

The Rävlidmyran Pit Lake before treatment, after liming, and after treatment with sewage sludge

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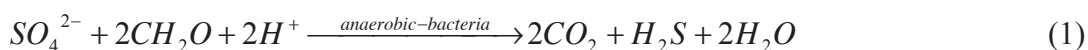
Abstract

The Rävlidmyran Pit Lake in Northern Sweden was studied during a whole-year cycle. This was followed by studies of two full-scale remediation treatments, liming and sewage sludge treatment, respectively. Before treatments, Rävlidmyran was an acidic lake with average pH of 3.6, and the lake water had high metal and sulphate concentrations. The lake was meromictic and oligotrophic. A permanent stratification was developed with three layers due to more saline groundwater inflow at depth; the mixolimnion at the top, in which the water was well mixed and saturated with oxygen; the monimolimnion in the deeper lake, which was poor in oxygen and which did not mix with upper water; and the chemocline, which separated the upper and deeper water. The distribution of elements such as Ca, Mg, Na, K, S, Mn, Fe and Zn was strongly controlled by the stratification and groundwater filling, with lower and constant concentrations in the mixolimnion, increased concentration in the chemocline and higher concentrations in the monimolimnion. The stratification remained intact, and elements such as Na, K and S were barely influenced by the treatments. However, the water in the monimolimnion developed to be anoxic. pH increased rapidly after liming. The effects of the liming on the dissolved elemental concentrations were distinct, especially in the upper oxic water layer. Elements such as Fe, Mn, Zn and Mg were largely removed in the upper oxic water, probably due to formation of oxyhydroxides. However, the concentrations increased towards pre-liming levels close to the bottom. Al and Cu were almost completely removed from the water throughout the water column, due to pH increase and precipitation of minerals such as gibbsite [Al(OH)₃]. Cu was probably removed from the water by sorption to gibbsite and Fe-oxyhydroxides. In the Rävlidmyran Pit Lake, liming will not be a long-term solution since there are acidic sources continuously flowing into the lake. The sewage sludge treatment did not show distinct effects on the water quality during the monitoring period, probably because it takes longer time for bacteria stimulated sulphate reduction to occur. Moreover, sewage sludge particles sank to the lake bottom rapidly, the major part within the first month after treatment. Therefore, organics in the sewage sludge do not seem to play an important role of scavenging metals in the water through sorption processes. The accumulation of organics at the lake bottom also indicates that if sulphate reduction will occur, this may be limited to the lake bottom.

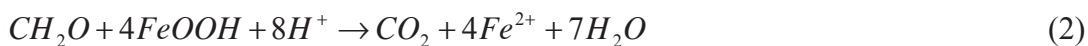
Introduction

Acidic mining pit lakes have attracted more and more attentions since the number of these water bodies increases and a growing awareness of the environmental risks arises. The water quality of these lakes is generally not desirable (Miller, *et al.*, 1996), although, depending on the mineral composition of the rocks surrounding a pit, pit lake water quality may vary. Pit lakes from sulphide ore mining generally have acidic water and a high content of toxic metals and sulphate due to oxidation of sulphide minerals (Miller, *et al.*, 1996, Levy, *et al.*, 1997). Overflow of surface water or outflow as groundwater from such lakes may be significantly detrimental to downstream areas.

Although water in an acid pit lake is also a kind of acid mine drainage (AMD), in situ treatment is more complicated in a pit lake than to drainage waters from waste deposits. Liming, as a simple and direct method for treatment of acid mine water, is often used and is proven to be a successful method in some cases (Fischer and Guderitz, 1996, Lewis, *et al.*, 2003). However, it is rather costly and if there is high availability of acidic sources, base neutralization will not be a long-term solution. Sulphide mining pit lakes often have high relative depth (the ratio between maximum depth and mean diameter), poor circulation, and a steady anoxic layer at depth. And the recovery could be stimulated by adding organics to create bacterially mediated titration. The mechanism behind the treatments is to use sulphate-reducing bacteria (SRB) to biodegrade sulphate and precipitate metals in AMD. SRB gain energy for growth by coupling oxidation of organic compounds of hydrogen with the reduction of sulphate to sulphide (Zehnder, 1988):



Reduced sulphur precipitates metals as sulphide minerals. For iron, as an example, microbial reduction of ferric iron will occur and the ferrous iron may be precipitated as a sulphide mineral. The net effect of these processes is that acidity in the water is partially neutralized and metal concentrations decrease:



The formed sulphide minerals are rather stable if the biological activity in the lake will be self-motivated and sustained. Stimulation of sulphate-reducing bacteria by addition of organic nutrients could potentially be a cost-effective means of dealing with these contaminated waters. It may be a long-term solution.

In Sweden, there are more than twenty pit lakes, and most of them originated from sulphidic base metal mining. However, few studies have been performed to study these special water bodies in Sweden. This paper presents a four years full-scale investigation of an abandoned sulphide mine pit lakes, the Rävliidmyran pit lakes in northern Sweden. The investigation includes geochemistry and limnology studies before treatments, and after liming and sewage sludge treatment, respectively.

Site Description

The Rävliidmyran mine is located in the western part of the Skellefte ore district of northern Sweden, about 180 km southwest of Luleå (Figure 1), and belongs to the Rävliidenfältet area ore bodies. The Kristineberg mine is located 5 km east of Rävliidmyran. The Rävliidmyran ore lies along a thin strip of graphite phyllitic rocks and limestone, which occupy the central axial zone of the Rävliidenfältet anticline. The rocks represent a c. 1.9 Ga old metamorphic transition sequence from the Skellefte volcanic series to the overlying Phyllite series. The surrounding rocks are quartz schists (with sericite, chlorite and biotite), limestone and graphite phyllites (Gavelin and Kulling, 1955, Roering, 1959). The mine contains several separated ore lenses: Sture ore, A-, B-, C-, D- G- and H- ores, among which the Sture ore body is the one that formed the present pit lake. This ore is a replacement ore occurring in a limestone environment, and it is pyrite-rich with Zn, Cu and Pb, and with minor Sb, Ag and Au. It has been localized by a drag fold in a limestone horizon and there is a large shear zone through this drag fold (Roering, 1959).

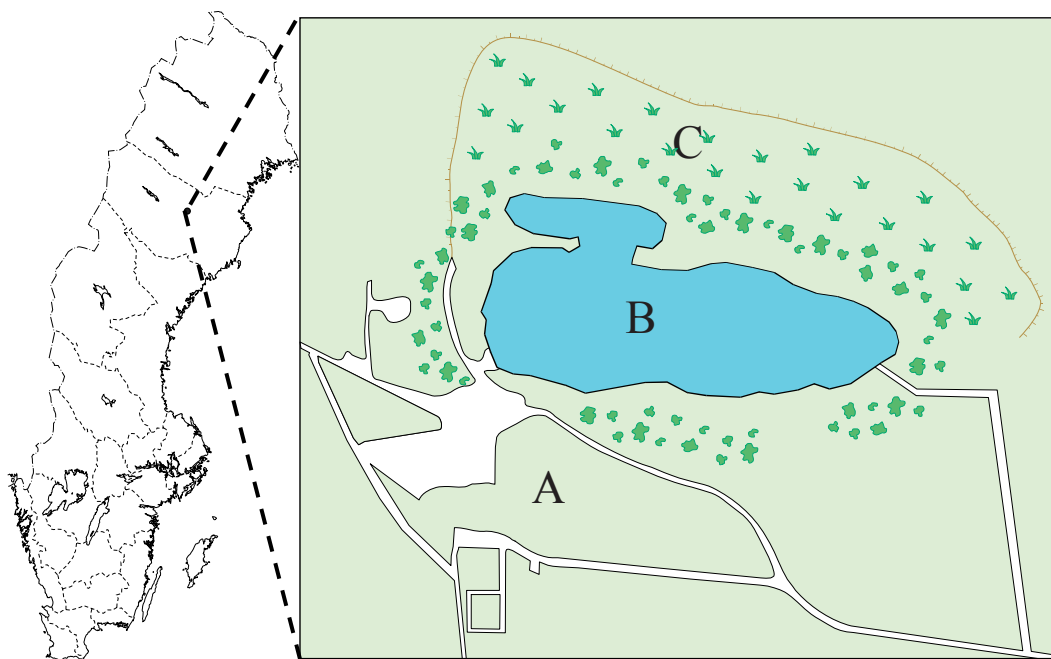


Figure 1 Rävliidmyran mine location map. The mining area comprises three parts. A-Industrial area and some backfilled smaller open pits; B-Sture ore, which formed the present Rävliidmyran Pit Lake; C-waste rock dump-site covered by till and planted with grass (Boliden, 1975, SGU, 1999).

Mining activities in the Rävliidmyran area were first started in 1953, and the ore was mined by both open pit and underground mining. The capacity of the mine was 300,000 tonnes per year, while the mean annual mining production was 230,000 tonnes. The Sture ore body (Figure 1) was the largest ore body in Rävliidmyran mine and it was estimated to contain 2,001,400 tonnes of ores with 4.12% Zn, 0.98% Cu, 0.67% Pb, and 23.4% S (Boliden, 1975). It also contained about 0.6 g/t Au and 48 g/t Ag. The Sture pit is about 450 m long and at most 200 m wide. Mining at the Sture pit ceased in the first half of 1974 (Boliden, 1975). To the north of the Sture pit is a dump in which about 500,000 – 600,000 m³ waste rock and the soil from the other pits is stored. The content of sulphide mineral in the waste rock is estimated to be about 2-5% (Boliden, 1992).

In its present state, the lake is a water body with a surface area of 49,000 m², and it contains a water volume of 527,000 m³. The maximum depth of the lake is 28.9 m and the average depth is 10.7 m (Figure 2). The relative depth of the lake is 12%. From mine closure in 1974 until spring 2003, the lake was left without any treatment until May 2003, when it was limed with 200 tonnes of lime (CaO) within three weeks. Two months later, 300 tonnes of sewage sludge, which was transported from Stockholm Vatten, was pumped into the lake. The sewage sludge, which is rich in organic carbon and the nutrients N and P, was transported from Stockholm Vatten. Composition of the sewage sludge is listed in Table 1.

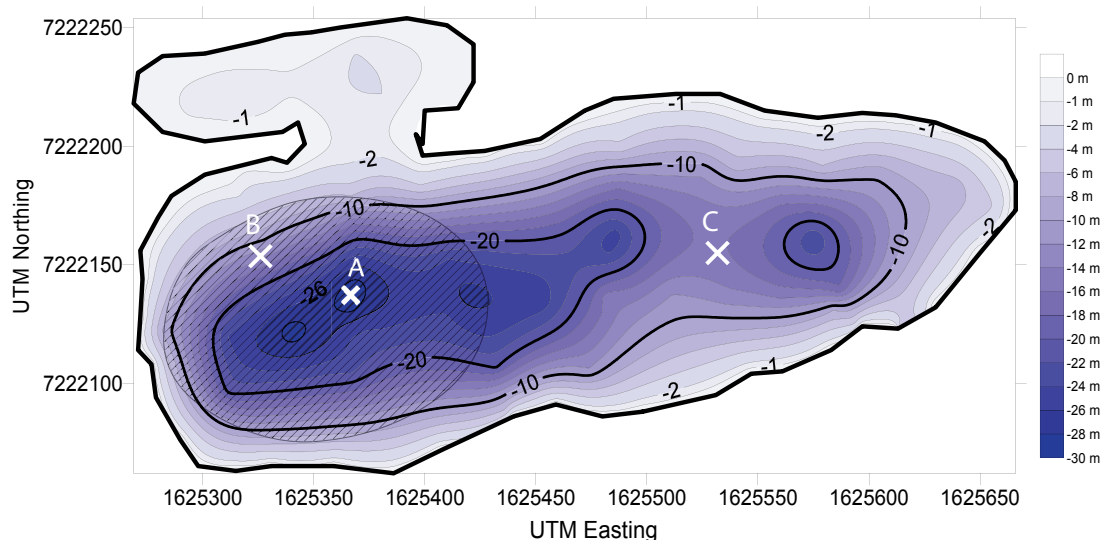


Figure 2 Bathymetric map of Rävildmyran Pit Lake. The white crossing points in the map are the sampling points in the lake. Results presented in this paper are all samples taken from site A. The sewage sludge was pumped in a certain area of the lake, which is shown by the shadowed area.

Sampling Methods

Before remediation treatment, sampling was performed six times from April 2001 till March 2002 to cover typical seasonal variations (Lu, et al., 2004). Two additional samplings were performed in May 2003 during the liming period, and in June 2003, one month after the whole liming treatment finished. After sewage sludge treatment, a full-year sampling cycle was performed, starting one week after sludge was pumped into the lake. During the first three months of the experiment, sampling was performed twice a month. In winter, since biological activity may be limited, the sampling frequency was reduced to only December 2003, when the lake was ice-covered. The last sampling was performed in August 2004. Each time, the samples were taken along the deepest profile of the lake, at station A in Figure 2. During the sewage sludge experiment, besides routine samplings at station A, samples were also taken from two random additional sites in the lake to investigate the horizontal distribution in the lake. It was found that the lake has very uniform horizontal distribution. Therefore, measurements from location A in this paper are used to represent the situation of the whole lake. Before water sampling, measurements including temperature, pH, conductivity, dissolved oxygen (DO) and redox potential were performed in situ with a Hydrolab Surveyor II water quality probe with half-metre or metre intervals. Immediately after measurement, samples were collected.

Eight to nine samples were collected on each sampling occasion, including the depths 0.5 m, 2 m, 5 m, 8 m, 10 m, 15 m, 20 m, 23 m and 25 m. A metal-free Ruttner sampler (1.7 l, Heraco AB) was used for collecting lake water. Samples were immediately filtered through a Nitrocellulose filter (0.22 μm , 25 mm ϕ , Millipore[®]) with a disposable plastic syringe (50 ml, Sartorius[®] AG, Germany). About 60 ml filtered water was saved in an acid-leached Azlon[®] HDPE bottle (Analytical AB, Sweden) for “dissolved” phase analysis. Throughout this paper,

the term “dissolved” refers to material that passes a 0.22 µm filter, including truly dissolved species, as well as colloids (Kimball, *et al.*, 1995, Stumm and Morgan, 1996, Langmuir, 1997). Another 120 ml without acid-wash was prepared following the same procedure to be used for anion analysis. Filters were saved in petri dishes for particulate metal determination. The volume of water that passed through the filters was recorded in order to calculate particulate element concentration. Both syringes and polycarbonate filter holders (25 mm φ, Sartorius® AG, Germany) were pre-rinsed with acid (5% HNO₃). Filters were also rinsed with 5% Acetic Acid for 24 hours before the sampling.

Table 1 Composition of sewage sludge (Stockholm Vatten. 2003)

Items	Levels	Items	Levels
pH	7.9	Fe mg/kg TS	115000.0
TS %	26.0	Al mg/kg TS	1547.0
CaO % TS	2.2	Zn mg/kg TS	520.0
MgO % TS	0.4	Cu mg/kg TS	380.0
K ₂ O % TS	0.3	Mn mg/kg TS	160.0
S % TS	0.96	Pb mg/kg TS	27.0
Total-P % TS	4.3	Cr mg/kg TS	22.0
Total-N % TS	4.4	Ni mg/kg TS	21.0
NH ₄ -N % TS	1.2	Co mg/kg TS	9.0
Total-C % TS	25.6	Cd mg/kg TS	1.1
TOC % TS	19.4		

TS % = percentage of dry weight

TOC = total organic carbon

Sediments from the pit lake floor were collected both during liming treatment and sewage sludge treatment. Before that, sediments were only collected in May and June 2001. The samples were kept in bottles (Analytical AB, Sweden) without headspace during transportation. Samples for organic carbon and nitrogen analysis were stored in glass bottles. Samples were exposed to air and dried at 50°C in the lab for 24 h before analysis. All the samples were kept in an icebox and were not exposed to light during transportation.

Analysis

Water and filter samples were analysed by Analytica AB (Sweden). Dissolved metals including Fe, Al, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, P, Pb and Zn were measured using ICP-SMS (high-resolution ICP-MS), and Ca, K, Mg, Na, S, Si and Sr were analysed by ICP-AES (Atomic Emission Spectroscopy). Data were reported after three to four runs on each instrument. The quality of the analyses was checked using synthetic standards. The precision determined in such conditions as \pm one standard deviation was generally better than 5%. Four instrumental blanks were also prepared and analysed as the samples.

Filters for particulate elements including Cu, Cd, Hg, Pb, Zn and S were dissolved with suprapur HNO₃ in closed Teflon bombs in a microwave oven, and then analysed by ICP-AES and ICP-SMS. Filters for other elements including Al, Ba, Ca, Co, Cr, Fe, K, Mg, Mn, Na, P, Si, Sr and Zn were wet-ashed in concentrated suprapur HNO₃ in platinum crucibles at 75°C, and then dry-ashed at 550°C. The ashes were fused with lithium metaborate in graphite crucibles at 1000°C. The formed beads were dissolved in 10% suprapur HNO₃ (Burman, *et al.*, 1978). The elements were then determined by ICP-AES. For each method, four field blank groups each containing four blank filters were prepared. They were digested and analysed following the same procedure. Blank contribution was calculated for each sample, and if it is

larger than 30%, the blank contribution was presumed to be too large and the result was unreliable and therefore not considered. The results from the laboratory were reported as μg total weight. If divided by the filtered water volume recorded during sampling, the particulate element concentrations can be reported as $\mu\text{g/l}$.

Sediment samples were also digested following the same procedure as filter samples, except the samples from 2001, which were only digested by the leaching process. Thus, elements such as Si and Al are lost in this case. However, elements such as Cu, Zn, Cd, Pb and S are comparable with the measurements of the 2003 and 2004 sediment samples. Part of the sediment samples were filtrated and dried in air. After drying, the material was prepared for mineralogical analysis by X-ray diffraction (XRD) analysis. Samples were measured over the range of 5° to 65° on a Philips XRD instrument using CuK_α radiation. X-ray diffraction (XRD) analysis was performed on the samples from 2001, June 2003 and September 2003.

Results and Discussion

Effects on pH, DO, conductivity, and redox

Before treatments, the annual monitoring of Rävlidmyran Pit Lake from April 2001 till March 2002 has demonstrated that it is a meromictic lake (Lu, *et al.*, 2004). The lake was permanently stratified and poorly mixed vertically. An anoxic layer, the monimolimnion, which was characterized by higher conductivity and higher elemental concentrations, was developed below a depth of 8 metres (Figure 3). Above 5 metres, the mixolimnion layer was characterized by well mixed oxygenated water. The chemocline between 5 and 8 metres distinctively separated the mixolimnion and the monimolimnion. The stratification and the strata were quite stable during the monitoring period. The lake was acidic, with an average pH level of 3.66. Redox potential remained positive and high (300-800 mV) despite the fact that dissolved oxygen concentration was very low in the deeper part of the lake.

The liming showed instant effects on pH and redox potential, but the stratification remained. Conductivity was slightly higher throughout the whole water column after liming. However, the deeper water was still denser than the surface water. This indicates that even though pumping of lime caused disturbances of surface water and at the depth which received lime, the density difference between upper and deeper water was strong enough to resist vertical mixing of the whole water column. The pH level increased in the whole water body after liming treatment (Figure 3). The highest pH, over 10, occurred between a depth of 2 m and 9 m during liming, May 2003, and between 6 m and 9 m one month after liming, June 2003. Most likely, this depth directly received lime, since the pipe through which lime was pumped was heavy and sank below the lake surface. The whole water volume was neutralized during the process when the lime sank to the lake bottom. With the increasing distance from the lime source, pH gradually dropped to around 7. After sewage treatment, pH in the lake dropped compared with after liming but the lake still was neutral or basic at most depths. Compared with after liming, pH distributed rather uniformly. The pH decrease indicates that there are sources of acidic water which still keep contributing into the lake. This is shown clearly by the profile of August 2004. The gradual drop of pH from 7 at 5 m down to 4.5 at 10 m most likely indicates the inflow of acidic water. During sewage sludge treatment, it was found that most of the sewage sludge sank rather rapidly down to the bottom and remained undissolved as a particulate phase. Therefore, although sewage sludge may also contribute to neutralizing of acidic water, since the pH of the sewage sludge is around 8, it has to be stressed that the neutral pH in the lake most likely still was an effect of the liming.

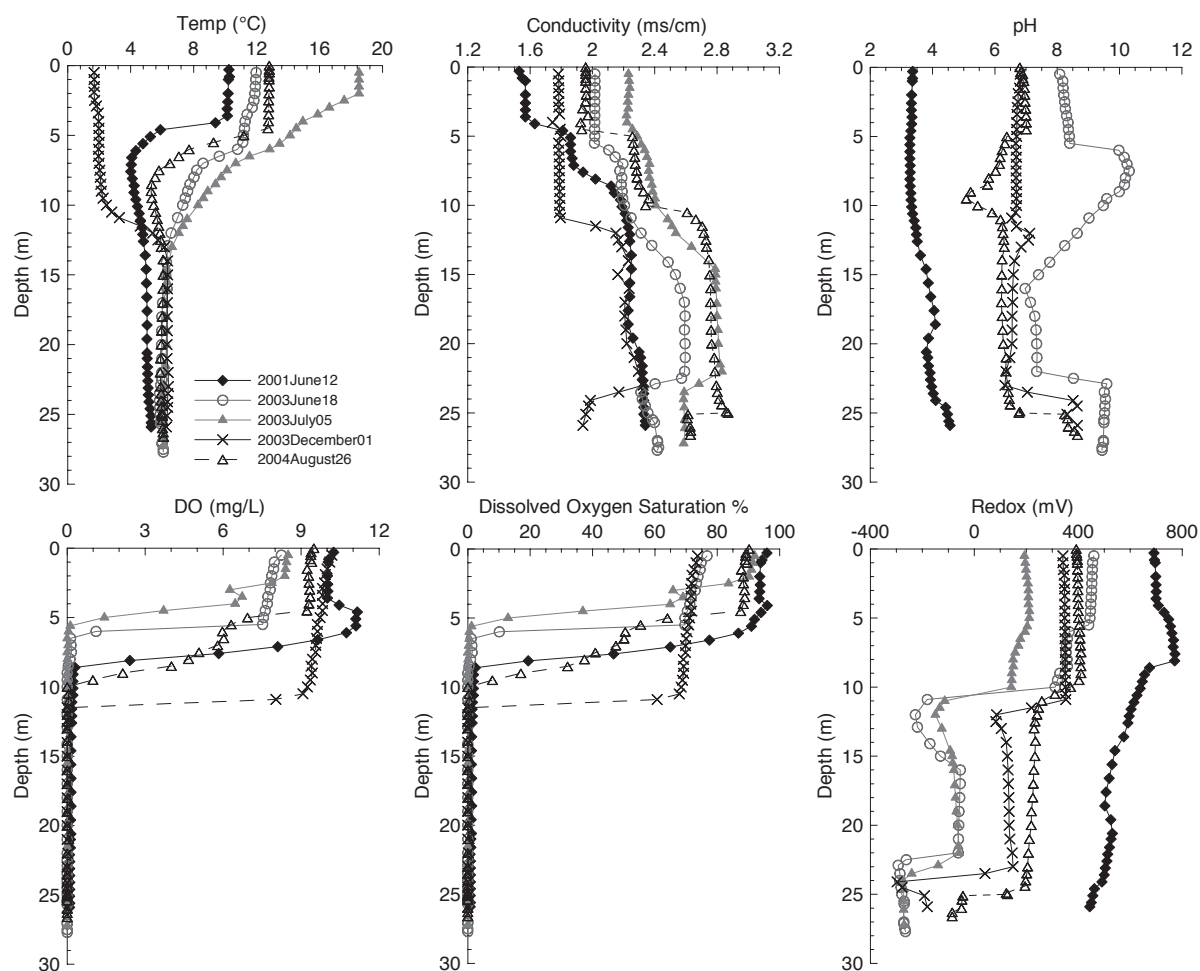


Figure 3 Results of in situ measurements of temperature, conductivity, pH, redox, dissolve oxygen and dissolved oxygen saturation for the Rävildmyran Pit Lake before treatments (2001 June 12), after liming treatment (2003 June 18) and different stages after sewage sludge treatment (2003 July 05 to 2004 August 26).

The lake remained stratified after both treatments, which prohibits oxygen diffusion into the monimolimnion. As a result, anoxic conditions remain in deeper water in the lake. Redox is obviously lowered by both liming and sewage sludge treatment due to increased pH, and limings caused the greater changes. Maximum decrease of redox of more than 700 mV, occurred after liming treatment, between 11 m and 15 m in June 2003. Before treatments, redox gradually decreased with depth. Sudden changes of redox potential did not occur. This was probably due to the presence of oxygen in the whole water column, although the concentration in the monimolimnion was close to zero. The redox couples O_2/H_2O together with other couples such as Fe^{2+}/Fe^{3+} in deeper water regulate the redox potential in the water, but they have not reached equilibrium conditions. However, sudden decreases of redox potential occurred after liming treatment and sewage sludge treatment. This indicates the change of dominating redox couples at different depth ranges. It was found that the distribution of redox potential in the upper water correlates with the distribution of dissolved oxygen. The oxic front always corresponds to strong decrease of redox. The redox potential decreased sharply to negative levels in the monimolimnion after liming treatment and until September 2003. However, after sewage sludge treatment, the redox level in deeper water

increased gradually with time. During later periods of sewage sludge treatment, December 2003 and August 2004, redox in deeper water became higher and positive due to decreased pH but was still lower than in the upper water and before treatment.

After both treatments, pH shows rapid increase near the bottom and becomes stable at higher pH down to the bottom (Figure 3). For example, after liming, pH was observed to increase about 2 units below a depth of 23 m, and was stable at the high level until the bottom. Water-rich unconsolidated slurry was found at the lake bottom, but it is difficult to determine where the sludge starts. The high pH probably indicates the presence of the sludge. Moreover, the increase of pH near the bottom coincides with decrease of conductivity and redox potential. This further strengthens the interpretation that the changes in these parameters near the bottom indicate the depth of the water-sediment interface. Therefore, the depth range where pH remains high and stable probably indicates the thickness of the sediment.

Sediment

Before treatments, the surface sediment appeared to be a thin layer of red-yellow coloured sludge without distinct horizons. After liming, several metres of dark green unconsolidated material was found to have settled at the bottom. As time developed after different treatments, the thickness, the mineral composition and the chemical composition in the sediment sludge changed. The sediment was thickest after liming, about 4.7 m. The thickness then gradually thinned to 3.7 m by 5 July 2003, one week after sewage sludge pumping was finished, 1.8 m in December 2003 and to 1.5 m in August 2004. The gradually thinned sediment could be due to the sediment getting denser by self-compacting processes. The highest percentage of dry weight (6.2%) was found during the last sampling.

The mineralogical composition also changed after different treatments. Before treatments, quartz (SiO_2), albite ($\text{NaAlSi}_3\text{O}_8$) and Fe-oxyhydroxides were the major minerals in the sediment. These minerals mainly arose from the material eroded from the bank and flushed into the lake. After the liming treatment, the sediment became rich in calcite (CaCO_3) due to the reaction of lime material with dissolved carbon dioxide in water:



where H_2CO_3^* represent the sum of dissolved CO_2 (aq) and its hydrous form of H_2CO_3 . Silicate minerals such as chlorite [$\text{Mg}_5\text{Al}_2\text{Si}_3\text{O}_{10}(\text{OH})_8$] and small amounts of amphiboles were also detected. The greenish colour of the sludge is an interesting phenomenon. The green colour totally disappeared after dehydration in the lab, and changed to yellowish brown, the characteristic colour of goethite (FeOOH) (Schwertmann and Cornell, 2000). This indicates that the greenish phases are not stable. A group of Fe(II)-Fe(III)-hydroxide salts, so called green rust, which structurally consists of alternating positively charged octahedral sheets and negatively charged sheets of exchangeable anions and water molecules, could give a green colour (Schwertmann and Cornell, 2000). The colour change after dehydration in the lab suggests that green rust is a dominant component of the sludge, giving its characteristic colour. The mineral composition changes indicate a stronger secondary mineral precipitation in the lake after the liming treatment. It is probable that large amounts of Fe-oxyhydroxides and gibbsite [$\text{Al}(\text{OH})_3$] also occur in the sediment after liming treatments as well as sewage sludge treatment, but since they occur as amorphous phases, they are not detected by XRD.

Table 2 Compositions of Rävlidmyran Pit Lake sediments before treatment (2001 June), after liming treatment (2003 June), and different stages after sewage sludge treatment (2003 July 05 till 2004 August)

Item	2001 Jun.	2003 Jun.	2003 Jul.05	2003 Jul.19	2003 Aug.	2003 Sept.	2003 Dec.	2004 Aug.
Fe ₂ O ₃ % TS	10.0	14.10	16.40	15.80	13.10	12.40	12.20	8.69
CaO % TS	-	17.10	16.00	6.56	11.30	10.30	11.00	3.49
MgO % TS	1.1	11.70	9.06	2.66	5.81	6.40	7.36	2.38
SiO ₂ % TS	-	4.14	4.82	11.60	10.20	16.90	10.60	58.80
MnO % TS	-	2.08	2.18	0.54	1.07	1.10	1.27	0.21
Al ₂ O ₃ % TS	-	0.89	1.42	3.46	2.69	4.11	2.90	12.10
P ₂ O ₅ % TS	-	0.03	0.74	6.07	3.52	2.95	3.27	0.40
K ₂ O % TS	-	0.31	0.23	0.70	0.55	0.86	0.51	2.75
Na ₂ O % TS	-	0.23	0.18	0.42	0.42	0.70	0.39	2.40
TiO ₂ % TS	-	0.02	0.04	0.38	0.25	0.31	0.25	0.66
LOI % TS	-	43.50	43.00	49.00	39.60	36.50	34.00	6.50
S mg/kg TS	1460	58700	75800	23000	44400	32400	29600	4820
Zn mg/kg TS	173	75500	59600	21200	41500	31600	35800	7600
Cu mg/kg TS	77.3	886	1030	539	638	723	737	444
Cd mg/kg TS	0.3	151	142	131	119	119	115	30
Pb mg/kg TS	92.1	13.4	21.1	37.1	36.8	48.0	30.5	112
C%	-	-	3.9	17.8	12.2	11.4	13.0	-
TOC% TS	-	-	0.4	17.9	7.3	6.6	10.2	-
IOC% TS	-	-	3.5	0	4.9	4.8	2.8	-
N %	-	-	0.08	1.7	1.1	1.0	1.08	-
TS%	-	-	1.2	1.9	0.6	1.7	3.5	6.2

- no measurement

TS = dry weight

LOI = loss on ignition

TOC = total organic carbon

IOC = inorganic carbon

The major components in the sediment changed from Al, Fe and Mg into Ca, Fe, S, Mg and Zn after liming, which are also the major constituents in sediment of the early stage of sewage sludge treatment. Si, Mn, Al and Cu are also important components in the sediment after the liming (Table 2). Due to lack of measurements of these elements before liming, the concentrations are not comparable. Almost all elements are found to have accumulated in the sediment after treatments, especially after liming. The sewage sludge settled rapidly at the lake bottom. This is shown by the present of increased organic content in the sediment shortly after the pumping. P, total organic carbon (TOC) and N showed the strongest accumulation during the first month after sewage sludge treatment. This indicates that if sulphate reducing reactions stimulated by organic matter will occur, this will be limited to the bottom. In the later stage of sewage sludge treatment (August 2004), stronger accumulation of Si, Al, K, Na in the sediment occurred. This is probably explained by erosion and flush of quartz and other silicates into the lake during 2004 caused by heavy rains.

The water column

Dissolved concentrations and distributions of elements such as Na, K and S were not influenced by either liming or sewage sludge treatment. Figure 4 shows Na, K, Ca, Mg, Fe,

Mn, Zn, S and Al profiles for comparison between before treatments, after liming treatment and early, middle and later stages after sewage treatment. Na, K and S have the same distribution pattern through the whole water column as well as similar concentrations. A mass calculation of the different elements in solution in the pit lake before and after liming has been performed to estimate the efficiency of treatment in removing metals. It shows that Na, K and S have almost the same total mass as before liming.

A change of the Ca concentration is obvious in the water after liming. The distinct increase of dissolved Ca concentrations is a direct result of the liming. Starting from 5 July 2003, dissolved Ca in the upper water gradually decreased. For example, dissolved concentration of Ca at 10 m had dropped 88 mg/l between 5 July 2003 and August 2004. Ca was probably precipitated as calcite, which was observed in the sediment. Moreover, decreased of pH from around 11 after liming treatment to near 7 at 5 m to 10 m also indicate the disappearance of Ca(OH)_2 , since Ca(OH)_2 normally buffers pH around 10 to 12. Ca removal from the water by precipitation is also evidenced by its accumulation in the sediment, as discussed in the sediment section.

Dissolved Mg was obviously lower in the uppermost 10 m after liming and the situation remained after sewage sludge treatment, which indicates the removal of Mg by the liming. It is calculated that about 62.4% of the Mg is removed from the dissolved phase in the upper water. However, below 10 m the concentration was higher, the total mass of Mg in the deeper water is calculated to increase about 7.2%. It is likely that Mg was removed from the upper water by precipitations which dissolved in deeper water. Therefore, the result was higher Mg concentration at depth. A possibility is that Mg precipitated as brucite [Mg(OH)_2] in the upper water where pH was much higher. The solubility of brucite is strongly pH dependent. At pH lower than around 10, Mg(OH)_2 will dissolve (Faure, 1991). However, PHREEQC modelling does not indicate that brucite may precipitate in the uppermost 10 m since the SI values are negative. Another possibility could be formation of $(\text{Ca, Mg})(\text{CO}_3)_2$, but due to lack of measurements of alkalinity, saturation index could not be modelled. However, it is concluded that there was transformation of Mg from the dissolved phase to particulate phases.

Dissolved Fe was strongly removed from the uppermost 10 m of water, with almost 100% removal efficiency, after liming treatment, and the concentration remained as similar low level after sewage sludge treatment, although the sludge contains significant amounts of Fe. The sewage treatment rather influenced particulate Fe concentration than dissolved Fe. The removal of dissolved Fe from the lake is mainly due to increased pH by liming combined with oxic conditions in the upper water (Figures 3 and 4). Dissolved Fe immediately increased at the depth where water was anoxic and the redox potential suddenly decreased. The process of Fe^{2+} oxidation and hydrolysis is an oxygen consumption and deprotonation process. Dissolved Fe may transform into particulate Fe in the form of goethite (FeOOH) and Fe(OH)_3 , especially in oxic water (Borggaard and Elberling, 2003). Particulate Fe shows increased concentrations after treatments. Down to the anoxic water after treatments, dissolved Fe increased several thousands times, but was still lower than the average level before treatments. The removal of Fe in the deeper water is probably due to the adsorption to the FeOOH formed in upper water and coprecipitation. Therefore, still around 66.4% of Fe was removed from deep water after liming treatment. Also, the formation of Fe(II)-Fe(III)-hydroxy salt, which is probably the major component giving the green colour to the sediment sludge found at the bottom, may also be a important process in removal of dissolved Fe at depth.

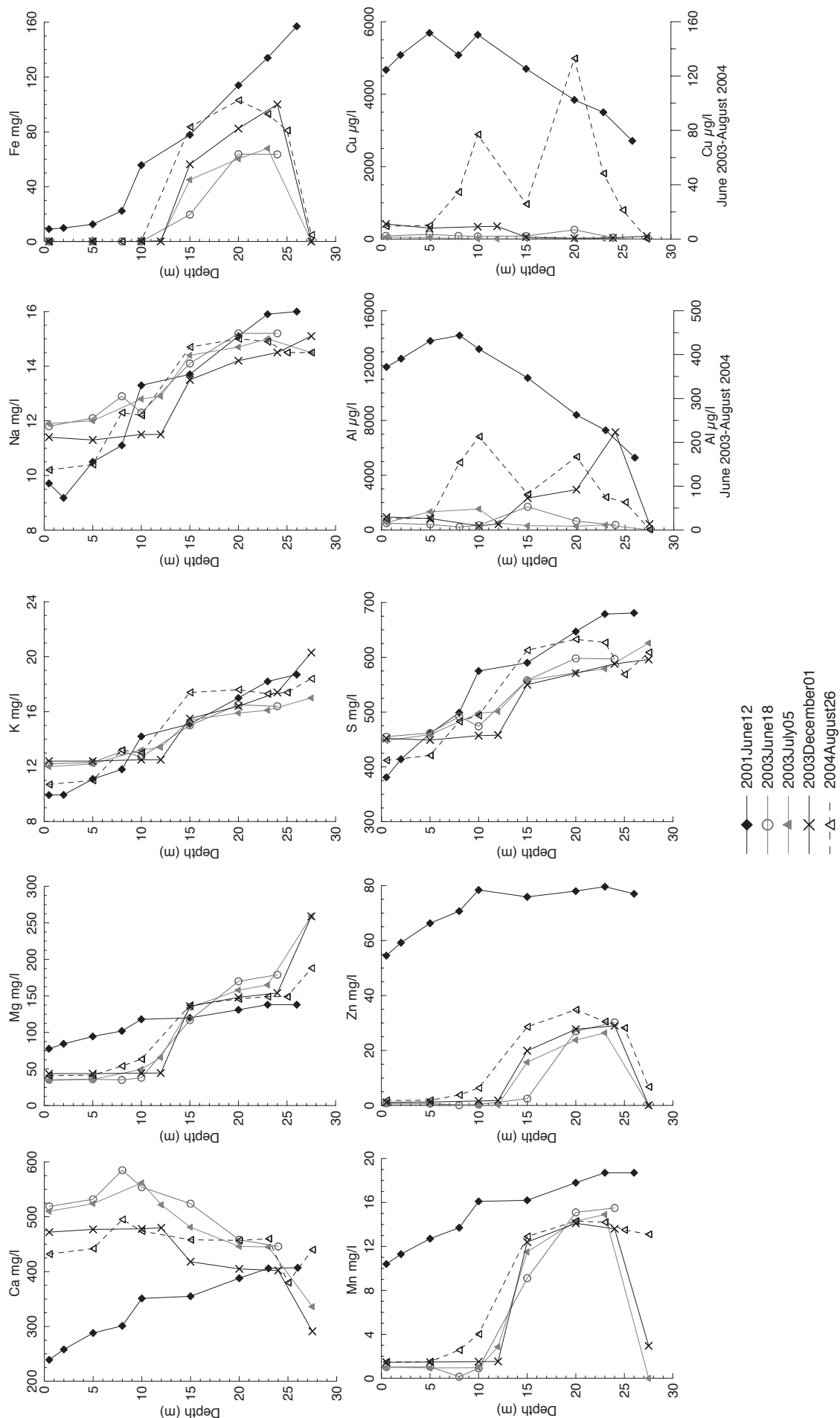


Figure 4 Concentration profiles of filtered Fe, Mn, Zn, S, Al and Cu concentrations in Rävildmyran Pit Lake before treatments (2001 June 12), after liming treatment (2003 June 18) and different stages after sewage sludge treatment (2003 July 05 to 2004 August 26).

The treatments had similar effect on Mn and Zn as on Fe. Both dissolved Mn and Zn were strongly removed from the water in the uppermost 10 m, with removal efficiency of 93.9% and 99.3% respectively. In the anoxic layer, their concentrations gradually increased and recovered close to the pre-liming average level. Therefore, removal of dissolved Mn and Zn was most likely the effect of liming, due to increased pH. Dissolved Mn most likely precipitated by forming the mineral manganite (MnOOH) in oxidized water (Stumm and Morgan, 1996). Dissolved Zn is likely to have been removed by forming Zn(OH)_2 within a pH range of around 8-10 (Stumm and Morgan, 1996). Besides, adsorption of Mn and Zn to Fe-oxyhydroxide may also have occurred since goethite as well as FeOOH are negatively charged when pH is higher than 8 (Langmuir, 1997). The precipitation of Zn and Mn resulted in high concentrations in the sediment (Table 2).

Al and Cu are the metals most strongly influenced by the treatments, especially by liming. Dissolved Al and Cu decreased dramatically after liming, and they were almost completely removed from the water. The mass calculation show that 99.9% of Cu and Al are removed from dissolved phase. Dissolved Al concentrations are heavily influenced by pH changes (Stumm and Morgan, 1996). Modelling shows that gibbsite [Al(OH)_3] has always been oversaturated in the lake after the treatments, indicating that precipitation of gibbsite may occur. Adsorption of Cu to gibbsite is probably an important process for removal of Cu from the water (Lee, *et al.*, 2002). Moreover, adsorption to Fe-oxyhydroxides and other minerals may also have been important since pH was rather high. In the Rävlidmyran pit lake, acid water with high concentrations of metals is continuously flowing into the lake. This is further shown by the gradually increased concentrations of Al and Cu after sewage sludge treatment. Cu and Al concentrations showed a significant change in the later period of sewage sludge treatment. The strong increase of Al and Cu coincide with the minimum level of pH in August 2004, illustrating inflow of acid flow in water at 10 m depth.

Conclusions

The Rävlidmyran Pit Lake is oligotrophic and meromictic. Before treatment, the lake had striking similarities with other sulphide mining lakes in terms of low pH and high metal and sulphate contents. The water is poorly mixed and permanently stratified. Three layers, the mixolimnion at the top, the chemocline below and the monimolimnion further below, are identifiable. Due to poor mixing, the monimolimnion contains very poor oxygen. However, the redox potential in the lake was positive and high before treatment. The density difference between the mixolimnion and monimolimnion is the key factor that prevents water cycling in the lake. Groundwater filling and stratification strongly controlled the elemental distributions in the lake. Most elements such as Ca, Mg, Na, K, S, Mn, Fe and Zn had the lowest and constant concentrations in the mixolimnion. Concentrations increased in the chemocline and kept rising in the monimolimnion. Fe was removed from the mixolimnion due to oxidation and precipitation, but precipitates redissolved in the monimolimnion. Scavenging processes by Fe-oxyhydroxides was not important due to the low pH. However, the formation of gibbsite [Al(OH)_3] was important in controlling Al concentrations, as well as Cu concentrations by adsorption.

Liming resulted in increased pH and decreased concentrations of metals such as Fe, Mn, Zn, Al and Cu as well as of other trace metals. However, elements such as Fe, Mn, Zn and Mg were strongly removed in the uppermost 10 m of the water column only, where oxygen was present. The stratification remained after liming treatment since the density differences between the mixolimnion and the monimolimnion was very strong. The monimolimnion

became anoxic and the redox potential decreased strongly. As a result, the concentrations of redox sensitive elements such as Fe and Mn were much higher than in the upper water. However, compared with before liming, metal concentrations in the monimolimnion were still lowered. Al and Cu were almost completely removed from the whole water column. Increased pH is the main reason for removal of dissolved Al from the water, due to precipitation of gibbsite. Almost all the metals are found to have accumulated in the sediment. However, liming is not a long-term solution as long as the acidic sources flow continuously into the lake. Therefore, the liming effect will not last long and it will be rather costly to continue liming.

Compared with liming, the sewage sludge treatment did not show strong and instant effects on the geochemistry of the lake water. The density stratification remained in spite of the disturbance by pumping sewage sludge. The sewage sludge treatment had the strongest influence on the particulate elemental concentrations, especially at the beginning of treatment. However, rather soon, the sludge particle settled at the bottom. Therefore, the organics in the sewage sludge may not have been able to stay in the water long enough to sorb ions, thereby affecting dissolved concentrations of metals. The accumulation of organics at the lake bottom also indicates that if sulphate reduction will occur, it may be limited to the lake bottom. During the monitoring period, no indication of sulphate reduction was detected. Sulphate-reducing bacteria is not likely to be active in the lake, yet. It is possible that stimulation of SRB in such a full-scale experiment may demand longer time to be able to observe the effects.

Acknowledgements

This study was financed and supported by the MISTRA research programme “Mitigation of the environmental impact from mining waste” (MiMi), Luleå University of Technology and Boliden AB. We would like to thank Boliden AB for co-operation and for providing us with background information. Special thanks are to Michael Sandberg from Boliden AB for great help in field work of sewage sludge pumping.

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