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# **How does urban discharge affect a lake in a recreational area in central Sweden?**

- A comparison of metals in the  
sediments of three similar lakes

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Madelene Holmblad (2014). **How does urban discharge affect a lake in a recreational area in central Sweden?** – A comparison of metals in the sediments of three similar lakes

Master thesis 30 credits in Physical Geography and Ecosystem Science

Department of Physical Geography and Ecosystems Science, Lund University

# **How does urban discharge affect a lake in a recreational area in central Sweden?**

- A comparison of metals in the sediments of three similar lakes

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Master degree thesis in physical geography and ecosystem science, 30 credits

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## **Abstract**

Metal contamination of lakes can bring negative effects to aquatic biota, and to the general health of the ecosystem. Urban discharge is a known source of common metals. In cold regions, snow disposal sites further enhances the risk of contaminating recipient lakes, due to accumulation of pollutants. The importance of this source is poorly known and is further investigated in this study. Metal content in the sediments of the urban Lake Lillsjön in central Sweden was analysed. Close to Lillsjön is an area with commercial activity, small industries, and a snow disposal site where melt water runs off to Lillsjön. The sediments of Lillsjön were compared with two reference lakes located in the same region. Samples were analysed with Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES) and X-ray Fluorescence (XRF) techniques. The uppermost sediment layer in Lillsjön indicate enhanced concentrations of almost all examined metals. In Lillsjön lead occurred in 16 times higher concentrations at 0-3 cm than the underlying sediment layers. Levels of typical “road metals” like copper, zinc, cadmium and lead deviate from Swedish EPA’s values for pristine lake sediments. There is a risk for negative consequences on biota in Lillsjön. The likely factor causing these enhanced metal concentrations in Lillsjön is the urban discharge with the snow disposal site as a substantial contributor.

## Sammanfattning

Metallföroreningar i sjöar kan orsaka negativa effekter på vattenlevande organismer, samt på hela ekosystemens hälsa. Avrinning från urbana miljöer utgör en källa för många vanliga metaller. Snötippor i kalla områden ökar risken att förorena recipienten ytterligare eftersom förorenande ämnen samlas där. Vikten av denna källa är inte klarlagd och kommer att undersökas vidare i denna studie. Förekomsten av metaller i sedimenten i urbant belägna Lillsjön i Östersund har analyserats. I området kring Lillsjön finns ett handelsområde och små industrier vilket medför mycket tung trafik och asfalterade ytor. Dessutom finns en snötipp där smältvattnet är en del av Lillsjöns tillrinning. Sedimenten i Lillsjön jämfördes med två referenssjöar belägna i eller strax utanför Östersund. Proverna analyserades med teknikerna Inductively Coupled Plasma-Atomic Emission Spectroscopy ICP-AES och X-ray Fluorescence XRF. De ytligaste sedimenten indikerar förhöjda koncentrationer av nästan alla undersökta metaller. I Lillsjön var förekomsten av bly 16 gånger högre vid 0-3 cm än i de djupare sedimenten. Typiska vägmetaller som koppar, zink, kadmium och bly avviker dessutom signifikant från naturvårdsverkets bakgrundsvärden för naturliga sjösediment. De höga metallhalterna utgör en risk för negativa konsekvenser på levande organismer i Lillsjön. Rimligen orsakas de förhöjda halterna i Lillsjön av de urbana inslagen i avrinningsområdet, där snötippen utgör en betydande faktor.

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# 1. Introduction

Since 2001, Sweden has 16 environmental quality objectives that shall permeate environmental actions until year 2020. One of these objectives “good quality groundwater”, is not thought to be achieved. Partly due to human undertakings. Water quality -especially in urban areas- is to a large extent affected by anthropogenic activities. Poorly treated storm water and other urban discharge have negative impact on water quality and ecosystem health status as it contains pollutants e.g. metals and contaminated sediments which accumulate in receiving water systems (SGU, 2004; SGU, 2012).

Accumulation of pollutants is enhanced during cold seasons due to large catchment surfaces made up by snowpacks (Marsalek et al., 2003). The main sources of pollutants during the winter season are cold-started and inefficient engines, wear of studs on tires, and de-icing chemicals used together with anti-skid agents (Engelhard et al., 2007; Marsalek et al., 2003). Urban storm water in cold climates is at present an environmental concern. Especially since snowmelt runoff was associated with enhanced metal concentrations and metals have been shown to accumulate in bottom sediments (Blecken et al., 2012).

Relatively few studies have been carried out on the subject of water contamination from urban discharge in cold climates, despite the fact that snowmelt runoff is a potential threat to healthy ecosystems (Marsalek et al., 2003). Many well-cited reports were written over ten years ago or even further back in time, and this subject needs to be brought back on the agenda. A number of studies from northern Sweden has investigated the quality of old snow, the sources of contaminants and has identified factors that determines the degree to which snow is polluted (Viklander, 1999; Reinosdotter & Viklander, 2005; Reinosdotter et al., 2003). However, there is a knowledge gap concerning the effects of melt water on receiving ecosystems, and the magnitude of contaminants that maintains a possible cause of damage. This is a challenging topic including numerous complex processes, which demands more attention and further investigations for better understanding (Luoma, 1983; Marsalek et al., 2003).

To investigate the topic further, the following case study was carried out studying a recreational lake situated in an urban area in cold climate: Lake Lillsjön in central Sweden.

Lillsjön is an urban lake found only 3 km from the centre of the city of Östersund in mid Sweden. The sediments are rich in calcium carbonate due to the bedrock and enables rare species to live there. The lake is situated approximately 150 m from the largest snow disposal site in the municipality. Large amounts of snow from the city are transported here and the melt

water from the snow dump is transported through a constructed sedimentation basin and a natural wetland before it reaches Lake Lillsjön (Östersund, 2011). To account for the possible negative effects the urban discharge might have on surrounding waters, the municipality of Östersund has carried out its own investigations and sampling which indicate an ongoing accumulation of heavy metals in Lillsjön (Östersund, 2012).

The lake provides an opportunity to study if urban discharge leads to enhanced levels of metals in the sediments.

### *1.1 Aim of this study*

The aim of this study is to investigate if an urban lake in Östersund shows elevated levels of metals in the sediments, compared to lakes situated further from the city. Lillsjön is affected by i.e. storm water from streets and melt water from an adjacent snow disposal site. For comparison, two reference lakes with similar characteristics but more pristine drainage areas are chosen. Samples from the top layers of the sediments in Lake Lillsjön are analyzed and compared with samples from two reference lakes. Because of the strong link between traffics impact on snow quality and the occurrence of heavy metals in snowmelt water, the focus of this study is mainly metals.

This study aims to answer the following questions:

- Do the sediments in Lillsjön contain higher concentrations of any metals than those in the reference lakes Rannåstjärn or Myckeltjärn?
- Are there differences in metal content between different sediment depths?
- Are the metal concentrations in the sediments of Lillsjön potentially harmful to biota?

### *1.2 Expectations*

Previous water samples show that the total metal content in water entering Lillsjön is higher than the outflowing water. This indicates that some metals are accumulating in the lake. Because of settling of particles, most of the metals eventually ends up at the bottom and accumulate in the deepest parts of the lakes. Partly because of that previous investigation, higher concentrations of so called “road metals” is expected in Lillsjön compared to the reference lakes. Higher levels are expected to be found in the deepest parts. But even without these results and kept in mind the geographical location, higher concentrations in Lillsjön are likely to be found. Close to Lillsjön an area with heavy traffic, small industries and a snow disposal site is found. In the surroundings of the reference lakes there is only one obvious and human induced

pollution source identified, highway E14 close to Rannåstjärn. The area around Lillsjön has urbanized mainly over the past 20 years, therefore it is expected to find higher metal concentrations in the top layers in the sediment than further down.

## **2. Background: Factors affecting ecosystem quality of urban lakes in cold climates**

To increase the understanding of the context of this case study, a description of the main factors for how runoff from urban areas can be a threat to water ecosystems is presented. First and foremost, there is a vital difference between pollution from snow and from rain which should be explained. The sedimentation of metals is another key factor for pollution of waters, and their toxicity to aquatic biota. A short presentation of some important metals and their toxicity is therefore included to bring understanding to why metals should be detected in ecosystems.

### ***2.1 Contamination of snow***

To avoid unsafe driving conditions, Swedish roads are cleared from snow. Furthermore, deicing and anti-skid agents are distributed when necessary. Approximately 250,000 metric tonnes of road salt, (sodium chloride NaCl) is used during each winter in Sweden. Risks associated with the use of NaCl are corroding vehicles, contamination of water and vegetation; further it can also affect the partitioning of dissolved metals in runoff (Reinosdotter & Viklander, 2005; Blecken et al., 2012). Sand is also used for improving road conditions in winter, which increases the amount of suspended solids in the melt water. These can in turn act as carriers of particle bound metals or other elements (Blecken et al., 2012). The main sources of pollutants during the winter season are cold-started and inefficient engines, wear of studs on tires, and de-icing chemicals used together with anti-skid agents (Engelhard et al., 2007; Marsalek et al., 2003).

Falling snowflakes have a relatively low velocity and big surface area and hence atmospheric pollutants can accumulate more efficient in snow than in raindrops (Engelhard et al., 2007; Oberts, 1994). As snow lies on the ground, more pollutants can accumulate with time; atmospheric deposition from various urban emissions and transported airborne contaminants is continuous. Thus snow packs in cold climate cities store a mixture of snow, water, chemicals, metals and solids (Marsalek et al., 2003).

The time the snow rests on the ground also affects the snow quality. Snow removed soon after snowfall is usually less contaminated than snow left for several days or weeks. Snow that has not been incorporated in the collection but rather pushed away by plows, ends up beside the road. This can build up small and sporadic piles of snow that in springtime appears as “black snow” because of particles and contaminants that have accumulated on the surface. Therefore,

even the last snow remains are necessary to take care of instead of leaving in the ditches to melt, even if it means an extra effort (Reinosdotter & Viklander, 2006). Viklander (1999) showed the importance of sediment in the snow and snow piles, because the concentration of pollution can be higher in the actual snow than in the melt water. This would then be true both on road sides and at snow disposal sites, which means that the melt water runs off, while contaminated sediment stays on the ground surface. Snow disposal sites also work as accumulation areas for polluted snow. Contaminated melt water is released during the final spring/summer melt as well as intermittent melts (Östersund, 2011). Intermittent melts can cause a concentration of pollutants in the bottom of the snow pack because of flushing of soluble compounds, which eventually brings a pulse of concentrated, acidic melt water running from the snow dump (Marsalek et al., 2003).

## 2.2 Metals from traffic

A study by Engelhard et al (2007) indicated that traffic density affect the heavy metal concentration in the street snow, although the results were not consistent for all elements. For example copper (Cu) was clearly elevated at high traffic density sites compared to low, while zinc (Zn) and lead (Pb) concentrations were high at both sites. However, the variation of heavy metal concentrations was always bigger at the densely trafficked areas (Engelhard et al., 2007), and traffic load is usually defined as an important factor for contamination of snow (Reinosdotter & Viklander, 2005; Sansalone et al., 2003). Heavy metals (infobox 3) most frequently found in runoff from roads and highways are: cadmium, chromium, copper, iron, lead, nickel and zinc (Reinosdotter et al., 2003).

### *Infobox 1. Description of the analysed half metals*

**Antimony** (Sb) is a half metal and somewhat similar to arsenic considering their toxic effects, antimony is possibly carcinogenic but is not bioaccumulating or biomagnifying. It has a long residence time in fresh water systems and can therefore be widely dispersed. Sb is used as flame retardants, alloys and in glass industries (IVL, 2002). Increased use and production has been observed during the latter 1900's although some lines of business try to replace the material for something else. In Sweden antimony is no longer allowed in brake pads, but elevated levels have been detected in trafficked areas because of imported car parts (IVL, 2002).

**Arsenic** (As) has toxic properties and is carcinogenic when exposed to humans by e.g. water and tobacco smoking (EPA, 2008). Elevated levels in nature can occur due to mining activities, agriculture or weathering processes. As mobility is determined by how and to what extent it is adsorbed to metal oxides, for example Mn-oxides (Lafferty et al., 2011). Considered a non-essential (half) metal.

A big source of particle contamination is the wear of tires and pavement, and with studded tires used during winter road conditions the wear is enhanced (Sansalone et al., 2003; Blecken et al., 2012). Tires were shown to be one of the main sources of zinc and cadmium emissions in Stockholm, capital of Sweden, in 2005 (Stockholm, 2007). An adjoining investigation showed that brake pads were a main contributor of copper emissions, and that emissions of lead and cadmium had decreased over the past years, probably due to changes in production. Use of

asbestos has been prohibited in Sweden since 1982, and in 1986 an additional inhibition concerning friction gear as brake pads was implemented. Copper replaced asbestos and since then the mean soil Cu concentrations in the Stockholm area has nearly doubled (EPA, 2002). Also relatively high levels of zinc and antimony (infobox 1) were discovered in brake pads in the mentioned study (Stockholm 2007a). Lead was previously added in petrol but is now prohibited in Sweden. It can still deposit from airborne pollutions and occurs in some colours as pigment.

One way of identifying the metals that are derived from traffic and cars is to analyse the waste water from car washes. Even though cadmium which is considered a very toxic metal, is only allowed for use in exceptional cases in Sweden, it frequently occurs in car washes and ends up in sewage plants from where the sludge can be used as fertilizers on farm land. Meaning that these metal then can leach to surrounding water systems. This is true not only for cadmium, but several other heavy metals like chrome, copper and mercury eventually reaches ground water or lake sediments this way (EPA, 2002).

If a metal is considered to be essential it must have some biological function, such as being part of an enzyme, work

as catalyst or inhibitor in enzymatic systems (infobox 2). Even though a metal might be essential, it will become toxic in too high concentrations; an optimal function is reached at an optimal concentration, while too high or too low concentrations causes a deficit or toxicity (Åhgren & Norrgren, 1996). If no biological function has been determined, the metal is not essential. The potential uptake of metals in biota depends on water quality and the potential is in general higher when; the water is “soft”, i.e., having low concentrations of Mg and Ca, low

*Infobox 2. Description of the analysed light metals*

**Aluminum** (Al) is a light metal and the most abundant metal in the earth’s crust. Its solubility is strongly dependent on pH and at low pH it is very toxic to fish (Åhgren & Norrgren, 1996). Aluminum is commonly used in constructions, packages and electronics. The function of aluminum is under debate, but is often considered as not essential (SGU web, NFA, 2013).

**Barium** (Ba) is a toxic trace element and mainly exist in nature as BaSO<sub>4</sub> or BaCO<sub>3</sub> and does not dissolve easily in water. It has been used as mouse poison and color in fireworks (SLU, 2007).

**Potassium** (K) is an alkali metal and naturally abundant. In bedrock and soils it occur mainly with silicates (SLU, 2007). K is essential and central in muscle and skeletal functions.

**Magnesium** (Mg) is like potassium mainly abundant with silicates. It is used for light material in constructions and cars, and in electronics (SLU, 2007). Essential.

**Sodium** (Na) makes part of the group alkali metals and is very reactive. Sodium is commonly known as part in the salt NaCl, found in oceans to where it is transported after weathering of bedrock (SLU, 2007). In Sweden Na occurs mainly with silicates in nature, and is used for deicing roads during the winter season. Sodium is essential for e.g. muscle functioning and is provided by food consumption (National Food Administration, 2013).

**Strontium** (Sr) has similar ionic radii as calcium and potassium. This brings risk for living organisms to assimilate Sr instead of Ca which then accumulates in the bone structure (SLU, 2007). Strontium can occur as a radioactive isotope and was part of the nuclear cloud after the Chernobyl accident in year 1986 (SLU, 2007). Not essential.

alkalinity and low pH, and when the amount of dissolved organic carbon (DOC) is low. This is due to elevated levels of free metal ions in the water during mentioned circumstances (Åhgren & Norrgren, 1996).

*Infobox 3. Description of the analysed heavy metals*

**Cadmium** (Cd) is found in the same group as zinc in the periodic table and have some similar properties. Cd is easily assimilated in fish and can accumulate and cause damage (SLU, 2007). It occurs naturally in zinc ores, and can be emitted from mining areas. Anthropogenic use has been in colour, batteries, corrosion protection, but since 1982 the use of Cd has been limited in Sweden due to regulations (Åhgren & Norrgren, 1996). Emissions are today smaller than deposition a plausible explanation is past emissions now being redistributed and acting as secondary sources (EPA, 2002). Not essential

**Chrome** (Cr) is at present mainly used in stainless steel and alloys, and historically to dye fabrics (SLU, 2007). The largest contamination source in Sweden is wear of tires and pavement. Other possible sources are colours and car paint (EPA, 2002). Chrome is an essential trace element.

**Copper** (Cu) is one of the most toxic metals for aquatic organisms, even though it is an important trace element and part of a few proteins (Åhgren & Norrgren, 1996). Cu reaches lakes and rivers through runoff from roofs and water pipes made out of copper. Wear of brake pads contribute largely to Cu emissions. It is essential for vegetation, animals and humans.

**Iron** (Fe) is crucial for oxygen transportation in the human body and is naturally part food and vegetables. Fe is a common element in the earth crust, Swedish bedrock and soils – especially in northern Sweden, and is economically important (SLU, 2007). Iron can also be toxic in aquatic environments and is thought to be pH-dependent (SLU, 2007). Essential.

**Manganese** (Mn) is important for photosynthesizing plants as is part of creating chlorophyll (SLU, 2007). It is toxic to aquatic organisms because of disrupted metabolism; it is suspected that the toxicity is negatively correlated to the calcium concentration in water (Åhgren & Norrgren, 1996). Naturally manganese often occur with oxides and carbonates and is extracted by reduction. Today the metal is mainly used in steel (SLU, 2007). Essential.

**Nickel** (Ni) is frequently used in the production of stainless steel. It is often part of stabile complexes in water, bound to compounds with oxygen, nitrogen and sulfur (Åhgren & Norrgren, 1996). Ni, Co and Fe have similar atomic radius which ease substitution and adjoining of these metals (SLU, 2007). Essential.

**Lead** (Pb) is a heavy metal and is considered to be toxic, particularly to children. Pb can damage the nervous system and cause paralysis, risk of low IQ and delayed development is associated with exposed embryos (National Food Administration, 2013). Lead is used in batteries, ammunition and fishing gear. Several big emissions sources have been identified in wear of tires and pavement, waste water from car washes, pigments from a popular Swedish house painting-color and lead shots (EPA, 2002). Several food products contain lead, elevated levels are found in hunted (game) meat because of the ammunition (National Food Administration, 2013). Lead can accumulate in the bone structure of humans, and in organs of other mammals. The uptake of lead by fish, and the concentration in water seems to be pH dependent and has shown a negative correlation (Åhgren & Norrgren, 1996). Not essential.

**Tin** (Sn) was discovered early and has been commonly used over a long time as tin cans (IVL, 2002), alloys and anti-fouling paint on boats. Organic tin compounds are very toxic to aquatic organisms (Åhgren & Norrgren, 1996), and humans as well (IVL, 2002). Not essential.

**Zinc** (Zn) has also been used by humans for a long time in brass and bronze alloys, as corrosion protection, in rubber procedures (tires) and batteries (Åhgren & Norrgren, 1996). In Stockholm, half of the zinc emissions are related to traffic due to wear of tires, brakes and pavement, and a big part is calculated to accumulate in the ground (EPA, 2002). Other sources are mining activities and steel works. Zinc is essential as part in human reproduction. It can have toxic effects on fish (Åhgren & Norrgren, 1996).

## 2.3 Runoff

Several studies have shown that melt water from snow can cause elevated concentrations of heavy metals and other pollutants in both recipient water and sediment (Marsalek et al., 2003; Oberts et al., 1994; Oliver et al., 1974). In Luleå northern Sweden, sediments of receiving water systems close to storm water outlets with snow impact had Cr, Cu and Ni concentrations that

well exceeded the background levels recommended by the Swedish EPA (Blecken et al., 2012). They concluded in the same study that fine-grained particles and their settling- and transport capacity have high impact on sediments. Fine material is more prone than coarse material to be flushed out of a snow pack during melting or rain on snow events (Oberts et al., 1994). Soluble contaminants are flushed even easier; when ice crystals re-freeze, the pollutants are not incorporated but rather pushed outside and moved downwards in the pile. By that, dissolved contaminants concentrate at the bottom and are released as a toxic and acidic “first flush” (Marsalek et al., 2003). Other studies have shown that the main part of metals in melt water is particle bound, over 80 % for Cu, Pb and Zn, which again point towards the importance of sedimentation of fine-grained material, and the sediment left on the snow disposal sites (Blecken et al., 2012; Marsalek et al., 2003).

## ***2.4 Sedimentation***

Since a big part of the contaminants found in snow are particle bound, sedimentation is an important process to reduce the toxicity of the water on its way towards the final recipient. As particles heavier than water eventually sinks to the bottom, the water becomes less polluted the longer this process is ongoing. When water in a river runs through dense vegetation the flow rate is reduced and the water becomes calmer. This reduces turbidity which in turn facilitates sedimentation (Blecken et al., 2012). Vegetation also works as a stabilizer of the bottom sediments due to the rooting systems. To settle very small or light particles like clay, the water needs to be almost entirely still. In turbid and fast flowing water, particles can transported over a very long distance. A relatively large surface and long water retention time are important factors when constructing a wetland or other settling areas, also a deeper section to prevent re-suspension and flush of settled material during storm or rain events (Strand, J. A., 2002). In lakes with varying depth material tends to settle and accumulate mainly in the deepest parts, so called accumulation bottoms (EPA, 2012).

## ***2.5 Bioavailability of metals***

Low pH increases solubility of heavy metals, and this is the single most important factor regulating adsorption-desorption equilibria of metals in the ground. The electrostatic attraction between a specific surface and a metal ion differs at different pH; cations are efficiently adsorbed at high pH while anions have the opposite relationship (EPA, 2006). This means that at lower pH the mobility of metal cations increase, they can occur as free ions or bind to organic matter instead of oxides which is the most important form of complex built by metals. Organic

particles are often small and have a big relative surface available for metal ions. Especially Cu and Hg are strongly bound to organic matter. Leaching to aquatic systems from soils is linked to low soil pH and the amount of DOC transported from the ground (EPA, 2006). In bottom sediments, high concentration of organic matter has shown to increase a systems buffering capacity for changes in pH (Jakobsson, 2005).

Heavy metals occur naturally as they are part of bed rock, soils, and the geochemical cycle. However, when these elements are present in elevated concentrations they cause damage to organisms and vegetation in the ecosystem. Some 20-30 years ago, the main source of metals to Swedish lakes were industries and atmospheric depositions, but today it is probably diffuse leakage from land (EPA, 2008b). Metal emissions from point sources like melting plants can cause lethal damage on fish due to limited function of gills and the gas exchange. A lower concentration and more constant exposure have more long term effects like changed structure of blood, damaged liver, skeletal deformation, and disturbed reproduction (Åhgren & Norrgren, 1996). The uptake of metals to aquatic biota depends on a number of parameters. Normally it is free ions or inorganically bound metals that show toxic effects (Skjelkvåle et al., 2001). Biota is exposed in two ways, by the surrounding water but also by food. Often the concentrations of metals are higher in food and is therefore the main source. Although ions might be particle bound when consumed, the low pH in the gut of invertebrates may cause the metal to dissolve (IVL, 2000). Unfortunately it is not only the essential elements that are assimilated by active mechanisms, because of structural similarities even non-essential metals can be ingested (Åhgren & Norrgren, 1996). As mentioned above, free metal ions in water is prone to build complexes and do so with organic matter, but also with fish gills because they too are negatively charged. This means that when there is more organic matter available, metal toxicity to fish is reduced (EPA, 2000). Several metals bioaccumulate in the organs of living organisms, so far the only metal known to biomagnify is mercury (EPA, 2000) which has caused the Swedish national food administration to set recommendations for consumption of fish from fresh water systems.

### **3. Methods**

The influx of metals to a lake can be difficult to measure, but by obtaining the concentrations in the sediments a fairly good interpretation can be made (EPA, 2000b). In order to analyse the heavy metal concentrations in the bottoms of the three lakes, it was necessary to collect sediment samples and perform the analysis in the lab. Mainly the upper parts of the sediment were collected, as the bottom material closest to the water column is what mainly can affect the aquatic biota. One can also assume that the most recently settled sediments are found in the top layers site (EPA, 2012), which in Lillsjön is affected by the polluted runoff from urban areas and the snow disposal site. Although samples down to 9 cm was collected to analyse sediments deposited also before the urbanisation using the general settling rate in Swedish lakes of 1 mm per year (EPA, 2012). It is relevant to compare Lake Lillsjön with other similar lakes, to find out if Lillsjön is in any ways diverging. Suitable reference lakes for Lillsjön would have sediments rich in calcium carbonates and presence of stonewort, but a drainage area without any clear sources of pollutants.

Two different methods for detecting metals and measure their concentrations in the samples were used: X-ray fluorescence (XRF) and Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). XRF was used to be able to analyse a relatively large amount of samples and get an overall view of the differences in the top sediments of the lakes. It was used as a complement to the more exact and expensive ICP-AES analysis which was used for more detailed analysis. To document any differences between the lakes, and to investigate whether metal concentrations show any correlation with organic matter or carbonate in the sediments, the method loss on ignition (LOI) was used to determine the total carbon and carbonate content.

#### **3.1 Study Area**

Lake Lillsjön (figure 1a) is located approximately 3 km from the city center of Östersund southwest of the highway E14, in the county of Jämtland, central Sweden. Östersund has an annual mean temperature of 2.5° C and precipitation of 530 mm, of which approximately 30 % falls as snow during winter time (SMHI, 2012). Lillsjön is a lake with large littoral zone, and a maximum depth of approximately 8 m (Table 1). Close to the lake is a big housing area, some smaller industries, and a shopping area. Storm water from these areas, and melt water from the snow dump placed 150 m from Lillsjön, eventually reaches the lake and makes up approximately 13 % of the incoming water. Approximately 60 % originates from a forested area, see Appendix A (Östersund, 2013). The bedrock in the Lillsjön area and the sediments in the

lake, consist of calcium carbonates which brings habitat to a unique flora and several endangered species.

In 1994, Blindow & Langangen identified several lakes in Jämtland as rare, important for birdlife and charofytes, and with high protective value. They also pointed out that it is central to follow up and further investigate these waters, regarding water chemistry and biodiversity or other aspects (Blindow & Langanen, 1994). The municipality of Östersund has acknowledged the area around Lillsjön as valuable for recreational purposes, and have ambitions to create a nature reserve to protect sensitive habitats and species (Östersund, 2013). The municipality takes water samples and plant fish in the lake, to stimulate bathing and fishing activities.

Table 1. Measured and calculated data on lake morphology and drainage areas for Lillsjön, Rannåstjärn and Myckeltjärn on average during year 2012. Lake size and volume is estimated in ArcGIS, and water bearing was calculated from the size of the drainage areas (Östersund, 2013).

	<b>Surface area (ha)</b>	<b>Volume (m<sup>3</sup>)</b>	<b>Average depth (m)</b>	<b>Maximum depth (m)</b>	<b>Water retention time (days)</b>	<b>Drainage area (ha)</b>
<b>Lillsjön</b>	20.3	494 000	2.4	7.8	58	840
<b>Rannåstjärn</b>	3.3	10 000	0.3	0.8	2-7	485
<b>Myckeltjärn</b>	32.9	310 000	0.9	6.5	74	635

### 3.2 Reference lakes

Both reference lakes have like Lillsjön for the area typical calcareous sediments. All three lakes have high alkalinity and clear water, and make habitat for several stonewort (*Chara sp.*) species (Blindow & Langangen, 1995). The first reference, Rannåstjärn was chosen because of its location relatively close to the city to evaluate if the metal content differ compared to Lillsjön, due to different drainage areas or is similar because of their urban proximity. The second lake, Myckeltjärn was chosen because of the opposite reason. It is not affected by urban activities and can therefore act as a more pristine reference.

Rannåstjärn is a shallow pond which is partly overgrown and has an estimated maximum depth of 0.8 m (Table 1). The pond is surrounded by forest- and further away some farm land, and the highway E14 running directly east of it. Rannåstjärn is located in a nature reserve and connected to a big greening area. Rannåstjärn is situated only a few kilometres from Lillsjön and they both have the proximity to the highway E14. Therefore the atmospheric deposition and impact from the highway is expected to be comparable. What clearly differs these two lakes is the drainage area where Lillsjön receives both melt water from the snow disposal site and storm water from

the commercial area. Further, Rannåstjärn is protected which lowers the risk of direct polluting and littering.

Myckeltjärn on the other hand is distanced from big roads and urban areas, and has no direct impact of polluting sources. It is found approximately 30 km north of Östersund. The drainage area is mainly forest land, like Lillsjön's was before the urbanization. Mycketjärn is similar to Lillsjön also regarding size and they both have a distinct deep area where an expected accumulation bottom is found (Table 1).

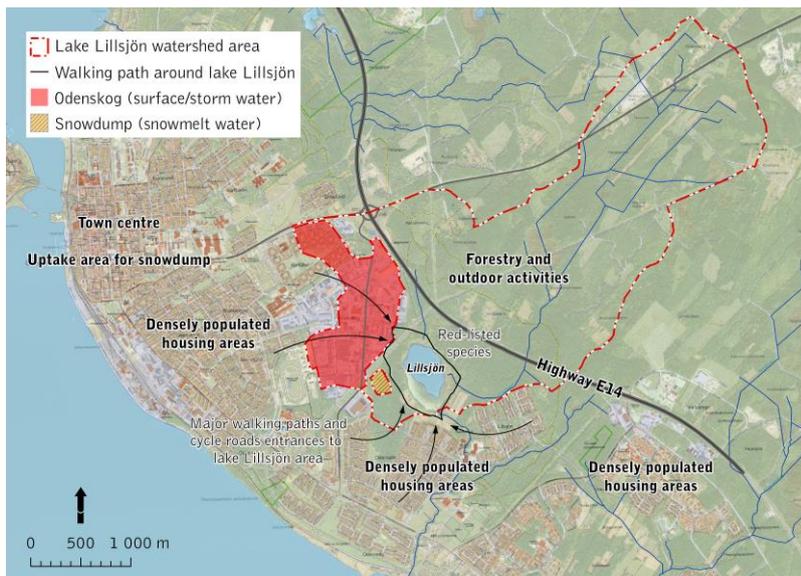


Figure 1 a.) Map showing the location of Lillsjön and its drainage area. (Reproduced with permission from the municipality of Östersund 2013).

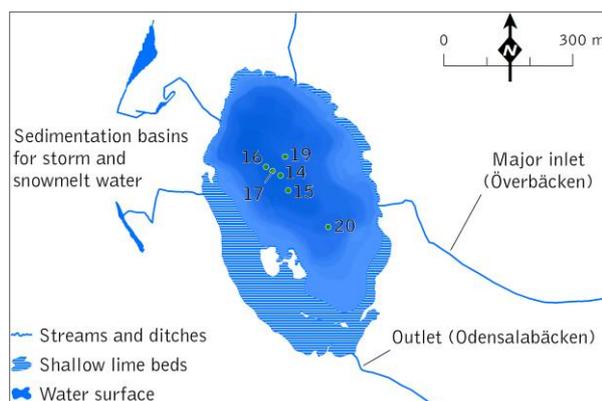


Figure 1 b.) Distribution of sample points in Lillsjön. Shallow areas have a light blue colour, and deeper have a dark blue colour. (Reproduced with permission from the municipality of Östersund 2013).

### 3.3 Sediment sampling

Sediment was sampled on the 2-4 of July 2013 from the lakes Rannåstjärn, Myckeltjärn and Lillsjön in the region around Östersund. Samples were collected using a kayak sampler, which

is a surface sediment catcher with a 40 cm long and 10 cm wide tube. This equipment was chosen instead of an Ekman bottom grab sampler to avoid the risk of losing fine grained material. It also enables slicing of a more or less exact depth of the sediment, and repeating the same procedure at all sampling points (EPA, 2012). In Lillsjön two sediment cores (sample points #15 & #19) were collected and divided into 3 samples each for ICP-AES analysis (six in total) (Figure 1b). Sampling for ICP-AES was done at the deepest parts found. Five samples were collected for XRF analysis over different depths, but due to missing coordinates for one sample point only four of them are visible in Figure 1b. The sediment core from point 17 was analysed as a sediment profile. It was divided into 1 cm slices down to 10 cm depth, 2.5 cm slices from 10 to 15 cm depth, and 5 cm slices from 15 to 35 cm depth. In the reference lakes one sediment core for ICP-AES was collected and divided into 3 samples, and five samples for XRF analysis. In Myckeltjärn all samples are from the deep areas in the lake. In Rannåstjärn the samples were collected from different depths which never exceeded 0.6 m.

Sediment samples for analysis with ICP-AES were cut into 3 cm slices, put in plastic jars, and stored in fridge before analysis to avoid molding. ICP-AES is a precise method even at low concentrations (Boss & Fredeen, 1997). It was therefore reasonable to divide the surface sediment into slices of 3 cm to evaluate differences in concentration with depth. Sampling for ICP-AES analysis was focused to the deepest part of the lake where settled particles remains and accumulate (EPA, 2012). Here it is easier to relate metal concentrations at different sediment depths to time. This method was chosen to obtain reliable results that hopefully can be compared to reference values or for future studies. The credibility is further enhanced by the fact that an authorized lab performed the analysis (see below).

Regarding samples for own analysis by X-ray fluorescence (XRF) and loss on ignition (LOI) the top 5 cm were sliced off and kept in zip lock bags. As the XRF method is not very precise for analysis close to the detection limit or on light metals, those samples were kept bigger than samples for ICP-AES (Boyle, 2000). One sample comprising 5 cm of sediment per sample point was collected, instead of comparing different layers per centimeter in the sediment surface (except for sample no 17). Furthermore, the top layers of the sediments are more affected by bioturbation and the time of settling cannot be directly linked to the “order” in the sediment layering (EPA, 2012). Collection for XRF analysis was spread out over the lakes, to see whether surface sediment concentrations is related to the lakes physical characteristics such as water depth. XRF analysis are relatively inexpensive which gave the opportunity to analyze numerous samples and produce more data for the study.

Other chemical parameters such as oxygen content, temperature and water transparency were also measured in field with oxygen meter, thermometer and secchi disc.

### 3.4 Analysis

#### 3.4.1 Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES)

Analyses with ICP-AES was done by an authorized ICP lab at the Department of Biology at Lund University, according to the Swedish standard SS 02 81 83 (EPA, 1998). The instrument used was an optic ICP of model Optima 8300 (PerkinElmer). The instrument directs argon gas into a radio frequency electric and magnetic field. A high-energy environment causes the Argon to break down to plasma. Hot plasma then atomizes the sediment sample and the high energy brings electrons to excitation and ionization processes. During those processes, atoms emit characteristic radiation and the wavelengths of the emitted lights are measured by a detector to identify the specific elements and at what concentrations they occur in the sample. Results are described as  $\mu\text{g/g}$  or ppm metal per dry substance sediment. More information is found in Boss & Fredeen (1997). Before the samples were put in the ICP-AES instrument, they were prepared in dilute nitric acid and put in an autoclave for 30 min in  $120^\circ\text{C}$ . Water content in percent was determined after drying a portion of each sample in  $105^\circ\text{C}$  until constant weight was reached. Loss of ignition (%) was obtained after burning samples in  $550^\circ\text{C}$  and samples were weighed before and after burning. Moist sediment corresponding to 1 g dry weight was added to 20 ml nitric acid for running in the autoclave, then diluted to 100 ml for analysis with ICP-AES.

The Swedish EPA (2000b) provides a classification system for metal concentrations in water and sediments in Swedish lakes. A range of values corresponds to one of five classes, based on deviation from the original concentrations compiled by EPA (2007). Class 1 represents values that show no deviation, class 2 slight deviation, class 3 significant deviation, class 4 large deviation and class 5 vary large deviation from reference values. Moreover, values categorized as class 1 can be considered to have no or negligible impact by anthropogenic sources. Class 2-4 indicate that the system is gradually becoming more affected and contaminated by local sources. Class 5 includes waters with an obvious impact from local sources (EPA, 2000b). The deviation is calculated from the recorded metal concentration divided by a reference value for natural, pristine levels in watercourses not affected by acidification or local emissions (EPA, 2000b). Another classification is also made, regarding the “current conditions” where the measured concentrations are compared to Swedish EPA’s published classification values (EPA, 2000b). Concentrations are divided into the classes’ *Very low*, *low*, *moderate high*, *high*, or *very high*. *Very low* or *low* concentrations brings no or slight risk of biological effects. Effects may

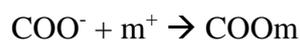
occur at *Moderate high* concentrations and the risk is increasing at *high*, or *very high* concentrations (EPA, 2000b).

### **3.4.2 X-ray fluorescence (XRF)**

Using a Niton XL3t GOLDD portable XRF analyzer (Thermo Scientific), sediment samples were analyzed for content and composition of metals. Samples were dried and homogenized before densely packed into a small cylinder covered with plastic film. The instrument shoots a beam with known energy towards the sample which causes electrons in the sample to excite. The emitted fluorescent X-rays from the electrons are unique for each element, which enables different metals to be quantified by measuring the energy in the X-rays. Each sample were analyzed for 2\*280 seconds and an average was calculated. The output provided the detected metals, and the concentration (ppm) in the dry sediment. The error for each analysis result was calculated (PANanalytical BV, 2010).

### **3.4.3. Loss on ignition (LOI)**

To measure the organic and carbonate content of the sediment samples, the method loss on ignition (LOI) was used (UCL, 2013). Previous studies have shown that sediments rich in organic matter in anoxic environments can act as a sink for metals (De Jonge et al., 2012), and it is therefore interesting to compile the carbon content of the examined sediments. Positively charged metals ( $m^+$ ) bind to organic matter via complexes with negatively charged carboxyles ( $COO^-$ ) in humic acids according to the following formula (EPA, 2006):



Further, the amount of carbon in the sediments can indicate whether the decomposing rates are relatively high or low. However, as all three lakes in this study are rich in calcium carbonate it can be of interest to compare the carbonate content. Calcium carbonate as settling material has proved to be an inefficient carrier of heavy metals (Sigg et al., 1987), possible correlation between metal concentration and  $CO_3$  will also be investigated in this study.

This method is straightforward and results can rapidly be produced. Wet sediment samples were placed in porcelain bowls and put to dry in a furnace for 48 h in 70°C. When dried, the samples were grinded and approximately 3 g was placed in a crucible with known weight and then dried in an air-circulation oven for 12 h in 105°C. Thereafter the samples were cooled in a desiccator for 1 h, weighed with the crucible and put in a muffle oven for 4h in 550°C with a warming up time of 1 h. Herewith, the organic matter is oxidized to carbon dioxide and ash (Heiri et al., 1999). After burning, the samples cooled in the desiccator for 2h and were then weighed again.

The LOI was calculated by the method of Heiri et al., (2001) to get an estimate in percent of the total organic matter in the samples.

$$\text{LOI}_{550^\circ} = ((\text{dry weight}_{105^\circ} - \text{dry weight}_{550^\circ}) / \text{dry weight}_{105^\circ}) * 100$$

Further, the samples were burned in a muffle oven for 4 h in 950°C which convert carbonates to oxides and are lost as carbon dioxide. The weight after burning in 950°C was subtracted from the dry weight (105°C) and calculated as content in percentage.

### ***3.5 Statistical analysis***

No statistical tests were carried out due to the low amount of data sampled for this study. Further sampling is needed to give evidence for significant differences.

## 4. Results

### 4.1 ICP-AES

One sediment core from each of the reference lakes was collected and divided into 3 cm slices for ICP-AES analysis, these will be referred to as Myckeltjärn and Rannåstjärn. In Lillsjön, two cores were collected at sample point 15 and 19 (Figure 1). These will be called Lillsjön A and B. At Lillsjön A, the core was divided into four samples of 3 cm each down to 12 cm sediment depth. At Lillsjön B three samples of the same range were collected down to a depth of 9 cm. Results from the ICP-AES analysis include an error percentage of  $\pm 5\%$ .

#### 4.1.1 Heavy metals

The following results are obtained by ICP-AES analysis and described as  $\mu\text{g/g}$  dry substance. The classification system provided by EPA (2000b) for a number of heavy (or toxic) metals: copper, zinc, cadmium, chromium, lead, nickel and arsenic are included. The measured concentrations in this study have been compared to the classification reference to show whether there are any deviations from a natural background value for each metal (Table 2). The colours in Table 2 correspond to the different classes described in Table 3. Despite the use of the term “significant”, no statistical relationships has been tested for these classifications but is a way of expressing the deviation from an approximated pristine concentration (EPA, 2000b).

For all metals but cadmium, Lillsjön was the only site to show concentrations higher than the EPA’s reference concentrations for pristine sediments. Zinc and nickel both show large deviation from the background values in Lillsjön. Arsenic is the only metal that overall does not reach any higher than class 2 (Table 3).

In the following figures the measured concentrations of these seven metals are shown to visualize the differences between depths and lakes. Error bars are included in the figures to represent the uncertainty of  $\pm 5\%$  from the true values.

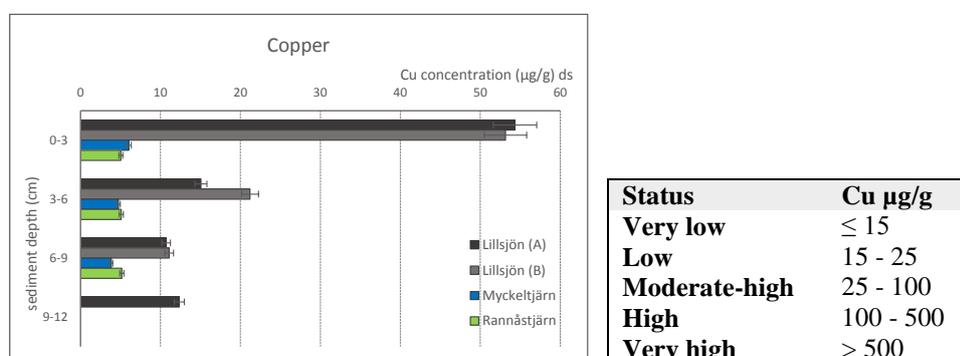
Table 2. Measured concentrations of metals in the four sediment cores from Lillsjön and the reference lakes. The colours corresponds to classifications according to the Swedish EPA (2000b), further described in Table 3.

Sample	Sediment depth cm	Cu $\mu\text{g/g}$	Zn $\mu\text{g/g}$	Cd $\mu\text{g/g}$	Cr $\mu\text{g/g}$	Pb $\mu\text{g/g}$	Ni $\mu\text{g/g}$	As $\mu\text{g/g}$
Lillsjön (A)	0-3	54.3	643	3.29	34.2	147	35.4	10.2
	3-6	15.1	144	2.36	10.7	9.1	15.4	5.5
	6-9	10.7	115	1.95	8.4	5.6	12.9	4.2
	9-12	12.4	136	1.78	10.9	5.9	13.6	4.6
Lillsjön (B)	0-3	53.2	514	3.60	35.2	124	57.1	8.4
	3-6	21.2	191	3.47	15.8	21.6	17.3	7.6
	6-9	11.1	120	2.56	9.4	8.1	12.2	5.6
Myckeltjärn	0-3	6.1	3.9	0.21	2.9	3.9	2.7	2.4
	3-6	4.7	4.7	0.30	2.4	4.7	2.6	2.6
	6-9	3.8	1.8	0.27	1.5	1.8	2.2	2.4
Rannåstjärn	0-3	5.0	0.1	0.39	3.8	0.1	3.7	1.3
	3-6	5.1	0.6	0.58	4.8	0.6	4.5	0.8
	6-9	5.2	1.1	0.70	4.5	1.1	6.7	1.6

Table 3. Classification scheme for deviation from reference values (EPA, 2000b).

Classes	Deviation
class 1	No
class 2	Slight
class 3	Significant
class 4	Large
class 5	Very large

Results from the ICP-AES analysis indicate that concentrations of copper is higher in Lillsjön than the reference lakes, and that in Lillsjön the highest concentrations are found in the top layers of the sediments (Figure 2a). The highest observed Cu level is 54.3  $\mu\text{g/g}$  in Lillsjön (A) which according to the Swedish EPA (2000b) is *Moderate high* (Figure 2b). Similar results were found for zinc (Figure 3a). *Moderate high* concentrations were measured at 0-3 cm sediment depth in Lillsjön (Figure 3b). Zn levels seem to decrease with sediment depth in Lillsjön, and to overall be higher in Lillsjön compared to the reference lakes.



Status	Cu $\mu\text{g/g}$
Very low	$\leq 15$
Low	15 - 25
Moderate-high	25 - 100
High	100 - 500
Very high	$> 500$

Figure 2 a). Results from ICP-AES analysis for Cu concentrations in the sediments of Lillsjön and the reference lakes. 2 b) Status of "current conditions" regarding Cu levels (EPA, 2000b).

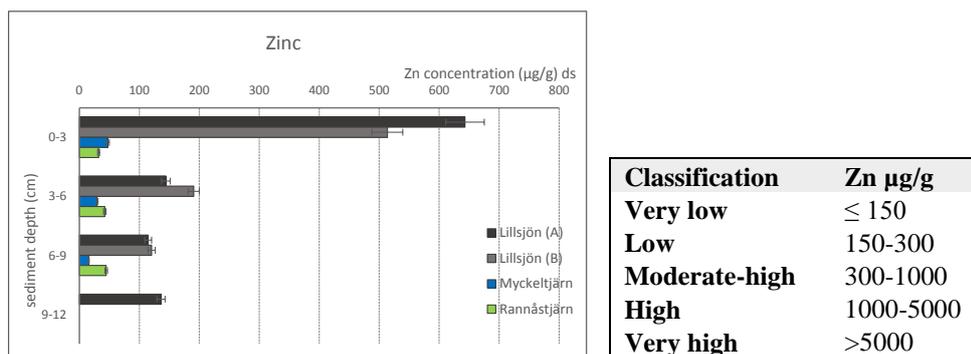


Figure 3 a). Results from ICP-AES analysis for Zn concentrations in the sediments of Lillsjön and the reference lakes. 3 b) Status of “current conditions” regarding Zn levels (EPA, 2000b).

Cadmium concentrations appear to be *moderate high* down to 6-9 cm sediment depth, although a slight decrease with depth is detected (Figure 4a & b). In Lillsjön, the highest Cd levels were found at 0-3 cm and concentrations decreased with depth. The collected samples also indicate that Lillsjön contains higher levels of Cd than the reference lakes, at all depths. Also chromium concentrations seem to have this same pattern, although it was only the samples from 0-3 cm that contained *moderate high* levels ( Figure 5a & b). Samples from deeper sediment strata showed *low* concentrations.

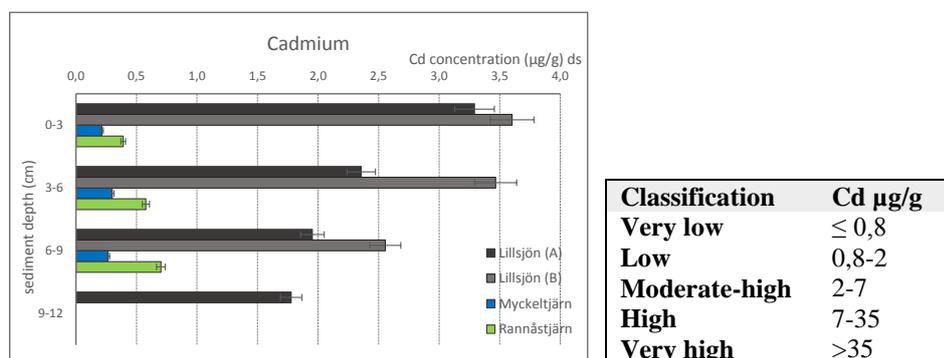
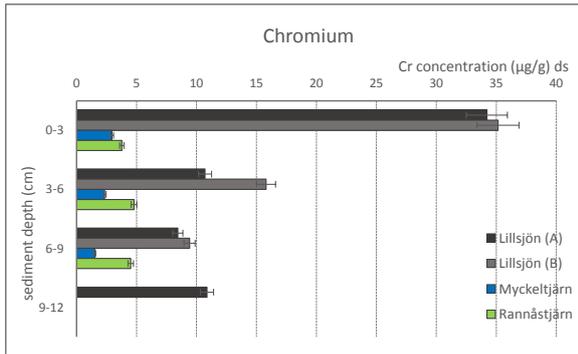


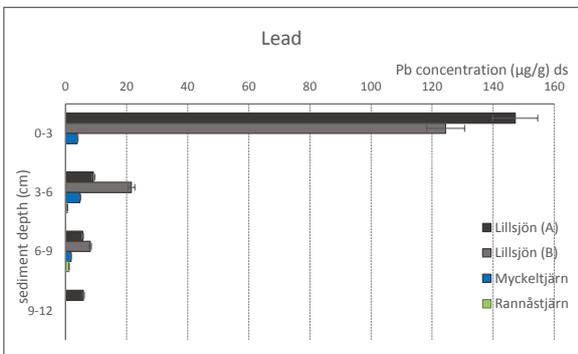
Figure 4 a). Results from ICP-AES analysis for Cd concentrations in the sediments of Lillsjön and the reference lakes. 4 b) Status of “current conditions” regarding Cd levels (EPA, 2000b).

Results regarding lead concentrations are somewhat different from other metals. Samples containing the highest concentrations (147 and 124 µg/g) were collected at 0-3 cm sediment depth in Lillsjön and are according to the Swedish EPA (2000b) considered *low*. The Pb content in Lillsjön seems to decrease rapidly from the sediment top and down as the samples from 0-3 cm depth showed concentrations approximately 16 times higher than those from 3-6 cm. Levels in Lillsjön never reach as low levels as the ones measured in the reference lakes (Figure 6).



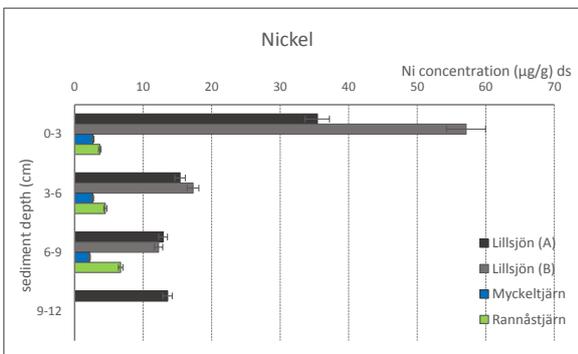
Classification	Cr µg/g
Very low	≤ 10
Low	10-20
Moderate-high	20-100
High	100-500
Very high	>500

Figure 5 a). Results from ICP-AES analysis for Cr concentrations in the sediments of Lillsjön and the reference lakes. 5 b) Status of “current conditions” regarding Cr levels (EPA, 2000b).



Classification	Pb µg/g
Very low	≤ 50
Low	50-150
Moderate-high	150-400
High	400-2000
Very high	>2000

Figure 6 a). Results from ICP-AES analysis for Pb concentrations in the sediments of Lillsjön and the reference lakes. 6 b) Status of “current conditions” regarding Pb levels (EPA, 2000b).



Classification	Ni µg/g
Very low	≤ 5
Low	5-15
Moderate-high	15-50
High	50-250
Very high	>250

Figure 7 a). Results from ICP-AES analysis for Ni concentrations in the sediments of Lillsjön and the reference lakes. 7 b) Status of “current conditions” regarding Ni levels (EPA, 2000b).

In the samples from Lillsjön, the highest Ni concentrations were detected. At 0-3 cm at point (B) levels seem to be *high* according to Swedish EPA (2000b) (Figure 7a & b). At both Lillsjön A and B levels were clearly higher at 0-3 cm than samples from deeper strata. Measured concentrations at point (A) 3-6 cm and point B 0-3 and 3-6 cm show *moderate high* levels. The concentrations decreased in the samples collected from deeper sediments in Lillsjön and was overall lower in the reference lakes. Regarding As, samples from Lillsjön showed higher levels at all depths, and at point (A) the maximum concentration was detected. Only that sample showed *moderate high* levels, whereas the rest of all samples contained *low* or *very low* levels of As. Communally for all mentioned metals except for cadmium, is a slight increase in concentration detected in the samples from Lillsjön (A) from 6-9 to 9-12 cm.

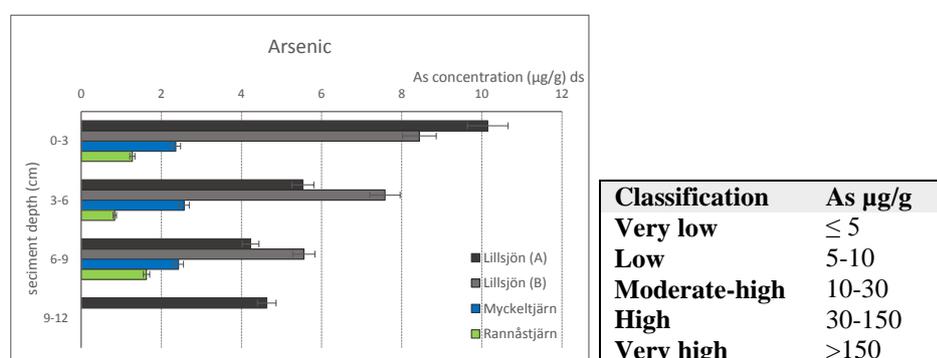


Figure 8 a). Results from ICP-AES analysis for Ni concentrations in the sediments of Lillsjön and the reference lakes. 8 b) Status of "current conditions" regarding Ni levels (EPA, 2000b).

#### 4.1.2 Light metals

The following section contain results mainly for light metals but also half metals and the heavy metals that have no corresponding classification values from the Swedish EPA. Table 4 shows a summary of the measured concentrations in the three lakes at different depths. Included is also the calculated uncertainty of  $\pm 5\%$ . The highest concentration for each metal is highlighted. Antimony is not included in the table as it was not detected in any sample.

The heavy metals iron and manganese were detected in all samples. Fe show decreasing levels with sediment depth in both Lillsjön and Myckeltjärn. The highest concentrations of Mn was detected at 3-6 cm depth in Lillsjön while it in the reference lakes decrease with sediment depth. Tin was only detected in the sediment surface of Lillsjön and can therefore not be compared to different depths or the reference lakes. However, this indicates that the levels of Sn are too low to be detected in the reference lakes, and that the levels are enhanced in Lillsjön.

Aluminum, barium, potassium, magnesium all showed their maximum concentrations in the sample from Lillsjön (A) at 0-3 cm. Jointly these metals also show a trend with decreasing

concentrations with sediment depth, in both Lillsjön and Myckeltjärn. The highest content of sodium was found in Lillsjön at 3-6 cm while for strontium it was in Rannåstjärn at 0-3 cm.

Table 4. Results obtained with ICP-AES analysis. The error margin is 5 % for each metal. The maximum value for each metal is highlighted.

Sample	Sediment depth cm	Fe µg/g	Mn µg/g	Al µg/g	Ba µg/g	K µg/g	Mg µg/g	Na µg/g	Sr µg/g	Sn µg/g
Lillsjön (A)	0-3	57269	2079	23979	257	7990	10771	258	134	<b>5,93</b>
	3-6	34126	2720	11843	252	4308	6545	<b>335</b>	242	
	6-9	29587	2555	10409	201	3467	5894	224	256	
	9-12	25907	2195	11819	204	3915	6234	237	240	
Lillsjön (B)	0-3	<b>58838</b>	2361	<b>26582</b>	<b>271</b>	<b>8819</b>	<b>11275</b>	286	121	4,28
	3-6	50198	<b>3297</b>	15189	232	5568	7638	251	219	
	6-9	40487	3057	10131	206	3788	5934	249	260	
Myckeltjärn	0-3	4909	724	2746	52	2068	1491	185	105	
	3-6	4455	615	2406	44	1765	1454	170	102	
	6-9	3846	539	1137	36	891	1048	143	104	
Rannåstjärn	0-3	9124	2283	4106	206	2930	4456	287	<b>396</b>	
	3-6	12097	1544	5126	189	3224	4981	314	352	
	6-9	13250	1295	4982	180	3033	5084	237	356	

## 4.2 XRF

To evaluate if the levels of a number of metals in Lillsjön was higher than in the reference lakes, the mean of the results from the XRF analysis was compared. In Rannåstjärn and Myckeltjärn n=5, while in Lillsjön n=4. All of these samples were collected in the same way, from the top 0-5 cm of the sediment. The XRF instrument could not detect all desirable elements because of low concentrations, and therefore all elements are not presented here. Metals included in the comparison were aluminum, iron, potassium, zinc, strontium, barium and manganese. Higher levels were found in Lillsjön for all metals except Sr, Ba and Mn (Table 5 and 6).

Table 5. Comparison of means between Lillsjön and Rannåstjärn..

Lillsjön/Rannåsen		
metal	mean Rannåsen µg/g	mean Lillsjön µg/g
Al	6539	33119
Fe	10739	28991
K	4904	19471
Zn	34	292
Sr	202	126
Ba	97	170
Mn	1985	1346

Table 6. Comparison of means between Lillsjön and Rannåstjärn.

Lillsjön/Myckeltjärn		
metal	mean Myckeltjärn µg/g	mean Lillsjön µg/g
Al	2922	33119
Fe	6039	28991
K	2349	19471
Zn	32	292
Sr	69	126
Ba	30	170
Mn	366	1346

### 4.2.1 Metal concentration and water depth

To see whether there is a variation in metal concentration within Lake Lillsjön samples were collected at different depths, both in the littoral and profundal zone. Below follows a presentation of the results provided by the XRF analysis in relation to water depth at the four sampling points. Samples were collected at 2.9, 4.4, 7 and 7.3 m depth. Only samples from the top 5 cm in the sediments of Lillsjön are included here.

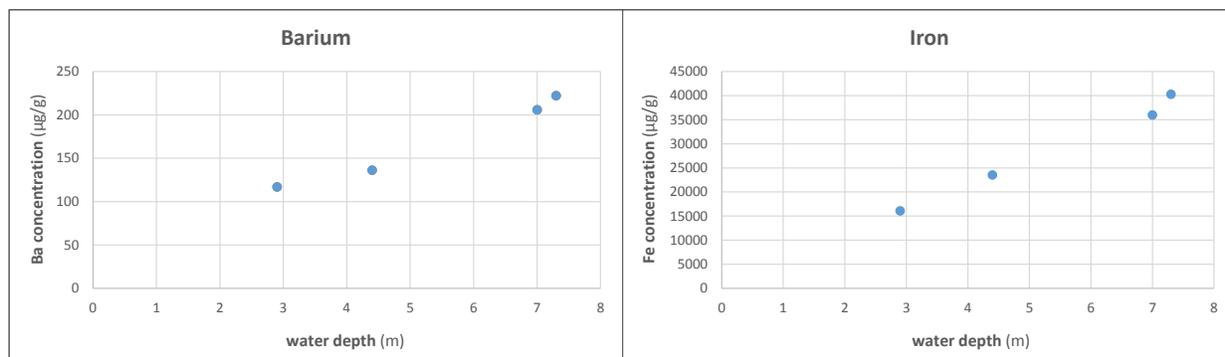


Figure 9 a) and b). Concentrations of barium and iron plotted against water depth at four sample points in Lillsjön.

Ba concentration seems to be correlated to water depth in Lillsjön (Figure 9a). Barium concentrations are elevated in the deepest parts of the lake compared to in the shallow. Levels increase with water depth, 116, 136, 205, 222 µg/g are the measured Ba content in order from lowest to highest water depth. A correlation between Fe and water depth is also indicated (Figure 9b). Iron concentration increase with water depth and the highest concentration, 40305 µg/g is found at 7.3 m depth. Lowest measured Fe concentration was 16107 µg/g where water depth was 2.9 m.

Figure 10a illustrates the correlation between chromium levels and water depth. The lowest concentration (53 µg/g) were found at the shallowest sampling point, and the highest Cr levels were 158 and 161 µg/g, found at 7 and 7.3 m depth. Mn concentrations in the sediments also seem to depend on water depth (Figure 10b). The highest manganese level (2060 µg/g) were found at

7.3 m depth and the second highest (1821  $\mu\text{g/g}$ ) at 7 m. At the more shallow depths, 2.9 and 4.4 m, the Mn concentrations were 742 and 759  $\mu\text{g/g}$  respectively.

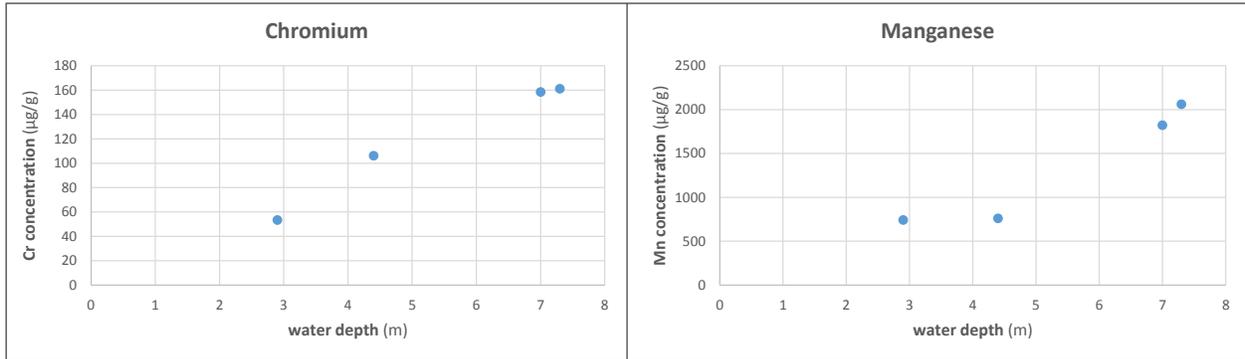


Figure 10 a) and b). Concentrations of chromium and manganese plotted against water depth at four sample points in Lillsjön.

The lowest Al concentration (20 267  $\mu\text{g/g}$ ) was found at 2.7 m depth, and the highest at 7 m (39461  $\mu\text{g/g}$ ). But there is only a relatively small difference in Al levels between 4.4 and 7.3 m (Figure 11a). Sediment with the highest Cu content was sampled at 7.3 m depth (35  $\mu\text{g/g}$ ). At 7 m, copper levels seems to be lower, and in the sample collected at the shallowest sample point the lowest Cu concentration was measured (15  $\mu\text{g/g}$ ). According to these results, levels of Cu in the sediments of Lillsjön consequently increase with water depth (Figure 11b). The highest and lowest K concentration was found at the second deepest (7 m) and the most shallow (2.9 m) sampling points, respectively (Figure 11c). At the three deepest sampling points, the concentrations are between 20 439 and 22 758  $\mu\text{g/g}$ , while at 2.9 m depth potassium content in the sediment is 12 478  $\mu\text{g/g}$ .

No correlation was indicated between zinc concentrations and water depth. Concentrations of magnesium and nickel are not presented here due to large errors in the results from the XRF method, combined with low concentrations.

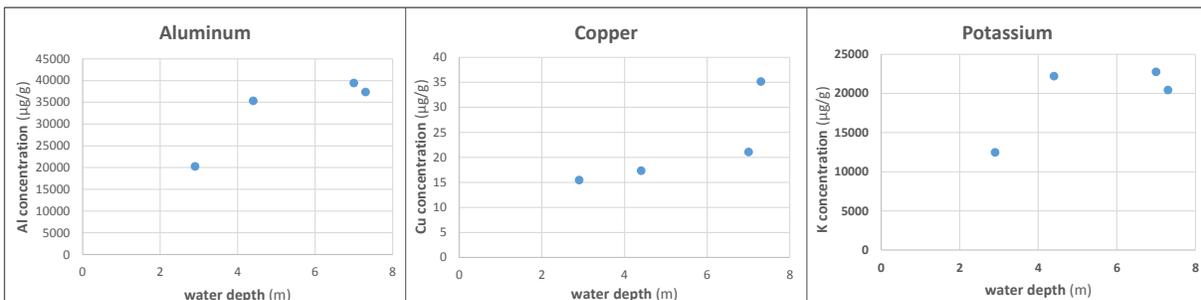


Figure 11 a), b) and c). Concentrations of aluminium, copper and potassium plotted against water depth at four sample points in Lillsjön.

#### 4.2.2 Sediment profile

At point 17 in Lillsjön where water depth was 7.1 m, one sediment core was collected and divided into several samples were to obtain a higher resolution. Between 0 and 10 cm samples included 1 cm of sediment, between 10 and 15 cm the range was 2.5 cm, and at 15-35 cm samples were divided into 5 cm slices. A picture of a sediment profile is found in Appendix B. Profiles from sample point 17 regarding barium, copper, chrome, zinc, aluminum and iron are presented below (Figure 13 and Figure 12). Detection for copper was only possible down to 10 cm depth, while the rest of the metals were detected in all samples. Consequently, elevated concentrations are found at 5-6 cm. All metals shown here have their maximum levels at the very same depth. Cu, Cr and Zn show similar trends where the sixth point distinctly shoots away to higher concentrations, whereas Ba, Al and Fe show a more successive increase towards maximum, seen from bottom to top. Before the clear increase, zinc showed relatively stable levels over a long time and have after its maximum decreased again. However, barium has its lowest concentration in the surface sediment after a steady decrease above maximum, whereas the other metals had lower concentrations deeper down in the sediment (except copper due to lack of results). These results should be interpreted with caution as they origin from only one sediment core and cannot be directly compared to other results.

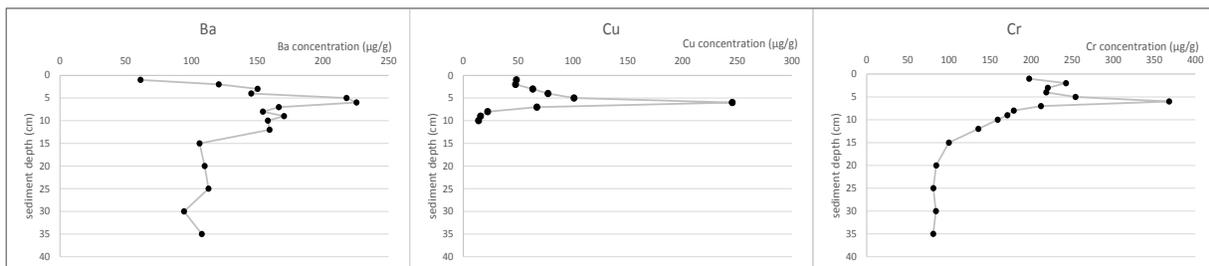


Figure 13. Barium, copper and cadmium concentrations at sample point 17 in Lillsjön. Ba and Cr show results down to a sediment depth of 35 cm and copper down to 10 cm.

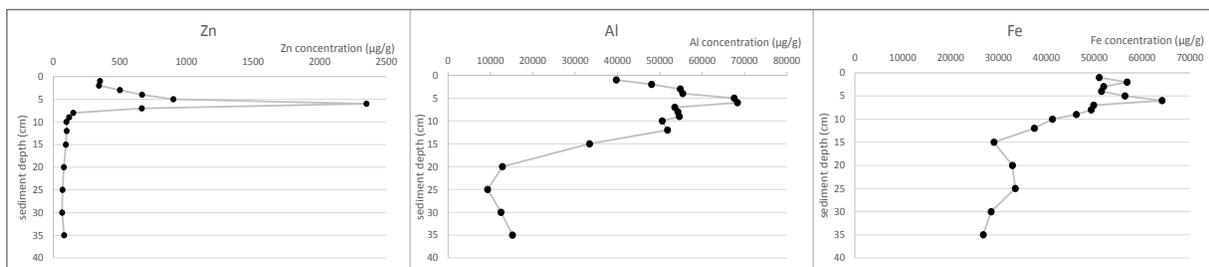


Figure 12. Zinc, aluminium and iron concentrations down to 35 cm in the sediment, at sample point 17 in Lillsjön.

### 4.3 Carbon & carbonate content

Carbon content was determined by loss on ignition in all samples collected for this study (Table 7). At sample point 15 in Lillsjön, four samples were collected down to 12 cm depth. Whereas for each of the other sample points, three samples were analysed. How carbon content varies with depth is different in Lillsjön compared to the reference lakes. In both samples from Lillsjön, the lowest carbon content is found in the top layer of the sediment, while the sample from 9-12 cm depth contained the most carbon. Myckeltjärn and Rannåstjärn contain overall less carbon in the sediments than Lillsjön. In Myckeltjärn there is a small difference between different sediment depths, and carbon content varies in the range 8.9 – 11.0 %. Variation in Rannåstjärn is bigger (6.4 – 10.9 %) and the carbon content decreases with sediment depth. The carbonate content was higher in Myckeltjärn (45-48 %) and Rannåstjärn (43-47 %) than in Lillsjön (27-36 %).

Table 7. Organic content expressed as percent in sediment samples from different depths in Lillsjön, Myckeltjärn and Rannåstjärn.

Sediment depth (cm)	Lillsjön (A)	Lillsjön (B)	Myckeltjärn	Rannåstjärn
0-3 cm	13 %	12.8 %	11.0 %	10.9%
3-6 cm	17 %	18.3 %	8.9 %	7.3 %
6-9 cm	17.4 %	18.3 %	10.8 %	6.4 %
9-12 cm	21.4 %			

No correlation with organic content was found for any of the detected metals in the three lakes. However, some metals show a negative correlation with increased carbonate content (Figure 14). Aluminum concentration in Lillsjön is lower while the carbonate content is higher. CO<sub>3</sub> varies between 27 and 36 % at the four sampling points (Figure 14a). The lowest K concentration was found where the carbonate content was highest (Figure 14b). It can be seen that chromium

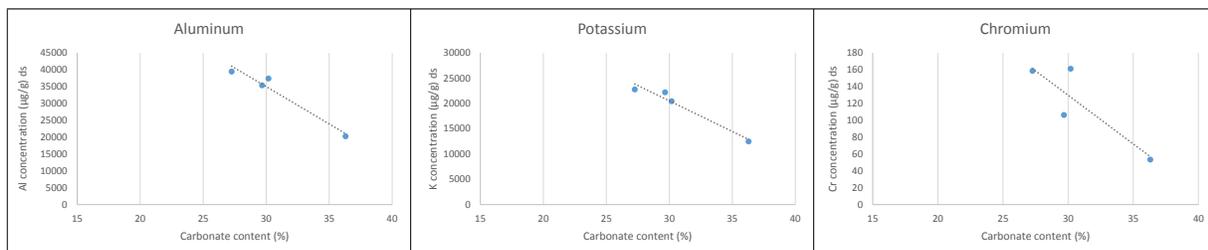


Figure 14 a), b) and c). Aluminum, potassium and chromium concentrations plotted against carbonate content expressed in percent. Samples collected in Lillsjön at 0-5 cm sediment depth.

concentration has some correlation with carbonate content (Figure 14c). Where the content of carbonate is highest, the lowest Cr concentration is found as well.

#### 4.4 Oxygen and temperature

As Lillsjön and Myckeltjärn are similar regarding size and depth, oxygen content and temperature are compared. These parameters were measured at each metre from bottom to top, at the deepest part of the lakes. Lillsjön had relatively high O<sub>2</sub> content in the surface water, at approximately 3 m depth it decreased rapidly with depth and close to the bottom the water contained 1.5 mg/l O<sub>2</sub> (Figure 15a). In Myckeltjärn the trend was somewhat reversed, from 1 to 5 m depth the oxygen content increased but in the deepest water there was a slight decrease to 10.9 mg/l O<sub>2</sub>. However, the oxygen content was lower at the surface than the bottom for Myckeltjärn, and the opposite for Lillsjön.

Regarding temperature, the both lakes show a similar trend (Figure 15b). In the surface water the temperature was relatively high, approximately 19 °C down to 2 m depth. In Lillsjön there was a rapid decrease at 3 m and 6 m depth, and the lowest measured temperature was 6.4 °C near the bottom. From 3 m and deeper, the temperature in Myckeltjärn was higher than in Lillsjön. The decrease was not as rapid in Myckeltjärn and minimum temperature was 11.1 °C in the bottom water.

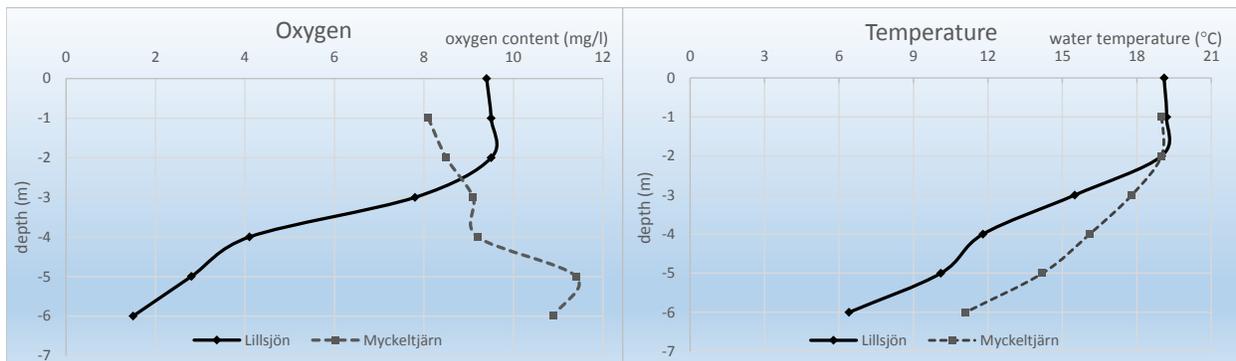


Figure 15 a) and b). Oxygen content and water temperature at different depths in Lillsjön, respectively.

It was not possible to produce a similar graph for water temperature and oxygen content in Rannåstjärn, as the water depth did not exceed 0.6 m at any point.

#### 4.5 phosphorous content

To try to link the amount of organic matter and oxygen in the sediment, also the content of phosphorus is presented. Seen over the entire sediment profile, Lillsjön has approximately two to four times higher levels of phosphorus. In the top sample (0–3) the concentrations were close to 600 µg/g in Lillsjön, 300 µg/g in Myckeltjärn and 225 in Rannåstjärn. In the deeper sediment layers of Myckeltjärn and Rannåstjärn, the levels of P clearly decreased to 134 and 102 µg/g, and 131 and 107 µg/g respectively. While in samples from Lillsjön the levels remained relatively high (Table 8).

Table 8. Phosphorous content in the sediments of Lillsjön and the reference lakes.

Phosphorous content (µg/g)				
sediment depth (cm)	Lillsjön (A)	Lillsjön (B)	Myckeltjärn	Rannåstjärn
0-3	562	625	299	226
3-6	595	596	134	131
6-9	471	536	102	107
9-12	494			

Water transparency was 2.5 m in Lillsjön and 4.1 m in Myckeltjärn, Rannåstjärn is shallow enough to see to the bottom.

#### 4.6 Comparison between ICP-AES and XRF

As two different methods was used to analyse the concentrations of the various metals in this study, the results for each metal were not exactly the same. Some metals were only detected with one of the methods, while others were obtained by both ICP-AES and XRF. Furthermore, two of the lakes: Lillsjön and Myckeltjärn were relatively similar regarding size and depth, and samples were collected at approximately the same water depth. Therefore the following section will include results from those two lakes, to be able to compare the used methods. XRF results from Lillsjön comprise three samples at 0-5 cm sediment depth collected at 7, 7.1 and 7.3 m water depth. From Myckeltjärn five samples analysed with XRF were included, from the top five centimetres of the sediment collected at 5.9, 6.4 and 6.8 (three samples) m water depth. The error values from the XRF results were divided by the concentrations, to picture how large the errors were in percent. For the ICP-AES results, a mean of the samples from 0 to 6 cm sediment depth was calculated. Samples were collected at 6.8 and 7.1 in Lillsjön and 6.2 m water depth in Myckeltjärn. Ergo,

metal concentrations in sediment samples from 0-5 cm analysed with XRF are compared to samples from 0-6 cm analysed with ICP-AES.

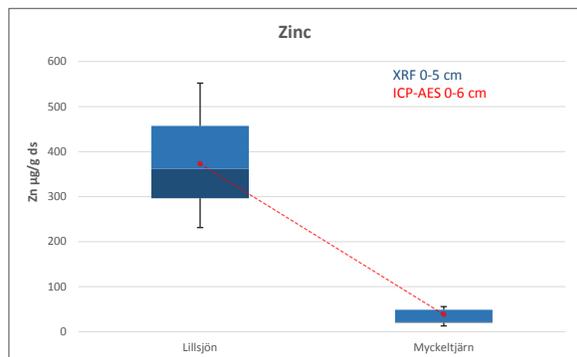


Figure 16. Boxplot with zinc concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

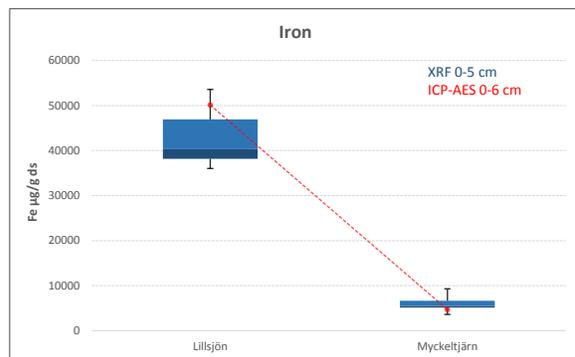


Figure 17. Boxplot with iron concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

The distribution of Zn concentrations measured with the XRF method is shown together with the mean of the ICP-AES values (Figure 16). For Lillsjön the range of values is bigger than for Myckeltjärn, and concentrations are higher too. The red point lies close to the median for Lillsjön which indicates that the methods correspond well. The distribution is relatively small in Myckeltjärn but the red point is within the error bars even there. For concentrations obtained by XRF in Lillsjön the error margin was 3.1, whereas in Myckeltjärn it was 21.8.

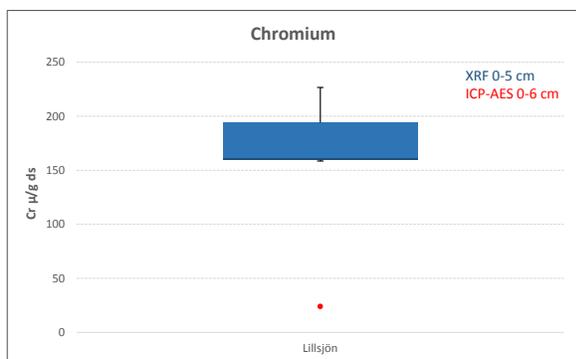


Figure 18. Boxplot with chromium concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

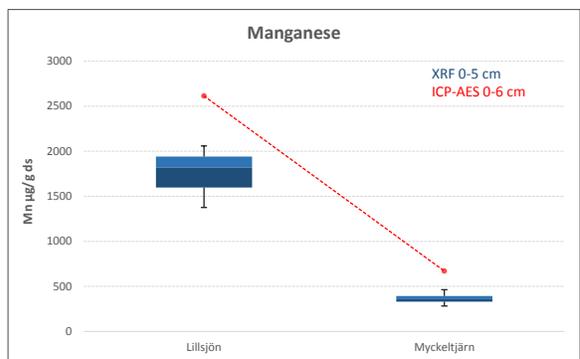


Figure 19. Boxplot with manganese concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

For iron analysis, the red point for ICP-AES values are within the error bars in the box for XRF regarding Lillsjön (Figure 17). In Myckeltjärn both methods give quite similar results for iron

content in the sediments. With XRF the error margins for Fe concentrations were 0.56 % in Lillsjön and 1.6 % in Myckeltjärn. The distribution of values is bigger for Lillsjön which also shows bigger error bars, than for Myckeltjärn.

No chromium was detected in the sediments of Myckeltjärn with the XRF method, therefore only results from Lillsjön is presented in Figure 18. XRF values are exceeding the mean of ICP-AES results, as the red point is far below the blue box. 29 % was the error margin for XRF results in the analysis of Cr. The distribution of Mn concentrations in Lillsjön and Myckeltjärn is represented by blue boxplots (Figure 19). The box is bigger for Lillsjön which means that the distribution is bigger, despite fewer data. The red points are well above the boxes, and ICP-AES values exceed XRF values. Error margins regarding XRF results were 5.7 and 14 % for Lillsjön and Myckeltjärn respectively.

In Lillsjön the aluminum concentrations vary within a bigger range than in Myckeltjärn and the error bars are bigger as well (Figure 20). The two methods seems to be comparable regarding the results for Myckeltjärn. The red point representing ICP-AES values lies close to the median in the box. While for Lillsjön the XRF values exceed the ICP and the red point is well below the box for Lillsjön. For Al results, the error margin for XRF was 2.9 and 59.6 % for Lillsjön and Myckeltjärn respectively.

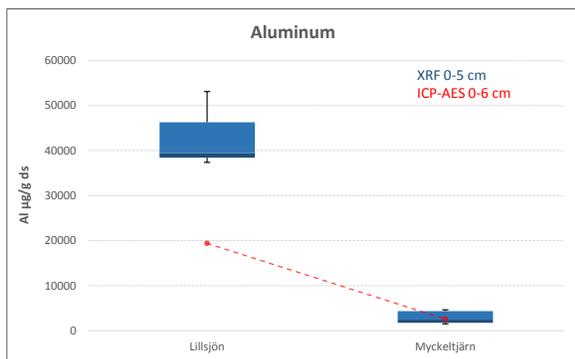


Figure 20. Boxplot with aluminum concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

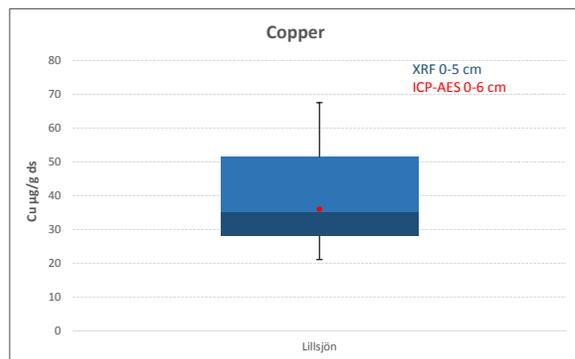


Figure 21. Boxplot with copper concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

Copper was detected only in Lillsjön, and not in Myckeltjärn. Therefore Figure 21 shows the distribution of Cu concentrations for Lillsjön alone. Close to the colour border in the blue box, the red point representing ICP-AES values is found. XRF and ICP-AES give similar results for Cu, and the methods seem to be comparable. The error margin for XRF results was 20.6 %.

Distribution of Ba concentrations is bigger in Lillsjön than Myckeltjärn (Figure 22). In Lillsjön the red point is found above the boxplot, which means that values from ICP-AES exceed values from XRF or that XRF underestimates the Ba concentrations in Lillsjön. In Myckeltjärn on the other hand, the red point is found near the median and the methods provide comparable values. Errors with the XRF method on barium was 17 % for Lillsjön and 53 % for Myckeltjärn.

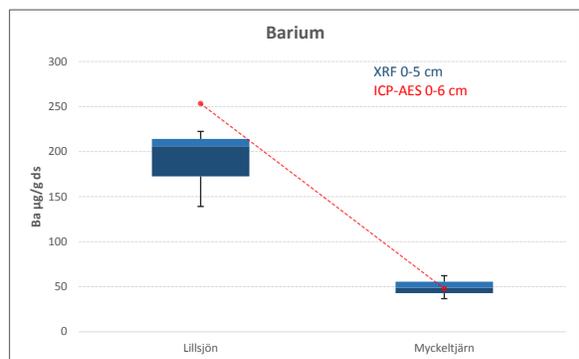


Figure 22. Boxplot with barium concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

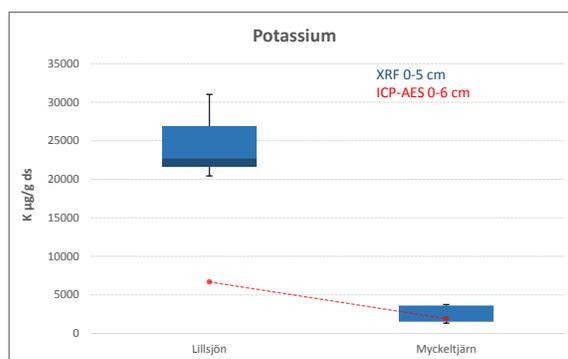


Figure 23. Boxplot with potassium concentrations in sediment samples from Lillsjön and Myckeltjärn analysed with XRF. Error bars represent the min and max values, light and dark blue segments are the 75<sup>th</sup> and 25<sup>th</sup> percentile and the border between them show the median. Red points show the mean of ICP-AES analysis.

Comparison between XRF and ICP-AES analysis regarding potassium is shown (Figure 23). The distribution of values is bigger for Lillsjön than for Myckeltjärn, and also concentrations are higher. ICP-AES values correspond well to XRF in Myckeltjärn, the red point is found within the error bars in the boxplot. For Lillsjön the results from each of the methods differ, XRF values exceed ICP-AES and the red marking is well below the blue box. Error margins for the XRF results were 1.2 and 7.2 % for Lillsjön and Myckeltjärn respectively.

## 5. Discussion

This study has a relevant topic as human impact on the environment is on the subject at all levels in society. In previous investigations on urban water quality the reader can come across the term “urban stream syndrome” (Blecken et al., 2012). This points to the fact that poorly treated storm water and other runoff is an obvious problem for water quality which in turn affects the ecosystems in the receiving water systems. Lillsjön is one example of such a lake. Below follows a discussion arguing that the urban environment surrounding Lake Lillsjön have a large impact on the ecosystem quality.

Lillsjön is as mentioned a popular recreational lake, further it is relatively small and located very close to a snow disposal site. Other studies investigating the of impact snowmelt on water systems, has done so in e.g. the Baltic sea or rivers running towards other larger waters (Blecken et al., 2012; Engelhard et al., 2007). In smaller lakes, the transporting and diluting effects are limited. Meaning that Lillsjön is perhaps not be suited for receiving the current urban discharge.

### *5.1 How Lillsjön differs from the reference lakes*

The results from ICP-AES analysis implies that Lillsjön contains higher levels of all the examined metals at all depths compared to the reference lakes, except for strontium and sodium. ICP-AES analysis further strengthens the indication that higher metal levels occur in Lillsjön. With an insecurity of only 5 % the results can be considered as reliable. Higher concentrations were found for Cd, As, Ba, Fe, Mg, Mn and Na which is 7 out of the 15 analysed elements. Clear differences were detected mainly when comparing Lillsjön to Myckeltjärn. This could suggest that levels in Rannåstjärn also are somewhat enhanced due to its location relatively close to the city. Even though levels are not high enough to be alarming. Myckeltjärn that act as a more pristine reference provides a clear evidence that lakes in this area not necessarily have to contain dangerously enhanced metal levels. This rules out the possibility that the high levels in Lillsjön is due to atmospheric deposition or bedrock geology. For many metals e.g. lead, the differences between the lakes were large but no statistical relationship could be established. If the number of observations would have been higher, a test for normally distributed data could have been done and significant differences might have been detected.

## ***5.2 Metal variation with sediment depth***

Most metals showed higher concentrations at 0-3 cm than underlying sediment layers.

Unfortunately it is still unknown if there are differences within the layers, but it is likely. Over the past 30 years the area around Lillsjön has developed which probably has altered the metal load reaching Lillsjön. However, it is clear that levels are lower in deeper strata, in sediments that probably deposited before the urbanisation and the snow disposal site was taken into use.

### **5.2.1 Sampling strategy**

For analysis with ICP-AES the sediment samples were collected from different depths to be able to study if there has been a change in metal load over time. The general trend in Lillsjön is that the sediment surface contains strongly elevated levels of metals compared to deeper sediment layers. This could mean that Lillsjön has received a bigger load of pollutants the past 30 years than further back in time. In Swedish lakes, the settling rate is estimated to 1 mm per year (EPA, 2012). The Swedish EPA recommends that sediment should be collected in areas where materials accumulate and that each sample should not comprise more than 1 cm (vertically) sediment. This is to enable a reliable link between time and sediment depth. Due to the limited budget for this study, samples were divided into parts of 3 cm down to 9 or 12 cm sediment depth, to obtain results from further down in the sediments. Of course this method has drawbacks, i.e. there can be big differences between the absolute top of the sediment and at 3 cm depth. This would not be detected as a mean of the concentrations is gained after mixing 3 cm of sediments.

### **5.2.1 Classifications**

The classification values for deviation from the Swedish EPA can work as a tool to relate metal concentrations in the sediments to human impact. The different classes for current conditions have a corresponding estimate of the potential biological effects instead. High concentrations naturally brings increasing risks of effects on biota (Blecken et al., 2012). Copper and zinc showed elevated concentrations in the top sediment layer in Lillsjön with at least two times the values further down. According to SLU (2001) neither copper nor zinc showed any increase in the uppermost sediment layers compared to the background value (30-32 cm deep) of the reference lakes in the northern half of Sweden, which they used for an environmental monitoring. This indicates that the difference between sediment layers is not commonly found in lakes from this area. Copper concentrations at 0-3 cm in Lillsjön were *moderate high* which brings a risk of negative effects on

biota, e.g. impact on reproduction and survival of some species (EPA, 2000b). The same sample showed a significant deviation from pristine lake sediments, whereas none of the other samples showed any risk of biological effects or deviation. Zinc analysis gave similar results as copper, *moderate high* concentrations and large deviation was found at 0-3 cm in Lillsjön. Further down in Lillsjön's sediments the deviation was slight, whereas no elevated levels were found in the reference lakes. Zinc normally shows increased concentrations in acidified regions and regional differences due to deposition of long distance pollutions (Skjelkvåle, 2001).

Samples from Lillsjön had enhanced levels of cadmium down to 6-9 cm, status *moderate high*. SLU (2001) points out that it is not unusual to find higher levels at the sediment surface than at 30 cm where background values can be found. All samples from Lillsjön, including 9-12 cm showed significant deviation from EPA's classification value. This indicates that even deeper sediment layers in Lillsjön are affected by contaminants and that Cd levels are higher than pristine sediments. Compared to other current sediment concentrations in Sweden they are still low. As mentioned for Zn, also Cd concentrations vary geographically in Sweden due to the transport of air pollutions from the southeast, and soil pH (Skjelkvåle, 2001). So the area around Lillsjön have the basic prerequisites for low Cd concentrations, disregarding from the urban impact.

No elevated levels of chromium were found in Myckeltjärn, Rannåstjärn or the deeper sediment strata of Lillsjön. In the top layer in Lillsjön, levels are *moderate high* and the deviation is significant. Cr together with arsenic were the only metals that showed no deviation in the deeper samples, which implies no anthropogenic impact on those sediment layers. According to Skjelkvåle et al (2001) Cr and As are not strongly affected by airborne pollutions, but are more influenced by bedrock and geochemistry. In the environmental monitoring by SLU (2001) chromium showed no trend of varying between different sediment depths. That corresponds well with the results from the reference lakes in this study, where only small differences were detected between the sediment layers. However, results from Lillsjön indicate impacts from pollutants down to 6 cm sediment depth. Kept in mind the relatively big samples, it is uncertain to say to which depth the Cr levels are elevated.

All samples in this study contained *very low* concentrations of lead, except for samples from the top layer in Lillsjön. There the concentrations were 124 and 147 µg/g which is close the limit for EPA's (2000b) status *moderate high* at 150 µg/g. SLU (2001) reports that the influx of Pb to

Swedish lakes is enhanced and that many lakes have higher concentrations in recent sediments than in deeper strata. As Pb easily bind to organic matter, a big amount of the deposited lead remains in the water system (Skjelkvåle, 2001). In Myckeltjärn the highest measured concentration was only 4.7 µg/g. So regarding concentrations of lead, Lillsjön diverge clearly from the reference lakes. This indicates that Lillsjön is strongly affected by its surroundings, as the atmospheric deposition cannot differ too much within the area of the lakes. Atmospheric deposition originating from Europe is known as one of the main sources of lead contamination (Skjelkvåle, 2001), but lake Lillsjön with its urban location is probably more affected by the traffic-related emissions of lead.

Nickel is the only metal in this study that showed levels with the status *high*. This was measured in the sample from 0-3 cm from Lillsjön (B). *High* levels bring a growing risk of negative impact on biota (EPA, 2000b). Deviation in top layers were significant and large. From 6-12 cm levels were *low* but the deviation was still slight. So at all measured depths in Lillsjön the indication is that Lillsjön is becoming more contaminated (EPA, 2000b).

Arsenic occurred in *low* or *very low* levels in both the reference lakes and Lillsjön, except for the top sample from Lillsjön (A) where levels were *moderate high*. According to SLU (2001) As has a tendency of enriching in the sediment surface, especially under low oxygen conditions where arsenic transport upwards and oxidize and thereafter stays in the surface layers. Both samples from Lillsjön showed the trend of higher concentrations in the sediment surface and decreasing downwards. Human impact seems limited to the top layers of the sediments in Lillsjön regarding As.

For many metals in Rannåstjärn, lower concentrations were detected in the sediment surface than further down. Rannåstjärn lies within an area that became protected in 1981 (CAB, 2009) and this could perhaps contribute to the decreased influx of metals over time. However, Myckeltjärn showed lower concentrations of several metals, but Rannåstjärns proximity to the densely trafficked highway E14 cannot be ignored.

### **5.2.3 Metals without classification values**

Al, Fe, K, Mg, Ba and Na all showed clear differences between sediment depths in Lillsjön. The top layers contained higher levels of these metals. Fe has the same character as arsenic of enriching in the top layers when oxygen levels are low in the sediment, this trend is not unusual for iron

(SLU, 2001). Also Myckeltjärn contained more Fe in the sediment top, but Rannåstjärn showed the opposite trend. Possible explanations for the distribution in Rannåstjärn is either that the influx of Fe simply has decreased, or that the shallow water depth brings constantly high oxygen conditions enabling accumulation further down.

In the reference lakes, Mn decreased with depth while in Lillsjön the highest levels were found at 3-6 cm at both sampling points. Mn is linked to Fe and As, and can also be enriching in sediments where the oxygen levels are higher (SLU, 2001). Sr influx to Lillsjön seems to have decreased over the past decades, whereas Rannåstjärn indicates the opposite. Rannåstjärn was also the lake with highest Sr levels overall. Na showed no clear trend regarding the differences with depth, though the levels in Lillsjön at 0-3 cm is significantly higher than levels at 6-9 cm. The variation was relatively small, and perhaps the influx of Na has not altered too much over the years.

### ***5.3 Biological effects***

Many of the above mentioned metal concentrations have been compared to classification values from the Swedish EPA, which identifies if there is a risk for biota with certain metal concentrations. To know that aquatic organisms are subject for possible negative consequences is not the same as stating that these effects are yet expressed. It is not the total concentrations, but the bioavailable concentration that determines the biological risks (EPA, 2007). Studies made on the impact on biota from heavy metals are made mainly in laboratories, and as the behaviour of metals cannot be assumed to stay the same in a lab as in a lake, the application to “real” conditions is complex (Luoma, 1983; Skjelkvåle, 2001). There are too many processes and factors involved to find a reliable simple method to determine the bioavailability.

For risk assessments, measuring the metal concentrations in water is more suitable (EPA, 2000b, Skjelkvåle, 2001) as sediment bound metals are not considered to bring as high risk as free ions in water (EPA, 2002) even though it is a concentrated pool of metals. As mentioned earlier, water analysis has been conducted in Lillsjön by the municipality of Östersund but the results are not presented here (Östersund, 2012). However, this provides good basic conditions for further studies on biological effects in Lillsjön.

One important mechanism for metal uptake by aquatic organisms is in connection with nutrient uptake as metals build complexes with e.g. proteins (Luoma, 1983). In the sediments it is detritus-feeding organisms that live in, or close to the bottom that are exposed to the high metal

concentrations. Fine-grained material is considered more important than coarse material in association with metals as adsorption-surfaces, regarding both transport and settling (Blecken et al., 2012).

Low water velocities enables fine material to settle. This is the purpose of transporting melt water from the snow disposal site in Östersund through a sedimentation basin and wetland before it reaches Lillsjön. Reducing the amount of fine-grained particles in Lillsjön also reduces the accumulation of particle-bound metals. During winter time Lillsjön is ice-covered and fine material that otherwise are redistributed by turbulence, can settle under the ice (Blecken et al., 2012). This study did not include grain-size analysis. The relationship between grain size and metal concentration in the sediment could be subject for another future investigation.

#### ***5.4 Variation with water depth***

Samples for XRF analysis were collected at different depths in Lillsjön, two from the believed accumulation bottom, and two from more shallow depths. A plot between metal concentration and water depth was created to see whether the deepest parts contain higher concentrations. Barium, iron, chromium and manganese concentrations all showed correlation with water depth. Aluminum, copper and potassium showed a vaguer trend. It was expected to find a correlation with water depth as Lillsjön has a large littoral zone and a distinct deep area where particles can settle (EPA, 2012). Four observations are relatively few and it would have been interesting to collect more samples over a depth gradient to see whether this correlation is valid all the way from 1 to 8 m depth.

#### ***5.5 Sediment profile***

One sediment profile down to 35 cm depth from Lillsjön was analysed with the XRF method. If the budget would have allowed to, several profiles would have been collected and analysed for comparison or the profile could have been analysed with ICP-AES instead. For Ba, Cu, Cr, Zn, Al and Fe the highest concentrations were found at 5-6 cm sediment depth. If 1 mm per year is assumed as the settling rate, this implies that the particles in the sediment settled 50 to 60 years ago. As Lillsjön is relatively nutrient rich (Blindow & Langangen, 1995) it is reasonable to believe that the sedimentation rate is somewhat higher (EPA, 2000b). Metal levels in Swedish sediments show a big increase up to, and partly during the 1970's due mainly to industrial developments (EPA, 2002). Perhaps the concentration peak in Lillsjön at approximately 5 cm depth corresponds

to the general load of metals in Sweden about 40 years ago. Also the local impact on Lillsjön was big during this time. Investigations by the county administrative board pointed out that the external load of pollutants endangered the good conditions in Lillsjön and the former snow disposal site was identified as a plausible cause (Östersund, 2011). In 1978, after several actions to diminish the inflow of pollutants Lillsjön was recovering and the water quality was improving (Östersund, 2011). The sediment profile in this study show a general decrease in metal concentrations from 5 cm and upward. After 1970 emissions of heavy metals have decreased (EPA, 2002). Partly due to the law of catalyts in Swedish cars, an emission control device that was implemented in year 1989 (ekonomifakta, 2010).

Results from the sediment profile do not follow the trend from the ICP-AES results where many metals show higher concentrations at 0-3 cm than further down. If samples for ICP-AES were divided per centimetre, a comparison could have been made. Unfortunately it is not known how the concentrations vary between 0 and 3 cm depth, and since only one profile was analysed with XRF it is difficult to draw any conclusions.

## ***5.6 Other parameters***

### **5.6.1 Carbon and carbonate content**

That the organic content was overall higher in samples from Lillsjön than the reference lakes can probably be explained by the fact that Lillsjön is more nutritious. This brings higher production and eventually more organic matter in the sediments (Blindow & Langangen, 1995). None of the metals in this study show any correlation with organic content. This was a bit surprising as Fe, Cr, Pb and Cu are known to be strongly associated to organic matter (EPA, 2000). In a study from Luleå LOI was positively correlated to Fe, Cd, Ni, Pb and Zn (Blecken et al., 2012).

In a study by Sigg et al (1987) calcium carbonate was concluded to be an inefficient carrier of trace metals, even though it can make up a considerable portion of the settling particles in a lake. Co-precipitation of metal ions seem unusual in general. However, an indication that Sr actually can co-precipitate with  $\text{CaCO}_3$  was noted as it has chemical similarities with Ca (Sigg et al., 1987). Aluminum, potassium and chromium show a negative correlation with carbonate content in the sediments of Lillsjön. Strontium was the only metal detected with ICP-AES with higher concentrations in Rannåstjärn than Lillsjön. It would be interesting to further investigate whether that can be linked to the higher carbonate content in Rannåstjärn.

### **5.6.2 Oxygen and temperature**

Oxygen and temperature curves was made for Lillsjön and Myckeltjärn, but Rannåstjärn is too shallow to make such analysis with the equipment used for this study. Both parameters vary with depth in Lillsjön and Myckeltjärn. Surface water is heated by the surrounding air and solar radiation during summer. In Lillsjön there is a clear limit (thermocline) where the warm surface water is divided from the underlying colder and denser water. In Myckeltjärn the difference was not as clear and the temperature deeper down was higher than in Lillsjön. In cold water, the potential for holding more oxygen is higher which also the water in Myckeltjärn did. In Lillsjön on the other hand, oxygen levels were strongly reduced close to the bottom. When the water is not mixing well due to the thermocline, no new oxygen reaches the bottom water and most of the oxygen is consumed in decomposition (EPA, 2007). Decomposing rates are slower with less available oxygen, which might be one further reason for the organic content being higher in the sediments of Lillsjön than Myckeltjärn.

### **5.6.3 Water transparency**

Water transparency decreases with high organic content as more planktonic algae are enabled to support from the food source. Suspended material in general deteriorate the light conditions in the water column (Kalff, 2001). The rare stonewort *Chara rudis* that are observed in Lillsjön demands high water transparency, and to some extent also nutrient-poor water (Odelberg, 2013). Phosphorous is taken up by the stonewort and limit the growth of other algae, which enables a relatively high water transparency. The bottom-living *Chara* algae also facilitates sedimentation, causing sediment-bound particles to be removed from the water column. If the phosphorous content is increased and the stonewort is damaged, water transparency will decrease and nutrients increase (Odelberg, 2013; Blindow & Langangen, 1995). According to Odelberg (2013) the P content in Lillsjön's water is higher than what is considered as suitable for stonewort. Together with the oxygen discussion above there is a risk that the stonewort species are disappearing from Lillsjön as the ecology is changing. Regarding the phosphorous content in the sediments, levels are higher in Lillsjön than in the reference lakes. Lillsjön has a history of high P values in the water during the 1970's, with sewage water, storm water and the former snow dump as reasonable sources (Östersund, 2001). The high values from then might be reflecting in the sediments today. Another contributing factor is the relatively bigger drainage area for Lillsjön compared to Myckeltjärn and Rannåstjärn. The high concentrations of phosphorous in the sediments, brings a

risk to Lillsjön as anoxic conditions seem to occur in the deepest bottoms. During anoxic conditions, P can be released from the sediments and yet again become available for production in the water column (Blindow & Langangen, 1995).

### 5.7 Method comparison

It was on beforehand known that XRF and ICP-AES differ in accuracy, price and procedure. Both methods have provided usable results for this study, although with varying concurrence. In an attempt to compare these methods a boxplot with XRF results was made, and the mean of the ICP-AES results for the same metal was plotted in the same graph. Note that results for XRF constitute sediments from 0 to 5 cm depth, and for ICP-AES from 0 to 6 cm sediment depth. Only results from comparable water depths were used in this comparison. As ICP-AES is a more precise method, the focus will be to establish whether XRF over- or underestimates the results from ICP-AES (Boss & Fredeen, 1997).

Regarding iron the methods are comparable, results from ICP-AES strikes within the error bars of the XRF boxplot. The error margins are small, probably due to the relatively high density of iron. Zinc is the only metal for which the ICP-AES results strikes within the blue areas (75<sup>th</sup> and 25<sup>th</sup> percentile) in the boxplot, for both lakes. Cu also shows concentrations within the same range with both methods.

XRF underestimates the Ba concentrations in Lillsjön, and overestimates Al and K. But in Myckeltjärn the results coincide and seem comparable. The error for Al in Myckeltjärn is 59.6 % and for some individual measurements even higher. These results should maybe not have been presented at all because of large errors, but were included since they correspond well with the ICP-AES results.

For Cr there is a large overestimation by the XRF method. The max value with ICP-AES was 35 µg/g and with XRF 226 µg/g. Chromium levels measured with ICP-AES was compared to the Swedish EPA's (2000b) classifications values and showed that they are *moderate high* and cause a significant deviation from pristine sediments. If the XRF results are accurate, the status would be *high* with very large deviation from natural concentrations.

Both methods have their advantages. For this study it was suitable to use ICP-AES to obtain reliable results even for lighter elements. Without the XRF method the number of observations

would have been considerably lower, and the analysis with depth and carbonate content would not have been possible.

## 6. Conclusions

The present study has resulted in several conclusions and straightforward results. The questions phrased in the beginning of this report are hereby answered.

### **Do the sediments in Lillsjön contain higher concentrations of any metals than Rannåstjärn or Myckeltjärn?**

XRF analysis shows that the sediment samples from Lillsjön contain higher levels of aluminum, iron, potassium, zinc and strontium than both reference lakes. Barium was found in higher levels in Lillsjön than Myckeltjärn. Regarding results from ICP-AES analysis copper, zinc, cadmium, chromium, lead, nickel, arsenic, barium, iron, manganese, aluminum, potassium all showed higher concentrations in Lillsjön at all depths, compared to Mycketjärn and Rannåstjärn. The only metals where Lillsjön did not contain the highest levels according to ICP-AES results were strontium and sodium.

### **Are there any differences in metal content at different sediment depths?**

All metals measured with the ICP-AES technique in Lillsjön showed big variation in concentrations with varied sediment depth. The general trend was that the sediment surface contained higher levels than the underlying layers. Strontium and sodium were not embraced by this trend.

### **Are the metal concentrations in the sediments of Lillsjön potentially harmful to biota?**

Results achieved by ICP-AES analysis were compared to classification values provided by the Swedish EPA. Ni was found at *high* concentrations which brings a progressive risk of negative biological effects. Zn, Cd, Cr and As levels were *moderate high* and this implies that negative effects can occur. Only Pb showed *low* concentrations, but was not far from reaching the status *moderate high* and the risk of affecting biota cannot be totally ruled out. It was also investigated how these concentrations deviate from concentrations found in pristine lake sediments, and Lillsjön is clearly affected by its incoming water. Several metals showed significant or large deviations which means that the influx of these metals to Lillsjön is enhanced.

Another conclusion drawn by this study is that metal concentrations were enhanced in areas where water depth is big and material can accumulate. At shallow depths levels were lower. The organic content in Lillsjön's sediments showed no correlation to metal concentrations, which on the other hand carbonate content did. Al, K and Cr show a negative correlation with carbonate content.

ICP-AES was a suitable method for the aim of this study, all desired metals were detected and measured, and could be presented here. XRF is also a usable method, although the exact concentrations should be interpreted with caution due to related errors.

The results of this study shows that the influx of metals are enhanced in Lillsjön compared to the reference lakes, and this should be kept in mind when planning the future for the lake and surrounding areas. Continued monitoring of the water quality is recommended to ensure a safe utilization of the lake. It is mainly the water quality that can give a trustworthy indication if the content of pollutants in Lillsjön can cause damage to biota.

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## Appendix A

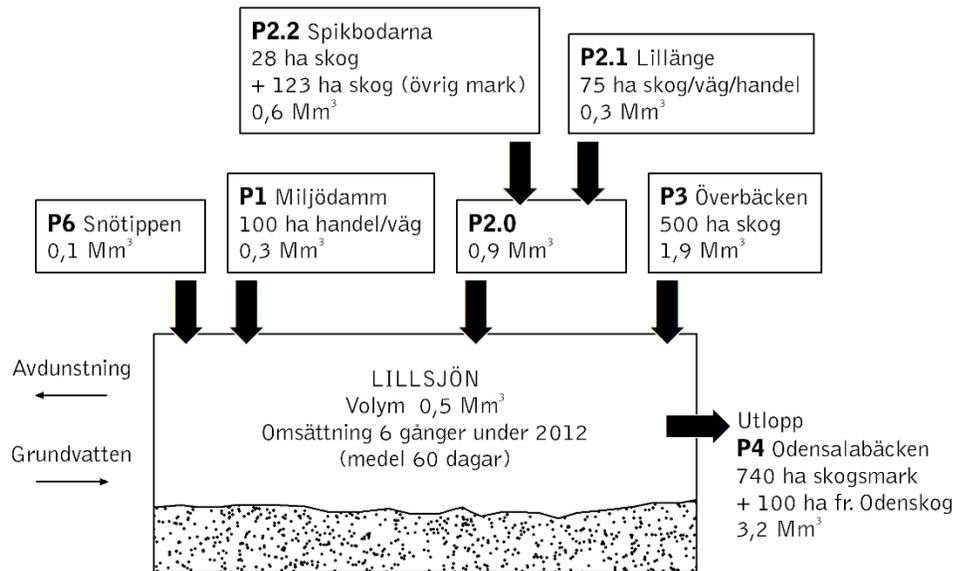


Figure 18. Schematic picture of the modelled water balance for Lillsjön during year 2012. The total waterflow through Lillsjön was estimated to 3.2 Mm<sup>3</sup>. Approximately 60% of the incoming water origins from drainage area P3 (Överbäcken). The water volume in Lillsjön is approximately 0.5 Mm<sup>3</sup> which theoretically means that the water was exchanged six times during 2012. The magnitude of groundwater inflow and evaporation is unknown (Östersund, 2013).

## Appendix B



*Figure 19. Sediment sample from Lillsjön. The core was approximately 35 cm and relatively dark, almost black.*

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