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Spatial patterns of groundwater-lake exchange – implications for acid neutralization processes in an acid mine lake

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Abstract:

Exchange of groundwater and lake water with typically quite different chemical composition is an important driver for biogeochemical processes at the groundwater-lake interface, which can affect the water quality of lakes. This is of particular relevance in mine lakes where anoxic and slightly acidic groundwater mixes with oxic and acidic lake water (pH < 3). To identify links between groundwater-lake exchange rates and acid neutralization processes in the sediments, exchange rates were quantified and related to pore-water pH, sulfate and iron concentrations as well as sulfate reduction rates within the sediment. Seepage rates measured with seepage meters (−2.5 to 5.8 L m^{-2} d^{-1}) were in reasonable agreement with rates inverted from modeled chloride profiles (−1.8 to 8.1 L m^{-2} d^{-1}). Large-scale exchange patterns were defined by the (hydro)geologic setting but superimposed by smaller scale variations caused by variability in sediment texture. Sites characterized by groundwater upwelling (flow into the lake) and sites where flow alternated between upwelling and downwelling were identified. Observed chloride profiles at the alternating sites reflected the transient flow regime. Seepage direction, as well as seepage rate, were found to influence pH, sulfate and iron profiles and the associated sulfate reduction rates. Under alternating conditions proton-consuming processes, for example, sulfate reduction, were slowed. In the uppermost layer of the sediment (max. 5 cm), sulfate reduction rates were significantly higher at upwelling (>330 nmol g^{-1} d^{-1}) compared to alternating sites (<220 nmol g^{-1} d^{-1}). Although differences in sulfate reduction rates could not be explained solely by different flux rates, they were clearly related to the prevailing groundwater-lake exchange patterns and the associated pH conditions. Our findings strongly suggest that groundwater-lake exchange has significant effects on the biogeochemical processes that are coupled to sulfate reduction such as acidity retention and precipitation of iron sulfides. Copyright © 2012 John Wiley & Sons, Ltd.

KEY WORDS groundwater-lake exchange; acid mine lake; seepage flux; pH-profiles; chloride profiles; acid neutralization processes

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INTRODUCTION

Lakes are an integral part of groundwater flow systems (Winter *et al.*, 1998). The qualitative and quantitative description of the exchange between groundwater and lakes is of central importance, for example, for the management of these water resources because it can determine the water balance of lakes and also their water quality (Winter *et al.*, 1998; Sophocleous, 2002). Several studies report seepage rates in lakes with values ranging from -7 L m^{-2} d^{-1} to values as high as +475 L m^{-2} d^{-1} (Lee, 1977; Lee and Cherry, 1978; Brock *et al.*, 1982; Shaw and Prepas, 1990b; Shaw and Prepas, 1990a; Taniguchi, 1993; Rosenberry *et al.*, 2000; Kishel and Gerla, 2002; Alexander and Caissie, 2003; Simpkins, 2006; Zielinski *et al.*, 2007). Locally, even higher rates up to -2630 L m^{-2} d^{-1} have been reported (Rosenberry, 2000). However, mostly groundwater-lake exchange rates are lower and typically range between -10 and +50 L m^{-2} d^{-1}. Advective groundwater flow into the lake and the seepage of lake water into groundwater are major pathways for the transfer of solutes – such as oxygen, carbon, nutrients, but also pollutants and acidity – across the lake-sediment interface. This transition zone is typically characterized by strong physical (e.g. hydraulic potential, temperature) and biogeochemical (e.g. dissolved oxygen, redox potential) gradients (Winter *et al.*, 1998), because of active mixing of the two adjacent water bodies with different chemical loadings. Groundwater-lake exchange has been shown to influence the lake sediment pore-water composition (Schafran and Driscoll, 1990; Schuster *et al.*, 2003; Blodau, 2005), biogeochemical processes in the lake sediments (Blodau, 2005) and lakeshore ecosystems (Sebestyen and Schneider, 2004). Direction and magnitude of the exchange rates are key controls for such effects, and a reliable quantification of exchange rates is an important prerequisite to better understand the underlying processes.

In this study, we investigated the effects of groundwater-lake exchange patterns and dynamics on acid neutralization processes in the sediments of an acid mine lake. Groundwater-lake exchange in former open pit mining areas is of major importance because it is directly related to the water quality of the lakes (Banks *et al.*, 1997). The usability of mining lakes for recreation or as

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water reservoirs is often severely restricted because of acid mine drainage following flooding with ground- and surface waters. Oxidative weathering of sulfide-containing minerals in the mining dumps leads to an enrichment of groundwater with dissolved ferrous iron and sulfate (Blodau, 2006). Groundwater-borne ferrous iron and its precipitation as iron oxides (e.g. schwertmannite or jarosite) at the groundwater-lake interface result in iron-rich and strongly acidic lake water (pH often < 3). The groundwater affected by seepage from the mining dumps is often only weakly acidic because of buffering processes; typical pH values lie between 3.5 and 6 (Blodau, 2006 and references therein). Hence, upwelling groundwater as well as downward seepage of acidic lake water can be assumed to exert a significant influence on biogeochemical processes at the groundwater-lake interface, which are linked to the overall acidity budget of a mining lake (Blodau, 2006).

To study these effects, we chose Mine Lake 77 (ML77) in the Lusatia mining area (East Germany), which is a well-characterized system, in terms of both hydrology (Knoll *et al*., 1999; Fleckenstein *et al*., 2009) and biogeochemistry (Blodau 2005, Knorr and Blodau 2006). Blodau (2005) attributed differences in sediment pore-water chemistry and calculated acidity balances observed between two locations at the northern and southern shore of ML77 to the different magnitudes of groundwater upwelling reported for these locations by Knoll *et al*. (1999). Flow conditions were not quantified in the study by Blodau (2005). Later, Fleckenstein *et al*. (2009) were able to demonstrate that ML77 was not only receiving groundwater inflows, as reported by Knoll *et al*. (1999), but instead, exchange patterns were more diverse and in the South, ML77 was predominantly losing water to the underlying aquifer. In this contribution, we link spatially explicit information on groundwater lake exchange rates with detailed synchronous measurements of key biogeochemical variables and processes directly at the respective sites. We hypothesize that despite spatial and temporal variability of exchange fluxes, characteristic exchange regimes can be identified, which are associated with distinct patterns in the key biogeochemical variables. We expect that the upwelling of only mildly acidic groundwater (pH 4 to 5) increases the pore water pH close to the water-sediment interface and, in turn, enhances sulfate reduction. Proton-consuming sulfate reduction has been reported to preferentially occur at pH values between 4 and 5 (Gyure *et al*., 1990; Küsel, 2003). If sulfate reduction exceeds iron reduction at favorable pH conditions, groundwater-borne iron can be retained in the sediments as iron sulfides, thereby reducing the iron flux and subsequently the acidity flux into the lake (Peine *et al*., 2000; Blodau, 2005; Knorr and Blodau, 2006). Such a dependency would have important implications for the generation and consumption of acidity at the groundwater-lake interface (e.g. by precipitation of iron-sulfides), not only in mining lakes.

The main objectives of this work were as follows: a) to characterize the dominant space and time patterns of groundwater-lake exchange and to quantify flux rates using direct and indirect methods, and b) to directly link the observed exchange patterns and rates to acid neutralization processes in the sediments at selected key locations. Exchange rates were measured directly using seepage meters. Indirect estimates were obtained from inverse simulation of vertical pore-water chloride profiles from pore-water peepers deployed next to the seepage meters and from mapped vertical temperature profiles. General pore-water chemistry was also obtained from the pore-water peepers. Acid neutralization processes were assessed based on the variables pore-water pH, sulfate and ferrous iron concentrations as well as sulfate reduction rates in the sediments. These variables are believed to be the key controls for the regulation of acidity at the groundwater-lake interface (Blodau, 2006).

MATERIALS AND METHODS

Study site

The study site – ML77 – is located in Lusatia, East Germany (Figure 1). This region has been impacted by mining activities since the 1890s. Abandoned open pits from lignite mining have been flooded, starting in the 1960s. ML77 formed during the late 1960s and is situated within a chain of lakes (connected by small canals) draining into the river Schwarze Elster. The mined 2nd Lusatia coal seam separates the lower regional tertiary aquifer from the upper aquifer complex, which consists of tertiary and quaternary sediments – mainly silt, sand and gravel (Nowel, 1994). These sediments were removed during active mining. The resulting mining dumps form the northern shoreline of ML77, whereas in the southeast, undisturbed tertiary sediments prevail (Fleckenstein *et al*., 2009). The regional groundwater flow direction is from north and northeast to southwest (Knoll *et al*., 1999). ML77 has a surface area of 24.4 ha and a maximum depth of about 8 m (Knoll *et al*., 1999). At the outlet of the downstream lake, a weir regulates the water level of the lakes upstream (including ML77). Chemically, ML77 is strongly affected by acid mine drainage, lake water chemistry is dominated by ferric iron and sulfate and characterized by a low pH of about 2.8 (Peine *et al*., 2000). The lake sediments at ML77 are rich in the iron minerals schwertmannite and goethite.

Seepage meter measurements

Exchange rates between groundwater and surface water were quantified using seepage meters, constructed according to (Lee, 1977). Modifications, described in detail in Fleckenstein *et al*. (2009), are mainly related to material and size of the open-end cylinder and the duration of measurements. The stainless steel seepage meters with a diameter and height of 0.5 m were pushed into the lake sediment. A closable valve on top of the seepage meters allowed the removal of trapped gas bubbles potentially emitted from the lake sediment. The valve was opened before and after the seepage meter measurements to check, if gas had collected in the seepage meter during the measurement. After equilibration and

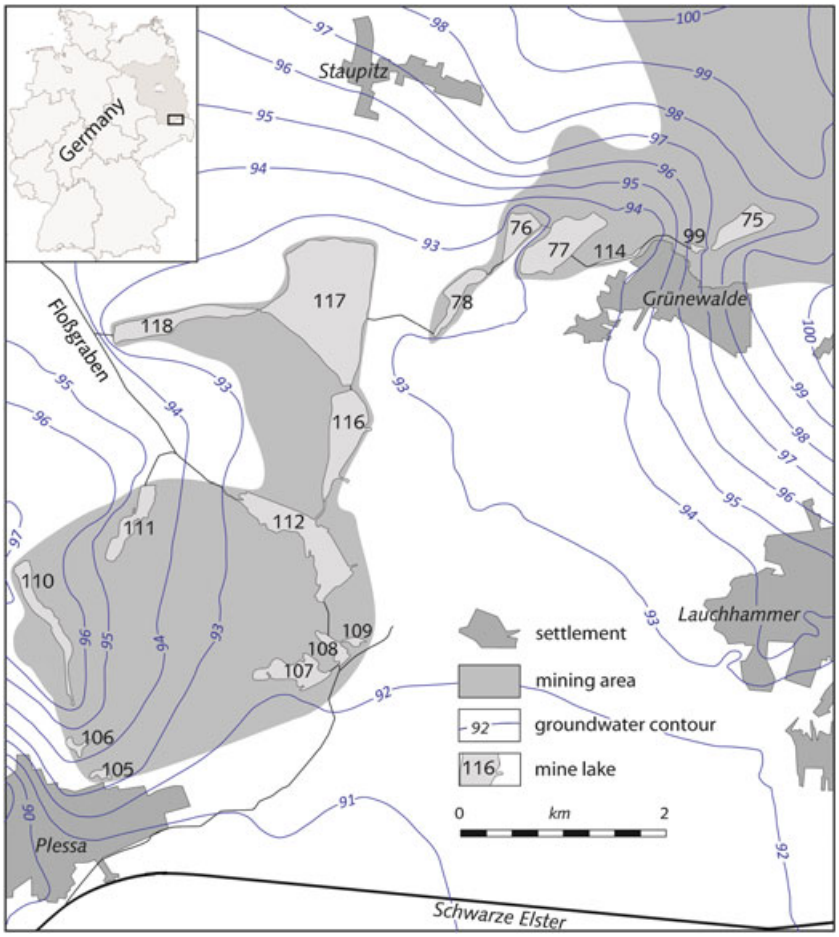

Figure 1. Map of the study area showing the different mine lakes, the surface water connections between them and the regional groundwater contours for the year 2008 – groundwater head data were obtained from the Lausitzer und Mitteldeutsche Bergbau-Verwaltungsgesellschaft - LMBV (adapted from Peine *et al*., 2000)

deaeration, 2-liter PVC-bags were connected to the seepage meters via a PVC-tube (inner diameter 12 mm). All bags were pre-filled with an initial volume of tap water (between 300 and 500 ml) to minimize the "bag-memory" effect as suggested by Shaw and Prepas (1989) and Blanchfield and Ridgway (1996). The tubes as well as the bags were air-free at the time of connection to reduce resistivity against water exchange (Sebestyen and Schneider, 2001; Murdoch and Kelly, 2003). Six sites were selected for the measurements based on the general exchange patterns described in Fleckenstein *et al*. (2009) and the characteristic shapes of the pore-water pH-profiles from the peeper measurements. They reflect the characteristic exchange regimes at ML77 with predominantly upwelling of groundwater (70–100 % of all measurements at the respective sites in this study) in the North (sites subsequently referred to as UP) and exchange fluxes alternating between upwelling and downwelling in the South (sites subsequently referred to as ALT). All six sites are in areas that are believed to be connected to the upper aquifer (tertiary and quaternary sediments), which in the North is affected by the seepage water from the mining dumps. Seepage meters at the deeper sites (~ 3 m water depth) were installed by scuba divers in the spring of 2008. At the shallow sites (0.6 to 1 m water depth; location: ALT-1, ALT-2, UP-1, and UP-2), the collection bags for seepage flux measurements were deployed at the lake bottom, whereas at the deeper sites (location: ALT-3 and UP-3), the bags were fixed to a buoy and lowered to about 0.5 m below the water surface to reduce the effect of wind and waves (Boyle, 1994). The bags were connected to the seepage meters for 12 to 24 hours. Using the weight of the bags before and after connection, seepage rates were calculated as described in Lee (1977). During the study period from February 2008 to June 2009, measurements were conducted at least once a month, except for the winter months when ice covered the lake.

Temperature mapping

To evaluate small-scale variability in exchange fluxes, sediment temperatures in the shallow lake sediments were mapped in the field (March 2009) using a stainless steel temperature probe containing eight thermocouples (Figure 2). Along two transects (water depths = 0.4 m and 0.8 m) at the northern shore, the probe was driven into the sediment to a depth of about 1 m with 4 m lateral spacing (for location of the transects, see Figure 3). After a 5-minute equilibration time, temperatures were recorded. Assuming a quasi-constant temperature of 11.7 °C in the deeper sediment (measured in a nearby piezometer screened at 4.5 m depth in the lake sediment), advective flux rates were

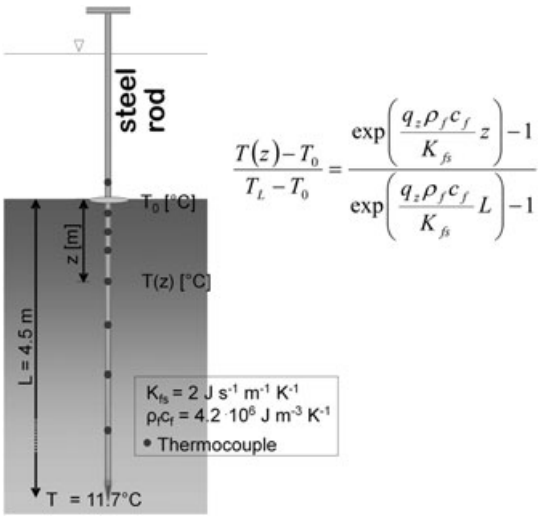

Figure 2. Schematic setup of the temperature probe and the analytical solution to the 1D steady state heat transport equation by Bredehoeft and Papadopulos (1965) used for the inversion of exchange flux rates

inverted from a steady-state analytical solution to the 1D heat flow equation from Bredehoeft and Papadopoulos (1965) as described in Schmidt *et al.* (2006).

Pore-water chemistry and sediment properties

Concentration-depth profiles of chemical species in the sediment pore-water were determined using 60 cm long pore-water peepers with a spatial resolution of 1 cm (Hesslein, 1976). They were pre-filled with deionized, degassed water, covered with a permeable membrane (0.2 µm pore size, HT Tuffryn membrane, PALL Corporation), and installed at the sediment-lake water interface. To minimize the effects of small-scale heterogeneity on the different flux estimation methods, peepers were placed within 1 m from the seepage meters. Equilibration time was at least 3 weeks, mainly to avoid effects from the sediment disturbance during installation. The time for the diffusive equilibration of concentrations is typically on the order of a few days for the used peepers with 5 ml chambers and a diffusive length of about 1 cm (Laskov *et al.* 2007). As for the seepage meters, peepers in deep water were installed by scuba divers and removed from the sediment between summer 2008 and spring 2009 (exact removal dates are indicated in Figure 3). After retrieval of the peeper, the pH was directly measured in the field using a sulfide-resistant pH-electrode (Mettler Toledo Inlab 412) in a sample aliquot. After transport to the lab, chloride and sulfate concentrations were measured on filtered samples (nylon syringe micro-filter, 0.2 µm, Roth) with ion chromatography (Metrohm IC-System Metrosep Anion Dual 3 column at 0.8 ml min^{-1} flow rate, conductivity detection after chemical suppression). Concentrations of dissolved ferrous iron were measured photometrically by the phenanthroline method at 512 nm (Tabatabai, 1974; Tamura *et al.*, 1974).

Lake sediment cores were taken in November and December 2008 by a gravity corer (Uwitec) in acrylic glass tubes. The cores were sliced according to physical properties

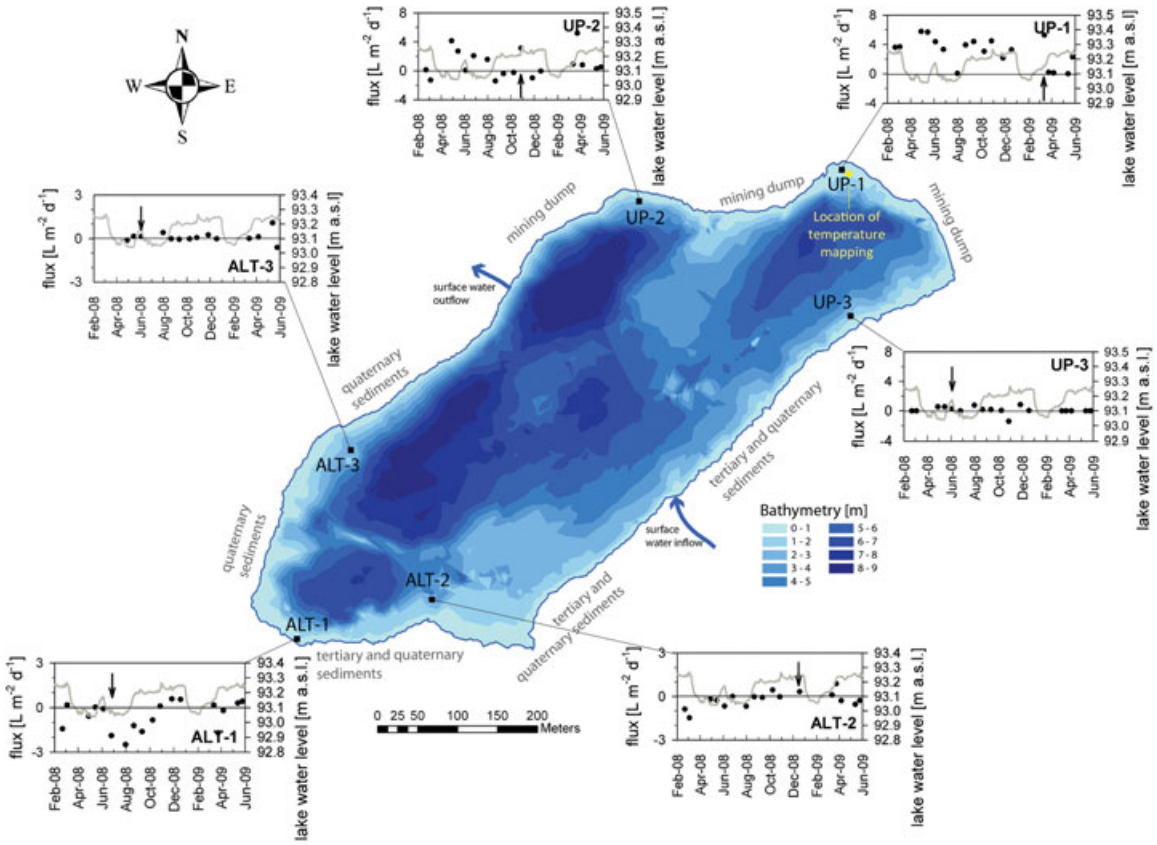

Figure 3. Seepage meter and pore water peeper sites and seepage rates (L m^{-2} d^{-1}) between February 2008 and May 2009 (positive = upwelling). The grey line in the seepage plots depicts lake water level, and the arrow indicates the date of the removal of the pore water peepers

(color, texture) as described by Peine *et al*. (2000). For each layer, porosity was determined by drying of a given volume of sediment until no further changes in weight could be observed. Sulfate reduction rates were determined for the uppermost layer (0 to 2.5. . .5 cm depth) using the radiotracer method (Jorgensen, 1978) in slurries from fresh sediment samples (sodium chloride solution 7‰). Samples were incubated with 40 kBq of oxygen-free ^{35}S solution (sodium sulfate, Perkin Elmer) for ca. 24 h at 10 °C. Total reduced inorganic ^{35}S was extracted under a N_2-stream and trapped in NaOH solution. An aliquot of the NaOH solution and of the residue were measured with a scintillation cocktail (Aquasafe 300Plus, Zunsser Analytic) on a Beckmann LS 6500 scintillation counter. Measured counts were corrected for counting efficiencies of the cocktail and the instrument. Sulfate reduction rates were calculated after Jorgensen (1978). The required sulfate concentration was measured in an aliquot of the slurry as described above. For comparison, the pH in the slurries was measured and found to be comparable to the pore-water pH (+/− 0.5 pH units), except for location UP-2 (pH of 3.0 in the slurry *vs* ~5 in the sediment).

Inverse modelling with VS2DT

In addition to the seepage meter measurements, groundwater-surface water exchange rates were inversely derived from vertical chloride profiles. Chloride, a common ion in (ground)water, is highly mobile, not involved in common geochemical reactions (Cox *et al*., 2007) and, therefore, an adequate conservative tracer. For inverse simulation, the 2-dimensional (2D) numerical code VS2DT (Healy and Ronan, 1996) was used. For transport, VS2DT uses a finite-difference solution to the advection-dispersion equation. To estimate the advective component of chloride transport and to fit the measured chloride concentration-depth profile, a 1D transport model for the upper sediment was set up. The length of the model domain was equal to the measured chloride concentration profile (depths of the pore-water peeper in the sediment). The model was discretized into 1 cm slices, each containing an observation point and run as a steady-state model for flow and transport. The upper and lower ends of the 1D model domain were treated as first-type boundary conditions (Dirichlet) for both flow and transport. Chloride concentrations at the boundaries were obtained from the cells of the pore-water peepers right at the water-sediment interface and at the lower end of the peeper. Variations in chloride concentrations at the lower end between sites are attributed to variability of chloride concentrations in the adjoining groundwater caused by differences in geology and sediment composition. The hydraulic gradients were fixed based on estimates from head measurements in nested piezometers at sites UP-1 and ALT-2 (−0.0024 and 0.0024, respectively), and the hydraulic conductivity was varied to fit the measured profile. In line with Fleckenstein *et al*. (2009) and based on Gelhar *et al*. (1992), hydrodynamic dispersivities of 0.01 m and 0.06 m were assumed for the shallow and deeper locations, respectively, reflecting differences in sediment texture. Table I summarizes the applied flow and transport parameters. The diffusion coefficient for chloride was calculated after Lerman (1978) from the self-diffusion coefficient for chloride of $2.3 \cdot 10^{-9}$ m^2 s^{-1} (Appelo and Postma, 2005) times the squared value of the sediment porosity.

Table I. Flow and transport parameters

		[cm]	[%]	[$m^2 s^{-1}$]
Shallow	ALT-1&2,	0. . .30.5	40	3.3 E-10
	UP-1&2	30.5. . .lower end	35	2.5 E-10
Deep	ALT-3, UP-3	0. . .20	90	1.6 E-9
		20. . .25	80	1.3 E-9
		25. . .30	70	1.0 E-9
		30. . .35	60	7.3 E-10
		35. . .lower end	50	5.1 E-10

RESULTS

Space and time patterns of groundwater-lake exchange

Measured seepage rates at ML77 were spatially as well as temporally variable (Figure 3). In the North, the lake predominantly received groundwater inflow. Rates of groundwater upwelling into the lake ranged from +0.1 to +5.8 L m^{-2} d^{-1}. Sites UP-2 and UP-3 with generally the lowest flux rates also had occasional periods of downwelling. In the South, downward seepage of lake water into the aquifer (>=50% of the time) as well as

Table II. Results from seepage meter measurements and inverse simulations of chloride profiles for all sites: measured rate [L m^{-2} d^{-1}] on the day of retrieval of the pore-water peeper and mean of measured rates [L m^{-2} d^{-1}]; modeled rate [L m^{-2} d^{-1}], range of the observed chloride concentrations – range Cl_{obs} [µmol L^{-1}], absolute and relative RMSE (root mean square error) between modeled and observed chloride concentrations [µmol L^{-1} and %], and coefficient of determination [ ]

location	ALT-1	ALT-2	ALT-3	UP-1	UP-2	UP-3
Date	24 June 2008	18 December 2008	03 June 2008	12 March 2009	28 October 2008	04 Jun 2008
Measured rate	−1.88	0.34	0.14	5.28	3.15	0.29
mean rate	−0.09	−0.27	0.04	3.68	0.82	0.23
modeled rate (s)	−0.03/0.03	0.04/0.23	−1.80/-0.21	8.14	0.27	0.82
range Cl_{obs}	1300–2150	981–1220	476–900	275–735	215–900	760–1146
RMSE [μ mol l^{-1}]	45/49	41/42	32/51	14	39	27
RMSE [%]	5.7	17.6	12.0	3.0	5.7	7.0
R^2	0.99/0.99	0.90/0.95	0.97/0.98	0.97	0.98	0.99

upwelling of groundwater into the lake were observed and ranged from −2.5 to +1.1 L m^{-2} d^{-1}. Mean seepage rates (Table II) were generally higher at sites adjacent to the mining dumps (locations UP-1, UP-2) than at sites with underlying geogenic tertiary and quaternary sediments (ALT-1–3) or sites characterized by the transition between mining dumps and geogenic sediments (UP-3). The mapping of vertical temperature profiles in the lake sediments at the northern shore (for location see Figure 3) revealed small-scale variations in temperatures in the sediment (Figure 4). Not only absolute temperatures but also the temperature gradients varied over short distances, indicating small-scale variations in advective heat and water fluxes. Calculated seepage rates ranged from 2.3 to 85.9 L m^{-2} d^{-1}.

Seepage rates fluctuated considerably at the sites ALT-1, ALT-2, UP-1 and UP-2 and were relatively steady only at the two sites UP-3 and ALT-3 (Figure 3). Lake water levels were characterized by moderate fluctuation over the measurement period (range was about 20 cm). Data from the sites in the North (UP-1, UP-2, UP-3) indicate some negative correlation between the observed upward seepage rates and lake water levels. In the South, at sites ALT-2 and ALT-3, flux rates are very low and show no clear correlation with lake water levels, whereas at site ALT-1 downward seepage rates seem to increase with decreasing lake water levels.

Pore-water chloride profiles and inverted seepage rates

Chloride profiles from the pore-water peepers as well as the simulated profiles and the associated flux rates at the six sites are shown in Figures 5 and 6. For the alternating sites (Figure 5), where observations could not be optimally represented by a single model, two simulated profiles for different flux rates are depicted, which envelope the observed concentrations profile. The root mean squared error (RMSE) between the measured and simulated chloride depth profiles is low to moderate, with generally lower values for the upwelling as opposed to the alternating sites

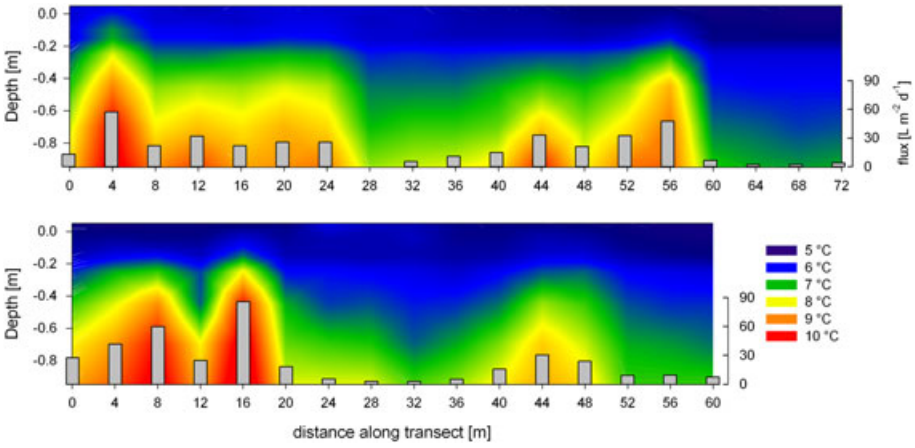

Figure 4. Temperature mapping in the lake sediments at the northern shore in 0.4 (upper panel) and 0.8 m water depth (lower panel). Bars indicate the calculated seepage rates (positive = upwelling)

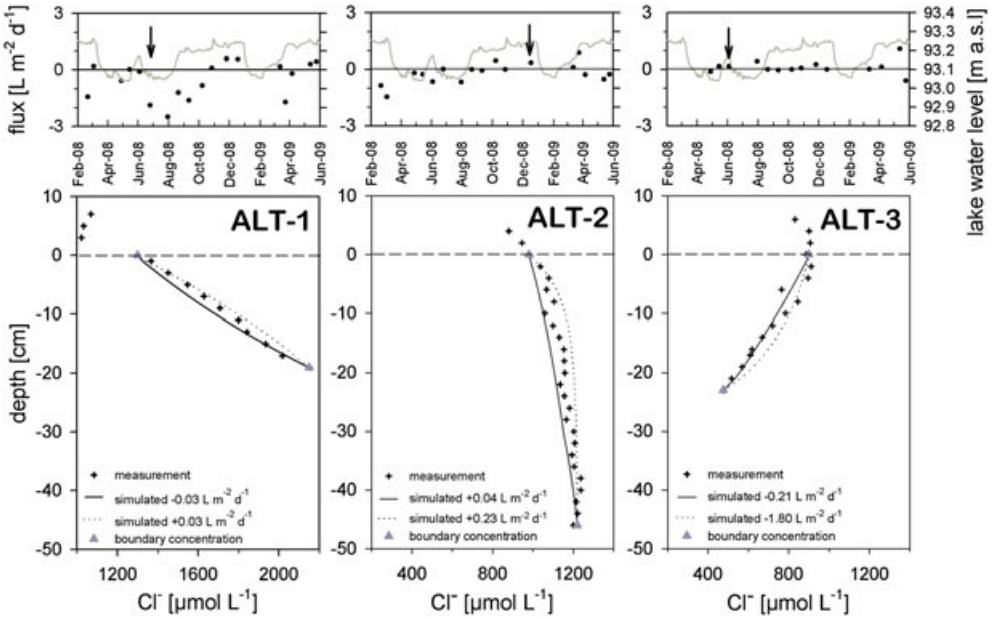

Figure 5. Measured and simulated pore water profiles of chloride (bottom) for sites with alternating flow (top). Note the different scale of the chloride concentration (x-axis) in the graph for ALT-1. Arrows in the scatter plots indicate the removal dates of the pore-water peepers

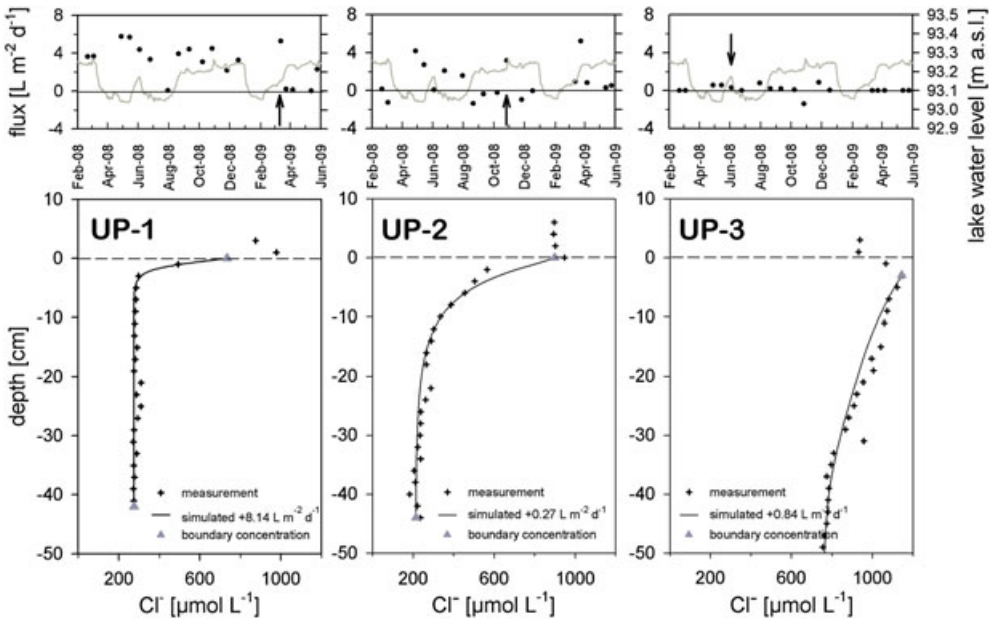

Figure 6. Measured and simulated pore water profiles of chloride (bottom) for sites with upward flow (top). Arrows in the scatter plots indicate the removal date of the pore-water peepers

(Table II). Relative RMSE values (RMSE normalized by the absolute concentration range in the profile) were below 7% at the upwelling sites as opposed to maximum values of up to 17% at the alternating sites (Table II). The temporal evolution of the flux rates from the seepage meters and the time of peeper removal are plotted in the top panel of Figures 5 and 6.

Mean chloride concentration in the lake water was around 1000 µmol L^{-1}. Concentrations in the sediment at the lower end of the peepers differed among the sampling sites. In the South where tertiary sands with remains of coal are partially overlain by quaternary material, concentrations between 1000 and 2000 µmol L^{-1} chloride were measured (ALT-1, ALT-2). In contrast, chloride concentrations of less than 400 µmol L^{-1} are typical for the sites adjacent to the mining dumps at the northern shore (UP-1, UP-2). Concentrations at the sites at the western (ALT-3) and eastern (UP-3) shores were intermediate with values between 400 and 800 µmol L^{-1}. The shapes of the chloride profiles at the alternating sites (Figure 5) clearly show signs of the transient flow conditions and deviate from the smoother shapes that would result from a flow regime at steady-state. For instance, the curvature in the upper part of the simulated profile at ALT-1 indicates upward flow, whereas it suggests downward flow in the lower part. At site ALT-2 the simulated flux rates (0.04 to 0.23 L m^{-2} d^{-1}) are in reasonable agreement with the seepage meter rate (0.32 L m^{-2} d^{-1}) on the day of the peeper removal (Table II). At ALT-1 the inverted flux rates (−0.03 to 0.03 L m^{-2} d^{-1}) underestimate the seepage meter rate from the day of peeper removal (−1.88 L m^{-2} d^{-1}), but reasonably agree with the mean flux rate over the measurement period (−0.09 L m^{-2} d^{-1}, Table II). At ALT-3 simulations suggest downward flow, whereas the seepage meter rate on the day of the peeper removal indicated a small upward flux (0.14 L m^{-2} d^{-1}). However, over the entire measurement period, seepage meter fluxes at this site frequently alternated in direction at very small rates.

The chloride profiles at UP-1 and UP-2 (Figure 6) show the steep concentration gradients close to the sediment-water interface that are indicative of significant groundwater upwelling (as opposed to a quasi-linear diffusive chloride profile that would be expected for negligible seepage rates). At UP-3, the concentration gradient right at the interface is less pronounced, and the highest chloride concentration with 1150 µmol L^{-1} is located 3 cm below the water-sediment interface (Figure 6). Some chemical transformation process, considered below in the discussion section, acts as an additional source of chloride in the uppermost layers. This elevated concentration was assigned as boundary condition in the VS2DT model. The modeled seepage rate was highest at UP-1 (8.14 L m^{-2} d^{-1}) and agrees reasonably with the seepage meter rate from the day of peeper removal (5.28 L m^{-2} d^{-1}). At site UP-2, where the flow direction from the seepage meter at the time of peeper removal was upward compared with downward right before and after the time of removal, the modeled rate (0.27 L m^{-2} d^{-1}) underestimates the seepage meter rate (3.15 L m^{-2} d^{-1}). However, as for ALT-1, the modeled rate agrees reasonably well with the mean flux rate over the measurement period (0.82 L m^{-2} d^{-1}). At UP-3, modeled as well as observed seepage rates are low (compared with the other two UP-sites) and the seepage meter rate on the day of peeper removal and the mean rate (0.29 and 0.23 L m^{-2} d^{-1}, respectively) both reasonably agree with the inverted rate (0.82 L m^{-2} d^{-1}). With increasing flow rates, the gradient of the chloride concentrations between lake water and groundwater extends over a shorter depth interval (becomes steeper) and is shifted towards the sediment-water interface (Figure 6, UP-1 as opposed to UP-2).

pH, SO_4 and Fe-II profiles and SO_4 reduction rates in the sediment

The pore-water pH increased with depth in the sediment at all sites from about 2.8, which represents

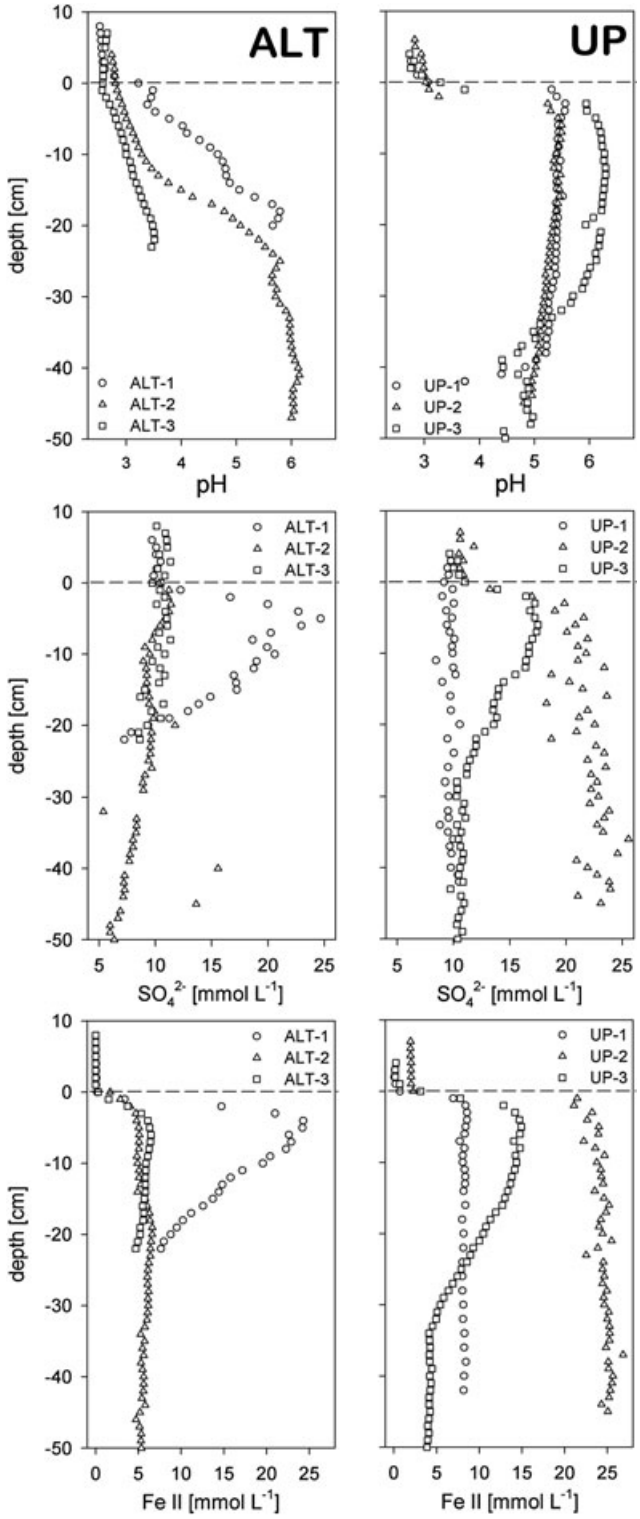

Figure 7. Pore-water pH, sulfate and ferrous iron profiles at all sampling sites. The dashed line (0 cm depth) marks the sediment-water interface. Sites are grouped according to their prevailing flow conditions: ALT for alternating conditions (left), UP for groundwater upwelling (right)

lake water pH, to values of 3.5 to > 6.0 (Figure 7). Depending on the predominant flow regime, characteristic pH-profiles had developed. At sites with alternating conditions (Figure 7, ALT), lake water with a low pH penetrated into the sediment, and maximum pH values were reached at the lower end of the profile. No sharp increase of the pH directly below the sediment-water interface occurred at these sites, and pH increased rather steadily with depth. At sites with upwelling conditions, the pH within the sediments increased from lake water pH to values of > 5 within a few centimeters below the sediment-water interface (UP, Figure 7). There, maximum pH-values were measured in the upper part of the profile, slightly decreasing with depth.

Sulfate concentrations above the surface water-sediment interface were close to 10 mmol L^{-1} at all sites (Figure 7). In two of the three sediments with alternating flow (ALT-2 and

ALT-3), sulfate concentrations somewhat decreased with depth and ferrous iron concentrations remained flat. Another site (ALT-1) was characterized by a combined sulfate and ferrous iron peak of >20 mmol L^{-1}. Sulfate and iron concentrations at sites with upwelling conditions reflected mostly the chemical composition of upwelling groundwater. Sites UP-1 and UP-2 had higher rates of upwelling groundwater with 8.14 and 0.82 L m^{-2} d^{-1} at this time, based on the modeling of chloride profiles (Figure 6). In agreement with faster advection rates, they were characterized by nearly flat sulfate and iron profiles near 10 and 25 mmol L^{-1}, respectively. At the site UP-3, with the smallest upwelling rate of 0.27 L m^{-2} d^{-1}, a peak of iron and sulfate occurred between 3 and 20 cm depth. This feature was matched by a pH increase. Both patterns are in line with slow groundwater upwelling in combination with iron reduction and schwertmannite disintegration. All of the sites with groundwater upwelling were characterized by steeper gradients of ferrous iron at the sediment-water interface than the sites with alternating conditions (Figure 7).

Sulfate was reduced in the uppermost sediment layer (0 to max. 5 cm) at rates of 22 to 698 nmol g^{-1} d^{-1} (Table III). Rates were significantly ($\alpha = 0.05$) lower at the ALT sites (< 220 nmol g^{-1} d^{-1}) compared with the UP sites (> 330 nmol g^{-1} d^{-1}).

DISCUSSION

Space and time patterns of groundwater-lake exchange

The observed spatial pattern of groundwater-lake exchange at ML77 was heterogeneous. Exchange rates were in the same range as values commonly reported for other lakes (e.g. (Lee, 1977; Shaw and Prepas, 1990b; Shaw and Prepas, 1990a; e.g. Boyle, 1994; Simpkins, 2006). Seepage rates obtained from the seepage meter measurements and the inverse simulation of chloride profiles indicated predominantly upward seepage of groundwater into the lake in the North and alternating conditions with a slight tendency for downward seepage of lake water into the aquifer in the South. This general pattern is in line with Fleckenstein *et al*. (2009) but in contrast to earlier work, which had characterized the lake as an inflow lake (Knoll *et al*., 1999). It reflects the regional groundwater flow direction from northeast to southwest. According to Freeze and Cherry (1979), ML77 can be classified as a through-flow lake. The evolution from an inflow lake to a through-flow lake reflects the changes in regional groundwater flow caused by the ongoing flooding of other large mining pits in the North of ML77. Rising groundwater levels in the North and Northeast of the lake (Figure 1) presumably raised lake water levels in ML77 slightly. In contrast, groundwater levels in the South of the lake remained relatively constant as they are buffered by the drainage level of the nearby river Schwarze Elster, which represents the main groundwater discharge area in the region. These changes reduced and eventually reversed the hydraulic gradient between groundwater and the lake in the South causing lake water to flow into the aquifer. The relatively low downward gradients compared with the larger upward gradients in the North can temporarily reverse in response to small changes in local hydrologic conditions (lake water level, hydraulic heads in the underlying aquifer).

Seepage rates in the South of the lake, where the aquifer is made up of undisturbed geogenic sediments, were lower and varied less in space than in the North, presumably because of the finer texture of the tertiary sands, which are spatially also more homogenous compared with the dumped material (LBV, 1995). In the North, where the subsurface consists of mining dump material, seepage rates were generally higher and showed more variability between sites. Similar spatial variations in seepage rates along the northern shore of ML77 have also been reported by Knoll *et al*. (1999) and Fleckenstein *et al*. (2009). The results from the small-scale temperature mapping at the North shore indicated significant temperature variations in the shallow sediments over short distances (Figure 4). The seepage rates inverted from the vertical temperature profiles varied by almost two orders of magnitude over less than 10 m. Although the absolute values of the inverted rates need to be viewed with caution, as the assumption of a thermal steady state could be violated locally (Schornberg *et al*., 2010), relative differences suggest significant small-scale variability in exchange fluxes. Subsequent seepage meter measurements at the thermal hotspot with the highest inverted flux rate (85 L m^{-2} d^{-1}, Figure 4, lower panel at 16 m) repeatedly recorded flux rates in excess of 55 L m^{-2} d^{-1}.

As opposed to much smaller rates in the immediate vicinity (data not shown). These small-scale variations in seepage rates cannot be explained by variations in macroscopic hydraulic boundary conditions (e.g. regional groundwater flow pattern) and are attributed to heterogeneities in the dumped material. Although no specific information on the dumping technique during mining and the resulting variations in texture and subsurface structure of the mining dumps at ML77 or for other mine lakes in the area (Hofmann *et al*., 2008) were available, the dumped materials are typically heterogeneous (Bozau and Strauch, 2002) and variations in the grain size distribution, bulk density and pore-volume of mine tailings within a few meters are common. Thin iron crusts that

Table III. Sulfate reduction rates [nmol g^{-1} d^{-1}] in the uppermost sediment layer

	Sampled depth [cm]	SRR [nmol $g^{-1}d^{-1}$]		Sampled depth [cm]	SRR [nmol $g^{-1}d^{-1}$]
ALT-1	0 - 3.0	75	**UP-1**	0 - 4.5	639
ALT-2	0 - 5.0	23	**UP-2**	0 - 3.5	336
ALT-3	0 - 4.5	212	**UP-3**	0 - 2.5	698

were locally observed at the top of or within the shallow lake sediments in the North shore may explain some of the observed variations.

Temporal changes in seepage rates can only partly be explained by variations in lake water levels, which were associated with water level changes in the connected lake ML76 (Figure 1) caused by the weir at the outflow of ML76 and periods of strong precipitation or evaporation. At the sites in the North (UP-1, UP-2, UP-3) seepage rates indicate a mild negative correlation with lake water levels and upward seepage fluxes are generally higher for lower lake water levels than for high lake water levels (Figure 3). This tendency is most pronounced at the sites with the highest exchange rates (UP-1, UP-2) and much less for sites with low exchange rates (UP-3, ALT-2, ALT-3). This is probably caused by a relatively quick equilibration between lake water levels and hydraulic heads in the adjoining aquifer at the sites that generally show small head differentials between lake and groundwater (UP-3, ALT-2, ALT-3). This can be seen at ALT-3, where the lowest seepage rates and minimal fluctuations, which practically do not correlate with lake water levels, were observed (Figure 3). Groundwater heads in the narrow ridge of quaternary sediments between the two adjacent lakes ML77 and ML76 (see Figure 1) are strongly controlled by the water levels in the lakes. As the two lakes are connected by a short canal and, therefore, have similar water level fluctuations, groundwater heads in the quaternary sediments adjacent to site ALT-3 quickly equilibrate to lake water levels. Consequently, the overall hydraulic gradients between the lake and the adjoining aquifer hardly change, resulting in the relatively steady flux rates observed at this site. At site ALT-1, the relationship between seepage rates and lake water levels is more complex and almost seems to be reversed. The highest rates of downward seepage were recorded during low lake water levels in late June and August of 2008. The transition from lower to higher rates of downward seepage between early June and August, when lake water levels were constantly low, probably reflects the seasonal decline in groundwater levels in the adjacent aquifer to the South of the lake. Similarly, the subsequent decrease in downward seepage rates and the eventual reversal to upwelling conditions between the later summer and fall is presumably caused by the seasonal recovery of groundwater heads after the dry summer period. At ALT-1, seasonal variations in groundwater heads in the adjacent aquifer seem to be the dominant control of seepage fluxes as opposed to fluctuations of lake water levels. These results highlight that lake water levels are not the only significant control for temporal patterns in groundwater lake exchange and instead seasonal changes and fluctuations in hydraulic potentials in the connected aquifers can dominate temporal variability in exchange fluxes. The geologic structure and heterogeneity of the aquifer also affect local groundwater head fluctuations by causing the system to react with different time delays and to different degrees to changes in the hydro-meteorological forcing. Such effects are presumably also the main reason for the short-term fluctuations that were observed at most sites. In some cases, these variations could be related to individual rainfall events, which may have caused spatially differentiated responses in local groundwater heads. The complex geology of artificial mine lakes including heterogeneous mining dumps and tailings can further exacerbate such effects (Fleckenstein *et al.*, 2009). However, similar fluctuations in groundwater-lake exchange rates have also been reported for natural lakes (Sebestyen and Schneider, 2001; Kishel and Gerla, 2002) and are likely quite common in most groundwater-lake systems.

Chloride profiles and modeled vs. measured seepage rates

Lake water chloride concentrations at the water-sediment interface were relatively uniform across the lake at values slightly below 1000 μmol L^{-1}. In contrast, concentrations in the sediments varied considerably with a general pattern of concentrations increasing from UP-2 to ALT-1 in clockwise direction around the lake and a decrease going back up along the western shore. This general pattern corresponds with changes in the geology surrounding the lake, with mining dumps in the North, a transition from mining dumps to geogenic tertiary and quaternary sediments in the East, geogenic tertiary and quaternary sediments in the South and quaternary sediments (Woberg discontinuity) in the Southwest (Fleckenstein *et al.*, 2009). It seems to reflect general differences in the geogenic availability of chloride in the different sediments that are underlying the lake. For the inversion of flux rates from the chloride profiles, these differences do not constitute a problem as long as the differences are accounted for in the lower boundary conditions of the site-specific models. At site UP-3, the highest chloride concentrations in the profile were found at 3 cm depth (Figure 6). The elevated chloride concentrations are attributed to a release of chloride from biogeochemical processes in the sediment. According to Bigham *et al.* (1990), chloride can partly replace sulfate in the tunnel structure of the precipitated iron sulfate-mineral schwertmannite, which may subsequently be released during the mineral transformation process into goethite. Such a release could increase chloride concentrations close to the sediment-water interface, where schwertmannite is preferentially transformed (Peine *et al.*, 2000), especially if subsequent removal by advection is slow. It was assumed that the shape of the chloride profile below the point of maximum concentration adequately reflects the advective-diffusive transport of chloride between the groundwater and the lake. Hence, the point of maximum chloride concentration was chosen as an upper boundary condition for the transport model.

The better agreement between simulated and observed chloride profiles at the upwelling sites (range of relative RMSE values: 3 to 7 %) as opposed to the alternating sites (range of relative RMSE values: 6 to 17 %) reflects the steadier flow regime at these sites. At UP-1 and UP-3 where seepage rates in the period before the removal of the pore-water peepers were relatively steady, the inverted flux rates reasonably agree with the seepage meter rate from the day of peeper removal (Table II). In contrast at UP-2, where

a relatively high upwelling flux on the day of peeper removal was preceded by a period with mild downwelling, the inverted flux rate is an order of magnitude lower than the seepage meter rate. However, it agrees reasonably well with the mean flux rate over the measurement period (Table II) reflecting the integral character of the peeper measurements. At all upwelling sites, the predominant direction of exchange and the relative differences in the overall magnitude of fluxes are adequately reflected in the shapes of the profiles as well as in the inverted flux rates (Figure 6). Local deviations between the simulated and observed chloride concentrations along the profile (most pronounced at UP-3) indicate fluctuations and reversals in the exchange fluxes over the period preceding the removal of the pore-water peeper.

Such deviations are also clearly evident in the chloride profiles at the alternating sites where observed values could only be bracketed by two simulated profiles for different flux rates (Figure 5). For the observed frequency of the changes in magnitude and direction of flow at these sites, chloride concentrations in the pore-water do not reach a steady state. The uneven shapes of the chloride profiles, which neither represent an idealized diffusive nor advective profile, as described by Lerman (1978) and Schlüter *et al*. (2004), reflect transients in the advective flux. Another reason for the shifting slopes in the chloride profiles (e.g. ALT-1, ALT-3) might be non-vertical flow components, which are precluded when using a 1D model. This simplifying assumption, which can lead to erroneous flux estimates (Schornberg *et al*., 2010) might not be strictly met at all sites. The inverted flux rates at these sites can hence only provide an envelope for the observed flux rates and a general indication of the direction and magnitude of flow. At these sites, estimates of absolute flux rates are problematic. At ALT-1 and ALT-3, the profiles are also less than 30 cm deep because the peeper could not be installed to greater depth. The profiles do not extend deep enough into the sediment to have reached a constant value that does not change further with depth. This may introduce additional uncertainty in the absolute flux estimate at these sites. However, the very low mean flux rates from the seepage meters at ALT-1 and ALT-3 (Table II) suggest a mainly diffusive exchange regime, which is also reflected in the somewhat linear trend in the profiles at these sites. Therefore, we suspect that with further depth, chloride concentrations will change at the same rate as in the uppermost 20–30 cm of the profile until ambient groundwater concentrations are reached. This would minimize potential errors in the flux rates inverted from these profiles.

At ALT-1 and ALT-2, the inverted fluxes rather reflect seepage rates from the previous seepage meter measurement. This highlights that seepage meters allow a more or less instantaneous measurement of flux rates, whereas the estimation from concentration-depth profiles integrates over time and hence reflects the flow regime from the preceding period. Nevertheless, the inverted flux rates that envelope the observed profiles (Figure 5) adequately reflect the transient flow regime in the preceding period and reasonably match magnitude and direction of either the mean (ALT-1) or instantaneous rates from the seepage meters (ALT-2). Only at site ALT-3 with the overall lowest seepage rates that fluctuate between upwelling and downwelling, the inverted flux from the chloride profile deviates from the instantaneous seepage meter rate in magnitude and direction.

Despite the discussed limitations, the method of estimating seepage rates by the inversion of chloride profiles was able to capture the same large-scale patterns of groundwater lake exchange that were derived from the repeated seepage meter measurements. At most sites, general magnitudes and directions of flow were also comparable between the methods. However, the inverted flux rates provide estimates that integrate over time, whereas seepage meter measurements are quasi-instantaneous. Therefore flux estimates obtained from both methods at the same point in time can only be compared, when the preceding exchange regime was relatively steady so that measured chloride profiles in the sediments could reach a steady state. If the exchange regime is characterized by strong fluctuations or even reversals in flow direction, as it is the case at several sites in this study, chloride profiles will be uneven, and inverted flux rates deviate from instantaneous rates and rather reflect average conditions over the preceding period. For studies on biogeochemical transformations in lake sediments, where the predominant exchange regime is often more important than the instantaneous rates or short-term fluctuations, the inversion of flux rates from chloride concentration profiles provides a viable alternative to seepage meter measurements. Pore water peepers have the additional advantage to enable the analyses of other dissolved species in the pore-water, which can provide further insights into the biogeochemical transformations at the groundwater-lake interface. As temporal variability of exchange fluxes seems to be a common feature in artificial (this study, Fleckenstein *et al*., 2009) and natural groundwater-lake systems (Sebestyen and Schneider, 2001; Kishel and Gerla, 2002), seepage meter measurements need to be frequent enough to capture the relevant temporal variability in fluxes.

Effects of exchange fluxes on pH and acid neutralization processes in the sediment

The quantification of groundwater-lake exchange rates at the iron-rich acid mining lake ML77 allowed us to interpret our biogeochemical data within a hydrologic framework: (1) the observed groundwater-lake exchange altered the pore-water pH-profiles, particularly close to the lake-sediment interface (Figure 7). Our data further (2) suggest that raised pH promoted sulfate reduction (Table III). The sulfate and ferrous iron concentrations among sites (3) also illustrate how the pore-water chemistry was modified by the interplay of advection and microbial iron reduction and related schwertmannite disintegration. Because we used identical locations for the determination of hydrological fluxes, pH, and sulfate reduction, we can link local processes directly to

hydrological conditions, which was not possible in previous investigations, such as presented in Blodau (2004, 2005)

The sediment pore-water pH in mining lake sediments results from proton-consuming and proton-producing processes and the interaction between the acidic lake and less acidic groundwater (Blodau, 2004). The pore-water pH measured deeper in the sediment was within the range observed in sediments with low carbonate contents in similar mine lake settings (Werner *et al*., 2001; Bozau and Strauch, 2002; Blodau, 2006). The pH values generally increased with depth and approached values typical for groundwater (pH $>$ 4.5, which is significantly higher than in the lake water) at depth no deeper than about 20 cm into the sediment. An exception is ALT-3, where groundwater in the narrow ridge between ML77 and ML76 (Figure 1) is probably strongly affected by the low-pH water of the adjoining lakes and does not represent genuine groundwater. In contrast to chloride concentrations, which showed significant variations between sites depending on the local geology, the pH in the deeper sediments was always higher than in the lake and reflected the values observed in shallow piezometers directly at the lake shore and in deeper groundwater wells up to several hundred meters away from the lake ($>$ 4.5, data not shown). The characteristic shapes of the pH-profiles (Figure 7) were clearly distinct for the different exchange regimes. At sites with upwelling groundwater, the pH sharply increased right below the sediment-water interface to values $>$ 4.5. The pore-water chemistry was further modified by release of ferrous iron and sulfate and their removal by groundwater advection (Figure 6 and 7). At the upwelling sites, inflow of groundwater with a relatively high pH may have triggered a further increase of the pH within the sediments because of an activation of proton-consuming, reductive processes (i.e. iron and sulfate reduction, Blodau, 2004). At the other sites, pH increased only gradually with depth and remained low near the interface, indicating a predominance of down-welling. Penetration of lake water with a low pH may have slowed proton consumption by sulfate reduction so that the pH remained low at these sites. Also here, some variation of pH occurred because of local conditions. Where the microbial activity in the sediment was strong and ferrous iron and sulfate were released (ALT-1, Figure 7), likely in response to increased input of organic matter from macrophytes along the shoreline, the pH was somewhat higher, yet without reaching the levels of the sites with upwelling groundwater. This was not the case at the sites with groundwater upwelling.

We further expected an impact of the water flux and pH level on sulfate reduction rates. Indeed, reduction rates in the uppermost sediment layers were significantly higher at the UP sites (Table III) at pH values of $>$ 5 compared with the ALT sites with values $<$ 4 (Figure 7). This pattern can be attributed to changes in the competition between iron and sulfate reduction, which is less competitive when pH is low (Blodau and Peiffer, 2003). Previous studies have postulated such a dependency: Blodau (2004) reported higher net-sulfate reduction rates along with higher pH-values near the northern shore at ML77 compared with the southern shore and linked this effect to the groundwater inflow rates reported by Knoll *et al*. (1999).

CONCLUSIONS

The combined use of frequent seepage meter measurements and chloride profiles from pore-water peepers to estimate groundwater-lake exchange rates provided detailed insights into the spatial and temporal patterns of groundwater-lake exchange at ML77. Exchange patterns were spatially and temporally heterogeneous. Relatively steady upwelling of groundwater into the lake in the North and alternating fluxes in the South were found. This was congruent with the regional groundwater flow direction from the Northeast to Southwest and generally corroborates the earlier work by Fleckenstein *et al*. (2009). The magnitude of flux rates varied with geology – artificial mining dumps in the North and tertiary and quaternary sediments in the South. At the smaller scale, variations within short distances were prevalent in the North, presumably caused by heterogeneous sediment texture, which is typical for man-made mining dumps. Flux rates at several sites varied significantly in time. Only at some sites variations were clearly correlated with fluctuations in lake water levels. At other sites, flux rates remained relatively constant, indicating synchronous fluctuations of lake water levels and hydraulic heads in the underlying aquifer or showed trends that were related to seasonal variations in groundwater levels. Flux rates inverted from chloride profiles provide time-integrated values as opposed to the quasi-instantaneous values provided by seepage meter measurements. Despite the simplifying assumptions that had to be made in the inverse modeling both methods provided similar results. This suggests that the relevant information on the exchange (e.g. predominance of flow direction, frequency of flow reversals, overall magnitude of flow), which is most pertinent for biogeochemical studies in sediments at the groundwater-lake interface, can be adequately deduced from pore-water peepers without the need for additional frequent seepage meter measurements. The observed spatial pattern of groundwater-lake exchange influenced the vertical profiles of sulfate, ferrous iron and pH in the sediment pore-water. The increased pH close to the sediment-water interface at the upwelling sites stipulated elevated sulfate reduction rates in the uppermost sediment layers. Such an effect had been postulated (Blodau, 2004), but a direct combination of synoptic flux measurements and biogeochemical sampling to demonstrate these mechanisms had been missing to date. This study thus confirms that groundwater exchange influences acid neutralization in acid mine lake sediments and suggests that knowledge of water exchange patterns is needed for the interpretation of biogeochemical processes in acid mine lake systems.

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