



# Chemistry of Acidic and Neutralized Alum Shale Pit Lakes 50 Years After Mine Closure, Kvarntorp, Sweden

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## Abstract

Several large pits were left after alum shale was mined from 1942 to 1966 in the Kvarntorp area of Sweden. Of these, the pit lakes Pölen and Norrtorpssjön are the focus of this study. They have elevated levels of Na, K, Mg, Ca, Al, Mn, Fe, and sulphate, as well as trace elements, from weathering of the exposed shale. Both lakes had a stable pH below 4 until 1996 when the pH in Norrtorpssjön started to increase, exceeding 8 in 2010, due to inflow of leachates from alkaline waste dumped in an adjacent waste deposit, similar to a large scale anoxic limestone drain (ALD). Iron and Al concentrations decreased as the pH increased, indicating formation of particulate species which accumulate as sediments. The Co, Ni, and Zn concentrations also decreased, probably due to association with the solid phases, while Cu was less affected by the increase in pH, possibly due to formation of complexes with dissolved organic matter. Vanadium concentrations show limited solubility, while Mo concentrations increased at higher pH. Uranium concentrations decreased from above 80 µg/L to below 10 µg/L before rising to 30–35 µg/L due to the formation of soluble carbonate complexes at higher pH levels. The elevated levels of Li, Sr, and U indicate that weathering has continued despite the pH change. Both pit lakes are stratified, but no seasonal overturn has been observed. Long-term behaviour of this large-scale ALD and its implications are also discussed.

**Keywords** Weathering · Leachate · Sediment · Vanadium · Molybdenum · Uranium

## Introduction

Alum shale (black shale), composed of muscovite-illite, quartz, and feldspar, with up to 15% pyrite and about 20% kerogene, is found in Kvarntorp some 200 km west of Stockholm, Sweden, N 59° 07', E 15° 17' (Andersson et al. 1985; Armands 1972). The crystalline basement in the area is covered by Lower Cambrian sandstone, Middle Cambrian green shale (mudstone), and on top, Upper Cambrian alum shale, up to 19 m thick (Bengtson 1971). There is also a layer of Ordovician limestone above the alum shale in the southern part of the area, but since the bedrock is dipping 0.5–1%

towards the south, the limestone cover thins to the north (Hessland and Armands 1978).

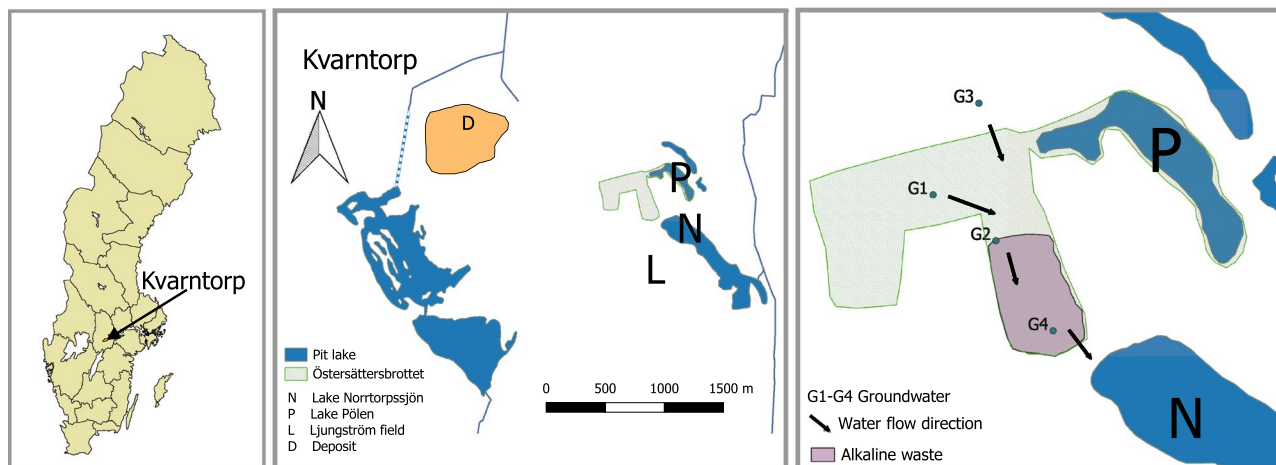
The shale has been subject to exploitation due to its content of up to 20% hydrocarbons (Andersson et al. 1985), as well as its high content of trace elements such as V (500 g/t), Mo (200 g/t), Ni (200 g/t), and U (150 g/t) (Hessland and Armands 1978). Large-scale mining of shale from open pits and production of oil started in 1942 and lasted until 1966. There was also small-scale recovery of U during the 1950s to test various separation processes that might be suitable for future large-scale operations. Residues from the oil production were deposited on site in some of the pits. Also, a total of ≈ 40 million m<sup>3</sup> of crushed and processed shale was put in the deposit with a final height of 100 m and a diameter of 700–800 m (Fig. 1). Most of the oil was produced by pyrolysis of the crushed shale and condensation of the gaseous phase. Oil was also extracted by heating the shale in situ using electrodes inserted through the limestone layer down into the alum shale (the “Ljungström method”, Sundqvist 1956). Hydraulic conductivity in the shale horizon was probably therefore increased.

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**Fig. 1** Location of Kvarntorp and the pit lakes in the area

The largest pit in the eastern part of the area is Östersättersbrottet, with the connected pits Alaborgsbrottet and Norrtorpsbrottet, now water-filled lakes (Pölen and Norrtorpssjön, Fig. 1). Large-scale mining started in the early 1960s in Östersättersbrottet, but was already occurring in the mid-1940s in open pits north and west of this area. Recovery of oil in situ started about the same time at the Ljungström field south of the area. Mining ended (north and west) in the late 1950s, and these areas were mainly backfilled with shale residues in the western area. The Ljungström field was closed in 1960, and large-scale mining in the major pit Östersättersbrottet ended in the mid-1960s. Since 1983, there has been a large industrial facility for treatment of hazardous waste at the Ljungström field site, and the Östersättersbrottet pit has, since 1985, been used to deposit industrial and municipal waste, as well as alkaline waste in the southern part of the deposit during 1996–2001 (Stenberg et al. 2002). The two pit lakes east and south of Östersättersbrottet, Pölen and Norrtorpssjön (Fig. 1), have been water-filled since the early 1970s.

Both the virgin alum shale and the residues from processing are potential sources of metals. Acid generation from weathering of the alum shale and similar materials containing pyrite, as well as neutralization by carbonates and silicate minerals, are well known and documented processes (e.g. Allard et al. 1991; Bäckström 2010; Chi Fru et al. 2016; Jaynes et al. 1984; Jeng 1991; Karlsson et al. 2012a, b, 2013; Lavergren 2008; Nicholson et al. 1988, 1989; Peng et al. 2004; Pihlak et al. 1985; Puura 1998; Puura et al. 1999; Ritsema and Groenenburg 1993; Scherlock et al. 1995). The two pit lakes in this study are in contact with the same shale horizon, which is subject to weathering and generation of acidic rock drainage (ARD) with a pH of 3.2–3.6. Figure 2 shows the alum shale profile at the northern shore line of



**Fig. 2** Photo showing the shale horizon at the northern shore of Norrtorpssjön

Norrtorpssjön. Shale in this horizon contains several strategic metals, such as V (420–450 g/t), rare earth elements (120–150 g/t), Mo (60–110 g/t), U (55–125 g/t), and Ni (30–55 g/t), besides Co, Cu, Zn, Cd, Pb, etc. at lower levels (Allard et al. 2014).

Lake Pölen has had a near-constant pH below 4 since the early 1970s, while a gradual increase in pH was recorded in Lake Norrtorpssjön, from less than 4 in 1996–97 up to 7 in 2003, and exceeding 8 in 2010–12. The pH increase was caused by leachate flowing into the lake through the alkaline waste that had been deposited in the southern part of Östersättersbrottet in 1996–2001 (Allard et al. 2011, 2014; Karlsson et al. 2012b), based on analysis of data from a monitoring programme that has been operated by the municipality since 1993 (Kumla kommun 1993–2017). Sampling

and analysis of water and sediments started in 2011 and has continued since 2015 in both lakes. The aim of this study was to further elucidate the processes in the eastern and southern pit lakes.

Worldwide, pit lakes display diverse water chemistry conditions. In many places, ARD causes pit lakes to have bad water quality. Bioremediation with municipal sewage and green waste (McCullough and Lund 2011), surface fertilization (Fisher and Lawrence 2006), and hydrogeochemical modelling to evaluate the potential efficiency of dilution, limestone treatment, and biological neutralization (Nixdorf et al. 2010) have been investigated. Yet another method is the use of anoxic limestone drains (ALDs), where crushed limestone neutralizes the ARD under anoxic conditions to prevent clogging by metal precipitation (e.g. Genty et al. 2012; Watzlaf et al. 2000). In the case of Norrtorpssjön, there was no planned remediation, but the dumping of alkaline waste resulted in a large-scale ALD, from which insight into remediation of this kind of lakes can be gained.

## Materials and Methods

### Sampling of Water and Sediments

Pölen (surface area 31,000 m<sup>2</sup>, depth 5–15 m) is mainly drained via the central landfilled section of Östersättersbrottet and into Norrtorpssjön, which also receives shallow groundwater from the area. Norrtorpssjön (surface area 167,000 m<sup>2</sup>, depth 5–10 m, with a 30 m deep section reaching down to the sandstone layer) drains into a small creek in the southern part of the lake. The water flow from Östersättersbrottet to the lake is  $\approx 175$  m<sup>3</sup>/day, i.e.  $\approx 63,000$  m<sup>3</sup>/year. Precipitation in the area is  $\approx 570$  mm/year (Kumla kommun 1993–2017). Average water flow from Norrtorpssjön to the creek is  $\approx 169,000$  m<sup>3</sup>/year, which indicates a total water exchange time of  $\approx 20$  years.

Water has been sampled regularly at the outlet of Norrtorpssjön since 1993 in a monitoring programme run by Kumla municipality (Kumla kommun 1993–2017). Reference samples have also been collected upstream of the area. Two groundwater wells were installed in the landfilled deposit area between Pölen and Norrtorpssjön in 2007, as well as a reference well upstream of the landfilled zone, at the mine site in the 1940–50s (G1, G2, and G3, Fig. 1). Sampling of groundwater has been carried out twice a year. Water was also sampled in the southern part of the deposit area in 2011 (G4, Fig. 1).

Water was sampled by Örebro University in both lakes during campaigns in 2011–12 and in 2017, when water was retrieved from different depths at the northern, middle, and southern part of Norrtorpssjön and from the western and middle part of Pölen. Regular sampling has

been conducted since 2015 at the outlet of Norrtorpssjön (monthly or every second month) and twice during 2017 in Pölen. Some samples were filtered (polycarbonate, 0.45  $\mu$ m), and some parameters were measured in the field (pH, Eh, electrical conductivity (EC) and temperature). Equipment used in the field was calibrated at the beginning of each field day. Samples for element analysis were acidified with HNO<sub>3</sub> to pH < 2. All samples were kept at 5–6 °C until analysis.

Sediments were sampled at several points in the two lakes in 2011 and 2017. Samples LN 20, LN 40, and LN 160 are from the northern part of Norrtorpssjön, LN 320 is from the middle, and LN 725 is from the southern part of Norrtorpssjön, while LP 45 is from the western part of Pölen and LP 255 from the middle part (Tables 2, 3). Water was sampled at various depths at the same points down to the maximum depth of the lake (28 m at one location). Sediment layers on top of the bedrock are thin and it was thus not possible to retrieve sediment cores. The samples from Norrtorpssjön in 2011 were recovered by means of a bottom sampler according to Van Veen (stainless steel, 250 cm<sup>2</sup>; Hydro-Bios) and from both lakes in 2017 with an Ekman dredge. The samples were dried at 30–35 °C until constant weight.

### Chemical Analyses

Water samples from the campaigns in 2011 and 2017 as well as from the regular monitoring programme since 2015 were analysed with respect to pH (Metrohm 6.0257.000 with temperature compensation), alkalinity/acidity (titrated with 0.02 M HCl or 0.02 M NaOH, respectively), EC (Radiometer CDC836T-6, with temperature compensation), elements (Al, As, B, Ca, Cd, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Mo, Ni, Sr, U, V, Zn; ICP-MS, Agilent 7500cx) and anions (Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>; HP<sup>3D</sup>CE, capillary electrophoresis, using sodium chromate buffer, 50 mM, containing TTAB 5 mM and a 40 cm  $\times$  50  $\mu$ m silica capillary). Samples from the monitoring programme run by Kumla municipality (Norrtorpssjön 1993–2017 and groundwater 2007–17) were analysed at certified laboratories (Kumla kommun 1993–2017).

The sediment samples were fused with borate flux in a high temperature controlled muffle furnace to analyse major elements, and the resulting beads were dissolved in dilute mineral acid. Trace elements were digested in aqua regia or in a 4-acid digestion (by MS Analytical). Elements were analysed by ICP-OES (Al, Ca, Fe, K, Mg, Mn, Na, and P) or ICP-MS (As, Cd, Co, Cu, Mo, Ni, Pb, U, V, and REE), and total sulphur and carbon by a Leco carbon and sulphur analyser. Analytical quality was verified by comparison with certified reference materials.

## Results and Discussion

### Water Chemistry: Major Components

Groundwater, with contribution from Pölen, flows from the north through Östersättersbrottet into Norrtorpssjön (Fig. 1). Groundwater from the area north of Östersättersbrottet (G3) is acidic due to the presence of weathering shale residues, just like the water from Pölen. Groundwater from the western area (G1) also passes through shale processing waste, but the pH is near-neutral due to the presence of limestone and construction waste in the landfill. Water flows through the deposit towards the southern end (G2), largely without contact with shale residues, but finally reaches the section with alkaline waste (G4), where a visible mirror of water was observed on the surface during the 2011 sampling. Thus, the water reaching Norrtorpssjön is a mixture, with contributions from weathered shale, limestone, and alkaline waste, surface water, and possibly original groundwater from the sandstone layer beneath the shale. There is also a diffuse flow of water from the Ljungström field, and flooding events have been recorded at least twice after heavy rain episodes (2006 and 2015).

Major components (anions and cations) are given in Fig. 3a, b and summarised in Table 1, which shows the composition in the sequence LP–G3–G1–G2–G4–LN from 2011 and 2017 (LP and LN denoting water from Pölen and Norrtorpssjön, respectively), as well as from 1994 (LN), one of the earliest measurements in the area. Shale weathering determines the water character in LP and G3, giving a Ca–SO<sub>4</sub>–water with a pH below 4. The balance between cations changes as the water flows through the pit (G2), and pH increases to near-neutral. There was not enough buffering capacity in the inflow to Norrtorpssjön in 1994 to neutralize the acid generation. However, after 1996, the alkalinity from the alkaline waste (G4) led to a gradual pH increase in the lake up to a near-neutral pH after 5–6 years, reaching a maximum level of 8.1 in 2011–13, and then decreasing slightly to 7.8 in 2017–18 (Fig. 3a). Given that a large part of the water reaching Norrtorpssjön passes through buried alkaline waste, a plausible reason for the buffering capacity is that the deposited alkaline waste might be working as an ALD. The anoxic conditions prevents precipitation reactions that might otherwise disable the functionality of the alkaline material (Watzlaf et al. 2000). The pH in Norrtorpssjön decreases from 7.8 to around 6.7 with increasing depth, while it increases with depth, from 3.3 to around 6.0, in Pölen.

Redox potentials were in the range of 260–310 mV down to a depth of 6 m in Norrtorpssjön (all sampling points), as expected for oxic conditions. This is below the

$Eh = 800 - 60 \times pH$  that has been suggested for water in equilibrium with air (see e.g. Garrels and Christ 1965) but is in fair agreement with the reported field measurements by Rai et al. (1980), who gave  $Eh = 730 - 55 \times pH$ . The redox potentials at depths of 8–10 m and below were generally in the range of 40–130 mV in Norrtorpssjön, and down to 20 mV in Pölen, corresponding to  $Eh = 1100 - 150 \times pH$ . This indicates anoxic conditions and that the potential at depth may be determined by the Fe<sup>2+</sup>/Fe(OH)<sub>3</sub>(s)-system (Pourbaix 1974), which is in fair agreement with what can be assessed from the measured iron concentrations vs. depth (Fig. 3c).

Sulphate concentrations are high (around 1300 mg/L or above) in all waters coming from the shale zones (LP, G3, LN) with a pH below 4 and are also high in G4, but may be decreasing or levelling out with time in Norrtorpssjön.

Alkalinity (total carbonate) is high in G1 and G2, but close to zero in G3 and Pölen (pH below 4) as well as in Norrtorpssjön until 1999–2000; thereafter, the alkalinity increased with increasing pH. Total carbonate level reached a maximum of  $\approx 100$  mg/L in 2011–13, and decreased the following years to around 80 mg/L in 2017, parallel to the decrease in pH.

Chloride concentrations ranged from 150 to 200 mg/L, in G1, G2, and G4 in 2010–12, but decreased with time to less than 100 mg/L, which may reflect the gradual depletion of Cl<sup>−</sup> from waste materials in the landfill, including municipal waste. The levels in Pölen and G3 are around 20 mg/L or below. Chloride from the landfill has reached Norrtorpssjön where concentrations increase with time, from ca 30 mg/L in 1994 to 150 mg/L in 2017, as well as with depth to above 250 mg/L in 2017. Some Cl<sup>−</sup> contribution may also be the result of intruding water from the Ljungström field (Svensson et al. 2005), where Cl<sup>−</sup> concentrations of up to  $\approx 300$  mg/L have been recorded in a groundwater well in the northern part of the area. There is no similar increase in Cl<sup>−</sup> concentrations in Pölen.

The Na concentrations are below 30 mg/L in Pölen and G3, but are increased in Norrtorpssjön by the contributions from G1, G2, and G4 in particular (Fig. 3b). The levels of K are similar to the Na levels but are not increasing in Norrtorpssjön. The Ca concentrations are fairly uniform in all of the waters, in the range of 300–500 mg/L except for G2, where the concentrations are less. Concentrations of Mg are high in G3, which may explain its high concentration in Norrtorpssjön in 1994, of  $\approx 100$  mg/L, decreasing with time and reaching 40 mg/L in 2017, similar to what has been recorded in Pölen.

Concentrations of Na, Mg, and Ca increase somewhat with depth in Norrtorpssjön, like the Cl<sup>−</sup>. Both lakes display similar Mg depth profiles, while Norrtorpssjön has higher concentrations of Ca, as well as strontium (Sr) than Pölen at all depths (see below and Fig. 3f). There are no data

**Fig. 3** Concentrations in water of selected components. Left: groundwater from the western part of the pit 2007–17; middle: water from Norrtorpssjön 1993–2017 and Pölen 2017; right: depth profiles from Norrtorpssjön and Pölen 2017: **a** pH, carbonate, sulphate, chloride; **b** Na, K, Mg, Ca; **c** Fe, Al, Mn; **d** Co, Ni, Cu, Zn; **e** V, As, Mo, **f** Li, Sr, U. The change of pH with time in Norrtorpssjön **a** is given as a reference in all of figures **b–f**

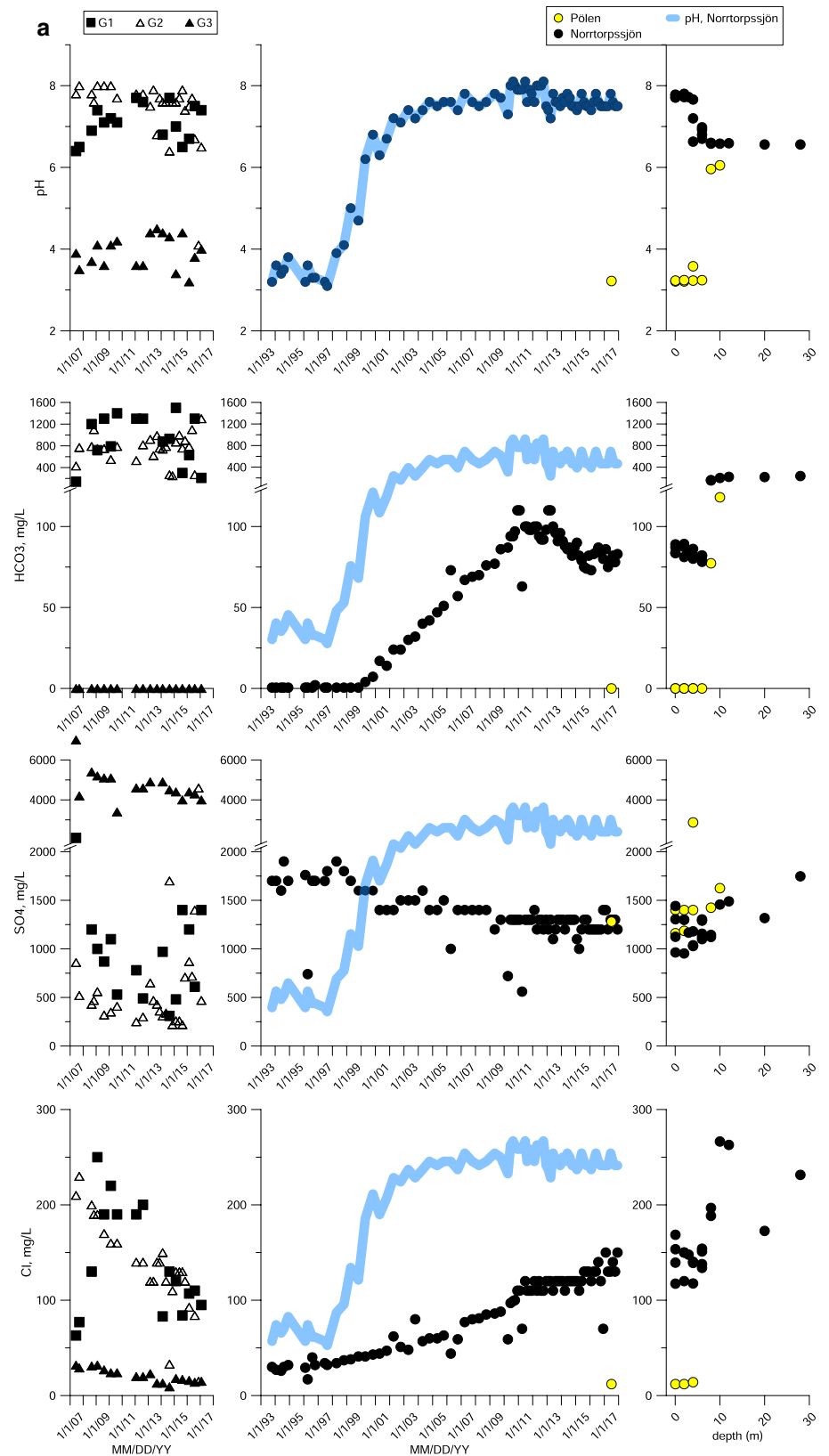


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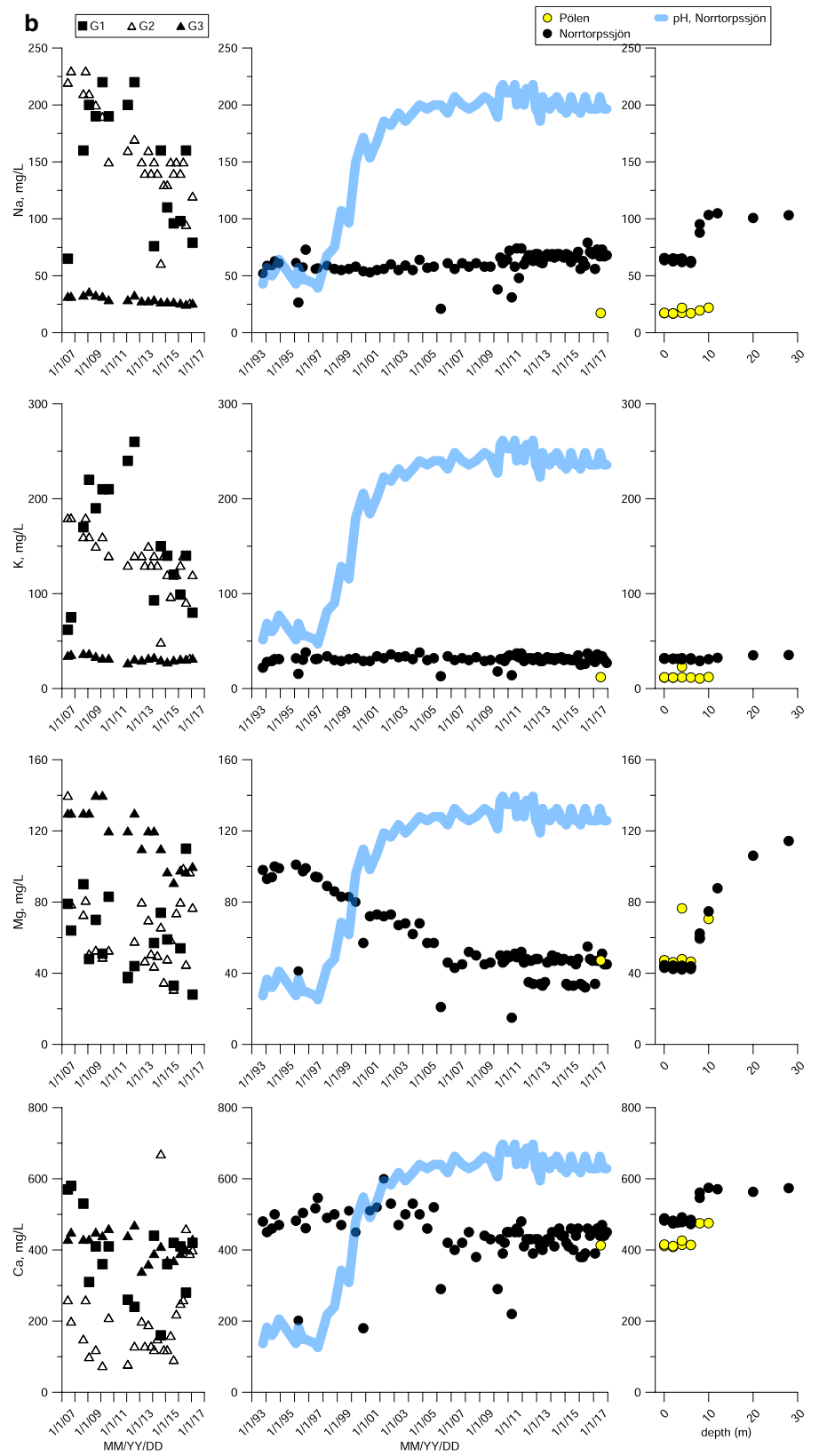
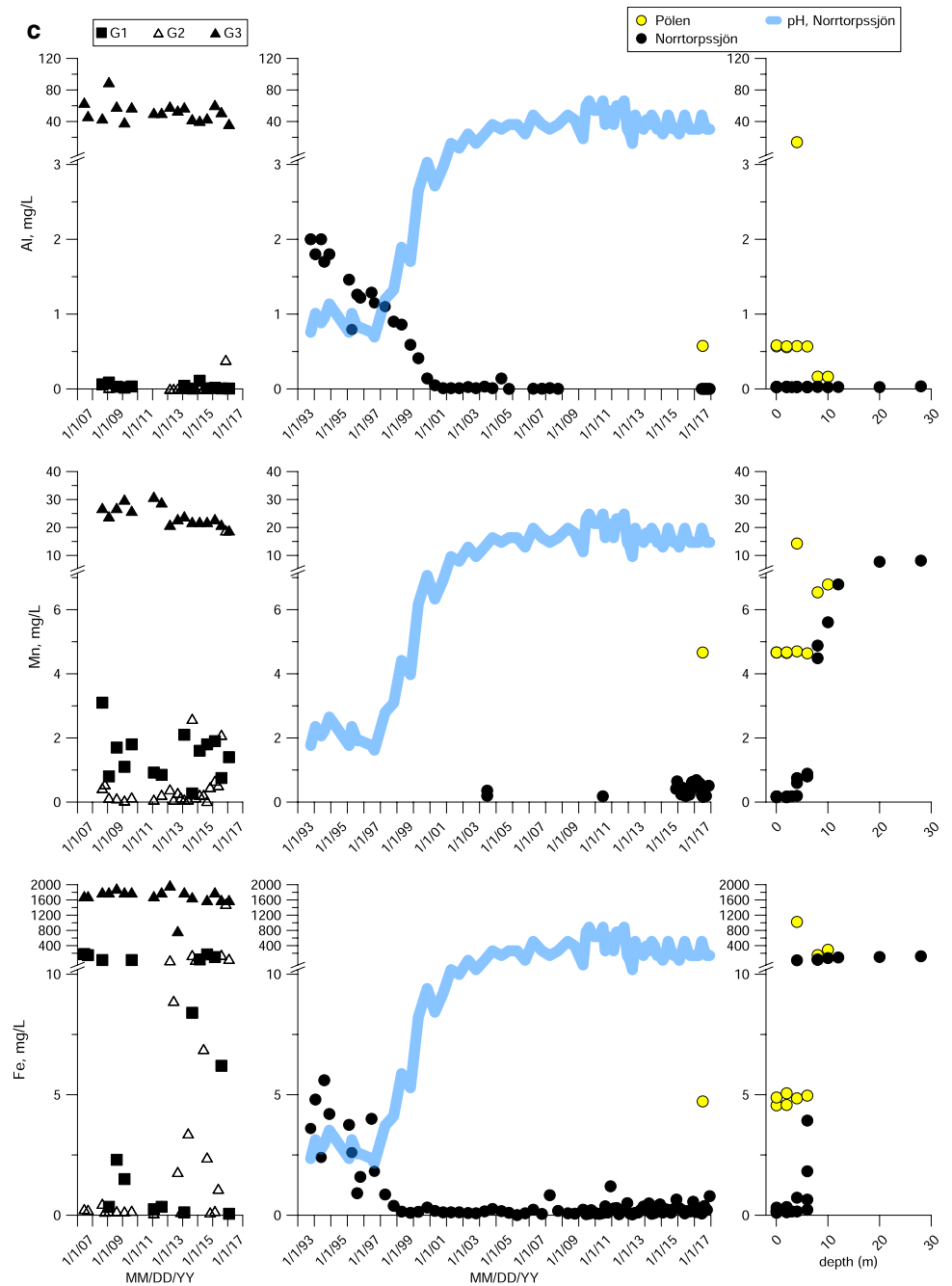


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available for these elements in the sandstone groundwater or in the intruding water from the Ljungström field. Calcium and sulphate concentrations in both Pölen and Norrtorpssjön indicate saturation, or even oversaturation, with respect to gypsum. The total carbonate concentrations in Norrtorpssjön, as well as the Pölen water at depth, indicate saturation with respect to calcite.

Iron (Fe) concentrations in the acidic water in G3 are in the range of 1600–1700 mg/L, indicating reducing conditions and the presence of Fe(II) (Fig. 3c). Concentrations of Al and Mn are  $\approx 50$  and 25 mg/L respectively, in G3. It is likely that the high Al concentrations upstream decrease due to precipitation as the water reaches the deposit and higher pH; both G1 and G2 had low Al concentrations. As the Al

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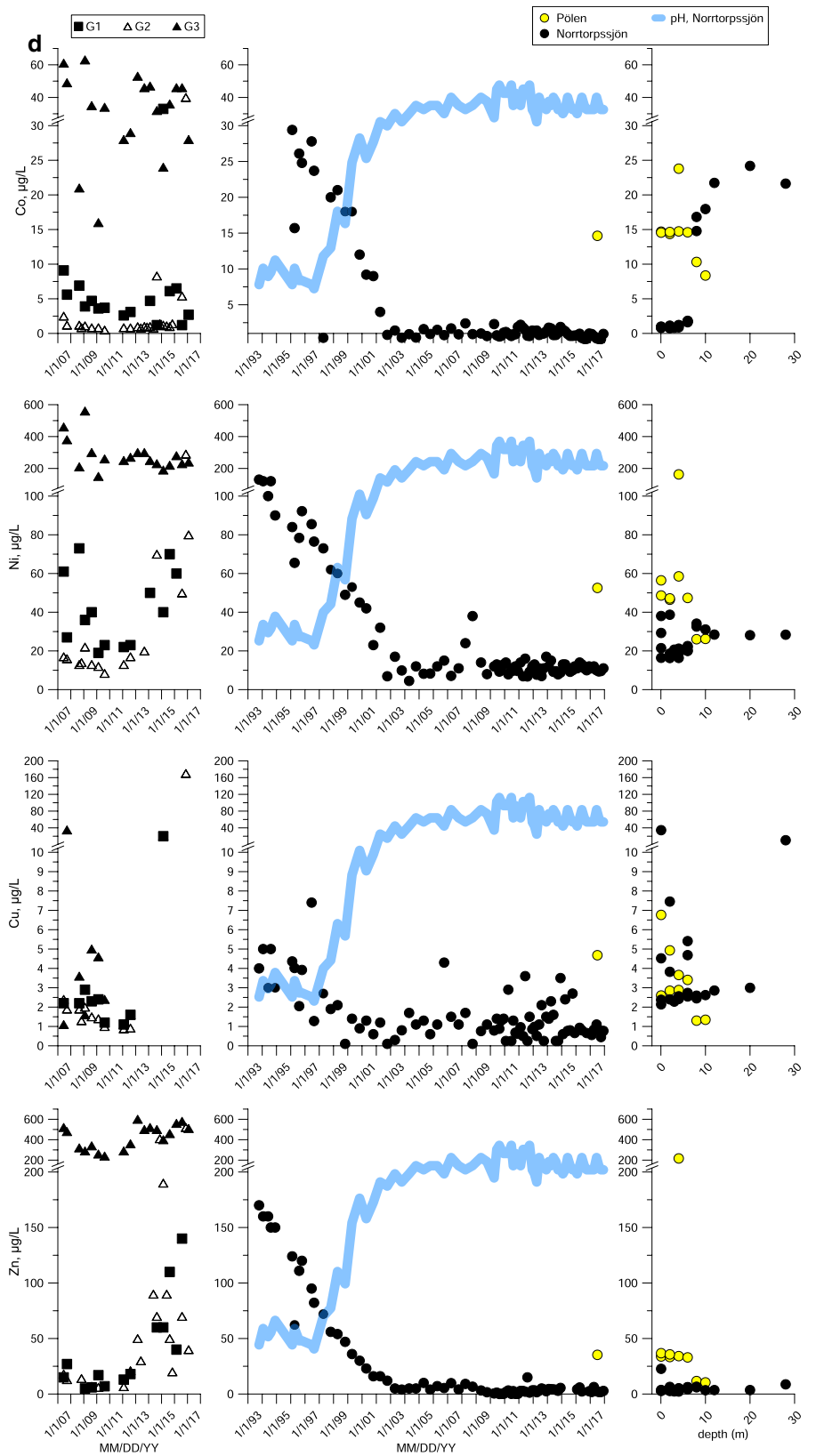




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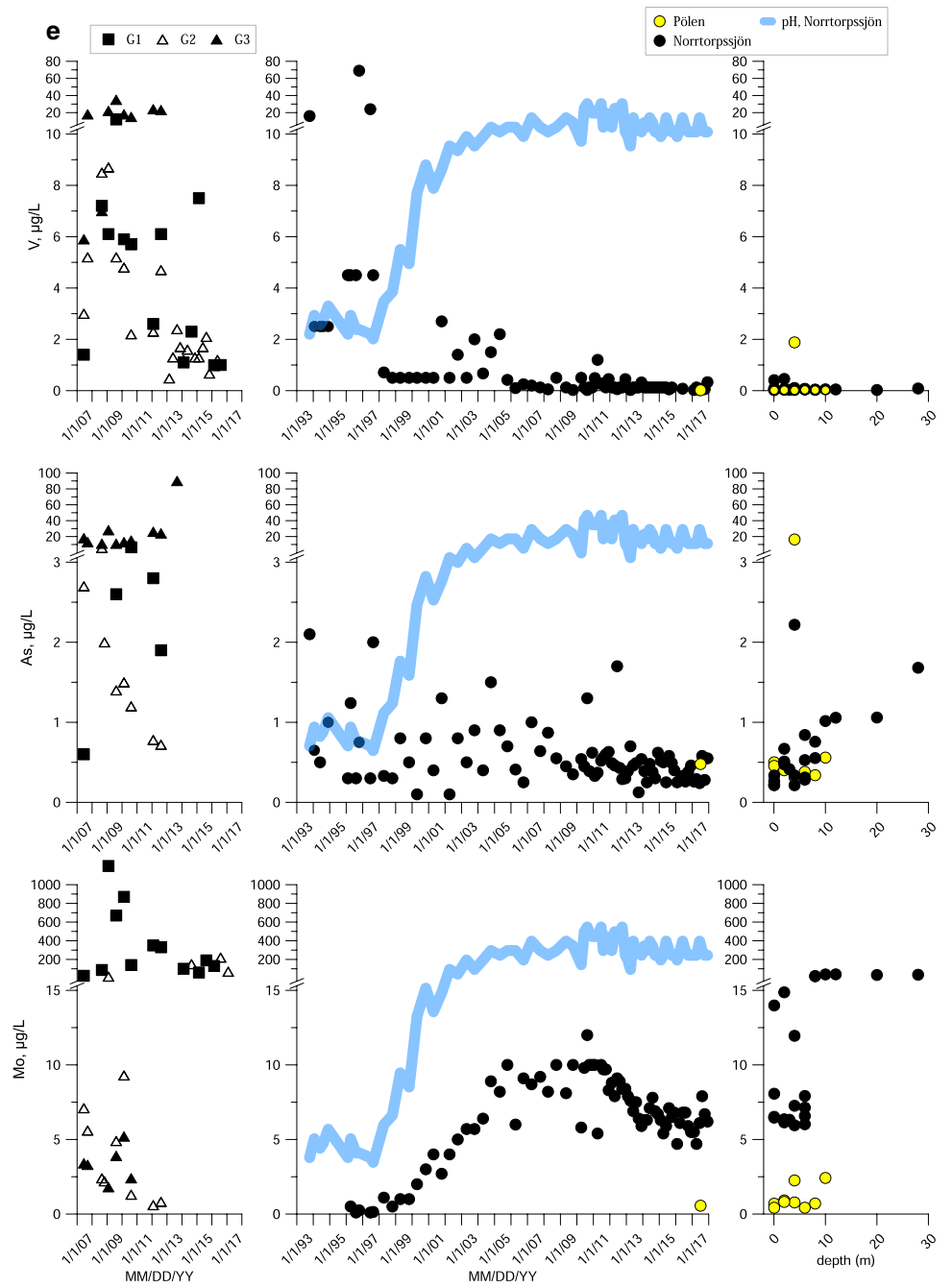
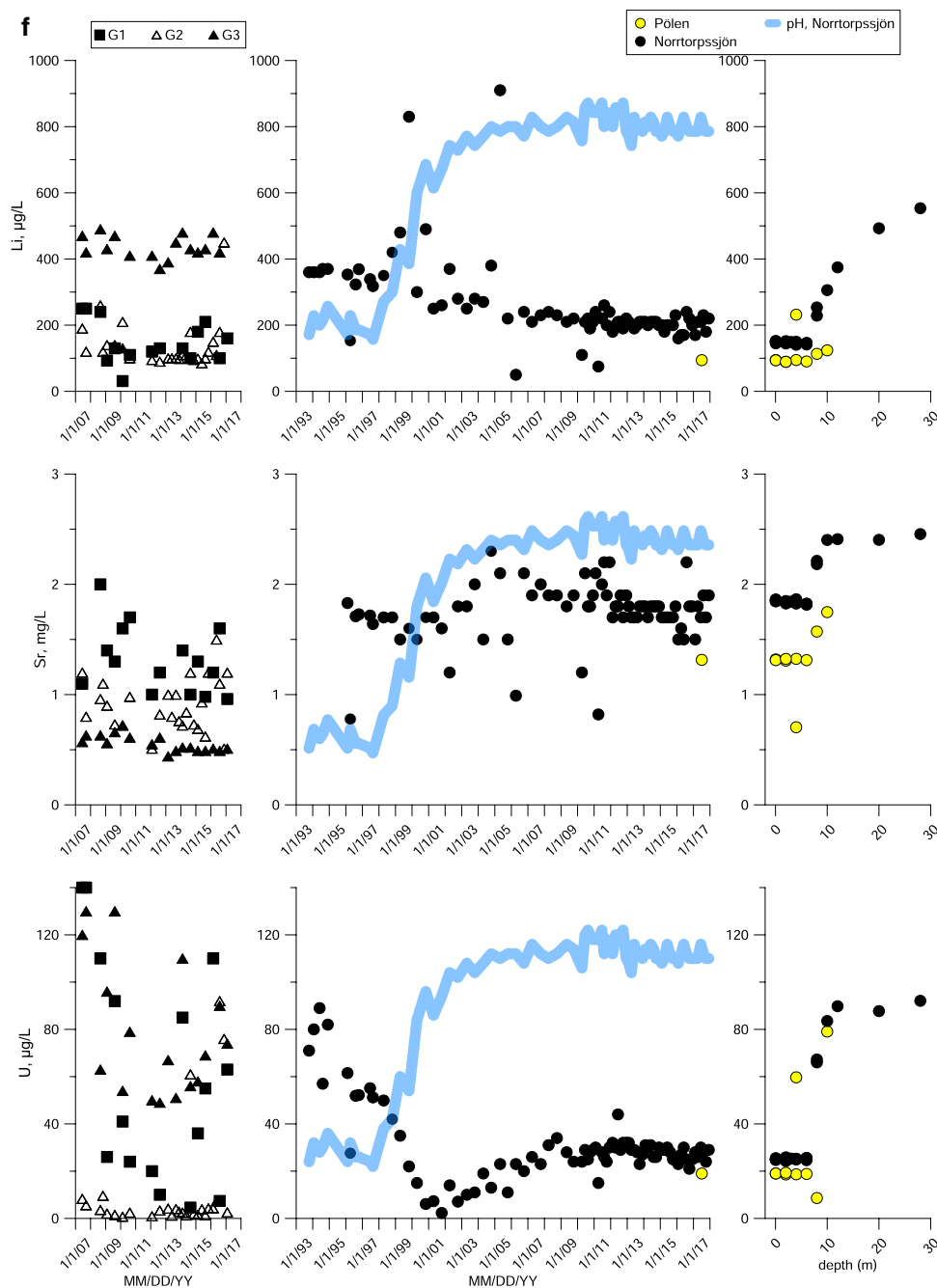


Fig. 3 (continued)



concentrations are already low when the water reaches the alkaline waste area, coating of the alkaline material or clogging is avoided. This might otherwise have prevented the alkaline waste from working as a long-term buffer (Watzlaf et al. 2000). Iron concentrations were  $\approx 5 \text{ mg/L}$  in Pölen and were  $\approx 5 \text{ mg/L}$  in Norrtorpssjön during the acidic period, but decreased to less than  $0.5 \text{ mg/L}$  as the pH increased to 6. Simultaneously, Al concentrations were reduced from

$2 \text{ mg/L}$  in Norrtorpssjön under acidic conditions to less than  $0.05 \text{ mg/L}$ . Manganese concentrations were in the range of  $4\text{--}5 \text{ mg/L}$  at all recorded pH values. The drastically reduced concentrations of dissolved Fe and Al in Norrtorpssjön, despite the fact that there is still a source of Fe and Al to the lake, indicate precipitation of the sparingly soluble Fe(III)-phases, notably ferrihydrite and at low pH, schwertmannite,

**Table 1** Concentrations (mg/L) of major components and pH in the Östersättersbrottet pit lakes Pölen (LP), Norrtorpssjön (LN) and in shallow groundwater from the deposit area of the pit (G1, G2, G3, G4)

	LN 1994	LP 2011	G3 2011	G1 2011	G2 2011	G4 2011	LN 2011	LP 2017	G3 2017	G1 2017	G2 2017	LN 2017
pH	3.2	3.2	3.8	7.4	7.7	12	7.4	3.2	4.0	7.4	6.5	7.8
Na	66	16	29	195	155	240	62	17.2	26	79	120	56
K	33	6.9	29	225	135	170	29	12	32	80	120	28
Mg	99	40	120	60	45	0.3	47	47	100	28	77	34
Ca	460	334	450	335	145	490	415	413	430	420	400	390
Cl <sup>-</sup>	34	11	22	190	150	240	110	12	15	95	95	150
SO <sub>4</sub> <sup>2-</sup>	1700	1410	4000	655	330	1800	1350	1280	4000	1400	470	1400
HCO <sub>3</sub> <sup>-</sup>	0	0	0	1350	660	n.a.	99	0	0	210	1300	86
DOC	n.a.	0.3 <sup>a</sup>	8	73	35	< 10	n.a.	n.a.	36	33	14	2

Years: 2011 (average 2010–12) and 2017, as well as 1994 (only LN)

<sup>a</sup>Grawunder et al. (2014)

and eventually goethite, as well as Al phases like boehmite, diaspore, gibbsite, and possible alunite.

There is a significant increase of Fe and Mn concentrations in the water with increasing depth in both lakes, which may result from a partial reduction of Fe(III) and desorption/dissolution of associated Mn species. The observed concentrations would, however, also include any suspended colloidal fraction that remains after filtration (0.45 µm filter).

### Water Chemistry: Minor Components

The concentration profiles of divalent trace metals with the highest concentrations in the leachate from weathering shale are given in Fig. 3d (Co, Ni, Cu, and Zn), and concentrations of elements sensitive to changing redox potential are given in Fig. 3e (V, As, and Mo) and 3f (U). Cobalt, Ni, and Zn exhibit similar changes in concentrations, i.e. high concentrations at low pH in Norrtorpssjön, ca 30, 130, and 175 µg/L, respectively, and decreases in concentrations by up to two orders of magnitude with increasing pH. Concentrations in the in-flow (LP-G3-G1-G2) are higher than in the neutralized Norrtorpssjön, indicating that a great fraction of these hydrolysable metals become associated with solid phases that are either suspended in the water phase or have settled. The concentration profile of Cu shows a similar

pH-dependence, with concentrations around 5 µg/L at low pH but a less evident reduction with increasing pH. This is possibly an indication of Cu affinity for dissolved natural organic matter leading to the formation of soluble complexes with organic ligands. Dissolved organic carbon (DOC) has not been regularly included in the monitoring programme operated by the municipality (1993–2017). However, DOC was measured in G1 and G2 (33 and 14 mg/L, respectively), in 2017 (Table 1), which may indicate and confirm the presence of organic waste material in the deposit. The concentration in G3, 8 mg/L of DOC (2010–12), is similar to the range of 6–9 mg/L in surface waters and shallow groundwater in the region (Kumla kommun 1993–2017). Lower levels are observed in the two lakes in 2011 (Pölen) and 2017 (Norrtorpssjön), respectively (Table 1). The dissolved organic matter, expected to be mostly natural hydrophilic acids (humic and fulvic acids), would have some impact on the speciation of Cu, as well as on the trivalent rare earth elements with total concentrations in the range 50–75 µg/L (Karlsson et al. 2012b).

Vanadium is enriched in alum shale with concentrations above 420 g/t. Concentrations in the groundwater samples, however, are not higher than 20–40 µg/L (G3), or below 4–5 µg/L, with some exceptions, in Norrtorpssjön at low pH,

and reduced to levels below 0.5  $\mu\text{g/L}$  with increasing pH. This indicates that the V in the shale has a limited solubility and is possibly incorporated as V(III) in suspended Fe(III) phases in the water. Leaching tests have shown that oxidative treatment of the shale can increase V solubility to a limited extent (Åhlgren et al. 2018). Other studies have confirmed that V mobility is limited in environmental systems and that desorption/dissolution from e.g. mine tailings and soil is relatively small (Yang et al. 2014).

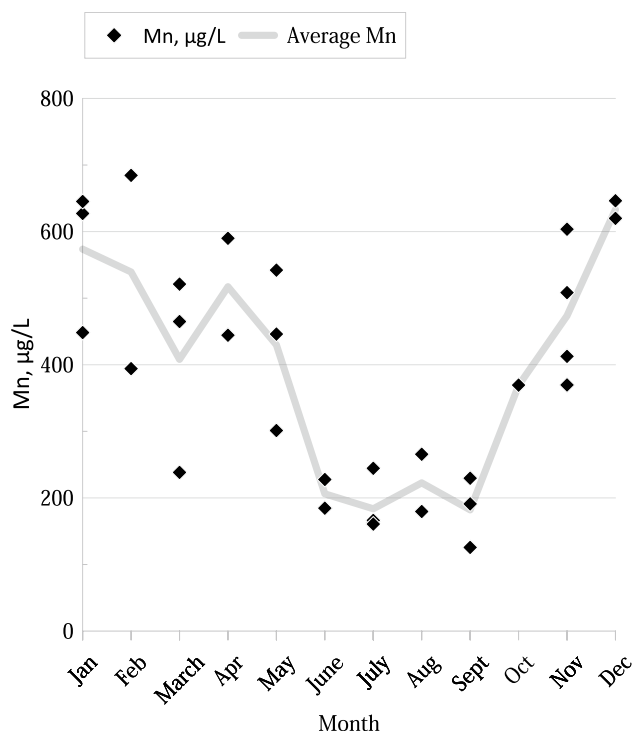
Arsenic would be penta-valent under oxic conditions and associated with any solid Fe(III)-phases in the system. Concentrations as high as 10–30  $\mu\text{g/L}$  were found in G3, but were less than 2  $\mu\text{g/L}$  in both lakes at low pH. Concentrations decrease to less than 0.5  $\mu\text{g/L}$  with increasing pH in Norrtorpssjön.

Molybdenum exhibits an evident pH-dependence, with concentration below 1  $\mu\text{g/L}$  at low pH in both lakes, but as high as 20  $\mu\text{g/L}$  in G3, and in the range of 700–1200  $\mu\text{g/L}$  in G1, 2009–10. Maximum concentrations of  $\approx 10$   $\mu\text{g/L}$  are recorded at a pH above 8, going down to 7  $\mu\text{g/L}$  at present pH of 7.8 at depth down to 4–6 m. The concentration increased with depth from 8 m and below in Norrtorpssjön, giving a maximum level of 40  $\mu\text{g/L}$  (Fig. 3e). This does not reflect a change of oxidation state, since Mo will be hexavalent, but may indicate that Mo under oxic conditions is associated with a suspended phase that disappears under reducing conditions, possibly Fe(III). The high levels in G1 groundwater from the deposit area is most likely not originating from the shale but from the industrial waste in the area.

Uranium concentrations (Fig. 3f) are around 80–90  $\mu\text{g/L}$  in Norrtorpssjön at low pH. Uranium is hexavalent (uranyl,  $\text{UO}_2^{2+}$ ) and behaves like divalent hydrolysable metals with decreasing concentrations with increasing pH, like Co, Ni, and Zn. Dissolved concentrations increase with pH above 6, which could be due to the formation of soluble carbonate complexes (c.f. Saleh et al. 2018; Stewart et al. 2010), reaching a final concentration of 30–35  $\mu\text{g/L}$  at pH above 7. Concentrations in Pölen are less than in Norrtorpssjön and G3, which might indicate differences between the two lakes in addition to the influence of the deposit. Possibly, Pölen is not in contact with the uppermost alum shale layer with the highest U content, considering the dipping of the bedrock with the shale layers towards the south. The concentrations in the groundwater samples vary from 2  $\mu\text{g/L}$  (G2) up to 140  $\mu\text{g/L}$  (G1). Similar to Mo, the U concentrations increase with depth in both lakes.

## Weathering

It has previously been discussed whether the weathering rate decreases with increasing pH or if it continues at the initial rate (Allard et al. 2014). Some elements could be used as



**Fig. 4** Seasonal variations of the manganese concentration in Norrtorpssjön outlet 2015–18

indicators of the weathering rate, since they are predominantly associated with the shale and not from the waste or the general surface water background. Lithium and Sr appear to be suitable as indicator elements (Fig. 3f). Lithium concentrations above 400  $\mu\text{g/L}$  have been recorded in G3, and from 400  $\mu\text{g/L}$  (low pH) to presently around 200  $\mu\text{g/L}$  in Norrtorpssjön, compared with the background in regional surface waters of less than 10  $\mu\text{g/L}$ . Strontium concentrations of 1.5–2 mg/L in Norrtorpssjön, at low as well as high pH, and similar levels in Pölen, are at least one order of magnitude above the regional surface water background below 0.1 mg/L. The Sr concentrations are high enough that precipitation of celestine ( $\text{SrSO}_4$ ) can be assumed, as indicated from calculated ion products. This can explain the low Sr concentrations in G3 (0.5 mg/L) where the sulphate concentrations are 4–5 g/L. Also, U is an obvious indicator element, and the present concentrations in both lakes are significantly higher than regional surface water levels of 5–10  $\mu\text{g/L}$  or less (Kumla kommun 1993–2017). Lithium and Sr contributions from the waste into Norrtorpssjön are too low to explain the levels in the lake, as indicated by the decreasing concentrations with time in G1 and G2, as well as the concentrations in G4 (2011). No water flow was observed from the deposit area into Pölen. Thus, it appears that weathering is also progressing at near-neutral pH and not only at low pH. The rate of weathering at high pH in comparison with low pH cannot, however, be deduced.

## Stratification and Seasonal Trends

In a previous study it was reported that Norrtorpssjön was stratified, with a thermocline extending from 8 to 11 m, whereas Pölen was not stratified (Karlsson et al. 2012b). There are, however, indications of stratification in both lakes based on data from 2017 with a thermocline also in Pölen, extending from 3–4 to 6 m and from 6 to 10 m. The depth profiles also show that pH increases with depth in Pölen whereas pH decreases with depth in Norrtorpssjön, and both lakes have higher carbonate concentrations at depth than at the surface (Fig. 3a).

Several elements show higher concentrations at depth than at the surface in Norrtorpssjön, e.g. divalent metals, including Mn and U (uranyl). An earlier investigation that modelled the groundwater pattern in the area indicated that there is an exchange of water between the water above the green shale layer and the underlying sandstone layer (Svensson et al. 2005). The changes in concentrations for many of the elements with depth indicate that chemical conditions change with depth. It has been suggested that settling solid Fe phases dissolve in the hypolimnion in Norrtorpssjön (Karlsson et al. 2012b) and, according to the results of this study, this could also be the case for Pölen. Also, Mn shows higher concentrations at depth, which may indicate reductive dissolution of Fe and Mn (hydr)oxides.

It was suggested that there would be seasonal variations in element concentrations and mobilities, including the transport of dissolved species and suspended matter further downstream and out of Norrtorpssjön (Karlsson et al. 2012b). No such seasonal trends can be clearly seen at the Norrtorpssjön outlet when samples from different months are compared, except for Mn (Fig. 4). This element was not analysed in the monitoring programme starting in 1993, but seasonal differences can be discerned for Mn with decreased concentrations during summer in the sampling 2015–17. Also, the pH showed indications of seasonal trends, with pH higher during the summer (median 7.48, May–August), and lower during winter (median 7.19, October–March). Sampling and analysis of the depth profile in the lake with time over the seasons of the year would be appropriate for a thorough investigation of possible implications of seasonal circulation in the lake. More frequent sampling at the outlet would be needed to make sure not to miss an outflow due to circulation. The Mn concentration variations do not necessarily indicate that accumulated Mn has become available due to circulation; they could, for instance, be a response to photosynthetic activity, such as previously reported in a study of diurnal variation of metals in a lake in Russia (Pokrovsky and Shirokova 2013). Maximum photosynthetic activity during daytime increased the pH, and it was proposed that lower Mn concentrations were due to adsorption of  $Mn^{2+}$  onto cyanobacterial cells. Decreasing pH at

night resulted in  $Mn^{2+}$  being desorbed. Thus, seasonal trends might exist and may be linked to the photosynthetic activity in Norrtorpssjön, with maximum activity during summer causing increased pH and adsorption of  $Mn^{2+}$ , while less photosynthesis in wintertime led to lower pH, and  $Mn^{2+}$  desorption from solid carrier phases.

## Sediments and Redistribution of Elements

Elements released from the shale due to weathering (Pölen and Norrtorpssjön) and from the deposited waste constitute the water chemistry in the lakes. There is a continuous transport of species in solution (dissolved and suspended) out of the lakes via Norrtorpssjön, but also a continuous accumulation of them on the lake bottoms due to adsorption on bottom materials as well as precipitation and sedimentation of new solid phases. The bottom material also contains fine-grained shale residues, and most likely material from the green shale zone beneath the alum shale horizon, and possibly carbonate phases in areas with neutral or high pH. Sediment/shale concentration ratios significantly above one would indicate the presence of new phases that have been carriers of elements from the water leading to an accumulation on the bottom. The average chemical composition (excluding Si, C, S, and O) of alum shale from the exposed horizon at the pit lakes and of shale with limestone (calcite) lenses from the upper part, is given in Table 2a–c, as well as the composition of the sampled lake sediments in 2011 and 2017.

Iron and Mn accumulated in the deep water as well as in the Norrtorpssjön bottom sediments in 2011 and in 2017. Precipitation of Fe(III) (pH 6.5 or slightly higher in both years) together with Mn, and/or settling of suspended Fe(III)-phases, is evident. Thus, there is either Fe–Mn hydroxide co-precipitation or possibly a separate Mn phase, e.g. of the birnessite type  $(Na, Ca)_{0.5}[Mn(III, IV)]_2O_4$ , that requires aerobic conditions. The dominant accumulation in the lake sediments of Fe, in a precipitating carrier phase with Mn as well as Ca and P, is further demonstrated by comparing it with the shale composition (Table 3).

There was an apparent enrichment of the divalent metals Co and Zn, and possibly also Ni (2011) and Cu (2017) in the sediments. These metals would adsorb on any precipitating or suspended Fe(III)-phase at pH above 6, possibly only partially for Ni, which requires a higher pH, and Cu, which can form complexes with organic (e.g. humic) acids. There was no evident accumulation of Cd (pH too low) or Pb. The enrichment of P in all sediment samples may indicate the formation of sparingly soluble phosphates, possibly with Ca, as well as with Fe. Precipitation of gypsum would also be expected. The enrichment of Ca was, however, higher, which may be due to the presence of carbonate phases in the sediment at this pH. There was no significant enrichment of the

**Table 2** Concentrations in shale and limestone lenses from the upper part of the shale horizon from Norrtorpssjön and [sediment/shale] concentration ratios 2011 (2a) and 2017 (2b) for lake bottom sediments from Norrtorpssjön (LN) and 2017 (2c) for sediments from Pölen (LP)

(a)	Shale	Lime-stone	Sediment LN 40, 28 m		Sediment LN 160, 8–10 m		Sediment LN 320, 8–10 m	
	Conc.(5)	Conc.(3)	Conc.(2)	Ratio	Conc.(3)	Ratio	Conc.(2)	Ratio
Li (mg/g)	0.024	0.005						
Na (mg/g)	1.38	0.134	1.76	1.27	2.15	1.56	1.68	1.22
K (mg/g)	31.5	4.12	12.9	0.41	15.1	0.48	8.49	0.27
Mg (mg/g)	3.91	1.45	3.18	0.81	3.42	0.87	2.39	0.61
Ca (mg/g)	3.29	319	20.5	6.23	42.6	12.9	9.11	2.77
Sr (mg/g)	0.087	0.281						
Al (mg/g)	49.5	8.48	33.3	0.67	36.5	0.73	20.0	0.40
Mn (mg/g)	0.068	0.416	0.400	5.88	0.119	1.75	0.877	12.9
Fe (mg/g)	31.9	7.76	246	7.71	237	7.42	340	10.7
Co (µg/g)	4.44	3.27	26.6	5.99	4.92	1.11	12.8	2.88
Ni (µg/g)	40.8	18.6	143	3.50	45.8	1.12	26.6	0.65
Cu (µg/g)	33.2	24.2	48.2	1.45	48.6	1.46	32.1	0.97
Zn (µg/g)	52.4	9.2	225	4.29	155	2.95	149	2.84
Cd (µg/g)	1.41	0.39						
Pb (µg/g)	33.7	13.3						
Ce (µg/g)	57.5	27.6	67.4	1.17	43.3	0.75	27.3	0.47
REE tot (µg/g)	132	71.8	197	1.49	107	0.81	68.6	0.52
P (µg/g)	275	155	927	3.37	736	2.68	549	2.00
V (µg/g)	434	57.6	122	0.28	90.2	0.21	38.3	0.09
As (µg/g)	28.9	10.7						
Mo (µg/g)	85.0	60.0	143	1.68	25.4	0.30	26.5	0.31
U (µg/g)	89.5	45.7	160	1.79	36.0	0.40	35.5	0.40
(b)	Shale	Lime-stone	Sediment LN 20, 8–10 m		Sediment LN 320, 10 m		Sediment LN 725, 10 m	
	Conc.(5)	Conc.(3)	Conc.(2)	Ratio	Conc.(2)	Ratio	Conc.(2)	Ratio
Li (mg/g)	0.024	0.005						
Na (mg/g)	1.38	0.134	0.814	0.59	0.519	0.38	2.97	2.15
K (mg/g)	31.5	4.12	6.60	0.21	10.5	0.33	12.0	0.38
Mg (mg/g)	3.91	1.45	1.20	0.31	3.19	0.82	2.17	0.55
Ca (mg/g)	3.29	319	9.69	2.94	145	44.1	16.3	4.95
Sr (mg/g)	0.087	0.281	0.089	1.03	0.121	1.39	0.071	0.81
Al (mg/g)	49.5	8.48	15.3	0.31	25.8	0.52	27.3	0.55
Mn (mg/g)	0.068	0.416	1.08	15.9	0.619	9.10	0.464	6.82
Fe (mg/g)	31.9	7.76	258	8.09	78.0	2.44	277	8.68
Co (µg/g)	4.44	3.27	16.2	3.64	6.40	1.44	7.00	1.57
Ni (µg/g)	40.8	18.6	31.7	0.78	20.1	0.49	22.9	0.56
Cu (µg/g)	33.2	24.2	77.1	2.32	30.8	0.93	33.8	1.02
Zn (µg/g)	52.4	9.2	138	2.63	34.0	0.65	49.0	0.93
Cd (µg/g)	1.41	0.39	0.795	0.56	0.13	0.09	0.21	0.15
Pb (µg/g)	33.7	13.3	31.8	0.94	13.2	0.39	18.1	0.54
Ce (µg/g)	57.5	27.6	32.2	0.56	45.5	0.79	30.5	0.53
REE tot (µg/g)	132	71.8	86.3	0.65	114	0.86	74.2	0.56
P (µg/g)	275	155	852	3.10	1267	4.61	612	2.22
V (µg/g)	434	57.6	86.5	0.20	68.0	1.18	48.0	0.11
As (µg/g)	28.9	10.7	70.5	2.44	21.5	0.74	37.3	1.29
Mo (µg/g)	85.0	60.0	162	1.91	35.2	0.41	109	1.28
U (µg/g)	89.5	45.7	130	1.45	59.5	0.66	68.2	0.76

**Table 2** (continued)

(c)	Shale	Limestone	Sediment LP 45, 5 m		Sediment LP 255, 12 m	
	Conc.(5)	Conc.(3)	Conc.(1)	Ratio	Conc.(1)	Ratio
Li (mg/g)	0.024	0.005				
Na (mg/g)	1.38	0.134	0.0741	0.054	8.53	
K (mg/g)	31.5	4.12	0.664	0.0211	22.1	0.702
Mg (mg/g)	3.91	1.45	0.301	0.077	4.04	1.03
Ca (mg/g)	3.29	319	3.78	1.15	11.5	3.49
Sr (mg/g)	0.087	0.281	0.0252	0.29	0.0929	1.07
Al (mg/g)	49.5	8.48	24.1	0.49	53.5	1.08
Mn (mg/g)	0.068	0.416	0.310	4.56	0.387	5.69
Fe (mg/g)	31.9	7.76	485	15.2	93.2	2.92
Co (µg/g)	4.44	3.27	1.30	0.29	14.6	3.29
Ni (µg/g)	40.8	18.6	10.5	0.26	125	3.06
Cu (µg/g)	33.2	24.2	17.1	0.51	39.5	1.19
Zn (µg/g)	52.4	9.2	33.0	0.63	172	3.28
Cd (µg/g)	1.41	0.39	0.18	0.13	1.47	1.04
Pb (µg/g)	33.7	13.3	5.90	0.17	20.2	0.60
Ce (µg/g)	57.5	27.6	46.9	0.82	73.4	1.28
REE tot (µg/g)	132	71.8	223	1.69	195	1.48
P (µg/g)	275	155	219	0.80	787	2.86
V (µg/g)	434	57.6	10	0.023	68.0	0.16
As (µg/g)	28.9	10.7	30.9	1.07	21.0	0.73
Mo (µg/g)	85.0	60.0	851	10.0	39.0	0.46
U (µg/g)	89.5	45.7	90.5	1.01	128	1.43

Average concentrations are given with number of samples within parenthesis. The distance from the western part of the pit (the deposit area) is given for the sediments (40, 160, 320 m, Norrtorpsjön, and 45, 255 m, Pölen), as well as the sampling depth (m) (Concentrations in shale and limestone from Allard et al. (2011) and Grawunder et al. to be published)

**Table 3** Average concentrations (g/kg) of major elements (except for silicon, carbon, and sulphur) in shale, limestone lenses, and lake bottom sediments

	Shale	Lime-stone	Norrtorpsjön 2011 LN 40, LN 160, LN 320 5 m, 8–10 m, 8–10 m			Norrtorpsjön 2017 LN 20, LN 320, LN 725 8–10 m, 10 m, 10 m			Pölen 2017 LP 45, LP 255 5 m, 12 m	
Al <sub>2</sub> O <sub>3</sub>	93.5	16.0	79.5	87.2	47.8	36.5	61.6	65.2	45.5	101
Fe <sub>2</sub> O <sub>3</sub>	45.6	11.1	352	339	486	369	111	396	693	133
K <sub>2</sub> O	38.0	4.96	15.5	18.2	10.2	7.95	12.6	14.5	0.80	26.6
MgO	6.48	2.40	5.27	5.67	3.96	1.99	5.14	3.60	0.50	6.70
CaO	4.60	446	28.7	59.6	12.7	13.6	203	22.8	5.29	16.1
Na <sub>2</sub> O	1.86	0.18	2.37	2.90	2.26	1.10	0.70	4.00	0.10	
P <sub>2</sub> O <sub>5</sub>	0.63	0.35	1.81	1.69	1.26	1.95	2.90	1.40	0.50	1.79
MnO <sub>2</sub>	0.11	0.66	0.63	0.19	1.39	1.71	0.98	0.73	0.49	0.61

trivalent rare earth elements, and no enhanced accumulation of Ce, relative to the total rare earth accumulation.

There was a similar accumulation of Fe and Mn in Pölen in the deepest sediment (12 m) in 2017, where pH was as high as 6, compared with 3.4 in the surface water. Cobalt and Ni were enriched, as well as P (and Ca). There was also an

accumulation of Fe and Mn in the sediment from the shallow depth (5 m), at a pH of ≈ 3.6, but without the divalent metals that would not be adsorbed by any suspended Fe(III)-phase at this pH. Molybdenum enrichment, not observed at pH 6 or at pH 6.5 (Norrtorpsjön), was evident.

## Conclusions

### Conditions in the Pit Lakes

The two pit lakes Pölen and Norrtorpssjön both receive leachates from weathering alum shale, resulting in a pH below 4 and elevated concentrations of major components in the water (Na, K, Mg, Ca, Sr, Al, Mn, Fe, as well as  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$ ) and of trace elements (Li, V, Co, Ni, Cu, Zn, As, Mo, U, rare earth elements; also Cd, Pb and others at low levels). Norrtorpssjön also receives leachates with metals as well as anions from the landfilled area of the Östersätterbrottet pit and the deposited waste, as well as from the adjacent Ljungström field.

A pH increase from 4 to 8 in Norrtorpssjön has led to a decrease of the concentrations of Al and Fe, and some of the associated trace elements, notably Co, Ni, Zn, V, and to some extent Cu. The pH increase is caused by an inflow of alkaline leachates from the deposited alkaline waste.

There is a continuous accumulation of sediments in both lakes, though Pölen is still acidic (pH below 4) while Norrtorpssjön is near-neutral (pH 7.8). Major components in the sediments are Fe and Ca, and minor components are K, Na, P, and Mn, as well as most of the trace elements at low levels. Iron and Mn exhibit the highest sediment/shale concentration ratios, which may indicate formation of an Fe-phase with co-precipitated Mn, or possibly a discrete Mn-phase separate from the Fe-phase (e.g. birnessite).

There are indications of seasonal variations of the Mn concentrations, and possibly also pH, in Norrtorpssjön that may reflect photosynthesis processes in the lake.

Norrtorpssjön has changed from being acidic to near-neutral, although it is still receiving leachates from the surrounding shale. This was not planned, engineered, or foreseen but the lake can be considered to be a “natural analogue” of an ALD, which can serve as a method for neutralizing acidic leachates. Norrtorpssjön also illustrates how this leads to transformation and redistribution of elements. Metals are transferred from water to the sediments, but it is also obvious that this transport could be reversed if/when the lake is once more acidified.

### Future Scenario

There was a significant decrease of total carbonate concentration in Norrtorpssjön, and a corresponding pH-decrease from the maximum level of 8.1 in 2011–13 to the present level of 7.8. This could indicate less input of alkaline leachates into the lake, which may be confirmed in the coming years.

Weathering of the shale is continuing, affecting both the acidic Pölen and near-neutral Norrtorpssjön. Thus, a decreasing pH can be expected in Norrtorpssjön, which

could lead to desorption/dissolution of trace elements from the bottom sediments. The progressing slight reduction in e.g. Li concentrations may, however, be an indication of depletion of accessible trace elements in the shale. A decreasing pH would result in higher levels of dissolved trace metals and increased outflow of metals from Norrtorpssjön downgradient.

Data are lacking on the concentration and composition of organic matter in the lakes. It is likely that speciation in the water as well as reactions in the sediments are affected by the presence of organics and by microbial activity. These processes may with time alter the chemistry of the lakes as well as the distribution and concentrations of trace elements and thereby the outflow from the lake into the next recipient downstream.

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