Research Papers

Organic Matter Diagenesis in Acidic Mine Lakes

Diagenese organischer Substanz in sauren Bergbaurestseen

C. Blodau, A. Peine,
S. Hoffmann, and S. Peiffer[1]

Keywords: Acid Mine Lake, NOM, Sulfate Reduction, Iron Reduction, Stable Isotope
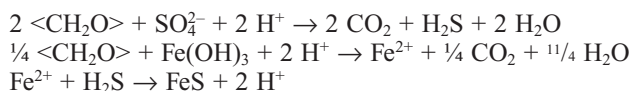
Summary: The significance of organic matter origin for carbon oxidation via sulfate and iron reduction in the sediments of three acid mine lakes is analyzed. Carbon reactivity was estimated by fitting first-order expressions to measured rates. Carbon oxidation rates via sulfate and ferric iron reduction ranged from 3.4 to 4.7 mmol m^{-2} d^{-1} and resembled those reported for freshwater lakes. The estimated reaction constants increased from about 10^{-3} a^{-1} at the interface to the former mine grounds to 0.05 to 0.2 a^{-1} at the current sediment-water interface. Aquatic organic matter accounted for an estimated 45...75% of total carbon oxidation rates while it amounted only to about 5...14% of the total organic matter that had been deposited. The results of this study suggest that in highly acidic mine lakes the reactivity of the deposited organic matter can rapidly increase after flooding, enhancing carbon oxidation and internal neutralization rates in the sediments.

Schlagwörter: saurer Restsee, NOM, Sulfatreduktion, Eisenreduktion, stabiles Isotop

Zusammenfassung: Der Beitrag aquatischer organischer Substanz an der Kohlenstoffmineralisierung durch Sulfat- und Eisenreduktion in den Sedimenten saurer Braunkohletagebaurestseen wird analysiert. Die Kohlenstoffreaktivität wird durch Anpassung von kinetischen Ausdrücken erster Ordnung an Mineralisationsraten bestimmt. Die Mineralisationsraten erreichten 3.4 bis 4.7 mmol m^{-2} d^{-1} und liegen damit im Bereich natürlicher Systeme. Die geschätzten Kohlenstoffreaktivitäten lagen zwischen 10^{-3} a^{-1} an der Grenzfläche zum früheren Tagebauboden und 0.05 bis 0.2 a^{-1} an der Sediment-Wasser-Grenze. Aquatische organische Substanz trug, trotz eines geschätzten Massenanteils von nur 5...15%, etwa 45...75% zur Kohlenstoffmineralisation in den Sedimenten bei. Die Ergebnisse der Studie dokumentieren die Bedeutung der Biomasseproduktion im Wasserkörper der Seen für die interne Neutralisation durch mikrobielle Prozesse in den Sedimenten.

1 Introduction

Surface mining of resources that contain pyrite and other sulfides causes severe environmental problems in Europe and other regions of the world [1]. After reclamation, lakes with pH values about 3 originate in the mine pits from the input of acidic ground- and surface waters which have passed zones of pyrite oxidation in adjacent mine tailings [1, 2]. The acidity in the lake water can partially be neutralized by the storage of reduced sulfur compounds in the sediments after microbial reduction of ferric iron and sulfate with organic matter as electron source [3, 4]:

$$2 <CH_2O> + SO_4^{2-} + 2 H^+ \rightarrow 2 CO_2 + H_2S + 2 H_2O$$
$$\tfrac{1}{4} <CH_2O> + Fe(OH)_3 + 2 H^+ \rightarrow Fe^{2+} + \tfrac{1}{4} CO_2 + {}^{11}/_4 H_2O$$
$$Fe^{2+} + H_2S \rightarrow FeS + 2 H^+$$

Similar processes have been found to occur in lakes affected by high inputs of sulfate and acidity from acid mine drainage [5], acid precipitation [6], and experimental acidification [7–9].

[1] Dipl.-Geoökol. Christian Blodau, Dr. Ariane Peine, Dipl.-Geoökol. Sabine Hoffmann, Dr. Stefan Peiffer, Limnological Research Station, University of Bayreuth, D-95440 Bayreuth, Germany

Correspondence to C. Blodau, Department of Geography and Center for Climate and Global Change Research, McGill University, Burnside Hall, 805 Sherbrooke Street West, Montreal H3A2K6, Canada
E-mail: cbloda@po-box.mcgill.ca

Little is known so far about the significance of organic matter quality for the neutralization processes in the sediments of highly acidic waters. It has, however, been hypothesized that the supply of easily decomposable organic matter of aquatic origin is crucial for the internal neutralization process [3, 4]. Generally, the organic matter (OM) in lake sediments is either of aquatic (AOM) or terrigeneous origin (non-AOM). The origin of the organic matter is closely connected to elemental and isotopic characteristics which can be used as indicators [10–13].
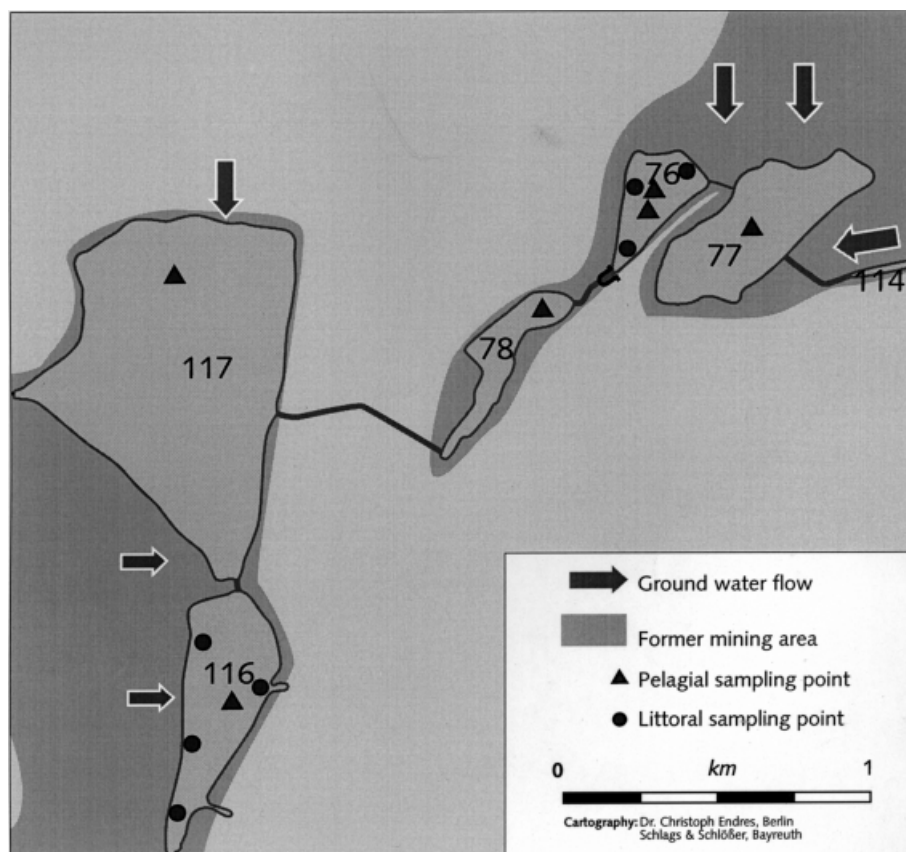
In this investigation we try to characterize and partition the organic matter in the sediments of three acidic mine lakes by elemental and carbon isotope analyses. These analyses are then used to assess the relative importance of the organic matter origin for the microbial metabolism in the sediments.

2 Study Sites

The lakes 77, 76, and 116 are part of an interconnected chain of strip mining lakes located in Brandenburg (Germany) (Fig. 1). Ground- and surface water move from lake 77 to 76 and, via two more lakes and a ditch, into 116. Surface areas, volume, and maximum depth are shown in Table 1. The strip mines were cut into clastic sediments containing lignite seams of 5 to 10 meters thickness. Groundwater driven flooding started in 1965-1968 and was completed some years later [14].

Fig. 1: Sampling sites. Only data obtained from the pelagial sampling points of lakes 77, 76, and 116 are presented.

Probenahmestandorte. Daten der pelagialen Standorte 77, 76 und 116 werden diskutiert.

Table 1: Surface, volume, and maximal depth of the studied lakes.

Oberfläche, Volumen und Tiefe der untersuchten Seen.

Lake	Surface area, m^2	Volume, m^3	Max. depth, m
76	89 500	260 810	5
77	244 000	–	7
116	331 200	1 294 350	11

The lakes receive most of their inflow by the ditch connecting the lakes and only secondarily from the aquifer (Weber, pers. communication). The sediments were sampled at maximum depth.

3 Methods

Sampling

Surface water profiles were sampled from January 1996 to May 1997 and analyzed for pH, ferrous and ferric iron, sulfate, and ammonium. Sediment cores were taken with a gravity corer (diameter: 6 cm) on several occasions (May 1996–November 1997) and transported to the laboratory within 10 hours. Sediment incubations began immediately after arrival. Preceding the solid phase analyses the cores were cut into segments. Diffusion chambers (cellulose acetate membrane; 0.45 μm pore diameter; 7 mL cell volume; [15]) were used to sample the pore-water of the sediments in the period of May, 1996 to February, 1997. The chambers were vertically inserted into the sediments by scuba divers and sampled three weeks later. Fe^{2+} concentrations and pH were determined immediately, while the other subsamples were frozen (–18 °C) and stored until analyzed.

Analytical methods

SO$_4^{2-}$, Ca^{2+}, and NH$_4^+$ were determined by ion chromatography (Metrohm 690), Fe^{2+} by the phenanthroline method [16], DOC by a total organic carbon analyzer (TOC5050, Shimadzu) and pH using an electrode (WTW E50, pH 7 and pH 3 buffers). Total iron was determined by flame atomic absorption spectrometry after digestion of dried sediment with concentrated nitric and hydrochloric acid (1 : 1 ratio) in a microwave digester. Reactive iron was extracted by treatment with HCl (c = 1 mol L^{-1}, [17]) and concentrations of Fe(tot) determined by flame atomic absorption spectrometry. The concentration of Fe(III) in the extract was calculated by the difference between Fe(tot) and FeS (AVS). Possible presence of FeCO$_3$ may have caused an overestimate of Fe(III). In case of lake 76 the acid ammonium oxalate method was used [18]. The content of total inorganic reduced sulfur compounds (TRIS: FeS$_2$, FeS, S°) and FeS (AVS) was determined by the method of Fossing and Jørgensen [19] and Canfield et al. [20]. Frozen sediment samples were thawed under N$_2$ and distilled with HCl (c = 5 mol L^{-1}; AVS and TRIS) and CrCl$_2$ (c = 0.15 mol L^{-1}, TRIS). The H$_2$S released into the nitrogen stream was trapped in 50 mL of NaOH (c = 0.15 mol L^{-1}) solution. The sulfide was precipitated by addition of zinc acetate and photometrically determined with a Varian Cary 1E at 665 nm [21]. The analytical recovery of a pyrite and a ZnS standard was 89 % and 96 %, respectively. In case of finely sectioned cores taken from lake 116, TRIS contents were estimated from the difference of total sulfur, dissolved sulfate, and the carbon contents assuming a molar C$_{org}$/S$_{org}$ ratio of 100 [22, 23]. Carbon, nitrogen, and total sulfur contents were determined with a C/N/S analyzer after drying of sediment. ^{13}C/^{12}C ratios were determined by gas-mass spectroscopy of CO$_2$ (combustion at 900 °C with cupric oxide and copper) after homogenizing, freeze drying, and grinding of the sediment samples. The δ notation is used in this paper with δ^{13}C defined as [U (sample)/U (standard) –1] · 1000, with $U = n(^{13}$C)$/n(^{12}$C) and unit ‰ [24].

Deposition rates and dating

The sediment age was estimated from finely sectioned cores. The position of the former mine ground was indicated by an abrupt change in bulk density within the profiles. The deposition rates and the approximate age of the sediments were estimated from the dry weight that had been deposited from that point on and assuming constant deposition rates. The approach was checked by ^{137}Cs dating of finely sectioned sediment cores [25, 26] and a comparison to data from sediment traps [27] which were sampled in 77 on a regular basis for one year. [137]Cs activities were determined by gamma spectrometry after freeze drying of sediment material.

Carbon oxidation rates via sulfate and ferric iron reduction

Carbon oxidation rates were approximated by the sum of <CH$_2$O> equivalents utilized in sulfate and iron reduction. These pathways probably prevailed in the sediments [28, 29]. Sulfate reduction rates were measured according to Jørgensen [30] in August to November 1996 (76 and 116) and November 1997 (77). From the sediment cores, 3 to 4 subcores (12 cm × 2.5 cm) were taken from 0 to 20 cm and $^{35}SO_4^{2-}$ injected in 2-cm intervals. The subcores were incubated for 10 to 14 hours at the in situ temperature of 7 °C,

subsequently plunged into liquid nitrogen and stored at –20 °C. The frozen subcores were sectioned into 2-cm segments, thawed in a solution of zinc acetate (30 mL, w(zinc acetate) = 5%), and distilled as described above [20]. The H$_2$S released into the nitrogen stream was trapped in 50 mL of NaOH (c = 0.15 mol L^{-1}), and counted on a Beckmann LS 6000 scintillation counter. Ferric iron reduction was estimated by two methods. The closed-vessel incubation technique [31] was utilized (in situ temperature: 12 °C) in lake 77 in June 1996. Pore-water modelling of dissolved ferrous iron profiles (in situ temperature: 7 °C) was performed under assumption of steady-state conditions, constant porosity, no bioturbation and not considering compaction and advective flow [28]. The turnover rate in a layer was calculated from Equation (1).

$$D_{s, Fe2+, out} \frac{\Delta C_{out}}{\Delta z_{out}} - D_{s, Fe2+, in} \frac{\Delta C_{in}}{\Delta z_{in}} = P \qquad (1)$$
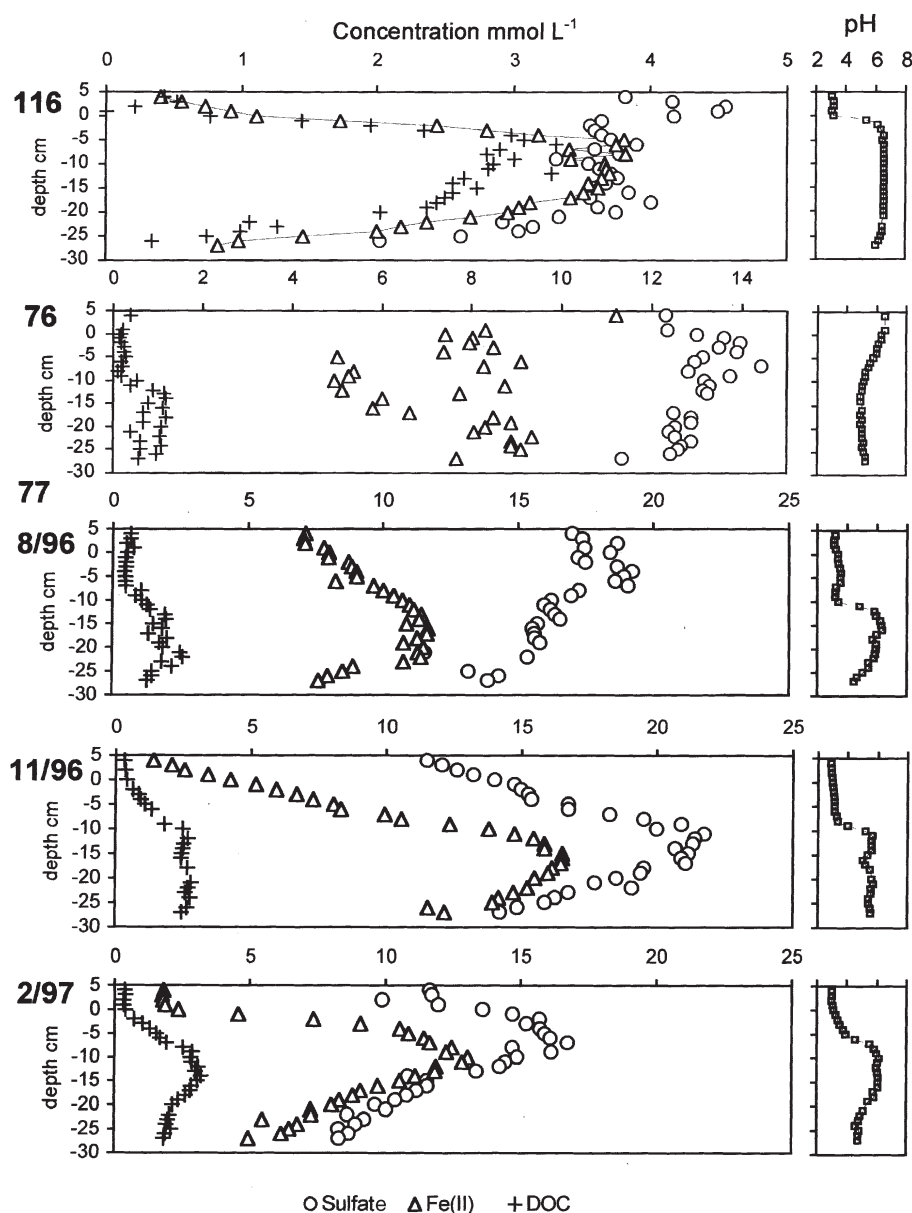
with

$(\Delta C/\Delta z)$: concentration gradient at the layer boundary (unit: nmol cm^{-4})
P: net turnover rate (unit: nmol cm^{-2} d^{-1})
$D_{s, Fe2+}$: whole-sediment diffusion coefficient for Fe^{2+} (unit: cm^2 d^{-1}).

The volume based turnover rate was calculated by dividing P by the diffusional length Δz.


Fig. 2: DOC, ferrous iron, sulfate, and pH in the pore waters of the sites 116 and 76 (December 1997), and site 77 (August, November 1996 and February 1997).

DOC-, Eisen(II)- und Sulfatkonzentration sowie pH-Wert im Porenwasser der Sedimente.

○ Sulfate   △ Fe(II)   + DOC

Since H_2S could not be detected by smell, it was assumed that all released H_2S reacted with Fe^{2+} to FeS. In order to correct for this precipitation reaction, the rate of sulfate reduction was added to the rates of iron reduction as determined by the mass balance calculation. The whole-sediment diffusion coefficient $D_{s,Fe2+}$ was determined from $^{35}SO_4^{2-}$ tracer diffusion experiments in three replicate subcores of each sampling location [30]. We did not correct for electric effects in estimating Fe^{2+} turnover, as has been done elsewhere [32, 33], since only Fe^{2+} and H^+ displayed strong concentration gradients (Fig. 2), and since H^+ concentrations above 1 μmol L^{-1} were restricted to the upper 2 cm of the sediment.
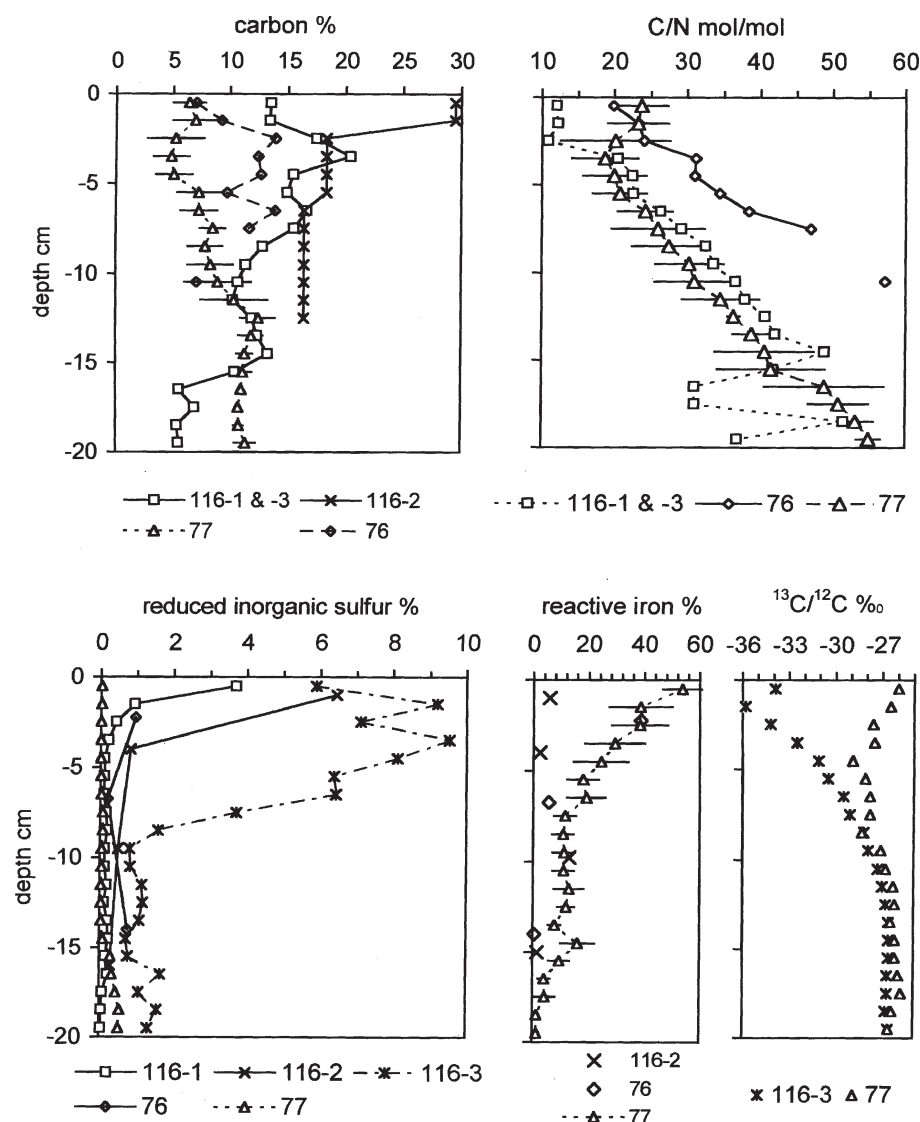
Fig. 3: Molar C/N ratios, carbon contents, reduced inorganic sulfur contents, reactive iron contents (FeOOH assumed; all in % of total dry weight), and isotopic ratios of carbon ($\delta^{13}C$) in the sediments.

Molare C/N-Quotienten, Gehalte an Kohlenstoff, TRIS und reaktivem Eisen sowie $\delta^{13}C$-Isotopenwerte in den Sedimenten.

Table 2: Deposition rates, accumulation rates of TRIS, and sediment thickness in the period 1968 to 1996 and 1986 to 1996. Deposition of AOC was estimated using Equations (2) and (3).

Depositionsraten (Gesamtmassen, Kohlenstoff, reaktives und Gesamteisen), TRIS-Akkumulationsraten und Sedimentmächtigkeit. Deposition von AOC wurde nach Gleichungen (2) und (3) berechnet.

Site	Total mass	OC	AOC	Fe_{rea} (Fe_{total})	TRIS	Sediment thickness
	g m^{-2} a^{-1}	g m^{-2} a^{-1}	g m^{-2} a^{-1}	g m^{-2} a^{-1}	g m^{-2} a^{-1}	cm
77, 1968	1700 (400...3 600)	165 (56...300)	3...6	81...98 (196)	0.1...1.3	16...35
77, 1986	–	120	6...13	145 (360)	0.5	13.5
76, 1968	190 (160...220)	23[2]	–	64[1,2] (90)	1.6[2]	5...7
76,1986	–	23	–	–	–	3
116, 1968	690 (620...720)	96 (86...106)	5...10	57[2] (276)	8.2 (1.3...17.1)	13...18
116, 1986	330	51 (51...52)	10...19	20[2] (146)	12.1 (1.6...22.1)	5...6

[1] oxalate dissolvable iron   [2] no replicates

Minimum long-term carbon oxidation rates were estimated from the TRIS inventory and the estimated age of the layers, assuming that all TRIS was initially reduced to H_2S by the oxidation of organic matter from oxidation state 0 to +4, and subsequently precipitated as FeS. Expressed in molar units of sulfur, this rate is equivalent to the TRIS retention rates.

4 Results

4.1 Surface and Pore Waters

The lakes followed a dimictic regime in 1996/1997, with clinograde O_2 profiles and the metalimnion extending from about 4 m downwards. During summer stratification the pH values were 2.8 (77 and 76) and 3.0 (116) in the epilimnion and increased to 3.5 (77) 5.6 (76) and 6.1 (116) towards the sediment-water interface. Sulfate (4.7...13.7 mmol L^{-1}), ferrous iron (maxima: 3.4...12.5 mmol L^{-1}), and ferric iron (0.3...1.9 mmol L^{-1}) concentrations decreased along the lake chain (77 > 76 > 116). The pore waters were dominated by SO_4^{2-}, Fe^{2+}, and Ca^{2+} with maximal concentrations of 10...22 mmol L^{-1} (77), 5...14 mmol L^{-1} (76), and 2...6 mmol L^{-1} (116) (Fig. 2). In 116 and 77 the pH increased with depth from 3 to 3.5 at the sediment-water interface to above 6. In lake 76 the pH peaked at the water-sediment interface and decreased with depth. Concentrations of Fe^{2+} (77 and 116) and DOC (77, 76, 116) increased below the sediment-water interface, peaking at depths of 10 cm to 20 cm (Fig. 2). Sulfate concentrations generally decreased at greater depths but showed differing patterns in the upper 10 cm of the sediments.

4.2 Solid Phases

Based on dry weight, reactive iron contents ranged from nearly 0% to 54% (77), 39% (76), and 13% (116), assuming the presence of FeOOH (Fig. 3). In 77 and 76 the iron contents clearly decreased with depth. Carbon contents covered a range of 2.7...13.3% in 77, 7...13.9% in 76, and 1...29.5% in 116 (Fig. 3). The molar C/N values of bulk samples ranged from 10 to 55. Visible lignite pieces showed values of 80 to 100. C/N values peaked at – 4 cm (77) and –0.5 cm (116 and 76). $\delta^{13}C$ values ranged from –25.8‰ to –35.8‰ and peaked at depths of –4.5 cm (77) and –1.5 cm (116). The TRIS contents increased from below 0.1% to 0.5% below depths of 14 cm in 77. In lake 76 TRIS contents were similar to 77 (0.2% to 0.9%), whereas at site 116 concentrations peaked close to the surface and at much higher values (3.8% and 9.5%).

4.3 Sedimentation and Dating

The mine ground-sediment interfaces were assigned to distinct changes in bulk density, indicating the beginning of sedimentation. The ^{137}Cs profile at site 116 (Fig. 4) displayed two distinct concentration peaks which we assigned to the fall out of the Chernobyl accident (1986) and the 1960's bombing period onto the former mine ground [25, 26]. Both "1960's-peak" and a distinct change in bulk density coincided, confirming this approach. Bulk density increased from 0.01 to 0.05 g cm^{-3} in the uppermost layers to values of 0.25...0.5 g cm^{-3} at the bulk density jump. The obtained deposition data substantially differed between the sites (Table 2). At site 77 high deposition of total sediment mass, carbon, and iron coincided with low TRIS accumulation. At site 76 little mass and carbon had been deposited, while the deposition of reactive iron was high in relative terms. Site 116 had an intermediate position with reference to the total mass and carbon
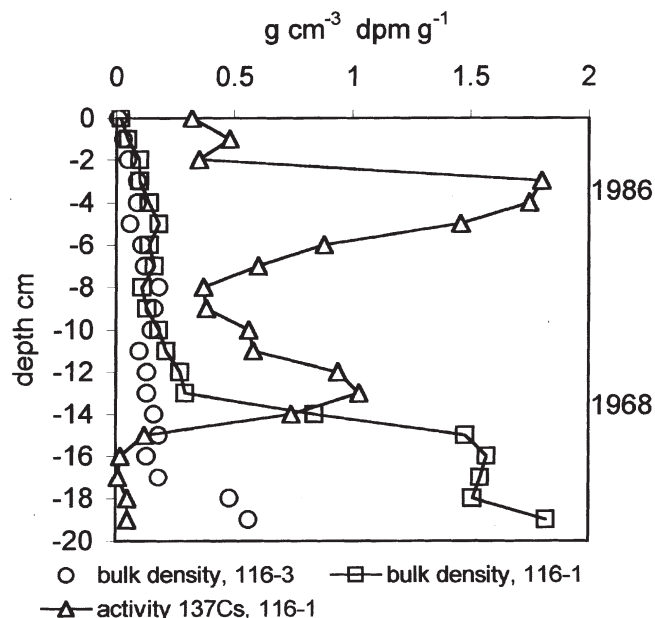

Fig. 4: Bulk density and activity of ^{137}Cs in the cores 116-1 and 116-3. Peaks of ^{137}Cs are assigned to fallout periods. The ^{137}Cs profiles are not decay corrected.

Lagerungsdichten und ^{137}Cs-Aktvitäten in den Sedimentkernen 116-1 und 116-3. Peaks der ^{137}Cs-Aktivität, unkorrigiert für radioaktiven Zerfall, sind Zeiträumen atmosphärischen Fallouts zugeordnet.

deposition. There, low iron deposition rates and high TRIS accumulation rates coincided.
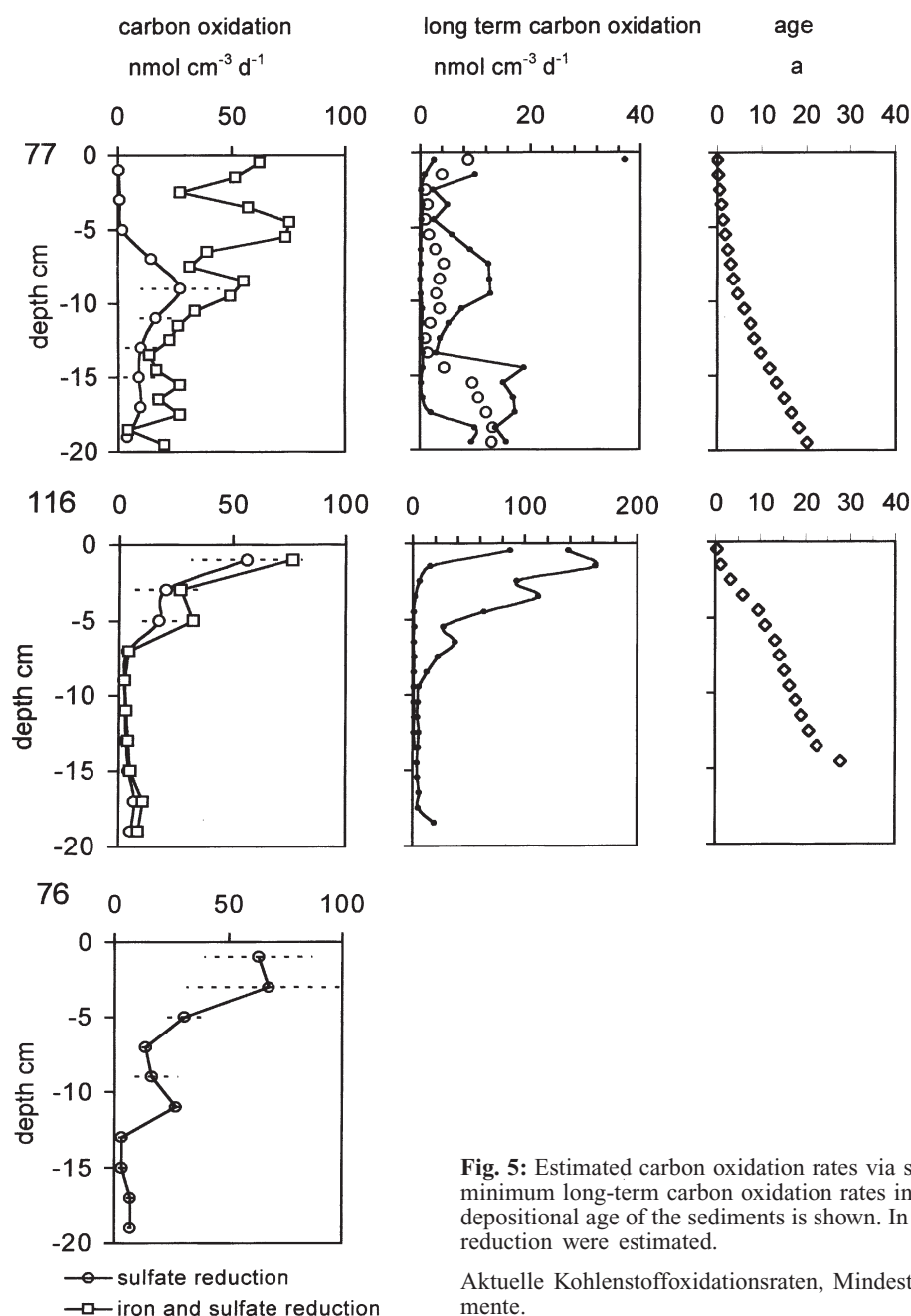
4.4 Estimated Carbon Oxidation Rates

Carbon oxidation rates via sulfate and iron reduction (Fig. 5) ranged from 4 to 75 nmol cm^{-3} d^{-1} (77), 3 to 68 nmol cm^{-3} d^{-1} (76, only sulfate reduction), and from below 1 to 78 nmol cm^{-3} d^{-1} (116). Based on the sediment surface area the rates ranged from 2.4 to 4.8 mmol m^{-2} d^{-1}. The relative contribution of ferric iron reduction rates was higher in 77 than in 116.

Minimum long-term carbon oxidation rates, obtained from the concentration of TRIS and the estimated depositional age of the sediments (Fig. 5) ranged, based on the sediment surface area, from 0.3 to 2.2 mmol m^{-2} d^{-1} in 77 and from 2.7 to 16 mmol m^{-2} d^{-1} in 116. They were therefore in 116 in average higher, and in 77 lower than the rates that had been determined by the turnover measurements.

5 Discussion

5.1 Carbon Oxidation Rates and Carbon Reactivity

The rates of carbon oxidation in the sediments of lake 77, 76, and 116 are in the wide range of rates that have been reported for aquatic systems (Table 3). Differences in rates may be caused by the incompleteness of the determined pathways and seasonal variations. In Lake Anna, the only lake that was influenced by acidic mine drainage [5], the carbon oxidation rates due to sulfate reduction exceeded the rates of the examined lakes by one or two orders of magnitude. Higher carbon oxidation rates have also been reported for freshwater wet-

Fig. 5: Estimated carbon oxidation rates via sulfate and ferric iron reduction and estimated minimum long-term carbon oxidation rates in lakes 77 and 116. On the right the estimated depositional age of the sediments is shown. In lake 76 only carbon oxidation rates via sulfate reduction were estimated.

Aktuelle Kohlenstoffoxidationsraten, Mindestlangzeitraten und geschätztes Alter der Sedimente.

lands and peatlands [31, 34–36], and coastal sediment [24, 37]. In contrast, rates in sediments of mesotrophic Little Rock Lake [38], Lake Sempach [39], and ten lakes of differing trophic status in Quebec [40] were similar to those estimated in this study. Similar rates have been reported for the continental margin sediments of eastern Skaggerak [41]. It can be concluded that carbon oxidation rates in the sediments are comparable to those in sediments of natural waters, despite pH values below 3 in the lake water and reported low primary production rates in acidic mine lakes [42].

It is remarkable that the long-term carbon oxidation rates at site 116, as estimated from the TRIS inventory, were higher than the rates obtained from turnover measurements (Fig. 5). Usually in lake sediments the rates of TRIS accumulation have been reported to be lower than the rates of turnover measurements, as at site 77, probably since TRIS is reoxidized [38].

The larger magnitude of the long-term carbon oxidation rates estimated for site 116 may reflect that in each newly deposited layer the most reactive organic matter is metabolized in weeks to months [43]. Consequently, the most reactive organic matter is not present any more when turnover measurements are performed in a layer that is older than some months. The current metabolic turnover rate in such a layer is then lower than the long-term turnover rate, as estimated by the TRIS inventory. For the sites 77 and 76 it also cannot be ruled out that "old" geogenic pyrite was included in the TRIS inventory and caused an overestimate of long-term carbon oxidation rates. For the site 116, though, such an overestimate seems unlikely based on ^{34}S isotope measurements [28].

The organic matter reactivity, expressed as a first order reaction constant, was within the range reported from other environments (Table 4). We assumed first-order kinetics since

Table 3: Carbon oxidation rates in aquatic environments. All values are integrated across the sampled profiles and were partly recalculated assuming oxidation of <CH₂O> to CO_2.

Flächennormierte Kohlenstoffoxidationsraten in aquatischen Ökosystemen.

Site	Method	Oxidation rate[#] mmol m^{-2} d^{-1}	Reference
Acid mine lake sediments			
Lake 116 Pelagial	Incubations, modelling	3.7, S, I	This study
Lake 116 Litoral	Incubations, modelling	14.7, S, I	[28]
Lake 76 Pelagial	Incubations	4.8, S	This study
Lake 76 Litoral	Incubations	9.2, S	[28]
Lake 77	Incubations	3.4, S, I	This study
Lake Anna	Incubations	3.42...452, S	[5]
Freshwater sediments			
Little Rock	Incubations	3.0...10.4, S	[38]
Lake Sempach	Pore water modelling	8.0, total	[39]
Quebec, 10 lakes	Benthic chambers, inc.	–3.0...60, total	[40]
Wintergreen	Incubations	30.6, S	[65]
Mendota	Incubations	200...440, S	[66]
Washington	Incubations	0.24, S	[67]
Freshwater wetlands			
Beaver pond	Incubations	79.6 ± 31.9, S, I, M	[31]
Beaver pond	Water-air flux	45, total	[35]
Peatland	Chamber flux	144...157, total	[36]
Ombrothrophic peatland	Incubations	36...70, S, M	[34]
Marine sediments			
Coastal (Limfjorden)	Incubations	26, S	[22]
Coastal (CapeLookout Bight)	Benthic chambers	98 ± 14, total	[37]
Shelf (Skaggerak)	Incubations	10.2...15.8, total	[41]
Continental margin	Pore water modelling	0.02...1.1, total	[45]

[#] S: Sulfate reduction; I: Ferric iron reduction; M: Methanogenesis; total: All pathways

Table 4: Carbon oxidation rate constants in sediments and soils.

Kohlenstoffoxidationsratenkonstanten in Sedimenten und Böden.

Environment	Method	Oxidation constant, a^{-1}	Source
Lake 116			
–1 cm	Turnover (TRIS eq.)	0.02...0.22 (0.27...0.73)	This study
–5 cm	Turnover (TRIS eq.)	0.004...0.02 (0.0004...0.03)	This study
–15 cm	Turnover (TRIS eq.)	0.0002...0.007 (0.001...0.003)	This study
Lake 77			
–1 cm	Turnover	0.03...0.07	This study
–5 cm	Turnover	0.02...0.10	This study
–15 cm	Turnover (TRIS eq.)	0.003...0.009 (0.0007...0.024)	This study
Lake 76			
–1 cm	Turnover	0.08	This study
–5 cm	Turnover	0.004	This study
Marine sediments			
Coastal marine	Decomp. experiments	7.2...8.8 (k_1) 0.84...1.02 (k_2)	[43]
Coastal marine	Porewater G-model	0.5 (k)	[50]
Coastal lagoon	Porewater G-model	0.7...11.2 (k)	[37]
Continental shelf	Ammonification rates	0.95 (k)	[51]
Continental margin	Porewater G-model	$1.3 \cdot 10^{-4}...4.1 \cdot 10^{-3}$ (k)	[46]
Deep Sea (Pacific)	Porewater G-model	$6.3 \cdot 10^{-4}...2.3 \cdot 10^{-3}$ (k)	[46]
Deep Sea (Pacific)	Porewater G-model	$9.5 \cdot 10^{-3}...7.9 \cdot 10^{-2}$ (k)	[44]
Deep Sea (Pacific)	Porewater G-model	$1.7 \cdot 10^{-4}...3.0 \cdot 10^{-2}$ (k)	[45]
Deep Sea	Porewater G-model	$0.5...7.8 \cdot 10^{-3}$ (k)	[45]
Deep Sea (Atlantic)	Porewater 2-G-model	1.4...16.4 (k_1) 0.013...0.035 (k_2)	[68]

Table 4 (Continued)

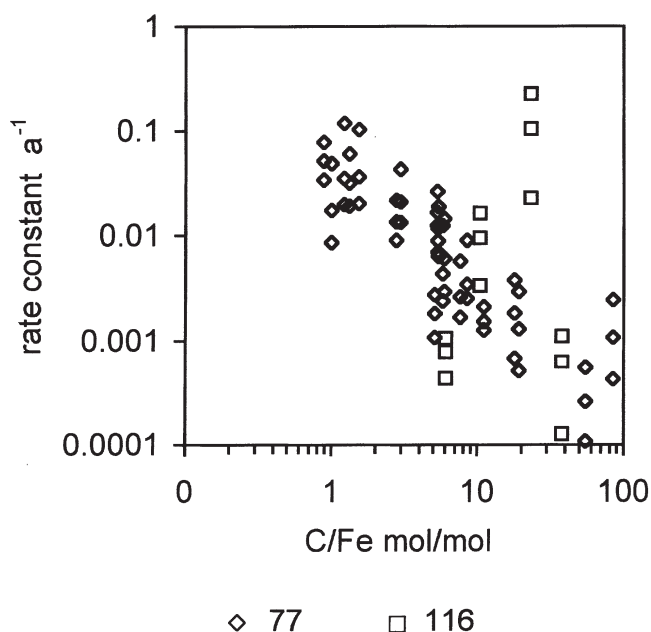| Environment	Method	Oxidation constant, a^{-1}	Source
Soils			
Agricultural temperate	Decomposition experiments; ^{14}C; Pool-model	4.2 ($k_{\text{decomposable plant}}$) 0.3 ($k_{\text{resistant plant}}$) 0.41 ($k_{\text{soil biomass}}$) 0.014 ($k_{\text{physically stabilized NOM}}$) $3.5 \cdot 10^{-3}$ ($k_{\text{chemically stabilized NOM}}$)	[47]
Grasslands temperate	Pool model; decomp. experiments; ^{14}C	0.14 (k_1); 0.0038 (k_2); 0.00013 (k_3)	[48]
Agricultural temperate (Ultisol)	^{14}C; pool model	0.1...1.0 (k_1); 0.01 (k_2); 0.001 (k_3); 0.0001 (k_4)	[49]
Grasslands/agricultural temperate	Incubation experiments; 1$^{\text{st}}$ order model	0.24...3.94 (k_1)	[69]

acetate amendment experiments had indicated that sulfate reduction was limited by the presence of utilizable organic compounds [28]. The comparison with other environments illustrates the rapid change of the organic matter reactivity occurring with depth. At greater depths ($10^{-4}...10^{-2}$ a^{-1}) the organic matter reactivity was as low as in deep sea sediments, which receive only recalcitrant NOM from the water column [44–46]. Similar values have been obtained for the most recalcitrant soil organic matter fractions [47–49]. In the uppermost layers, the oxidation rate constants (0.05...0.2 a^{-1}) were almost as high as for plant residues and algae residues in soils and coastal marine sediments [43, 47, 50, 51]. The highest reported constants were one to two orders of magnitude larger than in the sampled sediments [43, 47].

The reactivity of organic matter in sediments may be controlled by the adsorption of organic matter at mineral and iron oxide surfaces [52–54], as has been proposed for marine sediments [55]. This factor did not have a discernable effect at site 77, despite strong gradients in iron oxide concentrations. The rate constants were negatively correlated to the molar C/Fe ratios (Spearman $r^2 = 0.87...0.91$, $\alpha < 0.05$; Fig. 6). If adsorption of organic matter at iron oxide surfaces was an important factor controlling the organic matter reactivity, one should expect the rate constants to be positively correlated to the molar C/Fe ratio. At site 116 the data basis with respect to ferric iron concentrations was too small in order to be instructive (Fig. 6).

Fig. 6: Carbon oxidation rate constants vs. molar ratio carbon/reactive iron.

Kohlenstoffoxidationsraten vs. molare C/Fe-Verhältnisse.

5.2 Carbon Sources and Carbon Reactivity

The carbon oxidation rates in the sediments of acidic mine lakes should be related to the carbon origin. This is likely due to the differences in the age and the chemical characteristics of aquatic, terrestrial, and refractory organic matter [10–13]. Hence we tried to trace how much of the deposited organic matter stemmed from the biomass production within the lakes. The obtained concentrations of aquatic organic carbon (AOC) and non-AOC were then related to the carbon oxidation rates.

Three different sources of organic matter may be distinguished in lakes 77, 76, and 116. These sources can be labeled as lignite, aquatic, and terrestrial organic matter. It was assumed that the elemental and isotopic characteristics, which are indicative for these sources, had not been obscured during diagenesis. This is a reasonable approximation due to three reasons. First, the elemental and isotopic characteristics have been reported to be fairly stable during diagenesis [12, 13].

Second, the observed gradients were extraordinarily large compared to natural lake sediments [12]. Third, diagenesis seemed to be at an initial stage with respect to carbon oxidation. Probably less than 10% of the originally deposited carbon had been oxidized during diagenesis at all depths, with the exception of the uppermost layers of site 116 (20...45%). We estimated these numbers from (I) the total carbon concentrations and the carbon equivalents that had accumulated in the TRIS pool and (II) from the rates of carbon oxidation, the estimated age of the respective layer and the carbon equivalents in form of carbon and TRIS. Aquatic organic matter has generally narrow C/N ratios of about 10, and (^{13}C values of about –26...–44‰ [10–13]. Terrestrial organic matter has typically higher C/N ratios (20...60) and often higher (^{13}C values (–25...–28‰) [10, 11, 13]. Pieces of lignite, picked from the sediments in 77 and 116 at depths of about 20 cm, had C/N ratios of 80...100 and δ^{13}C values of 25‰.

The high C/N and δ^{13}C values at larger depths show that at the beginning terrestrial organic matter and lignite were deposited in the lakes (Fig. 3). The C/N and δ^{13}C values of the deposited organic carbon decreased with time. Hence a different organic matter source of low C/N and δ^{13}C values was increasingly deposited. We attribute this change in C/N and δ^{13}C values to the input of AOM. Assigning a C/N value of 11 and a δ^{13}C value of -35.8‰ to AOM, relative AOC contents (x) were estimated using Equation (2):

$$\delta^{13}(OC) = x\,\delta^{13}(AOC) + (1 - x)\ \delta^{13}(non\text{-}AOC) \qquad (2)$$

with
$\delta^{13}(OC)$: δ^{13} measured signature of the organic carbon (unit: ‰)
$\delta^{13}(AOC)$: -35.8‰
$\delta^{13}(non\text{-}AOC)$: -26‰

The AOC deposition rates for the period 1965–1997 and 1986–1997 were then estimated by using the relative content of AOC, the carbon concentrations, and dating data:

$$S_{AOC} = x\,S_{OC}/t_{dep\ period} \qquad (3)$$

with
S_{AOC}:   deposition of AOC (unit: g m^{-2} a^{-1})
x: relative content of AOC (unit: 1)
S_{OC}:   deposited carbon (unit: g m^{-2})
$t_{dep\ period}$:   deposition period (unit: a)

According to this approach AOC accounts for about 5% of the deposited carbon in 77 and for about 14% in 116 (see also Table 2). In both lakes the contribution of AOC has increased during the last decade (Fig. 7). Interesting is that it dropped again in 77 in 1995/1996 after an intermediate peak representing about five years. This drop is also indicated by the higher molar C/N ratio in the uppermost layer of 77 (Fig. 3).

In order to estimate the contribution of AOC to the carbon oxidation rates (Eq. (4)), we segmented the profiles with respect to their AOC content (Fig. 7). We used the carbon reactivity constant of the segment in which AOC was nearly absent as a proxy for the reactivity of non-AOC. This value was then assigned to the non-AOC in the segment in which both AOC and non-AOC were present (Eq. (7)). The contribution of AOC to the oxidation rates in this segment with mixed sources was given by the difference between the measured rate and the contribution of non-AOC. The difference between the measured rate and the contribution of non-AOC was calculated from the Equations (5) and (6).

$$Contribution_{AOC} = R_{AOC}/R_{measured} \qquad (4)$$

with

$$R_{AOC} = R_{measured} - R_{non\text{-}AOC} \qquad (5)$$

$$R_{non\text{-}AOC} = k_{non\text{-}AOC}\ c_{non\text{-}AOC} \qquad (6)$$

$$k_{non\text{-}AOC} = R_{measured\text{-}non\text{-}AOC}/c_{non\text{-}AOC} \qquad (7)$$

with
R_{AOC}:   oxidation rate of AOC (unit: nmol cm^{-3} d^{-1})
$R_{measured}$:   measured sum of sulfate and iron reduction in carbon equivalents (unit: nmol cm^{-3} d^{-1})
$R_{non\text{-}AOC}$:   oxidation rate of non-AOC (unit: nmol cm^{-3} d^{-1})
$k_{non\text{-}AOC}$:   first order constant of non-AOC oxidation rate (unit: d^{-1})

According to this approach the oxidized carbon stemmed to 42...58% (77) and 70...78% (116) from AOC, despite the fact that AOC amounted only to about 5% (77) and 14% (116) of the deposited organic carbon (Table 2). The importance of AOC for the carbon turnover in the sediments is therefore much higher than the relatively small deposition rates of AOC suggest.

Similar results were obtained when the carbon oxidation rates were fitted to first order expressions [43, 56, 57] by the Levenberg-Marquardt method. The first order expressions contained the concentration of AOC and non-AOC, and the age of the respective layer, which may have influenced the carbon reactivity. In order to adequately reproduce the rate profiles, a model that incorporated two carbon fractions and decreasing reactivity with depth, or age, was necessary (Fig. 7). Using Equation (8), 56% (77) and 75% (116) of the total carbon oxidation rate was attributed to AOC oxidation.

$$R_{model} = k_1\,t_{dep}^{-1}\,c_{AOC} + k_2\,c_{non\text{-}AOC} \qquad (8)$$

with
R_{model}:   carbon oxidation rate (unit: μmol cm^{-3} a^{-1})
k_1, k_2:   fitting parameters (unit: 1, a^{-1})
t_{dep}:   age of a layer (unit: a)
c_{AOC}:   amount-of-substance AOC concentration (unit: μmol cm^{-3})
$c_{non\text{-}AOC}$:   amount-of-substance non-AOC concentration (unit: μmol cm^{-3})

Overall the carbon oxidation profiles were fairly reproduced by expression (8), suggesting that carbon concentrations, quality, and age controlled the carbon oxidation rates (Fig. 7). We tested the validity of the approach by using the parameterized model of 116 to reproduce the carbon oxidation profiles of 77, and vice versa. Expression (8) was not adequate to predict the exact magnitude of the carbon oxidation rates when the best fit from the respectively other site was used. The depth integrated carbon oxidation rates were overestimated or underestimated by a factor 1.6 (Fig. 7). This discrepancy is not very dramatic since differences of this magnitude also occurred among replicated sulfate reduction rates.

We also tested whether the DOC concentrations were related to the carbon oxidation rates in 77 and 116. The mineralisation of organic matter in sediments is believed to be preceded by the extracellular hydrolysis of particulate organic matter into high molecular weight DOC and subsequent breakdown into low molecular weight DOC which is then utilized by microorganisms. This breakdown is also supposed to be the rate limiting step in this process [58, 59]. According to this concept, DOC concentrations should be positively correlated to the carbon oxidation rates. This was not the case in the examined lake sediments. The carbon oxidation rates in all sediments were weakly negatively correlated to the DOC concentrations in the pore waters (Fig. 8). The substrates for carbon oxidation via sulfate and iron reduction therefore were not provided by the majority of the DOC that was present in the pore waters. These considerations illustrate that in this system the sum parameter DOC is of little use when it comes to the utilization of DOC by microorganisms. DRIFT spectra of dissolved organic matter had further suggested that the average structural characteristics were rather invariable with depth. They also resembled the spectra of recalcitrant humic substances [28]. Based on these findings it seems unlikely that the majority of the DOC was actively involved in the carbon mineralization process.
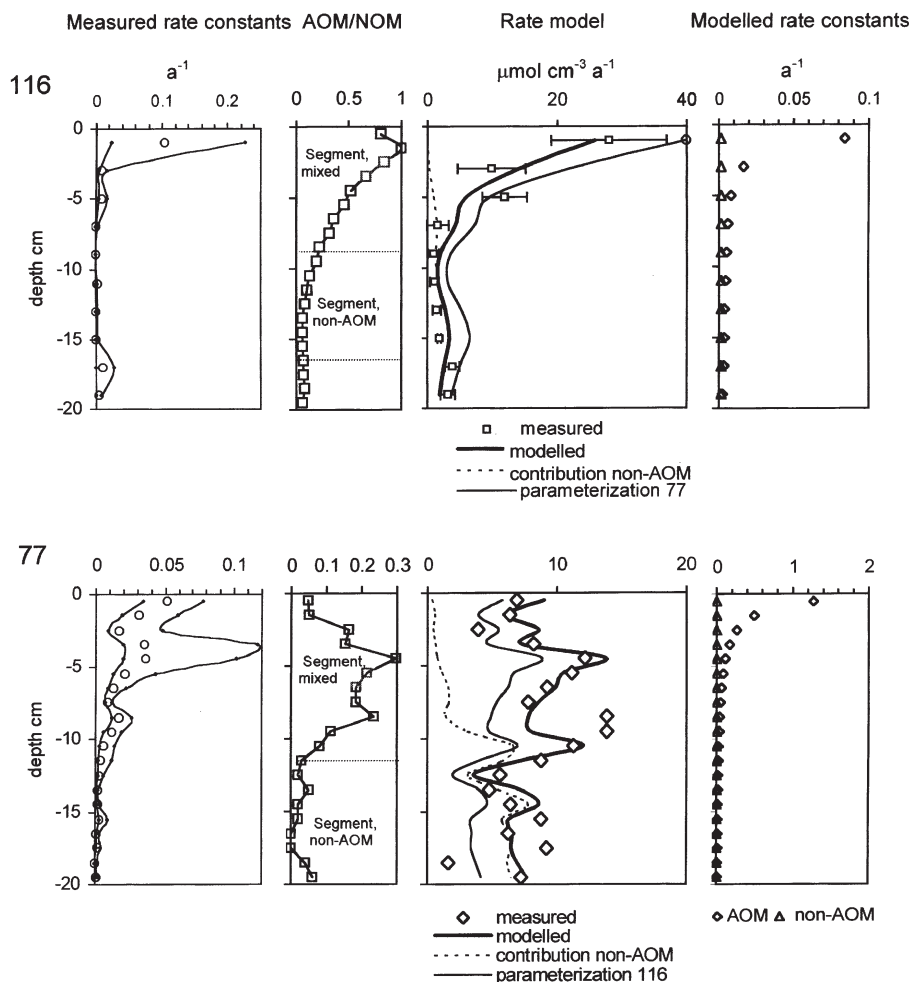
Fig. 7: Measured rate constants, relative content of AOC, measured, and modelled rates and modelled rate constants for AOC and non-AOC in lakes 116 and 77.

Aus Messwerten bestimmte Ratenkonstanten, relative Gehalte an AOC und gemessene und modellierte Raten und Ratenkonstanten für AOC und Nicht-AOC an den Standorten 77 und 116.
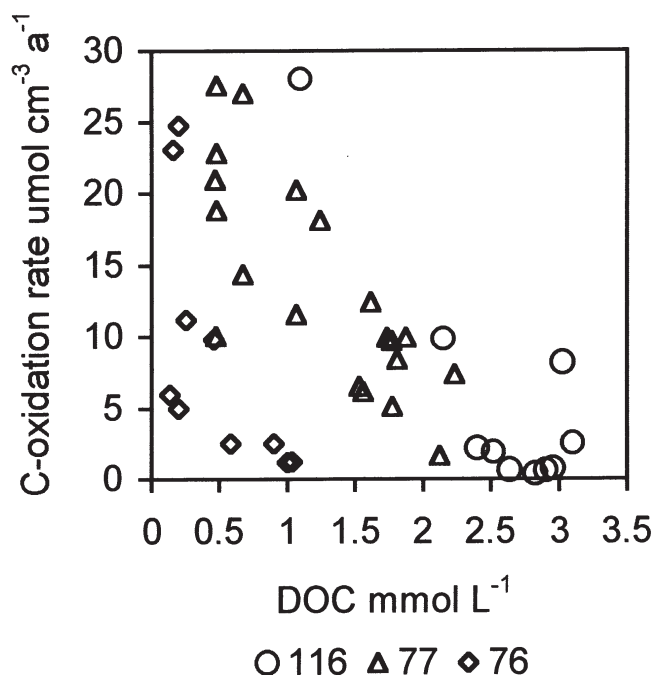
Fig. 8: Carbon oxidation rates vs. DOC concentrations.

Kohlenstoffoxidationsraten vs. DOC-Konzentrationen.

The DOC concentration seemed to be rather controlled by an interaction with dissolved ferrous iron. Both variables were correlated (Table 5), indicating that sources and sinks were similarly located. A co-release of iron oxide bound DOC during the reduction of ferric iron [60] and a chemical association of DOC and dissolved ferrous iron [61] may have contributed to this phenomenon. At site 76 a correlation between DOC and dissolved ferrous iron was not found, probably due to sampling and analytical errors being large compared to the small gradients of ferrous iron at site 76.

Table 5: DOC/Fe^{2+} ratios and correlation coefficients (Pearson) between dissolved ferrous iron and DOC in the sediments.

DOC/Fe^{2+}-Verhältnisse und Korrelationskoeffizienten zwischen gelöstem Eisen(II) und DOC in den Sedimenten.

Site/Date	[DOC]/[Fe]$^{\#}$	r^2	[DOC]/[Fe]$^{\varphi}$	r^2
77 August	0.27	0.77	0.20	0.67
77 November	0.20	0.96	0.19	0.69
77 February	0.23	0.73	0.25	0.88
116 December	0.81	0.92	0.70	0.91

$^{\#}$ upper section of profiles; $^{\varphi}$ lower section of profiles

6 Conclusions

About 30 years after the flooding of the mine pits carbon was utilized at similar rates as in many freshwater and marine sediments. A prerequisite for the internal neutralization of the lakes was therefore fulfilled. While the deposition of non-aquatic organic matter has prevailed since flooding, aquatic biomass was increasingly deposited. This AOC deposition increased the carbon oxidation rates in the sediments. Our estimates suggest that AOC, amounting to about 5...14% of the total carbon deposited, accounted for about 50...75% of the carbon oxidation rates. The deposition of aquatic organic matter probably ultimately limits carbon oxidation via sulfate and iron reduction rates in acidic mine lake sediments, as has been predicted earlier [3]. Our results suggest that this limitation diminishes over time as the lakes become more productive. This conclusion corroborates with predictions of other workers [62] and the considerable potentials for primary biomass production in the hypolimnion and close to the water-sediment interface which have been reported for other acidic mine lakes [63, 64]. Higher productivity and carbon mineralization rates, however, do not necessarily cause high neutralization rates, as can be seen from the low TRIS contents of lake 77 sediments. The combined effect of factors controlling the mineralisation rate, the competition between pathways of carbon mineralisation, and the reoxidation of TRIS requires further investigation.

Acknowledgements

List of Abbreviations and Symbols

AOM:	aquatic organic matter
AOC:	aquatic organic carbon
non-AOM:	lignite and terrestrial organic matter
non-AOC:	lignite and terrestrial organic carbon
DOM:	dissolved organic matter
DOC:	dissolved organic carbon
TRIS:	total reduced inorganic sulfur
$\delta^{13}C$:	isotopic signature of carbon, defined as $[U(\text{sample})/U(\text{standard}) -1] \cdot 1000$, with $U = n(^{13}C)/n(^{12}C)$ (unit: ‰)
$\delta^{13}(AOC)$:	$\delta^{13}C$ signature of AOC (unit: ‰)
$\delta^{13}(\text{non-AOC})$:	$\delta^{13}C$ signature of non-AOC (unit: ‰)
$\delta^{13}(OC)$:	measured ^{13}C signature of the total organic carbon (unit: ‰)
$\Delta C/\Delta z$:	vertical concentration gradient in the pore waters (unit: nmol cm^{-4})
c_{AOC}:	AOC concentration (unit: μmol cm^{-3})
$c_{\text{non-AOC}}$:	non-AOC concentration (unit: μmol cm^{-3})
$D_{s,Fe^{2+}}$:	whole-sediment diffusion coefficient for Fe^{2+} (unit: cm^2 d^{-1})
$k_{\text{non-AOC}}$:	first-order constant of non-AOC oxidation rate (unit: d^{-1})
k_1, k_2:	fitting parameters in carbon oxidation rate model (unit: 1, a^{-1})
P:	estimated net iron turnover rate (unit: nmol cm^{-2} d^{-1})
R_{AOC}:	oxidation rate of AOC (unit: nmol cm^{-3} d^{-1})
R_{measured}:	measured sum of sulfate and iron reduction in carbon equivalents (unit: nmol cm^{-3} d^{-1})
$R_{\text{non-AOC}}$:	oxidation rate of non-AOC (unit: nmol cm^{-3} d^{-1})
R_{model}:	modelled carbon oxidation rate (unit: μmol cm^{-3} a^{-1})
S_{AOC}:	deposition rate of AOC (unit: g m^{-2} a^{-1})
S_{OC}:	deposited organic carbon (unit: g m^{-2})
$t_{\text{dep period}}$:	deposition period (unit: a)
t_{dep}:	age of a sediment layer (unit: a)
x:	relative content of AOC (unit: 1)

References

[1] *Schnoor, J. L., Galloway, J. N., Moldan, B.:* East Central Europe: An Environment in Transition. Environ. Sci. Technol. *31,* 412A–416A (1997).

[2] *Evangelou, V. P., Zhang, Y. L.:* A review: Pyrite oxidation mechanisms and acid mine drainage prevention. Crit. Rev. Environ. Sci. Technol. *25,* 141–199 (1995).

[3] *Peine, A., Peiffer, S.:* Neutralization processes in acid mine lake sediments. Arch. Hydrobiol. Spec. Issues Advanc. Limnol *48,* 261–267 (1996).

[4] *Peine, A., Peiffer, S.:* In lake-neutralization of acid mine lakes. In: *Geller, W., Klapper, H., Salomons, W.* (Eds.): Acidic Mining Lakes. Springer, Berlin, 1998 pp. 47–63.

[5] *Herlihy, A. T., Mills, A. L.:* Sulfate reduction in freshwater sediments receiving acid mine drainage. Appl. Environ. Microbiol. *49,* 179–186 (1985).

[6] *Schindler, D. W., Turner, M. A., Stainton, M. P., Linsey, G. A:* Natural sources of acid neutralizing capacity in low alkalinity lakes of the Precambrian shield. Science *232,* 844–847 (1986).

[7] *Giblin, A. E., Likens, G. E., White, D., Howarth, R. W.:* Sulfur storage and alkalinity generation in New England lake sediments. Limnol. Oceanogr. *35,* 852–869 (1990).

[8] *Kelly, C. A., Amaral, J. A., Turner, M. A., Rudd, J. W. M., Schindler, D. W., Stainton, M. P.:* Disruption of sulfur cycling and acid neutralization in lakes at low pH. Biogeochemistry *28,* 115–130 (1995).

[9] *Sherman, L. A., Baker, L. A., Weir, E. P., Brezonik, P. L.:* Sedimentary pore water dynamics of Little Rock Lake, Wisconsin: Geochemical processes and seasonal and spatial variability. Limnol. Oceanogr. *39,* 1115–1171 (1994).

[10] *Bernasconi, S. M., Barbieri, A., Simona, M.:* Carbon and nitrogen isotope variations in sedimenting organic matter in Lake Lugano. Limnol. Oceanogr. *42,* 1755–1765 (1998).

[11] *Buffle, J.:* Complexation reactions in aquatic systems: An analytical approach. Ellis Horwood Limited, Chichester, 1988.

[12] *Hodell, D. A., Schelske, C. L.:* Production, sedimentation, and isotopic composition of organic matter in Lake Lugano. Limnol. Oceanogr. *43,* 200–214 (1998).

[13] *Meyers, P. A., Ishiwatari, R.:* Lacustrine organic geochemistry – an overview of indicators of organic matter sources and diagenesis in lake sediments. Org. Geochem. *20,* 867–900 (1993).

[14] LAUBAG (Lausitzer Braunkohle Aktiengesellschaft): written communication, 1996.

[15] *Hoepner, T.:* Design and use of a diffusion sampler for interstitial water from fine grained sediments. Environ. Technol. Lett. *2,* 187–196 (1981).

[16] *Tamura H., Goto, K., Yotsuyanagi, T., Nagayama, M.:* Spectrophotometric determination of iron(II) with 1,10-phenanthroline in the presence of large amounts of iron(III). Talanta *21,* 314–318 (1974).

[17] *Wallmann, K., Hennies, K., König, I., Petersen, W., Knauth, H.-D.:* New procedure for determining reactive Fe(III) and Fe(II) minerals in sediments. Limnol. Oceanogr. *38,* 1803–1812 (1993).

[18] *Canfield, D. E.:* Reactive iron in marine sediments. Geochim. Cosmochim. Acta *53*, 619–632 (1988).

[19] *Fossing, H., Jørgensen, B. B.:* Measurement of bacterial sulfate reduction in sediments: Evaluation of a single step chromium reduction method. Biogeochemistry *8*, 205–222 (1989).

[20] *Canfield, D. E., Raiswell, R., Westrich, J. T., Reaves, C. M., Berner, R. A.:* The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. Chem. Geol. *54*, 149–155 (1986).

[21] *Frevert, T.:* Hydrochemisches Grundpraktikum, UTB Birkhäuser, Basel, 1983.

[22] *Joergensen, B. B.:* The sulfur cycle of a coastal marine sediment (Limfjorden, Denmark). Limnol. Oceanogr. *22*, 814–832 (1977).

[23] *Urban, N. R., Bayley, S. E., Eisenreich, S. J.:* Export of dissolved organic carbon and acidity from peatlands. Water Res. *25*, 1619–1628 (1989).

[24] *O'Leary, M. H.:* Carbon isotopes in photosynthesis. Bioscience *38*, 328–335 (1988).

[25] *Rowan, J. S., Higgit, D. L., Wallin, D. E.:* Incorporation of Chernobyl derived radiocaesium into reservoir sedimentary sequences. In: *McManus, J., Duck, R. W.* (Eds.): Geomorphology and sedimentology of lakes and reservoirs. John Wiley & Sons, Chichester, 1993, pp. 55–72.

[26] *Wieland, E., Santschi, P. H., Hoehener, P., Sturm, M.:* Scavenging of Chernobyl ^{137}Cs and natural ^{210}Pb in Lake Sempach, Switzerland. Geochim. Cosmochim. Acta *57*, 2959–2979 (1993).

[27] *Bloesch, J., Burns, N. M.:* A critical review of sedimentation trap technique. Schweiz. Z. Hydrol. *42*, 15–55 (1980).

[28] *Blodau C., Hoffmann, S., Peine, A., Peiffer, S.:* Iron and sulfate reduction in the sediments of acid mine lake 116 (Brandenburg, Germany): Rates and geochemical evaluation. Water, Air, Soil Pollut. *108*, 249–270 (1998).

[29] *Peine, A., Küsel, K., Peiffer, S.:* Iron and sulfur cycling in iron-rich sediments of an acidic mine lake. Limnol. Oceanogr. (2000) (accepted).

[30] *Jørgensen, B. B.:* A comparison of methods for the quantification of bacterial sulfate reduction in coastal marine sediments. Geomicrobiology J. *1*, 11–47 (1978).

[31] *Roden E. R., Wetzel, R. G.:* Organic carbon oxidation and suppression of methane production by microbial Fe(III) oxide reduction in vegetated and unvegetated freshwater wetland sediments. Limnol. Oceanogr. *41*, 1733–1748 (1996).

[32] *Kuivila, K. M., Murray, J. W.:* Organic matter diagenesis in freshwater sediments: The alkalinity and total CO_2 balance and methane production in the sediments of Lake Washington. Limnol. Oceanogr. *29*, 1218–1230 (1984).

[33] *McDuff, R. E., Ellis, R. A.:* Determining diffusion coefficients in marine sediments: A laboratory study of the validity of resistivity techniques. Am J. Sci. *279*, 66–675 (1979).

[34] *Nedwell D., Watson, A.:* CH_4 production, oxidation and emissions in a UK ombrotrophic peat bog: Influence of SO_4^- from acid rain. Soil Biol. Biochem. *27*, 893–903 (1995).

[35] *Roulet, N. T., Crill, P. M., Comer, N. T., Dove, A., Boubonniere, R. A.:* CO_2 and CH_4 flux between a boreal beaver pond and the atmosphere. J. Geophys. Res. *102*, 29,313–29,319 (1997).

[36] *Wieder R. K., Yavitt, J. B., Lang, G. E.:* Methane Production and sulfate reduction in two Appalachian Peatlands. Biogeochemistry *10*, 81–104 (1990).

[37] *Martens, C. S., Klump, J. V.:* Biogeochemical cycling in an organic-rich coastal marine basin 4. An organic carbon budget for sediments dominated by sulfate reduction and methanogenesis. Geochim. Cosmochim. Acta *48*, 1987–2004 (1984).

[38] *Urban, N. R., Baker, L. A., Sherman, L. A., Brezonik, P. L.:* Sulfate reduction and diffusion in sediments of Little Rock Lake, Wisconsin. Limnol. Oceanogr. *39*, 797–815 (1994).

[39] *Furrer, G., Wehrli, B.:* Microbial reactions, chemical speciation, and multicomponent diffusion in pore waters of a eutrophic lake. Geochim. Cosmochim. Acta *60*, 2333–2346 (1996).

[40] *den Heyer, C., Kalff, J.:* Organic matter mineralization rates in sediments. A within and among lake study. Limnol. Oceanogr. *43*, 695–705 (1998).

[41] *Canfield, D. E., Thamdrup, B., Hansen, J. E.:* The anaerobic degradation of organic matter in Danish coastal sediments: Iron reduction, manganese reduction, and sulfate reduction. Geochim. Cosmochim. Acta *57*, 3867–3883 (1993).

[42] *Gyure, R. A., Konopka, A., Brooks, A., Doemel, W.:* Algal and bacterial activities in acidic (pH 3) strip mine lakes. Appl. Environ. Microbiol. *49*, 179–186 (1987).

[43] *Westrich, J. T., Berner, R. A.:* The role of sedimentary organic matter in bacterial sulfate reduction: The G model tested. Limnol. Oceanogr. *29*, 236–249 (1984).

[44] *Emerson, S., Fischer, K., Reimers, C., Heggie, D.:* Organic carbon dynamics and preservation in deep sea sediments. Dee-Sea Res. *32*, 1–21 (1985).

[45] *Heggie, D., Maris, C., Hudson, A., Dymond, J., Beach, R., Cullen, J.:* Organic carbon oxidation and preservation in NW Atlantic continental margin sediments. In: Geology and Geochemistry of Abyssal Plains. Geological Society Special Publication *31*, 215–236 (1987).

[46] *Reimers, C. E., Suess, E.:* The partitioning of organic carbon fluxes and sedimentary organic matter decomposition rates in the ocean. Mar. Chem. *13*, 141–168 (1983).

[47] *Jenkinson, D. S.:* Studies on the decomposition of plant material in soil. V. The effects of plant cover and soil type on the loss of carbon from ^{14}C labelled ryegrass decomposing under field conditions. J. Soil Sci. *28*, 424–434 (1977).

[48] *Parton, W. J., Schimel, D. S., Cole, C. V., Ojima, D. S.:* Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Sci. Soc. Am. J. *51*, 1173–1179 (1987).

[49] *Trumbore, S. E.:* Comparison of carbon dynamics in tropical and temperate soils using radiocarbon measurements. Glob. Biogeochem. Cycles *7*, 275–290 (1993).

[50] *Berner, R. A.:* A rate model for organic matter decomposition during bacterial sulfate reduction in marine sediments. In: Biogeochemistry of organic matter at the sediment-water interface. CNRS Int. Colloq., 35–45 (1980).

[51] *Billen, G.:* An idealized model of nitrogen recycling in marine sediments. Am. J. Sci. *282*, 512–541 (1982).

[52] *Gu, B., Schmitt, J., Chen, Z., Liang, L., McCarthy, J. F.:* Adsorption and desorption of different organic matter fractions on iron oxide. Geochim. Cosmochim. Acta *59*, 219–229 (1995).

[53] *McKnight, D. M., Bencala, K. E., Zellweger, G. W., Aiken, G. R., Feder, G. L., Thorn, K. A.:* Sorption of dissolved organic carbon by hydrous aluminum and iron oxides occurring at the confluence of Deer Creek with the Snake River, Summit County, Colorado. Environ. Sci. Technol. *26*, 1388–1396 (1992).

[54] *Stumm, W., Morgan, J. J.:* Aquatic chemistry. John Wiley & Sons, New York, 1996.

[55] *Hedges, J. I., Keil, R. G.:* Sedimentary organic matter preservation: an assessment and speculative synthesis. Mar. Chem. *49*, 81–115 (1995).

[56] *Berner, R. A.:* Early diagenesis: A theoretical approach, Princeton University Press, Princeton, 1980.

[57] *Middelburg, J.:* A simple rate model for organic matter decomposition in marine sediments. Geochim. Cosmochim. Acta *53*, 1577–1581 (1989).

[58] *Burdige, D. J., Gardner, K. G.:* Molecular weight distribution of dissolved organic carbon in marine sediment pore waters. Mar. Chem. *62*, 45–64 (1998).

[59] *Henrichs, S. M.:* Early diagenesis of organic matter in marine sediments: progress and perplexity. Mar. Chem. *39*, 119–149 (1992).

[60] *Chin, Y. P., Traina, S. J., Swank, C. R., Backhus, D.:* Abundance and properties of dissolved organic matter in pore waters of a freshwater wetland. Limnol. Oceanogr. *43*, 1287–1296 (1998).

[61] *Krohm, M. D., Sholkovitz, E. R.:* On the association of iron and manganese with organic matter in anoxic marine pore waters. Geochim. Cosmochim. Acta *42*, 607–611 (1978).

[62] *Kleeberg, A.:* The quantification of sulfate reduction in sulfate-rich freshwater lakes-a means for predicting the eutrophication process of acidic mine lakes? Water, Air, Soil Pollut. *108*, 365–374 (1998).

[63] *Nixdorf, B., Kapfer, M.:* Stimulation of phototrophic pelagic and benthic metabolism close to sediments in acidic mine lakes. Water, Air, Soil Pollut. *108*, 317–330 (1998).

[64] *Kapfer, M.:* Assessment of the colonization and primary production of microphytobenthos in the littoral of acidic mine lakes in Lusatia (Germany). Water, Air, Soil Pollut. *108*, 331–340 (1998).

[65] *Smith, R. L., Klug, M. J.:* Reduction of sulfur compounds in the sediments of a eutrophic lake basin. Appl. Environ. Microbiol. *41*, 1230–1237 (1981).

[66] *Ingvorsen, K., Zeikus, J. G., Brock, T. D.:* Dynamics of bacterial reduction in a eutrophic lake. Appl. Environ. Microbiol. *42*, 1029–1036 (1981).

[67] *Kuivila, K. M., Murray, J. W, Devol, A. H.:* Methane production, sulfate reduction and competition for substrates in the sediments of lake Washington, Geochim. Cosmochim. Acta *53*, 409–416 (1989).

[68] *Rabouille C., Gaillard, J.-F., Relexans, J.-C., Treguer, P., Vincendeau, M.-A.:* Recycling of organic matter in antarctic sediments. Limnol. Oceanogr. *43*, 420–432 (1998).

[69] *Aiwa, H. A., Rice, C. W., Sotomayor, D.:* Carbon and nitrogen mineralization in tallgrass prairie and agricultural soil profiles. Soil Sci. Soc. Am. J. *62*, 942–951 (1998).