THE TRACE OF METALS

USE, EMISSIONS AND SEDIMENT LOAD OF URBAN HEAVY METALS

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V. Jonsson, A. and L. Sörme: “Sources of Copper and Zinc to the aquatic recipients of Stockholm, Sweden” Manuscript
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Sammanfattning


Tidigare har miljöforskning mest sysslats med att undersöka föroreningar i naturen, deras spridning och effekter. På senare tid har det dock utvecklats flera forskningsfält som försöker identifiera potentiella miljöproblem på ett tidigare stadium, bland annat genom att analysera samhällets användning av olika material. Materialflödesanalys är ett verktyg som har använts för att studera dessa flöden. I denna avhandling presenteras en utökad materialflödesanalys, som även inkluderar flödet av metallerna i naturen, närmare bestämt till bottensediment i sjöar och hav. Fem metaller valdes ut: kadmium (Cd), koppar (Cu), kvicksilver (Hg), bly (Pb) och zink (Zn), och studieområdet är Stockholm. För dessa metaller knyts alltså användningen i samhället ("samhällsmetabolismen") ihop med utsläpp utomhus, till exempel via reningsverk och dagvatten, och belastningen på sedimentet.

Med hjälp av arkivmaterial, offentlig statistik, kontakter med branschorganisationer m.m. har användningen och utsläppen av dessa metaller i Stockholm uppskattats. För Cd, Pb och Hg har den historiska utvecklingen kunnat beskrivas. Denna utveckling har sedan jämförts med beräkningar av hur sedimentbelastningen har utvecklats, baserat på analys av sedimentprover från Mälaren och Stockholms skärgård.

Eftersom sedimenten i stora delar av Stockholmsområdet är syrefria, finns det inga bottenlevande organismer som blandar om dem. Detta gör att sedimentpartiklarna ligger i ordnade lager i den ordning de avsattes. I det lager som avsattes 1986 finns i sediment från Stockholmsområdet tydligt förhöjda halter av den radioaktiva isotopen Cs-137 som spreds över stora områden vid kärnkraftsolyckan i Tjernobyl. Med hjälp av denna markering kan man beräkna hur mycket sediment som avsättas per år, och följa den sedan området på ett viss nivå.
På så vis kan man med hjälp av sedimentkärnor beräkna hur belastningen av metaller har utvecklats över tiden.

Resultaten visar att Hg har använts i stora mängder under flera hundra år i Stockholm. Denna användning har ofta givit upphov till stora utsläpp till miljön. Efter andra världskriget ökade både användningen och utsläppen dramatiskt. Under de senaste 30 åren har dock användningen av Cd, Hg och Pb minskat som en följd av lagstiftning och teknisk utveckling. Detta har gjort att även utsläppen har minskat markant, liksom metalldepositionen från atmosfären, och att belastningen på sedimenten har blivit mindre. Däremot har sedimentbelastningen inte minskat lika snabbt som tillförseln av metaller till vattenområdena, vilket gör att det nu saknas någon källa i budgeten för dessa metaller i det studerade området. Sådana källor kan vara diffusa, icke-analyserade utsläpp, eller internbelastning, dvs gammalt förorenat sedimentmaterial återförs till vattnet och sedimentar igen. För Cu är tillförseln av metaller ungefär lika stor som sedimentationen, medan Zn verkar exporteras ut från området till öppna Östersjön.

Fortfarande är halten av de studerade metallerna mycket förhöjd i området, särskilt i Stockholms innerstad, där avvikelsen från naturliga halter för alla fem metaller bedömdes som ”mycket stor”, vilket är den högsta klassen i Naturvårdsverkets bedömningsgrunder för metaller i sediment. Situationen är särskilt allvarlig eftersom metallerna kan komma att återföras till vattnet, och komma in i näringskedjorna. En sådan utveckling har ibland beskrivits som en kemisk tidsbomb eftersom förändringen kan komma mycket hastigt.
Preface

This thesis has been written in an interdisciplinary environment. Among my co-authors are two engineers, a physical geographer, a historian, a chemist and a biologist. On top of that my supervisor has a PhD in entomology. It is my hope that this mix is reflected in the work presented, which combines a material flux perspective with environmental chemistry. A general aim has been to present an integrated view of metal fluxes in an urban environment. However, this view had to be broken down to be presented in the form of scientific papers. The work centres on combining the study of sediments with an analysis of the use and emission of metals from the human society, and these perspectives should not be separated. Neither was it appropriate to discuss the different metals separately. The papers, therefore, present a combination of these: The first one discusses the history of mercury use in Stockholm. The second presents data on present-day sediment loads of several metals. Paper III integrates the history of mercury use with the reconstructed sediment load data, from sediment cores by means of a model of urban mercury fluxes. Paper IV uses a budget approach to describe how the regulations imposed on different uses of cadmium and lead have reduced the environmental fluxes of these metals, including the sediment load. In Paper V a similar budget is presented for present conditions for copper and zinc. In this thesis I have concentrated on bringing together the results from the different papers and have taken the opportunity to make some comparisons not possible in the separate papers.
Introduction

Human society is becoming increasingly urbanized. In 1950 only 14% of the world’s population lived in cities, today the number is around 50% globally, and at least 75% in the industrialized world (Baccini and Brunner, 1991; Rees and Wackernagel, 1996). Since the process of urbanization has been paralleled by an increase in the utilization of energy and materials, cities have become nodes of the so-called industrial metabolism. Furthermore, as the emissions of many pollutants have shifted from local, well-defined point sources related to production activities, to diffuse consumption emissions, urban areas have become hot spots of pollution, for example in relation to heavy metals (Bergbäck, 1992).

Despite this, urban areas have generally not received much attention in terms of environmental research. More extensive habitats such as forests, agricultural land and the open ocean have attracted more heavily investigated.

The use of metals has been an essential aspect of industrialization (Bergbäck et al., acc.). In fact, metals have been intimately related to the technological development of mankind for thousands of years. Recently, metals have been widely used for such purposes as structural elements, plating, in electrical appliances, in pigments, and as additives in plastics, paints and fuels. Although the use of some metals has a long history, the 20th century has seen a rapid increase in the turnover of most of them, as well as the introduction of “new” metals, previously of little or no industrial interest. On a global scale, the fluxes of most metals through the society now exceed the natural fluxes from weathering, volcanic activities etc (Nriagu, 1990; Nriagu and Pacyna, 1988). Although in some environments natural sources may be considerable, in urban areas the anthropogenic fluxes are probably even more dominant.

Not all metals have the same environmental impact. Some are potent toxins, some are essential trace elements, and for some the ecotoxicological properties are not well known. The first of these categories includes metals such as lead (Pb), mercury (Hg) and cadmium (Cd). These are not thought to be essential to any species and their adverse effects, even at low concentrations, are well documented. Therefore, their use is now strictly regulated. For example, lead is no longer allowed as a fuel additive in most industrialized countries, and in Sweden the government has decided that the use of Hg should be totally eliminated (Gov. bill, 1990/ 91:90; 1993/ 94:163). The group of metals that are essential for living organisms also includes the ones most widely used in society, such as iron (Fe), copper (Cu) and zinc (Zn). These metals are major constituents of the so-called technosphere, i.e. the material dimension of human society. Therefore, they are
interesting from a material flux perspective, although their environmental impact is not of major concern in this context. In other environments, e.g. mine waste deposits, their environmental impact may be quite considerable. The third category includes metals such as platinum (Pt), rhodium (Rh) and iridium (Ir), metals that are increasingly used in catalysts and electronic components, but whose effects on the environment are not well studied. This situation is of great concern; we must try to avoid repeating past mistakes.

This thesis focuses on urban turnover and the environmental dispersion of five of these metals: Cd, Hg, Pb, Cu and Zn. This group includes three metals – Cd, Hg and Pb – that still constitute a threat to the environment and to public health, although they have caused extensive environmental concern for a long time. Little concern has centred on Cu and Zn, although from a material flux perspective they are interesting since they are widely used, especially in urban areas, and in products that are exposed to weathering. In the following section these five metals are discussed from an environmental and a toxicological perspective.

The specific aims of this thesis are:

- to investigate the history of the use of selected heavy metals in Stockholm;
- to estimate the metal emissions due to these uses;
- to evaluate the degree of contamination of surface sediments from different parts of the aquatic recipients of Stockholm;
- to calculate the input of metals to sediments in different parts of the aquatic recipients of Stockholm, by analysing the metal content of dated sediment cores;
- to reconstruct the history of this load;
- to compare these fluxes with other heavy metal fluxes in Stockholm, including turn-over at sewage treatment plants (STPs) and atmospheric deposition by applying a mass-balance approach; and
- to assess the relationships between use, emissions, sediment loads and other environmental fluxes of heavy metals.

The discussion relating to metals in the environment focuses on total fluxes of metals. Biological effects and speciation of metals are not addressed specifically, although this is a crucial point when assessing the impact of metals in the environment. For the mass-balance approach a quantitative measure is appropriate, whereas qualitative information would be needed for an in-depth discussion of environmental quality.
Metals in focus

The five metals studied in this work differ widely in their patterns of use, associated legislation, mobility and toxicity. Some brief environmental and toxicological characteristics of these metals are presented below. It should be emphasised that the biological effects of metal pollution are not central to this study, but are discussed to some extent in the following text. In the section below cited references refer to all the information given since the previous reference.

Cadmium (Papers II and IV)

Cadmium is a very rare element in the natural environment, the average concentration in the earth’s crust is 0.11 ppm. Compared with metals such as lead and mercury, it does not have a long history of use. Although discovered in 1817 it was not until the mid 20th century that it was used extensively. Cadmium is produced mainly as a by-product of zinc processing. The total world production in 1997 was 20 000 tonnes (Enghag, 2000).

There are five principal types of products in which Cd is used: pigments for plastics, glass and artists’ paints; stabilizers for PVC and other plastics; protective plating; in alloys; and batteries. In Sweden the ‘cadmium-ban’ has restricted the first three of these uses since the early 1980s, and has reduced the use of Cd in these applications. However, an increased use of NiCd batteries during the 1980s and 1990s has counteracted this trend, keeping the Cd turnover at a high level. The ‘cadmium ban’ has been effective in shifting use from exposed to protected products, thus it has effectively reduced the emissions (Bergbäck and Jonsson, 1998; Sörme et al., acc.-a), Paper IV. One, easily overlooked, source of Cd in the environment zinc, since zinc metal contains traces of Cd. Different publications quote very different concentrations - between 0.2 and 500 ppm (Lohm et al., 1997). Even low amounts of Cd in Zn metal may be important in comparison to other uses, since Zn is often used in exposed environments.

The major routes of human exposure to Cd are food and tobacco. In Sweden, the mean intake from food is approximately 15 µg/day, corresponding to 25 % of the recommended WHO limit (Alfvén, 1999; Swedish EPA, 1987). Absorption in the gut amounts to 5-8 % of the oral intake (Goyer, 1996). However, intake is highly variable, and may well exceed critical levels in some sections of the population, especially in polluted areas. In the population living close to a former battery plant in southern Sweden a significant correlation was found between Cd levels in urine and renal dysfunction and osteoporosis (Alfvén et al., 2000; Järup et al., 2000).
For the general population the major source of Cd is wheat. The Cd concentration in agricultural soils in Sweden is presently increasing by 0.2 % per year (Alfvén, 1999). The major sources are fertilizers and atmospheric deposition (Hellstrand and Landner, 1998). Cadmium in soil is easily absorbed by plants (Kabata-Pendias and Pendias, 1992) and thus, Cd is a more serious threat to public health than for example Pb or Hg in agricultural land.

A cigarette contains on average 1-2 µg of Cd, of which approximately 10 % is absorbed through the lungs (Goyer, 1996). Thus, smoking 5-10 cigarettes or more per day results in the body absorbing more Cd from cigarettes than from the food, assuming average Swedish intake from food.

In aquatic environments in Sweden high Cd concentrations are correlated with reduced phytoplankton diversity as well as with disturbed carbohydrate metabolism in perch (Perca fluviatilis). The mobility of Cd in soils is dependent on pH. Acid rain increases the runoff of Cd, thus increasing the Cd concentrations in softwater lakes. This adds to the stress already caused in other ways by acid rain. In marine environments, it is reported that high Ca concentrations inhibit the uptake of Cd, thereby reducing its toxicity. However, the relatively low salinity of the Baltic Sea in combination with eutrophication and the heavy load of pollutants, put pressure on many organisms, making them more susceptible to Cd pollution. Between 1980 and 1986 the concentration of Cd in Baltic herring (Clupea harengus) increased by 5-7 % per year. This may have been due to increased leaching of Cd from soils because of acid rain (Parkman et al., 1998).

**Lead (Papers II and IV)**

Lead is relatively abundant in the earth's crust (average 14 ppm), it can readily be extracted from natural minerals, mainly lead glance (PbS), and it has been extracted and used by man for thousands of years (Enghag, 2000). Renberg and co-workers have used sediment cores from lakes to reconstruct the history of lead pollution in Sweden, and found traces of pollution as early as 2000 BC, and more commonly during the Roman era, 200 BC-400 AD (Brännvall et al., 1999; Renberg et al., 2000; Renberg et al., 1994).

The use of lead in Sweden during the period 1880-1980 has been described by Bergbäck et al. (1992) and Anderberg et al. (1990) and its use in Stockholm was described by Lohm et al. (1997) and Sörme et al. (acc.-a). The major uses include fuel additives, pigments, accumulators and ammunition. In Stockholm considerable amounts are still present in cable shielding and pipe joints.

For adults the major route of exposure, besides work-place sources at smelters etc, is through food and tap water. The reduction in the use of lead-soldered cans for food and beverages has reduced lead exposure from food to less than 20 µg/ day, compared with the 400-500 in the 1940s (Goyer, 1996). The contribution from drinking water is less than 10 µg/ day and from inhalation 1 µg/ day.
Infants and toddlers, however, tend to have a much higher level of exposure, since they ingest several times these doses because of hand-to-mouth activities and while investigating the world orally. This behaviour may cause lead exposures detrimental to a child's psychological development and the lead concentrations of soils in the city of Stockholm have therefore caused some concern (Berglund et al., 1994). Dietary intake of lead in women may cause problems of pre-natal exposure. A foetus may be exposed to lead ingested by the mother, or because of mobilization of lead from her bones (Mushak and Mushak, 2000).

The environmental impact of Pb pollution is greatest in forest soils (Notter, 1993). Lead is strongly bound to organic matter, and may thus accumulate for several hundred years in organic soils (Kabata-Pendias and Pendias, 1992). Some Swedish soils have concentrations of Pb likely to affect soil organisms and reduce microbial activity. In heavily contaminated areas higher organisms such as birds and mammals have been affected (Bergbäck and Johansson, 1996). In lakes the bio-availability of Pb is increased by acidification, since the fraction of free Pb$^{2+}$ increases with decreasing pH. In polluted areas of the Baltic Sea there is a greater positive correlation between vertebral defects in fourhorned sculpins (Myoxocephalus quadriornis) and Pb concentrations than for other metals (Notter, 1993).

**Mercury (Papers I, II and III)**

Mercury is even less abundant in the earth's crust than Cd. The average concentration is only 0.05 ppm. Despite this, it has been known for thousands of years, since it is easily extracted from the mineral cinnabar (HgS) which was known as early as the classical Mediterranean antiquity as well as in ancient China (Enghag, 2000).

A detailed description of the history of Hg use in Stockholm is given in Paper I. Mercury was already in use in the late 18th century for gilding and mirror foliation, and during the 19th century its main use was medical (mainly as a treatment for syphilis) became the dominant use, reaching annual turnover rates comparable to modern levels. Interestingly, when antibiotics replaced Hg in medicinal use during the first half of the 20th century, Hg found a new way into the human body as dentists began using amalgam to fill teeth rather than pulling them. After World War II, the toxicity of Hg was made use of in a variety of biocides such as anti-fouling agents and in the pulp and paper industry. In the late 1960s, these biocides were banned in Sweden as the environmental effects of Hg became clear following the disasters at Minamata and Niigata in Japan. Electrical products such as batteries, switches and lighting appliances accounted for a considerable part of the Hg usage during the 1970s and 1980s. Since then, the use of Hg has been reduced through improved technology and new regulations (Paper I). Some uses that are not relevant in Stockholm still deserve a mention here. One is the use of
organic and inorganic Hg compounds as a fungicide treatment of seeds, which until the 1960s, caused considerable release of Hg directly into the environment (Berglund, 1970). Another is the use in chlor-alcali industries, which in the late 1980s accounted for 15 % of the total Swedish Hg turnover (Notter, 1993). Globally, the use of Hg for gold extraction is also of great importance, causing extensive atmospheric emissions (Lacerda and Marins, 1997).

The routes of exposure usually considered most important for humans are inhalation of Hg vapour and ingestion of organic Hg compounds. These forms of Hg readily pass from the lungs and the gut into the blood and then into the brain. In both cases the symptoms are primarily neurological (Goyer, 1996).

According to Goyer (1996), most human exposure is by inhalation. Mercury vapour is mainly an occupational health problem, although exposure via dental fillings has recently also become an issue of concern.

Most of what is known about the toxic effects of organic Hg compounds stems from the catastrophes in Japan and Iraq. The most widely discussed of these compounds is methyl-mercury (Me-Hg), which can be produced in several different processes including the activity of anaerobic micro-organisms (Hamasaki et al., 1995; Pelletier, 1995). Thus, Hg that is emitted in a relatively harmless form may be transformed into a very potent poison. This was the situation at Minamata and Niigata. Me-Hg is strongly bio-magnified: the concentration in fish is 25 times higher than in zooplankton, and the Me-Hg percentage of total Hg increases from 50 % in zooplankton to 90 % in predatory fish (Hellner, 1990).

In Sweden, the Hg issue has mainly focused on Me-Hg concentrations in fresh-water predatory fish. High Hg concentrations have been found in fish from lakes without local point sources, and although emissions have decreased, no reduction in concentrations in fish has been seen until recently (Johansson et al., acc.). Still, Hg concentrations in 1 kg-sized pike (Esox lucius) are estimated to be over 0.5 mg/ kg in 40 000 Swedish lakes. Therefore, the National Food Administration has advised women who are pregnant, or planning to become pregnant, to refrain from eating certain fish such as pike, perch and eel (Notter, 1993).

Like Pb, Hg is likely to have impaired the microbial activity in forest soils in southern Sweden and may also have adversely affected reproduction in fish-eating birds (Bergbäck and Johansson, 1996).

**Copper (Papers II and V)**

The average Cu concentration in the earth’s crust is 50 ppm. Of the worldwide deposits 90 % are sulphidic minerals, 9 % are oxidic, and 1 % is elemental copper (Enghag, 2000).

Copper is one of the most important metals in the history of technology. It was the first metal to be utilized by man in the late Neolithic period. Indeed,
some historians refer to the latter part of the Neolithic period as the Copper age. When it was discovered that a harder material was produced by mixing copper ore with tin ore before smelting, it was the beginning of the Bronze age (Enghag, 2000).

Today copper is used in a wide variety of applications in the city of Stockholm. The majority is used in protected locations for example in heavy electrical equipment and in cables. From an environmental perspective the exposed use of copper in roofs, water pipes, anti-fouling agents and brake linings is more important (Bergbäck et al., acc.; Sörme et al., acc.-b).

Humans are mostly exposed to Cu via tap water. In Stockholm there are some 6500 tonnes of copper in water pipes, releasing 4.3 tonnes to tap water annually (Sörme et al., acc.-b). This may not be a direct threat to the consumers’ health, since the uptake of copper via the gut is regulated (Goyer, 1996). However, much of the Cu ends up in sludge at sewage treatment plants. Tap water is considered to be the main source of copper in sewage sludge, and is one of the reasons that the concentration of copper in sludge is now close to the Swedish legal limit (Bergbäck et al., acc.).

Brake linings constitute a different source of copper exposure. In Stockholm they are estimated to release 3900 kg Cu/year in the form of fine particles (Westerlund, 1998), possibly fine enough to reach the alveoli when inhaled. They may also be a source of Cu in storm water, and hence, in the case of combined sewage systems, contribute to the high levels in sewage sludge.

Toxicologically copper is a relatively harmless element, although high copper concentrations in drinking water are thought to be related to “Indian childhood disorder”. It is an essential trace element, required for example by enzymes involved in haemoglobin synthesis. Thus, copper deficiency may lead to anaemia (Goyer, 1996).

Copper is strongly held by both organic and inorganic soil constituents. It is one of the least mobile metals and accumulates in the upper horizon of forest soils (Kabata-Pendas and Pendas, 1992). Studies from different areas of southern Sweden around 1980 indicated that whereas leaching of metals such as Zn, Cd, Cr and Ni exceeded deposition rates, Pb and Cu were still accumulating in forest soils (Notter, 1993). One source of this Cu is the emission from brake linings. Studies of polluted soils have shown that high Cu levels may adversely affect microbial activity (Bergbäck and Johansson, 1996).

In freshwater environments the bio-availability of Cu is highly pH-dependent, and like Pb it may be a problem in acidified lakes. The toxicity of Cu to marine organisms is affected by its speciation, since the free Cu^{2+} ion that is the toxic species only constitutes about 1 % of the total Cu concentration. The free Cu^{2+} ion is toxic to marine zooplankton and their larvae at concentrations as low as 0.03 and 0.003 µg/ l respectively, and is thought to have a limiting effect on algae
even at natural background levels. In the Baltic Sea the copper levels are high compared with the open ocean, suggesting that adverse effects on sensitive plankton species are likely (Notter, 1993).

**Zinc (Papers II and V)**

The average concentration of Zn in the earth's crust is 75 ppm. It exists mainly as the sulphide, sphalerite or zinc blende, which is found together with other minerals, such as galena (lead glance). Different Zn minerals were known and used during classical antiquity, and around 1000 AD Zn was being extracted from its oxide in India and China. (Enghag, 2000). Today it is used in a variety of products, many of which are highly exposed and are, therefore, potential emitters to the environment. In Stockholm most Zn is used in brass products such as water taps. Other alloys containing Zn are also extensively used. Steel produced for use in exposed environments, for example roofs, lamp posts and crash barriers, is often galvanized, thus exposing Zn to the environment, unless the surface is painted. Zinc oxide is used as a pigment in paints, and is also added to rubber produced for tires. Tires contain 1.6 % Zn, which in Stockholm makes tire wear the most important source of Zn in the environment, with an annual emission of 10 tonnes, most of which ends up in soils close to roads, or in storm water (Lohm et al., 1997; Sörme et al., acc.-a; Sörme et al., acc.-b).

Although Zn is a relatively harmless element, problems may arise due to its close relation to Cd, (see above).

More than 200 enzymes require Zn as a co-factor and deficiency results in a variety of symptoms. Excessive exposure, however, is relatively uncommon, and the body content is regulated by modulation of both uptake and excretion. However, inhalation of Zn fumes has been shown to cause metal fume fever.

Zinc mobility in forest soils is more dependent on pH than for example Cu. Thus, acid rain in southern Sweden has caused increased leaching of Zn from soils and has consequently increased concentrations in rivers, lakes and groundwater. No effects have been observed due to this increase so far. It is possible that zooplankton have been adversely affected by Zn in the Baltic Sea. In the Bothnian Sea the Zn concentrations in surface sediments are close to those known to affect benthic fauna (Notter, 1993).
The scientific landscape

Research, like all human activities, is always conducted within a specific context. To understand the research presented here, it is necessary to gain some insight into its wider context, which is described in the following section. I will do this by describing what the context looks like from where I stand. Some characteristics, which are close to my position, will be described in more detail, whereas other, more distant parts, will be described very briefly, or ignored. This section is intended to provide an introduction to the fields dealt with in this thesis, and also to define my own position in this scientific landscape.

Sustainability research

For a long time environmental research concentrated on measuring the levels of different pollutants in various media and assessing their impact on organisms. However, due to time lags associated with both environmental impact and the effects of measures taken to reduce this impact, such an approach does not give sufficiently rapid feedback for effective environmental management. A method of “early recognition” of environmental problems is required, ideally one that identifies problems before they arise. Such an approach is not reactive but proactive (Burström, 1998). This study therefore combined environmental monitoring with an assessment of the different uses of metals in the technosphere studied in a material flux analysis (MFA). The combination of these two viewpoints results in a description of the metal metabolism in the city of Stockholm, including the spatial dimension of metal dispersion in the environment. The thesis, therefore forwards the question “where do pollutants come from?” into environmental monitoring and the question “where do pollutants go?” into MFA.

In this section, a brief introduction is given to the research landscape of society-nature relationships. The aim is to identify ways of describing the spatial dimension of these relations.

The relationship between nature and human society has often been described as consisting of two more or less separate parts: the utilization of natural resources, and the emission of waste products. Although sometimes useful, this division is not entirely beneficial to the overall discussion, since resource scarcity and pollution are intimately linked and may even be seen as one and the same (Folke, 1991). During the 1990s interest focused on sustainable development, which stresses the close interdependency of nature-society relationships and economic growth and equal distribution of resources. Whereas the question of environmental protection initially mainly concerned natural scientists, sustainable de-
velopment has profound social implications. This has led to the development of a new research area analysing the wider relationships between society and nature (Anderberg, 1996).

When environmental problems entered the agenda of the western world in the 1960s, focus was on emissions of hazardous substances from point sources or otherwise easily identifiable sources. Environmental pollution concerns focused on industrial plants, off-gases and effluents. The problem was regarded as a technical shortcoming, and the proposed solutions were of an “end-of-the-pipe” kind. Eventually, however, it became clear that these solutions were insufficient. Measures to mitigate pollution could no longer rely on filters and wastewater treatment. The problem, and its solution, needed to be addressed earlier in the system. The causes of pollution were now seen as shortcomings within the industrial system and the solutions therefore required a system-based approach including fundamental changes within the society. In addition, pollution was increasingly seen in connection with resource and development issues. From these viewpoints, a new aim was identified for the worldwide work on these issues. This aim was formulated as “sustainable development” in the report of the World Commission for Environment and Development in 1987, (the Brundtland report) and subsequently during the United Nations Conference on Environment and Development in Rio de Janeiro in 1992. Since then much research has been undertaken to define the true nature of sustainable development, and to identify ways to evaluate and achieve it. This new field is still difficult to review since it is constantly evolving. This overview is based on the work of a number of authors (Anderberg, 1996; Fischer-Kowalski, 1998; Fischer-Kowalski and Hüttler, 1998; Graedel, 2000; Indigo Development, 1998; Lohm, 1998), and several views of the concept are described, which are relevant to the present study.

Research in this field has evolved in three main areas: industrial metabolism, ecological economics and industrial ecology. These categories are overlapping and do not encompass all aspects of the subject, but in this research context they are the most relevant. From my viewpoint in this research landscape these are the ones most adjacent, and the ones most related to my own work. As well as in the listed areas, significant work is being conducted in several research areas, including social and behavioural sciences, which deal for example with people's attitudes towards sustainability, and how sustainable development can be managed at local and regional levels, etc.

The three areas mentioned above clearly have a common basis in the analogy between natural ecosystems and society, or “nature’s household” (ecology) and “humankind’s household” (economics) (Ecological Economics, 2000). The connection lies in the perception that society, like the ecosystem, has a turnover, a metabolism of energy and material. This analogy can be used to describe and analyse society, as industrial metabolism. It may also be used as an inspiration for
organizing the industrial system to optimize its use of energy and matter, which is
the basis for some aspects of the field of industrial ecology. Thus, the analogy
implies that industrial systems should mimic natural ecosystems (Graedel, 2000)
as well as be integrated with them (Ecological Economics, 2000). The analogy,
however, also has some vital shortcomings, for example in relation to the way
that systems change and how they are regulated. Thus, it is imperfect, and should
not be extrapolated too far. In this context it is sufficient to establish that the
human and natural households have some basic properties in common, which
form a basis for the three areas of research presented below.

**Industrial metabolism**

Based on the analogy to the metabolism of plants and animals, industrial meta-
bolism has been defined as “the set of physico-chemical transformations that
convert raw materials (biomass, fuels, minerals, metals) into manufactured pro-
ducts and structures (i.e. ‘goods’) and wastes … industrial metabolism compre-
hends all the materials/ energy transformations that enable the economic system
to function.” (Ayres and Simonis, 1994). Thus “industrial” in this context is ap-
plied in the wide sense of the word, including the whole economic system. This
approach is usually attributed to Robert Ayres and Allen Kneese in the late 1960s
(Ayres and Kneese, 1969). Previously the concept of metabolism had been used
in connection with socio-economic activities, but had not been fully developed
(Fischer-Kowalski, 1998).

The analytical tool most often employed in studies of industrial metabolism is
described as material flux analysis, MFA (also known as material flow assessment).
Sometimes MFA is distinguished from SFA (substance flux analysis). The former
deals with bulk materials such as water and gravel, and the latter with separate
substances such as heavy metals or pesticides (Lohm, 1998). Alternatively, the
term material has been defined as “a chemical element ... and its compounds”
(Brunner et al., 1994), i.e. what is usually called a substance. As Anderberg (1996)
notes, this definition excludes agricultural products and fuels, regarding them
simply as carriers of ‘materials’. In this overview, therefore, the term MFA is used
for the analysis of fluxes of elements, compounds and complex products, in-
cluding industrially manufactured products as well as bulk materials such as
gravel and fossil fuels.

The traditional way of controlling pollution has been to regulate the emissions
to air and water. This has, however, only resulted in redirecting pollutants. Fly
ash that is separated from industrial off-gases is deposited in landfills, and metals
in sewage end up in the sludge that is spread on farmland. MFA provides a dif-
f erent, more holistic perspective. It deals with potentially hazardous substances
before they become pollutants to examine if and how they can be controlled earlier
in the process. This is sometimes referred to as early recognition. A sustainable
society has closed the cycles of such substances. The analysis of the fluxes of substances is, therefore, a relevant measure of sustainability (Ayres, 1994), although insufficient in isolation.

The MFA approach is especially suitable for persistent substances such as heavy metals and other elements, and certain organic substances, since these may be tracked through the different compartments of an industrial system.

An MFA model of the material fluxes within an industrial system may start with the extraction of raw materials from natural resources. These are refined and turned into products, which eventually become waste. Waste is then either recycled, incinerated or placed in landfills, depending on local practices and the nature of the waste. Each step in this chain, from the extraction of natural resources to the management of waste, can cause emissions of the substance to the environment.

MFA studies have been undertaken for cities (Newcomb et al., 1978), for individual companies (Eklund, 1995), for watersheds (Ayres and Rod, 1986; Brunner et al., 1994; Stigliani and Anderberg, 1994) and for nations (Ayres and Ayres, 1994; Bergbäck, 1992; Lohm et al., 1994).

The relationship between the technosphere and its surrounding natural environment is often handled by drawing boundaries (Fischer-Kowalski et al., 1994). This issue is certainly not trivial. Anderberg (1996) stresses that, if such boundaries are not defined and dealt with properly "grey areas" may arise, i.e. areas alternating between the societal and the environmental compartments. However, he feels that the need to resolve this problem is questionable: "After all," he asks, "isn’t a consequent separation between society and nature a rather impossible task?".

In MFA the surroundings of the industrial system are sometimes described by the concept of the hinterland, (literally “the land behind”). The hinterland is the region outside the system that supplies the necessary resources (versorgungshinterland) and receives the resultant wastes (entsorgungshinterland) (Obernosterer et al., 2000). In the case of metals in the city of Stockholm, the mines that supply the metal are part of the versorgungshinterland, and the Baltic Sea, to which metals are emitted is part of the entsorgungshinterland. Stating that the hinterland is “outside” the system does not necessarily mean that it is geographically remote, only that it is conceptually separate (Fischer-Kowalski et al., 1994). Based on this concept Obernosterer et al. (2000) talk about “the urban shadow” (der urbane Schatten) to describe the grey area identified by Anderberg (1996). The urban shadow is not of primary interest in most MFA studies, which usually focus on what goes on within the technosphere and on the magnitude of the fluxes to and from the hinterland — rather than on what happens to pollutants that have been emitted. The research programme “Metals in the urban environment” that was carried out by the Swedish Environmental Protection
Most industrial metabolism studies have a rather short time span, aiming to elucidate the fluxes through society during a year. Exceptions are the studies of the Hudson-Raritan basin (Ayres and Rod, 1986), the Rhine basin (Anderberg, 1996; Stigliani and Anderberg, 1994), several studies of heavy metals in Sweden and the United States (Ayres and Ayres, 1994; Bergbäck, 1992; Lohm et al., 1994), and the Stockholm study, of which the research presented in this thesis is a part. A general conclusion from these studies is that diffuse emissions related to consumption and waste treatment ("consumption emissions") have become increasingly important in relation to several heavy metals, and that they are more extensive than the emissions from extraction and production processes ("production emissions"). Since consumption emissions are largely connected to population centres, the conclusion has been drawn that cities are potential "hot spots" for metal pollution (Bergbäck, 1992). This was one of the motives behind the research programme "Metals in the urban environment" (Bergbäck et al., acc.).

Whereas most studies only deal with fluxes of materials, the Stockholm study also considered the stocks of materials that have accumulated in the technosphere (Sörme et al., acc.-b). The inclusion of stocks has also been developed by other authors, who have calculated the emissions from accumulated materials in various ways (Kleijn et al., 2000; Voet et al., 1999).

The entsorgungs-hinterland of some heavy metals in Sweden has been addressed spatially by Bergbäck and co-workers by introducing the concept of immission landscapes (Bergbäck, 1992; Bergbäck et al., 1994; Lohm et al., 1994). The invented term 'immission' is the inverse of emission, i.e. whereas emissions are the pollutants that leave the technosphere, immissions are the pollutants that are deposited in the environment. Thus the immission landscape describes the spatial distribution of pollutants in their final environmental sinks - soils and sediments. These studies constructed the immission landscape by calculating emissions from different sources (both production and consumption emissions) and attributing these to different media (water and air). This was conducted for all 70 Swedish 'A-regions'. As an approximation the emissions were assumed to have been deposited within the same A-region in which they had been emitted. Emissions to water were assumed to be deposited in sediments, and emissions to air were distributed between soils and sediments according to the land/water ratio of the A-region in question. In combination, all these regions constituted the immission landscape of Sweden.

A few studies have attempted to calculate historical emissions and trace them within the environment, using different environmental archives. In this they have some affinity the approach in the present study. Ayres and Rod (1986) used sedi-
ment cores as an independent check of the estimated emissions of PCB, mercury and lead in the Hudson-Raritan river basin. Eklund (1995) used sediments, soils and tree rings to analyse the redistribution of metal emissions from an alum-works, a copperworks and a battery plant.

An earlier historical perspective was used in a regional study on the development of metal and sulphur emissions associated with the industrialization of several iron-works in south-east Sweden during the period 1655-1920 (Svidén, 1996).

From the results of MFA and other work, it has been concluded that industrialized countries need to significantly reduce their use of various materials. This has led to the development of the research field of dematerialization. Examples include decarbonization of the energy sector, and the “factor 10 movement”, which argues that the use of materials in the industrialised world should be reduced by a factor of 10 (Hinterberger and Schepelmann, 1998).

**Ecological economics**

The field of ecological economics has evolved from two perceptions. First, that “the dynamics of economic systems are not independent of the dynamics of the ecological systems that constitute their environment” and, second, that “the dynamics of the jointly determined system become increasingly discontinuous, the closer economic systems get to the limits of the ‘assimilative’ and ‘carrying’ capacity of the environment” (Perrings et al., 1995). According to ecological economics, neither economics nor ecology in their conventional forms have adequately dealt with this interdependency and the discontinuities or threshold effects that may result from it (Perrings et al., 1995). Ecological economics is intended to be a new approach to both economy and ecology. It should make economy more aware of the dependency of economic systems on their physical environment, while at the same time making ecology more fit to deal with economic forces that affect the environment (Folke and Kåberger, 1991). Although other disciplines are represented, ecologists and economists dominate the field. Besides the viewpoint that economic and ecological systems are interdependent, the two disciplines are said to have much in common. For example they have a tradition of dealing with mathematics of non-linear, complex and even chaotic systems, and the biological concept of evolution has an analogue in the study of economic change (Perrings et al., 1995).

Ecological economists have spent considerable effort in finding integrative quantitative measures for natural resources and for the impact that society has on the environment. Among the measures that have been used are monetary units (e.g. cost-effectiveness analyses) and energetic measures. A spatial measure, the so-called ecological footprint (EF), has also been proposed and has received some attention (Rees and Wackernagel, 1996; Wackernagel and Rees, 1996; Bergh and Verbruggen, 1999). It can be described as the inverse of carrying capacity: Instead
of asking how big a population a certain region can support, it asks how large an area of productive land is needed to sustainably support a certain population – a household, a city, or a nation – wherever that area is located (Rees and Wackernagel, 1996). At least conceptually “support” includes all ecological services used by the population, both the supply of resources and the assimilation of wastes. In practice, however, it has been difficult to translate the effects of pollution into spatial measures, and hence the calculations usually do not deal with this, but concentrate on the supply of resources. The only exception I have found is that CO₂ emissions are accounted for by calculating “the area of average carbon-sink forest that would be required to sequester them” (Rees and Wackernagel, 1996). As questionable as such an approach may seem in the case of CO₂ (Bergh and Verbruggen, 1999), the problem is more serious when considering potentially toxic substances that are not readily degraded or otherwise rendered harmless. For example, we may wish to consider the size of the area that is needed to assimilate the Hg emissions from Stockholm. Another problem with the footprint approach as it has been described so far, is that it does not differentiate between land uses, which may have quite different effects on the environment (Bergh and Verbruggen, 1999). As defined, the EF is the area needed to sustainably support a given population. For example, at least principally, calculations assume that food is produced in a sustainable manner, which is usually not the case. Since neither of these shortcomings presently can be addressed, it is simply stated that they both result in an underestimation of the true footprint, i.e. the “real” footprint should be considerably larger than indicated by the calculations (Wackernagel and Rees, 1996).

Industrial ecology

Industrial ecology is perhaps the most vaguely defined concept of the three areas described in this chapter. Sometimes it is described as “the science of sustainability” including both industrial metabolism and ecological footprinting (Indigo Development, 1998). It can also be viewed more narrowly, as “getting inspiration from nature’s food chains for the design of different industrial systems” (Lohm, 1998). Erkman (1997) describes industrial metabolism as “essentially analytical and descriptive”, whereas industrial ecology goes further in determining how the industrial system “should be restructured to make it compatible with the way natural ecosystems function”. In either case, “industrial” here refers to the activities of commercial industries, i.e. the main perspective is that of the industrial enterprise. Approaches may be mainly technological such as pollution prevention and design for the environment, or integrate different perspectives, as in cleaner production, life cycle assessment (LCA), extended producer responsibility and eco-industrial parks (Graedel, 2000; Lohm, 1998). Erkman (1997), however, explicitly excludes some of these approaches from his definition of industrial ecology. On the con-
trary, he sees industrial ecology as an alternative to the strategies of pollution prevention and cleaner production, which he thinks are isolated and still share the end-of-the-pipe philosophy. Industrial ecology, to him, is a strategy for restructuring industrial systems on a supra-company level. Thus, he focuses on structural and organizational approaches like eco-industrial parks, and dematerialization.

The concept has been used in different contexts at least since the 1970s, but it was not until 1989 that it spread more widely in the sense described above. In a special issue of Scientific American two General Motors employees forwarded the thought that industrial systems should be developed to function analogously to biological ecosystems, optimizing their use of energy and material and thereby reducing their environmental impact (Frosch and Gallopoulos, 1989).

Among these perspectives, life cycle assessment has much in common with material flux analysis, especially the cradle-to-grave analysis. However, whereas LCA focuses on all kinds of environmental impacts from a specific product or activity, MFA deals with a specific material in whatever product or activity it is present. Thus, they can be seen as perpendicular, coinciding in the mutual interest in the use of a specific material in a specific product. In these intersections, LCA and MFA can contribute significantly to each other.

In summary, two different approaches have been identified that deal with society-nature relations in a spatial way: the ecological footprint, and the immission landscape. Since pollution issues are not easily addressed in ecological footprints, the approach adopted in this thesis was to analyse the immission landscape of heavy metals in Stockholm, by means of a material flux analysis, and by measurements of the sediment load. The use of sediment cores also facilitates a historical view, since the sediment load may be reconstructed (see below), and compared with estimates of past heavy metal use in Stockholm.

**Sediments and environmental archives**

Sediments are often used for monitoring aquatic environments, since they can provide integrated information about the environmental status of the water body. They can be regarded as “a bank of environmental information” (Håkanson and Jansson, 1983). There are several advantages of using sediments rather than water for monitoring aquatic environments. First, the concentrations of pollutants are much higher in sediments than in water bodies, which makes laboratory analysis easier and tends to produce more reliable data. Furthermore, whereas water concentrations of different pollutants may show considerable seasonal variation, sediment concentrations are relatively stable. Hence samples can be collected once, rather than several times over the year, as is required for water samples.
(although, of course, if seasonal variations are of interest in the study, water sampling is probably preferable). The short residence time of most pollutants in water also means that short pollution pulses may be missed in the snap-shots provided by water investigations, but can be found in the integrated picture provided by the sediments. Finally, assuming that the sediments are undisturbed, i.e. that neither physical nor chemical processes have altered the vertical distribution of the analyte, they may act as archives of environmental history.

Sediments may also be of primary interest, and not merely reflections of the environmental state of the water in the lake or coastal area. Horowitz (1985) discusses why sediments should be considered in water-quality studies. Apart from the possibility of reconstructing historical records, providing information about pollution history and background conditions, he mentions three ways in which pollutants in sediments may re-enter the food chain. Changing physico-chemical conditions such as pH and redox state, may result in the release of sediment-bound pollutants into the water phase. For example, improved sewage treatment during recent decades has reduced the emissions of nutrients and organic matter from Stockholm. As a result, the load of organic matter to sediments has been reduced, and thus less oxygen is consumed during the decomposition of this material. This may lead to a redox turnover, so that presently anoxic sediments become oxygenated. Such a turnover is likely to affect the binding characteristics of several metals. Oxygenation of sediments is likely to be followed by the return of bio-turbators, which speed up the redox-change, possibly causing more metals to be mobilized. This development has been described as a “chemical time bomb” (Stigliani et al., 1991). Further, several normally inert or environmentally harmless substances may be altered into mobile, bio-accumulating and seriously toxic pollutants. The methylation of Hg is a good example. Finally, Horowitz (1985) stresses that bottom sediments are continuously being resuspended by wind and wave action, which may constitute the most important source of metals to the water phase.

Apart from the eco-toxicological perspective, the concentrations of metals in sediments are not as interesting as the metal load, i.e. the input of metals to the sediment. Basically two approaches can be used to assess the flux. One is to use sediment traps in which settling material is collected over a defined period. The metal content of the material is then analysed and thus the sediment load of metals during that period can be estimated. The other approach, the one that has been used in this study, is based on dating of sediment cores. By determining the age of the sediment at a given depth in the core it is possible to calculate the amount of material that has settled during that time. There are several ways of dating sediment cores. The procedure may be based on the decay of radioactive isotopes such as Pb-210 or, if the sediments are distinctly laminated, on counting laminae. However, in this study the Cs-137 or the radiocesium method has been
used (Meili et al., 1998). Although Cs-137 is a radioactive isotope, the method is not based on its decay but on its distribution in the core. Two events caused widespread deposition of Cs-137 in this region: the atmospheric testing of nuclear weapons in the mid 1960s, and the Chernobyl accident in 1986. The latter event, particularly, is reflected in most cores from the Stockholm area (see below). A limitation of this method is that it is not possible to date every part of the core directly, only to determine the average sedimentation rate since 1986, which is then assumed to have been constant over the period studied. This dating method is further described in a later chapter.

To calculate the metal load of the whole lake or coastal area, sediment dynamics have to be investigated, i.e. the distribution of different bottom types has to be determined. Areas of continuous fine sediment accumulation (A-areas) are distinguished from areas of sediment erosion, and areas of sediment transport (E- and T-areas, respectively), since it is only in the A-areas that there is a continuous accumulation of sediment, and thus of pollutants. Thus, sediments from the whole water body are deposited in a smaller area (Håkanson and Jansson, 1983). This is referred to as sediment focusing.

In order to reconstruct the changing environmental load, it is necessary to find a medium that has not only a spatial but also a temporal dimension. Two conditions are crucial for environmental archives: it has to be possible to date samples accurately, and the measured composition of the sample must somehow reflect the environment in which it was formed. Several such archives have been suggested, including mosses, tree rings, herbarium specimens, human remains as well as ice, snow, peat and sediment cores (MARC, 1985). For sediments the two conditions imply, as mentioned previously, they have to be physically and chemically undisturbed. Physical redistribution may be caused by wind and wave action, dredging, slides and bioturbation, i.e. the activity of benthic organisms. Anaerobic sediments no such organisms are present, and hence there is no bioturbation. This results in the laminated sediments that can be found in large parts of the Baltic Sea, including the Stockholm archipelago (Jonsson, 1992; Östlund et al., 1998). The occurrence of laminae is a good indication that the sediments are physically undisturbed. Chemical redistribution can occur as a consequence of the redox conditions in the sediments, which may cause mobilization of metals from carrier particles. This process is more difficult to rule out, since it may take place between the layers of a laminated sediment, and should always be considered as a source of error in sediment investigations (Jonsson, 1992). Whereas physical disturbance affects the distribution of all elements equally, chemical processes act differently on different elements. Hence, although there is a sharp increase in the Cs profile presented in the methods chapter, indicating that this element has not been redistributed between sediment layers, this does not mean that all metals are equally undisturbed.
If sediment cores are sufficiently long, it is possible to use the oldest part of the core to calculate the pre-industrial load of pollutants, which can then be used as a natural background estimate (Håkanson and Jansson, 1983). In fact, the historical record may go even further; as mentioned above (p. 15) Renberg and co-workers have used sediment cores to study how the atmospheric deposition of Pb has changed during the last four millennia, showing that “pre-industrial” is far from equivalent to “natural background” (Brännvall et al., 1999; Renberg et al., 1994; Renberg et al., 2000). However, in the Stockholm area, with the long history of heavy metal pollution reported in Paper I, and with the high sediment deposition rates reported in Paper II, it was not possible even to determine the pre-industrial load – let alone the natural background – using this approach. Therefore, these levels had to be estimated by alternative means, as described below.
Materials and methods

Study area

Stockholm is the capital of Sweden and is located where the lake on the western side, Mälaren (area 1140 km², catchment area 22603 km²), meets the Baltic Sea (Figure 1). The water flows through a dense system of islands, which begins in the eastern part of Mälaren and gradually opens up to the Baltic Sea east of the city, constituting the archipelago of Stockholm. More than 75% of the water from Mälaren flows via one main channel, Norrström, in the very centre of Stockholm. There are also some minor streams and two locks within Stockholm. The average water level difference between Mälaren and the Baltic Sea is 0.6 m. The average water discharge from Mälaren is about 160 m³/s (Lännergren and Eriksson, 2000). The mixing of freshwater from Mälaren and the brackish water of the Baltic Sea creates a salinity gradient through the archipelago. This gradient ranges from 1 psu (practical salinity unit) in the central parts of the city to 5-6 psu.

Figure 1 The area investigated showing the 14 sub-areas sampled (separated by the black lines) and the municipality of Stockholm (the dark area). The distance from the centre of the city to the open Baltic Sea is approximately 50 km.
in the outer areas. The hydrodynamic flow pattern of the inner archipelago has not been extensively investigated, but the characteristics of the salinity gradients on different depths suggest that there is a main outward flow of surface water, which gradually mixes with an inward flow of more saline deep water. The tidal influence is negligible in the Baltic Sea. The central areas also receive storm water and effluent water from the four major sewage treatment plants of the Stockholm area (Lannergren and Eriksson, 2000).

Based on topographic characteristics, the study area was divided into 14 sub-areas - seven in eastern Mälaren (A-G) and seven in the inner parts of the archipelago (1-7) as shown in Figure 1. Except for sub-areas E and F, these are distributed along the main water course. Some characteristics of the sub-areas are shown in Table 1 (from Paper II).

**Table 1** Background data relating to the investigated sub-areas. Total water area, area of sediment accumulation (A-area, % of total area), maximum depth (Dmax), water volume (V) and basic water chemistry (mean values of surface and deep water during 1997 in the archipelago (1-7) and 1998 in Mälaren (A-G)): total organic carbon (TOC), surface water salinity (Sal. s), deep water salinity (Sal. d), pH and deep water oxygen concentration (O2). From Paper II.

<table>
<thead>
<tr>
<th>Sub-area (name)</th>
<th>Area (km²)</th>
<th>A-area (%)</th>
<th>Dmax (m)</th>
<th>V (Mm³)</th>
<th>TOC (mg/l)</th>
<th>Sal. s (psu)</th>
<th>Sal. d (psu)</th>
<th>pH</th>
<th>O2 deep (mg/l)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A (Lambarfjärden)</td>
<td>38.7</td>
<td>34</td>
<td>53</td>
<td>411</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>7.17</td>
<td>10.7</td>
</tr>
<tr>
<td>B (Kyrkfjärden)</td>
<td>22.0</td>
<td>22</td>
<td>22</td>
<td>116</td>
<td>6.9</td>
<td>-</td>
<td>-</td>
<td>6.73</td>
<td>10.8</td>
</tr>
<tr>
<td>G (E Ekerö, Fiskartjärden)</td>
<td>12.2</td>
<td>20</td>
<td>25</td>
<td>68.7</td>
<td>7.1</td>
<td>-</td>
<td>-</td>
<td>7.11</td>
<td>10.5</td>
</tr>
<tr>
<td>C (Klubben, Smedslätt)</td>
<td>3.8</td>
<td>42</td>
<td>36</td>
<td>48.1</td>
<td>7.3</td>
<td>-</td>
<td>-</td>
<td>7.11</td>
<td>9.9</td>
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<td>E (Ulvsundasjön)</td>
<td>2.6</td>
<td>27</td>
<td>22</td>
<td>19.7</td>
<td>7.6</td>
<td>-</td>
<td>-</td>
<td>7.50</td>
<td>11.1</td>
</tr>
<tr>
<td>F (Arstaviken)</td>
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<td>21</td>
<td>10</td>
<td>7.2</td>
<td>7.3</td>
<td>-</td>
<td>-</td>
<td>7.85</td>
<td>10.4</td>
</tr>
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<td>D (Riddarfjärden)</td>
<td>2.4</td>
<td>48</td>
<td>27</td>
<td>27.7</td>
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<td>7.49</td>
<td>11.2</td>
</tr>
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<td>1 (Salsjön)</td>
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<td>38</td>
<td>39</td>
<td>48.2</td>
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<td>1.3</td>
<td>4.5</td>
<td>7.14</td>
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<td>2 (Lilla Värtan)</td>
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<td>4.2</td>
<td>7.27</td>
<td>7.7</td>
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<td>3 (N Värmdölandet)</td>
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<td>59</td>
<td>552</td>
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<td>7.31</td>
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<td>5 (Solo- Torsbyfjärden)</td>
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<td>47</td>
<td>312</td>
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<td>6 (Trälavet)</td>
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<td>352</td>
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<td>4.0</td>
<td>4.8</td>
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<td>30</td>
<td>59</td>
<td>410</td>
<td>4.4</td>
<td>4.4</td>
<td>4.9</td>
<td>7.30</td>
<td>12.6</td>
</tr>
</tbody>
</table>

The system analysed by the metabolism study was defined as the municipality of Stockholm, which has about 700 000 inhabitants, corresponding to 8 % of the total Swedish population. The total area is 215 km² out of which 28 km² is covered by water (Utrednings- och Statistikkontoret, 1993). In the early 20th century Stockholm was heavily industrialized. Today the labour market is dominated by the trade, service, communications and financial sectors (Sörme et al., acc.-a). The sediment samples from Mälaren were mainly taken from within the city boundaries, but most of the samples from the archipelago were taken in other municipalities. Thus, this study investigates not only the stocks and flows within the
city’s system, but follows the flows of metals into the surrounding recipients, which constitute the so-called entsorgungshinterland, (the area outside the system which is affected by the activities that take place within it). However, it does not deal directly with activities in the versorgungshinterland, (fluxes related to metal production, refinement and processing).

**Industrial metabolism analyses**

**Use and emissions**

Since the quality of available data is highly varying, the data collection methods of material flux analyses such as the ones presented in this thesis have to be flexible and adjust to the type of data that can be found. No detailed description of the data sources is given here, only a brief overview of the different approaches taken and the types of sources that have been used. For more details see Lohm et al. (1996), Lohm et al. (1997) and Paper I.

The time period of the industrial metabolism studies for Hg were defined as 1795-1995 (Paper I) and the 20th century (Paper III). For Cd and Pb a shorter period was used - the last three decades (Paper IV), and the studies of Cu and Zn focused on the present situation (Paper V).

Several types of data sources were used for fluxes and accumulation:

- National (regional) figures, scaled down according to population ratios or other relevant proportions,
- Figures relating to the metal content of a product, scaled according to estimates of the number of such products in Stockholm, and
- Data directly available on the use of metals for certain purposes in Stockholm.

Based on the average lifetime of a product, the flux and the accumulated amount of metals could be calculated from each other:

\[
\text{Accumulation (kg)} = \text{average annual turnover (kg/y)} \times \text{average lifetime (y)}.\]

Estimating the diffuse metal emissions from different products is a difficult task. This problem has been addressed in three different ways.

In Paper I, all of the mercury used in different products was assumed to have been emitted either to air or to water and soils. Emissions were assumed to be instantaneous, i.e. they were assigned to the same year as the inflow. This is obvi-
ously a simplification, but since most of the products discussed have rather short lifetimes, the problem is not that serious.

Paper III develops this approach further, through a model partly inspired by Munthe and Kindbom (1997). The structure of the model is shown in Figure 2. Here the mercury consumed during a year for each purpose is distributed between different kinds of waste, recycling, and direct emissions to water and air. Direct emissions to soil/landfills were considered, but were not found to be relevant. Factors for emissions to water, air and soil/landfills were then assigned to the waste types. Changing patterns of use, and changing waste management was taken into consideration by allowing the distribution and emission factors to change over time.

A somewhat different approach was used in Paper IV. The estimates in this paper were based on the concept of emission coefficients as presented by Ayres and Ayres (1994). These coefficients are defined as “the fraction of the material in question that is released in mobile form (to the air or water) within a certain period”. Still, however, emissions were assigned to the year of consumption.
**Turnover at sewage treatment plants**

The fluxes of metals in sewage were studied in the annual reports of the sewage treatment plants (STPs) from 1975 to 1996. These reports give the amounts of metals that have been emitted with the treated water, as well as the concentration of metals in sludge, and the amounts of sludge produced. Assuming that no metals are added during treatment (an assumption that is likely to be valid for the metals discussed here) the amount of metals in the incoming water equals the sum of metals in the effluent water and in sludge. These fluxes are discussed by Östlund and Jonsson (1998), and summarized in Table 2.

**Atmospheric deposition of metals**

The atmospheric deposition of metals in Stockholm and its surroundings has been studied several times. Thus, data are available relating to both the regional background deposition, representing long-range transported metals, and local deposition in Stockholm, which also includes metals from sources within the city. Based on the results of these studies, the atmospheric deposition on the water surface of each sub-area was calculated.

The regional background was calculated from the analysis of mosses from areas in the region assumed to be sufficiently remote as to be unaffected by the city (Rühling et al., 1996; Statistics Sweden, 1990).

Investigations of metal deposition in Stockholm have been performed irregularly since 1970 (Johansson and Burman, 1998). Although different studies have used different methodologies (moss analyses and precipitation collection), and different sample station distributions (some have taken samples from the whole municipality of Stockholm, and others have concentrated on the central parts) they give indications of the trends in atmospheric deposition of metals in Stockholm.

A combination of these local and background deposition measurements was used to estimate the deposition in each sub-area. For example, the deposition measured in the city was assumed to be representative of sub-areas D, E, F and 1; sub-areas 6 and 7 were assumed to sufficiently distant to receive only the background deposition. The depositions calculated were then summed to give the total deposition on water in the whole area.

**Metals in storm water**

The 1994 fluxes of metals in storm water to all aquatic recipients of Stockholm were published by the Stockholm Water Company (1994). The emissions to recipients included in this study were calculated, and the same proportions were applied to the total emission figures for 1984 (The Stockholm Environment and Health Protection Administration, 1995).
Sediment analyses

Sediment dynamics and sediment sampling

During two cruises with the R/V Sunbeam of Uppsala (August 1997 in the archipelago, and June 1998 in Mälaren) the sediment dynamics of the sub-areas were investigated and sediment samples were taken. To determine the dynamic conditions, a side scanning sonar (EG & G Environmental Equipped model 260 Image Correcting Side Scan Sonar, with a 272-TD-Saf-T-Link Tow Fish, set at 100 kHz and a range of 100-200 m) was used in combination with a sediment echo-sounder (O.R.E. Geopulser pinger at 14 kHz). The former gives a horizontal picture of the sediment surface, similar to an aerial photograph. The sediment echo-sounder produces a depth profile of the sediment, differentiating between soft, hard and gas-containing sediments. Information from these instruments in combination with the results of water content and loss on ignition analyses, makes it possible to determine the distribution of areas of continuous sediment accumulation (A-areas) and areas of sediment erosion or transport (E-or T-areas respectively) (Håkanson and Jansson, 1983). From these data, sites were selected for sediment sampling and the total annual sediment deposition in each sub-area was calculated.

Sediment samples were taken from five to seven locations in every sub-area, using a Gemini gravity sediment corer with Plexiglass tubes. Only relatively undisturbed cores were accepted. They were divided immediately after sampling into 1 cm slices using a piston device. At some locations only surface sediments were taken (0-1; 1-2 cm). At one to four locations in every sub-area the whole sediment core was sectioned, taking every cm (0-1; 1-2 cm…) to 6 or 11 cm, then every fifth cm (10-11; 15-16 cm…) to the end of the core. The sediment material was transferred to polypropene containers and frozen immediately.

Laboratory work, dating and calculations

In the laboratory the water content (w) was determined either by drying the samples at 105 °C for 20 hours, or by freeze-drying for three days. These methods were compared and found to give consistent results for these sediments. The organic matter content was analysed as loss on ignition, heating sub-samples (<0.5 g dry sediment) at 550 °C for two hours.

The Gemini corer takes two sediment cores simultaneously, allowing one to be sectioned as described above, and the other to be kept for visual inspection and description of structural characteristics. Laminated sediments were found in most sub-areas because no higher organisms (bioturbators) were present. These laminae were used in combination with radiocesium analysis to determine the annual deposition of sediment material in each sub-area, as well as the age of every part
of the core. The Chernobyl accident in 1986 is usually reflected in the Cs-137 profile of sediments in the Stockholm area, which facilitates the identification of this year in the profile (Meili et al., 1998) (Figure 3). One to three cores in every sub-area were used to calculate the annual dry matter deposition (in g/ (cm²*y)). The total weight of dry matter deposited since 1986 was calculated and divided by the number of years that had passed (11 or 12). Dating was then based on the assumption that deposition has been constant throughout the whole period covered by the core. This last assumption is a weakness of the method, but when cross-checked the results were in agreement with those found by counting annual laminae, thus confirming the radiocesium dating.

Figure 3 The Cs-137 profile of one of the cores from sub-area 1 (Paper II). The deposition of Cs-137 from the Chernobyl accident is obvious in most sediment cores and facilitates the identification of the sediment layer from 1986. This in turn makes it possible to estimate the age of every layer in the profile. The sharp increase indicates that the sediment at this location has not been disturbed. The figure shows the profile of one of the cores taken in the centre of the city in 1998.

For the metal analyses <0.5 g of freeze-dried sediment, or a corresponding amount of wet sediment, was transferred to Duran glass bottles equipped with Teflon gaskets and polypropene caps. To each of these 20 ml of HNO₃ (7 M) was added and the bottles were heated to 120 °C for 30 minutes (Swedish standard SS 02 81 50). When the bottles had cooled, milli-Q water was added to a total volume of 50 ml and the bottles were left overnight to allow the residual sediment material to settle. The supernatant was then transferred to acid-washed
polypropene test tubes. On the day of analysis these solutions were further diluted by a factor of at least ten, and the internal standard was added. The analyses were performed using inductively coupled plasma - mass spectrometry (ICP-MS). The instrument used was a Perkin-Elmer Sciex Elan 6000 which was optimized according to the manufacturer's instructions (Perkin-Elmer Sciex, 1997). 10 ppb of rhodium (Rh) was used as an internal standard for all metals except mercury, for which thallium (Tl) was used. To eliminate memory effects 100 ppb of gold (Au) was added to all samples and standard solutions for the mercury analyses (Wolf et al., 1995). To validate the results of the ICP-MS analysis various amounts of a certified reference material (NRC PACS-2 “marine sediment”) were digested and analysed in the same way as the samples. For Cu, Hg, Pb and Zn the average concentrations were within the certified 95 % confidence interval, and Cd was on the upper limit. Average recoveries for Cr and Ni were 55 % and 82 %, respectively, which can be explained by incomplete digestion. The certification was based on total digestions, whereas the digestion procedures according to the Swedish standard described above left a significant mineral residual. The coefficients of variation (CV = standard deviation/mean value) for the series of the different digestions for all metals (including Cr and Ni) were less than 0.13, indicating an acceptable precision.

The metal concentration of the sediment sample (µg/g dw) was then multiplied by the annual deposition of dry matter, yielding the annual metal load per unit of A-area (µg/(y*cm²)). The investigations of sediment dynamics produced information on the total area of sediment accumulation in each sub-area. Multiplying the above result by this area and by a form factor, which corrects for the topographic variation of the bottom area (see Paper II), results in a value for annual metal deposition in each sub-area (kg/y). To facilitate comparisons this was then divided by the total water area of the sub-area to give the load corrected for sediment focusing kg/(y*km²). The surface sediments were used to estimate present-day loads in Paper II and V and the sediment cores were used in Papers III and IV to reconstruct historical loads.

As mentioned previously, the oldest layers of the sediment cores could not be used to calculate the natural background load of metals in this area. Instead the concentrations measured in the outer sub-areas were used. However, a number of processes along the salinity gradient affect the sorption properties and the sedimentation rate of metals. These must be corrected for. One way, as described in Paper II, is by normalization to an element that has sedimentation characteristics similar to those of the metals investigated, and that has no anthropogenic sources in the area. One suitable element was Ni. It correlated well in the surface sediments of sub-areas 6 and 7 with Cr, Cu, Pb and Zn. The Me/ Ni ratio in these areas (with a 95 % confidence interval) was used as an estimate of their relative natural occurrence. Thus, the natural background contribution of these metals
could be calculated for each sample using the Ni concentration of the sample and the estimated natural Me/Ni ratio. In Mälaren there is no salinity gradient, thus the problem of varying sedimentation characteristics is less serious. The natural background was estimated, therefore, using the lowest value found. For Cd and Hg the same method was also used in the archipelago.
General results and conclusions

The results are presented in detail in Papers I-V. The different metals are dealt with more or less separately in the five papers, and here the results will be summarized and compared at a general level. The results of the MFA study are discussed first, followed by an evaluation of the metal concentrations in surface sediments as well as in loads of metals to the sediments. Then the data is drawn together, comparing the different fluxes of metals into and within the aquatic recipient of Stockholm. Finally there are some concluding remarks relating to the results and the approaches that have been used during this research.

Metal metabolism

Use and emissions

Since the 1970s the use of Cd, Hg and Pb has decreased. This may be due partly to successful legislation against some uses of these metals, but at least for Hg technological developments, facilitating the substitution of Hg, seem to be equally or even more important (Paper I).

The calculated use and emissions of Hg and Cd, and the Pb emissions from petrol combustion are shown in Figures 4, 5 and 6 respectively. (Note that the emissions of Cd and Pb presented in Figures 5 and 6 are from the specified uses only, but the emissions in Paper IV also include production emissions.)

An important reason for the reduced Hg emissions to water indicated in Figure 4 is improved preventative dental care, which has reduced the need for amalgam fillings. With respect to the emissions to the air, much of the reduction is due to the installation of improved off-gas treatment at the solid waste incineration plant in the late 1980s. The mercury emissions to soil and landfill come mainly from sewage sludge, and the variation is, therefore, a consequence of changes in sludge management. Since the installation of off-gas treatment at the solid waste incineration plant, industrial waste has become a significant source of Hg to soils and landfill. Thus, improved treatment of sewage and of off-gases from incineration has re-distributed Hg fluxes from the air and water to soils and landfills. Unfortunately, it has not been possible to find much information relating to the fate of Hg in soils and landfills. It may therefore end up in sewage sludge used in agricultural soil improvement, as well as in a municipal landfill. These two alternatives represent two quite different environmental fates for the emitted Hg, although neither provides a stable end-point.
Cadmium was banned for several uses in the early 1980s, but this was soon followed – and partly counteracted – by a rapid increase in the use of batteries in various appliances, such as mobile telephones, laptop computers and cordless tools. Since these batteries are less exposed than the uses affected by the ban, less Cd is emitted to the environment. This is not, of course, to say that they do not constitute a problem. On the contrary: Cd in batteries constitutes a serious problem for waste management, and if not handled properly, discarded batteries will, and already do, release considerable amounts of Cd to the environment.
Figure 5 The use (top) and emissions (bottom) of Cd in Stockholm. The different uses are presented cumulatively. Note the different scales on the y-axis.

In 1968 the Pb concentration in petrol in Sweden was 0.63 g/l. Since then the concentration has gradually been reduced, and the petrol consumption has not increased as rapidly as before (Lohm et al., 1997). Thus, Pb emissions have steadily decreased.
For Cu and Zn the datasets did not facilitate reconstruction of the historical uses and emissions like the ones presented above. However, paper V presents a budget approach identifying the products that are contributing to the load of Cu and Zn to sewage treatment plants, to storm water and to the recipients. Cu was found to originate mainly from tap water, brake linings and copper roofs. For Zn galvanized goods and tyres were the main sources. Food is a considerable source relating to both metals.
Metals at sewage treatment plants

The fluxes of metals at the sewage treatment plants are summarized in Table 2. Both incoming and emitted water fluxes of all metals have decreased over the period studied. The most likely explanation is better treatment of industrial effluents connected to the sewage system. For Cu, Hg and Pb the fraction of the incoming metal that exits in the emitted water has decreased, but there are no clear trends for Cd and Zn relating to their fate at the STPs.

Table 2 Average fluxes of metals at sewage treatment plants in Stockholm, tonnes/year. Incoming fluxes have been calculated as the sum of the amounts in emitted water and sludge.

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>In</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1975-80</td>
<td>0.43</td>
<td>28</td>
<td>0.24</td>
<td>8.2</td>
<td>58</td>
</tr>
<tr>
<td>1981-90</td>
<td>0.084</td>
<td>14</td>
<td>0.11</td>
<td>2.8</td>
<td>32</td>
</tr>
<tr>
<td>1991-96</td>
<td>0.042</td>
<td>9.0</td>
<td>0.067</td>
<td>1.4</td>
<td>17</td>
</tr>
<tr>
<td><strong>Out</strong></td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>1975-80</td>
<td>0.12</td>
<td>5.3</td>
<td>0.092</td>
<td>0.96</td>
<td>18</td>
</tr>
<tr>
<td>1981-90</td>
<td>0.025</td>
<td>4.1</td>
<td>0.022</td>
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<td>1.0</td>
<td>0.010</td>
<td>0.091</td>
<td>4</td>
</tr>
<tr>
<td><strong>Sludge</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1975-80</td>
<td>0.30</td>
<td>23</td>
<td>0.15</td>
<td>7.2</td>
<td>40</td>
</tr>
<tr>
<td>1981-90</td>
<td>0.059</td>
<td>10</td>
<td>0.085</td>
<td>2.6</td>
<td>18</td>
</tr>
<tr>
<td>1991-96</td>
<td>0.030</td>
<td>8.0</td>
<td>0.056</td>
<td>1.3</td>
<td>12</td>
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</tbody>
</table>

Metals in surface sediments - evaluation of the present situation

The metal concentrations in surface sediments of the different sub-areas are presented in Table 3. They are classified by comparison with “natural” values for lakes and coastal areas (Swedish EPA, 1999a, b). Note that this classification is not based on the biological effects of metal concentrations, but on their statistical distribution.

Every sub-area was also compared with the sub-area with the lowest median concentration in Mälaren and the archipelago respectively, using a Mann-Whitney test. The significance levels of the differences are indicated in Table 3.

In table 5 Cu, generally, shows the most elevated concentrations, with large or very large deviations from natural levels in all sub-areas but one. The sediments of sub-area 1 (in the very centre of the city) display very large deviations with respect to all metals. The sediments from Mälaren, in general, do not deviate from natural levels as much as the sediments from the archipelago. These “comparative values” are, however, somewhat arbitrary and may not be entirely representative for this area.
Table 3 Median metal concentrations in surface sediments (0-1 and 1-2 cm) of the sub-areas investigated (Figure 1) in µg/g d.w. (Paper II) classified on the basis of their elevation relative to "comparative values" as presented by the (Swedish EPA, 1999a, b) for lakes and coastal areas. The classes are: 1 No deviation; 2 Slight deviation; 3 Obvious deviation; 4 Large deviation; 5 Very large deviation. Also indicated is the significance level of the deviation from the sub-area with the lowest median in Mälaren and the archipelago respectively, as given by a Mann-Whitney test: *=0.05; **=0.01; ***=0.001. n=number of surface sediment samples.

<table>
<thead>
<tr>
<th>Sub-area</th>
<th>N</th>
<th>Cd</th>
<th>Class</th>
<th>Cu</th>
<th>Class</th>
<th>Hg</th>
<th>Class</th>
<th>Pb</th>
<th>Class</th>
<th>Zn</th>
<th>Class</th>
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<tr>
<td>A</td>
<td>10</td>
<td>0.75***</td>
<td>2</td>
<td>49.9</td>
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<td>0.10</td>
<td>2</td>
<td>74.9***</td>
<td>2</td>
<td>255</td>
<td>3</td>
</tr>
<tr>
<td>B</td>
<td>12</td>
<td>0.43</td>
<td>2</td>
<td>63.6**</td>
<td>4</td>
<td>0.16</td>
<td>2</td>
<td>48.2</td>
<td>2</td>
<td>232</td>
<td>3</td>
</tr>
<tr>
<td>G</td>
<td>10</td>
<td>0.79***</td>
<td>2</td>
<td>87.3***</td>
<td>4</td>
<td>0.30***</td>
<td>3</td>
<td>72.6***</td>
<td>2</td>
<td>282**</td>
<td>3</td>
</tr>
<tr>
<td>C</td>
<td>12</td>
<td>1.07***</td>
<td>2</td>
<td>118***</td>
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<td>3</td>
<td>95.8***</td>
<td>3</td>
<td>311***</td>
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<tr>
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<td>192***</td>
<td>5</td>
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<td>4</td>
<td>185***</td>
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<td>F</td>
<td>12</td>
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<td>268***</td>
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<td>5</td>
<td>296***</td>
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<td>862***</td>
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<td>D</td>
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<td>5</td>
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<td>4</td>
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<tr>
<td>1</td>
<td>7</td>
<td>3.23***</td>
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<td>301***</td>
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<td>2</td>
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<td>1.26**</td>
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<td>0.16</td>
<td>3</td>
<td>40.2</td>
<td>3</td>
<td>201</td>
<td>3</td>
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</table>

Other recent studies include data on heavy metal concentrations in sediments in Stockholm (Blomqvist and Larsson, 1996; Östlund et al., 1998). Table 4 compares the metal concentrations in surface sediments of the present study with values from some of these previous studies and from the open Baltic Sea. The results agree reasonably well, although it should be noted that the other studies have used different sampling strategies, and that the areas investigated do not entirely coincide. This explains some of the differences between the results, especially the fact that in most cases the maximum concentrations found in the other studies are considerably higher than the values reported in Paper II. It is also striking that for all metals the medians from Paper II are higher than in the other studies in the archipelago, whereas in Mälaren they are lower. This too could possibly be explained by the different sampling strategies. The values for surface sediments from the open Baltic presented by Borg and Jonsson (1996) are considerably lower than those found in the archipelago for most metals. However, Cd and to some extent Zn are exceptions, indicating more widespread pollution over the whole Baltic Sea. Applying the same classification criteria to the surface sediments from the open Baltic, as described above, they fall into classes 4 and 5 with respect to all metals except Hg (class 2).
To summarize, the concentrations of metals in sediments in central Stockholm indicate very large deviations from the comparative values suggested by the Swedish EPA. According to the findings presented in Paper II the fluxes of all metals studied are also elevated. For Cd, Cu, Hg and Pb the increase is five-fold, and for Zn it is three-fold, compared to the surrounding areas.

Table 4 The concentration of metals (µg/g dw) in surface sediments (0-5 cm) in the municipality of Stockholm (only sub-areas C-F and 1-2). Data reported in this work and in other recent investigations. For comparison values for the open Baltic Sea are also included. n=number of samples included in this compilation. Refs: (1) this study (Paper II), (2) (Östlund et al., 1998), (3) (Blomqvist and Larsson, 1996), (4) (Borg and Jonsson, 1996). “Pre-industrial” refers to sediments below 10 cm depth in the open Baltic Sea. Note that for comparison some samples reported by Östlund et al. were excluded because they were taken from areas not included in the present study.

<table>
<thead>
<tr>
<th></th>
<th>Ref.</th>
<th>n</th>
<th>Cd</th>
<th>Cu</th>
<th>Hg</th>
<th>Pb</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mälaren</td>
<td>(1)</td>
<td>75</td>
<td>Min</td>
<td>0.31</td>
<td>52</td>
<td>0.03</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Median</td>
<td>1.8</td>
<td>174</td>
<td>0.92</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Mean</td>
<td>2.0</td>
<td>188</td>
<td>1.2</td>
<td>201</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>Max</td>
<td>4.2</td>
<td>308</td>
<td>4.3</td>
<td>539</td>
</tr>
<tr>
<td>Mälaren</td>
<td>(2)</td>
<td>57</td>
<td>Min</td>
<td>0.33</td>
<td>62</td>
<td>0.12</td>
<td>49</td>
</tr>
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<td>240</td>
<td>1.8</td>
<td>230</td>
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<td>2.4</td>
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<td></td>
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<td>7</td>
<td>940</td>
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<td>(1)</td>
<td>30</td>
<td>Min</td>
<td>1.2</td>
<td>120</td>
<td>0.94</td>
<td>91</td>
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<td></td>
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<td>458</td>
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<td>361</td>
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<td>85</td>
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<td>487</td>
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<tr>
<td></td>
<td></td>
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<td>1400</td>
<td>38</td>
<td>5700</td>
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<td>(3)</td>
<td>84</td>
<td>Min</td>
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<td>23</td>
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<td>Median</td>
<td>2.2</td>
<td>184</td>
<td>2</td>
<td>192</td>
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<tr>
<td></td>
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<td></td>
<td>Mean</td>
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<td>215</td>
<td>2.6</td>
<td>231</td>
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<tr>
<td></td>
<td></td>
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<td>13</td>
<td>608</td>
<td>18</td>
<td>895</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface</td>
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<td>Mean</td>
<td>2.9</td>
<td>63</td>
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<td>71</td>
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<td>28</td>
<td>0.05</td>
<td>32</td>
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<tr>
<td>Preindustrial</td>
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<td>Mean</td>
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<td>45</td>
<td>0.04</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
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<td>SD</td>
<td>0.19</td>
<td>13</td>
<td>0.02</td>
<td>15</td>
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</table>

The elevated concentrations of metals in the sediments may not seem to pose an immediate threat. However, because mobilization of metals may occur they
may constitute a potential threat if made available to the benthic biota. For example, an increased redox potential in the sediments, caused by a reduced load of organic material, may release substantial amounts of metals into the water phase. This development is what has been referred to as a ‘chemical time bomb’ (Stigliani et al., 1991). Once the redox conditions are high enough for higher organisms to be present, aeration of sediment increases, which promotes the release of more metals. Further, the fact that the fluxes are still elevated indicates that there are unmonitored fluxes of some heavy metals, which should be a cause of concern.

**Aquatic metal fluxes in Stockholm**

Because of high sedimentation rates, the time period covered by the sediment cores was very short in some sub-areas. Figure 7 shows the reconstructed loads in three sub-areas in which the cores facilitated reconstructions over the whole of the 20\textsuperscript{th} century. For each sub-area, the reconstruction presents the average of all samples from every decade (1900-1909; 1910-1919, etc).

In sub-area D, in the very centre of the city on the freshwater side, all metals show generally decreasing trends since the 1970s. Since the 1940s the anthropogenic deposition of Pb in the sediments in sub-area D seems to have increased relative to that of other metals. This may be due to the introduction of a more specific source of Pb: fuel additives. There is also another interesting characteristic in the reconstructions of metal loads in this sub-area. They all have a distinct maximum load in the 1930s, just before the opening of the first sewage treatment plants in Stockholm. Also note that Hg is the only metal whose sediment load decreases in the early 20\textsuperscript{th} century. This is interesting in the light of the findings presented in Paper I, that Hg compounds were extensively used for medical purposes during the 19\textsuperscript{th} century, and until the early 1900s when they were replaced by As compounds and later by antibiotics. In sub-area 1, closest to the city on the brackish-water side, the general decrease in all metal loads starts earlier than in sub-area D. The reduction coincides with the period when environmental legislation was implemented in Stockholm; treatment of domestic and industrial sewage was improved, and some metal uses were regulated. In 1989 the outlet of the STP at Bromma was moved from Mälaren (on the border between sub-areas C and G) to the innermost archipelago (sub-area 1). The amounts of metals emitted from Bromma in 1989 were 7 kg Cd, 600 kg Cu, 4 kg Hg, 60 kg Pb and 1300 kg Zn, which may explain the slight increase in the flux of all metals between the 1980s and '90s. In sub-area 4 the metal load is lower, because of the low sedimentation rate and lower metal concentrations. However, the concentrations of the metals studied are high enough to be classified as large or very large deviations from the comparative values for coastal areas. It should be
noted that only some of the water flows through this sub-area, the rest passes through sub-area 5.

**Figure 7** Reconstructions of the heavy metal loads corrected for sediment focusing (kg/ (y*km²)) in sub-areas D (top), 1 (middle) and 4 (bottom). The total number of cores used for the reconstruction was three each from sub-areas D and 1, and two from sub-area 4.

Unfortunately, it has not been possible to derive reconstructions like the ones presented in Figure 7 for all sub-areas. In sub-areas 2 and 5 the cores only covered approximately 20 years. Therefore, in Paper III several sub-areas had to be combined in order to reconstruct the total sediment load for the whole area. Paper IV focused on the last three decades, a period covered by using data presented in another study for two cores from sub-area 2 (Östlund et al., 1998).
Thus, it was possible to calculate the total metal input to the sediments across the whole area, and to describe the development of what has been called the immission landscape, i.e. the changing pattern of metal pollution in the area. In Figure 8 all the samples from one decade in one sub-area have been combined in one bar. The result is an illustration of how past pollution is being dispersed in time and space. As the metal load to these areas is reduced, so is the size of the area affected by the emissions. Some sub-areas, where the load was considerable during the 1970s have now returned to the background level. This illustrates that the immission landscape is dynamic, but that changes are much slower than changes in emissions.

**Figure 8** The developing immission landscape of heavy metals in the sediments of Stockholm (c.f. Figure 1). Unit: kg per km² water area and year.
A striking feature of the trends shown in Figures 7 and 8 is that the reconstructions of all metals are similar. This may imply that they have common sources, and that their fluxes to the sediment are governed by mutual factors. There is no simple relationship between the use of a metal and its sediment deposition. Improved sewage treatment has not only reduced the load of regulated metals such as Hg and Cd, but also of Cu and Zn. However, this reduction is merely a redistribution, illustrating the limits of end-of-the-pipe solutions. If the load of metals reaching the sewage treatment plant is not reduced, improved treatment will only redirect the metals, in this case into the sludge. Consequently, Cu in sludge is of increasing concern, as the levels are approaching the Swedish legal limits for agricultural use of sludge (Bergbäck et al., acc.).

For Hg, a comparison was made in Paper III between the calculated emissions to water and the reconstructed sediment load during the whole of the 20th century (Figure 9). It appears that the sediment load is poorly correlated to the emission estimate. Large amounts of mercury were emitted between 1950 and 1975 but can not be traced in the sediment. A possible explanation (see Paper III) is that much of these emissions may have been deposited very close to the source, and may therefore have been missed, or even avoided, during sampling for this study, which aimed at describing the general deposition pattern. Another explanation is the possibility of volatilization of mercury through microbial activity in the sediments (Benjamin and Honeyman, 1992). The rapid decrease in emissions since the 1970s has caused a reduced calculated Hg load to the aquatic environment, but the measured reduction in the sediment load is much slower. Thus, the area has gone from a balance close to a zero in the first half of the century, to a positive balance between 1945 and 1980 (indicating unknown sinks such as export or locally elevated sediment load), to a negative balance today (indicating unidentified sources, such as diffuse emissions from the city not included in the monitoring of metal fluxes, or resuspension of previously deposited, more polluted sediments). Over the whole period, emitted quantities closely match the sediment load. The calculations indicate that some 30 tonnes of mercury have been emitted to water, whereas the sediment cores indicate a total load of approximately 20 tonnes in the whole area.
In Paper IV a budget approach was used to compare the different fluxes of Cd and Pb to the aquatic recipient of Stockholm. The results are summarized in Table 5. They show that the sediment load of Cd and Pb has been reduced since the 1970s, but not by the same level as the emissions (see above) or as much as most other monitored fluxes. As a consequence, the metal sink (sedimentation) has changed from being smaller than the sources (at least for Cd, and probably also for Pb, see Paper IV) indicating export to the Baltic Sea, to being larger, indicating that there are unidentified sources as discussed above for Hg.

Table 5 Budget for the aquatic fluxes of cadmium and lead in Stockholm 1975-1995 (tonnes/year). 1) Mean value for the period 1975-1980. 2) 1970; 3) 1988; 4) 1980-81 (upper limit) and 1988 (lower limit); 5) 1984; 6) 1994; n.d. = no data available. A positive balance indicates that there are sinks that have not been identified, e.g. export to the Baltic Sea; a negative balance indicates unidentified sources, e.g. diffuse emissions and internal load.

<table>
<thead>
<tr>
<th></th>
<th>Cd</th>
<th></th>
<th>Pb</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Sources:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>From sewage treatment</td>
<td>0.12&lt;sup&gt;1)&lt;/sup&gt;</td>
<td>0.03</td>
<td>&lt;0.001</td>
<td>1&lt;sup&gt;1)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>0.1&lt;sup&gt;2)&lt;/sup&gt;</td>
<td>0.04&lt;sup&gt;3)&lt;/sup&gt;</td>
<td>0.01</td>
<td>8&lt;sup&gt;2)&lt;/sup&gt;</td>
</tr>
<tr>
<td>Storm water</td>
<td>n.d.</td>
<td>0.005&lt;sup&gt;5)&lt;/sup&gt;</td>
<td>0.005&lt;sup&gt;6)&lt;/sup&gt;</td>
<td>n.d.</td>
</tr>
<tr>
<td>Regional background</td>
<td>0.01-0.04</td>
<td>0.003</td>
<td>0.01-0.04</td>
<td>4-5</td>
</tr>
<tr>
<td>Sources, total:</td>
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<td>0.075-0.105</td>
<td>0.025-0.056</td>
<td>13-14</td>
</tr>
<tr>
<td>Sinks:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total sediment deposition</td>
<td>0.18</td>
<td>0.09</td>
<td>0.08</td>
<td>14</td>
</tr>
<tr>
<td>Balance (average):</td>
<td>0.065</td>
<td>0</td>
<td>-0.04</td>
<td>-0.5</td>
</tr>
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</table>
Present day budgets for Cu and Zn are presented in Table 6 (Paper V). Note that, in contrast to Cd, Hg and Pb, these metals show approximately zero balances, i.e. the sources of metals to the studied area are approximately balanced by the sediment load. For Zn, there even seems to be a positive result, indicating that this metal is exported to the open Baltic Sea.

It can also be noted that the regional background is more important for the fluxes of Cu and Zn than in relation to those of Cd and Pb. Regional background contributes to more than half of the total sediment load of Cu and Zn, approximately half of the Pb load and less than half of the total sediment load of Cd.

<table>
<thead>
<tr>
<th>Sources:</th>
<th>Cu 1995</th>
<th>Zn 1995</th>
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<tbody>
<tr>
<td>From sewage treatment</td>
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<td>4</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
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<td>2.3</td>
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<tr>
<td>Storm water</td>
<td>0.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Direct emissions 1</td>
<td>0.7</td>
<td>1.5</td>
</tr>
<tr>
<td>Regional background</td>
<td>3.8-4.5</td>
<td>13-16</td>
</tr>
<tr>
<td>Sources, total</td>
<td>6.4-7.1</td>
<td>22.1-25.1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sinks:</th>
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<tbody>
<tr>
<td>Total sediment deposition</td>
<td>6.6</td>
<td>20</td>
</tr>
<tr>
<td>Balance (average)</td>
<td>0.15</td>
<td>3.6</td>
</tr>
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</table>

**Table 6** Budget for the aquatic fluxes of Cu and Zn in Stockholm 1995 (tonnes/year) (Paper V). A positive balance indicates that there are sinks that have not been identified, e.g. export to the Baltic Sea. 1 Anti-fouling agents (Cu) and sacrificial anodes (Zn), from (Sörme et al., acc.-b).

**Reflections and concluding remarks**

This thesis presents an extended material flux analysis for metals in Stockholm, comprising both the metal fluxes within the society, the emissions from it and the dispersion of metals within the aquatic recipient. These different fluxes have been studied in different ways. In this section, the advantages and disadvantages of the different methods are discussed.

The information relating to societal material fluxes in the human society was gained through a material flux analysis (MFA) approach. This is a way of quantifying the “flows of materials in, out and through an economy-environment system” (Voet et al., 2000). The sources of information included interviews, official reports and trade statistics. Rarely was it possible to find answers to the exact question posed, and hence a number of assumptions were made about the representativeness of the data collected. For example, figures have been scaled down from a national level, or scaled up from an individual or a household level. It was
not possible to use standard methods, since MFA is a relatively new field of research and standard methods are only slowly and recently being developed (Voet et al., 1995).

For the environmental metal fluxes, standard methods are available. However, we must question whether the data collected is of value, and how best it can be interpreted. The sampling procedure is really nothing but a way of scaling up the information from a sample to the whole area. In relation to the chemical analyses we must question not only their validity in answering our questions (method validation), but also whether these questions are the relevant ones. For example, in this work the Swedish standard method was chosen for digestion of sediments. The standard method was chosen to enable comparison with other studies. Several other methods are available, and would have resulted in the mobilization of different quantities of metals. For example a total digestion using hydrofluoric acid would have mobilized more Cr and Ni. Thus, the analysis does not really tell the metal content of the sediment, but the amount of metal that is mobilized from it by the specified method. These uncertainties, though rarely noted, are as important as the more obvious simplifications and assumptions used in MFA.

There are also differences in the way uncertainties are dealt with in MFA compared with more traditional environmental investigations, where uncertainties in measurements can be reduced by taking more samples, analysing more replicates etc. This has no proper analogue in MFA. Normal statistics are not well suited to handling the types of uncertainties affecting MFA. For example, different sources present different figures relating to the use of a substance in a product. These figures cannot be represented in terms of confidence intervals. When the same number is presented, this does not necessarily increase the reliability of the information, since different sources may be referring to a single original source. An attempt to deal with these questions is presented by Hedbrant and Sörme (acc.), although the rationale presented does not exclude vague and subjective estimations.

To ensure a complete picture of heavy metal fluxes in an urban area, it is necessary to include several approaches. This thesis presents one way of doing this, by combining information on the industrial metal metabolism, with emission data, and reconstructions of the pollution history based on sediment cores. The relationships between these are not easily described, but an extended material flux analysis helps to create a fuller picture of urban heavy metal metabolism and its traces in the environment.

In their recent book Voet et al. (2000) question whether reducing metal emissions from various sectors has solved the environmental problems associated with heavy metals. The book deals with the Dutch situation, and their conclusion is that, currently, the influx to society of several metals is greater than the emissions, and therefore metals must accumulate in the technosphere. With the pres-
ent management regime this accumulation will result in increased emissions in the future. This, together with findings that environmental heavy metal concentrations are not declining, leads to their suggestion that the problems associated with heavy metals are far from solved. The present study concurs - reducing emissions from society does not solve the problem, it only shifts the emphasis. Even where metal emissions are reduced, it may take a long time before any changes in the environmental fluxes can be seen.

The results of this thesis suggest that:

- Mercury has a very long history of use in Stockholm, spanning at least 200 years. Over this period a number of uses have succeeded each other. These include small-scale industries, medical treatment, electric uses and dental fillings. After World War II, the total use increased dramatically through dentistry and new uses in anti-fouling agents and in the pulp-industry. Many of these uses have been very dissipative, causing extensive Hg emissions.

- The uses of Cd, Hg and Pb have recently been reduced substantially through technological development and legislative measures. For Cd, the restrictions on some uses have been partially counteracted by technological developments, which lead to an increase in the use of NiCd batteries increase in the late 1980s. Since the Cd in batteries is much less exposed than in, for example, cadmated surfaces, the ‘cadmium’ ban was still successful in reducing Cd emissions.

- Together with improved treatment of industrial waste-water the decrease in use has reduced the fluxes of Cd, Hg and Pb in Stockholm, including the sediment load. However, the sediment load has not decreased as quickly as the other fluxes, resulting in a negative balance in the budget of these metals in Stockholm’s aquatic recipients, indicating unidentified sources in this area. The importance of including sediment fluxes in environmental monitoring of metals is, therefore highlighted, as well as the need for a better understanding of the processes that affect the transport of metals from sources to sediment in this area, i.e. the metallic biogeochemistry of the city.

- The fluxes of Cu and Zn have also been reduced. The sources of these metals are approximately balanced by the sediment load in the whole area studied. For Zn, the area may even act as a source to the Baltic Sea.

- The Cu and Zn in the aquatic environment of Stockholm comes mainly from sewage treatment plants and from storm water. The products that contribute most to these emissions are tap water, brake linings and roofs
(Cu), and galvanized goods and tyres (Zn). Food is a considerable source of both of these metals.

- The concentrations of metals in surface sediments in central Stockholm are substantially elevated compared to the “natural” values suggested by the Swedish EPA. In the whole archipelago the deviations are large or very large for all metals, whereas in Mälaren they are a little lower, except for Cu.

- Elevated sediment loads were noted for all metals studied. For Cd, Cu, Hg and Pb the increase was five-fold, and for Zn it was three-fold, compared to the surrounding areas.

- The polluted sediments in this area may possibly be regarded as so-called chemical time-bombs. Metals may become bio-available through a number of chemical, physical and biological processes, which may act rather quickly and mobilize large amounts of metals in a rather short time.

- The extended material flux analysis presents a way of dealing with the complex system of metals in the urban environment - their use, emissions and environmental fate.
Acknowledgements

Five years ago, I moved from Stockholm to Linköping to write a thesis about Stockholm. This may seem paradoxical, but I soon realized that the research environment at the Department of Water and Environmental Studies (Tema Vatten) at the university of Linköping was more important for the work I was doing, than the proximity of the study area. Therefore I want to start by thanking everyone who has contributed – both socially and professionally – to this very special environment during these years.

There are some people that I especially want to thank. First of all, my supervisors, Ulrik Lohm at tema Vatten and Bosse Bergbäck at Kalmar University, have encouraged me and guided me in the scientific landscape, without interfering with my own exploration, giving me a considerable amount of freedom to find my own way.

The experienced advice and skilful assistance given by Lena Lundman have been of tremendous value. Her experience and know-how in the lab are priceless, and can not be sufficiently emphasized.

Martin Lindström has been an important companion along the whole journey - during sampling, as a co-author, and in discussions about ideas and manuscripts, sharing his knowledge about sediments.

All the members of the metal metabolism group have in different ways contributed to my work: John Svidén has broadened my historical perspectives, as well as my insights relating to environmental history and 'policy implications'. Louise Sörme has contributed not only with data relating to the urban metabolism of metals, but also with valuable perspectives, inspiring discussions and new ideas. The ever-enthusiastic Johan Hedbrant has a way of finding new ways to look at things. Discussions with him are a source of pleasure and inspiration. When I began working with the metabolism of metals, Catarina Östlund was my first co-worker. She generously shared her experiences in the field and helped me get into it.

The crewmembers of R/ V Sunbeam did a great job during the two sampling cruises, making these weeks unforgettable. Fantastic people on a wonderful ship!

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I am a little flattered by the number of people who have taken their time to improve the quality of my thesis by giving me comments and constructive criticism of the manuscript at different stages. They are too many for all of them to be mentioned by name, but I am grateful to you all! However, Bo Wiman at the University of Kalmar deserves special thanks, as well as John Blackwell who considerably improved my English.

My time at tema Vatten would not have been the same without the support and friendship of fellow PhD students, especially the D95 group, or my lunch companions in ‘matlaget’, who have literally sustained my metabolism.

I am also grateful to my family and to all my friends for their support in every way, and to those who every now and then have taken my mind off sediments and heavy metals; to ‘patrull Bävern’ and the rest of the SMU-scout troop of Linköping, and to Hammarby IF. I hope to be able to see much more of you all in the future than in the last few months.

My warmest thanks go to Elisabeth, for all her love and support, for always believing in me, and for being the wonderful person she is. This, however, can not be accurately expressed in this way, and I shall therefore present my gratitude to her at another occasion.

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