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# Seasonal and spatial distribution of redox zones during lake bank filtration in Berlin, Germany

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Abstract Redox processes during bank filtration were evaluated in Berlin, where bank filtered water is abstracted for drinking water production. The investigations included the mapping of the infiltration zone, a column study and hydrochemical analyses of the groundwater sampled between lake and production well. The organic carbon content increased and the permeability of the lake sediments decreased with distance from the shoreline. The most important changes with regard to the redox state of the infiltrate occurred within the first metre of flow. Infiltration was mostly anoxic, as oxygen was rapidly consumed within the organic rich sediments. The infiltration zone revealed a vertical redox stratification with hydrochemical conditions becoming more reducing with depth rather than with distance from the lake. The redox zones were found to be very narrow below the lake and wider towards the production wells, suggesting that other than differing flow paths, reaeration after infiltration may also occur and possible mechanisms are presented. Redox conditions were influenced by strong annual temperature variations of the surface water affecting the microbial activity. Aerobic infiltration only took place close to the shore in winter.

**Keywords** Lake bank filtration · Hyporheic zone · Redox processes · Seasonality · Organic carbon

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#### Introduction

Bank filtration of river and lake water is often induced by pumping of wells adjacent to the lake or river banks to gain water for potable use (e.g. Bouwer 2002). Induced aquifer recharge is generally practised as a method to conserve groundwater resources (e.g. Okubo and Matsumoto 1983). It is also considered to be an efficient and natural treatment technology and there are a number of benefits in the use of bank filtration for potable purposes. The surface water quality is improved during passage through the river bank and aquifer sediments due to the elimination of suspended solids, particles, biodegradable compounds, bacteria, viruses, and parasites as well as the partial elimination of adsorbable compounds. The quality improvement is caused by biotic and abiotic processes such as physical filtration, biodegradation, adsorption, chemical precipitation, and redox reactions (e.g. Kuehn and Mueller 2000; Hiscock and Grischek 2002; Tufenkji et al. 2002). Clearly, bank filtration has many advantages over the direct use of river water. However, since many rivers next to bank filtration sites are also used for sewage (or treated sewage) disposal, the occurrence of persistent pollutants in the river water can nevertheless represent a problem for the drinking water quality (e.g. Achten et al. 2002). In Europe, bank filtration has been successfully applied for more than 100 years (Hiscock and Grischek 2002; Schubert 2002).

The characteristics of the sediments covering a river, pond or lake bed, often referred to as the hyporheic zone (e.g. Brugger et al. 2001; Tufenkji et al. 2002) are of major importance for the behaviour of the entire bank filtration system, since they form the direct interface between surface water and groundwater. Clogging may reduce the permeability of the riverbed, for example due to the deposition of fine particles (Brunke 1999) or the formation

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of biofilms (Battin and Sengschmitt 1999). Although reduced infiltration rates may constitute a disadvantage with regard to productivity, the formation of a clogging zone can also have many advantages: it is potentially more effective in removing contaminants than the unclogged sands of the aquifer because the adsorption and reduction capacities are larger owing to higher proportions of organic and/or fine-grained material. In addition, the relatively low permeability slows down the travel times from the surface water to the production wells. Several authors showed that the most significant chemical changes which are related to microbial organic matter degradation occur within the first metres of infiltration (Hoehn et al. 1983; Jacobs et al. 1988; Dousson et al. 1997; Brugger et al. 2001), thereby also often effectively reducing the concentration of organic contaminants such as aromatic hydrocarbons (Juttner 1999). Hiscock and Grischek (2002) stated that the success of bank filtration schemes generally depends on microbial activity and chemical reactions which mainly take place in the very reactive river sediments.

The redox conditions during bank infiltration or other forms of aquifer recharge are of major importance, since they may cause the appearance of the undesired metals iron (Fe<sup>2+</sup>) and manganese (Mn<sup>2+</sup>) (Bourg et al. 1989; Bourg and Bertin 1993) as well as copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) (von Gunten and Kull 1986). They also influence the behaviour of a number of organic pollutants such as pharmaceutically active substances (e.g. Holm et al. 1995; Massmann et al. 2006), halogenated organic compounds (Bouwer and McCarty 1983; Bosma et al. 1996; Kao et al. 2003; Grünheid et al. 2005), pesticides (Agertved et al. 1992; Tuxen et al. 2000; Broholm et al. 2001; Patterson et al. 2002), or disinfection byproducts (Pavelic et al. 2005). Holzbecher et al. (2006) showed that the elimination of phages is redox dependent. In addition, redox conditions affect the pH and calcite solution capacity (Richters et al. 2004). Redox processes are mostly driven by organic matter degradation by terminal electron acceptors (TEAs) such as oxygen (O<sub>2</sub>), nitrate (NO<sub>3</sub>), manganese(MnIV)- and iron-(FeIII)oxides and hydroxides and sulphate  $(SO_4^{2-})$  which are typically consumed in a sequential order from the highest energy yield downwards (Froehlich et al. 1978; Champ et al. 1979; Berner 1981). The consequent formation of distinguishable redox zones, i.e. a redox sequence in flow direction has often been observed in aquifers recharged by bank filtration (von Gunten and Kull 1986; Jacobs et al. 1988; Bourg and Bertin 1993; Lensing et al. 1994; Dousson et al. 1997; Massmann et al. 2004).

The drinking water for the ~3.4 million inhabitants of metropolitan Berlin originates from the local groundwater reservoirs. Production well galleries of the Berlin Water Company (Berliner Wasserbetriebe) are located adjacent to the surface water system and artificial infiltration ponds, and 70% of the abstracted groundwater is estimated to be bank filtrate or artificially recharged groundwater (Pekdeger and Sommer-von Jarmersted 1998). Hence, besides other factors, the quality of the abstracted water is influenced by hydrochemical changes occurring during the process of infiltration. Monitoring and understanding of these water quality changes is therefore of great importance in order to ensure the sustainability of the drinking water production system.

Because information on the infiltration dynamics during bank filtration in Berlin is scarce, the infiltration zone of a field site at Lake Wannsee was investigated. The investigations included the mapping of the infiltration zone, the drilling of several cores close to the lake shore, a column study with an undisturbed core from the lake bed at the shore as well as groundwater sampling along a transect of observation wells oriented approximately in flow direction between Lake Wannsee and a production well. The objectives of the study were (i) to evaluate the spatial distribution of hydraulic conductivities and organic carbon contents of the sediment at the lake bottom, (ii) to investigate the spatial and temporal hydrochemical changes directly at the surface water/groundwater interface as well as (iii) within the aquifer between the lake and the production well. The results will provide an insight into infiltration dynamics in Berlin and similar lake bank filtration settings worldwide.

## Site description

The study site is located at Lake Wannsee, in the southwest of Berlin. Mapping was conducted along the shores of the lake up to a distance of ~200 m into the lake. Sediment cores for analysis and a column study were taken close to the shore in the shallow water next to a groundwater research transect. The transect consists of several observation wells screened in various depths and oriented roughly in flow direction between the lake and a production well. Two observation wells were placed inland of the production wells to investigate the composition of the ambient groundwater. The piezometers are made of high-density polyethylene (PE-HD) with a diameter of 0.05 m and a filter screen length of 2 m. Previous work at the site was done by Massmann et al. (2007). The locations of mapping and coring sampling points, groundwater observation and drinking water production wells are given in Fig. 1.

The sediments of the uppermost aquifer abstracting bank filtrate are Pleistocene, porous, glaciofluvial and fluvial sands of the Saale and Weichsel glaciation. The sands are underlain by a continuous organic-rich clay aquitard of the Holstein interglacial period, followed by an aquifer Fig. 1 Location of mapping (grid intersections) and coring sample points, groundwater observation and drinking water production wells at the field site. The inlets show the location of the field site within Berlin 55



composed of sands from the Elster glaciation, which are separated into two local units by a silt aquitard of Elster age. The production well (well three) of the adjacent water work Beelitzhof of the Berlin Water Company (Berliner Wasserbetriebe) is screened in three separate sediment layers. This paper focuses on the uppermost sandy aquifer recharged by bank filtration. A simplified cross section is given later in combination with the redox results. The maximum depth of Lake Wannsee is 9.8 m. Originally, the glacial valley below the lakes was much deeper, but it was subsequently filled with very fine-grained, organic-rich sediments (lacustrine sapropel) which presently are estimated to reach a thickness of tens of metres (Senat für Stadtentwicklung 2006).

## Methods

## Mapping of the lake sediments and sediment collection

In August and October 2004, 180 disturbed grab sediment samples were taken with a Van Veen sediment dredge from a swimming platform at the grid intersections given in Fig. 1. At each grid point, the recovered sediments were examined visually for grain size (finger test) and organic matter content as well as for colour and shell content. In addition, the water depth was noted at each point. Sediment samples were retrieved for subsequent analysis. In January 2004, seven sediment cores were drilled with a vibrocorer at 3 locations in 1.5, 20 and 40 m distance from the shore, corresponding to water depths of 0.15, 0.6 and 2.3 m at the time. Two undisturbed sediment cores of approximately 1 m length were drilled at each of the three distances for sedimentological examinations. The seventh sediment core of 1 m length was drilled at the 20 m distance location and captured in a transparent Perspex liner for a column experiment.

## Sediment analysis

Hydraulic conductivities  $k_f$  (m/s) were determined by transient permeability tests carried out with 75 disturbed samples from the mapping campaign (circles in Fig. 1). The samples were fitted into a little metal cylinder with a defined length l (m) and cross-sectional area A (m<sup>2</sup>), topped with a manometer tube with a cross sectional area a (m<sup>2</sup>). The decline of the hydraulic head from the original height  $h_1$  (m) to the final height  $h_2$  (m) over a time interval t (s) was measured. The hydraulic conductivity was calculated following Darcy's law as (e.g. Busch et al. 1993):

$$k_f = \frac{a \times l}{A \times t} \times 2.3 \times \lg\left(\frac{h_1}{h_2}\right).$$

The grain size distribution of a set of 26 sub samples was analysed by sieving with mesh sizes of 4, 2, 1, 0.5, 0.25, 0.125 and 0.063 mm according to DIN 4022. The

organic carbon content of the 178 grab samples (grid intersections in Fig. 1) from the mapping campaign was measured by loss of ignition at 550°C. Sediments from the cores were analysed for total organic and inorganic carbon and sulphur with a C–S–N analyser (CS-225, LECO).

## Column study

The column was installed in the laboratory at room temperatures of 20–22°C (Fig. 2). The column was operated downwards, with a water column of 0.2 m on top to ensure a head gradient similar to the one encountered in the field. This was done in order to maintain the field conditions since turning the core around might have disturbed the clogging layer. A pulsating pump was later installed when flow rates varied. Fresh surface water from Lake Wannsee was added from a container bubbled with air by an aquarium air pump to maintain constant saturation of oxygen. Nine sampling ports were installed in the sediment. Oxygen minisensors (optodes) were placed directly into the sediment of the column (for depth of the sensors refer to Fig. 2).

The column was operated for 12 months, starting in April 2004. The flow rate varied between 200 and 1,500 ml/day. The variability of the flow rate over time was most likely due to the degassing of the sediment during



Fig. 2 Column set-up in the laboratory. The column was operated in the downwards mode. The flow rate was measured regularly volumetrically with a beaker. Eh, pH and EC were constantly logged in the in- and outflow. Oxygen concentrations were detected with oxygen probes placed directly into the sediment. Depths of sampling ports are given to the *right* 

sampling, which increased the hydraulic conductivity followed by the formation of gas. However, the flow rate was estimated to be similar to the variation encountered in the field. The hydraulic conductivity of the column was  $2.2 \times 10^{-6}$  m/s, calculated by applying Darcy's law after measuring the flow-rate Q (m<sup>3</sup>/s), the length of the column (l) and the cross sectional area A (m<sup>2</sup>) and the head difference (h2–h1). The flow velocity through the column was  $6 \times 10^{-6}$  m/s (or 0.52 m/day) and the longitudinal dispersion coefficient was  $D_L = 8 \times 10^{-8}$  m<sup>2</sup>/s, both derived from a tracer test conducted with a NaCl solution in July 2004 at average flow rates of 600 ml/day. Since the flow rate varied during the experiment, these values are only representative at this particular flow rate.

Sampling at the ports was done monthly, while the inand outflow was sampled approximately weekly. Due to the low flow-rate, volumes of only ~30 ml were collected. Temperature, redox potential (Eh), pH and electrical conductivity (EC) were measured immediately after sampling. Water samples were analysed photometrically for Na<sup>+</sup> and K<sup>+</sup> (Eppendorf Elex 6361r), for Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>2+</sup> and Mn<sup>2+</sup> by atomic adsorption spectroscopy (AAS flame, Perkin Elmer 5000) and for  $Cl^-$ ,  $SO_4^{2-}$  and  $NO_3^-$  by ion chromatography (IC DX100). HCO<sub>3</sub> was determined by micro titration of 3 ml of sample with HCL. Full anion and cation analysis was done in order to ensure that the ion charge balance is correct. Only samples with a charge balance of <5% were included in the calculation of the medians presented later. For the optical oxygen measurements, adapted blue light is fed into an optical fibre with a fluorescence dye glued to its tip which is oxygen sensitive. The fluorescence light is reflected by the optical fibre and detected in a measuring devise. If oxygen is present, fluorescence is quenched and the concentration can be determined. The method is described in detail in Hecht and Kölling (2002).

## Groundwater sampling and analysis

Water sampling of surface water, observation and production wells was conducted monthly between January 2003 and August 2005. Measurements for redox potential, pH,  $O_2$ , temperature and electric conductivity were carried out in the field in a flow cell. Filtration with 0.45 µm membrane filters was done immediately after sample retrieval for analyses of cations and anions. Samples for cation analysis were preserved with concentrated nitric acid (HNO<sub>3</sub>). Alkalinity samples were collected in glass bottles that were carefully filled without any air entrapment. Samples were stored at 4°C, and full water analysis was generally performed one day after sampling.

Groundwater samples were analysed in the laboratory of the Berliner Wasserbetriebe/Berlin Water Company (BWB). Anions in the water were measured with ion chromatography, DX 500 (Dionex Coop.) using the DIN EN ISO 10304-1/2 procedure. Cations in the water were determined with an ICP (OES) IRIS (Nicolet) according to the DIN EN 11885-E22 method. The DOC measurements were carried out according to the DIN EN 1484-H03 method with a "High TOC" TOC/DOC-analyzer (Elementar).

## Results

## Sediments properties in the infiltration zone

The water depth of the mapped section of Lake Wannsee is shown in Fig. 3a. Within 200 m distance from the shoreline, the water depth drops from very shallow to more than 8 m. Here, the sediment surface flattens out to a wide lacustrine basin, with maximum depths of ~9 m. The sediment samples obtained during mapping were predominantly composed of fine-grained sands with variable organic and inorganic carbon contents. In shallow water depths of less than 2 m, the sands were coloured in light brown to greyish tones, frequently covered by a film of green organic substances and interspersed with remnants of vegetation. In depths from 2 to 6 m, the colour of the sands was transiently changing from grey to darker olive-brown and dark grey tones. At depths of more than 6 m, their colour darkened to olive-black and black. The sands generally became finer-grained with water depth. At a depth of more than 6 m, the fine-grained sands contained an increasing amount of silt. At depths of more than 7.2 m, the sediments appeared to be less densely packed. The granular structure was replaced by a watery, unconsolidated and non-granular structure of the sediments. At depths of more than 7 m, lacustrine sapropels, i.e. organic rich sludges, prevailed. With the exception of the sand sediments in low water depths of <2.5 m, all samples contained minor amounts of sulphides, already noticeable by greyish colours and a distinct odour. In depths of down to ~4.5 m, the sands were settled by colonies of mussels which were a few centimetres thick. With greater depths, layers of shells and detritus, increasingly crushed to finer fragments, replaced the mussel colonies. In depths exceeding 6 m shells and shell detritus disappeared; carbonate detritus of sand-grain size remained within the sands on the sediment surface. The lacustrine sapropels contained carbonate in a fine-dispersed form.

The distribution of the hydraulic conductivity  $(k_f)$  of the lake bottom sediments as determined by transient permeameter tests with disturbed samples is illustrated in Fig. 3b. The hydraulic conductivity generally decreased with distance from the shore and with water depth. In more than 7 m water depth, the hydraulic conductivity rapidly declined to values below  $1 \times 10^{-6}$  m/s reaching the lowest values of  $10^{-7}$  m/s towards the lake centre. We suspect that the real in-situ hydraulic conductivities are probably even considerably lower than those given in Fig. 3b, since tests were conducted with disturbed samples where the sediment structure had been destroyed. The hydraulic conductivities of the lake base are clearly lower than those of the aquifer which were mostly around  $10^{-4}$  m/s ( $k_f$  values derived from sieving of core BEE202).

The organic matter content (Fig. 4) of the lake bottom sands varied from 0.2 to almost 10 weight-%. Similar to the hydraulic conductivities, the organic carbon content showed a relation to distance from the shore, i.e. water depth, with increasing values with distance to the shore. In greater water depths the amount of organic matter exceeded values of 10 weight-%. The maximum organic carbon content measured at the field site was 25.7 weight-% in a loose, watery and unconsolidated lacustrine sapropel.

Fig. 3 a Water depth of lake Wannsee (m) and b hydraulic conductivities (m/s) of the lake base in the infiltration zone. The water depth was measured with a rope at each grid point, hydraulic conductivities were determined by transient Darcy experiments for 79 disturbed samples obtained at the circles. Boundaries were drawn by hand according to the test results and the sediment descriptions at the grid points. As the water depth increases, the hydraulic conductivity decreases





Fig. 4 Organic carbon content of the uppermost sediment layer of the lake base in the infiltration zone, showing a general increase with increasing water depth

Redox conditions of the infiltration zone

Two observation wells (Fig. 5) were placed in the shallow water to investigate the hydrochemical composition of the freshly infiltrated water. Both are screened in the ground-water below the lake at 5–7 (BEE206) and 4–6 (BEE205)

metres below the lake base, in a distance of  $\sim 1.5$  and ~20 m from the shore (shoreline moves slightly over the year) and at corresponding lake water depths of ~0.15 and  $\sim 0.6$  m (slightly variable over the year). They are located in an area where the sediments below the lake are partly unsaturated, since the groundwater level is lowered below the lake base due to the pumping of the production wells. The extent of the unsaturated zone below the lake varies. depending on factors such as the pumping performance and the season. Figure 5 gives the approximate minimum and maximum of the groundwater level. The existence of an unsaturated zone clearly illustrates that there is a resistance to flow across the lake bottom as a result of the lower hydraulic conductivity of the lake bottom compared to the aquifer. The distribution of the organic carbon content of the sediments in this zone was heterogeneous. Although the organic carbon content of the uppermost 0.3 m generally increased with distance to the shore (Fig. 4), the cores revealed that the uppermost sediment of the middle core (WS 2A) had a lower organic carbon content than the core close to the shore (WS 1A). However, the core furthest into the lake (WS 3A) clearly contained the highest amount of organic carbon.

Boxplots of both observation wells and the lake Wannsee are given in Fig. 6. In comparison to the lake water, the groundwater sampled was already considerably more reducing. But while BEE206 closer to the shore was still mostly aerobic, containing both  $O_2$  and  $NO_3^-$  at a median Eh of ~230 mV, BEE205 was mostly  $O_2$  and  $NO_3^$ free (Eh ~80 mV). BEE205 contained traces of ammonia (NH<sub>4</sub><sup>+</sup>), which is produced by organic matter degradation (Doussan et al. 1998). Mn<sup>2+</sup> concentrations derived from reductive dissolution of Mn(IV)-oxides or hydroxides were higher in BEE205 compared to BEE206, and BEE205 also contained traces of Fe<sup>2+</sup> from reductive dissolution of

Fig. 5 Cross section of the infiltration zone with groundwater observation wells and core sampling locations, extent of the unsaturated zone below the lake and organic carbon contents of the cores WS 1A, WS 2A and WS 3A





**Fig. 6** Boxplots of the redox sensitive parameters Eh (mV),  $O_2$ ,  $\text{NO}_3$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$  and DOC (mM) in Lake Wannsee and the shallow groundwater observation wells BEE205 and BEE206 below the lake from January 2003 to August 2004. The box represents the area of 50% of the average values, i.e. those which lie between the 25 and 75% percentile. The median is given as a *black line* within the *box*.

The *horizontal line* above and below the *box* are largest and smallest values, which were not classified as outliers. Outliers (distance to box 1.5-3 times the box height) are shown as *little circles*, extreme values as *asterisks* (distance to box >3 times the box height). The hydrochemical conditions of BEE206 closer to the shore are less reducing than in BEE205

Fe(III)-oxides or hydroxides, which was never detected at BEE206. Since organic carbon is believed to be the main electron donor, one would expect the DOC concentration to be lower in BEE205 than in BEE206, according to the larger consumption of electron acceptors in this well. The fact that the DOC concentrations were higher in BEE205 as in BEE206 is an indicator that particulate organic carbon (POC) might have acted as an additional electron donor and was dissolved in larger amounts in BEE205 than in BEE206, probably because of the higher content in the hyporheic zone.

Median concentrations over one year of the redox indicators in the column are displayed in Fig. 7. Since the column is an undisturbed core (WS 2C) taken from the lake bottom next to BEE205 (Fig. 1), its redox state resembled the conditions of the groundwater at BEE205. Oxygen and  $NO_3^-$  were completely consumed during passage through the column (Fig. 7). Both the column outlet and the groundwater well BEE205 were O2 and NO3 free. Oxygen disappeared from solution at a depth of 0.2 m, NO<sub>3</sub> at a depth of 0.9 m. On the other hand, the redox indicators Mn<sup>2+</sup>, Fe<sup>2+</sup> were generated during flow. Both the column outlet and BEE205 contained traces of Mn<sup>2+</sup> (median: 0.011 and 0.005 mmol/l, respectively) and  $Fe^{2+}$  (median: 0.005 and 0.020 mmol/l, respectively). A significant reduction of  $SO_4^{2-}$  was never observed in the column or groundwater well BEE205. The median DOC concentrations were 0.47 and 0.45 mmol/l, similarly reduced as compared to the surface water (0.59 mmol/l). Hence, the outflow from the column strongly resembled the ground-water of BEE205.

Redox conditions within the aquifer

The average concentration with standard deviations of the redox indicators O2, NO3, Mn2+, Fe2+ and SO4- plotted versus filter screen depth of the multi-level well nest BEE202 in approximately 30 m distance from the lake, as well as the corresponding concentrations in Lake Wannsee are shown in Fig. 8. The lake contained the TEAs  $O_2$ ,  $NO_3^$ and  $SO_4^{2-}$ . The concentrations of  $O_2$  and particularly  $NO_3^{-}$ displayed large seasonal variations, which are reflected in the large standard deviations. On average, the uppermost groundwater sample (filter screen depth 8.5-10.5 m below ground surface, mbgs) and, to some extent, the sample from the second filter screen (13.3-15.3 mbgs) contained  $O_2$  and  $NO_3^-$  in diminished concentrations. The second and, above all, the third sample (18.3-20.3 mbgs) displayed increased Mn<sup>2+</sup> concentrations. Fe<sup>2+</sup> was detected in low concentrations in the groundwater from the third filter screen, while Mn<sup>2+</sup> was still detectable. Finally, the groundwater from the fourth filter screen (23.1–25.1 mbgs) contained Fe<sup>2+</sup> at all times. The samples from the two lower screens were free of  $NO_3^-$  and  $O_2$  at all times. The

Fig. 7 Median concentrations of the redox indicators during the column passage and redox zones as characterised by disappearance  $(O_2, NO_3)$  or appearance  $(Mn^{2+}, Fe^{2+})$  of reactants. Post-oxic conditions are reached within less than 1 m of flow in the column

filter screen depth [m below ground]

5

10



**Fig. 8** Average concentrations (January 2003–August 2004, n = 20) of the redox indicators O<sub>2</sub>, NO<sub>3</sub>, Mn<sup>2+</sup>, Fe<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup> plotted versus filter screen depth (*middle* of the screen) of the mulit-level well nest BEE202. The corresponding concentrations in Lake Wannsee (May

2002–August 2004, n = 28) are shown for comparison (*circles*). *Error* bars represent  $\pm$  standard deviations. The groundwater becomes more reducing with depth

 $SO_4^{2-}$  concentrations of all groundwater samples were similar to the lake concentrations. The redox potential (not shown) decreased from the lake ( $261 \pm 80$ ) to the deepest sample ( $66 \pm 48$  mV). It becomes clear that the groundwater got increasingly more reducing with depth of the aquifer.

A cross-section of the entire groundwater transect is given in Fig. 9. Redox zones characterised by the disappearance ( $O_2$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ) or the appearance ( $Mn^{2+}$ ,  $Fe^{2+}$ ) of reactants as suggested by Champ et al. (1979) were drawn into Fig. 9 according to the average concentrations of the reactants. While the shallower wells contained  $O_2$ , and  $NO_3^-$  throughout most of the year (compare also Fig. 8), the deeper observation wells were  $O_2$  and  $NO_3^-$  free but contained  $Mn^{2+}$  and  $Fe^{2+}$ . While hydrochemical conditions were generally more reducing with increasing depth, the redox zones were narrower below the lake and thicker towards the production well.

Seasonal redox changes during infiltration

The redox conditions in the infiltration zone and the aquifer were not immobile, and redox boundaries were found to move seasonally. Figure 10 shows temperatures as well as  $O_2$  and  $NO_3^-$  concentrations over the sample period in the shallow bank filtrate, i.e. the bank filtrate with travel times in the order of months (Massmann et al. 2007). Grey bars mark the temperature threshold of 14°C which was found to be a limit below which microbial degradation is strongly limited (Prommer and Stuyfzand 2005). The shallow bank Fig. 9 Cross section of the bank filtration transect with approximate redox zones. Filter screens are given at rectangles. The production well 3 is screened in deeper aquifers too (not shown). The groundwater becomes more reducing with depth. The zones are narrow below the infiltration zone and widen towards the production well





Fig. 10 Time series of temperature (°C) and  $O_2$  and  $NO_3^-$  (mM) concentrations in the lake and groundwater observation wells BEE206, BEE202OP and BEE203 revealing a strong seasonality

filtrate (observation wells BEE206, BEE202OP and BEE203) underwent strong seasonal temperature changes. While temperatures in the lake and the shallow observation wells below the lake (BEE206) showed variations of ~25°C over the year, the more distant groundwater wells BEE202OP and BEE203 still underwent temperature variations of ~10°C. O<sub>2</sub> roughly disappeared at times when temperatures were highest, which was in summer or autumn, depending on the respective time lag to the well. It is

interesting to note that  $NO_3^-$  concentrations in the lake itself decreased to zero in summer, probably due to consumption by algae in the lake. Changes of total inorganic N due to algae growth have been observed in a recharge pond by Haeffner et al. (1998). The disappearance of  $NO_3^-$  in the observation wells therefore appears to simply reflect the input signal rather than a reduction in the aquifer itself.

## Discussion

Influence of sediment characteristics on hydrochemical conditions during infiltration

Sophocleous (2002) pointed out the need to evaluate the hydraulic properties of the interface between surface water and groundwater, in particular with regard to their spatial variability. There are large differences in the properties of the sediments covering the base of the surface water bodies of bank filtration sites. At relatively fast flowing rivers, there is often little natural sedimentation or colmation and/ or artificial clogging taking place. For example at the river Glatt (Hoehn et al. 1983) or the river Oder (Massmann et al. 2004), the sandy and gravelly river beds did not show any reduced hydraulic conductivities. At sites like these, finer-grained material may even be washed away with the flow and consequently increase the hydraulic conductivities. The comparatively low hydraulic conductivities encountered in Berlin are the result of the hydrologic characteristics of the Berlin surface water system. The total discharge of the rivers Spree and Havel flowing through Berlin is in the order of 46.3 m<sup>3</sup>/s (average 1991–1995), whereas rivers like the Rhine or the Elbe (where bank filtration is also practised) have an average mean annual discharge of 2335 m<sup>3</sup>/s and 631 m<sup>3</sup>/s, respectively (Senatsverwaltung für Stadtentwicklung Berlin 2006). At the same time, the water flows through wide lakes, resulting in a slow and sluggish flow. It is unclear to what extent the

clogging (colmation) is of anthropogenic origin. The sewage loading may have increased the naturally occurring colmation by enhanced algae growth or sedimentation of an organic carbon layer (Sophocleous 2002).

However, the investigations at the infiltration zone revealed more reducing hydrochemical conditions in the groundwater below the lake at ~20 m distance from the shore compared to the groundwater near the shoreline (BEE205 and BEE206, respectively). In the latter case, the infiltrated water was mostly aerobic, while slightly into the lake the aerobic conditions reached only decimetres into the sediments (column study). Dousson et al. (1997) reported from a study at the Seine River in France that percolation velocity through the river sediments and organic matter content of the river sediments are the two key factors governing the evolution of the bank filtrate. As the mapping and the cores taken close to the observation wells in Berlin revealed, the sediment's organic matter content increased rapidly with distance from the shore while the hydraulic conductivities decreased which are the likely causes of the differences in the hydrochemical conditions. The column and the field study showed that the most significant redox changes occurred within 1 m of sediment passage. The results confirm the findings of Sophocleous (2002) and others, stating that the biogeochemical processes within the upper few centimetres of the surface water body sediments have a profound effect on the chemistry of the infiltrating surface water. Microbiological studies revealed that the interface sediments are the most active zones with regard to microbial activity. For example Marmonier et al. (1995) reported gradients of decreasing concentrations for biodegradable organic carbon (BDOC), bacterial abundances and microbial activity in the first metre of the sediment of the Rhône River in France. Brugger et al. (2001) showed a sharp decline in TOC concentrations and bacterial activity within the first metre of the river bank of the Enns. The large redox gradients at the Berlin site result from the difference in the sediment characteristics between aquifer and hyporheic zone which, in the Berlin case, lead to mostly anaerobic infiltration.

## The origin of the vertical redox stratification

As explained above, the infiltration became anaerobic a short way into the lake, causing the redox zones in Fig. 9 to be very narrow below the lake. With distance from the lake, the redox zones widened. In addition, the redox boundaries were horizontal. Hence the hydrochemical conditions were vertically stratified and became more reducing with depth, rather than with distance from the lake as observed by von Gunten and Kull (1986), Jacobs et al. (1988), Bourg and Bertin (1993), Lensing et al. (1994) and Massmann et al. (2004). Other authors reported

rather vertical redox zones. Richters et al. (2004) described a vertical redox zonation at a bank filtration site at the Rhine River in Germany, ascribed to different flow-path lengths. The vertical zoning of the bank filtrate at the river Glatt in Switzerland was also caused by different flow lengths (Hoehn et al. 1983). Here, fresh, shallow bank filtrate was sitting on top of older bank filtrate which infiltrated upstream of the investigated transect, overlying native groundwater.

The vertical redox zoning in Berlin may partly be a result of the different groundwater ages. Massmann et al. (2007) applied multiple age-dating methods at the site and revealed that the groundwater from the deeper layers of the aquifer is considerably older than the shallow bank filtrate (decades compared to months). This vertical age stratification is suspected to be caused by the fact that the impermeable lake base inhibits infiltration everywhere except at the shores. Consequently, the bank filtrate originates from infiltration zones at the nearest lake shores as well as from infiltration zones at greater distances. However, the vertical redox zoning may also be caused by re-oxidation of more reducing bank filtrate by oxygen delivered into the bank filtrate after infiltration, i.e. between the lake and the pumping well. Additional oxygen could be transported into the aquifer with rain water percolating through the permeable unsaturated zone or by diffusion through the unsaturated zone. As a third possibility, oxygen delivery might be enhanced by the waterlevel fluctuations caused by the irregular pumping regime. To our knowledge, this has never been described in the literature in the context of bank filtration. The fact that production wells have to be regularly redeveloped due to clogging with iron-oxyhydroxides supports this theory. In addition, elevated excess air concentrations (>12%) which were calculated as a by product during tritium/helium age dating in the shallow wells provide further evidance. Excess air is characterized by gas concentrations larger than equilibrium values (Heaton and Vogel 1981). In another context Williams and Oostrom (2000) successfully tested the hypothesis that water table fluctuations increase the oxygen transfer from air to water via enhanced exchange from entrapped air bubbles. Bourg and Bertin (1993) investigated biogeochemical changes during bank filtration at the Lot River in France and described a reduced anaerobic zone close to the river with intense microbial activity followed by aerobic conditions nearer the production well. They concluded that the observed redox processes were reversible and the re-oxidation of Mn<sup>2+</sup> was caused by aeration through the permeable unsaturated zone in combination with decreasing microbial activity within the aquifer. The additional O<sub>2</sub> input was ascribed to recharge by rain and irrigation. The fact that the redox zones at the Berlin site widen strongly suggests that one or more additional sources deliver oxygen to the bank filtrate after infiltration. The relative importance of the potential sources has yet to be quantified and follow-up studies are in progress.

#### The temperature influence on the redox conditions

The redox conditions during infiltration displayed a strong seasonal variation. Aerobic infiltration was only encountered during winter and, according to Fig. 10, the redox zoning given in Fig. 9 and derived from average concentrations of redox indicators at the site was only that wide in winter. In summer, O<sub>2</sub> was consumed within the hyporheic zone. The seasonal influence was still seen in well BEE203, in 50 m distance from the shore. While the seasonality of infiltration processes has sometimes been neglected in bank filtration studies (e.g. Bourg et al. 1989; Matsunaga et al. 1993; Bourg and Bertin 1993; Dousson et al. 1997; Petrunic et al. 2005), several studies have described seasonal variations in the chemical composition of the river and groundwater. In the Glatt river study,  $O_2$  was mostly consumed at the surface water/groundwater interface during warm months (Jacobs et al. 1988), owing to temperature-induced variations of the microbial activity in the river water and in the sediments of the riverbed (von Gunten et al. 1991). The annual cycles affected the concentration profiles of trace heavy metals (Hoehn et al. 1983; von Gunten and Kull 1986). Microbiological studies could show that the seasonal chemistry changes were related to microbial activity. Marmonier et al. (1995) observed seasonal variations in the BDOC of the riverbed sediments of the Rhône River, where decreases of BDOC only occurred when the microbial enzymatic activities were high. Brugger et al. (2001) found that temperature appeared to regulate the metabolic activity of interstitial bacteria in the hyporheic zone of the Enns River in Austria. But other than in Berlin, the seasonal influence diminished at a distance of >1 m from the banks at both sites. Miettinen et al. (1996) regarded bacterial enzymatic activities in bank filtered groundwater at a lake in Finland with a travel time of 1 and 4 weeks, respectively. The enzyme activities which decreased with bacterial abundance and production activity were strongly affected by seasonal temperature changes and could be followed into the groundwater. Recent studies were able to successfully model the water quality changes in dependence on varying groundwater temperatures during artificial deep well recharge (Prommer and Stuyfzand 2005) and basin recharge (Greskowiak et al. 2006). Although within the present study the microbial activity was not investigated, it can be assumed that the seasonality in the shallow bank filtrate was the result of variations in the microbial activity, which were induced by the temperature changes. The deeper bank filtrate (e.g. BEE202UP) was not subject to annual variations since the long travel times have buffered the temperature influence. In the column study, temperature changes were not simulated. Therefore, the column study is representative for summer infiltration conditions only.

#### Summary and conclusions

This study investigated the spatial and temporal variation of redox zones below at a lake bank filtration site in Berlin. The redox chemistry at the sight was linked to the highly heterogeneous properties of the sediments in the hyporheic zone. Infiltration was only aerobic near the shore, where sands dominated and the organic carbon content of the sediment was low. With increasing distance from the shore, as organic carbon content increased and hydraulic conductivities decreased, infiltration was anoxic and oxygen and nitrate were consumed within decimetres of flow. The redox zones were found to be vertically stratified, with conditions becoming increasingly reducing with depth of the aquifer. The vertical zonation is believed to partly be the results of increasing travel times with depth of the aquifer. Redox zones also widened towards the production well and possible mechanisms for the reoxidation of the infiltrate presented include (i) oxygen input with rain water percolating through the permeable unsaturated zone, (ii) diffusion of oxygen through the unsaturated zone and (iii) oxygen delivery by entrapment of air, possibly enhanced by the frequent water-level fluctuations. The redox condition displayed a strong seasonality, most likely to be the result of variations in the microbial activity induced by strong temperature changes of almost 25°C in the lake and >10°C in 50 m lake distance. The seasonal variations could be followed up to a distance of 50 m. Overall, this study revealed the sensitivity of the hydrochemical system to sediment properties of the hyporheic zone, temperature variations and, most likely, water table oscillations which similar bank filtration or artificial recharge schemes may also be sensitive to. The study provides a consistent conceptual model of how redox environments evolve below lake bank filtration sites. In addition, it supplies a basis for subsequent investigations on the fate of trace organic compounds such as PhACs, which are often redox sensitive.

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