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Technical Article

Microbial Alkalinity Production to Prevent Reacidification of Neutralized Mining Lakes

Oliver Totsche[1], Andrew Fyson[1, 2], Christian E. W. Steinberg[3]

[1]Leibniz-Institute of Freshwater Ecology and Inland Fisheries, Müggelseedamm 310, 12587 Berlin, Germany; [2]Boojum Research, Ltd, 139 Amelia Str, Toronto M4X 1E6, Ontario, Canada; [3]Humboldt Univ at Berlin, Unter den Linden 6, 10099 Berlin, Germany; corresponding author's e-mail: totsche@igb-berlin.de

Abstract. Microbial alkalinity production was evaluated as a method to prevent reacidification of neutralized mining lakes by acidic ground and seepage water. We used 60 L mesocosms to represent the sediment and water column of a shallow acidic mine lake. To enhance alkalinity production, acidic and neutralized lake waters were treated with either phosphorus (controlled eutrophication) or organic matter (controlled saprobization). Controlled eutrophication could not produce enough autochthonous biomass as substrate for microbial alkalinity production to change the acidity of the water. Chemical pre-neutralization of the acidic water caused the inorganic carbon concentration to increase, but at the same time, hindered algae growth by reducing the availability of phosphate by sorption to the freshly precipitated iron hydroxide. This effect was so strong that even high phosphorus additions could not increase the algae biomass production. In contrast to controlled eutrophication, controlled saprobization produced significant alkalinity. Despite inhibition of the most important alkalinity producing process, namely microbial sulfate reduction, by low pH values, the microbial alkalinity production rate was not affected by pre-neutralization of the water column. Other alkalinity producing processes raised the pH in the reactive zone until sulfate reduction was no longer inhibited.

Key words: Acid mine lake; eutrophication; neutralization rate; saprobization; sulfate reduction

Introduction

There are more than 100 open pit lakes in the Lusatia region of eastern Germany. The mining lakes can be divided into two types based on the lignite extraction process: small shallow littoral lakes with a mean depth of less than 5 m and very large lakes with a mean depth of more than 20 m (Nixdorf and Kapfer 1998). Almost two-thirds of these mining lakes have a pH of 2.0 to 3.5 and high concentrations of acidity, iron, and sulfate (Geller 2005; Klapper and Schultze 1995). There is intense public interest in neutralizing these lakes, converting the former mining area to a recreation and tourist zone, and protecting the ground water resources.

To neutralize acidic lakes, three principal neutralization strategies are available: (1) flooding the lakes with neutral water, (2) producing alkalinity microbially, and (3) neutralizing with chemical reagents. However, once-neutralized lakes can reacidify due to the inflow of acidic ground and seepage water, and it is anticipated that acid production in mining areas will continue for hundreds or perhaps thousands of years (Kalin 2001; Nordstrom and Alpers 1999).

The first choice method for neutralization is flooding with neutral water. However with less than approximately 500 mm a^{-1} in the Lusatia region, too little water is available to flood all the lakes with neutral surface or ground water. In addition, it is too expensive and impractical to flood the many small and far-flung, shallow lakes in this region. Therefore this flooding method is mainly used on the large deep lakes in the region (e.g. Lake Geierswalde, Lake Greifenhain, and Lake Gräbendorf). For the neutralization of small shallow lakes, alternative methods have to be applied.

Microbial alkalinity production is an alternative neutralizing strategy in which the acidification process is reversed by sulfate and iron reduction. This process is carried out by bacteria under anoxic conditions in the hypolimnion and sediments of stratified lakes and sediments of non-stratified shallow lakes. Sulfate reduction requires the addition of organic substrates. This requirement is met through controlled saprobization or controlled eutrophication (Fyson et al. 1998a; Kalin 2001). Controlled saprobization means the addition of organic substances, such as agricultural waste, in such a way that complete anoxia of the water body is avoided. This method has been tested in a number of small-scale studies (Brugam and Stahl 2000; Brugam et al. 1995; Fyson et al. 1998a, b; Kalin 2001; Frömmichen et al. 2003; Frömmichen et al. 2004; Prasad et al. 1999). Although some laboratory experiments resulted in a complete neutralization of the water body (Brugam et al. 1995; Frömmichen et al. 2004;

Fyson et al. 1998a), this method has not yet been successfully applied to whole lakes.

Controlled eutrophication involves the sustainable addition of nutrients, to build up substrates for microbial alkalinity-generating processes through enhanced primary production. This autochthonous lake biomass is more readily decomposable than allochthonous material (Blodau et al. 1999). There is, however, information available that as long as the water is acidic, the potential for primary production is limited by the low concentration of inorganic carbon (Tittel and Kamjunke 2004).

With the third method of neutralization, the water is neutralized by alkaline substances, such as lime or sodium hydroxide. This method has the considerable disadvantage that it is not sustainable and can only neutralize the standing water volume. To inhibit subsequent acidification from inflowing acidic ground and seepage water (Bozau and Strauch 2002), a permanent and regular addition of the chemical agent is required. This need results in high costs for infrastructure and chemicals. Nevertheless, a lack of alternatives in Lusatia has led to projects (e.g. Lake Bockwitz, Horstteich) using chemical neutralization.

To avoid the expensive, constant and regular addition of neutralizing agents, microbial neutralization could be employed to inhibit re-acidification after chemical neutralization. This is possible through addition of either organic substrates (controlled saprobization) or nutrients to stimulate biomass production (controlled eutrophication). Thus, it is possible that at circumneutral pH, the acid-determined inhibition of sulfate reduction (Koschorreck et al. 2003b; Küsel 2003) can be eliminated and the subsequent alkalinity production will lead to an increased microbial alkalinity production rate. In addition, taking into account the higher inorganic carbon supply, Tittel and Kamjunke (2004) hypothesized that primary production may play a role in the long-term alkalinity budget of mining lakes, provided that neutral conditions are achieved. However, there is also one counteracting process that must be considered: under circumneutral conditions, phosphorus limitation to primary producers may occur due to the adsorption of phosphate on freshly precipitated, reactive iron hydroxides (Dzombak and Morel 1990). This can, in turn, lead to inhibition of primary production. To date, the net outcome of these two competing processes has not been tested either in the field or small-scale laboratory studies. This means that, although microbial sulfate reduction is a well studied process in acidic mine waters (Küsel 2003), it is unknown whether microbial alkalinity production can prevent reacidification of chemically neutralized shallow mining lakes, and which biological and chemical processes play a predominant role. This study is the first to compare controlled eutrophication and controlled saprobization in both acidic and neutralized mine waters. The underlying processes will be described and microbial alkalinity production rates calculated.

Materials and Methods

The studies were carried out with water and sediments from the small (10 ha), shallow (mean depth 4.5 m) mining lake Plessa 111 in Lusatia (51°29’ N, 13°38’ E). This lake, with a pH of 2.55 and an acidity of 14.5 mmol L^{-1}, may be considered as representative of shallow lakes in the region and, due to numerous previous studies (Bozau and Strauch 2002; Dzombak and Morel 1990; Friese et al. 1998; Frömmichen et al. 2003; Kapfer 1998; Koschorreck et al. 2003a; Frömmichen et al. 2004; Tittel and Kamjunke 2004), has been well characterized.

The experiment used 18 transparent PVC columns (mesocosms) with a diameter of 20 cm and height of 2 m. Approximately 4.5 L of littoral sediment were added to the columns and 50 L of epilimnion water from the lake were poured over the sediment layer. The columns were incubated at 13 °C and illuminated with daylight-spectrum fluorescent lamps (TrueLite fluorescent tubes) with a 16: 8 h light: dark cycle.

After the first sampling, half of the columns were neutralized (to pH 7) with sodium carbonate (Na_2CO_3). After 7 days, either 135 mg of sodium bisphosphate (to give a phosphate concentration of 500 µg L^{-1}) or 150 g of organic material, such as whole raw potatoes, were added to some of the columns. Potatoes were used as the organic material in accordance with previous positive results (Fyson et al 1998a, Fyson et al. 1998b) in mesocosm studies. The experimental treatments are summarized in Table 1. Each treatment was carried out in triplicate.

To simulate reacidification in the lake, 1.5 L of mesocosm water was removed monthly by a sample port in the side of the column at mid depth (middle of the water column) and replaced with fresh pH 2.55 epilimnion water from Plessa 111. After 8 months, the lower zone of the water column and the sediment pore water were studied using dialysis pore water samplers (Hesslein 1976). At the start and end of the experiment, sediment cores were taken and immediately frozen in liquid nitrogen. From these samples, TRIS (total reduced inorganic sulfur) was determined, according to Frömmichen (2001). Twenty four hours after phosphate addition to the water column, small samples of the uppermost

Table 1. Abbreviations and treatments

Abbreviation	Treatment
(C)	Control - no treatment
(E)	Eutrophication due to addition of phosphate
(S)	Saprobization due to addition of organic matter
(N)	Neutralization due to addition of soda ash
(NE)	Neutralization and eutrophication due to addition of soda ash and phosphate
(NS)	Neutralization and saprobization due to addition of soda ash and organic matter

sediment layer was taken by a silicone tube. These and the remaining sediment and potato samples were dried (105°C), and the total organic carbon (TOC) and total phosphorous (TP) content were determined.

In the monthly water samples taken from the middle of the water column, dissolved Fe, dissolved Al, TP, total inorganic carbon (TIC), and dissolved inorganic nitrogen (DIN, as the sum of ammonium, nitrite, and nitrate) were analyzed using standard German methods (German Institute of Standardization 2003). Their acidity was determined by titration with 0.1 M NaOH to pH 8.2. The fraction of alkalinity gain due to controlled eutrophication and saprobization (Figure 1) was calculated, taking into account acidity development in the control (C, N) treatments and the acidity of the added acidic mining lake water. The alkalinity gain for the different reactions (Table 2) was calculated by the equivalent sum of conservative cations less the sum of conservative anions. This equals, for acidic mine waters, the modified (Uhlmann et al. 2004) alternative alkalinity concept of Stumm and Morgan (1998).

$$\text{Alk} = 2[Ca^{2+}] + 2[Mg^{2+}] + [Na^{+}] + [K^{+}] + [NH_4^{+}] - 2[SO_4^{2-}] - [Cl^{-}] - [NO_3^{-}]$$

Light intensity directly below the water surface was measured with a spherical quantum sensor (LiCor Li-193 SA). Depth profiles of chlorophyll *a* fluorescence, pH, and redox potential were measured using a multi-parameter probe (YSI 6820) inserted into the water column. Maximum potential chlorophyll *a* concentrations (carrying capacity) were calculated according to Köhler et al. (2000). For carbon and nitrogen, the simplified calculation method, assuming a constant mean ratio of chlorophyll to carbon (0.02) was used (Sommer 1994). Values for the mean extinction coefficients of Plessa 111 (e_{wp}=0.9) (Krumbeck et al. 1998), the mean ratio of chlorophyll to dry weight (9.22 x 10^{-3}) (Behrendt and Opitz 1996), and the mean covered area per chlorophyll *a* concentration (0.01 m^2 mg^{-1}) (Sommer 1994) were derived from the literature. Geochemical speciation simulations were carried out using Version 2.4 of PHREEQC and stability diagrams with Version 5.0 of Geochemist's Workbench. Statistical comparisons of means and tests against zero were carried out with a two-tail *t*-test (α=0.05) for independent samples. The check for Gaussian distribution was accomplished by means of a Kolmogorov-Smirnov test (α=0.05).

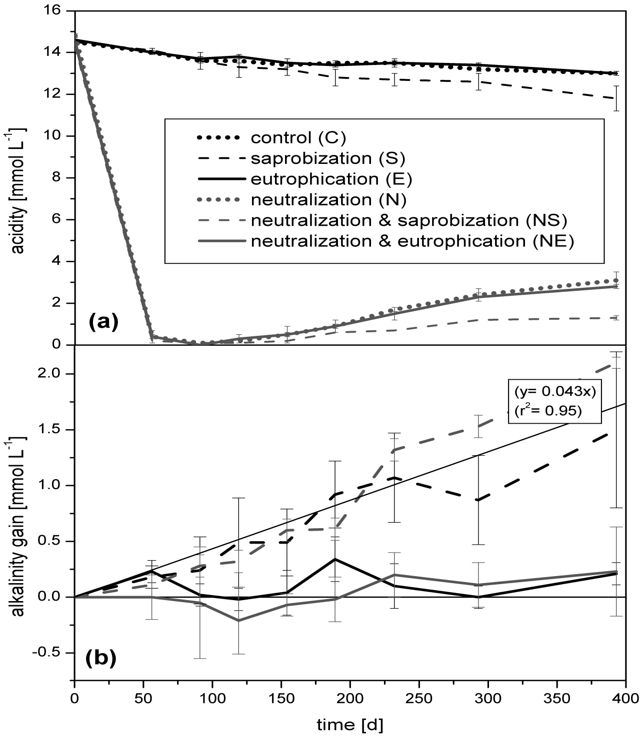

Figure 1. a) Mean and standard deviation (n = 3) of acidity in the water column of all experimental treatments. b) Mean and standard deviation (n = 3) of alkalinity gain in the saprobization (S, NS) and eutrophication (E, NE) treatments.

Results and Discussion

Through the course of the experiment, the acidity of the water in all acidic (C, E, S) treatments declined, while the acidity of the water in all mesocosms neutralized with soda (N, NE, NS) increased (Figure 1a). There are various processes that can explain this. The addition of acidic lake water was intended to simulate the continuous input of acidic ground water into the lake. In addition, in acid lakes, the production of biomass (Fyson et al. 1998a) and the transformation of minerals in the sediment (Peine et al. 2000) release acidity. Gains in alkalinity are associated with several anaerobic microbial respiration processes, especially sulfate reduction. The extent of the alkalinity gain depends on the

Table 2. Oxygen-, iron-, and sulfate-reducing processes and their alkalinity gains through transformed organic carbon (C_{org}), iron (Fe), and sulfur (S); an atomic C: N: P ratio of 400:16:1 was assumed, which reflects the measured ratio of the organic matter (potatoes) used in this experiment.

Type of reaction	alkalinity gain [mol]		
	per mol C_{org}	**per mol Fe**	**per mol S**
reduction of oxygen (respiration) $<CH_2O(NH_3)_{0.04}(H_3PO_4)_{0.0025}> + O_2 + 0.0375\ H^+ \rightarrow$ $CO_2\uparrow + 0.04\ NH_4^+ + 0.0025\ H_2PO_4^- + H_2O$	0.04	-	-
reduction of iron hydroxide $<CH_2O(NH_3)_{0.04}(H_3PO_4)_{0.0025}> + 4\ Fe(OH)_3 + 8.0375\ H^+ \rightarrow$ $CO_2\uparrow + 4\ Fe^{2+} + 0.04\ NH_4^+ + 0.0025\ H_2PO_4^- + 11\ H_2O$	0.04	0.01	-
reduction of dissolved ferric iron $<CH_2O(NH_3)_{0.04}(H_3PO_4)_{0.0025}> + 4\ Fe^{3+} + H_2O \rightarrow$ $CO_2\uparrow + 4\ Fe^{2+} + 0.04\ NH_4^+ + 0.0025\ H_2PO_4^- + 3.9625\ H^+$	0.04	0.01	-
sulfate reduction and iron monosulfide precipitation $<CH_2O(NH_3)_{0.04}(H_3PO_4)_{0..0025}> + 0.5\ SO_4^{2-} + 0.5\ Fe^{2+} + 0.0375\ H^+ \rightarrow$ $CO_2\uparrow + 0.5\ FeS\downarrow + 0.04\ NH_4^+ + 0.0025\ H_2PO_4^- + H_2O$	1.04	2.08	2.08
Sulfate reduction and irondisulfide (pyrite) precipitation $<CH_2O(NH_3)_{0.04}(H_3PO_4)_{0.0025}> + 0.5714\ SO_4^{2-} + 0.2857\ Fe^{2+} + 0.6089\ H^+ \rightarrow$ $CO_2\uparrow + 0.2857\ FeS_2\downarrow + 0.04\ NH_4^+ + 0.0025\ H_2PO_4^- + 1.2857\ H_2O$	1.18	4.14	2.07

composition (C: N ratio) of the organic substances. According to acid-base theory (Stumm and Morgan 1996), the alkalinity gain caused by respiration and, indirectly, iron reduction, is from the release of ammonium (NH_4^+) as a corresponding cation of a strong base (Table 2). The neutralizing effect of sulfate reduction is principally dependent on sulfate (anion of a strong acid) consumption in addition to ammonium release. Indeed, it is expected that only the net reactions are relevant. With sulfate reduction followed by re-oxidation of the sulfide, no net sulfate is consumed; nevertheless, a reduced alkalinity gain is achieved through ammonium release (Table 2). Nitrate reduction processes, which could also play a role in neutralization, are unimportant due to very low nitrate concentrations in the acidic mining lakes (Fyson et al. 1998b).

The decrease in acidity shown in Figure 1a for the control columns (C) was also observed in other experiments with acidic mine lake waters (Frömmichen et al. 2003; Fyson et al. 1998b) and is probably due to ammonium release through the decomposition (respiration and iron reduction) of the organic matter in the sediment (about 5% total organic carbon). The fraction of alkalinity gain due to controlled eutrophication and saprobization is shown in Figure 1b.

Controlled Eutrophication

The algal biomass in acidic mining lakes is very low compared to that of neutral lakes. The limitation of inorganic carbon responsible for this (Nixdorf et al. 2003; Tittel and Kamjunke 2004) can only be overcome through neutralization.

The measured chlorophyll *a* concentrations, used as a measure of algal biomass (Figure 2), show that chemical neutralization led to a decrease rather than an increase in algal biomass. In contrast, the addition of phosphate to the acidic water (E) led to a 10-fold increase in algal biomass.

To explain this negative effect of the chemical neutralization on algal biomass development, the carrying capacity or potential chlorophyll quantity was calculated based on the principal individual growth factors (light, nitrogen, carbon, and phosphorus). One can see from Figure 2 that light (230 $\mu E\ m^{-2}\ s^{-1}$ at the water surface) and nitrogen were not limiting algal growth in any of the treatments. In the control treatment (C), carbon and phosphate were close to being limiting (Figure 2a). In fact, although the chemical neutralization (N) treatment resulted in an increase in carrying capacity of carbon, it also simultaneously decreased the carrying capacity of phosphorus still further so that the algal biomass became phosphorus limited (Figure 2c). In the acidic eutrophication (E) treatment, the measured chlorophyll *a* concentration overshot the theoretical carrying capacity of carbon by an order of magnitude (Figure 2b). This implies that although the concentration of inorganic carbon was low, it was not limiting algal growth. This is probably attributable to the algae *Chlamydomonas* spp. and *Ochromonas* spp,

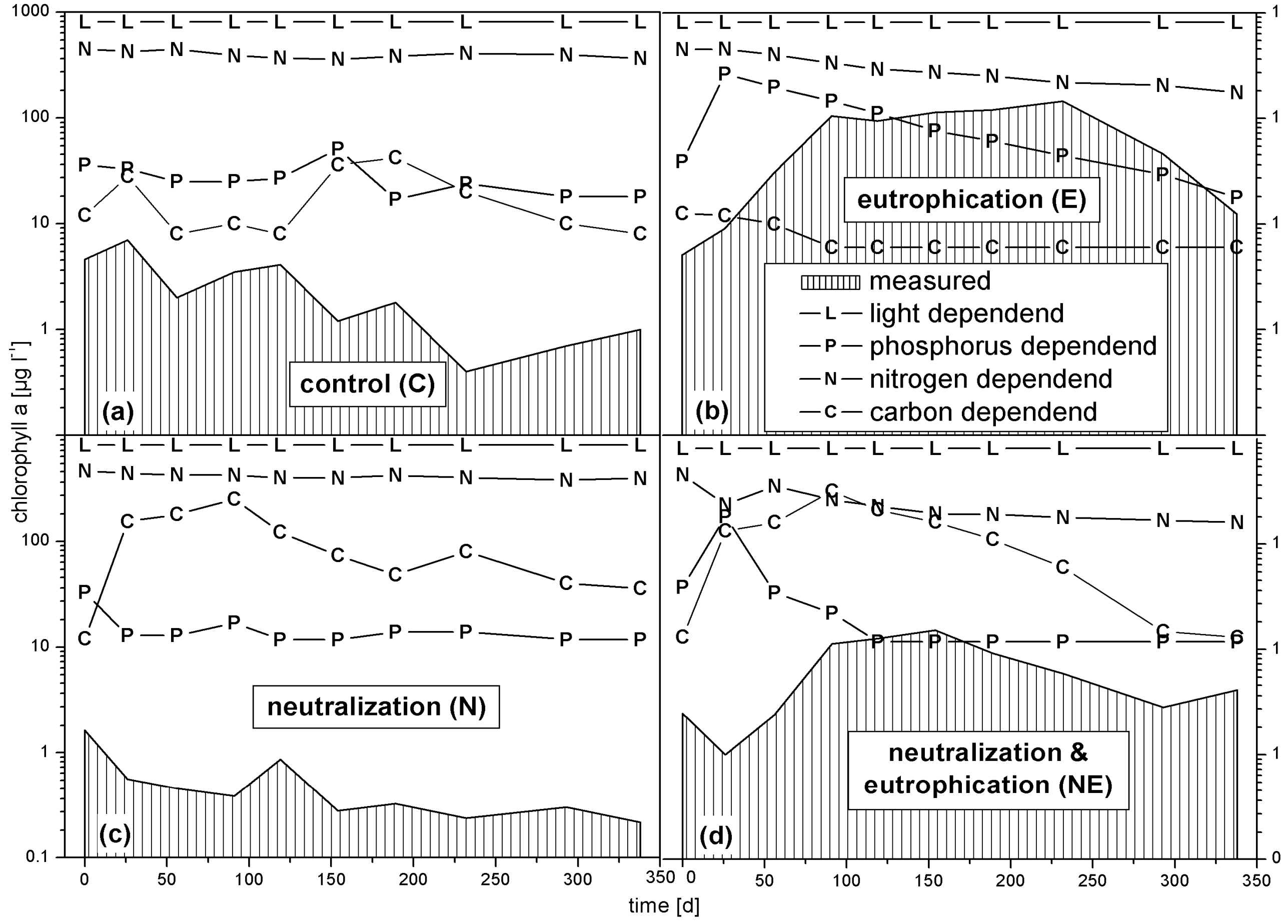

Figure 2. Chlorophyll a concentration and the maximum theoretical concentration based on calculated carrying capacity according to light, nitrogen, phosphorus, and carbon for the control (C) and the neutralized (N), the eutrophication (E), and the combined neutralisation and eutrophication (NE) treatments. The detection limits of 3 µg l^{-1} TP and 0.3 mg l^{-1} TIC does not allow carrying capacity values lower than 12 µg l^{-1} chlorophyll a for the phosphorus limited and 6 µg l^{-1} chlorophyll a for the carbon-limited carrying capacity to be determined, respectively. In all graphs, the lowest line is the limiting parameter.

which are dominant in the lake as well as in the mesocosms. These algae have the ability to grow mixotrophically, i.e. they can obtain their carbon requirements from dissolved and particulate organic matter in addition to inorganic carbon (Gerloff-Elias et al. 2005; Nixdorf et al. 2001; Tittel et al. 2005). Since inorganic carbon is not limiting, the eutrophication treatment is in fact phosphorus limited, but at a much higher level than in the controls. Since the dominating algae species were the same in all treatments the carbon limitation of the control treatment (C) is questionable. The combination of eutrophication and chemical neutralization (NE) led neither to a clear increase nor clear decrease in biomass compared to the controls (Figure 2d). After a short-lived decrease, algal biomass in the chemical neutralization with eutrophication (NE) treatment climbed almost exponentially as with the eutrophication (E) treatment. At the first measurement, 24 hours after increasing the phosphate concentration to 500 µmol L^{-1}, only about 50% of the added phosphate was detectable. At the next sampling, 4 weeks later, the concentration had already declined to below the initial concentration in the added mine lake water. After a further 4 weeks, algal growth stagnated due to phosphorous limitation.

An accumulation of phosphate was observed in the uppermost sediment layer, which consisted mostly of freshly precipitated iron hydroxides. Since in the chemical neutralization with eutrophication (NE) treatment, there was no visible precipitation, it is likely that phosphate had not been precipitated, but rather adsorbed by freshly precipitated iron hydroxides in the upper sediment layer. This hypothesis is supported by the good adsorption properties of iron hydroxides (Dzombak and Morel 1990) and a study on the sulfate adsorption of freshly precipitated mining lake sediments (Dzombak and Morel 1990; Totsche et al. 2003). Phosphate shares many of the chemical properties of sulfate, including its adsorption abilities. The adsorption capacity of the sediments probably decreases over time; however, because of the large quantity of sediment, one must expect that phosphorus is a long-term limiting factor to algal biomass. A continuous or semi-continuous addition of phosphate could solve this problem. However, the resulting large pool of phosphorus bound in sediments could be released following microbial neutralization with changes in redox conditions and could ultimately lead to excessive eutrophication (Kleeberg 1998).

In addition to phytoplankton (algal biomass) in the water column, benthic algae can also have an important role in biomass production (Kapfer 1998; Koschorreck et al. 2003a; Nixdorf and Kapfer 1998; Tittel and Kamjunke 2004). In this study, benthic algal biomass was not quantified; however, from visual evaluation, it appeared that the sediment surface in the eutrophication (E) treatment was more extensively colonized by algae than the controls (C) or the chemical neutralization (N, NE) treatments.

The alkalinity gains at the end of the experiment are insignificant both with the chemical neutralization plus eutrophication (NE) and the eutrophication (E) treatments (Figure 1b). This means that a neutralizing effect is not being observed either with addition of phosphate to the acidic water or with an addition to previously neutralized water. Obviously, the decomposition of autochthonously-produced, dead, and precipitated algae is insufficient to support measurable sulfate reduction. This is confirmed by the pH and redox potentials (ORP) profiles, which are almost identical to those of the controls (C) (Figure 3).

The fact that there was no neutralizing effect with the controlled eutrophication treatment under acidic conditions confirms the results of an earlier study (Tittel and Kamjunke 2004). The assumption that biomass development in neutralized water would be sufficient to generate measurable microbial alkalinity production with improved nutrient availability could not be confirmed due to the phosphorus limitation. Since the elimination of phosphorus from the water column and the resulting phosphorus limitation are also likely to take place in small, shallow mining lakes that have been previously chemically neutralized, controlled eutrophication is probably unsuitable for such lakes that have a risk of reacidification due to pyrite weathering. However, in large, deep-mining lakes with an extensive hypolimnion, the situation can be different as the phosphorus in the epilimnion would have hardly any contact with the iron hydroxide sediment and would remain in circulation as a nutrient for the algae.

Controlled Saprobization

In contrast to the controlled eutrophication (E and NE) treatments, controlled saprobization (S and NS) yielded a significant gain in alkalinity (Figure 1b). Generation of TRIS in the acidic (S) (0.275 mol m^{-2} a^{-1}) and neutralized (NS) (0.298 mol m^{-2} a^{-1}) treatments shows that controlled saprobization supports sulfate reduction and the subsequent precipitation of iron sulfides.

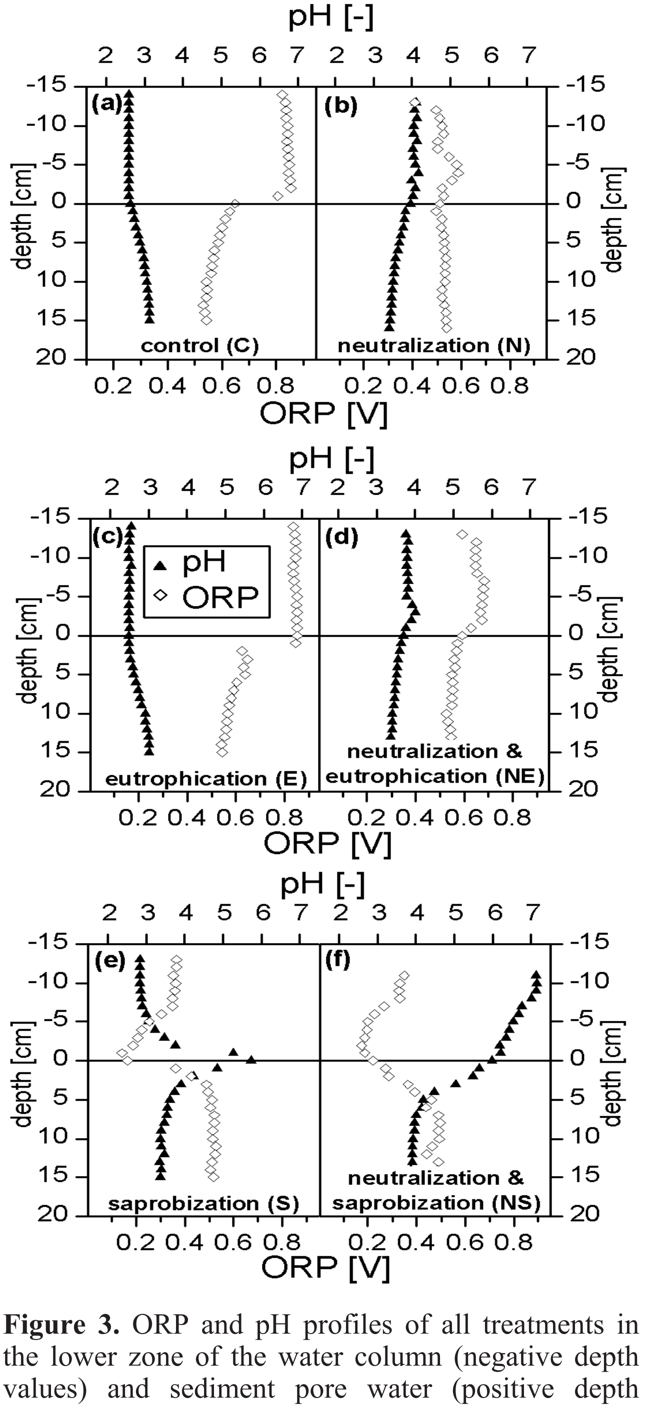

Figure 3. ORP and pH profiles of all treatments in the lower zone of the water column (negative depth values) and sediment pore water (positive depth values), 8 months after initial neutralization, eutrophication, and saprobisation

A comparison of the alkalinity gains between the decomposition treatments shows no significant difference between the acidic (S) and neutralized (NS) mesocosms. This means that chemical pre-neutralization had neither a positive nor negative effect on alkalinity generation; however, differing neutralization rates could be expected because sulfate reduction is inhibited by low pH (Küsel 2003). The reason for this lack of difference in microbial alkalinity production rates is clear from the pH and ORP profiles (Figure 3). The low redox potential at the sediment-water boundary in the acidic (S) and neutralized (NS) saprobization treatments shows that the zone in which the added organic material is found is microbially very active. In the acidic (S) treatment, there is a pH maximum at the same location, so the pH value is as high as in the neutralized (NS) treatment. This may be due to local ammonium release through microbial respiration or iron reduction in the acidic treatment at the sediment-water interface providing a sufficiently high pH to overcome inhibition of sulfate reduction. Interestingly, the alkalinity gains were not significantly below those of the pre-neutralized treatment (NS). In other words, even pre-neutralization did not cause an overall increase in bacterial sulfate reduction rates.

Since the alkalinity gain increased linearly in both cases, one can calculate a microbial neutralization rate of 2.6 mol m^{-2} a^{-1}. This value for a littoral sediment is, as expected, a little less than the neutralization rate calculated for a hypolimnion sediment in a comparable mesocosm experiment (3.6 mol m^{-2} a^{-1}) (Table 3). In a whole lake experiment, a neutralisation rate of 33 mmol m^{-2} d^{-1} was calculated (Brugam and Stahl 2000). For better comparison, this daily rate was converted to the annual rate of 12 mol m^{-2} a^{-1} (Table 3). Of course, this daily neutralisation rate is not directly comparable with the annual rates of the mesocosm experiments.

In addition to the water acidity values, one can use the accumulation of reduced sulfur compounds in the sediment to calculate microbial neutralization rates. For this calculation, only the alkalinity from the precipitated iron sulfide is considered. Alkalinity gain through respiration and dissolved or deoxidized iron is not considered here. If one accepts that non-sulfide iron (II) compounds such as iron carbonates are quantitatively negligible in alkalinity gains (since their concentrations are so low) and that the iron and sulfate reduction from the potato biomass as well as iron mono-sulfide formation and pyrite formation per mole sulfur is 2.08 (Table 2), one can calculate a microbial neutralization rate of 0.6 mol m^{-2} a^{-1} for this experiment from the TRIS content. The neutralization rates of the controlled saprobization, calculated from the TRIS content, are clearly higher than the natural microbial neutralization rates in the Lusatian mining lakes (Table 3). Microcosm studies with hypolimnion sediments and enclosure studies in Lake Plessa 111, with addition of Carbokalk®, a waste product of the sugar industry, provided clearly higher neutralization rates than those calculated for this study (Table 3). Determining hypolimnion sediment neutralization rates is valuable in assessing the maximum neutralization rate of the lake. The littoral sediment neutralization rate is probably much closer to an average neutralization rate in shallow lakes like Plessa 111.

Table 3. Microbial neutralization rates in the water column and sediment from the mesocosm experiment and the literature

Neutralization Rate [mol m^{-2} a^{-1}]		Experimental Design	Source
Water (titration)	Sediment (TRIS)		
2.6	0.57 … 0.62	Saprobization of acidic mine water with potatoes; mesocosm experiment; Lake Plessa 111, Lusatia, Germany	This study
3.6		Saprobization of acidic mine water with potatoes; microcosm experiment; Lake Koschen, Lusatia, Germany	(Fyson et al. 1998a)
12		Saprobization of acidic mine lake with cow manure; whole lake experiment; Lake Pit C, Illinouis, USA	(Brugam and Stahl 2000)
	0.02 …0.137	In-situ measurements of some acidic mining lakes; Plessa area, Lusatia, Germany	(Peine 1998)
	6.1-14.9[a]	Saprobization of acidic mine water with straw and Carbokalk, microcosm experiment; Plessa 111, Lusatia, Germany	(Frömmichen et al. 2004)
	14…23	Saprobization of acidic mine water with straw and Carbokalk® (a waste product of the sugar industry); enclosure experiment; Plessa 111, Lusatia, Germany	(Frömmichen 2001)

[a] other ferrous iron compounds, such as carbonates and phosphates, are included in this neutralization rate

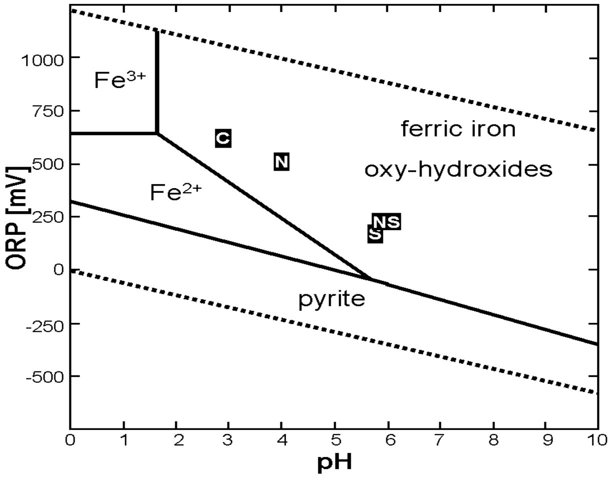

Figure 4. ORP-pH predominance diagram for dissolved di- (Fe^{2+}) and trivalent (Fe^{3+}) iron, iron hydroxide, and pyrite (at 13°C and activities of iron and sulfur of 0.01 mol/L, similar to measured concentration in the experiment at the sediment-water interface). The pH and ORP values of the sediment-water boundary in the control (C, N) and decomposition (S, NS) treatments are also provided.

Since the composition of organic substances, which contributed to total alkalinity, and sulfate reduction rates are known, one can calculate a coefficient of effectiveness (ratio of organic substance necessary for sulfate reduction to transformed organic substances). The 0.6 $mol\,m^{-2}\,a^{-1}$ alkalinity from iron sulfide formation has a carbon requirement of ≈ 0.5 mol (Table 2). For the 2 $mol\,m^{-2}\,a^{-1}$ alkalinity, which must derive from respiration of dissolved and re-oxidized iron, about 50 mol of organic carbon is required (Table 2). In total, this results in an efficiency of 1%. To derive the reason behind this low efficiency in the littoral sediment, a predominance diagram for the iron phase is useful (Figure 4).

The values of the sediment-water boundary in the control (C, N) treatments are located in the iron hydroxide zone. The saprobization (S, NS) sample values clearly lie nearer the iron sulfide (pyrite) zone (Figure 4). Despite the 99% organic carbon, which leads to a decline in redox potential through aerobic respiration (oxygen reduction) and anaerobic iron reduction, the ORP/pH conditions are still in the zone predominantly controlled by iron hydroxide. The evidence for the formation of iron sulfide from the sulfur fractionation is no contradiction, because in Figure 4, only the overriding current phase is shown. Although sulfate reduction under acidic (pH 3) conditions, was just found in the absence of ferric iron (Koschorreck et al. 2003b), under moderately acidic conditions (pH > 5), as in the saprobization treatments (S, NS), it can occur even with ferric iron present (Küsel and Dorsch 2000).

The fact that the ORP/pH conditions in the saprobization treatment remain in the iron hydroxide zone shows that the microbial neutralization rate is limited more by local water chemistry than substrate availability. To achieve higher sulfate reduction and microbial neutralization rates, the redox potential must be shifted into the pyrite zone. Such an ORP decrease could be achieved through stable stratification in deeper lakes, which would reduce the vertical transport of oxygen and dissolved iron (III). In the littoral sediments, however, this would require a sediment cover.

Similarly, to achieve a higher efficiency in algal productivity, the redox potential must be shifted into the pyrite zone, where no phosphorus adsorption occurs.

This study has shown that increasing microbial alkalinity is a suitable method to combat the continued input of acidic water from surrounding mine wastes. However, whether it can be used to inhibit reacidification depends above all on the alkalinity generation rate in the lake, the acidity of the water, and the quantity of acidic water input.

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