The influence by point sources on carbon, nitrogen and metals in two sedimentary environments

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Stockholm 2005
ABSTRACT

In this thesis sediment in two aquatic environments have been investigated. Both are anthropogenically affected and polluted. The focus has been on stable carbon and nitrogen isotopes, the carbon and nitrogen ratio, and heavy metals. The first study area is Höggarnsfjärden Bay in the inner parts of Stockholm Archipelago, Sweden. In the bay a garbage dump releases treated leach water. The effect on carbon and nitrogen situation close to the discharge is large, but 1200 m downstream the effect is diluted by the background discharge of the town of Stockholm and the Lake Mälaren, which drains into the archipelago. The same is valid for the metals. The main source is not the garbage dump itself, but the sediment close to the garbage dump shows high enrichment factors due to high sedimentation rate and adsorption, and low decomposition of organic matter. The enrichment factors of the metals of downstream sites are not higher than the upstream sites.

The second environment is Lake Verkasjön close to the north part of Lake Vättern, in the County of Örebro, Sweden. River Salaån flows through Lake Verkasjön on the way through a former mining area to the north part of Lake Vättern. Upstream of Lake Verkasjön an ore dressing plant site was used for a short period of time at the end of the 19th century for extraction of zinc. During that period the sediment of Lake Verkasjön received high loadings of metal loaded clastic material. Normal sedimentation after the closing of the ore dressing plant has lead to that the polluted sediment is found as a distinct layer at 18-22 cm. The layer is characterized by elevated metal concentrations in the pore water and solid phases, decreased organic matter content and increased stable carbon composition. The sediment that has accumulated above 18 cm works as a physicochemical barrier that seals the waste from the overlying sediment. At the time period when the ore dressing plant was active the signal of aquatic production in the sediment changed. In the sediment above the layer the proportion of aquatically produced material and the organic matter content has increased, implying changed land use in the catchment area.
The influence by point sources on carbon, nitrogen and metals in two sedimentary environments

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This doctoral thesis consists of a summary and four papers. The four papers are listed below and are referred to as Paper I-IV in the text:

Paper I
Hanna Bohlin, Carl-Magnus Mörth, and Nils G. Holm
Point source influences on the carbon and nitrogen geochemistry of sediments in the Stockholm inner archipelago, Sweden

Paper II
Hanna Bohlin, Carl-Magnus Mörth, Nils G. Holm
Anthropogenic pollution of heavy metals of sediments in the Stockholm inner archipelago
Submitted to Applied Geochemistry

Paper III
Mattias Bäckström, Hanna Bohlin, Stefan Karlsson, and Nils G. Holm
Element (Ag, Cd, Cu, Pb, Sb, Tl and Zn), element ratio and lead isotope profiles in a sediment affected by a mining operation episode during the late 19th century
(Manuscript)

Paper IV
Hanna Bohlin, Mattias Bäckström, Nils G. Holm, and Carl-Magnus Mörth
Carbon and nitrogen stable isotope variation in lake sediments influenced by a short mining episode in the late 19th century
(Manuscript)

My contribution to the papers is:
Paper I. Field sampling, sample preparation, data processing, and main part of data evaluation.
Paper II. Field sampling, sample preparation, participation in the ICP-analyses, main part of data processing, and data evaluation.
Paper III. Participation in the field sampling, sediment sample preparation, and participation in the data evaluation.
Paper IV. Participation in field sampling, sample preparation, and evaluation of data.

Stockholm, November 2005,

Hanna Bohlin
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INTRODUCTION

Lacustrine and marine sediments are often used as paleoenvironmental archives in environmental studies. The subaqueous sediments hold information of, for example, organic matter like carbon and nitrogen, and metals, which can be used to reconstruct the paleoecological and pollution history of the lakes/archipelagos and their catchments. The sources may be natural such as products of weathering and erosion or decomposition of organic matter, but also anthropogenic as urban areas, industries, mining, traffic, and agriculture. Vertical concentration profiles in lake sediments are commonly used as a tool to monitor levels of organic matter and metals in the environment (Brännvall et al., 2001; Bratton et al., 2003; Herczeg et al., 2001; Jia and Peng, 2003; Kendall et al., 2001; Lehmann et al., 2002; Lindström et al., 2001; Lücke et al., 2003; Mariotti et al., 1988; Meyers, 2003; Östlund and Palm, 1998; Östlund and Sternbeck, 2001; Preda and Cox, 2002; Renberg et al., 2002; Routh et al., 2004; Savage, 2005; Soto-Jiménez and Páez-Osuna, 2001; Sternbeck and Östlund, 2001; Voss et al., 2005).

In this thesis sediment from two aquatic environments have been investigated, both are anthropogenically affected and polluted. The focus has been on stable carbon and nitrogen isotopes, carbon and nitrogen ratios and heavy metals.

Sources of organic matter

Particulate organic matter, POM, is detrital terrestrial and aquatic organic material, that gives information about natural and anthropogenic activities within the drainage basin (Kendall et al., 2001). There are two general sources: organic matter produced in the aquatic system via photosynthesis (autochthonous), and terrestrial organic matter from the catchment delivered via tributaries (allochthonous) (Herczeg et al., 2001). Typical autochthonous sources of POM are phytoplankton, algae, and macrophytes, while typical allochthonous sources of POM are soil organic matter, plant detritus and soil humus. The aquatic and land derived organic matter is degraded by bacteria and other microbes. This process is going on in both the water column and in the sediment, even if the decomposition rate is slower in the sediment (Routh et al., 2004). A consequence is that only a few percent of the initially produced organic matter becomes buried in the sediment (Hoefs, 1997; Routh et al., 2004). The decomposition of organic matter consumes electron acceptors like oxygen and is slower during anoxic conditions (Lehmann et al., 2002; Meyers and Teranes, 2001; Stumm and Morgan, 1996).

The concentration of organic carbon gives information about the amount of organic matter in the sediment, and the C/N ratio identifies the proportions of algal and land-plant organic matter (Herczeg et al., 2001; Kendall et al., 2001; Meyers, 2003).

Another method used to appoint the source of carbon and nitrogen in organic matter is based on the use of isotopes. Isotopes are different species of the same chemical element, with the same number of protons but different number of neutrons in the nuclei (Hoefs, 1997). This give them slightly different atomic mass, which provide them slightly different chemical and physical properties (Kendall and Caldwell, 1998). Carbon has two stable isotopes, $^{12}$C with the abundance 98.89%, and $^{13}$C with the abundance 1.11% (Hoefs, 1997; Wang et al., 1998). Concordantly, nitrogen has two stable isotopes, $^{14}$N and $^{15}$N, with the abundance 99.64% and 0.36% respectively. The heavier isotope tends to be enriched in the compound with higher oxidation state, and between different phases of the same compound the heavier isotope tends to be enriched in the denser phase (Kendall and Caldwell, 1998). Further, organisms prefer the lighter isotope before the heavier ($^{12}$C and $^{14}$N before $^{13}$C and $^{15}$N) so the product is isotopically lighter than the residue (Kendall, 1998; Kendall et al., 2001). The reason for the fractionation mechanism is that lighter isotope generally react easier and are more mobile than those with the heavy isotope (Hoefs, 1997). The isotopic composition is normally expressed as a δ-value ($\delta^{13}$C, $\delta^{15}$N), where the ratio of the sample is compared to the same ratio of a standard;

$$\delta^{15}N \text{ or } \delta^{13}C (\%) = \left( \frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1000$$

where R is the ratio of heavy to light isotope, i.e. $^{15}$N/$^{14}$N and $^{13}$C/$^{12}$C. The standard used for calculating $\delta^{13}$C is PDB (PeeDee Belemnite), and for $\delta^{15}$N the standard used is N$_2$ in air (Hoefs, 1997; Wang et al., 1998). The stable isotope composition of C and N gives information about the proportion of different sources of C and N, and assimilation and degradation processes (Herczeg et al., 2001; Kendall et al., 2001).

Carbon

Stable isotopes of carbon in organic matter in sediments have frequently been used as indicator for sources of carbon, carbon assimilation during photosynthesis, changes in productivity rates, and changes in the proportion between terrestrial and aquatic produced organic matter (Herczeg et al., 2001; Hoefs, 1997; Kendall et al., 2001; Lücke et al., 2003; Meyers, 2003).

Terrestrial vascular plant material have atmospheric CO$_2$ as ultimate carbon source (-7 or -8‰) (Hoefs, 1997; Kendall et al., 2001; Wang et al., 1998). Most terrestrial photosynthetic plants incorporate the atmospheric CO$_2$ using the Calvin pathway (C$_3$) which gives them an average $\delta^{13}$C of -27‰ (Hoefs, 1997; Wang et al., 1998). The soil organic matter tends to reflect the $\delta^{13}$C of plants growing on the soil, and shows generally values around -27‰ for C$_3$-plants (Kendall et al., 2001).

Aquatic plants derive most of their carbon from dissolved inorganic carbon (DIC) i.e. in freshwater mostly dissolved atmospheric CO$_2$ or CO$_2$ from plant respiration
(-27‰) (Kendall et al., 2001) Other sources are DIC from dissolved carbonate rocks, the catchment and recycling of $^{13}$C depleted C from decay of organic matter in the water column and sediments (Kendall et al., 2001; Wolfe et al., 1999). Freshwater phytoplankton using DIC in isotopic equilibrium with the atmospheric CO$_2$ produces aquatic plants $^{13}$C commonly indistinguishable from the organic matter derived from the land surrounding area (Meyers and Teranes, 2001). However, the delivery of DIC by land runoff and land produced plant debris results generally in isotopically lighter DIC available for phytoplankton and algae (Kendall et al., 2001; Meyers and Teranes, 2001), and freshwater plankton usually have an average $^{13}$C of -30‰ (Kendall et al., 2001; Wolfe et al., 1999). Generally, land produced organic matter and aquatic macrophytes have $^{13}$C >-28‰ and lacustrine produced organic matter <$-25‰ (Lücke et al., 2003; Meyers and Teranes, 2001). Because of large variation of carbon sources (DIC) available for aquatic plants, POM derived from aquatic plants has a larger $^{13}$C variation than terrestrial plants, for which the carbon source mainly is atmospheric CO$_2$ (Kendall et al., 2001).

The main source of inorganic carbon for marine algae is dissolved bicarbonate, which has a $^{13}$C value of approximately 0‰. The result is that organic matter of marine origin (phytoplankton) has $^{13}$C values around -20‰ (Hoefs, 1997; Kendall et al., 2001). The 7‰ difference between $^{13}$C for land-plants and marine organic matter has been used as a distinction between continental and marine sources of sedimentary organic matter (Hoefs, 1997; Kendall et al., 2001).

Grain size is not significantly affecting the $^{13}$C. The early diagenesis of sinking and sedimenting organic material appears to have very small effect on the carbon isotopic composition of the material (Hoefs, 1997; Lücke et al., 2003; Meyers and Teranes, 2001), usually less than 2‰ (Neumann et al., 2002).

The degradation of organic matter in anoxic and reduced sediment is often carried out by bacterial methane production, which generally follows sulphate reduction in carbon rich sediment. The methane producing bacteria produce very $^{13}$C rich methane, resulting in pore water with significantly increased $^{13}$C (Hoefs, 1997; Kendall et al., 2001; Schlesinger, 1997).

Nitrogen

The stable isotopes of nitrogen have been used as indicators of nitrogen sources and processes in the environment in numerous studies. $\delta^{15}$N in organic matter can get a wide range of values, and may provide information about the proportions between algal- and land-plant organic matter, evidence of nitrogen fixation and enhanced algal production (Bratton et al., 2003; Kendall et al., 2001; Mariotti et al., 1988; Meyers, 2003; Routh et al., 2004; Savage, 2005; Voss et al., 2005; Voss et al., 2000; Wolfe et al., 1999) because of the characteristic $\delta^{15}$N values for different sources of dissolved inorganic nitrogen (DIN), even if isotopic studies of carbon in watersheds are more common (Meyers and Teranes, 2001).

The use of $\delta^{15}$N to identify organic matter sources is based on the difference of $\delta^{15}$N of the inorganic nitrogen available for land plants and plants in the water (Meyers, 2003; Meyers and Teranes, 2001). The ultimate nitrogen source for terrestrial N-fixing plants is N$_2$ in air, which by definition has $\delta^{15}$N=0‰ (Owens, 1987), while the nitrogen source for aquatic plants and algae commonly are DIN (Meyers and Teranes, 2001). The N-fixing terrestrial plants usually get $\delta^{15}$N values between 0 and +2‰ (Kendall et al., 2001; Meyers, 2003), and $^{15}$N in soils is influenced by soil depth, vegetation, climate, cultural history, etc., and range normally between +2 and +5‰ (Kendall et al., 2001).

DIN, which is an important nitrogen source for aquatic plants, algae and macrophytes is in pristine rivers mainly derived from mineralization of organic matter and subsequent nitrification (Kendall et al., 2001). However, the isotopic composition of DIN is modified by nitrification, denitrification, algal uptake and mineralization (Savage, 2005), processes that normally increase $\delta^{15}$N in the residual (Kendall, 1998; Mariotti et al., 1988). Much of the nitrate in larger river systems is also derived from agriculture, fertilizers and urban sewage, sources that generally gives nitrogen inputs into the ecosystem that is suggested to increase $\delta^{15}$N values of DIN (Hoefs, 1997; Kendall, 1998; Kendall et al., 2001; Mariotti et al., 1988; Voss et al., 2000). Runoff from fertilized fields may, for example, increase the $\delta^{15}$N value since fertilizers produced from manure usually have $\delta^{15}$N between +10 and +20‰ ($\delta^{15}$N around 0‰ are reported for artificial fertilizers) (Kendall et al., 2001; Mariotti et al., 1988). Consequently, $\delta^{15}$N of DIN available for aquatic plants are normally in the range of +7 to +10‰ (Meyers, 2003; Meyers and Teranes, 2001). The $\delta^{15}$N value of nutrients in the water is preserved in plankton and sediment, and an isotopic change in the sediment may subsequently be explained by anthropogenic input into the water (Kendall et al., 2001; Voss et al., 2000).

The largest fractionation is generally caused by denitrification (Kendall, 1998), which occurs in anoxic environments when heterotrophic organisms use oxidized nitrogen as electron acceptor and reduce the nitrogen to N$_2$. Denitrification does thus decrease the amount of N in the sediment (Stumm and Morgan, 1996).

$\delta^{15}$N tend to increase in soil during decomposition (Kendall et al., 2001), and even if nitrogen isotope ratios are not conservative over the long term since nitrogen undergoes various fractionation processes it is stable enough for use as a sediment tracer (Bachtiar et al., 1996). Studies show that there are no diagenetic isotopic effects on $\delta^{15}$N in the Baltic Sea (Voss et al., 2005).

C/N ratio

C/N ratios of organic matter have been used to distinguish between algal and land-plant origins of sedimentary
organic matter (Kendall et al., 2001; Meyers and Teranes, 2001) even if C/N values of terrestrial and aquatic plants may show considerable overlapping (Kendall et al., 2001).

Samples with C/N ratios lower than 8 are usually interpreted as dominated by plankton material (Kendall et al., 2001), since plankton and algae typically have C/N ratios of 4-10 (Kendall et al., 2001; Meyers, 2003; Meyers and Teranes, 2001). Sediment samples with a large proportion of terrestrial land plant content have higher C/N ratio since terrestrial vascular land plants usually have values above 20 (Meyers, 2003; Meyers and Teranes, 2001) and fresh plant litter may have ratios above 100 (Schlesinger, 1997). C/N ratios above 15 may indicate samples dominated by fresh plant input, or a combination of terrestrial plants and macrophytes (Kendall et al., 2001). The difference in C/N ratio between plankton and terrestrial plants is because of the high content of proteins (N-rich) in planktons and the cellulose and lignin (N-poor) in land plants and macrophytes (Meyers, 2003).

Studies show that C/N of organic matter may be changed during degradation (Kendall et al., 2001), but are usually preserved well enough in subaqueous sediments to retain reliable source information (Meyers, 2003; Meyers and Teranes, 2001; Voss et al., 2000).

Metals

The increasing industrialisation and human activities during the last century has intensified the emission of various pollutants such as heavy metals into the environment. A major process controlling the content of metal in aquatic environments is particle scavenging, and subsequent transport to the sediments. The particles on which metals and other pollutants in aquatic environments are scavenged may be of both inorganic and organic material (Stumm and Morgan, 1996), and the metals may be adsorbed to, complex bound to, or co-precipitated with the scavenger (Liaghati et al., 2003; Novotny, 1995). The main sediment fractions that interact with metal compounds in aerobic freshwater include Mn and Fe hydrous oxides, POM and clays (Jacobson et al., 2000; Novotny, 1995; Preda and Cox, 2002; Salomons et al., 1995; Schnoor, 1996). Under anaerobic conditions sulphate is microbially reduced to sulphide, which is an important scavenger of trace elements (Jacobson et al., 2000; Salomons et al., 1995). This process controls the solubility of many trace elements (Borg and Jonsson, 1996; Bourg, 1995; Schnoor, 1996). Metals may also be complex bound in the dissolved phase by, for example, sulphides, humic substances, organic acids and chloride ions (Stumm and Morgan, 1996).

When studying associations between different species in the sedimentary environment one method is to calculate the correlation coefficients of the species of interest. Metals showing high correlation coefficients with, for example, Al, Mn, Fe, organic carbon or S, are often regarded as associated with clays, (Liaghati et al., 2003) Mn and Fe oxides and hydroxides, organic matter (Bourg, 1995; Preda and Cox, 2002; Schnoor, 1996; Sternbeck, 1996; Sternbeck et al., 2000) and sulphide, respectively (Novotny, 1995). Al, Ni, Cr, Fe and Mn are known to be associated with clays (El Bilali et al., 2002). In anoxic sediments, association of Mn and Fe oxides with Cr, Cu, Ni, Pb and Zn is common (Bourg, 1995; El Bilali et al., 2002; Stumm and Morgan, 1996). These oxides are not normally present in anoxic sediments where they become reduced and dissolved (Bourg, 1995; Jacobson et al., 2000; Sternbeck, 1996). Cu, Pb and Zn are known to be associated with organic matter (El Bilali et al., 2002). Sulphides are important scavengers of Fe, Cu, Ni, Pb and Zn in anoxic environments (Hongve, 2003; Jacobson et al., 2000; Schnoor, 1996).

As many metals occur naturally in weathered materials and drainage systems due their presence in local rocks, the relative influence of natural and anthropogenic sources on the geochemistry of sediments are not always clear. The metals of different sources accumulate simultaneously in the sediment, and in order to distinguish between the natural and anthropogenic sources and to compensate for variations in rock and soil types, sediment rates and grain-size distribution data can be normalized. A common normalization method is to calculate the Enrichment Factor, EF (Covelli and Fontolan, 1997; Soto-Jiménez and Páez-Osuna, 2001; Vertacnik et al., 1997):

$$EF = \frac{\left[ \frac{Me}{X} \right]_{\text{Sample}}}{\left[ \frac{Me}{X} \right]_{\text{Reference}}}$$

The enrichment factor compares the ratio between the metal (Me) and a conservative element (X) in the sample with the ratio of the same elements in a reference material. An EF value below 2 indicates that the concentrations of metals are of natural origin, i.e. the metal concentration in the sample is near the mineralogical composition of the background. EF values between 2 and 10 suggest a possible anthropogenic impact, while EF values above 10 clearly indicate pollution (Vertacnik et al., 1997). The conservative element (X) should principally have natural sources in the sediment and similar sedimentological properties as the elements of interest (Lindström et al., 2001). The element should also be associated with the smaller grain size fractions like silt and clay (Covelli and Fontolan, 1997). In previous studies used elements are Al (Soto-Jiménez and Páez-Osuna, 2001), Fe (Vertacnik et al., 1997), Li (Soto-Jiménez and Páez-Osuna, 2001), Ni (Lindström et al., 2001), and Sc (Blomqvist and Larsson, 1996; Vertacnik et al., 1997). The ratio between the analyzed element and the conservative element should be compared with a reference level in order to get information about for example the intensity of anthropogenic contamination.
The metal concentrations of the reference should have a natural origin. Often used references are ‘average crust’ or ‘average shale’. These references do, however, require total digestion of the sediment samples (Liaghati et al., 2003), which is not always the extraction method used. Other often used references are deeper sediments of the studied area. This sediment is supposed to be mineralogically and texturally comparable with the rest of the sample (Covelli and Fontolan, 1997).

Comparisons have been done between absolute metal concentration data and enrichment factors data in soil. Liagathit et al. (2003) digested sediment with aqua regia, normalized to Al and used deeper sediments as reference material. In material with high clay content the absolute concentration data and enrichment factors covaried, but in cores with more irregular distribution of grain size there was negative correlation. The conclusion was that in highly heterogeneous environment interpretations based on absolute concentration of different elements alone could be misleading. Instead, the normalization procedure gave the best approach for sensible interpretation of data (Liaghati et al., 2003).

**Lead and lead isotopes**

Lead is good as pollution indicator and may give a general picture of changes in past atmospheric pollution. The natural sources of lead are weathered mineral matter in soil and bedrock (Renberg et al., 2002). Anthropogenic sources to the environment are, for example, mining, metal industry, burning of fossil fuels, and vehicles (Brännvall et al., 2001). The metal can be transported long distances in the atmosphere, but the mobility in soils and sediments is generally low and the transport from catchment soils is limited (Renberg et al., 2002). The geographical distribution of the lead pollution of today is similar to the map of the pollution of the past. In Europe today, as before, it is caused by a long-range, south-to-north atmospheric transport of anthropogenic lead and other pollutants (Brännvall et al., 2001).

The isotopic ratio of $^{206}\text{Pb}$ and $^{207}\text{Pb}$ is often used when tracing the sources of lead. The isotopic composition differs generally between sources such as bedrock (background), ores, and gasoline (Renberg et al., 2002), and can be used as a ‘fingerprint’ of anthropogenic Pb (Östlund and Sternbeck, 2001).

Swedish lake sediments at ‘pre-pollution’ depth have $^{206}\text{Pb}/^{207}\text{Pb}$ average of 1.52 (Brännvall et al., 2001; Renberg et al., 2002), and sediment with ratio above 1.3 may be interpreted as unpolluted background (Brännvall et al., 2001). Various anthropogenic lead sources depress the $^{206}\text{Pb}/^{207}\text{Pb}$ ratio; lead ores and coal in Europe have an average of 1.17 (Renberg et al., 2002), and lead in gasoline even lower, 1.10-1.2 (Monna et al., 1999). The atmospheric contribution of lead in Sweden during the 1980s and 1990s had a lead isotopic ratio between 1.12 and 1.16, due to the use of lead ores and coal and to traffic (Brännvall et al., 2001; Renberg et al., 2002). This has influenced the sediments of Swedish lakes, and sediments with $^{206}\text{Pb}/^{207}\text{Pb} <1.2$ are interpreted as polluted by ores and coal (Brännvall et al., 2001). Generally, the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios of Swedish lake sediments are not lower than 1.17. (Brännvall et al., 2001). However, lake sediments close to the Falu copper mine and in the Bergslagen region in the central part of Sweden have reported $^{206}\text{Pb}/^{207}\text{Pb}$ of 1.03 (Renberg et al., 2001; Renberg et al., 2002).

The first indications of atmospheric lead pollution in Swedish sediments is from 3500-3000 years ago (Brännvall et al., 2001; Renberg et al., 2002), most likely principally originating from metallurgy (Brännvall et al., 2001). The use of lead in the Greek-Roman (500 B.C.-400 A.D) and Medieval cultures (900-1400 A.D) as well as during the industrial period (1800-2000 A.D) is visible in Swedish soils and sediments (Brännvall et al., 2001; Renberg et al., 2002). The highest peak of lead in the sediment is from the 1970’s, and since then the atmospheric deposition of Pb recorded in Swedish lakes has decreased due to emission control, industrial cleaning techniques, closure of polluting industries and phasing out lead in petrol (Brännvall et al., 2001; Renberg et al., 2002).

**STUDY AREAS**

The two studied sites are Höggarnsfjärden Bay in the Stockholm inner archipelago and the Lake Verkajön in the county of Örebro. The first study site, Höggarnsfjärden Bay is located north of Ormingelandet in the Stockholm inner archipelago, east of Stockholm, Sweden (figure 1). For further site description, see papers I and II.

The second study site, Lake Verkajön, is located between Hammar and Zinkgruvan in the county of Örebro in the south of Sweden (figure 2). An additional site description is available in papers III and IV.

**SUMMARY OF PAPERS**

**Paper I: Point source influences on the carbon and nitrogen geochemistry of sediments in the Stockholm inner archipelago, Sweden**

The aim of the study has been to study the carbon and nitrogen in the sediments in the Höggarnsfjärden Bay in the inner parts of the Stockholm Archipelago, Sweden, and to detect possible sources of carbon and nitrogen. The sampling sites are located upstream, near, and downstream of the outflow of the treated leach water from a garbage dump. The sediments were sampled with a gravity corer, freeze-dried and analyzed for carbon and nitrogen isotope ratios ($\delta^{13}\text{C}_{\text{TOT}}$ and $\delta^{15}\text{N}_{\text{TOT}}$) and total contents of carbon and nitrogen ($\text{C}_{\text{TOT}}$ and $\text{N}_{\text{TOT}}$). Leach water samples were filtered and the particulate material (LW$_{\text{PS}}$) was analysed for $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$.

The sediment at site 1, close to the outflow of the garbage dump, is characterized by high $\delta^{15}\text{N}_{\text{TOT}}$, $\text{C}_{\text{TOT}}$, and low $\text{C}_{\text{TOT}}/\text{N}_{\text{TOT}}$ ratio compared to the other
sites of the study. The δ¹⁵N_TO, values of the sediment at the outflow site (+16 to +19‰) are clearly higher than the δ¹⁵N_TO of the other sites (around +8‰ at the sediment surface), and correspond to the average δ¹⁵N_TO of the particulate material in the leach water (+17 ‰). This suggests that the sediment in the area close to the garbage dump is strongly influenced by effluents from the dump. The outflow site has a high content of C_TO and N_TO compared to the other sites. This could be due to high loading of organic matter, but the major reason is low decomposition rate of the organic matter due to anoxia in the sediment. The anoxia is implied also by the δ¹³C data. The carbon of the outflow site has high δ¹³C (-22.4‰) compared to the other sites and the particulate material of the leach water (-30.7‰). The reason is that the sediment at the outflow is subjected to degradation by methane fermentation by bacteria.

The organic matter in the sediment samples from the downstream site is the result of mixing of material from the leach water, the outflow site, and material from upstream of the area. A nitrogen end member mixing analysis gives the estimation that about 8% of the nitrogen in the sediment at the downstream site originates from the leach water. Calculating the carbon end member mixing analysis at the downstream site gives the estimation that 14% of the carbon in the sediment at the downstream site originates from the leach water.

**Paper II: Anthropogenic pollution of heavy metals of sediments in the Stockholm inner archipelago**

This paper reports metal data from the sample sites in Höggarnsfjärden Bay, east of Stockholm. The sample sites are situated upstream (site 3, 4 and 5), near (site 1), and downstream (site 2) of the outflow of treated leach water from a garbage dump in the Höggarnsfjärden Bay, east of Stockholm, Sweden. Sediment cores were sampled with a gravity corer, freeze-dried, and digested with concentrated HNO₃ according to USEPA method 3051 in a microwave oven, and were then analyzed with ICP-OES, Varian Vista Pro AX for Cr, Cu, Ni, Pb, V, and Zn. Enrichment factors (EF) have been calculated with Al as normalizing element and deeper levels of the upstream samples as baseline. Correlation tests were made to determine relationships between the investigated metals and Al, Mn, Fe, C_TO, and S, respectively.

The sediments show increased enrichment factors of all analysed metals at site 1 (Cr: 11.5, Cu: 12.7, Ni:
The reason may be low decomposition rate of the organic matter due to anoxia in the sediment. At both the upstream and downstream sites Cu, Pb, and Zn, and to some extend Cr, show increased levels compared to baseline level. Ni and V in the sediment are in the same levels as the baseline. The major amount of the reported metals origin from areas upstream of the studied bay, closer to the city of Stockholm and the Lake Mälaren.

In the baseline sediments (the deepest sampled sediment of the upstream cores used in the enrichment calculations) Cr, V, and Zn are well correlated to Al and thus presumably to clay minerals. Ni and Pb are weakly correlated to Fe and S, implying iron sulphides. The metals in the present background of the Höggarnsfjärden Bay (uppermost 3 cm of upstream samples) show high correlation coefficients to C_TOT and Al, suggesting that they are bound to organic matter (Cr, Cu, Pb and Zn) and clay minerals (V). At site 1 all studied metals show high correlation with Al and S, suggesting accumulation simultaneously with clay particles and sulphides, due to the anoxic conditions. At site 2, the downstream site, Cu, Ni and Pb are strongest correlated to Fe and S, suggesting association with iron sulphides. V is due to high correlation with Al suggested to be associated with clay particles.

Paper III: Element (Ag, Cd, Cu, Pb, Sb and Zn), element ratio and lead isotope profiles in a sediment affected by a mining operation episode during the late 19th century

The aim of this paper was to study the concentration and mobility of some heavy metals in the sediment in Lake Verkasjön, which drains to Lake Vättern, the second largest lake in Sweden. Lake Verkasjön is part of the River Salaån which has a catchment area that is known for mining activities since the 14th century. Upstream of the Lake Verkasjön a former mining site is located, which was active during five years in the end of the 19th century (1877-1881). This source was identified in the sediment records, as well as an additional source, based on elemental ratios and historical data.

The mining operations during 1877-1881 resulted in increased minerogenic, sulphidic, metal loading into the lake. Normal sedimentation after the episode has buried the polluted sediment material which now forms a distinct layer at a depth of 18-22 cm below the sediment surface. This is suggested both by physical and chemical parameters, as well as by \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios. The layer is characterized by elevated metal concentrations in the pore water and solid phases, approximately neutral pH and sulphate concentrations below detection limit.

The sediment above the polluted sediment layer at 18-22 cm works as a physical as well as a chemical barrier that seals of the waste from the overlying sediment. Redox properties of iron in combination with continuous input of sulphate efficiently retain the trace metals through adsorption in oxic/post-oxic environments and sulphide formation in reducing strata. This processes works as redox barrier, preventing the metal waste from contact with the mobile water in the lake today.

The increased metal content in the uppermost 18 cm of the sediment originate from additional sources. This is implied by historical production records, trace element ratios and \(^{206}\text{Pb}/^{207}\text{Pb}\) ratios. Increased copper concentrations were observed before the activity of the ore dressing plant while the concentrations of antimony and thallium began to increase after this period. The elemental concentrations in the surface sediment are independent of the pollution event and are determined principally by release upstream, possible in combination with atmospheric deposition.

Paper IV: Carbon and nitrogen stable isotope variation in lake sediments influenced by a short mining episode in the late 19th century

The aim of this paper was to study the carbon and nitrogen in the sediment in Lake Verkasjön. The former ore dressing plant upstream of Lake Verkasjön (active 1877-1881) contributed minerogenic material which sedimented into the lake. This sediment event appears in the sediment at the depth of 18-22 cm as changed content of total carbon (C_TOT) and nitrogen (N_TOT), carbon isotope ratio (\(\delta^{13}\text{C}\)), C/N ratio, and lead isotopic data (\(^{206}\text{Pb}/^{207}\text{Pb}\)).

In the deeper parts of the sediment, between 50 and 25 cm, C_TOT, N_TOT, C/N, and \(\delta^{13}\text{N}\) are rather stable. The \(\delta^{13}\text{C}\) data suggest predominantly aquatically produced material in the lake sediment. The C/N ratio suggests a mixture of nonvascular and vascular aquatic plant contributions with terrestrial contribution.

At about 25 cm all variables change. C_TOT and N_TOT increase, suggesting that there is more organic matter in the sediment above 20 cm than below; and \(\delta^{13}\text{C}\) (decreases) and \(\delta^{15}\text{N}\) (increases) imply that this organic matter is more influenced by aquatic production than below. At the same depth the lead sources change from a predominantly origin of surrounding soil to a predominantly origin of tailings and atmospheric deposition. The change of lead source is a satisfactory dating tool of the sediment level of 20 cm, the contribution from the zinc ore dressing plant active during 1877-1881.

The decreased concentration of C_TOT and N_TOT increased C/N ratio and \(\delta^{13}\text{C}\) values, and rather unchanged \(\delta^{15}\text{N}\) values at the level of 18-22 cm compared to above and below imply that the most important at this level seems to be less input organic matter and the subsequent changed \(\delta^{15}\text{C}\) values caused by this changed influx of carbon.
**DISCUSSION**

### Höggarnsfjärden Bay

The sediment representing the present background of the studied area (site 4 and 5) shows δ¹³C (-25.5‰) and δ¹⁵N (+8‰) values (Paper I) in the range as previous studies in the inner parts of the Stockholm Archipelago (δ¹³C) (Jönsson et al., 2005) and Lake Mälaren (δ¹⁵N) (Renberg et al., 2001). The enrichment factors (EF) of Ni and V of the recent background of site 3 and 4 shows baseline values, i.e. principally natural sources, and the EF of Cr is close to baseline (Paper II). Cu, Pb and Zn show higher EF, suggesting that the sediment is polluted by these elements (Paper II). This implies that the background of the studied area is polluted by Cu, Pb and Zn.

δ¹⁵N values (+17.4‰ at site 1, +17‰ in LWₚ₉) indicate that the predominantly nitrogen source into site 1, close to the discharge of treated leach water, is the particulate material in the leach water (LWₚ₉) (Paper I). At the first sight the δ¹³C values of site 1 (-22.4‰) do not match the δ¹³C values of the LWₚ₉ (-30.7‰), but the higher δ¹³C of site 1 is probably caused by decreased decomposition rate of organic matter due to the anoxia. The methane producing bacteria prefer ¹²C before ¹³C, leaving the residue enriched in ¹³C, with an increased δ¹³C value as a result. The methane production is suggested also by the presence of bubbles of gas in the sediment, bubbles that most likely contain methane. The high accumulation rate at site 1 (more than 23 cm/15 years) (Paper I) may be caused by decreased decomposition rate of organic matter due to the anoxia.

The EFs of the studied metals for site 1 are high (10) for all metals (Cr, Cu, Ni, Pb, V, and Zn) (Paper II). Since also site 5 show increased EF values (Cr, Cu, Pb, Zn), the origin of the metals at site 1 is not only the garbage dump. The predominant sources are probably situated upstream of the studied area, in the urban area of Stockholm and Lake Mälaren. The high EF at site 1 is most likely due to the high accumulation of sediment at the site.

The metals are strongly correlated with Al and S implying accumulation simultaneously with clay particles and sulphides. The presence of the latter demands anaerobic or suboxic environments (van Loon and Duffy, 2003).

At the downstream site (site 2) the signs of released treated leach water from the garbage dump are not as obvious as at site 1, δ¹³C is in the range of DIN common in water (Meyers, 2003). An estimation is that about 8% of the nitrogen at site 2 origins from site 1 (Paper I). A major reason for the value is most likely dilution of the material by sources upstream of site 1, i.e. the urban area of Stockholm and Lake Mälaren. Burial in the sediment at site 1 and removal of nitrogen due to denitrification are also likely reasons. Coastal areas have been reported to act as filters of, for example, nitrogen from land and rivers. This is in accordance with nitrogen data of the

Stockholm Archipelago by the environmental monitoring program of the Stockholm Archipelago (Lännergren and Eriksson, 2005). Part of the nitrogen in the water in the inner archipelago never reaches the middle part of the archipelago, since the nitrogen is removed by the denitrification in the anoxic/suboxic sediments (Lännergren and Eriksson, 2005). In the coastal areas of the Baltic Sea the most important process of removing nitrogen from the water appears to be sediment denitrification (Lännergren and Eriksson, 2005; Nilsson and Jansson, 2002; Savage et al., 2004; Voss et al., 2005), but also sediment accumulation (Savage et al., 2004).

The carbon influence at site 2 from the LWₚ₉ is estimated to be about 14% (Paper I).

Ni, V, and Cr show EF values close to baseline at site 2 indicating natural sources in the area, while Cu, Zn and Pb show EFs indicating anthropogenic pollution sources (Paper II).

### Lake Verkasjön

The sediment of Lake Verkasjön offers an opportunity to study the environmental impact of a historical single major metal release. Metals that where released from the sulphide minerogenic material to the lake during 1877 to 1881 are today present in a distinct layer at the depth of 18-22 cm below the present sediment surface (Paper III). The layer is distinguished from sediments above as well as below by both physical and chemical parameters; the metal concentrations are high in both the pore water and the solid phase (Paper III), and the layer contains less organic matter and lower δ¹³C compared to the other sediments (Paper IV).

Below the sediment depth of 22 cm the sediment is characterized by metal concentrations close to or less than the Swedish background in the solid phase (Pb, Cd, Ag, Sb, and Tl) (Paper III). δ¹⁵N values are low and C/N ratios in the range suggesting that the organic matter in the sediment contains a mixture of nonvascular and vascular aquatic plants with a terrestrial contribution (Paper IV). The ²⁰⁶Pb/²⁰⁷Pb ratio suggests that the main Pb source is the surrounding soil.

Above the sediment depth of 18 cm the content of the sediment has changed. The content of organic matter has increased compared to below 22 cm, and δ¹³C, δ¹⁵N and C/N data indicate a higher proportion of aerobically produced organic material than before. The decreased δ¹³C and increased δ¹⁵N are most likely caused by changes in DIC and DIN assimilated by aquatic plants, algae and plankton. This change is probably caused by changed land use in the draining area for the lake and the river, for example changed (increased) use of fertilizers in the agriculture and reforestation. The decreased C/N ratio reflects a change from more land produced material to a higher proportion of aquatic produced material than earlier (Paper IV). ²⁰⁶Pb/²⁰⁷Pb ratios have decreased from values common in the Swedish background to values close to the mobile fraction of tailings in the area.
The diagenesis of the uppermost 18 cm has generated ordinary sediment that work as a physical as well as chemical barrier for the metals at 18-22 cm depth. The redox properties of iron in combination with a continuous input of sulphate above background levels effectively retain the trace metals through adsorption in oxic/post-oxic sediments and sulphide formation at reducing strata (Paper III).

Several metal sources have contributed with metals to the lake sediment due to studies of historical production records, trace elemental ratios, and dating of the cores by the $^{206}\text{Pb}/^{207}\text{Pb}$ ratios. During 1877-1881 the release from the ore dressing plant dominated the sediment content for all studied metals, except for Cu, Sb and Tl. The increased Cu concentrations were related to the use of a copper blast furnace between the 1830s to the 1860s. The levels of Sb and Tl began to increase around 1950, most likely by atmospheric deposition. At present, the metals concentration in the surface sediment are independent of the pollution event 1877-1881, and are determined principally by release upstream, possible in combination with atmospheric deposition (Paper III).

Acknowledgements

First, I would like to express my gratitude and thanks to my supervisors:

Nils Holm for kind and generous support, for always having time for questions and discussions, and for finding financial support.

Magnus Mörth for kind and generous support, encouragement and stimulating discussions.

-I am grateful to all help from both of you.

The research was financed by The Swedish Research Council (VR), Kinanders Foundation, Stockholm Marine Research Centre (SMF), and K&A Wallenbergs Stiftelse, resebidrag ur Jubileumsdonationen.

I would also like to thank Mattias Bäckström and Stefan Karlsson for their contribution to this work, interesting discussions and cooperation during the study of Lake Verkasjön.

I appreciate all the good advice and help from Birgitta Boström, Klara Hajnal and Heike Siegmund with laboratory work. I am grateful to Lars Erik Bågander and Rolf Hallberg for giving valuable comments on the manuscripts of this thesis. Arne Lif is acknowledged for computer support, Tomas Hjorth for good advice and discussions and Stefan Sädbom for sharing his knowledge of the mining history of Åmmebergs bergslag.

I would also like express my happy thanks to all friends and colleagues at the department for your kindness, interesting discussions (not always so scientific…) and many enjoyable moments.

Last, but not least, I would like to thank my family and my friends outside the department for understanding and encouragement during this journey. You will probably see more of me now...
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