Release of trace metals from sulphidic mine waste when turning a deposit into a golf course

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Abstract

The release of some selected metals was studied from a deposit of sulphidic mine waste that contains some 6×10^6 metric ton from extraction of zinc and lead ores. The deposit was in use from 1862 to 1976 and contains mainly a sand fraction, with minor amounts of tailings. The site is located on the shore of the second largest lake in Sweden, Lake Vättern and it was transformed into a golf course in 1980s. The impact of this hydrochemical change on trace metal (Al, Cd, Cu, Mn, Ni, Pb, Tl and Zn) mobility is discussed in this paper. Water quality measurements were made on surface water and groundwater from the golf course. Coefficients of distribution (Kd; $l\ kg^{-1}$) were determined in batch systems between pH 3 to 9 in order to elucidate the influence of pH on metal mobility.

The highest concentrations of dissolved metals were found in the groundwater (Pb; 15-278 µg/l in groundwater, 2-7 µg/l in surface water), except for zinc (32-167 µg/l in groundwater and 153-463 µg/l in surface water), and were rather typical for this kind of sulphidic waste. At present, the new use of the deposit does not seem to enhance weathering of the waste material.

Batch equilibrium tests showed that the mobility on average increased by three orders of magnitude at pH 3, in comparison to pH 9. For instance, at a pH around 6 a large decrease in Kd is seen and at the low pH about 30% of the lead and zinc content (average concentrations 5-10 g/kg and 15-100 g/kg, respectively) in the deposit will be mobile. There is no risk for increased metal mobility at present since the pH exceeds 6 and there is a high content of carbonates in relation to sulphides. The acid neutralising capacity is about 1400 meq/kg. The study points out the importance to include pH control in the maintenance of the golf course to minimise any future risk for an increase of metal transports from the area.

Introduction

Scope of the problem

Building a golf course on an old deposit with sulphidic mine waste may induce other environmental problems than commonly ascribed to this kind of material. Different chemicals such as weed killers and fertilisers are used in order to ascertain a good grass surface. At this specific golf course the use of weed killers is at a minimum and only inorganic fertilisers are added. The greens and tees are watered in the summer why there is an addition of water to the annual precipitation of 700 mm. From the natural water balance it has been concluded that some 350 mm $year^{-1}$ forms groundwater (Ekholm, 2002). Watering appears to be the only practice that might increase the metal transport, provided that they are mobile. The waste is toxic to the grass and it wilts as the roots come in contact with it through the shallow soil.

Weathering processes

Weathering of sulphidic waste occurs in aerobic as well as anaerobic environments. In the first pathway a truly chemical process is feasible although bacterial oxidation is most frequently reported (Kelley and Tuovinen, 1988). The latter is quantitatively important since the rate of the biological weathering is about 10,000 times faster. The result from both pathways of weathering is of course acidic leachates that have a high metal content. The latter reflects the composition of the weathering sulphides and any acid attack on the parent rock. Weathering occurs even under anaerobic conditions (Stumm and Morgan, 1996). In this process trivalent iron serves as electron acceptor, resulting in formation of sulphate and dissolved trace metals. A principal reaction pathway is summarised in figure 1.

In Sweden, the most frequent strategy to abate acid drainage from mine waste relies on either pH control or covering of the waste with an

impermeable layer, thereby preventing percolation of rain and minimising the access of oxygen. On this particular site the deposit has been turned into a golf course, which would influence the partial pressure of oxygen, pH and the fluctuation of the groundwater table. It is the aim of the present study to evaluate how this practice influences the release of trace metals from the waste in terms of their concentrations in soil and surface waters in relation to their pH dependent mobilisation from the waste.

Materials and methods

The Field Site

Before it was turned into a deposit, and later a golf course, this site was a bay of the second largest lake in Sweden, Lake Vättern (figure 2 & 3). The deposit is about 0.4 km^2 and the golf course covers almost all of this area. At the north shore of Lake Vättern mining waste from the Zinkgruvan processing plant containing sulphide residues (mainly sphalerite and galena) was deposited from 1862 and onwards. The dumpsite was in use until 1976 and altogether it contains some 6×10^6 metric ton of waste sand. Three separate sub areas are distinguished where each of them represents different enrichment processes in the plant. The oldest part, in use between 1862-1930, is called I. This waste was re-processed for lead and zinc from 1931 to 1965; the waste after the enrichment was then put in area III. Between 1930-1973 waste was deposited in area II, and after 1973 until the closing of the waste site in 1976, it was put in area Ia. Typical levels of zinc and lead in the waste are presented in table 1.

In 1980s the deposit site was turned into a golf course. The site was covered with a soil layer between just a few centimetres to some 40 cm in magnitude. To half of the area municipal sludge was added. The rill seen in figure 2 was moved closer to the main land and drains were built at various places to lower the groundwater level. The old rill grove did not completely dry out, instead puddles with vegetation formed. The water from these is led to the new rill that enters Lake Vättern through the marina, figure 3. The average annual water flow of rill is 10-30 m/s (ref. VBB (1975) in Ekholm (2002)). A few ponds were constructed along the rill and they are now almost completely covered with vegetation, notably reed (*Phragmites australis*) that increases the retention time of the water. Fountains that are supplied with surface water from Lake Vättern keep the water moving in ponds through out the golf course.

Sampling

In May 2001 groundwater, surface water and soil was collected at two sites, figure 3 and in September 2002 only soil was sampled.

Soil was, in 2001, sampled close to the two ponds (S1 and S2) at depths between 1 and 2 m, just below the groundwater surface. In 2002 groundwater wells in the northern part of the deposit were installed and soil samples were taken on both sides of the groundwater level as well as at the interface. These samples were mixed and pooled into two samples SMA and SMB, figure 3. The soil sampled in 2002 may contain roasted ore and therefore react differently than soil sampled 2001. Soil samples were stored in plastic bags.

Surface water was sampled at the same site as the soil, W1 and W2. They were taken by manually immersing a bottle in the pond.

Groundwater samples were collected from wells (GW1 and GW2) located in the southern part of the deposit. The wells were emptied and allowed to refill before sampling. A battery-operated Amazon-pump was used. At this occasion, the groundwater level was 1 m below the soil surface and the water samples were taken 1-1.5 m below the groundwater surface.

All water samples were collected in 1 litre polyethylene bottles that had been washed in nitric acid/18.2 MΩ-water (1:100) for 24 hr and then rinsed three times with 18.2 MΩ-water prior to packing in plastic bags. All samples were stored in a refrigerator prior to treatment.

Sample treatment

Acid soluble metals

Soil samples was digested in nitric acid (reagent grade, Scharlau), 20 ml to 0.3 g sample, for 10 minutes at 90°C, and then diluted to 40 ml with 18.2 MΩ-water. Digestion was performed with a microwave digester (prolabo, Microdigest 3.6).

Metal solid-solution distribution - batch experiment

The soil sample (35 g, d.w.) was dispersed in 500 ml 18.2 MΩ-water and the slurry was stirred in a beaker covered with a polyethylene film. After 24 hrs the pH of the water phase was measured and 15 ml was taken for analysis. The sample was stored in a closed vial in a refrigerator to minimise chemical and biological activity. Base (NH_3, 0.1-0.5 M, p.a., Merck) or acid (HNO_3, 0.5 M, reagent grade, Scharlau) was then added to the slurry in order to maintain pH at specified levels in the desired range of pH 3-9.3. The slurry was kept at each pH for 24 hrs with continuos stirring where after 15 ml of the water phase was sampled before the next lower pH was set.

The pH control was made with an automatic titrator operated in pH-stat mode (Radiometer, Titralab TIM900) and an automatic burette (Radiometer, ABU93 Triburette).

Analysis

Metals

Water samples (from batch experiments, ground- and surface water) were filtered through 0.4 µm polycarbonate filters and acidified with nitric acid (for trace analyses, Scharlau) to a final concentration of 2%. If necessary, samples were diluted prior to analysis. Analysis was performed with ICP-MS (Agilent, 4500) using ^{103}Rh (Merck) as internal mass standard. Both semi-quantitative and quantitative evaluations were performed.

Principal anions

Analysis of principal anions (Cl^-, SO_4^{2-}, F^-) was performed with capillary electrophoresis (HP, ^{3D}CE) using a chromate buffer with an osmotic flow modifier (5 mM $NaCrO_4$ and 0.5 mM TTAB) as electrolyte solution. Prior to analysis, the samples were filtered through 0.4 µm polycarbonate filters.

Results and discussion

pH

There is a close resemblance between pH measurements in batch and field systems, respectively. Consequently, the soil buffers the acid production from the acid waste, regarding both the production of sulphuric acid as well as hydrolysis of notably aluminium and iron. The high amount of acid soluble calcium in combination with a total CaO content of 8% (weight) of the waste suggest that the pH is controlled by calcium carbonate.

Water

The concentrations of Cr, Mn and Pb were all higher in the groundwater samples (GW1 and GW2) than in the surface waters (W1 and W2), whereas for Zn the opposite was observed (table 2). For Al, Ni, Cu, Cd and Tl no distinct differences in concentrations between groundwater and surface water were noticed. Due to the heterogeneous waste material, variations in metal concentrations are expected. The heterogeneity of the system is further emphasised by the fact that there was a considerable difference between the concentrations of zinc being 463 µg/l and 32 µg/l in surface and groundwater, respectively, at site W1/GW1.

Metal concentrations in the aqueous phase after equilibration for 24 hrs with pure water all reached levels exceeding those observed in the field, see below. Thus, it appears as if the weathering rate, in combination with redistribution processes and dilution with unpolluted groundwater control the metal mobility on the field site.

Acid soluble metals

The concentrations of acid soluble metals in the soil are high, table 4, notably for lead and zinc. The elements are heterogeneously distributed in the deposit, which indicates that the waste emanates from different periods of production and reflects different enrichment methods. Considering that about 6×10^6 metric ton waste is deposited in this area, the amount of metals in the soil is considerable, see table 4.

Batch equilibrium

The batch equilibration studies indicate different acid neutralising capacities in the waste material. Samples from the northern part had a pH of about 7 whereas those from the southern part were more than a unit higher, having a pH of 8.3. At a steady state pH of 3, the amount of acid added to the system infers a neutralising

capacity 1400 meq/kg. On the equilibration with water high concentrations of mobilised metals were found in solution, table 2. In comparison with groundwater (pH ~7.7) concentrations of Al, Cr, Ni, Cu, Zn and Tl in the batch equilibrium systems were 2-20 times higher. Manganese and lead showed similar concentrations in both systems. On the other hand, the concentration of cadmium was 55 times higher. The surface water also contains lower concentrations of all elements compared to the batch equilibrium system; the difference is about the same order of magnitude as compared to the groundwater.

The batch equilibrium experiments showed that the pH-dependent metal distribution is in general characterised by a pronounced release of most metals at pH 5 (Al, Fe) to 6 (Cd, Cr, Cu, Mn, Ni, Pb, Tl). A similar pH dependent release indicates that a more or less unspecific mechanism controls the distribution. The concentrations of the considered elements in the water phase do not reach saturation. Therefore, the mechanism behind the distribution would be adsorption. Considering the pH interval, several adsorbents are possible. The magnitude of the release differs substantially between sites as well as elements, figure 4 and 6. There appears to be a positive quantitative correlation between the age of the waste and the amount of metals that is released to the water phase. The old waste released up to 35% of its acid soluble content of lead and zinc, whereas fresh waste released only 10%. The same pattern is present for Cd (20% and 3%), Tl (7% and 2%), Al (25% and 3%) and Mn (15% and 2%).

The pH appears to be the single most important parameter that controls the distribution and thereby the mobility of the metals (figures 4, 5 and 6). The prominent release at pH 5-6 for all metals infers that the composition of the adsorbent is also important. In similar systems, ferric hydrous oxides with various contents of water are usually considered to be the primary adsorbents, both as discrete precipitates and as surface coatings. The pH of zero point of charge reported for most ferric hydrous oxides (Parks, 1967) is above the pH where metals are released in this system why other surfaces might serve as primary adsorbents. Since the concentrations of dissolved calcium and iron increase dramatically at pH below 7 and 5, respectively, we believe that the distribution of trace metals in this system is controlled by adsorption/occlusion to carbonate minerals. According to the concentrations of primary cations in the aqueous phase after equilibration with water and the acid soluble amount of these metals, both calcite and siderite are possible candidates.

Conclusions

The metals in the golf course can in the future become an environmental problem unless the pH of the waste is maintained above 6. Contrary to other sulphidic mine waste the high content of calcareous minerals in this particular waste counteracts metal mobility. On the other hand, all trace metals studied are released at pH 5.

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Table 1. Levels of zinc and lead in the deposition area according to sub area and amount waste (Ekholm, 2002).

Sub area	Active deposit	Zn (%)	Pb (%)	Amount ($\times 10^6$ ton)	Area (km^2)
I	1862-1930	~9.4	~1.3	1.5	0.10
Ia	1973-1976	0.4-0.5	0.2-0.3	1.13	-
II	1930-1973	1-2	0.4-0.6	3.5	0.23
III	1937-1965	3-7	0.7-2.3	1.0	0.07

Table 2. Concentrations of metals (µg/l) found in surface and groundwater (W1 & 2, GW1 & 2) and in the water phase of the soil sample/water batch experiments (S1 & 2, SMA & B).

	pH	Al	Cr	Mn	Ni	Cu	Zn	Cd	Tl	Pb
W1	7.98	0.79	0.18	2.9	0.98	1.2	463	0.34	0.27	7.1
W2	7.63	1.1	0.19	0.89	0.50	0.49	153	0.28	0.26	2.2
GW1	7.51	0.77	0.21	340	0.73	0.57	32	0.30	0.26	15
GW2	8.18	2.0	0.25	117	1.6	2.4	167	0.68	0.30	278
S1	8.3	10	2.2	378	2.4	2.9	1667	7.8	3.3	100
S2	8.3	9.3	2.3	22	3.4	4.3	2109	46	4.8	63
SMA	7.3	11	1.7	87	4.3	2.6	10286	57	4.3	154
SMB	6.9	10	2.8	449	5.6	3.5	34945	438	4.8	1112

Table 3. Principal anions in ground- and surface water as well as water from 24 hrs equilibration with mining sand (mg/l).

	GW1	GW2	W1	W2	S1	S2
Cl^-	12	18	7.0	3.2	0.4	0.4
SO_4^{2-}	251	660	353	14	54	40
F^-	2.4	2.6	1.6	0.7	1.0	1.0

Table 4. Acid soluble metals in the soil (g/kg).

	Al	Cr	Mn	Ni	Cu	Zn	Cd	Tl	Pb
S1	4.7	-	1.8	0.3	0.4	19	0.6	0.6	5.2
S2	6.9	-	1.8	0.3	0.5	15	0.7	0.7	4.9
SMA	5.7	7.8×10^{-2}	0.7	0.1	0.1	95	0.2	8.9×10^{-2}	9.8
SMB	5.2	0.1	0.7	0.2	0.1	118	0.2	8.7×10^{-2}	10

$$HS^- + Fe(III) \longrightarrow \text{oxidised S} + Fe(II) \quad (1)$$

$$Fe(II) + \text{oxidising organic molecule} \longrightarrow Fe(III) + \text{reducing organic molecule} \quad (2)$$

Figure 1. Schematic sketch over pyrite weathering.

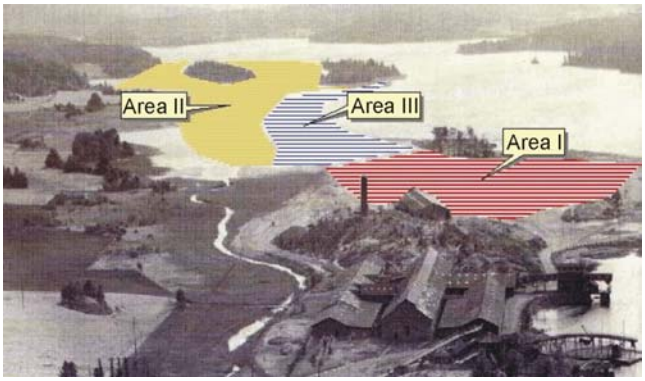

Figure 2. Photograph over the industry and a part of Lake Vättern. The marked areas are the deposition sites, further information regarding the sub areas see text and table 1 (with permission from Ekholm (2002) and Zinkgruvan Mining AB).

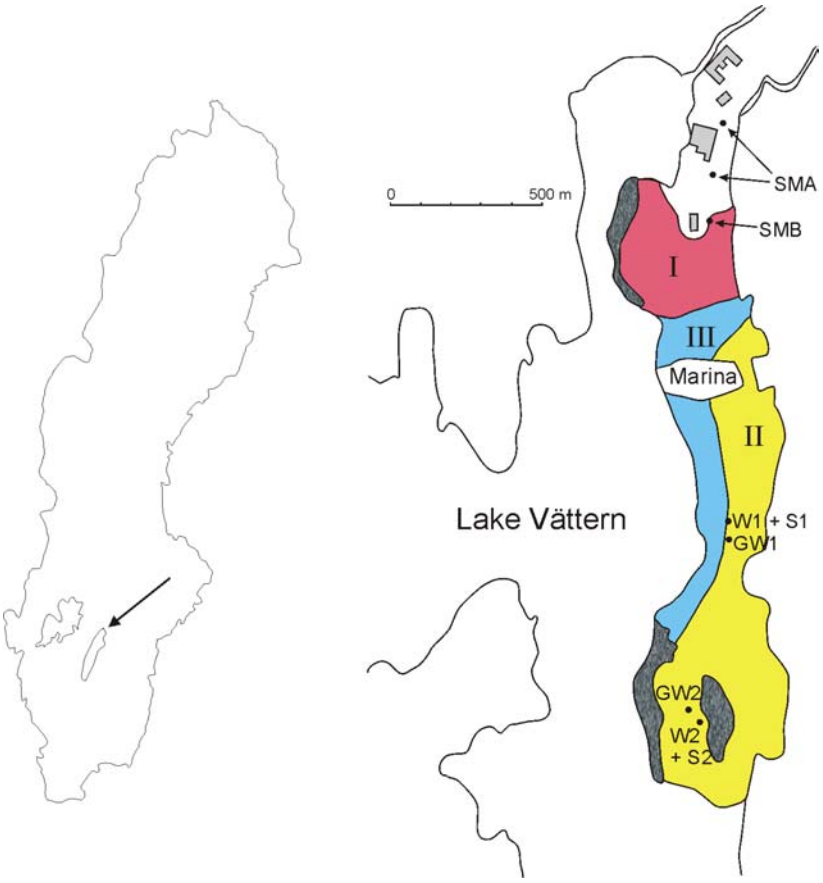

Figure 3. Location of the mining deposit in Sweden (to the left) and (to the right) a map over the deposition site with marked sampling sites.

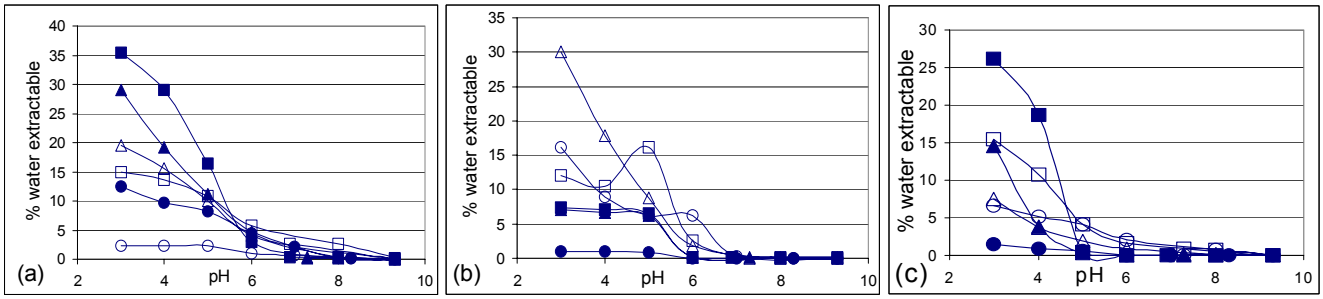

Figure 4. Solid solution distribution of Zn, Cd, Tl, Pb and Al in SMA (▲), SMB (■) and S2 (●), a) filled Zn, unfilled Cd, b) filled Tl, unfilled Pb, c) filled Al, unfilled Mn.

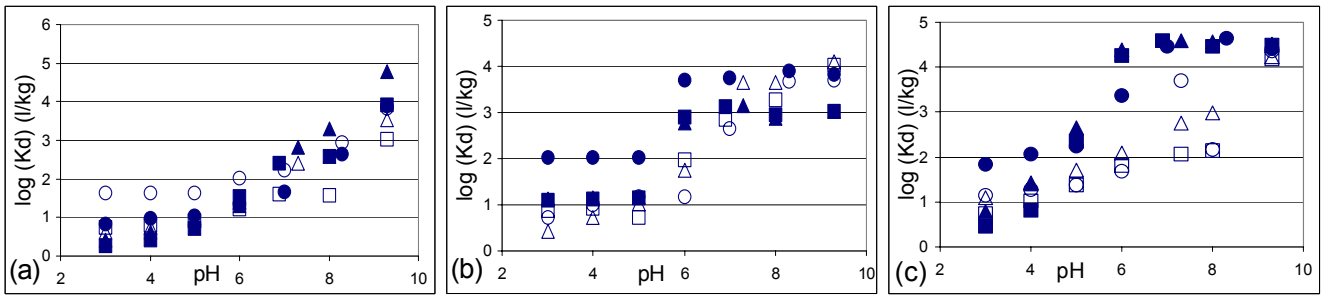

Figure 5. Distribution coefficient (log) for Zn, Cd, Tl, Pb and Al in SMA (▲), SMB (■) and S2 (●), a) filled Zn, unfilled Cd, b) filled Tl, unfilled Pb, c) filled Al, unfilled Mn.

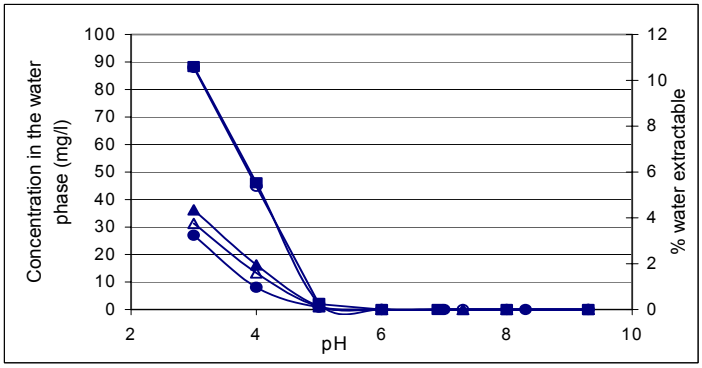

Figure 6. Iron found in the water phase of the extraction, in concentration (mg/l) (filled) and % water extractable (unfilled). SMA (▲), SMB (■) and S2 (●).