Vertical and Annual Distribution of Ferric and Ferrous Iron in Acidic Mining Lakes

Vertikale und jahreszeitliche Verteilung von Eisen(III) und Eisen(II) in pyritversauerten Tagebaurestseen

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Summary: The investigated coal mining lakes (ML 111, ML 117, and ML 107) in the Lusatian lignite mining district are extremely acidic. The concentrations of iron in these geogenic acidified lakes are orders of magnitude higher than in acidic bog lakes and softwater lakes acidified by atmospheric deposition.

Ferric iron was for the most part the predominant species by a Fe(III) to Fe(II) ratio of more than 10. Density stratification of the water column leads to vertical concentration gradients of ferrous iron. Extremely high concentrations of ferrous iron were found in the anoxic layers above the sediment of ML 111 and ML 107. High concentrations of Fe(II) were correlated with high concentrations of carbon dioxide. A microbial potential to reduce ferric iron was found in the sediments.

In ML 111 and ML 117 the concentrations of Fe(II) in the epilimnion were markedly higher than in the oxic hypolimnetic layers. It can be suggested that the occurence of ferrous iron in the epilimnion is of photochemical origin, as described for softwater lakes. Minimum concentrations of dissolved organic carbon in the epilimnion could be correlated to the increase of ferrous iron concentrations. Especially in springtime and summer the concentrations of Fe(II) in the epilimnion were higher than in the oxic hypolimnetic layer below.

Zusammenfassung: Die untersuchten Braunkohletagebaurestseen ML 111, ML 117 und ML 107 im Lausitzer Braunkohlerevier sind extrem pyritversauert. Die Eisenkonzentrationen in diesen geogen versauerten Seen liegen um Größenordnungen höher als in sauren Moorseen und atmosphärisch versauerten Weichwasserseen.

Eisen(III) war in der Regel die dominierende Komponente bei einem Konzentrationsverhältnis von Eisen(III) zu Eisen(II) von mehr als 10. Die Dichteschichtung der Wassersäule führte zu vertikalen Konzentrationsgradienten von Eisen(II). In der anoxischen Zone über dem Sediment wurden besonders hohe Eisen(II)-Konzentrationen beobachtet, und zwar in ML 111 und ML 107. Hohe Eisen(II)-Konzentrationen und hohe Kohlendioxidkonzentrationen traten parallel auf. In den Sedimenten gab es ein Potential für die mikrobielle Reduktion von dreiwertigem Eisen.

In ML 111 und ML 107 traten im Epilimnion deutlich höhere Eisen(II)-Konzentrationen auf als in der oxischen Zone des Hypolimnions. Es ist davon auszugehen, daß Eisen(II) im Epilimnion photochemischen Ursprungs ist, wie es in der Literatur für Weichwasserseen beschrieben wurde. Konzentrationsminima für gelösten organisch gebundenen Kohlenstoff konnten mit den erhöhten Konzentrationen von Eisen(II) im Epilimnion in Zusammenhang gebracht werden. Insbesondere im Frühling und im Sommer waren die Eisen(II)-Konzentrationen im Epilimnion gegenüber der darunterliegenden oxischen Zone des Hypolimnions erhöht.

1 Introduction

Limnological studies have provided much information about seasonal and vertical variations of iron concentrations in naturally acidified bog lakes (e.g., [1, 2]), and in atmospherically acidified soft-water lakes, and about the proportion of ferrous to total iron [3, 4]. The main subject of iron investigation in soft-water lakes was iron redox cycling and the effect of light.

Microbial [5], geochemical [6], and photochemical [7] aspects of the oxidation state of dissolved iron and its distribution as a function of time and depth were investigated in geogenically acidified surface waters. However, only few informations are available about the distribution of ferric and ferrous iron in geogenically acidified lakes.

Geogenic acidification caused by pyrite and marcasite oxidation was the subject of early investigations before 1950 (e.g., [8]). These minerals are commonly associated with coal and all sulfidic ores. During the lignite surface mining process the

geological strata are exposed to the atmosphere and pyrite reacts with oxygen and water to release acidity, iron and sulfate [9–11]. This process is accelerated by the action of acidophilic Thiobacilli [12, 13]. As acidic leachate flows through mine spoils and soil, dissolved materials such as iron, aluminium, manganese, and sulfate accumulate and are introduced into surface waters. The inputs from acid mine drainage lead to high ionic strength and high acidity.

The objective of the present study was to determine the seasonal and vertical distribution of ferric and ferrous iron in acidic coal mining lakes. The changes in ferrous iron concentrations were correlated with gradients of dissolved organic carbon and inorganic carbon. The study is part of a cooperate research project dealing with the ecological situation of a former lignite mining area and the development of environmental quality targets ("Leitbilder"). The limnological investigations of various acidic strip-mining lakes focus on abiotic and biotic characterization ("status quo") of these lakes. Based on these data an assessment of the potential development of these lakes will be attempted.

2 Study Sites

Three acidic lakes of the Lusatian lignite mining district were investigated. A short description of the lakes is given in Table 1. All lakes originated before 1956. The results presented here mainly focus on mining lake (ML) 111 because of its relatively stable stratification. For the experiment described in paragraph 3.6 and 4.5, water from ML Niemegk (near Bitterfeld, Saxony Anhalt) was used. The degree of acidification and the concentrations of dissolved iron and sulfate of ML Niemegk are comparable to the three Lusatian lakes as shown in Table 1. However its DOC concentration (≈ 0.35 mmol/L) exceeds the epilimnetic DOC of the Lusatian lakes (<0.05 mmol/L).

As shown in Table 1, the main components of dissolved substances are $CaSO_4$, $MgSO_4$, $Al_2(SO_4)_3$, $Fe_2(SO_4)_3$, and H_2SO_4 (oxic epilimnion). Calcium, magnesium, aluminium and silicon are dissolved by acid consuming reactions (weathering of calcite minerals and alumo silicates in the overburden) [14]. These reactions are consecutive processes of pyrite acidification. Manganese is dissolved by reduction of pyrolusite minerals with ferrous iron and consumption of protons under anoxic conditions [14]. Dissolution of manganese leads to partial elimination of iron by precipitation of $Fe(OH)_3$. However, concentration of dissolved iron exceeds concentration of dissolved manganese in highly acidified mining lakes. Sulfate is the dominant anion in acidic mining lakes. Especially in Lusatian lakes we found that contents of other anions like chloride are negligible compared to sulfate.

3 Experimental

3.1 Sampling

The water column was investigated monthly. Water samples were taken using a 3.5-L modified Friedinger-sampler (LIMNOS, Finland) in 1-m intervals. Samples for carbon (TIC, TOC, DOC) and ferric and ferrous iron analysis were filled bubble-free in glass flasks with obliquely cut glass stoppers. Samples for heavy metals analysis were filled in PE-bottles and stabilized with nitric acid to a final concentration of 28.7 mmol/L.

3.2 Temperature, O_2, and pH Measurements

Temperature profiles were measured by a ME multiparameter probe (ME Meerestechnik Elektronik, Trappenkamp, Germany), oxygen saturation and pH by WTW probes (Wissenschaftlich Technische Werkstätten GmbH, Weilheim, Germany). Since July 1996 all three parameters were measured by a Idronaut multiparameter probe (Idronaut Srl., Brugherio, Italy). The temperature sensors consisted of a platinum resistance thermometer (PT 100) with a accuracy of better than ± 0.05°C and a resolution better than 0.001°C. Oxygen sensors were of polarographic type with accuracies of better than 2% saturation. Calibration against air (100%) was performed minimum once per lake and day, i.e., before nearly every profile. The pH sensors consisted of an electrode with glass membrane and a reference sensor with a silver/silver chloride cell in a potassium chloride solid gel (3 mol/L). Accuracy was better than 0.05 pH units. Calibration was performed minimum once per campaign. Temperature and pressure compensation was performed automatically by means of build-in sensors.

3.3 Segmented-flow Analysis (Photometry): Fe(II)/Fe(III)-determination

3.3.1 Apparatus

Analyses were performed with a segmented-flow analyzer, which is shown in Figure 1. A dialyser and a dilution coil were integrated in the manifolds for automatic dilution. This was necessary because the concentrations of iron species varied over a wide range in the different acidic lakes: Maximum concentrations of β(Fe(II)) = 800 mg/L and β(Fe(III)) = 650 mg/L were found in ML 107. Minimum concentrations of β(Fe(II)) = 0.1 mg/L and β(Fe(III)) = 18 mg/L were found in ML 117.

The switching valves enabled the combination of the manifolds for Fe(II) and Fe(III) determination with different dilution coils. By this configuration it was possible to adjust the calibra-

Table 1: The three acidified lakes (Lusatian lignite mining district) and ML Niemegk.

Die drei pyritversauerten Seen (Lausitzer Braunkohlerevier) und ML Niemegk.

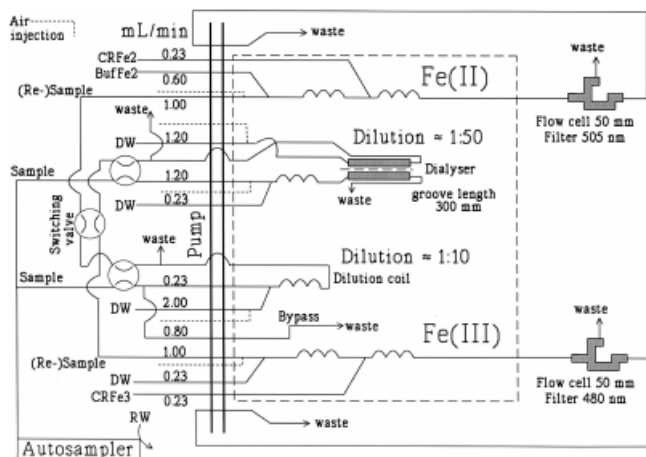| mining lake	area in m²	maximum depth in m	pH	sulfate	total iron	manganese	calcium c in mmol/L	magnesium	aluminium	silicon
111	$1.1 \cdot 10^5$	10	2.65	14	2.8	0.055	5.7	1.2	1.4	0.61
107	$1.0 \cdot 10^5$	4	2.35	28	9.8	0.2	8.9	1.8	1.9	0.66
117	$1.0 \cdot 10^6$	14	3.0	4.5	0.36	0.021	2.6	0.62	0.07	0.38
Niemegk	–	15	2.75	20	2.7	0.08	10	3.5	0.95	0.86

Fig. 1: Skalar SAN^{plus} segmented-flow analyzer (Skalar Analytical, The Netherlands).

Skalar-SAN^{plus}-segmented-flow-Analysator (Skalar Analytical, Niederlande).

Abbreviations

RW Rinsing reagent for sample needle and rinsing vessel: Distilled water, pH adjusted to 2.3 with hydrochloric acid.

DW Dilution reagent for dialyser or dilution coil, resp.: Distilled water, pH adjusted to 2.3 with hydrochloric acid, 1 mL M.S.D. (Skalar 13903, surface-active agent) per 1 000 mL solution.

CRFe3 Fe(III)-color reagent: 10 g KSCN, 10 mL acetone per 1 000 mL distilled water, pH adjusted to 1.0 with nitric acid (65%).

CRFe2 Fe(II)-color reagent: 1 g o-phenanthroline per 1 000 mL distilled water.

BufFe2 Buffer solution Fe(II)-determination: 50 g sodium acetate, 100 mg KH_2PO_4, 1 mL M.S.D. per 1 000 mL distilled water, pH adjusted to 5.0 with acetic acid.

tion ranges to the real concentrations of ferric and ferrous iron in the investigated acidic lakes. Only samples with $\beta(Fe(II))$ or $\beta(Fe(III)) > 200$ mg/L were prediluted manually.

The pH of calibration standards ($FeSO_4$ or $Fe(NO_3)_3$), resp.) was generally adjusted to 2.5 with H_2SO_4. Calibration curves were fitted to calculate the mean confidence intervals (95%). All relative deviations and error bars used in paragraph 4 were derived from the mean confidence intervals.

3.3.2 Cross Reactivities Fe(II) – Fe(III)

The cross reactivity of Fe(III) in the detection of Fe(II) was measured as shown in Table 2. The cross reactivity was not proportional to its concentration. The Fe(II)-values were not corrected, because the cross reactivity of Fe(III) was very low. When concentrations of Fe(III) were two orders of magnitude higher than Fe(II) concentrations, the measured Fe(II) concentrations were in the same order of magnitude as the determined cross reactivity. However, this had no influence on the qualitative informative value, because the relative variations of Fe(II) concentrations were high compared to the corresponding relative variations of Fe(III) concentrations.

The cross reactivity of Fe(II)-standards in the detection of Fe(III) was measured by separate experiments. For Fe(II) concentrations from 5 mg/L to 50 mg/L the cross reactivity of Fe(II) in the detection of Fe(III) was 20.6% ± 0.5%. All results of Fe(III)-measurement were corrected by substracting 20% of the determined Fe(II) concentration from the Fe(III)-value.

Table 2: Cross reactivity of Fe(III)-standards in the detection of Fe(II).

Querempfindlichkeit der Fe(III)-Standards bei der Bestimmung von Fe(II).

Fe(III)-standards	β in mg/L				
	40	80	120	160	200
Fe(II) measured, mean of 10 analysis runs	0.49	0.73	0.9	1.1	1.41
cross reactivity	1.22%	0.91%	0.75%	0.69%	0.71%

Unfortunately, the determination of the cross reactivity of Fe(II)-standards in the detection of Fe(III) was not reproducible. An experiment performed in January 1997 showed that the cross reactivity was less than 5% and was not proportional to Fe(II) concentration. An explanation could be that the cross reactivity of 20% as determined before resulted from impurities in the M.S.D. detergent. Such impurities might have catalyzed oxidation of Fe(II) during the segmented-flow analysis process. Therefore an uncertainty remains for those Fe(III) concentrations with corresponding high Fe(II) concentrations. In these cases the Fe(III) concentrations may have been underestimated. In samples from the anoxic hypolimnion the difference beetween the measured Fe(III) concentration and the correction can exceed 100% (of the corrected result) as demonstrated by following example. In ML 111, 24 Sept 1996, we found at 10 m depth 364 mg/L Fe(II), 66 mg/L Fe(III), and 414 mg/L total iron (determined as described in paragraph 3.4). Fe(III) was calculated by substracting 20% (73 mg/L) of the found Fe(II) concentration from the measured result of Fe(III) (139 mg/L). As a summary, the uncertainty of Fe(III) determination might be founded on the impurities of the used M.S.D., because the stability of this product is not clear.

3.4 Determination of Total Iron by ICP-OES

The total iron concentration was measured in all samples by inductively coupled plasma optical emission spectrometry (ICP-OES, OPTIMA 3000, Perkin-Elmer GmbH, Überlingen, Germany). Samples were prediluted as follows: ML 107: 1:25; ML 111: 1:20; ML 117: 1:2. 50-mL PP centrifuge tubes (Sarstedt, Germany) were used for dilution and measurement.

The advantage of ICP-OES is the broad linear range of calibration. Therefore only a two-point calibration (blank and 50 mg/L Fe) was performed. The calibration of iron was not affected by the matrix. Therefore standard addition calibration or matrix matched calibration was not necessary.

A comparison was performed for analysis data (altogether 235 single data pairs) from the three investigated mining lakes (only data from 1996). The sum of Fe(II) and Fe(III) (photometrical analysis) was compared with total iron (ICP-OES analysis). The correlation coefficient was 0.969 ($m = 0.952$; $n = 235$; $p < 0.05$). This correlation shows that the results of ICP-OES and the determination of Fe(II) and Fe(III) are in good agreement.

3.5 TOC/DOC/TIC-analysis

Samples were analyzed IR-spectrometrically by a Dima-TOC 100 apparatus (Dimatec, Essen, Germany). The injection volume for TIC-detection was 0.1 mL (160°C reactor temperature). For TOC-analysis samples were additionally acidified by

H_2SO_4 and gassed automatically (autosampler needle) by the carrier gas (oxygen) to eliminate the inorganic carbon. By this procedure TOC could be measured as TC (injection volume = 0.25 mL; reactor temperature = 850°C). For DOC-analysis 20 mL sample were filtered with 0.45 μm MILLEX-HV non-sterile filters (Durapore, PVDF, Millipore SLHV 025 NB). Calibration curves were fitted to calculate the mean confidence intervals (95%). All relative deviations and error bars used in paragraph 4 were derived from the mean confidence intervals.

3.6 Sunlight Exposure Experiment

Samples from ML 111 (sample date: 13 May 1997, exposure date: 14 May 1997) were exposed to sunlight in 100-mL quartz glass vessels for three hours. Vessels wrapped with aluminium foil served as dark controls. Fe(II), Fe(III), DOC, and TOC were measured as described above. Samples from ML Niemegk (sample date: 9 June 1997; exposure date: 11 June 1997) were exposed to sunlight in 100-mL quartz glass vessels for five hours. Brown glass vessels served as dark controls.

A solution of 0.12 mmol/L citric acid and 3.6 mmol/L ferric iron $(Fe_2(SO_4)_3)$ was adjusted to pH 2.3 with H_2SO_4. 100-mL quartz glass vessels and brown glass vessels (dark control) containing this light sensitive solution were exposed in ML 111 at distinct depths (0 m; 0.1 m; 0.25 m; 0.5 m; 1 m; 2 m) in the middle of the northern basin. ML 111 water (0 m; 0.25 m; 0.5 m) and ML Niemegk water (0 m; 0.1 m; 0.25 m; 0.5 m) were exposed as well. The experiment was started at 4:00 pm (date: 21 Aug 1997) and finished at 11:00 am (date: 22 Aug 1997). As a control either a quarz glas vessel and a brown glass vessel with the solution or ML 111 and Niemegk water, resp., were directly exposed to sunlight (outside the lake water) during the same time period.

4 Results

4.1 General Results

Fe(III) is the predominant species in acidic coal mining lakes. Table 3 shows some examples of Fe(III) : Fe(II) ratios. The minimum concentrations of ferrous iron were found in the hypolimnetic layers under oxic conditions. The highest concentrations of ferrous iron were generally found above the sediment of ML 111 and ML 107. The concentrations of DOC and TIC in the water column were generally very low. Maximum concentrations of organic and inorganic carbon were found

Table 3: Examples of Fe(III) : Fe(II) ratios (date of sample: 2/3 July 1996).

Beispiele für das Verhältnis von Fe(III) zu Fe(II) (Datum der Probenahme: 2. und 3. Juli 1996).

mining lake	depth in m	pH	c(oxygen) in mmol/L	c(Fe(II)) in mmol/L	c(Fe(III)) in mmol/L	ratio Fe(III):Fe(II)
ML 111	0	2.5	0.28	0.076	2.5	33
ML 111	5	2.54	0.081	0.026	3.4	130
ML 111	9	2.6	0	3.7	2.6	0.7
ML 107	0	2.3	0.26	0.67	8.6	13
ML 107	4	2.29	0	14.5	3.9	0.27
ML 117	0	2.83	0.32	0.032	0.39	12
ML 117	12	2.84	0.21	0.003 8	0.46	120

above the sediment. We presuppose that the measured TIC concentrations correspond to carbon dioxide concentrations, because equilibrium concentration of hydrogencarbonate is negligible at pH < 3.

Thermal stratification in ML 111 began in April 1995. Since that time a permanent stratification was observed in the deepest (>7.5 m depth) part of ML 111, which covers approx. 4% of the total area. The stratification persisted until the end of investigation. In contrast ML 107 and ML 117 were not permanently stratified. Stratification of ML 107 lasted from ice coverage in January – March 1996 until autumn 1996. ML 117 was stratified from the beginning of measurements in April 1996 until autumn 1996.

4.2 Seasonal Variations of Concentrations in ML 111 above the Sediment

In March 1995, oxygen concentration at 9 m depth exceeded 0.3 mmol/L. Anoxia developed within the following two
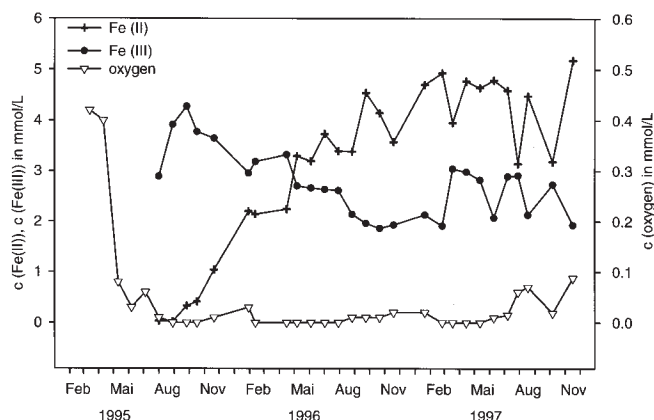
Fig. 2: Seasonal development of oxygen, Fe(II), and Fe(III) concentrations at a depth of 9 m in ML 111. The mean relative deviations were ±6.3% (ferrous iron) and ±6.8 % (ferric iron) (calculated as described in paragraph 3.3.1).

Jahresgang der Konzentrationen von Sauerstoff, Fe(II) und Fe(III) in einer Tiefe von 9 m in ML 111. Die mittleren relativen Fehler betrugen ±6.3% (Eisen (II)) und ±6.8% (Eisen(III)) (berechnet wie in Abschn. 3.3.1 beschrieben).

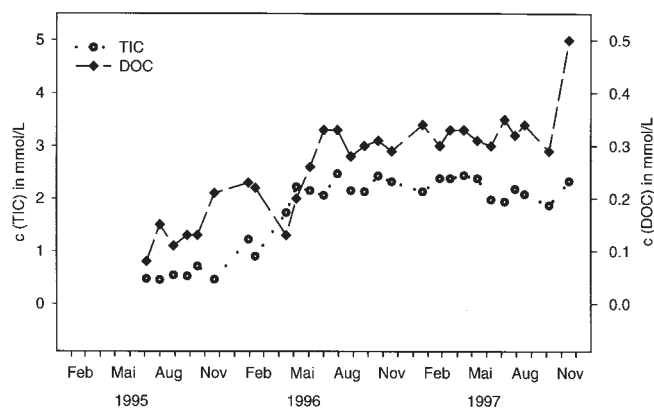**Fig. 3:** Seasonal development of DOC and TIC concentrations at a depth of 9 m in ML 111. The mean relative deviations were ±14.4% (DOC) and ±5.4% (TIC) (calculated as described in paragraph 3.5).

Jahresgang der DOC- und TIC-Konzentrationen in einer Tiefe von 9 m in ML 111. Die mittleren relativen Fehler betrugen ±14.4% (DOC) und ±5.4% (TIC) (berechnet wie in Abschn. 3.5 beschrieben).

months. Finally, the deepest part of ML 111 was permanently anoxic at a depth of 9 m and below (Fig. 2). Since the beginning of iron measurements in ML 111 (1 Aug 1995), a permanent increase of ferrous iron concentration was observed above the sediment (Fig. 2). The concentration of ferric iron reached its maximum at this depth in September 1995. Then the concentration of Fe(III) decreased, but not to the same degree as the Fe(II) increase. Generally, total iron concentration increased from 3 mmol/L in September 1995 to about 5 mmol/L in 1996.

The increase of TIC (Fig. 3) correlated with the increase of ferrous iron (Fig. 2). The correlation coefficient was 0.90 ($n = 29$; $p < 0.05$). The corresponding increase of DOC was not as predominant as the increase of TIC or Fe(II). As a summary the increases of Fe(II), DOC and TIC concentrations seem to be a consequence of the preceeding decrease of oxygen concentration in the deepest part of ML 111.

4.3 Vertical Gradients at the Sediment-Water Interface

Discussion focusses on ML 111 and ML 107, because in ML 117 never occured such steep gradients of ferrous iron above the sediment. Figure 4 shows vertical concentration gradients for TIC, Fe(II), and oxygen. Due to thermal stratifica-
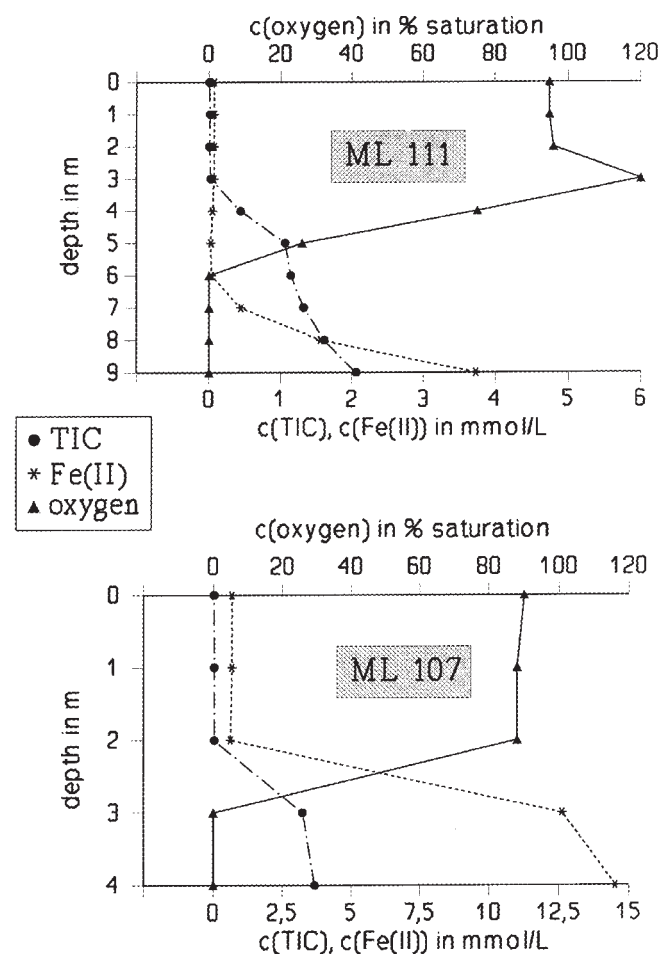
tion, in both lakes oxygen depletion occured above the sediment in July. For ML 111 and ML 107 the concentrations of TIC and ferrous iron were low in the epilimnion compared to concentrations at the sediment-water interface. In ML 107 no vertical concentration gradients were observed after the thermal stratification ended and circulation started in October 1996. In ML 111 the vertical gradient remained in 1996 due to the long lasting stratification. The vertical distribution of Fe(III) in ML 111 is shown in Figure 5.
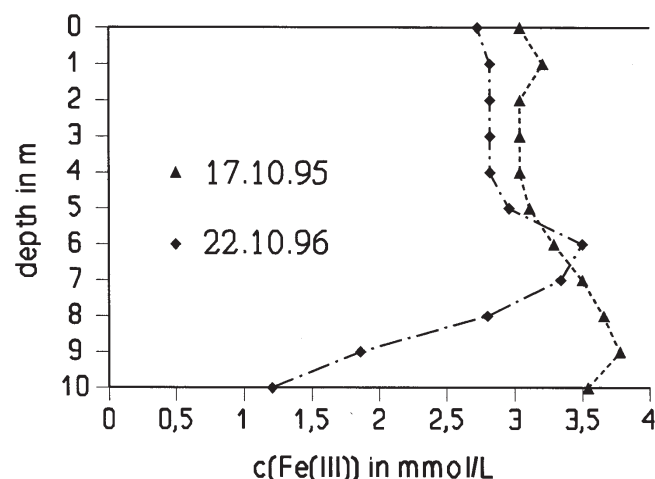

Fig. 5: Vertical distribution of Fe(III) in autumn 1995 and 1996 (ML 111).

Vertikale Verteilung von Fe(III) im Herbst 1995 und im Herbst 1996 (ML 111).

The concentration of ferric iron increased from the metalimnion to the oxic/anoxic boundary and then decreased towards the sediment. As a result, a permanent hypolimnetic maximum of Fe(III) was observed at a depth of 6...9 m. The decrease of Fe(III) concentration above the sediment occured considerably later than the beginning development of anoxic conditions (Fig. 2).

4.4 Seasonal Variations in the Epilimnion

At the surface of ML 111 the seasonal variations (Fg. 6) were quite different from those of 9 m depth (Fig. 2 and Fig. 3).
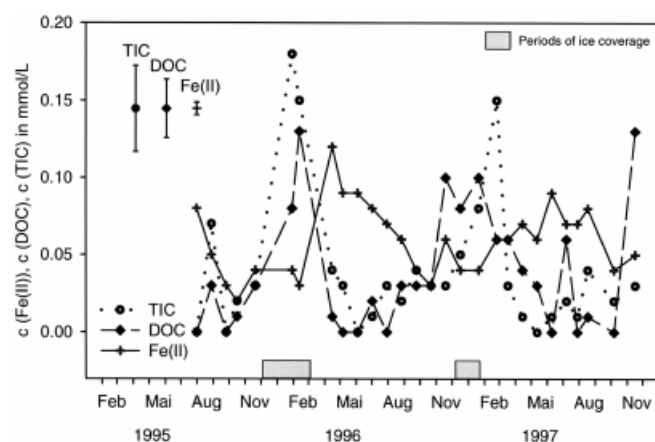

Fig. 4: Vertical distribution of TIC, Fe(II), and oxygen in ML 111 and ML 107, 2 July 1996.

Vertikale Verteilung von TIC, Fe(II) und Sauerstoff in ML 111 und ML 107 am 2. Juli 1996.

Fig. 6: Seasonal development of Fe(II), DOC, and TIC concentrations at 0...1 m in ML 111. Error bars show mean confidence intervals (see paragraphs 3.3.1 and 3.5).

Jahresgang der Konzentrationen von Fe(II), DOC und TIC in einer Tiefe von 0...1 m in ML 111. Die Fehlerbalken zeigen die mittleren Konfidenzintervalle (siehe Abschn. 3.3.1 und 3.5).
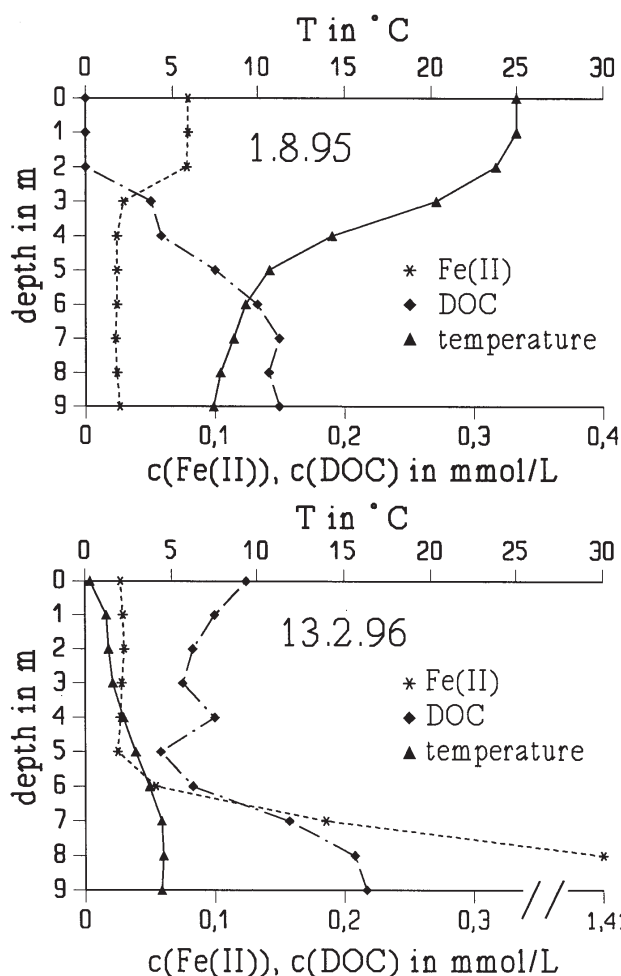
Fig. 7: Vertical distribution of Fe(II) and DOC at four different seasons (ML 111).

Vertikale Verteilung von Fe(II) und DOC zu vier verschiedenen Jahreszeiten in ML 111.
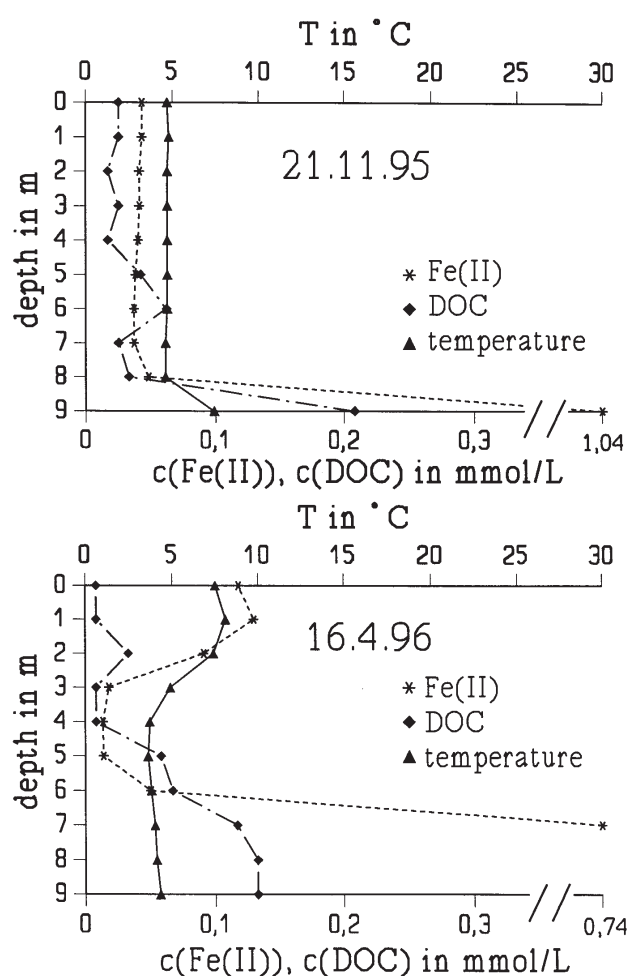

Fig. 8: Vertical distribution of Fe(II), DOC, and TIC (ML 117), 3 July 1996.

Vertikale Verteilung von Fe(II), DOC und TIC in ML 117 am 3. Juli 1996.

During the long period of ice coverage in winter 1995/1996 DOC and TIC concentrations were high compared to the situation in autumn before. In April 1996 the epilimnetic DOC and TIC disappeared nearly completely paralleled by a considerable increase in Fe(II) concentration (Fig. 6 and Fig. 7). In springtime 1997 we found again an increase in Fe(II) concentration and a decrease in DOC and TIC concentration.

The vertical profiles of Fe(II), DOC, and temperature showed a typical structure in springtime and summer (1 Aug 1995 and 16 Apr 1996, ML 111, Fig. 7; 3 July 1996, ML 117, Fig. 8): An increase of Fe(II) (towards the epilimnion) and a corresponding decrease of DOC was observed at the metalimnion. In November (21 Nov 1995) no distinct hypolimnetic minimum of Fe(II) was found. In winter under ice coverage (13 Febr 1996) the DOC concentration exceeded the Fe(II) concentration. In contrast to that, in springtime and in summer the DOC concentration was small compared to the concentration of ferrous iron.

4.5 Variation of DOC and Ferrous Iron Concentrations after Exposure of Samples to Sunlight

The production of ferrous iron was investigated by exposure of samples from acidic mining lakes to sunlight (Table 4

and Table 5). A predominant increase of Fe(II) concentration (90...370%) was observed after sunlight exposure compared to the dark control (Table 4). The concentrations of Fe(III) (1...5%), TOC (20...65%), DOC (0...60%) decreased. The relative increase or decrease, resp., was calculated as follows: {[Concentration (dark) – concentration (light)] / concentration (dark)} · 100%. The experiment was repeated (11 June 1997) with water from ML Niemegk (near Bitterfeld, Saxony Anhalt). This acidic mining lake has considerable higher DOC concentrations in the epilimnion than the investigated Lusatian lakes. The increase of ferrous iron was more than 1 000%, the decrease of DOC was more than 70% (Table 5).

As a summary, production of ferrous iron is paralleled by elimination of DOC under the influence of sunlight. The effect of sunlight as a function of water depth was investigated by an additional experiment (Table 6 and Table 7).

The relative elimination of DOC in the citric acid solution was about 50% at an exposure depth of 0...0.25 m, about 35% at an exposure depth of 0.5 m, and <10% at 1m and below (Table 6). The relative production of ferrous iron was about 500% at 0...0.25 m, about 350% at 0.5 m, and less than 100% below 1 m. The absolute elimination of DOC and the absolute production of ferrous iron were low below 1 m. The effect of light was clearly diminished within the first meter depth of acidic mining lakes.

The production of ferrous iron in samples from ML 111 and ML Niemegk exposed in lake water was more than five-fold less compared to the control samples directly exposed to sunlight (Table 7). The decrease of DOC was very small compared to the control. In contrast to that the concentrations of the citric acid solution exposed in lake water (0...0.25 m) were comparable to the control sample directly exposed (Table 6).

5 Discussion

The processes in acidic mining lakes derived from the investigated vertical and annual distribution of ferric/ferrous iron and DOC/TIC are summarized in Figure 9. As shown in ML 111 stratification leads to anoxic conditions above the sediment. In acidic mining lakes the most significant electron acceptors under anoxic conditions may be MnO_2, $Fe(OH)_3$ and SO_4^{2-}. Due to the redox potential manganese reduction is energetically favoured over iron reduction which again is favoured compared to sulfate reduction [15]. This reveals the order in which certain electron acceptors are used by bacteria. Thus the biogeochemical cycles of sulfur and of iron and to a certain degree of manganese have a strong impact in acidic mining lakes. Bacteria can reduce Fe(III) either by using it as an electron sink during fermentative activities or by using Fe(III) as terminal electron acceptor for anaerobic respiration [16, 17]. These processes require suboxic to anoxic conditions and organic carbon or molecular hydrogen. Such conditions are mainly found near or in the sediment, therefore this habitat plays an important role in iron redox cycling in lakes.

Anaerobic microbial activity at the sediment-water interface can be responsible for the accumulation of ferrous iron and carbon dioxide in the hypolimnion, as described for other acidic strip mine lakes [5]. Dissimilatory iron-reducing bacteria have also been found in a variety of freshwater sediments [17]. The steep gradient towards the sediment (Fig. 4) suggests that Fe(II) was produced there. Viable counts of iron-reducing bacteria were obtained by a most probable number method and calculated with the program described in [18]. Up to $3 \cdot 10^3$ cells
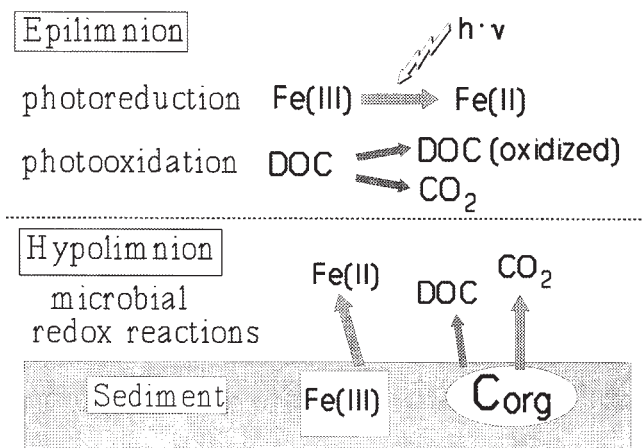

Fig. 9: Possible sources of ferrous iron.
Mögliche Quellen von Eisen(II).

per mL sediment (fresh volume) were found, but no iron-reducing bacteria were detected in the epilimnion. Sulfate-reducing bacteria, which may also be responsible for Fe(III) reduction in some habitats [19, 20], have been found in even higher numbers in ML 111 sediments [21].

As we found in ML 111 the decrease of the hypolimnetic Fe(III) concentration is not of the same magnitude as the increase of Fe(II) concentration. This indicates that solid Fe(III) is reduced in the sediment and the soluble product Fe(II) diffuses into the water column. The metabolism of organic matter at the water-sediment interface will be a subject of further investigation in order to explain the accumulation of DOC in the hypolimnion of acidic mining lakes.

A permanent input of groundwater might also contribute to the hypolimnetic accumulation of ferrous iron. The influence of groundwater input is yet unclear, detailed hydrogeological informations are still lacking.

There exist different possibilities for the origin of epilimnetic ferrous iron. Reduction of Fe(III) in oxygenated natural waters can occur in the absence of light through microbial processes [13] or via chemical reductants such as humic substances [22]. In sunlight, Fe(III) reduction can be accelerated by primary (direct ligand-to-metal charge transfer) or secondary (via intermediates) photo-processes [23]. As described before, we found no iron-reducing bacteria in the epilimnion. This supports the hypothesis that photochemical reactions are responsible for Fe(II) production near the lake surface whereas hypolimnetic Fe(II) is generated by microbial activity.

Many Fe(III)-organic complexes undergo photochemical ligand-to-metal charge transfer reactions, either on an iron oxide surface or in solution, much more readily than inorganic Fe(III) species [23]. Photochemical iron reduction by humic acids is thought to happen by a mechanism similar to that observed for simple Fe(III) carboxylates, such as citrate, oxalate or malonate [24]. Carbon dioxide is a possible product of the photolysis of an Fe(III)-organic complex as shown for the photodegradation of oxalate in various types of Fe(III) (hydr)oxides suspensions [25].

Hydrogen peroxide, a common constituent of lake water and freshwater, reacts with Fe(II), which results from photoreduction [26]. By this photo-Fenton reaction hydroxyl radicals are produced [27] (1).

Table 4: Effects of exposition of ML 111 water to sunlight.

Auswirkungen des Sonnenlichts auf das Wasser von ML 111.

| sample | $c(TOC)$ in mmol/L | | $c(DOC)$ in mmol/L | | $c(Fe(II))$ in mmol/L | | $c(Fe(III))$ in mmol/L | |
	light	dark	light	dark	light	dark	light	dark
0 m	0.067 ± 0.013	0.083 ± 0.013	0.025 ± 0.014	0.05 ± 0.013	0.111 ± 0.002 6	0.059 ± 0.002 4	2.96 ± 0.19	3.11 ± 0.19
5 m	0.042 ± 0.014	0.075 ± 0.013	0.017 ± 0.014	0.042 ± 0.014	0.110 ± 0.002 6	0.027 ± 0.002 2	3.11 ± 0.19	3.14 ± 0.19
6 m	0.067 ± 0.013	0.19 ± 0.014	0.05 ± 0.013	0.05 ± 0.013	0.123 ± 0.002 6	0.026 ± 0.002 2	3.16 ± 0.19	3.23 ± 0.19

Table 5: Effects of exposition of ML Niemegk water to sunlight.

Auswirkungen des Sonnenlichts auf das Wasser von ML Niemegk.

| sample | $c(DOC)$ in mmol/L | | $c(Fe(II))$ in mmol/L | | $c(Fe(III))$ in mmol/L | |
	light	dark	light	dark	light	dark
0 m	0.083 ± 0.017	0.28 ± 0.017	0.48 ± 0.086	0.038 ± 0.002 6	1.35 ± 0.19	1.43 ± 0.19
8 m	0.075 ± 0.017	0.35 ± 0.017	0.53 ± 0.084	0.044 ± 0.002 6	1.21 ± 0.19	1.41 ± 0.19

**Table 6:** Effects of exposition of a solution of citric acid and $Fe_2(SO_4)_3$ in H_2SO_4 (pH 2.3) to sunlight at distinct depths of lake water.

Auswirkungen des Sonnenlichts auf eine Lösung von Citronensäure und $Fe_2(SO_4)_3$ in H_2SO_4 (pH = 2.3) in unterschiedlichen Seewassertiefen.

| depth of exposure | $c(DOC)$ in mmol/L | | $c(Fe(II))$ in mmol/L | | $c(Fe(III))$ in mmol/L | |
	light	dark	light	dark	light	dark
outside the lake water	0.32 ± 0.029	0.67 ± 0.029	0.37 ± 0.012	0.058 ± 0.005 2	3.38 ± 0.21	3.61 ± 0.21
0 m	0.31 ± 0.029	0.72 ± 0.029	0.30 ± 0.013	0.048 ± 0.005 4	3.41 ± 0.21	3.52 ± 0.21
0.1 m	0.35 ± 0.029	0.71 ± 0.029	0.29 ± 0.013	0.043 ± 0.005 5	3.41 ± 0.21	3.54 ± 0.21
0.25 m	0.35 ± 0.029	0.73 ± 0.029	0.26 ± 0.013	0.039 ± 0.005 5	3.46 ± 0.21	3.59 ± 0.21
0.5 m	0.48 ± 0.029	0.75 ± 0.029	0.18 ± 0.014	0.038 ± 0.005 5	3.48 ± 0.21	3.57 ± 0.21
1 m	0.67 ± 0.029	0.73 ± 0.029	0.070 ± 0.005	0.041 ± 0.005 5	3.48 ± 0.21	3.5 ± 0.21
2 m	0.68 ± 0.029	0.73 ± 0.029	0.064 ± 0.005	0.036 ± 0.005 5	3.54 ± 0.21	3.57 ± 0.21

Table 7: Effects of exposition of ML 111 and ML Niemegk water to sunlight at distinct depths of lake water.

Auswirkungen des Sonnenlichts auf das Wasser von ML 111 und ML Niemegk in unterschiedlichen Seewassertiefen.

| depth of exposure | ML 111 water $c(DOC)$ in mmol/L | | $c(Fe(II))$ in mmol/L | | ML Niemegk water $c(DOC)$ in mmol/L | | $c(Fe(II))$ in mmol/L | |
	light	dark	light	dark	light	dark	light	dark
outside the lake water	0.049±0.019	0.14±0.018	0.21±0.014	0.038±0.005 5	0.19±0.018	0.29±0.029	0.18±0.014	0.035±0.005 5
0 m	0.13±0.018	0.19±0.018	0.054±0.005 2	0.024±0.005 5	0.3 ±0.029	0.32±0.029	0.033±0.005 5	0.017±0.005 5
0.1 m	–	–	–	–	0.28±0.029	0.31±0.029	0.024±0.005 5	0.018±0.005 5
0.25 m	0.15±0.018	0.18±0.018	0.041±0.005 5	0.023±0.005 5	0.32±0.029	0.31±0.029	0.023±0.005 5	0.018±0.005 5
0.5 m	0.15±0.018	0.16±0.018	0.026±0.005 5	0.027±0.005 5	0.3 ±0.029	0.31±0.029	0.018±0.005 5	0.017±0.005 5

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^\bullet + OH^- \qquad (1)$$
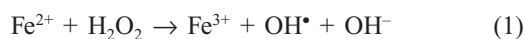
The photolysis of Fe(III) aquo complexes alone could easily account for the Fe(II) formation in acid mine drainage streams [7]. This photolysis directly generates hydroxyl radicals [26, 28] (2).

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + OH^\bullet + H^+ \qquad (2)$$
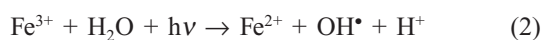
The hydroxyl radicals rapidly react with many organic substances in water and are potential oxidants of refractory synthetic and natural organic compounds that are resistant to degradation by other processes in natural waters [29].

The (local) epilimnetic maxima of ferrous iron (the absolute maximum in ML 111 was obviously above the sediment) in acidic mining lakes as shown for ML 111 and ML 117 are in correspondence with maxima known from acidic soft-water lakes [3, 4]. The epilimnetic minima of DOC in acidic mining lakes agree well with the described photochemical degradation of dissolved organic matter (DOM) as cited above [22–25, 29]. In contrast to the numerous investigations about ferrous iron no experimental data for DOC are available in the cited literature. It can be assumed that photochemical reactions participate in the epilimnetic production of ferrous iron and in the elimination of DOC in the epilimnion of acidic mining lakes. Results presented in paragraph 4.5 (Table 4 and Table 5) support this hypothesis.

From results in Table 6 and Table 7 it can be suggested that photochemical processes in acid mining lakes occur only within a thin layer at the water surface. The effect of light on lake water (samples from ML 111 and ML Niemegk) was very small, when they were exposed to sunlight in water of ML 111 compared to direct sunlight exposure (Table 7). Because it absorbs light, ferric iron can limit the penetration of light radiation into surface waters. However, free turbulence in epilimnion allows a continuous supply of photochemically degradable substances to the water surface.

The increase of ferrous iron in soft-water lakes qualitatively agrees with the increase in acidic mining lakes. Performing a similar experiment to that described in paragraph 4.5 Collienne [3] found an increase of ferrous iron from 0.000 16 mmol/L to 0.007 1 mmol/L after six hours sunlight exposure in a sample from an acid soft-water lake. The concentration of ferric iron decreased from 0.002 9 mmol/L to 0.000 8 mmol/L. The absolute concentration of Fe(II) in ML 111 after sunlight exposure was more than 10-fold higher than in the soft-water lake. Another distinct difference was the relative change of Fe(III) concentration. In the soft-water lake, the relative decrease of Fe(III) was in the same order of magnitude as the increase of Fe(II). Compared to that the relative decrease of Fe(III) in ML 111 after sunlight exposure was negligible.

Principally the vertical distribution in soft-water lakes showed a more than 10:1 ratio of Fe(II):Fe(III) in the epilimnion (oxic) and less than 1:10 in the hypolimnion (oxic) [3] in summer. In contrast to the described soft-water lakes [1–4] the pH-values of the investigated Lusatian mining lakes were considerably lower. The concentration of total iron was more than 20-fold higher compared to the soft-water lakes. The absolute amount of photochemically generated ferrous iron in acidic mining lakes is higher than in soft-water lakes. Therefore it can be assumed that the elimination of DOM will be more effective in acidic mining lakes. In spite of photochemical production of ferrous iron, ferric iron remains the predominant epilimnetic species in acidic coal mining lakes.

In contrast to sediment and hypolimnion, sunlight has an influence on epilimnetic biota. In many softwater lakes, attenuation of light is a function of DOM. Acidification has been shown to cause DOM concentrations to decline in lakes. This can cause a deepening of the euphotic zone [30]. This effect is of minor importance in the highly acidic strip mining lakes because attenuation of light is mainly caused by dissolved iron [31].

It was shown that the sources of epilimnetic ferrous iron are the same in acidic mining lakes as in the well investigated acid soft-water lakes [1–4]. As a consequence of extremely high concentrations of dissolved iron in acidic mining lakes photoreduction keeps the carbon budget low because organic carbon is oxidized finally to carbon dioxide or even to carbon monoxide [27] which leave the water in the gaseous form at very low pH. Availability of carbon is supposed to be a limiting factor for primary production in acidic waters [32, 33].

ML 111 is inhabited by small phytoflagellates of the genus *Ochromonas* and *Chlamydomonas* [34]. Peaks of chlorophyll a fluorescence and of the abundance of these phytoflagellates were mainly found in deeper layers (6...9 m water depth) [34]. It is known for these taxa to overcome inorganic carbon limitation by mixotrophy [35–37]. Some *Ochromonas* species must be regarded functionally as heterotrophic organisms [35]. The autotrophic system acts only as a reserve under conditions when the heterotrophic system is limited [35].

Higher concentrations of TIC and DOC were found in deeper layers. These conditions favour phytoplankton species like *Chrysophytes* or *Chlamydomonads* which are adapted to low light levels or are even independent from light supply. They are able to grow in the deeper layers or even just above the sediment. One can suppose that in spite of the chlorophyll a-peaks in the deeper layers primary production does not play an important role but is outranged by heterotrophic usage of DOC.

The low carbon budget might be one factor for the low diversity and biomass of pelagic primary producers in the epilimnion. In addition, intermediates of photochemical reactions may have a direct influence on aquatic biota.

Increased formation of OH-radicals that are produced as described before [7, 26–28] was suspected to result in direct toxic effects on the aquatic biota or to lead to the production of other toxic compounds via DOC [27]. Hydroxyl is a reactive, nonselective radical underlying the chemistry of many advanced oxidation processes for degrading organic compounds in water [38]. The instability of species like superoxide ($HO_2^\bullet$), hydrogen peroxide, and hydroxyl radicals poses a serious threat to aerobic organisms via toxic DNA damage [39]. Toxic effects by photochemical reactions might be more important in acidic mining lakes containing high amounts of dissolved iron than in acidic soft water lakes or neutral lakes.

In contrast to that, UV irradiation of humic compounds in surface water (humic lake in southern Sweden, pH 6.4) was reported to result in a substantial production of several low-molecular weight carboxylic acids (oxalic-, malonic-, formic-, and acetic acid) [40]. The formation of these compounds was demonstrated to constitute a significant carbon source for the indigenous microbial community. Even enhanced microbial growth was observed in UV irradiated samples compared to dark controls. We have no knowledge about the abundance of humic substances or production of carboxylic acids in acidic mining lakes. But we suspect that conditions for epilimnetic microbial growth are more disadvantageous in acid mining lakes than in other lakes because of toxic photochemical inter-

mediates and photochemical decomposition of ferric carboxylate complexes.

As a summary, photochemical reactions might be an additional growth limiting factor for aquatic biota beside the low pH-level, beside the low carbon budget, and beside high concentrations of dissolved heavy metals (e.g., zinc, nickel, cobalt, chromium) in acid mining lakes.

Acknowledgement

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