# THE ACIDIC LIGNITE PIT-LAKES OF GERMANY-MICROCOSM EXPERIMENTS ON ACIDITY REMOVAL THROUGH CONTROLLED EUTROPHICATION<sup>1</sup>

# A. Fyson<sup>2</sup> and B. Nixdorf<sup>3</sup>

<u>Abstract</u>: Pit lakes in the Lausitz lignite mining district of Germany are diverse in size and morphometry. Many are extremely acidic with  $pH \le 3$  and high in iron concentrations. Productivity in most of the mining lakes is generally low and they support only simple food webs; a few of the acidic lakes, with high nutrient concentrations, are highly productive. State planners hope to develop the lake region for recreation. To that end, various methods are being investigated to remove acidity from the lake waters. The microcosm experiment described here employs controlled eutrophication to enhance element cycling and sedimentbound alkalinity generating processes.

Sixty litre microcosms with water and sediment from Lake Grünewalde (pH 3.0, Fe 14 mg L<sup>-1</sup>, acidity (KB<sub>8.3</sub>) 2 mmol L<sup>-1</sup> and phosphorus 4  $\mu$ g L<sup>-1</sup>) were set up under laboratory conditions. Addition of nutrients (organic carbon and phosphorus) led to dramatic increases in primary production associated with blooms of green algae (*Chlamydomonas* sp.) and diatoms (*Eunotia exigua*) but no substantial removal of acidity. Generation of temporary anaerobic conditions through addition of potatoes led to removal of 85 % of acidity, all detectable dissolved iron, and an increase in pH from 3 to 7. These conditions were maintained with this treatment for the remainder of the 8 month observation period following removal of iron and protons from the water column.

Additional Key Words: aquatic chemistry, acid mine drainage, ecology, primary productivity, algal biodiversity

<sup>&</sup>lt;sup>1</sup> Paper was presented at the 2005 National Meeting of the American Society of Mining and Reclamation, Breckenridge CO, June, 19-23 2005. Published by ASMR, 3134 Montavesta Rd., Lexington, KY 40502.

<sup>&</sup>lt;sup>2</sup> Andrew Fyson, Boojum Research Ltd. 139 Amelia Street, Toronto, Ontario, M4X1E6, Canada e-mail:afyson@boojumresearch.com. <sup>3</sup>Brigitte Nixdorf, Professor, Department of Water Conservation, Brandenburg Technical University, Cottbus, Seestrasse 45, D-15546 Bad Saarow, Germany e-mail:b.nixdorf@t-online.de

Proceedings America Society of Mining and Reclamation, 2005 pp 361-378 DOI: 10. 21000/JASMR05010361

https://doi.org/10.21000/JASMR05010361

#### **Introduction**

In Germany, there are some 500 flooded, open-cast lignite pits (Tagebauseen). The morphometry, history and chemistry of these lakes are described in Nixdorf et al. (2001b). Many of these lakes are extremely acidic due to high concentrations of dissolved metals (mostly iron and aluminum) in addition to protons (low pH), and also have high sulfate concentrations. During mining operations, water was pumped from the open cast pits. Following closure, many pits filled with groundwater and acidified to pH around 3 through exposure and oxidation of iron sulfides (marcasite and pyrite) within the mining wastes and overburden material.

In the Lausitz region of eastern Germany, 168 pit lakes documented of which approximately half are extremely acidic (pH 2.4 - 3.4) (Nixdorf et al., 2001b). The water chemistry of some of these is summarised in Table 1 and is discussed in detail by Geller et al. (2000) and Uhlmann et al. (2004).

Parameter	Units	Concentration (mean)	Range
рН	-	2.9	2.4-3.4
Acidity (KB <sub>4.3</sub> )	mmol $L^{-1}$	4.9	0.1-26.6
Fe	$mg L^{-1}$	95	0.2-800
Sulfate	$mg L^{-1}$	1448	460-4636
Total organic C	mg $L^{-1}$	3.4	0.8-10.9
Total-N	$mg L^{-1}$	3.5	0.9-5.3
Total-P	$\mu g L^{-1}$	14.3	4-26
chlorophyll a	$\mu g L^{-1}$	2	0.5-5.0

Table 1. Summary of some chemical parameters for 75 acidic mining lakes (pH 2.4-3.4) in the Lausitz region. From Nixdorf et al. (2001b).

Acidic mine drainage (AMD) poses a major environmental problem in many countries. Remediation through constructed wetlands and anoxic limestone drains has been extensively developed, particularly in North America. However, long term, self-sustaining treatment of extremely acidic waters has not been demonstrated. Although the treatment systems have been described as passive, they are not self-sustaining and will require the periodic removal of precipitates and recharging of substrates. A truly passive system would require no ongoing management.

The water chemistry of the acidic Lusatian pit lakes is similar to that of the intensely studied acidic coal mine-drainages of the eastern United States with high concentrations of dissolved Fe

(III) and sulphate as well as low pH values (2-4). Most attention has been paid to acidity removal through promotion of sulfate reduction in sediments in anaerobic wetlands and other so called passive treatment systems (see Kalin et al. (1995), Skousen et al. (1998), Younger et al. (2002) and Brown et al. (2002) for reviews of these systems). Other processes, Fe (III) reduction and assimilation coupled to uptake of nitrate can also play a role. However as nitrate concentrations in such waters are generally low, sulphate reduction coupled to Fe (III) reduction and the sequestration of Fe and S as sulphides in the sediments remains the best prospect for acidity removal without the addition of expensive and only short-term effective direct addition of neutralising materials (e.g. lime).

Economically and environmentally acceptable methods are being sought to sustainably remove the acidity of the Lausitz pit lakes to assist in their development, mainly for recreational use (Totsche and Steinberg, 2004; Uhlmann et al., 2004). Neutral, nutrient-rich river water has been diverted into some of the larger lakes, but there is insufficient water to reduce the acidity for all lakes and for many smaller and already filled lakes, this method is impractical. Another method is to enhance *in-situ* alkalinity generating processes through addition of nutrients/or wastes and/or the sustainable enhancement of net carbon production (primary productivity) to feed such processes. This controlled eutrophication is the basis of the study reported here.

Although biodiversity in extremely acidic lake ecosystems is generally low (Wollmann and Deneke, 2004), productivity may be high in local situations where availability of nutrients, particularly phosphorus and carbon are high (Fyson and Ruecker, 1998; Nixdorf et al., 2003). Bacterial production in the acidic Lusatia pit lakes is typically in the range found in eutrophic, non-mining lakes in the region (Kamjanke et al., 2004; Nixdorf et al., 2003). However, primary productivity in such ecosystems is generally low (Nixdorf et al., 2003; Beulker and Nixdorf, 2004) and likely limited either by the intrinsically low dissolved inorganic carbon (DIC) concentrations at low pH values or the extremely low P concentrations attributable to the propensity of this phosphate to coprecipitate with iron (III) oxyhydroxides (Stumm and Morgan, 1996). Such DIC and P limitations have been documented for the acidic Lausitz pit lakes (Krumbeck et al., 1998; Beulker and Nixdorf, 2004). It is well known that the productivity of lakes, as reflected in chlorophyll concentrations, is closely tied to phosphorus concentration and the chlorophyll a to total phosphorus (TP) concentration for the acidic Lausitz pit lakes fits in with the general relationship (Fig. 1).

Algae may be able to grow mixotrophically in these lakes using organic carbon sources, both dissolved and particulate (Tittel et al., 2003). Incorporation of organic carbon into biomass makes no net addition to carbon pools. However, primary production does occur in the acidic Lausitz pit lakes and addition of phosphorus and inorganic carbon has been shown to enhance primary production in bottle experiments (Nixdorf et al., 2003; Beulker and Nixdorf, 2004). If primary production of these ecosystems can be enhanced with a net input of inorganic carbon to the system, the supply of carbon and nutrients to sediment-bound, alkalinity generating processes can also be increased. The continued enhanced cycling of nutrients and carbon may provide the basis of a sustained acidity removal system. Earlier experiments with water and sediments from Koschen, another acidic pit lake in the region, showed that addition of organic matter (potatoes) led to the rapid neutralization of the water following a burst of sulfate reduction (Fyson et al., 1998 a, b). The high pH values in the water column were maintained for the duration of the experiment (2 years). Other microcosm studies with water

and sediment from Lake ML111, another acidic pit lake in the region, have shown that additions of various organic substances can enhance sulfate reduction in the sediment and generate alkalinity (Fauville et al., 2004; Frömmichen et al., 2004).



Figure 1. The relationship between chlorophyll concentration and total phosphorus concentrations in Lausitz pit lakes in comparison to data for eutrophic non-mining lakes from Vollenweider and Kerekes (1982). The arrows indicate how these systems will likely develop over time.

With funding from the German government and the lignite industry, a multidisciplinary project, involving researchers from several universities and institutes in the region has investigated the use of controlled eutrophication to increase lake productivity and sustainably remove acidity through sediment bound and water column biologically mediated processes. The results of this project are described in Nixdorf and Deneke (2004). It has included basic research on particle transport in streams and lakes, pelagic food web interactions and submerged macrophyte metabolism as well as investigations on the roles of wetlands, bacterial interactions at the water-sediment interface (Wendt-Potthoff and Koschorrek, 2002, 2004) and modelling (Nixdorf and Uhlmann, 2002; Uhlmann and Nixdorf, 2002). This contribution focuses on the laboratory experiments on controlled eutrophication, described in more detail in Fyson and Gelbrecht (2004)

Microcosm experiments (60 L) were carried out to investigate the effect of phosphorus and organic carbon additions on the water chemistry and biology of acidic lake water in the presence or absence of sediment. An initial experiment was set up with lake water and amendments, but without sediment. This sought to determine the effects of changes in conditions on water chemistry. The results are described in Fyson and Gelbrecht (2004). Addition of phosphate and organic C (acetic acid) together resulted in higher primary production rates than in controls or with addition of phosphate alone. Phosphate concentrations declined rapidly coupled to removal of Fe. The enhanced primary production could enhance the supply of organic substrates for sediment-bound alkalinity generating processes such as iron and sulphate reduction. None of the treatments in this experiment resulted in substantial changes in pH or acidity over a 230 day period (Fyson and Gelbrecht, 2004). In the study described here, chemical and biological changes have been studied in 60 L microcosms with water and sediment from Lake Grünewalde to determine the effects of added nutrients on water and sediment chemistry, primary production, and colonization by algae.

# **Materials and Methods**

Laboratory microcosm experiments were carried out with clear PVC columns 2 m high and with an internal diameter of 0.2 m. These were filled with 60 L of lake water from Lake Grünewalde (Fig. 2) and with a 20 cm layer of sediment from the lake.



Figure 2. Lake Grünewalde (RL 117) from which water and sediments were used in the microcosm experiment.

Mean values of chemistry parameters for Lake Grünewalde (from Beulker and Nixdorf, 2004) are as follows: pH 3.0, Fe 14 mg  $L^{-1}$ , acidity (KB<sub>8,3</sub>) 2 mmol  $L^{-1}$  P 3 µg  $L^{-1}$  NH<sub>4</sub><sup>+</sup>-N 1.5-2.0 mg  $L^{-1}$  dissolved inorganic carbon (DIC) 0.2-0.3 mg  $L^{-1}$ ). The experimental set-up is shown in Fig. 3.

These microcosms were incubated at room temperature (18-22 °C) under artificial lighting (True Lite fluorescent tubes) with a near to sunlight light spectrum. Light intensity was approximately 50 W m<sup>-2</sup>.s<sup>-1</sup> at the top of the microcosms. Amendments were added as shown in Table 2. Three microcosms were set up for each treatment. Chemical and physico-chemical parameters were determined according to standard German methods (DEV) modified according to Zwirnmann et al. (1999). Measurements of pH, O<sub>2</sub> concentration, redox potential and electrical conductivity were made with YSI probes in the middle of the water column (0.9 m depth). Primary production (PP) was determined by the <sup>14</sup>C method as modified by Kapfer et al.

(1997) and bacterial production (BP) by a modified <sup>3</sup>H thymidine method (Nixdorf and Jander, 2003). Algal biovolume was determined for lugol-fixed samples by a modified Utermohl method (Rott, 1981) with the help of an inverse microscope. Sediment porewater was extracted by centrifugation of 200 mL sediment at 4 °C. The decanted porewater was filtered (0.45  $\mu$ m pore cellulose acetate filters)) and analyzed as described above. For analysis of the sediment, samples were dried at 60 °C, homogenized and analyzed in an Elementar C-N-S analyzer.



Figure 3. Microcosm set-up

Table 2. Microcosm experiment, treatments and amendments added (3 microcosms for each treatment). All microcosms had 60 L of Lake Grünewalde and except treatment 1, 4 L of sediment from the same lake.

Treatment		Amendment
1	Control without sediment	None
2	Complex organic	120 g fresh weight of potato (1 small potato) added to the sediment surface in a net bag with a stone to provide weight
3	Simple organic and phosphate	Addition of $Na_2HPO_4$ and acetic acid to give concentrations of 1.41 mM and 0.1 mM respectively
4	Control with sediment	Water and sediment from Lake Grünewalde
5	NaOH	NaOH added to raise pH from 3.0 to 3.5 (precipitate iron)

### **Results**

In the study described here, chemical and biological changes have been studied in 60 L microcosms with water and sediment from Lake Grünewalde to determine the effects of added nutrients on primary production and water chemistry as well as to establish the role of sediment-water interactions on changes in water chemistry and primary production. Additional treatments were applied with addition of NaOH to raise pH to 3.5 in order to precipitate iron, and with potatoes to generate conditions favourable for anaerobic alkalinity generating processes. The results are shown in Fig. 4, and Table 3.

In the microcosms with lake water alone, there were only small changes in measured parameters (P, Fe, pH, conductivity) over time. Some iron was lost as hydroxide precipitates and the pH remained stable (Fig 4 a). Primary production rates remained very low (Fig 4 f). Algal populations (biovolume) declined following the first sampling (19-21 days) as shown in Fig. 5. The algae were dominated by diatoms (*Eunotia exigua*) and green algae (*Chlamydomonas* sp.). Other algae present were the golden alga, *Ochromonas* sp. and two green algae, *Nanochlorum* sp. and an unidentified species (Table 4). These did not contribute substantially to algal biovolume in any treatment.



Figure 4. Changes in microcosm water-column chemistry and productivity: a, pH; b, Total dissolved iron; c, Total phosphorus (TP); d, Soluble reactive phosphorus (SRP); e, Electrical conductivity; f, Primary production (PP); g, Total inorganic carbon (TIC); h, Bacterial production (BP); a-e Mean ± SD (n = 3), f-h Single microcosms.

In microcosms with lake-water and sediment and no further additions, the conductivity declined substantially during the course of the experiment largely attributable to the decline in sulphate concentration from 346 mg  $L^{-1}$  to 278 mg  $L^{-1}$  presumably due to sulfate reduction in the sediment and precipitation of iron hydroxy sulfates (such as schwertmannite as described in Blodau and Peiffer, 2003). It is noteworthy that the Fe-concentration fell more rapidly than in the water-only microcosms (Fig 4 b). The pH climbed to 3.8 by the end of the measurement period and titratable acidity (KB<sub>8.2</sub>) declined from 2.1 to 0.47 mmol  $L^{-1}$ . Clearly, the sediment was able to generate alkalinity. With both these treatments, phosphate concentrations remained very low (Fig 4 c, d). Detectable nitrate disappeared. In the presence of sediment, ammonium-N concentrations increased, presumably due to decomposition of organic matter. Total inorganic carbon (TIC) and dissolved organic carbon (DOC) concentrations also increased in these microcosms indicating net release or carbon from the sediment from decomposition processes. Other parameters (Mn, Ca, Mg, Al, K, Na, Cl, Si) exhibited little change in concentrations. In the microcosms with sediment but no other additions, primary production (Fig 4 f) and algal biomass (Fig. 5) remained low and similar to values of water only microcosms and was similarly dominated by Eunotia exigua and Chlamydomonas sp. The increase in TIC was associated with high rates of bacterial production (Fig. 4 h).

meroeosin enperiment. Trean values for anee meroeosins.								
Parameter	Water only	Control	P/Acetic acid	NaOH	Potatoes			
	Days	Days	Days	Days	Days			
	0 245	0 245	0 245	0 245	0 245			
Fe [ mg $L^{-1}$ ]	4.0 1.3	5.7 <0.2	4.4 <0.2	2.8 <0.2	5.9 <0.2			
SRP [ $\mu g L^{-1}$ ]	4.8 6.1	5.1 3.5	143 3.1	3.2 3.6	3.0 6.6			
TP [µg L <sup>-1</sup> ]	2.9 3.9	4.1 4.7	169 3.8	5.2 3.8	2.5 24			
TIC [ mg L <sup>-1</sup> ]	0.04 0.2	0.25 1.5	0.3 1.9	0.1 31.6	0.1 637			
DOC [ mg L <sup>-1</sup> ]	1.0 0.8	1.0 2.2	6.2 0.8	1.0 1.3	0.9 5.1			
$NO_3^{-}-N [mg L^{-1}]$	0.08 0.35	0.06 0.3	0.06 0.2	0.07 0.3	0.06 0.2			
$NH_4^+ - N [mg L^{-1}]$	1.1 1.3	1.1 4.0	0.8 3.37	0.8 3.80	0.8 5.1			
$SO_4^{2-}$ [ mg L <sup>-1</sup> ]	345 343	346 278	346 256	345 292	344 116			
Si $[mg L^{-1}]$	6.8 4.9	7.3 6.5	7.0 3.9	7.2 6.0	7.3 8.8			
рН [-]	3.0 3.0	3.0 3.8	3.0 3.8	3.5 4.6	3.0 7.4			
Acidity [mmol L <sup>-1</sup> ]	2.1 1.8	2.1 0.47	2.1 0.54	2.1 0.23	2.1 0.29			
Cond. $[\mu S \text{ cm}^{-1}]$	1055 1169	1044 689	1055 671	848 683	1033 576			
$O_2 [mg L^{-1}]$	8.0 8.4	8.7 7.1	9.2 7.3	7.9 7.5	3.4 0.8			

Table 3. Changes in various parameters from set-up to the end of observations (245 days) in the microcosm experiment. Mean values for three microcosms.



Figure 5. Total algal biovolume and biovolume of the two dominant algae (*Eunotia exigua* and *Chlamydomonas* sp.) according to treatment, 19-21 days and 246 to 256 days after set-up. Mean values for samples from 2 microcosms

Table. 4. Algal biovolumes in second microcosm experiment after 19-25 and 246-256 days.

	Lake				Microcosm							
		Wat	er only	Cont	rol	PO	<sup>3-/</sup> acetic acid	NaOH		Potat	toes	
Incubation (days)		21	256	21 24	46-256	21	246-256	19-25	246-256	21 2	46-256	
Nanochlorum sp.	+	+	+	+	+	+	+	+	+	+	+	
Ochromonas sp.	+	+	(+)	+	+	+	(+)	+	+	+	+	
Eunotia exigua	+	+	(+)	(+)	(+)	+	+	+	(+)	+	-	
Chlamydomonas sp	<b>0</b> .+	(+)	(+)	+	+	+	+	+	(+)	(+)	(+)	
Chlorophyte	-	(+)	-	(+)	(+)	+	(+)	-	-	-	-	

With the addition of phosphorus and acetate, soluble reactive phosphorus (SRP) concentrations declined from a mean of 143  $\mu$ g L<sup>-1</sup> two days after addition to only 6  $\mu$ g L<sup>-1</sup> after 79 days, likely due to coprecipitation with iron hydroxides (Fig 4 c, d; Table 3). The decrease in sulfate concentration was similar to that of microcosms with sediment alone (Table 3). At the beginning of the experiment, the P and acetate additions led to a dramatic increase in primary production (PP) (Fig 4 f) but PP subsequently declined with sinking phosphorus concentration. However, values remained well above those of water only and water/sediment microcosms. Bacterial production, in contrast, remained high (Fig. 4 h). The low DOC concentration indicates the uptake and or breakdown (respiration) of the added acetate. Other parameters (N, TIC, metals) exhibited only small changes in microcosms with added phosphorus and acetic acid (Table 3). Si concentrations declined rapidly in association with the build up of the diatom *E. exigua* (Fig. 5) which uses this element to construct cell walls. After 21 days and 246-256 days, total algal biovolume in these microcosms was higher than with all other treatments (Fig. 5).

NaOH was added to some microcosms to increase the pH to around 3.5 to rapidly precipitate iron. During the course of the experiment, the pH climbed further to 4.6 (Fig 4 a, Table 3) and much of the titratable acidity was removed. With the exception of Na (added to the microcosms), the concentration of other parameters remained similar to those of microcosms with water and sediment alone. There was a greater development of *E. exigua* and higher overall algal biovolume in these microcosms (Fig. 5) than in the water-only and control microcosms.

With the addition of potatoes to the sediment surface and the resulting decomposition, oxygen concentrations decreased to below the detection limit  $(0.1 \text{ mg L}^{-1})$  within 4 weeks (data not shown). In these anoxic conditions, the pH values in the water column rose to more than 7 and remained circum-neutral for the remainder of the experiment (Fig 4 a, Table 3). At the same time, Fe concentrations increased for a short period with the release of Fe (II) from the sediment. The anoxic conditions were short lived with the subsequent slow recovery of oxygen concentrations. Iron concentration declined to less than 0.2 mg  $L^{-1}$  (Fig 4 b). There was a dramatic decline in sulphate concentrations from 344 mg  $L^{-1}$  to 124 mg  $L^{-1}$  (Table 3) presumably due to enhanced sulphate reduction. Conductivity decreased substantially to less than 600  $\mu$ S cm<sup>-1</sup>. There was a substantial increase in TP concentration in the water column of these microcosms in the early part of the experiment (149  $\mu$ g L<sup>-1</sup> after 49 days). Although subsequently declining, it remained well above that of other treatments (24  $\mu$ g L<sup>-1</sup>) at the end of the observation period. In contrast, SRP concentrations were similar to those of the controls probably indicating uptake and rapid recycling within the water column. A further consequence of the anoxic conditions in the potato microcosms was the increase in concentrations of ammonium-N, TIC and DOC. The overall release of nutrients resulted in very high primary reduction rates (Fig 5h) due to the proliferation of green sulphur bacteria (microscopic and pigment determination by J. Rücker). The algal biovolume remained low (Fig. 5).

The analyses of the sediments (Table 5 b) show that the sulfur content of sediments amended with potatoes was clearly higher than with other treatments indicating the net deposit of sulfur. This is best explained by the production of iron sulfides. The low redox potentials and high Fe concentrations in the sediment porewater (Table 5 a) for this and other treatments indicate iron reduction in anoxic conditions and the release of Fe(II) within the sediment. In all microcosms, the pore-water TP concentration was high (207-256  $\mu$ g L<sup>-1</sup>) and pH values were in the 6.7 to 6.9 range.

Table 5. a) Sediment porewater analysis and b) sediment composition of the microcosm experiment 245 days after set-up. Mean values from amalgamated samples from 3 microcosms

Amendment	Fe [mg/L]	Mn [mg/L]	TP [µg/L]	pН	Redox [mV]			
Control	186	0.8	207	6.7	-147			
Phosphate/Acetic acid	145	0.7	215	6.7	-141			
NaOH	148	0.9	251	6.7	-133			
Potato	144	0.7	256	6.9	-128			

b)	Sediment	carbon,	hydrogen,	nitrogen	and sulphur	(% dry	weight)
- /		,	,,		·····	(	

a) Sediment pore-water

	• •			
Amendment	Carbon	Hydrogen	Nitrogen	Sulfur
Control	10.8	1.49	0.20	0.46
Phosphate/Acetic acid	11.1	1.51	0.19	0.47
NaOH	10.8	1.49	0.20	0.45
Potato	11.0	1.54	0.21	0.54

# **Discussion**

Anaerobic microbially mediated alkalinity generating processes notably iron and sulfate reduction have been long-proposed as a means for removing acidity and metals from AMD. Much emphasis has been put on sulfate reduction. The enhancement of sulfate reduction through increasing the supply of organic substrates has been demonstrated in a number of laboratory experiments (e.g. Christensen et al., 1996: Fyson et al., 1998 a, b; Fauville et al., 2004; Frömmichen et al., 2004). Passive treatment systems such as compost (anaerobic) wetlands, the ARUM system and field bioreactor systems have been constructed, particularly in North America and the U.K have been shown to remove acidity from AMD at least for a short period (see Kalin et al. (1995), Skousen et al. (1998), Younger et al. (2002) and Brown et al. (2002) for reviews of these systems). Self-sustaining systems, i.e. with no ongoing management have not as yet been demonstrated and existing systems have only yet been shown to function for a few years, up to 6 years in the case of ARUM (Kalin and Smith, 1997). Internal carbon generating systems (through photosynthesis and carbon fixation) coupled to active internal recycling of nutrients are necessary for sustainability.

Increasing autochthonous primary production through controlled eutrophication (enhanced production through enhancement of nutrient supply) is therefore an attractive strategy for the long-term neutralisation of the acidic Lausitz pit lakes through sustained supply of organic material and nutrients to sediments. These lakes are characterised by extremely low phosphorus and dissolved inorganic carbon concentrations on account of the high iron (III) content and low pH respectively. The iron (III) precipitates as iron (III) oxyhydroxides with the coprecipitation of phosphorus. Subsequent reduction of these precipitates in anoxic conditions can re-release

the phosphorus. Experiments with water and sediments from the acidic Lausitz pit lakes have demonstrated that organic additions can stimulate alkalinity generation including sulfate reduction (Fyson et al., 1998; Fauville et al., 2004; Frömmichen et al., 2004).

The experiment described here has shown that increase in supply of nutrients can fuel increases in primary production in microcosm experiments with water and sediments from the acidic Lake Grünewalde. However, only the presence of sediment and with the addition of readily degradable organic material (potatoes) did neutral conditions in the water column and sequestration of iron and sulfur in sediments result. This requires the generation of anoxic conditions in and above the sediment. Increased phosphorus and carbon supply greatly enhances primary production and maintains carbon supply for the sediment-bound alkalinity generating processes. The experiment described here and others published elsewhere (Fyson et al., 1998; Fyson and Gelbrecht, 2004) show that once the acidity is removed, pH remains high and an enhanced supply of phosphorus to the water column is maintained. Whether this can sustain treatment of incoming acidic groundwater and remove acidity from the whole water column in the mining lakes has yet to be established. Enclosure experiments in Lake Grünewalde (Fyson and Gelbrecht, 2004) have shown enhanced productivity with addition of potatoes. However, as yet only short term experiments have been carried out and long-term experiments of whole lakes are necessary to establish this treatment technology.

The results presented here for Lake Grünewalde confirm earlier observations made in 20 L microcosm experiments with lake water and sediment from Lake Koschen (pH 3.1, Fe 21.0 mg  $L^{-1}$ ). In this previous study, anoxic conditions were temporary but neutral conditions with enhanced P concentrations were maintained until the end of the observation period (2 years after set-up) (Fyson et al., 1998a). Biological acidity removal clearly works in laboratory microcosms and enhanced P and C supply can greatly enhance primary production, support enhanced algal growth and sustain neutral conditions in the water column.

Beulker and Nixdorf (2004) have estimated potential supply of carbon to sediments in the acidic Lausitz pit lakes (including Lake Grünewalde) from primary production of 26 g C m<sup>-2</sup> a<sup>-1</sup> based on carrying capacity and concluded that organic carbon from phytoplankton can make an important contribution to alkalinity generation by the sediments. However, Long-term field experiments in large mesocosms (30 m diameter) are underway in Plessa ML 111 another acidic lake in the area (pH 2.6, Fe 150 mg L<sup>-1</sup>) have concluded that pelagic algae could contribute less than 2 % to acidity removal (Tittel and Kamjunke, 2004). These authors concluded that benthic (bottom living) algae were much more important in this role. In the experiment described in this paper, the primary production rates with addition of either acetic acid and phosphate or potatoes are high in relation to in situ determined rates (Beulker and Nixdorf, 2004) but it is not realistic to extrapolate to annual contributions to alkalinity generation in the field.

An understanding of the overall functioning of these ecosystems is essential for the development of ecotechnological remediation measures which optimise the role of biological alkalinity-generating processes for sustainable, environmentally acceptable acidity removal. Food webs in these lakes are relatively simple (e.g. top predators are coroxids (Wollmann et al., 2000)) and these relatively simple ecosystems provide model system for studies of trophic interactions and with the acquisition of further knowledge, both of ecosystem functioning and the geohydrological situation, integrated development strategies, incorporating long-term, self-

sustaining acidity removal may be developed. The role of bacteria in supply and utilization of carbon and nutrients in the water column is clearly important as bacterial production may exceed primary production (Kamjunke at al., 2004). There are many unanswered questions.

Together with modelling of the chemical processes in relation to lake morphometry (Nixdorf and Uhlmann, 2002; Uhlmann and Nixdorf, 2002), the results of the studies described here and those on other expects on functioning of the acidic, flooded lignite pit ecosystems will assist in the development of biologically based remediation strategies (Nixdorf and Deneke, 2004).

There is great interest in developing sustainable treatment for treatment of AMD. Most of the "passive" systems developed up to now (see Skousen (1998), Younger et al. (2002) and Brown et al. (2002) for reviews of these technologies) are not sustainable. Although they embrace the role of microbial alkalinity generating processes, especially sulfate reduction, they will require ongoing maintenance such as substrate replacement. In addition, it has not been clearly established that the metals and sulfides removed are in the form or stable sulfides in sediments. In order to develop truly sustainable technologies for AMD treatment, ecosystems must be designed and engineered to optimise the role of primary producers (macrophytes or algae) through enhanced biogeochemical cycling to maintain a supply of carbon for the anaerobic, alkalinity-generating processes. The ARUM process (Fyson et al., 1995; Kalin et al., 1995) employs such ecological engineering approach to treat AMD. In these systems, floating vegetation mats generate carbon to sustain anaerobic conditions in and above the sediments below and provide fuel for the alkalinity generating processes. Under certain conditions, such systems have been shown to remove acidity for at least 5 years (Kalin and Smith, 1997). Further research and long-term funding is clearly needed to understand how AMD treatment can be sustained indefinitely in both surface-flowing AMD and acidic pit lakes. Sustained enhanced carbon input coupled to enhanced nutrient cycling could provide truly passive AMD treatment systems.

#### **Summary**

Microcosm experiments with water and sediment form extremely acidic flooded lignite pits in Germany have demonstrated that supplementary supply of phosphorus and carbon to the water column (controlled eutrophication) can enhance primary production and maintain sedimentbound, alkalinity generating processes. Future studies will help develop treatment strategies which are environmentally acceptable and hopefully provide a sustainable alternative to chemical treatments for neutralisation of AMD.

# **Acknowledgements**

This study was funded by BMBF (Bundesministerium für Bildung und Forschung, FKZ 0339746) and LMBV (Lausitzer und Mitteldeutscher Bergbau Verwaltungsgesellschaft) grant 45016514. The authors wish to thank colleagues in the Department of Water Conservation, Brandenburg Technical University, Cottbus and the Institute of Freshwater Ecology and Inland Fisheries, Berlin for all their help.

### **References**

Beulker, C. and B. Nixdorf. 2004. Primärproduktion und Alkalinisierung p. 73-86. In Grundlagen und Maßnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.

- Blodau, C. and S. Peiffer. 2003. Thermodynamics and organic matter: Constraints on neutralization processes in sediments of highly acidic waters. Applied Geochem. 18: 25-36. http://dx.doi.org/10.1016/S0883-2927(02)00052-5.
- Brown, M., B. Barley and W. Wood. 2002. Minewater treatment, technology, application and policy. IWA Publishing, London, U.K.
- DEV Deutsche Einheitsverfahren zur Wasser-, Abwasser-, und Schlammuntersuchung, Fachgruppe Wasserchemie i. d. GDCh in Gemeinschaft mit dem NAW im DIN (Eds.). VCH Verlagsges., Weinheim, 1976-1998.
- Fauville, A., B. Mayer, R. Frömmichen, K. Friese and J. Veizer., 2004. Chemical and isotopic evidence for accelerated bacterial sulphate reduction in acid mining lakes after addition of organic carbon: laboratory batch experiments. Chemical Geology 204: 325-344. http://dx.doi.org/10.1016/j.chemgeo.2003.11.010.
- Frömmichen, R., K. Wendt-Potthoff, K. Friese and R. Fischer. 2004. Microcosm studies for neutralization of hypolimnic acid mine pit water (pH 2.6). Environ. Sci. Technol. 38: 1877-1887. <u>http://dx.doi.org/10.1021/es034863e</u> PMid:15074702.
- Fyson, A. and J. Gelbrecht. 2004. Kontrollierte Eutrophierung: Nährstoffzugaben und Induktion microbieller Stoffumsetzungen durch erhöhte Primärproduktion. p. 89-104. *In* B. Nixdorf and R. Deneke (ed.). Grundlagen und Maβnahmen zur biogenen Alkalisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.
- Fyson, A., M. Kalin and M.P. Smith. 1995. Microbially-mediated metal removal from acid mine drainage. In: M. Moo Young et al. (ed.) Environmental Biotechnology, Kluwer Academic Publishers. <u>http://dx.doi.org/10.1007/978-94-017-1435-8\_47</u>.
- Fyson A., Nixdorf, B., Kalin M., Steinberg, C.E.W. 1998. Mesocosm studies to assess acidity removal from acidic mining lakes through controlled eutrophication. Ecological Engineering 10: 229-245. <u>http://dx.doi.org/10.1016/S0925-8574(98)00007-X</u>.
- Fyson, A., B. Nixdorf and C.E.W. Steinberg. 1998. Manipulation of the sediment –water interface of extremely acidic mining lakes with potatoes: Laboratory studies with intact sediment cores. Water, Air and Soil Pollution 108: 353-363. <u>http://dx.doi.org/10.1023/A:1005190303508</u>.
- <u>Fyson, A. and J. Ruecker</u>. 1998. Die Chemie und Ökologie des Lugteiches eines extrem sauren, meromiktischen Tagebausees. *In*: M. Schmitt and B. Nixdorf (eds.) Gewaesserreport (Nr. 4). BTUC-AR 5/98: 18-34.

- Geller, W., K. Friese, P. Herzsprung, R. Kringel and M. Schultze. 2000. Limnology of sulphuracid lignite mining lakes. II Chemical main constituents and buffering systems. Verh. Internat. Verein. Limnol. 27: 1-5.
- Kalin, M., A. Fyson and M.P. Smith. 1995. Microbially-mediated metal removal from acid mine drainage. Proceedings of the Mining and the Environment Conference, (Sudbury, Ontario, Canada, May 28-June 1, 1995).
- Kalin, M and M.P. Smith, 1997. Microbial acid reduction in sediments Concepts and Application. p. 1323-1334. Proceedings of the Fourth International Conference on Acid Rock Drainage. (Vancouver, B. C., Canada, June, 1997).
- Kamjunke, N., J. Tittel and U. Gaedke. 2004. Mikrobielle Umsetzungen und Biomasseproduktion im Pelagial von Tagebauseen. p. 105-118. *In*: Grundlagen und Maßnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.
- Kapfer M., U. Mischke, K. Wollmann, H. Krumbeck. 1997. Erste Ergebnisse zur Primärproduktion in extrem sauren Tagebauseen der Lausitz . *In*: Deneke H. and Nixdorf B. (Eds.). Gewässerreport Nr. 3. Lehrstuhl Gewässerschutz, Brandenburg Technical University, BTUC-AR 5/97, 31-40.
- Krumbeck H., B. Nixdorf and A. Fyson. 1998. Ressourcen der Bioproduktion in extrem sauren Tagebauseen der Lausitz –Angebot, Verfügbarkeit und Umsetzung. In Schmidt, M and Nixdorf, B. (Eds.). Gewässerreport (Nr. 4), Lehrstuhl Gewässerschutz, Brandenburg Technical University. BTUC-AR 5/98, 7-17.
- Lessmann D., A. Fyson, B. Nixdorf. 2000. Phytoplankton of the extremely acidic mining lakes of Lusatia (Germany) with pH  $\leq$  3. Hydrobiologia 433: 123-128. http://dx.doi.org/10.1023/A:1004018722898.
- Nixdorf, B., H. Krumbeck, J. Jander and C. Beulker. 2003. Comparison of bacterial and phytoplankton productivity in extremely acidic mining lakes and eutrophic hard water lakes. Acta Oecologia 24 (Suppl. 1): 281-288. <u>http://dx.doi.org/10.1016/S1146-609X(03)00031-6</u>.
- Nixdorf, B. and R. Deneke, Eds. 2004. Grundlagen und Maßnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.
- Nixdorf, B. and J. Jander. 2003. Bacterial activities in shallow lakes A comparison between extremely acidic and alkaline eutrophic hard water lake. Hydrobiologia 506(1): 697-705. http://dx.doi.org/10.1023/B:HYDR.0000008623.73250.c8
- Nixdorf B., M. Mischke and D. Lessmann. 1998. Chrysophytes and chlamydomonads: Pioneer colonists in extremely acidic mining lakes (pH<3) in Lusatia (Germany). Hydrobiologia 369-370, 315-327. <u>http://dx.doi.org/10.1023/A:1017010229136</u>.

- Nixdorf B., A. Fyson and H. Krumbeck. 2001a. Review: plant life in extremely acidic waters. Environmental and Experimental Botany 46: 203-211. <u>http://dx.doi.org/10.1016/S0098-8472(01)00104-6</u>.
- Nixdorf B., M. Hemm, A. Schlundt, M. Kapfer and H. Krumbeck. 2001b. Tagebauseen in Deutschland ein Überblick. Umweltforschungsplan des Bundesministeriums für Umwelt, Naturschutz und Reaktorsicherheit Forschungsbericht 298 22 240 UBA-FB 000146.
- Nixdorf B., H. Krumbeck, J. Jander and C. Beulker. 2003. Comparison of bacterial and phytoplankton productivity in extremely acidic mining lakes and eutrophic hard water lakes. Acta Oecologica. 24, supplement 1: 281-288. <u>http://dx.doi.org/10.1016/S1146-609X(03)00031-6</u>
- Nixdorf B., W. Uhlmann. 2002. Ökotechnologische Steuerung der Gewässergüte in sauren Tagebauseen. Teil 1: Desulfurikation und Morphologie. Wasser und Boden 54, 16-21.
- Rott, E. 1981. Some results from phytoplankton counting intercalibrations. Schweiz. Z. Hydrol. 43: 34-62. <u>http://dx.doi.org/10.1007/bf02502471</u>.
- Skousen, J., A. Rose, G. Geidel, R. Evans, W. Hellier and others. 1998. ADTI handbook of technologies for avoidence and treatment of acid mine drainage. National Mine Land Reclamation Center, WVY, Morgentown, West Virginia.
- Stumm, W. and J.J. Morgan. 1996. Aquatic chemistry. 3rd. Edition. John Wiley and Sons.
- Tittel, J., V. Bissinger, B. Zippel, U. Gaedke, E. Bell, A. Lorke and N. Kamjunke 2003. Mixotrophs combine resource use to outcompete specialists: Implications for aquatic food webs. PNAS 100: 12776-12781. <u>http://dx.doi.org/10.1073/pnas.2130696100</u> PMid:14569026 PMCid:PMC240694.
- Totsche, O and C.E.W.Steinberg. 2004. Maßnahmen zur Neutralisierung saurer Gewässr- Eine Übersicht. p. 37-54 In Grundlagen und Maßnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.
- Uhlmann W. And B. Nixdorf. 2002. Ökotechnologische Steuerung der Gewässergüte in sauren Tagebauseen. Teil 2: Primärproduktion und Respiration. Wasser und Boden 54: 22-26.
- Uhlmann, W., H. Büttcher and M. Schulze. 2004. Grundlagen der chemischen und biologischen Alkalinisierung saurer Tagebauseen. p. 13-35. *In*: Grundlagen und Maßnahmen zur biogenen Alkalinisierung von sauren Tagebauseen. Weißensee Verlag, Berlin.
- Vollenweider, R.A. and J.J. Kerekes. 1982. Synthesis report-Cooperation program on monitoring of inland water (eutrophication control). OECD, Paris.
- Wollmann, K., R. Deneke, B. Nixdorf and G. Packroff. 2000. Dynamics of planktonic food webs in three mining lakes across a pH gradient (pH 2-4). Hydrobiologia 433: 3-14. http://dx.doi.org/10.1023/A:1004051629258 http://dx.doi.org/10.1023/A:1004060732467

- Younger, P.L., S.A. Banwart and R.S. Hedin. 2002. Minewater: hydrology, pollution, remedation. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Zwirnmann E., A. Krüger, A. And J. Gelbrecht. 1999. Analytik im Zentralen Chemielabor des IGB. Institut für Gewässerökologie und Binnenfischerei, Report 9. ISSN-Nr. 1432 508X.