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Biogeochemistry of the sediment–water interface in the littoral of an acidic mining lake studied with microsensors and gel-probes

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Abstract

Acidic mining lakes (pH < 3) represent a big environmental issue in former lignite mining areas. The acidity status of such lakes is mainly governed by the fluxes and the turnover of iron. No data are known about the iron cycling at the sediment–water boundary in the littoral of acidic mining lakes. In order to study the microstratification of iron cycling at the sediment–water interface, existing microsensor and gel-probe techniques (diffusive equilibration in thin-films, DET) were adapted to the extreme conditions of a mining lake. Microprofiles of O_2 and pH measured in situ by a profiler were compared with profiles measured in sediment cores immediately after sampling. The results indicate that microprofile measurements in cores from the littoral underestimate oxygen penetration into the sediment. Both advective pore water movement and pore water displacement during coring did influence concentration profiles. Measurement of sulfate and both ferric and ferrous iron was possible on a millimetre scale using DET. Based on different test measurements, a protocol for the application of gel probes for the analysis of iron and sulfate in acidic mining lakes was developed.

The combination of microsensor and DET data allowed the characterisation and localisation of iron turnover on a millimetre scale. As an example, results from the littoral of Mining Lake 111 (Lusatia, Germany) are presented. Pore water gradients indicated a flux of ferric iron and sulfate from the water into the sediment. There were no indications of iron reduction or oxidation in the uppermost 6 cm of the sediment. A relative comparison of the fluxes revealed that the iron and sulfur fluxes were probably driven by the formation of jarosite directly in the sediment.

Keywords: Acidic mining lakes; DET; Littoral; Microsensors; Sediment diagenesis

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1. Introduction

Acidic mining lakes (pH < 3) represent a big environmental problem in former lignite mining areas. The main sources of protons in such lakes are the inflow of acidic groundwater and the oxidation and hydrolysis of iron in the lake itself. Under acidic conditions, the microbial oxidation of ferrous iron is orders of magnitude faster than chemical oxidation (Nordstrom, 1982). Although at low pH ferric iron is rather soluble in water, acidic mining lakes are usually supersaturated with respect to iron hydroxosulfates. At low pH, the products of iron hydrolysis are iron-hydroxosulfates like schwertmannite (Peine et al., 2000) or jarosite (Bigham et al., 1996) rather than ferrihydrite. It is usually assumed that these minerals are precipitated in the water column and are then settling on the sediment surface.

Under anoxic conditions, on the other hand, the microbial reduction of iron or sulfate can remove acidity from the water (Anderson and Schiff, 1987):

$$15[CH_2O] + 4FeOOH_{(s)} + 8SO^{2-}_{4(aq)} + 16H^{+}_{(aq)} \Rightarrow 15CO_2 + 4FeS_{2(s)} + 25H_2O$$

The location of the different processes is governed by the availability of oxygen. Since the oxic zone at the sediment surface in lakes is usually only a few millimetres thick we expect a fine stratification of reductive and oxidative processes at the sediment surface of acidic mining lakes.

A common way to quantify microbial processes on a microscale is to measure microprofiles of substrates, or products of particular reactions, and calculate fluxes and turnover rates using Fick's law of diffusion (Berg et al., 1998). High resolution profiles of iron had been determined with microsensors (Brendel and Luther, 1995) or gel-probes (Davison et al., 1997). Gel probes as well as voltametric microsensors (Brendel and Luther, 1995) have the advantage that several parameters can be determined with one probe. Diffusive equilibration in thin-films (DET) has been used to study gradients of iron on a sub millimetre scale (Fones et al., 1998). In principal, a thin acrylamide gel is incubated in the sediment and then sampled, sliced and eluted. In the eluate, various pore water components can be analysed. In acidic mining lakes, we have to consider that under acidic conditions both ferric and ferrous iron are soluble in water. Ferrous iron, however, is not stable under oxic conditions. Oxidation or precipitation of iron has to be prevented during sample handling. A general disadvantage of gel-probes is that a small gel fragment is eluted in a comparable big volume of water that introduces a dilution step. Consequently, concentrations in the eluate can be low and the detection limits of the analytical methods might limit the application of the probes.

Gradients of oxygen and pH at the sediment–water boundary can be measured with microelectrodes. Microprofiles are often measured in sediment cores directly after sampling. It is generally assumed that in shallow water the lack of pressure and temperature effects and the possibility to sample carefully by hand minimises sampling artefacts like pore water allocation, oxygen depletion or changed rates due to temperature changes. To test if measurements in sediment cores give reliable results, we compared measurements in freshly sampled cores with in situ measurements in the lake.

While the profundal sediments of acidic mining lakes is comparatively well studied, no information exists about the biogeochemistry in the littoral. Littoral sediments are characterised by high heterogeneity and water movement. The resulting methodological difficulties are one reason, why most studies of the sediment–water boundary focused on the profundal of lakes.

The aim of this study was to evaluate and adapt existing methods to measure gradients of oxygen, pH, sulfate, ferric and ferrous iron on a millimetre scale in situ in an acidic mining lake. Combining the data obtained with different methods, the nature and localisation of microbial iron turnover in the littoral sediment of an acidic mining lake should be determined.

2. Material and methods

2.1. Study area

The study was carried out in Mining Lake 111 (ML111) in the Lusatian lignite mining district in eastern Germany (51°29′ north, 13°38′ east). The lake has a surface area of 107,000 m^2 and a mean depth of 4.5 m. The maximum depth is 10.5 m (Büttner et al., 1998). The lake has a pH of 2.6 and contains high amounts of SO_4^{2-} (13.6 mmol l^{-1}) and Fe (2.8 mmol l^{-1}) (Friese et al., 1998) but low (< 0.1 mmol l^{-1}) concentrations of organic and inorganic carbon (Herzsprung et al., 1998). Since the formation of the lake more than 30 years ago, no natural neutralisation of the water has taken place. For littoral sampling, a rather homogeneous looking level area on the western shore with about 0.5 m water depth was chosen. There were no higher plants or animals. Profundal sampling was carried out near the eastern shore at about 4 m depth.

2.2. Gel probes

Gel probes were prepared according to Krom et al. (1994). A total of 10 ml of 30% acrylamide–bis solution (37.5:1) were mixed with 10 ml H_2O and polymerisation was started by adding 60 μl ammonium peroxodisulfate (30%) and 20 μl TEMED 1 M. After polymerisation between glass plates (0.75 mm spacer) for 30 min at 40 °C, one glass plate was removed and the gel was hydrated in H_2O for 24 h. The membrane was also hydrated. We tested a 0.45-μm cellulose acetate membrane (Schleicher and Schuell OE67) and a 0.45-μm cellulose nitrate membrane (Schleicher and Schuell PROTRAN BA85) and could not see any difference. The gel and the membrane were fixed to a probe according to Krom et al. (1994) and stored in N_2 bubbled water for 2 days. The final gel had a water content of 89 ± 0.4%. The probe had a scale of scratches on the back used for the determination of the sediment surface.

For field application, the gel was pushed into the sediment either by hand (littoral) or fixed to the in situ profiler (profundal). After 24 h in the sediment, the probe was taken and sampled within 10–15 min as described by Mortimer et al. (1998). Particles were removed from the membrane with a dry paper towel. Then the gel was cut along the inner edge of the holding frame by a razor blade. The gel was also cut at the sediment water boundary,

which was indicated by sediment particles adhering to the probe. The membrane was carefully taken off and the gel transferred to a glass plate. There it was cut into 1 cm fragments. Each fragment was then further fragmented into smaller stripes by a razor blade. The gel stripes were pushed on the blade by a small spatula and transferred to preweight tubes. The exact length of each gel fragment, and hence the position in the sediment, was determined from the mass of the fragment.

2.3. Dialysis sampler and pore water extraction

Sediment pore water was sampled with a dialysis pore water sampler ("peeper"). Design and deployment were basically the same as described by Hesslein (1976). The peeper was inserted manually from a boat and left to equilibrate for 14 days. It was sampled with syringes immediately after retrieval.

For comparison, sediment cores were manually taken with 6 cm diameter tubes and sliced in 1 cm intervals immediately after sampling. The sediment was stored gas bubble-free in plastic bags, which were then stored in anaerobic bags (Anerocult®) until centrifugation and analysis in the laboratory.

2.4. Analytical techniques

Sulfate was analysed by ion chromatography (IC). For ferrous and ferric iron, three analytical methods were used: Reactive Fe, including HCl-soluble Fe(II) and hydroxylamine-reducible Fe(III), was determined in triplicates using ferrozine (Lovley and Phillips, 1987). Samples were centrifuged (16,000 × *g*, 10 min) instead of filtrated before photometry. Soluble iron species in acidified water (H_2O acidified with HCl to pH 2.6) were analysed colorimetrically by segmented flow analysis (SFA) as described by Herzsprung et al. (1998). Alternatively, the redox state of soluble iron was conserved using the selective chelator pair ethylenediamine tetraacetate (EDTA) for ferric iron and bathophenanthroline disulfonate (BPDS) for ferrous iron followed by direct photometric analysis of the ferrous iron–BPDS complex at 535 nm. Ferric iron can be measured after conversion of the Fe(III)–EDTA complex to Fe(II)–BPDS in the light (Wang and Peverly, 1998).

2.5. Microsensor measurement

Microsensor in situ measurements were carried out with a commercially available profiler (UNISENSE, Århus, Denmark) equipped with an O_2 and a pH microelectrode. The profiler was placed on the sediment and left to settle for at least 30 min. Tests had shown that after 30 min, the profiler did not sink further into the sediment. For calibration of the oxygen electrode, the oxygen concentration in the bottom water was determined by Winkler titration. The pH sensor was calibrated immediately before or after profile measurements using standard buffers, which were stored in the lake for temperature equilibration. Sediment cores for microsensor measurements were taken either by hand (littoral, 2.6 cm diameter tubes) or by a gravity corer (profundal, 6 cm diameter tubes). The cores were immediately brought to the shore and fixed to a pre-calibrated microsensor stand. Measurements of O_2 microprofiles were completed within 1 h after sampling.

During measurements, the cores were darkened using aluminium foil. The sediment surface was identified from a slight shift of the slope of the profiles. If optical verification was possible we always found a good agreement between optical and indirect determination of the interface.

2.6. Calculations

Diffusive fluxes were calculated using Fick's first law and temperature corrected diffusion coefficients (O_2 from Broecker and Peng, 1974; SO_4^{2-} and Fe from Li and Gregory, 1974). Fluxes of oxygen were determined from the gradient in the diffusive boundary layer. Fluxes of iron and sulfate were determined from gradients in the sediment and corrected for porosity. The diffusion coefficients in the sediment (D_s) were calculated from the molecular diffusion coefficient in water (D) and the porosity (Φ): $D_s = D \times (\Phi)^2$ (Lerman, 1988).

3. Results

3.1. Gel probes method

We tested the use of the standard methods used in our laboratory to analyse sulfate (IC), ferrous and ferric iron (SFA) in gel probe samples. We analysed gel fragments which were exposed to the overlying water and should contain the same concentration of solutes with different analytical methods (Table 1). The analysis of ferric iron with the segmented flow analyser (SFA) showed very low concentrations and the concentration of ferrous iron in the eluate was at the detection limit of the analytical method. The high dilution factors increased the analytical error. A comparison of results obtained from the same eluates using either SFA or direct photometry (Fig. 1) demonstrates the high scatter and low values of the SFA method. The method was not suitable to be used with gel probes at the iron concentration present in the lake. The colorimetric analysis in the redox stabilising buffer (Wang and Peverly, 1998) gave intermediate results while the ferrozine analysis (Lovley and Phillips, 1987) gave the highest values. In the case of ferric iron, both ferrozine and direct colorimetry gave comparable results.

In a test experiment, we also determined back equilibration times. It is important to keep back equilibration time as short as possible in order to prevent oxidation of iron. A gel was incubated in a standard solution. Different fragments of the gel were back equilibrated in acidified (pH 2.6) H_2O for different times (Table 2). It turned out that a

Table 1
Iron concentration in the overlaying water determined with different analytical methods

	Fe^{II} (mmol l^{-1})	Fe^{III} (mmol l^{-1})
Ferrozine 48 h extraction ($n=3$)	0.38 ± 0.02	3.03 ± 0.01
Wang and Peverly ($n=4$)	0.22 ± 0.1	2.87 ± 0.2
SFA ($n=4$)	0.34 ± 0.12	2.29 ± 0.54

Littoral ML111 August 2001.

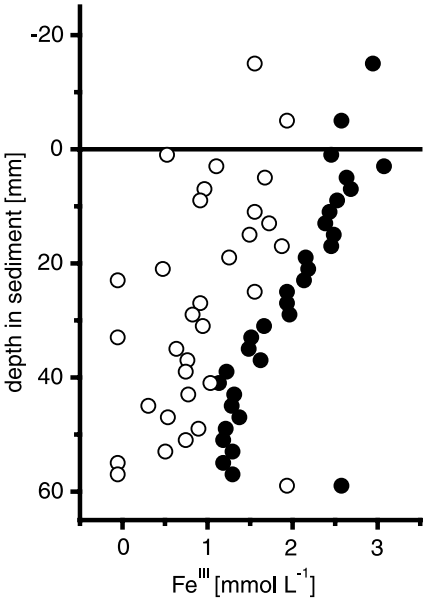

Fig. 1. Concentrations of ferric iron in a gel deployed in the littoral in August 2001 determined with direct colorimetric analysis (closed dots) and segmented flow analysis (open dots).

back equilibration time of 1 h was sufficient both for sulfate and iron. There was a slight (8%) overestimation of sulfate in the gel. The concentration of ferrous iron did not decrease with prolonged back equilibration time which means that oxidation was not a problem. We chose a back equilibration time of 24 h for all following experiments. The back equilibration experiment, however, confirmed problems related to the analysis of iron. If we used the ferrozine method, the concentration of ferric iron, and to a lesser extent ferrous iron, was overestimated. While using the method of Wang and Peverly, ferrous iron was underestimated with a high standard deviation and ferric iron was slightly overestimated (Table 2). Using standard protocols, both methods were obviously not suitable for the determination of iron in gel probes.

Table 2
Concentration of SO_4^{2-}, Fe^{II} and Fe^{III} (mmol l^{-1}) in a gel after different elution times in H_2O (pH 2.6) determined with different analytical methods ($n=3$)

Elution (h)	SO_4^{2-} [a]	Fe^{II} [b]	Fe^{II} [c]	Fe^{III} [b]	Fe^{III} [c]
Standard	26.6 ± 0.1	1 ± 0.06		2.7 ± 0.18	
1	28.9 ± 0.5	1.84 ± 0.04	0.41 ± 0.16	2.66 ± 0.42	3.01
5	29.3 ± 0.1	2.37 ± 0.18	0.40 ± 0.07	3.35 ± 0.75	3.12
24	29.0 ± 0.1	2.47 ± 0.29	0.68 ± 0.24	2.52 ± 0.65	2.84
48	28.6 ± 0.2	2.41 ± 0.28	0.52 ± 0.24	4.78 ± 0.44	

The gel was incubated for 24 h in a standard solution.
[a] IC.
[b] Ferrozine method.
[c] Wang and Peverly method.

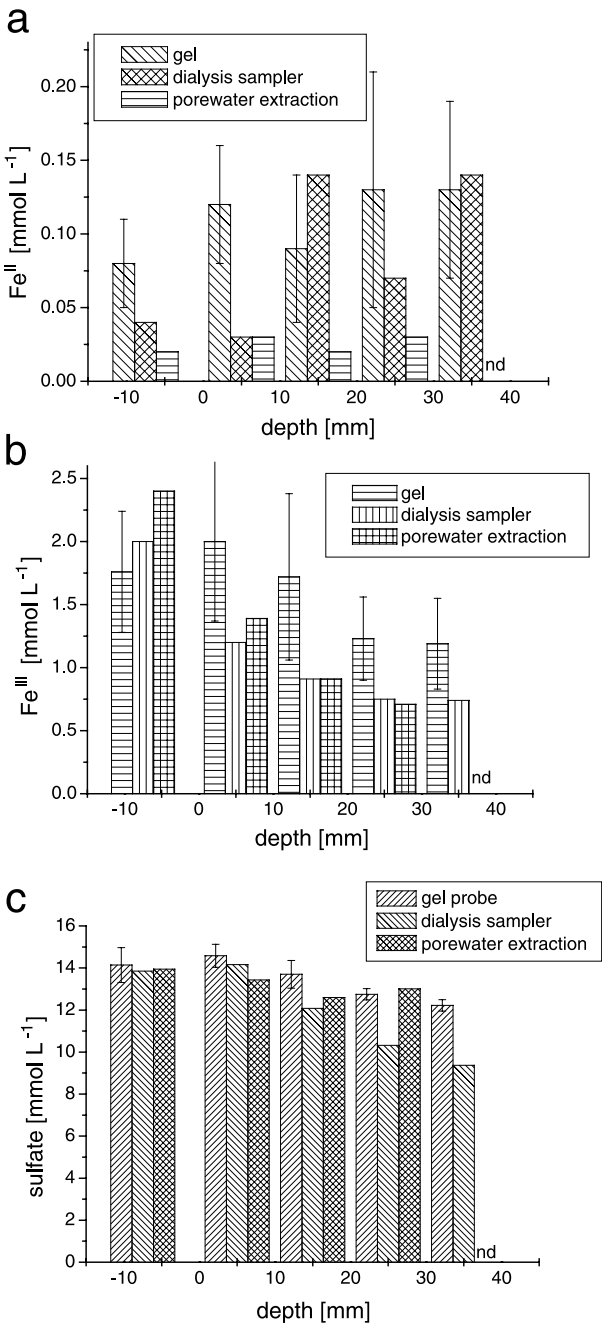

Fig. 2. Comparison of (a) ferrous, (b) ferric iron and (c) sulfate concentrations obtained with gel-probes, ordinary dialysis sampler and pore water extraction (November 2001) in cm intervals. The gel probe data are mean and standard deviation of the gel fragments from two gels covering 1 cm.

During the ferrozine procedure, the gel was directly eluted in hydrochloric acid or hydroxylamine solution. With this procedure, the total reactive iron in the gel was analysed. Thus, the ferrozine analysis included both solid and soluble iron, which probably led to the overestimation. To exclude this artefact, all following ferrozine assays were done on gels back equilibrated in acidified H_2O rather than in HCl. This introduces an additional dilution step but makes sure, that only soluble iron undergoes ferrozine analysis. We tried to match the pH of the lake water by acidifying unbuffered distilled water with HCl to pH 2.6. A direct comparison of H_2O (pH 2.6) and HCl (0.5 mol l^{-1}) extraction of gel fragments, which were exposed to lake water, gave significantly higher values of Fe^{II} with HCl extraction (0.2 ± 0.03) compared to the H_2O extraction (0.08 ± 0.03). This shows that indeed probably some precipitation of iron had taken place in the gel.

In November 2001, we sampled the littoral site with different sampling techniques. A comparison of gel probe data with extracted pore water or samples from a standard dialysis sampler (Fig. 2) showed some differences. We cannot, however, differentiate between methodological differences and spatial heterogeneity of the sediment. The standard deviation of the gel probe data from the overlying water (-10 to 0 mm) reflect the methodological error of the gels which was 6%, 24% and 27% for SO_4^{2-}, Fe^{II} and Fe^{III}, respectively ($n = 8$). A possible source of error is sample contamination during processing in the field. A test experiment had shown that drying of gel fragments during gel processing was a negligible error source (data not shown).

Fe^{II} concentrations were very low and there was no consistent pattern between methods except that the pore water analysis always gave the lowest results (Fig. 2a). For Fe^{III}, the gels gave higher concentrations than both other methods (Fig. 2b). The general shape of the profiles, however, was the same. The higher values were partly due to small-scale concentration peaks in one of the two gels (filled squares in Fig. 3b) which are not resolved by the other sampling techniques. The sulfate measurements showed good agreement between all sampling techniques (Fig. 2c).

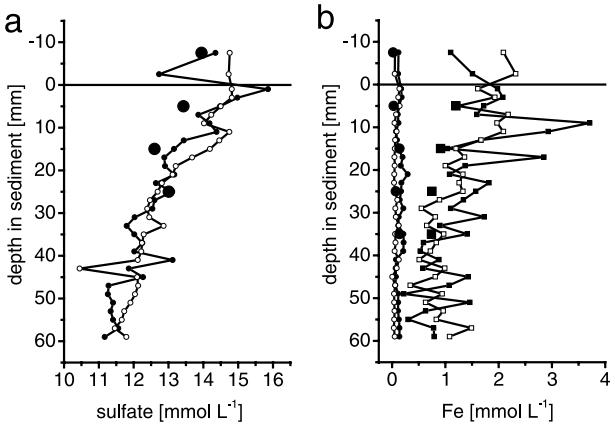

Fig. 3. Gel-probe data of littoral sediment November 2001. (a) Sulfate in two gel probes (small symbols) and direct pore water analysis (big dots). (b) Fe^{II} (circles) and Fe^{III} (squares) in two gel probes (small symbols) and in the pore water (big symbols).

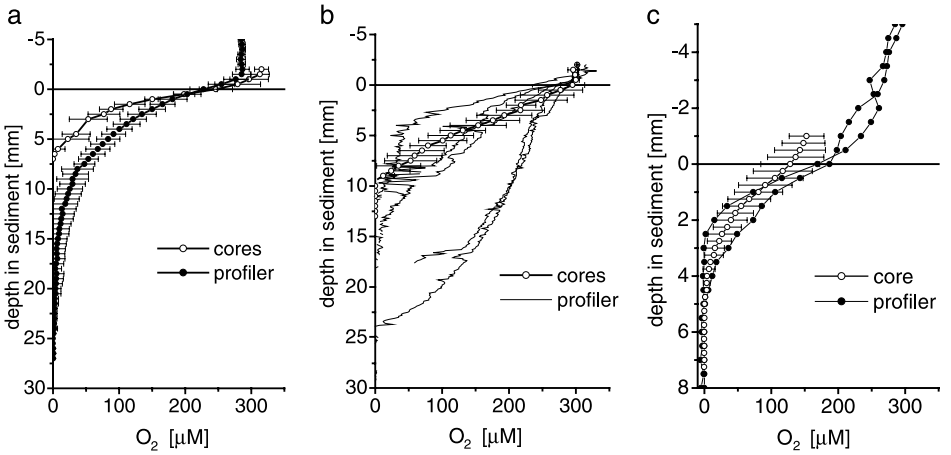

Fig. 4. Comparison of microprofiles measured in situ and in sediment cores (a) littoral August 2001: mean ± SD of six in situ profiles and mean of three profiles from two sediment cores . (b) Littoral November 2001: five different in situ profiles and mean of three profiles from two cores. (c) Profundal September 2001: two in situ profiles and mean of three profiles from one core.

3.2. Microsensor measurement method

On three occasions microprofiles of oxygen measured directly in the lake by the in situ profiler were compared with profiles measured in sediment cores immediately after sampling (Fig. 4). At the littoral site, profiles differed considerably between the two methods. In the sediment cores, oxygen penetration was much lower and the diffusive boundary layer (DBL) was smaller. The diffusive oxygen flux between water and sediment was unaffected in August but lower in the cores in November (Table 3). Usually, the heterogeneity between microprofiles was greater in situ than in cores. At the profundal site, oxygen penetration was the same with both methods but the oxygen concentration at the sediment surface was lower in the core (Fig. 4c).

3.3. In situ measurements

In November 2001, we measured a complete dataset in the littoral of ML111. Oxygen penetration was between 11 and 24 mm (mean about 15 mm) (Fig. 5a). There was a considerable heterogeneity between different oxygen profiles.

Ferric iron decreased with depth until a constant concentration was reached in about 4 cm depth (Fig. 3b). The decrease of ferric iron with depth was not accompanied by an

Table 3
Comparison of oxygen fluxes calculated from oxygen profiles measured in situ and in cores (mmol m^{-2} day^{-1})

	Littoral August	Littoral November	Profundal September
In situ	6.6 ± 0.9 (n = 6)	6.1 ± 3.5 (n = 6)	5.9 (n = 2)
Core	6.8 ± 0.4 (n = 3)	2.6 ± 0.2 (n = 3)	4.6 ± 2.2 (n = 3)

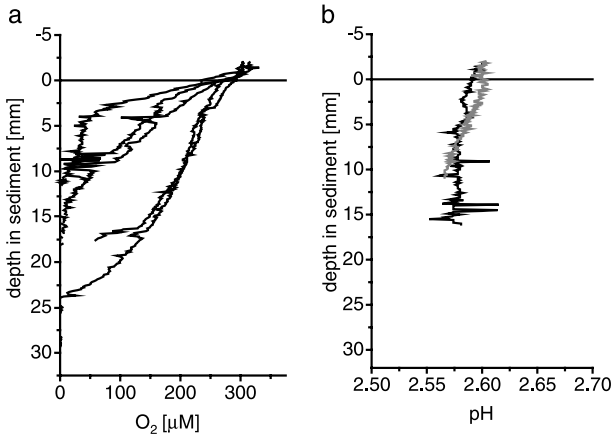

Fig. 5. Microprofiles of (a) oxygen and (b) pH in the littoral sediment measured in November 2001.

increase in ferrous iron. Sulfate also decreased with depth from 15 mmol l^{-1} at the sediment surface to 11.5 mmol l^{-1} in 6 m depth (Fig. 3a). There was good agreement between data from two different gels. The scatter of the profiles was higher for iron than for sulfate.

The pH decreased from 2.6 to 2.58 in the uppermost 5 mm (Fig. 5b). The fluxes from the water into the sediment were 6.1 ± 3.5 mmol O_2 m^{-2} day^{-1}, 1 mmol Fe^{III} m^{-2} day^{-1} (0.87 and 1.06 for the two probes, respectively) and 4.4 mmol SO_4^{2-} m^{-2} day^{-1} (4.54 and 4.17 for the two probes, respectively).

4. Discussion

4.1. Gel probes method

Published back equilibration times for sulfate and iron are 20 min in a freshwater standard (Krom et al., 1994) and 24 h in seawater (Mortimer et al., 1998). The authors recommend 1 h (freshwater) and 48 h (seawater) back equilibration time. In our case, 1 h proved to be enough but for convenience we choose 24 h. If a gel was applied in seawater, about 3% to 7% of the sulfate was retained in the gel (Mortimer et al., 1998). The authors suggest the application of a correction factor, which is obtained by comparing gel data from the water above the sediment with data directly measured in the overlying water (Mortimer et al., 1998). We did not observe a retention of sulfate in the gel but a slight overestimation of sulfate in the gel. We also observed some precipitation of iron in the gel. It is possible that some sulfate adsorbed to solid phase iron in the gel, which can explain the elevated sulfate concentration in the gel.

Theoretical considerations revealed that the spatial resolution of the gel is limited by lateral diffusion in the gel between retrieval from the sediment and cutting of the gel (Davison et al., 1994). If only total iron is to be analysed, the gel can be fixed in

NaOH. This is not possible when both redox states of iron are to be analysed. Our experience is that a gel can be taken from the sediment, transferred to a glass plate and cut into 1 cm fragments within 5 min. Depending on the number of fragments, the gel can be further sampled into preweight Eppendorf tubes in 10 min by two people. If the gel fragment with the steepest gradient is processed first, a spatial resolution of about 2 mm should be possible. If rapid processing of the gel is practically difficult, the use of a constrained DET probe with individual gel compartments (Fones et al., 1998) should be considered.

As a result of the different methodological tests, we recommend the following procedure for the application of gel probes in acidic mining lakes:

- 24 h deployment of the gel in situ,
- sampling, immediate cutting of the gel (at least 2 mm intervals); storage of the gel fragments is possible in the cold,
- back equilibration 24 h in H_2O which was adjusted to in situ pH with HCl,
- analysis of sulfate using ion chromatography,
- analysis of the ferrous and ferric iron in the eluate using the ferrozine method.

Profiles obtained with this procedure were similar to profiles obtained with pore water extraction or dialysis sampler.

4.2. Microsensor measurement method

The comparison of in situ measurements with measurements in sediment cores showed that at the littoral site core measurements gave different results. The discrepancy can partly be explained if we assume other transport processes which are faster than diffusion. One major effect of coring is that water movement above the sediment is lowered and groundwater flow is blocked. Both water movement and groundwater flow can increase oxygen transport in the sediment. Exclusion of mass transport by coring would thus reduce oxygen transport and oxygen penetration into the sediment. This is supported by the observation that the oxygen penetration in the profundal was the same with both methods. In the profundal water, movement was very low. The DBL was more than 2 mm thick. The sediment in the cores contained less oxygen than the sediment in situ. The difference between integrated profiles was 1.5 mmol O_2 m^2 in August. With the calculated flux of 6.8 mmol m^{-2} day^{-1}, it would need 4.5 h to consume the missing oxygen in the sediment. The profiles were, however, all measured within 1 h after sampling. The most reasonable explanation is, that oxygen containing pore water was flushed out of the sediment during sampling. Pore water movement during sampling is facilitated by the sandy texture of the littoral sediment. At the muddy profundal site, no lack of oxygen was observed. One way to overcome this problem is to use tubes with a bigger diameter. In sandy sediments, however, it is practically difficult to get sediment cores with a bigger diameter. In the littoral of ML111, it was not possible to get surface sediment cores with a diameter of 9 cm.

We conclude that only under conditions when transport is dominated by diffusion and conditions allow sampling of bigger cores, core measurements can give reliable results and

at least the extension of the oxic zone can be estimated. In case of water movement, however, core measurements cannot be used to determine the distribution and flux of oxygen in the sediment. In this case, profiles have to be measured in situ or in sophisticated laboratory setups which mimic the natural flow conditions. To avoid artefacts due to changed flow conditions or pore water allocation, we recommend the use of an in situ profiler. The calculation of fluxes or process rates using diffusion models gives limited information under such conditions. The comparison of in situ with core measurements, however, gives the possibility to assess the influence of non-diffusive transport processes on the distribution of solutes in the sediment.

The differences between different oxygen profiles were not artefacts but demonstrate the heterogeneity of the system. Under such conditions, many microelectrode profiles have to be measured or a 2D technique like the recently developed planar optodes (Glud et al., 1996) have to be used to get a realistic picture.

4.3. Iron turnover at the sediment–water interface

Although all methods suffered from certain disadvantages, the combination of the data gives a picture of the iron turnover in the surface layer of the littoral sediment.

The data clearly indicate fluxes of O_2, Fe^{III} and SO_4^{2-} from the water into the sediment. To maintain the observed gradients, iron and sulfate removing processes in the sediment must exist. Possible fates of ferric iron and sulfate in the sediment are (1) reduction, (2) adsorption or (3) precipitation.

Although the sediment was anoxic below 2.5 cm depth, we have no indications that iron reduction occurred. The concentration of ferrous iron was relatively low. H_2S, which might have precipitated ferrous iron, was not present and no sulfate reduction could be detected using ^{35}S tracer techniques (data not shown). Microbial alkalinity production did not take place in the surface littoral sediment of ML111.

Adsorption stops when all surfaces are saturated. Given the age of the lake of more than 30 years, it seems improbable that absorption is still an important process of net iron and sulfate fixation in the sediment. This leaves only precipitation as possible iron and sulfate sink. Possible iron-sulfate minerals formed at low pH are jarosite ($NaFe_3(OH)_6(SO_4)_2$) or schwertmannite ($Fe_8O_8(OH)_x(SO_4)_y$) (Bigham et al., 1996).

Under the assumption that iron and sulfate are equally affected by advection, the quotient of iron and sulfate flux gives the stoichiometry of iron and sulfur "consumption" in the sediment. At the littoral site, the Fe/S flux ratio was 0.23. The number is close to the molar ratio of iron and sulfur in jarosite, which is 0.375, but much lower than in schwertmannite, which is 4.7. The assumption that iron is precipitated as jarosite is further supported by the Fe/S ratio of the surface sediment of ML111, which is 0.09 ± 0.04 ($n = 6$) (unpublished data). These findings modify our view of the early diagenesis of mining lake sediments (Peine et al., 2000). A significant amount of minerals is probably not formed in the water column but directly in the upper centimetres of the sediment. A major mechanism of sediment diagenesis might be the growth "from below" rather than particle sedimentation. This has to be considered when discussing the chemical conditions of mineral formation in acidic lakes (Bigham et al., 1996; Peine et al., 2000; Bachmann et al., 2001), especially when sediment trap data are used.

5. Conclusions

Microsensors and gel probes are suitable tools to study the biogeochemistry of the sediment–water interface in the littoral of acidic mining lakes. A protocol for the use of DET probes was developed. Site heterogeneity, flow conditions and artefacts due to sediment coring make the use of in situ techniques necessary.

The combined results of DET and microsensor data suggest that the most important iron and sulfur converting process in the nearshore sediment of Mining Lake 111 was the precipitation of jarosite.

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