Tracing Copper from society to the aquatic environment
Model development and case studies in Stockholm

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Summary

Copper remains at elevated levels in the aquatic environment of Stockholm due to diffuse urban sources. Management of these diffuse sources requires their quantification but they cannot be measured directly by field observations. The working hypothesis of this thesis was that Copper levels in the sediments of urban lakes would reflect diffuse emissions within their catchment areas. In order to test this hypothesis, a source – transport – storage conceptual model was developed for tracing the urban diffuse sources of Copper to the sediment in the urbanised catchment. A substance flow analysis (SFA) approach was taken in the source module and a fate, mass-balance model was applied in the lake module. Five separate urban lakes (Judarn, Laduviken, Långsjön, Räcksta Träsk and Trekanten) within the Stockholm area and a main water flow pathway from Lake Mälaren to the inner archipelago of the Baltic Sea, through Stockholm, were selected as case studies.

In comparison to actual source strength data in the literature for the five case study lakes, the SFA approach gave similar results to previous models, but with reduced uncertainty. The SFA approach was also able to indicate the actual sources of urban copper, which was not accomplished by the other approaches and which is a great advantage in managing the sources. For the five lakes in Stockholm, traffic and copper roofs were found to be major contributors of Copper. For the three more polluted lakes, good agreement was obtained between simulated sediment copper contents and independent field observations, thereby supporting the applicability of the model in such cases. Furthermore, simulation results showed sediment copper content to be linearly dependent on the urban load. While this suggests that the urban copper sediment level reflects the urban load, considerable integration of this load over time (decade(s)) was suggested by the simulation results, so time must be allowed in order to detect a change in the urban load by field monitoring of the sediments.

Published data on the main water flow pathway from Lake Mälaren to the archipelago showed a peak in sediment copper content close to the city centre, confirming a considerable urban influence. An approach to quantitatively follow Cu from its urban source through such a complex, aquatic system was developed and applied to Stockholm. The compliance of future quantitative model results with monitoring data may help test the choices made in this conceptual model and the applicability of the model. Data availability proved to be a major obstacle to achieving a quantitative model, particularly as several municipalities with different levels of data availability surround the main water flow pathway studied.

Finally, the applicability of the quantitative, coupled source – transport – storage was demonstrated in a simplified scenario analysis. The ability of the model to estimate the copper load to air and soil and to the urban aquatic environment was also demonstrated.
Keywords: Diffuse source, source analysis, sediment pollution levels, urban lake, Copper, Stockholm archipelago, SFA
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Stockholm, Dec 2009

Qing Cui
List of Appended Papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals:


The contribution of the author was the work on formulating the conceptual model, establishing the numerical model, data collecting, model simulation and analysis of the simulation results. The author was responsible for carrying out the research and writing the paper. The author also made an oral presentation of the paper at the conference.


The contribution of the author was the work on modifying the numerical model, data collecting, model simulation, and the sensitivity and uncertainty analyses. The author was responsible for carrying out the research work and writing the paper.


The author was part of the research group, took part in discussions on this work and contributed to the literature search and data collection.
# Contents

Summary ............................................................................................................................................... i
Acknowledgements ................................................................................................................................... iii
List of Appended Papers ........................................................................................................................ iv
Contents .................................................................................................................................................... v

1. Introduction ........................................................................................................................................... 1
   1.1 Background and study motivation ..................................................................................................... 1
   1.2 Aims and objectives ............................................................................................................................ 2

2. Background information from previous studies ..................................................................................... 5
   2.1 Copper .............................................................................................................................................. 5
      2.1.1 The life cycle of Copper .............................................................................................................. 6
      2.1.2 The toxicity and environmental effects of Copper .................................................................... 6
   2.2 The urban water system in Stockholm, Sweden ................................................................................ 6
   2.3 Copper sources, fate and environmental levels in Stockholm ............................................................. 8
      2.3.1 Anthropogenic sources of Copper in Stockholm ...................................................................... 9
      2.3.2 The sediment copper levels in the aquatic system of Stockholm ............................................. 10
   2.4 Models estimating the urban load of diffuse emissions ..................................................................... 11
      2.4.1 Two major approach for estimating the urban load of diffuse emissions ............................... 12
   2.5 Model for the fate of Copper in lakes ............................................................................................... 13
   2.6 Lake sediment as recorder of human activities ............................................................................... 15

3. Model description .................................................................................................................................... 16
   3.1 Source model ................................................................................................................................... 17
   3.2 Lake model ...................................................................................................................................... 20
   3.3 The basin-strait approach for a complex aquatic system .................................................................. 21

4. Case studies ......................................................................................................................................... 23
   4.1 The urban lakes in Stockholm: Case study at Level I ..................................................................... 23
      4.1.1 Background information on the studied urban lakes in Stockholm ...................................... 23
      4.1.2 Model simulations and analysis at Level I .............................................................................. 27
   4.2 The aquatic water system in Stockholm - Case study at Level II ................................................... 28

5. Results .................................................................................................................................................. 29
   5.1 Gradient of sediment copper content in the Stockholm aquatic system ...................................... 29
1. Introduction

1.1 Background and study motivation

Stockholm, the capital of Sweden, is a city built on the waters, with 30% of the central urban area being water. Urban development in Stockholm is causing water pollution and the degradation of water quality (Stockholm Environment and Health Protection Administration, 1999). The accumulation of heavy metals (e.g. Cu) in the aquatic environment throughout the central urban area of Stockholm has been shown in several monitoring programmes (Lindström et al., 2001; Sternbeck et al., 2003; Rauch, 2007). The water quality problem caused by urbanisation is one of the important environmental management issues in Stockholm. A few of the aims of the Stockholm Water Programme 2006-2015 concerned the environmental effect of urban runoff to recipient waters and the pollutant levels in the sediment in:

“...1.1 The quality of run-off water shall be such that a good water status is achieved in the city’s lakes and watercourses. ...

1.6 Polluted land and sediment areas which have a major impact on surface water and groundwater shall be cleaned up...”

----- Stockholm Stad, 2006

In Stockholm, diffuse emissions were recognised as a major source of water quality problems (e.g. heavy metals; Sörme et al., 2001; Ahlman and Svensson, 2005). Therefore, estimating and managing urban diffuse emissions became a crucial issue for laying out environmentally friendly development of a regional watershed in Stockholm.

This thesis concerns Copper in water bodies, with Copper being one of the most important heavy metals in Stockholm. Copper was probably the first metal employed by man and is still one of the most widely utilised materials causing concern to resource economists and environmental scientists. Copper is one of the conventional pollutants in the priority list for environmental protection (European Commission, 2001; Eriksson et al., 2007). This study benefited greatly from the large number of previous studies on Copper in Stockholm, e.g. through data availability and quality.

Rodrigues et al. (2009) indicated that it is necessary to make reasonable quantitative estimates not only of environmental pathways, loads and concentrations, but also of socioeconomic drivers and ‘upstream’ control measures, which requires a clear understanding of the cause-effect relationship of copper pollution. To manage diffuse sources of Copper in the urban area, it is necessary to quantify the sources. However, it is clearly impossible to monitor these sources of Copper directly. To get around this problem, diffuse loads have been estimated by different models in the literature. As an alternative approach, the significance of the sources has been inferred by monitoring the levels of Copper in the aquatic environment. In particular, the load of
Copper to a number of lakes in Stockholm was estimated based on land use related to the copper concentration in urban runoff (Larm, 2000; Stockholm Vatten, 2000; Rule, 2006). However, this approach was not able to identify the actual urban sources. A substance flow analysis (SFA) approach proposed by Sörme and Lagerkvist (2002) estimated the urban load of Copper to waste water treatment plants in Stockholm from the leaching process of materials/goods in use. While this approach gathered a great amount of information from different fields such as urban transportation, municipal construction, etc., it was not applied to estimate the load of Copper to the natural lakes of Stockholm.

Lindström and Häkanson (2001a) used a fate model for Copper in lakes along with monitored copper levels in the aqueous phase and the sediment to estimate the load of Copper to a few lakes in Stockholm and indicated the fate of Copper in those lakes. The environmental levels of Copper in terms of concentration of Copper in the aqueous phase and in the accumulation bottoms of a number of discrete lakes and coupled water bodies has been reported from monitoring campaigns and regular monitoring programmes (Lännnergren, 1991; Ekvall, 1999; Lindström and Häkanson, 2001; Lindström et al., 2001; Sternbeck and Östlund, 2001; Lithner and Holm, 2003; Sternbeck et al., 2003; Rauch, 2007; Andersson et al., 2008).

Thus, while a number of models have attempted to address the diffuse urban source strengths and the aquatic concentrations of Copper for lakes in Stockholm, previous research did not attempt to connect the two and was not able to trace the actual source of Copper in the urban environment. Furthermore, little attempt has been made to trace the fate of Copper in recipient lakes and through the connected water bodies of the urbanised area of Stockholm, as is needed to account for the actual diffuse sources of copper levels observed in the aquatic environment.

1.2 Aims and objectives

As outlined in the previous section, despite extensive previous research (Stockholm Vatten, 2000; Larm, 2000; Lindstöm and Häkanson, 2001; Sternbeck and Östlund, 2001; Sörme and Lagerkvist, 2002; Lithner et al., 2003; Sternbeck et al., 2003), there is still a lack of understanding of the actual diffuse sources of Copper to the natural aquatic recipients in Stockholm and the fate of Copper in the lakes. The underlying hypothesis in this thesis was that the copper concentration in the aquatic environment reflects the strength of current diffuse sources and can thus be used as an indirect measure of this strength. The main aim of the thesis was to test this hypothesis through:

1) Investigating the links between the observed levels of Copper in the aquatic environment of Stockholm and the strength of urban sources of Copper.

2) Quantifying the response of the environmental concentration of Copper to a change in the source strength and the time taken for this response.

A secondary aim of the thesis was to estimate the actual urban sources of Copper in the aquatic environment of Stockholm and to deduce the distribution of urban diffuse emissions in this environment.
To achieve these two aims, a source – transport – storage conceptual model for tracing the fate of Copper from sources to the sediment store in the urbanised watershed was developed. The model was designed to integrate current knowledge originating from different disciplines and then quantify the relationship between urban emissions and environmental levels in lake sediment. The model was then applied in case studies at two levels.

Level I: The simple watershed – an individual urban lake and its drainage area.

At this level, the model was refined, applied and tested on a few discrete cases studies of urban lakes in Stockholm. The objectives of the studies on this level were to:

- Develop a SFA model for the urban load of Copper and test the model by comparison with the concentration-based approach.
- Couple the source model to a model for the fate of Copper in the lake and test the applicability of the combined model for simulating the copper flow from urban diffuse sources to the copper content in lake sediment.
- Use the coupled source – transport – storage model to indicate main sources and fates of Copper in a few lakes in Stockholm.
- Investigate the response of the environmental concentration of Copper to a change in strength of the urban source and the time taken to achieve this response.
- Investigate the sensitivity and uncertainty of the combined model in order to identify key factors in the fate of Copper and the quality of the model simulations, and identify additional monitoring needs.
- Discuss the potential use of the combined model for supporting urban planning and environmental management through the model simulation.

Level II: The complex aquatic system – the natural urban water system with coupled water basins.

The studies at this level were based on a case study of the aquatic system in Stockholm. The major question was not how the urban load contributes to the primary recipient, but rather how far downstream in the urban aquatic system the diffuse emission is reflected. The objectives of this section were to:

- Develop a conceptual model for the fate of Copper in a complex, natural water system.
- Review the gradient of sediment copper content along a main water flow path through Stockholm from the literature in order to identify the importance of urban sources to copper concentrations in the case of Stockholm.
- Use the case study of Stockholm to discuss the data availability and the difficulties in developing a quantitative model for a complex watershed.
The aims of this thesis were achieved step by step in three papers. In Paper I, we present the conceptual model for coupling information from urban society and the surrounding aquatic environment. An SFA-based source model and a dynamic lake fate model were adapted and connected to create the concept for the conceptual model. We tested and verified the combined model with the case of the fate of Copper in Lake Trekanten and its drainage area. Based on the case of Lake Trekanten, we then evaluated the use of sediment copper content as an indicator of urban copper emissions.

In Paper II, based on the work in Paper I, we refined the source model for more comprehensive and transparent evaluation of the urban load and the diffuse source. We then tested the model in more cases in Stockholm with various pollution levels and with different characteristics of the urban land use in the drainage area. We evaluated and analysed the model simulation results by comparing the results with field observations and previous estimates, and through carrying out sensitivity and uncertainty analyses.

In Paper III, we attempted to apply the model to a broader and more complex case of the urban aquatic system in Stockholm. We first reviewed the aquatic system of Stockholm and the spatial trend of copper concentration in sediment along the main path of the water flow, then suggested a conceptual approach for dealing with the case of a complex system of urban recipients. This paper also discussed the potential difficulties in applying the conceptual approach.

In this thesis, Chapter 2 summarises knowledge from the literature, Chapter 3 describes the conceptual model and the quantitative models used at each level and Chapter 4 introduces the cases studied and the strategies applied in the two levels of case study. Chapter 5 summarises the main results of the research, while Chapter 6 discusses the use of sediment copper levels to indicate urban diffuse sources and the understanding of the fate of Copper in the urbanised watershed in Stockholm based on the model simulation and the model analysis. Chapter 7 draws conclusions on the results obtained from the model simulation and the case studies.
2. Background information from previous studies

2.1 Copper

Copper is an abundant trace element in nature (28th most frequently found in the earth’s crust; Landner and Reuther, 2004). In the technosphere, Copper is one of the oldest materials, having been in use for at least 10,000 years. Nowadays, Copper is still used extensively in various fields, such as coinage, household products, architecture, industry, electrical, biomedical and chemical applications (Table 2-1).

Table 2-1. Applications of Copper in the technosphere (Richardson, 1997; Sörme et al. 2001; Sviden et al., 2001)

<table>
<thead>
<tr>
<th>Field</th>
<th>Usage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coinage</td>
<td>A component of coins</td>
</tr>
<tr>
<td>Household products</td>
<td>Drinking water piping, cookware and dinnerware, water heating systems, etc.</td>
</tr>
<tr>
<td>Architecture and Art</td>
<td>Roofing, lightening rods, wood preservative, statues, paint, etc.</td>
</tr>
<tr>
<td>Industry</td>
<td>Electroplating, ship painting, brake linings, etc.</td>
</tr>
<tr>
<td>Electrical applications</td>
<td>Copper wire, electromagnets, circuit boards, etc.</td>
</tr>
<tr>
<td>Biomedical applications</td>
<td>Fungicides, radiotracers</td>
</tr>
</tbody>
</table>

Figure 2-1. The technological copper cycle in the anthroposphere (modified from Spatari et al., 2005). The successive life stages plotted from left to right: extraction & production, fabrication & manufacturing, use and waste. Dashed rectangle indicates the life stages involved in our study.
2.1.1 The life cycle of Copper
Copper is a finite but recyclable resource. The international copper association estimated Copper as the third most recycled metal. It is reported that more than 95 percent of all Copper ever mined and smelted has been extracted since 1900 (Spatari et al., 2005). Many studies focused on the life cycle of Copper (Figure 2-1) in multi-scope from the city level to the global level (Bergbäck et al., 2001; Bertram et al., 2002; Graedel et al, 2004). It is reported that 53% of the discarded Copper was recovered and reused or recycled in the global level (Graedel et al, 2004) and 48% in the overall Europe (Bertram et al., 2002). In the field of resources and waste management, the studies stressed that whether the copper would be scarce over this century or not, with different opinions (Graedel et al, 2004, Tilton and Lagos, 2007).

2.1.2 The toxicity and environmental effects of Copper
Copper is one of the essential elements for all organisms, since it is incorporated into a large number of proteins for both catalytic and structural purposes. However, Copper is also toxic to organisms ingesting or exposed to excess levels. At high concentrations, Copper inhibits growth and interferes with a number of cellular processes, such as photosynthesis, respiration, enzyme activity. Therefore, Copper is considered hazardous for the environment, especially the aquatic ecosystem (Flemming and Trevors, 1989).

The wide use of Copper in the technosphere (Table 2-1) influences the copper load to the environment and is leading to increasing copper content in the urbanised aquatic system. When the copper concentration in the environment exceeds a certain level, microbial diversity, populations and activities are affected (Flemming and Trevors, 1989; Landner and Reuther, 2004; Boivin, 2005). Since microorganisms play an important role as primary decomposers in the aquatic ecosystem, Copper is considered a pollutant in the aquatic ecosystem. Therefore the copper content in the environment, such as in the soil, water and sediment, needs to be considered in environmental management/monitoring programmes (Bulter and Davies, 2000; Swedish EPA, 2000; Brils, 2008).

2.2 The urban water system in Stockholm, Sweden
Water flow is the dominant carrier of urban copper loads to the water recipient, so the urban water system contains important information for understanding the sources and fate of Copper in Stockholm. The water system in Stockholm in general is presented in Figure 2-2. There are three input pathways of water into the drainage area: the water supply system, precipitation and surface runoff from the upstream aquatic system. The water provided through the supply system goes into various fields of human life, such as household, business, etc. After use, the water becomes wastewater and is transported to a wastewater treatment plant (WTP) through the sewer system. The wastewater is then discharged to the water recipient after being treated. In Stockholm, three major wastewater treatment plants (WTP), Bromma, Henriksdal and Käppala, are in use, and the discharge points of these are located downstream of the city (see Chapter 4).
Precipitation is another important input to the urban water system. Surface cover in the urbanised drainage area comprises impervious cover and the natural ground cover (USEPA, 2003), and the relative distribution of these characterises the water paths out of the drainage area. When rain falls on impervious surface cover, i.e. urban hard surfaces, it washes off pollutants and particles from these surfaces and forms stormwater (Figure 2-2). In Stockholm, part of the stormwater is discharged into the surrounding water recipient and part goes into the combined sewer system (for details see Chapter 4). When the rain falls on natural ground cover, part of the water goes into the surrounding water recipient through the pathway of surface water, and part infiltrates into the deeper ground and becomes groundwater. The groundwater also contributes to the water recipient, but is mostly stored in the aquifer.

Figure 2-2. The urban water system in Stockholm. The ovals show cover types with different runoff characteristics in the drainage area, the block arrows show inflow pathways of the water, the rectangles are the outflow pathways, and the single-line arrows show the flows of the water runoff.

Surface runoff is one of the natural pathways of water flow through the drainage area (Figure 2-2). In the drainage area, it accepts some of the precipitation from the natural ground, but its most important function is connecting the water recipient with the upstream/downstream system.

The characteristics of the drainage system in Stockholm lead to a focus on different water pathways in studies at different scales:

- For urban lakes without the upstream recipient in Stockholm, such as the case studies at Level I, the wastewater in Figure 2-2 is excluded from the studied system, while the stormwater is the dominant carrier of the urban copper load. This kind of small watershed is the major type involved in this study.

- For the complex aquatic system in Stockholm in Level II, all kinds of water pathways shown in Figure 2-2 are involved in the studied system. However, in the basins without the discharge
point of WTPs in the aquatic system of Stockholm, the pathway of wastewater is still excluded.

2.3 Copper sources, fate and environmental levels in Stockholm
As a result of industrialisation and urbanisation, the use of Copper increased rapidly in the 1900s. In Sweden, electrification (including Cu, Pb) started at the turn of the 19th century and culminated in 1920-1960; the tap water system changed from Fe and Zn to Cu in the 1950s. According to Bergbäck (2001), the total copper stock of Stockholm was about 123 000 tons in 1995. The accumulation in the city of Stockholm has continued, with a ratio of outflow to inflow of 3 to 23 (Figure 2-3).

![Copper flow diagram]

Figure 2-3. Copper flows in Stockholm, Sweden, 1995 (data from Bergbäck, 2001). ‘Protected’ means that this part of copper stock is not exposed to the natural environment. ‘Exposed to Air/Soil/Water’ means the copper applications are exposed to the elements (Air, Soil and Water) and these kinds of copper stock are potential sources of diffuse emissions.

In Stockholm, the copper load to the natural environment is around 5% of the copper flow to solid waste, and the copper load to the aquatic environment is <1% of this (Figure 2-3; Bergbäck et al., 2001). Thus, when estimating the cycle and fate of anthropogenic Copper, the flow to the
natural environment is normally neglected or considered as losses. However, it is exactly this part of the anthropogenic copper cycle that is the focus of the present study.

2.3.1 Anthropogenic sources of Copper in Stockholm

Since the 1970s, the emissions from copper production (the main point source) have decreased considerably (Sörme, 2001), because industries have to a large degree moved out of the city and those remaining have improved various pre-treatments of their effluent. Thus, the contribution of diffuse sources becomes more and more dominant to the copper load in the urbanised watershed in Stockholm.

In this thesis, the cases studied were at city level (Level II) or even lower level (Level I), where the copper stock is mostly in the ‘use state’ (Figure 2-1). The majority of the copper stock is not exposed to the weather or wear processes (the stock under protection in Figure 2-3), and only 38% of the urban copper stock in Stockholm is exposed to the natural environment (Water, Air and Soil; Figure 2-3). Sörme et al. (2001) indicated that electrical applications, such as power cables, telephone cables, consumer electronics, etc. are a major store of Copper in Stockholm (more than 86 000 ton) but are not exposed to the environment and thus Copper emitted from this kind of stock is negligible.

The stocks exposed to the environment in Stockholm are potential sources of copper release. Sörme et al. (2001) summarised copper goods in the anthroposphere of Stockholm in terms of their emissions and the environmental receiver. The copper stocks in vehicles (brakes, tyres, protective paint on boats, petrol, car washing), building materials (roofing, electrical earthing, drinking water pipes) and infrastructure (aerial lines and road surfacing) were judged to be the major sources. Hedbrant (2001) indicated that in the last century the emissions of Copper from drinking water systems increased from <0.5 to ~4.5 tons/year based on the stock of Copper. An estimated 11.5-12.4 tons/year of Copper were emitted from those sources in Stockholm in 1995 (Bergbäck et al., 2001). In addition, about 0.25 tons of Copper were released by the fireworks within Stockholm during the 2000 New Year’s celebrations, a fraction of which arrived at nearby recipients (Burman, 2000). This indicates that fireworks might be a substantial temporary, but non-dominant, source of Copper in Stockholm.

Based on the case of Henriksdal wastewater treatment plant (WTP) in Stockholm, Sörme and Lagerkvist (2002) classified the various copper sources into seven categories: households, drainage water, businesses, atmospheric deposition, traffic, building materials and pipe sediment (Figure 2-4). According to the urban water system in Stockholm (see Figure 2-2), copper emissions from those sources are collected and transported by the wastewater or/and stormwater, and then goes to the recipient directly or indirectly. A source-based approach based on the view of SFA was used to evaluate the diffuse emissions from the stock of copper goods, and applied in the case of the Stockholm City (Sörme et al., 2001) and urban load to Henriksdal WTP (Sörme and Lagerkvist, 2002). In Henriksdal WTP, 90% of Copper came from the sewage water, of
which ~60% derived from households. The copper content in the stormwater mostly originated from traffic and copper roofs (Sörme and Lagerkvist, 2002).

Figure 2-4. Copper sources to the aquatic system in Stockholm (modified from Sörme and Lagerkvist, 2002).

2.3.2 The sediment copper levels in the aquatic system of Stockholm
In the aquatic system in Stockholm, the sediment copper contents were monitored in several studies (Lindström et al. 2001; Sternbeck et al., 2003; Rauch, 2007) to identify the effect of human activities in the city of Stockholm. Lindström et al (2001) divided the main water course through Stockholm into 14 sub-areas, and the sediment samples showed sediment deposition was increased about 5 fold of Copper in the central area of Stockholm, compared to the surrounding areas. Lindström and Håkanson (2001b) also concluded Copper is most dependent on urban influences, according to the regression analysis for sediment copper concentration versus land use parameters in ten urban lakes in Stockholm.

Sternbeck et al. (2003) determinated the occurrence of WFD priority substances (including Cu) in sediments from Stockholm and the Svealand coastal region and sludges in Bromma and
Henriksdal WTPs. The results indicated that Copper were enriched in central Stockholm and the lakes relative to the coast region. Although Copper was found in both sediments and sludge, the spatial trends in the sediments suggest that these substances are also released by other sources than WTPs. Rauch (2007) analyzed the trace metals (Cu) according to 18 sediment samples collected in the outflow of Lake Mälaren and in lakes in the Stockholm area. It showed that Copper and other metals were found at elevated concentrations in the urban area relative to background sites. In Stockholm, Copper is detected in sediment in a range of 27 to 475 mg/kg dw and most sampled sites was in the state of high copper concentrations according to Swedish EPA sediment concentration guideline (Swedish EPA, 2000).

In addition, the sediment contents of heavy metals were used as the evidence of long-term pollution of heavy metals in Lake Mälaren (Renberg et al, 2001; Olli and Destouni, 2008).

2.4 Models estimating the urban load of diffuse emissions

Many studies and models on diffuse emissions, especially at the watershed scale, stress the importance of urban runoff. These studies estimate the copper load from the concentration of pollutants in the runoff through the so-called concentration-based approach. For example, the Storm Water Management Model (SWMM) proposed by USEPA is a dynamic rainfall-runoff simulation model that examines the generation and transportation of urban runoff and its pollutant loads from the urban area. StormTac is a watershed management model for the quantification of pollutant loads with rainfall-runoff simulation and for the design of stormwater drainage and treatment (Larm, 2000). In 2000, the Stockholm water programme estimates the copper load to the lakes and watercourses in Stockholm by the concentration-based approach (Lä nnergren, 2009). Since the pollutant load in urban runoff is already a mixed load, this approach is not able to indicate urban diffuse sources.

Some researchers have attempted to explain emissions of heavy metals from the perspective of material metabolism, namely the source-based approach. STOCKHOME is a spreadsheet model to present flows and stocks of the metal consumption process and emissions at the urban level (Hedbrant, 2001). The model has been used to present metal metabolism in Stockholm from 1990-1995. STOCKHOME indicated the importance of the stock of heavy metals in long-lived materials and goods, e.g. Copper in the tap water system in Stockholm, but was not suited for studying the effect of the emissions on the recipient. Sörme and Lagerkvist (2002) linked the copper load in WTP with the urban sources (material/goods in use) based on the SFA structure (see Section 2.3.1). A model called SEWSYS was then developed for tracking copper transport and treatment in the sewer system (Ahlman and Svensson, 2005). SEWSYS has been used for studying wastewater in Gothenburg, Sweden. The studies based on the source-based approach focus on the origins and flows of Copper related to human activities in the anthroposphere, but not the water environmental effect.

STOCKHOME focused on estimating the diffuse load from urban storage, i.e. materials and goods in use, but did not involve the distribution of the load in the recipient. SWESYS estimated
the diffuse loads from urban sources, but it mainly focused on the scope of the urban sewage (wastewater) system. StormTac estimated urban loads from the water quality of urban runoff and the effect on water quality in the recipient, but urban sources were not involved. SWMM focused on the quality and quantity of urban runoff in the drainage system (pipes, channels, etc.), and the scope of SWMM was similar to StormTac for estimating urban diffuse emissions in the watershed. These models simulated the copper transportation along with stormwater from the urban area to natural recipient in part (Table 2-2), but none of them was able to present the relationship between the strength of urban diffuse sources and the copper levels in the recipient.

### Table 2-2. Scope and characteristics of models for urban loads

<table>
<thead>
<tr>
<th>Model</th>
<th>Urban load quantification</th>
<th>Scope Scope</th>
<th>Source</th>
<th>Recipient</th>
<th>Water flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>STOCKHOME¹</td>
<td>source-based</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SEWSYS²</td>
<td>source-based</td>
<td>*</td>
<td>*</td>
<td>-</td>
<td>Quantitative</td>
</tr>
<tr>
<td>StormTac³</td>
<td>concentration-based</td>
<td>*</td>
<td>*</td>
<td>Water</td>
<td>Quantitative</td>
</tr>
<tr>
<td>SWMM⁴</td>
<td>concentration-based</td>
<td>*</td>
<td>*</td>
<td>Sediment</td>
<td>Quantitative</td>
</tr>
</tbody>
</table>

¹Hedbrant, 2001  
²Ahlman and Svensson, 2005  
³Larm, 2000  
⁴Rossman, 2004

#### 2.4.1 Two major approach for estimating the urban load of diffuse emissions

According to the models mentioned above, two major approaches for quantifying the urban load, a source-based approach from the perspective of material metabolism (Substance Flow Analysis, SFA) and a concentration-based approach from the perspective of urban runoff, were introduced.

- The source-based approach estimates the copper load according to the stock in various sources (good/material in use) in the drainage area and the leaching factor caused by the wear or weathering of goods/material in use.
- The concentration-based approach quantifies the copper load to lakes by stormwater flux and the copper concentration in the stormwater, which vary according to the land uses in the catchment area.

In tracing urban diffuse sources, information is needed on the diffuse sources of the copper load, for which the source-based approach is more appropriate due to its starting point and quantification strategy (Table 2-3). For example, the copper load in a residential area probably involves contributions from copper roofs, traffic emissions in the road through the residential area and atmospheric deposition. Thus the source-based approach attributes the copper load to the original sources directly and achieves source analysis of the copper load.

The source-based approach involves an amount of social data, the uncertainty in which cannot be investigated by statistical analysis. Hedbrant and Sörme (2001) analysed the uncertainty in urban
Chapter 2: Background information from previous studies

heavy metal data and proposed a quantification approach to deal with the uncertainty of social data based on the sources and scope of the data. Danius (2002) developed and applied this approach in the MFA (Material Flow Analysis) case study. Larm (2000) discussed the uncertainty in the concentration-based approach based on the StormTac model. Several case studies indicated that the uncertainty in StormTac was caused by the monthly runoff coefficients ($\beta$) and the copper concentration ($C$). The uncertainties of those parameters were indicated by the minimum and maximum value in the database of StormTac (Larm, 2000).

Table 2-3 Characteristics of the source-based and concentration-based approaches for source analysis

<table>
<thead>
<tr>
<th>Source-based approach</th>
<th>Concentration-based approach</th>
</tr>
</thead>
<tbody>
<tr>
<td>Start point</td>
<td>Urban runoff</td>
</tr>
<tr>
<td>Quantification</td>
<td>$E(t) = L \cdot S(t)^a$</td>
</tr>
<tr>
<td>Required input data</td>
<td>$F = Q \cdot C; Q = A \cdot P \cdot \beta^b$</td>
</tr>
<tr>
<td>Database</td>
<td>The area of each land use</td>
</tr>
<tr>
<td>Database</td>
<td>Average/standard copper concentration in urban runoff; Average/monitored precipitation</td>
</tr>
<tr>
<td>Output</td>
<td>Copper emissions and the copper load; The distribution of copper emissions to the environment; The contribution of various sources; The contribution of various land uses</td>
</tr>
<tr>
<td>Output</td>
<td>The copper load in the urban runoff; The contribution of various land uses</td>
</tr>
</tbody>
</table>

$^aS(t)$ is the size of the stock at time $t$ and $L$ is the leaching factor. (Elshkaki et al., 2005).

$^bC$ is the copper concentration in runoff, $Q$ is the flux of the runoff, $A$ is the area of the studied area, $P$ is the precipitation and $\beta$ is the coefficient of runoff (Larm, 2000).

2.5 Model for the fate of Copper in lakes

For estimating the environmental effect of pollutants in lakes, various models for quantifying the fate of pollutants in lakes have been developed (Table 2-4). Lindstöm and Håkanson (2001a) calculated heavy metal loads to urban lakes from observed concentrations in lake sediment and water using a dynamic lake mass-balance model. Lindstöm and Håkanson (2001a) found that the predicted sediment metal concentrations were close to field observations but the metal concentrations in water were not well predicted. In this model, the dissolved/particle metal fraction (DF/PF) was the factor causing most uncertainty in the model prediction. Here, this lake mass-balance model is adopted as a submodel for the case study of shallow lakes (see Chapter 3). The model presents six major physical processes of Copper in the lake: inflow, outflow,
sedimentation, resuspension, diffusion and burial. The quantification processes for these can be seen in Chapter 3 and Papers I and II.

Håkanson et al. (2004) extended the lake model with a two-part water compartment for simulating seasonal variations in pollutants (such as P and radiocaesium) in the lake. The model divided the water compartment into two parts, surface water and deep water, with the theoretical wave base introduced by considering wind-wave influences. The lake model then quantified the mixing process between the surface and deep water through the stratification in the lake water. The lake model with two-part water compartment was used to simulate the mass-balance of phosphorus in 41 lakes from the northern hemisphere and the factor inflow contributed the most uncertainty in the simulated TP (Total Phosphorus), followed by the sedimentation rate and the dissolved/particle metal fraction (Håkanson and Bryhn, 2008). Sinha (2009) and Cursino da Cruz (2009) applied the lake model with two-part water compartment in several cases in Stockholm.

Table 2-4. Models for determining the fate of Copper in lakes

<table>
<thead>
<tr>
<th>Model source</th>
<th>Compartments</th>
<th>Physical transport</th>
<th>Chemical reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lindström and Håkanson (2001a)</td>
<td>Well mixed</td>
<td>ET-area A-area</td>
<td>*</td>
</tr>
<tr>
<td>Håkanson and Bryhn (2008)</td>
<td>Surface water Deep water</td>
<td>ET-area A-area</td>
<td>*</td>
</tr>
<tr>
<td>Mackey et al. (1983)</td>
<td>Well mixed</td>
<td>One part</td>
<td>*</td>
</tr>
<tr>
<td>Adams and Chapman (2003)</td>
<td>Well mixed</td>
<td>Aerobic Anaerobic</td>
<td>*</td>
</tr>
<tr>
<td>Rippey et al. (2004)</td>
<td>Well mixed</td>
<td>-</td>
<td>*</td>
</tr>
</tbody>
</table>

Mackey et al. (1983) developed the Quantitative Water Air Sediment Interaction (QWASI) model based on the concept of fugacity for describing the fate and transport of chemicals in aquatic systems. Adams and Chapman (2003) published a water column/sediment model for assessing the hazard of metals and inorganic metal substances in the aquatic system that focused on physical transport and chemical action in lake sediment. Rippey et al. (2004) developed a simple generic model for investigating the steady-state concentration of heavy metals (Pb, Zn, Cu) in lake water by the metal load and retention time of water and metal. The characteristics of these models are summarised briefly in Table 2-4.

In addition, Engqvist and Andrejev (2003) proposed a cascade framework modelling approach for describing water exchange and contaminant transport in the complex aquatic system in the case of the Stockholm archipelago. This model has also been applied in the case of Forsmark, a Baltic Coastal Region in Sweden (Engqvist et al., 2006).

The models for the fate of Copper in lakes (Table 2-4) and in the archipelago/coastal region (Engqvist and Andrejev, 2003) focus on transportation and distribution of Copper in the aquatic
system, which requires urban copper load as an input for predicting the future copper concentration in water and sediment for presenting the environment effect of urban load. However, the lake model is unable to present any information on the sources and fluxes of Copper in the drainage area. Thus, this thesis tries to combine the source model with a lake model in order to trace the entire fate of Copper in the watershed.

2.6 Lake sediment as recorder of human activities

Sediment is one of the important indicators of the environmental quality of the aquatic system in Sweden (Swedish EPA, 2000) and in the European Water Framework Directive (Brils, 2008). Bulter and Davies (2000) suggested that sediment could qualitatively assess the recipient impacts of urban discharges. The impacts of urban discharges in sediment are on a decade scale, while for water mixing in lakes the temporal scale of the impacts is only hourly to weekly (Bulter and Davies, 2004).

Moreover, in studies of the aquatic system, the sediment record is commonly used to investigate spatial and temporal variations in the pattern of the metal pollution and to reflect the influence of human activities (Zhang et al., 1996; Lindström, 2001; Renberg et al., 2001; Sternbeck and Östlund, 2001; Olli and Destouni, 2008).

Zhang et al. (1996) showed that the heavy metal (Zn, Cd, Mn and Cu) concentration in sediment in several lakes in China increased rapidly after the 1970s, correlated with human activities. Lindström (2001) demonstrated that urban status (land use) influences dominated the lake fluxes and sediment concentration of Copper by correlating the sediment copper concentration with the land use in the catchment based on 10 headwater lakes in Stockholm, Sweden. In that study, the urban status was described by the area of various land uses in the drainage area and the index of total anthropogenic influences as:

\[
AI = \frac{\text{The sum of the area of traffic, building, garden, cultivate land, park, small forest and other hard area}}{\text{The area of the drainage area (ADA)}} \times 100\%.
\]

Renberg et al. (2001) showed through the lead concentration in sediment cores that several basins in Lake Mälaren, upstream of Stockholm, were polluted in the 19th century and earlier from extensive metal production and processing in the catchment. Olli and Destouni (2008) reported that waterborne metal pollution by Zn and Cu is still increasing in Karlskärsviken bay, part of Lake Mälaren, according to the sediment evidence. Olli and Destouni (2008) also pointed out that the sediment metal contents were dominated by local discharges in the inner Karlskärsviken bay, while in the outer bay they were mainly affected by regional discharges.

The studies above illustrated the capacity of sediment to reflect the influence of human activities, but did not focus on tracing the anthropogenic sources of sediment pollutant loads, especially when diffuse sources dominated the copper load in the urban discharges. This thesis therefore analysed and investigated how sediment reflects the urban load from diffuse emissions through case studies and simulations using the source – transport – storage model.
3. Model description

This chapter introduces the conceptual model, called the source – transport – storage model (Figure 3-1, Papers I and II), for tracing copper sources and copper flows in the urbanised water system. According to the scope of this study, the spatial system of the model is defined as the water recipient and the urban drainage area: for a simple case (Level I), it is a lake and its drainage area; for a complex case (Level II), it is the network of connected recipients and their drainage areas. The conceptual model focuses on various urban sources and the fate of Copper in the aquatic phase in the studied system, but also includes atmospheric deposition (Figure 3-1).

In the drainage area, Copper is widely used in materials and goods in people’s lives, such as copper roofs, water pipes and brake linings (Section 2.3). Because of the weathering and wear process, Copper is emitted from materials/goods in use to water, air and soil (Figure 3-1). The water pathways, including stormwater and surface water, taking the diffuse copper emissions to the lake are reviewed in Section 2.2, Figure 2-2).

Part of the copper from air goes to the natural surface water (surface runoff and the lake) and the drainage area by atmospheric deposition. Another part of the copper in air is exported out of the study system and is deposited elsewhere. In the drainage area, if the copper settles on the impervious cover it is carried by stormwater. If the copper settles on the natural ground, i.e. the soil, it is considered to be stored in the soil and its further fate is discussed as the fate of Copper.
in soil. In addition, air is not a pure internal source, since Copper from sources outside the catchment is imported and deposited within the drainage area (Figure 3-2).

The copper in soil goes to the lake partly through surface runoff and partly through the groundwater (Figure 2-2). The groundwater pathway for Copper is neglected in this study since it has been estimated that the contribution of Copper with groundwater only contributes around 1% of the total flux from the anthroposphere (Landner and Reuther, 2004). Nevertheless, the groundwater is an important store of Copper (Aastrup and Thunholm, 2001). In the lake, Copper is distributed between the water and particles. Subsequently, part of Copper is transported downstream by the water flow and part settles and is accumulated in the sediment.

In applying the conceptual model in two levels of cases, the quantitative model is different:

- **Level I: The simple watershed (a lake with its drainage area).**
  
  The conceptual model is achieved by coupling a source model based on the SFA approach (Section 3.1) for estimating the copper load in the drainage area with a lake model (Section 3.2) for the copper fate in the lake. These two models are connected by the total copper load to the lake ($F_{in}$).

- **Level II: The complex case with coupled basins (the aquatic system in Stockholm).**
  
  A basin-strait approach (Paper III, Section 3.3) is introduced for assessing the contribution of urban sources along the flow path. Since the focus in Level II is on tracing how far downstream in the aquatic system the diffuse emissions are reflected, it is necessary to estimate the fate of Copper along with the water flow, whereas neither the source model nor the lake model included this information.

### 3.1 Source model

The source analysis submodel accounts for the diffuse emissions following the SFA approach of Sörme and Lagerkvist (2002) and thereby quantifies the total copper load from the drainage area to the lake. The source analysis involves two types of information in the drainage area: source type and land use (Papers I and II). The source model is implemented as a spreadsheet in Microsoft Office Excel 2007.

As mentioned before, Copper is widely used in the urban area so that the diffuse sources in the drainage area have various origins. In Paper I, the source model adopted the sources list of stormwater from Sörme and Lagerkvist (2002, Figure 2-4). For enhancing understanding on the origins of urban diffuse emissions, Paper II extended the source list by considering the interactions among environmental compartments (water, soil and air) and classified the sources in the drainage area into three groups:

- **The primary sources are material/goods in use, which emit Copper through the wear and weathering process.** Based on the work of Sörme and Lagerkvist (2002), the major diffuse
sources in the urban area were divided into two major sectors: the traffic sector (brake linings, tyres, asphalted road and catenaries for railway) and building materials (copper roofing).

- The secondary sources are the consequences of the emissions from the primary sources from the perspective of urban diffuse sources, but can also be considered as sources of copper load to the lake. The secondary sources include air (dry and wet atmospheric deposition), soil (farmland, forest and other open areas) and parking in the traffic sector.

- The other sources are gathered under point sources and case-specific sources, such as landfill and combined sewer overflow.

The source classification and the flux of copper emissions in the drainage area are shown in Figure 3-2. As mentioned before, the main source of Copper in our study system belongs to the life stage of use (Figure 2-1). Thus, the quantification in the source model mainly assumes the leaching mechanism of emissions (Elshkaki et al., 2005). The emissions from the material or goods in use (primary sources) are quantified by:

\[ E(t) = L \times S(t) \]  

where \( S(t) \) is the size of the stock at time \( t \) and \( L \) is the leaching factor. It is defined as the ‘source-based approach’ and is used in the traffic and building materials sector in this study. The detailed application is described in Papers I and II.

For the secondary sources, both the source-based and concentration-based approaches are applied to quantify the emissions based on the available data. For quantifying the copper load from the air and parking, the quantification is analogous to Eq. 1 and considers the area, \( A \) (\( m^2 \)) as the stock and the runoff rate (mg/m²/year) as the leaching factor. For soil and other sources, the store and leaching information is lacking for our cases. In order to manage this, we introduce a ‘concentration-based’ quantification approach as a complement (see Section 2.4.1), which is land use-based but not source-resolved, and quantifies the emissions by a kind of land use or case-specific standard copper concentration in the water along with the water runoff from the selected area as:

\[ E = Q \times C_{Cu} \]  

where \( C_{Cu} \) is the empirical copper concentration in water flows from different land use area (µg/l, Larm, 2000; C. Lännergren, pers. comm., 2009), and \( Q \) is the flux of water (m³/year).

The total copper load from drainage area to lake (\( F_{ln} \)) is calculated from the emissions (\( E \)) from each source (\( m \)) and the fraction to lake (\( \beta \)) in different land uses (\( n \)) as:

\[ F_{ln} = \sum_m \sum_n E_{mn} \beta_n \]
Figure 3-2. Source list and flux of copper emissions in the drainage area. The rectangles are the primary sources quantified in Eq. 1, the ovals are the secondary sources, the diamond is other sources and the thick arrows show the pathway to quantify the copper load ($F_{in}$) in the source model. Factor $\alpha$ shows the portion of emissions from the traffic sources to the water pathways according to the particle size of the emissions, factor $\beta$ the portion of stormwater/surface runoff going to the lake according to the type of land use (see Papers I and II).

In the conceptual model of the source – transport – storage model, the total copper load to the lake ($F_{in}$) is the connection point to the lake submodel. The proportion of the total emissions that is transmitted to the recipient has to be quantified (Figure 3-2). In the traffic sector, a factor $\alpha$ is involved to quantify the fraction of the diffuse emissions that goes to the stormwater (Papers I and II). For other sources, we calculated the copper load in the water phase directly. However, only some of the water flux goes to the recipient from various water courses (Figure 2-2), so the fraction of the water fluxes to the lake also needs to be considered. Here, we introduced a factor $\beta$ (the fraction to lake) to represent the portion of the water flux that is collected and transmitted to the lake, and it is determined by the land use. For the urban area, $\beta$ means the portion of stormwater to the lake; for the natural ground, $\beta$ means the fraction of the rainfall on the natural ground to lake. The value of $\beta$ is given by Larm (2000) and Lännergren (pers. comm., 2009).
3.2 Lake model

The lake model is used to represent the fate of Copper in the lake when the copper loads from the drainage area go into the lake. It was adapted from Lindström and Håkanson (2001a) and applied in case studies in Level I, a simple lake and its drainage area (Papers I and II).

The lake model (Figure 3-3) contains three compartments: the water (W), the sediment of the erosion and transport bottoms (ET), and the active accumulation bottoms (A, 0-2 cm). As a simplification, the water compartment is assumed to be well mixed and thermal and concentration stratification is neglected. Six processes, inflow, outflow, sedimentation, resuspension, burial and diffusion, are included in the lake model.

![Figure 3-3. Structure of the lake model. The block arrow is the connection point with the source model, the rounded rectangles are the three compartments in the lake system, and the arrows stand for the transport processes between the compartments. Passive sediment is considered to be outside the system boundary of the lake model.](image)

Copper entering the water pillar is partly transported out of the lake with outflow and partly deposited in the sediment by the sedimentation process. Sediment settled in the ET-area is mobile because of the erosion and transportation process. Copper in the ET-sediment is resuspended to both the water and A-area. In the A-area only the uppermost part (0-2 cm) is considered active sediment in the lake model since it is assumed that only this part has substance exchange with the lake water directly, while the deeper sediment (depth >2 cm) is considered passive. Copper settling in the A-area is buried in the deep, passive sediments but may also be released to the water pillar through diffusion.
Chapter 3: Model description

The transfer of Cu between the different compartments in the lake model is quantified by first-order approximations, as suggested by Lindström and Håkanson (2001a) and discussed by Paper I and II:

\[ F_j = R_j M_i \]  

where \( F_j \) (kg/year) is the Cu flux of process \( j \), \( M_i \) (kg) is the mass of Cu in compartment \( i \), and \( R_j \) (year\(^{-1}\)) is the transfer rate constant of process \( j \) (for details, see Paper II). The quantifications of the transfer rate constants are empirical, but process-based. The model was implemented through a graphical interface, dynamic, causality model approach in Simile v 5.4.

3.3 The basin-strait approach for a complex aquatic system

As mentioned before, it is necessary to assess the influence of urban copper loads along the water path in the complex aquatic system. In Level II, a basin-strait approach from Engqvist and Andrejev (2003) was introduced to present the net water flow and to obtain the copper flow between water recipients (Paper III).

For the complex aquatic system, the boundary of the aquatic system where the influence of the urban activities is insignificant must first be defined (broken line in Figure 3-4). This may be estimated from source term considerations or through monitored environmental levels of the pollutant. Then considering the water flow, the aquatic system needs to be divided into connected basins and straits based on geometric form (Figure 3-4). To simplify determination of the fate of Copper along the water path, we assumed straits as non-reactive channels for the copper due to an associated, expected lower water residence time, such that sediment deposition and internal loading of Copper are insignificant. Therefore, we proposed that the fate model only be applied in basins but not in straits in the complex aquatic system, while source analysis would be applied in both basin and strait for resolving the contribution of urban diffuse emission to each part of the aquatic system.

Furthermore, considering the contribution of water flow and urban copper load of each tributary basin to the major flow, the basin-strait structure of the defined aquatic system could be simplified by excluding the unimportant tributary basins. The basins and straits are coupled in the model by the outflow in the lake model taking account of the incoming mass-balance, such that the copper outflow of an upstream basin arrives in a downstream basin.

The drainage area of the defined aquatic system is set in each basin and strait separately, according to the topographical characteristics as well as the local discharge of stormwater. If there are some point sources, such as WTP discharge points, it may be convenient to extend the considered area to the catchment boundary of WTPs.

This approach is discussed systematically and in detail in the case of the aquatic system of Stockholm in Chapter 5.
Figure 3-4. Conceptual model of the basin-strait approach for a complex aquatic system (from Paper III).
4. Case studies

To evaluate the source-transport-storage model we described in Chapter 3, we applied the model in the urban lakes (Level I) and the aquatic water system (Level II) in Stockholm, Sweden. Stockholm is the capital of Sweden, and is situated between the fresh water Lake Mälaren in the west and the archipelago of the lightly saline Baltic Sea in the east (see Figure 4-1). The city is built on the islands, with 30% of the inner city area being water. In 2007, the county of Stockholm had 1 950 000 inhabitants, with about 65% within the urban area. Historically, the water bodies surrounding Stockholm received extensive amounts of urban pollutants from households and factories. Today, the situation was improved a lot: the wastewater from households and other kinds of buildings and part of the stormwater are transported to and treated in WTP before discharged to the downstream recipient of Stockholm. However, according to the observations, many pollutants such as heavy metals still accumulated in the lake sediments (Lindström et al., 2001; Sternbeck et al, 2003, Rauch, 2007) and the urban runoff to the lakes is dirtier than the natural inflow (Larm, 2000).

In this chapter, we outline the situation of the cases involved in our study and introduce the case methodology in both Level I and II. Section 4.1 describes the characteristics of several urban lakes in Stockholm and the strategy of the model evaluation and simulation applied in Level I. Section 4.2 presents the direction of water flow and the composition of the aquatic system, and introduces the case methodology in Level II.

4.1 The urban lakes in Stockholm: Case study at Level I

In Level I, the study structured a combined model, a source model coupled with a lake model, for tracing the fate of Copper from urban sources to the sediment store in a simple urbanised watershed. The study chose the independent lake without the upstream aquatic system. To test the source model, the combined model coupling the source model with the lake model (see Chapter 3), we chose five small lakes in Stockholm, Sweden (Figure 4-1) as our case studies. They are all very small and shallow lakes (0.036-0.29 km$^2$ with maximum depth 2.3-7.0 m), even from a Stockholm perspective. The characteristics of the lakes and their drainage areas are shown in Paper II.

4.1.1 Background information on the studied urban lakes in Stockholm

The copper sources of the chosen lakes are relatively simple and local, without the contribution from any upstream system. The main water pathways of the copper are stormwater and natural surface runoff from the drainage area. In the case of Trekanten, due to the artificial activity the lake has another important inflow, pumped drinking water, which is still a local source. In addition, except for Lake Laduviken, the other four lakes are connected with the major water flow Lake Mälaren, so that the results in those cases could probably be useful when discussing the complex aquatic system in Stockholm.
Since we assessed the fate of Copper in these studies, the copper level in the lake (sediment) was another criterion in choosing suitable cases. The studied lakes have different sediment copper levels (for details see Paper II). The sediment copper levels in Lake Råcksta Träsk, Trekanten and Långsjön are significantly higher than in the other two cases, Lake Judarn and Laduviken, in which the sediment copper contents are relatively low.

In addition, one of the important aims of the model was to estimate the urban diffuse sources in the drainage area. The cases were chosen as involving significant copper sources, such as copper roofs in the case of Trekanten or specific sources such as the landfill in the case of Råcksta Träsk and the combined sewer overflow in the case of Långsjön.

![Figure 4-1. Lakes and water courses in Stockholm, Sweden. Black line is the boundary of the City of Stockholm; the block arrows show the major direction of water flow; the blue area is the aquatic water system; 4-point stars mark the locations of the five urban lakes. Sediment sampling points from Literature: 1. Lambarfjärden, 2. Bornsjön, 3. Ekerö, 4. Klubben, 5. Reimersholme, 6. Riddarfjärden, 7. Strömmen, 8. Kastellholmen, 9. Saltsjön, 10. Fjäderholmsområdet, 11. Värmdölandet, 12. Vaxholmsfjärdarna, 13. Kovik/Tynningö, 14. Torsby-Solöfjärden and 15. Trähhavet. Note that points 1,2,14 and 15 are not shown on the map but the arrows point to their locations (results shown in Figure 5-1, Paper III). The distribution of the diffuse sources is related to land use in the drainage area, which is also considered in the source model. Thus, the structure of the land use and the urban proportion in the]
drainage area are factors we considered for choosing the cases (Figure 4-2). For the various distribution of land uses, there is the simple case of Långsjön, which is almost a unitary residential area with a local road. In other cases, the drainage area combined major roads, residential areas and railway/metro in different proportions. For the various proportions of urban area (involving roads, buildings and other urban constructions), we chose a lake with very little urban area (Judarn 12%) and a lake with a highly urbanised drainage area (Långsjön 74%).

Figure 4-2 The distribution of various land use in the drainage area of the studied cases (data from Stockholm Vatten, 2000).

4.1.1.1 Monitoring information on stormwater in the case of Lake Trekanten

The estimated results of urban loads could be tested with observations on the stormwater through the concentration-based approach. However, stormwater observations were not available for all the urban lakes involved in this study. This section introduces detailed information on Region Nybohov in the case of Lake Trekanten, for which a few observations on stormwater are available.

Region Nybohov is a residential area in the south of Trekanten, occupying 15% of the drainage area of Lake Trekanten, but with about 95% copper roofs in the drainage area located there. From
Feb-Nov 1998, Larm and Holmgren (1999) monitored copper concentrations in stormwater at several monitoring points in Nybohov that collected the stormwater from part or all of Nybohov, see Figure 4-3. Considering the land use in all of Nybohov or Nybohov A (Table 4-1), the copper loads estimated from the observations of stormwater were fit for testing the quantification of emissions from copper roofs in this thesis. Nybohov is a residential area with a local road passing through, while Nybohov A is a single residential area without any traffic contribution (Table 4-1).

![Figure 4-3. Location and scale of Nybohov (as a whole and Nybohov A) and the related sampling position of stormwater (information from Larm and Holmgren, 1999). The shallow blue area is the lake surface, the green area is the area of natural ground, the shadow area is the area of urban land use, the darker gray area is the area of highway and the light tan area is the area of Nybohov A.](image)

<table>
<thead>
<tr>
<th>Land use</th>
<th>Nybohov</th>
<th>Nybohov (whole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Road</td>
<td>0</td>
<td>29 459</td>
</tr>
<tr>
<td>Building</td>
<td>1 623(543)</td>
<td>12 944(2 409)</td>
</tr>
<tr>
<td>Other hard area</td>
<td>1 785</td>
<td>20 529</td>
</tr>
</tbody>
</table>

1First figure is area of buildings; figure in brackets is area of copper roofs in use
2Other hard area is other impervious surfaces excluding all type of buildings and traffic area.
4.1.2 Model simulations and analysis at Level I

In the five cases in Stockholm, the input data of the source model, such as the land use, the distribution of copper roofs and the traffic volume on the major road were collected from different sources in the ten-year period 1996-2006. The temporal variability of the input data in those cases in the study period was neglected. Thus, the estimated copper loads ($F_{in}$) in the cases were taken as the average in the study period and then introduced as static input data to the lake model. The initial state in the lake model is set by the observations of copper concentrations in water and A-area in 1996 (Lindström and Håkanson, 2001a). The lake model was used to run a six-year simulation for simulating the copper concentration in water and A-sediment in the years 1996-2001 (for details see Papers I and II).

4.1.2.1 Model test

The diffuse sources of pollutants are hard to monitor (Mitchell, 2005). It is impossible to find observations on diffuse urban emissions. Commonly, the load of diffuse emissions is estimated from the observations on urban runoff. However, the monitoring data for the specific cases are too limited to verify the results of our model simulations. Therefore, we tested the model results, especially the estimated total copper load in the drainage area and the simulated copper concentrations in sediment, in three steps:

- Testing the source model using monitoring data from Region Nybohov in the drainage area of Lake Trekanten. This test focused on the sector building materials (copper roofs; Paper I).
- Testing the estimated urban load ($F_{in}$) from the source analysis with previous estimations (Larm and Holmgren, 1999; Larm, 2000; Stockholm vatten 2000) in five cases of urban lakes in Stockholm, Sweden (Papers I and II).
- Testing the simulation of the combined model with observations of copper concentration in lake sediment during the period 1996-2001 (Papers I and II).

4.1.2.2 Simulating the water and sediment copper content with changes in copper load

In order to understand the relationship between copper load and the sediment copper content, we used the lake model to simulate the temporal and quantitative response of the copper concentration in the lake compartments (water and A-area) to changes in the copper load caused by human activities in the drainage area. Starting from steady state, the lake model ran with the step (halving the initial $F_{in}$) and pulse changes (100 times of the initial $F_{in}$ in one week) of the inflow, i.e. the copper load from the drainage area ($F_{in}$), respectively, until a new steady state was reached.

4.1.2.3 Sensitivity analysis and uncertainty analysis

The sensitivity analysis of the source model was based on the estimated results on the contribution of sources directly, since the source model presented a static and linear relationship
(see Eq. 3). Since the source model was based on the SFA approach, the model uncertainty was analysed by the approach proposed by Hedbrant and Sörme (2001) and developed by Danius (2002). Details are shown in Paper II.

The sensitivity of the lake model was analysed by varying the dominant factors in each process, while the uncertainty of the lake model was expressed as the ‘extreme’ cases (minimum and maximum) of the simulated copper concentrations in water and A-area (see Paper II).

4.2 The aquatic water system in Stockholm - Case study at Level II

Chapter 5 summarises field observations in Lake Mälaren and the inner archipelago of the Baltic Sea during the period 1996-2006 (Lindström et al., 2001; Sternbeck et al., 2003; Rauch, 2007) and presents the copper gradient in sediment in the aquatic system through the central city of Stockholm. The study at Level II involves the application of the basin-strait approach (Section 3.3) in the case of the aquatic system in Stockholm.

Generally, the complex aquatic system in Stockholm contains three parts: Östra Mälaren, the inner archipelago, and the small lakes in Stockholm (Figure 4-1; Rolli, 2009; Paper III). The major water flow Mälaren-Inner Archipelago involves:

- Östra Mälaren within the city, divided into different areas: Kalbergskanalen-Klara sjö, Ulvsundasjön and Bällstaviken, Essinge fjärden, Riddarfjärden, Åstraviken;
- Fractions of the inner Archipelago water: Saltsjön, Lilla Värtan, Hammarby sjö, Djurgårdsbrunnviken (more fractions in the inner Archipelago see Paper III);
- Lakes: Räcksta Träsk, Judarn, Lillsjön, Trekanten.

According to Figure 4-1 and Stockholm water program (Stockholm Vatten, 2000), the two water flows from the upstream of Lake Mälaren gather into Essinge fjärden, and the islands Kungsholmen and Södermalm divide the water flow into three directions: to Ulvsundasjön, to Riddarfjärden and to Årstaviken. The lake Ulvsundasjön gathers the water flows from Bällstaviken and Essinge fjärden, and the water flow from Ulvsundasjön inflows to Riddarfjärden through Klara sjö. The water flow gathered into Riddarfjärden goes to Lake Saltsjön in the inner archipelago, while the water flow to Årstaviken also goes to Lake Saltsjön through Hammarby sjö. The water flow from Lake Saltsjön is divided into two directions, one going to Fjäderhomsområdet directly and one going to Fjäderhomsområdet through Djurgårdsbrunnviken. In addition, the outflow of the small lakes goes to the major water flow in different parts according to their locations.
5. Results

In this chapter, we summarise the major results from the three papers and some extended results described in Appendix I and II:

In Level I, a simple urbanised watershed, a combined model (a source model – lake fate model) was applied to determine the link between urban diffuse emissions and the copper levels in lakes. Here, the applicability of the combined model was tested with observations and previous estimates based on case studies in urban lakes in Stockholm (Section 5.2). Section 5.3 then presents the simulated fate of copper in the simple watershed and reveals the relationship between urban diffuse emissions and sediment copper content in the recipient. Section 5.4 identifies the sensitive factors in the fate of copper by a sensitivity analysis and evaluates the quality of model results through a uncertainty analysis.

In Level II, we reviewed the copper gradient along the water flow in the sediment in the aquatic system in Stockholm according to previous reports and monitoring programmes. This is helpful for understanding the effect of urban diffuse emissions to the aquatic system in the case of Copper (Section 5.1). Several relevant issues for achieving a quantitative model for tracing Copper in the case of the aquatic system in Stockholm are discussed (see Section 5.5).

5.1 Gradient of sediment copper content in the Stockholm aquatic system

As mentioned in Section 2.3.2, sediment copper contents have been monitored in published studies to investigate the pattern of metal distribution in the aquatic system spatially and temporally. This thesis evaluated several groups of monitoring data during 1997-2006 (Lindström et al., 2001; Sternbeck et al., 2003; Rauch, 2007) along the major direction of water flow discussed in Section 4.1, and summarised the gradient of the sediment copper content from east Mälaren to the inner archipelago of the Baltic Sea (Figure 5-1, Paper III). The sediment copper level in the central city is as much as three times the background levels in the upstream and downstream regions. Thus, the city of Stockholm is considered a strong source of copper for the surrounding aquatic system.
Figure 5-1. Gradient of sediment copper concentration (0-2 cm) along with the water flow from Lake Mälaren (start from 1. Lambarfjärden) to the inner archipelago of Baltic Sea (end at 15. Trälhavet). Details of the sampling points are presented in Figure 4-1 and Paper III. Data reported by Lindström et al. (2001), Sternbeck et al. (2003) and Rauch (2007).

5.2 Test of the combined model in the case of urban lakes
As mentioned in Section 4.1.2, the source model was tested with the observations on stormwater in Region Nybohov in the case of Lake Trekanten and with previous estimations for the five urban lakes in Stockholm. The simulated sediment copper contents in the combined model for the simple watershed were compared with the field observations in those five cases.

5.2.1 Test of the source model: Building material sector
Region Nybohov is a residential area with copper roofing (Section 4.1.1). Thus, the copper load in the stormwater could be considered as predominantly coming from the emissions from copper roofs. The load estimated for the building materials sector (copper roofs) in the source model was therefore tested with the monitoring data on stormwater in Region Nybohov. The monitoring points and the collection area of stormwater samples are shown in Figure 4-3. The source model showed that the copper loads in Nybohov A and in the whole Nybohov area were dominated by the copper roofs (>98). The results in Table 5-1 show that the copper loads estimated in the source model agreed with the results obtained from the monitored concentrations of copper and water flow of the stormwater. This indicates that the performance of the source model, especially for building materials, is reasonable.

For the traffic sector of the source model, there was no suitable case and monitoring information available for testing the model. However, for the whole drainage area of Lake Trekanten (Paper I, Table 5-2), the estimated copper load of the source model is in good agreement with previous analyses suggesting a total copper load of 7.9-15 kg/year (Larm and Holmgren, 1999; Stockholm Vatten, 2000; Lindström and Håkanson, 2001a). In addition, the traffic sector contributed about
55% of the total copper load to Lake Trekanten (for details see Table 5-3). The applicability of the traffic sector of the source model appears acceptable.

Table 5-1. Copper load in part or all of Nybohov

<table>
<thead>
<tr>
<th>Copper load from diffuse emissions (kg/year)</th>
<th>Nybohov A</th>
<th>Nybohov (whole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Estimated in the source model</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Traffic</td>
<td>0</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper roofs</td>
<td>1.1</td>
<td>5.1</td>
</tr>
<tr>
<td>Atmospheric deposition</td>
<td>0.0056</td>
<td>0.11</td>
</tr>
<tr>
<td>Total</td>
<td>1.1</td>
<td>5.2</td>
</tr>
<tr>
<td>Estimated from field observations</td>
<td>1.1</td>
<td>8</td>
</tr>
</tbody>
</table>

1 Quantification concentration-based, see Table 2-3 in Chapter 3, data from Larm and Holmgren, 1999.

5.2.2 Test of the source model: Total copper load (F\textsubscript{in})

As mentioned in Section 3.1, the unmodified source list used in Paper I (Figure 2-4) was proposed by Sörme and Lagerkvist (2001), then the source model was modified in Paper II (Figure 3-2) by involving the copper load from Parking, Railway/Metro and Soil (natural ground in the drainage area: forest, farm, garden etc.). Copper loads estimated by the modified source model were slightly increased by about 3-13% from the unmodified source model in the five case study lakes (Table 5-2). Considering the uncertainty of the estimated copper load (F\textsubscript{in}), enlargement of the sources list to include the contribution from parking, railway/metro and the soil thus did not markedly change the results of the copper load (F\textsubscript{in}) in the cases studied. However, the modification in the source model showed a more comprehensive understanding of urban diffuse sources (see Section 3.1).

Table 5-2 shows comparisons of the results of the source model base on the SFA approach (Section 2.4.1) with the copper load estimated by the concentration-based approach (StormTac and Stockholm water programme) and the lake model (Lindström and Håkanson, 2001a). The information on land use was used for estimating the copper load in both source-based and concentration-based approaches (Table 2-3). In the former approach, the area of land use was considered as the store of Copper (S(t), Eq.1) in the air and parking sector and the type of land use was used to define the portion of stormwater to the lake (β), as the runoff coefficient in the concentration-based approach. In the latter approach, the area of land use was used to estimate the flux of water to the lake. Since no monitoring data were available for the concentration-based approach in those cases, the estimation of copper load was based on the database of the average copper level in stormwater from different land use area in Stockholm (Stockholm water program, 2000) or Sweden (StormTac, Table 5-2; Papers I and II).

The results of two studies based on the concentration-based approach, StormTac and Stockholm water programme, agreed well with each other due to the similarity of the input data and the estimated approach. The estimated copper loads for all the cases in our source model fell within a factor of 1.5 of the previous estimations by the concentration approach. Thus, the source model
for tracking the copper sources of urban load and the previous studies with the concentration-base approach validated each other.

<table>
<thead>
<tr>
<th>Case</th>
<th>Source-based Source model</th>
<th>Total copper load ($F_{in}$, kg/year)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Unmodified</td>
<td>StormTac$^c$</td>
</tr>
<tr>
<td></td>
<td>Modified$^b$</td>
<td>Stockholm water program$^d$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lindström &amp; Håkanson$^e$</td>
</tr>
<tr>
<td>Laduviken</td>
<td>5.4</td>
<td>6.1 (4.2-8.8)</td>
</tr>
<tr>
<td>Råcksta Träsk</td>
<td>25</td>
<td>27 (21- 35)</td>
</tr>
<tr>
<td>Judarn</td>
<td>5.5</td>
<td>5.8 (4.1-8.2)</td>
</tr>
<tr>
<td>Trekanten</td>
<td>11</td>
<td>12 (9.4-16)</td>
</tr>
<tr>
<td>Långsjön</td>
<td>16</td>
<td>16 (12-22)</td>
</tr>
</tbody>
</table>

$^a$Source model presented by Sörme and Lagerkvist (2002), applied in Paper I
$^b$Source model with the enlarged source list (Details in Paper II)
$^c$Quantified according to the database in StormTac (2000)
$^d$Data from Stockholm Vatten (2000)
$^e$Data from Lindström and Håkanson, 2001a as estimated by the lake model,
$^f$Data in brackets show the uncertainty of the model results.

For all five case study lakes, the copper loads quantified by both the source-based and concentration-based approach were generally higher than the loads quantified by the lake model (Lindström and Håkanson, 2001a). However, the results of the source model in the case of Lakes Trekanten and Långsjön were in good agreement with the copper load suggested from the lake model (Table 5-2, Lindström and Håkanson, 2001a).

### 5.2.3 Model test: The coupled source – transport – storage model

According to the objective of the source – transport – storage model, i.e. coupling the information flow between the urban society and the natural aquatic environment, we introduced the estimated copper load ($F_{in}$) in the source model into the lake model as the copper inflow of the lake (Paper II). It was assumed that the copper loads ($F_{in}$) from the drainage area in all five cases remained stable in the period 1996-2002. We then simulated the copper levels in both water and sediment through the lake submodel. Neither the source model nor the lake model was calibrated.

The simulations of copper concentration in A-sediment ($C_S$) were tested by comparing with independent monitoring data (Östlund et al., 1998; Lithner et al., 2003; Sternbeck et al., 2003), except for the field data in year 1996 used as the initial point of the simulations. (Figure 5-2; Paper II). Due to the data gap in copper concentrations in water, except for the monitoring data used as the initial point of the simulation, there were few or no observation data to evaluate the simulations on the water copper contents in the five cases. Thus, here the model test focus on the sediment copper levels ($C_s$) in the lake, while the simulations of water copper concentration in water ($C_W$) are shown in Paper II.
Figure 5-2 Copper content in sediment in the active accumulation bottoms (A-sediment) in five lakes during 1996-2002 (from Paper II). a. Lake Laduviken; b. Lake Råcksta Träsk; c. Lake Judarn; d. Lake Trekanten; e. Lake Långsjön. Full lines show model predictions and markers show monitoring data (Östlund et al., 1998; Ekvall, 1999; Lindström and Häkanson, 2001a; Lithner et al., 2003; Sternbeck et al., 2003), dashed lines describe the uncertainty of the combined model, dotted lines show the uncertainty caused by uncertainty in $F_{in}$ (the source model) alone.

In the case of Lakes Råcksta Träsk, Långsjön and Trekanten, the simulated copper concentrations in the A-sediment ($C_S$) over time agreed reasonably well with the monitoring data, considering the model uncertainty (Figure 5-2 b, d and e; Paper II). For the case of Laduviken and Judarn, the model predicted higher sediment copper concentrations than observed and there was an increasing trend in simulated sediment copper contents, but the field observations showed a steady state of sediment copper levels over the reported years (Figure 5-2 a and c). The results shown in Figure 5-2 indicate that the model result agreed with the field observations for the more polluted lakes.
such as Lakes Rääksta Träsk, Långsjön, and Trekanten (Figure 5-2 b, d and e). Thus, it is suggested that the source – transport – storage model is applicable to the simple, urbanised watershed, urban lake and its drainage area, especially in cases with higher sediment copper levels in the lake.

5.3 Urban copper load and fate in the simple urbanised watershed

One of the major objectives of this study was tracing urban diffuse sources of the sediment copper content through the source – transport – storage model. This section presents the results obtained from the combined model in the five case study lakes: the contribution of urban diffuse sources to the copper load ($F_{in}$), the fate of copper in each lake and the relationship among the diffuse sources, the copper load ($F_{in}$) and the sediment copper content.

5.3.1 The source analysis of the copper loads

Even though the proportion of the urban area in the studied cases varied between 12 and 74% (Figure 4-3), urban diffuse sources dominated the total copper load in all of the drainage areas (83-93%, Paper II). The source analysis in the studied cases of urban lakes showed the traffic sector contributed 50-80% of the copper load in the drainage area, with in particular brake linings of vehicles contributing 41-63% (Table 5-3, Paper II). The results indicated that in the five cases, brake linings in the traffic sector dominated the copper load ($F_{in}$) to lakes. Copper roofs were also a very important urban source of Copper in some cases, with a contribution that varied between the cases (4-43%).

Table 5-3. Results of the source model in the five lakes (from Paper II)

<table>
<thead>
<tr>
<th>Source (kg/year)</th>
<th>Laduviken</th>
<th>Rääksta Träsk</th>
<th>Judarn</th>
<th>Trekanten</th>
<th>Långsjön</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traffic</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brake linings</td>
<td>3.9</td>
<td>11</td>
<td>3.44</td>
<td>4.89</td>
<td>8.69</td>
</tr>
<tr>
<td>Tyres</td>
<td>0.0016</td>
<td>0.0040</td>
<td>0.0011</td>
<td>0.0022</td>
<td>0.0028</td>
</tr>
<tr>
<td>Asphalt</td>
<td>0.58</td>
<td>1.4</td>
<td>0.40</td>
<td>0.79</td>
<td>1.02</td>
</tr>
<tr>
<td>Parking</td>
<td>0.32</td>
<td>0.76</td>
<td>0.03</td>
<td>0.417</td>
<td>0.25</td>
</tr>
<tr>
<td>Railway/Metro</td>
<td>0.128</td>
<td>0.0067</td>
<td>0.0041</td>
<td>0.46</td>
<td>-</td>
</tr>
<tr>
<td>Building materials</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper roof</td>
<td>0.18</td>
<td>8.4</td>
<td>1.50</td>
<td>5.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>To lake</td>
<td>0.24</td>
<td>1.82</td>
<td>0.15</td>
<td>0.45</td>
<td>1.5</td>
</tr>
<tr>
<td>To hard area</td>
<td>0.45</td>
<td>0.090</td>
<td>0.10</td>
<td>0.3375</td>
<td>0.0038</td>
</tr>
<tr>
<td>Soil</td>
<td>0.36</td>
<td>1.0</td>
<td>0.22</td>
<td>0.14</td>
<td>0.21</td>
</tr>
<tr>
<td>Others</td>
<td>-</td>
<td>2.42</td>
<td>-</td>
<td>-</td>
<td>0.24</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>6.2</strong></td>
<td><strong>27</strong></td>
<td><strong>5.8</strong></td>
<td><strong>12</strong></td>
<td><strong>16</strong></td>
</tr>
</tbody>
</table>

Appendix I shows the distribution of copper diffuse emissions into the environment. Copper emitted from urban materials/goods in use (primary sources) in the study cases amounted to about 26-102 kg/year, but only 18-23% of these emission loads went to the lake. Meanwhile,
other pathways of diffuse emissions went to air and soil or stayed where they were (i.e. not emitted). Details are shown in Appendix I.

5.3.2 Fate of Copper in the lake

After evaluating the copper load ($F_{in}$) from the drainage areas in each case, the lake model was used to calculate the fate of Copper in the lake system. In the case of Råcksta Träsk, Trekanten and Långsjön, the simulation of sediment copper content was in fair agreement with the reported field data (Section 5.2.3, Figure 5-2) and thus the simulated fate of Copper in 2002 is shown in Figure 5-3. The contributions of the fate processes in all five lakes are shown in Paper II. In the cases studied, the sediment and burial processes (Table 5-3, Paper II) dominated the fate of Copper in the lake, except for the case of Råcksta Träsk (discussed in Paper II). This means the copper load from the local drainage area was preferentially accumulated in the lake sediment rather than being transported further through the water flow.

![Diagram of copper fate in lakes](image)

**Figure 5-3.** Simulated fate of copper in the lake system in the case of (a) Råckstra Träsk, (b) Trekanten and (c) Långsjön in 2002

In the lake model, the water retention time ($T_W$) determined the flux of outflow. In the sedimentation process, the flux of Copper is related to the ratio of the fraction of particle-
combined Copper with the mean depth of the lake ($D_m$), since another relevant parameter, the sedimental velocity ($v_s$), is set as the same level, 100 m/year (for details see Paper II). Except for the case of Råcksta Träsk, the transport rate of outflow ($R_{out}$) was greater than the rate of sedimentation ($R_{sed}$). The calculated transport rate of sedimentation was about 2.5-17 times $R_{out}$. Therefore, the fate of Copper in the lake (staying in lake or going downstream) was dominated by the three lake parameters water retention time ($T_W$), mean depth of the lake ($D_m$) and the particulate fraction (PF).

**5.3.3 Correlation between sediment copper content and urban diffuse discharge**

Based on the five cases of urban lakes in Stockholm, the field data on sediment copper content were linked with several parameters in the drainage area, including:

- Information on urban diffuse sources: Copper load ($F_{in}$) quantified by the source model, traffic volume ($T$, a dominant parameter of diffuse emissions, Paper I)
- Basic watershed information: Area of the drainage area (ADA)
- Land use information: Area of urban area, area of road, index of general anthropogenic influences ($AI = \frac{A_{\text{Traffic}}+A_{\text{Building}}+A_{\text{Garden}}+A_{\text{Park}}+A_{\text{Small forest}}+A_{\text{Other}}}{\text{ADA}} \times 100\%$, Lindström, 2001)

Even though five lakes was a little too limited a number to make a correlation analysis, the results in this thesis showed that the sediment copper content was positively correlated with the estimated copper load from urban diffuse sources (Figure 5-4 a, $R^2=0.8496$, n=5). According to the source analysis (Table 5-3), the emissions from brake linings dominated the copper load in the five case study lakes. Thus, the sediment copper content also showed a positive correlation with the source factor for estimating the contribution of brake linings, traffic volume ($T$), see Figure 5-4b ($R^2=0.7346$, n=5). Lake Trekanten was the outlier in the correlation between traffic volume and sediment copper content owing to the higher contribution of the secondary dominant urban source (Figure 5-4 b), copper roofs (43%) to the total copper load in Lake Trekanten.

Moreover, since the traffic volume ($T$) showed a good correlation ($R^2=0.9914$, n=4) with the area of the drainage area (ADA) for all lakes except the outlier Lake Trekanten, the monitored sediment copper concentrations also showed a linear correlation with ADA (Figure 5-4 c). This correlation between $C_S$ and ADA needs to be further investigated for more cases in the watershed. Compared with the source-related factor, the field observations of sediment copper content ($C_S$) showed a much weaker correlation with the land use information on traffic area and urban area (Figure 5-4 d-f). The results based on those five cases showed that the sediment copper content is more appropriate for reflecting the urban source strength than the situation of land use.
Chapter 5: Results

Figure 5-4. Copper sediment content (average of the field data from 1991-2006) as a function of the information in the drainage area based on the five cases: (a) The estimated copper load from the source model (F_{in}, kg/year), (b) The traffic activity in the drainage area (T), (c) The area of the whole drainage area (ADA), (d) The index of general anthropogenic influences (AI= the sum of the area of traffic, building, garden, cultivated land, park, small forest (<0.05km^2) and other hard areas/ADA*100%, Lindström, 2001), (e) The area of the urban drainage area (including all the traffic area, building area and other type of hard area), and (f) The area of the road in the drainage area.
5.3.4 Response of water and sediment copper content to change in urban loads

In order to understand the relationship between copper load and sediment copper content, characteristics of the lake response to changes in the copper load caused by human activities in the drainage area were examined.

As shown in Papers I and II, for halved $F_{in}$ the copper contents in the water and A-sediment eventually were linearly dependent on $F_{in}$ with a proportion of 1:1. The response time of water and A-sediment, defined as the time to reach 95% of the change in copper concentration from the initial steady state to the new steady state, differed. In the cases studied, the response time of the water compartment was at the annual level, while in the same situation, the response time of the A-sediment was at the decade level (Paper II).

For a pulse change in the copper load, i.e. 100 times the initial copper loading in one week, the quantitative and temporal responses of the copper concentration in both water and sediment (A-area) were simulated in the five case study lakes (Figure 5-5 and 5-6). The water copper concentration increased to 7-57 times the initial level in response to the pulse, while the simulated sediment copper content ($C_S$) showed only a 20-40% increase (Figure 5-5).

In the five case study lakes, the quantitative response in water and sediment (A-area), shown by the ratio of the simulated max copper concentration and the initial copper concentration ($\frac{C_{max}}{C_0}$) was correlated with the copper retention time in lake water and sediment (Figure 5-6). In the lake model, the higher rate of copper outflow and sedimentation indicated the smaller copper retention time ($T_{cu}$) in water in the lake. It was assumed that the rate of the burial process indicated the copper retention time in A-sediment, since the burial process was the dominant outflow of A-sediment (Figure 5-3, Paper II). Thus, the longer Copper stayed in lake water and A-sediment, the smaller the quantitative response of the copper concentration ($C_w$ and $C_S$) in water and A-sediment to the pulse changes in copper load.

The water copper concentrations ($C_w$) reached their peak at the time the pulse change occurred, but the sediment copper concentrations took six months or one year to reach their peak after the pulse increase in the copper load (Figure 5-5). According to the temporal response in the lake model, the water copper concentration returned to the initial level within a year, whereas the sediment copper contents took at least a decade to return to their original level. This shows that the sediment copper content indicates the long-term effect of urban loads to the lake environment. Although less sensitive to pulse changes in the copper load ($F_{in}$), the sediment is appropriate for monitoring programmes since it can record pulse events of emissions over several years.
Figure 5-5. Simulated copper content in water (vertical axis on left) and A-sediment (vertical axis on right) upon a one-week pulse in the copper load in the fourth year.
Figure 5-6. Simulated response for a pulse in the copper load ($F_{\text{in}}$), shown as the ratio of the max and the initial copper concentration, as a function of copper retention time in (a) water and (b) A-sediment. For details of the quantification of R in the lake model see Paper II.

5.4 Sensitivity and uncertainty analyses of the combined model

The sensitivity and uncertainty of the combined model were analysed in the source model and the lake model, respectively. The output of the source model ($F_{\text{in}}$) is the input of the lake model, so the uncertainty analysis of the lake model also involved the uncertainty from the source model.

5.4.1 The source model

The source model quantified the copper load to lakes by a static and additive approach, so the overall result of the source model, i.e. $F_{\text{in}}$, was most sensitive to the dominant sources and their parameters. In the cases presented in Paper II, the copper load ($F_{\text{in}}$) proved most sensitive to brake linings in the traffic sector, further to parameters related to the traffic emission such as road length ($L$) and traffic volume ($T$) on the major roads, the copper content in brake linings ($M$), the wear rate of brake linings ($W$), the fraction to stormwater ($\alpha$) and the collected fraction of stormwater ($\beta$, i.e. the runoff coefficient in StormTac).

Table 5-2 shows the estimated copper load and the relevant uncertainty estimated by the source model (the source-based approach) and the database of StormTac (the concentration approach) in the five cases. The uncertainty of estimated copper load ($F_{\text{in}}$) from the source model was much smaller than the uncertainty shown by StormTac. It is suggested that the source model much reduced the uncertainty of the results ($F_{\text{in}}$) by involving the case-specific data and the data from laboratory studies, while StormTac quantified the copper load from the land use and the database of $C_{\text{cu}}$ and $\beta$ estimated from the monitoring data from Stockholm, Sweden or even other European countries. The data uncertainty in StormTac was taken as the maximum and minimum value in its database.
Figure 5-7. Uncertainty in the estimated copper load ($F_{in}$) caused by each source (in the five studies cases, a–e) and only caused by brake linings and related parameters (in the case of Lake Råcksta Träsk). The diamond marker represents the normalised total copper load ($F_{in}/F_{in}$), the error bar shows the normalised minimum and maximum deviation value in the source model.

The importance of the sources to the model was directly related to the contribution of the sources to the copper load to lake ($F_{in}$, see Table 5-3). Thus, the uncertainty analysis of the source model showed that the primary source, especially the traffic sector, introduced the most uncertainty in the model (Figure 5-7). In Paper II, it was also shown that the wear rate of brake linings ($W_B$), the fraction of Copper emitted from brake linings to stormwater ($\alpha_B$) and the fraction from the road to the lake ($\beta_{Road}$) were the largest contributors to the uncertainty in the source model in the cases studied (Figure 5-7f). In the case of Lakes Råcksta Träsk and Trekanten, the building materials sector (copper roof) was an important contributor to the copper load to lake (F-
Lake Råckast Träsk 31%, Lake Trekanten 44%). Thus, the building materials sector in those two cases was also important for the model uncertainty (Figure 5-7 b and d).

The quantification of the load from soil was based on the concentration-based approach, which was estimated with a big uncertainty (Table 5-2). The contribution of the soil sector to the model uncertainty is related to the proportion of natural ground in the drainage area (Table 5-3). The more natural ground in the drainage area, the more important the soil sector for model uncertainty (Figure 5-7 a, b and c).

5.4.2 The lake model

To reveal the dependence of the water and sediment copper levels on the model parameters, we carried out a sensitivity analysis of the lake model in Paper II. In agreement with the previous studies of Lindström and Håkanson (2001a, 2004), the sensitivity analysis of the lake model (Paper II) showed that both water and sediment copper concentration ($C_W$ and $C_S$) were sensitive to the processes inflow ($F_{in}$, i.e. the copper load from the drainage area), sedimentation $(v_s)$ and bury (sed). In addition, the sediment copper content was sensitive to the fraction of the accumulation bottom ($D_A$), which is the important factor determining the distribution of copper sedimentation to A-sediment (Paper II).

The uncertainties of the combined model are shown in Figure 5-2. The uncertainty analysis (Figure 5-8) showed that the processes inflow, sedimentation and burial dominated the uncertainty of the simulated sediment copper concentration in the A-area ($C_S$). The contribution to the model uncertainty was generally related to the contribution of the copper flux in the transport process to the lake system. In the case of Laduviken, Judarn and Långsjön, the sedimentation and burial processes were the largest contributors to the uncertainty of the whole model, followed by the inflow (Figure 5-8 a, c and e).

In contrast, the contributions of inflow were larger than the contribution of the sedimentation and burial processes in Lakes Råcksta Träsk and Trekanten (Figure 5-8 b and d), in which the flux of sedimentation was 44% and 69% of the inflow ($F_{in}$) respectively. In addition, the outflow process in the case of Råcksta Träsk dominated the fate of Copper, whereas the sedimentation and burial process dominated in the other cases. Therefore, only in the case of Råcksta Träsk did the outflow contribute substantially to the simulation uncertainty (Figure 5-8 b).

The sensitivity analysis and the uncertainty analysis of the lake model indicated that decreasing the uncertainty in $F_{in}$ and $v_s$ was the key point in improving the quality of model simulations. This proved the advantage of using the source-based approach to estimate the copper load to lake, since the source-based approach decreased the uncertainty of $F_{in}$ considerably compared with the concentration-based approach (see Table 5-2). In addition, the value of settling velocity $(v_s)$ in the lake model was assumed to be based on the literature values. To improve the reliability of the model simulation, observations of the lake-specific settling velocity $(v_s)$ are required.
Figure 5-8. Uncertainty in the normalised copper concentration in A-sediment, estimated in the lake model (in the steady state) for all five cases. The triangle markers represent the normalised copper concentration in A-sediment \( \frac{C_s}{C_a} \), the error bars show the normalised minimum and maximum deviation value in the lake model and each process.

5.5 Towards a quantitative model on the fate of Copper in Stockholm

As reviewed in Section 5.1, the gradient of Copper in the aquatic system in Stockholm (Figure 5-1, Paper III) showed an increased trend of Copper in the aquatic sediment in central Stockholm. Three WTPs collect all the sewage and part of the stormwater in Stockholm, treat and discharge in downstream of the city (Paper III). Thus, the urban copper load to the WTPs did not contribute
to the trend of increasing copper concentration in the aquatic sediment in central Stockholm and should be explained by the urban diffuse loads direct to the aquatic recipients.

Because of copper transport along with the water flow in the aquatic system, it is not clear which is the dominant source of sediment copper content in a basin in the aquatic system – the load from the upstream system or the local urban emissions. To manage the urban diffuse sources and improve the environmental quality of the aquatic system in Stockholm, it is necessary to know where the dominant contributions of Copper come from. Therefore, the link between the urban loads and the sediment copper levels in the complex aquatic system in Stockholm must be known. This section presents a model for the aquatic system of Stockholm through the basin-strait approaches (see Section 3.3).

5.5.1 Defining the system boundary of the aquatic system

To structure a quantitative model for the complex aquatic system in the case of Stockholm, the first thing is to establish the system boundary of the aquatic system (Paper III). This study focused on the major flow from Lake Mälaren to Baltic Sea inner archipelago, which goes through central Stockholm, so other non-relevant lakes and streams were excluded. The upstream boundary of the studied aquatic system was taken as the Stockholm municipal boundary (Figure 5-9). While there are several distant cities and municipalities that may contribute Copper to Lake Mälaren upstream, this was attributed to regional waterborne discharge in order to assess the contribution of urban copper sources in Stockholm.

The downstream boundary is taken as the water body Fjäderholmsområdet after the WTP discharge point (Paper III) in this thesis, whereas Paper III presents a boundary scaled to the exchange point between the inner and outer archipelago. There are two major reasons for simplifying the aquatic system of Stockholm:

- First, the gradient of sediment copper concentration is decreased by more than half in the water body Fjäderholmsområdet, after which the sediment copper concentrations are under 100 mg/kg dw, close to the reference value (Figure 5-1).
- Second, the water flow divides into two directions after Fjäderholmsområdet (Figure 5-9): to Lilla Värtan and to Askrikefjärden. The water body Lilla Värtan not only receives water from the flow through the central city of Stockholm, but also from another complex aquatic system with urban influence in the north of Stockholm. This situation makes the aquatic system after Fjäderholmsområdet very complicated.
5.5.2 Structuring the network of copper flow in Stockholm through the basin/strait approach

Urban diffuse emissions in Stockholm were distributed along the aquatic system. As shown in Figure 5-10, the aquatic system is divided into many basins and straits. The water bodies involved in Stockholm aquatic system can be divided into three types:

1. An individual basin without upstream recipients: all the small lakes, i.e. Lake Räcksta Träsk, Judarn, Lillsjön and Trekanten. In most of the basins, the copper source and flow in the basin were described as discussed in Chapter 5.3 (one source model for the drainage area and one lake model for the lake).

2. A basin with local copper loads that also receives copper loads from upstream: Östra Mälaren, Ulvsundasjön and Bällstaviken, Riddarfjärden, Åstraviken, Hammarby sjö, Djurgårdsbrunnviken and Fjäderholmsområdet. In this case both source model and lake model are needed, but the inflow in the lake model should involve the copper load from upstream, i.e. the outflow in another lake model.

3. The water strait, which only transports the copper load from a basin to another basin taking into account the urban diffuse discharge: Essingejnäden, Klara sjö and Saltsjön. In these cases only the source model is needed.

All the basins and straits are then connected according to the water flow as described in Figure 5-10. The transport of copper load from one basin/strait is estimated as the outflow in the lake.
model. For identifying and excluding/including the individual lakes or tributaries in the studied aquatic system, further investigation are required on whether they make a significant copper contribution to the major water flow.

Figure 5-10. Basin-strait structure estimated in the aquatic system of Östra Mälaren-Inner Archipelago through the city of Stockholm.

5.5.3 Defining the urban drainage area of the studied aquatic system
The drainage area of the aquatic system of Stockholm was considered as the aggregation of the drainage areas of each basin/strait, evaluated by Stockholm Vatten (2000). Thus, the urban copper loads to each fraction of the aquatic system needed to be estimated separately considering the geographical pattern and the stormwater discharge system in the basin-strait approach.

5.5.4 Choice of lake model based on water depth
In the aquatic water system in Stockholm, the depth of basin/strait is in a wide range, from 1-20 m (Rolli, 2009). The thermal stratification in the water pillar becomes increasingly important for the simulation of sediment copper content with increasing lake depth. Kalada et al. (2005) concluded that the character of thermal stratification generally occurs when the water depth is greater than 5-6 m, based on the case of Polish lakes. Häkanson et al. (2004) suggested providing consistent information to define the boundary between surface and deep water by the ‘critical’ depth from water temperature to obtain seasonal variations, which was not the focus of this thesis. Thus, the lake models with one or two water compartment were suggested in the aquatic system of Stockholm (Table 5-4, Paper III).

It has been suggested that the lake model with a one-part water compartment be used for shallow urban lakes ($D_m<5m$) to avoid introducing more uncertainties from the empirical quantification
and information (Rolli, 2009). For deep lakes, the lake model with two-part water compartment has been suggested (Cursino da Cruz, 2009).

Table 5-4 the suggested lake model for basins/straits in the aquatic system in Stockholm

<table>
<thead>
<tr>
<th>Lake model</th>
<th>D_m</th>
<th>Lakes</th>
</tr>
</thead>
<tbody>
<tr>
<td>One-part water compartment</td>
<td>≤5m</td>
<td>Råcksta Träsk, Jurdan, Lillsjön, Trekanten, Karlbergskanalen-Klara sjö, Hammarby sjö, Djurgårdsbrunnviken,</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Two-parts water compartment</td>
<td>&gt;5m</td>
<td>Saltsjön, Lilla Värtan, Ulvsundasjön and Bällstaviken, Essingefjärden, Riddarfjärden, Åstraviken</td>
</tr>
</tbody>
</table>

5.5.5 Data availability
The availability of data to apply the conceptual model in the Stockholm aquatic system is discussed in Paper III. Most of the information for the source analysis, including land use area, copper roofing, stormwater discharge and traffic volume, in the studied basin, is well-documented. The data gap in the source model was that most of the traffic volume on the local road is unknown.

Hydrodynamic information is essential in the basin-strait approach, since the copper flows along with the water between these basins/straits. The water exchange in the inner archipelago has been estimated by Engquist and Andrejev (2003). However, for parts of Lake Mälaren and the transition zone to the archipelago, for example the water change between Hammarby sjön and Lake Saltsjön, the water exchange is unknown, and thus the water retention times needed in the lake model are missing for some basins. Cursino da Cruz (2009) suggested quantifying the net water exchange through simple hydraulic models, such as the Manning Formula.
6. Discussion

A source – transport – storage model is proposed in this thesis to test the hypothesis that the copper concentration in the aquatic environment reflects the current diffuse source strength (Chapter 3). Compared with other studies and models focusing on diffuse emissions, STOCKHOME, SEWSYS, StormTac and SWMM (Chapter 2), the source – transport – storage model provides a more comprehensive understanding of urban diffuse sources and their contribution to the aquatic recipient.

6.1 Level I: The case of the simple watershed

The applicability of the combined model (source model and lake model) for tracing the copper from urban sources to the lake was tested using the five urban lakes in Stockholm, with available field observations and previous estimates. The source model applied in Paper I was adapted from a model for tracing the sources of heavy metals in a WTP (Sörme and Lagerkvist, 2002). In contrast to the WTP, the lake also received discharges from natural ground and atmospheric deposition (Figure 2-2). This was considered in the source model modified in Papers I and II and helped to clarify the contribution of urban diffuse sources to the total copper load (83-93%, Section 5.3.1). An extension of the original source list to include the soil (natural ground such as grassland, forest), railway/metro and parking did not markedly change the results of the estimated copper load (F_in) in the cases studied (Section 5.2.2).

The SFA source model much improved the quality of estimated copper loads compared with the concentration-based approach (StormTac, Table 5-2). The uncertainty in the estimated copper load in the source model varied by a factor about ±30%. In the case without the case-specific observations, the concentration-based approach estimated the copper load through a uniform copper concentration given by the land use, for example in the case of Nybohov (area with abundant copper roofs in use) and the drainage area of Lake Långsjön (few copper roofs in use). However, the SFA source model is able to identify the actual activities within the land use area that yield the copper load. Obviously, it is more appropriate to estimate the copper load from the area of copper roofs through the SFA source-based approach than though a concentration-based approach for which no site-specific monitored data are available.

The weakness of the SFA source model is that this approach requires very specific data in both model input and parameters, such as the traffic volume on each road, extent of copper roofing in the drainage area, and copper content in the source materials/goods. This required information is generally not available through the routine environmental monitoring programme and therefore must be obtained from the statistical data, e.g. government reports in the relevant fields, even the social aspect. If the specific data are still unavailable, assumptions based on similar cases or situations are needed.

In the five cases of urban lakes in Stockholm, the results showed that 50-80% of the copper load in the drainage area was from the traffic sector and 4-43% from the weathering of copper roofs.
The estimated contributions of diffuse sources to urban lakes were different from the study on the Henriksdal WTP in Stockholm (Sörme and Lagerkvist, 2002), in which the copper load in stormwater was dominated by copper roofs (72-77%) followed by the traffic sector (23-28%). The different results on the contribution of urban sources between the urban runoff to the WTP and the urban lakes in Stockholm could be explained by the engineering design of the combined drainage system in Stockholm. In Stockholm, the drainage system discharges some of the stormwater from the traffic area to the local recipient. This means that to manage diffuse emissions, the focus for pollutant abatement measures might be different in different drainage areas and thus it is necessary to estimate urban sources not only at the city level but also in the smaller watersheds.

The correlation analysis based on the five cases indicated that the sediment copper content had a good correlation with the source strength, but a relatively weak correlation with the land use information. This is in agreement with Lindström (2001), who concluded that Copper in surface sediment of small lakes is dominated by the urban status, which was estimated based on land use. However, our five cases did not reproduce the relationship of sediment concentration versus the index of urban status (the index of general anthropogenic influences based on land use, AI%; Lindström, 2001).

According to case studies, the capacity of the lake model is limited to simulate the water copper content. The simulated water copper concentration in the lake model was overestimated within a factor of three compared with field observations in all five cases in this study (Paper II). This level of model performance agreed with that of models by Lindström and Håkanson (2001a) and of the QWASI model (Sinha, 2009). In the lake model, the uncertainties in the dominant processes, inflow (the copper load, \( F_{in} \)), sedimentation and burial, were crucial for the simulated copper concentration in sediment. Lindström and Håkanson (2001a) concluded that the uncertainty for each process in the lake model made an equal contribution to the overall uncertainty. Since uncertainties in dominant fluxes should be more crucial than uncertainties in minor fluxes, the results of uncertainty analysis in this thesis are more reasonable.

The model simulations of the trend of copper sediment content in the five case study lakes from 1996-2001 (Figure 5-2) showed in the case of Råcksta Träsk, Långsjön and Trekanten that the simulated copper concentrations in the A-sediment (\( C_S \)) over time agreed fairly well with the monitoring data considering the model uncertainty. This indicated the applicability of the combined model in the simple urbanised watershed, especially the case with higher sediment copper levels in the lake. The demonstration of the model applications is shown in Appendix II, based on the case of Lake Trekanten.

6.2 Level II: The complex aquatic system

Our review of the gradient of sediment copper concentration along a water path in the aquatic system of Stockholm (Figure 5-1) showed the sediment copper level in the central city to be about three times the background levels upstream and downstream. This indicates the importance
of the urban influence in the aquatic system studied, as has been discussed in previous studies (Lindström et al., 2001; Sternbeck et al., 2003; Rauch, 2007).

In the case of the aquatic system in Stockholm, the urban area is situated in the connection point of Lake Mälaren and the archipelago, where the freshwater mixes with slightly brackish water. Copper is accumulated naturally in sediment in estuarine environments through flocculation and precipitation processes caused by the change in salinity when freshwater meets saline coastal water (Flemming and Trevors, 1989). The salinity in the waters within Stockholm City varies with the different recipients and increases with the distance from Lake Mälaren discharge (summarised by Rolli, 2009). The natural accumulated copper level in estuaries is reported to be around 0.0014-0.012 g/m²/year in other European countries (Flemming and Trevors, 1989). Thus, the accumulation rate caused by the gradient of salinity is much less than the actual accumulation rate of Copper in sediment in the aquatic system of central Stockholm, which is 0.41 g/m²/year, as reported by Sternbeck and Östlund (2001). Therefore, the gradient of sediment copper concentration indicates that anthropogenic influences dominate sediment accumulation of Copper in this aquatic system, considering the accumulation caused by the natural situation of this aquatic system in Stockholm.

In this thesis and Paper III, the aquatic system in Stockholm was presented as a group of coupled basins/straits (Figure 5-8). The coupling of such multiple models causes large uncertainty in the model simulation, which is one of the difficulties in simulating the copper flow from urban sources to the sediment in the Stockholm aquatic system. The copper flow is connected by the copper load with water flow, i.e. the outflow of the upstream basin is the inflow of the downstream basin. The outflows of Copper from basins were estimated by the lake model. In the single basin, Lakes Räcksta Träsk, Judarn and Trekanten, the uncertainty of the water copper content in the combined model for one simple watershed varied between a factor of 1.5 and 2.5 (Paper II). Thus, the lake model showed large uncertainty in the simulated copper concentrations in water. In practice, some small lakes had little or insignificant surface water exchange with the major water path and we concluded that it was possible to exclude them, which was beneficial for avoiding unnecessary complexity of the model and reducing the data demands and model uncertainties (Section 5.5.2). However, this needs to be further investigated.

6.3 Evaluating the sediment content as an indicator of urban emissions

As mentioned above, urban diffuse emissions dominated the sediment copper content in the studied cases, which is a precondition for using sediment copper content as an indicator of urban diffuse emissions.

The source – transport – storage model developed in this thesis accurately traced urban diffuse sources of sediment copper content in the simple urbanised watershed. According to the model simulations, the sediment copper content is positively correlated with the estimated copper load ($F_{in}$) from urban diffuse sources and with the factors related to urban source strength, such as traffic volumes in the five cases investigated here (Figure 5-4 a and b). Moreover, the model
simulation of a step change in $F_{in}$ showed that the sediment copper content was eventually linearly dependent on $F_{in}$ with a proportion of 1:1 (Paper II). In addition, the sensitivity analysis of the lake model indicated the copper load ($F_{in}$) to be the most sensitive factor for the fate of Copper in the lake (Section 5.4.2). These results supported the hypothesis that the copper concentration in the aquatic environment reflects the strength of current diffuse sources. The observed decade-long response of sediment copper content agreed with the temporal scale of the impact of urban discharge on the recipient sediment (Bulter and Davies, 2000). This implies that a substantial integration of the load over time will be recorded in sediment copper level.

In addition, urban diffuse emissions comprise the low-density continuous load to the lake recipient and thus the copper load is generally estimated in the annual level. According to the model simulations, the quantitative response in water and sediment is correlated with the copper retention time in water and sediment (Section 5.3.4). The longer the copper retention time, the less the water and sediment copper content responds quantitatively to a particular pulse change in the copper load. According to the five studied cases here the copper retention time in water is less than 0.4 year, but in sediment it is around 3-8 years (Figure 5-6). Thus, it is more reasonable to use sediment copper content to reflect the annual copper load than water copper content.

Summarising the results in case studies of urban lakes and the aquatic system of Stockholm, sediment copper content can be taken as an indicator of urban diffuse emissions in the case of Stockholm.
7. Conclusions

The major contributions of the thesis are integration of the information flow on urban diffuse sources, the transport of Copper with urban runoff and the fate of Copper in lakes; and revelation of the links between urban diffuse sources and sediment copper content in lakes through a source – transport – storage conceptual model. Three submodels were proposed to achieve the conceptual model in the case of urban lakes and the Stockholm aquatic system:

- An SFA source model for estimating urban diffuse sources and their contribution to the total load in the drainage area.
- A lake model for simulating the distribution of the urban load between different compartments of the lake system.
- A basin-strait approach for presenting the fate of Copper along with water flow in an complex aquatic system.

The applicability of the source – transport – storage model is analysed in the case of individual urban lakes (Level I) and an entire, natural aquatic system in Stockholm (Level II).

A review of the reported sediment copper contents along a main water flow path from upstream Lake Mälaren to the Baltic Sea archipelago through Stockholm showed elevated levels close to the city centre (see Section 5.1), and source analysis in the case of urban lakes showed a dominant contribution of urban sources (83-93%) to the copper load (Section 5.3.1). These results indicate the importance of urban diffuse sources for sediment copper content in the entire aquatic system and in individual lakes in Stockholm.

The results of a SFA source model for the urban copper load to five case study lakes in Stockholm (Trekanten, Laduviken, Långsjön, Räcksta Träsk, and Judarn) were similar to those obtained by the conventional concentration-based estimation method (e.g. StormTac) thereby validating both model approaches (See Section 5.2). Source analysis indicated that the dominant source of Copper in the cases studied was traffic, especially vehicle brake linings, with copper roofing also being important in some cases.

The SFA approach reduced the uncertainty in source strength estimates compared with the concentration-based model (see Section 5.4, Table 5.2) and also allowed identification of actual urban sources of Copper, thereby providing the possibility to manage those. The weakness of the source-based approach is that it requires very specific data in both model input and parameters, e.g. the traffic volume on each road and copper content in the source material/goods, which is not included in routine environmental monitoring programme or even unavailable.

Based on the generally good agreement between simulated copper contents in sediment and independent field observations, (Figure 5-2), we suggest that the coupled source –transport – storage model is applicable for urban lakes with significant urban diffuse sources and/or high level of copper contents. The observations of sediment copper concentration showed a fairly
good correlation between estimated copper load and traffic activity (the dominant factor of source strength, Figure 5-4a and b), confirming that the sediment copper content reflects the strength of urban sources as initially hypothesised. However, the copper fate model showed poorer agreement between simulated and observed copper concentrations in the aqueous phase (see Section 5.4).

Simulated copper contents of the sediment and the aqueous phase were shown to respond linearly to a step change in the copper load for a simple watershed (Paper II). For a pulse load of Copper, the maximum copper concentration was found to be related to the copper retention time in water and A-sediment (Figure 5-6). In the water compartment, it related to the water retention time ($T_W$), the depth of the lake water ($D_m$) and the particular fraction (PF); while in the A-sediment, it related to the form factor of the lake ($V_d$) and the sedimentation rate (sed). While the response to a step or pulse change in the copper load occurred quickly in the aqueous phase, the change in the sediment was slower (on the timescale of years). Altogether, the simulation results imply that the sediment copper content reflects the urban load, but that there is a considerable integration of the load over time, causing a delay in detection of the change. This means that monitoring results correspond to the load over decades, so time must be allowed to indicate the effect of recent changes in the strength of urban sources. The potential application of the combined model in the field of water management and urban planning in the watershed is shown in Appendix II.

Sensitivity and uncertainty analyses (Section 5.4) showed the copper load from the drainage area ($F_{in}$) to be most sensitive to parameters quantifying the copper contribution from brake linings in the traffic sector. The wear rate of brake linings ($W$), the fraction of emissions to the water phase ($\alpha$) and the fraction of stormwater from the road that goes to the lake ($\beta$) in the traffic sector were responsible for most of the uncertainty in $F_{in}$ (Figure 5-7f). In the lake model, the sedimentation process ($v_S$, PF) was dominant in determining both the simulated water and sediment copper concentration ($C_W$ and $C_S$), and also contributed most uncertainty, along with $F_{in}$. Thus, in order to decrease the uncertainty of the source model, the factors, $W$, $\alpha$ and $\beta$, in particular would need to be better constrained. The uncertainty of the coupled model could be further decreased by more precise information on the factors, $v_S$ and PF, in particular.

In the formulation of a conceptual model for the sources and fate of Copper in a series of coupled recipients, it is proposed that the basin-strait approach for water flow in the archipelago by Engqvist and Andrejev (2003) may be useful. Major conceptual difficulties in the proposed model relate to the establishment of system boundaries, level of spatial discretisation of the coupled recipients into basins and straits, and partitioning of the urban sources into individual basins/straits of the model. For application in a quantitative site model, while most of the necessary field data are available for the municipality of Stockholm, data from adjacent municipalities are less readily available. Handling of the temporal variation in water flows and directions between different basins also constitutes a model difficulty, primarily due to lack of data (cf. Cursino da Cruz, 2009).
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Glossary and Abbreviations

Anthroposphere Also referred as technosphere, is that part of the environment that is made or modified by humans for use in human activities and human habitats.

Drainage area The entire geographical area drained by natural and artificial tributaries into an aquatic recipient. Also called catchment area, drainage basin or watershed.

LCA Life cycle analysis, the investigation and valuation of the environmental impacts of a given product or service caused or necessitated by its existence.

QWASI Quantitative Water Air Sediment Interaction model, based on the concept of fugacity and developed by Mackay et al. (1983)

Sensitivity analysis Determination of the effect of a small change in model parameters on the model results

SEWSYS A source-based pollution load model for simulation of transport and treatment processes in sewer systems, developed by Ahlman and Svensson (2005)

Sewer An artificial conduit (or pipe) or system of conduits used to remove sewage (human liquid waste from household, sanitation, commerce and industries) and to provide drainage.

SFA Substance flow analysis, a method of analysing the flows of a substance in a well-defined system.

STOCKHOME A spreadsheet model of urban heavy metal metabolism, including both of the MFA perspective and the utilisation perspective (Hedbrant, 2001).

StomTac A watershed-based spreadsheet stormwater model, was developed by Larm (2000)

Stormwater Water originating during precipitation events and not soaking into the ground but becoming surface runoff, which either flows into surface waterways or is channelled into the storm sewer.

SWEPA Swedish Environmental Protection Agency

SWMM A dynamic rainfall – runoff – subsurface runoff simulation model, used for single-event to long-term (continuous) simulation of the surface runoff/subsurface runoff quantity and quality from primarily urban/suburban areas. Model developed by USEPA.

Uncertainty analysis Determination of the uncertainty of the model simulations due to uncertainty in model parameters, inputs, of initial state.

Urban runoff Surface runoff of rainwater is created by urbanisation. During urbanisation, impervious surfaces, such as road, parking lots and rooftops, are constructed. This kind of surface tends to carry the rainfall to the storm drains instead of allowing it to percolate through soil.

USEPA United States Environmental Protection Agency

Verification The determination that a model or simulation implementation represents the developer’s conceptual description and specifications in an acceptable level.
Appendix I: The distribution of diffuse copper emissions in the drainage area

As presented in the conceptual model (Figure 3-1), the urban diffuse emissions were distributed to the environment compartments (Water, Air and Soil). Appendix I attempts to estimate the distribution of urban diffuse emissions to the environment in the simple watershed (Level I) through the source model.

In the source model, the copper load to the aquatic recipient ($F_{in}$) was quantified from the emission strength ($E$, see Eq. 3) by considering the factor $\beta$ (the fraction of water runoff to the lake), where the fraction (1 - $\beta$) of emissions to the soil is considered (Figure 3-2). In the traffic sector, the distribution of the emissions ($E$) to the stormwater was also estimated by the factor $\alpha$ (the fraction to water, Papers I and II). In the building materials sector, the corrosion rate and runoff rate of copper roofs were used to quantify the respective emissions and load to water runoff from the copper roofs. During the data collection of those factors, the contributions of these urban emissions to other environmental compartment (Air and Soil) also became available. Thus, the distribution of each source was reviewed in Table A-1.

<table>
<thead>
<tr>
<th>Compartment Sources</th>
<th>Water</th>
<th>Air</th>
<th>Soil</th>
<th>Not-emitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brake linings¹</td>
<td>20</td>
<td>49</td>
<td>-</td>
<td>31</td>
</tr>
<tr>
<td>Tyres and Asphalt²</td>
<td>40</td>
<td>60</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Railways/Metro³</td>
<td>20</td>
<td>80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Copper roof⁴</td>
<td>31</td>
<td>-</td>
<td>-</td>
<td>69</td>
</tr>
<tr>
<td>Landfill⁵</td>
<td>40</td>
<td>-</td>
<td>60</td>
<td>-</td>
</tr>
</tbody>
</table>

¹Legret and Pagotto, 1999
²Sörme and Lagerkvist, 2001
³Assumed to be the same as brake linings
⁴He et al., 2001
⁵Larm, 2000

In the five study cases, Copper emitted from urban materials/goods in use (primary source) was about 26-102 kg/year (Figure A-1~5), but only 18-23% of these emissions went to the lake (details presented in Chapter 5.3.1 and Paper II). Meanwhile, other emissions went to air and soil or stayed where they were (i.e. not emitted). In these study cases, 31-46% of the total urban diffuse emissions went to the air, 30-43% were not emitted in the study area and the rest went to the soil (see Figure A-1 to A-5).

In the source model, we neglected the spatial differentiation of atmospheric deposition, i.e. the copper load from the air sector was evaluated by the average level in Stockholm, but did not consider the local influence of traffic emissions, which affect the copper content in the air around the traffic area. Thus, the traffic contribution of Copper to the soil through the path ‘Traffic
source-Air-Soil’ could not be estimated in the source model (shown as the marker “?” in Figure A-1 to A-5).

In the air compartment, around 15-23% of the copper inflow from primary sources was deposited to the soil and water locally, while the rest stayed in air and was transported to the downstream system. However, the estimated copper loads in and out of the soil in the source model showed that over 88% copper loads to the soil in the drainage area were accumulated locally and only a few (3-12%) were transported to the lake as secondary sources.

The copper load not emitted to the environment mainly includes copper emissions from the wear of brake linings and the corrosion products of copper roofs. According to previous studies, 31% of copper wear from brake linings is not emitted from the vehicles (Legret and Pagotto, 1999) and 69% of corrosion products from copper roofs are not washed off with urban runoff (He et al., 2001). The former, the non-emitted Copper in vehicles, was separated out of the studied system because of the copper emissions ending up in the waste water through car washing (Sörme and Lagerkvist, 2002). The latter formed a corrosion layer adhering to the surface of copper roofs.

Figure A-1. Diffuse emissions of Copper to the surrounding environment – Lake Laduviken (kg/year). Insert: nd = no data for quantifying the copper load, marker “?” means the copper load through the pathway ‘traffic sector-air-soil’ is not available in the source model. The first value for ‘Primary sources’ in the top left of the figure is the copper load to the water recipient from the primary sources and the second value is the total copper emissions from primary sources.
Appendix I: The distribution of diffuse copper emissions in the drainage area

Figure A-2 Diffuse emission of Copper to the surrounding environment – Lake Råcksta Träsk (kg/year).

Figure A-3 Diffuse emission of Copper to the surrounding environment – Lake Judarn (kg/year)
Figure A-4 Diffuse emission of Copper to the surrounding environment – Lake Trekanten (kg/year).

Figure A-5 Diffuse emission of Copper to the surrounding environment – Lake Långsjön (kg/year).
Appendix II: Demonstration of the model application in the case of Lake Trekanten

The source – transport – storage model is designed as a supporting tool of urban planning and environment management for estimating urban diffuse emissions and their environment effect. This section discusses some scenarios of the case of Lake Trekanten, which is helpful for understanding how the model could be applied in practice.

Trekanten is a highly eutrophic lake, while the level of Lead and Copper is among the highest documented in any lake in Stockholm. For restoring the environmental quality of the lake system, various measures aimed at different pollutants have been implemented in both the lake and its drainage area:

- Removing or replacing copper roofs (Scenario I)
- Engineered water in/outflows for bringing down the phosphorus level decreasing the water retention time from 3 years to 1 year (Scenario II)

In addition, due to urban development, the traffic situation and land use in the drainage area has changed. For example, the traffic density on the highway Essingeleden and Södertäljevägen has increased to 135 000 and 53 700 vehicles/day since 2002 due to the development of municipal transportation, and some new buildings constructed in the original parking area in the drainage area (S. Thörlöf, pers. comm., 2008). According to these changes, we formulated three scenarios and discussed the usefulness of the proposed model for reflecting human activities on the copper load ($F_{in}$) and on the sediment copper concentration.

**Scenario I: Changes in diffuse copper sources in the drainage area**

According to the environmental quality criteria of lakes and water courses established by the Swedish EPA, the sediment copper concentration in Lake Trekanten (Table 4-2) is classified as Class 4 (High concentration, 100-500 ug/kg dw. Thus, it is suggested to limit the copper load (12 kg/year) in the case of Lake Trekanten to decrease the sediment copper concentration. According to the source analysis (Section 5.3.1), the dominant sources of Copper in Trekanten are traffic emissions (50%) and copper roofs (43%).
Based on the changes in the traffic and building (copper roof) sector presented above, the study formulated four different states (State 0-3), then the source model estimated the change in the copper load ($F_{in}$) and the lake model simulated the reflection of the copper concentration in A-sediment in Figure A-6, respectively, as:

**State 0**: Remains unchanged in terms of urban diffuse sources: $F_{in}$ kept as 12 kg/year.

**State 1**: All copper roofs removed; $F_{in}$ decreased by 43% to 7.1 kg/year.

**State 2**: Traffic activity increased according to S. Thörnelöf S. (pers. comm., 2008): $F_{in}$ increased by 4% to 13 kg/year.

**State 3**: Considering changes in traffic activity and the replacement of copper roofs; $F_{in}$ decreased to 7.6 kg/year.

Figure A-6. Simulated sediment copper content in the period 2007-2037. Assumptions: the initial state of the copper in the sediment in 2007 is 475 mg/kg dw (Rauch, 2007), and the lake is in the steady state in 2007; the copper load ($F_{in}$) is invariable in the simulated period.

According to Scenario I, the source-based approach applied in the combined model was able to estimate the change in $F_{in}$ caused by the actions related to urban diffuse sources directly, compared with the concentration-based approach.

**Scenario II: Changes in land use in the drainage area**

Urban development will cause changes in the land use in the drainage area, for example enlarging the urban area and constructing new residential buildings in a parking area, which also directly or
Appendix II: Demonstration of the model application in the case of Lake Trekanten

indirectly affects the copper load to lakes. Since the source model considered the information on both the diffuse sources (material /goods in use) and the land use, it is possible to reflect on the effect of changes in the land use in the results of the source model. According to the source model, the relationship between the copper load from each source and the land use (the parameter $\beta$) in the drainage area is analysed as follows:

- In the air sector, the load is related to the area of hard surface (i.e. impervious ground). Enlargement of the urban area will increase the area of impervious ground and the copper load from atmospheric deposition will be affected.
- In the soil sector, the load is quantified from the area of natural ground. If the area is changed following urbanisation, the quantification of the copper load from soil could reflect the changes in land use ($\beta$).
- In the building materials sector, the load from building materials is not estimated from the land use directly, but is related to the number of additional copper roofs or other copper material used in the new construction.
- In the traffic sector, traffic emissions are indirectly affected by changes in land use. For example, if increasing the residential area and business area leads to increasing human activities and traffic volume in the relevant area, then the copper load from the traffic will increasing accordingly. Thus, additional information on how the changes in land use affect traffic volume in the local road is required.

In the case of Trekanten, it is reported that two areas of parking (around 9400 m$^2$) were used to construct the new residential building and no copper roofs were used (Thörnelöf, 2008). According to this information, the copper load was estimated again in the source model. The results showed that the copper load from the building materials, air and soil was not affected by this shift of land use, since no relevant parameter was affected. The decrease in the copper load ($F_{in}$) caused by the change in the parking area is <1%, which could be neglected. The effect of the newly constructed building on traffic volume on the local road is unknown, e.g. whether the traffic volume is increased due to the increased population in new residential buildings. Since the traffic volume in the drainage area is dominated by the two major highway Essingeleden and Södertäljevägen (>70%), it was considered that the effect of the newly constructed building is
negligible in this case. Therefore, the source analysis showed that the shift of parking to residential area (9400 m$^2$) did not affect the copper load to Lake Trekanten.

Scenario 2 showed the possibility of estimating the effects of changes in land use on the copper load, but also that some specific information is needed.

**Scenario III: Decreasing the water retention time by engineered water flows**

To decrease the phosphorus level in Lake Trekanten, Stockholm Water Company started diverting drinking water to Trekanten from 1982, and also installed a pump in the bottom for pumping out the bottom water of Trekanten to Lake Mälaren. Those measures changed the water retention time of Lake Trekanten from 3 years to 1 year.

The lake model simulated the effect of decreased water retention time on the lake sediment content (Figure A-7). The simulation showed that if the water retention time decreased to one-third, the sediment copper content decreased by around 30%. This indicates that the measures for managing the eutrophication in this case also bring the positive effect of reducing the copper content in the lake sediment.

![Figure A-7. Simulated sediment copper content during the period 1976-2012. Assumptions: the initial state of Copper in the sediment in 1976 was 630 mg/kg dw (Lännergren C., pers. comm., 2009), and the lake was in the steady state in 1976; The urban copper load ($F_{in}$) and other lake-specific factors were constant in the period 1982-2010; $F_{in}$ is 12 kg/year, as estimated in the period 1996-2002.](image-url)
Because of the assumptions in Figure A-7, the variation in copper load (F_in) is not considered in the simulation and the simulated copper concentration in A-sediment (C_S≈450 mg/kg dw) in 1996-2002 is lower than the observed value (C_S≈600 mg/kg dw) presented in Figure 5-2d. The underestimation indicated the realistic copper load in the earlier period should be higher than the estimated value during the period 1996-2002.

Scenario 3 identified that if there are environmental measures or other human activities changing transport processes in the lake, the lake model is able to reflect their effect on sediment copper levels.
Sediment metal contents as indicators of urban metal flows in Stockholm

Cui, Q., Brandt, N. and Malmström, M. E. (2009)

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Sediment metal contents as indicators of urban metal flows in Stockholm

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Abstract

In Stockholm, Sweden, diffuse emissions have become the dominating source of copper to water. This paper couples source strengths in the urban area with environmental levels of copper through modeling. A MFA/SFA source analysis and a dynamic lake model are adopted from the literature and combined. The combined model is applied in a case study of Lake Trekanten, Stockholm, Sweden. It is shown that the source model, which was made as transparent as possible, matched results of previous studies. The lake submodel showed better predictive capacity for copper in sediment than in water. While we judge our approach as promising, further studies are needed to test if the sediment metal contents can be used as indicators of the urban emissions through this model.

1. Introduction

Metals are widely used in society and they can be considered as “nutrients of technology” (Kapur and Graedel, 2006). At the same time, some metals are common pollutants. The environmental problems caused by these metals have already been considered and solved to some extent in the last decades for some parts of the world. Despite the decrease in the point sources, heavy metals in the environment still maintain at a stable, enhanced level because of diffuse urban emissions (Sörme et al., 2001). In Stockholm, the metal contents in the uppermost sediment of lakes are frequently monitored and reported (Sternbeck et al., 2003; Lithner et al., 2003; Andersson et al., 2008; Rauch, 2007). In Lake Trekanten (Stockholm, Sweden), which is the case study of this work, the copper content of the sediment is still classified as high (Class 4, high level 100-500 mg/kg dw, Swedish EPA; Rauch, 2007) although the local industries moved out the drainage area.
Understanding of the coupling between the pollutant load and the monitored, environmental status is critical for managing urban emissions of pollutants. In this, it is not enough to be able to understand the response of the environment to historical changes of the emissions, but it is also necessary to be able to predict the response to planned activities, such as change in land use or application of pollution remediation or prevention methods. In this study, we assess the coupling between the urban, diffuse emission and the monitored content of copper in lake sediments.

In the literature, the urban loads of metals have previously been estimated by material/substance flow analyses (MFA/SFA). MFA/SFA is an important analytical tool in the research field of Industrial Ecology and is used to analyze the stocks and flows of metals in scales ranging from local to global (Elshkaki et al., 2004; Graedel et al., 2004; Spatari et al., 2005). Several studies/models on MFA/SFA in the urban system have been done for Stockholm. For example, Stockhome, a spreadsheet model based on the MFA approach, has been used to represent the urban metabolism of copper in Stockholm (Hedbrant, 2001). The sources of copper to the Henriksdal wastewater treatment plant (WTP) in Stockholm were investigated in 1999 by the MFA/SFA approach (Sorme and Lagerkvist, 2002). A similar approach will be applied in this paper.

Moreover, there are a variety of models quantifying the fate of metals in the environment, especially lakes, available. For example, Dynabox is a multi-media fate model for real-world situations of Cd, Cu, Pb, Zn in Netherlands (van der Voet et al., 2000). In Canada, the fate of metals in contaminated lake has been simulated by QWAS1 and MINTEQA2 (Woodfine et al., 2000). The fate of heavy metals in Swedish lakes has been modeled by a dynamic model (Håkanson, 1996a,b; Lindström and Håkanson, 2001). This model is adopted for the work in this paper.

In summary, both SFA and dynamic lake models are available in the literature. In this work, we adopt models from the literature in order to address the fate of copper using the small lake Trekanten in Stockholm, Sweden and its urban drainage area as a case study. We also attempt to advance the understanding of the coupling between the urban emissions and the monitored, environmental conditions by combining these two kinds of models. Such a combined model can potentially be used to understand the pollution situation of today and historically and may also be used to assess different scenarios for future changes of the system. The objectives of this paper are:
To adopt models for source analysis of urban emissions and copper fate in lakes from the literature;

To couple and test the source analysis and lake sub-models by historic data in a case study;

To apply the lake submodel for predicting the responses of sedimental copper content to a change in urban load;

To use the combined model to evaluate the use of sediment copper contents as an indicator of the urban metal emission.

2. Case study – Trekanten

Trekanten is a small lake in the urban area of Stockholm, Sweden. It is highly eutrophic with low transparency and high contents of heavy metals (StockholmVatten, 2000). The basic information on Lake Trekanten is shown in Table 1. All major water in/out flows are engineered: an underground outflow goes to Lake Mälaren, a tributary leads drinking water to the lake, and four discharge points distributed in the lakeside are responsible for transporting storm water into the lake (Figure 1).

Figure 1 Map of Lake Trekanten and its drainage area. Source: Miljöförvattningen Stockholm, 2001
Until the early 1960s, the lake was flanked by small scale industries, such as tanneries, and dye- and creosote works. Today, a timber trade north of the lake is the only remaining industrial operation in the drainage area of Trekanten, but it has little effect on the copper emission (Thörnelöf, 2007). Today, the land use in the drainage area can be divided into residential, business and traffic area (including highways, roads through residential and business area, parking lots and a traffic center; Table 2). A considerable part of the drainage area is green areas, including parks, lake front promenades and other recreational areas.

**Table 1** Information on Lake Trekanten used in the lake model.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Trekanten</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water retention time(^a)</td>
<td>T</td>
<td>years</td>
<td>1.6</td>
</tr>
<tr>
<td>Lake surface area(^a)</td>
<td>A</td>
<td>m(^2)</td>
<td>1.3×10(^5)</td>
</tr>
<tr>
<td>Area of the drainage area(^a)</td>
<td>A(_D)</td>
<td>m(^2)</td>
<td>5.7×10(^5)</td>
</tr>
<tr>
<td>Lake volume(^a)</td>
<td>V(_W)</td>
<td>m(^3)</td>
<td>5.0×10(^5)</td>
</tr>
<tr>
<td>Mean depth(^a)</td>
<td>D(_m)</td>
<td>m</td>
<td>3.86</td>
</tr>
<tr>
<td>Maximum depth(^a)</td>
<td>D(_{max})</td>
<td>m</td>
<td>6.5</td>
</tr>
<tr>
<td>The form factor(^a)</td>
<td>V(_d)</td>
<td>-</td>
<td>1.78</td>
</tr>
<tr>
<td>Fraction of A-area(^a)</td>
<td>D(_A)</td>
<td>%</td>
<td>29</td>
</tr>
<tr>
<td>Sedimentation velocity(^a)</td>
<td>(v_s)</td>
<td>cm/year</td>
<td>0.71</td>
</tr>
<tr>
<td>The depth of A-area(^a)</td>
<td>T(_A)</td>
<td>cm</td>
<td>2</td>
</tr>
<tr>
<td>The age of ET-sediment(^a)</td>
<td>T(_{ET})</td>
<td>year</td>
<td>1</td>
</tr>
<tr>
<td>The age of A-sediment(^a)</td>
<td>T(_A)</td>
<td>year</td>
<td>2.8</td>
</tr>
<tr>
<td>Diffusion constant(^a)</td>
<td>C(_{diff})</td>
<td>year(^{-1})</td>
<td>0.35</td>
</tr>
<tr>
<td>Settling velocity of the particles(^a)</td>
<td>V</td>
<td>m/year</td>
<td>100</td>
</tr>
<tr>
<td>Particle fraction(^a)</td>
<td>PF</td>
<td>%</td>
<td>10</td>
</tr>
<tr>
<td>Loss of ignition(^b)</td>
<td>LOI</td>
<td>%</td>
<td>31(^2)</td>
</tr>
<tr>
<td>Water content in sediment(^b)</td>
<td>W</td>
<td>%</td>
<td>95(^2)</td>
</tr>
</tbody>
</table>
aSee Lindström and Håkanson, 2001
bSee Sternbeck et al., 2003

Table 2 Land use, hard area and copper roofs in the drainage area of Lake Trekanten. Source: Larm and Holmgren, 1999

<table>
<thead>
<tr>
<th>Geographic regions</th>
<th>Traffic A_R</th>
<th>Residential A_R</th>
<th>Business A_B</th>
<th>Green area</th>
<th>Hard area A_H</th>
<th>Cu roofs A_b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nybohov</td>
<td>89,789</td>
<td>51,337</td>
<td>12,146</td>
<td>983</td>
<td>25,323</td>
<td>64,466</td>
</tr>
<tr>
<td>Liljeholmen</td>
<td>77,631</td>
<td>50,117</td>
<td>142</td>
<td>3,873</td>
<td>23,499</td>
<td>54,132</td>
</tr>
<tr>
<td>Katrineberg</td>
<td>63,916</td>
<td>27,298</td>
<td>5,949</td>
<td>15,521</td>
<td>15,147</td>
<td>48,768</td>
</tr>
<tr>
<td>Gröndal</td>
<td>72,044</td>
<td>25,416</td>
<td>12,029</td>
<td>454</td>
<td>34,146</td>
<td>37,899</td>
</tr>
<tr>
<td>Essingeleden</td>
<td>10,652</td>
<td>9,892</td>
<td>0</td>
<td>0</td>
<td>760</td>
<td>9,892</td>
</tr>
<tr>
<td>Others</td>
<td>271,766</td>
<td>24,460</td>
<td>1,468</td>
<td>9,403</td>
<td>235,654</td>
<td>35,331</td>
</tr>
<tr>
<td>Sum</td>
<td>585,798</td>
<td>188,520</td>
<td>31,734</td>
<td>30,234</td>
<td>334,529</td>
<td>250,488</td>
</tr>
</tbody>
</table>

The drainage area is divided into several geographical regions (Figure 1): 1. Nybohov, 2. Liljeholmen, 3. Katrineberg, 4. Gröndal, and 5. Essingeleden. In the drainage area of Trekanten, two major traffic routes, Essingeleden (300 m) and Södertäljevägen (200m) pass through and there is a traffic centre in Liljeholmen (Region 2). In Nybohov, copper roofs are used in several buildings (Larm and Holmgren, 1999).

The copper load to storm water from the drainage area and the water/sediment quality in Trekanten has been monitored in previous studies (Larm and Holmgren, 1999; Lindström and Håkanson, 2001; Sternbeck et al., 2003; Rauch, 2007). In 1996,
Lindström and Håkanson (2001) measured the mean copper concentration of five surface water samples during the year as 3.15 μg/L, and the average concentration from five sediment samples in different sites in the winter as 569 mg/kg dw. In 2001, the copper contents in Lake Trekanten were monitored as 3.7 μg/L in water and 591 mg/kg dw in lake sediments (Lithner et al., 2003).

3. Model description

3.1. The conceptual model

For this work, the conceptual model is designed to link the information from the technosphere and the biosphere—water, air and soil (Figure 2). In the technosphere, copper is widely used in many different products and materials, such as, cables, wires, electrical products, roof materials, pipes for plumbing, heating and ventilation, and pesticides and for decoration. Because of the multiple applications of copper, there is a huge store of it in the urban area. Due to the weathering and wearing processes of this store, there are diffuse emissions of copper to the surrounding biosphere (soil, water and air; Figure 2).

Considering the fate of copper from urban drainage areas to a natural aquatic recipient, such as a lake, several pathways are involved. Copper emitted to storm water or sewer is mainly collected by the storm water/waste water system, and then parts of them are transported to the lake. A small part of the copper in the stormwater goes to soil, due to not all water being collected.

The copper content in air is partly from the local urban emissions and has partly been transported from other places. A part of the copper content in the air will reach the recipient lake by deposition in the lake directly. In addition, atmospheric deposition also goes to the drainage area (hard area and soil); the copper deposited to the hard area will to a great extent be collected by the stormwater and be transported to the lake. Most of the copper emitted to the local soil is immobile, but can to some extent be transported to the lake by ground water.
The fate of copper follows geochemical principles, when it goes into a natural, aquatic system. Once copper reaches the lake it may be transported downstream by the water flow or adhere to lake particles and settle in the sediments.

In order to connect the technosphere and the lake in this urban system, we use two submodels: a source analysis and a lake submodel (Figure 2). The source analysis/urban emissions submodel accounts for the possible diffuse emissions following the approach of Sörme and Lagerkvist (2002) and using an as transparent as possible quantification. The fate of copper in the recipient lake is represented in a lake submodel following the approach of Lindström and Håkanson (2001). This approach is based on quantifying fluxes between compartments representing different physical units of the lake system by process-based, empirical transfer equations. To connect the two submodels, the result/output file of the source analysis, is used as the indata/input file of the lake mass-balances model.
3.2. The source analysis submodel

The focus of the source analysis submodel is on the diffuse emissions of copper from the urban area in the drainage area and the subsequent pathways of copper emissions to the lake. Copper arrives a lake by upstream tributaries, ground water, wet and dry deposition from air and by urban runoffs through the stormwater system as well as by wastewater discharge (Lindström and Håkanson, 2001; Lindström et al., 2001; Jonsson et al., 2002). In Lake Trekanten, there is no waste water discharge into the lake; therefore, only stormwater is considered for estimating the amount of urban diffuse copper emission with water. It has been suggested that heavy metal transport through ground water in the Stockholm area is very low (Aastrup and Thunholm, 2001), so the contribution of ground water is also neglected here.

To estimate the urban emission of copper, the drainage area is divided into several geographic regions as mentioned before. The source analysis submodel focuses on two types of information in each region: land use and source type (Figure 3). The land use information provides influence factors, such as traffic density, area of hard area, and the fraction of stormwater that goes to the lake, for quantifying the copper load from different source in the drainage area. The source type includes the possible materials or products that may emit copper, which can be classified into five groups: traffic, building materials, atmospheric deposition, pipe sediment, people and animals.

According to Sörme and Lagerkvist (2002), the contribution of pipe sediment is insignificant compared to other sources in the case of heavy metals in Stockholm. Furthermore, the sector of people and animals, which has been evaluated by Larm and Holmgren (1999) in the case of Trekanten, is also negligible. Therefore, the major urban contributing source types in the case of Trekanten and the only ones considered in this work are traffic, building materials, and atmospheric deposition (Figure 3).
Figure 3 Urban sources of copper in the drainage area of a lake

From the view of SFA, the urban emissions are through the mechanisms of delay and leaching (Elshkaki et al., 2005). Delay refers to the discarding of the products and is related to the life span of the products. Leaching means the emissions of the substance from the products in use. Generally, the urban copper emission from traffic and building material to the water system is considered to follow the leaching mechanism (Elshkaki et al., 2005) and is given by:

\[ E(t) = C \cdot S(t) \]  

(1)

where \( S(t) \) is the size of the stock at time \( t \), and \( C \) is the leaching factor. The following sections detail the quantification made in this work for the different sources types and land uses (compare Figure 3).
3.2.1. Traffic

In the urban drainage area, copper is contributed from the traffic sector by emissions from vehicle parts and roads (Figure 3). The emission from the traffic sector is calculated as (Westerlund, 2001):

\[ E_j = \sum_i M_i W_i T_j \alpha_i \]  

(2)

where \( M_i \) is the metal content of vehicle parts/roads \( i \) (% m/m); \( W_i \) is the wear of vehicle parts/roads \( i \) (mg/km vehicle); \( T \) is the average annual traffic work (km vehicle/year), and equal to traffic density (\( D_v \), vehicle/day) times the length of the road (\( L \), km; US FHWA, 2001) and time (365 day/year). \( \alpha \) is the fraction of copper emission from vehicle parts/roads (%) that goes to stormwater. Equation 2 is evaluated for the different geographic regions \( (j) \), separately.

There are two types of brake linings: original (40%) and replacement (60%). The average metal content (\( M_B \)) equals to original metal content * 0.4 + replacement metal content * 0.6.

The first is the value for front break linings, and the latter is the value for rear break linings. In Eq. 2 \( M_i = M_{front} W_{front} + M_{rear} W_{rear} \)

The first is the value of private cars, and the latter is the value of heavy vehicles.

The default values of \( M, W \) and \( \alpha \) are shown in Table 3. Private cars and heavy vehicles contribute different amounts of copper, therefore, their wear rates \( (W_i) \) are separated in Table 3, and their different traffic work taken into account when evaluation Equation 2. To estimate the traffic work \( (T = D_v L 365) \) based on available, limited data on Lake Trekenenten, several assumptions are made:

Traffic density in the drainage area is invariable with time in the estimated period. Since the fraction of private car and heavy vehicle varies between the function areas, the roads are divided into three types: highways, traffic center, local roads (roads through business area and roads through residential area). The fractions of the total traffic work done by private car and \( D_v \) of different road type are shown in Table 4.
### Table 3: The parameter setting of the source analysis

<table>
<thead>
<tr>
<th>Section</th>
<th>Catalog</th>
<th>Parameter</th>
<th>Symbol</th>
<th>Unit</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traffic</td>
<td>Brake linings</td>
<td>Cu content</td>
<td>(M_b)</td>
<td>% m/m</td>
<td>0.01/0.074(^{a,b})</td>
<td>Westerlund et al, 2001</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wear rate</td>
<td>(W_b)</td>
<td>mg/vehicle km</td>
<td>10.5/5.13(^b)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Faction to stormwater</td>
<td>(\alpha_b)</td>
<td>%</td>
<td>20</td>
<td>Hulskotte et al., 2006</td>
</tr>
<tr>
<td>Tires</td>
<td></td>
<td>Cu content</td>
<td>(M_t)</td>
<td>mg/kg</td>
<td>1.8</td>
<td>Legret and Pagotto, 1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wear rate</td>
<td>(W_t)</td>
<td>mg/vehicle km</td>
<td>100/400(^c)</td>
<td>Larm and Holmgren, 1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Faction to stormwater</td>
<td>(\alpha_t)</td>
<td>%</td>
<td>40</td>
<td>Sörme and Lagerkvist, 2002</td>
</tr>
<tr>
<td>Asphalt</td>
<td></td>
<td>Cu content</td>
<td>(M_A)</td>
<td>mg/kg</td>
<td>14</td>
<td>Legret et al, 2005</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wear rate</td>
<td>(W_A)</td>
<td>mg/vehicle km</td>
<td>5000/20,000(^c)</td>
<td>Larm and Holmgren, 1999</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Faction to stormwater</td>
<td>(\alpha_A)</td>
<td>%</td>
<td>40</td>
<td>Sörme and Lagerkvist, 2002</td>
</tr>
<tr>
<td>Building materials</td>
<td>Copper roof</td>
<td>Impregnated wood</td>
<td>Runoff rate</td>
<td>(C_{\text{roof}})</td>
<td>2100</td>
<td>He et al., 2001</td>
</tr>
<tr>
<td>Building materials</td>
<td>Copper roof</td>
<td>Impregnated wood</td>
<td>Runoff rate</td>
<td>(C_{\text{wood}})</td>
<td>660</td>
<td>Persson and Kucera, 2001</td>
</tr>
<tr>
<td>Atm. deposition</td>
<td></td>
<td>Deposition rate</td>
<td>(C_D)</td>
<td>mg/m(^2) year</td>
<td>2.5</td>
<td>Burman and Johansson, 2000</td>
</tr>
<tr>
<td>Residential</td>
<td></td>
<td>(\beta_{\text{Residential}})</td>
<td>%</td>
<td></td>
<td>35</td>
<td>Larm and Holmgren, 1999</td>
</tr>
<tr>
<td>Traffic</td>
<td></td>
<td>(\beta_{\text{Traffic}})</td>
<td>%</td>
<td></td>
<td>90</td>
<td>Larm and Holmgren, 1999</td>
</tr>
<tr>
<td>Business</td>
<td></td>
<td>(\beta_{\text{Business}})</td>
<td>%</td>
<td></td>
<td>90</td>
<td>Larm and Holmgren, 1999</td>
</tr>
</tbody>
</table>
To evaluate the road length in the residential and business areas, it is assumed that:

$$\frac{L_R}{L_B} = \frac{A_R}{A_B}$$ (3)

where $L_R$ and $L_B$ are the road length in residential and business areas respectively, and $A_R$ and $A_B$ is the area of residential and business areas in the same region. The total length of local road in a region equals the sum of road lengths in the residential and business areas, and the total road lengths are shown in Table 4.

Except for the high ways (Essingeleden and Södertäljevägen), the local road system is branched. Thus, vehicles will not pass the total length of the road. It is assumed that each vehicle only passes 50% of the total road length.

**Table 4** Traffic work in the drainage area of Lake Trekanten.

<table>
<thead>
<tr>
<th>Regions</th>
<th>Road type</th>
<th>$D_V$ vehicle/day</th>
<th>L km</th>
<th>Fraction of private cars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nybohov</td>
<td>local road</td>
<td>4,000&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>1.13</td>
<td>96/80&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>Liljeholmen</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Södertäljevägen</td>
<td>highway</td>
<td>45,000&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.20</td>
<td>96&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>Liljeholmstorget</td>
<td>traffic center</td>
<td>8,000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>1.06</td>
<td>50&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>Katrineberg</td>
<td>local road</td>
<td>4,000&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>0.53</td>
<td>96/80</td>
</tr>
<tr>
<td>Gröndal</td>
<td>local road</td>
<td>4,000&lt;sup&gt;a,b&lt;/sup&gt;</td>
<td>2.53</td>
<td>96/80</td>
</tr>
<tr>
<td>Essingeleden</td>
<td>highway</td>
<td>120,000&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.30</td>
<td>96</td>
</tr>
</tbody>
</table>

<sup>a</sup>Larm and Holmgren, 1999

<sup>b</sup>$D_V$ in the local roads are assumed equal to the traffic density of local road in Nybohovsbacken (Larm and Holmgren, 1999).

<sup>c</sup>From StockholmVatten, 2000

<sup>d</sup>The former value is faction of private cars in the roads in the residential areas, refer to Sörme and Lagerkvist (2002); the latter value is in the roads in the business areas, refer to Larm and Holmgren (1999).
In the traffic sector, copper is normally emitted as particles, of which the larger particles are deposited on the road directly and then transported with the stormwater (Sörme and Lagerkvist, 2002). Thus, only a fraction $\alpha$ (see Table 3) goes directly to the stormwater. It is this fraction that is accounted for directly in the traffic source. The smaller particles go to the air as aerosols and some of this is deposited in the close by soil; this is accounted for by the atmospheric source in this work. Another part of the smaller particles are transported with air to more distant areas and escapes from the urban drainage area and is excluded from further consideration in the source analysis.

3.2.2. Building materials

For building materials, it is reported that copper emitted from copper roofs, asphalt covering roof, and impregnated wood. The emission from building materials is calculated as

$$E_b = C_b \times A_b$$  \hspace{1cm} (4)

where $C_b$ is the copper runoff rate of material $b$ (g/m$^2$ year, see Table 3), and $A_b$ is the exposed area of this material in the drainage area (m$^2$).

3.2.3. Atmospheric deposition

Atmospheric deposition (wet and dry) is divided into two parts: deposition into the lake directly and deposition into hard area in the drainage area. Here, it is assumed that in the drainage area, only the atmospheric deposition to hard area can be collected by stormwater system, and copper deposited on soil is considered immobile, and will not be transported to the lake. Generally, the atmospheric contribution of copper is quantified as:

$$E_{atm} = C_{atm} \times A_H$$  \hspace{1cm} (5)

where $C_{atm}$ is the total atmospheric deposition rate of copper (including wet and dry deposition; g/m$^2$ year, see Table 3), and $A_H$ is the area of hard surface and/or lake surface in aimed region (m$^2$).
3.2.4. Copper emission to the lake

Most of stormwater in this urban drainage area is collected by the stormwater system, but still some of the stormwater is absorbed by the soil in the drainage area. As stormwater is the important carrier of urban copper emissions, the fraction (β) caught by the stormwater system greatly influences the urban inflow of copper to the lake. This fraction is determined by the land use (see Table 3). The urban inflow of copper to the lake (\( F_{in} \)) is quantified as:

\[
F_{in} = E_{atm,lake} + \sum_m \sum_n \beta_n E_{mn} \tag{6}
\]

Where \( E_{mn} \) is the diffused copper emission from source type \( m \) in the \( n \) land use area, as calculated by Equations 2-4 for the different source types and \( \beta_n \) (see Table 3) is the fraction of the stormwater that goes to the lake (\%).

3.3. The lake submodel

The fate of copper in the lake is presented in the lake submodel (Figure 4), which contains three compartments: the water (\( W \)), the erosion and transport sediment (ET), and the active, accumulated sediment (A). As a simplification, the water compartment is assumed well-mixed and thermal and concentration stratification is neglected. Copper entering the water pillar is partly transported out of the lake and partly deposited into the sediments. Sediment in the ET-area is affected by erosion and transportation. It is thus mobile and considered as contributing to the internal loading in the lake, and is also responsible for some of the copper transport to the A-area. Sediment is accumulated in the A-area, of which only the upmost part (0-2cm) is considered here as only this part is assumed to have exchange with the lake water, while the deeper sediment is considered as passive. From the A-area, copper is buried into the deep sediments but may also be released to the water pillar through diffusion.
Six major transport processes (j) are involved: inflow, outflow, sedimentation, resuspension, diffusion and burying. The inflow of copper to the lake ($F_{in}$) is imported from the source analysis submodel (Equation 6), thereby connecting the two submodels. The fluxes of the other processes are calculated as

$$F_j = M_i \times R_j$$  \hspace{1cm} (7)$$

Where $F_j$ is the copper flux of process j (kg/year), $M_i$ is the mass of copper in compartment i (kg) and $R_j$ is the transfer rate of process j (year$^{-1}$). The equations for calculating the transfer rates are summarized in Table 5.
Table 5 Process quantifications in the lake submodel

<table>
<thead>
<tr>
<th>Process</th>
<th>Quantification&lt;sup&gt;d&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Outflow&lt;sup&gt;a,c&lt;/sup&gt;</td>
<td>$F_{out} = M_W * R_{out}$&lt;br&gt;$M_W = C_W * V_W$&lt;br&gt;$R_{out} = 1.386/T^((30/(T+30-1)+0.5/1.5))$</td>
</tr>
<tr>
<td>Sedimentation&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$F_{sed-ET} = F_{sed} * D_{ET}$;&lt;br&gt;$F_{sed-A} = F_{sed} * D_A$;&lt;br&gt;$F_{sed} = M_W * R_{sed}$;&lt;br&gt;$D_{ET} = 1 - D_A$;&lt;br&gt;$R_{sed} = P_F * v / D_m$</td>
</tr>
<tr>
<td>Resuspension&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$F_{res-A} = F_{res} * V_d / 3$;&lt;br&gt;$F_{res-W} = F_{res} * (1 - V_d / 3)$;&lt;br&gt;$F_{res} = M_{ET} * R_{res}$;&lt;br&gt;$R_{res} = 1 / T_{ET}$</td>
</tr>
<tr>
<td>Bury&lt;sup&gt;b,c&lt;/sup&gt;</td>
<td>$F_{bur} = M_A * R_{bur}$&lt;br&gt;$M_A = C_s * A * t * D_A * d^*(1 - W / 100)$&lt;br&gt;$R_{bur} = 1 / T_A$&lt;br&gt;$d = 100 * 2.6 / (100 + (W + LOI) * (2.6 - 1))$</td>
</tr>
<tr>
<td>Diffusion&lt;sup&gt;a&lt;/sup&gt;</td>
<td>$F_{diff} = M_A * R_{diff}$&lt;br&gt;$R_{diff} = C_{diff} / LOI$</td>
</tr>
</tbody>
</table>

<sup>a</sup>See Lindström and Håkanson, 2001  
<sup>b</sup>See Håkanson and Bryhn, 2008  
<sup>c</sup>See Lindström and Håkanson, 2001  
<sup>d</sup>$C_W$, $C_s$ are the copper concentration in water and A-sediment, respectively. Both are state-variables in the model.
3.4. Application in case study and numerical implementation

The model is formulated and tested in the case of Lake Trekanten in Stockholm, Sweden. A past time period, 1998-1999, is simulated for testing the source analysis submodel. The whole drainage area and two regions in the drainage area, Nybohov and Essingeleden, are addressed, separately. Based on the available information of Lake Trekanten, another time period, 1996-2001, is chosen for testing the lake submodel. Subsequently, the lake submodel is run with a half of the original copper inflow in a 30-year period in order to test the response of the sediment copper content to the urban emission.

The source analysis is based on the structure of substance flow analysis (SFA) and is implemented as a spreadsheet in Microsoft Office Excel 2007. The lake submodel is implemented through a graphical interface dynamic causality model approach in Simile v 5.1.

4. Results and discussion

4.1. Results and verification of the source analysis submodel

Based on historic information from a one-year period, 1998-1999, the source analysis submodel is applied in the case of Trekanten and its drainage area. In this source analysis, the copper load to Lake Trekanten is estimated from land use (Table 2) in the drainage area and three source types (Table 3). The copper emissions to lake from the different sources in the five geographic regions are shown in Table 6. The total urban inflow of copper to Lake Trekanten is estimated to 11.5 kg/year. To test the source analysis submodel, the result is compared with published monitoring and previous modeling results (Table 6), including Nybohov (Region 1), Essingeleden (Region 5) and the entire study area.
Table 6 Estimated copper load in the different drainage regions and in the entire drainage area for Lake Trekanten

<table>
<thead>
<tr>
<th>Cu/kg/year</th>
<th>Nybohov</th>
<th>Liljeholmen</th>
<th>Katrineberg</th>
<th>Gröndal</th>
<th>Essingeleden</th>
<th>Lake/other</th>
<th>Sum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Traffic</td>
<td>0.2</td>
<td>1.3</td>
<td>0.1</td>
<td>0.5</td>
<td>3.4/0.6&lt;sup&gt;1&lt;/sup&gt;</td>
<td>5.5/2.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Building material</td>
<td>5.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
<td>5.3</td>
<td></td>
</tr>
<tr>
<td>Atm. deposition</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
<td>0.02</td>
<td>0.3</td>
<td>0.7</td>
</tr>
<tr>
<td>sum</td>
<td>5.4</td>
<td>1.5</td>
<td>0.3</td>
<td>0.6</td>
<td>3.4/0.6</td>
<td>11.5/8.7&lt;sup&gt;a&lt;/sup&gt;</td>
<td></td>
</tr>
<tr>
<td>Monitoring data&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8</td>
<td></td>
<td></td>
<td></td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Larm and Holmgren, 1999</td>
<td>7.7</td>
<td>2.8</td>
<td>1.8</td>
<td>1.2</td>
<td>1.2</td>
<td>--</td>
<td>15</td>
</tr>
<tr>
<td>StockholmVatten, 2000</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>7.9</td>
</tr>
<tr>
<td>Lindström and Håkanson, 2001</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>8</td>
</tr>
</tbody>
</table>

<sup>1,a</sup>The former value is the original value from the source analysis submodel; the latter values is the results adjusted according to reported monitoring data
<sup>b</sup>See Larm and Holmgren, 1999

According to the information of source type, copper roof is the major source in the building material sector in this study area and about 96% of them are located in Nybohov. So this region is used to test the source model of the building material sector. From the source analysis submodel, the total copper load in Nybohov is estimated as 5.40 kg/year and the emission from copper roof (5.06 kg/year) contributed 94% of the copper load in this region. The modeled copper load in Nybohov is around two thirds of the copper load implied by the monitoring data (8 kg/year, Table 6). Despite this difference, we judge the performance of the model for the building material sector as reasonable in this case study, particularly given the wide range of $C_R$ previously reported in the literatures (770-2600 mg/m$^2$/year; Larm, 1999; He, 2001; Persson, 2001),
Table 6 shows that the dominating source in Essingeleden is the traffic sector. The calculated copper load of Essingeleden in this model (3.4 kg/year) is about 6 times higher than that derived from monitoring results (0.6 kg/year). In Essingeleden, there is an underground oil separator for the stormwater from the highway. Although there is no field data available to test this, we assumed that the separator facility may reduce the copper load and, at least in part, cause the observed discrepancy between model results and monitoring data. In the following, we used the load based on the monitoring result for Essingeleden. The other regions are not equipped with oil separators and for those we use the model estimates.

With these adjustments, the total urban copper load to the lake is estimated to 8.7 kg/year (Table 6). This estimated load is in good agreement with previous analyses suggesting a total copper load to Lake Trekanten of 7.9-15 kg/year (Table 6; Larm and Holmgren, 1999; StockholmVatten, 2000; Lindström and Håkanson, 2001).

4.2. Lake submodel

The estimated load of copper from the source analysis submodel (8.7 kg/year) is used as the inflow of copper in the lake submodel. The initial state of the lake is set by the monitoring information in 1996. The lake submodel is run in a 5-year period, 1996-2001, assuming that the urban copper emission in this 5-year period is invariable with time.

Figure 5 shows model predictions of copper concentrations in water and sediment (accumulation bottoms, “A-areas”) over the considered time period along with monitoring observations from 1996 (initial conditions for the model; Lindström and Håkanson, 2001) and 2001 (Lithner et al., 2003). The modeled concentration of copper in the sediment is close to constant over the considered time, which is consistent with the monitoring results (Figure 5b). In year 2001, the model results deviate less than 5% from the monitoring results. For the water pillar, the model predicts roughly a doubling of the copper concentration from year 1996 to 2001 (Figure 5a). The monitoring data, on the contrary, suggests a slight decrease in the concentration.
Figure 5 Copper concentration in Lake Trekanten as function of time: a. Water; b. Sediment (Aarea). Curves show results of the lake model and symbols show the monitoring data from Lindström and Håkanson (2001) and Lithner and Holm (2003).

Generally, discrepancy between model results and field observations may be due to (1) inconsistencies made in the comparison or (2) inefficiency of the model to reproduce the real system behaviour, due to conceptualisation, formulation or...
We conclude that the model predicts a copper concentration in the accumulation sediment that agrees well with monitoring results. For the water pillar, model and monitoring results, although differing, agree within a factor of 2.4 in the year of 2001; preliminary, we accept this discrepancy, given the uncertainties in the source analysis and the simplifications made in the lake submodel and in the comparison of model and monitoring results.

The fate of Cu in Lake Trekanten as given by the model is shown in Figure 6. About 1/3 of the copper in the inflow is transported out of the lake system, with a major part being accumulated in the lake. In addition to the urban inflow, the sediments both in the ET- and A-areas provide copper to the lake water, which is about 20% of the total load. About 60% of the copper flow to the A-sediment is from the ET-area. The copper content in the A-area is buried into the deeper, passive sediment. This part is considered as stored in the lake system, but it is out of the system boundary of the
lake submodel. The sediment content of copper is at close to the steady-state and burial to deep sediments, thus, dominantly accounts for the difference between in- and out-flows with water.

Figure 6 The fate of copper in Lake Trekanen in year 2001 as given by the model. Fluxes are given in kg of copper per year.

4.3. Modelled response of sediment/water contents of copper to the urban emission

In order to test the response of the sediment copper content to the change in urban inflow, the lake submodel was run from steady state, halving the inflow at year 6. The modeled copper concentrations in the sediment and the water during 30 years are shown in Figure 7. Following the decrease in copper inflow, both the modelled sediment and water copper contents decreased. The modeled copper concentration in water decreases rapidly, and approaches a new steady state in less than 3 year. Here, this response time is defined as the time needed for the copper concentration to
reach 95% of the new steady-state value from the initial steady-state. The decrease of the modeled sediment copper content is much slower, taking 10 years to approach a new steady state. At the new steady state, both the water and sediment copper contents are half of the initial, corresponding to the decrease in the inflow by 50%. The results indicate that if the inflow is changed, the response time of sediment content of copper is around three times that of the water copper content.

*Figure 7* The modeled CW (a) and CS (b) as function of time. In the simulation, the copper load is increased from 8.7 to 4.35 kg/year in year 6, starting from steady state conditions of the lake submodel (inflow=8.7 kg/year) in Figure 5.
The result in this test indicated that the response of the sediment copper content is much slower than water content. Because of the slower response of the sediments to change in the load, it is easier to improve the water quality (in terms of copper concentrations) than to reduce the copper content in the sediments. Even when the water quality has improved, the sediments will retain elevated copper concentrations, and contribute to internal pollutant loading. On the one hand, this indicates that the sediment content of copper may be less sensitive to the fluctuations in the load, as due to temporal variations not concerned in this study, than the water concentration and thus yield a more reliable indicator of the urban load. On the other hand, slow response means that change of load will not be detected in the sediment copper content until after considerable time.

5. Conclusion

This paper made an attempt to match information from the technosphere and the surrounding environment using a model on the local level. The work is based on the case of copper sources and fate in Lake Trekanten and its urban drainage area in Stockholm, Sweden. For this, we adopted a SFA structure from Sörme et al (2002) and an empirical lake model by Lindström and Håkanson (2001) and Håkansson (2004). Both submodels were presented in an as transparent as possible way and were connected through the urban copper load to the lake.

Both submodels were tested against previously published monitoring and model data. Our modeled urban copper emissions estimated by the source analysis submodel were in reasonable accordance with previously published results. The lake model was evaluated using monitoring data from the 5-year period, 1996-2001. It was shown that the performance of the lake model is reasonable, taking uncertainties and simplifications into account, and is better for copper content in sediment than in water. We suggest that remaining discrepancies may be due to inevitable inconsistency in comparison of model and monitoring results or errors/uncertainties in model formulation or parametersation.

Both the water and sediment copper contents respond proportionally to a change in the copper load, but the response is slower for the sediments. This implies that the sediments may be less sensitive to fluctuations in load, yielding a reflection of the time integration of the load. This may yield more reliable signatures of the urban load, but also in a slowly responding indicator. We find the approach of coupling source analysis
and pollutant fate submodels promising and worthy of further investigation, with specific focus on the use of sediment copper contents as indicator of urban emissions.

### 6. Acknowledgements

We are greatly indebted to Dr. Arne Jonsson and Stina Thörnelöf, Environment and Health Administration, Stockholm, Sweden, for help with case study data and for discussion the idea of this paper. We are also indebted to Prof. Lars Håkanson, Department of Earth Science, Uppsala University, Sweden, who gave many valuable advices on the lake modeling.

### 7. References


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Copper content in lake sediment as tracer of urban emissions: evaluation through a source – transport – storage model

Manuscript submitted
Copper content in lake sediments as a tracer of urban emissions: Evaluation through a source – transport – storage model

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Abstract

Diffuse sources in the urban area are becoming increasingly important as point sources of e.g. heavy metals, are managed. To manage these diffuse sources, their extent and origins must be understood. A coupled source – transport – storage model was developed to determine the origin and path of copper from materials/goods in use in the urban drainage area and the fate of copper in local recipient lakes. The model was applied and tested using five small lakes in Stockholm, Sweden. In the case of the polluted lakes Räcksta Träsk, Trekanten and Långsjön, the source stresses of copper identified by the model were found to be well linked with independently observed copper contents in the lake sediments through the model. The model results also showed that traffic emissions, especially from brake linings, dominated the total load in all five cases. Sequential sedimentation and burial proved to be the most important fate processes of copper in all lakes except Räcksta Träsk, where outflow dominated. The model indicated that sediment copper content can be used as a tracer of urban diffuse copper sources, but that the response to changes in source strength is fairly slow (decades). Major uncertainties in the source model related to management of stormwater in the urban area and the rate of wear of brake linings and weathering of copper roofs. The uncertainty of the coupled model is also affected mainly by parameters quantifying the sedimentation process, such as particulate fraction and sedimentation rate. Here, we applied the model to demonstrate how it can be used to guide pollution abatement.

Keywords: Diffuse source, lake sediment, urban drainage area, copper

1. Introduction

Due to environmental legislation and improved techniques, the point sources of heavy metals have been well managed and limited in many industrialized cities (Sviden et al., 2001; Sörme and Lagerkvist, 2002). Nevertheless, heavy metals are still present in the environment at elevated levels, with diffuse sources becoming dominant in the anthroposphere, especially in urban areas. Urban lakes are valuable natural resources in the urban area and an important part of the urban water system that supplies water and material transfer pathways. Urban water quality is therefore a very important element of sustainable urban development. Due to the spread of urban construction, the urban water environment is deteriorating in most cities (Booth and Jackson, 1997; Wang and Wang, 2005). In Sweden, diffuse or non-point source pollution is recognized as a major source of water quality problems in surface waters and groundwater(Ahlman and Svensson, 2005). Therefore, this study focuses on the effect of diffuse emissions, e.g. sediment metal content, on the environmental quality of urban lakes.

1Proof to Malmström on the above address
To manage diffuse sources in the urban area, it is necessary to quantify the sources. It is difficult to monitor the diffuse sources of heavy metals themselves, but easier to monitor the environmental metal levels (e.g. sediment metal level in the lake). Such environmental levels are commonly used for classification of pollution severity. In order to use the sediment metal content as an indicator of the urban source, we need to understand how it reflects the heavy metals emitted from materials/goods in use in the urban drainage area. This coupling is governed by the fate of the metal in the local recipient and its drainage area. It is thus particularly important to identify and quantify the dominant processes and factors affecting this fate. In order to choose appropriate abatement methods, it is also important to understand the response of the actual sediment metal level to a change in the urban load and the time taken to achieve this response (response time).

To understand the relationship between lake sediment content of heavy metals and the urban load, information from the anthroposphere and the surrounding environment is needed. Such information is usually obtained from different fields of study. Diffuse sources in an urban catchment are often evaluated by the pollutant concentration in water in combination with water flow (Larm, 2000; Rule et al., 2006; Tiefenthaler et al., 2008). In Stockholm, Sörme and Lagerkvist (2002) proposed evaluating urban emissions from substance flow analysis (SFA) and using this approach, they quantified urban copper emissions to a centralized sewer treatment plant. In the field of environmental modelling, a variety of models are available that quantify the fate of metals in aquatic systems, especially lakes. These include e.g. Dynabox (van der Voet et al., 2000), QWASI (Woodfine et al., 2000) and a dynamic lake mass-balance model from Lindström and Håkanson (2001).

Previously, we presented a dynamic source – transport – storage model quantifying the diffuse sources and fate of copper in the local recipient and its drainage area, thereby providing a coupling between sediment metal content and urban diffuse emission (Cui et al., 2009). Malmström et al. (2009) discussed how this approach can be used for a system of coupled recipients and drainage areas within an urban area. In the previous study by Cui et al. (2009), a model test based on the case of Lake Trekanten in Stockholm, Sweden showed that this approach of coupling the source analysis and pollutant fate model is promising, but needs to be further evaluated. In this paper, we deepen the studies of this model with the overall aim of evaluating the use of sediment copper content as an indicator of urban diffuse emissions. Specific objectives of this work were to:

1) Refine the source model through extending the source list and complementing the source-based approach (SFA) with a concentration-based approach, and to test the approach.

2) Identify the dominant processes and factors in the fate of copper in lakes and their watersheds using model simulations and a sensitivity analysis.

3) Test the source – transport – storage model in five cases using independent monitoring data and identify the major sources of uncertainty.

4) Investigate the response (response time and proportionality) of the sediment metal content to a halving of the urban load over time using the model.

Most previous studies of urban diffuse emissions focus on the quality of the urban runoff, i.e. stormwater and sewage (Rule et al., 2006, Göbel et al., 2007). Therefore, they cannot give the emission strength from each source directly. Those previous approaches were tailored to guide end-of-pipe control of pollution, but are not sufficient for source control of urban diffuse emissions, as those are not individually resolved. Therefore, our source – transport – storage model adopts an SFA approach in the source analysis, thereby enabling estimation of the individual diffuse sources and their contributions to
the local environment. In this paper, we also test and evaluate the proposed SFA approach by comparison with the conventional concentration-based approach.

In management of diffuse sources, the source – transport – storage model is expected to be helpful for evaluating the dominant sources and their contribution to the total urban load through the source analysis. The lake model is expected to help address the associated effect on the environmental quality of the lake. The lake fate model could also help estimate the load that the lake can accept while still keeping within the national standards for lake quality. As the model involves land use information, it could be used to predict the environmental effect of different urban development strategies, e.g. construction of new roads or enlargement of the urban component in the drainage area.

2. Case studies

This study involved five lakes in Stockholm, Sweden (Figure 1). They are all very small and shallow lakes (0.036-0.29 km², maximum depth 2.3-7.0 m), even from a Stockholm perspective. The characteristics of the lakes and their drainage areas are shown in Table 1. The water inflows of the lakes are relatively simple, including stormwater and natural surface runoff from the local drainage area. One exception to this is Lake Långsjön, which also receives short duration combined sewer overflow (CSO) under extreme meteorological conditions (e.g. heavy rainfall). The second exception is that drinking water is pumped to Lake Trekanten as an engineered (and sole) tributary.

![Figure 1. Location of case studies in Stockholm. Inserts: Lakes and their drainage areas, 1. Laduviken; 2. Råcksta Träsk; 3. Judarn; 4. Trekanten; 5. Långsjön. In the maps of the lakes and drainage areas, light grey shows the lake, while the black, filled arrows around the lake are the stormwater discharge points. Darker grey in the drainage area is the urban area, including residential, business area, etc. and the white area indicates natural area, including forest, grassland and other open areas. Black lines through the drainage area represent roads: thicker lines are major motorways and thin lines are local roads.](image-url)
The land uses in the drainage areas of the five case study lakes (Stockholm Vatten, 2000) are shown in Figure 1. Laduviken is situated in the National City Park ‘Ekoparken’ and the catchment area largely comprises pasture and forest. Part of Stockholm University, which is the largest urban development in the drainage area of Lake Laduviken, is located at the western edge of the catchment. The motorway Roslagsvägen (0.7 km) with a traffic volume of 47 000 vehicles/day (Miljöförvaltningen, 2003) and the local railway Roslagsbanan pass through the western part of the drainage area. East of the lake are a few minor houses and commercial buildings (copper-roofed, 125 m²; GIS information from A. Arnerdal, Environmental and Health Administration, Stockholm, pers. comm. 2009).

Table 1. Lake specific parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Symbol</th>
<th>Units</th>
<th>Laduviken</th>
<th>Råcksta Träsk</th>
<th>Judarn</th>
<th>Trekanten</th>
<th>Långsjön</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water retention time(^a)</td>
<td>(T_w)</td>
<td>year</td>
<td>0.25</td>
<td>0.05</td>
<td>0.9</td>
<td>1</td>
<td>0.8</td>
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<tr>
<td>Lake surface area(^a)</td>
<td>A</td>
<td>m(^2)</td>
<td>5.3×10(^3)</td>
<td>3.6×10(^3)</td>
<td>7.4×10(^4)</td>
<td>1.4×10(^5)</td>
<td>2.9×10(^5)</td>
</tr>
<tr>
<td>Area of the drainage area(^a)</td>
<td>ADA</td>
<td>m(^2)</td>
<td>1.1×10(^6)</td>
<td>3.6×10(^6)</td>
<td>8.0×10(^5)</td>
<td>6.0×10(^5)</td>
<td>2.4×10(^6)</td>
</tr>
<tr>
<td>Lake volume(^b)</td>
<td>(V_w)</td>
<td>m(^3)</td>
<td>1.2×10(^5)</td>
<td>4.7×10(^4)</td>
<td>1.8×10(^5)</td>
<td>5.7×10(^5)</td>
<td>6.2×10(^5)</td>
</tr>
<tr>
<td>Mean depth(^b)</td>
<td>(D_m)</td>
<td>m</td>
<td>2.2</td>
<td>1.5</td>
<td>2.2</td>
<td>4.4</td>
<td>2.2</td>
</tr>
<tr>
<td>Maximum depth(^b)</td>
<td>(D_{max})</td>
<td>m</td>
<td>3.2</td>
<td>2.3</td>
<td>3.7</td>
<td>7</td>
<td>3.3</td>
</tr>
<tr>
<td>Sedimentation rate(^b)</td>
<td>sed</td>
<td>g/cm(^2)/year</td>
<td>0.037</td>
<td>0.29</td>
<td>0.057</td>
<td>0.063</td>
<td>0.06</td>
</tr>
<tr>
<td>Particle fraction(^b)</td>
<td>PF</td>
<td>%</td>
<td>13</td>
<td>28</td>
<td>24</td>
<td>10</td>
<td>24</td>
</tr>
<tr>
<td>Loss of ignition(^b)</td>
<td>LOI</td>
<td>%</td>
<td>41</td>
<td>22.5</td>
<td>48.5</td>
<td>29.8</td>
<td>44.5</td>
</tr>
<tr>
<td>Water content in sediment(^b)</td>
<td>W</td>
<td>%</td>
<td>97.2</td>
<td>91.2</td>
<td>97.4</td>
<td>93.7</td>
<td>97.1</td>
</tr>
<tr>
<td>Form factor(^c)</td>
<td>(V_d)</td>
<td>-</td>
<td>2.06</td>
<td>1.96</td>
<td>2.19</td>
<td>1.89</td>
<td>2.00</td>
</tr>
<tr>
<td>Dynamic ratio(^c)</td>
<td>DR</td>
<td>-</td>
<td>0.1</td>
<td>0.13</td>
<td>0.1</td>
<td>0.08</td>
<td>0.24</td>
</tr>
<tr>
<td>Sediment bulk density(^c)</td>
<td>(\rho)</td>
<td>g/cm(^3)</td>
<td>1.02</td>
<td>1.23</td>
<td>1.02</td>
<td>1.04</td>
<td>1.02</td>
</tr>
<tr>
<td>Depth of A-area(^d)</td>
<td>t</td>
<td>cm</td>
<td>2</td>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Age of ET-sediment(^d)</td>
<td>(T_{ET})</td>
<td>year</td>
<td>1</td>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Settling velocity of particles(^d)</td>
<td>(v_s)</td>
<td>m/year</td>
<td>100</td>
<td>1</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diffusion constant(^d)</td>
<td>(c_{diff})</td>
<td>year(^{-1})</td>
<td>0.0035</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

- a. Data from Stockholm water programme (2000)
- b. Data from Sternbeck (1998) and Lindström and Håkanson (2001)
- c. Data calculated from the lake form information (a). \(V_d=3D_m/D_{max}\); \(DR=(\text{Area}10^5/0.5/D_m); \rho=\rho_i\rho_m/(\rho_w+(\rho_i-\rho_m)w)\) (Håkanson and Bryhn, 2008)
- d. Data are the model default settings. t is defined based on the sediment sampling, \(T_{ET}\) is taken from Håkanson (2004), \(c_{diff}\) from Lindström and Håkanson (2001) and \(v_s\) is set according to literature values (Lindström and Håkanson, 2001) and Stock’s law.

Råcksta Träsk is a small lake with high levels of copper in the western suburb of Stockholm. Twenty percent of the drainage area is composed of residential buildings, with 4000 m² copper roof in use (Stockholm Vatten, 2001), located north of the lake. In the north, a traffic route Bergslagsvägen (3 km, 32 000 vehicles/day) and an aboveground stretch of metro (2.6 km, 200 trains/day) pass through the catchment. An abandoned landfill, Johannelundstippen, is located in the north-west of the lake’s drainage area. This area is considered a point source (contaminated soil).
Lake Judarn is located east of Råcksta Träsk. The lake is surrounded by open forest, while a few residential buildings with 720 m² copper roofs (GIS information from A. Arnerdal) are situated in the far west of the drainage area. The traffic situation in the drainage area is similar to that for Råcksta: Bergslagsvägen (1.6 km, 26 000 vehicles/day) and aboveground metro (1.4 km and 200 trains/day) pass through in the north (Stockholm Stad, 2006).

In the drainage area of Trekanten, two major traffic routes, Essingeleden (0.3 km with traffic volume as 120 000 vehicles/day) and Södertäljevägen (0.2 km, 46 000 vehicles/day) pass through the drainage area and there is a traffic centre to the east of the lake. To the south of the lake, copper roofs (2460 m²) are used in many buildings (Larm and Holmgren, 1999).

Lake Långsjön is located in the south of Stockholm. Its drainage area is an old residential neighbourhood and low-density residential buildings (2000 m² copper roof, information from A. Arnerdal) occupy about 60%. There is no major traffic route but there is a complex net of local roads (23.8 km) in the drainage area. In this study the traffic volume on those roads had to be assumed according to the situation in another case in Stockholm: 4000 vehicles/day in low-density residential area, 8000 vehicles/day in high-density residential area (Larm and Holmgren, 1999), as the traffic volumes on the local roads had not been measured.

3. Methods

3.1 Model description

The source – transport – storage model is designed to couple the urban diffuse sources to the sediment metal content in the lake. In this study, the system under study was defined as the lake and its drainage area. The conceptual model focuses on various water transport pathways of copper in the system under study, but also includes atmospheric deposition (Figure 2).

![Conceptual model](image)

Figure 2. The conceptual model and its system boundary. The fully drawn rectangle is the urban sources (store); the square box with rounded corners is the water recipient (lake); the ovals are other natural recipients, such as soil and air; and the open arrows show copper flows between the sources and recipients. The dotted line represents the system boundary of the conceptual model and shows the partitioning into two submodels. The single-line arrows represent the pathways of copper from other environmental compartments (air and soil) to the water system.
In the drainage area, copper is widely used in materials and goods in daily life, e.g. in copper roofs, water pipes and brake linings. Because of weathering and wear processes, copper is emitted from these materials and goods in use to the environment (water, air and soil; open arrows in Figure 2). The direct pathway of the diffuse copper emissions to the lake is through urban runoff (stormwater). The emitted copper also goes to air and soil (ovals in Figure 2), which become secondary sources of copper to the aquatic recipient (squares with rounded corners in Figure 2). The copper in air partly goes to the natural surface water (surface runoff and the lake) by direct atmospheric deposition, and the copper settling in urban hard areas may go to the lake by urban runoff. Another part of the copper in air is exported out of the catchment area and is deposited elsewhere. Similarly, copper from sources outside the catchment is imported by air and deposited within the catchment (Figure 2).

The copper in soil goes to the lake partly through the surface runoff and partly through the groundwater (Figure 2). The contribution of copper from the groundwater is hard to estimate using the SFA approach, but Landner and Reuther (2004) estimate that copper in groundwater only contributes around 1% of the total flux from the anthroposphere in Stockholm. Therefore, the groundwater pathway for copper is neglected in the present study, even though the groundwater is an important store of copper (Aastrup and Thunholm, 2001).

In the lake, copper is distributed between the dissolved phase and particles. Subsequently, part of the copper is transported downstream by the water flow and part is settled and accumulated in the sediment as described below.

To represent the linkage between urban diffuse sources in the drainage area and the copper content in the lake sediment, two submodels, a source model for the drainage area and a fate model for the lake, were taken from the literature and connected in this study.

### 3.2 Source model

The source analysis submodel accounts for the diffuse emissions and their contribution following the approach of Sörme and Lagerkvist (2002) and thereby quantifies the copper load from the drainage area to the lake. The source analysis is based on the structure of substance flow analysis (SFA) and is implemented as a spreadsheet in Microsoft Office Excel 2007. To estimate the urban emissions of copper, the source analysis focuses on two types of information in the drainage area: source type and land use. The parameter setting is shown in Tables 2 and 3.

As mentioned before, copper is widely used in the urban area so the diffuse sources in the drainage area have various origins. In a previous study (Cui et al., 2009), the source model classified urban diffuse sources into three sectors: traffic, building materials and atmospheric deposition, based on the work of Sörme and Lagerkvist (2002). In this study, we enlarged the list of source types and included soil (farmland, forest and other open areas) as a new sector. Here, we ignored the contribution from the groundwater, as discussed above, but included the contribution by surface water. We also added vehicle parking and railway/train traffic to the traffic sector. In addition, a combined sewer overflow (CSO) and a landfill were considered point sources, depending on the case.

As shown in Figure 3, this study divides urban copper sources into three groups. The primary sources are material/goods in use (traffic materials and building materials), which emit copper through wear and weathering processes. The secondary sources are the consequences of emissions from the primary sources from the perspective of urban diffuse sources, but can also be considered sources of copper load to the lake. These secondary sources include parking, air and soil. Some specific sources, such as
point sources and combined sewer overflow in different cases, are considered a third type of sources (others).

Figure 3. Structure of the source analysis. The three rectangles represent the major source types of the urban diffuse sources: the primary source, the secondary source and others. The oval is the copper load to the lake from the diffuse sources in the drainage area \( F_{\text{in}} \) through various pathways shown in Figure 2. In the equation of \( F_{\text{in}} \), \( E_{\text{atm,lake}} \) is the emissions from source \( m \) in the land use \( n \); \( E_{\text{atm,lake}} \) is the atmospheric deposition directly to the lake; \( \beta \) is the fraction of the total stormwater/surface water from land use \( n \) that goes to the lake directly, without passing a treatment facility.

3.2.1 Quantifications in the source model

The quantification in the source model is based on the assumption that leaching is the dominant mechanism of emission (Elshkaki et al., 2005). The emissions from materials or goods in use (primary sources) are quantified by:

\[
E(t) = C*S(t) \tag{1}
\]

where \( S(t) \) is the size of the stock at time \( t \) and \( C \) is the leaching factor, which is expressed in the form of Equation 2 for the traffic sector and Equation 3 for the building materials sector, and is referred to as the ‘source-based approach’ in this study.

In the traffic sector, the major sources, e.g. brake linings, tyres, asphalt and catenaries, emit copper through the wear process. Copper from the traffic sector is normally emitted as particles, the larger particles being deposited on the road directly and then transported with the stormwater (Sörme and Lagerkvist, 2002). Thus, only a fraction \( (\alpha, \text{see Table 3}) \) goes directly to the stormwater, and is accounted for directly in the traffic source (Figure 2). The smaller particles go to the air as aerosols and some of these are deposited in neighbouring soil; these being accounted for by the secondary sources of air and soil, respectively, in this work. Another fraction of the small particles is transported with air to more distant areas and escapes from the urban drainage area, so it is excluded from further consideration here. The emissions to stormwater in the traffic sector \( E \), kg/year) are calculated as:

\[
E = T*L*M*W * \alpha \tag{2}
\]
where \( M \) is the copper content in the wearing material (ppt, m/m), \( W \) is the wear rate (mg/vehicle km), \( T \) is the annual traffic volume (private cars/heavy vehicle/train) on the road (vehicles/year), \( L \) is the road length (km) and \( \alpha \) is the fraction of the emissions that goes to the stormwater. Here \( T*L*M \) is considered as the stock \( S(t) \) and \( W*\alpha \) corresponds to the leaching factor \( C \) in Equation 1. Parameter setting is shown in Tables 2 and 3.

Table 2. Parameter setting for the source model (see also Table 3)

<table>
<thead>
<tr>
<th>Sector (m)</th>
<th>Wear rate (mg/vehicle km)</th>
<th>Cu content (ppt)</th>
<th>Fraction to SW (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Traffic</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Brake linings</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Front</td>
<td>10.5(^a)</td>
<td>0.09(^a)</td>
<td>20(^b)</td>
</tr>
<tr>
<td>Rear</td>
<td>5.13(^a)</td>
<td>0.068(^a)</td>
<td></td>
</tr>
<tr>
<td>Tires</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Private car</td>
<td>100(^c)</td>
<td>0.000018(^d)</td>
<td>40(^e)</td>
</tr>
<tr>
<td>Heavy vehicle</td>
<td>400(^c)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Road(Asphalt)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Private car</td>
<td>5000(^c)</td>
<td>0.000013(^e)</td>
<td>40(^e)</td>
</tr>
<tr>
<td>Heavy vehicle</td>
<td>20000(^c)</td>
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<tr>
<td>Railway/metro(^f)</td>
<td>35.75</td>
<td>0.014</td>
<td>20</td>
</tr>
<tr>
<td>Parking(^g)</td>
<td>15.5</td>
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<tr>
<td><strong>Building materials</strong></td>
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<tr>
<td>Copper roofing(^h)</td>
<td>2275</td>
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</tr>
<tr>
<td><strong>Air</strong></td>
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<td>Atmospheric deposition(^i)</td>
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<td>Farmland</td>
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<td>Forest</td>
<td>6.5</td>
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<tr>
<td>Open area</td>
<td>15</td>
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</tr>
<tr>
<td><strong>Combined sewer overflow(^j)</strong></td>
<td>150</td>
<td></td>
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</tr>
</tbody>
</table>

a. Westerlund (2001)
b. Hulskotte et al. (2006)
c. Larm and Holmgren (1999); Larm (2000)
d. Legret and Pagotto (1999)
e. sörme and Lagerkvist (2002)
f. Calculated from the measured concentration of PM\(_{10}\), the traffic volume of the subway (Johansson and Johansson, 2003)
g. \( R_{parking}=C_{Cu} \times P - R_{atm} \), where \( C_{Cu} \) is the standard copper concentration in the parking area (Larm, 2000), \( P \) is the annual precipitation, and \( R_{atm} \) is the runoff rate for the total atmospheric deposition.
h. Cui et al (2009)
i. Burman and Johansson (2000)
j. Personal communication from C. Lännergren, Stockholm Vatten

In the building materials sector, the emissions from copper roofs are caused by the weathering of materials. The quantification is:

8
\[ E = A_{\text{roof}} \times R_{\text{roof}} \]

where \( A_{\text{roof}} \) (m\(^2\)) is the area of copper roof considered as the stock \( S(t) \) and \( R_{\text{roof}} \) is the runoff rate of copper (mg/m\(^2\)/year), which is equal to the leaching factor \( C \) in Equation 1.

For the secondary sources, there are two approaches to quantify the emissions according to the available data in Table 2. The first approach is analogous to Equation 3 and considers the area \( A \) (m\(^2\)) as the stock and the runoff rate \( R \) (mg/m\(^2\)/year) as the leaching factor. This approach is applied here to quantify the emissions from the air and parking.

From the air, copper undergoes atmospheric deposition (wet and dry) back to the drainage area. This load is divided into two parts: direct deposition into the lake (\( E_{\text{atm,lake}} \), see Figure 3) and deposition onto hard areas in the drainage area. Here, it is assumed that copper deposition to the hard areas is collected by the stormwater system and transported to the lake. In addition, copper deposited into other areas, e.g. farmland, forest and so on, is considered to go to another natural store (the soil) and is not involved in the air sector.

In the parking area, the copper load is from both the wearing of vehicle parts (brake linings, tyres, etc.) and atmospheric deposition. The atmospheric deposition part is already calculated in the air sector, since parking is a type of hard area in the drainage area. Therefore, the copper load in the parking area in this study comprised the emissions from vehicles. However, the copper load in the parking area could not be traced back to the emissions from individual vehicles and quantified by Equation 2 because of data gaps. Firstly, data on the traffic volume in parking areas were lacking for all five cases in this work. Secondly, the wear of vehicle parts in parking has not been estimated and is different from the wear on the road, since the dominant driving state of vehicles is different. Thirdly, it is hard to define the travel length of vehicles in the parking areas. Therefore, parking is separated from other sources in the traffic sector and classified as a secondary source. The emissions are calculated by the area of parking (m\(^2\)) and the runoff rate in the parking area (mg/m\(^2\)/year).

As mentioned in the conceptual model, the soil receives emissions from urban diffuse sources and the air (Figure 2). Most of the copper in the soil is immobile, but some is still transported by surface runoff and groundwater. Therefore, the soil (forest, farmland and open area) was considered here as a secondary source to the lake. As mentioned previously, we ignored the transport of copper with groundwater, but included transport from soil by surface water to the lake (see below).

Combined sewer overflow (CSO) is a special source, which appears only in the case of Lake Långsjön. The overflow only happens during heavy rainfall to relieve the flood pressure on the municipal drainage system. It is complex work to quantify the original source of copper in CSO. Firstly, the overflow contains not only stormwater but also sewer water, and the diffuse sources of copper in sewers are not involved in the list of source types in Figure 3. Secondly, the drainage area of the lake in Figure 1 is defined by the surface runoff and the stormwater flow. For evaluating copper emissions in the sewer, the drainage area of the lake needs to be redefined, as the wastewater may be collected from parts outside the surface/stormwater catchment of the lake. Therefore, CSO is considered as a point source here in order to simplify quantification.

For soil and CSO, storage and leaching information was lacking for our cases. In order to handle this, we introduced a ‘concentration-based’ quantification approach as a complement to the SFA approach. The concentration-based approach is land use-based but not source-resolved, and quantifies the emissions by a land use or case-specific standard copper concentration in the water along with the water runoff from the selected area as follows:
\[ E_{\text{CSO}} = Q \cdot C_{\text{Cu}} \text{ for the CSO} \] (4)
\[ E_{\text{s}} = A_{s} \cdot P \cdot C_{\text{Cu}} \text{ for the soil} \] (5)

where \( C_{\text{Cu}} \) is the standard copper concentration in stormwater in the selected area (µg/l), as quantified in Stockholm Vatten (2000), \( Q \) is the flux of CSO (m³/year), \( A_{s} \) is the area of selected soil (m²) and \( P \) is the mean annual precipitation in Stockholm (m/year). The parameter setting is shown in Table 2.

### 3.2.2 Linking the source model to the lake model

Not all copper that is emitted goes to the lake. Here we assumed that a fraction \( \alpha \) of the diffuse emissions goes to the stormwater, and a fraction \( \beta \) of the stormwater goes directly to the recipient, without passing through a stormwater treatment facility. The \( \beta \) factor represents the proportion of the stormwater that is collected and transmitted to the lake, and it is determined by the land use (Figure 3; values given Table 3). Therefore, in the source model, the copper load to the lake \( (F_{\text{in}}) \) is calculated from the emissions from each source \( (m) \) and the fraction to the lake \( (\beta) \) in different land uses \( (n) \), thereby linking the sub-models.

<table>
<thead>
<tr>
<th>Land use</th>
<th>Fraction to lake</th>
<th>( \beta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>n</td>
<td></td>
<td>%</td>
</tr>
<tr>
<td>Road</td>
<td>85</td>
<td></td>
</tr>
<tr>
<td>Railway</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Settlements</td>
<td>35</td>
<td></td>
</tr>
<tr>
<td>Business</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Farmland</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>Forest</td>
<td>7.5</td>
<td></td>
</tr>
<tr>
<td>Open area</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

For our cases, it was assumed that the input was static and \( F_{\text{in}} \) was taken as the average during the period 1996-2006. Since the emissions data were collected from different sources of information (urban planning and transportation), all data could not be obtained for the same year even for one case. In this study, we used data that were generally collected in the ten-year period 1996-2006. Data on land use are given by Stockholm Vatten (2000), the distribution of copper roofs in Stockholm was estimated in 1997 (Ekstrand et al., 1997), and the traffic volumes on major roads for the period 1996-2006 are listed in several reports (Stockholm Vatten, 2000; Miljöförvaltningen, 2002, Miljöförvaltningen, 2003; Stockholm Stad, 2006). This approach was deemed sufficient since from the perspective of urbanization, the temporal variability in required information in our cases was very small over a decade, as Stockholm is a well-developed city with slow further development.

### 3.3 Lake model

The lake model represents the fate of copper from the drainage area in the lake (Figure 4). The fate model, which is based on the mass balance model from Lindström and Håkanson (2001) and has been further tested by Cui et al. (2009), is based on quantifying fluxes between compartments representing different physical units of the lake system by process-based, empirical transfer equations. The model is implemented through a graphical interface, dynamic, causality model approach in Simile v 5.1.
Figure 4. Structure of the lake model and quantification of the fate processes (Lindström and Håkanson, 2001; Håkanson, 2004). The transport process (arrow) involves: 1. Inflow, which is the connection point to the source model, 2. Outflow, 3. Sedimentation, 4. Resuspension, 5. Burial and 6. Diffusion. In Process 3 Sedimentation, $D_a/D_{ET}$ represents the distribution of the sedimentation to the A/ET area. In Process 4 Resuspension, the lake form (Vd) determines the distribution of resuspension to the water and the A-area. For parameter, values see Table 1.
The fate model contains three compartments: the water (W), the sediment of the erosion and transport bottoms (ET), and the active accumulation bottoms (A, 0-2 cm). As a simplification, the water compartment is assumed to be well mixed and thermal and concentration stratification is neglected. Copper entering the water pillar is partly transported out of the lake and partly deposited into the sediments. The sediment in the ET-area is affected by erosion and transportation. It is thus mobile and considered as contributing to the internal loading in the lake by resuspending the copper to both the water pillar and the A-area. Sediment is accumulated in the A-area, of which only the uppermost part (0-2 cm) is considered here, as only this part is assumed to have exchange with the lake water, while the deeper sediment is considered passive. From the A-area, copper is buried into the deep sediments but may also be released to the water pillar through diffusion.

In summary, six processes are involved: inflow, outflow, sedimentation, resuspension, diffusion and burial. The inflow ($F_{in}$) is imported from the source model (see Figure 3), thereby connecting the two submodels. The quantifications of the other processes are through expression such as:

$$F_j = M_i \times R_j$$  \hspace{1cm} (6)

where $F_j$ is the copper flux of process j (kg/year), $M_i$ is the mass of copper in compartment i (water/ET-area/A-area, kg) and $R_j$ is the transfer rate constant of process j (year$^{-1}$). The details are summarized in Figure 4.

### 3.4 Model simulation

The results of source analyses ($F_{in}$) were introduced as input data to the lake model, which simulates the fate of copper. In the initial state, the copper mass in water and the A-area ($M_{i,W}$, $M_{i,A}$) were taken from the 1996 monitoring data on copper concentrations (Lindström and Håkanson, 2001). The copper mass in the ET-area ($M_{i,ET}$) was set as the copper mass in the ET-area in the steady state with the initial $M_A$. From the initial state, the lake model ran a six-year simulation, representing the years 1996-2001 for which monitoring data of aqueous and sediment copper contents were available for the five lakes.

### 3.5 Sensitivity and uncertainty analyses

In this part, we assessed the sensitivity of model results to different processes and parameters in order to identify the dominant features governing the sources and fate of Cu. In order to highlight important further data needs, we also assessed the uncertainty in model input and parameters and how they were reflected in the model output.

#### 3.5.1 The source model

The source model used in this study includes a linear relationship between the resulting load and the model input parameters. Thus, the source analysis is simply sensitive to the dominant source types and the parameters involved for quantifying the contribution, and a more sophisticated assessment is not required.

Because both the input data and parameters originated from different sources, their quality and precision varied. Unlike data in natural sciences, most of the data in the source model are not multiple-sampled or reproduced. Thereby, their uncertainty cannot be defined in statistical terms (e.g. standard deviation). In MFA/SFA studies, the data uncertainties are instead normally described as uncertainty intervals (Hedbrant and Sörme, 2001).
The method of uncertainty analysis used here was proposed by Hedbrant and Sörme (2001) and modified by Danius (2002). The first step is to classify the uncertainty level (intervals) of the input data and parameters according to the data sources. The uncertainty interval is defined as asymmetric intervals, */y. If data $X$ have the uncertainty intervals */y, the uncertainty range is $X/y_{X}X_{Y}X_{Y}$. Since all the case-specific input data (e.g. road lengths, copper roof area) are on the local level, their uncertainties are defined as */1.1 according to the classification of Danius (2002). According to Danius (2002), the uncertainty of the parameters is as follows: the fraction of copper emitted from the wearing materials to stormwater ($\alpha$) and the runoff rate of copper roof ($R_{\text{roof}}$) has uncertainty */1.33; the wear rate ($W$) has */1.5, and that of all other parameters in Tables 2 and 3 is */1.1. The uncertainties of the standard copper concentration ($C$, in a range of */1.25~2.8) and the fractions to lake ($\beta$, in a range of */1.1~2.5) were adopted according to Larm (2000). The secondary step of the uncertainty analysis is to calculate the uncertainty of the model results ($F_{in}$) through error propagation.

3.5.2 The lake model

For the sensitivity analysis of the lake model, we adopted the dominant factors in each process ($F_{in}$-inflow, DA-sedimentation, t-burial, $T_{E}$-resuspension, $c_{diff}$-diffusion, $T_{W}$-outflow, $v_{T}$&$v_{S}$—both sedimentation and burial, see Figure 4) and varied them by a factor of 0.25, 0.5, 2 and 4, from the base case of Lake Långsjön. Note that the burial process is directly related to the sedimentation process, and the sedimentation rate (sed) is related to the settling velocity of particles ($v_{S}$) (Blake et al., 2004). Therefore, when $v_{S}$ is changed in the sensitivity analysis, sed is changed to the same extent. In the sensitivity analysis, the simulation results are presented after normalization to results of the base case for Lake Långsjön.

In the uncertainty analysis, the coefficient of variation (CV), defined as SD/MV, where SD is the standard deviation and MV is the mean value of the parameter, was considered for each parameter representing a dominant process. These processes and parameters and their associated uncertainties are:

1) The uncertainty from copper inflow, $F_{in}$, is deduced from the uncertainty analysis of the source model.

2) The uncertainty from the sedimentation process (see Equation of Process 3 in Figure 4) is considered through the governing parameters $P_{F}$ and $D_{A}$. The uncertainty of $D_{A}$ and $v_{S}$ was set to CV=0.1 and CV=0.5, respectively, according to Håkanson (2004). For PF, CV=0.28 was used, based on data for the five cases (Lindström and Håkanson, 2001).

3) The uncertainty from the burial process (see Equation of Process 5 in Figure 4) is estimated from the uncertainties in BF and $v_{S}$. Sternbeck (1998) measured the sedimentation rate (sed) and the burial velocity ($v_{D}$) using $^{210}$Pb, yielding CV=0.1, which was adopted here. The uncertainty of the BF was deduced from its relationship to the uncertainty in sed through the gross sedimentation (GS; see caption to Figure 4).

The results of the uncertainty analysis are expressed as the extreme values (minimum and maximum) of water and sediment copper content obtained by simultaneously varying the parameters according to their individual uncertainties.

4. Results
4.1 Source analysis

Table 4 (left column) shows the estimated total load to the five lakes in Stockholm, Sweden, from our source model. The value outside the brackets is the best estimate, while the values within the brackets represent the uncertainty, as explained in Section 3.4.1. Since there were no direct observations of the total urban load ($F_{in}$) against which to test the results of the source model, we compared our results with two other estimates in the literature made through the concentration-based approach:


2) The quantifications from the StormTac model (Larm, 2000).

These comparisons showed that our results, based on the SFA approach, were similar to those of the concentration-based approach, except for the case of Lake Långsjön, for which our model yielded only half the load of the other approaches (Table 4). No reliable information on the traffic volume was available for Lake Långsjön, as described in Section 2, and the traffic volume assumed for the area caused uncertainty in the model results. This is probably one of the reasons for the difference between present and previous results.

Table 4. Estimated copper loads to the recipients from their urban drainage area

<table>
<thead>
<tr>
<th></th>
<th>Our source model</th>
<th>Copper load (kg/year)</th>
<th>StormTac*</th>
<th>Water programme</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laduviken</td>
<td>6.1 (4.2-8.8)</td>
<td>8.1 (1.7-12)</td>
<td>4.5 (0.81-7.0)</td>
<td>6.5</td>
</tr>
<tr>
<td>Råcksta Träsk</td>
<td>27 (21-35)</td>
<td>38 (10-78)</td>
<td>4.2</td>
<td>36</td>
</tr>
<tr>
<td>Jugarn</td>
<td>5.8 (4.1-8.2)</td>
<td>8.0 (2.0-22)</td>
<td>7.9</td>
<td></td>
</tr>
<tr>
<td>Trekanten</td>
<td>12 (9.4-16)</td>
<td>25 (5.9-43)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Långsjön</td>
<td>16 (12-22)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a. Quantified according to Larm (2000)

b. Results reported in Stockholm Vatten (2000)

Figure 5 shows the total copper loads to the lakes and the contribution of the various diffuse sources in the drainage area. In all five cases, the urban diffuse source dominated the total copper load in the drainage area (83%-93%), with the contribution from air and soil (the secondary sources) being minor. The additional sources included here (emissions from parking and railway in the traffic sector; the soil) compared with the previous analysis of Lake Trekanten (Cui et al., 2009) contributed less than 11% of $F_{in}$ in the five cases.

In all cases, the traffic sector provided the biggest contribution to the copper load (50-80%, Figure 5a). Within the traffic sector, brake linings of vehicles dominated copper emissions (80%--90%, Figure 5b). Copper roofs also proved to be a very important urban source of copper, with a contribution that varied from 43% of total load in the case of Trekanten to only 4% in the case of Laduviken (Figure 5a).

Sensitivity and uncertainty of the source analysis

A sensitivity analysis was carried out in order to show the dominant processes and parameters in the source model. The source model produced a linear relationship between the diffuse sources and the
total copper load in the drainage area (Equation in Figure 3). Thus, the overall results of the source model were most sensitive to parameters quantifying the dominant sources, in our case the brake linings in the traffic sector. Following Eq. (2), the model was thus most sensitive to road length (L) and the traffic volume (T) on major roads, the copper content in brake linings (M), the wear rate of brake linings (W), the fraction to stormwater (α) and the fraction of stormwater to the lake (β).

Figure 5. Total copper load ($F_{in}$) and contribution of the different diffuse sources in the drainage area of five cases in Stockholm, Sweden from the source model. (a) the contribution of all source types. The notation ‘others’ means the sources (diffuse or point) that are not common to all the cases, e.g. landfill in the case of Råcksta Träsk, CSO in the case of Långsjön (NB: Bars show fractions of the total load, with this load being printed under the horizontal axis); (b) the contribution from different components in the traffic sector.

An uncertainty analysis was carried out in order to deduce both the uncertainty in the load estimate and the major contributor to this uncertainty. The uncertainty in the estimated $F_{in}$ from the source model is shown in Table 4. The uncertainty analysis showed that the traffic sector made the largest contribution to the uncertainty, since it was the dominant source sector. Resolution of the uncertainties in the traffic sector showed that the wear rate of brake linings (W), the fraction of the copper emitted from the
brake linings that goes to stormwater ($\alpha_B$), and the fraction to stormwater that goes to the lake ($\beta_{\text{Road}}$) were the largest contributors to uncertainty in the source model.

### 4.2 Fate analysis

Figure 6 compares the simulation results (full lines in Figure 6) of the lake model for the period 1996-2002 in the five cases in Stockholm with monitoring data (Östlund et al., 1998; Ekwall, 1999; Lindström and Håkanson, 2001; Lithner et al., 2003; Sternbeck et al., 2003). Here, it should be noted that the models were not calibrated, and that the monitoring data in 2002 can be seen as independent of those used in the model. In the case of Lakes Råcksta Träsk, Långsjön and Trekanten, the simulated copper concentrations in the sediment agreed reasonably well with the monitoring data throughout the simulation, considering the model uncertainty (dashed line in Figure 6). Moreover, the trend with time (if any) shown in the simulations of Lakes Råcksta, Långsjön and Trekanten agreed with the observations (Figure 6d, 6h and 6j).

For Lakes Laduviken and Judarn the model predicted higher sediment copper contents than those observed. In addition, the model predicted increasing contents with time, while field data remained fairly constant over the reported years (Figure 6b and 6f). In the sixth year, the simulated sediment copper concentrations exceed the observed levels by a factor 4-6. An obvious difference between the cases in which the model was able to predict sediment copper contents (Råcksta Träsk, Trekanten, and Långsjön) and those in which it performed worse (Judarn and Laduviken) is that in the latter, the urban area is situated at greater distance from the lake (>0.5km, Figure 1), with natural areas surrounding the lake. Thus, we suggest that some of the copper is lost, for example as ‘pipe sediment’ (Sörme and Lagerkvist, 2002) or by retention in the soil, on its path to the lakes in these cases, thereby leading to an overestimation of the actual copper load to these lakes and the resulting copper contents.

Furthermore, the actual copper levels in lake sediment in the cases of Lakes Laduviken (115~160 mg/kg dw) and Judarn (50~80 mg/kg dw) and the copper pollution level in those two cases can be considered to be outside the scope of the combined model applied. For cases with higher copper levels, based on the agreement between simulation results and monitoring data in Figure 6d, 6h and 6j, we suggest that the source – transport – storage model is applicable.

Apart from the monitoring data used as the initial points, there were few or no data available to evaluate the simulations of the water copper contents in our five lakes. In Figure 6, the simulated copper concentrations in water are not close to the observations in Lakes Råcksta, Judarn and Trekanten, but fall within a factor of 3 of the monitored concentrations. This level of agreement between model results and monitoring data is similar to the performance of the original lake model in previous studies (Lindström and Håkanson, 2001; Cui et al., 2009). For Lake Råcksta Träsk, the agreement between simulated water concentrations of copper and observations is similar to that obtained by the QWASI model as shown by Sinha (2009). Generally, the model reproduced the copper content of water less well than the copper content of sediment. In the following, we thus focus on the latter.

The flow of copper in the different processes in the lakes as interpreted by the model for 2002 is shown in Figure 7 as the proportion of the total load $F_{\text{tot}}$. Since the internal loading in the lake (resuspension and diffusion) also contributes to the fate of copper in the lake and since sedimentation and burial occur in series, the sum of the proportions exceeds 100%. The sedimentation and burial processes dominated the fate of copper in all lakes except Lake Råcksta Träsk, where outflow dominated. Outflow was also an important process in the case of Lake Trekanten. The internal loading, resuspension and diffusion provided copper corresponding to 15-21% of the inflow in the five cases.
Figure 6. Simulations of copper content in water (left column) and sediment in accumulation bottoms (A-sediment, right column) in five lakes during 1996-2002. Full lines show model predictions and markers show monitoring data (Lännergren, 1991; Östlund et al., 1998; Ekvall, 1999; Lindström and Håkanson, 2001; Lithner et al., 2003; Sternbeck et al., 2003). Cs corresponds to copper concentration in the accumulation bottoms and is plotted together with sediment monitoring data, as it is the accumulation bottoms that are sampled, while the erosion/transport (ET) bottoms are generally not sampled. Dashed lines describe the uncertainty of the combined model, dotted lines show the uncertainty caused by uncertainty in Fm (the source model) alone, and markers represent the measured copper concentrations. In (d), m shows the total uncertainty of the source – transport – storage model, n is the uncertainty caused by the source analysis and m-n is the uncertainty caused by the lake model.
Sensitivity analysis and uncertainty of lake model

The sensitivity analysis of the lake model focused on the parameters involved in quantifying sedimentation, burial and outflow, which are the dominant processes for the fate of copper (Figure 7). The inflow \(F_{in}\) is the connection of two submodels and a major process, so it also needs to be considered. Figure 8 shows the results of a sensitivity analysis using the seven parameters \(F_{in}, D_A, t, T_{ET}, c_{diff}, v_s & sed, T_w\) that are key factors in quantification of the dominant processes, based on the case of Lake Långsjön. Lake Långsjön represents a lake where retention of copper in the lake is more important than downstream transport, which was the case for all our case study lakes except Lake Råcksta Träsk (see Figure 7).

![Figure 7](image_url)

Figure 7. Magnitude of the different processes as percentage of inflow in the five lakes from model results for 2002.

The results show that the copper concentrations in both water and sediment \(C_W\) and \(C_s\) were sensitive to \(F_{in}\) and the connected parameters \(v_s & sed\) (both quantifying \(R_{sed}\)). This agrees with the sensitivity test for the original fate model (Lindström and Håkanson, 2001, Håkanson, 2004). \(C_W\) and \(C_s\) had a positive, linear correlation with \(F_{in}\) but a negative, nonlinear correlation with \(v_s & sed\). Furthermore, the sediment copper concentration was sensitive to the fraction of the bottom characterized as accumulation bottom, since \(D_A\) determined the distribution of the sedimentation flux between A and ET-areas, and thus the mass of copper in the A-sediment. Neither \(C_W\) nor \(C_s\) was sensitive to \(c_{diff}\) in the diffusion process, in agreement with previous studies (Lindström and Håkanson, 2001), which is also consistent with diffusion not being a major process (Figure 7).

The propagated uncertainty in the source – transport – storage model is shown as dashed lines in Figure 6 (dashed line), representing 'worst cases' as explained in the methods section. The uncertainty in \(F_{in}\) is given special attention, as \(F_{in}\) is deduced from the source sub-model. Dotted lines in Figure 6 represent the uncertainty caused by the source model, i.e. the uncertainty caused by \(F_{in}\) alone. The difference between the dotted and dashed lines is considered to be the uncertainty caused in the lake model, disregarding the inflow (see distances m and n in Figure 6d).

Even though most of the data uncertainties in the lake model were set as equal between the different cases, the resulting uncertainty was different for each cases. In the cases of Lakes Laduviken and Judarn (Figure 6b and 6f), the uncertainty was caused almost entirely by the uncertainty in \(F_{in}\) (the source
model). For other cases where the simulated sediment copper content agreed with field observations, the lake model provided around 55-65% of the total uncertainty of simulated sediment copper content in the coupled model (Figure 6d, 6h and 6j). According to the sensitivity analysis, the lake model is sensitive to the factors $v_s$&sed, which means that the sedimentation process, along with the inflow, has a great impact on both simulated $C_w$ and $C_s$. Therefore, the propagation of uncertainty in $v_s$ and $PF$, which govern the quantification of the sedimentation process, contributes most to the overall uncertainty of the sediment copper content in the coupled model.

![Figure 8](image)

Figure 8. Normalised simulated copper concentration (a: in water, b: A-sediment) as function of normalised parameters in the lake model for the case of Lake Långsjön. Both simulated copper concentrations ($C_w$ and $C_s$ at the steady state) and the model parameters ($F$) are normalized for the base-case and shown as $C/C_0$ and $F/F_0$, respectively. Note that the parameter values were varied one at a time, leaving the others at their original value. Parameters include $F_{in}$ (copper load to the lake), $D_A$ (fraction of lake bottom area in accumulation bottoms) for the inflow, $t$ (depth of the active sediments in the accumulation bottom) for the burial process, $T_{ET}$ (average age of the ET bottom) for the resuspension, $c_{diff}$ (rate constant for diffusion from active accumulation bottoms to water pillar) for the diffusion, $v_s$&sed ($v_s$ is the particle settling velocity and sed is the sedimentation rate) for both sedimentation and burial processes, $T_w$ (the water retention time) for the outflow.

### 4.3 Response of sediment copper content to changes in copper load ($F_{in}$)

In order to test the response of the sediment copper content to a change in the urban copper load, the simulation of the fate model started from Steady state 0, in which the total copper load ($F_{in}$) had the values given by the source analysis. Then $F_{in}$ was decreased to half at year 5, and the fate model was run to a new steady state (Steady state 1). The model results show that in the new steady state, both the water and sediment copper contents had halved, thus linearly corresponding to $F_{in}$ (Figure 9). While the response to a change in conditions was thus similar between the different compartments, the time taken to achieve this was different, as shown in Figure 9. For all the lakes the response time, defined as
the time needed to achieve 95% of the change in the copper concentration, was in the order water< ET-area< A-area, as further detailed in Table 5.

Figure 9. Normalised simulated mass of copper in each lake compartment (W-water, A-sediment of accumulation bottoms, and ET-sediment erosion and transport bottoms). At 5 years, the copper load, Fin, is instantaneously halved, to eventually reach steady state 1 Fin. The response time (T) of water and ET-/A-sediment is defined as 95% of the time taken to achieve the change between the steady states.

Table 5. Response time of the different compartments in the fate model upon halving the urban copper load

<table>
<thead>
<tr>
<th>Response time T'/year</th>
<th>Laduviken</th>
<th>Råcksta Träsk</th>
<th>Judarn</th>
<th>Trekanten</th>
<th>Långsjön</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>4.3</td>
<td>1.2</td>
<td>0.4</td>
<td>2.0</td>
<td>1.0</td>
</tr>
<tr>
<td>A</td>
<td>26</td>
<td>17.2</td>
<td>11.7</td>
<td>21.1</td>
<td>12.8</td>
</tr>
<tr>
<td>ET</td>
<td>5.1</td>
<td>4</td>
<td>3.4</td>
<td>4.4</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Water retention time T_w/ year | 0.25 | 0.05 | 0.9 | 1 | 0.8 |

When we instead applied a pulse of 100 times the initial copper load during one week, the concentration of copper in the water increased 7- to 60-fold immediately after the pulse and then returned to the initial value within weeks for our five cases. The sediment, on the other hand, showed just a 20-40% increase in the simulated copper concentration occurring half or one year after the pulse and slowly returning to the initial level over year(s) (results not shown). We found that due to the rapid response-recovery character of the water compartment, it is possible to miss an unexpected unknown pulse of copper from the drainage area in regular monitoring (monthly or quarterly) of the lake water. However, although less sensitive to changes in the load, the sediment could record pulse events of emissions over several years, as appropriate for most monitoring programmes.

5. Discussion
5.1 Source analysis: Comparison of the source (SFA)-based and concentration-based approaches

The source model involves two different approaches to estimate the copper load in the drainage area. The source-based approach is based on the structure of SFA and quantifies the emissions from the stock of copper in the diffuse sources, as shown in Equation 1. In the source model, this approach dominates the quantification of the copper load in the drainage area. For the five cases in this paper, at least 94% of $F_{in}$ was estimated using the source-based approach (Figure 5, traffic sector, copper roofing and atmospheric deposition). The other approach is the concentration-based approach, which quantifies the copper load by the water flux and standard copper concentrations in the water (e.g. stormwater) in different land use areas. This approach has been widely used in previous studies (Larm, 2000; Karvelas et al., 2003; Rule et al., 2006), but it was only used as a complement in this study when data necessary for the source-based approach were lacking, for example for quantifying the copper emissions from soil and with the combined sewer overflow (CSO).

From the view of system boundaries, the source-based approach represents a broader system than the concentration-based approach. The former starts from ‘material/goods in use’ (see Figure 2) in the conceptual model, but the latter starts from ‘urban/surface runoff’. Therefore, the source-based approach sets up a clearer classification of the sources (Figure 3) and provides direct information on the emissions from diffuse sources. This is the most important benefit of using the source-based approach in the source model.

While the total copper loads were similar between the two approaches (Table 4), the apparent contributions from individual sources differed (Table 6) due to the difference between the concepts of models. According to the comparison in Table 6, the source analysis of this work identified the traffic sector as a major contributor of copper (50-80 % in the five cases), while the results from Stockholm Vatten (2000) and the StormTac model identified built-up areas as the major contributor. This apparent difference is due to all traffic emissions in all land use types being accounted for in the SFA approach, whereas the concentration-based approach employed in StormTac and by Stockholm Vatten only includes those traffic emissions occurring in traffic areas (roads, parking and railways). In the concentration-based approach, the remaining traffic emissions are attributed to the other land use area, resulting in relatively higher values for the building and soil sectors (see Table 6 for an example). We therefore concluded that the source-based approach represents a more transparent and specific accounting for the urban diffuse sources than the concentration-based approach.

The weakness of the source-based approach is that much specific information is needed as input data, such as the traffic volume on each road and the extent of copper roofing in the drainage area, and parameter values. The data gap becomes the biggest problem of the source analysis, exemplified by the traffic volume in the case of Lake Långsjön, so that the source model needs to make some assumptions. Various data sources and assumptions caused great uncertainty in the source model. Nevertheless, compared with the concentration-based approach, e.g. through StormTac, the source-based approach decreased the uncertainty of the source quantification remarkably (Table 4).

5.2 Effect of different spatial and temporal scales of model and field observations

As seen in Figure 6, the model is better at predicting the sediment copper concentration ($C_s$) than the water copper concentration ($C_w$). This can be explained from both the monitoring and the modelling view. The sediment observations we used correspond to the model simulation results, as the model simulates the annual copper concentration and the sediment copper concentration changes only slowly.
(Figure 9). The sediment is sampled in the uppermost 0-2 cm, yielding one or two years of average copper concentration according to the age of the A-sediment.

However, the water observations used as references are averages of 4-5 surface samples from 1 m depth during a year, which do not correspond to the simulated annual water concentration. Firstly, the observations show the surface water concentration (1 m depth), but not the mean concentration of the whole water pillar as used in the model. Secondly, even though the field water samples are averages from 4-5 sampling campaigns during a year, the measured copper concentration in water is affected by temporal variations, for example weather (rainfall, snow), as the response time of water is short, and may differ from the annual averages represented by the model. Therefore, we propose that the annual level description of the transport process in the lake model is sufficient to simulate the copper concentrations in sediment, but may be too crude to simulate the concentrations in water.

5.3 Application results of the source – transport – storage model

Considering the model performance and data availability discussed above, the sediment content is more suitable for reflecting the copper load in the drainage area than the water concentration. Furthermore, the decade response time of A-sediment (Table 5), which is in agreement with general pollutant accumulation time-scales in sediment as summarised by Butler and Davies (2004), means that the sediment copper content is suitable for indicating long-term changes in F_{in}. The results of source analysis in the source – transport – storage model identified traffic as the most dominant diffuse source of copper in the drainage areas of the five catchments studied here (Figure 5, Table 6). The lake model simulated the resulting long-term environmental copper levels in the lakes (Figure 6). From the perspective of environmental sustainability, the ultimate way to manage urban development in the drainage area would be source control of pollutants, reducing the urban impacts below critical, acceptable levels. Here, we used the coupled model to evaluate the acceptable copper load for a specific lake according to the environmental quality standards of the lake sediment. We used the source model to indicate the types of urban sources that need to be reduced and the coupled model to assess the time needed to obtain an increase in quality. For example, in the case of Trekanten, the sediment copper content in 2007 corresponded to Class 4 (100-500 mg/kg dw) according to the Swedish EPA classification (Rauch, 2007). To restore the lake sediment copper content to Class 3 (25-100 mg/kg dw), the urban load of copper needs to be limited. Model simulations show that F_{in} needs to be decreased to <3.8 kg/year and that a decade will be needed to meet Class 3 criteria. According to the source analysis, the dominant sources of copper in the drainage area of Trekanten are traffic (69%) and copper roofs (23%). Thus, reducing copper roofing and traffic in the catchment would be efficient ways to meet this requirement. Indeed, copper roofing in this drainage area had greatly decreased by 2008, but the volume of traffic on the highway has increased 12-19% during the last 5-6 years (S. Thörnelöf, pers. comm. 2008).

6. Conclusions

This study attempts to link the information on copper sources in the urban area and the fate of copper in the local aquatic recipient in a source – transport – storage model.

Our source model extended the list of source types to including parking and metro/railway in the traffic sector, farmland, forest and other open land in the soil sector, and some case-specific sources, such as combined sewer overflow (CSO). This enlargement made the source model more comprehensive, but did not markedly change the results of the copper load, F_{in}, in the cases studied. However, a comprehensive list of source types may be necessary for improving the applicability of the model in
other cases. The source analysis indicated that the traffic sector (especially brake linings) was the dominant diffuse source in the drainage area in all five cases assessed here (see Figure 5). In the case of Lake Trekanten, copper roofs were also an important source.

Similarity between model results validated both the source-based approach and concentration-based approach used here (Table 4). However, the source-based approach provided clearer knowledge on the contribution of individual, urban, diffuse sources. The major weakness of the source-based approach is the specific data requirement, with resulting large uncertainty in the source analysis. Therefore, the source-based approach did not improve the source analysis in the modelling uncertainty aspects markedly, compared with the concentration-based approach.

Tests of the coupled source – transport – storage model in five cases in Stockholm indicated that the model is applicable to urban catchment areas with elevated copper levels in the sediments (Lakes Trekanten, Råcksta Träsk and Långsjön) but is not so accurate for cases with lower environmental levels of copper (Lakes Laduviken and Judarn; see Figure 6). The model was also better at predicting the copper content in sediment than in water, which may be related to the agreement of the spatial and temporal resolution of the model, the model input, and the field observations used to test the model. The lake fate model suggested that sedimentation and burial processes dominated the fate of copper in all cases except Lake Råcksta Träsk, where outflow actually is the dominant process, due to the low water retention time of this recipient (Figure 7).

The sensitivity analysis and uncertainty analyses showed the copper load from the drainage area (F_i) to be most sensitive to parameters quantifying the copper contribution from brake linings in the traffic sector. The wear rate of braking lining (W) and the fraction of stormwater from the road to the lake (β) in the traffic sector were responsible for most of the uncertainty in F_i. In the lake model, the sedimentation process (v_s, PF) was dominant in determining both the simulated water and sediment copper concentration (C_W and C_s), and also contributed most uncertainty, along with F_i. Thus, in order to decrease the uncertainty of the source model, β and W in particular would need to be better constrained. The uncertainty of the coupled model could be further decreased by more precise information on v_s and PF in particular.

The response of the A-sediment to a change in the copper load (from the drainage area F_i) showed that the simulated sediment copper concentration (CS) linearly reflected F_i, but with a temporal delay on the decade level. Based on this, we suggest that sediment can be used to indicate long-term variations in the urban load.

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8. References


Sources and fates of heavy metals in complex, urban aquatic systems: Modelling study based on Stockholm, Sweden

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Sources and fates of heavy metals in complex, urban aquatic systems: modelling study based on Stockholm, Sweden

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Abstract

Despite management of point sources, heavy metals today remain at an elevated level in the urban environment, with diffuse sources dominating the emissions. In order to manage these pollutants, it is necessary to understand the coupling between the urban sources of heavy metals and their monitored, environmental levels, for example in aquatic sediments. In this work, we suggest a simple approach to quantitatively model Cu from its urban sources through a complex aquatic system. We apply the proposed model to Stockholm, situated between Lake Mälaren and the archipelago of the Baltic sea, and discuss data availability along with conceptual difficulties. Using literature data, we show that Cu occurs at elevated levels in the aquatic sediment close to the centre of Stockholm, Sweden.

*Keywords: source, fate, copper, modelling, urban, aquatic system.*

1 Introduction

Despite management of point sources, heavy metals today remain at an elevated level in the urban environment, with diffuse sources becoming dominant and with extensive internal loading within the aquatic systems. In order to manage these pollutants, increased knowledge of the sources and fates of urban metals is required. Particularly, there is a need for understanding the coupling between the urban sources of pollutants and their monitored status in the environment. This need stems from the fact that while policies and regulations aim at altering the strength of the diffuse sources, this strength can never be directly measured by...
field observations. A change in the strength of the diffuse source may, however, propagate to the environmental level of the pollutant, and thereby be indirectly detected. In order to understand the monitored levels of pollutants in response to their historical sources and to predict the effect of alteration of today’s sources on future environmental levels of the heavy metals, it is important to be able to couple the monitored levels to the actual source terms.

In this study, we attempt assessing the coupling between sediment copper content, often analysed in environmental monitoring programs, and the urban sources of Cu in a complex, urban, aquatic system. Stockholm, Sweden, is such an example where diffuse sources are distributed over many urban activities and emitting into many, coupled basins from the upstream Lake Mälaren to the downstream archipelago of the Baltic Sea.

Source analyses of Cu for isolated recipients or entire municipalities have been frequently published in the literature [1–4]. Fate models for Cu in lakes have been suggested by e.g., Lindström and Håkanson [5], Woodfine et al. [6], Mackay et al. [7] and Heijungs [8]. Cui et al. [9] coupled a source analysis with a fate model for the small Lake Trekanten in Stockholm. In this work, we advance this coupling by suggesting an approach to assess a complex water system, where a multitude of diffuse, urban sources emit into many, coupled water bodies. The objectives of this communication are to:

- Present a conceptual model for the Cu flow from urban sources through a complex series of natural recipients;
- Test and demonstrate the conceptual model using Stockholm, Sweden, as a case study;
- Use literature data to deduce the trend in sediment Cu content along a flow path from Lake Mälaren, through Stockholm towards, the Baltic Sea.

2 Urban sources of copper and delivery to the environment

Today, major point sources of Cu have been managed in many urban environments in the industrialised world, and diffuse sources have become dominant [1]. As shown in Figure 1, important diffuse sources of Cu include traffic and building materials (see e.g., Sörme and Lagerkvist [2]). Copper is released to air or water, depending on the nature of release, e.g. as particles (traffic) or by leaching by precipitation (building materials). Airborne Cu may be scavenged to soil or surface water or is exported out of the recipient’s catchment.

The fractions of waterborne Cu that go to storm water, surface water or groundwater is determined by the landuse, e.g. traffic, residential, business, or recreational area (see summary in Cui et al. [9]). Depending on the storm water collection system, a part of the storm water may go directly to the recipient, while another part may be treated in a storm water treatment plant (SWTP). Generally, a major part of the Cu that has been deposited in the soil is retained there, but a minor fraction may be transported to the recipient either directly with the groundwater (groundwater discharge) or by prior release to the surface water system (Figure 1).
The diffuse urban sources of Cu brought to the recipient with the storm water can be estimated in at least two conceptually different ways. The first way to estimate the source term strength, \( F \) [kg/year], is based on the volume of leachate \( V \) [m³ year⁻¹] and standard concentrations, \( C_{std,n} \) [kg m⁻³], of Cu for storm water from different landuses \( n \):

\[
F = \sum_{n} V_n C_{std,n}
\]  

(1)

where \( V_n \) can be measured or estimated from precipitation, \( P \) [m year⁻¹], runoff coefficients, \( \gamma \) [-], and the fraction, \( \beta \) [-] of storm water that goes directly to the recipient, without passing a SWTP. This type of quantification was used by the municipality of Stockholm for some of the lakes in the case study in Section 5 [10] and is detailed in connection to the Stormmac model [11].

The second way of quantify the source term is based on the actual activities \( m \) in the catchment of the recipient:

\[
F = \sum_{m} \sum_{n} \alpha_m \beta_n E_{mn}
\]  

(2)

In Eqn. (2), \( \alpha \) [-] is the fraction of released Cu that goes to storm water. \( E \) [kg/year] is the emission by the activity, e.g. road traffic of presence of Cu roof, with a quantification that is based on activity specific wear or leaching rates of the goods [2, 9]. Cui et al. [12] compares the two approaches. Groundwater and surface water contributions and atmospheric deposition of Cu can be handled in analogy to Eqn. (1) or (2) (see, for example, Cui et al. [9, 12]).

Urban point sources of Cu may include SWTP and industrial and municipal waste water treatment plants, landfills, and industrial and potentially environmental hazardous activities within the catchment. Point source can be quantified similarly to Eqn. (1), based on specific source information.

Figure 1: Pathways for Cu from the sources to the recipient in the urban environment.
3 Fate of copper in the recipient

Copper from urban activities enters the recipient in particle form and dissolved in the aqueous phase through the pathways shown in Figure 1. Within the recipient, the limnology governs the fate of the Cu (Figure 2), where chemical conditions determine the partitioning between the dissolved and the particle form. Copper may leave the recipient in both forms. Particle-bound Cu is also subject to deposition in the sediments. Particles deposited into erosion or transport bottoms (ET-bottoms) are readily resuspended again. Particles deposited into accumulation bottoms (A-bottoms) rest there. The sediment in the accumulation bottoms is with time buried, and is then prevent from direct interaction with the water pillar. In both A- and ET-areas, dissolved Cu may be transported between the sediments and the water pillar through diffusion and advection.

The transfer of Cu between the different compartments in Figure 2 can be quantified by first-order approximations, as suggested by Lindström and Håkanson [5] and discussed by Cui et al. [9, 12]:

\[ F_j = R_j M_i \]  

(3)

where \( F_j [\text{kg year}^{-1}] \) is the Cu flux of process \( j \), \( M_i [\text{kg}] \) is the mass of Cu in compartment \( i \), and \( R_j [\text{year}^{-1}] \) is the transfer rate constant of process \( j \). In the literature, the quantification of the transfer rate constant has been empirical, but process based (see e.g., Håkanson [13]).

![Diagram](image)

Figure 2: Fate of Cu in the recipient (modified from Lindström and Håkanson [5] and Cui et al. [9]). The arrows represent transfer of Cu between the different compartments for Cu in the aquatic environment (water pillar, surficial sediment in accumulation, erosion and transport bottoms and the deep sediment).

The conceptual model in Figure 2 assumes the water pillar to be fully mixed. However, water bodies with little flow and/or considerable depth may become stratified, preventing mixing of surficial water with bottom water. For these types of systems, a compartmentalisation of the water pillar into upper and lower
water masses, with only partial and episodic mixing, may be relevant. The mixing fluxes can be handled similarly to other transfers, Eqn. (3), after handling of the timing of mixing. (see e.g., Håkanson and Bryhn [14]).

4 Conceptual model for copper sources and fate in a complex system of urban recipients

In this work, we are interested in following Cu from its urban source through the surface water system, in order to see if the anthropogenic contribution can be traced along the flow path. In the following, we suggest a conceptual model for this assessment. For clarity, we address the general case in Figure 3, where the flow path of interest is marked by a dotted line, and Cu is released from a multitude of activities in the urban area and emitted into several recipients. Challenges in formulating a quantifiable conceptual model for such a system include particularly the establishment of system boarders, the description of the fate of the pollutants in the coupled recipients, and the definition of the urban catchment for the source quantification. These issues are discussed here and the implementation of the approach in a case study is explained in Section 5.

![Diagram](https://via.placeholder.com/150)

**Figure 3:** General geographic structure of the urban pollutant catchment system along a considered flow path (dotted line). Basins and straits (grey) and their surface water catchments (hatched areas); storm water catchments (full line), storm water treatment plants (SWTP) and municipality boarders (dash-dot line). Thick, broken lines show upstream and downstream boarder for urban Cu sources.

4.1 System boarders

We suggest that the upstream system boarder can be set where the urban source is insignificant (broken line in Figure 3). This boarder may be estimated from
source term considerations (see Sections 2 and 4.3) or through monitored environmental levels of the pollutant. The downstream system boarder is set by the extension of the considered flow path out of the urban area. As discussed in the case study below, it may be convenient to extend the considered area to municipality/surface or storm water catchment boarders. Note that all surface waters with an urban source of Cu that are connected to the considered path must be included in the assessment.

4.2 Propagation and fate of copper downstream of the source

To consider the transport of Cu through the system of recipients, we propose to follow the approach of Engqvist and Andrejev [15] and divide the surface water into connected basins and straits based on geometric form, with straits being narrow, with an associated, expected lower water residence time (Figure 3). In order to trace the Cu through the system, the water flow through the straits between the basins must be established. Here, it must be noted that if the flow is bidirectional, partial mixing of water between basins must be considered, which complicates the mathematical coupling of the basins.

As a first approximation, we suggest considering straits as non-reactive channels for the Cu, such that sediment deposition and internal loading of Cu is insignificant; urban sources of Cu may, however, contribute Cu to the straits (compare Figure 3). We propose to use the methods described in Section 3 to quantify the fate of Cu in each basin. We suggest that basins and straits are quantitatively coupled in the model through mass-balance considerations, such that the Cu outflow of an upstream basin arrives in a downstream basin.

4.3 The urban catchment of copper

In quantifying the sources of Cu, we suggest that each basin and strait must be considered separately, as Cu may be significantly retarded in upstream basins. In the source quantification, a crucial part is to delineate the urban catchment of each basin and strait. Here, the catchment of ground- and surface water carrying Cu must be considered (compare Section 2 and Figure 3). However, a dominant contribution of Cu generally comes with storm water and cleaned waste water, which also must be considered. Each urban area has its own water management plan, which may cut over municipality boarders, that needs to be considered. As explained in Section 2, storm water may go directly to the recipient, be treated in a SWTP, or go to the soil, with the distribution being case-specific, and not necessarily well known.

This also implies that a storm water source may be geographically separated from its recipient, with water being lead to the recipient after potential treatment in a (distant) SWTP. Further redirection of precipitation within the urban area may occur as an effect of snow removal, in which case placement of snow deposits must be considered. It is noteworthy that the Cu sources that affect the considered flow path may be situated in several municipalities, possibly with separate storm water treatment facilities and environmental monitoring plans, thus providing separate “data catchments”.
5 The Stockholm case study

Stockholm is the capital of Sweden and is situated between the fresh water Lake Mälaren in the west and the archipelago of the lightly saline Baltic Sea in the east. The city is built on the islands and the coast line of the two water bodies, with 30% of the inner city area being water. In this study, we assess the flow path depicted as a dotted line in Figure 4 that also represents the main water flow direction from Lake Mälaren towards the Baltic Sea, transecting the municipalities of Stockholm, Lidingö, Nacka, Vaxholm, and Värmdö.

In 2007, the county of Stockholm had 1,950,000 inhabitants, with ~65% within the urban area. Historically, the water bodies surrounding Stockholm received extensive amounts of urban pollutants through unmanaged point sources and waste water [16]. Today, point sources of Cu have been largely managed and diffuse sources dominate [1]. Important diffuse sources include copper roofs, traffic (through brake linings, asphalt wear, and tires) and atmospheric deposition of Cu originating in more distant areas. Part of the Cu emitted from the diffuse sources goes directly to the recipient, while a major part is stored in the soil [17, 18], and yet a dominant part goes to the storm water treatment facilities (compare Section 2).

![Map of Stockholm with labeled points and lines](image)

Figure 4: The urban area of Stockholm (white area) is situated between Lake Mälaren in the west and the Baltic Sea archipelago in the east. The dotted line marks our considered flow path and numbered spots refer to locations of reported sediment Cu contents (Figure 5). The full line is the water system border of our model. The broken line shows municipality boarders.

Jonsson and Sörme [19] suggest that within the municipality of Stockholm, ca 1 tonne of Cu per year goes directly from the diffuse sources, dominated by traffic, and another 0.25 tonne year\(^{-1}\) through the storm water treatment plants, after 90% removal, to the recipients. The sewage/storm water treatment plants...
(generally combined) contribute another 0.65 tonne year\(^{-1}\) of Cu to the recipients [19], as a point source, mainly from the tap water system (brass/copper pipes and taps) and food faeces, with a small contribution from car washes [2]. Discharging groundwater provide a minor contribution of \(~30\) kg year\(^{-1}\) to the recipients within the municipality of Stockholm, according to Aastrup and Thunholm [20].

Burman [21] reports that ca. 0.25 tonne of Cu was distributed by the fireworks within Stockholm during the 2000 New Year's celebration, a fraction of which arrived to the nearby recipients. This indicates that fireworks may be a substantial, but non-dominant Cu contributor in the considered system. Antifouling bottom paints on boats are possibly also a source of Cu. Elevated sediment Cu contents have been detected in one of the marinas just outside the considered system [22], but there are not yet any estimates of the annual emissions of Cu from these sources within Stockholm in the literature.

Diffuse and point sources of Cu within the municipality of Stockholm are generally well known and documented as shown above. Emissions of Cu within the other municipalities affecting the considered flow path (Figure 4) have to a lesser degree been reported in the literature, but must also be considered.

![Diagram showing Cu content in different locations](image)

Figure 5: Average of the sediment Cu content in the upper 2 cm during 1997-2006 along the flow path in Figure 4 as reported by Lindström \textit{et al.} [23], Rauch [24], and Sternbeck \textit{et al.} [25]. The arrow shows the extent of the city centre and the main water flow direction.

5.1 Trends in sediment copper contents along a flow path

Figure 5 shows the average of the Cu content in the upper sediments along the flow path in Figure 4 as reported for 1997-2006 [23–25]. It is noteworthy that in Lake Mälaren, west and upstream of Stockholm, the Cu content is relatively low,
increasing along the flow path as it passes through Stockholm. The Cu content in the sediment is lower east of the city centre, approaching and passing through the inner archipelago. This confirms a considerable urban effect on the Cu content of the sediments.

5.2 Copper source and fate conceptual models for Stockholm

Following the conceptual model in Section 4, the water system boarder was defined by the expected area of urban Cu contribution and the major water exchange path (see Figure 4, full line). According to Figure 5, this system includes the area with evidently elevated sediment Cu content. While several distant upstream cities and municipalities may contribute Cu to the considered system, this contribution is expected to be low, as surface water concentration of Cu generally is low. For convenience, we have thus used the Stockholm municipality boarder as our western system boarder. We include the bays of Edsviken and Stora Värtan north of the considered flow path, as it was estimated that non-negligible sources of Cu can be expected from the roads and traffic in the nearby areas [26]. A few lakes in this area were excluded from the system, but may need to be considered as recipients of part of this Cu (not shown).

Figure 6: The subdivision of the considered water system (Figure 4) into basins (ellipses; deep – full contour; shallow – dashed contour) and straits (arrows; surface water – filled; underground/groundwater – dotted). Neglected basins within the more urban area have been crossed out. Broken line divides the inner archipelago from Lake Mälaren/transition zone. Triangle with exclamation mark shows the approximate position of WTP water outlet.

As the eastern boarder of the system, we propose to use Oxdjupet, close to Point 15 in Figure 4, as this represents the major water exchange point between the inner- and the outer archipelago, neglecting two smaller exchange points to
the west (marked by dashed arrows in Figure 4). The water exchange point to the
south at Skuru has also been excluded, as only little water is exchanged between
the considered system and the southern archipelago, not assessed here. Tentatively, we ignore contributions of Cu from the Baltic sea.

For the archipelago, Engqvist and Andrejev [15] already suggested a
partitioning into basins and straits; for Lake Mälaren and the transitional region,
we consider the water bodies with slender form as straits, whereas others were
considered as basins (Figure 6). Basins with a maximum depth of more than 10m
were considered deep (full contour ellipse in Figure 6), whereas the rest were
considered shallow (dashed contour ellipse in Figure 6). We suggest that the
shallow basins can be modelled as fully mixed, whereas thermal stratification in
the deep basins requires their compartmentalisation into a deeper and a shallower
part in the lake fate model (see Section 3). A few small basins with no or little
connection to other parts of the water system under consideration were neglected
for simplicity (crossed-out basins in Figure 6). Furthermore, many lakes in some
more rural areas, south and east of the city centre, were not considered as they
will neither contribute nor prevent Cu from reaching the flow path, as a first
approximation (not shown in Figure 6).

6 Discussion

6.1 The conceptual model and its quantification

In this work, we have proposed a way to assess the urban copper sources and the
fate of copper as it is transported through a complex aquatic system (Section 4).
The approach is based on a source quantification, through a substance flow
analyses (Section 2), that is coupled with a dynamic fate modelling (Section 3).
Application of the model to the case of Stockholm (Section 5) highlighted a
number of scientific challenges that will be discussed here.

6.1.1 System boarders

While the definition of the geographical system boarders may be unproblematic,
the handling of small lakes within the system may pose considerable difficulty.
Including lakes that are unimportant for the considered flow path adds
unnecessary complexity to the model, and demands a greater amount of field
data. We propose that small lakes with no or insignificant surface water
exchange with the considered flow path need only to be considered as sinks for
the urban Cu in the source analysis, and can be excluded from the fate model.
However, this needs to be further investigated. In Section 5.2, we discuss that
urban waters judged to contribute little Cu may be considered to be left out of the
system; in our case, Edsviken and Stora Värtan and their catchments were
tentatively kept within the system.

6.1.2 Propagation and fate of copper downstream of the source

Mapping the water system into basins and straits is obviously a source of
uncertainty in the proposed model, as is the partitioning into shallow and deep
basins. In our case study, we have implicitly suggested a rather rough handling, with for example small bays being lumped with bigger basins or straits. The choice of spatial discretisation can be investigated using a sensitivity analyses in a quantitative model. Availability of input data for the source and fate models as well as of monitoring data to test the model will ultimately limit the level of geographical details that is meaningful to describe.

We have identified water exchange between basins and particularly bidirectional flow between and episodic mixing of basins as major conceptual difficulties to overcome, and also associated with data gaps in our considered case study. As a first approximation, we suggested the straits to be handled as non-reactive channels for Cu, in order to ease the source quantification. The implications of this simplification must be tested.

6.1.3 The urban catchment of copper

A major difficulty in the source quantification is the establishment of the urban catchment, as detailed in Section 4.3. The actual source quantification within the catchments is associated with further uncertainty. This uncertainty is related to data availability with respect to traffic work, amount of Cu bearing goods and its leaching rates, the collection and treatment of storm water, etc. Also in well-investigated municipalities, like the municipality of Stockholm, not all data are at hand. The effect of such uncertainties on predicted levels of Cu, as the uncertainties propagate through the model, can be assessed by sensitivity analyses.

6.2 Towards a quantitative model for Stockholm – data availability

In a case study, we propose a coupling of source and fate sub models for Cu along a main water flow path through Stockholm. Dominant information needed in the source quantification includes landuse area, storm water collection, and traffic work, as well as extent of copper roofing (see summary by Cui et al. [9]). For the central municipality of Stockholm, the Cu emissions have been well researched and documented, as summarised above for the municipality as a whole.

For the individual basins/straits the information is in many cases also available in the literature [27] or through the authorities (e.g., Stockholm EPA). A detailed assessment of the small Lake Trekanten, just south of the considered flow path in Figure 4, was reported by Cui et al. [9] and a few additional lakes north of the flow path is being reported by Cui et al. [12]. For the municipalities surrounding Stockholm, less information is readily available. Monitoring data of particularly sediment Cu content over time in several basins/straits along with data for source quantification will be essential for model testing.

Particularly important data needs for the fate model include water exchange between basins. Through the work of Engqvist and Andrejev [15], this is generally available for the inner archipelago (Figure 6). However, for the parts of Lake Mälaren and the transition zone to the archipelago, less information is readily available. Here, it must be emphasized that it is not sufficient with the net water exchange between basins, as episodic change of flow direction implies a
partial mixing of waters with potentially different Cu levels. We suggest that model sensitivity tests may help deducing the level of details needed in this water flow description, in order to match other uncertainties in the fate model.

7 Conclusions

Using literature data, we showed that there is a peak in the Cu content of the upper, aquatic sediments sampled during 1997-2006 close to the city centre of Stockholm (Figure 5). Upstream (west) of Stockholm, in Lake Mälaren, and downstream, in the inner Baltic Sea archipelago, the Cu content is lower, confirming the urban origin of this Cu (see also Lindström et al. [23], Rauch [24], and Sternbeck et al. [25]). We proposed that such elevated levels of Cu in the aquatic sediment can be quantitatively coupled to the urban Cu sources.

We also proposed an approach to quantitatively follow Cu from its urban source through a complex, aquatic system. The approach combines a substance flow analysis [2] for the urban sources of Cu with a mass-balance model for its environmental fate [5] through a series of natural recipients (Section 4). As detailed site data generally is an obstacle to site or case modelling, the approach is simple, rather than sophisticated.

We applied the proposed model to a main water path from Lake Mälaren to the Baltic Sea archipelago, through Stockholm, in Sweden (Figure 4). This represents a case where a multitude of point and diffuse sources, distributed over many urban activities, emit into many, coupled water bodies. In the case study, we proposed definition of the system boarders and partitioning of water bodies into straits and deep and shallow basins, based on geometric form (Figure 6). We suggested that compliance of future quantitative model results with monitoring data may help testing the choices made in this conceptual model. We proposed that data needed for such model testing includes particularly sediment Cu contents at a few separate times for several of the basins/straits along with source quantifications during a similar time period.

Here, we propose that the quantitative coupling of the urban sources and the monitored levels of pollutants, as aimed for in this study, is crucial for understanding monitoring results in the light of historical sources, which may help formulating policies and assessing different management scenarios. Furthermore, model results and sensitivity analyses may help establishing the monitoring needs, in order to follow the response of environmental Cu levels to different pollution management actions and city developments within a complex aquatic system.

References


