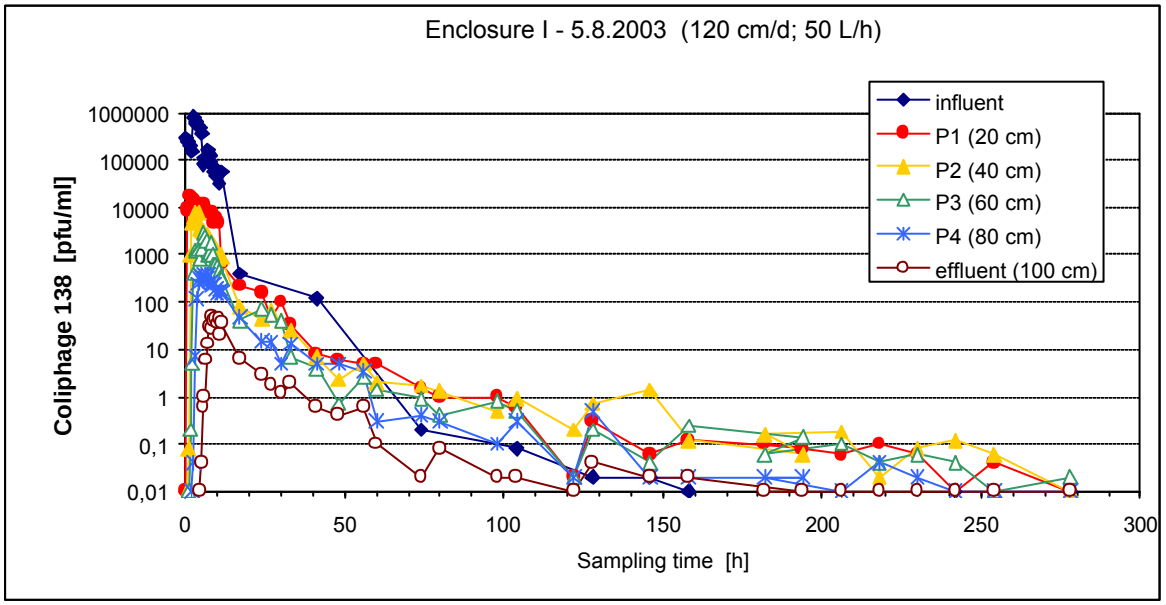


Fig. 11: Concentration of coliphage 138 in the different sampling levels of the enclosure

The data were handed over to the “model group” for detailed analysis. For preliminary analysis, retention and breakthrough ratios were estimated using from cumulative breakthrough curves (Fig. 12).

Breakthrough of coliphage 138 was observed synchronic with the tracer salt NaCl at all sampling sites. Despite the rapid breakthrough of some phages, retention of phages in the column was high. After 20 cm or 100 cm 96,5 % or 99,9 % of the inoculated phages were retained, respectively. (Fig. 12, Table 3).

After an operation time of 278 h, the relative breakthrough of coliphage 138 at each sampling site remained at the same level as observed after 12 h (Fig. 12, Table 3).

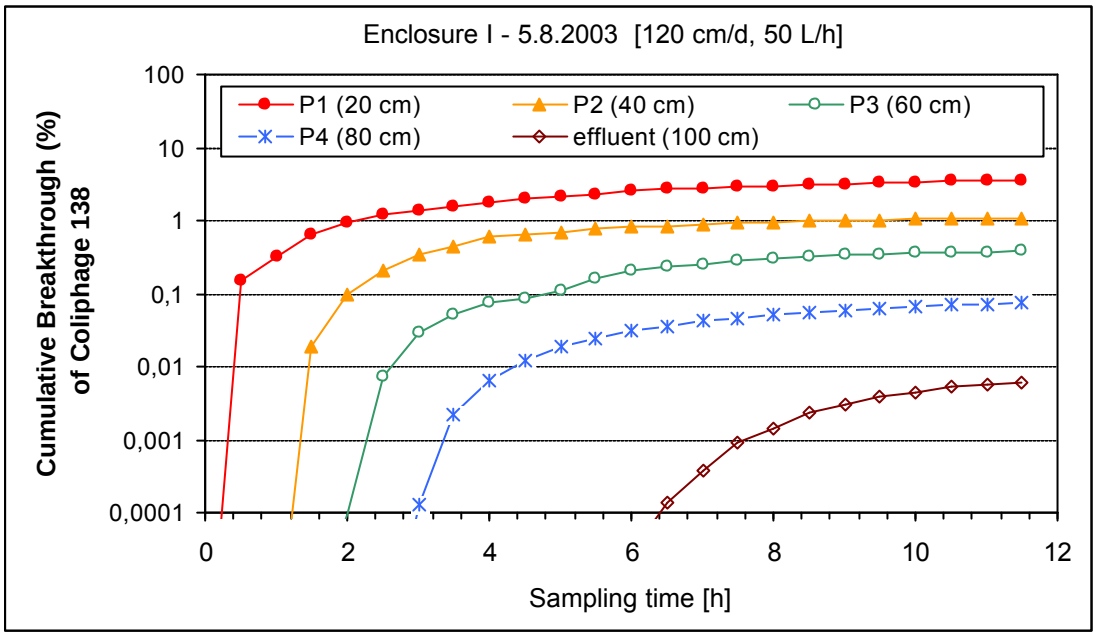


Fig. 12, Table 3: Cumulative breakthrough of coliphage 138 at different sampling sites of the enclosure at a filtration rate of 120 cm/d

	CPHG138	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	effluent (100 cm)
within 12 h	Breakthrough (%)	3,47	1,09	0,38	0,07	0,01
	Retention (%)	96,5	98,9	99,6	99,9	99,99
within 278 h	Breakthrough (%)	3,55	1,11	0,41	0,09	0,01
	Retention (%)	96,45	98,84	99,57	99,89	99,99

Concentration of coliphage 241 was much lower in the reservoir after inoculation compared to coliphage 138. Only 2000 pfu/ml were detected and concentration decreased to 40 pfu/ml during a percolation time of 24h (Fig. 13).

The data were handed over to the “model group” for detailed analysis. For preliminary analysis, retention and breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 14).

Detection of coliphage 241 in filtrate samples was synchronic with the tracer NaCl at all sampling sites. Despite the low initial concentration of phages in the influent, a relatively high amount of coliphage 241 break through the filter. After a percolation time of 12 h, 8 % of inoculated viruses were detected in filtrate samples from the 20 cm drain tube. At 80 cm and 100 cm 0,14 % or 0,01 % of the influent concentration were, respectively (Fig. 14, Table 4).

Coliphage 241 was detected in all filtrate samples during continued operation of the filter for up to 278 h, but at relatively low concentrations (Fig. 13). The breakthrough ratios of coliphage 241 were calculated as 12,3 % for 20 cm, 3,3 % for 40 cm, 0,4 % for 80 cm and 0,07 % for 100 cm (Table 4).

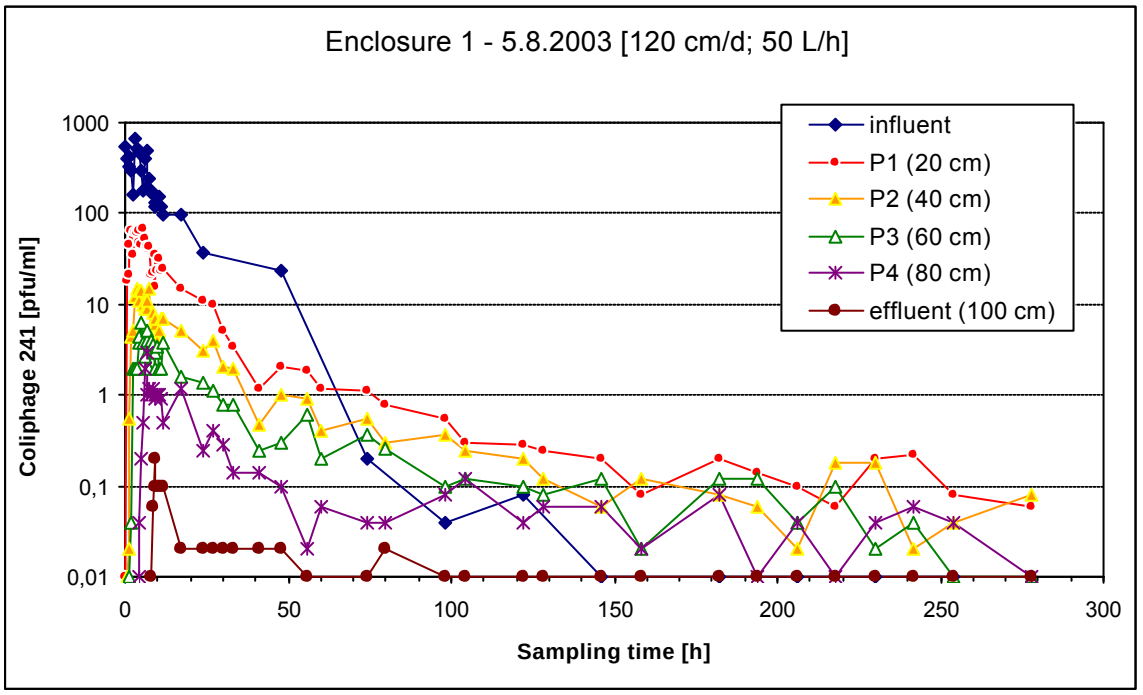


Fig. 13: Concentration of coliphage 241 at different levels of the enclosure at a filtration rate of 120 cm/d without clogging layer.

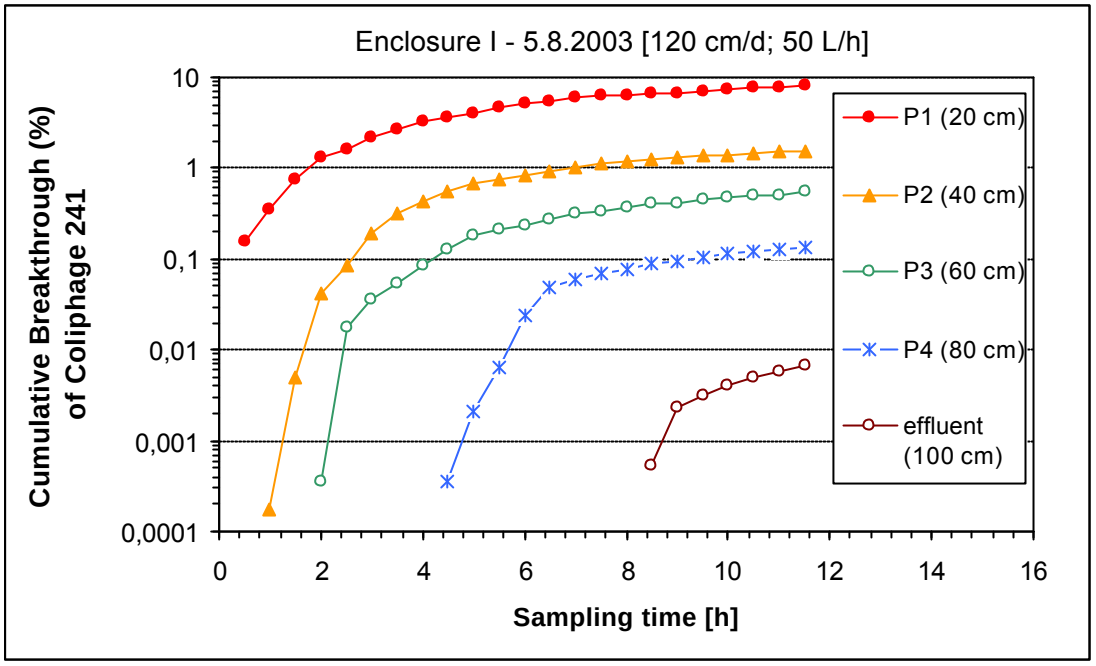


Fig. 14, Table 4: Cumulative breakthrough of coliphage 241 at different sampling levels of the enclosure at a filtration rate of 120 cm/d without clogging layer.

	CPHG241	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	effluent (100 cm)
within 12 h	Breakthrough (%)	8,0	1,6	0,5	0,14	0,007
	Retention (%)	92,0	98,4	99,5	98,9	99,99
within 278 h	Breakthrough (%)	12,3	3,3	1,3	0,4	0,1
	Retention (%)	87,7	96,7	98,7	99,6	99,9

5.2.2.2 Experiment II (10.09.03, with clogging layer)

The experiment was started after the formation of a clogging layer on the surface of the filter. All reference chemicals and coliphage 138 were inoculated into the water reservoir of the enclosure which was operated at a flow rate of 50 L/d corresponding to 120 cm/d. The initial concentration of coliphage 138 was 6.2×10^4 pfu/ml (Fig. 18). Concentration decreased by about 4 log units during the 140 h of operation. Similar curves were obtained at the different filtration levels at lower concentrations (Fig. 15).

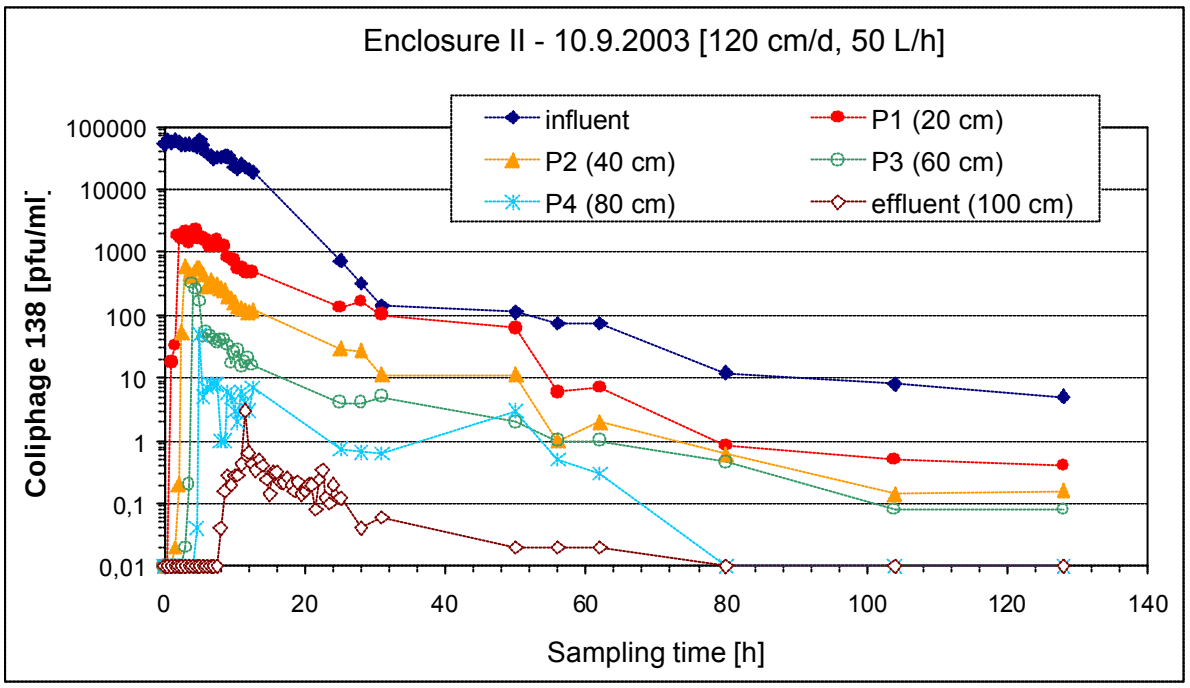


Fig. 15. Concentration of coliphage 138 at different levels of the enclosure at a filtration rate of 120 cm/d with clogging layer.

The data were handed over to the "model group" for detailed analysis. For preliminary analysis, retention and breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 16).

Again, coliphage 138 occurred synchronic with the tracer NaCl in all filtrate samples. The retention of coliphage 138 was slightly better than in the previous experiment without clogging layer. After an operation time of 12 h, the retention of coliphage138 amounted 97 % or 99 % at a filtration path of 20 or 40 cm, respectively., The elimination rates of coliphages attained 3 or 4 log units at the sampling sites of 80 cm and 100 cm depths (Fig, 16, Table 5). Similar relative retentions were obtained at the end of operation after 140 h (Table 5).

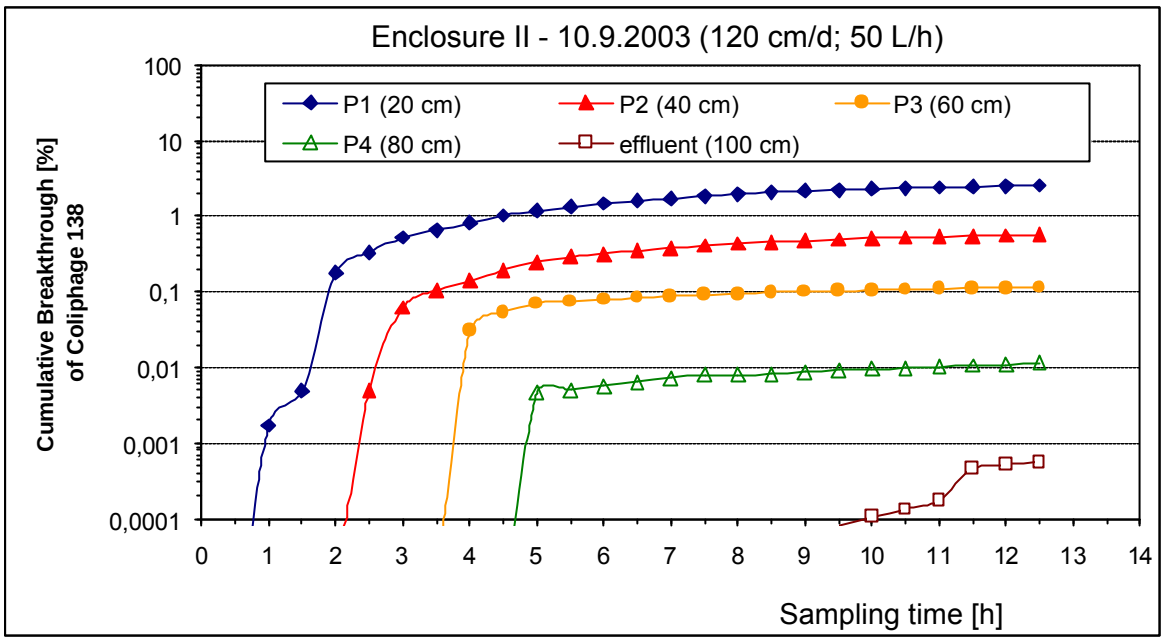


Fig. 16, Table 5: Cumulative breakthrough of coliphage 138 at different sampling sites of the enclosure at a filtration rate of 120 cm/d with schmutzdecke

	CPHG138	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	effluent (100 cm)
within 12 h	Breakthrough (%)	2,6	0,6	0,1	0,01	0,001
	Retention (%)	97,4	99,4	99,9	99,99	99,999
within 140 h	Breakthrough (%)	3,3	0,7	0,1	0,02	0,001
	Retention (%)	96,7	99,3	99,9	99,98	99,999

5.2.2.3 Experiment III (17.09.03, with clogging layer)

Coliphage 241 was inoculated into the water reservoir of the enclosure in a second experiment with clogging layer. The enclosure was operated at a flow rate of 50 L/d corresponding to 120 cm/d.

Indicator bacteria (*E. coli* and enterococci) were added to the enclosure at the same time as coliphage 241 (see chapter 5.4).

The initial concentration of coliphage 241 was 2.1×10^3 pfu/ml (Fig. 17). Concentration decreased about 3 log units during the first 100 h of operation. Similar curves were obtained

at the different filtration levels at lower concentrations. Coliphage 241 was detected in low numbers from all drain samples up to an operation time of 800 h (Fig. 17).

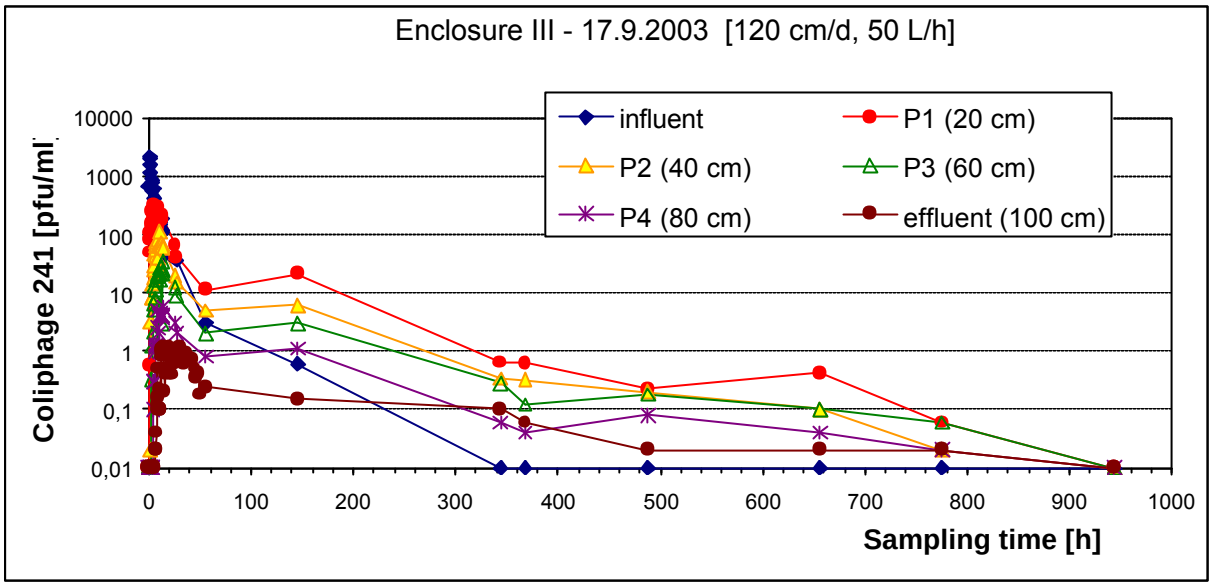


Fig. 17 Concentration of coliphage 241 at different levels of the enclosure at a filtration rate of 120 cm/d with clogging layer.

The data were handed over to the "model group" for detailed analysis. For preliminary analysis, retention and breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 18, Table 6).

Also in this experiment, coliphages occurred synchronic with the tracer NaCl in all filtrate samples (Fig. 18).

The retention of coliphages 241 at all sampling sites was lower than in experiment I with clogging layer. About 30 % or 8 % of inoculated phages were retrieved in water samples from 20 cm or 40 cm depth, respectively (Table 6). During a filtration time for 12 h, water samples from the outlet of the enclosure (100 cm) contained 0,04 % of the coliphges inoculated. After 51 h of operation, breakthrough of coliphage 241 rose to 57 % within 20 cm, 23 % within 40 cm, and 0,4 % in total effluent of the enclosure at a depth of 100 cm.

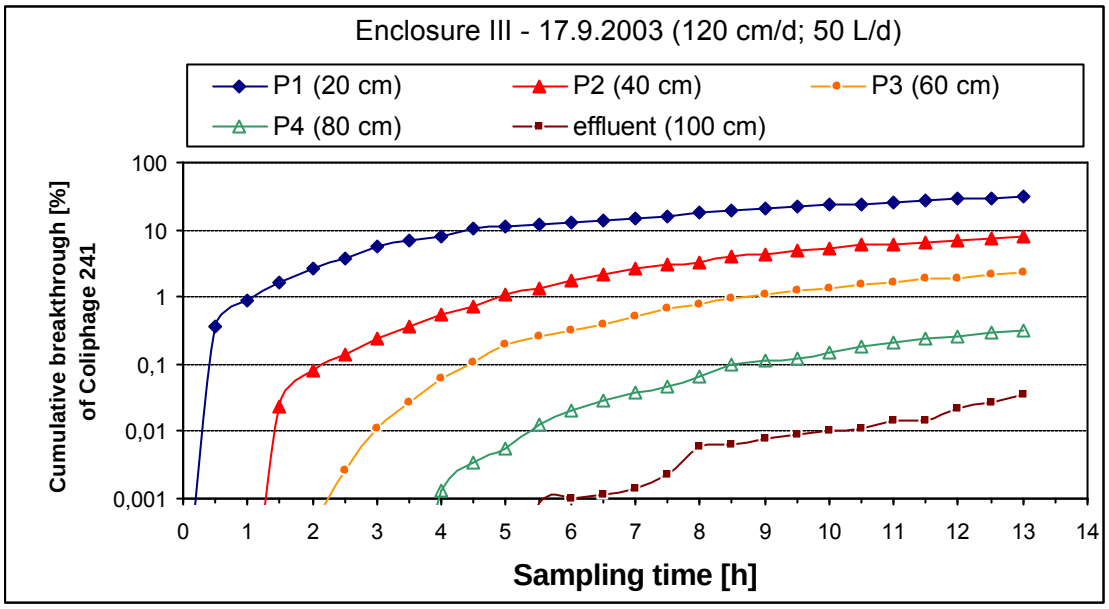


Fig. 18, Table 6: Cumulative breakthrough of coliphage 241 at different sampling levels of the enclosure at a filtration rate of 120 cm/d with clogging layer.

	CPHG241	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	effluent (100 cm)
within 12 h	Breakthrough (%)	29,9	7,7	2,3	0,3	0,04
	Retention (%)	70,1	92,3	97,7	99,7	99,96
within 51 h	Breakthrough (%)	57,2	22,9	7,3	1,8	0,4
	Retention (%)	42,8	77,1	92,7	98,2	99,6

5.2.3 Investigations in the filtration ponds

The sand filtration pond of Marienfelde consists of a sandy soil bed with a surface area of 6m x 6m and a vertical filtration path of 80 cm. Hydro dynamical conditions were regulated to obtain a comparable flow rate as for the enclosure experiments (3000 L/d corresponding to 120 cm/d).

The first experiment in the filtration pond was carried out without any clogging layer on the surface of filter. After the formation of a schmutzdecke, the filtration experiment was repeated with the same flow rate. No consistent difference was detected between these experiments and the data are, therefore, analysed together.

All reference compounds including a stock suspension of coliphages 138 and 241 were suspended in 50 L pond water containing 25 % NaCl as tracer. This suspension was mixed within 10 min into the surface water column of the filtration pond containing 40000 l ground water. Samples from influent and effluent of the pond were taken at regular intervals.

5.2.3.1. Experiment I (120 cm/d without clogging layer)

Immediately after inoculation of the filtration pond, the density of coliphage 138 reached 5.10^5 pfu/ml in the surface water and then gradually decreased to 5.10^4 pfu/ml after 6 h (Fig. 19). After 48 h of operation 100 pfu/ml were detected. The concentration of coliphage 138 in the effluent reached 200-300 pfu/ml after 5-24 h and subsequently declined to 1 pfu/ml during further operation up to 90 h.

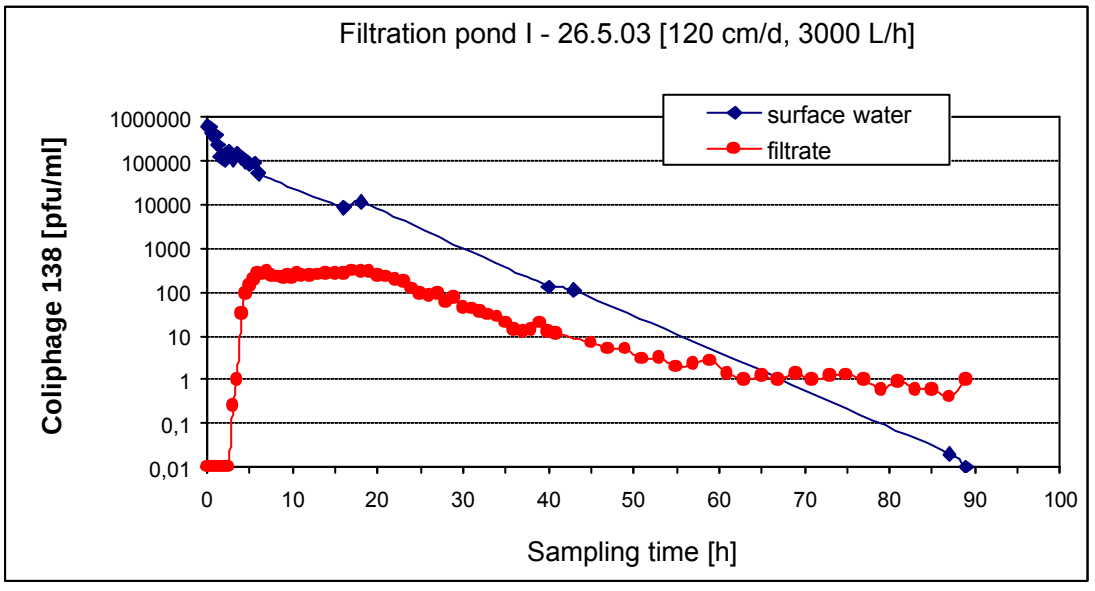


Fig. 19: Concentration of coliphage 138 in influent and effluent of the filtration pond at a flow rate of 120 cm/d without clogging layer.

The detection of coliphage 138 in the filtrate samples was synchronic with the increase in electro conductivity (Fig. 20).

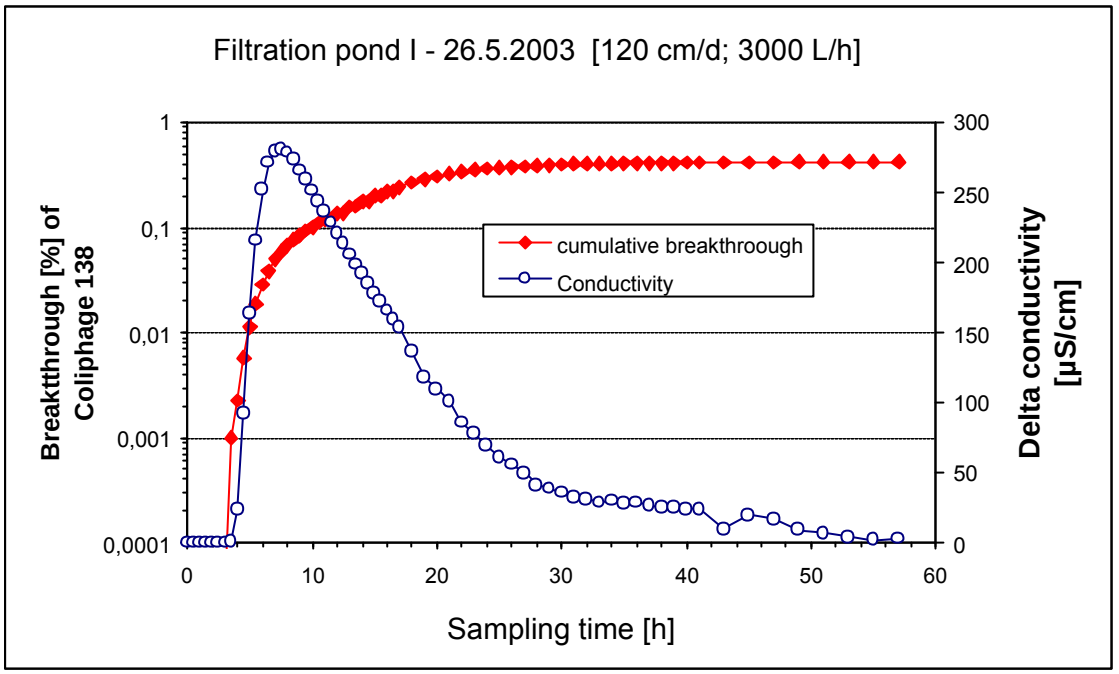


Fig. 20: Cumulative breakthrough of coliphage 138 and tracer min slow sand filtration pond at a filtration rate of 120 cm/d (3000 L/h) without clogging layer.

The data were handed over to the "model group" for detailed analysis. For preliminary analysis, breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 20, Table 7).

The breakthrough ratio of coliphage 138 was calculated as 0.14 % and 0.4 % after a filtration time of 12 h or 150 h, respectively (Table 7).

After inoculation of the filtration pond, the concentration of coliphage 241 was much lower than that of coliphage 138. It averaged 10^3 pfu/ml in the surface water and decreased to 170 pfu/ml during a filtration period of 6 h (Fig. 21). Concentrations of coliphage 241 in the effluent were very low (<3 pfu/ml) but positive results were obtained from all filtrate samples during a filtration time of 151 h.

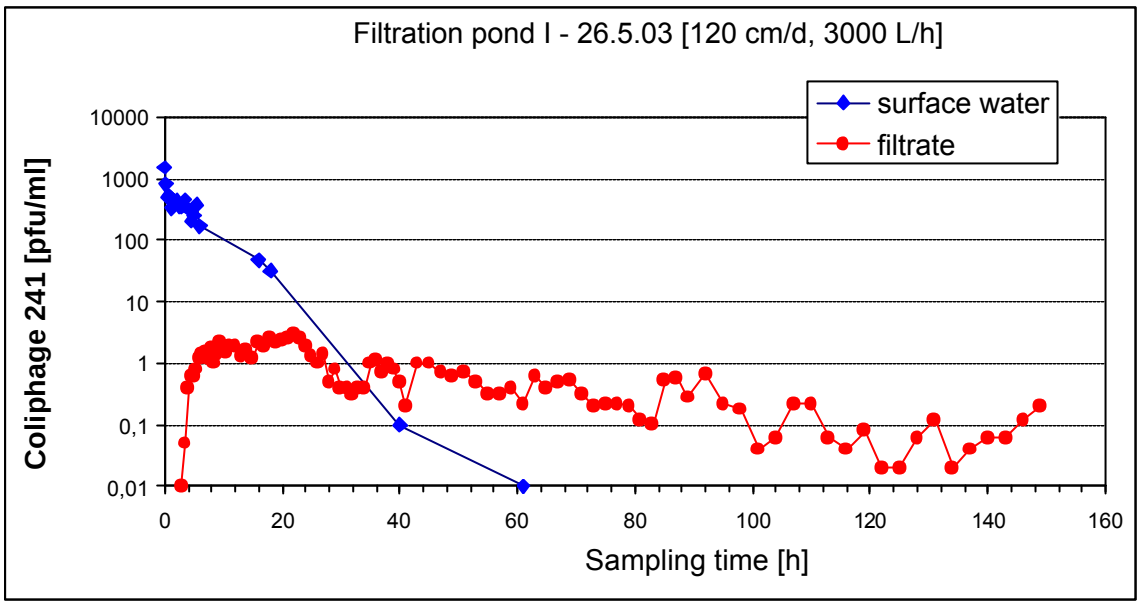


Fig. 21: Concentration of coliphage 241 in influent and effluent of the filtration pond at a flow rate of 120 cm/d without clogging layer.

The detection of coliphage 241 in the filtrate samples was also synchronic with the increase in electro conductivity (Fig. 22).

The data were handed over to the “model group” for detailed analysis. For preliminary analysis, breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 22, Table 7).

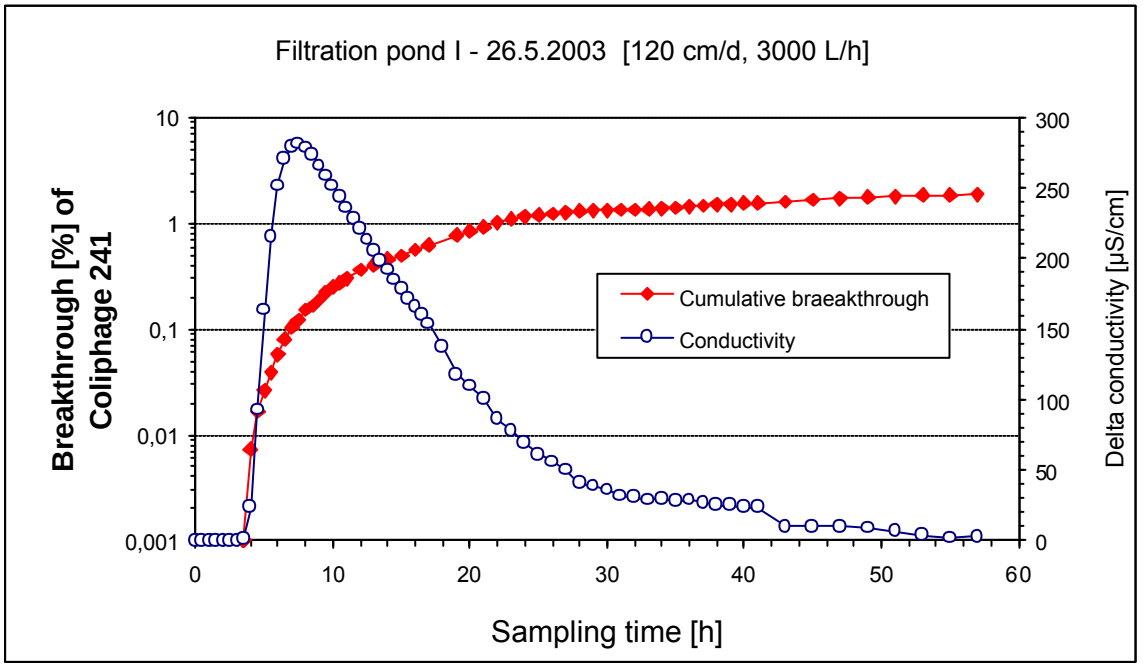


Fig. 22: Cumulative breakthrough of coliphage 241 and tracer in slow sand filtration pond at a filtration rate of 120 cm/d (3000 L/h) without clogging layer.

Retention of coliphage 241 in the filter was not as good as for coliphage 138. Breakthrough rates reached 0.4 % or 2.2 % after a percolation time of 12 h or 150 h, respectively (Table 7).

Table 7: Breakthrough ratio (%) of coliphage 138 and 241 in slow sand filtration pond at a filtration rate of 120 cm/d before and after formation of a clogging layer

Filtration time (h)	**Coliphage 138**		**Coliphage 241**	
	without Schmutzdecke	with Schmutzdecke	without Schmutzdecke	with Schmutzdecke
12	0,14	0,13	0,04	1,23
24	0,36	0,15	0,18	1,68
60	0,42	0,16	0,19	2,37
90	0,43	0,16	0,22	2,37
150	**0,43**	**0,16**	**0,24**	**2,37**

5.2.3.2. Experiment II (120 cm/d with clogging layer)

Spiking of coliphages was repeated after a clogging layer had formed on the filter. The clogging layer was not uniform but patchy with different thickness and structure. Filtration rate was set to 120 cm/d as in the previous experiment.

Coliphage 138 reached a concentration of about 10^5 pfu/ml in the pond water after inoculation which rapidly declined to 1000 pfu/ml within 12 h (Fig. 23). In the effluent concentrations of 100 pfu/ml were detected after 4 h of operation. Concentration declined gradually to 0.1 pfu/ml after 100 h.

The initial concentration of coliphage 241 in pond water was low (about 100 pfu/ml) and rapidly decreased to below detection limit i.e. less than 1 pfu/100 ml. Only very low concentrations with a maximum of about 0.1 pfu/ml were detected in the filtrate (Fig. 23).

Coliphages 138 and 241 were already observed in the frontal fractions of filtrates (Fig. 24).

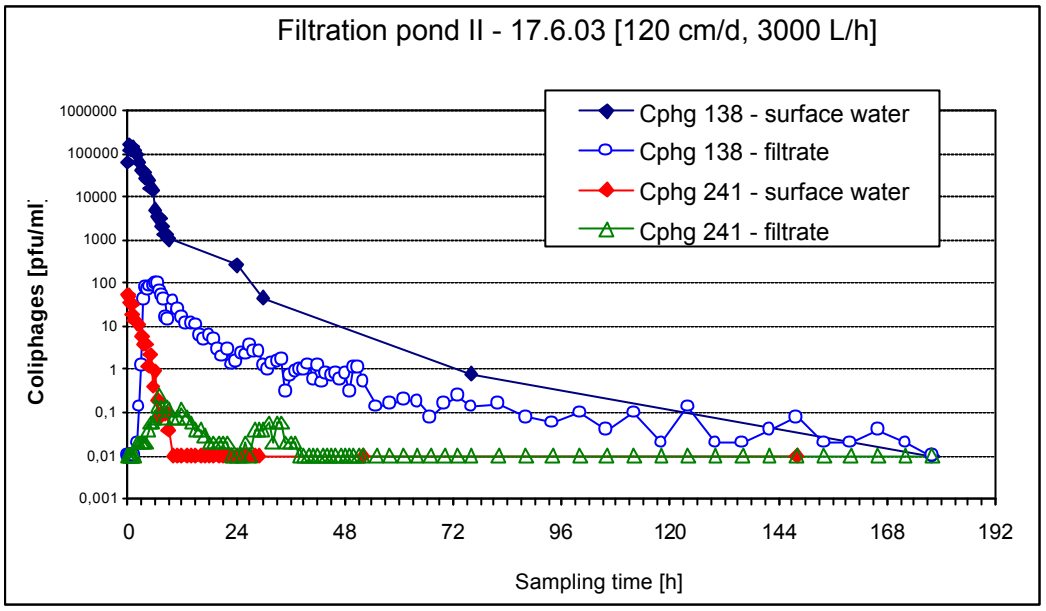


Fig. 23: Concentration of coliphages 138 and 241 in influent and effluent of the filtration pond at a flow rate of 120 cm/d with clogging layer.

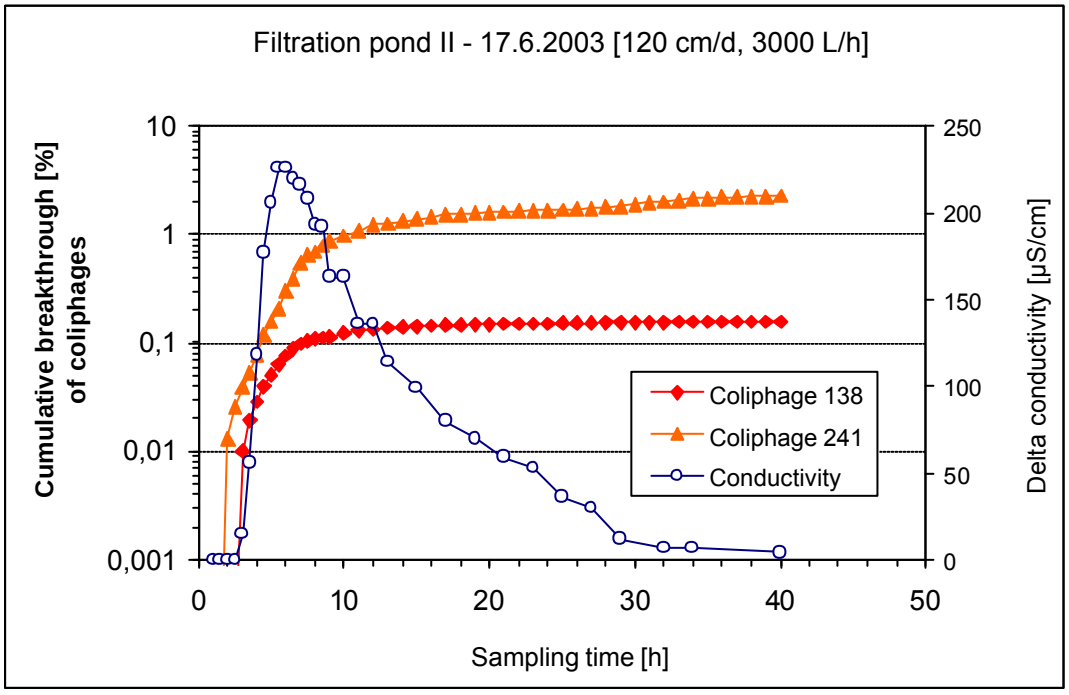


Fig. 24: Cumulative breakthrough of coliphage 138, 241 and tracer in slow sand filtration pond at a filtration rate of 120 cm/d (3000 L/h) with clogging layer.

The data were handed over to the “model group” for detailed analysis. For preliminary analysis, breakthrough ratios were estimated using cumulative breakthrough curves (Fig. 24, Table 7).

Breakthrough ratios of coliphage 138 were calculated as 0.13 % within 12 h and 0.16 % for 60 h which did not change up to the end of the experiment after 150 h (Table 7). These ratios were comparable to the ratios obtained without clogging layer.

Breakthrough ratios of coliphage 241 were higher in this experiment than in the previous experiment without clogging layer. Breakthrough ratios were calculated as 1.2 % after 12 h and as 2.4 % at the end of the experiment after 150 h.

5.3 Effect of flow rate on migration of coliphages in the sandy soil column

After 35 d of percolation (see 5.2.1), the flow rate of lake water through the column was increased from 0.5 L/h (1 m/d) to 4 L/h (8 m/d) for the next three weeks without any additionally inoculation of the column with coliphages. Subsequently, the flow rate was further increased to 12 L/h (24 m/d) for a further 3 weeks.

The concentrations of coliphage 138 were very low after the first 35 h of operation. Nevertheless, an increase in concentration was detected at all sampling points after increase in flow rate (Fig 25). After two weeks, the densities of coliphages 138 further decreased to values close to the detection limit. Therefore, the possible effects of a further increase in flow rate could not be detected.

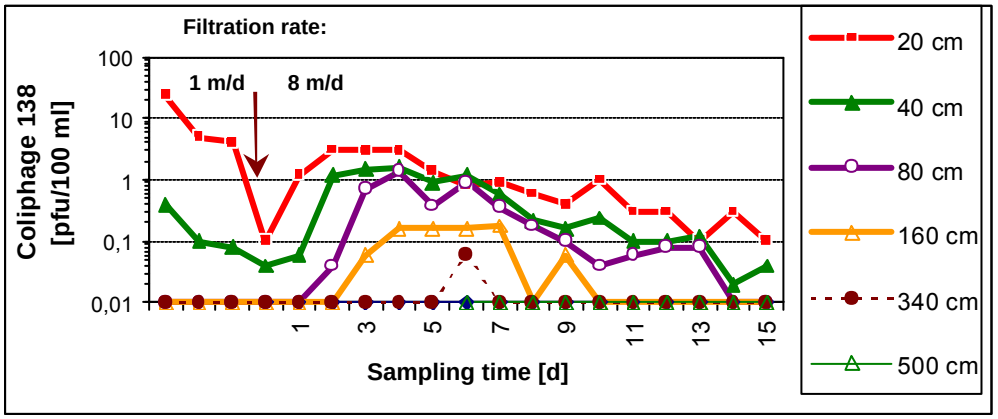


Fig. 25: Concentration of Coliphage 138 in the sandy soil column after an increase in flow rate to 8m/d

The densities of coliphages 241 within the column high of 20 cm did not change by increasing the flow rate to 8 m/d (Fig. 26). But migration of coliphages was significantly induced at all other levels of the column. At the sampling sites of 40 cm and 80 cm, coliphage 241 concentrations attained the highest level following a percolation of 2 and 3 days. At all other sampling sites, the densities of coliphages continuously increased up to 7 days and remained at this level until the end of experience.

A further increase in flow rate to 24 m/d did not alter the concentrations of coliphages 241 in the water samples from the drain tubes of 20, 40 and 80 cm high, but clearly induced coliphage mobilisation at a column high of 340 and 500 cm (Fig. 26).

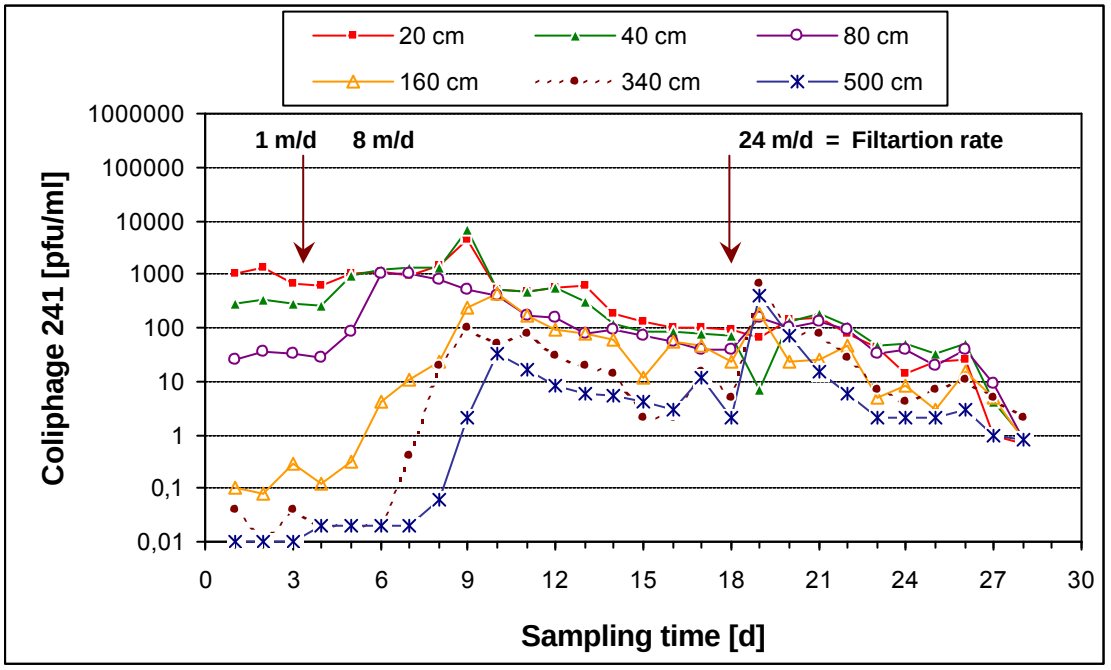


Fig. 26: Concentration of coliphage 241 in the sandy soil column after increase in flow rate to 8m/d and 24 m/d.

5.4 Investigations in the enclosure with bacteria.

After a naturally grown clogging layer had formed on the surface of the sediment, microcystin, coliphage 241, and indicator bacteria were inoculated into the surface water column of the enclosure which was percolated at a flow rate of 50 L/d corresponding to 120 cm/d as described in 5.2.2 (Enclosure III).

The bacteria *E. coli* and *Enterococcus faecalis* were added to the enclosure at the same time as coliphage 241. The addition of bacteria was possible for this experiment since the investigations with the trace chemicals had already been completed. Simultaneous addition of trace chemicals and bacteria was previously not allowed due to expected interactions.

Coliphages and bacteria occurred synchronic with the tracer NaCl in all filtrate samples. Due to the lower detection limit, single bacteria were detected even before an increase in the concentration of the tracer was detectable.

The results concerning the retention of coliphage 241 is described in chapter 5.2.2.3.

Initial concentration of *E. coli* in the influent was 10^8 cfu/100 ml. Concentration decreased about one log unit during the first 14 h of the experiment (Fig. 27). Concentration in the effluent stabilized at about 1000 cfu/ 100 ml.

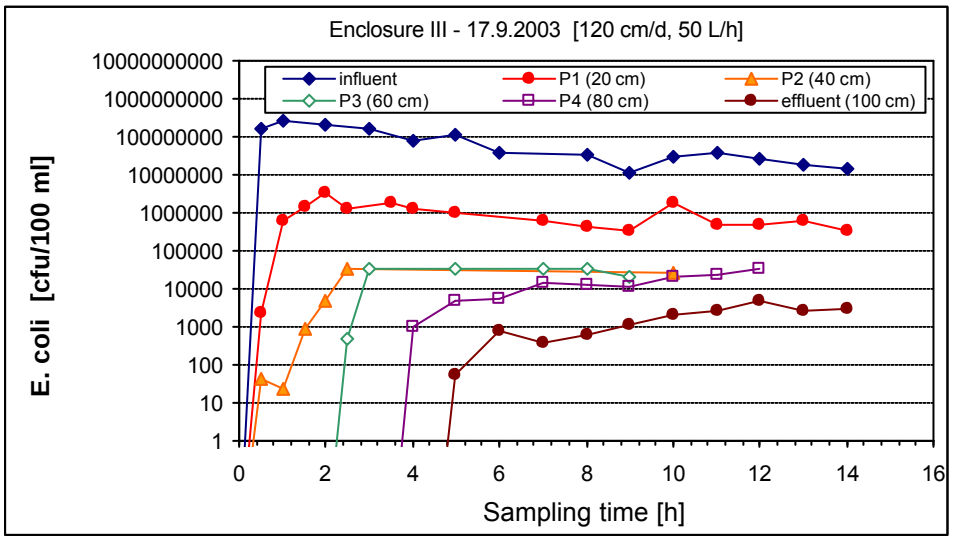


Fig. 27. Concentration of *E. coli* at different sampling sites in the enclosure at a filtration rate of 120 cm/d with clogging layer (detection limit 10-15 cfu/100 ml)

Retention of *E. coli* in the enclosure was higher than that of the coliphages. About 99 % of the inoculated *E. coli* were eliminated after 20 cm of filtration after 14 h of operation. The retention rate reached 99,99 % after 80 cm (Fig. 28, Table 8).

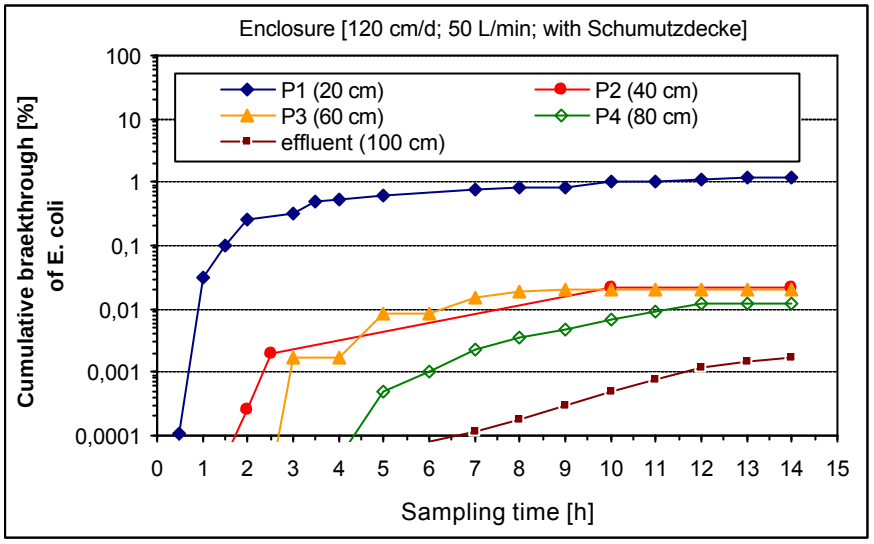


Fig. 28, Table 8: Cumulative breakthrough of *E. coli* at different sampling sites of the enclosure at a filtration rate of 120 cm/d with clogging layer

	E. coli	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	Effluent (100 cm)
within 14 h	Breakthrough (%)	1,18	0,022	0,02	0,012	0,001
	Retention (%)	98,74	99,978	99,98	99,99	99,999

The concentration of enterococci in the influent was about 10^6 cfu/100 ml after inoculation (Fig. 29). Survival potential of these enterococci was much lower than that of the *E. coli* strain. Their concentration in the influent rapidly decreased during the experiment and after 3 h only 1000 cfu/100 ml were detected. As for *E. coli*, the retention of enterococci was higher than that for coliphage 241. No enterococci were detectable in the effluent. The retention rates were 99 % at 20 cm, 99,9 % at 60 cm and more than five log units at 100 cm filtration depth (Fig. 30, Table 9).

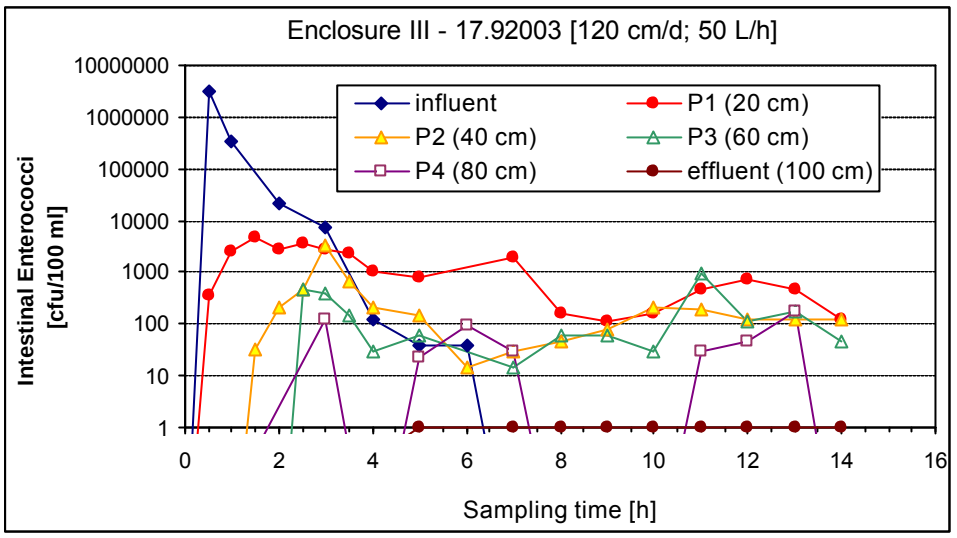


Fig. 29: Concentration of *Enterococcus faecalis* at different sampling sites in the enclosure at a filtration rate of 120 cm/d with schmutzdecke (detection limit 10 cfu/100 ml)

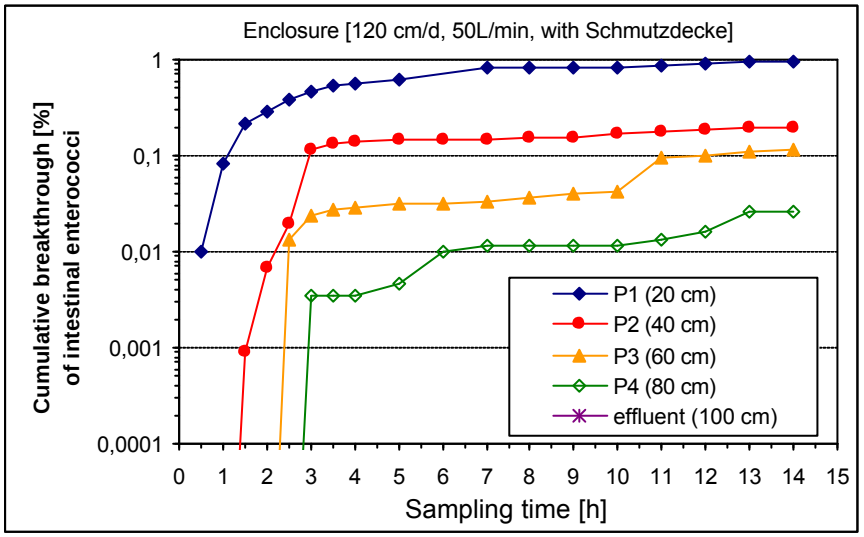


Fig. 30, Table 9: Cumulative breakthrough of *Enterococcus faecalis* at different sampling sites of the enclosure at a filtration rate of 120 cm/d with clogging layer.

	Intestinal enterococci	P1 (20 cm)	P2 (40 cm)	P3 (60 cm)	P4 (80 cm)	effluent (100 cm)
within 14 h	Breakthrough (%)	0,94	0,2	0,11	0,03	<0,001
	Retention (%)	99,06	99,8	99,89	99,97	>99,999

The experiment was continued for another four weeks with a constant flow rate of 120 cm/d. The flow was, however, interrupted several times due to technical problems.

During further percolation the concentration of *E. coli* in the influent further decreased to 800 cfu/ 100 ml after 50 h (Fig. 31). *E. coli* was detected at all sampling depths for up to 500 h in concentrations of 20 to 300 cfu/ 100 ml (sample at 20 cm not analysed). The concentration in the effluent decreased to about 1000 cfu/ 100 ml and 100 cfu/ 100 ml after 30 h or 60 h, respectively. After 500 h, the concentration in the effluent was in the range of 10-20 cfu/ 100 ml (detection limit 1 cfu/ 100 ml).

Enterococci were only detected sporadically in the influent and at all sampling sites of the enclosure during the prolonged percolation. Concentrations ranged from 1-30 cfu/ 100 ml (detection limit 1-10 cfu/ 100 ml).

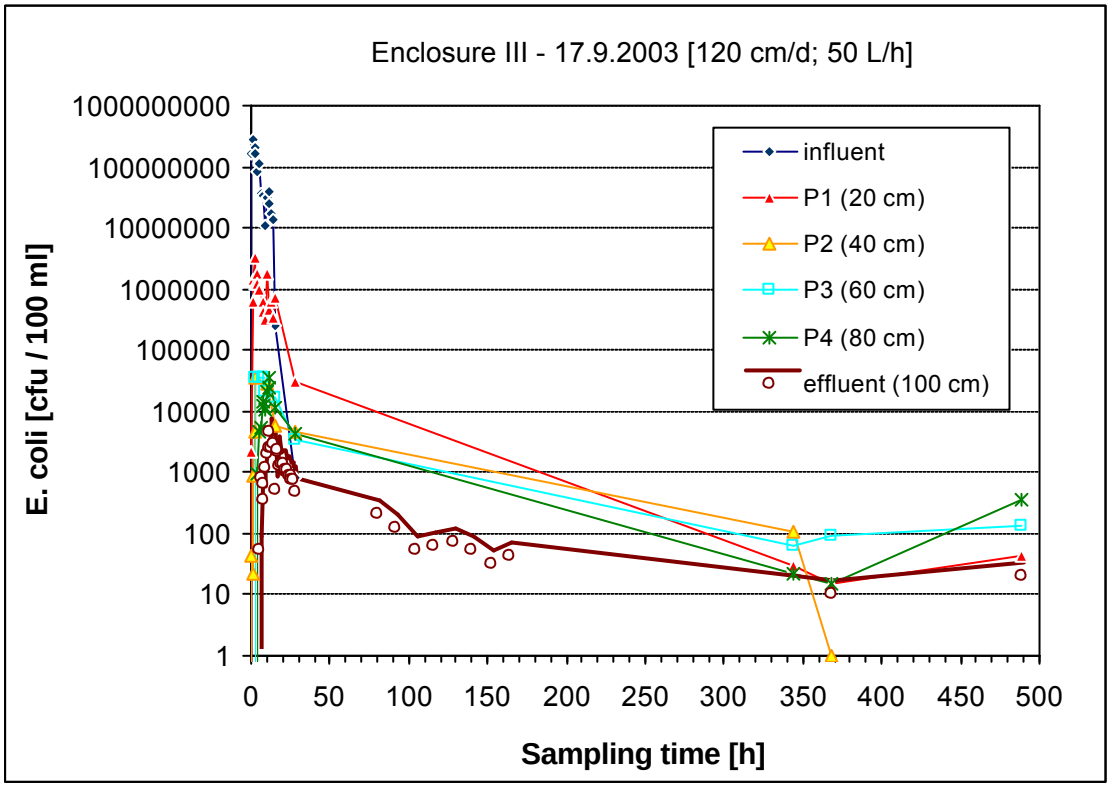


Fig. 31:Concentration of *E. coli* at different levels of the enclosure at a filtration rate of 120 cm/d with clogging layer (detection limit 1-15 cfu/100 ml).

5.5 Investigations inside the filter

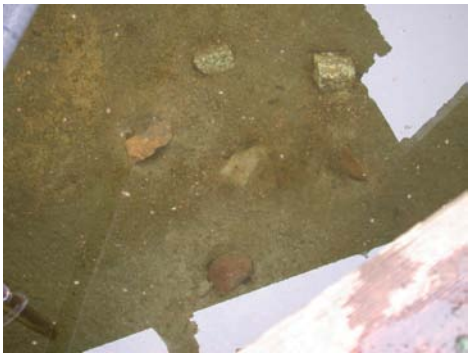
Seven cores of the filter material in the enclosures were taken before and during the filtration experiment at days 1, 3, 4, 11, 23, 53, and 71. The cores were divided into 5-10 cm sections which were analysed for total bacteria (DAPI), *E. coli*, enterococci as well as the two coliphages. Additionally, the clogging layer and the core samples were examined microscopically.

5.5.1 Characterisation of the clogging layer

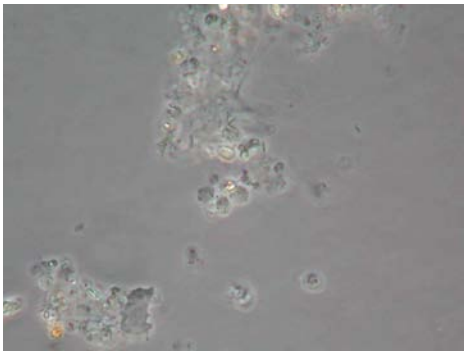
The dominating organisms found in the clogging layer were algae of different groups (diatoms, gold and green algae) together with amoebae. Occasionally higher organisms (e.g. gastrotrichs) were found (Table 10, Fig. 32). The cyanobacterium Microcystis, which had been applied to the filter together with the microcystin was found in the clogging layer at all sampling times.

Table 10: organisms identified in the clogging layer

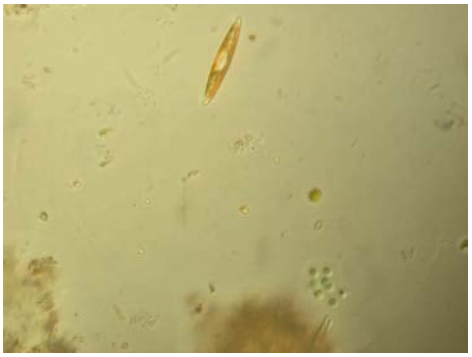
Cyanobacteria :	Microcystis spec.
Diatoms :	Navicula spec. Synedra spec. Anomoeoneis spec. Nitzschia spec.
Gold algae :	Dinobryon spec.
Green algae :	Chlorococcum spec. Euastrum spec.
Amoebae :	Actinosphaerium spec. Testacea , ambiguous
Gastrotichs :	Chaetonotus spec.



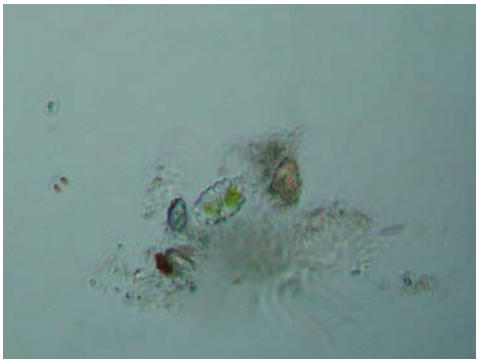
„Schmutzdecke“ enclosure



Amoeba, sediment et al.
magnification1000



Diatoms and single cell greenalgae
magnification 400



„Jochalge“ Euastrum spec.
magnifigation 1000

Fig. 32: typical organisms in the upper sand layers of the enclosure

5.5.2 Examination of the filter cores

Filter cores were analysed for total bacteria using DAPI staining and fluorescence microscopy. Concentrations between 10^8 and 10^9 cfu/g dry weight were found in all samples (Fig. 33). No correlation between the concentration of the bacteria and the depth of the filter was detected. Similar results were obtained from the GWA Tegel (results not shown, will be discussed in a later report).

The filter cores were analysed for both bacteriophages since the previous experiment had been carried out with coliphage 138. Coliphage 138 was still detected in concentrations of

10-70 pfu/g wet weight in the beginning of the experiment. After 23 days, these coliphages were only detected sporadically in very low numbers (< 1-3 pfu/ g, data not shown).

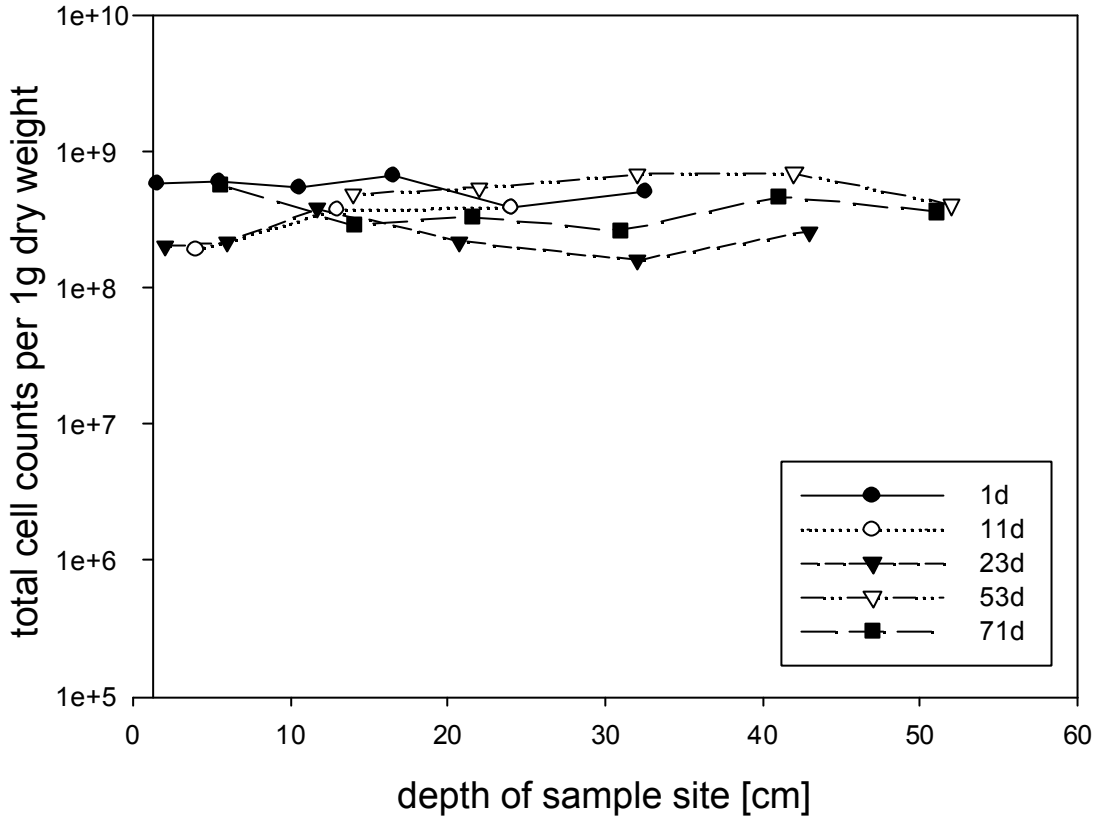


Fig. 33: Total cell counts per 1g dry weight determined by DAPI staining in sediment samples taken from the enclosure during the filtration experiment.

Coliphage 241 was detected in very low concentrations (1-5 pfu/g wet weight) before the start of the experiment in all sampling depths. High concentrations were found at day 3 and 4 after inoculation. Concentrations decreased with depths (Fig. 34). In the upper layers concentrations ranged from 3×10^3 – 1.5×10^4 pfu/g wet weight. In the lower layers, concentrations increased from day 2 to day 3 from 10 to several hundred pfu/g. Coliphage 241 was still present after 23 days in all sampling depth at concentrations of 100-300 pfu/g.

Enterococci were not detected in core samples before inoculation. After inoculation, concentrations were in the range of $1\text{-}8 \times 10^4$ cfu/g wet weight in the upper layers and decreased to about 1000 cfu/g in a depth of 40-50 cm (Fig. 35). Concentrations decreased after 2-3 weeks to 100-600 pfu/g in the upper layers and to below detection limit in 40-50 cm

depth. Enterococci were detected in only one core sample at day 53 and in none of the core samples at day 71.

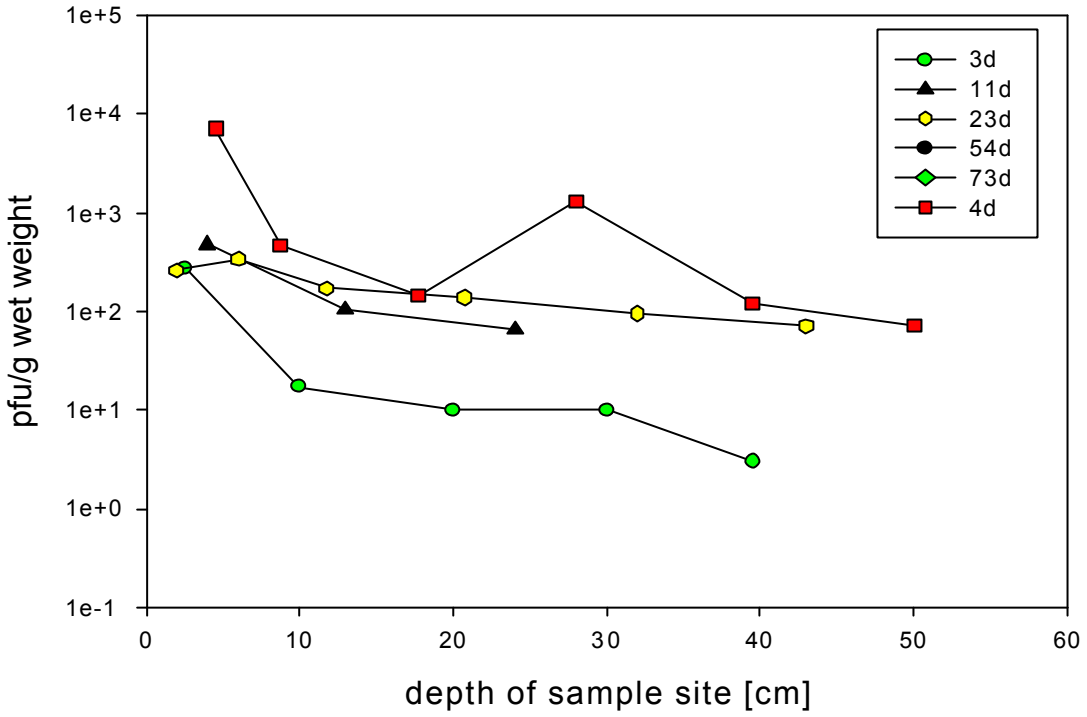


Fig. 34: Concentration of coliphage 241 in sediment samples taken from the enclosure during the experiment (no data at day 54 and 73).

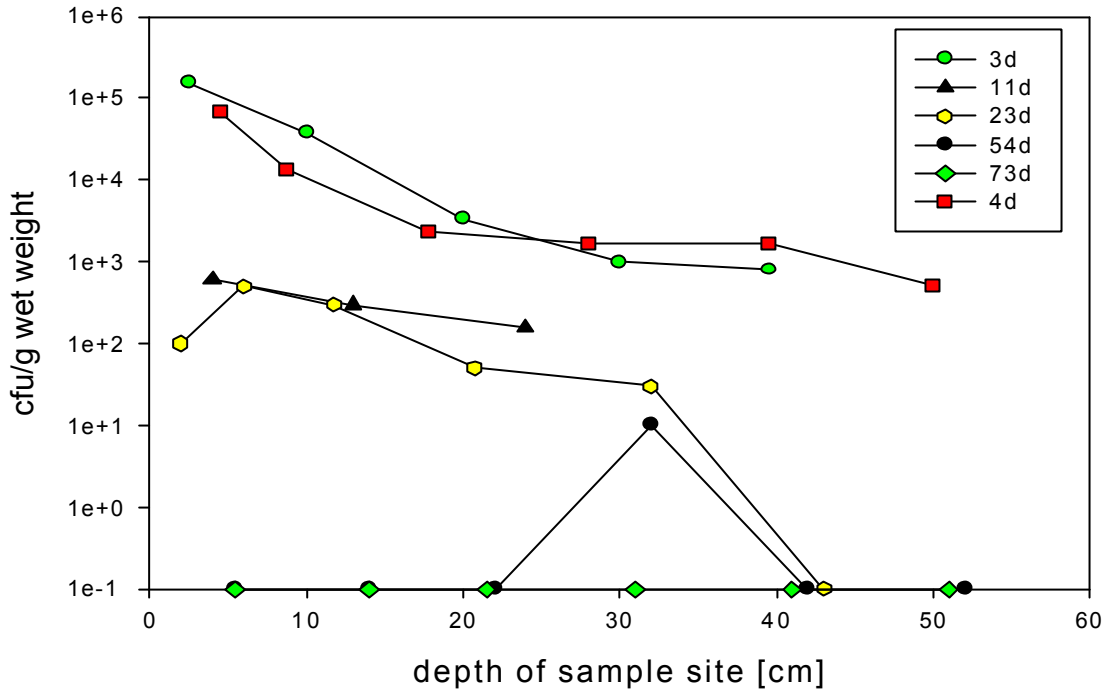


Fig. 35: Concentration of enterococci in sediment samples taken from the enclosure during the filtration experiment (detection limit 1 cfu/g).

E. coli was not detected in core samples before inoculation. Concentrations were above the detection limit at day 3 after inoculation (data not shown). At day 4 very high concentrations of 10^5 cfu/g wet weight were detected in the upper layers of the filter (Fig. 36). Concentrations decreased with depths and were in the range of 10^3-10^4 cfu/g in 20-50 cm. *E. coli* survived better in the filter than the enterococci. Concentrations of 1-100 cfu/g were detected in all core samples even after 71 days of percolation.

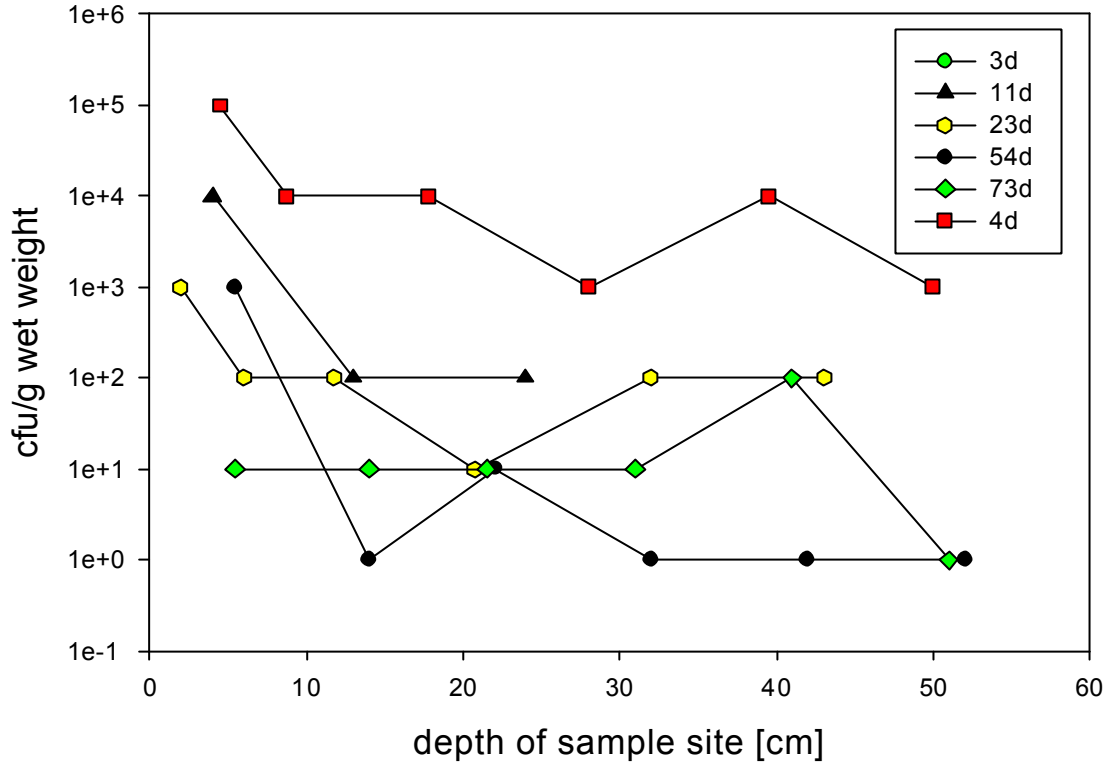


Fig. 36: Concentration of *E. coli* in sediment samples taken from the enclosure during the experiment (no data at day 3, detection limit 1 cfu/g).

6 Discusion

6.1 Results in lakes Wannsee and Tegel and in its respective transects

In both surface waters the concentration of Intestinal Enterococci never exceeded 10 cfu in 100 ml, and that of E.coli only occasionally was higher than 100 cfu in 100 ml. The highest concentration of coliphages observed amounted to 300 pfu in 100 ml (Fig. 1). Clearly, the concentration of indicator bacteria and coliphages, both in lake Wannsee and lake Tegel, never was so high as to allow a quantitative approach of its elimination along the transects.

Surprisingly, the water in the observation well was not always free of indicators. In fact this water, specially in the shore of lake Wannsee, frequently contained indicators (Table 1 and 2). It is not clear if these findings are due to shortcuts in the underground along the water passage or to external contaminations occurred post infiltration.

6.2 Reduction of viruses by filtration in the column in Marienfelde

Both phages, the somatic phage 241 and the F+-phage 138 were eliminated very efficiently in the first 100 cm of the column, but even during this initial part the elimination began to become poorer with increasing filtration path (Figs. 2-10). Beyond the first 100 cm of the column the reduction performance decreased dramatically. Fig. 37 shows the filter distance that would be required for reducing the concentration of the phages by a factor of ten, if one would calculate this distance from the results obtained at different column heights. For the sake of simplicity we will refer to this distance as the “one-log distance”. For phage 138 (red triangles in Fig. 37) the one-log distance between the bottom of the column (the column was operated from bottom to top) and the 20 cm point was 13 cm. However, between the 80th and the 160th cm the estimate for the one-log distance is 133 cm, i.e., ten times as much. Further pursue of the fate of the phage 138 beyond 160 cm was not possible due to the die-off of the phages in the reservoir feeding the column.

Opposite to the phage 138, phage 241 was not continuously inoculated. Instead, a high number of phages 241 was injected as an one-time dose into the basis of the column at the beginning of the experiment. With this procedure we intended to delay the die-off of the phages in order to be able to follow up its fate along deeper layers of the column. In fact, this was possible up to 340 cm distance from the bottom. This experimental design had however the disadvantage that no value for the input concentration was available. For estimating the one-log distances, we took the concentration observed at 20 cm as the input concentration. With this phage, two estimates were carried out: the first one, using the concentrations

obtained during the first 4 weeks of the experiment (purple squares). As substantial numbers of phages kept coming after this time, we continued the measurements and repeated the estimate with the values obtained during the first nine months after the beginning (blue squares).

As was the case with phage 138, the one-log distances of the phage 241 increased with increasing column depth. From a one-log distance of 23 cm after 20 cm filter path (note that with this phage the 40th cm of the column corresponds to a filtration path of 20 cm) to 346 cm after 320 cm filter path. We can not explain at this stage the differences between the four and the forty weeks values at the 160th cm of the column. But we hope that a more thorough mathematical analysis might explain this discrepancy.

What could be the reason for the decreasing performance of the column? In principle, the reasons might be found either in the column itself –different chemical or physicochemical conditions with increasing depth- or within the viral suspension used for the experiment. Concerning the conditions prevailing in the different parts of the column, we are in the process of looking out for possible reasons which would explain the different reduction rates. With respect to the viral suspension used for the experiment, it can not be ruled out that it consisted of a combination of monodispersed viruses together with viral aggregates. The aggregates might comprise two, three or, in fact, thousands of viral particles. Besides being aggregated, the viruses might be partially embed in cellular debris, a fact that would make its retardation kinetics very unpredictable.

Two mechanisms may be envisaged by which the heterogeneity of the viral suspension might be responsible for increasing one-log distances: different viral “populations” will percolate the column with different velocities. Obviously, the slower fractions will remain in the rear whereas the fastest fractions will take the lead. After a certain distance the fastest fractions will be in the front of the viral cloud and its speed will be register as the highest.

As a second possibility, the viruses might enter the column as aggregates of several or many viral particles. With time, these aggregates might get dispersed into smaller ones or even to single viral particles along the filtration path. But as these forms, aggregates and single viral particles alike, are all detected as single Plaque Forming Units, the impression will be given as if the viral reduction in the deeper layers of the column be less pronounced than in the superficial ones.

Any one or all three possibilities might explain why the viral reduction rate gets worse with increasing filter distance. In any case, it is important to keep in mind that these effects also might be encountered in real-life water works, when fecally contaminated surface waters are bank-filtrated to obtain potable water. Unfortunately, as any one of the causes mentioned above might be present in a variable degree, prediction of the filter distance necessary for producing safe water by means of mathematical modelling could become very complex and might be not sufficient for warranting safe water. Along with estimates of the filter path of a bank filter, one will have to contemplate to monitor the quality of the filtrated water by other means.

6.3 Reduction of viruses and bacteria by filtration in the enclosure and in the infiltration pond in Marienfelde

The results of the enclosure (Figs. 11-18) point to the same direction. The one-log distances have the tendency of become larger with increasing filtration distance (Fig. 38. But disregard the experiment of 17.09.03., green symbols, because here the filter bed was sampled –and disturbed- during the experiment).

The data obtained in the infiltration pond (Figs. 19-24) can not be analysed with respect to a variable filter path, since these results were obtained after 80 cm filter path only and not after different filtration distances as was the case with the other devices. The one-log distances estimated from the 80 cm filtration path (two times 28 cm for the phage 138 as well as 23 and 42 cm for the phage 241) are in the same range as the ones gained from the work carried out with the column (first 100 cm.) and with the enclosure. Table 10 summarizes the results of the three experimental sites in Marienfelde.

Even the lowest degree of elimination observed at 340 cm column depth appears acceptable in the light of the requirement specified by the US EPA. The requirement is that the treatment of surface water or surface water influenced groundwater must warrant a reduction of viruses of at least four logs in order to be accepted as sufficiently safe to be used for drinking water production. The table shows that assuming the worst one-log distance observed in the column –346 cm- this requirement would be achieved by passing the water through a path of 14 meters, provided the other conditions considered in the column are met.

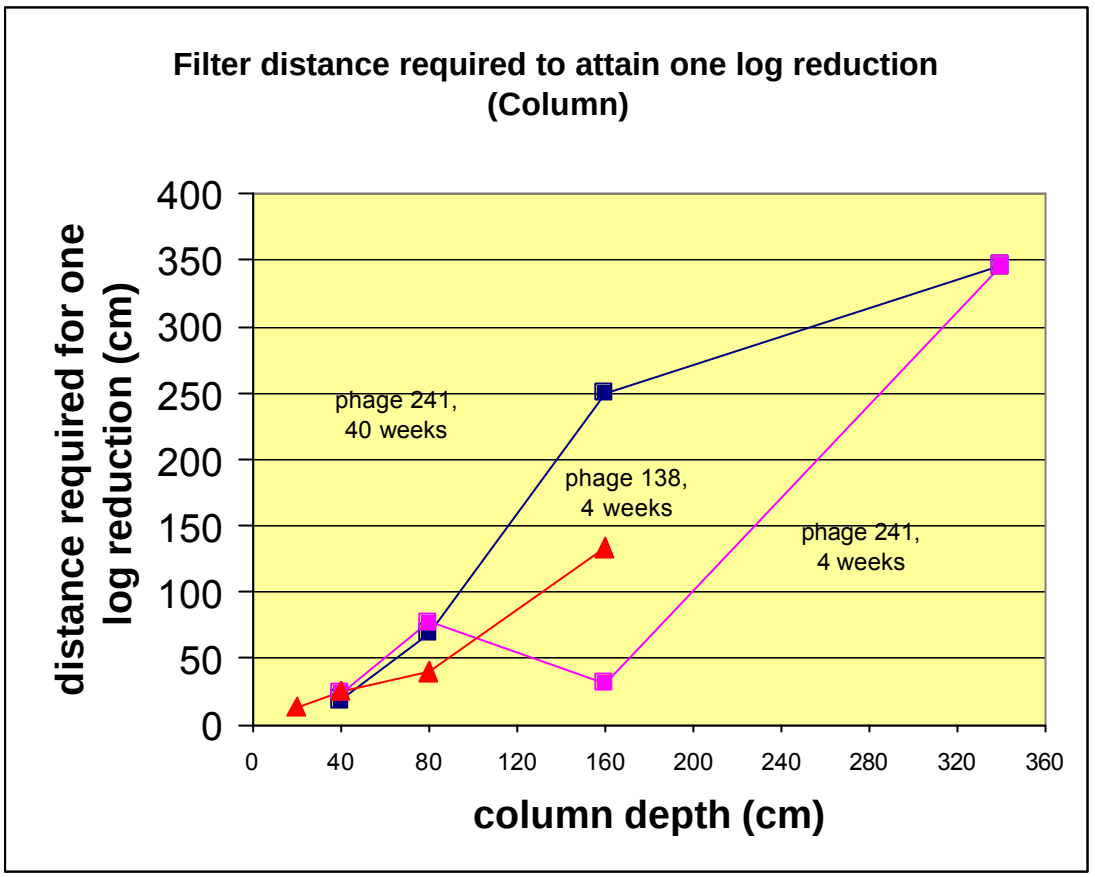


Fig. 37: Filter path of the column in Marienfelde required to reduce the concentration of phages by one log with respect to the concentration observed in the observation point located immediately before.

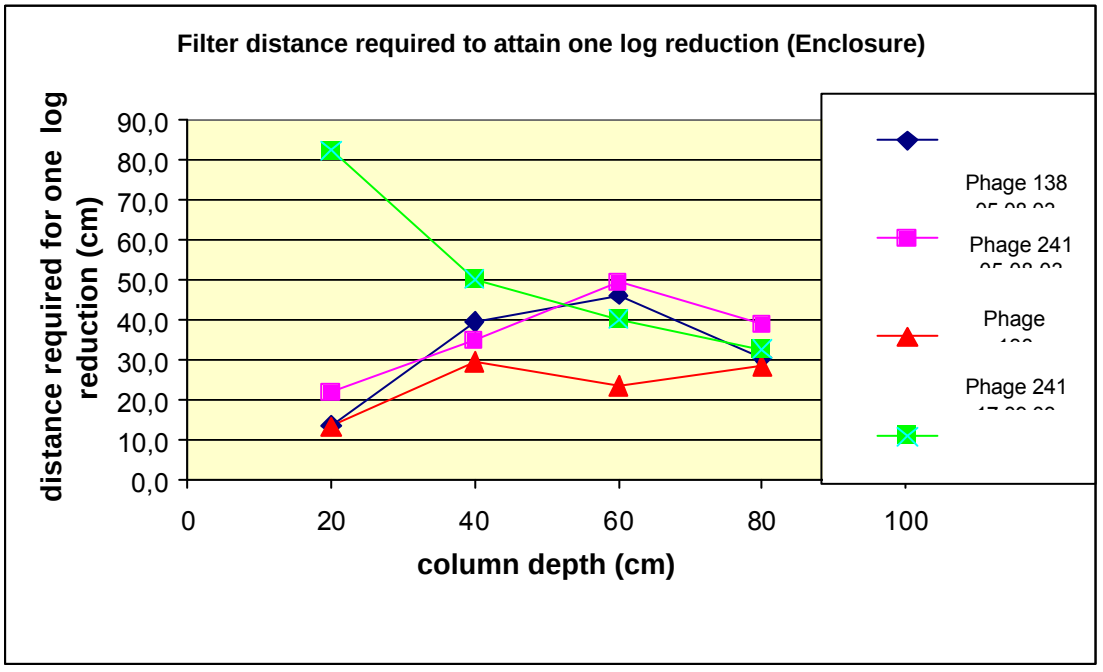


Fig. 38: As in Fig 37., but in the enclosure.

Table 10

Filter path required for reducing the phage concentration by one log (cm)

	Column Marienfelde (100 cm/d, 20 cm depth)	Column Marienfelde (100 cm/d, 80-160 cm depth)	Column Marienfelde (100 cm/d, 160-340 cm depth)	Enclosure (12 120 cm/d, 20-80 cm depth)	Infiltration Pond (120 cm/d, 80 cm depth)
Phage 138	13	135	-	Phage 138, 14-46 cm	Phage 138, 28 cm (two experiments)
Phage 241 (first month)	25	31	346	Phage 241, 22-50 cm	Phage 241, 23 and 42 cm respectively
Phage 241 after 10 months	25	250	346		

6.4 Influence of the percolation velocity in the elimination of viruses

In the Fig. 26 it can be seen how the increase in percolation rate from 1 to 8 m/d influences the mobility of the virus 241. At 160 cm column height and beyond the mobilization is very pronounced and the concentrations reached might be one thousand times higher than before the percolation rate was increased. At lower column heights the mobilisation is less manifest but the concentrations become still at least one order of magnitude higher. Another additional increase of the percolation velocity from 8 to 24 m/day further increased the mobility of the viruses. The results obtained with the virus 138 point into the same direction (Fig. 25).

The influence of the percolation rate is important for the practical design and management of bank filtration water works, since horizon fluctuations of the surface water feeding the plant might very well influence the filtration rate and have direct consequences for the

microbiological water quality. Further investigations aimed to quantitatively predict the consequences of water velocity increase on viral mobility are underway.

6.5 Investigations in the enclosure with bacteria. Investigations inside the filter

There will be circumstances where bank filtration can not be carried out according to optimal standards, be it that the soil does not possess the suitable properties, that the filter path required can not be attain, or that the underground water velocity is too high. For these occasions it seems prudent to envisage quality control programs of the filtered water, designed to supervise its hygienic quality. One could think of measurements of E.coli, intestinal enterococci or/and coliphages.

In order to enhance the value of such programmes from a risk assessment perspective we are studying the relationship between the mobilities of E.coli, intestinal enterococci and coliphages (Figs. 27-31). Moreover, it is equally important to assess potential hazards resulting from log-living pathogens resting in the filters for months or even years. To gain sufficient information regarding the tenacity of viruses and bacteria inmobilized in the filters, we have carried out studies in which sand cores were analysed for several microorganisms (Figs. 32-36). These investigations are still going on. The conclusions from the results will be elaborated upon at a later point.

7. Perspectives / Intended tasks for the upcoming project period (January – December 2004)

Task	comments
Continuing: Measuring indicator bacteria and coliphages in surface water and in different wells along the transects 1 and 2 of the Lake Wannsee	By working observation wells 207OP, 207 MP1, 207MP2, and 207UP, sampling will be more frequently continued.
Continuing: Spiking the bank filtration plant of Marienfelde with cultured coliphages, sampling of the water and detection of coliphages in filtrate samples	In collaboration with working group of Dr. Chorus (UBA)
Continuing: Inoculation of coliphages and indicator bacteria into the slow sand filtration pond pf Marienfelde, variation of hydrodynamic conditions (flow rate, forming colmation layer)	In collaboration with working groups of Dr. Chorus (UBA) and Dr. Nützmann (IGB)
Continuing: Spiking the enclosure I and II with suspensions of cultured indicator bacteria and coliphages as well as with wastewater at different concentrations, sampling at different filtration time and velocity, determination of coliphages and bacteria in filtrate samples	In collaboration with working groups of Dr. Chorus (UBA) and Dr. Nützmann (IGB)
Continuing: Measuring indicator bacteria and coliphages in water samples from the sandy soil column	In collaboration with working group of Prof. Jekel (TU-Berlin)
Repeatedly spiking the sandy soil column with coliphage cultures, variation hydrodynamic conditions.	