

# Ni, Cu, Zn, Cd and Pb in sediments in the city- centre of Stockholm, Sweden

Origins, deposition rates and bio-  
availability

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<p><b>Title and subtitle of the report</b> Ni, Cu, Zn, Cd and Pb in sediments in the city-centre of Stockholm, Sweden Origins, deposition rates and bio-availability</p>	
<p><b>Summary</b> This study had three aims:</p> <ul style="list-style-type: none"> <li>• To estimate yearly fluxes of the metals Ni, Cu, Zn, Cd, Ba, Sb and Pb to the sediments in the city centre of Stockholm.</li> <li>• To estimate the flows of the metals Ni, Cu, Zn, Cd, and Pb to the sediments in the city centre of Stockholm from the important sources in the city: atmospheric deposition, storm water runoff from buildings and other infrastructure including roads, and WTPs.</li> <li>• To assess the bioavailability to the benthic organisms of the metals Cr, Ni, Cu, Zn, As, Cd and Pb dissolved in the sediment pore water. The bioavailability was defined according to the SEM/AVS (Simultaneous extraction of metals/Acid volatile sulphur) ratio.</li> </ul> <p>The major conclusions from the study were:</p> <ul style="list-style-type: none"> <li>• The concentrations of Cu in the water samples from both Lake Mälaren and Saltsjön are below the PNECs derived by the chronic Cu BLM (EURAS version 109), MEC/PNEC = 0.04 - 0.3.</li> <li>• The surface sediments in the city centre of Stockholm are far from toxic with regards to pore water concentrations of the metals Cr, Ni, Cu, Zn, As, Cd and Pb according to SEM/AVS.</li> <li>• Differences in surface sediment concentrations for the metals Ni, Cu, Zn, Cd and Pb between the sediments in freshwater Lake Mälaren and brackish water Saltsjön can be explained by a combination of sources and speciation. There has been a decrease compared to 1996 in the city centre of Stockholm of Cu, Zn (Lake Mälaren and Saltsjön), Cd and Pb (Lake Mälaren).</li> </ul>	
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## **Abstract**

A study on the sediments in the city centre of Stockholm was undertaken in August and September 2010. This study had three aims:

- To estimate yearly fluxes of the metals Ni, Cu, Zn, Cd, Ba, Sb and Pb to the sediments in the city centre of Stockholm.
- To estimate the flows of the metals Ni, Cu, Zn, Cd, and Pb to the sediments in the city centre of Stockholm from the important sources in the city: atmospheric deposition, storm water runoff from buildings and other infrastructure including roads, and WTPs.
- To assess the bioavailability to the benthic organisms of the metals Cr, Ni, Cu, Zn, As, Cd and Pb dissolved in the sediment pore water. The bioavailability was defined according to the SEM/AVS (Simultaneous extraction of metals/Acid volatile sulphur) ratio.

Sediments were sampled at locations which reflect the impact of four different point sources of significance: the city itself with its infrastructure including roads, the discharge points of Lake Mälaren into the brackish water Saltsjön in the Baltic Sea, the discharge points of the two WTPs Bromma and Henriksdal. The emissions from the city itself and its traffic are discharged as storm water at several points in the study area. At each site two sediment cores were collected. One of the cores was sectioned the  $^{137}\text{Cs}$   $\gamma$ -activity for each sediment sub-sample was measured to estimate the accumulation of sediment dry matter at that station in  $\text{g dw}/\text{cm}^2$  since 1986. The other core was sectioned and the sub-samples were analysed for Ba, Cd, Cu, Ni, Pb and Zn using ICP-AES and Sb which was analysed using AAS. Sediments for the testing of bioavailability according to the SEM/AVS ratio of the metals As, Cd, Cu, Ni, Pb, Zn were sampled by pooling the top 8 to 10 cm of three samples collected by a grab sampler at each location. Total organic carbon (TOC) in these sediment samples was also determined.

The conclusions from the study were:

- The concentrations of Cu in the water samples from both Lake Mälaren and Saltsjön are below the PNECs derived by the chronic Cu BLM (EURAS version 109),  $\text{MEC}/\text{PNEC} = 0.04$  to  $0.3$ .
- The sediments in both Lake Mälaren and Saltsjön the city centre of Stockholm is far from toxic with regards to pore water concentrations of the metals Cr, Ni, Cu, Zn, As, Cd and Pb according to the SEM/AVS method.
- Differences in surface sediment concentrations for the metals Ni, Cu, Zn, Cd and Pb between the sediments in freshwater Lake Mälaren and brackish water Saltsjön can be explained by a combination of differences in local sources and differences in metal speciation
- The surface sediment concentrations of Cu and Zn have decreased since 1996 in both Lake Mälaren and Saltsjön in the city centre of Stockholm.
- The surface sediment concentrations of Cd and Pb have decreased since 1996 in Lake Mälaren in the city centre of Stockholm.
- Direct runoff of roads can make up a major portion of the Cu and Zn that is buried in Lake Mälaren sediments in the city centre of Stockholm.
- The effluents from the WTPs can make up significant parts of the Ni, Cu, Zn and Cd that is buried in the sediments in Saltsjön in the city centre of Stockholm.

However, the locations of the measured sediment fluxes in relation to the discharge points of the WTPs indicate that this is not the case.

- Runoff of copper-roofs can only be an insignificant source of Cu to the sediments in Lake Mälaren and Saltsjön in the city centre of Stockholm.

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## 1 Introduction

Metals are natural and in many instances essential (e.g. Cu and Zn) constituents of the aquatic environment including sediments. In population centres the additional loads of metals from infrastructure, industrial activities and human consumption to surface waters and sediments have frequently caused concern for environmental risks. These concerns have motivated studies and monitoring programs aiming at estimating the loads from diffuse or background sources such as atmospheric deposition and land use (roads, railways and soil), point sources such as wastewater treatment plants (WTP), effluents from industrial activities and contaminated sites such as landfills. The capitol of Sweden, Stockholm, with a population of approximately 1.5 million including suburbs is no exception. For example studies of burial rates and concentrations of metals in sediments in lakes and in the brackish Baltic Sea, both around and in central Stockholm, have been conducted several times during the last decade or so (e.g. Östlund et al., 1998; Lindström et al. 2001; Sternbeck et al., 2003; SVAB 2010). Other studies have looked at the emissions of metals from various sources to the environment in Stockholm. These sources include road traffic (Furusjö et al., 2007; Hjortenkrans et al., 2007); copper in building materials (Ekstrand et al., 2001; Odnewall-Wallinder et al., 2009) and WTPs (Pettersson and Wahlberg, 2010). Finally, some studies have estimated the atmospheric deposition of metals (Stockholm Stad, 2000) and some the combined, total load of metals from all sources (Sörme and Lagerkvist, 2002; Cui et al., 2010). However, considering the fact that all metals naturally exist in the aquatic environment with large variations in concentrations it is equally important to study the speciation and bio-availability of these metals in the aquatic environment, e.g. sediments of the Stockholm area (Sundelin and Eriksson, 2001).

The present study has three aims. The first is to estimate yearly fluxes of the metals Ni, Cu, Zn, Cd, Ba, Sb and Pb to the sediments in the city centre of Stockholm. The metals Ni, Cu, Zn, Cd, and Pb are among the most commonly monitored in the aquatic environment due to their potential toxicity and large anthropogenic loads in relation to background fluxes in the environment (Benjamin and Honeyman, 1998). Specifically, the concentrations of these metals in the aquatic environment are of interest since they have many important sources in the urban environment such as runoff from buildings and roads (Göbel et al., 2007; Jartun et al., 2008). Concentrations of Ba and Sb in the sediments are used as tracers for the metal emissions from the wear of brake linings, which is a major source of Cu from road traffic (Sternbeck et al., 2002; Furusjö et al., 2007). The sediments investigated are located both in the easternmost part of the freshwater Lake Mälaren, and in Saltsjön, which is the area where Lake Mälaren discharges into the brackish Baltic Sea. The second aim is to estimate the flows of the metals Ni, Cu, Zn, Cd, and Pb to the sediments in the city centre of Stockholm from the important sources in the city: atmospheric deposition, storm water runoff from buildings and other infrastructure including roads, and WTPs.

The third aim is to assess the bioavailability to the benthic organisms of the metals Cr, Ni, Cu, Zn, As, Cd and Pb dissolved in the sediment pore water. These metals readily form solid phases with sulphur, sulphides, in the reducing environment at or below the sediment

surface. The formations of these sulphides drastically decrease the pore water concentrations of these metals, making them far less bioavailable considering the exposure through pore water. Recognizing the importance of these sulphides, a method called SEM/AVS which relates the binding strength of these metals (Simultaneously Extracted Metals) to the sediment and the supply of sulphur for the formation of these sulphides (Acid Volatile Sulphur) has been developed and widely used to assess bioavailability (e.g. Ankley, 1996; Di Toro et al., 1990; ICMM, 2007). The SEM/AVS method also allows for assessing the importance of other inorganic and organic ligands with regards to metal bioavailability (Sundelin and Eriksson, 2001). With an adequate experimental set up, these other fractions can be identified in increasing binding strength as exchangeable (labile), carbonates, Fe-Mn-Oxides, sulphide/organic matter and residual (Kelderman and Osman, 2007)

## **2 Materials and methods**

Sediment and water samples were collected on 31<sup>st</sup> of August 2010 in Saltsjön and 9<sup>th</sup> of September in Lake Mälaren. The locations of the sampling sites are shown in Fig. 1. The sampling locations were chosen to reflect the impact of four different point sources of significance: the city itself with its infrastructure including roads, the discharge points of Lake Mälaren into the brackish water Saltsjön in the Baltic Sea, the discharge points of the two WTPs Bromma and Henriksdal. Bromma and Henriksdal WTPs have 294000 and 705000 persons connected, respectively. The emissions from the city itself and its traffic are discharged as storm water at several points in the study area. As the surface water flows along the general direction of west to east in Lake Mälaren, additional S2 is also downstream of the discharge point of the Bromma WTP. The most easterly sampling location S3 is downstream of the discharge point of Henriksdal WTP.

### Water samples

At each site, water was collected 0,5m above sea or lake bottom and 0,5m below the water surface. The temperature, salinity, conductivity of the water samples was determined directly using a CTD. Oxygen concentration was determined using Winkler's method. Redox potential was determined in situ. The pH was measured directly on board for the samples from Lake Mälaren, whereas for the samples from Saltsjön it was measured in the laboratory two days after sampling. Dissolved organic carbon (DOC) was determined at Eurofins laboratory in Lidköping. DOC was determined by the difference of total carbon (TC) and total inorganic carbon (TIC). TC and TIC was determined by combustion of the sample with non-dispersive infrared detection. The major constituents of TIC are carbonates, which are protonated first with acid, HCL, so that CO<sub>2(g)</sub> is produced.

The concentrations of calcium and magnesium were determined using ICP-AES. Water hardness was calculated as the sum of Ca+Mg. Cu was determined filtrated (0.45µm) and un-filtrated using ICP-MS.

### Sediment samples

At each site two sediment cores were collected using a Kajak sampler. One of the cores was sectioned in cm as: 0 – 2; 2-4; 4-6; 6-8; 8-10; and then 1cm sections till 30 or 40cm length. These samples were frozen, freeze-dried and milled at IVL, before being sent to Uppsala University for dating by measuring the  $\gamma$ -activity from  $^{137}$ -Cs. The other core was sectioned in cm as: 0-2; 2-4; 4-6; 6-8; 8-10; 14-16; 20-22 and 28-30. These sediments samples were analysed for Ba, Cd, Cu, Ni, Pb and Zn using ICP-AES and Sb which was analysed using AAS. The analyses were carried out by Eurofins in Lidköping, Sweden.

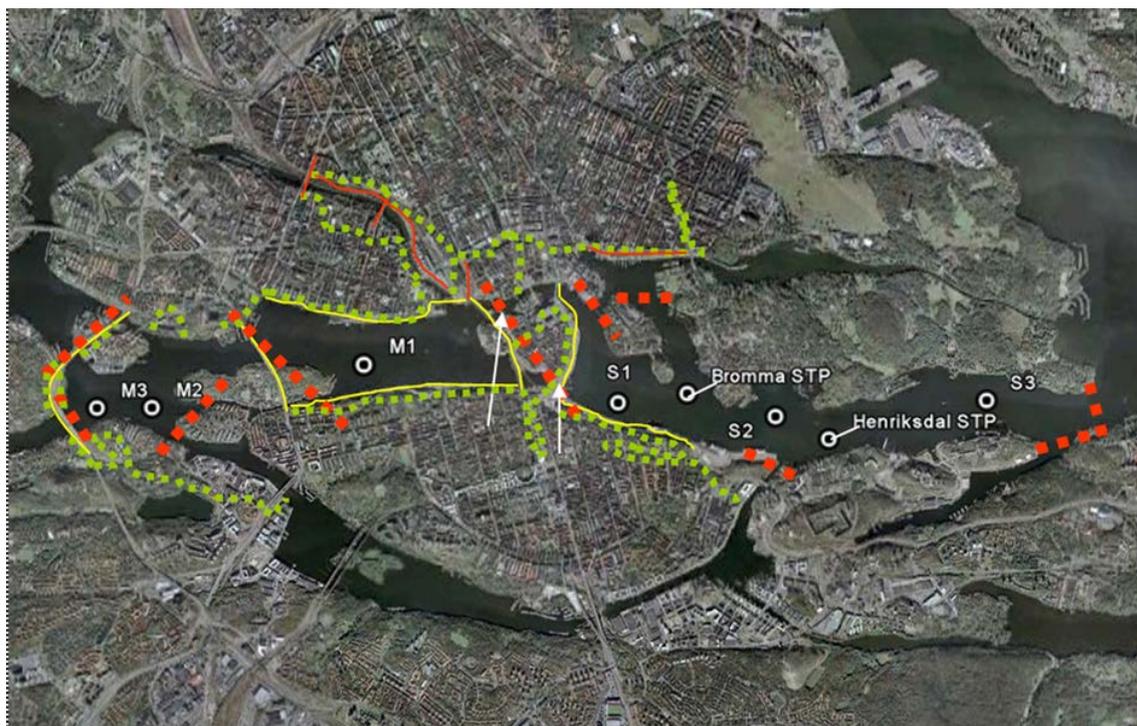
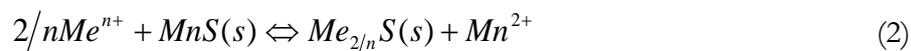
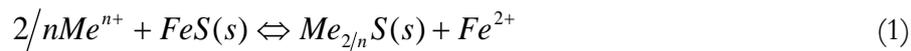


Figure 1. Satellite picture of Stockholm showing the sampling locations M1 – M3 in freshwater Lake Mälaren and S1-S3 in Saltsjön, part of the brackish Baltic Sea. M1 is located in the easternmost part of Lake Mälaren called Riddarfjärden, where the lake discharges into Saltsjön in the Baltic Sea at the locations indicated by the two white arrows, Norrström to north and Söderström to the south. The three sub-areas of the study area is divided by red thick hashed lines. The areas are from west to east: E Lake Mälaren, Riddarfjärden and Saltsjön. The thick green hashed lines indicate the areas with major roads that are drained directly to the study area without any treatment of stormwater (SVAB 2010b). Major roads within these areas are indicated by solid yellow lines. Major roads drained directly to adjacent surface waters are indicated by solid red lines. These receiving water areas are indicated by red arrows, Klara canal to the West and Nybroviken to the East. The discharge points of the two WTPs, treating both storm and waste water are indicated on the map.

Sediment for the testing of bioavailability of the metals As, Cd, Cu, Ni, Pb, Zn were sampled by pooling the top 8 to 10cm of three samples collected by a grab sampler at each location. This sediment depth interval represents the relevant part where benthic organisms will get exposed to metals in dissolved form in pore water when bioturbating. To test for the bioavailability of these metals in the sediment samples, the SEM/AVS-ratios were analysed by Vito. According to this method the bioavailability or toxicity of the

metals are operationally defined as the ratio between SEM (simultaneously-extracted metals) to AVS (acid volatile sulphides). The AVS is considered to be the most reactive part of the sulphides, the iron mono-sulphides. These sulphides are available for forming insoluble metal-sulphide complexes that are non-bioavailable. The concept behind the AVS approach is that most metals have higher solubility products than most iron and manganese mono sulphides, with the exception of pyrite. Hence these metals can displace iron (and manganese) from its sulphide complex on a mole to mole basis, forming insoluble sulphide complexes with minimal biological availability (Ankley, 1996).



If all the metal in sediment is in the form of solid MeS phases, i.e. AVS in excess, then the free metal ion activity is controlled by dissolution of these phases.

In anoxic sediments, chromium also forms sulphides ( $Cr_2S_3$ ) with lower solubility products than most metals. Therefore, the stoichiometry of equations 1 and 2 above also applies to Cr.

The operational definition of AVS is those sulphides that are readily extracted by the cold extraction of sediment in 1M HCl acid. In reality this means that other solid and organic phases will be included in the AVS. SEM is defined as the metal which is simultaneously extracted under the same conditions under which the AVS content is determined. In the present case where multiple metals are investigated, the term total SEM or  $\Sigma$ SEM should be used instead. The concentration of the metals was determined using ICP-AES.

When the measured AVS concentrations exceed the concentration of SEM the pore water levels of free metal ions should be very low according to the SEM-AVS model. This means that when SEM/AVS < 1, the SEM-AVS model predicts no toxicity with regards to these metals.

Total organic carbon (TOC) in sediment samples was determined by the difference of total carbon (TC) and total inorganic carbon (TIC). TC and TIC was determined by combustion of the sample with infrared detection. The major constituents of TIC are carbonates, which are protonated first with acid, HCL, so that  $CO_{2(g)}$  is produced.

The accumulation of sediment dry matter at each station was estimated by measuring the  $^{137}Cs$   $\gamma$ -activity for each sediment sub-sample. In this way the peak from the fallout from the 1986 Chernobyl accident could be identified. The yearly average sediment accumulation rate in cm or g dw per  $cm^2$  since 1986 could be estimated by dividing either the height or mass of dry matter respectively of sediment accumulated since 1986.

### 3 Results

The physical and chemical parameters and Cu concentrations for the water samples are presented in Table 1 below.

Table 1. Measured values of physical and chemical parameters including Cu concentrations in water samples.

	M3		M2		M1		S1		S2		S3	
Depth(m)	0.5	23	0.5	20	0.5	16	0.5	27	0.5	27	0.5	27
Temp(°C)	16.4	11.2	16.6	12.0	16.5	14.4	16.2	5.62	16.0	5.59	16.7	5.41
Conductivity (mS/m)	19	21	19	21	20	20	239	907	226	902	121	900
Salinity(‰)	0.080	0.090	0.090	0.090	0.090	0.10	1.2	5.1	1.2	5.0	0.60	5.0
O <sub>2</sub> (mg/l)	8.3	0.30	8.4	<0.2	8.2	1.5	7.8	6.0	7.6	5.3	7.6	4.3
Redox (mV)	280	115	272	98.7	235	242	218	210	188	158	200	208
pH	7.7	7.7	7.7	7.7	7.8	7.8	8.0	7.9	8.0	7.9	8.1	7.9
Ca (mg/l)	17	20	17	19	17	19	32	72	31	72	25	73
Mg(mg/l)	4.2	4.5	4.1	4.5	4.2	4.4	45	170	35	170	20	170
°dH <sup>1</sup>	3.3	3.8	3.3	3.7	3.3	3.7	15	49	12	49	8.1	49
DOC (mg/l)	9.3	9.3	8.9	9.6	9.3	8.8	7.1	4.2	7.2	4.3	7.6	4.5
Cu filtrated (µg/l)	2.7	2.5	3.0	2.4	3.7	2.8	5.7	2.8	4.7	2.3	3.2	1.7
Cu non filt-rated(µg/l)	3.4	3.3	4.2	3.5	4.9	3.2	5.6	3.9	4.9	3.9	3.3	1.9

<sup>1</sup> °dH (German degrees) is the unit commonly used for water hardness in Sweden. 1°dH is equivalent to 1mg CaO (= 0.71mg Ca) per 100 cm<sup>3</sup> water or the equivalent amounts 0.72 mg MgO (=0.43mg Mg) and 1.28mg FeO (= 1.00mg Fe) per 100 cm<sup>3</sup> of water.

The concentrations of the metals as a function of sediment depth at the different locations are presented in Figs. 2 – 8 below.

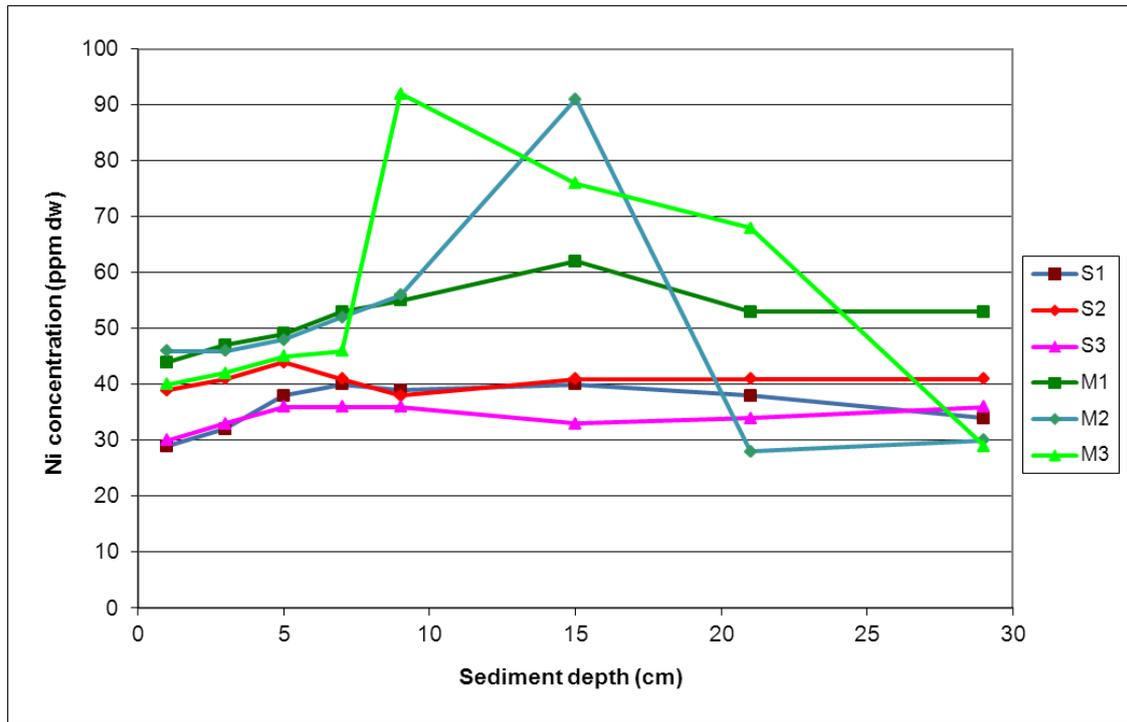


Figure 2. Ni concentrations in ppm dry weight as a function of sediment depth in cm.

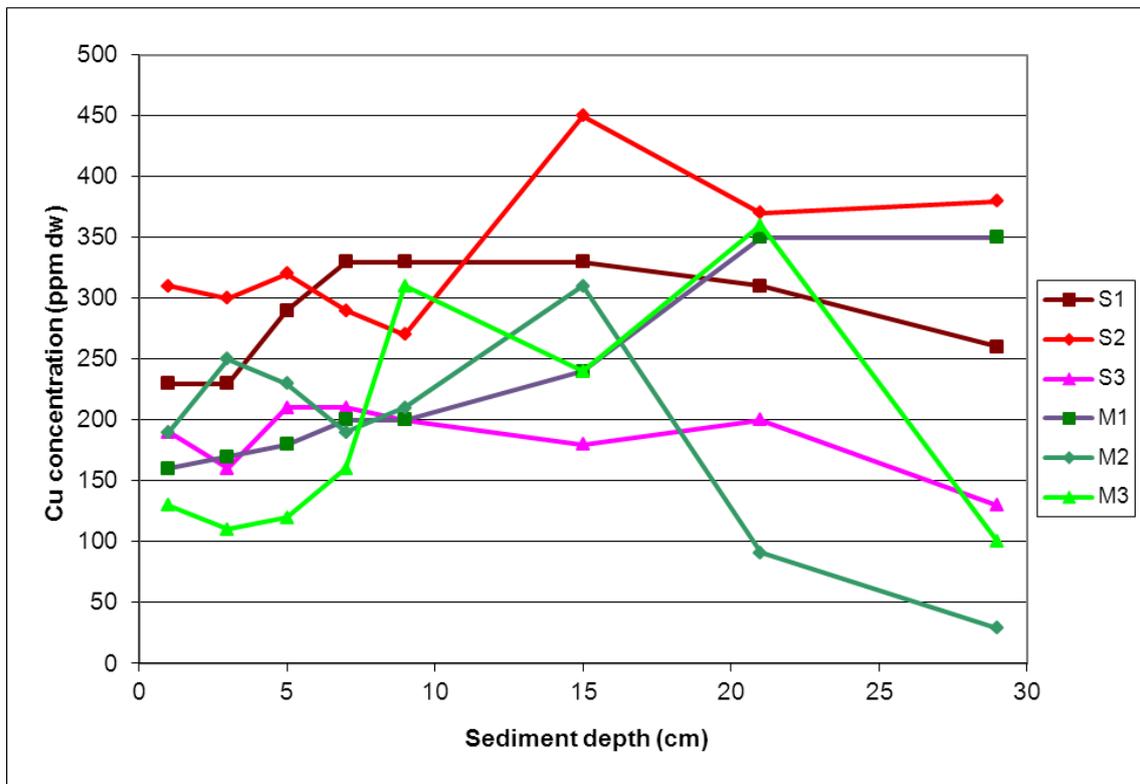


Figure 3. Cu concentrations in ppm dry weight as a function of sediment depth in cm.

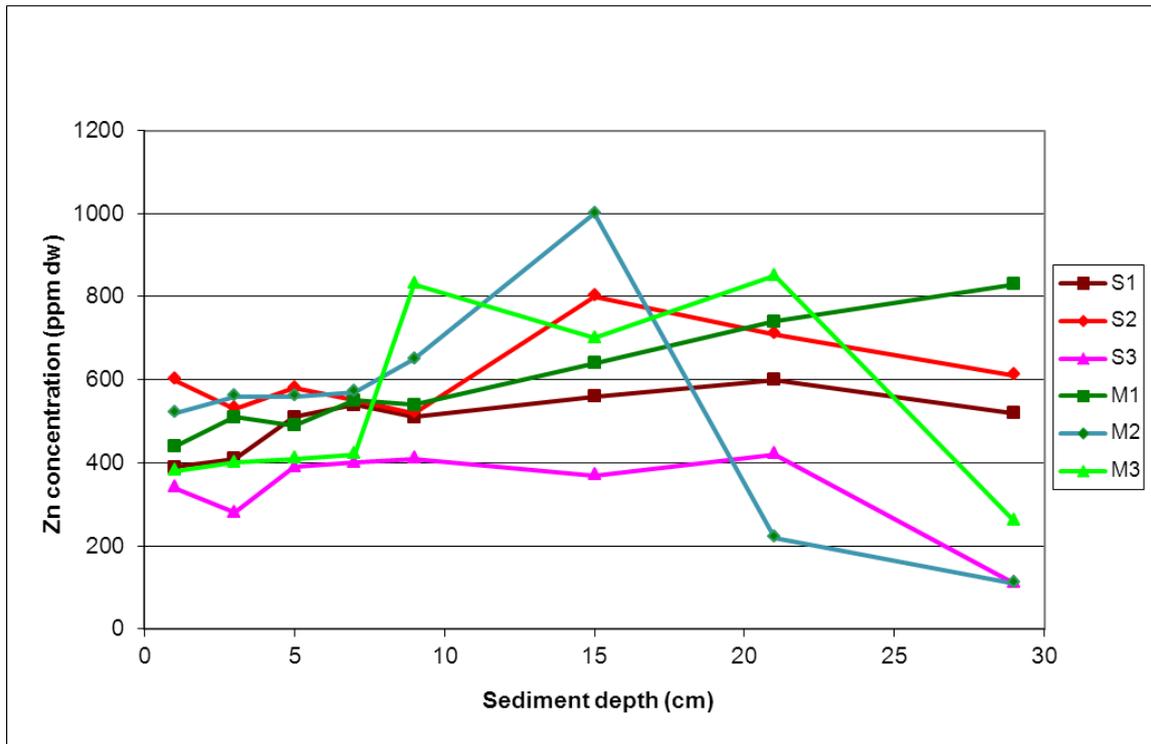


Figure 4. Zn concentrations in ppm dry weight as a function of sediment depth in cm.

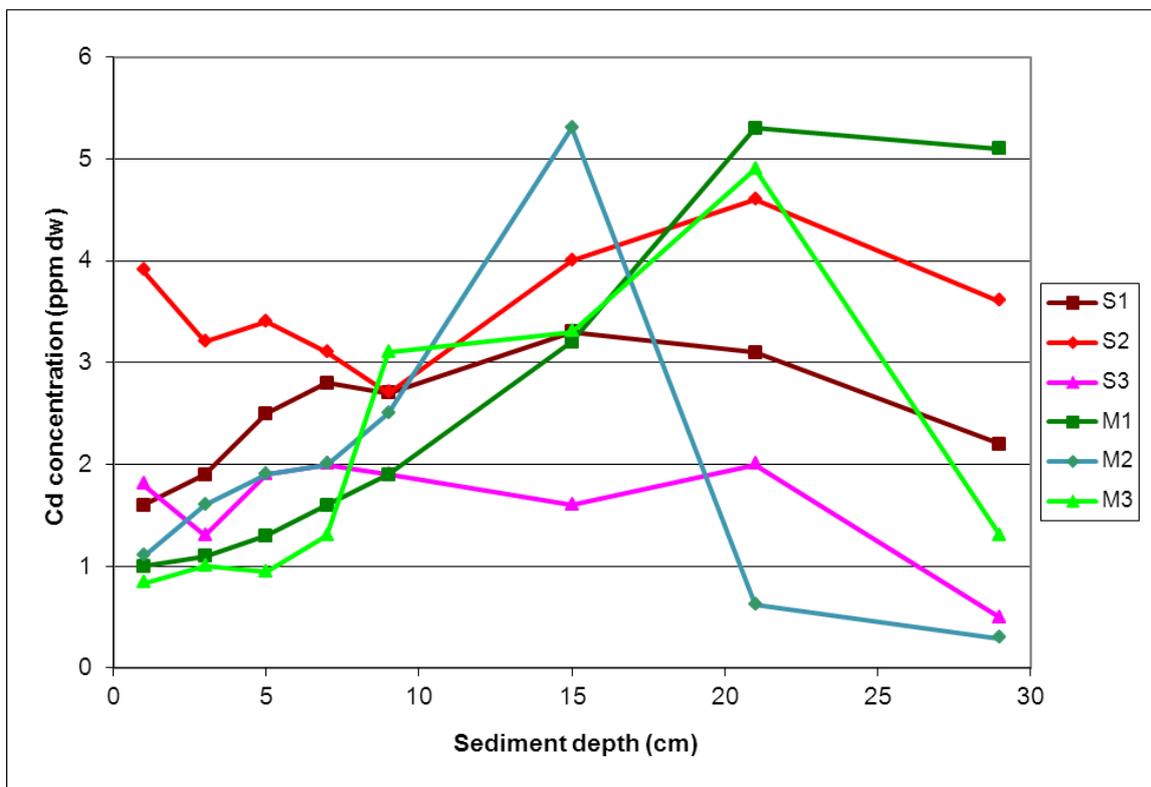


Figure 5. Cd concentrations in ppm dry weight as a function of sediment depth in cm.

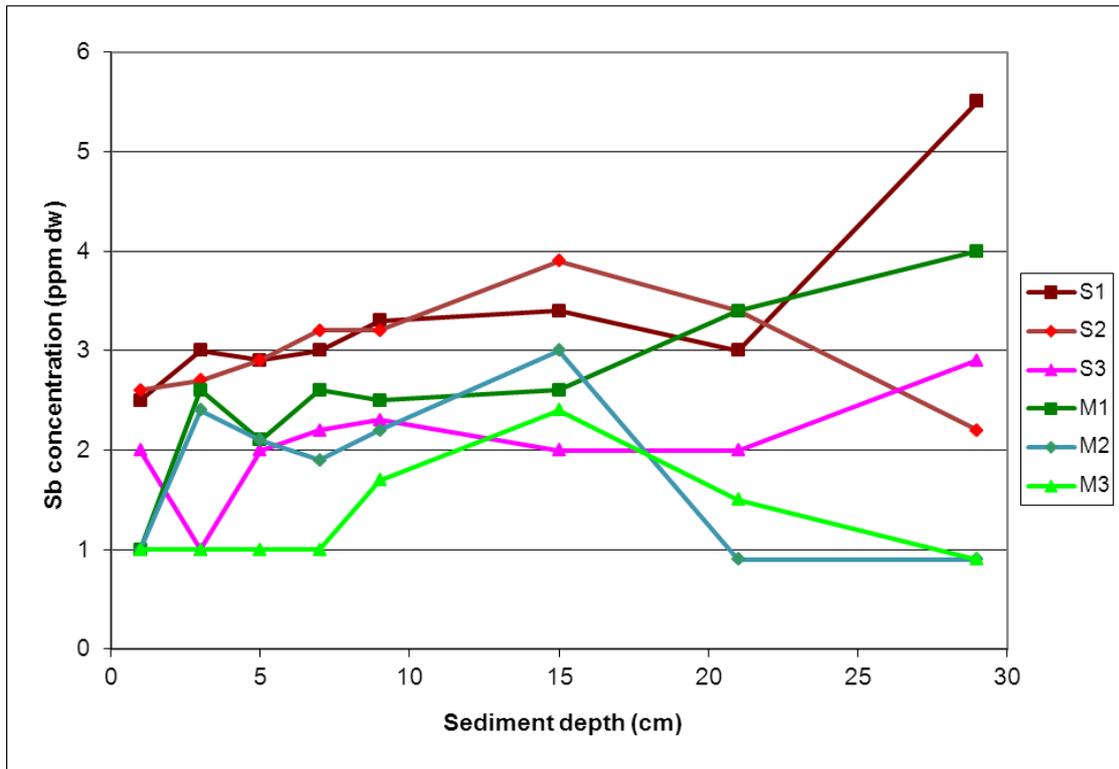


Figure 6. Sb concentrations in ppm dry weight as a function of sediment depth in cm.

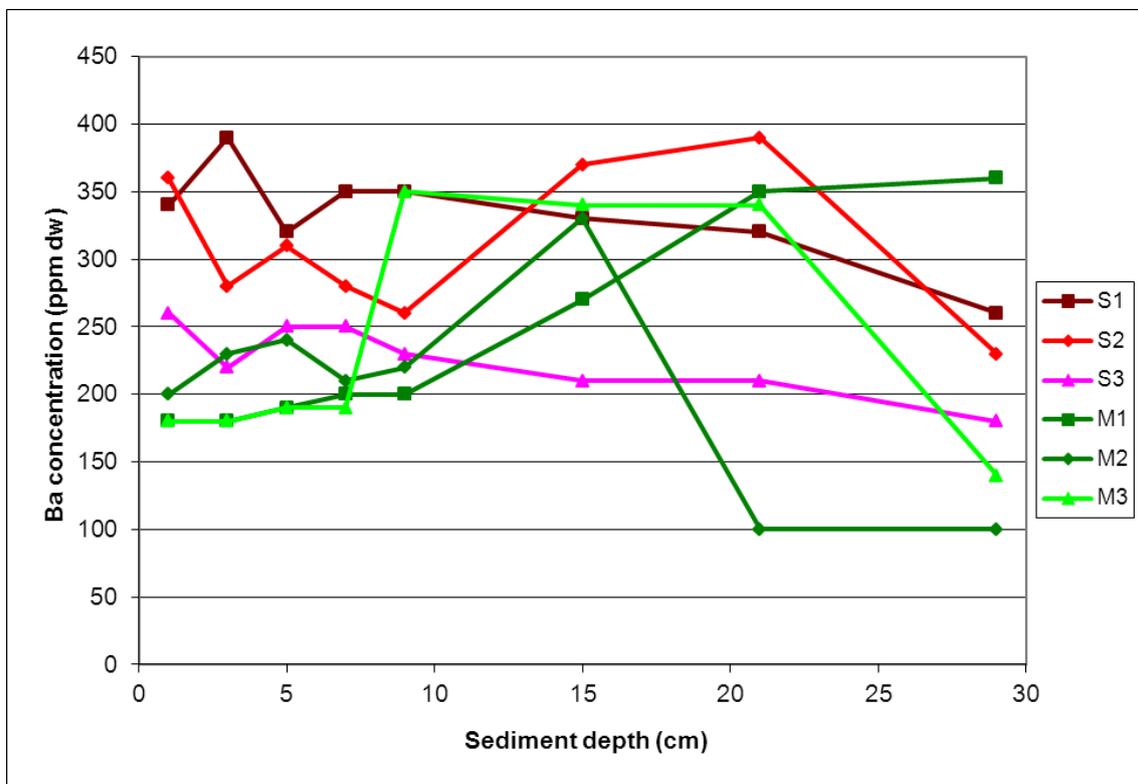


Figure 7. Ba concentrations in ppm dry weight as a function of sediment depth in cm.

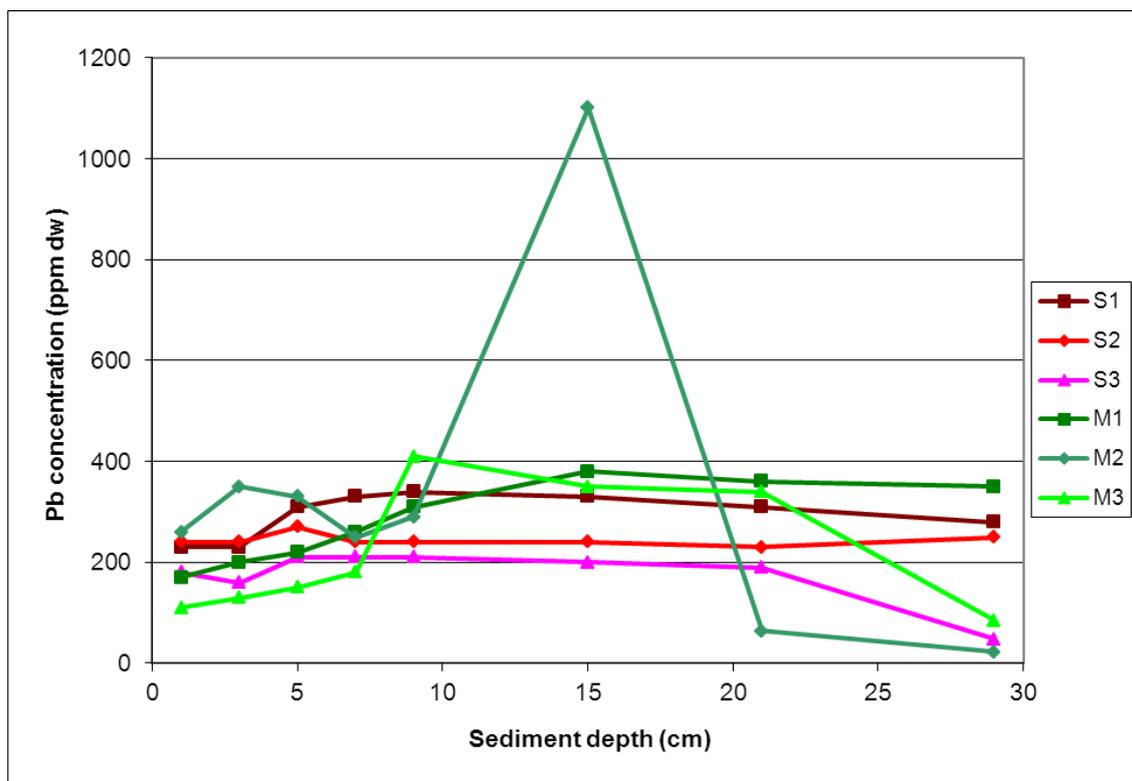


Figure 8. Pb concentrations in ppm dry weight as a function of sediment depth in cm.

The concentrations of total organic carbon (TOC) at the different sampling locations are given in Table 2 below.

Table 2. Concentration (% dw) of TOC in sediment samples.

Sediment depth (cm)	M3	M2	M1	S1	S2	S3
0-2	5.7	6.3	6.1	8.4	8.7	6.2
2-10	6.4	6	6.3	7.7	6.8	6.3

The accumulation rates of dry matter and metals at the different sampling locations are given in Table 3 below. In figures 9 to 13 the concentrations of the metals Ni, Cu, Zn, Cd and Pb are presented as functions of sediment age. The sediment ages are calculated assuming no compaction of sediment and average dry matter deposition figures for the period 2010 – 1986 as given in table 3. The lower boundary is determined either by the length of the core or the occurrence of erosion and transport sediments, which are defined as having water contents less than 50 and 75 % respectively. Since the sediment accumulation rate is a constant the changes in concentrations with sediment depths corresponds to the same changes in fluxes to the sediment.

Table 3. Accumulation rates of dry matter and metals at the surface at the different sampling locations as inferred from dating of sediments using activity of <sup>137</sup>Cs. The sediment depth corresponding to the year 1986 when the Chernobyl accident and subsequent fallout of <sup>137</sup>Cs occurred as indicated by the  $\gamma$ -activity is also given.

	M3	M2	M1	S1	S2	S3
Accumulation (g/cm <sup>2</sup> /yr.)	0.23	0.29	0.17	0.52	0.31	0.40
year 1986 (cm)	14	17	10	>30	19	21
Ba (µg/cm <sup>2</sup> /yr.)	51	69	31	170	95	94
Cd (µg/cm <sup>2</sup> /yr.)	0.34	0.69	0.23	1.3	1.0	0.72
Cu (µg/cm <sup>2</sup> /yr.)	39	67	30	150	99	78
Ni (µg/cm <sup>2</sup> /yr.)	12	16	8.2	19	12	14
Pb (µg/cm <sup>2</sup> /yr.)	46	120	38	150	75	79
Zn (µg/cm <sup>2</sup> /yr.)	110	190	84	260	180	150
Sb (µg/cm <sup>2</sup> /yr.)	0.27	0.61	0.36	1.7	0.94	0.78

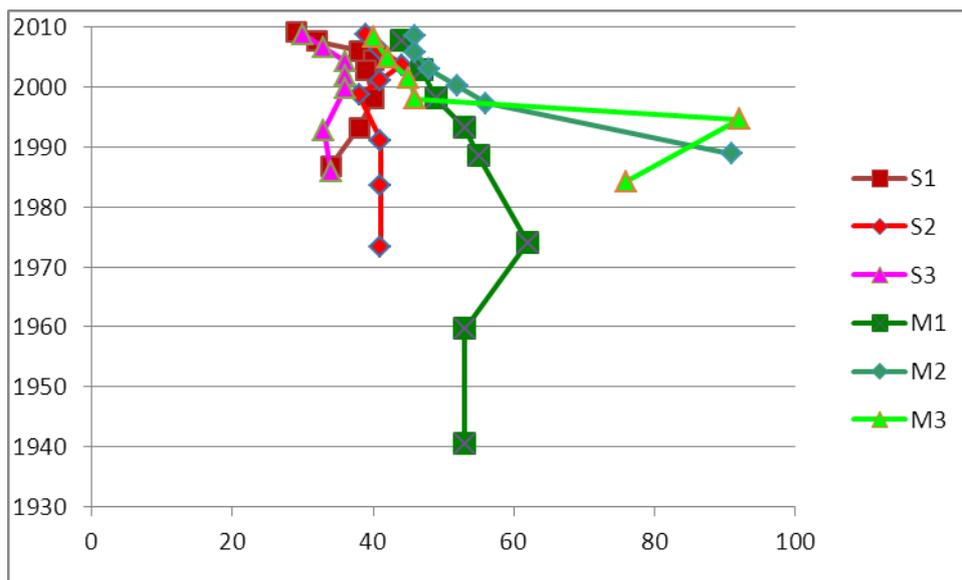


Figure 9. Ni concentrations in ppm dry weight as a function of sediment age in years A.D.

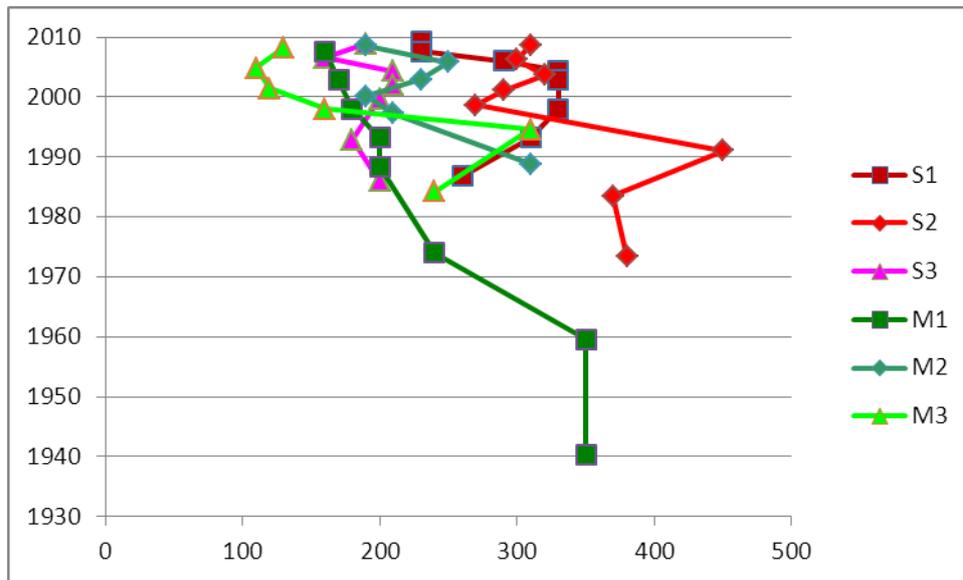


Figure 10. Cu concentrations in ppm dry weight as a function of sediment age in years A.D.

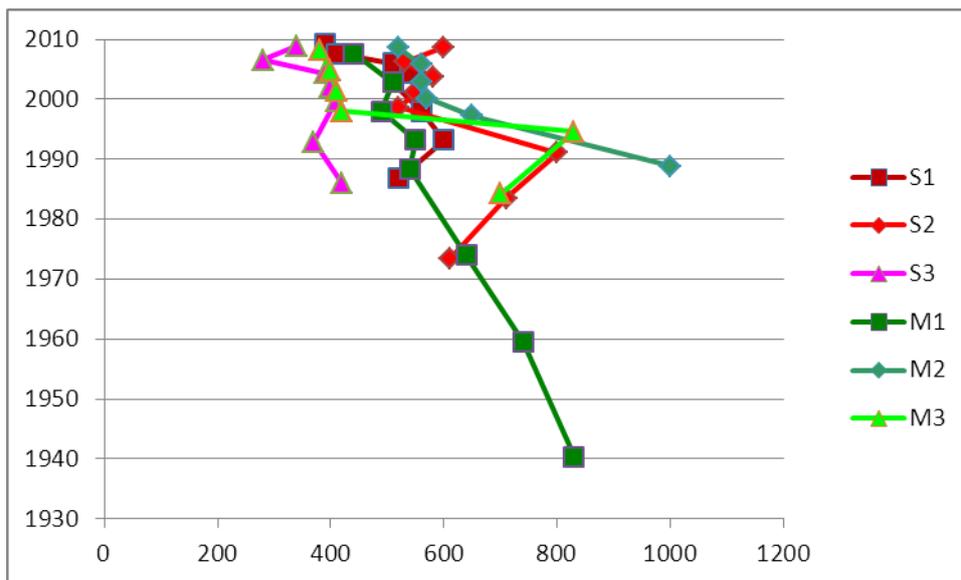


Figure 11. Zn concentrations in ppm dry weight as a function of sediment age in years A.D.

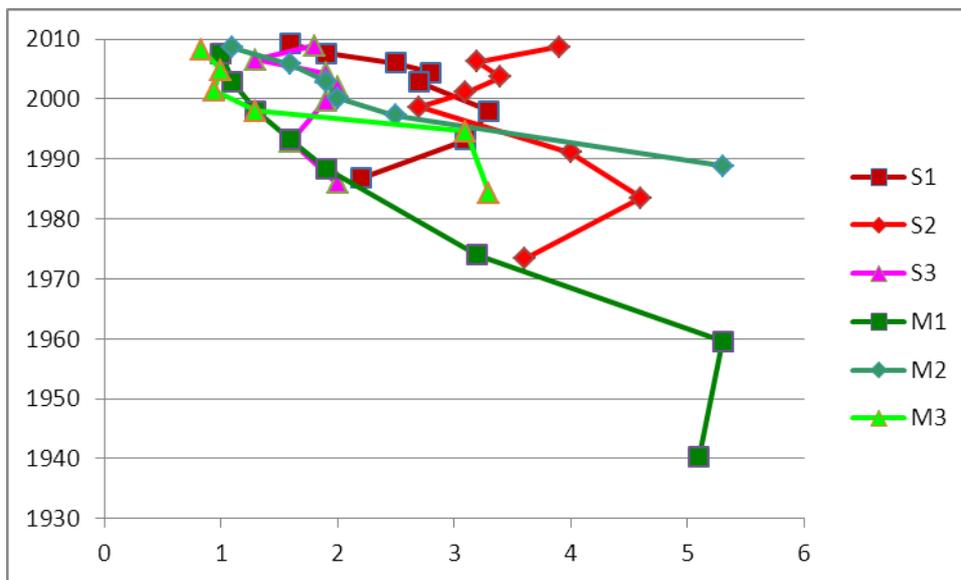


Figure 12. Cd concentrations in ppm dry weight as a function of sediment age in years A.D.

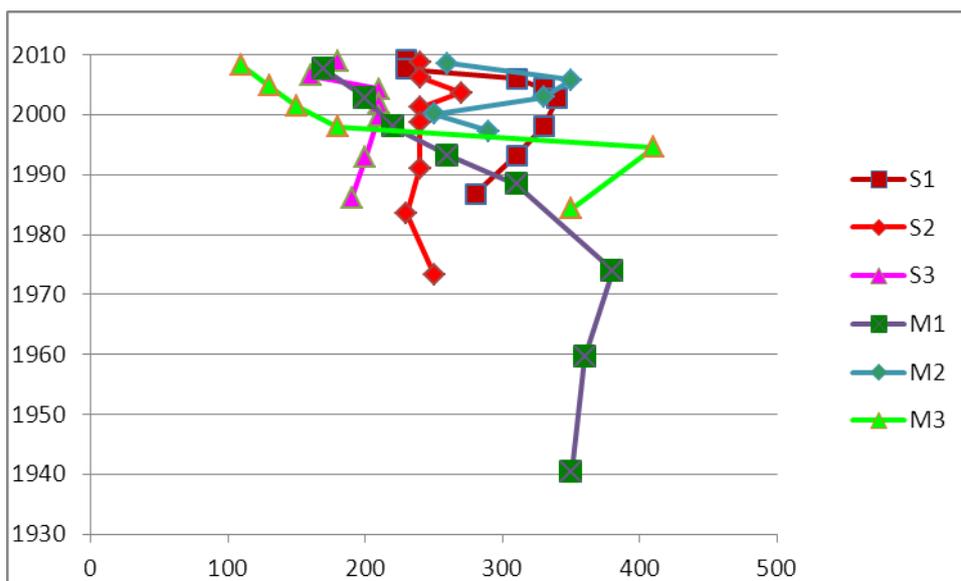


Figure 13. Pb concentrations in ppm dry weight as a function of sediment age in years A.D.

The load of the metals Ni, Cu, Zn, Cd and Pb from the three major types of point sources considered in this study: storm water from buildings and roads, Lake Mälaren itself, and WTPs were estimated using different sets of data. The annual load of metals from storm water draining major roads were estimated by multiplying the length of the road considered in each area with the annual average daily traffic volume in 2006 times 365 (Stockholm Stad, 2006) with the emission factors for vehicle traffic for each metal (Sörme and Lagerkvist, 2002). The lengths of the roads considered were measured using Google Earth™. The data for the estimated metal load from vehicle traffic to each of the areas is presented in Table 4 below.

Table 4. Data for estimating metal loads to each area from road traffic

Area	Road length (km)	Vehicle traffic (annual daily average)	Emission factors: Brake linings + tires and asphalt (Kg per 11 billion vehicle km)
E. Lake Mälaren	1.4	153165	Ni: 4 <sup>1</sup> Cu: 1435* Zn: 2760 Cd: 0,88 <sup>2</sup> Pb: 271
Riddarfjärden	5.6	189568	
Saltsjön	2.3	45143	

<sup>1</sup>Ni: data for tires not included; <sup>2</sup> Cd: emissions from brake linings estimated using Hjortenkrans et al. 2007; \*a similar value of 1.76 mg Cu/km was concluded as European average in the copper Risk assessment report, appendix C (EU, 2008)

The metal load in treated sewage water from the two WTPs Bromma and Henriksdal to Saltsjön, were calculated using concentration data from samplings carried out 1-8<sup>th</sup> of October 2007 and 14<sup>th</sup> to 21<sup>st</sup> of April in 2008 (Pettersson and Wahlberg, 2010). These concentrations were then multiplied with the average of the daily average sewage water flow for 2007 and 2008 times 365 for each WTP. The estimated annual discharges of treated sewage to Saltsjön were thus 0.0465 Km<sup>3</sup> for Bromma and 0.0905 Km<sup>3</sup> for Henriksdal. The metal load from Lake Mälaren to Saltsjön in the brackish Baltic Sea in the city centre of Stockholm at Norrström and Söderström was calculated for the year 2008 using data from Centralbron in Stockholm in the national environmental monitoring programme (SEPA, 2011).

The annual loads from these three sources can be compared with the annual accumulation in the sediments and the total atmospheric deposition. Since only sediments where net accumulation takes place are considered in this study, the sediments are considered a (net) sink only. To estimate the accumulation for each area, the accumulation rates in Table 3 were multiplied with the areas of accumulation sediments. The distribution of accumulation areas were determined using side scan and depth penetrating sonar (Jönsson, in prep.) For Eastern Lake Mälaren the total metal accumulation in the sediments was estimated by using the average accumulation rate of M2 and M3 multiplied with 81 ha. For Riddarfjärden the accumulation rate for M1 was multiplied with 111 ha. Finally for Saltsjön the average accumulation rates for S1, S2 and S3 was multiplied by 256 ha. The data for total (wet + dry) atmospheric deposition of Ni, Cu, Zn, Cd and Pb are from 1998 and 1999 (Stockholm Stad, 2000). In Figs. 14 to 18 the estimated sources and the sediment sink is presented for each metal investigated.

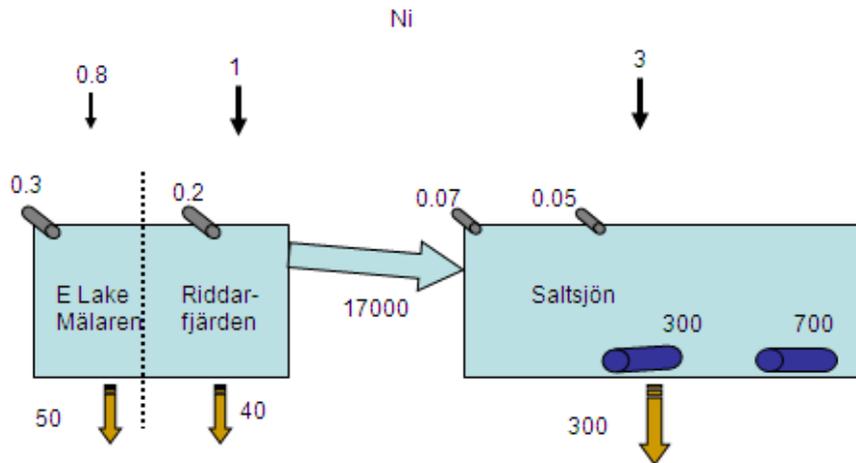


Figure 14. Flows of Ni in Kg/year: total atmospheric deposition (black arrows), storm water runoff from roads (grey pipes), Lake Mälaren discharge to Saltsjön in brackish Baltic Sea (light blue arrow), treated sewage water from WTPs (dark blue pipes), burial in sediments (dark yellow arrows).

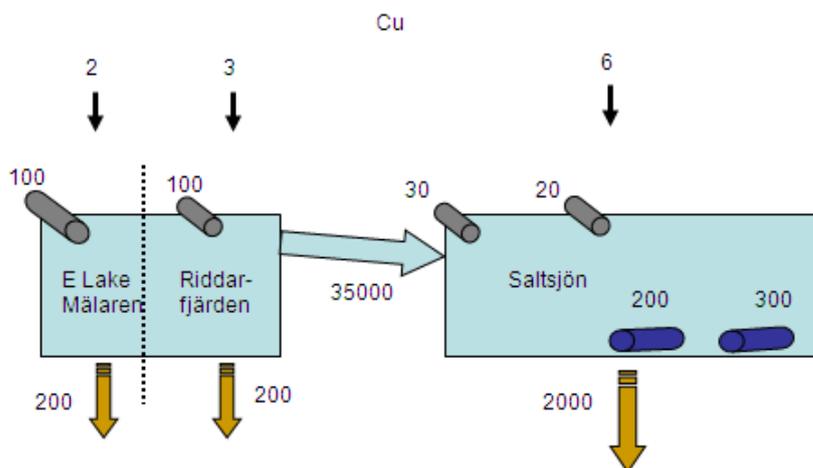


Figure 15. Flows of Cu in Kg/year: total atmospheric deposition (black arrows), storm water runoff from roads (grey pipes), Lake Mälaren discharge to Saltsjön in brackish Baltic Sea (light blue arrow), treated sewage water from WTPs (dark blue pipes), burial in sediments (dark yellow arrows).

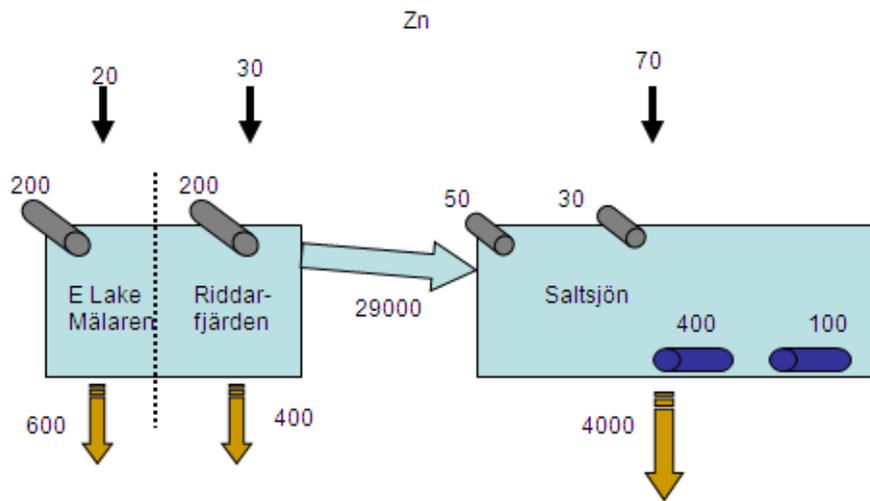


Figure 16. Flows of Zn in Kg/year: total atmospheric deposition (black arrows), storm water runoff from roads (grey pipes), Lake Mälaren discharge to Saltsjön in brackish Baltic Sea (light blue arrow), treated sewage water from WTPs (dark blue pipes), burial in sediments (dark yellow arrows).

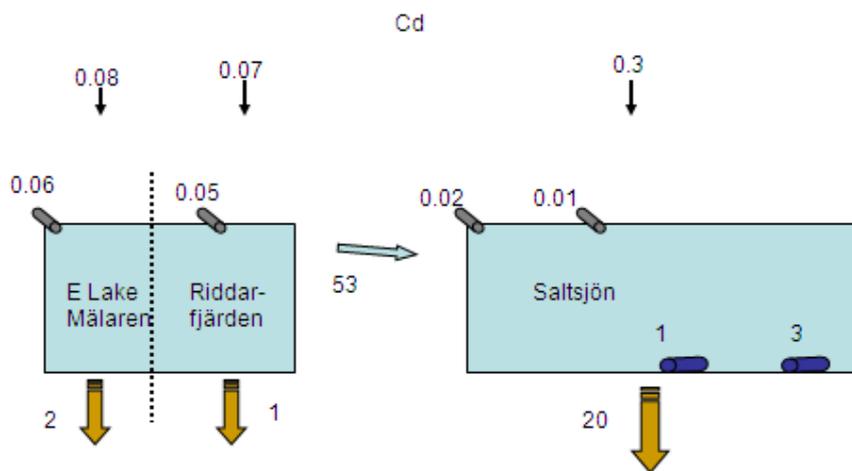


Figure 17. Flows of Cd in Kg/year: total atmospheric deposition (black arrows), storm water runoff from roads (grey pipes), Lake Mälaren discharge to Saltsjön in brackish Baltic Sea (light blue arrow), treated sewage water from WTPs (dark blue pipes), burial in sediments (dark yellow arrows).

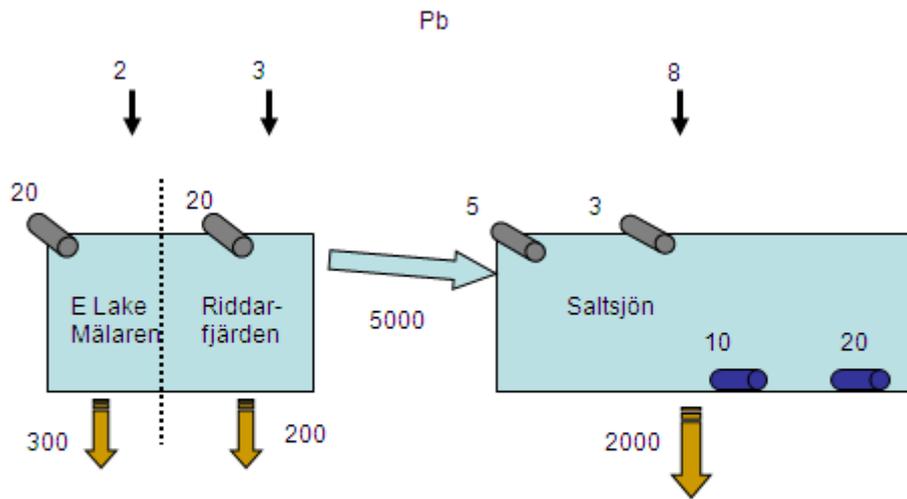


Figure 18. Flows of Pb in Kg/year: total atmospheric deposition (black arrows), storm water runoff from roads (grey pipes), Lake Mälaren discharge to Saltsjön in brackish Baltic Sea (light blue arrow), treated sewage water from STPs (dark blue pipes), burial in sediments (dark yellow arrows).

The results from the SEM-AVS analyses are presented in Table 5 below.

Table 5. Results from the SEM-AVS analyses: Concentrations of AVS (acid volatile sulphides in mmoles/kg dw) and metals (mg/kg dw) in the solid phase of the sediment samples, concentrations of simultaneously extracted metals (SEM) (mmoles/kg dw) and the ratio of SEM to AVS.

	S1a (mmol/ Kg dw)	S1b (mmol/ Kg dw)	S2 (mmol/ Kg dw)	S3 (mmol/ Kg dw)	M1a (mmol/ Kg dw)	M1b (mmol/ Kg dw)	M2 (mmol/ Kg dw)	M3a (mmol/ Kg dw)	M3b (mmol/ Kg dw)
dw %	18.3		19.1	22.7	22.9		24.9	21.3	
TOC (%C dw)	7.87		6.76	5.87	5.86		5.88	5.5	
AVS	91	110	130	170	100	100	130	150	140
As	21		20	17	12		18	14	
Cd	4.6		4.7	3.1	2.8		4.1	1.5	
Cr	130		126	119	117		118	102	
Cu	377		370	248	223		249	164	
Pb	339		289	226	292		304	199	
Ni	51		54	47	66		74	55	
Zn	607		632	470	540		680	451	
SEM									
Cd	0.024	0.025	0.025	0.015	0.015	0.015	0.022	0.01	0.01
Cr	0.39	0.39	0.39	0.26	0.41	0.41	0.44	0.29	0.31
Fe	199	212	164	241	331	339	322	330	329
Cu	0.76	0.3	0.22	0.6	0.84	0.83	0.41	0.37	0.21
Pb	1.3	1.4	1.1	0.88	1.1	1.1	1.1	0.73	0.66
Mn	1.8	1.9	1.8	2.7	5.1	5	5.9	9.9	9.5
Ni	0.19	0.2	0.19	0.18	0.39	0.39	0.43	0.36	1.7
Zn	6	6.5	6.2	4.2	6.5	6.4	8.2	5	4.7
SEM	8.664	8.815	8.125	6.135	9.255	9.145	10.602	6.76	7.59
SEM/ AVS	<b>0.095</b>	<b>0.080</b>	<b>0.063</b>	<b>0.036</b>	<b>0.093</b>	<b>0.091</b>	<b>0.082</b>	<b>0.045</b>	<b>0.054</b>

## 4 Discussion

### Physical and chemical parameters including Cu of water samples

The pH-values from the samples in Lake Mälaren (Table 1) are in the normal range. Usually the pH in Lake Mälaren is between 7.5 and 8.0, with excursions above 8.0 (SEPA, 2011) in conjunction with intense pelagic primary production. Lake Mälaren is stratified because of temperature gradients during summer. At the time of this sampling in late summer or early fall, the temperature gradient has decreased. The alkalinity at the monitoring station Centralbron is generally between 0.8 and 1.0 meq/l (SEPA, 2011). The concentrations of Mg and Ca generally are between 0.32–0.50 and 0.80–1.2 meq/l, respectively (SEPA, 2011). The results from this study are within these ranges (Table 1).

At these alkalinities and in this range of pH-values, the total carbonate carbon concentration,  $C_{T,CO_2}$ , can be estimated to be in the range of 1 – 1.2 mM (Deffeyes, 1965).

The concentrations of DOC in the samples from Lake Mälaren are within the normal range of TOC at the monitoring station, 6 – 10 mg/l (SEPA, 2011), considering that DOC usually makes up 90 – 95 % of freshwater TOC (Wetzel, 2001; Algesten et al., 2003).

The transition from freshwater Lake Mälaren to brackish Baltic Sea at Saltsjön is evident from the values of the physical and chemical parameters in Table 1. As can be seen when looking at the values of parameters such as conductivity, salinity, Ca, Mg and dH, the freshwater discharge from Lake Mälaren is transported as a less dense plume on the denser, more saline brackish Baltic Sea water below. Saltsjön is usually stratified because of salinity and temperature gradients (SVAB 2010b).

Looking at the concentration of dissolved organic carbon (DOC) in Table 1, one can see that in Lake Mälaren there is no surface to bottom gradient. However, in Saltsjön there is almost twice as much DOC in the surface water compared to the bottom water. The explanation for this difference is the same as for the other parameters: the surface water consists mainly of freshwater from Lake Mälaren. Lake Mälaren has around twice as high concentrations of DOC as compared to bottom water in Saltsjön, see Table 1. Lake Mälaren is a major source of TOC to the inner Stockholm Archipelago of the Baltic Sea, where Saltsjön is located. Although 95% of the TOC that is discharged from Lake Mälaren to the inner Stockholm Archipelago passes through on its way to the outer parts of the Stockholm Archipelago and the open Baltic Sea, about 1/3 of all the TOC buried in the sediments is of Lake Mälaren origin (Jönsson et al., 2005). This massive transport of TOC also has implications for the speciation and sedimentation of metals, which will be discussed in the sections below. From Table 1, it is possible to see the smallest difference between unfiltered and filtered concentrations of Cu, is for the surface water samples in Saltsjön of mixed freshwater from Lake Mälaren and brackish Baltic Sea water. The largest differences in filtered and unfiltered concentrations of Cu, thus indicating a greater importance of organic ligands in the operationally defined particulate phase, are in the Lake Mälaren samples and the bottom water samples at S2 and S3.

For the samples from Lake Mälaren the range of total (non filtrated) Cu concentrations is 3.2 to 4.9 µg/l (Table 1), which corresponds to 50 to 77 nM. In the ranges of pH (7.5 – 8) and alkalinity of 1 – 1.2 mM, the dominant Cu-species when considering inorganic complexes only is  $\text{CuCO}_3^0$ , while the fraction of  $\text{Cu}_{(aq)}^{2+}$  is less than 0.1 (Snoeyink and Jenkins, 1980). In Saltsjön the total Cu concentrations are in the same range but as alkalinity increases, the fraction  $\text{Cu}_{(aq)}^{2+}$  will be smaller than in Lake Mälaren (Snoeyink and Jenkins, 1980). In Lake Mälaren and Saltsjön, the concentrations of DOC are sufficient to make organic ligands important complexing agents for Cu and other metals. Speciation studies have shown that copper tend to occur as organic matter complexes to a very high degree in both fresh and estuarine waters and thus significantly contribute to bring the concentrations of free Cu ion below toxic levels (Kim et al., 1999; Dryden et al., 2007; Santos-Echeandia et al., 2008; Louis et al., 2009). Considering the good supply of organic and inorganic ligands in both Lake Mälaren and Saltsjön, and the modest levels of total concentrations of Cu ( $\approx 0.1$  µM), the levels of free cupric ion are expected to be far below toxic levels for plankton and crustaceans (1 to 10 nM) according to studies in freshwater, estuarine and marine waters (Kim et al., 1999; Dryden et al. 2007; Louis et al., 2009). According to the chronic Cu Biotic Ligand Model (EURAS version 109, available from <http://www.eurocopper.org/copper/copper-ra.html>), the PNECs for the freshwater samples collected in Lake Mälaren (both close to the bottom and surface) and in Saltsjön (surface only) are in the range 37 to 48 µg/L (0.58 to 0.91 µM) of dissolved (filtrated) Cu. For the bottom water samples from Saltsjön (brackish water with salinity 5 ‰), the corresponding marine PNECs with one safety factor and OC-normalisation (copper risk assessment report [http://echa.europa.eu/chem\\_data/transit\\_measures/vrar\\_en.asp](http://echa.europa.eu/chem_data/transit_measures/vrar_en.asp) and Foekema et al., 2011) are in the range – 8-9 µg/L (0.13 µM) of dissolved Cu. Regarding the sensitivity of microbes to bio-available Cu, the concentrations in the freshwater samples of this study (Lake Mälaren and surface water in Saltsjön) are well below the PNEC of 0,23 mg/l dissolved Cu (Cha et al., 2004). For the brackish water samples from Saltsjön, some papers have demonstrated higher sensitivity of the microbes e.g. cyanobacteria compared to algae (Brand et al., 1986). Other papers suggest that cyanobacteria produce copper chelating agents to cope against copper toxicity (e.g. Dryden et al., 2007) and the copper risk assessment (EU, 2008) concluded that that there is no indication that cyanobacteria populations have a sensitivity  $< 10$  µg Cu/l for a coastal marine water with 2 mg DOC/L. The marine PNEC (5.2 µg Cu/l; EU, 2008 and Foekema et al., 2011) is therefore considered as protective to cyanobacteria. Studies on bioaccumulation of Cu (and other metals) in the same area as the present study, indicate that Cu is not bioavailable at toxic levels. Studies on fish, *Perca fluviatilis* show no response for metallothionein (Hansson et al., 2006) and no enrichment of Cu were found in mussels, *Dreissena polymorpha*, compared to reference sites (Lithner et al., 2003; Landner and Reuther, 2004).

#### Sediment surface concentration of Ni, Cu, Zn, Cd and Pb in the city centre of Stockholm

An interesting ground for comparison of sediment surface metal concentrations exists with three previous studies in the same areas: Östlund et al. (1998), Lindström et al. (2001) and Sternbeck et al. (2003). In all three studies, sediment from accumulation bottoms was

sampled, which make it possible to compare the changes in surface sediment metal concentrations over time. However, in the study by Östlund et al. (1998), sediment from erosion and transport bottoms was also sampled. This is indicated by the very low loss on ignition (LOI) and high dry matter content) figures for some of the samples. Therefore, data for comparison with the present study must be selected carefully in order to make comparisons meaningful. Also the data from Östlund et al. (1998) do not always include the 0 – 2 cm sediment depth interval. In those cases, data from the 2-4cm sediment depth interval were used instead. The extensive study carried out by Östlund et al. (1998) had as one objective to study the effects of some of the present and historical local point sources. Therefore one would expect the data from this study to have a larger variance. Indeed sediment concentrations data often have positively skewed distributions e.g. lognormal (Jönsson et al., 2003). A summary of the data from the studies by Östlund et al. (1998), Sternbeck et al. (2003) and the present one is presented in Figs. 19 – 23 below. The data in Lindström et al. (2001) is not reported in a form which allows boxplots. Instead the data from the study by Lindström et al. (2001) will be presented in Table 6 below.

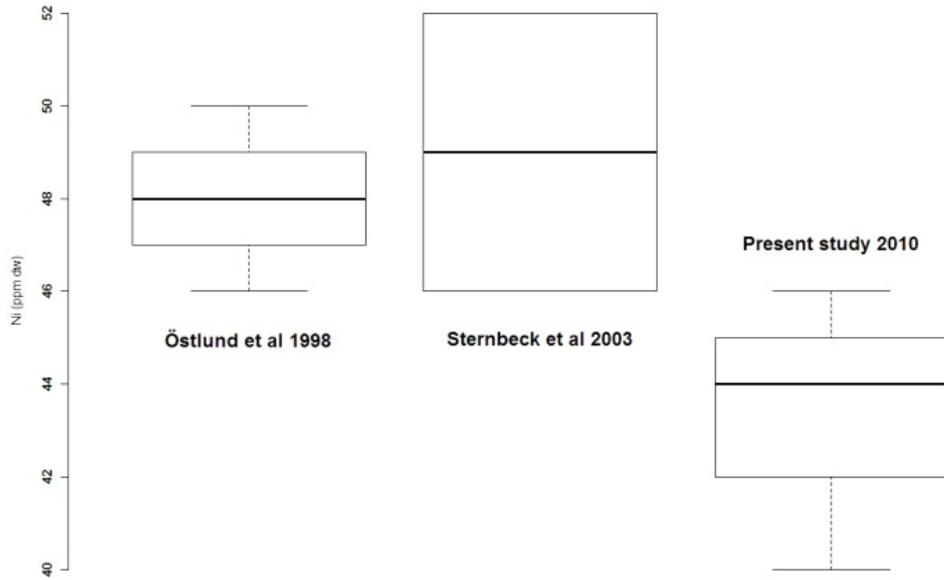
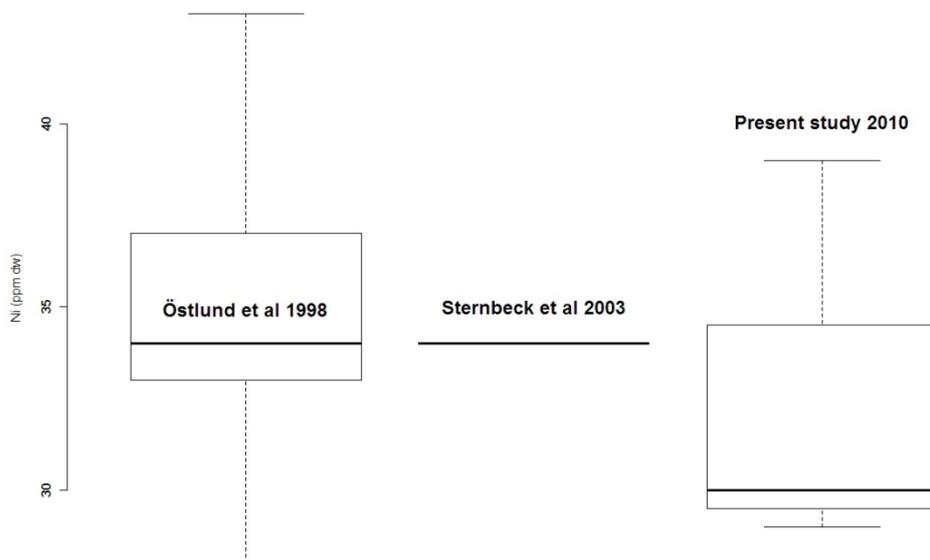


Figure 19. Ni concentrations (ppm dw.) in surface sediments in Lake Mälaren (above) and Baltic Sea (below) in the city centre of Stockholm in three different studies: Östlund et al. (1998), n=6 and n=5, respectively; Sternbeck et al. (2003), n=2 and n=1, respectively; present study (2010), n=3 and n=3, respectively.



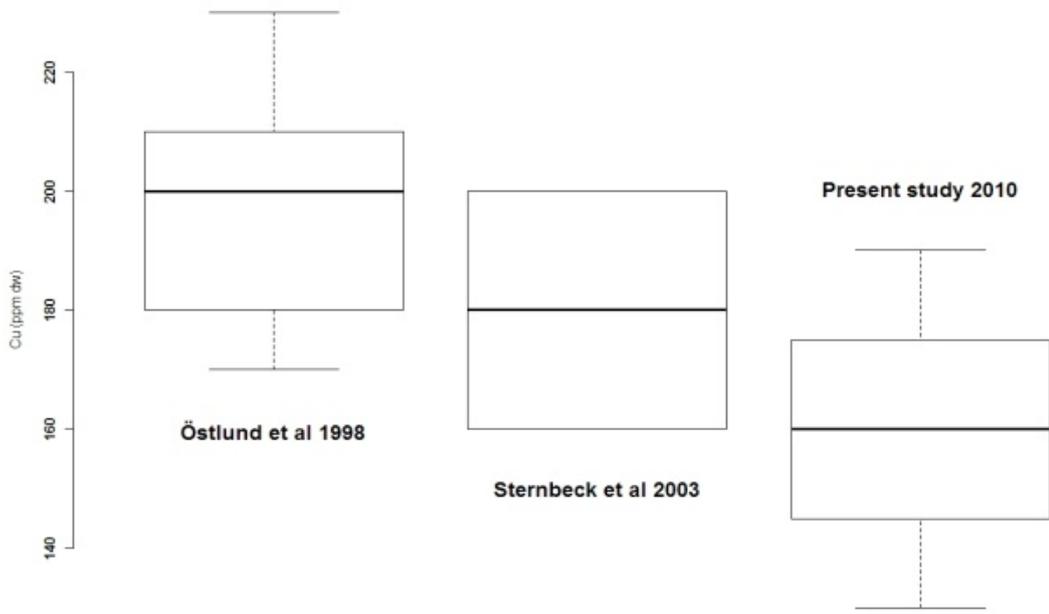
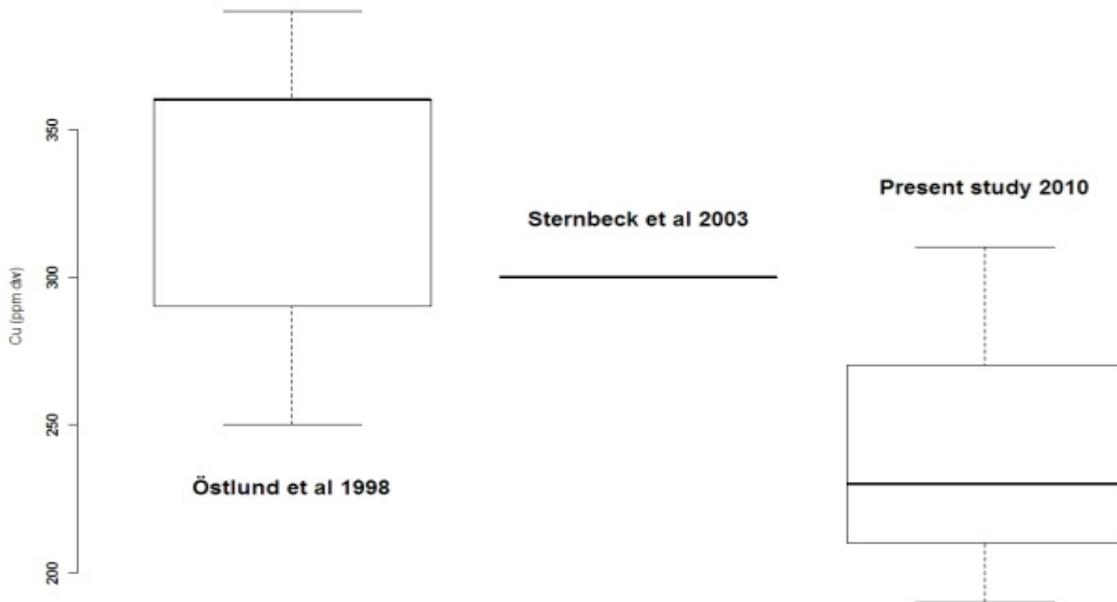


Figure 20. Cu concentrations (ppm dw.) in surface sediments in Lake Mälaren (above) and Baltic Sea (below) in the city centre of Stockholm in three different studies: Östlund et al. (1998), n=6 and n=5, respectively; Sternbeck et al. (2003), n=2 and n=1, respectively; present study (2010), n=3 and n=3, respectively.



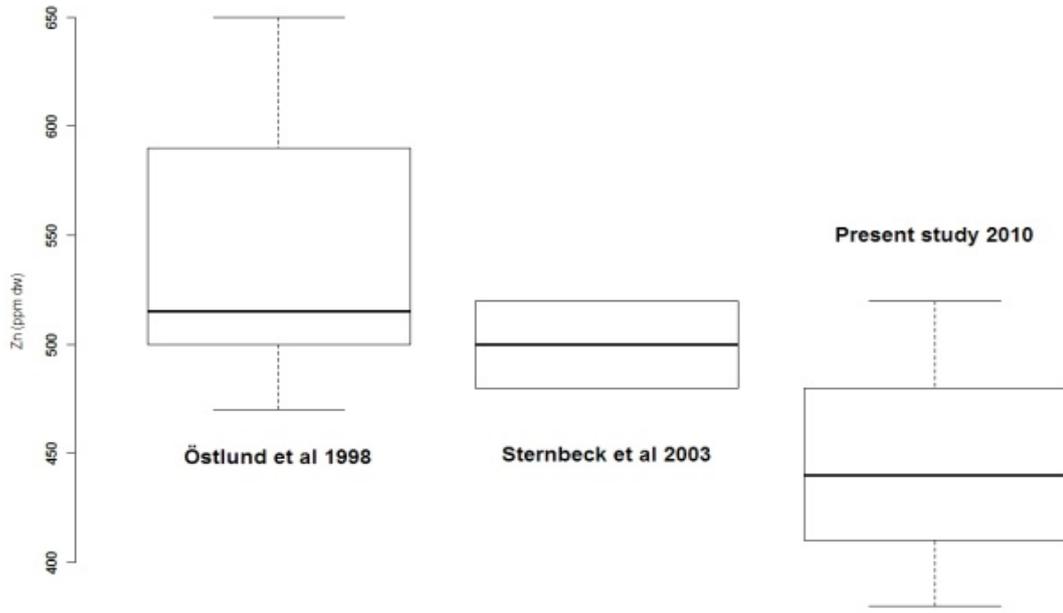
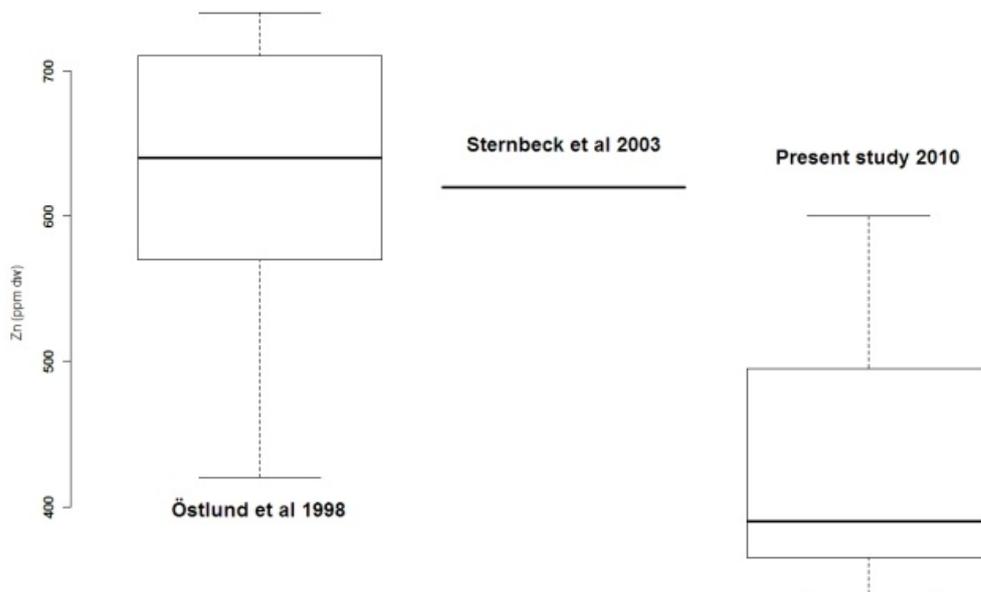


Figure 21. Zn concentrations (ppm dw.) in surface sediments in Lake Mälaren (above) and Baltic Sea in the city centre of Stockholm (below) in three different studies: Östlund et al. (1998), n=6 and n=5, respectively; Sternbeck et al (2003), n=2 and n=1, respectively; present study(2010), n=3 and n=3, respectively.



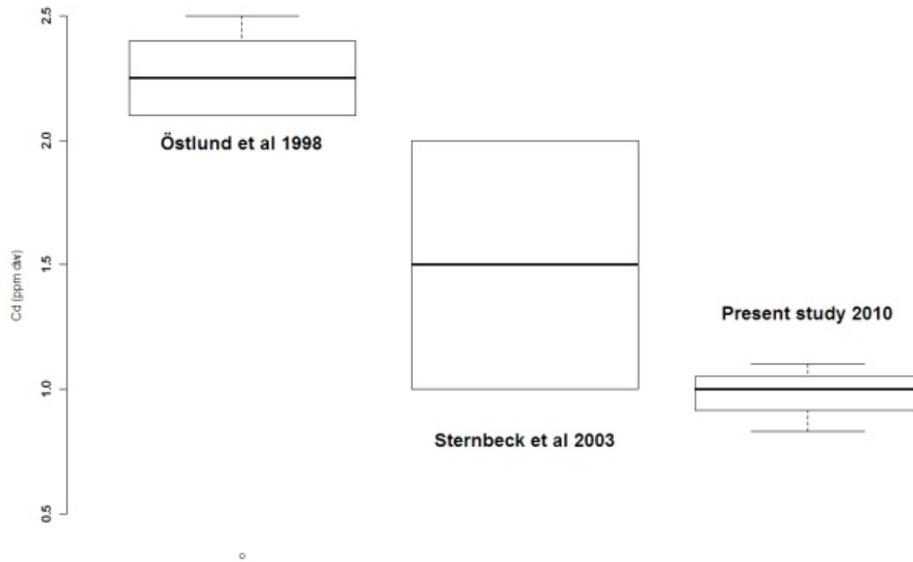
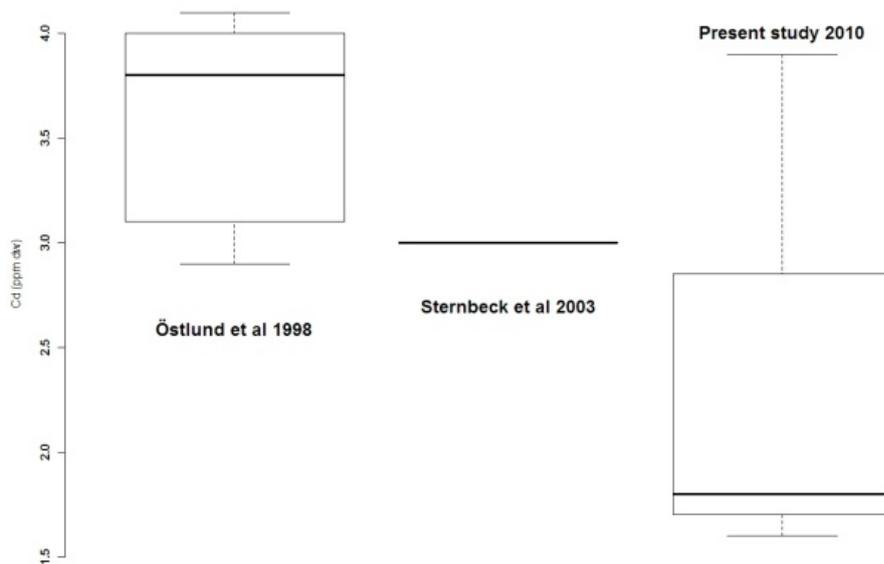


Figure 22. Cd concentrations (ppm dw.) in surface sediments in Lake Mälaren (above) and Baltic Sea in the city centre of Stockholm (below) in three different studies: Östlund et al. (1998), n=6 and n=5, respectively; Sternbeck et al (2003), n=2 and n=1, respectively; present study(2010), n=3 and n=3, respectively



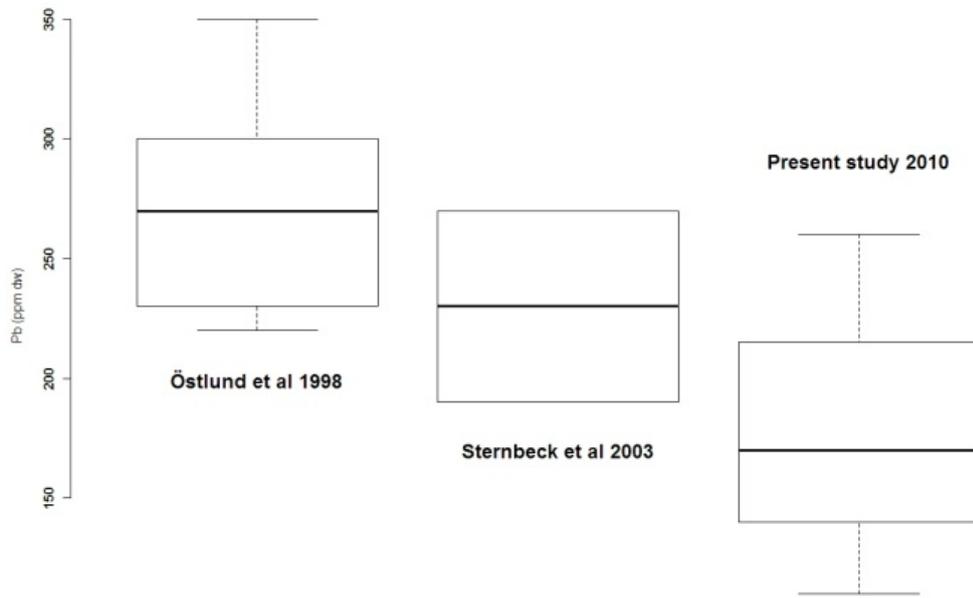


Figure 23. Pb concentrations (ppm dw.) in surface sediments in Lake Mälaren (above) and Baltic Sea (below) in the city centre of Stockholm in three different studies: Östlund et al. (1998), n=6 and n=5, respectively; Sternbeck et al (2003), n=2 and n=1, respectively; present study(2010), n=3 and n=3, respectively.

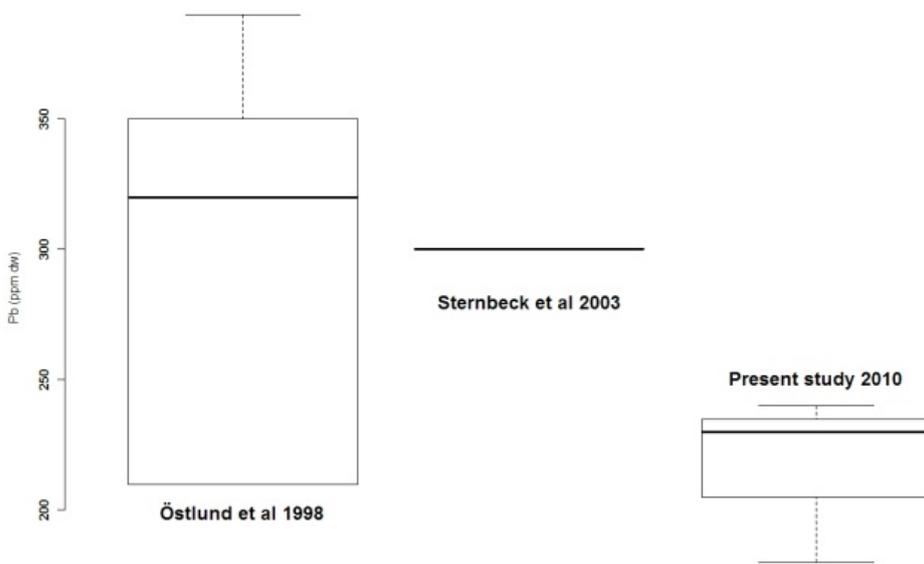


Table 6. Metal concentration (mg/Kg dw.) in surface sediments in Lake Mälaren and Baltic Sea in city centre of Stockholm. Data from Lindström et al. (2001).

	Ni	Cu	Zn	Cd	Pb
Lake Mälaren (n =4)	45.7 (0.16)	161 (0.14)	468 (0.2)	1.57 (0.2)	233 (0.22)
Saltsjön (n=5)	38 (0.16)	298 (0.23)	613 (0.16)	3.22 (0.27)	332 (0.21)

From the boxplots in Figs. 19 – 23 one general trend is evident. The surface sediment concentrations at both locations have decreased from 1996 to 2010. A second less evident trend is that there seems to be higher concentrations in the brackish Baltic Sea (Saltsjön) than in the freshwater Lake Mälaren in the city centre of Stockholm, with the exceptions of Ni and Zn. To check if there indeed are these differences two one-sided hypotheses were tested using a Wilcoxon rank sum test, equivalent to the Mann-Whitney test.

The first hypothesis tested was that the mean concentration of the metal in question (e.g. Ni, Cu, Zn, Cd or Pb) for each area (Saltsjön or Lake Mälaren) in 1996 was equal to that of 2010. The alternative hypothesis was then that the mean concentration in 1996 was higher. Data consisted of same observations as in the boxplots in Figs. 19-23. The outcomes of the testing of this hypothesis for the different cases are presented in Table 7 below.

Table 7. P-values for testing hypothesis of decreasing surface sediment concentrations between 1996 and 2010. M denotes Lake Mälaren and S denotes Saltsjön (Baltic Sea).

	Ni-M	Cu-M	Zn-M	Cd-M	Pb-M	Ni-S	Cu-S	Zn-S	Cd-S	Pb-S
p-value	0.0186	0.0460	0.0974	0.0833	0.0460	0.393	0.0669	0.0714	0.125	0.184

As can be seen in Table 7 there has been a decrease in sediment surface concentrations between 1996 and 2010 on a 90% confidence level with the exception of Ni in both Lake Mälaren and Saltsjön and Cd and Pb in Saltsjön. The data from Lindström et al. (2001) in Table 6 fits this trend in the case of Lake Mälaren.

The second hypothesis tested was that the mean concentrations of the metal in question (e.g. Ni, Cu, Zn, Cd or Pb) in 2010 was equal in Saltsjön and Lake Mälaren. The alternative hypothesis was then that the mean concentration in Lake Mälaren was lower. Data consisted of the same observations as in the boxplots in Figs. 19-23. The outcomes of the testing of this hypothesis for the different cases are presented in Table 8 below.

Table 8. P-values for testing hypothesis of higher mean sediment surface concentration in Baltic Sea (Saltsjön) than in Lake Mälaren in city centre of Stockholm

	Ni	Cu	Zn	Cd	Pb
p-value	1	0.0606	0.65	0.05	0.35

The results from the testing of the second hypothesis in Table 8 show that it is only the concentrations of Cu and Cd that are higher in the brackish Baltic Sea (Saltsjön) than in Lake Mälaren surface sediments in the city centre of Stockholm. These results are also in line with the observations made by Lindström et al. (2001) as presented in Table 6.

Some explanations for the existence or absence of these two trends will be presented in the following section.

### Sediment fluxes of Ni, Cu, Zn, Cd and Pb in the city centre of Stockholm: implications for sources and flows

Although the relative strengths of the sources and the environmental fate of the metals investigated can differ, there are some common patterns that become evident when assessing the various flows for the metals in Figs. 14 to 18. One observation is that the flow of metals from Lake Mälaren to Saltsjön in the brackish Baltic Sea is the largest flow by far. During the period of 1996 – 2008 the yearly transport of these metals from Lake Mälaren to Saltsjön had the following mean, standard deviations, minimum and maximum in tonnes:

- Ni (15,5; 5,87; 7,45; 27,5)
- Cu (21,2; 9,82; 8,90; 36,8)
- Zn (28,1; 19,7; 7,49; 76,5)
- Cd (0,0524; 0,0227; 0,0196; 0,0943)
- Pb (4,47; 5,55; 19,5; 0,851)

As can be seen the yearly transport of Ni, Cd and Pb from Lake Mälaren to Saltsjön in figures 14, 17 and 18 are close their respective means for the period 1996 – 2008. In the cases of Cu and Zn (figs. 15 and 16), the values are similar to their max and minimum values respectively for the period 1996-2008. In the cases of Pb and Cd the sediment fluxes in Saltsjön is of the same magnitude as the yearly transport from Lake Mälaren to Saltsjön. Another observation is that no external flow can wholly make up for accumulation of metals in the sediments in either area, except for Ni in Saltsjön. In the cases of Cu and Zn storm water from roads can make up a significant part of metal accumulation in sediments in Eastern Lake Mälaren and Riddarfjärden, whereas WTPs can make up a significant part in Saltsjön. In the Figs. 14 to 18, the storm water discharges into Riddarfjärden does not account for the load of metals from the major roads that are drained into the Klara canal, which discharges into Riddarfjärden just before Lake Mälaren discharges into Saltsjön at Norrström. If all of these loads were considered to end up in Riddarfjärden, the figures for the storm water load to Riddarfjärden would not change since the increase would only be 1 to 3 decimals. In a similar way, one can assess the metal load from storm water from the major roads which is discharged into the area just north of Saltsjön, Nybroviken. In Figs. 14 to 18, these loads are not accounted for. By assuming that nothing of these metals sediment in the Nybroviken area itself, but is carried to Saltsjön, the storm water flow figures need to be adjusted somewhat for Ni, Zn and Pb. The adjusted figures would be 0.1Kg, 70Kg and 7Kg respectively. Still, these flows would be far too small to account for the sediment burial fluxes of these metals in Saltsjön.

The similarities and differences of the relative strengths of the sources and sinks considered for the different metals can be analysed considering three different aspects:

- 1) The city centre as a source of metals

- 2) Transport of organic matter from Lake Mälaren and subsequent flocculation and sedimentation in Saltsjön in the brackish Baltic Sea
- 3) Differences and similarities in chemical and physical properties of the metal species under consideration

For the metals considered in this study, there are many sources to storm water but they can be divided into two groups (Sörme and Lagerkvist, 2002): traffic (asphalt, brake linings and tires); buildings and other constructions (copper roofs and galvanized steel). The storm water is either discharged with or without treatment (e.g. sedimentation ponds) to Eastern Lake Mälaren, Riddarfjärden and Saltsjön or led to the WTPs Bromma and Henriksdal. After treatment in the WTPs, which includes flocculation using FeSO<sub>4</sub>, the storm water is then discharged with the waste water to Saltsjön. As can be seen in Fig. 1, it is only narrow stretches of land, including bridges, which contain building and road infrastructure where storm water is drained directly to the Lake Mälaren or Saltsjön. In this study only the metal load from major roads in these areas were considered.

One way to gauge to what extent this is an underestimation is to compare the contributions to storm water led to Henriksdal WTP between traffic and buildings infrastructure (Sörme and Lagerkvist, 2002):

- Cu 5% (traffic) and 13 – 17% (buildings), i.e. buildings app. 3 times greater
- Zn 10 – 11% (traffic) and 24 % (buildings), i.e. buildings app. 2 times greater
- Pb and Ni buildings insignificant
- Cd both traffic and buildings contribute 1%

Applying these ratios would mean that the flows from storm water to Eastern Lake Mälaren, Riddarfjärden and Saltsjön should be multiplied by four in the case of Cu and three in the case of Zn. These additional loads of Cu and Zn would mean that storm water could alone sustain the sediment burial of these metals in Eastern Lake Mälaren and Riddarfjärden. However, in Saltsjön storm water would still be an insignificant source to the sediment burial.

Another way of estimating the part that traffic contributes to the total metal load to the storm water is to compare emission factors for the different types of land use. This has been done for the Riddarfjärden drainage area (Stockholms Stad 2011a):

Cu:

- 3 Kg/year from traffic ( roads with 20000 vehicles /day )
- 4,1 Kg/year from traffic (parking spaces and roads with less than 20000 vehicles/day and railways)
- 7 Kg/ year from buildings

Zn:

- 11 Kg/year from traffic ( roads with 20000 vehicles /day )
- 22 Kg/year from traffic (parking spaces and roads with less than 20000 vehicles/day and railways)
- 17 Kg/ year from buildings.

If one applies these ratios between major roads (i.e. more than 20 000 vehicles per/day) and other contributions from traffic and buildings for the loads of Cu( $11,1/3 \approx 4$ ) and Zn ( $39/11 \approx 4$ ) to the storm water, these flows should be increased by a factor of five in Figs. 15 and 16. These additions would make the flows of Cu and Zn from storm water in Eastern Lake Mälaren and Riddarfjärden sufficient to sustain the sediment burial rates there but far from sufficient in Saltsjön.

Note that if the flows of Cu and Zn to Riddarfjärden derived from land use are compared with the storm water flows Cu and Zn in the present study, which only accounts for emissions from traffic, one can see that the former is less than the latter.

If one compares the distributions of areas where the storm water is discharged directly to either Lake Mälaren or Saltsjön without treatment (Fig. 1) with the distributions of copper roofs in the city of Stockholm (Ekstrand et al., 2001) one can see that the storm water from the vast majority of the copper roofs in Stockholm are led to Bromma and Henriksdal WTPs. The storm water from the small fraction of copper roofs which is drained directly to the surface water without any treatment is discharged to Riddarfjärden at Norrström. This immediately before Lake Mälaren is discharged into Saltsjön and the copper from the roofs would therefore end up in Saltsjön. Due to the location of the sampling station for the national environmental monitoring program (Fig. 1), not all of this copper load will be accounted for in the estimates of the Cu load from Lake Mälaren to Saltsjön. However, since the vast majority of Cu from copper roofs ends up in the WTPs one can deduce that the minor part entering the surface waters without any treatment can only be an insignificant part to the sediments in Saltsjön since the contributions from WTPs can at the most only be a minor part of the Cu that is buried in the sediments in Saltsjön (Fig. 15). Applying a runoff-rate of 1g Cu per square meter copper roof and year (Odnewall Wallinder et al., 2009) to a total copper roof area of 622 590 m<sup>2</sup> for the city of Stockholm (Ekstrand et al., 2001) and disregarding the small direct runoff of Cu to the recipients, a yearly load of 600 Kg of Cu to the WTPs Henriksdal and Bromma is estimated. Since at least 96 % (Peterson and Wahlberg, 2010) of Cu is removed during treatment at the WTPs, a maximum of 2Kg of Cu from copper roofs are discharged in Saltsjön from the WTPs which is an insignificant fraction of the annual load of Cu from the WTPs (Fig. 15).

The wear for brake linings have been identified as a major source from traffic for the metals Cu, Zn, Cd, Sb, Ba and Pb (Sternbeck et al., 2002; Furujsjö et al., 2007). Applying the emission factor for Cu, Zn, Cd and Pb for brake linings from Sternbeck et al. (2002) would for the present study result in the following loads

	E. Lake Mälaren	Riddarfjärden	Saltsjön
Cu 1	10 Kg	10Kg	3 Kg
Zn	20 Kg	10Kg	5 Kg
Cd	0.02 Kg	0.02Kg	0.006 Kg
Pb	3 Kg	2Kg	0.8 Kg

A comparison between these loads from brake linings with the estimated loads from traffic (storm water) in Figs. 14 – 18 indicates that only in the cases of Zn and Cd can brake linings be a major source of metals to the storm water. However if any of the ratios

reported for the composition of the brake lining material Cd:Sb:Zn:Cu = 0.064:710:1000:3800 (Hjortenkrans et al., 2007) or the composition of PM<sub>10</sub> particles emitted from the wear of brake liners Cd:Sb:Zn:Cu = 0.068:780:1000:3100 (Furusjö et al., 2007) or from metal emission factors dominated by brake lining wear Cu:Zn:Cd:Sb:Ba = 1:1.3:0.0016:0.26:1.3 (Sternbeck et al., 2002) is compared with the ratios for these metals in any of the sediment samples (Figs. 2 - 8) there is no consistent indications of contributions from the wear of brake lining material.

Waste water from households and industries also contain a significant part of the metal load to the WTPs. It was estimated by Sörme and Lagerqvist (2002) to vary from 39% for Ni to 91 % for Cu for Henriksdal WTP in 1999. The sources of metals to wastewater are car washing, industrial operations, pipes and taps and drinking water (Sörme and Lagerqvist, 2002). After treatment in the WTPs, which includes flocculation using FeSO<sub>4</sub>, the storm water is then discharged with the sewage water to Saltsjön.

One way to gauge the total impact from the infrastructure in Stockholm city is to compare sediment concentrations along a transect from West to East. Starting in Lake Mälaren, passing the city centre and continuing to the outer Stockholm Archipelago in brackish Baltic Sea.

By comparing sediments from outside the island of Stora Essingen, directly upstream and West of the city centre of Stockholm in Lake Mälaren with sediments from Riddarfjärden, Årstaviken and outside the island of Reimersholme in the city centre of Stockholm in Lake Mälaren the following positive (i.e. increasing concentrations) trends can be observed (Sternbeck et al., 2003)

- Ni: None (factor 1)
- Cu: Weak (factor 1 to 2)
- Zn: Weak (factor 1 to 3)
- Cd: Weak (1 to 3)
- Pb: Weak (factor 2 to 3)

If one compares the sediment concentrations outside the island of Stora Essingen with sediment concentrations further West of Stockholm, outside the island of Färingsö, there is a weak negative trend (i.e. decreasing concentrations) for the metals Cu, Zn and Pb, with factors between 1 and 2 (Olli and Destouni, 2008). At Färingsö, there is no direct impact from the infrastructure in the city of Stockholm, only the general background load of these metals. By using the maximum factor of 2 for correcting for the potential influence from the infrastructure in the city of Stockholm on the sediment concentrations at Stora Essingen, the above trends should be adjusted for Cu, Zn and Pb:

- Cu: Weak (factor 1 to 4)
- Zn: Weak to Moderate (factor 1 to 6)
- Pb: Weak to Moderate (factor 2 to 6)

By comparing sediment concentrations from Saltsjön in the brackish Baltic Sea in the centre of Stockholm with sediment concentrations from the outer Stockholm Archipelago

in the Baltic Sea the following negative (i.e. decreasing concentrations) trends can be observed (Sternbeck et al., 2003, SVAB, 2010)

- Ni: Weak (factor 1 to 2)
- Cu: Very strong (factor 10 to 15)
- Zn: Moderate (factor 3 to 6)
- Cd: Strong (5 to 10)
- Pb: Strong (factor 6 to 12)

By comparing the trends in Lake Mälaren from outside of the city to the city centre of Stockholm and in the brackish Baltic Sea from the city centre of Stockholm to the outer and middle archipelago, one can divide the metals into two groups. For Cu, Cd and Pb a weak to moderate increase in concentrations in Lake Mälaren is followed by a strong to very strong decrease in the brackish Baltic Sea. For Ni and Zn, no and weak to moderate increases in sediment concentrations in Lake Mälaren is followed by weak to moderate decreases in concentrations in the Baltic Sea. For the former group, the change in the strength of trend indicates that there has to be a major source of Cu, Cd and Pb in Saltsjön in the Baltic Sea in the city centre of Stockholm. For the latter group, there can be no significant additional sources in Saltsjön compared to those in Eastern Lake Mälaren and Riddarfjärden. From the Figs. 14 to 18 it is evident that the additional sources in Saltsjön in the cases of Cu, Cd and Pb have to be either the two WTPs or the discharge of Lake Mälaren. By comparing the flows from the WTPs with the sediment fluxes it is clear that for both Cu and Cd; the WTPs can only contribute a minor part, while for Pb the contributions from the WTPs have to be insignificant. However, there is one indication that also the contributions of Cu and Cd to the sediments in Saltsjön from the WTPs may not be significant. As is the case for Pb, the sediment fluxes of Cu and Cd decrease as from S1 to S2 to S3 (Table 3). If they there were any significant contributions from the WTPs it would be the other way round, since the discharge points are located between S1 and S2 and S2 and S3 and the discharge pipes are designed so that the treated effluents travel eastward, away from the city, towards the Stockholm archipelago in the Baltic Sea.

Instead, one explanation for the increase in the sediment burial rates of Cu, Cd and Pb in Saltsjön is the sedimentation of these metals caused by the flocculation of organic matter from the freshwater Lake Mälaren when it is discharged into Saltsjön in the brackish Baltic Sea. The flocculation and coagulation of organic matter (incl. Fe-Mn-organic complexes) caused by the increase in conductivity as the freshwater is mixed with more saline waters in estuaries is well known (Benjamin and Honeyman, 1998). So is the subsequent sedimentation and scavenging of metals, particularly Cu (Benjamins and Honeyman, 1998). In a study by Jönsson et al. (2005), it was found that about 4% of the total amount of TOC that was discharged from Lake Mälaren to the Baltic Sea was buried in the sediments Inner Stockholm Archipelago, which includes Saltsjön. However, because of the large amount of TOC that is discharged from Lake Mälaren, e.g. 50 million Kg in 2008 (SEPA, 2011), this amounts to about 1/3 of all TOC buried in the sediments of the Inner Stockholm Archipelago. Since Saltsjön is at the actual discharge points, the proportion would probably be higher here. This is indicated by the decreasing sediment burial rates of TOC from S1 to S2 to S3 (Tables 2 and 3).

For Pb, one complementary process of increased sedimentation in Saltsjön can be the formation of  $\text{PbSO}_4$  ( $\log\beta=7,8$  ;  $I=0$ ), which would be an analogy to the main removal mechanism of  $\text{Ba}^{2+}$  from marine surface water (Broecker and Peng, 1982). The relative increase in relation to dry matter in sedimentation of Ba in Saltsjön compared to Lake Mälaren can be explained by this mechanism. However, the fraction of dissolved Pb or Pb complex with weak inorganic ligands in the freshwater from Lake Mälaren entering Saltsjön is probably minor, considering the amount of TOC, carbonates and particle surfaces (Schnoor, 1996) so for this process to be of importance the Pb has to preferentially form  $\text{PbSO}_4$ .

In the following section, the environmental fates of the different metals will be discussed in the context of their respective aqueous chemistries.

### Ni

$\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  compete with  $\text{Ni}^{2+}$  for the strong organic ligand-complexes. Therefore the concentrations of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  will affect how strong the binding will be between  $\text{Ni}^{2+}$  and DOC (Hassan et al., 2008).  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  have slower kinetics than  $\text{Ni}^{2+}$  because of their higher charge and ion potential. This in turn leads to higher stability constants for  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  (Hassan et al., 2006).

The chemical properties of DOC influence how effective the formation of organic complexes is, to the extent that at a given concentration of DOC, the concentration of  $\text{Ni}_{aq}^{2+}$  will vary with a factor 2 (Doig and Liber, 2006). The chemical properties of DOC will thus influence the number of different ligands and how stable these complexes will be (Santos-Echeandia et al., 2008). Chemical properties of organic matter can be expressed on a bulk basis as the ratios of different elements, e.g. C:H:N, which can be used as an indicator of the amount of functional groups (Benner et al., 1992). This ratio is determined by the origin of organic matter, i.e. terrestrial, freshwater or marine, and age (Jönsson et al., 2005).

It is evident from studies on the speciation of Ni in waters with similar chemical properties, that a large proportion (e.g. 30 – 80 %) of Ni may be in the form of free ion or dissolved or as complexes with very small and weak organic and inorganic ligands in Lake Mälaren and Saltsjön (Benjamin and Honeyman, 1998; Turner and Martino, 2006; Van Laer et al., 2006). The importance of complexes with DOC will disappear as soon as the water reaches the brackish water in Saltsjön (Turner and Martino, 2006). Thus, one possible explanation for the fact that there are no differences between the concentrations of Ni in the sediments of Lake Mälaren and Saltsjön, and that there has been no decrease in the sediment concentrations over time, is that Ni is to a relatively large extent transported in the truly dissolved form and other complexes which will not sediment with organic matter and particles in the increased flocculation in Saltsjön. This would explain why the sediment flux in Saltsjön (Fig. 14) is the smallest for Ni in relation to the input from Lake Mälaren (1,7%) for all of the metals. The sedimentation of Ni that takes place may not due to sedimentation of organic matter but of re-suspended clay particles, as will be described for Zn, Cd and Pb.

### Cu

Looking at Figure 15, it is evident that the sediment fluxes in both Lake Mälaren and in Saltsjön are large in relation to the anthropogenic loads from direct discharges of storm water and WTPs. The sum of these sediment fluxes (2400 Kg/year) can be compared to the figure of 500 to 5000 Kg/year estimated by Östlund et al. (1998). In relation to the input from Lake Mälaren, the sediment burial of Cu in Saltsjön is about 6%, close to the corresponding figure for TOC of 4% (Jönsson et al., 2005). That the environmental fate of Cu would be to a large extent governed by organic matter dynamics is in accordance with aqueous chemistry of Cu in natural waters, where the dominant dissolved part is bound to organically (incl. Fe-humic) complexes and the rest to inorganic carbon (Schnoor, 1996; Benjamin and Honeyman, 1998). The inorganic complexes become more important in marine waters. The formation of organic complexes is stronger for Cu than adsorption to particles and therefore the main sedimentation mechanism is Cu bound to either organic particles or to inorganic particles coated with organic matter (Benjamin and Honeyman, 1998). The importance of the sedimentation of organic matter due to flocculation can be indicated by comparing the sediment burial rates of Cu at M1 with that at S1. As can be seen in Table 3, the sediment burial rate of dry matter is almost exactly 3 times as high at S1 compared to M1. If the sediment burial rate of Cu at M1 is multiplied by three and divided by the corresponding rate at S1, a ratio of 0.6 is obtained. This ratio can be interpreted as the additional sediment load caused by flocculation and sedimentation of organic matter, including Fe- Mn-organic complexes.

A higher binding of copper to suspended solids in marine/estuarine waters compared to freshwater was also concluded from comparing  $K_D$ s for respectively freshwater, estuarine waters and marine water (EU, 2008), see below.

	<b>Freshwater log <math>K_D</math></b>	<b>Freshwater <math>K_D</math> (L/kg)</b>	<b>Estuarine log <math>K_D</math></b>	<b>Estuarine <math>K_D</math>(L/kg)</b>	<b>Marine log <math>K_D</math></b>	<b>Marine <math>K_D</math>(L/kg)</b>
50 <sup>th</sup> centile	4.48	30,246	4.75	56,234	5.12	131,826
10 <sup>th</sup> centile	3.76	5,752	4.19	15,488	4.58	38,019
90 <sup>th</sup> centile	5.29	194,228	5.42	263,027	5.66	457,088

### Zn, Cd and Pb

These three metals are in between the two extremes of Cu and Ni, which form the strongest and weakest complexes with organic matter (Benjamin and Honeyman, 1998). The metals Zn, Cd and Pb can be expected to have fractions of truly dissolved species (i.e. free ion) in between the two extremes of Cu and Ni. As the formations of complexes with organic matter for these metals are less important than for Cu, the adsorption to particles will instead increase in importance (Benjamin and Honeyman, 1998). This difference between the speciation of these metals and Cu will have an effect on their environmental fate if flocculation and sedimentation of organic matter in Saltsjön is an important removal mechanism. In a similar way as that of Cu, the sediment fluxes of Zn, Cd and Pb at M1 and S1 can be compared. The corresponding ratios are 1; 0,5 and 0,7 respectively. The equally low ratio for Cd as that of Cu is difficult to explain. Of the three metals, Cd is the one with

weakest sorption to particles and it does not form any strong complexes with organic matter (Schnoor, 1996; Benjamin and Honeyman, 1998). Zn is the only one of these three metals where a significant fraction could be truly dissolved in Saltsjön (Benjamin and Honeyman, 1998). As salinity increases the concentrations of cations which compete for sorption sites on particles also increase. Therefore the stability constants for Zn and Cd decrease with salinity (Turner, 1996). Also, the concentration of  $Cl^-$  increase with salinity, and this anion can form complexes with Zn and Cd, further reducing the capability of Zn and Cd to sorb to particles (Turner, 1996). This effect actually makes Cd much more soluble in seawater than in freshwater and  $CdCl_2^0$  is the major dissolved species in seawater (Snoeyink and Jenkins, 1980). Thus a decrease in sedimentation would be expected. However, the ratio between the sediment fluxes in Saltsjön (Figs. 16-18) and the input of these metals from Lake Mälaren is actually higher for the metals Zn (13%), Cd(36%) and Pb(38%) than for Cu (6%). In turbid tide-water controlled estuaries, the re-suspension of sediment particles can have a major influence on the transport and speciation of metals, particularly Pb but also Cd and Ni (Martino et al., 2002). In the Baltic Sea there are no tidal currents to speak of, but the plume from the discharge of Lake Mälaren into Saltsjön erodes the sediment at Norrström and Söderström (Jönsson, in prep.). The sediments that area eroded here are glacial clays, thus clay particles are re-suspended, creating an injection of particles to adsorb to. These clay particles will sink to the bottom and sediment as the turbulent flow of the water ceases further east; where the accumulation sediments are formed (e.g. S1). This process would probably be most important for Pb since it is strongly adsorbed to particles (Schnoor, 1996; Benjamin and Honeyman, 1998; Turner and Millward, 2000) but could also play a role for Cd and Ni (Schnoor, 1996; Martino et al., 2002). For Zn the sedimentation of organic complexes themselves may be of importance since a significant part of the Zn being transported with water from Lake Mälaren may in complexes with organic ligands (Benjamin and Honeyman, 1998). This is not the case for Cd but another possible removal mechanism is that colloidal iron oxides coagulate as salinity increases which lead to the formation of Fe-oxide-organic aggregates (Benjamin and Honeyman, 1998). Cd can be adsorbed to these Fe-oxides (Balistreri et al., 2007) and thus be buried in the sediments as the Fe-organic aggregates flocculate and sink to the bottom.

In the study by Östlund et al. (1998) the annual sediment fluxes in the city centre of Stockholm were estimated to be between 1200-12000 Kg for Zn, 5-50 Kg for Cd and 500-5000 Kg for Pb. The corresponding sediment fluxes estimated by the present study are (Figs. 16-18) 5000Kgs for Zn, 22 Kg for Cd and 2500 Kg for Pb.

#### Bioavailability of Ni, Cu, Zn, Cd and Pb in sediment in the city centre of Stockholm

As can be seen in Table 4, the bioavailability of the metals investigated is very low according to the SEM/AVS ratio, which is always below 0,1. This is at least 10 times lower than the threshold of AEM/AVS ratio of 1, where a toxic effect due to bio-availability may be expected (Ankley, 1996; Peesch et al., 1995). The main reasons for the low SEM/AVS ratio are the large amounts of AVS (i.e. sulfides), organic matter and inorganic ligands present in these anoxic and sub oxic sediments (Sundelin and Eriksson, 2001). Because of the presence of both high concentrations of TOC and inorganic ligands, these sediments show low toxicity in terms of mortality and embryonic malformations of amphipods with regards to the metals Hg, Cu, Zn, Cd, Hg and Pb even after oxygenation and bioturbation

for several months (Sundelin and Eriksson, 2001). The importance of the different binding forms sulphides, organic matter, Fe-Mn-(hydr)oxides can vary from metal to metal (Kelderman and Osman, 2007). The distribution of the metals between the different phases can also change after e.g. an oxidation of the AVS due to bioturbation, so that the metals form new phases e.g. carbonates (Kelderman and Osman, 2007). The concentration of AVS typically decreases close to the sediment surface with increasing redox, but the AVS concentration can vary further down in the sediment in the top 10 cm (Van den Berg et al., 1998; Sundelin and Eriksson, 2001; Van den Berg et al., 2001). As an operational definition AVS can be made up of different fractions (e.g. phases), with different kinetics and stabilities to oxygen (di Toro et al., 1996). In the unlikely situation where no AVS was present and all the SEM present in the top centimetre of the sediment, the SEM/AVS would possibly reach 1 in some cases, since all the ratios in this study is below 1/10 and the samples consisted of the top 8 to 10cm of sediments, see Table 4. However the concentration of organic matter in the upper 10cm is fairly constant in the sediments investigated in this study, see Table 2. Therefore even under these unlikely circumstances with no AVS and all SEM in the top cm of the sediments, considering the high concentrations of TOC the sediments in the city centre of Stockholm, all of the top 10cm of sediments should be considered to have low toxicity with regards to the metals investigated (Mahony et al., 1996; Sundelin and Eriksson, 2001).

There has been an improvement during the last decade or so, in the oxygen conditions of the surface sediments in the Saltsjön area (Karlsson et al., 2010). One of the possible explanations for the improved oxygenation of the sediments in this area, according to Karlsson et al. (2010) is the migration of the polychaeta *Marenzelleria spp.* to the Baltic Sea from North America and Russia (Arctic Sea). This organism is tolerable to sub-oxic conditions and its bioturbation will improve the oxygenation of the sediments. Indeed, (freeze-dried) remains of animals were found at several depths in sediment samples from the locations S1, S2 and S3. At depths of 2-4 cm the relative large *Isaduria Entomon* (up to 7 cm) and deeper down in the sediments, 4 – 8cm below the surface, remains of a worm-like animal was found, probably the polychaete *Marenzelleria spp.* As explained above and indicated by the SEM/AVS ratios in table 4, due to the presence of high concentrations of not only AVS but also TOC and inorganic ligands, the bioturbation of the sediments by these animals is not sufficient to make the sediments more toxic with regards to metals. Even after several months of bioturbation and oxygenation, the sediments from Saltsjön still had a low toxicity with regards to metals (Sundelin and Eriksson, 2001).

### Historical deposition of metals in the sediments in the city-centre of Stockholm

By multiplication of the average accumulation rates of dry matter since 1986 at the locations in this study (Table 3) with the concentrations at different sediment depths (Figures 9-13), the corresponding accumulation rates of metals at different ages can be estimated. By using the average accumulation rates of dry matter since 1986, the assumption is made that there has been no trends in the sedimentation rates during the time prior to 1986. The information regarding the variability in sedimentation accumulation rates both prior to and after 1986 is lost. Nevertheless, it can be meaningful to compare the results in this study to that of Östlund et al. (1998). Instead of using  $^{137}\text{Cs}$  to estimate sediment accumulation rates, Östlund et al. (1998) used  $^{210}\text{Pb}$ . Using this radioactive isotope has the advantage that sediment accumulation rates can be estimated for each sub-sample more than 100 years back. Thus in the study by Östlund et al. (1998), metal accumulation in the sediments were estimated for the period 1900 to 1998. In the study by Östlund et al. (1998), four stations are located close to stations M2, M1, S1 and S2+S3 in this study. The station 59 is located in between S2 and S3 along the West-East transect from the discharge points of Lake Mälaren (Norrström and Söderström) in Saltsjön. Therefore the average of the metal accumulation rates in S2 and S3 are compared with that in station 59 in the study of Östlund et al. (1998). A comparison of the timing and rates of maximum metal accumulation of metals in sediments of the city centre of Stockholm is presented in Table 9 below.

Table 9. Comparison of timing and size of maximum metal sediment fluxes in the city centre of Stockholm in present study and that of Östlund et al. (1998)

Station	M2	18	M1	34	S1	52	S2 + S3 59		
Period start	1989	1937	1940	1920	1987	1960	1973	1986	1936
Period end	2009	1996	2008	1996	2009	1996	2009	2009	1996
Average mass accumulation rate (g/cm <sup>2</sup> yr)	0.29	0.20	0.17	0.20	0.52	0.22	0.31	0.40	0.13
Average sediment burial rate (cm/yr)	0.71	0.44	0.42	0.36	1.3	0.6	0.79	0.88	0.26
Ni(g/m <sup>2</sup> yr)	0.30	0.25	0.10	0.13	0.21	0.10	0.13	0.15	0.070
Year(s)	1986	1988	1986	1984	98,04	1980	2004	02,04,07	1982
Cu(g/m <sup>2</sup> yr)	0.90	0.70	0.40	0.80	1.7	1.3	1.4	0.85	0.60
Year(s)	1986	1988	1986	1962	98,03,04	1970	1998	02,04	1982
Zn (g/m <sup>2</sup> yr)	3.0	2.0	1.1	2.5	3.0	4.0	2.4	1.7	1.0
Year	1986	1988	1986	1944	1993	1970	1991	2000	1982
Cd(mg/m <sup>2</sup> yr <sup>1</sup> )	15	12	5.3	14	17	18	14	8.1	7.0
year	1986	1970	1986	1962	1998	1970	1991	1986	1982
Pb (g/m <sup>2</sup> yr <sup>1</sup> )	3.2	0.90	0.63	1.2	1.7	1.3	0.83	0.85	0.50
Year(s)	1986	1988	1986	1962	2003	1970	2004	00,02,04	1982

The estimated rates of maximum accumulation of the metals Ni, Cu, Zn, Cd and Pb in the sediments in the city centre of Stockholm is to a large extent similar between the present study and that of Östlund et al. (1998). The largest difference is a factor of 2 and that occurs only for the cases Ni in Saltsjön (S1/52 and S2+S3/59), Cu in Mälaren (M1/34), Zn in Mälaren (M1/34), Cd in Mälaren (M1/34) and Pb in Mälaren (M2/18 and M1/34). If the metal accumulation rates in S2 and S3 are compared individually to that in 59, there is a difference of a factor 2 for S2/59 for Cu, Zn and Cd. For S3/59 there is only a factor 2 difference in the case of Ni. Since two different methods have been employed, <sup>137</sup>Cs (present study) and <sup>210</sup>Pb (Östlund et al., 1998), there are several explanations for the

deviations and similarities of the results. The  $^{137}\text{Cs}$ -method leads to estimated average accumulation rates for the period 1986-2010, which for M1 and S2 were used beyond that period. This can be one explanation for the deviations between M1 and 34. At M1 the sediment accumulation rates of Cu, Zn and Cd would then be higher during the period 1944/1962 to 1986 because of higher mass accumulation rates during that period compared to the average mass accumulation rates for the period 1986-2010 given by the  $^{127}\text{Cs}$ -method. That this might be the case is indicated by the average mass accumulation rate for the period 1920-1998 of  $0.20 \text{ g/cm}^2\text{yr}^{-1}$  given by the  $^{210}\text{Pb}$ -method in Östlund et al. (1998), which is higher than the average for the period 1986-2010,  $0.17 \text{ g/cm}^2\text{yr}^{-1}$ , given by the  $^{137}\text{Cs}$ -method. The sediment concentrations of Cu, Zn, Cd and Pb are also slightly higher in the corresponding sediment depth interval at 34 (Östlund et al., 1998) compared to that of M1 in the present study. Thus the combination of slightly higher sediment concentrations and higher sediment mass accumulation rates is the probable explanation for the maximum sediment fluxes of these metals being reached in 1944 and 1962 in the study of Östlund et al. (1998). In the case of Pb at M2 and 18, the explanation is the high concentration (1100 ppm) at sediment depth 15cm at M2 of the present study. This value is possibly an artefact and should at present be excluded from further discussion. If this value is disregarded the maximum Pb accumulation rate would be  $1.0 \text{ g/m}^2\text{yr}^{-1}$  (2006), which is close to 0.90 at station 18 in the study by Östlund et al. (1998). For Ni there are both higher sediment concentrations and mass accumulations rates (S2) and higher mass accumulation rates only (S3) compared to that at 59 (Östlund et al., 1998), which explain the higher sediment fluxes.

Apart from the deviations described previously, there are only small differences (less than a factor 2) in maximum sediment fluxes of Ni, Cu, Zn, Cd and Pb in the city centre of Stockholm in this study and that by Östlund et al. (1998) although different methods and periods were used. This observation is supported by the findings by Östlund et al. (1998), that there are only small differences (less than a factor 2) both temporally and spatially in mass accumulation rates in the city centre of Stockholm.

By looking at the timing of the maximum accumulation rates of Ni, Cu, Zn, As and Pb in Table 9 and the change of sediment surface concentrations between 2010 and 1996 in Figures 19-23 and Table 7, the following tentative conclusions can be made:

- The sediment fluxes of Cu and Zn are decreasing since the 1980s in Lake Mälaren
- The sediment fluxes of Cu and Zn are on a more recent decline in Saltsjön
- The sediment fluxes of Cd and Pb are decreasing since the 1980s in Lake Mälaren

These conclusions can only be tentative since average mass accumulation rates for the period 1986-2010 have been used to estimate sediment fluxes of Cu, Zn, Cd and Pb. However, the observed trends in sediment fluxes in this study is supported by Sternbeck and Östlund (2001), who found decreasing trends in sediment fluxes in the city centre of Stockholm for Cu, Cd and Pb from the 1980s, although the trend was only significant for Cd. The reasons Cd and Pb show decreasing sediment fluxes can be due to restrictions on their use. Cd in pigments, stabilizers and as a protective for corrosion was banned during the 80s in Sweden (Sörme et al., 2001). However, the use of Cd in sintered plated batteries (NiCd) increased during end of the 1980s and into the 1990s and some of the products banned have a long-term use, which means that emissions of Cd can continue long after a

ban (Sörme et al., 2001). Additionally, Cd is emitted to the environment via the use of fertilizers in agriculture. Pb as an additive in petrol was banned in 1995 in Sweden. But the use of Pb overall decreased only slightly up till the end of 20<sup>th</sup> century, since the main application of Pb in accumulators, had no replacement. For Cu and Zn, there was no decrease in the usage of consumer goods or industrial applications till the end of the 20<sup>th</sup> century (Sörme et al., 2001). The changes in use, due to restrictions and otherwise (e.g. shifting the discharge point of Bromma WTP from Lake Mälaren to Saltsjön), of these metals will be reflected in the sediment fluxes in Lake Mälaren and Saltsjön if they are sufficiently large in relation to background sources. The observation that the sediment fluxes of Cu and Zn have decreased in Lake Mälaren since the 1980s but only recently in Saltsjön, can be explained by looking at Figures 15 and 16. Since the discharge of Cu and Zn with Lake Mälaren water into Saltsjön is the largest source by far, it is the flocculation, particle sorption and subsequent sedimentation which determines the sediment fluxes of Cu and Zn in Saltsjön. Thus, although the sediment fluxes of Cu and Zn have decreased in Lake Mälaren in the city centre of Stockholm, reflecting decreased emissions to locally or to the Lake Mälarens drainage area, this does not significantly reduce the sediment fluxes in Saltsjön if the load of Cu and Zn to Saltsjön is sufficiently high. There has been no increase or decrease in the load of Cu and Zn from Lake Mälaren during the period 1999 – 2008 at the 0.10 significance level according to the non-parametric Mann-Kendall test for detecting trends using data from Centralbron (SEPA, 2011).

For Cd and Pb the discharge from Lake Mälaren is not at all as dominating compared to the discharges from the WTPs into Saltsjön. Therefore, although the emissions of Cd and Pb to Lake Mälarens drainage area have decreased, as reflected by the sediment fluxes, if the sediment fluxes in Saltsjön is to decrease the if the emissions from the WTPs have to decreased as well.

There has been no increase or decrease in the load of Cd and Pb from Lake Mälaren during the period 1999 – 2008 at the 0.10 significance level according to the non-parametric Mann-Kendall test for detecting trends using data from Centralbron (SEPA, 2011).

## 5 Conclusions

- The concentrations of Cu in the water samples from both Lake Mälaren and Saltsjön are below the PNECs derived by the chronic Cu BLM (EURAS version 109), MEC/PNEC = 0.04 to 0.3.
- The sediments in both Lake Mälaren and Saltsjön in the city centre of Stockholm are far from toxic with regards to pore water concentrations of the metals Cr, Ni, Cu, Zn, As, Cd and Pb according to the SEM/AVS method.
- Differences in surface sediment concentrations for the metals Ni, Cu, Zn, Cd and Pb between the sediments in freshwater Lake Mälaren and brackish water Saltsjön can be explained by a combination of differences in local sources and differences in metal speciation
- The surface sediment concentrations of Cu and Zn have decreased since 1996 in both Lake Mälaren and Saltsjön in the city centre of Stockholm.
- The surface sediment concentrations of Cd and Pb have decreased since 1996 in Lake Mälaren in the city centre of Stockholm.
- Direct runoff of roads can make up a major portion of the Cu and Zn that is buried in Lake Mälaren sediments in the city centre of Stockholm.
- The effluents from the WTPs can make up significant parts of the Ni, Cu, Zn and Cd that is buried in the sediments in Saltsjön in the city centre of Stockholm. However, the locations of the measured sediment fluxes in relation to the discharge points of the WTPs indicate that this is not the case.
- Runoff of copper-roofs can only be an insignificant source of Cu to the sediments in Lake Mälaren and Saltsjön in the city centre of Stockholm.

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