

## Water chemistry and trace metal concentrations in an acidic alum shale pit lake – effects of liming

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**Abstract** A former open pit where alum shale was mined during 1942–65 has been water filled since 1966. The water chemistry was dominated by calcium and sulphate and had a pH of 3.5 until 1997–98, when pH was gradually increasing. This was due to the intrusion of alkaline leachates from a dry part of the pit into the lake. A stable pH of around 7.5 was obtained after 6–7 years. The chemistry of the pit lake has changed due to the neutralisation. Concentrations of some dissolved metals, notably zinc and nickel, have gone down while other metals, notably uranium and molybdenum, still are present at elevated levels. Weathering of shale is still in progress despite the high pH.

**Key Words** Alum shale, pit lake, liming, neutralisation

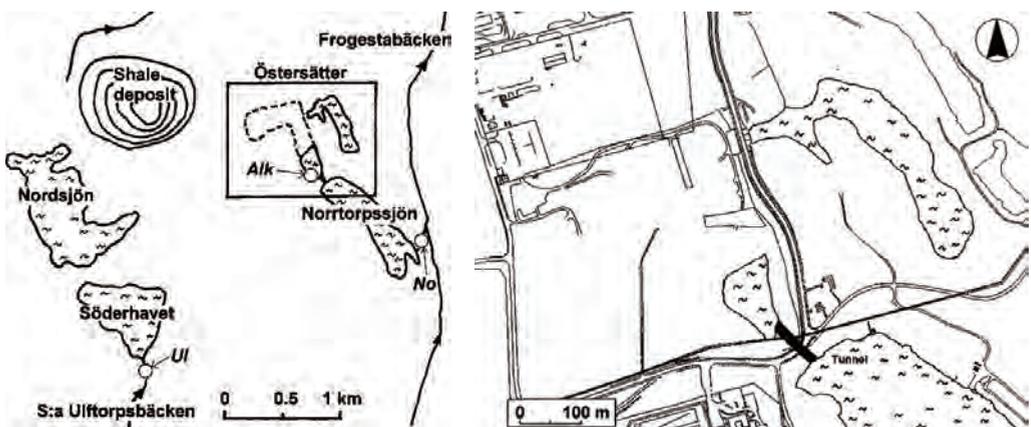
### Introduction

Alum shale was mined and processed for recovery of hydrocarbons in Kvarntorp, some 200 km SW of Stockholm, Sweden, during 1942–66. The shale that is of Late Cambrium age has an organic carbon content in the range 15–18 % and a sulphur content in the range 6–9 % (as metal sulphides), as well as a range of metals at trace levels, notably vanadium, molybdenum, uranium, rare earth metals etc. Remains from the mining is a deposit (height 100 m, diameter some 700 m) containing some 40 milj. m<sup>3</sup> crushed shale residues.

There are several large open pits in the area, most of them water-filled. One of the pits, the Östersätter quarry, was originally divided into two

parts connected by a tunnel under a road (fig. 1). After closure of operations around 1965 the tunnel was filled. The westerly part of the pit has been used as a deposit area for industrial waste, while the easterly part (lake Norrtorpssjön) was gradually filled with water from run-off and precipitation, as well as groundwater, partly penetrating through the filled tunnel from the westerly pit area.

Water quality has been monitored in the area, occasionally since 1970 and regularly since 1993, in the pit lakes, in surface run-off and rivers etc. By 1996 the lake water in Norrtorpssjön had reached a fairly constant composition in terms of concentrations of major ions and pH (in the range



**Figure 1** The Kvarntorp area (N 59°08', E 15°17') with the former Östersätter quarry – the partly water-filled westerly part and the completely filled easterly part, Lake Norrtorpssjön. Also Lake Nordsjön and Lake Söderhavet are pit lakes. Locations for water sampling are indicated: No: outlet from Lake Norrtorpssjön; Alk = alkaline leachate from the westerly part; Ul = surface water representing back-ground conditions

3.2–3.6). The low pH reflects the continued weathering of sulphides in the water exposed shale horizons that constitute the steep vertical shore lines of the lake.

In 1996 large volumes of alkaline residues from a local cement factory were dumped in the deposit area of the westerly part of the former pit, and dumping of alkaline residues has continued since then (Stenberg et al, 2002). There was a rapid response in terms of changes in pH and water composition in the easterly part of the pit, i.e. lake Norrtorpssjön. Evidently, the hydraulic contact between the westerly and easterly part of the pit, through the filled tunnel, allowed a transport of alkaline leachates from the, since the late 90-ies, partly water-filled westerly part into the lake. Thus, this has turned out to become a full-scale neutralisation experiment, although not at all planned.

The purpose of the present project is to analyse the neutralisation process and consequences in terms of changes in water chemistry and transport of metals from the weathering shale in the pit lake by draining rivers out of the mining area. Of particular interest are vanadium, molybdenum and uranium, since recovery of these metals from the shale and the processing waste has been considered.

**Methods**

Data from the monitoring program (regular sampling since 1993 plus a few data from the 70-ties) have been collected and analysed. A new water and sediment sampling program started in 2011. Water samples are analysed with respect to major dissolved components as well as trace elements originating from the weathering shale. Shale samples have been collected and analysed with respect to major components as well as some selected trace elements.

**The alum shale**

The Late Cambrium alum shale at Kvarntorp and in other regions in central Sweden typically con-

sists of K-feldspars (3–8%), illite (24–41%), chlorite (1–5%), calcite (1–4%), quartz (18–34%), pyrite (5–17%) and organic carbon (5–18%), as well as some other minerals (up to 8%) (Armands, 1972; Andersson et al, 1985).

Shale samples were taken from the vertical shore line in the northern part of lake Norrtorpssjön at different depths and were analysed by ICP-MS, after dissolution in strong acid (tab.1). Concentrations of organic carbon and sulphur (not analysed in the Norrtorpssjön samples) are reported to be in the range 15.2–17.7 % and 5.9–8.6 %, respectively (Assarsson and Grundulis, 1961). The upper level samples were dominated by CaCO<sub>3</sub> giving high levels of calcium (around 90 mol-% of the cations (tab. 5). The brownish middle level samples, as well as the black lower level samples, were rich in iron and aluminium, and particularly the lower level samples were poor in calcium. The composition of the middle and lower level samples are in fair agreement with the previously reported analyses of shale from the same pit.

The calcite-rich upper level samples also have high concentrations of strontium, while high levels of vanadium are observed for the middle and lower level samples (tab. 2). Also molybdenum is present at high concentration levels, as well as boron (not analysed in the Norrtorpssjön samples). Boron levels in the range 110–120 mg/kg have previously been reported (Andersson et al, 1985).

**The water of the pit lake Norrtorpssjön**

The water in Norrtorpssjön (fig. 1, tab. 3) is initially dominated by calcium and sulphate, close to saturation with respect to gypsum, and with pH in the range 3.2–3.4 (tab. 3). Additional cations are magnesium and sodium, as well as potassium at a lower level. The total concentration, as indicated by the conductivity, is about one order of magnitude above representative back-ground. There is no direct correspondence between the molar ratios in water and shale (tab. 1 and 5). Evidently the

**Table 1** Composition of shale from Lake Norrtorpssjön - major elements, besides oxygen (weight-%). Upper level samples: U-Ge and U-P3; middle level samples: M-Pb, M-Gb and M-P2; lower level samples: L-Gs and L-P1; previously reported concentration ranges: K-H (from Assarsson and Grundulis, 1961)

Sample	Si	Fe	Al	K	Ca	Mg	Ti	Na
U-Gc		0.64	0.84	0.40	30.8	0.26	0.046	0.011
U-P3	2.77	2.28	0.77	0.31	36.0	0.25	0.033	0.046
M-Pb	28.2	5.62	7.51	3.40	3.24	1.28	0.31	0.13
M-Gb		3.76	4.60	2.95	1.14	0.38	0.32	0.14
M-P2	27.5	7.36	8.83	2.68	1.23	1.98	0.60	0.40
L-Gs		2.45	5.06	3.28	0.43	0.35	0.34	0.14
L-P1	23.4	2.38	5.55	3.55	0.12	0.40	0.36	0.18
K-H		5.6-7.9	5.8-7.2	2.7-3.4	0.36-1.5	0.46-0.77	0.35-0.48	0.15-0.41

**Table 2** Composition of shale from Lake Norrtorpssjön - minor elements (mg/kg).

Sample	As	Cd	Co	Cr	Cu	Li	Mo	Ni	Pb	Sr	U	V	Zn
U-Gc	9.8	0.62	2.7	6.2	20	4.1		17	320	260	61	49	64
U-P3	32		4.2	19	23		60	39	14	300	31	51	68
M-Pb	32		4.9	42	36		110	34	20	62	77	320	58
M-Gb	25	0.82	5.1	40	38	21		47	37	94	71	420	36
M-P2	43		15	73	52		2.3	53	26	36	3.0	110	120
L-Gs	26	0.40	1.9	22	16	24		26	38	82	61	460	11
L-P1	32		1.2	36	15		170	12	17	62	53	300	46

**Table 3** Water concentrations - major components (mg/L), and conductivity (mS/L). Average values per year based on 2–4 samples, usually from February – April and August – October (from Kumla kommun, 1994–2009). Samples from the outlet of Lake Norrtorpssjön are denoted No-year, Ulfstorsbäcken, representing back-ground, Ul-year and the alkaline leachate Alk

Sample	pH	Cond	K	Ca	Mg	Na	Sr	ΣCO <sub>3</sub>	Cl	SO <sub>4</sub> <sup>2-</sup>	Fe	Al
No-93	3.2	220	22	480	98	52		0	30	1700	3.6	2.0
No-94	3.4	220	30	460	95	60		0	30	1650	2.8	1.9
No-96	3.25	240	33	460	99	66	1.7	0	34	1700	2.1	1.3
No-97	3.15	220	31	530	94	57	1.7	0	33	1750	2.9	1.2
No-98	4.0	290	32	490	87	58	1.7	0	36	1850	0.63	1.0
No-99	4.85	280	30	490	83	55	1.5	<1	40	1650	0.13	0.73
No-00	6.4	230	30	450	77	56	1.6	5.6	42	1600	0.23	0.27
No-01	6.5	250	32	520	72	54	1.6	15	46	1400	0.16	0.025
No-02	7.15	250	34	560	72	58	1.5	24	57	1450	0.12	<0.003
No-03	7.25	250	34	490	67	57	1.9	31	64	1500	0.085	0.015
No-04	7.5	250	35	510	64	59	1.8	41	59	1500	0.19	0.025
No-05	7.55	250	31	490	57	58	1.8	49	62	1450	0.13	0.075
No-06	7.4	210	34	420	46	61	2.1	57	59	1100	0.079	0.0013
No-07	7.7	220	31	410	44	59	1.9	68	79	1400	0.14	0.0030
No-08	7.55	240	31	410	51	60	1.9	73	83	1400	0.18	0.0065
No-09	7.7	240	29	430	46	58	1.8	81	87	1250	0.071	0.0023
Ul-09	7.8	24	2.4	41	1.6	5.6	0.053	87	12	20	1.0	0.14
Alk	12.0	470	170	490	0.3	240	0.028	(<0.1)	240	(1800)	0.19	0.052

upper shale layers contribute with calcium, while the middle layers may contribute with magnesium and potassium, and the lower layer with potassium in particular. Both sodium and potassium exhibit larger mole fractions in the water than in any of the shale samples.

The intrusion of alkaline solutions into the lake that started in 1996 led to a gradual increase in pH during 1998–2005 when present levels in the range 7.5–7.8 were reached (tab. 3) with a corresponding increasing level of alkalinity from pH around 5 and above. The volumes of alkaline leachates from the deposit entering into the lake are not estimated. However, the chloride concentration has increased by a factor of three since 1998, which indicate the gradually increasing fraction of the leachates in the lake water. The decrease in magnesium concentrations by a factor

of two may also be an indication of the increasing fraction of leachates rather than a reduced weathering rate of the exposed shales in the lake. The sodium concentrations are almost at the same level since 1993, while there is a reduction of the calcium levels by some 20% since 1998.

The concentrations of metals, associated with sulphide (pyrite) in the shale, are high in the water until the intrusion of alkaline water started in 1997 (tab. 4). This is particularly the case for zinc and nickel, as well as to some extent lead and cadmium. The concentration decreases with increasing pH. This can be due to a reduced weathering rate at high pH, but more likely to the adsorption of these metals on solid surfaces, notably on the precipitating iron and aluminium that decrease in concentration in solution with increasing pH.

The levels of lithium decrease in a similar way

**Table 4** Water concentrations – minor elements ( $\mu\text{g/L}$ ). Denotations as in tab. 3

Sample	As	B	Cd	Co	Cr	Cu	Li	Mo	Ni	Pb	U	V	Zn
No-93	2.1	230	1.1		1.0	4.0	360		130	1.9	71	16	140
No-94	0.5	220	0.65		0.65	3.4	360		110	1.3	83	<5	84
No-96	<0.6	220	0.53	27	0.45	3.4	350	<0.2	84	1.8	54	9	120
No-97	<0.6	220	0.49	26	0.35	4.3	330	0.15	81	1.2	53	16	88
No-98	0.32	220	0.36	10	0.28	2.3	390	0.95	67	0.32	46	0.45	64
No-99	0.65	240	0.31	19	0.15	1.1	480	1.0	55	0.25	29	<1	51
No-00	0.45	230	0.25	15	<0.2	1.2	390	2.5	49	0.45	10	<1	30
No-01	0.85	160	0.19	9.1	0.50	0.95	260	3.4	32	0.85	4.8	1.3	19
No-02	0.45	180	0.12	2.4	0.25	0.65	330	4.5	19	0.45	11	0.75	14
No-03	0.70	170	0.070	0.90	0.45	0.55	270	5.7	13	0.70	11	1.3	4.5
No-04	0.95	220	0.055	0.56	0.60	1.4	320	7.8	8.4	0.15	16	1.1	5.0
No-05	0.80	220	0.080	1.3	1.8	0.95	220	9.1	8.3	0.8	17	1.3	7.0
No-06	<0.5	210	0.34	0.76	<0.6	4.3	240	9.1	15	<0.5	20	<0.5	5.4
No-07	0.82	240	0.11	2.3	0.30	1.3	220	8.9	9.1	0.050	25	<0.2	7.0
No-08	0.71	240	0.058	1.6	0.081	1.7	230	9.1	31	0.083	32	0.051	7.6
No-09	0.40	220	0.022	0.76	0.095	0.93	220	9.0	11	<0.04	26	<0.05	2.4
Ul-09	1.4	12	0.033	0.39	0.43	2.1	<50	2.7	1.3	0.23	4.9	1.3	2.2
Alk	9.0		0.63	0.77	9.8	2.7							

as magnesium, which is an indication of the increased fraction of alkaline leachates in the lake. However, the almost constant levels of boron, coming from the shale, and the levels of molybdenum, increasing with pH as expected for an anion ( $\text{MoO}_4^{2-}$ ), indicates a progressing weathering of the shale despite the increasing pH. The constant levels of boron and strontium, not coming from the intruding leachates, are clear indications of a continued weathering of the shale also at high pH in the lake.

Levels of arsenic are low, both in the initial acidic state as well as after neutralisation. The reduction of arsenic with increasing pH may reflect the presence of a precipitating scavenging iron phase. Levels of chromium, which would be anionic, are low during the whole period.

The concentrations of uranium are high at low pH, which illustrate the high leachability of this metal. Concentrations in solution decrease with

increasing pH, as expected for a cationic hydrolysable species ( $\text{UO}_2^{2+}$ ), but reaches a minimum around pH 6.5 and then increases with pH. This illustrates the formation of the neutral carbonate complex, and also possibly a fraction of the anionic dicarbonate in solution. Also molybdenum (anionic, as  $\text{MoO}_4^{2-}$ ) levels are increasing with pH.

#### Processes behind the release of metals

The release of major elements and associated minor components from the shale, and the evolution of an acidic water in the pit lake, illustrates the natural weathering of the shale, largely driven by the oxidation of the sulphides (pyrite). The acidic leachates are to some extent neutralised by the dissolution of calcium carbonates present primarily in the upper layers. There are no indications of a congruent dissolution, as would have been indicated by similarities in molar ratios be-

Sample	Fe	Al	K	Ca	Mg	Ti	Na
U-Gc	1.4	3.7	1.2	92.2	1.3	0.1	0.1
U-P3	4.1	2.9	0.8	90.9	1.0	0.1	0.2
M-Pb	16.4	45.4	14.2	13.4	8.6	1.1	0.9
M-Gb	18.2	46.0	20.4	7.7	4.2	1.9	1.6
M-P2	19.7	48.8	10.2	4.6	12.2	1.9	2.6
L-Gs	12.4	53.0	23.8	3.0	4.1	2.0	1.7
L-P1	14.4	55.0	24.3	0.8	4.4	2.0	2.1
No-93/97	0.3	0.3	3.8	62.0	20.4		13.2
Alk	<0.1	<0.1	16.1	45.2	0.1		38.6
No-06/09	<0.1	<0.1	5.2	68.0	9.9		16.9

**Table 5** Composition of shale and water – major metals (% of  $\mu\text{mol/kg}$  and % of  $\mu\text{mol/L}$ ).

**Table 6** Composition of shale and water – minor elements (% of  $\mu\text{mol}/\text{kg}$  and % of  $\mu\text{mol}/\text{L}$ ).

Sample	As	Cd	Co	Cr	Cu	Mo	Ni	Pb	U	V	Zn
U-Gc	2.5	0.1	0.9	2.3	6.0	(12)	5.5	29.2	4.9	18.1	18.5
U-P3	9.0	0.1	1.5	7.7	7.6	13.2	13.9	1.4	2.7	21.1	21.8
M-Pb	3.8	0.1	0.7	7.2	5.1	10.2	5.2	0.9	2.9	56.0	7.9
M-Gb	2.6	<0.1	0.7	5.9	4.6	(9)	6.1	1.4	2.3	63.2	4.2
M-P2	7.1	0.1	3.1	17.3	10.1	0.3	11.1	1.6	0.2	26.5	22.6
L-Gs	2.7	<0.1	0.2	3.3	1.9	(14)	3.4	1.4	2.0	69.8	1.3
L-P1	4.2	<0.1	0.2	6.7	2.3	17.4	2.0	0.8	2.2	57.4	6.8
No-93	0.5	0.2	8.9	0.3	1.1	<0.1	40.6	0.2	5.8	5.1	37.3
No-08/09	1.7	0.1	5.1	0.6	3.8	17.7	32.0	0.1	21.3	0.2	17.4

tween shale and water (tab. 5 and 6). There is no apparent pattern in terms of element ratios in the solid shale matrix that are preserved as concentration ratios in solution. An exception may be cadmium that is associated with zinc. The enhanced fraction of calcium in solution would be result of the dissolution of calcium carbonate. The high proportions of sodium, but low of potassium, illustrate the incongruent character. Thus, the release process can not be deduced solely from analysis of the pit lake water.

The release of vanadium is low both initially and after neutralisation, which may illustrate the behaviour of a metal that is cationic in the whole pH-range, and not primarily associated with sulphides. Molybdenum may be associated with sulphides, but the anionic molybdate would be adsorbed on positively charged surfaces at low pH and only desorbed at pH above the point of zero charge. The release of uranium is not primarily associated with the oxidation of sulphides. The high levels observed after neutralisation indicates the formation of neutral or anionic species, which is probable considering the alkalinity, above 1 mM (total carbonate). This may, in fact, indicate a higher rate of release from the shale at high pH than at low pH.

Concentrations of vanadium are presently at back-ground levels, while concentrations of molybdenum are above back-ground by a factor of three (and about one order of magnitude above average back-ground). The uranium levels are above back-ground by a factor of five and 1–2 orders of magnitude above back-ground levels in surface water from areas where the bed-rock is free from discrete uranium mineralisation.

### Conclusions

The somewhat arbitrary deposition of highly alkaline industrial waste from 1996 and onwards in the westerly part of the former pit close to the water-filled pit lake Norrtorpssjön has led to a neu-

tralisation of the lake water from around 3.5 to 7.5 over a period of some 6–7 years. This has led to significant changes in water chemistry, however still dominated by calcium and sulphate.

Cationic metals that are present at high concentrations at low pH, particularly zinc and nickel, and to some extent lead and cadmium, decrease in concentration with increasing pH. This decrease is likely to be the result of adsorption on exposed solid surfaces, including on precipitating iron and aluminium phases.

There are no firm indications that the rate of weathering of the shale that is exposed in the pit lake is reduced due to the increase in pH from 3.5 to 7.5. The acid that is released due to oxidation of sulphides and hydrolysis of ferric iron is efficiently neutralised. Released metals are likely to be deposited on the bottom of the lake instead of being transported out as dissolved species. Levels above back-ground levels of particularly molybdenum, nickel and uranium are observed also at the high pH that has been established in the lake

The question whether the rate of weathering and release of metals from exposed shale is affected by the change of pH is not fully answered. The weathering rate as a function of pH is presently studied as a continuation of this project that so far has been focussed on field measurements.

Another issue that will be followed-up is the pH-dependence of the uranium concentration in solution. Uranium is one of the few trace metals in the out-flow from the pit lake that is present at levels significantly above representative back-ground concentrations, the others being molybdenum and nickel (as well as boron, lithium and some of the major elements; c.f Förstner and Wittman, 1981; Allard, 1995).

### Acknowledgements

The authors thank Kumla municipality for access to data from the water monitoring program, as well as

access to the pit lake for sampling of shale and water for analysis. The assistance in field work and analytical work in the present phase of the project by V Sjöberg, A Grandin and L Karlsson is gratefully acknowledged.

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