Distribution of Rare Earth Elements and Other Metals in a Stratified Acidic Pit Lake in Black Shales 45 Years after Mine Closure

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Abstract
Opencast mining of black shale for extraction of oil was undertaken from 1942 to 1966 at Kvarntorp, Sweden, and the pits are now water filled. The shale is rich in sulphides (S 5-8%), so the leachates have a pH of 3-3.5. The shale contains a wide range of metals, including rare earth elements and uranium, at concentrations 50-500 g/ton. Water samples were collected (profiles and transects) in two pit lakes and analysed for general hydrochemical conditions and metals. The results indicate an incongruent release of metals from the shale. Heterogeneous distributions of trace metals, including the rare earth elements, were observed with concentrations that varied with depth and with the distance from water exposed shale horizons. This heterogeneity reflects pH, redox conditions and dissolved organic matter, as well as lake stratification, presence of adsorbing particulate matter and the formation of precipitates that accumulate on the bottom creating secondary metal rich sediments. The incongruent release of metals from the weathering shale is also demonstrated from the accumulation and distribution in secondary minerals that are precipitated directly on shale surfaces above the water level.

Key Words: black shales, pit lake, rare earth elements, hydrogeochemistry

Introduction
In Sweden the organic rich black shales are commonly known as alum shales because of their content of alum ($KAl(SO_4)_2$), which was sought for during the 18th and 19th centuries (Eklund *et al.* 1995). In many regions where black shales are available, the remains of past operations are visible as piles of burnt shale. Production of hydrocarbons from the organic rich black shale (up to 18% organic carbon) in the Kvarntorp area in south central Sweden began during the Second World War. The shale was excavated in open pits, crushed, sieved and pyrolysed, and the volatile organic hydrocarbon fraction was recovered. The heated shale residues were put on a single pile together with a fine-grained shale fraction that was discarded since it was not suitable for pyrolysis. The production continued in full operation until the mid 1960s when it ceased because of the production costs (Dyni 2006). In the later stage of the operation the shale was also extracted for uranium, by sulphuric acid leaching, but only some 62 tonnes were produced. The original shale as well as the different shale waste materials have a high pollution potential because of their concentrations of metals such as uranium, vanadium, nickel and molybdenum in combination with pyrite and other acid generating metal sulphides. These elements, together with some rare earth elements (REE), make the materials economically attractive for future extraction from both the waste fractions as well as the pristine shale. Hence, it is essential to understand the chemical mechanisms behind metal release and redistribution in this complex system.

The two pit lakes in this study receive water that has passed through untreated waste shale along their shores as well as the original strata in the surrounding soil. A part of the shallow groundwater that reaches Lake Norrtorpsjön has passed through a backfill of alkaline waste from the production of construction materials from limestone. There is also some diffuse seepage of water from the adjacent municipal waste landfill. Lake Norrtorpsjön is roughly 30 m deep so it is thermally stratified during summers and winters. On the other hand, Lake Pölen is not stratified and acidic. These different conditions within the same catchment provide a nice opportunity to study the impact of several hydrochemical conditions on metal mobility and availability for downstream transport. Here, we focus on the speciation of a selected range of elements with respect to their size, charge and dominating redistribution processes.

Materials and Methods

The field site

Kvarntorp is located some 20 km south of Örebro, 200 km west of Stockholm (Figure 1) and the former mining area covers some 8 km^2. The black shale horizon that has a thickness of 5-15 m is of late Cambrium age. Usually it is found beneath a layer of Ordovician limestone but at this site the black shale has been lifted to the surface due to faulting which is why it is easily accessible. Major mineral components of the shale are quartz (18-34%), illite (24-41%), K-feldspars (3-8%), chlorite (1-5%), calcite (1-4%), as well as pyrite (5-17%) and organic carbon (5-18%). Emissions of sulphuric acid, metals and hydrocarbons, including PAHs, PCBs and dioxins during the shale processing period have made the area one of the most polluted sites in Sweden (SWECO VIAK, 2005).

The small acidic and shallow Lake Pölen (S1) has a maximum depth of 8 m and receives water only from the shale residues and groundwater. Lake Norrtorpsjön (S2) is 30 m deep and receives water from the same shale waste but also diffuse seepage from the municipal waste deposit to the NW. In addition, a backfill in the NW corner of the lake contains alkaline waste from production of building materials from limestone.

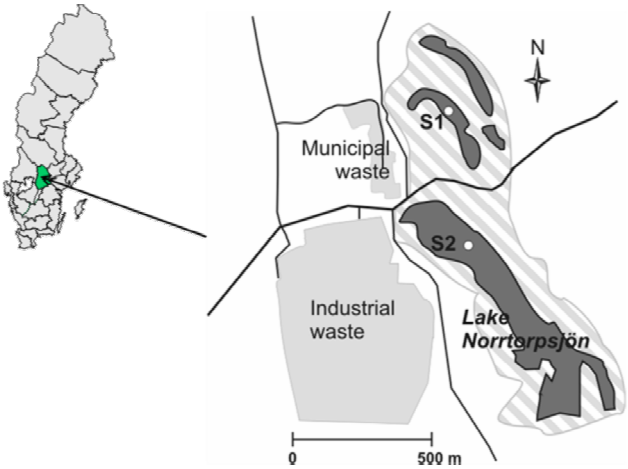

Figure 1. Map of the area with the pit lakes

Sampling and analysis

The two pit lakes were sampled in mid June and July 2011. On both occasions a conventional water sampler was used and the samples were poured into 1 L polypropylene bottles and transported to the laboratory for further processing of general hydrochemical parameters. Sampling depths were determined after an initial recording of temperature and oxygen saturation with a combination probe. Samples from Lake Norrtorpsjön were taken at 1 m (epilimnion), 8 m (thermocline), 12 m (hypolimnion) and 27 m (bottom water). Samples from Lake Pölen were collected at 1 m and 3 m. Samples for speciation were collected in separate 1 L triplicates, also in polypropylene bottles.

The speciation procedure separates the metals according to size and charge. Phase separations were made in a clean room (class 10/100) by filtration through 47 mm polycarbonate membranes with defined pore sizes of 1, 0.4 and 0.2 µm, respectively. Plastic syringes were used, and the filtration was made below the filter clogging point to minimize the risk of inducing redistribution. The filtrates were acidified with sub boiled distilled nitric acid and stored until analysis. Acidified original water samples represent "total" element concentrations. Anionic metal species were captured on pre-conditioned (ionic strength and pH) DEAE cellulose anion exchange resins. An excess of the resin was added to a 1 L sample bottle immediately after sampling and intermittently shaken for one hour. Triplicate samples were prepared for each depth. The bottles were then transported to the laboratory and the resin was allowed to settle. A sub-

volume (50 ml) of the aqueous phase was decanted, acidified with nitric acid and stored until analysis. An additional sub-sample was taken after 8 hours.

Temperature, electrical conductivity, pH, Eh and dissolved oxygen were measured in the profiles on site with a multi-probe. Electrical conductivity and pH were also measured in the laboratory. Principal anions (F^-, Cl^-, Br^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}) were quantified by ion-chromatography in 0.2µm filtrates using a Dionex AS12A column and a running buffer (1 ml/min) with 10.5 mM Na_2CO_3/0.5 mM $NaHCO_3$. Total organic carbon (TOC) and inorganic carbon (IC) were quantified with a TOC-analyser (Shimadzu TOC-V CPH). Metals were quantified with ICP-MS (Agilent 7500 cx) operated with a Micromist nebulizer. The REEs were determined with the same instrument but with an ultrasonic nebulizer unit equipped with a dryer (CETAC U6000AT$^+$) to minimise interferences from oxides and hydrides. All sample treatment and metal analysis were performed in a clean room (class 10/100). The saturation index (S.I.) for relevant solid phases was calculated with the geochemical software PHREEQC.

Results and Discussion

General hydrochemistry

The profiles of temperature, dissolved oxygen and Eh show that Lake Norrtorpsjön was stratified, with the thermocline extending from 8 m to 11 m. For the principal anions the common pattern was low concentrations in the epilimnion and an increase towards and across the thermocline (Figure 2). In the hypolimnion the concentrations were rather constant.

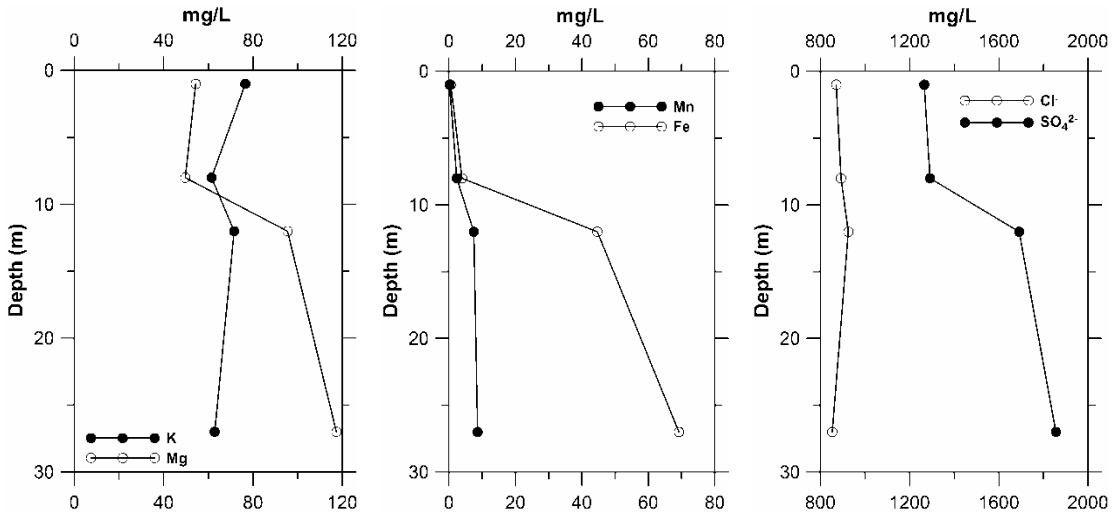

Figure 2. Examples of depth profiles, Lake Norrtorpsjön.

For most anions, the concentrations are quite high (Table 1) and it is evident that there were different sources for them. High sulphate concentrations are expected from sulphide weathering, but this source cannot account for the high concentrations of chloride and nitrate as well as the presence of bromide. The proximity to the municipal waste site is a clear indication of the origin of these ions (Figure 1) whereas elevated concentrations of fluoride originate from shale, shale waste and municipal waste.

Lake Pölen was not deep enough to stratify and the oxygen saturation as well as concentrations of anions were similar at both depths. The lower oxygen saturation (10%) at the surface in comparison with Lake Norrtorpsjön might indicate a lower photosynthetic activity in the former, in comparison with oxygen consuming processes. These conditions are not uncommon in acidified lakes (pH 3.2) where input of organic matter from the soil exceeds carbon fixation in the lake. A comparison with analyses of shallow groundwater and leachates from other sites suggest that this lake is not contaminated by either the

municipal waste or the alkaline backfill. Hence, the concentrations of principal anions would represent "background" conditions due to black shales in the area better than Lake Norrtorpsjön.

The alkaline waste in the tributary to Lake Norrtorpsjön had a large impact on its pH since at 1 m depth in Lake Pölen and Lake Norrtorpsjön pH was 3.2 and 7.4, respectively. In Lake Norrtorpsjön pH drops to 6.4 and 5.9 at 8 m and 27 m, respectively which indicates acid producing processes below the thermocline. This change coincides with oxygen consumption as reflected by an oxygen saturation of roughly 90% at the surface and 3% at 27 m. The TOC concentrations were below detection throughout the profile so other processes than mineralization of carbon compounds is expected.

Table 1. General hydrochemical parameters (b.d. below detection)

Site	Depth m	pH	El.Cond mS/cm	Eh mV	O_2 %[a]	IC mg/L	TOC mg/L	F^- mg/L	Cl^- mg/L	Br^- mg/L	SO_4^{2-} mg/L	NO_3^- mg/L
L. Norrtorpsjön	1	7.42	1.978	23	85	19.7	<0.01	0.88	871	1.52	1265	3.18
	8	6.76	2.135	-39	29	24.3	<0.01	1.03	892	1.47	1291	6.21
	12	6.42	2.512	-110	20	33.8	<0.01	1.38	925	2.76	1690	8.68
	27	5.97	2.947	-108	3	27.4	<0.01	1.39	853	2.55	1855	b.d.
L. Pölen	1	3.18	1.796	490	10	1.52	0.74	0.63	792	b.d.	1406	b.d.
	3	3.18	1.834	360	8	1.05	1.17	0.64	819	b.d.	1412	b.d.

[a] Percentage of equilibrium concentration with the atmospheric partial pressure.

The impact of the different wastes in the tributary is reflected by the concentration levels as well as depth profiles of the principal cations (Tables 1 and 2, Figure 2). The concentrations of sodium, potassium and calcium are elevated (Karlsson 2011) but common in this calcite dominated environment. These elements have their highest concentrations above the thermocline where some 10% is retained by all filter pore sizes. The calcium concentrations are in both lakes close to saturation with gypsum (S.I. -0.02). None of these elements were retained by the anion-exchangers indicating that they were present as dissolved cations.

Magnesium, iron and manganese have very similar depth profiles, with low concentrations in the epilimnion and an abrupt increase across the thermocline (Figure 2). Such profiles would indicate the formation of settling particles above the thermocline (iron 28% particulate > 0.2 µm), followed by dissolution/release below it (iron 4% particulate > 0.2 µm). This is confirmed by the saturation indices for ferrihydrite that indicate oversaturation above the thermocline (S.I. 4.9) but below saturation limiting concentrations in the hypolimnion (S.I. -4.4). The presence of particulate/colloidal iron corresponds to depths where the oxygen saturation exceeds 20%.

Evidently the redox potential and dissolved oxygen did not allow for the precipitation of iron sulphides as evidenced by the elevated concentrations of sulphate (Table 1). Consequently, reductive dissolution occurs below the thermocline and contains a significant amount of iron and associated elements that will be transported during lake circulation. The relatively low fraction of particulate iron in the oxic zone above the thermocline indicates two possible mechanisms: i) a rapid formation of large ferrihydrite particles that quickly settle below the thermocline or ii) that photoreduction maintains iron in its divalent state (c.f. McKnight and Bencala 1988). No magnesium, iron or manganese was retained by the anion exchanger. Irrespective of the contributing mechanisms, it is evident that bottom waters of the lake contain a high amount of dissolved iron.

Lake Pölen was close to equilibrium with ferrihydrite (S.I. 0.08). Manganese had similar depth dependence as iron in Lake Norrtorpsjön but contrary to iron it was dissolved throughout the water column and no solubility limiting stoichiometric phases were identified by geochemical modelling and no anionic species were found empirically. High dissolved Mn concentrations found in all samples from Lake Pölen likely resulted from the impact of pH on Mn solubility.

Table 2. Principal cation concentrations in unfiltered samples (b.d. below detection)

Site	Depth m	Al mg/L	Ca mg/L	Fe mg/L	K mg/L	Mg mg/L	Mn mg/L	Na mg/L
L. Norrtorpsjön	1	0.135	520	0.55	37.8	54.3	0.18	76.5
	8	0.092	496	3.91	32.0	49.6	2.35	61.4
	12	0.113	503	44.6	28.3	95.4	7.47	71.5
	27	0.920	454	69.2	31.2	117.4	8.58	62.8
L. Pölen	1	0.85	334	5.0	6.9	40.4	4.59	16.0
	3	0.78	321	4.7	6.3	38.7	4.49	15.5

Table 3. The fraction (%) of principal elements in the 0.2 µm filtrates (nd not different (p 0.05) from unfiltered sample)

Site	Depth m	Al %	Ca %	Fe %	K %	Mg %	Mn %
L. Norrtorpsjön	1	21.0	10.4	27.8	14.5	16.1	8.1
	8	23.2	7.5	15.4	12.6	7.0	6.5
	12	35.1	7.0	4.3	9.0	4.4	2.2
	27	37.9	6.8	3.5	11.0	12.3	7.8
L. Pölen	1	2.8	3.1	4.4	5.1	3.1	1.8
	3	3.9	3.5	5.3	6.2	2.5	0.6

Concentrations of aluminium in the acidic Lake Pölen (Table 2) do not reach saturation with solid hydroxides or hydroxysulphates phases and only 3-5% (Table 3) is retained by the finest filter (> 0.2 µm). Conditions are different in Lake Norrtorpsjön (Figure 3) where Al is 20-40% is particulate (> 0.2 µm) although total-Al concentrations are low (Table 2). The reason for low dissolved concentrations of Al is the entire aqueous system is supersaturated or close to saturation for several hydroxides and hydroxysulphate Al species. Aluminium in Lake Norrtorpsjön and Lake Pölen did not form any anion exchangeable species. In Lake Pölen, although there were detectable concentrations of TOC, the similar Al between the filtered and original samples indicate the Al was entirely in a dissolved form.

To summarise, the chemistry of Lake Norrtorpsjön is influenced by the inputs from three different sources (shale, alkaline solid waste and municipal waste) while Lake Pölen is only influenced by the surrounding shale/limestone. As a result of the alkaline waste, Lake Norrtorpsjön has a higher pH which induces precipitation of aluminium hydroxides and hydroxysulphates. Ferrihydrite is formed in portions of Lake

Norrtorpsjön with high levels of dissolved oxygen. Upon settling to the hypolimnion, ferrihydrite is dissolved through reduction. Oxygen partial pressure in the hypolimnion is maintained at levels that prevent iron sulphide formation, probably because of limited primary production. Manganese does not participate in the formation of particulate/colloidal matter. None of the principal metals form anionic species. Hence, the dominating trace metal carrier phases would be the inorganic precipitates of aluminium and iron.

Trace metals

In Lake Norrtorpsjön, depth profiles for copper, nickel, molybdenum and uranium were similar to iron, i.e. low concentrations above the thermocline and higher in the bottom water (Table 4). Detectable particulate fractions (> 0.2 µm) up to 5% of the total uranium, 12% of the total copper and 15% of the total nickel were found below the thermocline (Table 5). Molybdenum was not significantly (p 0.05) retained by the filters above the thermocline but up to 38% below. No stoichiometric solid phases were identified from geochemical modelling for nickel, molybdenum and uranium which is why particulate forms would be controlled by coprecipitation/adsorption to solid carrier phases. Above the thermocline, copper concentrations were at equilibrium with malachite and oversaturated with respect to tenorite and cupric ferrite. Cationic species dominated since only uranium had significantly (p 0.05) lower concentrations in the aqueous phase after the samples had been in contact with the anion-exchanger. Above the thermocline, 5-15% of the U was anionic and below it increased to 30-40%. The latter results are much higher than the 6.5% of negatively charged uranium complexes indicated by geochemical modelling, which call for further studies on a more detailed level.

For the acidic Lake Pölen, concentrations were slightly higher for nickel and copper, not different for uranium and lower for molybdenum (Table 4). Ni, Cu, U and Mo particulate fractions did not exceed 5% of the total. With the exception of Mo, this is likely a result of their higher solubility at lower pH. Of the trace metals, only uranium was retained by the anion exchange resin with values up to 30%.

Table 4. Selected trace metal concentrations (b.d. below detection)

Site	Depth m	Cd µg/L	Cu µg/L	Mo µg/L	Ni µg/L	Pb µg/L	U µg/L	V µg/L	Zn µg/L
L. Norrtorpsjön	1	0.10	18.8	9.4	18.8	0.40	36.6	35.0	199
	8	0.04	25.6	13.6	25.6	0.10	32.4	30.8	176
	12	0.05	66.6	23.5	66.6	18.8	58.8	29.3	193
	27	0.05	49.2	12.6	49.2	1.20	55.9	41.9	185
L. Pölen	1	0.41	69.0	0.6	69.0	1.79	22.8	38.5	216
	3	0.36	60.0	b.d.	59.9	1.40	22.4	18.8	204

Table 5. The fraction (%) of trace elements in the 0.2 µm filtrates
(nd not different (p 0.05) from unfiltered sample)

Site	Depth m	Cd %	Cu %	Mo %	Ni %	Pb %	U %	V %	Zn %
L. Norrtorpsjön	1	16.0	6.0	nd	9.8	69.9	2.8	17.5	12.1
	8	19.0	6.6	nd	12.8	80.3	2.5	28.8	9.4
	12	59.2	12.8	37.5	9.9	99.9	4.4	29.6	9.8
	27	49.6	11.9	29.5	11.4	98.3	6.8	32.7	8.9
L. Pölen	1	nd	4.8	5.6	3.5	nd	5.3	33.9	nd
	3	nd	2.0	5.9	2.0	nd	3.7	31.0	nd

Zinc had similar concentrations throughout the depth profile in Lake Norrtorpsjön. 10% of the Zn was particulate (> 0.20 µm). No anionic Zn species were identified. Since Zn concentrations were below saturation with known solid phases suggest that Zn in the particulate phase results from sorption. In Lake Pölen, zinc concentrations were slightly higher than in Lake Norrtorpsjön and no zinc was retained either by the filters or by the anion exchanger.

A similar behaviour would be expected for cadmium, because of its chemical similarity with zinc, although concentrations are much lower. In Lake Norrtorpsjön, the cadmium concentration was fairly consistent except for high concentration at 1 m depth. Approximately 50% of the Cd was particulate (> 0.2 µm) although the concentrations were below saturation, which indicates the importance of sorption to carrier phases. The only similarity with zinc in Lake Norrtorpsjön is that no anionic Cd species was found. In Lake Pölen, cadmium concentrations were slightly higher and were all present in a cationic form.

Lead (Table 4) in Lake Norrtorpsjön increased below the thermocline while in Lake Pölen it was homogeneously distributed. There was, however, a large qualitative difference since approximately 35% and 95% of the Pb in Lake Norrtorpsjön was particulate (> 0.4 µm, > 0.2 µm) at 1 m and 27 m, respectively, while no particulate lead (p 0.05) was found in Lake Pölen. In Lake Norrtorpsjön, 1-3% and 20% of Pb was anionic, above and below the thermocline, respectively, while 10% was anionic in Lake Pölen. In spite of the pH differences in the two lakes, concentrations of vanadium were similar (Table 4) and approximately 30% was particulate (> 0.2 µm). In both lakes, vanadium was anionic. No solubility limiting phases were found for either lead or vanadium indicating that the solid phase resulted from sorption.

Rare earth elements

The surrounding black shale is a source for the REE, including scandium and yttrium. Lowering the pH through pyrite oxidation should increase their concentration in adjacent water bodies. This is evident in Lake Pölen where several REEs are found at high concentrations, in relation to non-shale environments (Table 6). REE are not significantly retained by the filters or anion exchange resin so their speciation would be dominated by dissolved cationic complexes (Table 7).

REE concentrations were quite different in Lake Norrtorpsjön where only dysprosium, erbium and scandium had quantifiable concentrations. Possibly, the low concentrations resulted from precipitation with up to 70% of the total concentrations found in the particulate (> 0.2 µm) fraction. The REE distribution is evidently related to the redox conditions, since the highest particulate fractions were found below the thermocline. Another feature in Lake Norrtorpsjön is that REE were retained by anion

exchange. In the bottom water up to 20% was anionic while just a few percent near the surface. The increased pH between coupled with slightly negative Eh seems to generate particulate carrier phases that redistribute the elements within the system.

Table 6. Selected rare earth element concentrations (b.d. below detection)

Site	Depth m	Ce µg/L	Dy µg/L	Er µg/L	Eu µg/L	Gd µg/L	La µg/L	Nd µg/L	Sc µg/L	Sm µg/L	Tb µg/L	Y µg/L	Yb µg/L
L. Norrtorpsjön	1	b.d.	0.08	0.06	b.d.	b.d.	b.d.	0.02	0.11	b.d.	b.d.	0.01	b.d.
	8	b.d.	0.07	0.06	b.d.	b.d.	b.d.	b.d.	0.07	b.d.	b.d.	b.d.	b.d.
	12	b.d.	0.06	0.08	b.d.	b.d.	b.d.	0.01	0.17	b.d.	b.d.	0.09	b.d.
	27	b.d.	0.13	0.09	b.d.	b.d.	b.d.	b.d.	0.17	b.d.	b.d.	0.06	b.d.
L. Pölen	1	12.0	15.4	9.91	0.31	1.87	3.77	6.84	0.05	1.41	0.24	0.40	0.72
	3	12.9	16.9	10.8	0.31	1.98	0.30	7.38	b.d.	1.52	0.23	0.41	0.81

Table 7. The fraction (%) of rare earth elements in the 0.2 µm filtrates (nd not different (p 0.05) from unfiltered sample)

Site	Depth m	Dy %	Er %	Tb %
L. Norrtorpsjön	1	11.0	7.2	12.2
	8	22.3	26.1	14.1
	12	73.1	65.5	48.5
	27	72.9	67.1	67.9
L. Pölen	1	nd	nd	nd
	3	nd	nd	nd

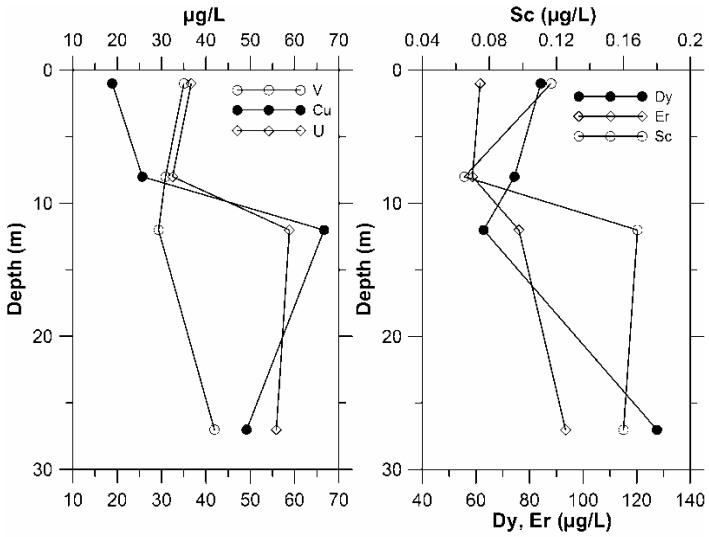

Figure 3. Examples of concentration profiles for selected elements

Statistical interpretation

The entire data set was evaluated with Hierarchical cluster analysis in R-mode and Q-mode to examine the relationships between variables and samples, respectively. The Lake Norrtorpsjön samples grouped in three main clusters. Group A were samples from a depth of 9 m and deeper; group B were samples from between 5 m and 8 m, and group C were samples from above 5 m. Samples from the epilimnion, thermocline and hypolimnion were separated with this strategy for data evaluation.

R-mode cluster analysis divided the analytical parameters into two main clusters, A and B. Two main sub-groups were identified in cluster A. The sub-group A1 includes electrical conductivity, calcium, iron, gallium, magnesium, molybdenum, nickel, scandium, sodium and uranium while the sub-group A2 includes aluminium, lead, potassium, vanadium and zinc. Cluster B also divided into two main sub-clusters. B1 includes cerium, europium, gadolinium, lanthanum, lutetium, neodymium, praseodymium and yttrium while B2 includes cadmium, copper, gadolinium and pH. R-mode cluster analysis indicates that the different clusters of parameters possibly have different origins or behaviour in the different compartments of the lake. This relationship depends on the chemical environment and properties of the individual element. One critical parameter is depth and another is pH. In order to better understand the system, water level fluctuations in the catchment should be measured and it should be sampled under different hydrochemical conditions, such as winter stratification and autumn and spring turn over.

Environmental consequences

The present data set is not sufficient for a complete spatial or temporal evaluation, but some remarks can be made concerning the impact of the pit lakes on downstream systems. During stratification, only the epilimnion is active in lateral transport process. Retention time and downstream response time would be a fraction of the theoretical residence time for the lake. Individual rain storms would result in a large downstream transport of elements and biological impact since the elements are mainly dissolved species.

The relatively high pH in Lake Norrtorpsjön results in an accumulation, or at least a temporal retention, for many environmentally hazardous elements. The major process seems to be adsorption to autochthonous solid phases of aluminium and iron. Possibly the retention capacity is somewhat counteracted by the redox conditions since settling iron phases evidently dissolve in the hypolimnion. In a “natural” system with this depth, primary production in combination with the inflow of high molecular carbon compounds (e.g. humic substances) would lead to an accumulation of organic matter at the sediment surface. During stratification oxygen would be consumed and with the high sulphate

concentrations in the system sulphide formation would precipitate several trace metals and REEs. This is evidently not the case not even during summer stratification, as indicated by the concentrations and empirical speciation of iron, oxygen saturation and Eh in the system. Thus, when autumn circulation occurs, the total metal inventory would be available for transport further downstream.

Conclusions

The neutralised pit lake, Lake Norrtorpsjön retains a number of metals from the surrounding sources during summer stratification because of its rather high pH, which facilitates precipitation of ferrihydrite and aluminium hydroxides and hydrated sulphates and adsorption of trace metals. Zinc and vanadium are exceptions because of their speciation. Both allochthonous and autochthonous sources of high molecular weight carbon compounds are too low to allow for a redox potential that is low enough to induce sulphide formation in the hypolimnion. Hence, metals that are accumulating below the thermocline are available for further transport downstream once the autumn circulation begins.

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