

Metal mobility in alum shale from Öland, Sweden

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Abstract

A study was initiated to analyse metal flows from alum shale to the environment in an area in Öland, Sweden. The study was performed by elemental analysis and leaching experiments of alum shale together with analysis of groundwater and surface water samples.

The metal concentrations in non-weathered alum shale were much higher than in weathered or burnt shale, especially for cadmium (Cd), nickel (Ni) and zinc (Zn), indicating a loss of metals during weathering or burning of the shale. The release of metals through weathering was clearly demonstrated by the leaching tests. A 36-week leaching period of non-weathered shale resulted in a drastic drop in pH and a significant increase in metal concentrations in the leachate. The metal concentrations in groundwater were inversely related to the pH. For surface waters, the concentrations of Cd, copper (Cu), Ni and Zn were generally increased compared to background values.

In conclusion, metals are released through weathering or burning of alum shale, as well as from heaps of weathered or burnt shale. The release of metals is strongly related to low pH, especially for Cd, Ni and Zn.

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1. Introduction

Metals are natural resources used by man over several millennia. Mining and various other industrial activities have, however, often resulted in a significant environmental impact. In order to assess the environmental state of an area, anthropogenic influences, as well as natural processes such as bedrock weathering, must be considered.

In 1999 high concentrations of cadmium (Cd), copper (Cu), nickel (Ni) and zinc (Zn) were detected in sewage sludge from a small wastewater treatment plant

(WTP) in Degerhamn, Sweden. The bedrock in the area is rich in alum shale, which earlier formed the basis for the local industry, mainly alum works. As the wastewater pipe system is directly located in a layer of alum shale, weathering processes were suspected to be a major source of sewage metals, especially Cd. Through infiltration of groundwater to the old leaky cement pipes, mobilized metals were able to eventually reach the WTP.

However, mobilized Cd, or other metals with a high concentration in alum shale, could constitute environmental risks for the area on a more general level. Weathering of similar bedrock has previously been shown to affect the geochemistry in some areas, resulting in elevated concentrations of potentially toxic elements such as Cd, Zn, molybdenum (Mo), uranium (U) and arsenic (As) in soils, sediments, waters and biota

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(e.g. Loukola-Ruskeeniemi et al., 1998; Lee et al., 1998). Therefore, a study was initiated in 2002 to analyse metal flows, primarily Cd, Cu, Ni, Zn and As, from alum shale to the environment. This introductory study was performed by elemental analysis and leaching experiments of alum shale in different weathered conditions together with analysis of groundwater and surface water samples.

2. Background

Alum shale is a sedimentary rock belonging to what are termed the 'black shales'. The Swedish occurrences of alum shale were formed during the latter part of the Cambrian era and up to the first part of the Ordovician era, approximately 540–480 million years ago (Hessland and Armands, 1978).

2.1. Composition and metal content of alum shale

The alum shale consists of various silicate minerals, sulphide minerals, calcite, lenses of bituminous limestone ('stinkstone') and kerogen (organic substances). Alum shale was formed from the sediment material in the oceans under anaerobic and relatively stagnant conditions with an intense supply of organic and inorganic material. Under these conditions, the organic material is incompletely oxidized, which leads to the reduction of sulphate (SO_4^{2-}) to hydrogen sulphide (H_2S). Sulphide ions (S^{2-}) may precipitate heavy metals in the environment into sulphide minerals such as pyrite (FeS_2). Other heavy metals such as Cd, Cu, lead (Pb) and Zn may also precipitate as solid sulphides in the sediments (Jeng, 1992). Affinity between metal ions and organic substances, like kerogen, could also fix metals into the alum shale sediments. However, the metal content in alum shale varies due to the heterogeneous nature of the material.

2.2. Weathering processes in alum shale

Alum shale is easily weathered when exposed to air and moisture. The process can be divided into two principal steps: [1.] oxygen and water may oxidize the sulphide minerals, generating H_2SO_4 and free metal cations; [2.] the sulphuric acid attacks and destabilizes the silicate minerals and kerogen, eventually releasing the elements within them (Jeng, 1991, 1992). Reaction models showing the oxidation of sulphide minerals such as FeS_2 and the subsequent acid production are well documented (e.g. Evangelou, 2001; Holmström, 2000; Jeng, 1991; Puura, 1998; Salomons,

1995; Strömberg, 1997). The produced acid may be buffered by calcium carbonate, precipitating the metals as metal hydroxides for example. Eventually the buffer capacity might be exceeded, resulting in a substantial decrease in pH and an increased release of elements from the solid to the solution phase. This release changes the shale structure and subsequently leads to the formation of unstable secondary minerals (Jeng, 1991, 1992). Visible changes due to weathering are increased fissility together with precipitations of gypsum at the shale's surface.

The shale kerogen also degrades easily when exposed to air (Eklund et al., 1995) resulting in a release of imbedded metals. Acidic rain plus physical and biological weathering can accelerate this process.

2.3. Alum shale—occurrence and use

Black shales, of various geological ages, exist in all continents of the world. Particularly large deposits are found in Russia, the USA, Australia, China and Brazil. Alum shale has also been formed in several places in Sweden, for example Öland and Scania. However, the shale is commonly covered by other kinds of rocks. Alum shale has been utilized as a raw material in the manufacture of alum, red paint, oil and gas, uranium, sulphur and nitrogen. It has also been used as fuel when burning lime and producing alum. Furthermore, shale ash has been used as an ingredient in porous concrete (Hessland and Armands, 1978).

2.4. Alum production

Alum [$\text{KAl}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$] had a wide range of uses in the eighteenth and nineteenth centuries, as a mordant, pigment and to produce a writable surface on rag paper. At the end of the nineteenth century, shale-based alum production was replaced by aluminium sulphate or other substances produced from different raw materials, and paper manufactured from cellulose was beginning to replace rag paper. These changes led to the end of the alum era in Sweden, with production ceasing entirely around the turn of the twentieth century. Production was based on alum shale as the major raw material. The shale was mined in opencast mines and then burned for as long as organic material remained in the shale (up to three months). High temperature in the heaps ($\sim 700^\circ\text{C}$) led to the production of sulphuric acid and iron oxide. The acid reacted with the silicate minerals in the shale and an alum salt was formed. The burnt shale was then leached with water to dissolve the alum salt and the leachate was concen-

trated by evaporation. The alum solution was then left for several days to cool, after which precipitated alum could be collected (Eklund et al., 1995, 1996).

3. Study area

Degerhamn is located in the southwest of the Swedish island of Öland and is a part of the municipality of Mörbylänga (Fig. 1). The village has a population of about 500. The major activities in the area are agriculture and limestone-based cement production. The bedrock of Öland consists of sedimentary rocks such as limestone, alum shale, sandstone and clay shale. As the bedrock layers slope to the east, the alum shale is only visible as the top rock layer in the southwest of Öland. The alum shale layer in Degerhamn is approximately 17 m thick. The total amount of alum shale in southwest Öland is estimated at approximately six billion tonnes (Andersson et al., 1985). The soil layer on top of the bedrock is thin in many places with the result that the alum shale is easily exposed to weathering processes.

In the Degerhamn area, alum shale has formed the basis for local industries. From the 18th century into the 20th century a huge amount of alum shale has been mined and burned on site for production of alum and lime (Eklund et al., 1995). This has led to a substantial change in the landscape topography, apparent as open-cast mines in the alum shale wall together with a large number of heaps of burnt and weathered shale.

The historical emissions from these industrial processes may still be influencing the environmental situation in the surrounding area through leaching of heavy metals from the heaps of burnt/weathered alum shale (Bergbäck et al., 1997). Furthermore, non-weathered

alum shale may be a significant source of metals if exposed to air and acidic rain.

4. Materials and methods

A number of analyses were carried out in order to study alum shale as a source of heavy metals. The studies focused on elemental analysis and leaching of alum shale as well as the spatial dispersal of metals in the area. Primarily Cd, Cu, Ni, Zn and As were studied.

4.1. Alum shale—metal concentrations and leaching test

4.1.1. Elemental analysis and pH determination of alum shale samples

Twenty-five different samples of non-weathered (NAS, $n=5$), weathered (WAS, $n=6$) and burnt (BAS, $n=14$) alum shale were collected from the area. A proportion of each sample was crushed and milled (Retsch centrifugal ball mill S 100) to a particle size of <0.25 mm. The milled samples were sent to XRAL Laboratories (Canada) for elemental analysis by ICP-MS after digestion (Mina and Mills, 2001), in which 1 g of the sample first was heated in 2 ml HNO_3 to 80–90 °C for 30 min. After cooling, 4 ml HCl was added and the sample again was heated for two hours. Determination of the pH of the milled shale samples was carried out according to Balsberg-Påhlsson (1990).

4.1.2. Leaching test and leachate analysis

The leaching test was based on a simplified column arrangement adapted to imitate the natural weathering

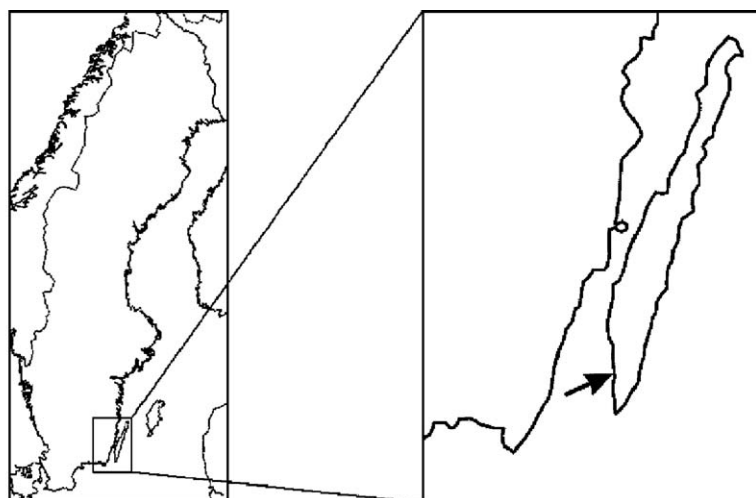


Fig. 1. The location of the study area Degerhamn, Sweden.

processes in alum shale. Twelve different samples of NAS ($n=3$), WAS ($n=3$) and BAS ($n=6$) were selected; 200 g of each sample were crushed and sieved to yield particles of suitable size (2 to 8 mm), which were placed in a 500 ml separation funnel fitted with a sintered glass filter in the bottom (Fig. 2). After one week the leaching procedure started, in which each sample was exposed to 200 ml milli-Q water, adjusted to pH 4.0 by addition of HNO_3 , for two hours on each occasion. The water was then tapped out and solids were removed from the leachate by filtration through fine-meshed filter paper and a Millipore filter (size 0.45 μm). Leachate pH was determined and 100 ml was acidified (conc. HNO_3) and sent to Analytica Laboratory in Luleå (Sweden) for metal analysis by ICP-AES/ICP-MS. The leaching process was monitored over a period of 36 weeks, during which 12 leachate samples were collected. For practical reasons, the time between leachings was gradually increased from one week to eight weeks (the time between leachings 1–4 was one week, between leachings 4–8 two weeks, between leachings 8–10 four weeks and between leachings 10–12 eight weeks). The Liquid (litres)/Solid (kg) ratio (the L/S ratio) thus increased during the leaching test from 1 to 12 l/kg. The L/S ratio describes the accumulated amount of liquid that has been in contact with the solid material. A leaching test thus describes a course of time while the L/S ratio increases with time

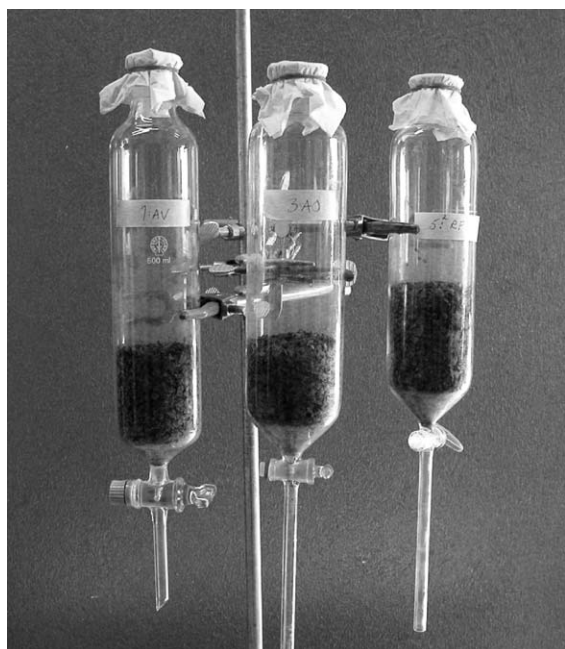


Fig. 2. Separation funnels used for the leaching test of alum shale.

as more water has infiltrated the solid material (Nordt-est, 1995).

4.2. Water analysis

4.2.1. Groundwater

Samples from six groundwater pipes (PEH, \varnothing 63 mm) were collected three times during autumn 2002; pH, temperature and conductivity were determined in situ (WTW pH/Cond 340i/SET). Water samples for metal analysis were filtered through a membrane filter (pore size 0.45 μm), acidified and sent to Analytica for metal analysis by ICP-AES/ICP-MS. For sample points, see Fig. 3.

4.2.2. Surface water

Surface water samples (from a total of 17 sample points) from areas close to alum shale walls and heaps with burnt alum shale were collected three times in spring 2002. To get the total amounts of metals transported, unfiltered water samples were taken, pH was determined in situ (WTW pH 330/SET) and the water samples were sent for metal analysis to Analytica. The samples were prepared by digestion in HNO_3 (2 ml for 20 ml water sample) in a microwave oven (50 min at 600 W in closed vessels) and then analysed by ICP-AES/ICP-MS. For sample points, see Fig. 3.

5. Results and discussion

5.1. Metal concentrations in alum shale

The metal concentrations in the different NAS (non-weathered), WAS (weathered) and BAS (burnt) alum shale samples are presented in Table 1.

The NAS in the area is, as expected, rich in metals compared to the average concentrations in the earth's crust. The variation in metal concentrations is, however, large even between only a few samples ($n=5$). For the samples of WAS and BAS, the Cd, Ni and Zn concentrations are significantly lower, though the variation is also great within these groups. On average, the WAS and BAS samples have Cd and Zn concentrations that are only 15–20% of those in NAS. For Ni, the corresponding figures are approximately 45–50%. Thus there are clear indications that during weathering and burning of alum shale, these metals are released from the shale structure. The different pH values also support the hypothesis of increased metal release when going from NAS to WAS or BAS samples. The high pH in NAS is probably due to high carbonate content.

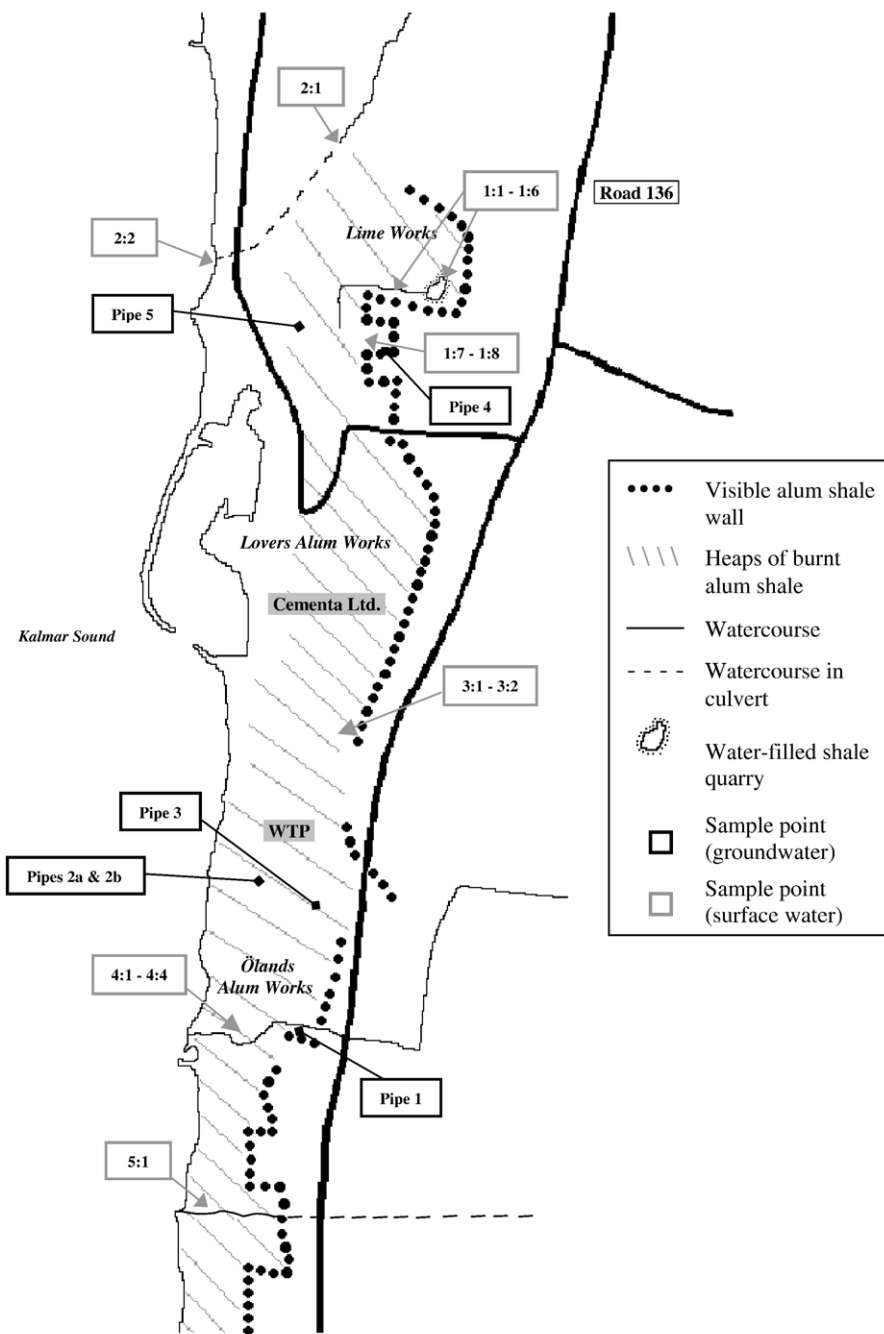


Fig. 3. Area map with historical activities and sample points, Degerhamn, Sweden.

During the weathering process of alum shale, as mentioned above, sulphuric acid is produced. A similar process, with production of SO_2 and H_2SO_4 , takes place when the shale is burnt. The low pH, caused by weathering or burning, probably facilitate the metal release from the shale. The pH of the BAS samples, however, varies from 3 to 9 due to the different histor-

ical activities where alum shale was used. High pH values are connected to areas with quicklime production, while alum production areas have a low pH.

For As and Cu, the release from alum shale during weathering or burning seems to be more limited, indicating that these elements are bound in more stable minerals and thus are less sensitive to changes in pH.

Table 1

Metal concentrations^a (mg/kg) and pH (min–max) in non-weathered (NAS), weathered (WAS) and burnt (BAS) alum shale from Degerhamn, Sweden

Sample	Cd	Cu	Ni	Zn	As	pH
	mg/kg					
NAS (<i>n</i> =5)	5.5 1.3–13	117 97–158	107 88–147	277 77–623	121 91–138	9.1–9.5
WAS (<i>n</i> =6)	1.1 0.4–1.9	100 51–140	52 20–81	43 16–65	75 54–112	3.1–5.4
BAS (<i>n</i> =14)	0.8 0.2–2.2	77 39–157	47 21–115	41 7.0–88	93 33–201	3.1–9.2
Average value in the earth's crust ^b	0.1	50	80	75	1.5	–

^a Top value indicates the mean value whereas the lower shows the interval.

^b After Enghag (2000).

5.2. Leaching test of alum shale

In order to analyse metal release and changes in pH related to weathering processes, a series of leaching tests was performed. Here pH 4.0 adjusted deionised water was used (cf. Methods). For NAS, a drastic drop in pH (from 8 to 3) was observed over the period (Fig. 4). Acid was apparently produced during the leaching process. The pH changes were accompanied by a significant release of Cd, Cu, Ni and Zn, especially after more than 8–12 weeks (Fig. 5).

Samples of weathered (WAS) and burnt (BAS) alum shale were also used in the leaching tests. Table 2 shows the release (in %) of metal from each sample during the test period.

For the NAS samples, the metals with the highest mobility were Cd, Ni and Zn (amount released 4–17%). Corresponding figures for Cu were 1–3%, while leaching of As was negligible. The changes in pH are, as shown earlier in Fig. 4, significant.

Metal release from WAS and BAS samples was generally very limited and the changes in pH were small. These samples have probably released most of their easily leachable elements during previous weathering or burning. There are, however, three exceptions: samples 1: WAS, 5: BAS and 6: BAS. In the first two samples, the pH was initially low and remained at the same level throughout the 36 weeks; the proportion of metals that leached out was very high. Here, buffering reactions with Al- and Fe-hydroxides may be of importance (Holmström et al., 1999), as indicated by high concentrations of dissolved Al and Fe in these samples. In the third sample (6: BAS) pH decreased from 7.4 to 3.3, mostly during the second half of the period. The

buffer capacity in this sample was probably exhausted during the initial leachings, resulting in an increased oxidation rate, acid production and release of metals to the leachate. This illustrates the heterogeneity found within the different shale samples from the Degerhamn area, with different degrees of weathering. In some areas the burnt shale is also mixed with lime residues from historical industrial activities.

The concentration of As in the leachates was low for all samples throughout the tests, probably due to retention in the mineral structure of sulphides, oxide minerals and hydrous metal oxides. Released As may also be adsorbed to the edges of clays and on the surface of calcite (Smedley and Kinniburgh, 2002). A higher As release was observed when unfiltered samples were analysed (on one of the 12 occasions), a behaviour also observed for Cu release. This indicates that As and Cu to a large extent are bound in, or at the surface of particles.

Since pH 4.0 adjusted deionised water instead of natural rainwater was used in this experiment, the leaching of metals was probably enhanced. Deionised water has a lower ionic strength than its natural analogue and is therefore likely to leach more strongly. This experiment thus does not give any indications of the time scales in the leaching under natural conditions. Further, only the size fraction 2–8 mm of the samples was used in the leaching experiment. This could also have affected the pace of the leaching, compared to natural conditions.

5.3. Analysis of water

Initial monitoring of groundwater and surface water in the Degerhamn area (Fig. 3) was also carried out with a limited number of samples and sampling occasions (*n*=3).

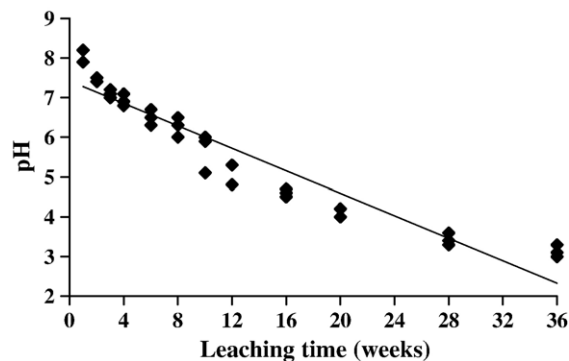


Fig. 4. Changes in pH in leachate from NAS samples after 1 to 36 weeks.

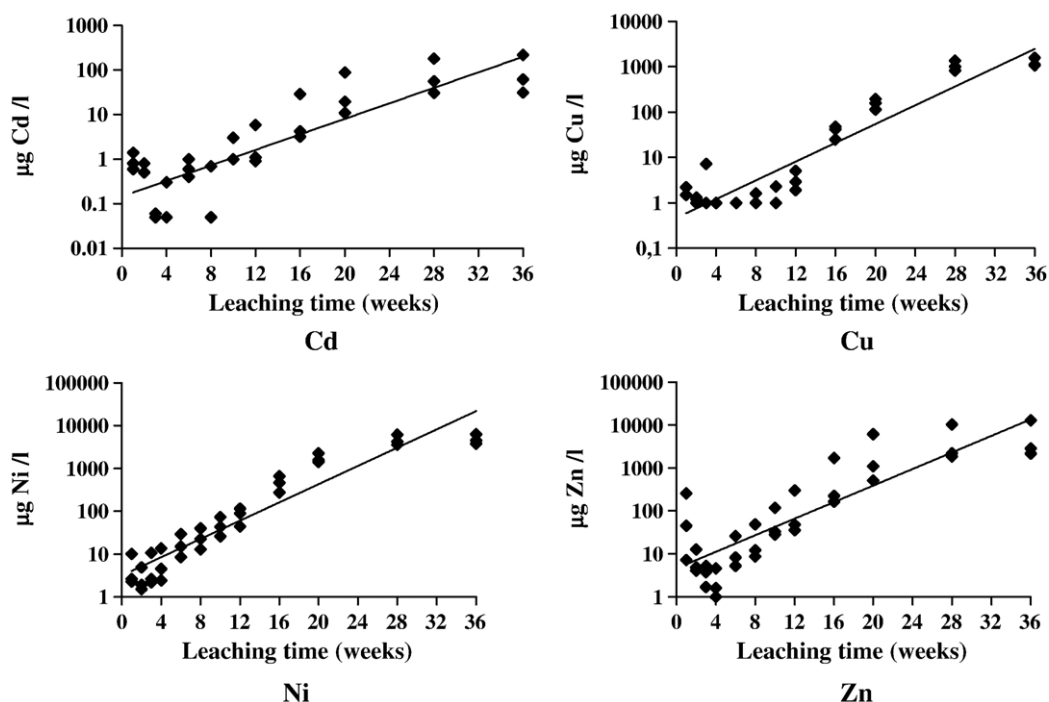


Fig. 5. Cd, Cu, Ni and Zn concentrations ($\mu\text{g/l}$) in leachate from NAS samples after 1 to 36 weeks. Logarithmic y-axis.

The metal concentrations in groundwater (Table 3) were, as expected, high when pH was low. Two samples with a pH of approximately 4.5 showed strongly elevated metal concentrations, and the conductivity was twice that of the other samples. Here the heaps consist of large amounts of slightly burnt shale, which facilitates the infiltration of both air and water, creating good conditions for weathering processes. The local wastewater treatment plant is situated in this area. The sewage

sludge is probably strongly affected by metals in the groundwater, infiltrating the old cement sewage pipes. In other sampled areas, the pH was approximately 7 and the metal concentrations were often low.

The watercourses are few and small in the Degerhamn area and all run dry in the summer months. The sampled surface waters, however, represent the existing local environments fairly well. Some of the watercourses discharge into Kalmar Sound in the Baltic

Table 2

The proportion of the metal content (%) leached out after a 36-week period for samples of non-weathered (NAS), weathered (WAS) and burnt (BAS) alum shale

Sample ^a	Cd		Cu		Ni		Zn		As		pH v. 1- v. 36
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	
1:NAS	1.3	6.2	98.8	3.2	92	17	77	6.5	137	0.03	7.9→3.0
2:NAS	13	4.0	158	1.5	147	6.5	623	5.1	115	0.04	8.2→3.3
3:NAS	2.1	6.9	114	1.8	108	9.8	114	5.7	138	0.05	8.2→3.1
1:WAS	1.8	28	109	12	80.6	7.1	65	26	91.7	0.05	2.6→2.9
2:WAS	1.9	1.4	108	0.09	71.9	1.6	32	3.8	102	0.01	4.2→3.8
3:WAS	1.5	1.3	135	0.1	52.5	0.4	60	0.8	54.3	0.05	4.5→4.5
1:BAS	0.87	0.3	81.5	0.06	50.4	0.1	35	0.4	52.7	0.3	8.0→7.2
2:BAS	2.2	0.2	105	0.06	115	0.02	79	0.2	171	0.4	7.2→7.3
3:BAS	0.65	1.5	77.6	0.05	53.2	2.5	24	1.2	39.6	0.1	7.5→6.4
4:BAS	0.27	0.9	39.3	0.05	21	0.2	7	4.2	33.3	0.06	6.2→5.5
5:BAS	1.0	39	157	28	51.4	46	88	24	156	0.4	2.5→2.2
6:BAS	0.48	4.8	62.7	0.7	33.2	5.6	20	5.3	80.6	0.01	7.4→3.3

^a For each sample, the original metal concentrations (mg/kg) and the change in leachate pH are given.

Table 3

Metal concentrations ($\mu\text{g/l}$, min–max), conductivity (cond., $\mu\text{S/cm}$) (min–max) and pH (mean) in groundwater, Degerhamn, Sweden. $n=3$, Autumn 2002

Sample	Cd	Cu	Ni	Zn	As	pH	Cond.
	$\mu\text{g/l}$						$\mu\text{S/cm}$
Pipe 1 (next to an alum shale wall)	<0.05	<1	0.5–1.0	4.3–13.1	<1	7.3	135–144
Pipe 2A (in a heap of burnt shale)	11.9–13.6	220–240	514–629	74–852	<1–10	4.6	225–249
Pipe 2B (in a heap of burnt shale)	18.2–18.7	362–382	831–862	1220–1300	<1–10	4.1	274–284
Pipe 3 (in a heap of burnt shale)	0.8–2.8	1.9–3.0	42.2–155	39.9–93.3	<1	7.2	150–250
Pipe 4 (next to an alum shale wall)	<0.05	<1–1050	3.3–4.0	6.0–12.8	<1	6.9	167–169
Pipe 5 (in a heap of burnt shale)	0.06–0.2	4.8–4.9	5.2–6.0	10.6–104	<1	7.2	103–109
Natural median value in Sweden ^a	0.03	0.8	2.2	17.0	0.1	–	–
Swedish threshold values for drinking water ^b	5	2000	20	1000	10	–	–

^a Aastrup and Thunholm (2001).

^b Swedish NFA (1989).

Sea (points 2:2, 4:1 and 5:1, see Fig. 3). The results in Table 4 indicate that the concentrations of Cd, Cu, Ni and Zn in the surface water in the area were generally increased compared to background values. For As, the concentrations were mostly below the detection threshold.

However, sample points 1:7 and 1:8, with the highest metal concentrations, differ considerably from the others, both in pH and size. Here a small countersink in the alum shale bedrock, where rainwater accumulates, seems to act as nature's own 'leaching test'. In total, the annual metal flows in these surface waters are small, mostly due to limited water flows.

6. Conclusions

Alum shale is relatively common worldwide. It is rich in metals fixed for example as sulphides or to organic substances like kerogen. During weathering processes acid is produced and metals are released from the solid to the solution phase. Oxygen and water are essential for these processes, while buffering substances counteract them. As indicated by this study,

release of metals from alum shale to recipients may be important.

In Degerhamn the shale is visible along the coast, facilitating the natural weathering processes. Furthermore, the burning of shale to produce alum has induced similar processes and metal flows. There has thus been both a natural and an anthropogenic environmental impact in the area.

The metal concentrations in non-weathered alum shale were much higher than in weathered or burnt shale, especially for Cd, Ni and Zn. This crude comparison alone indicates a loss of metals during weathering or burning of the shale. The release of metals through weathering was clearly demonstrated by the leaching tests. A 36-week leaching period of non-weathered shale resulted in a drastic drop in pH and a significant increase of the metal concentrations in the leachate. The proportions of metals released from the weathered and burnt samples were generally limited and the changes in pH small, probably due to steady state conditions. However, if the pH decreased or was initially low, metal release was also observed from these samples.

Table 4

Metal concentrations ($\mu\text{g/l}$, min–max) and pH (mean) in small watercourses, Degerhamn, Sweden. $n=3$, spring 2002

Sample	Cd	Cu	Ni	Zn	pH
	$\mu\text{g/l}$				
1:1 – 1:3 (Water-filled shale quarry)	<0.05–0.5	1.5–19.2	17.2–34.7	5.9–34.7	6.9
1:4 – 1:6 (Outlet channel from quarry, through burnt shale)	<0.05–0.08	1.6–3.9	16.2–22.3	4.7–22.7	7.6
1:7 – 1:8 (Small shale quarry)	0.3–0.8	10.5–37.6	26.3–53.8	10.5–98.3	3.5
2:1 – 2:2 (Runoff from cultivation area)	<0.05–0.07	2.9–6.3	0.6–3.7	<4–22.7	7.6
3:1 – 3:2 (Next to alum shale wall)	<0.05–1.1	1.0–7.3	12.2–54.5	8.1–55	7.4
4:1 – 4:4 (Runoff from cultivation area, through burnt shale)	0.08–0.3	2.6–6.4	5.6–26.8	5.8–32.7	7.8
5:1 (Runoff from limestone quarry, through burnt shale)	0.08–0.2	<1–1.6	3.6–10.5	5.5–6.7	7.8
Background conc. in small watercourses in southern Sweden ^a	0.016	0.5	0.4	2.0	–

^a Swedish EPA (1999).

To obtain an initial overview of the environmental state of the Degerhamn area, limited monitoring of ground and surface water was carried out. The metal concentrations in groundwater were high when the pH was low. These samples were collected in areas where the heaps consist of large proportions of slightly burnt shale, which facilitates the weathering processes. As the local wastewater treatment plant is situated in this area, the sewage sludge is probably strongly affected by metals in the groundwater, infiltrating the old sewage system. For surface water, the concentrations of Cd, Cu, Ni and Zn were generally increased compared to background values. Again, the metal concentrations were high when the pH was low. However, the annual metal flows in these surface waters are small, mostly due to limited water flows.

To conclude, metals are released through weathering or burning of alum shale as well as from heaps of weathered or burnt shale. The metal release is strongly related to pH, especially for Cd, Ni and Zn. For an environmental risk analysis of these metal flows, further data are required. An expanded study therefore begun in late 2003, including extended analyses of alum shale, groundwater and surface water and different leaching tests.

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