Metal release and mobility in an arctic lake due to artificial drainage

Effects of mining and sulfide oxidation

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Abstract

The aim of this report was to investigate the potential effects of sulfide oxidation in sediments of an arctic lake, N Luossajärvi, induced by lowered water level. Lake water, potentially contaminated by metals, was pumped into a mine tailings impoundment. The water quality in the receiving water was evaluated to see if the drainage have had an effect on the water quality. Six sediment profiles were sampled. Each profile were divided into 5 cm sections and analyzed for major elements and trace metals. Water chemistry were analyzed at six sites. As, Ni and Cu had high concentrations within undrained sediments, where As levels were classified as highly contaminated (> 27 mg kg^{-1} dw). Trace metals had strong statistical correlation to each other indicating a common source. The PCA analyzes performed suggests that trace metals are controlled by a common factor and drained sediments showed two additional factors controlling the variance of metals. Water chemistry had overall good status, but As, Cd, Ni and Cu exceeded natural background values. Historical data on the other hand showed no statistical difference from measured values. No effects on water quality could therefore be seen after draining of the lake, proposing high precipitation of metals within the tailing or that metals is still prevailing in the drained sediments. Metal mobility were seen within the drained sediments, where only As and Cd were presumed connected to chemical weathering and where erosion and soil properties seems to be responsible for most metal mobility.

Key words: Arctic environment, Sulfide oxidation, Metal leakage, Contaminated soils, Mine tailing.

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1 INTRODUCTION AND AIM

1.1 Introduction

Sources of acidification, natural and anthropogenic, became highlighted under the 1980´s due to rising and severe environmental issues, with low pH and the following mobilization of metals. The importance of distinguishing between anthropogenic and naturally sources of acidification is apparent when discussing measures to prevent acidification, and which ways to proceed when there are both have natural and artificial inputs (Land and Öhlander 1997).

Two major sources for acidification of surface waters and release of toxic amounts of metals are acid sulfate soils and mining activity. Sulfuric sediments form naturally in the sulfur cycle where sulfate is reduced to sulfide. The process of forming insoluble metal sulfides from aqueous sulfate take place under anoxic condition where little oxygen is present, usually near the bottom of lakes and ocean, due to absence of mixing of water (Broberg and Jansson 1994). Microorganisms catalyzes this process in forming sulfide. Pyrite (FeS_2) can usually be formed in sediments when sulfide reacts with iron. Under reducing environments sediments rich in pyrite remain stable, but when these sediments are exposed to air oxidation of pyrite occurs. Pyritic sediments, oxidized or not, are typically known as acid sulfate soils, or ASS (Dent 1986). Oxidation of ASS produces high concentrations of sulfuric acid and metal ions, which in turn effects surrounding environment and soils where more acid-soluble metals and trace metals can be mobilized. Leaching of toxic amounts of different elements into adjacent streams and lakes can have a profound impact of the ecosystem (Sammut et al. 1996, Boman et al. 2010). Naturally formed ASS is occupying an area of ca. 17 million ha worldwide, where Finland has the highest amounts of ASS in Europe (Andriesse and van Mensvoort 2002). Japan (Vuai et al. 2003), Australia (Hinwood et al. 2006) and West Africa (Andriesse and van Mensvoort 2002) also shows some abundance of ASS and it´s effects.

Metal leakage, due to acidic conditions, from mining activities is a more evidential and easily foreseeable source compared to leakage from sediments. Human activities within the bedrock enable oxygen and water to penetrate and act upon freshly exposed bedrock surfaces, producing acid waters. Sulfide rich bedrock is often related to high metal concentrations, and has great potential for mobilization of those metals. The mining company LKAB in Kiruna, northern Sweden, have started a project in which a nearby lake is to be partly emptied. The one third of lake N Luosajärvi that has been emptied now has the potential of producing acid metal rich water, due to dried sediments. To reduce the environmental risks most of the lake water has been pumped into the mine tailings impoundment (Fig. 1 B), in the hope that adsorption of metals could take place.

1.2 Aim

The aim of this study was to examine the potential effects on water quality of sulfide oxidation in sediments following drainage of an arctic lake (N Luossajärvi). Moreover the water quality downstream the active mine tailings impoundment was also to be investigated, to see if the artificial draining of the lake has had any interference concerning water quality.

2 BACKGROUND

2.1 Study area

The city of Kiruna is located in the north of Sweden, ca 140 km north of the arctic circle. Kiruna belongs to the county Norrbotten, which is the northernmost county in Sweden as well as the biggest, ca 20 000 km² (LKAB 2009). The population of the town was ca 18 200 by the end of year 2010 (SCB 2012).

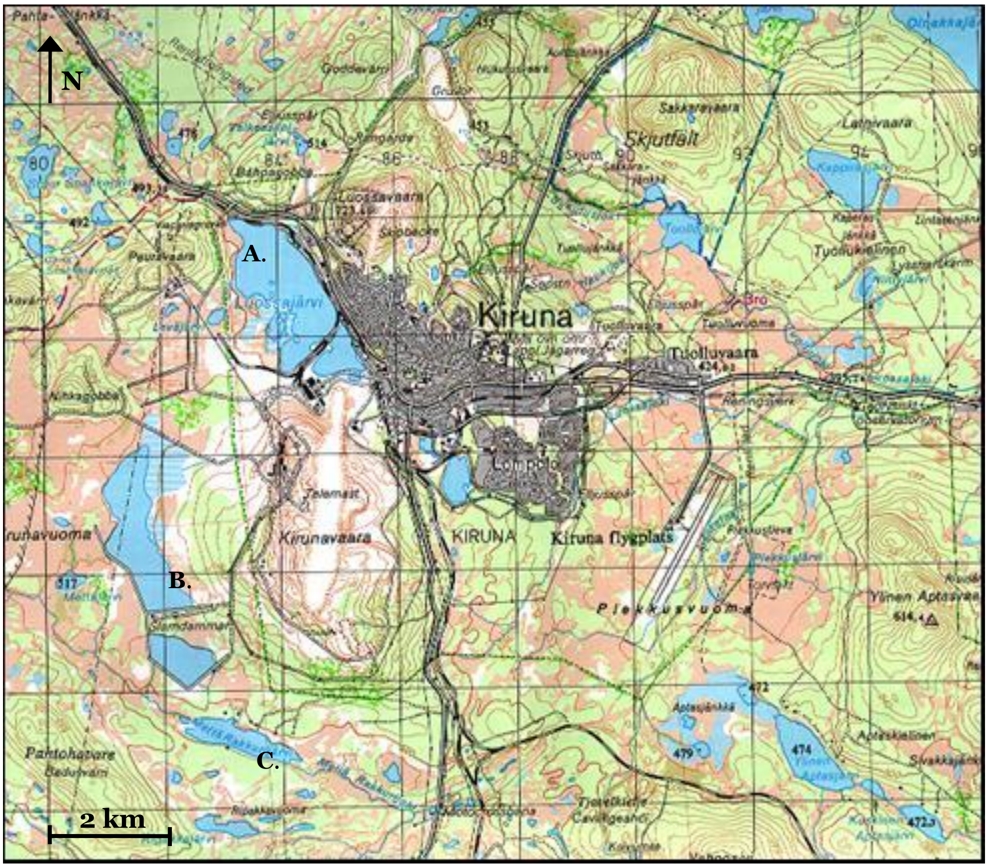

Figure 1. An overview of Kiruna, with lake N Luossajärvi in the north end of the town (A). West of mountain Kirunavaara is the tailings impoundment and clarification pond for the mining industry (B). South of the tailing is lake Mettä Rakkuri and the combining streams (C).

The Rakkuri water system, which is of interest in this study, consists of three lakes with five combining streams. The lake Mettä Rakkuri (488 m.a.s.l., Fig 1 C) is closest to the tailings impoundment (with a water level of 527 m.a.s.l.), and is located just south of the impoundment (LKAB 2009). The outgoing water from the clarification pond have an inlet to Mettä Rakkuri, which therefore is the primarily source of mining waste. The stream Rakkurijoki, from Mettä Rakkuri, later on converge into the beginning of Kalix river. Kalix river has its source within the Kebnekaise massif and mouths in the Gulf of Bothnia close to the city of Kalix.

Lake N Luossajärvi lies in direct contact to the mining area of Kirunavaara and to the main city of Kiruna (Fig. 1 A). The length of the lake is 3 km, in N-S direction, and between 0.6 and

1.2 km wide. Mean depth is ca 4 m, with an maximum depth of 18 m. Before the present drainage of the lake, it's total volume was estimated to 11.3 Mm^3. The catchment area is around 15.3 km^2, of which the lake occupy 14 % of the catchment area (2.2 km^2) (LKAB 2009). Two minor inlets occur to the lake, in the West and in the North. Because of prior drainages of the lake only one artificial outlet existed, through a culvert from the southern parts of the lake. Due to the ongoing drainage and planning of the new industry area for the southern parts of the lake, the new and present outlet of N Luossajärvi is in the North through streams and ending into the Torneriver, up north of Kiruna.

Around the shores of Mettä Rakkuri the bedrock is characterized of an gabbro intrusion (Edsfeldt and Sundström 1995). Here gabbro is usually rich in silica and sulfide minerals (SNA 2009). Along Rakkurajoki, downstream of the mining area and Mettä Rakkuri, granite and granite shale rich in sulfides occur by the stream, with some occurrences of conglomerates (Edsfeldt and Sundström 1995, SNA 2009). The bedrock underlaying lake N Luossajärvi in the North is the gabbro intrusion, with some granite and sulfide rich shale occurrences in the West and Southwest. The Kiruna greenstones (basic vulkanites) are also occurring in the whole area. Along the Northwestern shore of N Luossajärvi a copper mine was in operation in the past, called the Viscaria mine (Fig. 1 A). The Viscaria mine was active until 1997 and is preumed to be one of Swedens largest copper deposits.The copper levels have been around 2-3 %, and the ore was contained within sedimentary bedrock rich in greenstones (SNA 2009).

Till, deposited by glacial drift and the melting of the Weichselian ice-sheet (~ 10 000 years ago), is the dominating soil in the area (SNA 2009). Large areas of open mires also exist. Vegetation is dominated by birch and low growing shrubs. Low growing vegetation and open mires results in a great openness to the landscape, where close location to the tree-line exists (LKAB 2009, SNA 2009).

The yearly mean temperature for Kiruna is -0.3 °C, where the coldest months are January and February (mean temperature of ca -11 °C) and the warmest months are June, July and August (mean temperature of 12 °C). All data refer to the time period of year 2000 to 2010 (SMHI 2012). Annual rain fall is around 600 mm for Kiruna, with higher amounts closer to the mountains in the West. The most prevailing wind directions during summer is from South and Southwest, and second common most from North. During winter the prevailing wind direction is also from Southwest, followed by wind from South. Wind strengths during all seasons often reach values in average between 0.5 to 5 m/s (LKAB 2009, SMHI 2012).

2.1.1 Mining activities

Luosavaara-Kirunavaara AB (henceforth called LKAB) is Swedens largest mining company and has been active since the 1890's. The phosphorus rich iron ore contained in mountain Kirunavaara exists as a leaning disc, which is 4 km wide, 80 m thick and approximately 1500 m deep. The ore disc is leaning with its depth towards the city, causing subsidence of the earth within the city upon mining at deep depth, which could have severe consequences for the city. As mining started, some 100 years ago, the company used an open pit, but relatively soon mining also took place underground. Present underground mining takes place at depth of ca 1 km, but it is planned in a relatively short future to expand even further down (LKAB

2009). Lake Loussajärvi was early, in the beginning of the 1900's, divided into two lakes, by a railway, creating the north and south Luossajärvi. Several drainages of S Luossajärvi have taken place, in order to prevent water leakage from the lake into the mine shaft. In the end of 1990's the present shape of N Luossajärvi was taken, where the last parts of S Luossajärvi was emptied (LKAB 2009). To prevent water leakage and dangerous subsiding of the ground, and for establishing a sustainable future for mining, N Luossajärvi have transformed again, where the southernmost third of the lake has been emptied. The dam was finished around September 2011, in which the drainage started. Within the timeframe of this study most lake water already had been pumped to the tailings impoundment, where only the deepest parts of the emptied lake contained water. The purpose of pumping the lake water to the tailings impoundment was to enable a treatment for the water in which metals and other elements would react with the tailings, which may adsorb potential dissolved fractions. LKAB is also treating the mine waste on a daily basis, mostly through liming, to minimize environmental effects of the tailings. Metal retention from lake water should therefore be accomplished within the tailings. This study is therefore unique in a way that it both have influences from potential AS soils and mine tailings, in which sediments can mobilize metals and the tailing retain the dissolved metals. Figure 2 shows the lake N Luossajärvi and the building of the dam.

Figure 2. Photograph of Lake N Luossajärvi seen from above (dam marked with a black line) and a photography of the construction of the dam, in the Western part.

2.2 Geochemical interactions in soil and water

Sediments rich in sulfide form under anoxic conditions, mostly due to biological decomposition in the sediments, can induce mineralizations and primarily the formation of iron sulfides (FeS and FeS_2) (Dent 1986, Sohlenius 2011). When sulfide minerals come in contact with air reactions with oxygen occur and oxidation takes place. Oxidation of iron sulfides (i.e. pyrite, FeS_2), reaction 1, produces iron hydroxides, sulfate and protons (H^+) (van Breemen 1973, Sohlenius 2011).

$$4FeS_2 + 14H_2O + 15O_2 \rightarrow 4Fe(OH)_3(s) + 16H^+ + 8SO_4^{2-} \qquad (1)$$

Large quantities of protons and sulfate can in turn produce sulfuric acid, which has the potential of lowering soil pH dramatically. pH values of 3-4 is usual in oxidized sulfate soils (van Breemen 1973, Sohlenius 2011). Acid conditions enhance weathering rates in the soil, contributing to some metal mobilization from the sediments. A study by Sundström et al. (2002) proposes that leakage of Ni and Cd from acid sulfate soils (AS soils) in Finland are of much greater magnitude than all of Finlands industrial emissions. So the potential of metal mobilization by sulfide oxidation can not be ignored. Mobilized metals have only partially been bound to the sulfide mineral it self, where the largest amounts of metals mobilized are suggested to originate from other surrounding minerals, primarily silicates. Thus, even if large amounts of metals is mobilized from AS soils the soils themselves normally do not contain higher metal concentrations than other fine grained soils (Sohlenius 2011). Even though AS soils are formed naturally in the sea and in lakes, most oxidations are humanly induced, i.e. by ditching, agriculture and building in the ground. Or as is the case in this study, induced by artificial drainage of a lake in order to enlarge mining activities. However, naturally induced processes occur as well, i.e. by isostatic land uplift in Finland (and undoubtedly also Sweden) near the coastline (Boman et. al 2009). Moreover, some research has proposed that oxidized AS soils can leach acid and metal rich water for up to a 100 years, proposing that long term effects could be more extensive than the immediate effects after oxidation (e.g. Åström and Björklund 1995, Lax and Sohlenius 2006).

Pyrite oxidation and it´s acid producing features is also of great concern for the mining industry. Tailings produced due to mining can consist of relatively high concentrations of pyrite and other iron sulfides, which in contact to the air undergo the same oxidation as described above. Outflow of acidic water from tailings and mines is also referred to as acid mine drainage (AMD) (MiMi 2004). Areas of extensive mining, e.g. the Skellefteå district in Northern Sweden, can often be heavily affected by AMD where adjacent downward streams often show low pH followed by limited biological activity. Acid rock drainage (ARD) often occurs naturally within mining areas, due to naturally high sulfur contents in the geology and mineralizations. Distinguishing between naturally induced acid leakage (ARD) and leakage connected to AMD is therefore hard. The Skellefteå district possesses higher metal concentrations in till and waters, due to natural weathering processes from the bedrock, than other surrounding areas without mines (different geology) (Andersson 2010). It is therefore important to recognize local background levels whenever some kind of environmental status is being evaluated (Naturvårdsverket 2007, Andersson 2010). The bedrock in Kiruna, however, does not contain as much S as the Skellefteå district, with probable lower amounts of AMD from the tailings. This study is unique in that matter that it combines both AS soils and AMD, in order to evaluate any metal mobility and surface water content.

Oxidation of iron sulfides in sediments also include the metastable iron sulfides, with a stoichiometry of FeS1.1, which may oxidize with relatively fast kinetics, reaction 2 (van Breemen 1973, Boman et al. 2009).

$$10FeS_{1.1} + 24O_2 + 26H_2O \rightarrow 10Fe(OH)_3(s) + 5.5H^+ + 11SO_4^{2-} \quad (2)$$

Oxidation of pyrite (reaction 1) has on the other hand rather slow kinetics, at least initial (Boman et al. 2009). A general feature for both reactions is that as the dropping of pH occurs the concentration of dissolved Fe^{3+} increases. Lower pH favor more dissolved Fe^{3+}, which in turn acts like an oxidation agent (stronger than O2) and keeps the reactions going right, towards more acid producing components and higher potential for weathering and metal mobilization (Eriksson et al. 2005, Boman et al. 2009). Other features of importance in the oxidation is that bacteria, *Acidithiobacillus ferrooxidans*, act as catalysts for the process (Boman et al. 2009).

Release of elements in minerals and rocks through weathering is controlled by many environmental factors. Vegetation, frost action, organic matter, temperature, pH, water and redox potential are some of the most important factors. Some parameters also affect the sorption of different elements onto adsorption sites, e.g. clay minerals and iron hydroxides (Eriksson et al. 2005). Large surface area of minerals, high temperatures, available water and high amounts of dissolved cations (Fe^{2+}, Ca^{2+} etc.) are factors that increase the chemical weathering rates in soils. Organic matter has been proven to be of significant importance in term of weathering, as organic matter provides organic acids, adsorption sites and CO2 from degradation of organic matter (Stumm 1992, Broberg and Jansson 1994). Water plays important roles both as a reactant and as a transportation medium for dissolved and particulate elements. Interactions between metal ion and particles are further dependent of the composition of water, where complex formation (e.g. chelates), pH and redox potential affect ions in the water. Release of adsorbed elements or adsorption of elements to particles and different complexes is often a result of changing water conditions (Eriksson et al. 2005, Naturvårdsverket 2007).

Mobilization and dissolution of metals is most of all related to acidic environments, where mobility of e.g. Al, Cd, Cu, Fe and Ni is well connected to enhanced acidity (Löfgren et al. 2003, Eriksson et al. 2005, Sohlenius 2011). AS soils, in particular, inhibit potential for high outflows of acidic and metal rich water, when snowmelt occurs and the frost cracked soil can transport large amounts of water. Atmospheric deposition, long transported groundwater and local point sources are also factors affecting metal distribution in the surface waters (Grip and Rhode 2003, Eriksson et al. 2005). Comparing total concentrations of metals in soils to the leachable fraction (e.g. through humidity cell tests) is an indicator of how strong the bond between mineral and metals, i.e. information about the mobility of elements and the potential for the metals to reach surface waters. High amounts of leachable elements do not always correlate well with high total concentrations. For example Pb which occurs mostly in an immobile and stable form, where leachable fraction is low. Leachable fractions of Cu on the other hand correlates well with higher total concentrations, where higher total concentrations generate higher leachable fractions (Tarvainen et al. 1997, Lax and Sohlenius 2006, Fältmarsch et al. 2008). Surface waters is also variable in its chemistry depending on how far downstream in the catchment area you go. As you go further downstream in the catchment area surface waters get more influenced by inflow of groundwater, where discharge areas are generated. Long transported and old groundwater is characterized by high concentrations of base cations, low oxygen content and high conductivity, which in turn will affect surface water chemistry upon mixing where potential precipitation of metals and elements can occur (Grip and Rhode 2004). Waters rich in Fe2+ can oxidize and precipitate as solids, e.g. goethite, jarosite, schwertmannite and ferrihydrite. Humic matter can also change adsorption potential and immobilize more metals (Broberg and Jansson 1994, Grip and Rhode 2004, Eriksson et al. 2005). Similar precipitation also occurs downstream of S rich tailings, where water rich in dissolved metals becomes buffered and pH starts to rise, as other surface waters is being mixed. The result can be a relatively thick bed of precipitated metals (usually Fe) some distance below the tailings impoundment, making streambeds reddish and hindering vegetation and fish life (MiMi 2004).

2.3 Trace elements

Mobility of metals and trace metals is dependent on precipitation reactions, ion substitutions at particle surfaces and adsorption processes, both in water and sediments (Eriksson et al. 2005). Table 1 shows the estimated regional background levels of trace metals (µg/l) in minor water streams in northern Sweden, as well as preindustrial natural background levels in Sweden established by Swedish EPA, table 2 shows parallel background levels in sediments together with benchmarks for contaminated environments (KM and MKM, where KM is used for planing of more sensitive land use, e.g. schools). Table 3 shows criterias for classification metal contents (µg/l) in steam waters established by Swedish EPA and criterias for toxic levels of metals for aquatic life according to Canadian CCME guidelines, which are more preservative more strict compared to European guidelines .

Table 1. Estimated background levels of some trace metals (µg/l) in minor water streams in northern Sweden, and natural background levels in Sweden established by Swedish EPA (1999).

Estimated background amounts of metals (µg/l) in minor stream waters	As	Cd	Cr	Cu	Ni	Pb	Zn
Natural origin - Sweden	0,06	0,002	0,1	0,3	0,3	0,02	1,0
Northern Sweden	0,06	0,003	0,1	0,3	0,3	0,04	0,9

Table 2. Estimated background levels of some trace metals (mg/kg dw) in sediments in northern Sweden, natural background levels in Sweden established by Swedish EPA (1999) together with established benchmarks for contaminated environments (Naturvårdsverket 2008).

Estimated background levels of metal (mg/kg dw) in sediment	As	Cd	Cr	Cu	Ni	Pb	Zn
Natural origin - Sweden	8	0,3	15	15	10	5	100
Northern Sweden	10	0,8	15	15	10	50	150
Contaminated soil - KM	10	0,5	80	80	40	50	250
- MKM	25	15	150	200	120	400	500

Table 3. Classification of metal contents (µg/l) in steam waters established by Swedish EPA (1999) and toxic levels according to CCME (2007).

Trace metal (µg/l)	Class 1 Very low	Class 2 Low	Class 3 Moderate	Class 4 High	Class 5 Very high	CCME
As	< 0,4	0,4 - 5	5 - 15	15 - 75	> 75	5
Cd	< 0,01	0,01 - 0,1	0,1 - 0,3	0,3 - 1,5	> 1,5	0,017
Cr	< 0,3	0,3 - 5	5 - 15	15 - 75	> 75	8,9
Cu	< 0,5	0,5 - 3	3 - 9	9 - 45	> 45	2 - 4
Ni	< 0,7	0,7 - 15	15 - 45	45 - 225	> 225	25 - 150
Pb	< 0,2	0,2 - 1	1 - 3	3 - 15	> 15	1 - 7
Zn	< 5	5 - 20	20 - 60	60 - 300	> 300	30

As mentioned earlier, the properties of single metals gives elemental information about mobility and which metals that should be of concern in different studies and locations.

Arsenic (As) is commonly found in various bedrock and rock minerals, especially as Arsenopyrite, FeAsS, and in sedimentary bedrocks and schist. As is a metalloid (semi-metal), which inherits some characteristics of ordinary metals like ability for heat and electrical conductivity, however not as strong as other metals (Eriksson et al. 2005, Andréasson 2006). As is a relatively immobile element in the presence of Fe and Mn hydroxides, which has high potential to adsorb As. Arsenite (AsO_3^{3-}) is one exception as it is relatively mobile in nature. Together with pH the reduction of Fe is the strongest property for mobilization and immobilization, which both determine adsorption potential on Fe hydroxides and amount and species of aforementioned (Naturvårdsverket 1999, Löfgren et al. 2003, Eriksson et al. 2005).

Cadmium (Cd) is a relatively soft metal with similarities to zinc and mercury. Cd, like As, derives mostly from schist and sedimentary bedrocks (Andréasson 2006). Organic matter, such as humic particles in water, and clay minerals has strong adsorption of Cd, controlling it´s occurrences in soils and waters (Bydén 1992). pH is the major factor controlling solubility, where low pH releases more Cd to soluble fractions. Sulfuric acid, nitric acid and hydrochloride acid can dissolve and leach Cd, when formation of $CdSO_4$, $Cd(NO_3)_2$ and $CdCl_2$ forms. Cd is present together with zinc in the mineral zincblende (ZnS) due to their close chemical relationship creating obvious correlations between the elements (Stumm 1992, Stumm and Morgan 1994, Naturvårdsverket 1999, Eriksson et al. 2005).

Chromium (Cr) is mostly present in mafic bedrock and minerals. Solubility for Cr is strongly dependent to redox potential, where Cr (+III) is immobile and Cr (+VI) is more mobile. Cr (+III) is however predominating. pH can also control some mobility of Cr, where adsorption processes on metal hydroxides and humic substances is affected (Broberg and Jansson 1994, Naturvårdsverket 1999, Eriksson et al. 2004).

Cupper (Cu) can be present in many types of bedrocks and minerals, where carbonates, sulfides and schist minerals are most common. The natural occurrence of Cu in sulfide minerals makes it relatively easy to mobilize from soils. Leakage of Cu can therefore be seen to have strong correlation to sulfur contents. Low pH increases adsorption of Cu to Fe hydroxides, making pH a controlling parameter for mobility (Naturvårdsverket 1997). Cu and organic matter often results in complex formations with strong bonds. Organic matter can both act as a transportation agent, as immobile Cu in particles, and as solvents, where dissolved organic matter complex binds Cu making it soluble (Broberg and Jansson 1994, Eriksson et al 2005, Andréasson 2006).

Iron (Fe) is a frequent and normally found metal in the environment, as it exists in many bedrocks and minerals with great sulfide and oxide forming characteristics. Two states of Fe are common in soils and waters. Fe^{2+} is usually found in reduced conditions in solutions, where Fe^{3+} is predominant in oxidized conditions in particulate forms, e.g. as precipitated metal complexes (hydroxides), adsorbed to different particle surfaces and complex bond to organic matter. Reduction of Fe^{3+} to Fe^{2+} in soils can contribute to high leakage of Fe to waters (Bydén 1992, Broberg and Jansson 1994, Eriksson et al. 2005).

Lead (Pb) in bedrocks can be found in silicate minerals and in galena, PbS. Organic matter (i.e. TOC and DOC), Fe hydroxides and pH are the most determent factors controlling movements of Pb in waters and the environment (Eriksson et al. 2005). Acid conditions can easily leach Pb from sulfide minerals. pH and Pb therefore have a strong negative correlation to each other. TOC, hydroxides and clay minerals on the other hand have positive correlation to Pb, as it is adsorbed well onto those particles in neutral conditions. TOC also serves as a transportation agent, where Pb in soils can be moved to waters (Broberg and Jansson 1994, Grip and Rhode 2003, Eriksson et al. 2005).

Nickel (Ni) is in nature correlated well with Cu and Fe, and rarely exists by itself. Slow oxidation of Ni in contact with air and in room temperature makes it corrosive resistant, as a protective oxide surface is formed. Like for Cu and Pb, pH and TOC are the controlling factors for mobilization of Ni (Broberg and Jansson 1994, Naturvårdsverket 1999, Eriksson et al. 2005).

Sulfur (S) is a non-metal that derives mainly from bedrock, in form of sulfides (e.g. pyrite). S also exists in sedimentary bedrocks and in present sediment formations. Sulfate (SO_4^{2-}) can serve as an indicator of pyrite weathering, but can also determine metal mobility (Broberg and Jansson 1994). Sulfate adsorption to TOC and metal colloids is pH dependent where acid conditions favors binding of sulfate. Sulfate can moreover bind dissolved metals onto particles and create colloids, when high concentrations of ions prevail (Broberg and Jansson 1994, Grip and Rhode 2004, Eriksson et al. 2005, Andréasson 2006).

Zinc (Zn) is often present as exchangeable fractions in different minerals in soils. Silicate and sulfide minerals are mostly occurring, where Zn is a chalcofile and means that Zn has higher affinity for sulfides than oxides, e.g. as zincblende (Andréasson 2006). Zn and Cd are correlated to each other, and can serve as indicators for weathering processes and the geochemistry of the catchment. pH and humic substances determine adsorption potential for Zn to particles and dissolved fractions. High pH values favors adsorption of Zn to metal hydroxides. High content of humic substances and low pH leaches dissolved Zn via run-off water to lakes further downstream in the catchment (Broberg and Jansson 1994, Naturvårdsverket 1997, Grip and Rhode 2004, Eriksson et al. 2005).

2.4 Chemical parameters

To assess quality of waters and its status some physical and chemical properties usually is taken into account. Accepted and used parameters for status control include pH, alkalinity, electrolytic conductivity, turbidity, temperature, total organic carbon (TOC), redox potential and amount oxygen (Bergil and Bydén 1995, Grip and Rhode 2004, Eriksson et al. 2005). These different parameters all affect the status of streams and water bodies. Moreover these parameters can also indicate how metals will behave in streams and lakes, effecting amounts of metals, solubility, mobility and specification of metal elements (Grip and Rhode 2004, Eriksson et al. 2005).

One of the most used and important factors influencing environmental health and metal mobility in waters is pH. The pH in waters vary both during daily timescales as well as on yearly basis. In surface waters the lowest pH values can be observed during spring snowmelt and autumn rains. Lower pH connected to higher run-off is often explained by higher transport of organic matter from land to streams and waters together with low biological activity at those times. During winter baseflow occurs, which has a higher amount of older and more nutrient rich ground water (Grip and Rhode 2003). In the summer when biological activity is at its peak, pH can vary during day and night. A high productivity during day can induce releases of carbondioxide (CO_2) during night when organic matter is being decomposed. Normal pH values for surface waters in Sweden usually ranges between 6 and 7 (Bydén 1992). According to Swedish EPA surface waters with mean pH higher than 6,8 should be classified as neutral, as seen in table 4.

Table 4. Classification of pH in surface waters from criteria established by Swedish EPA (1999).

pH	***Classification***
>6,8	Neutral
6,8 – 6,5	Weakly acid
6,5 – 6,2	Moderate acid
6,2 – 5,6	Acid
≤5,6	Significant acid

When mean pH gets below 5,6 the classification system indicates that surface waters is acid and that some acidification source should be present. pH is also one of the most important factors controlling the amount of dissolved metals in waters. When pH is low excessive amounts of protons (H^+) is present which, through ion exchange reactions, competes with metal ions bound to different complexes in waters and soils which can mobilize metal ions. Retention times for metals has been shown to increase with increased pH. As oxidation of sulfide minerals also shows, there is a negative correlation between many metals and pH where e.g. Cd and Zn increases in their dissolved fraction with decreasing pH (Stumm 1992, Stumm and Morgan 1994, MiMi 2004, Eriksson et al. 2005).

Alkalinity is a measurement that gives the capacity of waters to buffer acid and neutralize addition of H^+. Acid neutralizing substances mainly consists of HCO_3^- and CO_3^{2-} and dictate buffering capacity of waters. Both alkalinity and pH can serve as indicators of acidity, but where alkalinity foremost is a indicator of the sensibility for acidification, i.e. how long the buffering processes can proceed (Bydén 1992, Eriksson et al. 2005). According to Swedish EPA, surface water with alkalinity over 0.2 mekv/l should be classified with very good buffering capacity (table 5).

Table 5. Classification of alkalinity in surface waters from criteria established by Swedish EPA (1999).

Alkalinity (mekv/l)	***Classification***
>0,20	Very good buffering capacity
0,20 – 0,10	Good buffering capacity
0,10 – 0,05	Weak buffering capacity
0,05 – 0,02	Very weak buffering capacity
≤0,02	None/Insignificant buffering capacity

Alkalinity shows little temporal variation and is more stable over time. Alkalinity is therefore a good measurement for occasional sampling. Alkalinity can have effects on dissolved fractions of different metals where metals cam be adsorbed to HCO_3^- and CO_3^{2-} and compete with particle adsorption sites (Grip and Rhode 2003, Eriksson et al. 2005).

Electrolytic conductivity (EC), henceforth called conductivity, is a measurement of the amounts of dissolved ions in the water. In surface waters the dominating anions are HCO_3^-, Cl^- and SO_4^{2-}, and the dominating cations are Na^+, K^+, Ca^{2+} and Mg^{2+} (Bydén 1992, Eriksson et al. 2005). More dissolved ions generates higher conductivity, where larger amounts of metal ions also generates water with higher conductivity. According to Grip and Rhode (2004) conductivity in surface waters is a reflection of the geochemistry in the catchment and provides information of soil conditions in the area, but it can also be used as an indicator for deviations due to natural and anthropogenic sources, such as industries or atmospheric deposition.

Turbidity is connected to other variables like amount of suspended particles, color and secci depth. Measurements of turbidity is able to establish the light-absorbing properties of waters by emitting infrared light, used units for turbidity is Formazin Nephelometric Unit (FNU). Table 6 gives the classifications for turbidity in Swedish surface waters, usually measured at 0.5 m depth (Naturvårdsverket 1999).

Table 6. Classification of turbidity in surface waters from criteria established by Swedish EPA (1999).

Turbidity (mg/l)	***Classification***
>7,0	Strong turbidity
7,0 – 2,5	Considerably turbidity
6,5 – 6,2	Moderate turbidity
6,2 – 5,6	Weak turbidity
≤5,6	No/insignificant turbidity

Turbidity have an direct correlation to the amount of suspended particles, where sand, clay, organic complexes and metal hydroxides is the most common particles, however the relationships cannot be quantified with good precision (Bydén 1992). All these particles in turn gives waters different chemical and biological properties, depending on which type and the amount of particles in the water. The amounts of organic complexes especially effects biological, physical and chemical properties of waters, where it can determine pH, biological activity, oxygen demand and indirect the amount of dissolved metals. Organic complexes, TOC in particular, can both act as source for dissolved metals at low pH and act as a sink for dissolved metals at higher pH when more active adsorption sites is available (Broberg and Jansson 1995, Eriksson et al. 2005).

Chemical oxygen demand (COD (mg O_2/l)) can be considered as a measurement of the the theoretical oxygen demand that a water possess, i.e. the amount of oxygen the can be used in a chemical total oxidation of all suspended and dissolved substances. The amount of oxygen available for oxidation is measured by the consumption of added strong oxidation agents, usually Mn or Cr, where COD_{Mn} is more common in surface waters and COD_{Cr} in industrial waters and drinking water (Bydén 1992, Bergil and Bydén 1995).

Temperature, total organic carbon (TOC) and redox reactions is also of importance for monitoring water quality. Temperature affect biological activity, with higher production with higher temperatures, and indirect the amounts of dissolved oxygen in waters, both by temperature it self but also from biological processes. Lake stratification can also be induced by temperature, hindering mixing of water an affecting water properties (Broberg and Jansson 1995). As described above TOC can affect pH and metal concentrations in waters. TOC´s strong impact on pH is especially notable under high run-off seasons, i.e. springmelt and autumn (Laudon et al. 2004). Fulvic acids is one of many components in TOC which can act like metal carriers and increase solubility and mobility of different metals, e.g. Pb, As and Hg. Complex formations with organic substances can on the other hand reduce solubility of metals, e.g. Al, Fe and Mn (Broberg and Jansson 1995, Eriksson et al. 2005). Redox reactions are of importance for dissolved metals in surface waters. Redox reactions refer to transfers of electrons between different elements, and naturally occurs as oxidation of organic matter followed by a reduction of oxygen. Reduced conditions can occur where the O_2 level is depleted and low redox potential (pe) occurs. Redox potential is one of the most important factors controlling metals in surface waters, in which redox sensitive elements like iron and sulfur is clearly affected and can become soluble. Redox reactions is generally slow but temperature, pH and biological activity can have large impact on the speed of the reactions, where low temperature and high pH promotes high redox potential and a higher retention of metals (Bydén 1992, Broberg and Jansson 1995, Eriksson et al. 2005)

3 METHOD

3.1 Sampling sites

One primary part of this study was to institute a sampling plan, with descriptions of the analyses proposed, amounts of samples and sampling points. For the investigation of effects on the water quality in the receiving water streams, downstream of the tailings impoundment, a total number of six sites were sampled (Fig. 3). All sites, except NL01 Mette, are within LKAB control programs. NL01 Mette was choosen exclusively in this study due to its location, size and different surruonding, with more mires and because it is a smaller stream.

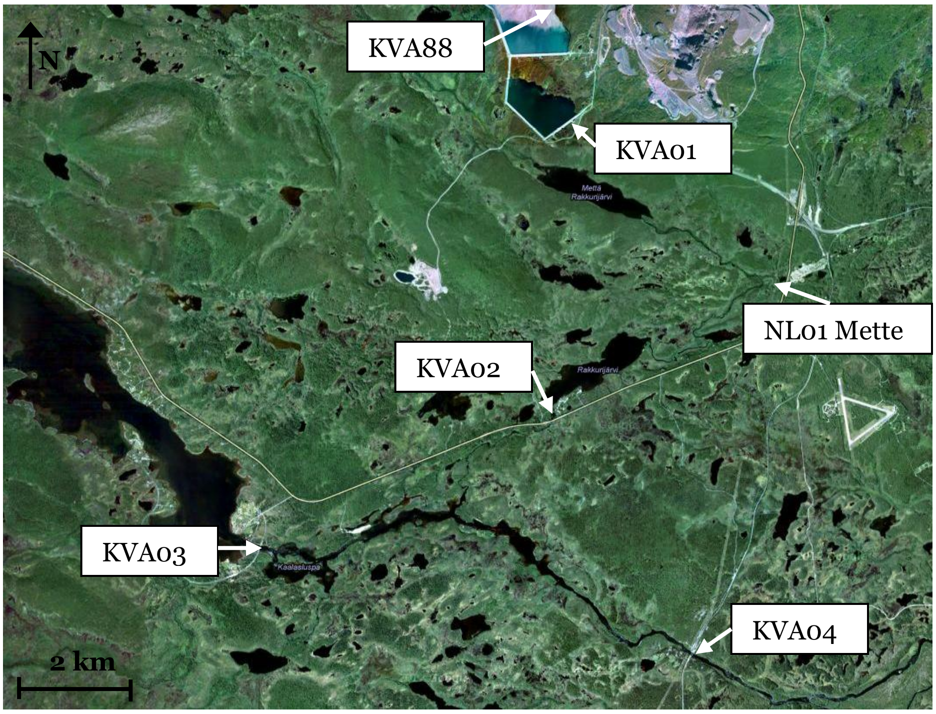

Figure 3. The six sites sampled in this study. Process water from the mine (KVA88), Outlet water in the receiving water stream (KVA01, NL01 Mette, KVA02 and KVA04) and a control site (KVA03).

The Mettä Rakkuri system is composed of several small streams connected by minor lakes and ponds, which, as mentioned above, eventually drain into the Kalix river that leads all the way to the Gulf of Bothnia. The six sites were chosen because of their connection within and location downstream of the tailings impoundment, which should be reflected in the waters's chemical composition. By choosing sites progressively further away from the impoundment, downstream in the system (i.e KVA01, NL01 Mette, KVA02 and KVA04), the potential effects of mining should be present together with some information on how the water chemistry changes. The effects of mining can further be evaluated when samples of mining process water (KVA88) and a control site upstream in Kalix river (KVA03) are added to the evaluation of quality and chemical changes within the system from impoundment to receiving water. Most sites were also chosen for their previous and current use as control points for LKAB and their assessments of the environmental effects of mining activity. Historic data are therefore available and used in this report, where historic deposition in waters streams can be evaluated.

As described above, Lake N Luossajärvi has undergone some transformation, where approximately one third of the lake (the Southern part) was emptied in 2012. Previous studies on sediments in N Luossajärvi (Lundkvist 1991, Ramböll 2008, Golder Assosiates 2011) have been performed. Lundkvist (1991) and Ramböll (2008) aimed to determine the status of sediments regarding trace metals, whereas Golder (2011) investigated the potential for metal mobilization during humidity cell tests. For the sampling of the sediments in this study the aim was to assess changes since the draining of the lake, in order to establish the extent to which sulfide oxidation may have occurred and to detect potential signs of weathering processes together with obtaining a deeper understanding of correlations between elements.

A total number of six sites were sampled (Fig. 4), four sites were located along a W-E transect within the part of the lake which has been emptied (i.e. NL 01- NL04, called NL sediments) together with two additional sites further north in the part of the lake that is remaining (i.e. NNL01 and NNL02, called NNL sediments). The W-E transect was chosen of two main reasons. Firstly a large ditch was under construction in the area, where the new drainage system is planned, and fresh dug surfaces were exposed down into the sediment. The mean depth of the ditch was about 3 m. Sampling of profiles was therefore simplified. Secondly, the W-E transect captures differences in the topography in the bottom surface, where shallower parts of the emptied lake occur in the western parts and more deeper sediments can be found more eastwards. The two additional sediment samples were taken at different depths in the Northern part of the remaining lake. Figure 4 shows the sampling sites for sediment cores in N Luossajärvi.

A clarification for the up coming text: NNL sediments consist of the two northern sites, and NL sediments refer to the W-E transect of drained sediments in the southern part of N Luossajärvi.

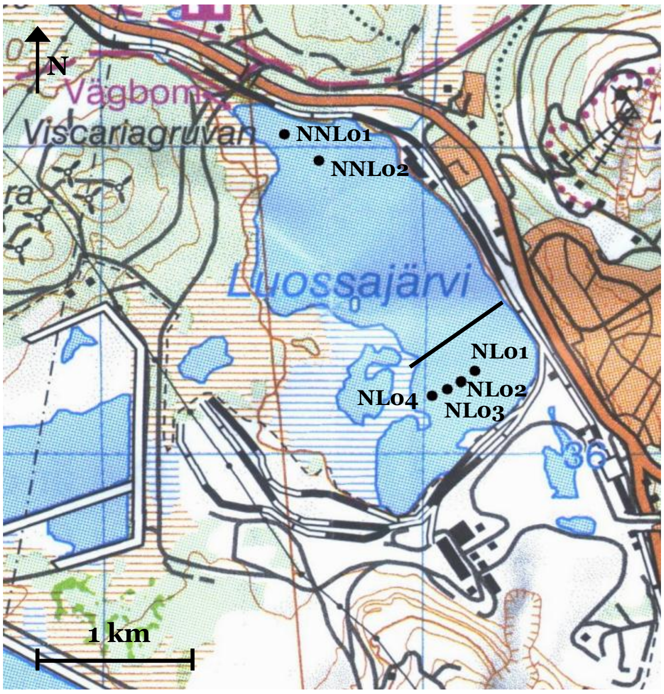

Figure 4. Sediment sampling sites, NL01-04 within the emptied part of the lake and NNL01-02 within the remaining part of the lake.

3.2 Field sampling and analysis

Water samples were collected in the spring of 2012, during one week in April (23-26 April). At each site four samples were collected. First a 250 ml polyethylene bottle was filled (non-filtered) for determination of turbidity, alkalinity (HCO_3^-), COD_{Mn} and sulfate (SO_4^{2-}). Another 250 ml bottle was filled (non-filtered) and preserved (in field) with 1 ml of zincacetate for determination of sulfide (S^{2-}). Two 125 ml acid-washed polyethylene bottles were also filled for analysis of metal concentrations, with one bottle of non-filtered water and the other with filtered water (0.2 µm, in field). Sampling was conducted according to Swedish standard (ISO 5667-6:2005). All water analyses were performed at ALS Scandinavia (accredited laboratory). In addition to the above given parameters the following elements were analyzed: As, Cd, Co, Cr, Cu, Fe, Mo, Ni, Pb, S, V and Zn. The non-filtered water samples should represent total amounts of the regarded elements, both particulate and dissolved (e.g. Broberg and Jansson 1994). Filtration by a 0.2 µm membrane filter in this study is different than the normally used 0.45 µm membranes. The purpose of using a more fine filter, such as 0.2 µm, is for a more accurate determination of the amount of dissolved elements. There is some possibility for colloids and particulate complexes to pass through a 0.45 µm filter (e.g. Eriksson et al. 2005). Therefore using a 0.2 µm filter dissolved concentrations and correlations may be deduced more accurately. Because of the time sensitivity of some variables prior to analysis all samples delivered to the laboratory within 1-2 days. In the field measurements of water pH, conductivity, temperature and oxygen content were also conducted.

Sediment samples were collected at the same time as the water sampling was executed. The four profiles sampled in the emptied (southern) part of N Luossajärvi were collected using a steel cylinder (*geokrycka*). Composite samples were collected in 5 cm sections down to 30 cm depth, an additional sample at 3 m depth (in the bottom of the ditch) was also collected as a potential reference sample. The two sediment cores in the remaining part of the lake were collected using a kayak sampler (Renberg and Hansson 2008) from the lake ice. Each core was subsequently sliced into 5 cm thick sections, to establish a complete profile with coarse resolution. At site NNL01 a depth of 25 cm was reached, and a depth of 30 cm at NNL02. In addition to sampling of sediment pH, oxygen content, conductivity and temperature profiles were measured in the lake at the sampling sites, for the purpose of determine prevailing conditions in the water. Figure 5 shows equipment and sampling of sediments in the northern part of the lake.

Figure 5. Sampling and field equipment for the sampling of NNL01 and NNL02.

Sample preparation, including drying and milling, was conducted in the laboratory before analysis. Samples were weighed and dried to standard dry weight at 105°C for three days, in order to calculate the water content. Analysis included trace element concentrations using a wave-length dispersive x-ray fluorescence spectrometer (XRF), loss-on-ignition (LOI) at 550°C (a proxy for organic matter) and concentrations of Cu in porewater (NNL01 and NNL02). Porewater samples were obtained from sediments using vacuum filtration (1,2 µm filter) and analyzed according to standard methods (SS 028150, SS 028152). Main elements (Al, Ca, Fe, K, Mg, Mn, P, S and Si) and trace elements (Cr, Ni, Cu, Zn, As and Pb) were measured on 0,5 g of dried and homogenized samples using a Bruker S8 Tiger (WD-XRF). The calibration was based on the analysis of 35 certified reference materials. Accuracy for all trace metal elements was within ± 9 % (except Pb ± 14 %) and reproducibility was ≥ 93 % for all trace metals. Details on calibration and accuracy are given in the paper by De Vleeschouwer et al. (2010).

3.3 Data treatment

Historical water data from the monitoring sites were given by LKAB; some of the study sites have data reaching back to 1990 (however not all sites). These water samples were analyzed approximately once a month, usually analyzed for trace metal concentrations together with e.g. S, SO_4^{2-}, P, total-N, turbidity, pH conductivity, color and suspended material. Both historical and current data were processed statistically in MS Excel 2010 and IBM SPSS 20. Control of normal distribution, correlations, t-test, ANOVA and principal component analysis (PCA) were performed on the data. Pearson's correlations and ANOVA used log-transformed concentrations, whereas PCA used z-scores. Significant levels (α) were set to 0.05 and a significant correlation is seen when $r^2 > 0.50$.

Principal component analysis (PCA) is primarily used to reduce the number of components in a large data set and to find patterns within the data, i.e. to identify differences and similarities in the data with connection to several facors. A PCA extracts patterns within the data set and analyzes variation due to different components. These components can later on be evaluated, where the first component explains most of the variation and the second components explans the second most etc., and some knowledge can be acquired as to what the controlling factors are on that specific data set (Smith 2002).

4 RESULTS

4.1 Lake water profiles

Water profiles from the two sites in the remaining northern part of the lake (NNL01 and NNL02) both show similar patterns and concentrations regarding pH, O_2 concentration, temperature and conductivity. NNL01, which is most north of the two sites (Fig. 4), is closer to the shoreline of the lake and therefore has a shallower depth than NNL02. The depth in NNL01 was measured to 3.5 m, whereas the depth in NNL02 was 7.5 m. pH values ranged between 7.1 and 7.4 in the NNL01 profile and between 6.8 and 7 in the NNL02 profile. NNL01 and NNL02 have the same variation in O_2 concentration, varying from 11 to 8.3 mg/l and 11.6 to 7.6 mg/l respectively, where higher O2 concentrations prevail at the lake surface in both cases (Fig. 6 and 7). The temperature ranged from 0.3°C in the surface water to 2.5°C near the bottom in NNL01, and for NNL02 between 0.2°C near the surface and 2.4°C near the bottom. Both profiles have similar shape regarding temperature, where temperature increases closer to the bottom. Conductivity also has similar pattern in both profiles, where conductivity increases with depth in the water until the sediment surface where conductivity drops (Fig. 6 and 7). Conductivity in NNL01 ranges from 679 µS/cm to 1023 µS/cm, and in NNL02 from 887 µS/cm to 1409 µS/cm.

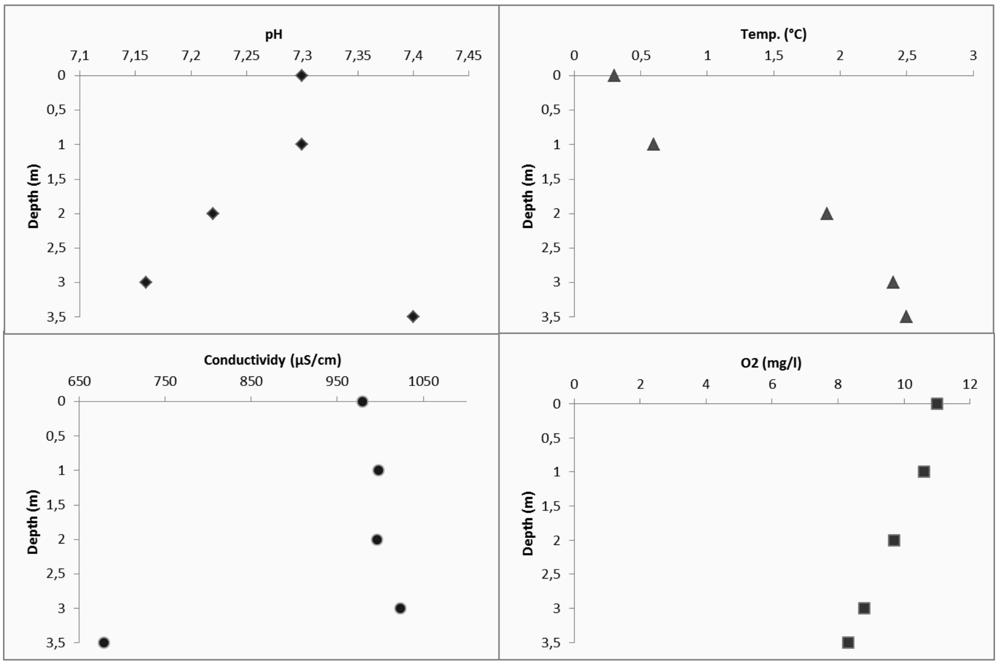

Figure 6. Lake water profiles for site NNL01 regarding concenration of O_2, pH, temperature and conductivity, April 24th 2012.

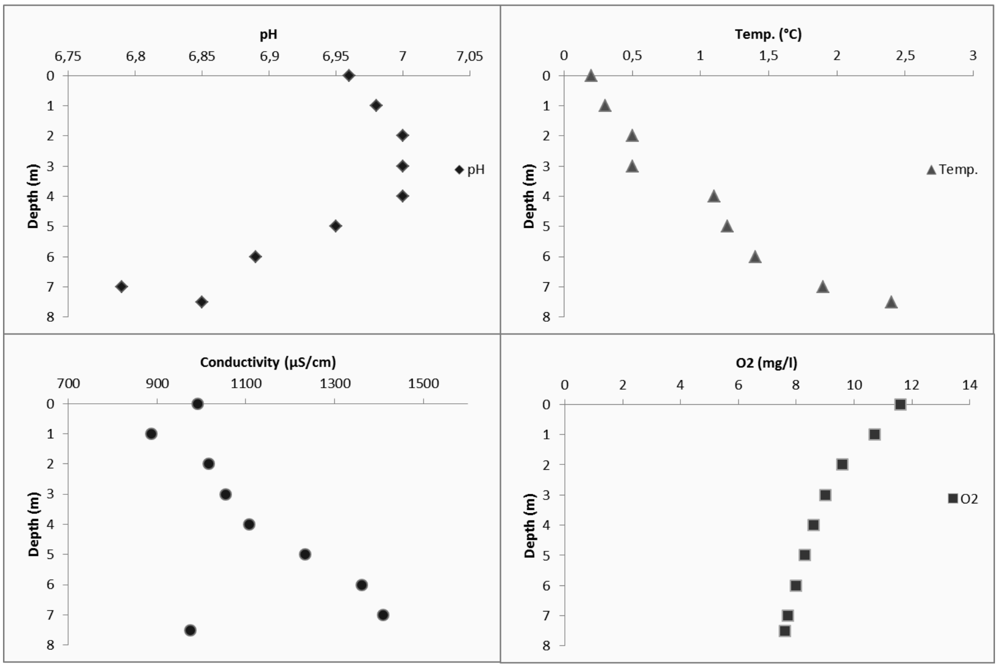

Figure 7. Lake water profiles for site NNL02 regarding concentrations of O_2, pH, temperature and conductivity, April 24th 2012.

4.2 Sediment geochemistry

At the NL sites in the emptied part of the lake the sediments generally had a light grey color, except at the surface of the sediments where some iron had been oxidized and formed a reddish precipitate. The occurrence of reddish colored sediment was primarily apparent at NL 03 and NL 04. Moreover, observed visually, the sediment consisted mainly of silt and clay, but with significant elements of sand and fine sand. Along the face of the ditch some indications for laminated sediments could be seen as well. No clear occurrence of organic matter could be seen. For the NNL sediments the color was more brownish with a clear influence of organic matter, where also some vegetation fragments could be seen. The sediment was composed mostly of clay, organic matter and silt. Some sulfurous odor could be detected in the profile, however sporadically. Concentrations of trace metals in all sediment samples ranged over several orders of magnitude and had an average concentration order of: Zn > Cr > Cu > Ni > As > Pb (Table 7). Compared to mean values for the four NL samples the two sediment profiles in NNL sediments (northern part of the lake, Fig. 4) had lower concentrations of Al, Si, K, Ca and Mg - major constitutes of mineral elements. NL on the other hand had higher concentrations of S, Ni, Cu, Zn, As, Pb – ore-related elements, LOI (%) and water content (H_20), whereas concentrations are similar for P, Mn and Cr (Table 7).

Table 7. Concentrations of trace metals and elements of specific interest for this study (mean ± SD; dry weight) in sediments from all sites, northern sites in the lake (NNL) and southern sites in the emptied part of the lake (NL). Regional background values for trace metals in sediments are also shown (Swedish EPA 1999).

	Al	Si	P	S	K	Ca
Site	g/kg	g/kg	mg/kg	mg/kg	mg/kg	mg/kg
All	50 ± 18	236 ± 50	1259 ± 326	7444 ± 12533	14294 ± 5672	29279 ± 8395
NL	60 ± 8	261 ± 31	1262 ± 296	1716 ± 4309	17466 ± 2777	33460 ± 5451
NNL	23 ± 5	173 ± 25	1251 ± 408	22024 ± 14868	6222 ± 1266	18636 ± 3747
	Mn	Fe	Mg	Ni	Cu	Zn
Site	mg/kg	mg/kg	g/kg	mg/kg	mg/kg	mg/kg
All	1427 ± 2291	69851 ± 38414	13397 ± 5976	22 ± 22	63 ± 78	95 ± 78
NL	1497 ± 2696	53905 ± 25040	16658 ± 2986	12 ± 7	25 ± 9	54 ± 16
NNL	1248 ± 517	110441 ± 37285	5095 ± 2451	47 ± 27	160 ± 91	200 ± 74
Northern Sweden				10	15	150
	As	Pb	Cr	LOI	H2O	
Site	mg/kg	mg/kg	mg/kg	%	%	
All	11 ± 13	12 ± 19	90 ± 45	10 ± 14	37 ± 35	
NL	5 ± 5	4 ± 2	91 ± 49	1 ± 3	15 ± 9	
NNL	27 ± 15	29 ± 28	87 ± 33	31 ± 4	91 ± 2	
Northern Sweden	10	50	15			

Comparing the mean trace metal concentrations in the two data sets (NL and NNL) to regional background levels some elements have significantly higher concentrations in NL and NNL, suggesting a strong influence of point sources. Cr concentrations are, for both NL and NNL, 5 to 6 times higher than the regional background value established by Swedish EPA (1999) and also classified as contaminated soil (KM level, Swedish EPA 2007) where the benchmark is surpassed (80 mg Cr kg^{-1}). Ni and Cu are around the regional background values when looking at NL data, for NNL the values are 4-5 times higher than regional background levels, also surpassing the benchmarks for contaminated soils (Swedish EPA (2007) KM level; 40 mg Ni kg^{-1} and 80 mg Cu kg^{-1}). NNL sediments also exceed the MKM level for As (25 mg As kg^{-1}) proposing some potential negative effects on the environment, NL concentration is around half the regional background value. Other elements like Al, Fe, Si propose a more minerogenic soil for NL sediments, with higher concentrations in NL than NNL, in agreement with observations in the field and by Eriksson et al. (2005).

Looking at the sediment profiles at the different sites, various trends can be seen for some elements and parameters (Fig. 8A and Fig. 8B). For base cations, K and Ca, together with Al, and Mg two trends can be found, where the concentration decreases downwards in the NNL profiles but increases downwards for the NL profiles. This is especially obvious for K and Mg. Moreover the samples collected at a depth of 3 m correspond to values at 30 cm depth, for the NL sediments. For Fe, Cu, Mn, Pb, Zn, Ni and S the overall trend is that the concentrations decrease with depth in the profile, however more profound in the NNL profiles where the highest concentrations can be found at the surface of the sediment profile. NL profiles vary less than NNL profiles, showing only slight decrease for the above mentioned elements and where some profiles in the NNL sediments can be seen to have a complex chemistry. Profiles for As, Cr, Si and P are harder to interpret and no clear trend can be seen. However As and Si concentrations seem to increase with depth down the profile, and Cr and P concentrations tend to decrease with depth. Water content in the profiles decreases with depth for the NL sites, whereas it is the same for the NNL sites. LOI is shown to decrease with depth as well in the NL profiles, but in contrast seem to increase with depth for the NNL sites, especially for NNL02. Here as well all the samples collected at 3 m, as a background reference sample, all had concentrations similar to the concentrations measured at 30 cm depth. Concentrations of Cu in porewater from NNL sediments show the same overall trend as for Cu concentration in sediment, it decreases with depth, except one section (15-20 cm) in the NNL01 profile which has the highest amount of Cu (0.028 mg Cu l^{-1}).

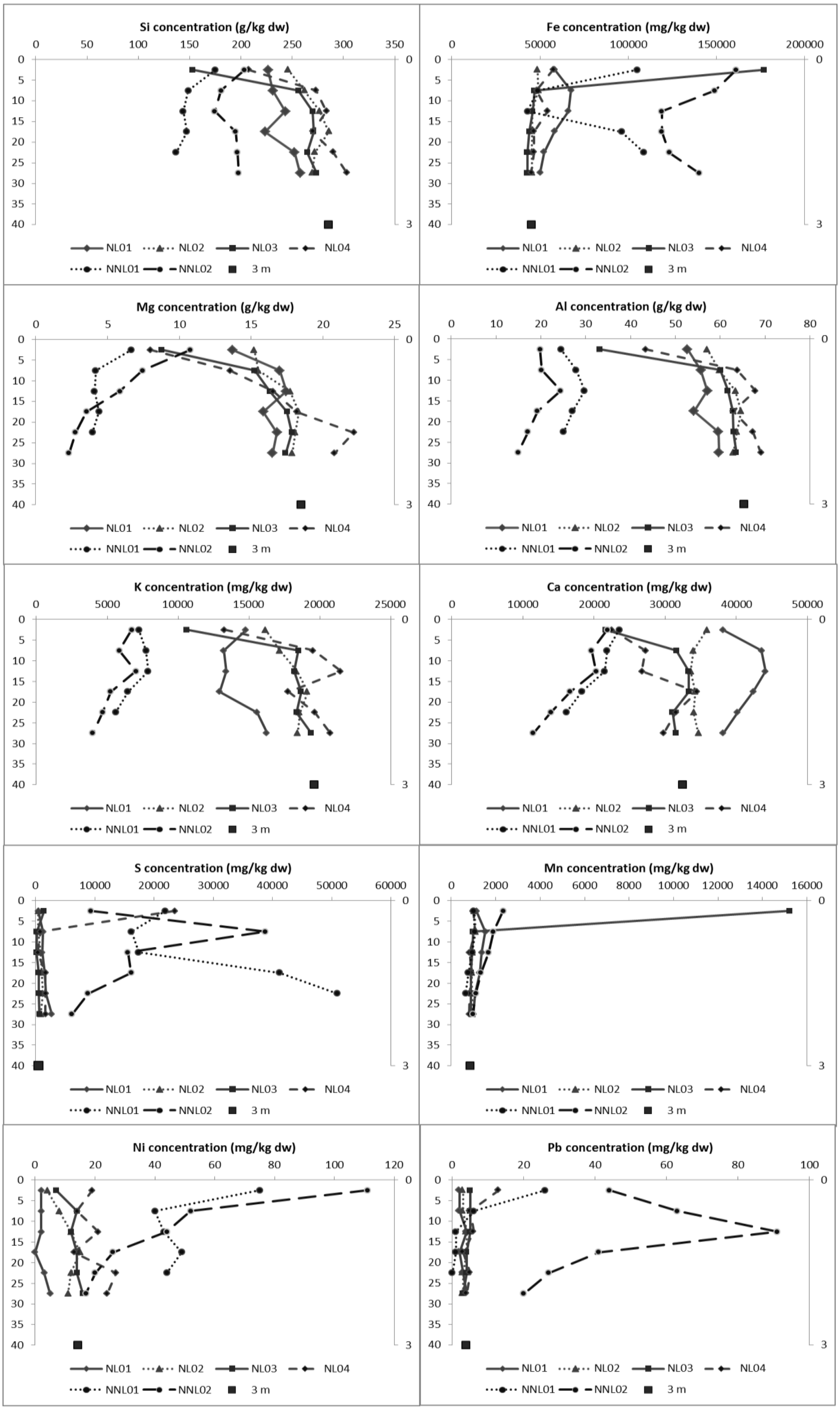

Figure 8A. Concentrations of metals, trace metals and for this study interesting elements down with depth for the six sampling sites (NL01-04, NNL01-02). Every profile is sampled in 5 cm thick sections down to 30 cm depth and a representative background sample at 3 m in the W-E transect (NL samples).

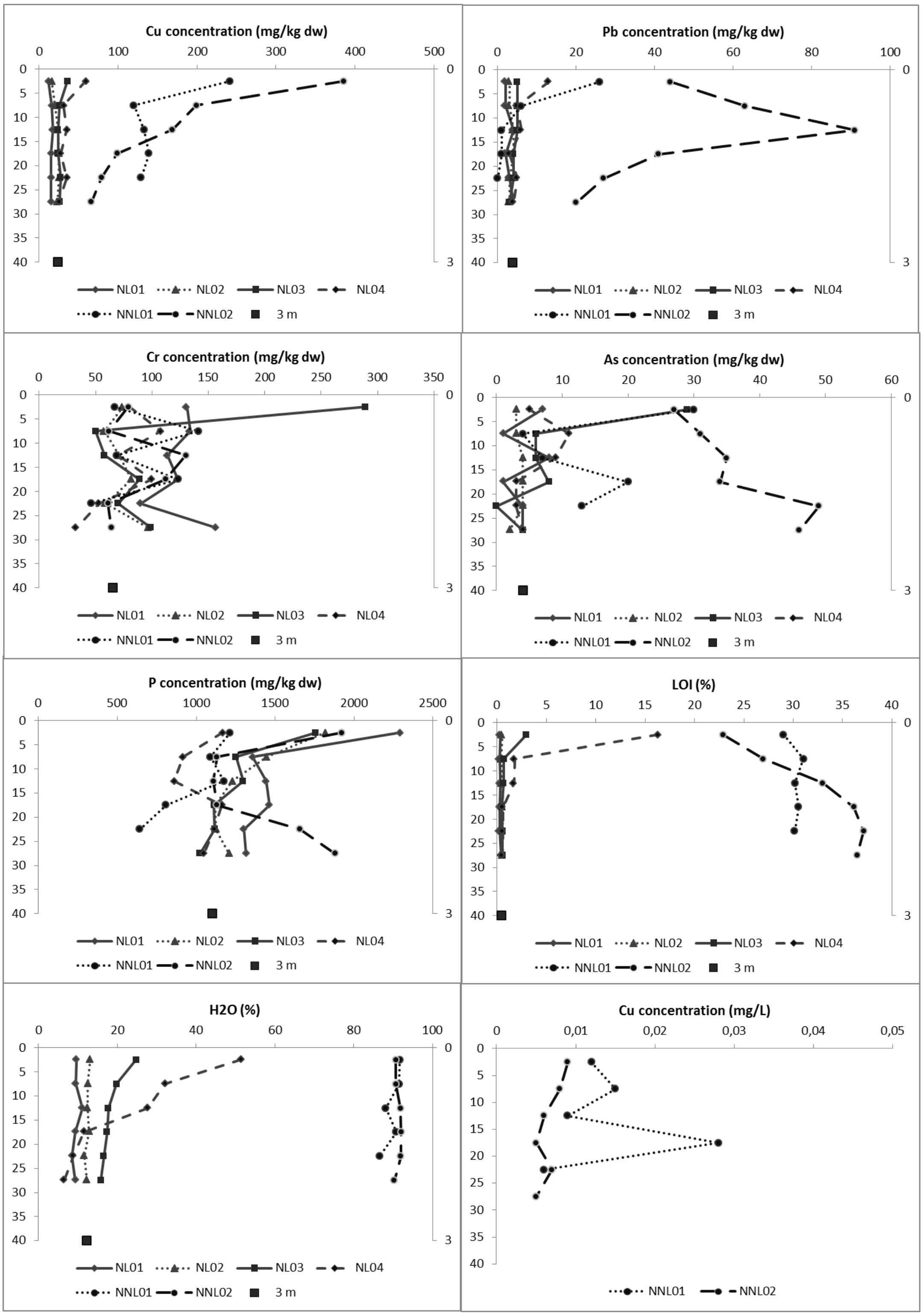

Figure 8B. Concentrations of trace metals water content and LOI down with depth for the six sampling sites (NL01-04, NNL01-02). Every profile is sampled in 5 cm thick sections down to 30 cm depth and a representative background sample at 3 m in the W-E transect (NL samples).

Looking at the trace metal concentrations separately in every 5 cm section, more information is given about how the metals have or will behave. For example, it can be seen that the concentrations of Ni, Cu, Pb and Zn all have their highest values within the NNL profiles, which in many cases exceed the benchmarks for the classification of contaminated soils according to the Swedish EPA (2007) (table 8). As and Cr also exceed the benchmarks in many cases, especially in the NNL profiles; however, multiple Cr concentrations can also be seen higher than the benchmarks in other profiles. NNL02 have distinctive higher concentrations of As, where all values give the whole profile a status of strong contamination (above MKN level). In table 8, red marks concentrations higher than MKM levels and yellow marks concentrations higher than KM level (Naturvårdsverket 2007). Looking at Cu concentrations in porewater downcore in the two NNL profiles, some values are high enough to give them the classification class 4 – high amounts (9-45 µg Cu l^{-1}) according to the Swedish EPA (1999). However, if the CCME levels are to be followed, all samples should be classified as toxic, where the toxic level for Cu is 2-4 µg l^{-1} (CCME 2007).

Table 8. Trace metal concentrations with depth down the profiles of the sediments for the six sites. Cells filled in yellow denote cnocentrations with higher values than the benchmarks for contaminated soils, KM level. Red color denotes concentrations above the more sensitive MKM level according to Swedish EPA (2007). High Cu concentration in porewater is marked with dark yellow to note the classification: class 4 (high concentrations) established by Swedish EPA (2007).

		Metal	As	Cr	Cu	Ni	Pb	Zn	Cu(H2O)
Site	Depth (cm)		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	µg/l
NL01	0-5		7	131	12	2	2	45	
	5-10		1	134	16	2	2	51	
	10-15		8	114	17	2	4	48	
	15-20		1	123	15	0	2	45	
	20-25		4	90	15	3	3	47	
	25-30		4	157	15	5	4	46	
	300		6	68	23	11	4	52	
NL02	0-5		3	74	16	4	3	41	
	5-10		3	58	20	8	3	48	
	10-15		4	71	24	12	4	51	
	15-20		4	82	25	15	4	53	
	20-25		4	59	25	12	3	52	
	25-30		2	97	23	11	3	53	
	300		7	55	22	10	3	49	
NL03	0-5		29	289	36	7	5	128	
	5-10		6	50	26	14	5	50	
	10-15		6	58	24	12	5	48	
	15-20		8	89	24	14	4	50	
	20-25		0	70	27	14	4	50	
	25-30		4	99	26	16	3	51	
	300		2	38	27	16	4	54	
NL04	0-5		5	80	59	19	13	82	
	5-10		11	108	31	14	5	51	
	10-15		9	70	35	21	6	61	
	15-20		3	100	27	13	3	47	
	20-25		3	53	35	27	5	49	
	25-30		4	33	25	24	4	49	
	300		1	101	24	20	4	50	
NNL01	0-5		30	67	242	75	26	218	12
	5-10		4	141	120	40	6	135	15
	10-15		7	69	133	43	1	123	9
	15-20		20	123	139	49	1	167	28
	20-25		13	46	129	44	0	166	6
NNL02	0-5		27	79	386	111	44	338	9
	5-10		31	62	199	52	63	304	8
	10-15		35	130	169	44	91	275	6
	15-20		34	112	99	26	41	178	5
	20-25		49	61	79	20	27	152	7
	25-30		46	64	66	17	20	140	5

The statistical treatment of the data for all sediment samples show that the trace metals are more or less correlated to all investigated elements. Fe, Ni, Cu, Zn, As and Pb all have strong positive correlation to each other and to S, LOI and water content, $r^2 > 0.58$ for all elements, except for Fe-Ni, As-Ni, Pb-Ni, S-Pb, where no significant relationships prevail. Higher concentrations of trace metals are therefore connected to each other and S, LOI and water content in the sediment. Significant negative correlations for Fe, Ni, Cu, Zn, As occur with Mg, Al, Si, K and Ca ($r^2 < -0.54$) except for Ni-Mg, Ni-Si, Ni-K, where no statistical correlation exists. Strong negative correlations also prevail for LOI to Mg, Al, Si, K, Ca ($r^2 < -0.83$), the same negative correlation also occurs for water content ($r^2 < -0.81$). LOI and water content on the other hand have strong positive correlation to S ($r^2 = 0.87$ and $r^2 = 0.80$, respectively). Cr has no significant correlation to the investigated elements, except for a positive correlation to Mn ($r^2 = 0.57$).

Dividing the data set into subsets can reflect sediment status in a better way, as the sediment characteristics, such as grain size (observed visually) and organic content, can vary among the data set. The obvious subsets in this study are NL sediments (the W-E transect, Fig. 4) separated from NNL sediments (the two northern sites, Fig. 4), which by observations have different characteristics. Comparing correlations within the NL dataset to all sediment data, weaker and fewer correlations can be found generally. Fe and Zn is still though negatively correlated to Mg, Al and Si ($r^2 < -0.65$). Ca is negatively correlated to all trace metals, except Cr and As, as well as with LOI and water content ($r^2 < -0.67$). The strong positive correlations between trace metals are here less profound, where only Pb is correlated to Ni, Cu and Zn ($r^2 > 0.54$), Zn is correlated to As and Cu ($r^2 = 0.51$ and $r^2 = 0.64$, respectively) and Cu is correlated to Ni and Zn ($r^2 = 0.76$ and $r^2 = 0.64$). Positive trace metal correlations to LOI and water content is also weakened in the NL data set, where only Cu and Zn have positive correlation to LOI and water content (Cu $r^2 = 0.76$ and $r^2 = 0.72$, respectively; Zn $r^2 = 0.72$ and $r^2 = 0.60$, respectively). S has no correlations to investigated elements, except to LOI ($r^2 = 0.57$) in the NL data set, compared to strong correlation between S and investigated elements for the whole data set.

In comparison to the previous data sets, the NNL data set shows some large differences. Mg is here positively strongly correlated to Ni, Cu and Zn ($r^2 > 0.84$), in contrast to some negative correlations within all data and NL data. The same trend, a change from negative to positive correlation, can be found with Si, where Si is positively correlated to Fe, As and Pb ($r^2 > 0.71$) in the NNL data set. Ca and K on the other hand goes from a negative correlation to Ni and Cu within all data, and partly within NL data, to a strong positive correlation in the NNL data (Ca $r^2 > 0.79$ and for K $r^2 > 0.63$). LOI also goes from a positive correlation to Ni, Cu and Zn to a strong negative correlation within the NNL data set ($r^2 < -0.63$). Like the previous data sets, NNL data also have strong positive correlation between Ni and Cu ($r^2 = 0.97$), Cu and Zn ($r^2 = 0.78$), Pb and Zn ($r^2 = 0.65$) and Pb to water content ($r^2 = 0,74$). Some new correlations also occur within NNL data, where depth is negatively correlated to Ni, Cu and Zn (r2< -0.60). Worth a notice is also that Cu concentrations in porewater do not correlate well to any trace metal in solid phase, especially not to Cu.

From the one-way ANOVA ($\alpha = 0.05$) performed for all elements together with LOI and water content some interesting results can be distinguished, where site concentrations (using log-transformed values) are compared to each other. For Cr and Mn, all six sites show no statistical difference in concentrations, where the significant values are 0.35 and 0.26, respectively. For all other elements and parameters the concentrations differ statistically between sites (sig. < 0.007).

The succeeding post-hoc test (Tukey's test) distinguishes at which sites the concentrations are different. Mg, S, K and Zn all show the same development where concentrations between sites NL01-04 and NNL01-02 has a statistical difference, but where the concentrations within the two subsets do not have any statistical difference, i.e. sites NNL01 and NNL02 has significantly higher concentrations than NL01-04 but do not when compared to each other. Water content in sediments also have a similar pattern where NNL01-02 has significantly higher water content and lower Ca concentrations than NL01-04. However not within the subsets themselves, except for a significant difference in water content between NL01 and NL03 and a difference between NL01 and NL03-04 plus NNL01-02, where NL03 has higher water contents and NL01 higher concentrations of Ca. Concentrations of P are overall very similar for all sites; however, NNL01 has significantly lower concentrations than NL01 and NNL02. For Si and Al concentrations sites NL01-04 are not significantly different from each other, but where NNL01 has lower concentrations than all other sites, including NNL02, and likewise for NNL02 which has lower concentrations than NL01-04 but higher than NNL02. Site NNL02 is also the only site with statistically higher concentrations of Fe and Pb compared to all other sites. All the other sites do not differ compared to each other. The same applies for As, with higher concentrations in NNL02 than the others, with the exception than NNL01 and NNL02 are not significantly different to each other and where NNL01 does not differ from any site. For Cu sites NNL01-02 have significantly higher concentrations than sites NL01-04, but not when compared to them selves, sites NL01 and NL04 are also significantly different where NL04 has higher concentrations. Site NL01 has statistically lower concentration of Ni than all the other sites and where NNL01 has statistically higher concentrations than NL01-04. Some differences in Ni concentration also occur between NNL02 and NL01-03, where NNL02 has significantly higher concentrations. LOI has, as observed, some different values comparing the sites, where NNL01-02 have statistically higher amounts of organic matter than NL01-04, but not compared to themselves, NL01 also has significantly lower amounts of organic matter than NL04.

To understand and recognize some underlying factors that potentially control the amounts of metals in the sediment and surrounding waters, a PCA was made involving the regarded elements, LOI, depth and water content. The results from the PCA, including all data, show that four components explain 85.4 % of the total variance in the data set, where component 1 explains 58.8 % and component 2 explains 13.6 %. A clear grouping can be seen for trace metals (Pb, Ni, Zn, Cu, As), S, LOI and Fe as well as for Mg, Al, Si, K and Ca (Fig. 9), where trace metals seem to be positively related to components 1 and 2 and the other group seem to have a negative relationship to components 1 and 2.

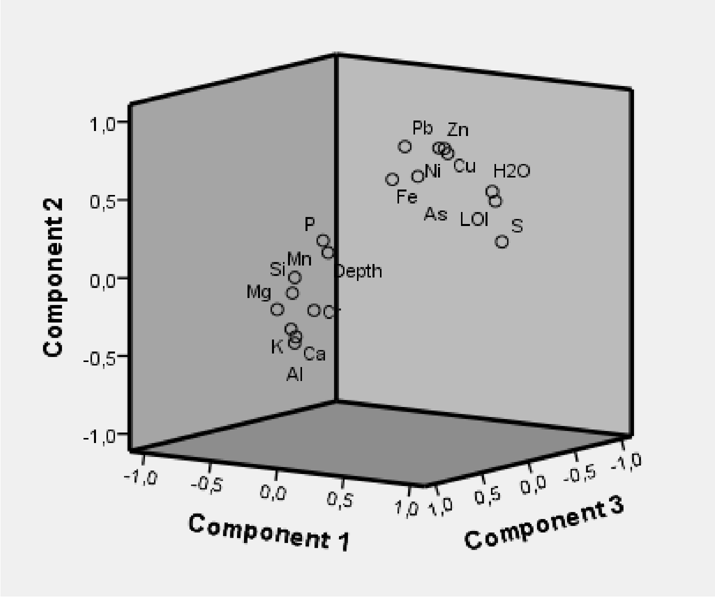

Figure 9. Component plot in rotated space for investigated elements and parameters, for all data.

Table 9 shows the values of the factor loadings, which further showe the observed groupings of elements and parameters. It can also be seen that trace metals seem to be more connected to component 2 than to component 1, in contrast to major elements, which has stronger and negative connection to component 1. Components having greater factor loadings than 0.3 as well as lower than -0.3, is taken as a measure of strong connection and potential for controlling the element in question.

Table 9. Factor loadings to the different components for the investigated elements and parameters. Principal components analysis, rotation Varimax with Kaiser normalization.

	Component			
	1	2	3	4
Mg	-,874	-,358		
Al	-,762	-,567		
Si	-,861			
P				-,797
S	,840			
K	-,780	-,477		
Ca	-,693	-,507		
Cr			,874	
Mn			,944	
Fe	,417	,693	,470	
Ni	,375	,760		
Cu	,415	,810		
Zn	,490	,844		
As	,447	,682		
Pb		,814		
LOI	,816	,517		
Depth	-,383			,655
H2O	,798	,577		

Dividing the whole data set into subsets are again favorable, bearing in mind that NL and NNL subsets differ in their composition and origin. PCA analyzes were further made on the NL separately and the NNL data separately. The result from the PCA, including the four NL sites, states on the other hand that three components should be considered. The three components explain 86.5 % of the variance in the subset, where component 1 explains 45.8 % and component 2 explains 28.3 %. Several groupings can be seen in this data set, where more trace metals and Fe groups together, Cu, Pb, LOI, S and water content also groups together and where Si, Al, K, Mg form one group.

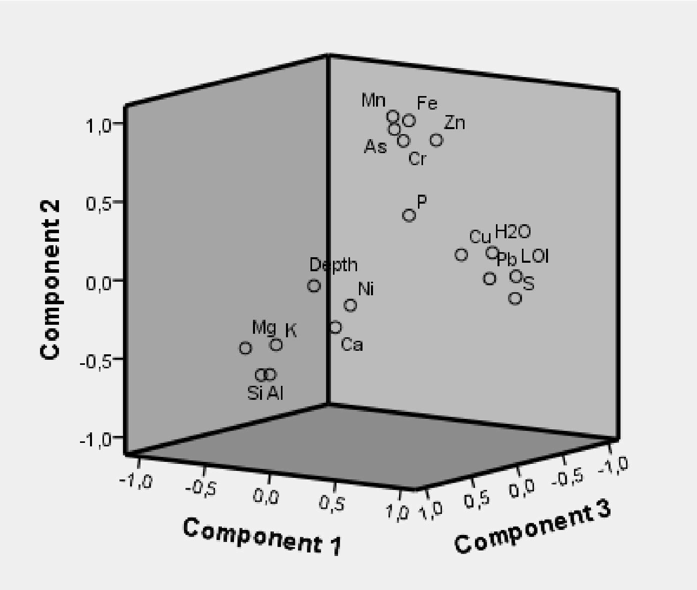

Figure 10. Component plot in rotated space for investigated elements and parameters, data from the four NL sites.

Table 10 shows values for factor loadings, and underlines some of the observed groupings. It also shows that all elements seem to be divided between more variable between the components, where Pb, Cu, LOI, Ca, S and Mg are in relation mostly to component 1 and Zn, As, Fe and Cr are related to component 2. Ni, K, Al, Si and P on the other hand are related to component 3.

Table 10. Factor loadings to the different components for the investigated elements and parameters. Principal components analysis, rotation Varimax with Kaiser normalization.

	Component		
	1	2	3
Mg	-,571	-,456	,568
Al	-,343	-,583	,721
Si		-,561	,772
P			-,768
S	,911		
K		-,340	,900
Ca	-,635	-,485	-,507
Cr		,764	-,462
Mn		,968	
Fe		,926	-,329
Ni	,425		,842
Cu	,896		,301
Zn	,430	,874	
As		,913	
Pb	,960		
LOI	,962		
Depth			,428
H2O	,905		

The result from the PCA, including the two NNL sites, states, unlike the others, that five components should be considered when investigating underlaying factors. The five components explain together 95.8 % of the variance in the NNL subset, where component 1 explains 36.8 % and component 2 explains 34 %. No clear grouping of elements can be seen in the loading plot (Fig 11). However some trace metals, Ni, Cu and Zn, seem to be located together.

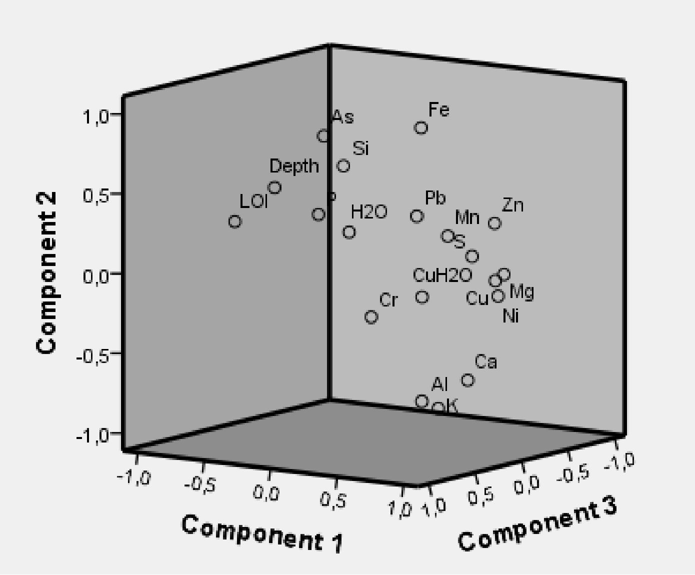

Figure 11. Component plot in rotated space for investigated elements and parameters, data from the two NNL sites, including porewater concentrations of Cu.

As shown in table 11 most of the investigated elements are related to component 1 and 2, with only few strong correlations for components 3 to 5. Ni, Cu, Mn, Ca and Mg have strong positive relation to component 1, whereas depth and LOI have the opposite, a strong negative relation to component 1. Al, Ca and K have strong negative relation with component 2, whereas Si, Fe and As have positive connection to component 2. S and P are connected to component 3, and Cr connected to component 4. Porewater concentration of Cu and Pb have connection to component 5.

Table 11. Factor loadings to the different components for the investigated elements and parameters. Principal components analysis, rotation Varimax with Kaiser normalization.

	Component				
	1	2	3	4	5
Mg	,990				
Al		-,891	-,364		
Si		,727	,575		
P		,462	,843		
S			-,946		
K	,465	-,850			
Ca	,697	-,649			
Cr		-,334		,858	
Mn	,719				,452
Fe	,357	,902			
Ni	,965				
Cu	,983				
Zn	,839	,338			,378
As		,841	,305		
Pb	,334	,347		,426	,746
LOI	-,919				
Depth	-,829	,390			
H2O			,372	,843	
CuH2O			-,322	,419	-,786

4.3 Water geochemistry

The investigated elements for the six sites had a predominant concentration order of: S > Mo > Zn > Cu > Ni > V > As > Fe > Co > Cd > Cr > Pb. Table 12 shows unfiltered concentrations for the investigated elements, filtered concentrations are shown in table 13.

Table 12. Concentrations of trace metals, Fe, Mo, V and S for unfiltered water samples.

		KVA88	KVA01	NL01 Mette	KVA02	KVA03	KVA04
Fe	mg/l	0,16	0,02	5,54	0,22	0,18	0,22
As	µg/l	1,13	1,00	1,00	1,00	1,00	1,00
Cd	µg/l	0,08	0,05	0,05	0,05	0,05	0,05
Co	µg/l	0,77	0,44	0,28	0,10	0,06	0,10
Cr	µg/l	0,05	0,05	0,05	0,05	0,05	0,05
Cu	µg/l	2,89	1,93	2,00	1,00	1,00	1,00
Mo	µg/l	72,40	71,80	0,50	16,80	0,58	1,76
Ni	µg/l	3,11	2,04	0,89	0,79	0,95	0,93
Pb	µg/l	0,20	0,20	0,20	0,20	0,20	0,20
V	µg/l	1,76	2,62	0,42	0,05	0,05	0,13
Zn	µg/l	2,00	2,00	2,00	18,50	2,00	2,00
S	mg/l	305,00	295,00	3,75	136,00	1,63	11,30

Table 13. Concentrations of trace metals, Fe, Mo, V and S for filtered (0.2 µm) water samples.

		KVA88	KVA01	NL01 Mette	KVA02	KVA03	KVA04
Fe	mg/l	0,004	0,004	1,43	0,04	0,08	0,07
As	µg/l	1,06	1,00	1,00	1,00	1,00	1,00
Cd	µg/l	0,06	0,08	0,05	0,05	0,05	0,05
Co	µg/l	0,39	0,35	0,15	0,09	0,07	0,08
Cr	µg/l	0,05	0,05	0,05	0,05	0,05	0,05
Cu	µg/l	1,59	1,77	1,00	1,00	1,00	1,00
Mo	µg/l	75,90	74,70	0,50	16,50	0,67	1,70
Ni	µg/l	3,41	1,16	1,66	1,54	0,93	1,46
Pb	µg/l	0,20	0,20	0,20	0,20	0,20	0,20
V	µg/l	1,49	2,38	0,15	0,05	0,06	0,05
Zn	µg/l	2,00	2,00	6,17	7,86	2,00	3,28
S	mg/l	303,00	291,00	3,63	134,00	1,66	11,60

Total concentrations for As, Cd, Co, Cr, Cu, Mo, Ni, Pb and S seem to mostly consist of dissolved fractions (< 0.2 µm) where all elements have levels above 79 % dissolved fractions (except Cu and Co at KVA 88, 55% and 51 %, respectively).

Trace metal concentrations have more or less variation between the sites (Fig. 12). Ni and Cu are shown to have a sharp, almost exponential, decrease and Co and As have more of a slight decrease, whereas Pb, Cd and Cr have little variation. Concentrations of S also decreases downstream but show larger variation between sites, Fe concentrations is relatively stable through out the system, however with a large peak at NL01 Mette (Fig 13). Weak relationship between S and Fe proposes that Fe is being oxidized and precipitated, and the produced acid is presumably neutralized by Ca carbonates as pH values are relatively high. The peak in Fe concentration at NL01 Mette is seen to relate to the drop in concentration for S at the same site. Mo concentrations is seen strongly connected to S concentrations, indicating potential Mo bearing sulfide minerals.

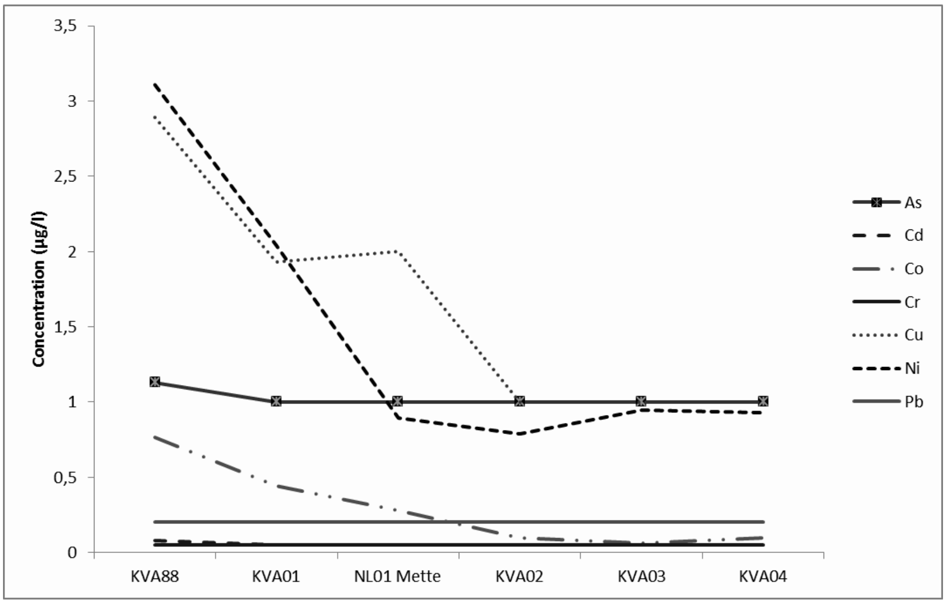

Figure 12. Regression of trace metal concentrations from the tailings impoundment into the water system.

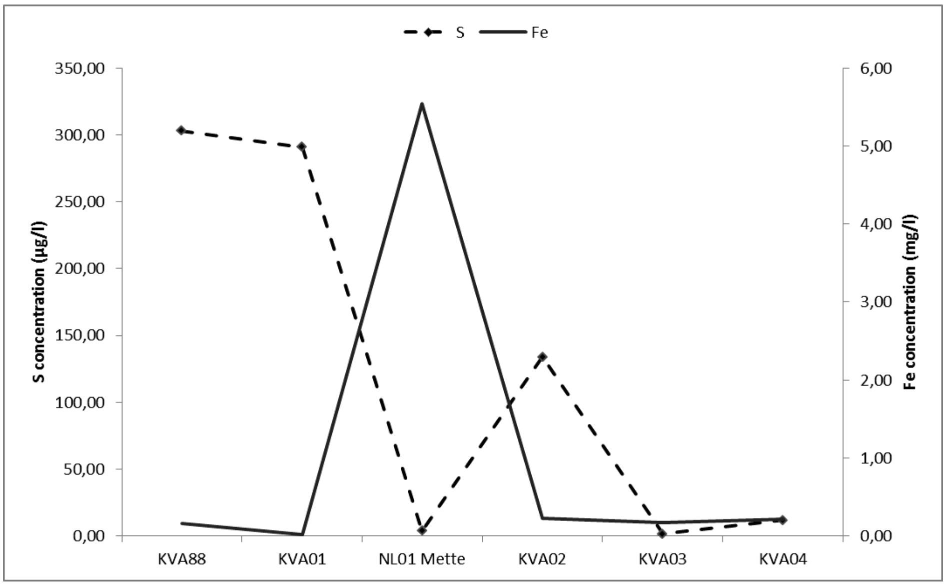

Figure 13. Iron (Fe) and sulfur (total S) concentrations from the tailings impoundment and into the water system.

Looking at unfiltered concentrations only Cd concentrations can be classified as high, according to Swedish EPA (1999), where Cd concentrations are a class 4 for all sites (values over 0.3 µg l^{-1}). No other trace metal is shown to have high values (above class 2) in this study. Looking at CCME's benchmarks though, both Cd and Cu exceeds the toxic levels for aquatic life (0.017 µg Cd l^{-1} and 2 µg Cu l^{-1}) (Fig. 14). Cd exceeds the CCME level at all sites, however Cu only exceeds the level at two sites, KVA88 and NL01 Mette (and on the border to exceed at site KVA01). Unfiltered concentrations for other trace metals all have low classification status, all below class 3 (Swedish EPA 1999) and CCME benchmarks (CCME 2007).

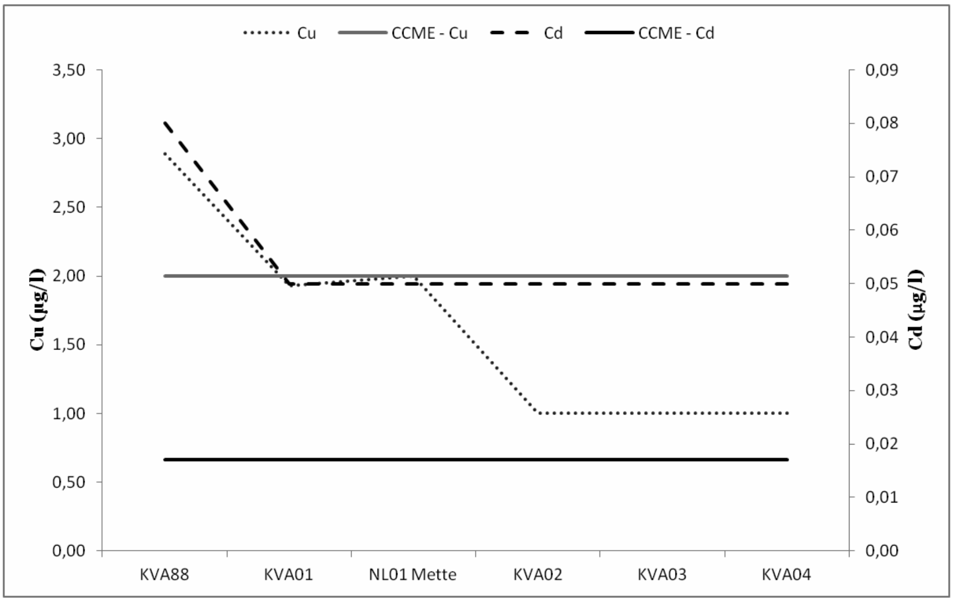

Figure 14. Decline of Cd and Cu within the water system and distance to the tailings impoundment, together with CCME guidelines.

The other analyzed parameters in the unfiltered water samples have similar patterns as e.g. trace metals, with declining concentrations further downstream from the tailings impoundment, se table 14. High bicarbonate concentrations, especially near the impoundment, indicate a very high alkalinity, with a good buffering capacity, according to Swedish EPA (1999). Turbididty is generally very low, with the exception of KVA88 which has strong turbidity (Naturvårdsverket 1999) which in turn may have an influence on the elevated alkalinity downstream of the tailings impoundment due to dissolution of solid phases.

Table 14. Concentrations of S, alkalinity, turbidity, sulfate, sulfide and chemical oxygen demand (COD-Mn) in and downstream of the tailings impoundment.

		KVA88	KVA01	NL01 Mette	KVA02	KVA03	KVA04
S	mg/l	305,00	295,00	3,75	136,00	1,63	11,30
HCO3	mg/l	490,00	59,00	51,00	56,00	15,00	18,00
Turbidity	FNU	1000,00	0,69	12,00	0,76	0,55	0,66
SO4	mg/l	1010,00	943,00	16,80	448,00	5,26	37,60
S2-	mg/l	0,05	0,05	0,05	0,05	0,05	0,05
COD-Mn	mg/l	50,00	0,87	2,24	1,52	1,15	0,76

Physical and chemical parameters of the water also varies as you go downstream (Fig. 15). Conductivity and temperature declines with distance to the tailings impoundment, whereas pH and O_2 levels are more stable. pH values between 6 and 8 generates the classification of neutral to weakly acid conditions, according to Swedish EPA (1999). Worth mentioning is that the conductivity levels at KVA88 and KVA01 are relatively high in comparison to the other sites.

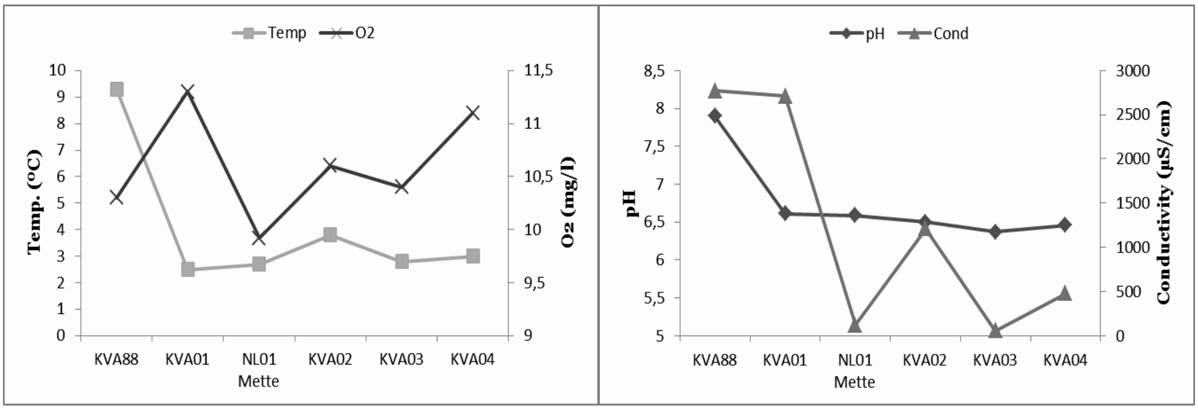

Figure 15. Variation of pH, temperature, oxygen amount and conductivity within the water system and distance to the tailings impoundment.

The one-way ANOVA analysis (data from KVA01-04 during September 2011 to present) showed that only some elements had significantly different concentrations when KVA01, KVA02, KVA03 and KVA04 were compared. Pb, Zn, Cr and Fe did not have any statistical difference in concentration within the sites. Turbidity, Cu, Ni, Co, Cd and As on the other hand have significantly higher concentrations in KVA01 than the other sites. No difference prevailed between the other sites. For sulfate and conductivity KVA01 and KVA02 have significantly higher concentrations than the other sites, as well as significantly different from each other.

Only a few negative correlations could be found among the data set, where Cr is negatively correlated to pH (r^2= -0.63) and to temperature (r^2= -0.69). Otherwise Cr, together with Zn, do not have any correlation at all to the investigated elements and parameters. As, Cd and Co are, in contrary, strongly positive correlated to pH, conductivity, turbidity, sulfate, alkalinity, Cu and Ni (r^2> 0.73, except As-Cu r^2= 0.55 and As-Pb r^2= 0.58). Ni and Cu are, like in the sediments, highly correlated, r^2= 0.90. Trace metals seem overall more correlated to each other, than the other elements, in contras to Fe which is highly correlated to the physical and chemical parameters together with themselves. Conductivity and pH are the strongest parameter correlated to the other parameters (r^2> 0.72, except for Turb. pH r^2= 0.58)

5 DISCUSSION

The two lake water profiles, obtained for O_2, pH, conductivity and temperature, are both relatively stable down with depth. Slightly higher O_2 concentrations at the surface, i.e. first meter (Fig. 6 and 7), are negatively related to the temperature. As dissolved O_2 concentrations in water are known to decrease with higher temperature (Bydén 1992), these profiles imply that temperature is controlling the O_2 levels together with diffusion, where oxygen transport in thermally stratified lakes are governed by diffusion. Conductivity increases down towards the bottom and where the bottom itself have lower concentrations again, at both sites. The conductivity profile would indicate that dissolved ions are released from sediment surface and water interactions. Conductivity levels at around 900 µS cm^{-1} are, compared to average values in Swedish surface waters (50-400 µS cm^{-1}), very high especially for northern lakes. However this lake is so affected by historical mining, industries and multiple transformations together with unique bedrock geology, that high values should not be surprising. The mixing and disturbance of sediments when building the dam is also one likely factor for elevated concentrations of dissolved ions. Stable pH, around 7, in both cases shows that lake water is neutral and not acid, as to expect in Swedish northern lakes (Bydén 1992). Considering all parameters, the lake during this sampling period is likely stable and not in a mixing state. This would also suggest that the lake is dimictic, with two circulations every year (spring and fall) and two stable periods (winter and summer) when some stratification can occur, like in this study.

The abundance order for metals in the sediments are of the same order as in soils around a zinc smelter in Odda, Norway (Svendsen et al. 2007). That would propose a similar origin to the elevated metal concentrations. The observed difference for several element concentrations between NL and NNL sites could mostly be explained by the difference in sediment texture, where NL sediments are more coarse with a more sandy like texture. This is also supported by the higher Si, Al, K and Ca concentrations in NL sites compared to NNL sites. Higher water content and LOI (a proxy for organic matter) in NNL shows more characteristics of normal sediment composition, and would implicate that NL sediments have been disturbed. The main reason would in that case be the artificial drainage. It seems like the drainage of lake water have mobilized the finest sediments, at the sediment surface, possibly into the deeper part of the drained area where lake water still exists. The sediment profiles also support this development. Some lower concentrations of Ca, K, Al, Mg, Si, Cu, Ni and S at the surface of NL soils would imply that these elements have been partly leached from the surface downwards in the profile. The same trend is observed for Zn and Pb at NL01 and NL02. However the origin of elements within the sediments could have varied within the formation of the sediments over several centuries, where further investigations need to deduce different origins for different elements. Most of these metals are on the other hand known as non mobile elements (or for Cu limited mobility). Normal lake sediments would be saturated with water even after a drainage preventing downward percolation of water in soil profiles, further preventing metal mobility; however, this is not seen to be the case for the NL sediments. Drained NL sediments are more like a sandy silty soil than lake sediment, which may be explained by a loss of fine-grained and organic rich substances due to mechanical factors (erosion), such as rainfall and frost actions. Comparing NL data to NNL data confirms a clear difference in soil composition. NL soils are more rich in lithogenics, supporting a more sandy like composition. Organic matter can therefore have been lost upon the exposure of the sediments, as NNL sediments and other studies show that organic rich sediments prevail in the lake. The main reason for leakage of the mentioned elements from NL soils on the other hand would be weathering, due to oxidation. This occurrence is also shown in podzol formations, in the E-horizon, when elements get dissolved by weathering and precipitate downwards in the profile (B-horizon) (Eriksson et al. 2005). That NL01 and NL02 have a more distinctive loss of these elements could be due to a more fine grained texture of the sediments than NL03 and NL04. Fine-grained sediments have a larger specific area, in which more chemical interactions can occur and change the geochemistry, especially considering that the groundwater table has been lowered significantly and water within the sediments will in time percolate downwards (Eriksson et al. 2005). NL03 and NL04 also showed more occurrences of a reddish rust horizon at the surface, likely Fe and Mn precipitates, that could protect the soil from weathering. Close proximity to mires for NL03 and NL 04 could potentially be a source for Fe, through the transportation of organic matter from the mires. Higher LOI and water content at the surface at those sites further contributes to that theory, especially distinctive at NL04. The short timescale from drainage to present is on the other hand not long enough for extensive weathering processes to have occurred, making the theory of weathering of NL soils only one possible explanation. The convergence of concentrations for elements at 30 cm depth would imply that local background values are almost reached at that level. Mean values at 3 m at all NL sites further supports that assumption, with some elements showing similar concentrations at 30 cm and 3 m.

NNL sediments, as mentioned above, do not have the same features as the NL sediments, mostly due to its origin of undisturbed sediments at the lake bottom. Unlike NL sediments, NNL sediments had higher concentrations for trace metals, Fe, Mg, Ca and K at the first 10 cm, near the surface. This would suggest that some accumulation of these elements have occurred in this layer. According to Leeder (1999) normal sedimentation rates in northern lakes in the world care about 15 cm per 100 years, which would suggest that N Luossajärvi have been receiving metals from point sources for at least 80-100 years, almost the same historic timeframe that mining has been active in the area. The higher concentrations of e.g. trace metals within NNL sediments compared to NL sediments further support the statement that the drainage has affected NL soils. Mechanical weathering, e.g. by rainfall, seem to be a more stronger factor for metal mobilization than chemical weathering and oxidation, where metals seem to be strongly bound to organic matter and fine particles. High concentrations of SO_4^{2-} and dissolved ions in the lake water, which has been shown for N Luossajärvi (LKAB 2009), can on the other hand create soluble fractions of As and Cd. High correlation between As and Cd to water content in the sediments and could be a result of that process.

Compared to both Lundkvist (1991) and Ramböll (2008) this study shows higher concentrations of some trace elements in N Luossajärvi. As, Cu and Ni levels are higher compared to Lundkvist (1991), and As levels, partly together with Cu levels, are higher compared to Ramböll (2008). However this is less pronounced for the NL sediments, where lower concentrations of all trace metals exists. Differences in analytical methods for the sediments between the studies may be one explanation of why e.g. As concentrations is different when compared, where XRF analysis has been used in this study and ICP-MS in the other studies. The small amount of samples (two sites) for the NNL sediments could also give a divergence of concentrations from the real mean concentrations in the lake, where additional samples could give more representative concentrations looking at the whole lake. Higher concentrations of these metals in this study may also be an effect of the disturbance of sediments when constructing the dam, migrating fine sediments to deeper parts of the remaining lake. Higher concentrations of As in NNL02 compared to NNL01 agrees with this conclusion, in which NNL02 is deeper and can be classified as a accumulation bottom. This can also be one reason why the NNL sediments are classified as contaminated soils considering As, Cu, Ni and partly Zn, according to Swedish EPA (2008) in this study.

Some porewater concentrations of Cu within the NNL sediments exceeds the classifications of high concentrations, class 4 according to Swedish EPA (2007). Compared to leached concentrations from humidity tests by Golder Associates (2011) the values in this study does not exceed those, implicating that the result by Golder Associates (2011) is valid considering that porewater in this study is vacuum filtrated (1.2 µm). Vacuum filtrated concentrations therefore contains particulate and non dissolved fractions, which will imply that some Cu in the porewater has the ability for sedimentation and to adsorption to other elements and will presumably not mobilize that far. The proposed weathering of 17 kg Cu per year from the drained sediments (Golder Associates 2011) should therefore be considered as a "worst case" scenario, also considering that those calculations were conducted with the assumption that weathering would take place all year around, which is not likely due to low kinetics for chemistry reactions at low temperatures (Eriksson et al. 2005).

Strong correlations between Ni-Cu, Cu-Zn and Pb-Zn through all the data sets ($r^2 > 0.63$) for the sediments indicates that those metals exists together and respond on a similar way to different factor acting on them, this is also in agreement with Svendsen et al. (2007) at contaminated soils near a smelter in Norway. These metals may therefore be deduced to smelter and mining activities, however bedrock geology can also have had an effect. The strong negative correlation between depth and Ni, Cu, Zn in the NNL profile underline the previous assumption that surface sediments are affected by the historic mining activities or bedrock geology. The lack of correlations between trace metals and depth in the other data set proposes that something has happen to the sediments during drainage of the lake. The negative correlation between K, Ca and trace metals also support the theory of weathering of sediments in the NL transect. Overall, the correlations within and between NL and NNL data set are hard to interpret, due to the changing positive and negative correlations. Very variable concentrations through the profiles of the sediments can therefore be affected by several causes, such as micro climate and local chemical composition.

The PCA performed for all data concludes that factor 1 explains most variation, and that factor 1 mostly controls major elements (lithogenics), LOI and water content (table 9). Factor 2 also explains some variation and seem to control the occurrences of trace metals and weak negative loadings for lithogenic elements. This means overall that when lithogenic element concentrations are high the trace metal concentrations get diluted, and vice versa. Without further analyzes the assumption would be that factor 2 is somewhat related to mining activity and is responsible for higher proportions of trace metals in the sediments. The component plot illustrates this as well, where a clear grouping can be seen from trace metals. Looking at only the NL data an even stronger grouping seem to take place where trace metals get divided into two main groups, As together with Zn and Cu together with Pb. Factor 1 seem to control Pb and Cu concentrations, whereas factor 2 seem to control Zn and As. Ni on the other hand seem to be controlled by factor 3. The conclusion made from this would be that Cu and Pb is related to sediment texture, as water content, LOI and S are also controlled by factor 1. Factor 2, controlling Zn and As, and factor 3, controlling Ni, is harder to determine but both could derive from some chemical interactions, like pH or amounts of sulfate. The PCA for the NNL data had no clear groupings, and where a total of five factors contribute to the variance of the data. The only clear indication given is that metals overall seem to be related to factor 1, and could presumably be signs of a point source (i.e. mining). The one-way ANOVA also further states that the NNL sediments and NL sediments are significantly different ($\alpha=0.05$) for most investigated elements, but that various variation within the data sets occur frequently. Even some significantly differences between NL01-02 and NL03-04 tells us that they are under different stage in the soil development, like the different stages of the formation of podzols. However podzols usually forms with the interaction of vegetation cover, which lacks here, and could propose an alternative factor acting on the sediments in different steps (Eriksson et al. 2005). The one-way ANOVA also supports the assumption that NL sediments have been acted on by erosion or weathering processes, presumably mostly erosion due to the short timeframe available for weathering processes to take place.

Concentrations (unfiltered) for trace metals at KVA01 in this study have almost the same range as the mean values at the same site for the period September 2011 to present, the time period for the drainage, except for As, Ni and Zn where all of these elements have higher values in this study, and could indicate elevated concentrations for these metals. Compared to mean values of trace metals for year 2008 at KVA01 on the other hand, only Cd concentrations had higher values in this study. The results for water chemisitry in this study are moreover, as mentioned earlier, in the same range as mean concentrations after the start of the drainage in 2011. This therefore indicates that the water quality at KVA01 has not changed since the lake was drained, except potentially for Cd. However looking at mean concentrations for 2004, the concentrations of Cd in this study are not elevated, indicating that annual variation is larger than the effect of metal leakage from oxidized sediments. Effects of water quality in KVA01 due to the oxidation of sediments in N Luossajärvi can therefore not be seen statistically. However the amounts of Cd in the water at all investigated sites, even the control site (KVA03, Fig. 3) exceeds the classification of high concentrations (class 4, Swedish EPA (1999)) and proposes a potential local natural source of Cd. Cu levels at KVA88, KVA01 and NL01 Mette also exceeds CCME bencmarks (CCME 2007), as well as Cd levels for all sites. Worth noting is that CCME guidelines are lower and more strict compared to Swedish EPA classifications, and that CCME concentrations should be used together with Swedish EPA classifications as that is the commonly used system in Sweden.

Trace metals overall in the water system seem correlated to each other and to some physical parameters, such as pH, turbidity, conductivity and O_2. High correlation among trace metals gives some evidence that they all derive from the same source. The source would then be the tailings impoundment. One-way ANOVA further supports that statement as many metal concentrations in KVA01 are significantly higher than the sites downstream, and further implicates that precipitation of all trace metals occur quickly after KVA01. Some trace metals even had no significant difference downstream of KVA01. The low COD-Mn at most sites, not KVA88, also indicates that the waters downstream have strong potential for precipitation of metals with much O_2 available, where high pH and alkalinity also possess the same characteristics. A quick decrease of sulfate after KVA02, indicates that sulfate does not have an environmental effect, as well as it supports that metal precipitation can occur after KVA02, when sulfate concentrations drop and potential dissolved metals can oxidize or bind to particles and chelates. The relatively high and equal percentage of dissolved fractions, in this study, for most elements at all sites on the other hand does not indicate that high precipitation occur.

Even though concentrations of Cu in porewater is classified as high, according to CCME, no effect can be seen in the tailings impoundment and in the downstream sites from the drainage of N Luossajärvi. The fact that the drainage water was pumped up north in the impoundment close to vegetation, could have had an effect of mobility for trace metals. More vegetation and longer transportation for the drained water favor precipitation of dissolved metals. On the other hand the leakage of Cu, Ni, As and Zn from the NL soils could also be trapped and bound to fine particles in the part of the lake that still has some water left, the deepest part. The possibility remains that trace metals were transported, e.g. by rainfall, to the deeper part when the sediment were exposed to the atmosphere. So both the potential for high adsorption in the impoundment and the possible occurrence of strongly bound metals to particles can explain why no obvious signs from the drainage can be seen in the water chemistry. The proposed adsorption of 40 % for Cu (Golder Associates 2011) can therefore be much higher, as shown in other tailings impounds in northern Sweden in a present study by Lövgren et al. (2012, in review) and in MiMi (2004).

Though Cd concentrations, filtered and unfiltered, in KVA03, a reference site upstream the impound, also shows the same concentration as the other sites, the classification of high, class 4, can be discussed. Without any further investigation the natural contribution of Cd to streams would be a factor worth considering, contributing that the tailings impoundment do not have any effects on water chemistry, not even after the drainage of lake N Luossajärvi. However, as previously studies have indicated, AS soils have the potential for leaching low pH waters with high metal content for up to 100 years (Åström and Björklund 1995, Sohlenius 2011). This would implicate that treatment of the exposed soil, e.g. liming and vegetation cover, are of large interest for LKAB and that water chemistry within the Rakkuri system still can be affected by the drainage, but with a delay. So active monitoring of the water chemistry is still important, and should be for the next upcoming years.

Sampling of the drained water was, unfortunately, not possible in this study where more indications of different processes could have been seen. That would be desirable in future studies. To achieve a more detailed understanding of metal mobility within the exposed sediments of N Luossajärvi seasonal and annual investigations would also be preferable. The fact that this study was conducted during winter can have some effects on the results, where perhaps some metals are immobile due to ice in the soils and are more leached during spring melt. However the time period from the start of the drainage until winter should be long enough to see indications of weathering, as observed in this study. Also during winter the weathering processes slows down, which could have made some of the presented results hard to interpret. Examples for future investigations could be to look at sediment profiles with an electron microscope, to see if any weathering have taken place. Using a electron microscope would also contribute to further understanding of which weathering processes that have occurred, mechanically or chemically or even perhaps bacterial induced weathering. A more quantitative study, with more samples, could also be of interest which would create an even more statistically certain investigation. More data, preferably with over 12 different sampling sites, which is a commonly proposed number for statistical certainly, are of interest when you want a good statistical background. Sampling of several media within the impoundment and downstream sites would also be preferable, e.g. vegetation, till and sediments, as it has been proven that temporal and site distinctive anomalies can be reduced, and natural variation within the catchment area can be observed (Salminen and Tarvainen 1995).

6 CONCLUSIONS

Lake N Luossajärvi is most likely a dimictic lake, and show some winter stratification during this study. Neutral pH values and normal O2 concentrations point to a healthy state for the lake. High conductivity levels support relatively high productivity in the lake, and is most likely derived from leakage of mining waste. The created sediment disturbance when constructing the dam could also be an affecting factor.

Drained sediments in N Luossajärvi can be seen to have been transformed compared to undrained sediments. Erosion of fine-grained particles seem to have occurred. Some weathering also seem to have had an effect on the NL sediments after the drainage, where a leakage of elements is seen near the surface, comparable to a podzol E-horizon. Leakage of As, Ni, Cu, S and Zn from drained sediments are of importance, and have presumably occurred due to erosion and weathering of NL sediments, also underlined statistically. However if the mobility of trace metals occurred by erosion or chemical weathering was hard to see. Higher metal concentrations are usually related to fine-grained sediments which are easily eroded and moved. Nevertheless some strong correlation exists between Ni, Cu and Zn within all sampled sediments, which could imply a mechanically derived process (erosion) as dissolution of these elements is small in neutral to alkaline conditions which prevails in N Luossajärvi. As and Cd on the other hand could have been leached and mobilized through chemical weathering as high concentrations of SO_4^{2-} and other dissolved ions would make them soluble.

A statistically significant difference in concentrations exists between drained and undrained sediments. NNL sediments have high concentrations of especially As, Cu and Ni, in the surface layers. Those elements are well above natural background levels and would therefore indicate inputs from at point source. Stable background values are, in this study, found at a depth of 30 cm, which would correspond to a generalized time span of ca 250-300 years, without any further investigation of site specific sedimentation processes affected by mining. Higher sedimentation rates could be presumed near an active mine due to the elevated emissions of dust and particles from the mine activities. Relating these concentrations to contaminated soil benchmarks (Swedish EPA 2008), KM levels are exceeded for Cu and Ni, and MKM levels exceeded for As. However, when these sediments lay under water not much contamination is possible, but some interest must be take in the future for these sediments, especially concerning As. NL sediments on the other hand have lower concentrations of trace metals, due to weathering, but where Cr concentrations exceed KM level for identification of contaminated soils (Swedish EPA). Due to the upcoming treatment of the drained sediments, liming and soil coverage, no special concern must be taken to the Cr concentrations. Continued monitoring is although needed also in the future as AS soils has shown to have the potential of leaking metals for centuries.

PCA analyzes of the sediments are interpreted as that a point source, likely mining, is responsible for variations and amounts of trace metals. Two other factors can be seen to control the mobility of some variation of trace metals, however these are hard to derive to something obvious. Weathering of some kind was expected, but no clear relation could be found.

Leached trace metals from drained sediments can not be seen to have had an effect on the water quality downstream of the tailings impoundment. The annual and seasonal variation is larger than the observed elevated concentrations for As, Ni and Zn, especially comparing to year 2008. Porewater concentrations of Cu further validate the study by Golder Associates (2011) that potential leakage of Cu from drained sediments is not more than 17 kg Cu. Precipitation of leached trace metals can also seen higher than the assumed level of 40 %, when Cu levels did not raise that much after drainage, although more investigation is needed for presentation of exact numbers. High precipitation within the tailing could be caused by the treatment of the deposited mine wasting, e.g. liming, or by the fact that the drainage water was emptied into a vegetated site within the impoundment or that most trace metals still prevails bound to unaffected fine-grained particles eroded to still water containing parts of the drained area.

Significantly lower concentrations and a regression of trace metals can be shown for the investigated sites downstream of the tailings impoundment, probable related to precipitation and sedimentation processes. High pH and O2 amounts together with low COD in this study all favor short mobility of trace metals within the Rakkuri water system.

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