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Trace Elements in Stockholm Sediments

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Under åren 2004-2008 driver Miljöförvaltningen tillsammans med Stockholm Vatten AB projektet Nya gifter – Nya verktyg med finansiering ur stadens Miljömiljard. Projektets mål är att ta fram information om vilka ämnen som bör prioriteras i stadens miljögiftsarbete, både i form av åtgärder och miljöövervakning. Det ska också beskriva var i staden de prioriterade ämnena används, hur de når stockholmsmiljön och vad staden och andra aktörer kan göra för att minska de problem som är förknippade med miljögifter i Stockholm.

En sammanfattande slutrapport kommer att publiceras under våren 2008.

Varje författare ansvarar för innehållet i respektive delrapport.

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Abstract

Stockholm is Sweden's largest city with a population of 1,200,000. As in most cities, human activities are resulting in environmental contamination and previous studies have shown the occurrence of elevated heavy metal concentrations in Stockholm sediments. The present study aims at determining the level of platinum group elements and other relevant metals in Stockholm sediments. Platinum, rhodium, antimony, cadmium, chromium, copper, lead, silver, tin, tungsten and zinc were analysed in a set of 18 sediment samples collected in the outflow of Lake Mälaren and in ponds and lakes in the Stockholm area.

This study shows that these elements are found at elevated concentrations in the urban area relative to background sites. Platinum and rhodium concentrations range from 2.4 to 25 ng g^{-1} and from 0.3 to 5 ng g^{-1}, respectively. Antimony, silver, tin, tungsten have concentrations in the range 0.1 to 8.9 μg g^{-1}, 0.2 to 8.5 μg g^{-1}, 1.2 to 38 μg g^{-1}, 1.1 to 37 μg g^{-1}, respectively. Cadmium, chromium, copper, lead and zinc have concentrations of 0.4-4 μg g^{-1}, 27-77 μg g^{-1}, 27 to 475 μg g^{-1}, 15-772 μg g^{-1} and 76-1200 μg g^{-1}, respectively. Copper is present at high concentrations at most sampled sites according to Swedish EPA sediment concentration guideline. Zinc and lead are only present at high concentrations at specific sites. In addition, Ag concentrations exceed the apparent threshold concentration for Ag at several sites, whereas it is exceeded at one site for antimony. No guidelines exist for platinum, rhodium and tungsten.

Sources of trace elements include automobile traffic, urban surfaces (road pavement), buildings and combustion, as well as location specific sources. The spatial distribution of trace elements in sediments demonstrates that the contamination is the result of diffuse sources and it is therefore difficult to control. Automobile traffic is a major source of trace elements, including platinum, rhodium, antimony and tungsten, and traffic reduction policies to be implemented in Stockholm may help reduced trace element input. In addition, several elements, including tungsten, antimony and lead, are locally elevated and the determination of location specific sources (possibly industrial emissions) may also allow to reduce locally elevated concentrations.

Introduction

Trace elements occur typically at small concentrations (less than 0.1%) in the environment. However, the concentration of many trace elements is increased as a result of human activities. The environmental relevance of a number of metals and metallic compounds has been studied and demonstration of their toxicity has resulted in the regulation of their emissions (Merian et al., 2004). Although emission of metals is not entirely new, rapid technological development is resulting in the emission of new metallic contaminants before potential risks have been sufficiently assessed. Because of potential risks associated with the emission of metallic contaminants, a timely assessment of potentials risks, i.e. prior to emission or at an early stage, is needed.

Metals or metallic compounds, which are used in new technologies and poorly studied, include antimony (batteries, automobile brakes, tire rubber and flame retardants), gold (electronics), silver (electronics) and platinum group elements (catalysts and electronics), as well as new chemical forms of commonly used metals, e.g. tin, copper and zinc organometallic species. Emission essentially occurs during use and disposal, with possible emission as point source during mining and manufacturing. Elevated concentrations of some of these contaminants have already been reported in the Swedish environment (Rauch et al., 2001; Lithner and Holm, 2003; Grahn et al., 2006; Karlsson et al., 2006), raising concern over their potential accumulation in the biosphere. The determination of associated risks is however hampered by the lack of knowledge on environmental pathways, bioaccumulation mechanisms and toxic effects.

Stockholm is Sweden's largest city with a population at approximately 770,000 and a total of 1,200,000 inhabitants in the urban area. As in most cities, anthropogenic activities are causing environmental contamination, including contamination of aquatic systems (Jonsson, 2000; Lindström et al., 2001).

The project described in this report aims at determining the level of platinum group elements used in automobile catalysts, namely Pt, Pd and Rh (Pd was however not included here because of analytical difficulties, as described in the method section), and other relevant trace elements in Stockholm sediments. Platinum group elements are emitted by both mechanical abrasion of the catalyst surface and physico-chemical processes (Palacios et al., 2000; Moldovan et al., 2002; Moldovan et al., 2003), resulting in the occurrence of platinum group elements in particles ranging from sub-micrometer to over 63 μm (Gomez et al., 2002; Rauch et al., 2005). Emitted catalysts particles deposit on the road surface or in the roadside environment, and transport in stormwater has resulted in the contamination of aquatic systems (Rauch et al., 2004). Although little is know about the toxicity of these elements, uptake by benthic organisms has been reported (Moldovan et al., 2002), raising concern over potential chronic effects. Other relevant trace elements to be studied include Sb (emitted from automotive parts, listed as priority pollutant by the European Union and the USEPA) and W (used in tyre studs) as well as more commonly studied elements including Cd, Cu, Cr, Pb and Zn.

Method

Description of sampling sites

Sediments samples were collected from the outflow of the Mälaren to the Baltic sea, where Stockholm is located. Sampling was performed by a Stockholm Vatten crew in December 2006. Samples include 11 samples from the outflow of Lake Mälaren into the Baltic Sea (Lambarfjärden, Klubbensborg, Gröndal, Riddarfjärden, Kastellholmen, Ulvsundasjön, Barnhusviken, Saltsjön, Årstadal, Årstaviken, Lilla Värtan and in the Archipelago downstream from Stockholm) and 6 samples from lakes and ponds in the Stockholm area (Trekanten, Drevviken, Bornsjön). In Drevviken, three samples were taken in a gradient from the outlet of traffic storm water from a small-scale treatment facility.
Two of the sites are considered as background for this study, i.e. Björnsjön and Lambarfjärden. Both sites are located outside the city area and Lambarfjärden, which is part of Lake Mälaren, is upstream from Stockholm. These sites are also used as dirnking water supply for Stockholm.
Collection was performed using piston corers. The top 4 cm were collected in 2 slices and the top slice (0-2cm) was retained for analysis. This layer is estimated to represent approximately 2-5 years of sediment accumulation. In addition, 2 sediment cores were collected in Lake Mälaren outflow (Riddarfjärden and Kastellholmen). Locations of sampling sites are provided in Figure 1 and Table 1.

Table 1. Sampling site list.

Sampling site	Samples
Lambarfjärden	59°21'31.07"N – 17°47'43.17"E
Klubbensborg	59°18'38.76"N – 17°57'39.18"E
Gröndal	59°19'11.52"N – 18° 0'10.68"E
Riddarfjärden	59°19'26.82"N – 18° 2'5.76"E
Kastellholmen	59°19'15. 54"N – 18° 5'11.28"E
Ulvsundasjön	59°20' 31.08"N – 17° 59'40.44"E
Barnhusviken	59°20' 9.36"N – 18° 2'35.76"E
Årstadal	59°18'33.24"N – 18° 2'10.92"E
Årstaviken	59°18'14.76"N – 18° 3'38.10"E
Saltsjön	59°19' 6.54"N – 18° 7' 3.12"E
Lilla Värtan	59°19'31.92"N – 18°10' 3.78"E
Archipelago	59°21'58.80"N – 18°20'58.80"E
Trekanten	59°18'41.52"N – 18° 0'58.08"E
Drevviken (3 sites)	59°14'49.20"N – 18° 7'22.08"E; 59°14'57.90"N – 18° 6'26.34"E; 59°14'47.82"N – 18° 6'40.50"E
Bornsjön (2 sites)	59°14'15.84"N – 17°42'46.38"E; 59°13'8.04"N – 17°46'27.78"E

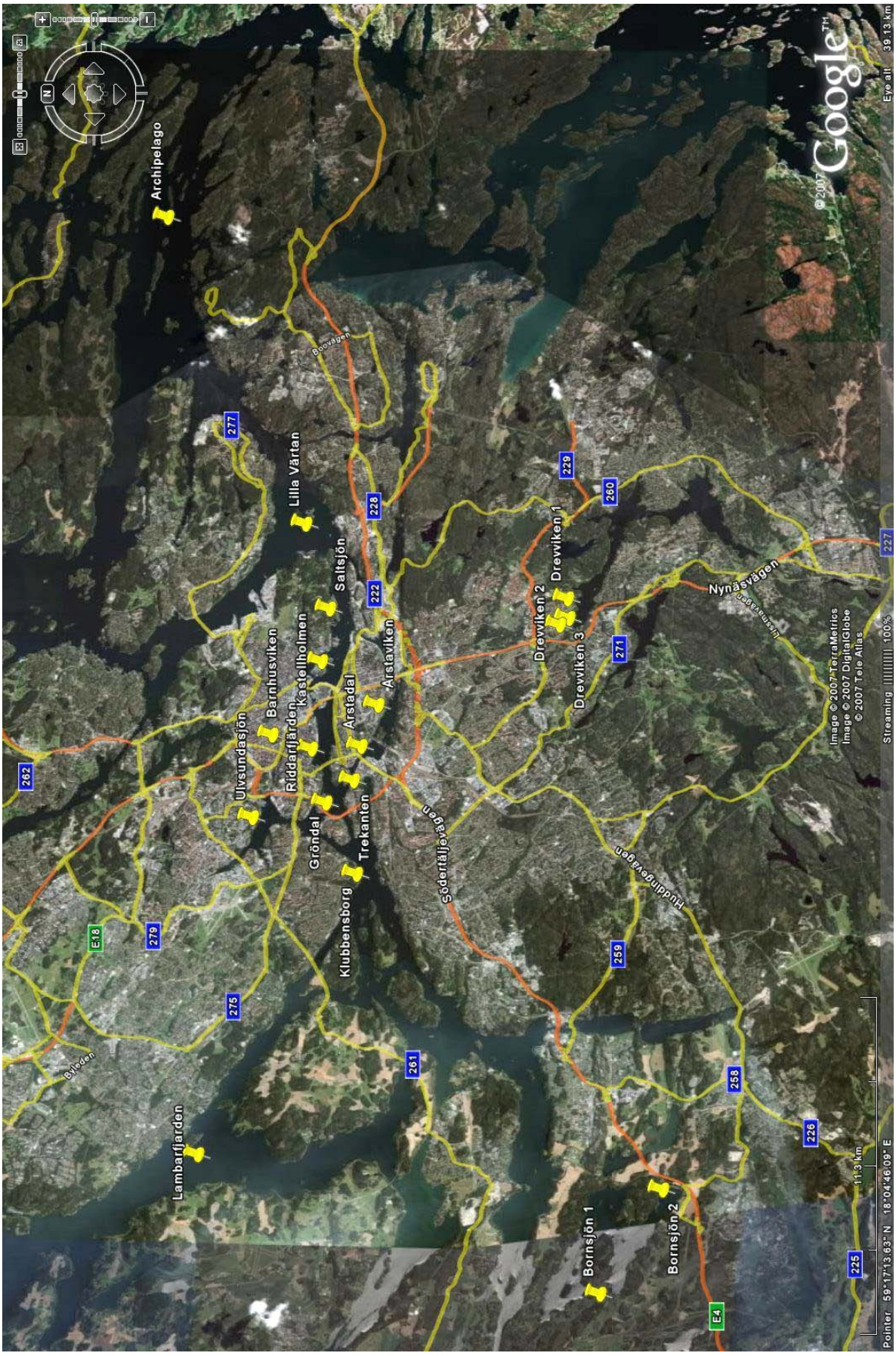

Figure 1. Sampling sites across Stockholm. Satellite image from Google Earth.

Sample preparation and analysis

Samples were prepared by microwave-assisted acid digestion (Mars5, CEM, USA) and analyzed by inductively coupled plasma-mass spectrometry. Sediment samples were dried overnight at 105°C (the possible loss of volatile Cd or Sb species was not taken into consideration here, but concentration levels, variations and distributions indicate that patterns of anthropogenic activity were preserved and loss are therefore expected to be small, if any). Dry sediments were then sieved and the 0-75 μm fraction was retained for analysis. 0.5 g of dry sediments were placed in microwave digestion vessels. Digestion was performed in closed vessels after addition of 8 ml *Aqua regia* (6 ml HCl + 2 ml HNO_3) using 2-step temperature increase to 185°C and a maximum allowed pressure of 200 psi. It is important to note that the procedure does not provide a full digestion, but a strong leach usually suitable for the study of anthropogenic metals in sediments. The leachate was then slowly taken to dryness on a hot plate and redissolved in 5% HNO_3. *Aqua regia* was selected for sample preparation because it is one of the only reagents that dissolve Pt.
Prepared samples were analysed by inductively coupled plasma-mass spectrometry (ICP-MS) using a quadrupole system (Elan 6000, Perkin Elmer, USA) with pneumatic injection (cross flow nebulisation) and using standard operating conditions. Calibration was performed by the analysis of multi-element standard solution, except for Pt and Rh for which solution of individual elements were analysed due to interference issues. Interference on Pt and Rh determination were corrected mathematically (Moldovan et al., 2001; Rauch et al., 2001). Pd results are not included in this report because interference on Pd analysis (especially from YO and ArCu) could not be excluded, raising concern over the accuracy of measured Pd concentrations.

Precautions and quality control

Because of the importance to provide accurate results, several precautions and quality control steps were implemented in the study. These include acid washing of all containers, the use of high purity acids (Suprapure grade, Promochem AB, Sweden) and water (18 MΩ cm, Milli-Q, Millipore, USA), the analysis of procedural blanks (prepared and analysed randomly). In addition, reference material BCR-723 (Road dust (Zischka et al., 2002)) was analysed to assess the accuracy of Pt and Rh concentrations.

Results

Metal concentrations across Stockholm

The concentration of most metals in surface sediments was found to vary across the sampling area. Concentrations are typically higher in the urban areas than at background sites, although variations were found for different metals. A further description of concentration variations is provided below for each metal, with concentrations presented as box plot (mean, standard error, standard deviation; the mean value represents replicates obtained from 3 sub-samples obtained after homogeneisation) and distribution maps (mean values of 3 replicates).

Platinum and rhodium

Average Pt and Rh concentrations in surface sediments across Stockholm range from 2.4 to 25 ng g^{-1} and from 0.3 to 5 ng g^{-1}, respectively. The distribution of Pt and Rh is presented in Figures 2 and 3, respectively.

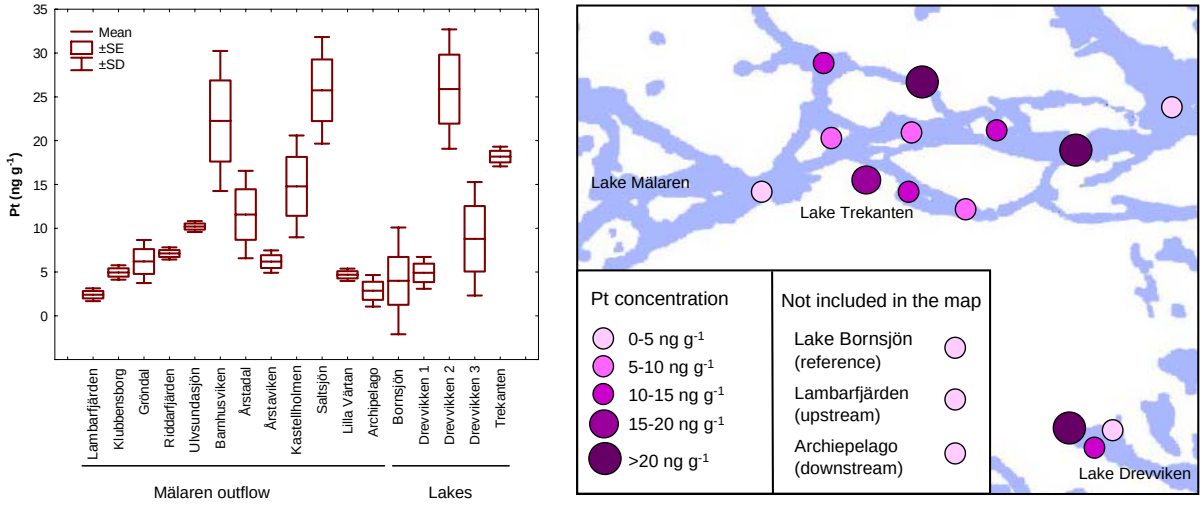

Figure 2. Pt concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

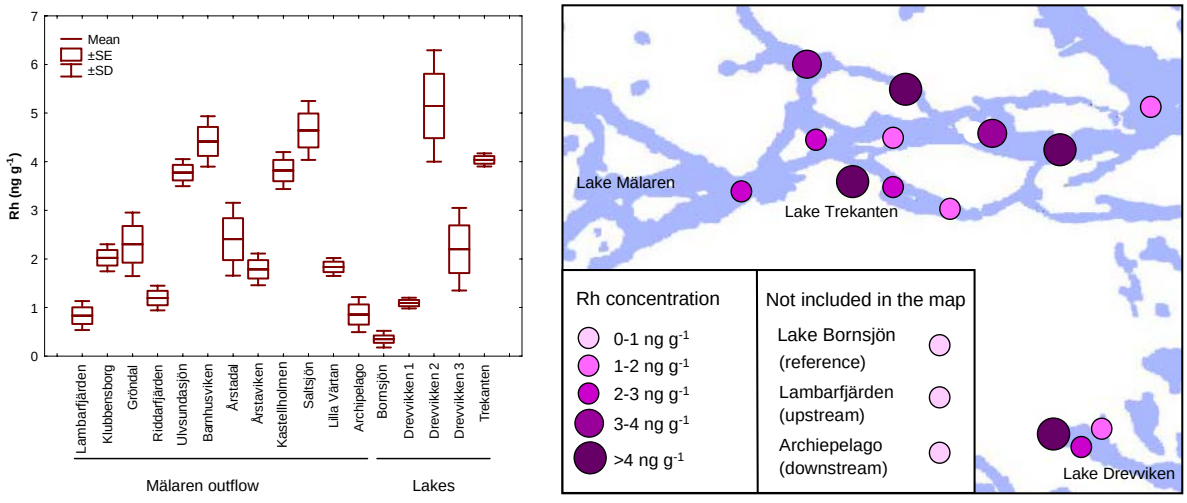

Figure 3. Rh concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

The lowest concentrations were measured at the Mälaren site and at Lake Bornsjön, as well as in the outflow into the Baltic Sea (Archipelago site). The average Pt concentration at Lake Bornsjön is 4.0 ng g^{-1} as a result of 1 outlier value. Without this outlier, the average Pt concentration is 1.3 ng g^{-1}. The highest concentrations were measured in the inner city (Barnhusviken and Saltsjön) and in Lakes Trekanten and Drevviken. In Drevviken concentrations exhibit a decreasing gradient with a decreasing gradient from the road and stormwater input.
Platinum and Rh concentrations measured in Stockholm are in the expected range for an urban area with dense automobile traffic. Platinum and rhodium concentrations in the urban area are lower than concentrations measured in an urban river in Göteborg (collected in 1999; Pt 54 ng g^{-1}; Rh 9 ng g^{-1}, Moldovan et al., 2001). The lower concentrations measured in Stockholm are likely to be the result of dilution because the river in Göteborg has a much smaller flow and sediment accumulation than the outflow of Lake Mälaren. Platinum and Rh concentrations in Lakes Drevviken and Trekanten are similar to concentrations in recent sediments obtained from a lake in Massachusetts, USA (Pt 25 ng g^{-1}; Rh 4 ng g^{-1}), where PGE accumulation rates were found to increase following the introduction of automobile catalysts (Rauch et al., 2004).

Silver

Silver concentrations in surface sediments across Stockholm range from 0.2 to 8.5 µg g^{-1}. Lowest concentrations are observed at background sites (Bornsjön and Lambarfjärden) and highest concentrations are found in the inner city area (Barnhusviken, Kastellholmen, Saltsjön and Trekanten), as shown in Figure 4. The relatively high Ag concentration in the Archipelago downstream from Stockholm indicates an export of Ag into the Baltic Sea.

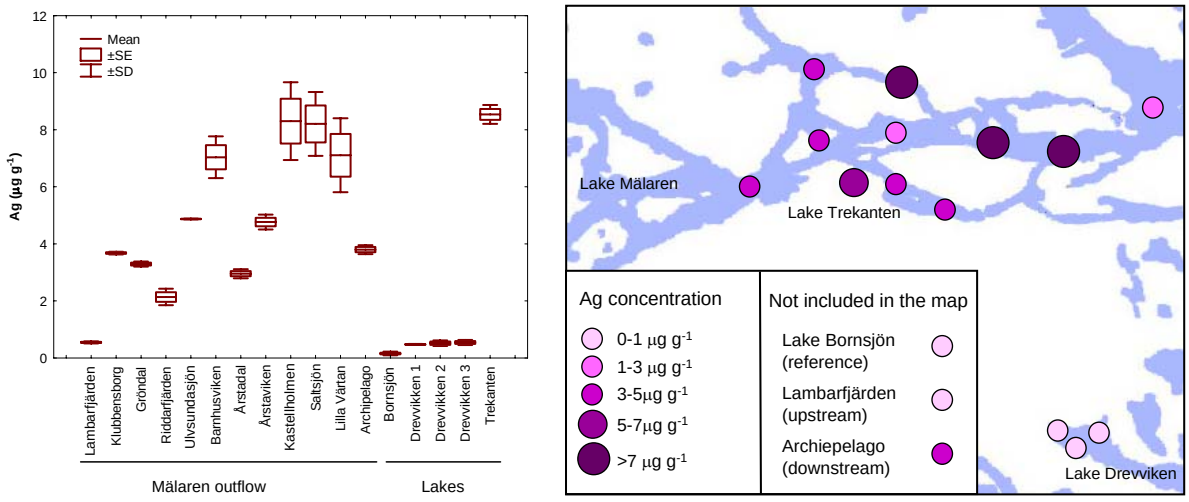

Figure 4. Ag concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

Tungsten

Tungsten concentrations in surface sediments across Stockholm range from 1.1 to 37 µg g^{-1}. Relatively low concentrations were found at most sampling sites and elevated concentrations were only present at a limited number of sites. Average concentrations at Kastellholmen, Trekanten and Årstadal exceed 20 µg g^{-1}, as shown in Figure 5.

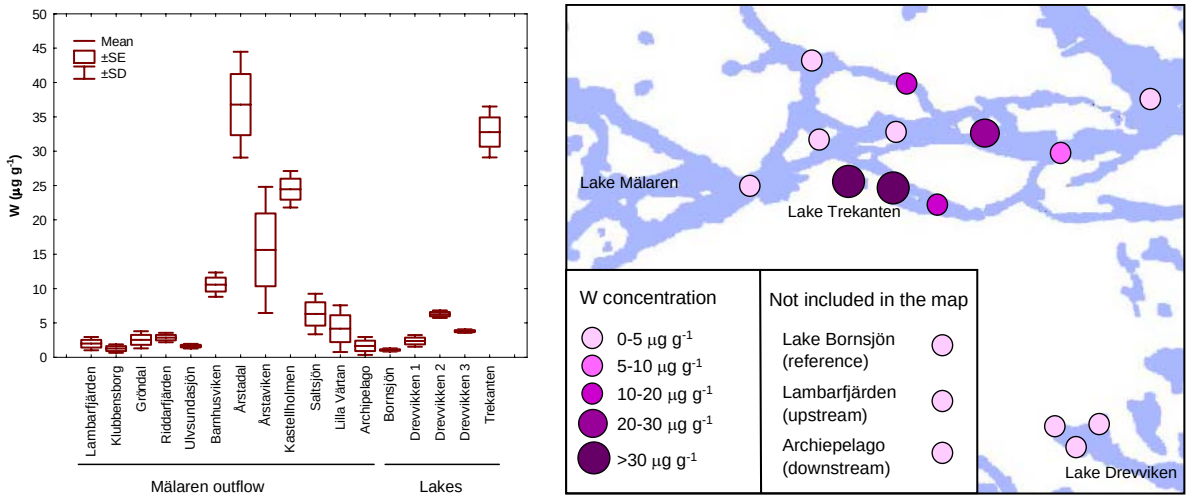

Figure 5. W concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

Antimony

Antimony concentrations in surface sediments across Stockholm range from 0.1 to 8.9 µg g^{-1} (Figure 6). The lowest concentration was found at Lake Bornsjön. Average concentrations do not exceed 2.5 µg g^{-1}, except for Årstadal, where an average concentration of 8.9 µg g^{-1} was measured.

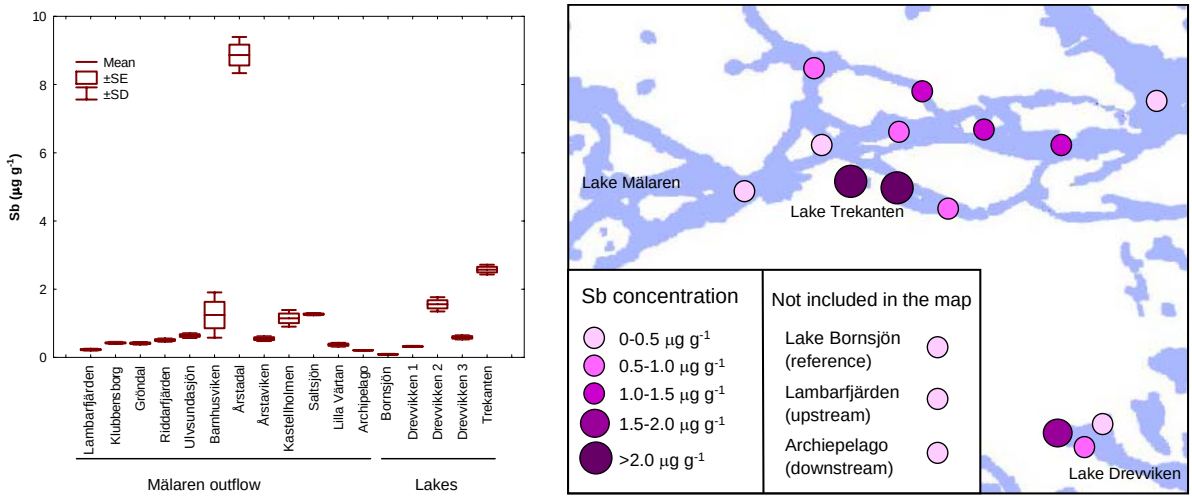

Figure 6. Sb concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

Tin

Tin concentrations in surface sediments across Stockholm range from 1.2 to 38 µg g^{-1} (Figure 7). The lowest concentration was found at Lake Bornsjön and maximum concentrations were measured at Barnhusviken. Average concentrations at Barnhusviken, Årstadal, Kastellholmen and Saltsjön exceed 25 µg g^{-1}.

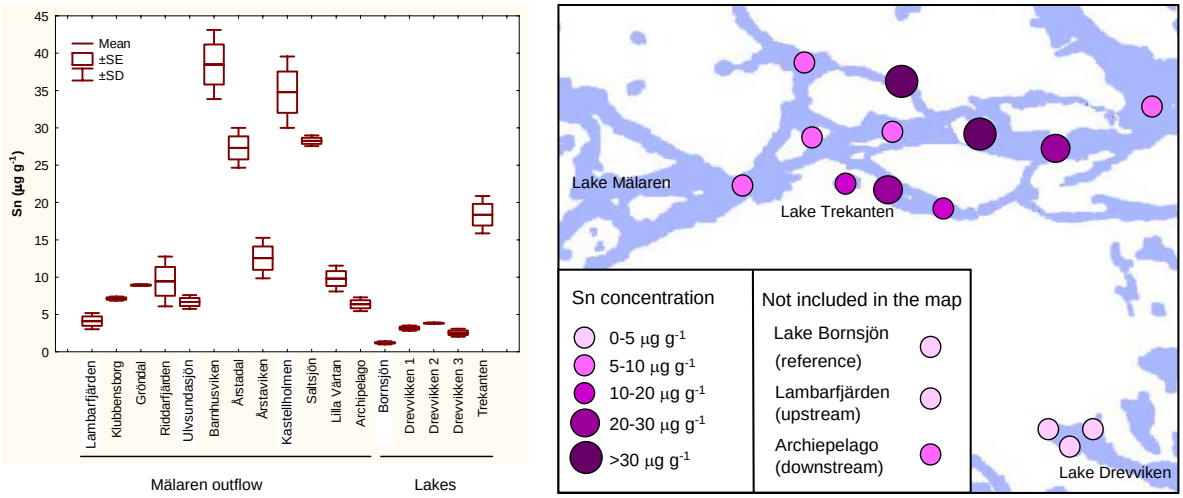

Figure 7. Sn concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution.

Copper, zinc, lead, chromium and cadmium

Copper, zinc, lead, chromium and cadmium are among the metals for which the Swedish Environmental Protection Agency (EPA) has provided guideline concentrations for sediments (Table 2).

Table 2. Swedish EPA classification of metal contaminated sediments (mg/kg dry weight, surface sediments (0–1 cm)).

Metal	Class 1 Very low content (Mycket låg)	Class 2 Low content (Låg halt)	Class 3 Moderately high content (Måttligt hög)	Class 4 High content (Hög)	Class 5 Very high content (Mycket hög)
			µg g^{-1}		
Cd	< 0,8	0,8–2	2–7	7–35	> 35
Cr	< 10	10–20	20–100	100–500	> 500
Cu	< 15	15–25	25–100	100–500	> 500
Pb	< 50	50–150	150–400	400–2000	> 2000
Zn	< 150	150–300	300–1000	1000–5000	> 5000

Copper concentrations in surface sediments across Stockholm range from 27 to 475 µg g^{-1}. Concentrations are presented in Figure 8 according to the Swedish EPA sediment concentration categories. The lowest concentration is observed at Lake Bornsjön, whereas in Lake Mälaren (Lambarfjärden) had moderately high concentration and highest concentrations are found in the city area. Cu concentrations were found to be high according to Swedish EPA categories at most sampling sites. Low Cu concentrations were only found at Lake Bornsjön, whereas Cu concentrations were moderately high in Lake Mälaren sediments.

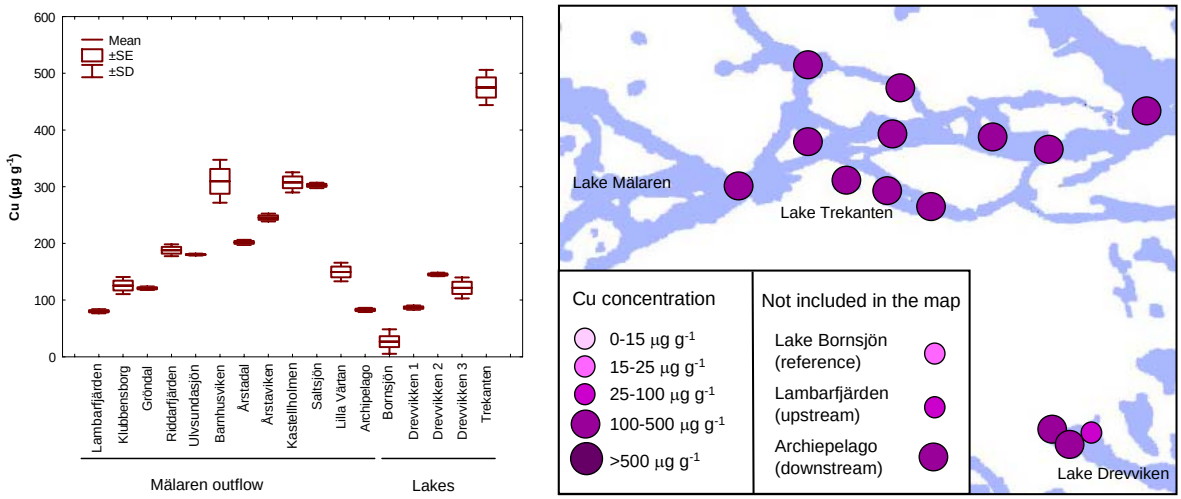

Figure 8. Cu concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution (categories corresponding to Swedish EPA sediment classification (Table 2)).

Zinc concentrations in surface sediments across Stockholm range from 76 to 1200 µg g^{-1}. Concentrations are presented in Figure 9 with the map showing concentrations according to the Swedish EPA sediment concentration categories. The lowest concentration is observed at Lake Bornsjön, whereas concentration in Lake Mälaren (Lambarfjärden) is moderately high. The highest concentrations are found in the inner city area, where concentrations are moderately high at most sites and high at Lake Trekanten.

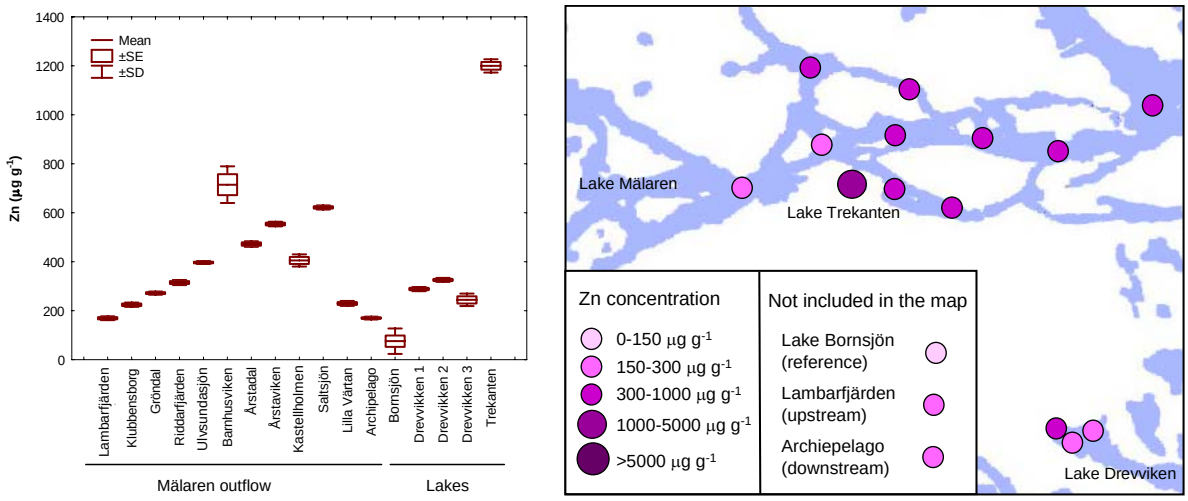

Figure 9. Zn concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution (categories corresponding to Swedish EPA sediment classification (Table 2)).

Lead concentrations in surface sediments across Stockholm range from 15 to 772 µg g^{-1}. Concentrations are presented in Figure 10 with the map showing concentrations according to the Swedish EPA sediment concentration categories. The lowest concentration is observed at Lake Bornsjön, Lambafjarden and Klubbensborg. Urban concentrations are in general moderately high, with high concentrations only observed at Årstadal.

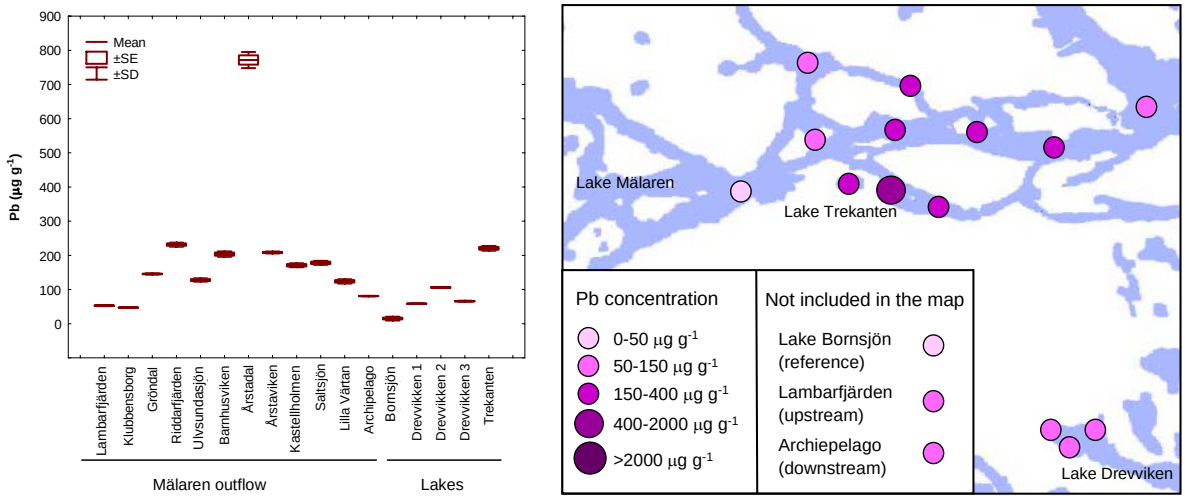

Figure 10. Pb concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution (categories corresponding to Swedish EPA sediment classification (Table 2)).

Cadmium concentrations in surface sediments across Stockholm range from 0.4 to 4.0 µg g^{-1}. Concentrations are presented in Figure 11 with the map showing concentrations according to the Swedish EPA sediment concentration categories. The lowest concentrations are observed at Lake Bornsjön and at Lambarfjärden. Urban concentrations are in general low or moderately high.

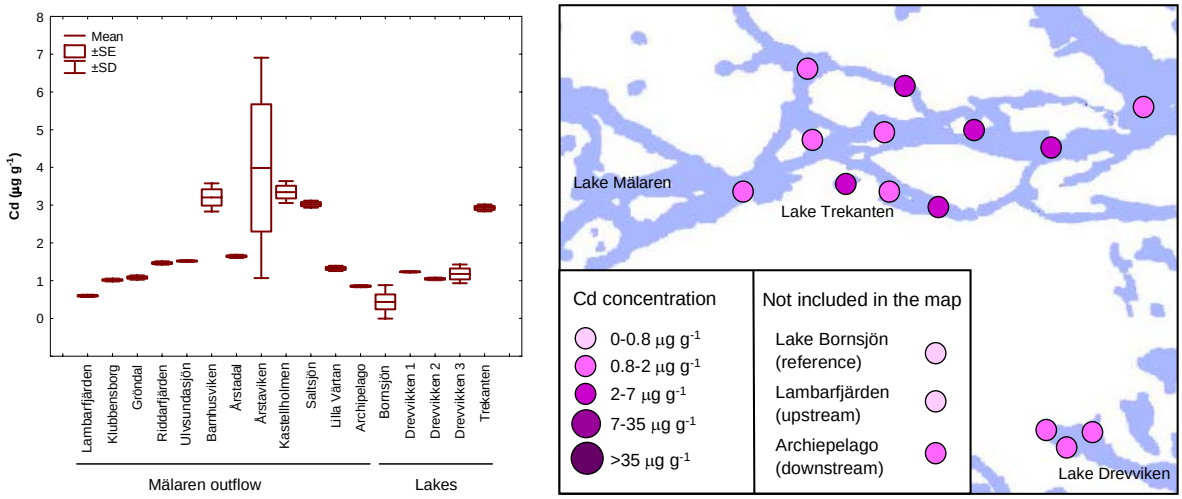

Figure 11. Cd concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution (categories corresponding to Swedish EPA sediment classification (Table 2)).

Chromium concentrations in surface sediments across Stockholm range from 27 to 77 μg g^{-1}. Concentrations are presented in Figure 12 with the map showing concentrations according to the Swedish EPA sediment concentration categories. All measured concentrations were moderately high. The lowest concentration is observed at Lake Bornsjön and concentrations in the outflow of Lake Mälaren were higher than in the lakes.

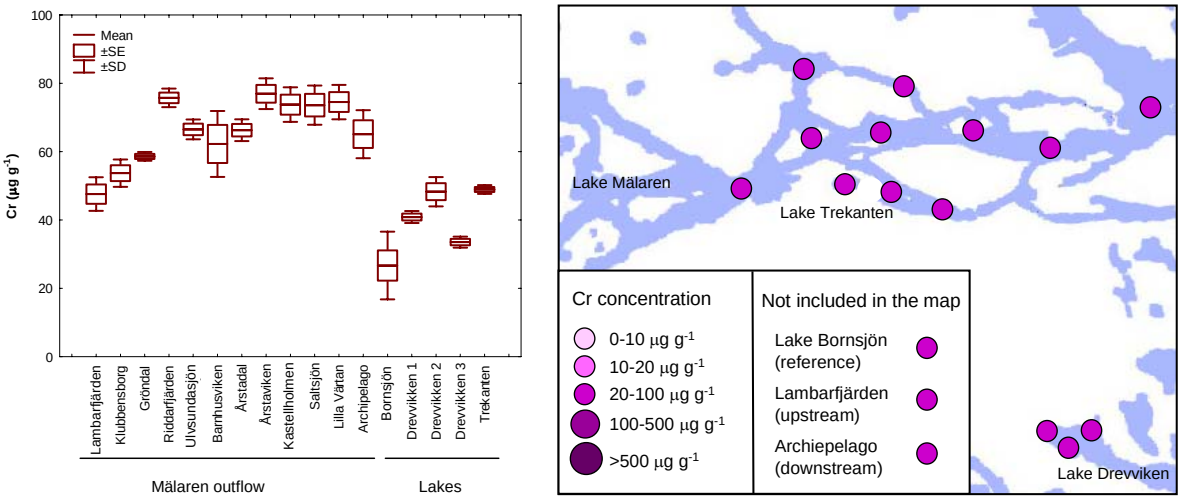

Figure 12. Cr concentrations in surface sediments across Stockholm; (left) Concentration box-plot; (right) Map presenting average concentration distribution (categories corresponding to Swedish EPA sediment classification (Table 2)).

Background concentrations

Comparison of Lake Bornsjön and Lake Mälaren (Lambarfjärden)

Because Lake Mälaren is the primary drinking water supply for Stockholm and Lake Bornsjön provides an alternative drinking water source in case of contamination of Lake Mälaren waters by upstream activities, it is important to determine the concentrations of potential contaminants in these lakes. In addition, these 2 lakes provide background sites for this study owing to relatively low metal contamination (Figures 2-12).
Comparison of the two sites for measured elements is provided in Table 3. The results show that concentrations for most elements are lower in Lake Bornsjön than in Lake Mälaren, possibly due to upstream sources. Several municipalities are located on the shores of Lake Mälaren, including Västerås which has a population over 100,000 and is an important industrial center. Anthropogenic contamination of Lake Mälaren is therefore likely, but the contamination measured at Lambarfjärden is moderate. Because contamination upstream from Stockholm might affect concentrations at Lambarfjärden, concentrations measured in Lake Bjornsjon are used as background for this study.
Average concentrations estimated for the Earth's upper continental crust (UCC) (McLennan, 2001; Peucker-Ehrenbrink and Jahn, 2001) provide an indication of expected natural levels despite local variations in crustal composition. UCC concentration estimates are given in Table 3 for comparison. UCC concentrations in the lakes are in general in the same order as in Lake Bornsjön, indicating that contamination at this site is limited.

Table 3. Comparison of trace element concentrations in the Upper continental crust and in Lake Bornsjon and at Lambafjarden.

Element	UCC	Bornsjön	Lambarfjärden
Pt, ng g^{-1}	0.5	1.3	2.4
Rh, ng g^{-1}	0.03	0.3	0.8
Ag, μg g^{-1}	0.05	0.16	0.5
W, μg g^{-1}	2.0	1.1	2.0
Cu, μg g^{-1}	25	27	80
Zn, μg g^{-1}	71	75	170
Cr, μg g^{-1}	83	27	48
Pb, μg g^{-1}	17	15	53
Cd, μg g^{-1}	0.1	0.4	0.6
Sn, μg g^{-1}	5.5	1.2	4.1
Sb, μg g^{-1}	0.2	0.1	0.2

Comparison of background and contaminated sites

The comparison of concentrations at background and contaminated sites gives an indication of the anthropogenic input of specific elements. Table 4 gives concentrations at Lake Bornsjön (background) and selected contaminated sites (Lake Trekanten and Kastellholmen), as well as maximum measured concentrations for each element. The maximum-to-background ratio provides information on the maximum level of contamination. This was preferred to median or mean because each site is considered important.

Table 4. Comparison of trace element concentrations in Bornsjön (mean of the two samples), Trekanten, Kastellholmen and maximum measured concentrations.

Element	Lake Bornsjön	Lake Trekanten	Kastellholmen	Max. concentration	Max.-to-background ratio
Pt, ng g^{-1}	1.3	18	15	26	20
Rh, ng g^{-1}	0.3	4	3.8	5.1	17
Ag, μg g^{-1}	0.16	8.5	8.3	8.5	53
W, μg g^{-1}	1.1	33	24	37	34
Cu, μg g^{-1}	27	475	308	475	18
Zn, μg g^{-1}	75	1200	405	1200	16
Cr, μg g^{-1}	27	49	74	77	3
Pb, μg g^{-1}	15	221	171	772	51
Cd, μg g^{-1}	0.4	2.9	3.3	4.0	10
Sn, μg g^{-1}	1.2	18	35	38	32
Sb, μg g^{-1}	0.1	2.6	1.1	8.9	89

Except for Cr, trace element concentrations at the selected contaminated sites are at least 1 order of magnitude larger than background concentrations, indicating an anthropogenic input. The maximum-to-background concentration ratio ranges from 3 for Cr to 89 for Sb with Sb, Ag and Pb having ratio larger than 50. Both Pt and Rh were found to have ratios of approx. 20. However, the maximum-to-background concentration ratio may only reflect input at one site and further analysis is needed to determine if elevated concentrations is a local problem (linked to a specific local source) or a general problem (resulting from widespread sources) in Stockholm.

Trace element source characterization

The determination of trace element sources to sediments in the Stockholm area was determined by comparison with background concentrations, the study of spatial patterns and statistical analysis of the concentration dataset.

Reported urban trace element sources

Sources of analysed trace elements reported in the literature are listed in Table 5. Whereas several elements have multiple sources, few elements have a single (Pt, Rh, W) or a limited number of sources (Ag, Cr) making them useful tracers for source characterization.

Table 5. Reported sources of analysed trace elements.

Element	Source	Note	Reference
Pt	Vehicles (catalysts)		(Palacios et al., 2000)
Rh	Vehicles (catalysts)		(Palacios et al., 2000)
Ag	Sewage (from photographic use) Electronics		(Bothner et al., 1998) (Sternbeck and Östlund, 1999)
W	Vehicles (tyre studs)	Sweden	(Karlsson et al., 2006)
Cu	Vehicles (tyres, brakes) Boat paints Buildings (roofs/fronts) Drinking water pipes Aerial powerlines and electrical grounding Road pavements	Stockholm	(Bergbäck et al., 2001)
Zn	Vehicles (tyres, brakes) Boats (Sacrificial anodes) Buildings (roofs/fronts) Galvanised goods Road pavements	Stockholm	(Bergbäck et al., 2001)
Cr	Vehicles (tyres, brakes) Road pavements	Stockholm	(Bergbäck et al., 2001)
Cd	Vehicles (tyres, brakes, petrol) Road pavements Paint Fertilizers Combustion (fossil fuel, waste)	Stockholm	(Bergbäck et al., 2001) (WHO, 1992)
Pb	Vehicles (tyres, brakes, petrol) Buildings (chimney collars, wood preservatives)	Stockholm	(Bergbäck et al., 2001)
Sn	Boats (antifouling paints) Buildings (wood preservatives, PVC stabilisers) Textiles and materials	Organotin compounds	(Hoch, 2001)
Sb	Vehicles (brakes, fuel) Flame retardants (especially waste deposits and incineration) Combustion products (fuel, waste incineration, metal smelting)		(Sternbeck and Östlund, 1999)

Interpretation of spatial trends

Several spatial trends are of interest in the perspective of source characterization, as described below.

1. an increase in concentration from Lambarfjärden to Klubbensborg and Gröndal indicates an urban source;
2. a decrease in concentration from Saltsjön to Lilla Värtan and the archipelago further supports the urban source (1), although the absence of such a trend could be the result of transport downstream and does not invalidate assumption 1.
3. Elevated concentrations at specific sampling points indicate a local source, possibly industry;
4. A concentration gradient at Drevviken in the order Drevviken 2 > Drevviken 3 > Drevviken 1 supports an automobile or traffic-related source owing to the proximity to the highway and stormwater input. Only elements with a ratio of 2 (Drevviken 2 : Drevviken 1) are listed for the trend to be significant.

The evaluation of potential sources based on these criteria is presented in Table 6. In summary,

- Most elements were found to have urban sources.
- Concentrations were elevated for several elements at Årstadal and/or Trekanten.
- Several elements were found to have an automobile-related source.

Table 6. List of sources of metals determined based on spatial trends.

Source characterization	Elements
Urban (criterion 1; confirmed by criterion 2 in bold)	**Pt**, **Rh**, Ag, **Sb**, **Sn**, **Cu**, **Zn**, **Pb**, **Cd**, Cr
Elevated concentrations at specific sampling points (criterion 3)	W (Årstadal, Trekanten), Sb (Årstadal), Sn (Årstadal, Trekanten), Cu (Trekanten), Zn (Trekanten), Pb (Årstadal)
Automobile traffic (criterion 4)	Pt, Rh, W, Sb

Most elements analyzed were found to have urban sources characterized by a concentration increase from Lambarfjärden to Klubbensborg, and in most cases a decrease from Saltsjön to the archipelago site. The only exception is W. Typical sources of metals in the urban environment include automobile traffic, sewage and leaching from building materials. Several metals were found at elevated concentrations at Årstadal and/or Trekanten, i.e. W, Sb, Sn, Cu, Zn and Pb. The sampling locations are located within 2 km of each other and it is possible that specific local sources affect both sites. The Årstadal watershed includes 12% characterised as environmentally hazardous comprising industries and a goods terminal (Stockholm Vatten, 2000). Industries include Sandvik Coromant, an enterprise which has a permit to emit W and Co. Sb is not meantioned in the permit but may be present in the emissions.

Pt, Rh, W and Sb were found to have an automobile source. In addition several elements displayed a trend at Lake Drevviken, but did not fulfill the 2x criterion, i.e. Cu, Pb, Cr, Zn and Sn. Among these elements, Pb has formerly been used as fuel additive and even if Pb use is now banned, contamination occurs in the fuel supply chain as a result of remaining Pb traces (Degobert, 1995).

Statistical source characterization

Statistical methods were applied to source characterization for elements.

1. Correlation between elements
2. principal component analysis

Correlation between 2 elements provides a strong indication for a single source. Therefore, coefficient of determination (R^2, square of the correlation coefficient) were calculated and are provided in a correlation matrix (Table 7). The matrix allows to determine groups of metals correlating with each other.

- Cu, Zn, Cd, Ag, Sn
- W, Sb, Pb
- Pt, Rh

Table 7. Numerical correlation (R^2) matrix; Values in bold correspond to R^2>0.8 and p<0.05.

	Cr	Cu	Zn	Ag	Cd	Sn	Sb	W	Pb	Pt	Rh
Cr	*1.00*	0.55	0.41	0.70	0.64	0.60	0.32	0.37	0.50	0.42	0.33
Cu	0.55	*1.00*	**0.96**	**0.84**	**0.88**	**0.81**	0.55	0.79	0.60	0.76	0.74
Zn	0.41	**0.96**	*1.00*	0.73	**0.81**	0.71	0.61	0.78	0.62	0.72	0.72
Ag	0.70	**0.84**	0.73	*1.00*	**0.80**	0.79	0.32	0.56	0.39	0.65	0.56
Cd	0.64	**0.88**	**0.81**	**0.80**	*1.00*	**0.81**	0.41	0.67	0.51	0.65	0.63
Sn	0.60	**0.81**	0.71	0.79	**0.81**	*1.00*	0.61	0.72	0.67	0.67	0.69
Sb	0.32	0.55	0.61	0.32	0.41	0.61	*1.00*	**0.84**	**0.97**	0.44	0.48
W	0.37	0.79	0.78	0.56	0.67	0.72	**0.84**	*1.00*	**0.83**	0.51	0.51
Pb	0.50	0.60	0.62	0.39	0.51	0.67	**0.97**	**0.83**	*1.00*	0.42	0.45
Pt	0.42	0.76	0.72	0.65	0.65	0.67	0.44	0.51	0.42	*1.00*	**0.94**
Rh	0.33	0.74	0.72	0.56	0.63	0.69	0.48	0.51	0.45	**0.94**	*1.00*

Further observation of the data (Figure 13) shows that correlation or absence of correlation may be the result of outliers. For instance, the absence of correlation between Sb and Cu is due to the presence of 2 data points with elevated Sb concentrations (Årstadal and Trekanten). In contrast, the correlation between Pb and W is largely due one data point with elevated Pb and W concentrations.

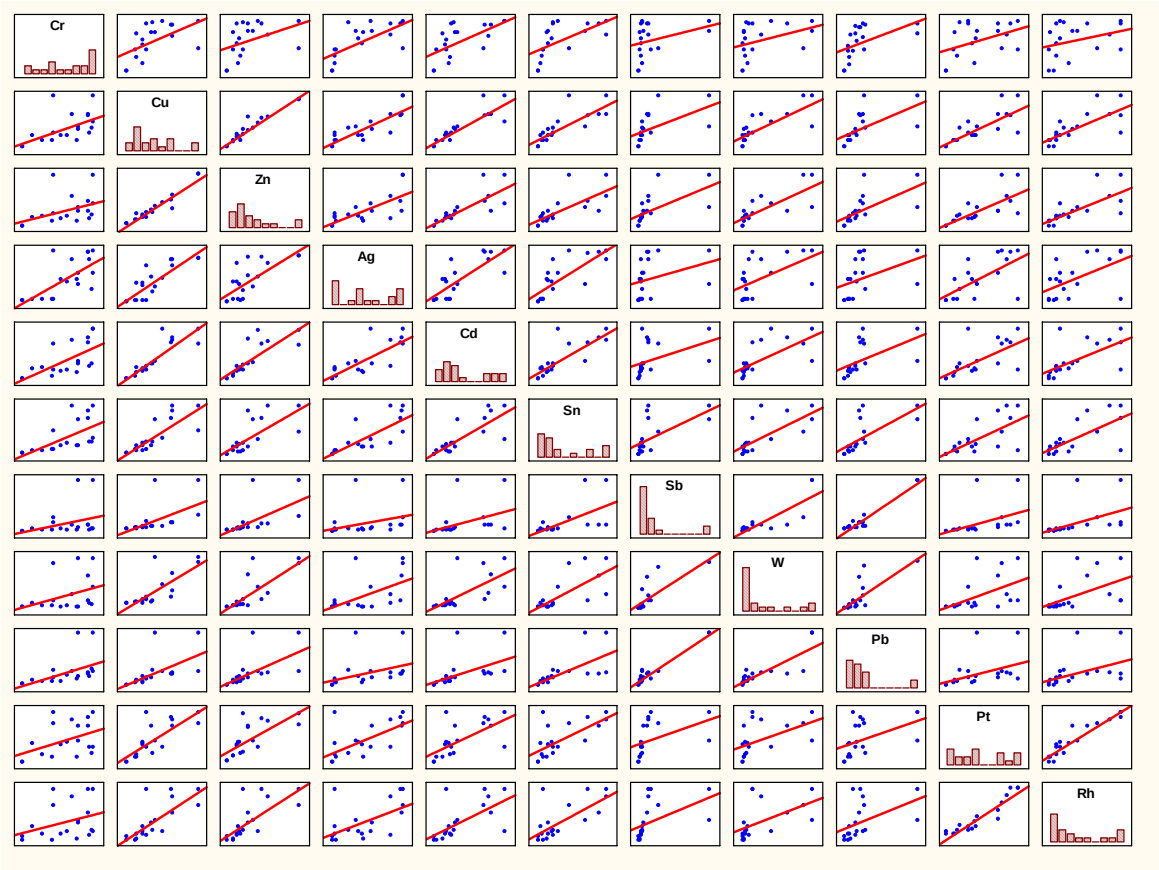

Figure 13. Graphical correlation matrix. The correlation matrix shows all the data points used in the calculation of correlation (Table 7) and provide further details on the absence or presence of correlation between 2 elements. Bar graphs describe the distribution of data points across the concentration range.

In addition, characterization of potential sources was performed by principal component analysis (PCA). PCA is generally used to reduce the number of variables and detect structures in the relationship between variables. This technique was therefore applied to the dataset to determine structures (groups) of elements based on their spatial distribution. Result of the PCA are presented as projection of factors 1, 2 and 3, which represent 87% of the variability in the dataset, thereby accounting for most of the variability (Figure 14).

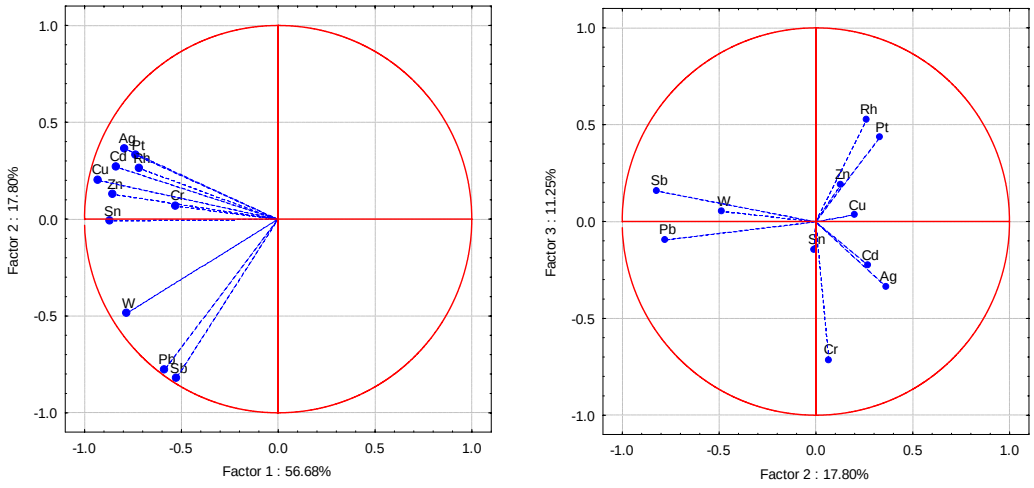

Figure 14. Projection on the factor plane of PCA factors 1, 2 and 3.

The PCA shows that Factor 1 does not allow separating elements from each other and Factor 1 is therefore a common feature of all elements, possibly the higher concentrations observed at urban sites (especially in the inner city) compared with non-urban sites. In contrast, Factors 2 and 3 allow separating analysed elements into distinct groups. Based on Factor 2, W, Pb and Sb are identified as 1 or 2 distinct groups. In addition, based on both Factors 2 and 3, (Pt, Rh), (Cd, Ag), (Zn, Cu) and (Pb,W, Sb) were identified as groups. It is important to note that only (Pb,W, Sb) could be distinguished from the other elements based on Factor 2 and therefore, some similarities exist between (Pt, Rh), (Cd, Ag) and (Zn, Cu).

Sources of trace elements in Stockholm

Platinum and rhodium

Platinum and rhodium are elements with limited uses (Table 5). Automobile catalysts, which use Pt and Rh for the treatment of exhaust gases from the engine, are the main application for these elements. Other important applications of Pt include jewelry and electronics, but emission from these uses is expected to be relatively limited. Pt and Rh are emitted from the catalysts during vehicle operation (Palacios et al., 2000; Moldovan et al., 2003) and catalysts have been identified as the main source of Pt and Rh in the urban environment (Zereini and Alt, 2000; Ely et al., 2001; Rauch et al., 2001; Gomez et al., 2002; Rauch et al., 2004; Zereini et al., 2004). An automobile source in Stockholm is supported by spatial distribution, as well as an average Pt/Rh ratio of 4.5±1.0 in the urban area and at the site closest to the road at Lake Drevviken, the ratio reflecting typical catalyst composition.

Lead, antimony and tungsten

Sb and W have been found to have an automobile source based on concentrations at Lake Drevviken. However comparison with Pt and Rh (absence of correlation, PCA and relative concentrations at Lake Drevviken and in the city area) indicates that vehicles are not the main source of W in the inner city (Årstadal, Årstaviken, Kastellholmen and Trekanten). Similarly, automobile emissions are a major source of Sb, although undefined sources are an important local source of Sb at Årstadal and Trekanten.

Pb concentrations only exhibit a relatively small gradient at Lake Drevviken. Although this indicates that traffic is a relatively small source of Pb due to the ban of leaded gasoline, comparison of urban levels and concentrations at Drevviken indicate that traffic is a relatively important source of Pb in Stockholm. Other sources (chimney collars, wood preservatives) are also contributing to urban Pb levels. In addition to diffuse sources, the distinctly high Pb concentration at Årstadal indicates the presence of a local source, possibly also contributing to levels in Lake Trekanten.

Elevated Pb, Sb and W concentrations at Årstadal and Årstaviken indicated an industrial source at these sites.

Silver and cadmium

Ag is present at elevated concentration throughout the urban area indicating a widespread urban source for this element. Concentration levels and spatial patterns at Lake Drevviken does not support an automobile source. Ag concentrations are elevated at all urban sites starting from the entrance into the urban area (Klubbensborg) with highest concentrations in the inner city, indicating an urban emission of Ag. Ag has been used as a tracer for sewage input as a result of the use of Ag in photography (Bothner et al., 1994; Bothner et al., 1998; Bothner et al., 2002). Despite the decreasing use of Ag in photography (due the increasing use of digital cameras), photography may still be a source of Ag. Another potential source of Ag

is the use of Ag as antibacterial agent in products including refrigerators, clothes (especially underwear) and medicinal equipments.
As for Ag, Cd was not found to have an automobile source. Table 5 lists road pavements, paint, fertilizers and combustion of fossil fuels and wastes. However, fertilizers are probably a small source at urban sites where highest concentrations were found. A road pavement source was assessed by comparing concentrations with road area in the catchment corresponding to each site, although sedimentation and upstream input render the comparison difficult. The comparison shows however that road pavements are a viable source of Cd.
Apparently, there are no common sources for Ag and Cd. This study shows however that these 2 elements have a similar distribution pattern, possibly due to the distribution of emissions across Stockholm.

Copper and Zinc
Copper and Zinc were found to have similar distributions and are therefore expected to have similar sources. Both metals were found to be released by automobile traffic, but traffic is not expected to be the main source in the urban area. Buildings (roofs/fronts) are likely sources as this is a common use for both elements. Other sources (Table 5) may also contribute to the measured concentrations.

Chromium and tin
Neither Cr nor Sn were found to be associated with any other elements, indicating that these elements have distinct sources. Cr concentrations are moderate throughout the city area, but the maximum-to-background concentration ratio of 3 indicate that anthropogenic sources are of relatively limited importance, possibly including automobile emissions and leaching from roads. A possibly important source of Sn in the aquatic environment is antifouling paints used to protect ships from algal growth. Other Sn sources may include leaching from building materials.

Potential risks

Sediment quality guideline values have been defined by the Swedish EPA for several elements, including Cu, Cd, Cr, Pb, and Zn (Table 2). Copper is present at high concentrations (100-500 $\mu g\ g^{-1}$) at most sites with the exception of Lake Bornsjön, Lambarfjarden and one site in the Lake Drevviken (Figure 9). In contrast, other elements have high concentrations at a limited number of sites and therefore Cu is a major concern, although none of the Cu concentrations are very high. Zn and Pb concentrations are only high in Lake Trekanten. Both Cd and Cr are not found at high concentrations, but Cr is present at moderately high concentrations at all sampling sites.
In addition to guidelines from the Swedish EPA, probable effect concentration (PEC, concentration above which adverse effects are expected) and apparent effect threshold concentrations (AET, concentration of a selected chemical above which statistically significant biological effects always occur) provide further indicators of potential risks (Table 8). Measured concentrations exceeded PEC at 9 sites for Cu, 5 sites for Zn and 9 sites for Pb. PEC concentrations were not exceeded for Cd and Cr.
The AET concentration for Sb is exceeded at Årstadal where a concentration of 8.9 $\mu g\ g^{-1}$ has been measured, whereas concentrations at all other sites were below the AET concentration. The AET concentration for Ag is exceeded at 7 sites. Ag concentrations at 9 sites also exceed the guideline value of 3.7 $\mu g\ g^{-1}$ associated with frequent adverse effects to marine organisms (Bothner et al., 1998), raising concern over Ag concentrations in the Stockholm area.

Other elements have no define guideline values and the potential risks associated with their elevated concentrations are therefore difficult to define.

Table 8. Sediment quality guidelines values.

Metal	High/very high content (Swedish EPA)	Apparent effect threshold[a]	Probable effect concentration[b]
		$\mu g\ g^{-1}$	
Cd	>7	7.6	4.98
Cr	>100	280	111
Cu	>100	840	149
Pb	>400	260	128
Zn	>1000	520	459
Ag	--	4.5	
Sb	--	3.0	

a. (Cubbage et al., 1997)
b. (USEPA, 2000)

Another important point is the large export of Ag into the Baltic Sea expected from the relatively high Ag concentrations downstream from Stockholm. Further work is needed to quantitatively assess this export and its environmental relevance.

Uncertainties

Sampling and sample heterogeneity

Sample heterogeneity appears to have a limited influence on concentrations for most elements and most sampling sites (Figure 2-12). Although concentrations may vary locally, the observed concentration variability indicates that concentration levels and spatial trends are consistent.

Sample preparation and analysis

Analysis of blanks, reference material BCR-723 and comparison with previous results provide confidence in the sample preparation and analysis. Measured Pt and Rh concentrations in BCR-723 (road dust) were in the certified range. Results for Cd, Cr, Cu, Pb, Zn are in the same range as previously reported and similar spatial trends were found (Jonsson, 2000; Lindström et al., 2001). Procedural blanks were prepared and analysed randomly. Blank values do not show any sign of contamination.

Note on the cores

Two sediment cores were collected in the outflow of Lake Mälaren (Riddarfjarden and Kastellholmen). None of the expected trends, e.g. increasing Pt and Rh concentrations following the introduction of automobile catalysts and decreasing Pb concentrations resulting from the ban of leaded gasoline, were found. It is likely that the sediment record is poorly preserved due to unstable accumulation resulting from water flow at the sampling locations. An unstable accumulation is also supported by the absence of trends in water content (average water content, core 1 (Kastellholmen) = 86%, core 2 (Riddarfjarden) = 71%) and organic content (average loss of ignition based on dry weight, core 1 (Kastellholmen) = 17%, core 2 (Riddarfjarden) = 9%) in the cores. Results are therefore not provided here.

Conclusions

The present study shows that elevated trace element concentrations are found in sediments in Stockholm as a result of urban contamination. Copper is present at high concentrations at most sampled sites according to Swedish EPA sediment concentration guideline, indicating a potential risk. Zn and Pb are only present at high concentrations at specific sites. In addition, Ag concentrations exceed the apparent threshold concentration for Ag at several sites, whereas it is exceeded at one site for Sb. Urban emissions of Pt, Rh and W were also found, but no guideline exist for these metals making the assessment of potential risks difficult. Measured Pt and Rh concentrations are typical of urban areas with dense automobile traffic. Sources of trace elements include automobile traffic, urban surfaces (road pavement), buildings and combustion, as well as location specific sources. The spatial distribution of trace elements in sediments demonstrates that the contamination is the result of diffuse sources and it is therefore difficult to control. Automobile traffic is a major source of trace elements and traffic reduction policies to be implemented in Stockholm may help reduced trace element input. The determination of location specific sources (possibly industrial emissions) may also allow to reduce locally elevated concentrations. In contrast, leaching from building materials and road pavement is difficult to reduce.

Recommendations

- Contamination of Lake Mälaren upstream from Stockholm is resulting in higher sediment concentrations than in Lake Bornsjön. Although the level of this contamination is low, regular analysis needs to be performed to ensure that this contamination is not a threat for the use of Lake Mälaren as drinking water supply. Lake Bornsjön provides a safer drinking water supply.
- The source of trace elements pollution at Årstadal and Trekanten should be identified and controlled.
- Trace element levels at Lake Trekanten are high and the recreational use of the lake needs to be carefully reconsidered with additional measurements in the water.
- The treatment of stormwater from the highway at Lake Drevviken does not efficient remove trace metals. Improvements need to be made to improve the performance of this facility.
- Pt and Rh are useful tracers for contamination from automobile traffic. As the city of Stockholm is planning to implement a new policy that is expected to lead to less traffic in the city area, monitoring Pt and Rh in sediments, as well as in the other urban samples (stormwater and road dust), could provide an assessment of the impact of the policy on trace metal pollution.

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