Controls on trace metals in urban stream sediments – implications for pollution monitoring using sediment chemistry data

Paula Kuusisto-Hjort

Department of Geography
Faculty of Science
University of Helsinki
Finland

Academic dissertation
Supervisors: Professor Matti Tikkanen, Department of Geography, University of Helsinki, Finland

Dr. Juhani Virkanen, Department of Geography, University of Helsinki, Finland

Pre-examiners: Professor Miska Luoto, Department of Geography, University of Oulu, Finland

Dr. Timo Tarvainen, Geological Survey of Finland, Espoo, Finland

Opponent: Dr. Raimo Heikkilä, Finnish Environmental Institute, Joensuu, Finland
Contamination of urban streams is a rising topic worldwide, but the assessment and investigation of stormwater induced contamination is limited by the high amount of water quality data needed to obtain reliable results. In this study, stream bed sediments were studied to determine their contamination degree and their applicability in monitoring aquatic metal contamination in urban areas. The interpretation of sedimentary metal concentrations is, however, not straightforward, since the concentrations commonly show spatial and temporal variations as a response to natural processes. The variations of and controls on metal concentrations were examined at different scales to increase the understanding of the usefulness of sediment metal concentrations in detecting anthropogenic metal contamination patterns.

The acid extractable concentrations of Zn, Cu, Pb and Cd were determined from the surface sediments and water of small streams in the Helsinki Metropolitan region, southern Finland. The data consists of two datasets: sediment samples from 53 sites located in the catchment of the Stream Gräsanoja and sediment and water samples from 67 independent catchments scattered around the metropolitan region. Moreover, the sediment samples were analyzed for their physical and chemical composition (e.g. total organic carbon, clay-%, Al, Li, Fe, Mn) and the speciation of metals (in the dataset of the Stream Gräsanoja).

The metal concentrations revealed that the stream sediments were moderately contaminated and caused no immediate threat to the biota. However, at some sites the sediments appeared to be polluted with Cu or Zn. The metal concentrations increased with increasing intensity of urbanization, but site specific factors, such as point sources, were responsible for the occurrence of the highest metal concentrations. The sediment analyses revealed, thus a need for more detailed studies on the processes and factors that cause the “hot spot” metal concentrations. The sediment composition and metal speciation analyses indicated that organic matter is a very strong indirect control on metal concentrations, and it should be accounted for when studying anthropogenic metal contamination patterns.

The fine-scale spatial and temporal variations of metal concentrations were low enough to allow meaningful interpretation of substantial metal concentration differences between sites. Furthermore, the metal concentrations in the stream bed sediments were correlated with the urbanization of the catchment better than the total metal concentrations in the water phase. These results suggest that stream sediments show true potential for wider use in detecting the spatial differences in metal contamination of urban streams. Consequently, using the sediment approach regional estimates of the stormwater related metal contamination could be obtained fairly cost-effectively, and the stability and reliability of results would be higher compared to analyses of single water samples. Nevertheless, water samples are essential in analysing the dissolved concentrations of metals, momentary discharges from point sources in particular.
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1. Introduction

1.1. Contamination of urban water bodies

Following the urban sprawl of the 20th century, human actions have altered the form and function of many water bodies either directly or indirectly as a result of catchment land use changes (Walsh et al. 2005a; Gurnell et al. 2007). Today one half of the world's population lives in cities and towns, while the corresponding figure for developed countries is 75% (The state of the world population report 2008). The continuously growing urban population leads to the spreading of urban land use, which is bound to affect increasingly more streams and rivers. In addition, the current aims towards more sustainable cities in many western countries tend to emphasize the need for higher compactness (Hall 2002; Jabareen 2006; Laine 2008), which may intensify the anthropogenic influence on existing urban water bodies.

The aquatic effects of urbanization are nowadays often driven by the quantity and quality of urban stormwater discharges (Walsh et al. 2005a), while other possible anthropogenic impacts of urban areas include for instance sanitary and combined sewer overflows, wastewater treatment plant effluents or industrial discharges (Wei & Morrison 1993; Bubb & Lester 1994; Paul & Meyer 2001; Ramessur & Ramjeawon 2002; Miltner et al. 2004). Channelization often leads to rerouting of urban runoff and increased drainage density. Furthermore, covering of soil by impermeable surfaces (soil sealing) interferes with the functioning of soil and the natural hydrological cycle by reducing infiltration and filtering of rainwater (European Commission 2002). These changes in the hydrological conditions may cause increased flooding and morphological modifications of stream channels (Hammer 1972; Neller 1989; Booth 1991; Schueler 1994; Gregory 2002). Stormwater quality is also degraded showing high concentrations of nutrients, pathogens, organic pollutants and trace metals (Line et al. 1996; May et al. 1997; Nurmi 1998; Rose et al. 2001). The physical and chemical changes of urban runoff and stream channels may further impose various biological alterations (Wang et al. 2001; Walsh et al. 2005b).

In urban areas metals originate from different natural and anthropogenic sources, which include wet and dry deposition, traffic, industrial areas, various chemicals and corrosion products of buildings and paving materials (Svensson & Malmqvist 1995; Bergbäck et al. 2001; Ministry of the environment 2005) (Table 1). In addition to exhaust fumes, the traffic sources include leakage of motor oil and corrosion and abrasion of vehicle parts (Brinkmann 1985; Sörme & Lagerqvist 2002). The dramatic increase of traffic has made it a major source of many metals in addition to the roofs and siding materials of buildings (Good 1993; Svensson & Malmqvist 1995; Gromaire-Mertz et al. 1999; Davis et al. 2001; Sörme & Lagerqvist 2002). During dry periods metals from different sources build up on impervious surfaces that typically cover a high proportion of urban areas. When rainfall starts, these metals are effectively washed off the surfaces to the stormwater system and receiving water bodies. In natural areas a higher proportion of the metals are retained in the soil and vegetation following the downward percolation of water and uptake by plants.

Some trace metals like Cu and Zn are essential for the metabolism of aquatic organisms in small amounts, but in high concentrations they can pose acute or chronic toxic effects (Adriano 2001; Londesborough 2003). Indirectly, high contaminant concentrations can cause changes in community structure and biodiversity (Reynolds 1987; Förstner 1989). The toxicity of metals depends on their bioavailability rather than their total concentration, i.e. the amount of metal available for biological action, such
as uptake by organism. Due to the high risk they cause to the aquatic environment, Pb, Cd, Ni and Hg have been selected as priority substances by the European Union (EC 2001). Cu, Zn and Cr are additionally regarded as essential to water protection goals in Finland, since they typically occur in relatively high concentrations and have adverse effects on surface water ecosystems. However, these metals were not classified as national priority substances and no quality objectives were laid down. Instead, they should be taken into account while considering the ecological status of waterbodies (Ministry of the environment 2005).

Stormwater related metal contamination of aquatic systems has been recognized as a major issue since the 1970’s (Malmqvist & Svensson 1978; Wilber & Hunter 1977; Melanen 1981; Brinkman 1985). In the past, urban diffuse pollution was overshadowed by excessive discharges of treated or untreated sewage that were primarily responsible for deterioration of urban water bodies (Ruth & Tikkanen 2001; Taylor et al. 2008). However, following the decline in point sources, diffuse metal sources and stormwater quality have gained increasing attention worldwide, as well as in Finland (Falk & Stahre 2000; Ministry of the environment 2005; Nurmi et al. 2008; Taylor et al. 2008). Numerous studies have demonstrated high stormwater metal concentrations (Melanen 1981; Gromaire-Mertz et al. 1999; Tuccillo 2005), and it is nowadays widely recommended to decrease metal loading using best management practices and low-impact design (EPA 2000; Ahponen 2005; Kloss & Calarusse 2006).

Anthropogenic activity also increases the release of trace metals from natural sources, such as acid sulphate soils, which are common in the western and southern coastal regions of Finland (Åström & Björklund 1995; Tarvainen et al. 1997). Ditching and construction activity related to urbanization may enhance the oxidation of sulphide minerals and leaching of trace metals (e.g. Co, Ni, Zn, Cu and Ti) from acid sulphate soils (see Åström 2001).

Metal concentrations of the water phase show strong temporal variations which can reach several orders of magnitude within a short time period (Förstner & Wittman 1981; Dong et al. 1984; Horowitz et al. 1990; Ruth 2004). Consequently, individual samples are involved with considerable uncertainty, which may impede the meaningful interpretation of spatial variations or temporal monitoring data (see Wilber & Hunter 1977; Bubb & Lester 1994). Due to the varying nature of water quality, intensive sampling and high costs are associated with water monitoring, and information concerning the metal loads of different urban areas is still limited. Therefore, the extent of stormwater induced metal pollution and its dependence on land use have remained relatively unclear, and further research on the topic is urgently needed (Williamson 1986; Goonetilleke et al. 2005; Ministry of the environment 2005; Taylor et al. 2008).

Table 1. Major (bold) and minor sources of metals in urbanized areas (Good 1993; Bergbäck et al. 2001; Davis et al. 2001; Sörme & Lagerqvist 2002).

<table>
<thead>
<tr>
<th>Source</th>
<th>Cu</th>
<th>Zn</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buildings</td>
<td>Copper roofs, gutters, building</td>
<td>Galvanized steel (roofs, gutters), building walls</td>
<td>Brick walls, old (Pb containing) paint</td>
<td>Galvanized materials (roofs, gutters), building walls</td>
</tr>
<tr>
<td>Traffic</td>
<td>Brake wear</td>
<td>Atmospheric deposition</td>
<td>Brake wear, brake wear, asphalt, motor oil</td>
<td>Petrol, tire wear, asphalt</td>
</tr>
<tr>
<td>Others</td>
<td>Atmospheric deposition</td>
<td>Atmospheric deposition</td>
<td>Atmospheric deposition</td>
<td>Atmospheric deposition</td>
</tr>
</tbody>
</table>

Table 1. Major (bold) and minor sources of metals in urbanized areas (Good 1993; Bergbäck et al. 2001; Davis et al. 2001; Sörme & Lagerqvist 2002).
1.2. Sediment assessment

One possibility to study the aquatic metal pollution is using sediment chemistry analysis (e.g. Förstner & Wittman 1981; Heikkilä 1999). Most trace metals tend to be associated with particulate matter and their transport and deposition is strongly controlled by the behaviour of suspended sediment. Metals may be associated with solids already as they enter the stream, or the partitioning of metals between dissolved and particulate phases may be altered following physical or chemical processes (Fig. 1). Thus, the dissolved metals can be gradually assimilated by the suspended sediments within the stream system (Droppo et al. 2001). In stormwater the particulate bound proportion of metals can be very variable typically exceeding 50% (Williamson 1985; Morrison et al. 1990; Garnaud et al. 1999; Tuccillo 2005).

As a consequence of the tendency to accumulate in the particulate phase, a major part of the metals carried by streams are eventually deposited in stream beds, floodplains or reservoirs as sediments (Tessier & Cambell 1987). In the active channels fine grained sediments of the depositional and near-bank sites best represent the material carried in suspension (Ciszewski 1998; Horowitz et al. 1999). The most recently deposited flocculated material often forms an unconsolidated surface floc layer (or surface fine-grained lamina) characterized by a porous structure and high water content (Droppo & Amos 2001). Floodplains and reservoirs mostly act as longer-term storages of metals and sediments, while sediments are usually stored only temporarily in channel bed (Owens et al. 2001; Walling et al. 2003; Figure 1. Key factors and processes controlling the composition and metal concentrations of stream bed sediments.)
Taylor et al. 2008). Although biostabilization often increases the strength of fluvial sediments (Droppo et al. 2001), the loose top layer of the fine grained sediments is remobilized during high discharge events. The channel bed sediments rarely last longer than a year (Owens et al. 2001; Taylor et al. 2008). Thus, the fine grained stream sediments offer a media to trace the quality of recently deposited suspended sediments.

Sediments can indicate the spatial distribution of contamination and thus help in identifying the sources and pathways of contaminants ( Förstner & Wittman 1981). Sediments have been suggested to be more stable media for tracing metal sources compared to water ( Förstner & Wittman 1981; Bubb & Lester 1994; Owens et al. 2001). While individual samples of the aqueous phase usually represent metal concentrations on a time scale from minutes to hours (Breault & Granato 2000), sediments may represent time-integrated concentrations. Furthermore, concentrations of metals are often orders of magnitude higher in sediments than solution (Luoma 1989; Arakel 1995). Thus, sediments have also been increasingly employed to assess the contamination of fluvial systems also in urban areas (Wilber & Hunter 1979; Wei & Morrison 1993; Callender & Rice 2000; Sutherland 2000; Mellor 2001; De Carlo & Anthony 2002; Ramessur & Ramjeawon 2002). In addition to sediments, also biogeochemical samples, such as plant roots and mosses, have been used in metal contamination assessments (Lax & Selenius 2005).

The sediment assessment approach is, however, not without some drawbacks. The most serious problems concerning the interpretation of results are created by the spatial variations of suspended sediment components and their deposition. Contaminant concentrations in the settled bed sediments may be controlled by the sediment composition rather than the location of contaminant sources (Combest 1991; Bubb & Lester 1994; Breault & Granato 2000; Walling et al. 2003). The composition of suspended sediments is affected by the properties of the primary sediment sources as well as the proportion of remobilized sediment (Fig. 1). In urban environments sediment may be derived from different parts of the catchment, and from numerous anthropogenic and natural sources. Sediment supply is also regulated by human actions such as street cleaning (Charlesworth & Lees 1999a, 1999b). Suspended material is additionally controlled by chemical processes (e.g. dissolution) which are often driven by the prevailing pH or redox-conditions (Jenne 1968) (Fig. 1).

Complex processes, such as flocculation, may enhance or impede the deposition of fine grained particles by altering the hydrodynamic characteristics of suspended sediment (Nicholas & Walling 1996; Droppo et al. 1997). Moreover, variations in the energy of the environment lead to contrasting depositional patterns for different sediment components (Kersten & Smedes 2002). The stream velocity and thus, the depositional conditions are controlled by various environmental factors, including gradient and morphology of the channel (Knighton 1980; Thoms 1987; Webster 1995; Ciszewski 1998; Ladd et al. 1998; Rhoads & Cahill 1999; Church 2002) (Fig. 1). A deeper insight into the relationship of sediment components with trace metals is needed in order to predict the areas of naturally high metal accumulation. The ability to distinguish the anthropogenic effects from natural variations is a prerequisite for utilization of sediment for pollution monitoring and control.

The sampling procedure and sampling site selection further controls the effect of sediment composition on trace metals. The selection of the most appropriate methods is dependent on the purpose of the study. For geochemical mapping, inorganic sediments are sampled, while organic sediments are preferred for environmental assessments (Salminen et al. 1998; Lahermo et al. 1996). In source detection studies samples are often collected from depositional zones where the sediment is homogeneous and fine-grained, while other types of sediments should also be
sampled for more comprehensive sediment quality studies, such as risk assessments (Ciszewski 1998; Ladd et al. 1998; Förstner & Heise 2006).

Sediment resuspension or chemical and biological reactions altering the composition of bed sediments (diagenesis) may cause post-depositional changes in metal concentrations (Breault & Granato 2000; Tao et al. 2005). This may further increase the discrepancy with the aquatic contamination loads. As a result of these processes, sediments may also become a secondary source of pollution in the future (Förstner & Heise 2006). The consequent release of contaminated particles and associated metals to the water phase may have impacts on the entire downstream water body.

Compared to terrestrial environments, identification of metal sources in fluvial environments is additionally hampered by the transport of sediment and metals (Fig. 1). Mixing of material of local origin with sediment transported from upstream reaches may disguise the spatial distribution of metal sources.

The factors and processes described above act on the sediment at different spatial scales and therefore lead to different spatial patterns of metal concentrations. The metal concentrations may change gradually in response to regional changes in controlling factors, or form local clusters of high or low concentrations (Combest 1991; Ladd et al. 1998; Mellor & Bevan 1999; Callender & Rice 2000; Sutherland 2000). On the other hand, differences in the intensities of controlling factors and processes within a small area may locally induce highly variable metal concentrations (van der Perk & van Gaans 1997; Rhoads & Cahill 1999). The spatial variations of the controlling factors and consequently different spatial patterns determine how the interpretation and reliability of the metal concentration results are affected. The information of the spatial patterns and the dominating scale of variations can be utilized to adjust the sampling scheme to obtain the desired information (Arakel 1995; Birch et al. 2001).

The importance of sediment bound metals goes beyond the practical aspects of sediments as archives of past and recent contamination. The sediments are also an essential part of the aquatic ecosystem, since they form habitats for a variety of organisms dwelling on the surface and within the sediment (Brils & de Deckere 2003; Stronkhorst et al. 2004; Allan & Castillo 2007). High metal concentrations of the sediment are particularly dangerous for organisms living within the sediment (Förstner & Wittman 1981), since many of them are exposed to contaminants via ingestion of the sediment (Luoma 1989; Allan & Castillo 2007). However, these invertebrates also serve as food for higher animals. Meaning that the quality of sediment may directly affect the biotic health of the stream.

1.3. Research objectives

An assessment of metal contamination (Cu, Zn, Pb, Cd) of urban streams in Helsinki Metropolitan region was conducted using sediment analysis. The aim of this study is to determine the key factors controlling the bed sediment metal concentrations, and to contribute to the current discussion on the role of sediment assessment in pollution monitoring particularly in urban areas.

Helsinki is the capital of Finland and is surrounded by the largest continuous urban area of the cities in Finland (Ristimäki et al. 2003). Numerous streams in the region are primarily located within urban settlement, and so the impacts of urbanization on metal concentrations in the streams are likely to be pronounced. However, the extent of aquatic metal contamination has not been comprehensively determined in the region. The information available is restricted to a few studies on the metal concentrations of urban pond sediments (Marttila 2007), stormwater (Nurmi 1998, Karvinen 2009 (unpublished data)) and stream water (dissolved metals) (Ruth 2004). This study also aims at increasing the knowledge of the spatial
distribution of metal contamination in the region especially with reference to different land use patterns.

So far, studies dealing with the controls, particularly of land use, on metal concentrations in urban fluvial sediments have mostly been descriptive. Therefore, knowledge of land use relationships with sedimentary metal concentrations is basic. This study aims at utilizing statistical relationships to obtain a quantitative assessment of the controls of sediment composition and land use on metal concentrations.

Spatial variations are a phenomenon that is intrinsically accepted as interfering with sediment chemistry analyses, but the magnitude and consequences for sampling and interpretation of results are rarely quantified. Spatial patterns are often the focus of urban stream sediment studies, but only the broad-scale patterns are identified and explained (c.f. Mellor & Bevan 1999; Callender & Rice 2000; Sutherland 2000). The finer scale patterns, such as local clustering of high and low values (autocorrelation) are nearly always neglected in sediment studies (for exceptions see van der Perk & van Gaans 1997; Ladd et al. 1998). The influence of fine-scale spatial variations and temporal variations on metal concentrations have been studied more frequently even in urban environments, but mostly from a geomorphological viewpoint (e.g. Rhoads & Cahill 1999; Birch et al. 2000, 2001). Here, an attempt is made to quantitatively evaluate the dominating scales of variation, and to identify the nature of the local scale spatial autocorrelation structure in stream sediments, and consequently to assess the implications for contaminant source detection studies.

The specific objectives of this study are to 1) quantify the metal contamination degree of urban stream bed sediments and establish a preliminary estimate of the possible biological effects, 2) investigate the controls on sediment composition and determine the influence of sediment on metal concentrations, 3) determine the impact of land use on metal concentrations, 4) assess the main scales of metal concentration variations and local scale metal patterns and 5) evaluate the applicability of sediment chemistry analysis for spatial contamination monitoring and source detection in urbanized areas.

This study reports Cu, Zn, Pb and Cd concentrations of depositional bed sediments. These metals have previously been shown to be good indicators of anthropogenic contamination, stormwater and traffic sources in particular (Williamson 1986; De Carlo & Anthony 2002; Singh et al. 2002; Bäckström et al. 2004). In addition, Cr and Ni concentrations were measured, but the concentrations were very low and the analytical method used did not provide reliable results. The data of the study can be separated to two sets. The first (the Gräsanoja dataset) contains sediment samples collected from the Stream Gräsanoja and its tributaries. The stream drains a catchment that is dominated by residential land use with small commercial and industrial districts particularly in the lower part of the catchment. The second dataset (areal dataset) includes sediment samples collected from independent headwater streams whose catchments range from mainly forested to industrial and commercial land use. According to Walsh (2000), small streams are particularly valuable for assessing the impacts of catchment urbanization, since they are located close to the built-up areas. To be able to distinguish the differences in metal concentrations between land use types, the streams of the areal dataset were selected so that the catchments would represent different land use types. Each catchment should, however, be as homogeneous as possible with regard to land use.
2. Study area and sampling catchments

2.1. The Helsinki Metropolitan region

Stream bed sediment samples were collected from the Helsinki Metropolitan region on the southern coast of Finland (Fig. 2). In addition to Helsinki, the metropolitan region of Helsinki includes the surrounding municipalities of Espoo, Vantaa and Kauniainen. At the beginning of 2008 the population of the region was 1 007 600 inhabitants (YTV 2009).

The metropolitan region consists of extensive suburban areas surrounding the central business district of Helsinki. The suburbs extend almost continuously to 15–20 km distance from the Helsinki city centre, and the suburban fringes are still expanding outwards (Halonen et al. 2002). Until the Second World War, urban settlement was rare in the region surrounding the city centre and only a few suburban areas were located along the railroads (Schulman 1990). By 1965 urban areas consisting of single-family houses were already common in the region comprising the urban areas today. Despite a couple of exceptions, the high density apartment building areas and industrial, commercial and institutional areas were constructed after 1965. Urbanization in the Helsinki Metropolitan region was most intense during the 1960’s and 1970’s (Schulman 1990), but the area continues to face population growth and construction of built-up areas (Halonen et al. 2002). However, despite the urbanization process, green areas still comprise 56% of the Helsinki Metropolitan region (Halonen et al. 2002). In the future, new urban construction will be located in the fringes of the Metropolitan region as well as within the existing urban structure (City of Espoo 1994, 2008; City of Helsinki 2003; City of Vantaa 2007).

The climate of the region is boreal with a large temperature difference between winter and summer. The mean annual temperature

Figure 2. Location of the sampling sites within the Helsinki Metropolitan region. The administrative boundaries represent the situation in 2008.
of the normal period 1971–2000 was 5.6 °C while monthly mean temperatures fluctuated from 15.8 °C in July to -4.9 °C in February. The area received rainfall on the average 642 mm/a (Finnish Meteorological Institute 2002). Rain is fairly evenly distributed throughout the year, but highest rainfall is received in summer and autumn. Average monthly runoff is highest in the spring (in March and April) during the snow melt period, but high average values are also recorded for late autumn months (October to December) (Korhonen 2007). Despite the lower average runoff in summer and winter, high momentary runoff peaks often occur throughout the year as a response to individual storms or snow melt (Ruth 2004).

2.2 The catchment of the Stream Gräsanoja

The catchment of the Stream Gräsanoja is located about 15 km west of Helsinki city centre (Fig. 2). The Stream Gräsanoja is a third-order perennial stream with a catchment area of about 25 km². In addition to the 9-km-long main channel, the stream network consists of two major tributaries (Stream Lukupuro and Stream Merituulenoja) and several smaller perennial tributaries (Fig. 3). Numerous seasonal ditches also bring drainage water to the streams in the high flow periods.

A majority of the catchment is located <20 m above the sea level (Fig. 4a). The hills between the low-lying sediment plains rise just above 40 m asl. The upper slopes of the hills are mostly rocky or covered by a thin layer of glacigenic till, while the lower slopes and the valley bottoms are covered by thick clay and silt deposits reaching depths more than 5 metres (Maaperäkartta 1:10 000 GEO 10 M Espoo) (Fig. 4c). In the upper reaches the stream flows through a small coarse silt deposit. Peat deposits are located in the upper reaches of the catchment, as well as in the catchment of the Stream Lukupuro (Map of Quaternary deposits 1:20 000, sheets 203403...
and 203212). The southern and central parts of the Stream Lukupuro catchment and the areas surrounding the main channel close to the confluence of the Stream Lukupuro are covered by organic rich gyttja deposits. In the central parts of the catchment of the Stream Lukupuro sulphide rich sediments, accumulated during the Litorina phase of the Baltic Sea, have been observed below the surficial layers (Ojala & Palmu 2007). The bedrock of the catchment is dominated by granite, particularly in the southern parts. In the northern parts of the catchment gneisses and amphibolite can also be found (Bedrock map 1:100 000, sheet 2032 Siuntio).

The main channel has steeper upper reaches (average gradient 5.8 m/km) compared with a very low-gradient in the lower parts.

Figure 4. a) Topography, b) land use and c) surficial deposits of the Stream Gräsanoja catchment (Map of Quaternary deposits 1:20 000, sheets 204303 and 203212).
reaches (average gradient 0.6 m/km) (Fig. 5a). The elevation drop in the main channel totals 24 m. In the upper reaches the stream is narrow and consists of alternating riffles and pools. At 6.5 km distance the stream channel becomes wide and shallow-watered (Fig. 5b, 6), and the gradient decreases. Apart from the upper reaches, the stream channel is rather uniform and lacks any well-developed geomorphological features. This is partly due to artificial modification of the stream reaches. Particularly in the middle and lower reaches, the stream consists of an artificially straightened channel with a simplified bank profile.

Most of the catchment is drained by a separate sewer system. Therefore, stormwater is discharged directly and untreated into the receiving waters, while sewage is channelled into the wastewater treatment plant. The majority of the built-up areas in the Stream Gräsanoja catchment are drained by underground storm water sewers. The density of the storm sewer network is highest in the southern parts of the catchment, where the tributaries are fed by numerous stormwater outlets.

The catchment of the biggest tributary,

![Figure 5. a) Longitudinal profile of the main stem of the Stream Gräsanoja and b) channel cross-section profiles at sites located in the upper, middle and lower reaches (the locations of the cross-sections are shown in the longitudinal profile).](image)
Stream Lukupuro, is mostly covered by forested headwater areas and extensive, formerly cultivated fields in the lower parts of the catchment (Fig. 4b). The fields were still mostly cultivated at the time of the sampling. Two sampling sites, located in the least disturbed, forested parts of the catchment, were considered to represent baseline conditions, since their catchments are only weakly impacted by direct anthropogenic activity. The rest of the Stream Gräsanoja catchment is mostly suburban and the built-up areas comprise 46% of the catchment area. Low density residential areas are the dominant type of urban land use (27%). High density residential areas (5%) and small industrial, commercial and institutional districts (11%) can be found scattered around the catchment. The source of the main channel is located in an industrial area that is mostly dominated by warehouse and industrial activity. The industrial area in the lower parts of the catchment is a combination of commercial activities and light industry. The lower reaches of the Stream Merituulenoja is surrounded by commercial areas. With the exception of five sites in the Stream Lukupuro catchment (sites 49, 50, 54, 55, 56, see Fig. 4b), all sites were categorized as urban sites in the statistical analyses.
Each of the three highways with traffic densities of over 30,000 vehicles per day run across the study catchment (Fig. 3). Ring Road II was opened for traffic in 2000, while the other two highways are considerably older. A municipal solid waste landfill, closed in 1986, is located close to the main channel in the upper part of the catchment. Except for occasional overflows, the leachate discharges from the landfill have been channeled to the wastewater treatment plant since 1980 (Jäppinen 2001). A municipal wastewater pumping station is located adjacent to the main channel of the Stream Gräsanoja just above the confluence of the Stream Lukupuro.

Water quality in the Stream Gräsanoja is monitored at five sites by Espoo Water twice a year. In general, the water in the Stream Gräsanoja was brownish and contained high concentrations of N, Fe and Mn. The concentrations of Cu, Zn, Pb and Cd were low and showed no apparent spatial trends. The average suitability of the water bodies for recreation was passable or poor (Jäppinen 2001, 2005).

2.3. Catchments of the areal study

Sediment samples were additionally collected from 67 small streams located throughout the Helsinki Metropolitan region (Fig. 1, 7, 8). The study sites represent a wide range of different land use types (Appendix 1). Seven sites are located in unbuilt catchments that could be regarded to represent baseline conditions. The rest of the catchments were

![Figure 7. Examples of the urban streams of the areal dataset. Sampling sites located in a) Varisto, b) Kannelmäki (West), c) Olari, d) Rajakylä and e) Hakuninmaa (for more details of the sites see Appendix 1).](image)
dominated by residential or industrial land use types.

The bedrock of the Metropolitan area is mainly composed of granite and gneiss (Bedrock map 1:100 000, sheets 2032, 2034 and 2043). Most of the catchments were located in the upstream reaches of the streams, and the drainage areas upstream of the sampling locations cover mostly less than 2 km². At the sampling sites the streams are small, approximately 0.5–1.5 m wide with water depths up to 0.5 m. No study catchments were located in the highly urbanized central areas of the city of Helsinki, where a combined sewer system is in use. The industrial, commercial, high density residential and modern low density residential areas are drained by underground storm sewers, whereas the oldest low density residential areas are partly drained by open ditches.

3. Materials and methods

3.1. Sampling and sample pre-treatment

The Gräsanoja dataset comprises bed sediment samples collected at 53 locations along the main channel of the Stream Gräsanoja and its tributaries in mid – late September 2003 (Fig. 4b). The average distance between adjacent sites was approximately 200 metres. In order to study the temporal variation of sediment quality, seven sites were re-visited and re-sampled in late September – mid October. These sites were also used for the study of fine-scale spatial variation. Therefore, two field replicate samples were collected at these sites during the latter sampling period. The spatial replicate samples were collected from one depositional zone at the sampling site within a distance of about ten metres. Altogether 67 samples were collected from the Stream Gräsanoja and its tributaries. The summer and autumn were generally fairly dry with average monthly rainfall of 48 mm, both during the summer months (June-August) and in the first two autumn months (September-October) (Finnish Meteorological Institute 2009). However, a few episodes of heavy rainfall were received during the entire sampling period and consequently between the collection of the two temporal replicates.

The areal dataset includes 67 sediment and 67 water samples collected from small streams in the Helsinki metropolitan area (Fig. 2) in July – August 2004. All sediment
sampling was conducted during low-flow periods. However, a very wet period preceded the sampling session, since the summer 2004 was unusually wet with monthly rainfall of 104, 201 and 78 mm in June, July and August, respectively (Finnish Meteorological Institute 2009). Additional water samples of the areal dataset were collected during snow-melt related high-flow periods in March – April 2009.

Only depositional zones of the streams, where the sediment is fine-grained, were selected as sampling sites in order to reduce the natural variability of the sediments induced by granulometric differences. Three to five subsamples collected within a stream distance of a couple of metres were composited at each site. The number of subsamples and the size of the sampling site were dependent upon the availability of suitable fine grained sediment at the site. The top layer of the sediment (approximately 1 – 2 cm) was collected using a plastic spoon from shallow waters near the shores of the stream (Shelton and Capel 1994). These localities have been proposed as being most suitable for geochemical sampling and monitoring of river pollution (Ciszewski 1998; Salminen et al. 1998).

First the sediment was sieved through a 2 mm sieve to remove the coarse plant fragments and inorganic particles. Then the sediment was wet sieved through a 63-µm nylon mesh using the ambient water. The sediment left on the sieve corresponded to the sand fraction (63µm – 2mm) (in the Gräsnöja dataset). The sediment that passed the sieve (the mud fraction, <63µm) was then allowed to settle for a few days at 8°C until the water was clear. The water was decanted, and most of the sediment was stored frozen. The sediment samples (both size fractions) were freeze-dried before any chemical analyses were conducted. For the areal dataset, a part of the sediment was stored in the refrigerator before any grain-size analysis was carried out. The use of <63µm sediment fraction is recommended, because it usually contains the highest concentration of pollutants, and represents the fraction of sediment that is transported in suspension (Salomons & Förstner 1984; Horowitz & Elrick 1987). This fraction has also been shown to be less prone to small scale spatial variation compared to bulk sediment (Birch et al. 2001).

The water samples of the areal dataset were collected into new or acid washed 1000 ml polyethylene or polypropylene bottles. The samples were transported to the laboratory in a cooler as quickly as possible after the sampling. In the laboratory water samples were stored deep-frozen until analysed. Electrical conductivity, pH and oxygen content of the water were measured in the field during the sampling.

### 3.2. Chemical and physical analyses

The chemical and physical analyses of the sediment samples were conducted in the Laboratory of physical geography at the University of Helsinki. For the determination of the acid extractable concentrations of metals (FeAE, MnAE, Al, Li, CuAE, ZnAE, PbAE, CdAE), the fine fraction of the sediment (<63 µm fraction) was digested with 14M HNO₃ using the method EPA 3051. The dissolution technique is non-selective, in that it extracts various labile and relatively stable fractions of metals, including metal in organic matter and a part of metals incorporated with amorphous metal hydroxides, biotite and clay minerals (Lahermo et al. 1996; Siiro & Kohonen 2003). Although some of the silicate minerals may also be partially digested (see Hämäläinen et al. 1997), quartz minerals and unweathered feldspars are mostly unaffected (Lahermo et al. 1996).

Metal speciation studies provide a better insight into the binding behavior and possible mobility and pollution sources of metals (Tack & Verloo 1995; Filgueiras et al. 2002). Among the available methods to partition the metals into different chemical phases are numerous single and sequential extraction techniques (Tessier et al. 1979; Chao 1984; Förstner & Kersten 1988; Ure et al. 1993; Usero et al. 1998). However, the
extractants dissolve operational phases that are determined by the method used, rather than well-defined chemical forms of metals (Tessier et al. 1979). Sequential extraction techniques, where extractants are applied sequentially to the sample with progressively increasing dissolution strength, are more commonly used than single or simultaneous selective extractions (Chao 1984; Hlavay et al. 2004). However, the efficiency of these techniques suffers from non-selectivity or the dissolution, re-adsorption of metals and losses of metals along with sample washing (Tessier et al. 1979; Rendell et al. 1980; Kheboian & Bauer 1987). Although the simultaneous extractions are also associated with non-selectivity problems (Chao 1984; Kersten & Förstner 1995; Dong et al. 2000), they are less time-consuming and involve less sample manipulation compared to sequential extraction (Bendell-Young et al. 1992).

Thus, the metals bound to different operational phases of the sediment were here determined utilizing a simultaneous selective extraction procedure (Table 2) as described by Bendell-Young et al. (1992): (1) easily reducible Mn and Fe (MnER, FeER) and associated metals (CuER, ZnER), (2) reducible Fe (FeR) and associated metals (CuR, ZnR), (3) organically bound metals (CuOrg, ZnOrg) and (4) pseudoresidual metals (CuRes, ZnRes). The easily reducible Mn and Fe correspond to the Mn-oxides and freshly precipitated, “reactive” amorphous Fe-oxides, while the reducible Fe includes crystalline Fe-oxides (Chao 1984; Stecko & Bendell-Young 2000). To obtain the pseudoresidual metal concentrations, the metals in the easily reducible, reducible and organically bound phases were subtracted from the acid extractable metal concentrations. Since the HNO3-extraction does not produce “total” metal concentrations, some of the metals bound to the resistant silicates are not included in the pseudoresidual metal concentrations calculated here (CuRes, ZnRes) (Andersen & Kisser 2004).

Flame atomic absorption spectrometry (FAAS) was used for the determination of Fe, FeER, (FeER+FeR), Mn, MnER, Li, Al, ZnAE, CuAE, ZnOrg, CuOrg, ZnR, CuR and ZnER (SFS 3044). Graphite furnace atomic absorption spectrometry (GFAAS) (SFS 5074) was used for the determination of PbAE and CdAE. ICP-MS was used to analyze all trace metals from the water and SPM samples, and for the determination of CuER, PbaE and CdER (ISO 17294-1; ISO 17294-2). For the water and SPM samples, the mean of the reagent blanks was subtracted from the ICP-MS results. For the bed sediment samples no subtraction was performed (the blanks showed very low concentrations compared to the samples) but the blanks were used to ensure that no contamination of the reagents was evident.

The total organic carbon (TOC) was measured by a sulfochromic oxidation method (ISO 14235). The primary grain size distribution of the mineral component (<63µm fraction (clay and silt) and 63µm–2mm fraction (sand) was measured by laser diffraction using a Coulter LS200 particle size analyzer, after organic matter removal and chemical (sodium pyrophos-

<table>
<thead>
<tr>
<th>Extractant</th>
<th>Phase extracted</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1N NH2OH.HCl in 0.01 N HNO3 for 0.5 hrs.</td>
<td>Easily reducible (MnER, FeER, CuER, ZnER, PbER, CdER)</td>
</tr>
<tr>
<td>0.1N NH2OH.HCl in 25% HOAc at 95°C for hrs.</td>
<td>Easily reducible + reducible (FeER+FeR, CuER+CuR, ZnER+ZnR)</td>
</tr>
<tr>
<td>1N NH4OH for 1 wk.</td>
<td>Organically bound (CuOrg, ZnOrg)</td>
</tr>
<tr>
<td>14N HNO3 (EPA 3051)</td>
<td>Acid extractable (CuAE, ZnAE, PbAE, CdAE)</td>
</tr>
</tbody>
</table>

Table 2. Simultaneous extraction scheme (Bendell-Young et al. 1992) used for the partitioning of metals in sediments.
phate) and ultrasonic dispersion (Agrawal et al. 1991). For the Gräsanoja dataset, dried sediment was used, and organic matter was removed using KOH (10%), since the commonly used \( \text{H}_2\text{O}_2 \) digestion did not disperse the aggregates of the dried sediment. For the areal dataset, wet sediment was used for the particle size analysis (see Förstner 2004), and organic matter was removed using \( \text{H}_2\text{O}_2 \)-digestion. The percentages of the clay (<2\( \mu \)m) and coarse silt (10-63\( \mu \)m) fractions of the material <63\( \mu \)m were used as grain-size parameters in further statistical analyses. Despite the dispersion methods used, slight differences in grain-size parameters between the datasets could be assigned to the differences of methods used, since freeze-drying can result in particle aggregation (Barbanti & Bothner 1993).

The suspended particulate matter concentrations (SPM) in the water samples were determined by filtration of accurately determined volume of water through 0.4 \( \mu \)m polycarbonate membrane (Whatman 111107 for low-flow samples and Whatman Cyclopore Track Etched Membrane for both low-flow and high-flow samples). The trace metal content of the SPM was determined by digestion of the filter membranes, using 14 M \( \text{HNO}_3 \) (EPA 3052). The digest and filtered water samples were then analyzed for trace metals by ICP-MS (ISO 17294-1; ISO 17294-2).

The metal concentration of the material left on the membrane, measured as dry weight, was called the SPM metal concentration. The concentration of these metals (left on the membrane) in the water sample, measured as mg/l, was called the particulate metal concentration. It was obtained as the product of the SPM metal concentration and the suspended sediment concentration. The metal concentration of the water that passed the filter membrane was denoted as the dissolved metal concentration. The sum of the particulate and dissolved metal concentrations was called the total metal concentration in water. The proportion of particulate metals was calculated by dividing the particulate metal concentration by the total metal concentration in water.

### 3.3. Quality control

The quality control procedure of sediments included analyses of a certified reference material with a roughly similar composition to the study samples (NIST River sediment 4350b) and analytical duplicates of samples. In the \( \text{HNO}_3 \)-digestion one reference sample was added in every second digestion and two analytical duplicates were analyzed for every sample. In the selective extractions, analytical duplicates were analyzed for several samples (altogether 14 duplicates for the extraction of the easily reducible fraction and 20 duplicates for the other two extractions).

The precision of the replicate analyses was quantified by calculating the relative standard deviation (RSD, \%). For more than two replicates RSD was obtained by dividing the standard deviation of the replicates by their average. RSD was expressed as percentages by multiplying the obtained value by 100. RSD between duplicate result \( a \) and \( b \) was calculated as (Clesceri et al. 1998):

\[
RSD = \frac{\left| X_a - X_b \right|}{(X_a + X_b)/2} \times 100\% \tag{1}
\]

The median of the relative standard deviations (RSD) obtained for the duplicates were <5\% for Al, Li, ZnAE, CuAE, CdAE, FeAE, MnAE, MnER, ZnER, PbER, CdER and CuOrg, <10\% for PbAE, FeER, FeR+ER, ZnR+ER, and <25\% for the rest of the measured concentrations. The RSD values of the 14 replicate samples of the reference material were <5\% for Zn, <15\% for Li, Cd, Pb, Mn, Fe, and <25\% for Cu and Al. For the TOC analysis, two analytical replicates for every sample were determined, and the relative standard deviations were <4\%.

The quality control procedure of the water samples collected in 2004 included replicates of ten samples for the determination of suspended solids and particulate metals,
and replicates of 23 samples for the determination of dissolved metals. For the dissolved metals, medians of the RSD were <10% for Cu, Zn and Cd and <25% for Pb. The RSD-values of suspended particulate matter and metal concentrations were very high (medians for particulate metals 33-48% and for SPM 100%). The SPM concentration of the first replicate was consistently higher than that of the second replicate. Accordingly, the particulate metal concentrations were consistently lower for the first replicate. The high variation between the replicates was interpreted as resulting from the higher content of metal poor coarse particles in the first replicate. The water samples were very dilute, and the occurrence of individual coarse particles with high settling velocities did apparently cause substantial variation between replicates. Thus, in order to maximize the comparability of the results between sampling sites, only the results of the first replicates were used for further analyses.

For the water samples collected in 2009, replicates were analysed for 5–10 samples. The median RSD values between the replicates were <5% for particulate and dissolved Cu and Zn, <10% for particulate Pb and Cd and dissolved Cd and <15% for SPM and dissolved Pb. In addition, certified reference material (HR-1, NMRI Canada) was also filtered (five replicates) and analyzed for SPM and particulate metals. More than 90% of the mass of the reference material was retained in the filter membrane, and in total 66–95% of the reference material was recovered (dissolved and particulate matter together). The average RSD-value of the SPM concentration of the reference materials was 14%. The trace metal concentrations of the particulate reference material (retained in the filter) were on the average 120-126% of the certified values for HNO3-digestion (EPA 3051), and RSD between the replicates was less than 5%.

3.4. Derivation of catchment characteristics utilizing GIS analyses

The catchments of the areal dataset and the subcatchments of each sampling site in the Gräsanoja dataset were delineated in MapInfo 8.5. The delineation was based on the contour lines of the 1:20 000 topographical maps (Basic map 1:20 000, sheets 203211, 203212, 203403, 203406, 203409, 204110, 204301, 204304, 204307) and maps presenting the location of storm sewers in the municipalities of the study area. The catchments were assigned a number corresponding to the number of the sampling site.

The catchment characteristics were investigated utilizing two different scales: the entire catchment scale and the partial catchment scale. In previous studies a number of different relatively simple methods, such as different buffers and circles, have been presented to define a partial catchment (Al- lan et al. 1997; Wang et al. 2001; Walton et al. 2007). However, these methods lack hydrological foundation and therefore, a region (immediate upstream catchment) representing the part of the catchment that is hydraulically close to the sampling site was delineated (Fig. 9). The region was defined as areas in the contributing catchment that are located up to 50 metres from the stream channel up to 150 metres distance upstream from the sampling site. The immediate upstream catchment also included areas surrounding (50 m buffer) stormwater pipes which discharge to the stream (up to 150 metres upstream from the sampling site). Catchment characteristics of the entire upstream catchment are indicated by c (for example the proportion of institutional land in the entire upstream catchment=INST_c, see Table 3 for the abbreviations of land use classes). Characteristics of the immediate upstream catchment are indicated by i (e.g. the proportion of institutional land in the immediate upstream catchment=INST_i). For the Gräsanoja dataset, the local riparian buffer zone was delineated as the 20 metre
wide (in each side of the stream) area surrounding the stream up to 50 metres upstream from the sampling site.

Figure 9. Determination of the immediate upstream catchment boundaries.

Topography has an influence on sediment transport and deposition processes, and thus on the sediment composition. In order to assess the control of topography on sediment composition, topographical indices (mean altitude and mean slope angle) were calculated from a digital elevation model (DEM). The raster DEM with 20 m grid size was calculated by linear interpolation from digital contour lines, provided by the National Land Survey of Finland, Uusimaa district survey office (011/UUMA/02), using Arc/Info’s TOPOGRID command. A slope map (20 m grid) of the study area (the Metropolitan region of Helsinki) was produced from the DEM by using ArcGIS Spatial Analyst toolbar. Mean of the altitude and mean slope angle in degrees for each catchment or subcatchment was calculated using the Zonal statistics as table command of ArcGIS Spatial analyst.

The composition of sediments is a function of the characteristics of various sediment sources in the catchment. The erosion of surface soils in the catchment is an important source of both mineral and organic sediments. Therefore, the proportions of different Quaternary sediment types out of the total catchment area were assessed for the catchments of the areal dataset. The Quaternary sediment (vector format) data was obtained from the Geological Survey of Finland (Map of Quaternary deposits 1:20 000, sheets 203211, 203212, 203403, 203406, 203409, 204110, 204301, 204304, 204307). Quaternary sediment data was missing from some of the densely built areas, where the data was supplemented by field inspections and utilising information obtained from the maps of Quaternary deposits produced by the municipalities of Espoo and Helsinki (Maaperäkartta 1:10 000 GEO 10 M Espoo; Geotekninen kartta 1:10 000 GEO 10 M Helsinki). The Quaternary deposit data was transferred to raster data (20 m grid) using ESRI ArcMap 9.3, and the areas of the different sediment types in each catchment and subcatchment (including immediate upstream catchments) were calculated using the Tabulate area command of ArcGIS Spatial analyst. Percentages were obtained by dividing the areas by the total area of the catchment.

Land use data (Table 3) was obtained by digitizing the regions of seven different land use types using MapInfo 8.5 software. Identification of different land use regions was conducted based on the information provided by topographical maps (Basic map 1:20 000, sheets 203211, 203212, 203403, 203406, 203409, 204110, 204301, 204304, 204307) and database of buildings provided by the National Land Survey of Finland, Uusimaa district survey office (011/UUMA/02). Internet sites (Vantaan kartta-ja paikkatietopalvelu SpatialWeb 5 2008, Iglo/karttahaku 2008) were also utilized to identify the land use types of the catchments. In addition to the buildings, the land use regions included the surrounding yards, parking areas and local and collector streets. Individual buildings with surroundings were, in most cases, not digitized as land use regions, but the land use regions contained several buildings. Finally, the land use regions were transformed to raster data (20 m grid) in ESRI ArcMap 9.3, and the areas of
the land use regions within each catchment were calculated using the Tabulate area command of ArcGIS Spatial analyst. Proportions (%) of the land use types were obtained by dividing the areas by the total areas of the catchments.

For further analysis, several land use types were combined to form more general land use metrics. Urban land use (URBAN) includes all built-up areas (LDR+HDR+INST+COMM+IND), and dense urban land use (DENSE) refers to the sum of HDR, INST, COMM and IND.

A land use classification was created for the study catchments of the areal dataset. Firstly, in order to decrease the number of land use classes, land use types HDR, INST and COMM were combined to form a new land use class: high density residential, commercial & institutional. Then the sites were grouped into four land use classes according to the dominating land use type of the entire upstream catchment.

The percentage of impervious surfaces associated with rooftops (TIA Roof) was obtained as the total area of buildings inside the catchment using the buildings database (National Land Survey of Finland, Uusimaa district survey office 011/UUMA/02). The impervious surfaces associated with transport areas (TIA Trans) were digitized utilizing a Spot satellite image (pixel size 2.5 metres) produced by Metria in 2002. Total percentage of impervious area (TIA) was obtained as the sum of TIA Roof and TIA Trans. The calculation of impervious surface metrics was conducted using MapInfo 8.5 software. The proportion of effective impervious areas (EIA, those directly connected to watersheds) was estimated using the method proposed by Sutherland (1995), where the EIA is a function of TIA and the intensity of stormwater drainage of the catchment (see Table 4):

$$EIA = a \times TIA^b$$

The TIA of the riparian zone in the Gräsanoja dataset was calculated by digitizing the impervious surfaces utilizing the aerial photographs (photo taken 2007) obtained from the internet site for municipality of Espoo (The City of Espoo Map Service 2008). Traffic density (TRAFFIC) was calculated for each study catchment and subcatchment. First, a traffic volume estimate was assigned for each street and highway of the street database (vector data) of the National Land Survey of Finland (Uuma/109/03). Measured traffic volume values were obtained for highways, main streets and collector streets (Ajoneuvoliikenne Espoossa 2002, 2003, 2007; Autoliikenne Vantaalla 2006; Liikennemäärät Helsingin pääkatuverkossa 2007). Only some traffic volume measurements were available for local streets. The average traffic volumes of local streets were

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Land use type</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDR</td>
<td>Low density</td>
<td>Single family houses, row houses and semi-detached houses</td>
</tr>
<tr>
<td>HDR</td>
<td>High density</td>
<td>Apartment buildings</td>
</tr>
<tr>
<td>INST</td>
<td>Institutional</td>
<td>Institutional buildings, such as churches, schools, administrative buildings or office buildings</td>
</tr>
<tr>
<td>COMM</td>
<td>Commercial &amp; traffic</td>
<td>Stores and shopping centres, commercial warehouse buildings and commercial sport centres, highways, major roads and collector streets within forested areas</td>
</tr>
<tr>
<td>IND</td>
<td>Industrial</td>
<td>Industrial buildings and surrounding streets, parking lots and warehouse areas</td>
</tr>
<tr>
<td>UNB</td>
<td>Unbuilt</td>
<td>Forests, mires, cultivated fields, meadows, parks, football fields</td>
</tr>
</tbody>
</table>

Table 3. Variables of land use (%) and their description.
650 and 210 vehicles per day in Helsinki and Espoo respectively (Ajoneuvoliikenne Espoossa 2007; Hellman 2008). The traffic volumes of local streets were estimated to be 500 vehicles per day for commercial, industrial, institutional and high density residential (apartment buildings) areas, 300 for medium-density residential (row houses and semi-detached houses) areas and 100 for low density residential areas (single-family houses). The average daily vehicle kilometres of each street were calculated as the product of the traffic volume and the length of the street. Traffic density was obtained by dividing the average daily vehicle kilometres of travel by square kilometre of land area for each catchment.

### 3.5. Data analysis

#### 3.5.1. General statistical methods

The statistical methods used in this study were based on covariances or linear correlations (Legendre & Legendre 1998). Therefore some of the variables were transformed in order to achieve normal distributions and linear relationships between variables. Trace metal concentrations (in both datasets), Clay-%, Fe and Mn (in the areal dataset), traffic density were log10-transformed. The arcsine transformation was applied for the percentages of land use and surficial sediment types, and proportions of metals in different binding phases (\(y' = \arcsin(\sqrt{y})\)) (see Legendre & Legendre 1998). The statistical analyses were conducted using SPSS 12.0.1 for Windows. Some of the dissolved metal concentrations and metals of the suspended particles were below the detection limit of the analysis, or above the calibration range. If the percentage of censored data was relatively small (<12%), these missing values were removed from correlation analyses and box-plot representations. Before this operation the data was analysed carefully to make sure that the missing values would not strongly impact the results. If the percentage of censored data was high (>25%), no correlation analyses were performed, because the results would involve too much uncertainty due to missing observations from the low and high ends of the data range.

Principal component analysis (PCA) was applied in order to summarize the data and relationships between different variables (Table 5). The principal components were extracted from the correlation matrices, and the components with eigenvalues larger than one were interpreted (Legendre & Legendre 1998). Because the initial principal components were relatively easy to interpret, the component solutions were not rotated. Correlation coefficients were further used to describe the relationship between different

<table>
<thead>
<tr>
<th>Catchment type</th>
<th>Description</th>
<th>a</th>
<th>b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average catchment</td>
<td>Mainly curbs and gutters, roofs of single family houses not connected to storm sewer or street curb</td>
<td>0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>Highly connected catchment</td>
<td>As average basin, but residential rooftops mostly connected to streets or storm sewers.</td>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Totally connected catchment</td>
<td>All impervious surfaces are directly connected to storm sewer system</td>
<td>1.0</td>
<td>1.1</td>
</tr>
<tr>
<td>Somewhat disconnected catchment</td>
<td>At least 50% of urban areas are not storm sewered by grassy swales or road-side ditches. Rooftops not connected.</td>
<td>0.04</td>
<td>1.7</td>
</tr>
<tr>
<td>Extremely disconnected basin</td>
<td>Only a small percentage of the urban area is storm sewered.</td>
<td>0.01</td>
<td>2.0</td>
</tr>
</tbody>
</table>

Table 4. Catchment properties and corresponding coefficients used in calculating EIA (Sutherland 1995).
variables. The relationships of metals with sediment components at the fine spatial and temporal scales were calculated as partial correlations (Legendre & Legendre 1998). The dominating impact of concentration differences between sites was removed by controlling for the site variables (seven dummy variables indicating the site where the concentration has been measured).

Linear regression models were built using forward selection. Variables were entered to the model one by one according to which variable produces the largest increase in coefficient of determination ($R^2$). Variables were added to the model as long as the new variable exceeded the significance level of 0.05. For dummy variables, the selection between two models (one includes the dummy variable/variables and the other does not) was conducted based on the F-test of nested models ($p<0.05$).

### 3.5.2. Scales of variation

The overall variability describes the total variation in the data without any reference to the spatial arrangement of the values, but the total variation can be disintegrated into different spatial or temporal scales. In this study, overall variability is expressed using

<table>
<thead>
<tr>
<th>Objective</th>
<th>Data</th>
<th>Data analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Metal contamination degree of urban stream bed sediments. - A preliminary estimate of the possible biological effects.</td>
<td>Both datasets: metal concentration (Cu, Zn, Pb, Cd) (acid extractable and easily reducible).</td>
</tr>
<tr>
<td>3</td>
<td>The impact of land use on metals.</td>
<td>Both datasets: Land use metrics of the entire and immediate upstream catchments, acid extractable metals Gräsanoja dataset: easily reducible metals.</td>
</tr>
<tr>
<td>4</td>
<td>Assess the main scales of metal concentration variations and local scale metal patterns.</td>
<td>Gräsanoja dataset: acid extractable metal concentrations at all sites, including the spatial and temporal replicates at seven sites.</td>
</tr>
<tr>
<td>5</td>
<td>Applicability of sediment chemistry analysis for spatial contamination monitoring and source detection in urbanized areas.</td>
<td>Both datasets: data of objectives 1–4. Areal dataset: metal concentrations in water and SPM. Gräsanoja dataset: easily reducible and acid extractable metals of the mud fraction and acid extractable metals of the sand fraction at 20 sites.</td>
</tr>
</tbody>
</table>
the coefficient of variation, or relative standard deviation. Here, the overall variability was expressed at different scales: 1) the total variation in the Gräsanoja dataset (n=53), 2) the fine-scale spatial variation between two field replicate samples at seven sites, and 3) the temporal variation between two temporal replicates at the seven sites. The total variation was calculated as the distribution of RSD-values calculated between two randomly selected sites within the urban sites, since the aim was to compare the fine-scale and temporal variations with the regional variations in the urban reaches. The fine-scale variation corresponds to variations within a site with spatial extent of about 5–10 m, and the temporal variation describes the variation at a certain site between two sampling campaigns separated by about a month.

3.5.3. Spatial autocorrelation

The spatial patterns of metal concentrations were further studied using the concept of spatial autocorrelation. It is a measure of the similarity of a variable between closely located sites (Goodchild 1986). Spatial autocorrelation has been commonly assessed for terrestrial environments, but rarely in aquatic systems, including fluvial environments (Peterson et al. 2006). In stream networks one of the difficulties involved in assessing the magnitude of spatial autocorrelation is the determination of distances between sites. Symmetric straight-line distances are not applicable to systems, where connections between sites are strongly determined by a directional process, such as stream flow (Ganio et al. 2005; Peterson et al. 2006; Ver Hoef et al. 2006). Thus, unidirectional hydrological distances between sites were measured here, i.e. distance from upstream site to downstream site along the stream channel network (for discussion on distances along networks see Peterson et al. 2006; Ver Hoef et al. 2006).

Here, spatial autocorrelation between sites separated by a certain distance (d) was calculated as the value of Moran’s I (Upton & Fingleton 1985):

$$ I_d = \left( \frac{n}{S_0} \right) \frac{\sum \sum W_{ij} (y_i - \bar{y})(y_j - \bar{y})}{\sum (y_i - \bar{y})^2} $$

where n is the number of samples, \( y_i \) and \( y_j \) are the concentrations of a metal at sites i and j, \( \bar{y} \) is the average of \( y \) and \( W_{ij} \) is the measure of spatial proximity of sites i and j. When water flows from site i to site j, and they are located within the distance of lag d, \( W_{ij} = 1 \), and otherwise \( W_{ij} = 0 \).

$$ S_0 = \sum \sum W_{ij} (i \neq j) $$

Moran’s I varies between -1 (maximum negative autocorrelation) and +1 (maximum positive autocorrelation). The mean and variance of the sampling distribution of I are obtained from:

$$ E(I) = -1/(n-1) $$

$$ \text{var} I = \frac{k(n(n-1)S_1 - 2nS_2 + 6S_0^2)}{(n-1)(n-2)(n-3)S_0^2} - \frac{1}{(n-1)^2} $$

where \( k = m_r^2 \); \( m_r = 1/n \sum (y_i - \bar{y})^2 \);

$$ S_1 = \frac{1}{2} \sum_i \sum_j (W_{ij} + W_{ji})^2 (i \neq j); $$

$$ S_2 = \sum_i (W_{i0} + W_{0i})^2; $$

$$ W_{0i} = \sum_j W_{ji}; $$

The significance of the I values can be obtained by comparing the probabilities of normal distribution with z (z = (I - E(I))/\sqrt{\text{var}(I))}.

The spatial autocorrelation was calculated for the raw data of trace metals and the standardized metal concentrations.

For the residuals of a linear model, the calculation of Moran’s I is slightly different. The residuals (\( \hat{e} \)) of a model \( y = bx + e \) (E(e)=0) are given by \( \hat{e} = y - \hat{y} \), where \( \hat{y} \) is the estimated value of \( y \). In the case of residuals, the spatial autocorrelation is calculated for \( \hat{e} \) values
in order to predict the pure impact of land use on metal concentrations. The set of land use variables used for modelling included the traffic density and percentages of impervious areas and different land use types (low density residential, high density residential, institutional, commercial and traffic, and industrial) in the entire upstream catchment and in the immediate upstream catchment. The rest of the land use metrics were derivatives of the above mentioned variables or their constituents, and were omitted from the analysis due to problems of multicollinearity.

In the first stage, the complete dataset was used to construct the model, and the fitted model is called the final model. The studentized residuals of the final models were examined in order to reveal heteroscedasticity, unlinear behaviour or the existence of outlier observations. Knowing that the studentized residuals follow $t_{n-k-2}$ distribution, the outlier observations were identified using the confidence level of 0.05 (Weisberg 1985). To evaluate the performance of the model for the calibration data, three fit statistics were used: coefficient of determination ($R^2$), Spearman’s rank correlation coefficient ($r_s$) between the observed and predicted values, and the average absolute bias (AB) (Guisan & Zimmerman 2000; Kozak & Kozak 2003). AB was obtained by:

$$ AB = \frac{1}{n} \sum_{i=1}^{n} |\hat{y}_i - y_i| $$

Where $y_i$ is the observed value and $\hat{y}_i$ is the estimated value of the response variable at site $i$.

Since the predicted errors of the final model were not independent of the data used to construct the model, the predictive accuracy of metal concentration models were assessed using tenfold cross-validation (Kozak & Kozak 2003). Although cross-validation involves some weaknesses, including loss of information and stability (Harrell 2001; Kozak & Kozak 2003), it provides a way to determine the predictive ability of the models.

### 3.5.4. Linear regression models of the metal concentrations

The relationships between metal concentrations and different environmental factors were studied using several explanatory methods. Further, it is of interest to determine how well the metal concentrations could be predicted using the information provided by sediment composition and land use metrics.

Therefore, linear regression models were created. Firstly, the metal concentrations were modelled using sediment composition and land use metrics as explanatory variables. Thus, in addition to the land use data, the area specific impact of sediment composition was accounted for. Secondly, metal concentrations standardized for the contents of clay and organic matter (see chapter 3.6.1.) were modelled as a function of land use data in order to predict the pure impact of land use on metal concentrations. The set of land use variables used for modelling included the traffic density and percentages of impervious areas and different land use types (low density residential, high density residential, institutional, commercial and traffic, and industrial) in the entire upstream catchment and in the immediate upstream catchment. The rest of the land use metrics were derivatives of the above mentioned variables or their constituents, and were omitted from the analysis due to problems of multicollinearity.

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$$ I_k = \frac{\hat{e}' W \hat{e}}{\hat{e}' \hat{e}} $$

where $W$ is a matrix containing the distances between sites (0/1). The mean and variance of the residuals are calculated by:

$$ E(I_k) = \frac{tr(MW)/(n-k)}{(n-k)(n-k+2)} $$

$$ \text{var}(I_k) = \frac{tr(MWMW') + tr(MMW)}{(n-k)(n-k+2)} $$

$$ + \frac{(tr(MW))^2}{(n-k)(n-k+2)} - E(I_k)^2 $$

where

$$ M=I-X(X'X)^{-1}X. $$

The magnitude of spatial autocorrelation was measured for acid extractable metal concentrations and standardized metal concentrations, and residuals obtained from a regression model that related metal concentrations to sediment composition. Thus, these residuals represent the variation of trace metals that is left when the influence of sediment composition is removed.

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and variability associated with model building (variable selection and estimation) (Harrell 2001). Because the dataset of this study was fairly small, cross-validation was more suitable for model evaluation compared to data splitting (Harrell 2001). However, similarly to data splitting techniques, cross-validation does not validate the model of the complete dataset but models developed on subsets of the data (Harrell 2001).

Here the complete dataset was divided into ten subsets at random. The first nine subsets were used to construct a calibration model. The calibration stage included the selection of variables and estimation of model parameters. Then, the calibration model was used to predict the response for the remaining 1/10th of the samples, and the accuracy of the prediction was assessed by comparison to the observed values. The linear model (calibration model) created using the construction set is

$$ Y = X\beta + \epsilon $$

The predicted value of an observation \( i \) for a given set of values of the predictor variables \( (x_i) \) in the estimation set is \( \hat{y}_i = x_i^T \hat{\beta} \), where \( \hat{\beta} \) is the estimate of \( \beta \) obtained from the fitted model of the construction set (Weisberg 1985). Prediction bounds for an individual response in the estimation set are obtained by

$$ \hat{y}_i \pm t_{\alpha/2} S \sqrt{1 + x_i^T (X^T X)^{-1} x_i} $$

Where \( t_{\alpha/2} \) is the appropriate point based on \( T_{n-k-1} \) distribution (Milton & Arnold 1990). Since \( x_i^T (X^T X)^{-1} x_i \) was close to zero in this study, the prediction bounds were calculated as \( \hat{y}_i \pm t_{\alpha/2} S \). \( S \) was estimated as the square root of the residual mean square \( \sigma^2 \) of the calibration model (see Weisberg 1985). The performance of the set of calibration models was assessed using three prediction statistics, comparable to those for the final model: R², \( r_s \) and average absolute bias (AB). Finally, the predicted values and prediction bounds (log-transformed) were transformed back to metal concentrations in order to graphically present the agreement of the prediction with observed values. The back-transformation of the predicted value \( \hat{y}_i \) produced the median of the predictive distribution of metal concentrations (Weisberg 1985).

### 3.5.5. Logistic regression models of the very high metal concentrations

The occurrences of very high metal concentrations, i.e. those that exceed the pollution level (for Cu and Zn) or the intervention level (for Pb and Cd) of dredged material (Table 7) were modelled by logistic regression. The metal concentrations were transformed to binary (0/1) variables (called here CuHigh, ZnHigh, PbHigh and CdHigh) according to the observed concentration in reference to the sediment quality guidelines. Thus, the new variables obtained value 1 (present sites, presence of high concentration) if the standardized metal concentration at the site was above the sediment quality guideline in question, and 0 (absent site, absence of high concentration) if the concentrations was below the guideline.

In a logistic regression model the response variables are the logarithms of odds. The odds express the likelihood of an occurrence (or presence) \( (p_i) \) relative to the likelihood of a non-occurrence. The odds are linearly dependent on the exposure to a set of risk factors (the explanatory variables). A linear combination of the explanatory variables is also called the linear predictor (LP) (Backhaus et al. 2000; Dobson 2002). The logistic model is of form:

$$ \log \left( \frac{p_i}{1-p_i} \right) = x_i^T \beta = LP $$

Where \( x_i \) is a vector containing the values of the explanatory variables at site \( i \) and \( \beta \) is the parameter vector. The parameters are estimated using maximum likelihood. In order to obtain the probabilities of occurrence, the model may be transformed to form:

$$ p_i = \frac{e^{x_i^T \beta}}{1 + e^{x_i^T \beta}} $$

The logarithmic regression produces, thus,
probabilities $p_i$ of occurrence (presence) that range between 0 and 1 (Dobson 2002). A classification of sites to those with predicted occurrence (presence) and predicted non-occurrence (absence) is obtained by comparing the probabilities of occurrence to a threshold value.

The explanatory variables were selected using backward elimination with a criterion of 0.05 for variable inclusion. The model thus created was called the final model. Similarly to the validation of the linear regression models, the predictive accuracy of the logistic regression models was assessed using tenfold cross-validation.

The fit statistics (final model) and prediction statistics (cross-validation) for the models included the area under the ROC curve statistic (AUC), Cohen's Kappa, sensitivity, specificity, positive prediction power and overall accuracy. All statistics, except AUC, were based on the predicted presences and absences. The cutoff threshold used in order to obtain presence or absence predictions based on the probabilities of presence was calculated as the prevalence (proportion of present sites) across the entire data (Liu et al. 2005). Cohen's Kappa coefficient measures the correct classification rate after the probability of chance has been removed (Cohen 1960). Thus, kappa measures whether or not the model predicts better than chance. Based on the Kappa coefficient, the discrimination ability of the model can be described as poor ($\kappa < 0.4$), good ($0.4 < \kappa < 0.75$) or excellent ($\kappa > 0.75$) (Landis & Koch 1977).

Sensitivity measures the proportion of correctly predicted sites among the present (observed) sites. Specificity describes the proportion of correctly predicted sites among the absent sites. Positive predictive power is the probability that a site is actually a present site if the model classifies the site as present. Accuracy is the proportion of all correctly predicted sites (Fielding & Bell 1997; Pearce & Ferrier 2000).

All the above mentioned fit and prediction statistics use only one cutoff threshold value, and are dependent on the choice of the value. AUC, on the other hand, provides a threshold independent measure of the discrimination ability. A ROC plot presents the sensitivity values against the corresponding value of false positive fraction (1-specificity) for all threshold values (Pearce & Ferrier 2000). AUC is the proportion of the area of the entire graph that lies beneath this ROC curve (Swets 1988). If the value is 0.5, the predicted probabilities of presence do not differ between the actual present and absent sites, and the model has no discrimination ability (Fielding & Bell 1997). AUC values 0.5-0.7 indicate poor discrimination capacity, values 0.7-0.9 indicate discrimination ability that is useful for some purposes, and values greater than 0.9 indicate very good performance (Swets 1988).

3.5.6. Significance of multiple statistical tests

The significance of a single statistical test was assessed using the p-value which describes the probability that the null hypothesis will be rejected when the null hypothesis is actually true (Type I error). Alpha ($\alpha$) is a threshold probability which defines the maximum p-value considered to indicate a significant result. When several tests are performed, each test has a chance to yield a significant result, and the chance of obtaining at least one significant result increases with the number of tests performed (even when $H_0$ is true for all of the tests). Traditionally, the change of declaring tests falsely significant is controlled using the Bonferroni correction meaning that, the $\alpha$-thresholds of single tests are adjusted so that the probability of obtaining at least one significant result is $\alpha$ (the familywise error rate or the overall significance level) (Verhoeven et al. 2005). This method does not, however, take into account the number of tests declared significant, or the lack of independence between the tests (Moran 2003; García 2004). As a result, it is unlikely to obtain significant results when a large number of tests are performed and the probability of Type II errors (accepting
H₀ when it is actually false) is high (Cabin & Mitchell 2000; Moran 2003; Nakagawa 2004; García 2004, Verhoeven et al. 2005).

Thus, the errors in multiple testing (in correlation tables, regression analyses and pairwise comparisons of means) were controlled here utilizing the false discovery rate (FDR), introduced by Benjamini and Hochberg (1995). It controls the fraction of false rejections among the significant hypotheses, instead of protecting against any false rejections, and provides a compromise between Type I and Type II errors (García 2004; Verhoeven et al. 2005). The following procedure controls FDR at a level less than or equal to α (Benjamini & Hochber 1995; Benjamini & Yekutieli 2001): Let \( p_{(1)} \leq p_{(2)} \leq \ldots \leq p_{(m)} \) be the observed p-values in ascending order, and denote by \( H(i) \) the null hypothesis corresponding to \( p_{(i)} \). Let \( k \) be the largest \( i \) for which

\[
p(i) \leq i/m*\alpha; \quad (16)
\]

then reject all \( H(j) \) for \( j = 1, 2, \ldots, k \). This procedure controls FDR in the case where all tests are independent or positively correlated (Benjamini & Hochber 1995; Benjamini & Yekutieli 2001, Verhoeven et al. 2005). The FDR controlled statistical significance (table-wise control) of the tests presented here were indicated as follows: *** (FDR<0.001), ** (0.001≤FDR<0.01), * (0.01≤FDR<0.05).

3.6. Metal pollution assessment

3.6.1. Metal enrichment over baseline

The severity of contamination related to urban land use was assessed by comparing the metal concentrations in sediments to the natural level of these metals. One of the most critical issues in contamination assessment is how the natural concentrations of metals are estimated (Förstner & Müller 1981; Prohić & Juračić 1989; Covelli & Fontolan 1997; Rubio et al. 2000; Apitz & Power 2002). Natural background concentrations of metals in fluvial sediments can be estimated using several methods. These include 1) average shale content, 2) average crustal abundance, 3) preindustrial lake, marine and river sediments or 4) recent sediments of fairly natural and unpolluted areas (Förstner & Müller 1981; van der Weijden 2002). The use of average shale content is problematic due to varying local geology and thus high spatial differences in the natural metal concentrations (Salminen & Tarvainen 1997; Matschullat et al. 2000; van der Weijden 2002). Preindustrial lake or marine sediments may be used to obtain the geochemical background concentration which represents the conditions prior to widespread industrial revolution. On the other hand, recent sediments even on remote sites are impacted by regional atmospheric pollution. Therefore, the concentrations of recent unpolluted sediments can not be expected to reflect the geochemical background, but rather the baseline concentration (see definition by Rice 1999) that refers to the concentration that has not been affected by direct anthropogenic inputs.

In this study, recent stream sediments of relatively unpolluted areas, where direct contamination from anthropogenic activity is assumed to be weak, were selected to estimate the baseline concentration of the area. While assessing the anthropogenic effect of urban land use, it is more meaningful to compare the concentrations of the urban sites to these baseline concentrations than to the geochemical background. Thus, the baseline concentrations were calculated as the average metal concentrations of the two baseline sites in the Stream Gräsanoja catchment (in the forested headwaters of the Stream Lukupuro) and seven baseline sampling sites of the areal dataset (the locations of the baseline sites are presented in Fig. 13). The catchments were dominated by forests or old fields which were not cultivated at the time of the sampling. It was estimated, that these sites did not receive substantial inputs of metals directly from anthropogenic sources. For the sediment contamination assessment using easily reducible metal concentrations in the Stream Gräsanoja, the baseline
concentrations were calculated as the average metal concentrations of two baseline sites of the Stream Gräsanoja catchment.

Several measures, such as enrichment factors, geoaccumulation indexes and sediment pollution indexes, have been used to establish the extent of contamination over background or baseline (Müller 1979, Sutherland 2000, Singh et al. 2002). In this study the contamination over baseline was estimated by calculating the enrichment factors of the metal concentrations in the sediments. Enrichment factors for metal concentrations (EF) were calculated as follows:

\[
EF = \frac{Metal_{sample}}{Metal_{baseline}}
\]

where \(Metal_{sample}\) is the concentration of metal and \(Metal_{baseline}\) is the best estimate of concentration (average) of metal in the baseline samples (Sutherland 2000, Andrews & Sutherland 2004). A five category ranking system of pollution proposed by Sutherland (2000) was adopted:

1. \(EF < 2\) Minimal enrichment, minimal or no pollution
2. \(EF 2 – 5\) Moderate enrichment, moderate pollution
3. \(EF 5 – 20\) Significant enrichment, significant pollution
4. \(EF 20 – 40\) Very high enrichment, very strong pollution
5. \(EF > 40\) Extreme enrichment, extreme pollution signal

Metal concentrations of both the urban stream sediments as well as natural baseline sediments vary according to sediment properties. Thus, normalization of metal concentrations is usually needed in order to differentiate between natural variability and anthropogenic input of contaminants (Rubio et al. 2000; Kersten & Smedes 2002). A normalization method recommended for coastal marine sediments in Finland was adopted here (Siiro & Kohonen 2003), i.e. metals were normalized to organic matter and clay percentage (metal concentrations were converted to correspond with concentrations of standard sediment (10% organic matter, 25% clay) (Ministry of the Environment 2004). For acid extractable metals, standardized metal concentrations were used for the calculation of enrichment factors, and the best estimate of baseline concentration was calculated as the average of the standardized baseline concentrations. For easily reducible metal concentrations no standardization was performed prior to the calculation of enrichment factors (baseline concentration was estimated as the average of the two baseline sites of the Gräsanoja dataset).

### 3.6.2. Evaluation sediment quality with reference to soil screening values and dredged material quality guidelines

Since no sediment quality criteria or environmental quality standards (EQS) have yet been proposed for metals in the freshwater sediments in the EU or in Finland, the sediment metal concentrations were compared with the quality guidelines proposed nationally for soil and dredged material (Table 6).

The soil screening values concerning Cu, Zn, Pb and Cd are mainly based on ecotoxicological grounds. Three levels have been established, an threshold level, and two guideline levels for different land use categories (Table 6). The threshold level is defined as ecotoxicologically relatively safe concentration level (Reinikainen 2007). The lower guideline level can be assumed to be safe to 50% of the species.

The quality criteria of dredged material are established as guidelines for managing disposal of dredged material (Ministry of the environment 2004). The criteria include two concentration levels. If the metal concentrations of the dredged material are lower than the lower level (intervention level), the material can be regarded as harmless. If the metal concentrations fall between the two levels, the material is defined as possibly polluted. Polluted material whose metal concentrations exceed the higher level (pollution level) cannot usually be disposed to sea (Ministry of the environment 2004).
Prior to comparison with the quality criteria (Table 6), sediment metal concentrations have to be normalized (Metalst) using clay and organic matter content to correspond with standard sediment (clay content 25%, organic matter 10%). The criteria are based on background concentrations and international toxicity assessments (Ministry of the environment 2004).

3.6.3. Hazard assessments

The ecological risk assessment of sediments usually includes the determination of hazard and risk that the sediment poses on the environment. Hazard is the potential for adverse ecological effects. Risk, on the other hand, is defined as the product of hazard and the probability of exposure (Apitz & Power 2002, Förstner & Heise 2006). In this study a hazard assessment was conducted using sediment chemistry information.

The quality guidelines for dredged material were utilized to identify the sites that show highest pollution potential. Hence, the sites where at least one of the metals exceeded the pollution level of dredged material (PLDM) were denoted as sites of concern. A further hazard ranking (modified after Heise et al. (2004)) was employed to the sites of concern based on acid extractable metal concentrations in the sediment. The sites were classified into 3 classes:

Class 1: indication of potential hazard, indicating that one metal exceeds the PLDM, but only by a small extent (up to 1.5 times with Cd and Pb; up to 2 times with Cu and Zn)

Class 2: higher certainty that hazard is present, when the PLDM is exceeded by at least two metals

Class 3: indication of potentially high hazard when concentration of at least one metal is more than 1.5 times (Cd and Pb) or 2 times (Cu and Zn) the PLDM

Class 0 was assigned to the sites not included in the group of sites of concern (no or weak indication of hazard).

4. Sediment composition results

4.1. Chemical and physical properties of the sediments

The general composition of the sediments was fairly similar between the datasets (Table 7). Al showed highest variation between sites – and between datasets. While Al concen-
trations are generally low in the areal dataset, the sediments of the Gräsanoja datasets show higher concentrations and variability. The range of variation was relatively high for clay-% in the areal dataset, but for both datasets clay-% lay between 15 and 25% at most sites.

4.1.1. Gräsanoja dataset

Figure 10 demonstrates the spatial pattern of the sediment properties in the Stream Gräsanoja and its tributaries. The spatial variations of the grain size distribution, clay-% in particular, were low, but one very distinct pattern can be identified. In the upper parts of the catchment, the sediment is particularly coarse grained, and the proportion of coarse silt reaches almost 60%. This pattern is apparently associated with strong supply of coarse silt from the small coarse silt deposit around site number 8. The effect can be detected in the sediment for 1 km downstream. The Li and Al concentrations roughly follow the relative variations in the proportions of coarse and fine silt, increasing with decreasing coarse silt-% (the proportion of particles with size between 10 and 63µm in the silt and clay fractions (<63µm)). However, Al concentrations are very high in the sediments of Lukupuro, compared to the grain-size parameters.

The major factors behind the spatial variations of sediment composition in the Stream Gräsanoja and its tributaries were determined using principal component analysis. Three factors were extracted (Table 8), and together the explained 74% of the variation in the data. The first component is strongly associated with fine grained sediment, since strong loadings are attained by clay-% and coarse silt-% (negative loading), as well as Li and Al. The high loadings of Fe- and Mn-oxides as well as TOC further show that, metal oxides and organic matter are associated with the fine sediment. The component therefore reflects the general accumulation of fine grained flocs which consist of soil aggregates as well as organic matter and metal oxides. The component is, thus, named as the component flocs and aggregates. The spatial distribution of the component scores showed that, the component of flocs and aggregates increases in the downstream direction in the main channel (Fig. 11). High scores were also recorded at the sites of the Streams Merituulentie and Lukupuro. Accumulation of flocs and aggregates were particularly low in the upper reaches of the main channel (sites 8–13).

PCA2 was mostly defined by Fe-oxides, amorphous Fe-oxides and TOC, which indicates that, the component further reflects the occurrence of flocs composed of metal oxides and/or organic matter. However, this component has a weakly negative associated

<table>
<thead>
<tr>
<th></th>
<th>Gräsanoja dataset</th>
<th>Areal dataset</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC (g/kg)</td>
<td>59.1 (20.6–90.2)</td>
<td>68.9 (21.3–126.1)</td>
</tr>
<tr>
<td>Fe (%)</td>
<td>5.37 (2.68–8.56)</td>
<td>4.08 (1.90–10.90)</td>
</tr>
<tr>
<td>Fe-oxides (mg/kg)</td>
<td>19.3 (7.3–56.2)</td>
<td></td>
</tr>
<tr>
<td>Amorphous Fe-oxides (mg/kg)</td>
<td>1.31 (0.60–3.31)</td>
<td></td>
</tr>
<tr>
<td>Mn (mg/kg)</td>
<td>0.48 (0.24–0.93)</td>
<td>0.44 (0.19–1.83)</td>
</tr>
<tr>
<td>Mn-oxides (mg/kg)</td>
<td>0.16 (0.01–0.48)</td>
<td></td>
</tr>
<tr>
<td>Al (%)</td>
<td>3.17 (1.53–8.31)</td>
<td>2.28 (1.12–5.07)</td>
</tr>
<tr>
<td>Li (mg/kg)</td>
<td>33.1 (15.6–48.7)</td>
<td>25.7 (11.7–40.1)</td>
</tr>
<tr>
<td>Clay-% (&lt;2µm)</td>
<td>24.0 (16.0–35.6)</td>
<td>20.9 (13.5–64.6)</td>
</tr>
<tr>
<td>Coarse silt-% (10–63µm)</td>
<td>36.0 (22.5–56.6)</td>
<td></td>
</tr>
</tbody>
</table>

Table 7. Medians and range (in parenthesis) of sediment properties in the two datasets.
with Li and Clay-%, which indicates that fine mineral matter, i.e. soil aggregates, are not incorporated in the flocs. The component is named simply the floc component. The floc component was high in the sediments of the Stream Merituentie. In the main channel, the highest accumulation of these flocs was recorded in the middle reaches. Contrary to the other two components, the component of organic and metal oxide flocs obtained low scores in the lower reaches of the main channel.

PCA3 is associated with Al and TOC bearing sediments which contain a low amount of amorphous Fe-oxides. Although the interpretation of this component is not straightforward, it may be related to organic matter is associated with Al-rich clay minerals or precipitates of Al-oxides and hydroxides (Al-mineral component). This component seems to be associated with sediments originating from the catchment of Lukupuro, since particularly high scores of the component were recorded in the sediments of Lukupuro, as well as in the main channel of the Stream Gräsanoja below the confluence of the Stream Lukupuro.

The first three principal components explained the majority of variation in the sediment components, with the exception of Mn-oxide which showed no marked trends in the study area. The spatial variation of Mn-oxide content might be partly related to variations in the redox-condition. For exam-

**Figure 10. Composition of the sediment samples of the Stream Gräsanoja. Clay fraction: <2µm, fine silt: 2–10µm and coarse silt: 10–63µm.**
Table 8. Results of the PCA analysis performed for the sediment composition of the Stream Gräsanoja and its tributaries. Clay particles: <2µm, coarse silt particles: 10–63µm. Bold text denotes absolute loadings greater than 0.3 (Legendre & Legendre 1998).

<table>
<thead>
<tr>
<th></th>
<th>PCA1</th>
<th>PCA2</th>
<th>PCA3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay-%</td>
<td>0.88</td>
<td>-0.20</td>
<td>-0.36</td>
<td>0.95</td>
</tr>
<tr>
<td>Li</td>
<td>0.76</td>
<td>-0.47</td>
<td>-0.07</td>
<td>0.81</td>
</tr>
<tr>
<td>Al</td>
<td>0.65</td>
<td>-0.12</td>
<td>0.51</td>
<td>0.69</td>
</tr>
<tr>
<td>Fe-oxides</td>
<td>0.63</td>
<td>0.54</td>
<td>0.16</td>
<td>0.72</td>
</tr>
<tr>
<td>Mn-oxides</td>
<td>0.51</td>
<td>0.23</td>
<td>-0.06</td>
<td>0.32</td>
</tr>
<tr>
<td>TOC</td>
<td>0.42</td>
<td>0.45</td>
<td>0.53</td>
<td>0.66</td>
</tr>
<tr>
<td>Am. Fe-oxides</td>
<td>0.14</td>
<td>0.71</td>
<td>-0.54</td>
<td>0.81</td>
</tr>
<tr>
<td>Coarse silt-%</td>
<td>-0.94</td>
<td>0.15</td>
<td>0.19</td>
<td>0.94</td>
</tr>
<tr>
<td>% of variation</td>
<td>3.5</td>
<td>1.3</td>
<td>1.0</td>
<td></td>
</tr>
</tbody>
</table>

The results of the principal component analysis are strongly dependent on the variables included in the analysis. Therefore, the strong effect of grain size indicators (clay-%, coarse silt-%, Al, Li) is partly a result of the variable selection process. Some direction of variation that is only represented by one

Figure 11. Site scores of the first three principal components of the Gräsanoja dataset.
variable is probably overshadowed by directions represented by several variables.

4.1.2. Areal dataset

In the principal component analysis of the areal dataset two factors were extracted which together explained 65% of the variation in the dataset. The first component (PCA1) was positively related to clay-%, Al, Li and Mn, and negatively related to TOC (Fig. 12). Usually clay aggregates are flocculated to form flocs composed of soil particles, organic matter and metal oxides. Therefore, a positive relationship is generally observed between organic matter and decreasing particle size (Borovec 2000; Lin et al. 2003). However, here the fine grained soil particles were deposited mainly as soil aggregates instead of flocs. Thus, this component reflected the occurrence of clay rich soil aggregates in the sediment (soil aggregate component). The observed behavior implies that, the accumulation of fine grained mineral material may be due to very strong supply of soil material through erosion: channel erosion, or enhanced surface erosion, as a result of for example construction activities.

The second component (PCA2) attained highest loading on Fe followed by TOC. The component was called the floc component, since it reflected the accumulation of flocs composed of Fe and organic matter. The weak positive loadings of Al and Li on the component indicate the weak tendency of clay minerals to be incorporated in flocs. The variation related to this component was, however, much weaker when compared to the soil aggregate component, and its effect on the sediment composition may be easily overshadowed by the soil aggregate component.

The intensity of urbanization appeared to be weakly related to the scores of the first principal component (Figure 12). The densely built urban areas attained lower scores than the non-urbanized or low density residential catchment. The difference between the two groups was statistically significant (p<0.05), when determined using the Mann Whitney U-test.

According to correlation analyses (results not shown here) sediment components of the areal dataset were not related to the percentages of surficial sediment types or topographical variables.

5. Metal concentration results

5.1. Metal concentrations

5.1.1. Baseline concentrations

The baseline sites of both datasets were combined to present the baseline concentrations of metals. Concentrations were slightly lower in the outskirts of the metropolitan region but, overall, the concentrations exhibited relatively low variation (Figure 13). The average acid extractable metal concentrations...
of the nine background sites were for Zn 108 mg/kg, for Cu 24.0 mg/kg, for Pb 12.1 mg/kg and for Cd 0.22 mg/kg.

5.1.2. Metals at the urban sites

The acid extractable metals in the silt and clay fraction (<63 µm) displayed high variability of concentrations among the urban sites of both datasets (Fig. 14). The differences between the two datasets were relatively low, and the average concentrations of the datasets were close to one another. All metals showed very high concentrations at several sites. Which sites were exceptionally enriched varied, however, according to the metal in question. In the sand fraction, Cu and Zn concentrations were on the average slightly lower than in the silt and clay fraction, although the range of concentrations was very high. The concentrations of the metals in the easily reducible phase (in mg/kg) of the silt and clay fraction ranged between 9–218 for Zn, 0.01–7.6 for Cu, 0.08–0.75 for Cd and 0.02–10.5 for Pb (Fig. 26).

5.2. Metal enrichment at the urban sites

The standardized metal concentrations were utilized to calculate the enrichment factors over baseline (Fig. 15). The metals showed mostly moderate contamination signals in both datasets. The sediments appeared to be most enriched with respect to Cu. More than 30% of the sites showed significant or a very strong pollution signal (EF>5). The sediments appeared to be the least contaminated with Cd and Pb. In the Gräsanoja dataset in particular over 40% of the sites showed no pollution signal with respect to Pb (EF<2). The median enrichment factors of the metals were 4.2 and 4.4 for Cu, 3.5 and 3.9 for Zn, 2.0 and 2.8 for Pb and 2.3 for Cd in the Gräsanoja dataset and the areal dataset, respectively.

The enrichment factors for easily reducible phase of the metals were 4.2 and 4.4 for Cu, 3.5 and 3.9 for Zn, 2.0 and 2.8 for Pb and 2.3 for Cd in the Gräsanoja dataset and the areal dataset, respectively.
Figure 14. Boxplot of the acid extractable metal concentrations of urban sites in the two datasets. The box represents the 25th percentile, median and the 75th percentile. The bars indicate the minimum and maximum values.

Figure 15. Ranking of the urban sites to different pollution categories according to enrichment factors of acid soluble metal concentrations.
ble Cu and Pb were considerably higher than for acid extractable concentrations (Fig. 16). More than 60% of the sites for Cu and 30% of the sites for Pb appear to be significantly, very strongly or extremely polluted. For Zn and Cd the enrichment was higher for acid extractable concentrations.

5.4. Comparison to soil screening values and dredged material quality guidelines

In absence of appropriate sediment quality guidelines, the sediment metal concentrations were compared to quality guidelines proposed for soil and dredged material (Fig. 17 and 18). Unstandardized metal concentrations were used to compare the results with the soil screening values, while comparison with the dredged material quality guidelines was carried out using standardized metal concentrations. The results indicate that the Pb concentrations of the sediments were mostly below the threshold level of soils and the intervention level of dredged material. Cd concentrations are also mostly unpolluted according to soil screening values, but 40 and 55% of the sites are possibly polluted according to the quality criteria for dredged material. Both quality guidelines indicate that the sediments are substantially more polluted with respect to Cu and Zn. The comparison with soil screening values suggests that the Cu concentrations of the sediments are less than the threshold value at more at 50% of the sites. However, the Cu concentrations exceed the upper guideline level (proposed for industrial/commercial and traffic areas) at some sites. According to the soil screening values, the sediments are most polluted with Zn. More than 70% of the sites in both datasets show Zn concentrations that exceeded the lower guideline value defined for residential and recreational sites. The comparison of Cu and Zn concentrations to the quality criteria for dredged material further indicates that the sediment may be polluted at almost all sites.

The sites of the Gräsanoja dataset were further ranked as hazard classes according to the metal concentrations in relation to the dredged material quality guidelines (Fig. 19). The sites of the hazard classes 1-3 can be denoted as sites of concern, since these sites are associated with a potential hazard due to high metal concentrations. In this study, the metals that were responsible for the hazard potential were Zn but particularly Cu. The sites of concern are located in the urban headwater streams as well as in the lower reaches of the main channel. The forested, agricultural and low density residential areas show mostly only weak signs of potential hazard (class 0). The results further indicate, that high hazard potential is found at only three sites. At the site located in the estuary
the potentially high hazard is primarily due to the exceptionally high binding capacity of the organic rich and fine-grained sediment.

6. Results of the spatial and temporal variations

6.1. Variation across scales

The variation of trace metals at the fine spatial and temporal scales were compared to the corresponding variations within all urban sites of the Gräsanoja dataset. The fine-scale spatial variations of acid extractable trace metals (Fig. 20) were mostly low and nearly of the same order as the analytical variation (Fig. 20). The fine-scale variations were generally lower than the differences between the replicate sites, and between randomly selected sites in the Gräsanoja dataset (Fig. 21). Thus, the fine-scale variations of acid extractable metals were unlikely to be responsible for major spatial differences in the data. The fine scale variations of the metals were somewhat higher in the easily re-
ducible fraction than in the acid extractable fraction (Fig. 22). However, the concentrations showed very strong variations within the urban sites, and the fine-scale spatial variations played no role in the ability to interpret spatial trace metal patterns (Fig. 21).

The temporal variation between two base flow sampling campaigns was considerably higher than the fine-scale variation for all trace metals (Fig. 20). This result suggests that small spatial differences in metal concentration between sampling sites do not have a meaningful interpretation. The temporal variations of the easily reducible metals, particularly CuER and PbER, may be very high (Fig. 22). However, figure 23 shows that the temporal variations are unlikely to mask major broad-scale spatial variations.

6.2. Spatial autocorrelation

Trace metals received moderately high positive values of Moran's I in the shortest distance lags, which suggests moderate spatial dependence (Figure 24). However, none of the autocorrelation values were statistically significantly higher than the expected value under the null hypothesis of no spatial autocorrelation. This may be related to the low number of site pairs particularly in the shortest distance lag (20 pairs). The correlo-

Figure 19. Ranking of study sites to hazard classes in the Stream Gräsanoja. Class 0: no or weak indication of hazard, class 1: indication of potential hazard, class 2: higher certainty that hazard is present, class 3: indication of potentially high hazard.
grams suggest that weak spatial dependence exists despite the lack of significance. For Cu and Pb the strongest spatial autocorrelation extends to 0.75 km, for Cd to 1 km and for Zn 1.25 km distance.

The spatial autocorrelations of standardized metal concentrations were somewhat weaker especially for Cu and Cd. No statistically significant spatial autocorrelation was recorded, although some weak autocorrelation appeared to extend to 0.75 km for Cu, Zn and Pb and 1 km distance for Cd.

The residuals from the sediment composition model were also tested for statistical autocorrelation in order to show how much of the local spatial pattern is attributable to other factors than sediment composition (the residuals show that part of metal concentration variations that is independent of sediment composition). The values of Mo-

Figure 20. Fine-scale spatial and temporal variation of trace metals (both analytical replicates shown).

Figure 21. Variation between the fine-scale spatial replicates at seven sites (circles), and the distribution of the variation between two randomly selected urban sites in the Gräsanoja dataset. The box represents the 25th percentile, median and the 75th percentile. The bars indicate the minimum and maximum values.
ran’s I for the residuals show that the spatial autocorrelation is weak for Cu, Zn and Cd, whereas Pb shows spatial autocorrelation at the two shortest distance lags (Fig. 25). No statistically significant autocorrelation was measured for the residuals.

Figure 22. Fine-scale spatial and temporal variation of easily reducible metal concentrations.

Figure 23. Variation between the temporal replicates at seven sites (circles), and the distribution of the variation between two randomly selected urban sites in the Gräsanoja dataset. The box represents the 25th percentile, median and the 75th percentile. The bars indicate the minimum and maximum values.
Figure 24. Spatial correlograms (Moran’s I) for metal concentrations and standardized metal concentrations (both log-transformed).
7. Results of the control of sediment composition on metals

7.1. Control of sediment composition on acid extractable metals in the Gräsanoja dataset

7.1.1. Regional variations

Principal component analysis was used to study and graphically represent the relationships between acid extractable metals and sediment components (Fig. 26). The first two components, which explained 57% of the variation, reflected the association of metals with sediment components. The first component was strongly positively related to all of the metals as well as most of the sediment components. Only coarse silt-% was strongly negatively related to this component. The axis represents the primary association of metals with fine grained sediments rich in organic matter and metal oxides. The second principal component (24% of variation) was also positively related to all of the metals. Sediment components defined by this component were coarse silt-% (positive loading) and clay-%, Al, Fe-oxides and Mn-oxides (negative loading). When the fine grained sediment is not associated with high organic matter content, the component reflects the tendency of fine grained sediments to contain low metal concentrations.

The correlations between metals and sediment components support the graphical representation of the PCA analysis (Appendix 2). However, nearly all of the correlations were non significant, due to the small amount of independent observations estimated. The most important sediment parameter controlling the metal concentrations was TOC for Cu, Zn and Cd. For Pb, the impact of sediment composition appeared to be very complex. Clay-% did not play an important role in defining the acid extractable metal concentrations.

7.1.2. Fine-scale spatial and temporal variation

The control of sediment composition on the fine-scale spatial and temporal variation of metals was studied by calculating the partial correlograms (Fig. 25). The correlograms show the spatial autocorrelation of the residuals of the sediment composition models for Cu, Zn, and Cd. The correlograms indicate the spatial relationships between the metals and the sediment components.

Figure 25. Spatial correlograms (Moran’s I) for the residuals of the sediment composition models of metals.
correlations between sediment components and metals, controlling for the effect of variations between sampling sites. The results were more variable than at the regional scale. The most consistent pattern is the negative correlation of coarse silt-% with all metals. The correlation matrix demonstrates that Cu and Zn concentrations were positively related with sediments composed of organic matter and Fe-oxides (Table 9). Pb and Cd did not demonstrate the positive dependence on TOC, making the results different to those of Cu and Zn.

The temporal variations of Cu, Zn and Pb were also strongly related to the changes in the TOC content of the sediment (Table 9). In addition, Fe- and Mn-oxides were related with the concentrations of Zn and Pb.

7.2. The effect of sediment composition on trace metals in the areal dataset

The relationships between metals and sediment components were summarized and graphically represented using principal component analysis (Fig. 27). Two components were extracted and, accounted for 63% of the total variation. The first component is closely positively related with all metals and TOC, and strongly negatively related with Clay-%. Li, Al and Mn were also negatively associated with the first component. The component probably reflects the impact of recent soil erosion on metal concentrations. These fine grained sediments dilute both the trace metal and organic matter concentrations in the sediment. Consequently metal concentrations are closely associated with organic matter and negatively related with properties indicating fine grained sediment.

The second principal component was most strongly related to Li and Al which reflect the abundance of clay minerals. The component was also positively related to Clay-%, Mn and Fe as well as all metals. Highest loading was attained by Cd, lowest by Cu. The component reflects the association of metals with fine grained rather than coarse grained sediments if the sediments contain an equal amount of organic matter.

The correlations further revealed that the most important sediment parameter affecting the metal concentrations was TOC that
showed significant positive correlation with all metals. In addition, the metals correlated statistically significantly with Clay-% (negative relationship) (Appendix 3).

The results of both the principal component and correlation analyses show that the metals had relatively similar relationships with the sediment components. This is because the metals shared a common spatial distribution between sampling sites, since the correlations between metals were mostly relatively high ($r>0.48$). Highest correlation was observed between Cu and Zn ($r=0.87$).

![Figure 27. PCA analysis of metals and sediment components in the areal dataset.](image)

Table 9. Partial correlations between sediment components and metals for the spatial and temporal replicates (<63µm fraction), controlling for the effect of concentrations differences between sampling sites (df=5).

<table>
<thead>
<tr>
<th></th>
<th>Fine-scale spatial variation</th>
<th>Temporal variation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>log$_{10}$Cu</td>
<td>log$_{10}$Zn</td>
</tr>
<tr>
<td>TOC</td>
<td>0.90</td>
<td>0.75</td>
</tr>
<tr>
<td>Am. Fe-oxides</td>
<td>0.65</td>
<td>0.58</td>
</tr>
<tr>
<td>Fe-oxides</td>
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<td>0.76</td>
</tr>
<tr>
<td>Mn-oxides</td>
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<td>0.08</td>
</tr>
<tr>
<td>Clay-%</td>
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<td>0.41</td>
</tr>
<tr>
<td>Coarse silt-%</td>
<td>-0.10</td>
<td>-0.47</td>
</tr>
<tr>
<td>Al</td>
<td>-0.72</td>
<td>-0.52</td>
</tr>
<tr>
<td>Li</td>
<td>-0.47</td>
<td>-0.42</td>
</tr>
</tbody>
</table>
7.3. Metal partitioning in the Gräsanoja dataset

7.3.1. Metal concentrations in different binding phases

On the average, the easily reducible phase constituted 50% (range 19.7–94.4%) of the acid extractable Cd, 17% (range 5.2–29.5%) of Zn, 2.5% (range 0.2–19.6%) of Pb and 1.4% (range 0.0–8.3%) of Cu. Hence, Cd and Zn appeared to be distinctly more mobile compared to Cu and Pb.

A large proportion of Cu and Zn appeared to be associated with the pseudoresidual phase (on the average 29.7% of Zn and 39.8% of Cu) (Figure 28). According to the results of the selective extraction, Zn was preferentially bound to the metal oxides (on the average 47.0%), and it was found to partition in the order residual = reducible > easily reducible > organic phase. Cu on the other hand showed a strong tendency to be associated with organic compounds (on the average 39.9%), and it partitioned in the order residual = organic > reducible > easily reducible phase.

Although the proportions bound to different phases varied somewhat among the sites, the variations of Cu and Zn in most of the operational phases followed closely the acid extractable metal concentrations closely. Hence, the concentrations of metals in all phases increased with increasing acid extractable metal concentration and the proportions of Cu and Zn between the operational phases were quite stable over the study area. In the headwater reaches of the main channel Cu was, however, strongly bound to the reducible phase and the proportion bound to the organic phase was lower than elsewhere. On the contrary, the proportion of Cu in the residual phase was low compared to other sites in the coarse-grained sediments of sites 8 and 9 as well as at sites 20–22. For Zn, the spatial variations of the relative importance of different binding phases were equally small. The proportion of the residual phase can be assumed to be exceptionally low at sites 8 and 9, since the sum of Zn in the three most mobile phases was even greater than the acid extractable Zn concentration.

Table 10. Correlation coefficients between sediment components and arcsine-transformed metal proportions in different binding phases. Degrees of freedom for the calculation of statistical significance=22 (24–2). Bold text denotes significant correlations.

<table>
<thead>
<tr>
<th></th>
<th>TOC</th>
<th>FeER%</th>
<th>FeR</th>
<th>MnER%</th>
<th>Clay-%</th>
<th>Coarse silt-%</th>
<th>Li</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdER%</td>
<td>-0.51</td>
<td>0.24</td>
<td>-0.14</td>
<td>0.10</td>
<td>0.05</td>
<td>0.09</td>
<td>-0.22</td>
<td>-0.19</td>
</tr>
<tr>
<td>PbER%</td>
<td>-0.58*</td>
<td>-0.30</td>
<td>-0.59*</td>
<td>-0.34</td>
<td>-0.38</td>
<td>0.48</td>
<td>-0.37</td>
<td>-0.26</td>
</tr>
<tr>
<td>ZnER%</td>
<td>-0.23</td>
<td>0.22</td>
<td>-0.43</td>
<td>-0.21</td>
<td>-0.51</td>
<td>0.56*</td>
<td>-0.60*</td>
<td>-0.62*</td>
</tr>
<tr>
<td>ZnR%</td>
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<td>-0.03</td>
<td>-0.09</td>
<td>-0.42</td>
<td>0.38</td>
<td>-0.26</td>
<td>-0.21</td>
</tr>
<tr>
<td>ZnOrg%</td>
<td>0.03</td>
<td>0.05</td>
<td>0.12</td>
<td>0.24</td>
<td>0.06</td>
<td>0.01</td>
<td>-0.24</td>
<td>0.32</td>
</tr>
<tr>
<td>ZnRes%</td>
<td>0.15</td>
<td>0.09</td>
<td>0.21</td>
<td>0.11</td>
<td>0.57*</td>
<td>-0.59*</td>
<td>0.59*</td>
<td>0.40</td>
</tr>
<tr>
<td>CuER%</td>
<td>-0.67*</td>
<td>-0.14</td>
<td>-0.58*</td>
<td>-0.27</td>
<td>-0.25</td>
<td>0.37</td>
<td>-0.32</td>
<td>-0.36</td>
</tr>
<tr>
<td>CuR%</td>
<td>-0.25</td>
<td>-0.03</td>
<td>0.22</td>
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<td>0.25</td>
<td>0.03</td>
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<tr>
<td>CuRes%</td>
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<td>-0.04</td>
<td>0.28</td>
<td>-0.34</td>
<td>0.40</td>
<td>0.07</td>
</tr>
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</table>
7.3.2. Control of sediment composition on metals in different phases

The correlations between sediment components and metal proportions in different binding phases showed that easily reducible metals decrease with increasing TOC (Table 10). Furthermore, CuER% and PbER% have a negative relationship with FeR concentration. Fine grained sediments were positively associated with high proportions of Zn and Cu in the residual phase, which reflected the high metal concentrations of clay minerals. With decreasing grain-size the proportion of easily reducible Zn also decreased. While TOC had relatively low concentrations with the proportions of metals in the reducible, organic and residual phases, their corresponding concentrations were positively associated with increasing TOC.

8. Results of land use impacts on metals

8.1. Relationships between land use and sediment composition

In the areal dataset TOC was positively associated with urbanization, since the baseline sites showed statistically significantly lower TOC concentrations when compared with
the urban sites (Fig. 29). The baseline sites had higher proportions of the clay fraction. Within the urban sites, TOC was positively and clay-%, Li and Al negatively related to the percentage of high density residential areas (correlations not shown here). The rest of the correlations between land use and sediment composition were relatively low.

8.2. Relationships between land use and metal concentrations

8.2.1. Acid extractable metals in the Gräsanoja dataset

Based on figures 30 and 31 the association of trace metals with urbanization is evident. With the exception of a few sites, the suburban sites exhibited considerably higher metal concentrations when compared with the non-urbanized Stream Lukupuro.

Within the urban sites, metal concentrations showed substantial variation unrelated to the degree of urbanization (Fig. 31). Thus, the correlations between metals and urban land use were only moderate (Table 12). The percentages of dense urban areas and impervious surfaces were among the most important correlates. In addition, commercial and traffic areas were strongly related with Cu and Zn (Fig. 29). Within the urbanized areas, low density residential areas had a negative relationship with metal concentrations, which showed that low density residential areas contribute less to the metal load of streams compared to more densely built areas.

Within the urban sites, the metals correlated equally strongly with the land use metrics at the immediate upstream catchment scale when compared with the entire upstream catchment scale. The percentages of impervious areas of the riparian zone showed relatively high correlations when compared with the correlations at the entire and immediate upstream catchment scales (Table 11). Thus, the local land use appears to be important in the urban environment.

The spatial distribution of all metals was very similar, which suggests that these metals have primarily common sources in the study area. However, the metals had slightly different correlation patterns with land use metrics. The most distinct differences between the metals were the low standardized concentrations of Pb in the stream Merituulenoja compared to the high concentrations of Cu, Zn and Cd. The spatial distribution of metal concentrations (Fig. 30) further reveals that the Pb concentrations are exceptionally high at sites 11, 12, 14 and 15. This is related to the proximity of the sites to the heavily trafficked Turunväylä highway which is located nearby.
Figure 30. Spatial distribution of standardized acid extractable metal concentrations in the Stream Gräsanoja.
8.2.2. Easily reducible metals in the Gräsanoja dataset

The easily reducible concentrations of metals also demonstrated the association of metals with urban land use. Metal concentrations were generally higher at the urban sites than the non-urban sites in the Stream Lukupuro, although concentrations comparable to those of the Stream Lukupuro were also recorded at several urban sites (Fig. 32). High easily reducible metal concentrations were located close to densely built areas (high density residential, institutional, commercial and industrial areas), although the Cu and Pb seem to differ from Zn and Cd in the spatial distribution of the highest concentrations. Pb and Cu concentrations remained very high for a long distance downstream of the industrial area of Karasmalmi in the upper reaches of the main channel even though the areas surrounding the stream

<table>
<thead>
<tr>
<th></th>
<th>Cu&lt;sub&gt;st&lt;/sub&gt;</th>
<th>Zn&lt;sub&gt;st&lt;/sub&gt;</th>
<th>Cd&lt;sub&gt;st&lt;/sub&gt;</th>
<th>Pb&lt;sub&gt;st&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Entire upstream catchment</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban (%)</td>
<td>-0.01</td>
<td>0.15</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>Dense urban (%)</td>
<td>0.13</td>
<td>0.23</td>
<td>0.14</td>
<td>0.23</td>
</tr>
<tr>
<td>TIA (%)</td>
<td>0.14</td>
<td>0.22</td>
<td>0.09</td>
<td>0.30</td>
</tr>
<tr>
<td>EIA (%)</td>
<td>0.12</td>
<td>0.21</td>
<td>-0.00</td>
<td>0.21</td>
</tr>
<tr>
<td>Low density residential (%)</td>
<td>-0.22</td>
<td>-0.16</td>
<td>-0.20</td>
<td>-0.40</td>
</tr>
<tr>
<td>High density residential (%)</td>
<td>-0.03</td>
<td>0.16</td>
<td>0.12</td>
<td>-0.08</td>
</tr>
<tr>
<td>Institutional (%)</td>
<td>0.02</td>
<td>-0.00</td>
<td>0.07</td>
<td>0.22</td>
</tr>
<tr>
<td>Commercial &amp; traffic (%)</td>
<td>0.25</td>
<td>0.25</td>
<td>-0.05</td>
<td>-0.09</td>
</tr>
<tr>
<td>Industrial (%)</td>
<td>-0.01</td>
<td>0.11</td>
<td>-0.25</td>
<td>-0.04</td>
</tr>
<tr>
<td>TIA_Roofs</td>
<td>0.04</td>
<td>0.17</td>
<td>0.00</td>
<td>0.12</td>
</tr>
<tr>
<td>TIA_Transport areas</td>
<td>0.20</td>
<td>0.25</td>
<td>0.13</td>
<td>0.36</td>
</tr>
<tr>
<td>Traffic density</td>
<td>0.25</td>
<td>0.06</td>
<td>0.22</td>
<td>0.16</td>
</tr>
<tr>
<td>Population density</td>
<td>-0.07</td>
<td>0.17</td>
<td>0.06</td>
<td>-0.48</td>
</tr>
<tr>
<td><strong>Immediate upstream catchment (local)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urban (%)</td>
<td>0.16</td>
<td>0.22</td>
<td>0.22</td>
<td>0.01</td>
</tr>
<tr>
<td>Dense urban (%)</td>
<td>0.27</td>
<td>0.16</td>
<td>0.16</td>
<td>0.10</td>
</tr>
<tr>
<td>TIA (%)</td>
<td>0.21</td>
<td>0.14</td>
<td>0.22</td>
<td>0.04</td>
</tr>
<tr>
<td>Low density residential (%)</td>
<td>-0.12</td>
<td>0.15</td>
<td>0.15</td>
<td>-0.12</td>
</tr>
<tr>
<td>High density residential (%)</td>
<td>0.10</td>
<td>0.02</td>
<td>-0.00</td>
<td>-0.01</td>
</tr>
<tr>
<td>Institutional (%)</td>
<td>0.03</td>
<td>0.06</td>
<td>0.20</td>
<td>0.12</td>
</tr>
<tr>
<td>Commercial &amp; traffic (%)</td>
<td>0.29</td>
<td>0.12</td>
<td>0.19</td>
<td>-0.11</td>
</tr>
<tr>
<td>Industrial (%)</td>
<td>0.15</td>
<td>0.09</td>
<td>-0.07</td>
<td>0.30</td>
</tr>
<tr>
<td>TIA_Roofs</td>
<td>0.20</td>
<td>0.34</td>
<td>0.25</td>
<td>-0.09</td>
</tr>
<tr>
<td>TIA_Transport areas</td>
<td>0.19</td>
<td>0.08</td>
<td>0.19</td>
<td>0.07</td>
</tr>
<tr>
<td><strong>Land use of the local riparian zone</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TIA</td>
<td>0.26</td>
<td>0.29</td>
<td>0.29</td>
<td>0.16</td>
</tr>
</tbody>
</table>
Figure 31. Relationships of standardized metal concentrations with TIA and the percentage of commercial and traffic areas in the entire upstream catchment (land use percentages of the entire upstream catchment arcsine-transformed). Urban sites: open circles, agricultural and baseline sites: filled circles.
were dominated by low density residential housing. Zn and Cd also showed elevated concentrations in the headwater sites close to the industrial area, but concentrations decrease more rapidly in the downstream direction.

The easily reducible concentrations of all metals were relatively strongly correlated with the general indices of urbanization within the urban sites (Table 12). In addition, particularly Cu and Zn correlate positively with the percentages of commercial and traffic areas, and industrial areas. The correlations of the easily reducible metals were considerably stronger when compared with the results of the acid extractable metals.

Figure 32. Spatial distribution of easily reducible metals in the Stream Gräsanoja.
8.2.3. Areal dataset

The most striking difference in metal concentrations occurred between the unbuilt and the urban catchments (Fig. 33 and 34). While metal concentrations at the baseline sites were very low, all of the other land use groups, including the low density residential areas, showed statistically significantly higher metal concentrations (Fig. 33). The differences between the urban land use groups were fairly small, and the only statistically significant differences were recorded for Pb and Cu concentrations between the groups of low density residential areas and high density residential, institutional, commercial and traffic areas. Industrial sites showed the highest median concentrations of Zn, Cd and Pb. However, the industrial sites also showed highest variation of metal concentrations, and the concentrations did not differ statistically significantly from other urban land use types. The land use categories explained 56, 54, 45 and 39% of the standardized concentrations of Cu, Zn, Pb and Cd, respectively. For the urban sites the percentages were substantially lower, namely 18% for Cu, Pb and Cd and 6% for Zn.

Within the urban sites of the areal dataset correlations between metals and urban land use metrics were moderate (Table 13), and Cu, Pb and Zn concentrations increased with increasing density of urbanization. The correlations with metals were lower for the individual land use types, but the negative correlation between low density residential areas and metals shows that the dense urban land use types are essential for the occurrence of high metal concentrations within the urban catchments (Fig. 32).

The population density was weakly or negatively related with metals (Table 13). Since industrial, commercial and institutional areas decrease the correspondence between population density and metal concentrations, the correlations were calculated separately for the residential sites (where the residential areas accounted for more than 50% of the built-up areas). The correlations were not, however, substantially stronger except for Pb (the correlation coefficients were 0.06 for Cu, 0.21 for Zn, -0.06 for Cd and 0.37 for Pb).

The correlations were higher for the land use of the entire upstream catchment, when compared to the immediate upstream catchment (Table 13). This highlights the importance of the entire upstream catch-

<table>
<thead>
<tr>
<th>Land Use Category</th>
<th>CuER</th>
<th>ZnER</th>
<th>CdER</th>
<th>PbER</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban (%)</td>
<td>0.43</td>
<td>0.44</td>
<td>0.31</td>
<td>0.45</td>
</tr>
<tr>
<td>Dense urban (%)</td>
<td>0.27</td>
<td>0.43</td>
<td>0.36</td>
<td>0.29</td>
</tr>
<tr>
<td>TIA (%)</td>
<td>0.38</td>
<td>0.42</td>
<td>0.31</td>
<td>0.41</td>
</tr>
<tr>
<td>EIA (%)</td>
<td>0.38</td>
<td>0.41</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>Low density residential (%)</td>
<td>-0.06</td>
<td>0.27</td>
<td>0.13</td>
<td>0.04</td>
</tr>
<tr>
<td>High density residential (%)</td>
<td>-0.10</td>
<td>0.04</td>
<td>0.17</td>
<td>-0.00</td>
</tr>
<tr>
<td>Commercial &amp; traffic (%)</td>
<td>0.37</td>
<td>0.39</td>
<td>0.19</td>
<td>0.08</td>
</tr>
<tr>
<td>Institutional (%)</td>
<td>0.45</td>
<td>0.19</td>
<td>-0.09</td>
<td>0.22</td>
</tr>
<tr>
<td>Traffic density</td>
<td>-0.22</td>
<td>-0.03</td>
<td>0.04</td>
<td>-0.25</td>
</tr>
<tr>
<td>Population density</td>
<td>-0.18</td>
<td>0.27</td>
<td>0.03</td>
<td>-0.28</td>
</tr>
</tbody>
</table>

Table 12. Correlations between easily reducible metals and land use metrics of the entire upstream catchment for the urban sites of the Gräsanoja dataset (log-transformed metal concentrations and densities, arcsine-transformed land use percentages) (df=17).
ment in determining the quality of aquatic sediments.

8.2.4. The relationship of TIA with metals for both datasets

The graphical presentation of metal concentrations against TIA of the entire upstream catchment demonstrates that the changes in average metal concentrations are steeper with higher imperviousness (Fig. 35). The metal concentrations increase only modestly until TIA reaches 3-40% level, but considerable variation is present in the concentrations. Cd demonstrates very gently increasing trend with increasing TIA. However, the non-urban sites (TIA<15%) showed constantly low concentrations of all metals. With increasing TIA the metal concentrations become even more variable, and both very low and high values are recorded. Thus, high urbanization does not necessarily cause high metal concentrations, but, conversely, high concentrations that exceed the pollution level for Zn and Cu and intervention level for Cd and Pb are related to high imperviousness (TIA>30%). However, several high Pb concentrations occured even with very low levels of TIA, which indicates that factors causing Pb enrichment are not directly associated with the intensity of urbanization in the entire upstream catchment. Figure 35
further shows that the metal concentrations are not elevated at all industrial sites, but a high proportion (over 50%) of the industrial sites show metal concentrations above the pollution level (Cu and Zn) or intervention level (Cd and Pb).

### 9. Results of the modelling of the trace metal concentrations in urban catchments

#### 9.1. Linear regression models

The metal concentrations were modelled using one combined dataset, which included independent urban sites (urban >30%) from both datasets. From the Gräsanoja dataset, only 24 sites, separated by more than 750
Figure 34. Relationships of standardized metal concentrations with TIA and the percentage of low density residential areas in the entire upstream catchment (arcsine-transformed land use percentages). Urban sites: open circles, baseline sites: filled circles.
metres, were included in the model to avoid the lack of independence of observations.

Firstly, linear regression models were constructed using sediment composition variables and land use metrics as explanatory variables (Table 14). All of the models included TOC as explanatory variable. The rest of the variables varied between the metals. However, all of the models indicated that metal concentrations increased with increasing intensity of land use. The models were relatively unbiased and did not show substantial heteroskedasticity (Figure 36). However, several sites were identified as outliers. Most of these sites were, however, not influential, and were not discarded from the analyses. Some of the outlier (negative residual) sites may represent exceptional environmental conditions, such as very coarse grain size that cannot be accounted for by the model. The high positive residuals, on the other hand, are likely to reflect other metal sources in addition to the diffuse metal pollution from urban areas, represented by the bulk of the samples.

The models were evaluated using tenfold cross-validation. The predictive ability at sites not used for model construction appeared to
be moderate (Table 14). The coefficient of determination decreased substantially compared to the final model, but the Spearman's correlation coefficient between the observed and predicted values was more stable. Cu and Zn models showed less deterioration between the final model and the cross-validation compared to Pb and Cd. Thus, Cu and Zn concentrations can to some extent predicted at new unvisited sites based on the sediment composition and metal concentrations. This is also supported by the graphs representing the predicted median concentrations and observed concentrations of metals (Figure 37). The median value offers some indication of the metal concentration level at the site. However, the 5% confidence bounds for individual concentrations are very wide compared to the range of the predicted median concentrations.

Next, linear regression models were constructed for the standardized metal concentrations using land use metrics as explanatory variables (Table 15). The models explained only a low proportion of the total variation, since the coefficient of determination was less than 15% for Zn, Pb and Cd. The lower explanation power of the current models compared to the models described above is partly attributable to the fact that the sediment composition is accounted for using standardization instead of incorporation in the model. However, the results show that within the urban zone, metal concentration differences are not strongly determined by land use variations.

For validation data, the predictive performance of the models was even weaker (Table 15). The models failed to explain even a small percentage of the variation. For Cd no statistically significant explanatory variables were found for the calibration dataset, and thus no statistics for the validation dataset can be presented. Although the observed metal concentrations showed strong deviation from the predicted concentrations (Fig. 38), the Spearman's correlation coefficients indicated some correlation between the observed and predicted values. However, the correlations were smaller than for the final model.

The average bias of the land use-metal concentration models was slightly higher than the corresponding values for the land use-sediment composition-metal concentration models, which shows that the incorporation of the sediment composition in the models does provide better predictive performance compared to standardization of metal concentration according to the instructions given for dredged material.

Table 14. Linear regression models. Explanatory variables selected from the set of sediment composition variables and land use metrics (see Table 4 for the land use abbreviations). Evaluation of the models: coefficient of determination ($R^2$), Spearman's rank correlation coefficients ($r_s$) between observed and predicted values of the dependent variables and average absolute bias ($AB$). Land use percentages were arcsine-transformed and densities log10-transformed.

<table>
<thead>
<tr>
<th>Model formula</th>
<th>Final model</th>
<th>Cross-validation</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\log_{10}Cu = 1.515 + 0.004 \cdot \text{TOC} + 0.326 \cdot \text{COMM}_c + 0.146 \cdot \text{HDR}_b + 0.001 \cdot \text{Trafﬁc density}$</td>
<td>$R^2 = 0.42$ $r_s = 0.66^{***}$ $AB = 0.12$</td>
<td>$R^2 = 0.20$ $r_s = 0.55^{***}$ $AB = 0.14$</td>
</tr>
<tr>
<td>$\log_{10}Zn = 1.914 + 0.004 \cdot \text{TOC} + 0.292 \cdot \text{COMM}_c + 0.233 \cdot \text{TIA}_b + 0.006 \cdot \text{Li}$</td>
<td>$R^2 = 0.46$ $r_s = 0.67^{***}$ $AB = 0.10$</td>
<td>$R^2 = 0.27$ $r_s = 0.58^{***}$ $AB = 0.11$</td>
</tr>
<tr>
<td>$\log_{10}Pb = 1.229 + 0.004 \cdot \text{TOC} - 0.181 \cdot \text{LDR}_c + 0.001 \cdot \text{Trafﬁc density} - 0.226 \cdot \text{COMM}_b$</td>
<td>$R^2 = 0.36$ $r_s = 0.66^{***}$ $AB = 0.16$</td>
<td>$R^2 = 0.02$ $r_s = 0.36^{***}$ $AB = 0.19$</td>
</tr>
<tr>
<td>$\log_{10}Cd = -0.884 + 0.005 \cdot \text{TOC} + 0.431 \cdot \text{IND}_c + 0.010 \cdot \text{Li} - 0.180 \cdot \text{IND}_b$</td>
<td>$R^2 = 0.35$ $r_s = 0.57^{***}$ $AB = 0.13$</td>
<td>$R^2 = 0.02$ $r_s = 0.47^{***}$ $AB = 0.15$</td>
</tr>
</tbody>
</table>
9.2. Logistic regression models

The occurrence of concentrations higher than the dredged material quality guidelines was modelled using logistic regression. Thus, the occurrences of metal concentration above the pollution (Cu, Zn) or intervention level (Pb, Cd) were used as the dependent variables (CuHigh, ZnHigh, PbHigh, CdHigh), and logistic regression models were created using land use metrics as explanatory variables (Table 16). Using the complete dataset, final models were obtained for Cu, Zn and Pb. For Cd, no statistically significant variables were identified.

The predictive ability of the final model was good for Zn, while the models of Cu and Pb were poor according to Cohen’s Kappa (K). The model for Zn showed a high predictive ability. For Cu and Pb, the models were not as effective. Table 15 shows the results of the logistic regression models.

Table 15. Regression models of standardized metal concentrations (see Table 4 for the land use abbreviations). Evaluation of the models: coefficient of determination (R²), Spearman’s rank correlation coefficients (rs) between observed and predicted values of the dependent variables and average absolute bias (AB). Land use percentages were arcsine-transformed and densities log10-transformed.

<table>
<thead>
<tr>
<th>Model formula</th>
<th>Final model</th>
<th>Cross-validation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R²</td>
<td>rs</td>
</tr>
<tr>
<td>Log₁₀Cuₜₜ = 1.885 - 0.114 · LDRₜₜ + 0.163 · HDRₜₜ + 0.001 · Traffic density</td>
<td>0.24</td>
<td>0.53***</td>
</tr>
<tr>
<td>Log₁₀Znₜₜ = 2.266 + 0.493 · TIAₜₜ</td>
<td>0.12</td>
<td>0.40***</td>
</tr>
<tr>
<td>Log₁₀Pbₜₜ = 1.635 - 0.261 · LDRₜₜ</td>
<td>0.13</td>
<td>0.37**</td>
</tr>
<tr>
<td>Log₁₀Cdₜₜ = -0.313 + 0.276 · INDₜₜ</td>
<td>0.10</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Figure 36. Studentized residuals of the models linking metal concentrations to sediment composition and land use. Outliers: filled circles (G=Gräsanhoja dataset).
ppa or moderate according to the coefficient of AUC (Table 16). The values of positive prediction power show that the proportion of present sites (those, where observed concentration exceeds the guideline) among the sites that were predicted to be present sites is considerable higher than among the complete dataset. However, only 64–67% of all the sites were correctly predicted.

The models were then evaluated by calculating the predicted probabilities of guideline exceedance using tenfold cross-validation. The models, particularly that for Pb, showed some deterioration compared to the final model (Table 17). However, the logistic regression model of Zn performed almost equally as well. The predictive capacity of the Zn-models remained moderate-good even when applied to data not used in the calibration of the models. Both the threshold independent AUC and kappa that used the prevalence cutoff indicated poor performance for Cu and Pb. However, the more detailed investigation of the statistics reveals that the Cu model performs slightly better than the very poor model of Pb. The predicted presences or absences of Pb guideline exceedance seem to be no better than those obtained by chance. The proportion of actually present sites in the group predicted
to be present is nearly the same as in the complete dataset. Thus, the model does not appear to provide any potential for screening of the data for the occurrence of guideline exceedance. Cu model, on the other hand, does not show any better overall performance, but the grouping of sites according to the predicted presence or absence does produce some concentration of actually present sites to the group predicted to be present.

10. Results of the differences between mud and sand size fraction

The sand fraction (63-200µm) left on the sieve was analysed for some sediment parameters in order to estimate the impact of sieving on the reliability of the results. The concentrations of trace metals were measured from the sand fraction, and the concentrations were on the average between 70 and 77% of the concentrations in the mud fraction (Figure 14). Thus, the somewhat lower trace metal concentrations reflect the diluting effect of the sand fraction, i.e. the lower trace metal concentrations and bind-

![Figure 38. Observed metal concentrations and the median predicted concentration from the 10-fold cross-validation (explanatory variable group: land use).](image-url)
ing capacity of the coarse grained sediment particles.

Sediment composition had a stronger influence on trace metal concentration in the sand fraction compared to the mud fraction (Table 18). Metal concentrations were highest in sediments containing abundant organic matter, corresponding with the results of the silt and clay fraction. Furthermore, metal concentrations appear to increase within decreasing grain size (Al, Li) and increasing Fe and Mn concentrations, which were not observed in the finer fraction.

The control of sediment composition on the fine scale variation was also stronger for the sand fraction (Table 18), since most of the correlations were statistically significant. In the sand fraction, Cu and Zn correlated strongly with Fe, Mn and Al, which reflects the importance of sediment grain-size, and

<table>
<thead>
<tr>
<th>Dependent variable</th>
<th>Cust &gt; pollution level</th>
<th>Znst &gt; pollution level</th>
<th>Pbst &gt; intervention level</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model formula</td>
<td>LP=-1.897 +2.101-HDR_b +0.01-Traffic density</td>
<td>LP=-21.854 +11.746-TIA_b +6.186-LDR_c +8.713-HDR_c +15.433-COMM_c +5.885-IND_b</td>
<td>LP=-0.756 -2.978-LDR_c +1.677-LDR_b +2.599-IND_b</td>
</tr>
<tr>
<td>AUC</td>
<td>0.755** (moderate)</td>
<td>0.917*** (very good)</td>
<td>0.752** (moderate)</td>
</tr>
<tr>
<td>Cutoff threshold</td>
<td>0.58</td>
<td>0.15</td>
<td>0.26</td>
</tr>
<tr>
<td>Kappa</td>
<td>0.277** (poor)</td>
<td>0.426*** (good)</td>
<td>0.278** (poor)</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>0.57</td>
<td>0.83</td>
<td>0.67</td>
</tr>
<tr>
<td>Specificity</td>
<td>0.74</td>
<td>0.78</td>
<td>0.67</td>
</tr>
<tr>
<td>Positive prediction</td>
<td>0.75</td>
<td>0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>Accuracy</td>
<td>0.64</td>
<td>0.79</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Table 17. Predictive performance of the logistic regression models in the 10-fold cross-validation (the evaluation data was not used for model construction). AUC=area under the curve.
the occurrence of clay minerals and Fe-oxides. Organic matter was, however, not as strong a control on metals as in the mud fraction.

The fine-scale spatial variation of the sand fraction appeared to be slightly greater than that of the mud fraction (<63µm). However, due to the high variations between sites in the sand fraction, the fine-scale variations did not strongly interfere with the interpretation of spatial patterns in metal concentration data. The analytical variation is also higher in the sand fraction compared to the more homogeneous mud fraction (Fig. 39), but these variations are also overshadowed by the strong regional variations of metals in the sand fraction.

The correlations of trace metals with the land use variables were of the same magnitude when compared to the mud fraction, although there were some differences between the two size fractions (Table 19). Particularly the general indicators of urbanization (TIA and percentages of urban and dense urban land use) were more weakly related with metals in the sand fraction.

**Table 18. Correlations of Cu and Zn with sediment components in the sand fraction (entire data, degrees of freedom=18) and partial correlations between sediment components and Cu and Zn for the spatial replicates (sand fraction), controlling for the effect of concentrations differences between sampling sites (df=5).**

<table>
<thead>
<tr>
<th></th>
<th>Entire data</th>
<th>Spatial replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log₁₀Cu</td>
<td>Log₁₀Zn</td>
</tr>
<tr>
<td>Organic matter</td>
<td>0.73**</td>
<td>0.75**</td>
</tr>
<tr>
<td>Fe</td>
<td>0.61*</td>
<td>0.71**</td>
</tr>
<tr>
<td>Mn</td>
<td>0.43</td>
<td>0.49</td>
</tr>
<tr>
<td>Al</td>
<td>0.37</td>
<td>0.37</td>
</tr>
<tr>
<td>Li</td>
<td>0.54*</td>
<td>0.57*</td>
</tr>
</tbody>
</table>

11. Water analysis results

11.1. Water chemistry and trace metal concentrations

The waters of the sampling sites in the areal dataset were generally of near neutral pH, well oxygenated and had moderate conductivity (Table 20). During the snow-melt period, however, several sites, both baseline and urban sites, were acid with pH of less than five. During the low-flow period only one baseline sites had pH lower than five. The snow-melt period also demonstrated lower electrical conductivity and higher SPM concentration and oxygen content than the summer low-flow period. The baseline sites showed lower pH-values (<7.1 during the low-flow period and <5.6 during the snow-melt period) and considerably lower electrical conductivity when compared to the urban sites.

All of the metal concentrations, except dissolved Pb and Cd, were higher in the high-flow than low-flow samples. The trace metal concentrations of the suspended particulate matter associated with snow-melt period were higher than the bed sediment metal concentrations, while the low-flow concentrations were mostly comparable to the sediment concentrations (Table 21). Cu, Cd and Pb showed higher association with the particulate phase during the snow-melt
period, while there was no difference in the partitioning of Zn between the two sampling campaigns.

Pb showed very strong affinity to the solid phase, and during the snow-melt period it was almost completely associated with the particulates (Table 21). Cd showed similar tendency to occur in the particulate phase during the high-flow period, although the proportion of dissolved Cd was considerable during the low-flow period. Cu was the element showing the weakest association with the particulates.

The sediment metal concentrations appeared to be fairly strongly associated with the high-flow metal concentrations of SPM and water phase (Table 22). The relationship was relatively strong for SPM metal concentrations even during the low-flow conditions.

Table 19. Correlations between land use variables (entire upstream catchment) and metal concentrations in the sand (63µm-2mm) fraction of the urban sites in the Gräsanoja dataset. Land use percentages are arcsine-transformed and traffic density log10-transformed.

<table>
<thead>
<tr>
<th>Land use variable</th>
<th>Log$_{10}$Cusand</th>
<th>Log$_{10}$Znsand</th>
<th>Log$_{10}$Cdsand</th>
<th>Log$_{10}$Pbsand</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urban (%)</td>
<td>0.01</td>
<td>-0.25</td>
<td>-0.11</td>
<td>0.05</td>
</tr>
<tr>
<td>Dense urban (%)</td>
<td>0.19</td>
<td>-0.15</td>
<td>-0.02</td>
<td>0.19</td>
</tr>
<tr>
<td>TIA (%)</td>
<td>0.17</td>
<td>-0.06</td>
<td>-0.01</td>
<td>0.28</td>
</tr>
<tr>
<td>Low density residential (%)</td>
<td>-0.34</td>
<td>0.05</td>
<td>-0.06</td>
<td>-0.24</td>
</tr>
<tr>
<td>High density residential (%)</td>
<td>0.08</td>
<td>-0.03</td>
<td>-0.11</td>
<td>-0.05</td>
</tr>
<tr>
<td>Institutional (%)</td>
<td>0.06</td>
<td>-0.08</td>
<td>-0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>Commercial &amp; traffic (%)</td>
<td>-0.05</td>
<td>0.39</td>
<td>0.25</td>
<td>0.27</td>
</tr>
<tr>
<td>Industrial (%)</td>
<td>-0.03</td>
<td>0.11</td>
<td>-0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>Traffic density</td>
<td>0.04</td>
<td>0.28</td>
<td>0.23</td>
<td>0.28</td>
</tr>
</tbody>
</table>
11.2. Controls on metal concentrations in the water phase and SPM

The differences in SPM metal concentrations between catchments dominated by different land use types showed that the major differences in metal concentrations were caused by distinctions between the baseline and urban sites (Fig. 40). With the exception of Pb during the low-flow period, the SPM metal concentrations were statistically significantly lower at the baseline sites when compared with the urban sites. In the high-flow samples there were also significant differences between the urban land use categories for all metals with industrial sites showing higher metal concentrations than the other two urban types. Furthermore, Cu was significantly lower in the low density compared to high density residential, institutional and commercial areas.

The total aqueous metal concentrations were lower in the baseline sites when compared with the urban sites for Cu and Zn during high-flow conditions (Fig. 41). In the low-flow samples no statistically significant differences between the land use categories were observed. High-flow Cu and Zn also showed the most distinct differences between different urban land use types. For these metals, industrial areas showed significantly higher concentrations than the low density residential areas. For Cu, there was also a difference between the low density residential areas and the high density residential, institutional and commercial areas.

Within the urban sites, the metal concentrations of SPM showed substantially higher correlations with the percentage of impervious surfaces during the high-flow conditions when compared with low-flow conditions.

Table 20. Median and range (in parenthesis) of water quality parameters of the entire areal dataset

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low-flow period</th>
<th>Snow-melt period (high flow)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>7.09 (4.87–8.45)</td>
<td>6.94 (4.17–7.97)</td>
</tr>
<tr>
<td>Electrical conduct-</td>
<td>424 (52–1460)</td>
<td>331 (55–2151)</td>
</tr>
<tr>
<td>ivity (µS/cm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diss O$_2$ (%)</td>
<td>74 (34–140)</td>
<td>92 (61–120)</td>
</tr>
<tr>
<td>SPM (mg/l)</td>
<td>16.8 (3.1–74.1)</td>
<td>51.3 (0.6–399)</td>
</tr>
</tbody>
</table>

Table 21. Median and range (in parenthesis) of acid extractable metal concentrations in water (total concentration in water = particulate + dissolved) and suspended particulates (SPM), in addition to the particulate and dissolved metal concentrations and the proportion of particulate metals in the areal dataset.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Low-flow</th>
<th>Total conc. in water (µg/l)</th>
<th>Particulate (µg/l)</th>
<th>Dissolved (µg/l)</th>
<th>Particulate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>Low-flow</td>
<td>106 (7.1–594)</td>
<td>9.1 (1.9–16.9)</td>
<td>1.5 (0.2–5.9)</td>
<td>7.3 (1.8–11)</td>
</tr>
<tr>
<td></td>
<td>High-flow</td>
<td>237 (21.0–1780)</td>
<td>18.9 (2.3–61.7)</td>
<td>12.4 (0.1–47.0)</td>
<td>9.0 (1.3–27.3)</td>
</tr>
<tr>
<td>Zn</td>
<td>Low-flow</td>
<td>476 (46.5–4194)</td>
<td>13.6 (3.3–70.9)</td>
<td>7.7 (0.9–61.5)</td>
<td>4.5 (1.5–110)</td>
</tr>
<tr>
<td></td>
<td>High-flow</td>
<td>829 (81.5–3141)</td>
<td>69.0 (7.5–479.5)</td>
<td>46.5 (0.4–159)</td>
<td>26.0 (1.9–320)</td>
</tr>
<tr>
<td>Pb</td>
<td>Low-flow</td>
<td>24.9 (0.07–213)</td>
<td>0.56 (0.02–2.26)</td>
<td>0.48 (0.002–2.22)</td>
<td>0.06 (&lt;0.02–1.1)</td>
</tr>
<tr>
<td></td>
<td>High-flow</td>
<td>45.6 (14.2–191)</td>
<td>2.3 (0.04–17.1)</td>
<td>2.8 (0.02–17.1)</td>
<td>0.02 (&lt;0.004–0.45)</td>
</tr>
<tr>
<td>Cd</td>
<td>Low-flow</td>
<td>1.1 (0.1–9.1)</td>
<td>0.04 (0.01–0.19)</td>
<td>0.02 (0.003–0.13)</td>
<td>0.02 (&lt;0.01–0.22)</td>
</tr>
<tr>
<td></td>
<td>High-flow</td>
<td>0.8 (0.3–4.9)</td>
<td>0.08 (0.02–0.35)</td>
<td>0.04 (0.0004–0.15)</td>
<td>0.03 (0.01–0.26)</td>
</tr>
</tbody>
</table>
The association of SPM metal concentrations with TIA was even stronger than that for the bed sediment. However, the metal concentrations of the bed sediment reflected the land use of the catchment better than low-flow SPM. The particulate, dissolved and total metal concentrations in water had mostly low correlations with TIA in the urban samples during both sampling periods (Fig. 42, Appendixes 5 and 6). However, total and dissolved Cu concentrations were closely related to the degree of urbanization during the high-flow period, and the correlations were only slightly lower than those for SPM.

Table 22. Correlations of sedimentary trace metal concentrations with the corresponding metal concentrations in water and SPM (log-transformed concentrations).

<table>
<thead>
<tr>
<th></th>
<th>Correlation: Sediment–SPM</th>
<th>Correlation: Sediment–total concentration in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low-flow</td>
<td>High-flow</td>
</tr>
<tr>
<td>Cu</td>
<td>0.62***</td>
<td>0.71***</td>
</tr>
<tr>
<td>Zn</td>
<td>0.67***</td>
<td>0.73***</td>
</tr>
<tr>
<td>Pb</td>
<td>0.18</td>
<td>0.59***</td>
</tr>
<tr>
<td>Cd</td>
<td>0.49***</td>
<td>0.42**</td>
</tr>
</tbody>
</table>

Figure 40. The influence of the dominant land use type of the catchment on SPM metal concentrations in the areal dataset during low- and high-flow (snow-melt) periods. The box represents the 25th percentile, median and the 75th percentile. The bars indicate the minimum and maximum values.
those for SPM and bed sediment. Contrary to the other metal concentrations, the dissolved Pb had a negative association with urbanization in the high-flow samples. In the baseflow samples SPM metal concentrations decreased with increasing suspended sediment concentrations (Table 23). This was probably a result of metal dissolution via erosion. The metal concentrations in water were, on the other hand, positively related to SPM reflecting increasing particulate metal concentration.

During the high-flow period SPM metal concentrations were related to the electrical conductivity of water, which is predominantly a reflection of the differences between baseline and urban samples, since baseline sites are associated with low electrical conductivity and SPM metal concentrations.

During the high-flow sampling campaign the discharge conditions and the areas contributing discharge changed somewhat, although the snow melted almost gradually during the sampling period. The suspended sediment concentrations increased at the urban sites towards the end of the period with corresponding increases in pH. The total metal concentrations of the water phase were strongly related to the SPM concentration, which shows the importance of particulate metals in controlling the variations of total metal concentrations. Hence, increasing suspended matter concentration tends to increase the total amount of metals in the water. The metal concentrations were also strongly related to pH, which is prob-

![Figure 41. The influence of the dominant land use type of the catchment on total metal concentrations in water in the areal dataset during low- and high-flow (snow-melt) periods. The box represents the 25th percentile, median and the 75th percentile. The bars indicate the minimum and maximum values.](image)
ably a result of the similar temporal variations of SPM and pH during the sampling campaign.

12. Discussion

12.1. Sediment composition

12.1.1. The influence of surficial deposits

The stream bottom sediment is a composite of materials derived from a variety of sources and from different parts of the catchment. The characteristics of the sediment material of each source and the relative contribution of different sources influence the eventual characteristics of sediments deposited on the

Table 23. Correlations of metal concentrations in water (total concentration) and SPM with water quality parameters in low-flow and high-flow samples. Metal concentrations, SPM and electrical conductivity log-transformed.

<table>
<thead>
<tr>
<th></th>
<th>Low-flow period</th>
<th></th>
<th>High-flow period</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH</td>
<td>Electrical conductivity</td>
<td>SPM</td>
<td>pH</td>
</tr>
<tr>
<td>Cu</td>
<td>0.23</td>
<td>0.17</td>
<td><strong>-0.39</strong></td>
<td>0.06</td>
</tr>
<tr>
<td>Water (µg/l)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>0.26</td>
<td>0.34*</td>
<td><strong>-0.40</strong></td>
<td>0.13</td>
</tr>
<tr>
<td>Water (µg/l)</td>
<td>-0.12</td>
<td>0.03</td>
<td>0.28</td>
<td><strong>0.54</strong>*</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.03</td>
<td>-0.17</td>
<td>-0.22</td>
<td>0.14</td>
</tr>
<tr>
<td>Water (µg/l)</td>
<td>-0.13</td>
<td>-0.26</td>
<td><strong>0.36</strong></td>
<td><strong>0.63</strong>*</td>
</tr>
<tr>
<td>Cd</td>
<td>0.07</td>
<td>0.06</td>
<td><strong>-0.48</strong></td>
<td>0.02</td>
</tr>
<tr>
<td>Water (µg/l)</td>
<td>-0.34*</td>
<td>-0.21</td>
<td>0.14</td>
<td><strong>0.58</strong>*</td>
</tr>
</tbody>
</table>
channel bed. These original sediment components have undergone various physicochemical and biological processes both in the water phase as well as within the sediment, which complicates the connections between sediment and the contributing catchment (Fig 1.).

The main sources of the inorganic sediment in lowland catchments include erosion of surface soils by water, channel erosion, resuspension of channel bed sediments, construction sites, the road network and material from point sources (Carter et al. 2003; Taylor et al. 2008). In most cases erosion of topsoil or channel banks is the dominating source of inorganic sediment (Carter et al. 2003; Taylor et al. 2008). Thus, the geology and geomorphology of the catchment have an impact on the characteristics of the sediment transported (Walling & Moorehead 1987). The sediments collected from the Stream Gräsanoja and its tributaries as well as the small streams of the areal dataset were relatively fine grained. The clay fraction accounted for approximately 20-25% of the mud fraction (clay and silt). A great majority of the bulk sediment belonged to clay, silt and sand size fractions (<2 mm), since the amount left on the 2 mm sieve was almost negligible. The fine sediment grain size is a reflection of the role of clays as one of the dominant surface sediment types in the Helsinki area. In addition, the sediments were collected from depositional areas of the streams, rather than transport or erosion sites where the sediment is composed primarily of sand and gravel were avoided.

Statistical relationships between surficial deposit type and stream sediment components could not be confirmed in the areal dataset. In the Gräsanoja dataset variations of proportions of different surficial deposit types were low, since bedrock and clay deposits dominate the entire catchment. Consequently, the variations of grain-size distribution were also weak. The results of this study indicate that in a geologically relatively homogeneous region, such as the Helsinki Metropolitan region, the rock and soil types of the catchment have a relatively low influence on the variations of bed sediment characteristics when compared with other catchment characteristics such as land use.

A few patterns of sediment characteristics in the Gräsanoja dataset could, however, be connected to the surficial sediments of the catchment. In the upper parts of the catchment the stream flows through a small coarse silt deposit. This is apparently associated with the strong supply of relatively coarse inorganic material to sediment with simultaneous decreases in the proportions of clay particles and organic matter. In addition, the stream has a steep gradient in the area, which is likely to further weaken the deposition of flocs and aggregates of fine mineral and organic sediment. The peat deposits located in the middle reaches of the main channel impact upon the organic component of the sediments, possibly in conjunction with the old waste landfill of the area. Water draining from these areas may be rich in dissolved/colloidal organic matter, Fe and Mn, which enhances the formation and settling of organo-metallic flocs (PCA2) in the main channel.

In the sediments of Lukupuro stream clay-% is high and principal components of flocs and aggregates (PCA1) as well as Al-minerals (PCA3) also show high loadings. The high amount of flocculated fine grained, organic and metal oxide rich material is related to the agricultural land use or gytta-dominated Quaternary sediments of the catchment. Erosion of organic rich fine grained soil material is likely to be eroded and transported to streams since extensive fields surround the main channel of Lukupuro. Furthermore, the input of fine grained sediment from the the Stream Lukupuro increased the proportion of fine sediment and other flocculated material in the lower reaches of the main channel. The sediments of Lukupuro also showed high loadings of Al-mineral component and the Al-concentrations of the sediments were very high when compared to Al-concentrations reported for clay soils of the area (Tarvainen &
This indicates very strong leaching of Al from the sulphide containing soils of the central parts of Lukupuro catchment (see Ojala & Palmu 2007).

The influence of surficial deposits was more easily discernible in the Gräsanoja dataset when compared to the areal dataset. It may be related to the fairly dense spatial sampling which enables the detection of gradual but relatively small changes in sediment composition. In the areal dataset with only one sample per catchment, the relationship between distinct surficial deposit types and sediment composition was more difficult to detect due to various disturbing factors, such as differences in abiotic and biotic conditions and anthropogenic effects.

12.1.2. Flocculation and soil aggregates

The sediments showed evidence of flocculation of organic matter, metal oxides and fine grained inorganic particles. In the Gräsanoja dataset the intensity of in-stream flocculation appeared to be the dominating control on sediment composition. In the areal dataset it had a substantially lower importance, since the variations of sediment composition appeared to be dominated by the accumulation of soil aggregates. The organic matter poor fine-grained sediments were indicative of freshly eroded soil from channel or surface erosion, whereas high signals of flocculation suggest that the sediment has strongly altered from the original source sediments due to in-stream processes, such as flocculation (c.f. Droppo 2001; Taylor et al. 2008).

The difference between the datasets may be primarily related to the characteristics and sizes of the catchments. The strong influence of soil aggregates in the areal dataset indicates that, the sediments represent material which has recently eroded from primary sources and subsequently deposited. The location of sampling sites in the headwater reaches may explain the low flocculation degree of the inorganic matter. Thus, the dense soil aggregates were deposited on the stream bed rapidly after reaching the stream channel (see Nicholas & Walling 1996; Droppo et al. 2005) and was influenced by in-stream processes. In the higher order reaches of the Stream Gräsanoja the majority of the sediment has thus been transported a long distance and altered by flocculation processes. The influence of local input of soil aggregates was weaker in proportion to the total sediment volume. The sediment may also have been involved in various sedimentation/resuspension cycles.

12.1.3. Sediment transport and deposition

Processes of sediment transport and deposition are traditionally regarded as being primarily dependent upon the hydraulic conditions of the stream and the properties of the sediment, such as settling velocity, which is dependent on the grain-size, shape and density of the particles (Lick 1986; Bridge 2003). On the scale of an entire drainage network, there is a usually a continuous downstream decrease of gradient, and a corresponding decrease of bed material grain size (Knighton 1980; Thoms 1987; Webster 1995; Church 2002). There are no direct measurements on the flow conditions of the Stream Gräsanoja. However, the gradient decreases downstream accompanied by increasing channel width, which is likely to be associated with downstream decreasing flow velocities despite increasing discharge. The spatial distribution of sediment components in the drainage network suggests that there may be some dependence on the longitudinal changes in energy of the flow, since the grain size distribution demonstrates a slight shift towards finer grain sizes in the downstream direction. This trend is considered to result from progressive downstream sorting and abrasion of particles (Knighton 1980; Bridge 2003). When being transported by a flow of decreasing velocity, largest and densest grains tend to be deposited first owing to their highest settling velocity (Bridge 2003). Therefore, sediment sorting takes place and downstream reaches with low flow velocities...
are associated with deposition of fine grained and organic rich material.

In addition to downstream changes, hydraulic conditions and consequently grain size properties of the sediments show typically strong local variations according to the local morphology (Rhoads & Cahill 1999). Depositional zones with slowly flowing or quiescent water and fine grained sediments are encountered for example in shallow water areas near the shores, on pointbars, downstream from obstacles or in stagnation zones at confluences (Shelton & Capel 1994; Wood & Armitage 1997, 1999; Rhoads & Cahill 1999). The sediment samples of this study were mainly collected from such depositional areas. Thus, local grain size variations are not expected to be considerable, but local flow velocities may have some influence on sediment composition.

Although the hydraulic environment is theoretically the determining factor behind the settling of sediment, the traditional approach involves some problems. Since majority of the finest sediment particles does not settle as discrete particles but as composite particles, the fine sediment content is not dependent on the settling velocity of the primary particles (Raudkivi 1990; Bridge 2003). Aggregation increases the actual size and settling velocity of the particles thus enabling them to be deposited in the sediment (Raudkivi 1990; Droppo & Stone 1994b; Nicholas & Walling 1996; Droppo et al. 1997). Thus, the formation and deposition of flocs may cause an increase of fine sediment particles and organic matter without a decrease of flow competence (Nicholas & Walling 1996; Droppo et al. 1997). Droppo and Stone (1994b) further state that in addition to the energy gradient, chemical and biological gradients are important, as they may control the formational processes that affect the nature of fine-grained material. Thus, the grain size variations observed here are related to the formation and deposition of flocs and aggregates as well as the velocity of the flow. The component of flocs and aggregates showed an increase in the lower reaches, below the confluence of Lukupuro. The increased flocculation in the lower reaches of the main channel may be related to the increased transport of organic matter and fine grained particles, since the concentration of suspended solids influences the rate of flocculation/deflocculation (Droppo et al. 1997, 1998). The low gradient and the wide and uniform channel morphology in the lower reaches of the main channel may increase the deposition of flocs due to decreasing flow velocities (c.f. Droppo et al. 1997, 1998). In addition, the shores of the lowermost reaches are mostly vegetated, which enhances sedimentation as the suspended material may be effectively trapped by the vegetation (c.f. Ciszewski 1998).

12.1.4. Land use impacts

The results of the areal dataset suggest that increasing urban land use increases the organic matter content and decreases the clay percentage of the depositional sediments. High scores of soil aggregate component were also found to dominate in the forested and low density residential catchments when compared with more dense urbanized catchments. In other studies, very controversial results have been found concerning the grain size distributions of urban stream beds. Schoonover et al. (2005, see also McBride & Booth 2005; Finkenbine et al. 2000) have obtained results similar to those reported here with relatively coarse sediments occurring in urbanized areas. Booth and Jackson (1997), on the other hand, claim that increased surface runoff increases the accumulation of fine sediment, which is also supported by similar results from May et al. (1997) and Thoms (1987).

Three main reasons for the observed land use-sediment composition correlation patterns can be distinguished: 1) the impacts of soil sealing, 2) the sources of anthropogenic sediment material and 3) the changes in hydraulic processes due to urbanization. Soil sealing leads to low availability of fine grained soil material for erosion (see Wol-
man 1967), which decreases the proportion of fine particles in sediment. In addition, when open channels are replaced with storm drains the supply of fine grained inorganic material by means of channel erosion decreases. The weakness of erosion is likely to increase the proportion of organic matter, since abundant organic material such as leaf litter is washed down from urban areas (Allison et al. 1998; Ruth 2004; Miller & Boulton 2005).

Particles washing down from the street surfaces include abrasion products of pavement and traction sand as well as particles emitted from tyres, brakes and corrosion of vehicles (Neller 1993; Kupiainen et al. 2003; Robertson et al. 2003). The road deposited particles have been shown to be fairly coarse grained (Chad et al. 2002; Robertson et al. 2003; Lau & Stenstrom 2005; Adachi & Tainosho 2005), although hydraulic sorting results in a shift towards finer grain sizes during sediment transport (Stone & Marsalek 1996; Droppo et al. 1998; Vaze & Chiew 2002, 2003; Sutherland 2003).

In the highly urbanized catchments water is conveyed through storm water pipes, where deposition of the larger grains is hindered. Thus, all sediment grain size fractions are primarily transported to receiving water bodies (Graf 1975; Walling & Moorehead 1987; Nelson & Booth 2002). When stormwater is discharged to open channels the coarsest grains are also deposited to the stream bed (Neller 1993) forming a fairly heterogeneous sediment.

High organic matter content of sediments in dense urban catchments is in agreement with high organic matter concentrations detected in suspended sediments of stormwater in Finland (Kivikangas 2002; Tarvainen et al. 2005). However, the exact reasons for the coarse grain-size and high organic matter content are not clear. The observed pattern is a result of many factors, and the sediment properties are likely to vary between urban areas depending on local conditions such as soil type, structure of stormwater drainage system and runoff processes.

12.2. Connections between sediment components and metals

12.2.1. Relationships in the sediment of the Stream Gräsanoja

The PCA-biplot and correlation matrix of metals and sediment composition demonstrated the association of metals with different sediment components. The PCA plot showed that high concentrations of Cu, Zn, Cd and Pb were recorded in similar sediments. The metals appeared to be strongly associated with sediments which showed strong signals of flocculation or coating of mineral grains: fine grained sediments which also contained abundant organic matter and metal oxides. The high specific surface area and high trace element binding capacity of clay particles, Fe- and Mn-oxides and organic matter is already widely known (Horowitz & Elrick 1987). The additional impact of flocculation on metal adsorption has rarely been documented, although Droppo et al. (1998) claim that flocculation alters the chemical and biological behaviour of sediments in terms of how it interacts with contaminants. Flocs tend to have a high specific surface area (Chu & Lee 2004; George et al. 2007), but the control of flocs on contaminant adsorption/desorption involves all floc constituents (living and non-living organic matter, inorganic compounds and water) and may be much more complicated than pure physical attraction. These constituents may influence interactions with contaminants through their functional processes, such as microbial activity, formation of fibrillar extracellular polymeric material and anaerobic/aerobic processes (Droppo et al. 1997).

The second principal component demonstrated the negative effect of organic poor fine grained sediments on metal concentrations. Similarly, the basin-scale differences of metals show almost no relation to the grain-size parameters, Al and metal oxides. The low or negative relationships between metals
and clay-% were surprising, since they are contrary to the general geochemical behaviour of trace metals (Förstner & Wittman 1981; Horowitz & Elrick 1987; Borovec 2000). The input of clay particles should increase the potential of the sediment to bind trace metals, since clay fraction has been regarded as a strong scavenger of trace metals (Wilber & Hunter 1979; Dong et al. 1984; Horowitz & Elrick 1987; Jain & Ram 1997; Förstner 2004). A number of authors have also claimed amorphous Fe- and Mn-oxides to be the most important scavengers of trace metals in sediment (Jenne 1968; Horowitz & Elrick 1987).

The weak relationships between trace metals and grain-size properties were partly related to the relatively low grain-size variations of the data. Since only fine-grained depositional sites were sampled and the sediments were sieved before any chemical analyses were carried out, the grain-size variations have an unusually low impact on trace metals. In addition, it appears that sediments representing freshly eroded and deposited soil aggregates (indicated by low scores of the second principal component) did not show high metal concentrations. Hence, a strong supply of clean sediment from soil and channel banks dilutes the concentrations of trace metals transported through storm water.

The correlations suggest that organic matter is the major control on the binding of Cu, Zn and Cd (for further discussion on the role of organic matter, see chapter 9.2.4.). Pb is less strongly related to TOC compared to other metals. Pb has probably accumulated in the surface soil during the years when leaded gasoline was used. Therefore the erosion of Pb-rich surface soils at parts of the catchment strengthens the relationship between Pb and soil aggregates, and at the same time weakens the relationship between Pb and TOC.

In this study, normalization of metal concentrations with respect to clay-% and organic matter was conducted prior to analysing the relationships with land use metrics. The aim of the normalization was to highlight the anthropogenic signals by reducing the variations in grain-size and mineralogy caused by differing depositional conditions (energy of the environment). The natural metal concentrations increase with the clay content, since the finest particles are composed of metal-bearing minerals, and they have a high capacity to bind trace metals as coatings (Kersten & Smedes 2002). In this study, low and even negative correlations between clay-% and metals were observed, which contradicts the natural metal-grain-size associations. However, the observed relationships were not merely a reflection of the energy of the environment, but rather the observed relationships were dominated by the mixing of sediments of different origins and grain-size distributions: uncontaminated fine-grained soil and material that originates from urban surfaces. The results cannot be interpreted to infer that the most coarse-grained particles would have the highest metal binding capacity. Instead, it can be assumed that the established relationships between metals and grain-size are valid also for the two sediment components that dominate the sediments of this study. Therefore, the normalization method proposed for marine sediments in Finland was adopted here. The clay-% and organic matter content were, however, relatively close to those of the standard sediment, and the normalization did not strongly alter the original metal concentrations.

On the small spatial and temporal scales, the relationships between metals and sediment components were stronger but less consistent. The organic matter appeared to be the most important sediment parameter having mostly a positive relationship with the metals. However, the relationship of TOC with Pb for instance was positive at the temporal scale but negative at the spatial scale. Therefore, it seems that the correlations are somewhat arbitrary, and may be strongly affected by variations at a single site. The only consistent relationship recorded was the negative relationship between met-
als and coarse silt. Hence, the proportion of coarse particles tends to decrease the metal concentrations at the small spatial and temporal scales. Overall, the results were quite difficult to interpret, and due to the small number of replicate sites, the correlations are not very robust. Therefore, further analysis using more sites is needed for more profound analysis of the effects of sediment composition on the small-scale spatial and temporal variations of metal concentrations.

The partitioning of metals between different operational phases gave an indication of the functional relationships between metals and sediment components. Although the correlations of metals with sediment components were relatively similar, they demonstrated very different binding behaviour for operational phases. The easily reducible phase that represents metals bound to Mn-oxides and reactive Fe-oxides was important for the binding of Zn and particularly Cd, although the statistical relationships with metal oxides were low. Furthermore, Zn showed strong affinity to the reducible phase (Fe-oxides) and Cu to the organic phase. Although the partitioning results mostly do not correspond with the statistical relationships observed, the findings are in accordance with most studies on metal speciation in stream and pond sediments (Lee et al. 1997; Liebens 2001; Johannesson et al. 2003; Marsalek et al. 2006). However, very contradictory results have also been presented (Charlesworth & Lees 1999a; Sutherland 2000); Zn in particular has been reported to be more strongly associated with the organic phase than the results of this study would suggest (Johannesson et al. 2003; Marsalek et al. 2006; Charlesworth & Lees 1999a). Accordingly, the binding behaviour of metals may be slightly site or area specific, as suggested by Charlesworth and Lees (1999a).

12.2.2. Statistical relationships in the areal dataset

In the areal dataset, the factors affecting the sediment-metal relationships were roughly the same as in the Gräsanoja dataset in that, the organic matter is be the single most important sediment parameter affecting the metal concentrations. The first principal component showed that the metals were positively related with organic matter and negatively to grain-size parameters and metal oxides. This component is comparable to the second principal component of the Gräsanoja dataset, which reflects the low metal scavenging ability of soil aggregates. Thus, due to the dominating control of the soil aggregate component on the sediment composition, the metals are negatively related to the sediment fines.

The second principal component reflects the impact of sediment grain size on metal accumulation. If the organic matter content of sediments is equal, fine grained sediments tend to be stronger metal scavengers compared to coarse grained sediments due to higher specific surface area. In addition, the metal oxide content is usually higher in fine grained sediments. This is also indicated by the positive loadings of Fe and Mn in the component.

The observed correlations in both the Gräsanoja and the areal dataset indicate that the availability of fine material is not the limiting factor for the accumulation of trace metals in the stream bed sediments. As concluded by Nicholas and Walling (1996), the different origins of composite particles in streams control the effective size, shape and density of the sediment. The results presented here further indicate that the origin of the composite particles, particularly the effect of in-stream processes including flocculation, has a strong influence on the accumulation of trace metals. Other reasons for the lack of generally observed relationships between grain size properties and metals may be related to the granulometric homogeneity of the sediments and the sieving procedure undertaken in the pre-treatment of the samples.
12.2.3. The role of TOC in determining the metal concentrations

TOC has a strong impact on the large scale distribution of metals for both datasets as well as on the fine scale spatial and temporal variations of metal concentrations. For Cu, the strong correlation with TOC concorded well with the high proportion of Cu bound to the organic phase in the Gräsanoja dataset. Therefore it seems likely that the organic matter is a strong causal and direct control on the Cu distribution in the sediments. This is in agreement with the typical occurrence of Cu in organic complexes (Jaïry et al. 1999; Åström & Corin 2000). The low percentage of Zn bound to the organic phase is, however very controversial with the observed high correlation between Zn and TOC. Similarly, the strong affinity of Zn to the reducible phase does not support the low correlation between Zn and the reducible Fe.

The correlations between Cu, Zn, Pb and Cd in the areal dataset as well as their similar spatial distributions in the Stream Gräsanoja sediments indicate that the sources and controlling factors are largely the same for all metals, although the speciation between different binding phases is very different. It appears that, despite their operational significance, the differences in the strengths of various binding phases do not strongly determine the spatial distribution of metals. Since there are strong statistical relationships between metals and TOC in both datasets, organic matter appears to reflect the controlling factors behind the spatial distributions of metals. Organic matter content is probably a good indicator of properties which affect the ability of the sediment to accumulate metals, such as flocculation degree of sediment. However, based on the speciation study, TOC is not the most important causal determinant at least for Zn and Cd.

Possible reasons for the contradiction between the correlations and Zn speciation may be related to the selective extraction scheme used. Incomplete dissolution of organic compounds from urban sediments, and alternatively weak bonds between metals and organic matter have been suggested as reasons for similar disparities between the correlations and binding phases (Flores-Rodríguez et al. 1994; Turner et al. 2001). In the present study, it is possible that a large proportion of the metals is bound to very stable organic compounds, such as bitumen or tire tread, that may not dissolve in the extractant of the organic phase. However, it is not likely that these compounds would exert such a strong influence, since their concentrations in urban air and soil are relatively low (Fauser et al. 2002).

Organic matter can have indirect positive impacts on the trace metals by enhancing their adsorption on other phases (Jenne 1968; Davis & Leckie 1978; Warren & Zimmerman 1994; Nelson et al. 1995), but the exact causes of the co-effects of organic matter and other phases are not understood. According to Jenne (1968), this could result from the control of organic matter on the reduction and oxidation of Fe-oxides. The organic matter would in this manner maintain the oxides in an amorphous high surface area state (Jenne 1968), which favours trace metal adsorption. According to Warren and Zimmerman (1994) the indirect impact of organic matter could be related to ‘a change from repulsive to attractive electrostatic interaction by the sorbed organic matter or the formation of oxide-Cu-organic matter bridges’. The complexity of the relationships between the sediment components and metals may be further enhanced by other biological and physical processes (Jenne 1968; Davis & Leckie 1978; Horowitz & Elrick 1987; Nelson et al. 1995, 1999; Stecko & Bendell-Young 2000).

The dominant role of TOC regulating the concentrations of Cu, Zn, Pb and Cd might also be due to the same sources of metals and organic matter in the study area (see Flores-Rodríguez et al. 1994; Turner 2000; Filgueiras et al. 2004; Fan et al. 2002; Tsai et al. 2003). The association of organic matter with the urban pollution has been widely reported, but mostly in relation to
sewage and waste inputs (Lin & Chen 1998; Matthai et al. 1998; González et al. 2000; Orescanin et al. 2004; Yau & Gray 2005). However, this study catchment is drained by a separate sewer system so one can expect the input from sewage sources to be fairly small. Nevertheless, diffuse runoff from urban areas, especially in districts with high traffic densities, may also be an important source of organic matter (Williamson 1985; Flores-Rodríguez et al. 1994; Svensson & Malmqvist 1995; Gromaire-Mertz et al. 1999; Kivikangas 2002; Ruth 2004). In the räsanoja dataset TOC appeared to be independent of land use, but in the areal dataset a linkage between sediment composition and land use was clearly observed. Organic matter content increased and clay-% decreased with increasing intensity of urbanization. Hence, the control of organic matter content on metals may be partly explained by their common sources.

The correlations between metals and sediment components, especially organic matter content, have often been used to assess the relative binding affinities of various sediment phases for metals (Bubb & Lester 1994; Tsai et al. 2003; Orescanin et al. 2004). Care should, however, be taken when using the correlation approach to make deductions on the binding modes of metals. The issue has been discussed previously by claiming that strong correlations between various sediment parameters make it difficult to distinguish between the effects of organic matter and other sediment components (Horowitz & Elrick 1987; Horowitz et al. 1989; Combest 1991; Flores-Rodríguez et al. 1994). The results of the present study confirm that even strong correlations between metals and a matrix component of the sediment do not provide a reliable estimate of the dominant binding phases of the metals, or the potential mobility and bioavailability of metals.

12.2.4. Control of sediment composition on the partitioning of metals

In addition to the organic phase TOC appeared to also increase the Cu and Zn concentrations in the pseudoresidual and reducible phases. Thus, organic matter increased the binding capacity of Fe-oxides oxides as suggested by Jenne (1968) and Warren and Zimmerman (1994). Surprisingly, there was only a weak correlation between the reducible metals and the corresponding matrix component (FeR). The pseudoresidual Cu and Zn were, however, correlated with clay-%, Li and Al. This implies that Zn and Cu concentration in the mineral lattices are high in clay rich sediments, which is in good agreement with the higher trace metal content of the micaceous minerals of the clay fraction compared to feldspars and quartz that dominate the coarser fractions (Salminen & Tarvainen 1997).

TOC had an opposite impact on the easily reducible metals compared to the metals in the other phases. Organic matter content and reducible Fe had negative relationships with easily reducible Cu and Pb concentrations. The negative associations were even stronger when the proportions of the easily reducible metals were considered. Apparently, Cu and Pb have so high affinities to organic matter and Fe-oxides that by competing for the Cu and Pb in solution, organic matter and Fe-oxides diminish the adsorption of these metals to the most mobile phase. And conversely, the affinity of Cu and Pb to the easily reducible phase is very weak. Therefore, they bind to the easily reducible phase in significant amounts only in conditions where the sediment contains minimal amounts of competing phases, including organic matter or reducible iron oxyhydroxides. The role of organic matter (Wei & Morrison 1993; Coquery & Welbourn 1995; Morillo et al. 2002) and Fe and Mn oxides (Adriano 2001) in decreasing the mobility and bioavailability of metals has also been reported. Compared to Pb and Cu, Zn and Cd have stronger affinity to the amor-
phous Fe-oxides and Mn-oxides. Therefore, the easily reducible Zn and Cd seemed to decrease less with increasing concentrations of the matrix components of the competing phases.

It seems that the total amount of MnER, FeER and FeR were not the limiting factors for the accumulation of metals in the easily reducible and reducible phases of the sediment. In addition to the above mentioned reasons, the lack of correlation might be related to variations in the crystallinity and age of the precipitates as well as to the various types of occurrence of these oxides, for example as coatings on mineral grains or as discrete particles (Jenne 1968; Lee 1975).

### 12.3. Sediment quality assessment

#### 12.3.1. Metal concentrations at the baseline sites

The baseline sites of this study represent catchments that receive only limited direct contaminant inputs from anthropogenic sources. The baseline concentrations of metals in the stream sediments were a result of weathering of minerals in the surficial sediments and bedrock, metal release from litterfall and atmospheric deposition (e.g. Starr et al. 2003). Here, direct inputs from wastewater, stormwater or other human sources can be assumed to be small at the baseline sites. Some of the catchments have been previously cultivated, and therefore, minor amounts of metals from fertilizer use can be washed down to the streams in association with soil particles. The concentrations of metals are, however, even slightly lower than the regional average of stream sediments in Southern Finland (Table 24).

The metal concentrations of the baseline sites of this study compare well with the metal concentrations of subsoil and pre-industrial sediments in the Baltic Sea and lakes located in southern Finland (Table 24). The close correspondence shows that the stream sediments of undisturbed catchments display negligible enrichment in relation to the geochemical background which represents conditions unimpacted by anthropogenic effects. This is slightly surprising, since the baseline sites are located around the suburban zone of the Helsinki Metropolitan region. Even sites surrounded by built-up areas do not show metal concentrations substantially above the geochemical background values, which suggests that regional and long distance transport of airborne pollutants do not markedly increase the natural metal concentrations of the stream sediments. The small difference may, however, be partially an artefact caused by differences in sediment composition (grain size, organic matter content). In addition, the chemistry of stream sediments is a result of complex processes involving both release and retaining of metals in the drainage basin (e.g. Starr et al. 2003), which may interfere with the accumulation of depositional metals in sediments.

Pb and Cd concentrations were lower than the corresponding baseline concentrations in humus samples. These metals are preferentially bound to the humus layer of soils (Tarvainen et al. 2006) and are not easily carried to waterbodies. This may explain the low baseline concentrations in the stream sediments. The strong role of sediment composition and catchment processes on the baseline metal concentrations is further supported by considerably higher metal concentrations reported for organic rich sediments in small ponds with non-urbanized catchments in Helsinki (Marttila 2007).

It is acknowledged that the choice of baseline concentrations is critical concerning the results of sediment enrichment (Rubio et al. 2000). Based on the low metal concentrations of the baseline sites in this study, the baseline sediments are likely to reflect the natural metal concentrations with minor additions from atmospheric pollution. Bias should not result from differing geologies either, since the baseline sites are located within the same geological area with the suburban sites. Thus, the sediments fulfill many of the criteria proposed for obtaining
representative background values (Förstner & Müller 1981). However, a more comprehensive picture of the natural variation of baseline concentrations would be obtained with a higher number of baseline sites.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Size fraction</th>
<th>Dissolution method</th>
<th>Zn</th>
<th>Cu</th>
<th>Pb</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Baseline stream sediments of this study (median)</td>
<td>&lt;63μm</td>
<td>Partial dissolution</td>
<td>113</td>
<td>25</td>
<td>13</td>
<td>0.2</td>
</tr>
<tr>
<td>Urban stream sediments of the Gräsanoja dataset (median)</td>
<td>&lt;63μm</td>
<td>Partial dissolution</td>
<td>360</td>
<td>108</td>
<td>31</td>
<td>0.6</td>
</tr>
<tr>
<td>Urban stream sediments of the areal dataset (median)</td>
<td>&lt;63μm</td>
<td>Partial dissolution</td>
<td>356</td>
<td>95</td>
<td>31</td>
<td>0.5</td>
</tr>
</tbody>
</table>

| Pre-industrial sediments                                                |               |                    |     |     |     |     |
| Pre-industrial marine sediment (Laajalahti Bay, Gulf of Finland) 2)     | Bulk          | Partial dissolution| 100-125 | 20-30 |
| Pre-industrial marine sediment (Gulf of Finland) 3)                     | <2mm          | Partial dissolution| 86.7 | 22.2 | 14.9 | 0.14|
| Pre-industrial lake sediment (Valkea-Kotinen, Southern Finland) 4)      | Bulk          | Partial dissolution| c. 100 | c. 21 | c. 10 | c. 0.6|
| Pre-industrial lake sediment (Hirvilampi, Southeastern Finland) 4)      | <2mm          | Partial dissolution| c. 90 | c. 15 | c. 10 | c. 0.25|

| Recent background sediments                                             |               |                    |     |     |     |     |
| Regional average of organic stream sediments (median)                   | <2mm          | Partial dissolution| c. 130 | c. 30 | c. 17 | 0.35-0.4|
| Median of clay soils (subsoil) in the areas surrounding the metropolitan region of Helsinki 5) | <2mm          | Partial dissolution| 108 | 42  | 17  | <0.1|

| Urban soils and sediments (medians)                                     |               |                    |     |     |     |     |
| Urban baseline concentrations of humus (in the area surrounding the metropolitan area of Helsinki) 5) | <2mm          | Partial dissolution| 63  | 9   | 49  | 0.4|
| Concentrations of organic top-soil (parks in Helsinki) 6)              | <1mm          | Partial dissolution| 82  | 44  | 51  | 0.3|
| Urban baseline concentrations of humus (natural soils in Helsinki) 6)  | <1mm          | Partial dissolution| 48  | 16  | 59  | 0.2|
| Street dust (Turku, Finland) 7)                                         | <43μm         | Total dissolution  | 222 | 101 | 38  | 0.5|
|                                                                       | 43–100μm      | Total dissolution  | 172 | 67  | 25  | 0.3|


12.3.2. Metals at the urban sites

Zn and Cu concentrations in both datasets compare well with concentrations reported for urban sites in the United States (Rice 1999). However, metal concentrations of urban stream sediments exhibit very high variations between studies (Rice 1999;
Sutherland 2000; Webster et al. 2000; Mel- lor 2001; Andrews & Sutherland 2004; De Carlo et al. 2005), probably depending upon the size of the drainage area, geology of the area, the intensity of urban land use and properties of the collected sediments. The Zn and Cu concentrations of the Helsinki region seem to be lower than those reported for streams of similar size in O‘ahu, Hawai‘i (De Carlo et al. 2005). However, larger streams with forested upstream catchments show lower Cu and Zn concentrations in their urban lower courses compared to the concentrations obtained here (Webster et al. 2000; Andrews & Sutherland 2004).

Enrichment factors offer a possibility to compare metal contamination with other areas that may be dominated by different basic geology. Zn enrichment of stream sediments in the Helsinki region is comparable to other urban areas, where the median enrichment factors range between 1.5 and 5 (Sutherland 2000; Andrews & Sutherland 2004; De Carlo et al. 2005). Meanwhile, Cu enrichment is relatively high in the Helsinki region when compared with the two catchments in Hawaii, where low enrichment factors of Cu (1.5-2) have been reported for urban areas.

In contrast to Cu and Zn, Pb concentrations from the studied streams in Helsinki region were low. Almost 75% of the sites in both datasets are below the minimum values reported for many urban and suburban catchments (Wei & Morrison 1993; Sutherland 2000; Webster et al. 2000; De Carlo & Anthony 2002; De Carlo et al. 2005). Median values of Pb are usually at least twice as high as reported in this study. The differences cannot be accounted for by different background concentrations, since the enrichment factors obtained in this study were also very low. As much as 10 times higher enrichment has been detected in other studies (Sutherland 2000; Andrews & Sutherland 2004; De Carlo et al. 2005).

The low concentrations of Pb in the Helsinki region demonstrate the positive effect of the use of unleaded gasoline and paint. The atmospheric Pb input declined rapidly during the 1980’s until the input from gasoline sources practically reached zero in 1994, when no leaded gasoline was for sale in Finland (Pietarila et al. 2001; Environmental statistics 2005). However, the Pb storage of the surficial layers of soils responds slowly to the reduction of emissions (Van Metre et al. 1998). The high concentrations reported in other studies reflect the long period in the 20th century when leaded gasoline was a major source of Pb. The effects are still widely evident in stream sediments and road deposited particles through the erosion of roadside soils (Sutherland 2000, 2003; DeCarlo & Anthony 2002; Brown et al. 2008). The high Pb concentrations observed at individual sites in this study are also a result of the mobilization of previously contaminated roadside soils. The catchments analysed in this study were dominated by single-family houses until 1960’s, when the construction of suburbs started outside the city centre (Schulman 1990). The relatively low age of the suburban districts and the short duration of Pb accumulation are the most probable reason for the generally low Pb concentrations in Helsinki.

The Pb concentrations have almost reached the background levels at most of the urban sites. Results on urban marine sediments in Helsinki have also shown that Pb concentrations almost reached the background level in the 1990’s (Tikkanen et al. 1997). However, the concentrations of Pb in organic stream bed sediments have, in fact, increased from the year 1990 to 2000 in Southern Finland (Ténhola & Tarvainen 2008). Therefore, it must be acknowledged that other Pb sources exist in the urban environment, including atmospheric deposition, car tires and paints (Good 1993; Davis et al. 2001; Hjortenkrans et al. 2007).

Cd concentrations of the small streams in Helsinki region were well below those reported in previous studies (Rice 1999; Sutherland 2000; De Carlo et al. 2005). In most studies Cd concentrations of urban stream sediments are around 0.9 mg/kg (Rice 1999; Sutherland 2000; De Carlo et al. 2005). As a
comparison, the median Cd concentrations obtained here were 0.6 in the Gräsanoja dataset and 0.5 in the areal dataset. However, based on the enrichment factors, the anthropogenic input of Cd to the aquatic environment is almost as high as the input of Zn.

The results demonstrate that the anthropogenic pollution exerts a widespread impact on the Zn and Cu concentrations of sediment in the suburban stream reaches. The sediments are mainly moderately polluted with respect to Cu and Zn (EF 2–5) (Fig. 15), but some sites show significant or even very strong pollution particularly with respect to Cu. In contrasts, Pb shows very low pollution signals. In the urban baseline study of Tarvainen (2006) Pb and Cd were found to reflect the atmospheric deposition and other anthropogenic input better than Zn and Cu. This shows that in urban areas Pb and Cd were strongly affected by atmospheric transport and deposition, while Cu and Zn are transported to the aquatic system directly from the contamination sources (traffic areas, buildings) by stormwater. Comparison to street sediment metal concentrations further reveals that, traffic is not the only substantial source of Zn in the urban environment. In addition to the regional atmospheric deposition, Cd appears to have direct sources in the urban environment, since the Cd concentrations are higher in urban stream sediments when compared with the baseline humus samples.

Sediment deposits provide habitat for many benthic organisms, which are thus in direct contact with the interstitial and sediment-bound metals. Many organisms can accumulate metals either by adsorption from the interstitial or overlying water to the body wall or respiratory surfaces, or from the solid phase through ingestion of the sediment (Tessier & Cambell 1987; Förstner 1989; Wang et al. 1999). Sediment quality guidelines have been developed to be able to identify sites where adverse effects on benthic organisms may occur based on sediment metal concentrations (Canadian Council of Ministers of the Environment 1999). No sediment quality guidelines have been proposed by the Finnish authorities or the EU. Therefore, sediment metal concentrations were compared with the Finnish soil screening values and the quality criteria proposed for dredged materials in Finland. These guidelines are not intended for contamination assessment of stream sediments (Degree 214/2007), and therefore they can only be used as a preliminary indication of potential risks associated with the sediments.

Cd and Pb can be considered as the most dangerous metals of those determined in this study. They have been included in the list of priority substances in EU (Water framework directive, EC 2000). Their concentrations were, however, low when compared with the soil screening values and dredged sediment quality guidelines, which indicates a low risk of ecological effects. Cu and Zn concentrations in the studied sediments were considerably higher compared to Cd and Pb. The concentrations were widely above the intervention criteria for dredged material, and the pollution level was exceeded at numerous sites. The soil screening values suggest, however, that the sediments are much less contaminated with Cu than Zn. Zn concentrations were above the guideline value at more than 75% of the sites. The results suggest that ecological effects are probable to occur due to high concentrations of Zn and possibly also Cu. The metal concentrations in this study were measured for the mud fraction (<63µm), while the soil screening values and dredged material quality guidelines are reported for the fraction <2mm. Therefore, the proportion of sites where metal concentrations exceed the criteria levels may be somewhat overestimated.

Although sediment quality guidelines (SQGs) have a central role in many sediment investigations, their use is dispute throughout the scientific community (Apitz & Power 2002). They have been criticized of lack of predictive ability concerning the biological effects, particularly of long-term exposure to the contaminant (Chapman & Mann 1999; Chapman et al. 1999; O’Connor &
Paul 2000; Mowat & Bundy 2001; Burton 2002). However, despite the weaknesses related to the use of SQG, they offer a preliminary indication of where biological effects might be expected (Roach 2005). The results demonstrated that the anthropogenic pollution exerted a widespread impact on the Zn and Cu concentrations of sediment in the suburban stream reaches. The concentrations were so high that they may even have toxicological effects on stream biota. Meanwhile, despite the dangerous nature of Pb and Cd, their concentrations were not high enough to cause adverse biological impacts on the streams of the Helsinki region.

12.3.3. Possible bioavailability and mobilization of metals

Sediment is considered polluted, when the metal concentration is high enough to cause harmful effects on biota (Burton 2002). The concentrations obtained here by partial dissolution do not, however, adequately reflect the potential impacts of the metals to the biota, since part of the metals are bound to relatively stable fractions of the sediment (Mowat & Bundy 2001). Only a small part of the total metal concentrations, the bioavailable fraction, is taken up by sediment-dwelling organisms (Mayer et al. 1996; Birch et al. 2001). According to Mayer et al. (1996) only 1-10% of the total Cu in sediments was bioavailable. Although a thorough assessment of biological effects should include methods that rely on direct toxicity measurements, in situ studies of metal concentrations in biota or changes in community structure or a combination of these methods (Ankley et al. 1994; Chapman et al. 1999; Ingersoll et al. 2001), an estimate of the biological reactivity of the sediment can be obtained using sediment chemistry (Tessier et al. 1979; Luoma 1989; Bryan & Langston 1992). Particularly metals bound to the most labile phases of sediment correspond with the metals in the biota (Tessier & Cambell 1987; Luoma 1989; Pempkowiak et al. 1999).

In this study the most mobile and bioavailable phase was represented by the easily reducible metal concentrations, which have been found to be the most important factor concerning the bioaccumulation of metals in the bivalve mollusc Macoma balthica (common name the Baltic macoma) (Thomas & Bendell-Young 1998). The results demonstrated that a considerable proportion of the total Zn and particularly Cd may possibly be taken up by benthic organisms. However, due to low acid extractable concentration of Cd the concentration of bioavailable Cd was also relatively low. Pb and Cu were highly unavailable to biota, since the proportion of easily reducible phase constituted a low percentage of the acid extractable concentrations. The enrichment factors and comparison to quality guidelines proposed for soil and dredged material suggest that Cu and Zn may pose the highest risk for environment. When considering the possible bioavailability of these metals, it is clear that Zn may be more available to biota, and can thus be of higher concern from the ecological point of view.

The sediment bound metals may further cause adverse effects through mobilization of metals. The increase of metal concentrations in the interstitial water can pose impacts on the overlying water quality and the sediment-dwelling biota (Stumm & Morgan 1996). Ecological impacts may also extend to lower reaches as a consequence of downstream movement of contaminated water.

Major controls on the mobilization of metals to the interstitial water in (sub)oxic sediments are changes in the metal binding phases (Whiteley & Pearce 2003; Ouddane et al. 2004; Tao et al. 2005). Here, Zn and Cd were most strongly bound to the Fe and Mn-oxides that are particularly sensitive to changes in redox conditions (Jenne 1968; Salomons & Förstner 1984; Stumm & Morgan 1996). Small changes in pH and redox-conditions can lead to reduction and dissolution of the Mn-oxides and reactive Fe. As a consequence, metals bound to the easily reducible phase, particularly a high
proportion of Cd, could be released to interstitial water and migrate to the overlying water. The reducible phase constitutes compounds which require lower redox-potential and pH for reductive dissolution. Therefore, fairly strong changes in the environmental conditions are needed in order to mobilize significant amounts of Zn from the solid phase. The strong association of Cd and Zn with the metal oxides suggests that the stable redox conditions of the streams are essential to prevent the mobilization of these metals. According to Charlesworth and Lees (1999a) environmental conditions are continuously changing in urban waterbodies, which increases the potential for metal mobilization. However, fairly high (6.4-7.9) and constant values of pH have been recorded in urban streams in Helsinki (Ruth 2004). Regardless of the chemistry of the overlying water, changes of redox conditions can also result from early diagenesis of sediments (Salomons & Förstner 1984).

Organic matter had the strongest impact on the speciation of Cu. Thus, the slow microbial decomposition of organic matter may also result in the release of considerable Cu storage from sediment to the interstitial water (Ouddane et al. 2004; Audry et al. 2006). Dissolved organic matter is also produced in association with organic matter destruction, which may lead to complexation of the released metals and thereby affect their partitioning between the solid and dissolved phases (Förstner 1989; Ouddane et al. 2004; Audry et al. 2006).

The spatial distribution of easily reducible metals suggests that metals are more mobile and available to the biota in the headwater reaches. In particular, Cu and Pb showed high concentrations in the smaller tributaries and in the upper reaches of the main channel, while spatial variations of Zn ad Cd were considerably weaker. The observed pattern strongly reflects the immobilizing effect of organic matter and iron oxides on Cu and Pb. As a consequence, the fairly high acid extractable metal concentrations in the lower reaches of the main channel are probably relatively harmless to the biota. This would suggest that the anthropogenic inputs of metals are more of a concern in the smaller headwater streams when compared with larger streams, where the abundance of flocculated fine grained and organic rich sediment immobilizes a large fraction of the metals. Previous studies have also demonstrated the occurrence of phase changes during transport from source to deposit in the urban environment (Flores-Rodriguez et al. 1994; Charlesworth & Lees 1999a). Flores-Rodriguez et al. (1994) reported a similar downstream shift towards more stable forms as observed in this study.

### 12.3.4. Hazard assessment

The assessment of sediment quality is often the basis for further management strategies or actions. This sediment quality evaluation does often take the form of a risk assessment, which aims to define the probability of various impacts of sediment contamination (Apitz & Power 2002). The first step of quality or risk assessment is usually to compare the sediment chemistry with SQGs (Chapman et al. 1999; Apitz & Power 2002). Despite the drawbacks of the use of SQGs, the information they provide can be used as a screening tool to prioritize the sites that most urgently need further analysis (Chapman et al. 1999; Canadian Council of Ministers of the Environment 1999; Apitz & Power 2002; Förstner & Heise 2006). In this study, the dredged material quality guidelines were the basis for identifying the sites that may be of concern. In the Gräsanoja dataset, the possibility of a hazard in the fine grained sediments is fairly common in the suburban areas, especially in the high density residential, commercial and industrial areas. In the agricultural, forested or low density residential areas the hazard is classified as non-existent or weak. Thus, the potential for ecological effects at the low density residential areas is probably low, even though the sediments cannot be regarded to represent natural conditions based on the mainly moderate en-
richment over baseline.

These results may act as an initial estimate of the locations most vulnerable to contamination induced biological effects. However, it is acknowledged that the sediments represent only the depositional sites that constitute a small proportion of the total sediment storage of studied streams. Thus, no actual estimate of the stream-scale biological effects can be made. Sediment samples representative of the different sediment types need to be collected in order to make an accurate assessment of sediment quality (Ladd et al. 1998). In addition, the framework for assessing sediment quality is usually a tiered approach, where by different chemical and biological analyses of sediment, interstitial water and biota are combined to evaluate the potential for adverse biological effects (Mowat & Bundy 2001; Apitz & Power 2002; Crane 2003; Förstner & Heise 2006).

12.4. Land use impacts

12.4.1. Intensity of urbanization

The association of metals with urban pollution is already well known. Increasing sediment metal concentrations have been reported for streams flowing through urban areas (Dong et al. 1984; Sutherland 2000; Andrews & Sutherland 2004). Furthermore, smaller urban catchments tend to be associated with higher sediment metal concentrations when compared with agricultural and forested catchments (Rice 1999; De Carlo et al. 2005). The results of this study are parallel to those reported before. Metal concentrations in the urban catchments of the areal dataset were statistically higher than at the unbuilt catchments. Moreover, metal concentrations were lower at the forested and agricultural sites when compared with most of the urban sites in the Gräsanoja dataset.

However, the impact of increasing urbanization has rarely been shown statistically, although Schueler (1994) claimed in his widely cited article “The importance of imperviousness” that urban water pollution is directly related to the percentage of impervious areas in the contributing catchment. May et al. (1997) also belong to the few who have found a relationship between metals and increasing urban land use and imperviousness. The results of the areal dataset further support the view that metal concentrations, especially Cu, Zn and Pb, are dependent upon the proportions of dense urban land use and impervious surfaces. However, while the metal concentrations of the non-urban and weakly urban sites were consistently low, the more urbanized sites were associated with a high variability of metal concentrations. In fact, the increasing variation of metal concentrations with increasing TIA was the most striking feature of the metal–TIA relationships. Hence, the results demonstrate that within the urban sites high metal concentrations do not result directly from a high degree of urbanization.

Variations between sites may be strongly affected by point sources and differences in the spatial proximity of the stream to contaminant sources. The weakness of correlation between the population density and metal concentrations in the residential catchments further shows that contamination is not directly dependent on the degree of urbanization of the catchment.

The usefulness of the observed metal–land use relationships for applications, such as land use planning or environmental management, are dependent on the selection of proper land use metrics. The land use indicator should reflect the occurrence of various pollution sources, while also being easily measurable and related to different land use policies. The results of this study confirm the widely accepted view that imperviousness is a very useful indicator of land use impact on aquatic systems (Schueler 1994; May et al. 1997; Wang et al. 2001). TIA and the percentage of dense urban areas correlated with the metals most consistently out of all the land use metrics within the urban sites. TIA is, however, likely to reflect the variations of
metal concentrations relatively well also in weakly urbanized catchments (see Fig. 43). Impervious surfaces are feasible predictors of aquatic pollution loads, since they accumulate pollutants from different sources and effectively deliver these pollutants to watersheds during storm events (Schueler 1994). The impervious surfaces are not necessarily the original sources of pollutants, but TIA is an index that integrates a variety of hydrological changes induced by land development (Schueler 1994; Booth & Jackson 1997; Zandbergen 1998). Although the use of TIA is tempting, the calculation may be expensive (May et al. 1997). However, the recent development of GIS based techniques for automatic classification of remote sensing data enables fast determination of the percentage impervious surfaces from over extensive areas (Carlson & Arthur 2000; Elgy 2001).

Walsh (2000) claims that TIA alone is not an appropriate indicator of aquatic impacts, since the variations in hydrological connection have to be taken into account. Connectivity is possibly even the dominant factor controlling water pollutants in urban areas (Hatt et al. 2004). EIA is a measure which accounts for the variations in the connectivity of the impervious surfaces to watersheds. However, the estimated percentages of EIA did not appear to be more closely related to metal concentrations in this study.

According to a classification of headwater urban streams (see Schueler 1994), streams with TIA below 10% show no degradation, and water quality tends to be good. When TIA is between 10 and 25%, some degradation is usually apparent, and water quality tends to be fair. When TIA exceeds 25%, streams are in poor condition with fair-poor water quality, low biodiversity and highly unstable channels. These thresholds correspond well with the results of this study concerning the metal concentrations of sediments. Zn, Cu and Cd concentrations were very low at the baseline sites with TIA<8%. When TIA is between 8 and 25–30%, metal concentrations remain mostly relatively low, but biological effects due to high concentrations of Cu and Zn are possible at nearly all sites. When TIA exceeds 25–30%, the range of concentrations is very high and biological effects are probable at numerous sites due to very high concentrations of Cu and Zn. Therefore, the TIA thresholds of c. 10 and 25% can be used as general guidelines for the estimation of the urbanization impacts upon stream sediments, although the metal concentrations do not appear to increase in a stepwise manner.

### 12.4.2. Transport areas and rooftops

Impervious surfaces composed of transport areas and rooftops were both related to the metal concentrations in the areal dataset. However, Zn and Cd showed considerably higher correlations with the percentage of rooftops. In the Gräsanoja dataset correlations were weak for both components. Since the differences between the two impervious surface types were relatively small, both rooftops and transport areas appear to be substantial metal sources.

Results of most stormwater studies and loading calculations infer that transport areas are the leading source of at least Pb and Cu, although buildings may also contribute substantially to Cu loads (Bannerman et al. 1993; Bergbäck et al. 2001; Davis et al. 2001; Gray & Becker 2002; Sörme & Lagerqvist 2002; Van Metre & Mahler 2003). Despite the reduction of Pb loads due to unleaded gasoline, traffic is still the most important Pb source in the urban environment according to Pakkanen et al. (2001). Pb is contained in brake linings and tires, although their concentrations have decreased substantially over the last years (Hjortenkrans et al. 2007). In addition, Pb may be derived from historical emissions through erosion of previously contaminated surface soil close to transport areas (c.f., Bergbäck et al. 2001; Sutherland & Tolosa 2001; Jonsson et al. 2002; De Carlo et al. 2004). The statistical relationships obtained in this study for stream sediments do not support the commonly reported
dominating role of transport areas as sources of Cu and Pb. However, the transport areas showed stronger relationships with Cu and Pb than with Zn and Cd, which is in accordance with previous studies.

Cd and Zn are, according to most loading studies, derived from both transport areas and buildings. The results of this study suggest, however, that the role of the rooftops is more important than that of the transport areas. It is worth noting that the results on the relative contribution of transport areas and buildings in stormwater metal loads show considerable variation depending on the type of land use and building materials (Bannerman et al. 1993; Bergbäck et al. 2001; Davis et al. 2001; Gray & Becker 2002; Sörme & Lagerqvist 2002; Van Metre & Mahler 2003).

In stream sediment studies traffic sources have often been considered the most important control on trace metal concentrations (Dong et al. 1984; Callender & Rice 2000; Sutherland 2000). The assumed importance of transport areas is supported by the fact that roads, yards and parking lots account for the majority (50-80%) of the total impervious surfaces in the study area. Moreover, transport areas are usually better connected to the storm drain system when compared with rooftops particularly in residential areas (Schueler 1994). However, the results of this study strongly indicate that both traffic and buildings are major sources of metals. This suggests that loading calculations might overestimate the importance of transport areas.

The relationship between metals and traffic density of the catchment was also studied here, because metal loads associated with transport areas have been claimed to be largely controlled by the amount of traffic (Rose et al. 2001; Robertson et al. 2003). The correlation of traffic density with trace metals was, however, equal to that of the impervious areas composed of transport areas. Thus, the information concerning the amount of traffic did not increase the correspondence between metals and traffic areas.

The analyses based on correlations with metal concentrations do not provide direct estimates of the actual contributions of transport areas and rooftops to metal loadings. In addition, the metal concentrations are not solely determined by the areal coverage of the two impervious surface types or the traffic amounts. The control of rooftops on metals is complicated by the variety of different materials in use. The fact that age of the buildings varies further enhances the diversity of roof materials and possible metal loads. In many studies the metal sources are simply separated into transport areas and rooftops, although siding materials have also been shown to be potential metal sources (Davis et al. 2001). Moreover, the metal loads of traffic are additionally determined by the driving habits, distribution of traffic lights and the road conditions (Brinkmann 1985; Hjortenkrans 2008).

12.4.3. Impacts of different urban and use types

Metal concentrations increased with increasing proportions of dense urban land. Increasing proportion of low density residential areas on the other hand resulted in lower metal concentrations relative to dense urban land use. However, the individual dense urban land use types (high density residential, institutional, commercial and industrial) showed weaker relationships with the metals than the combined group of dense urban land, and no consistent differences could be established between these land use types with regard to correlations with metals. The difference between the land use types was also reflected in the median metal concentrations between different catchment categories, since catchments dominated by low density residential areas exhibited lower metal concentrations when compared with other urban catchments. However, statistically significant differences were recorded only for Cu and Pb between low density residential catchments and the group of high density residential, commercial and institu-
tional catchments.

The fairly high metal concentrations of dense urban areas observed in this study are related to higher traffic volumes and densities of buildings and roads when compared with low density residential areas (c.f. Karouna-Renier & Sparling 2001). The dominating building materials may also vary between different land use types. For example, steel roofs are the dominant roof type in Finland, but brick roofs are most common in residential buildings (Kytölä 2008). However, the metal loads related to different construction materials have not been determined unambiguously, and further research on this subject is needed.

Catchments dominated by industrial land use showed the highest median metal concentrations, but the variation within the group was very strong, and no statistically significant difference with other land use groups was detected. However, many of the highest metal concentrations occurred at industrial catchments. This corresponds well with studies that report highest metal concentrations in stream sediments or soils in areas that are presently or have been formerly industrialized (Mellor & Bevan 1999; Mellor 2001). In addition to high diffuse pollution levels, the elevated metal concentrations may be due to point sources of metals from industrial activity, outside storage or traffic. The strongly varying metal concentrations in industrial areas emphasize the need for site-specific investigations as the foundations for decisions concerning stormwater management and treatment.

Within the urban sites low density residential areas were negatively related to metal concentrations. A similar result has been presented by Wilber and Hunter (1977), who found a decrease of stormwater metal concentrations with increasing residential land use. These results are explained by the fact that the land use percentages are not independent variables. The increase of one land use type percentage leads to a decrease in the percentages of one or more other land use classes (King et al. 2005). Therefore, the impact of dense urban land uses can overshadow the independent impact of low density residential areas. The spatial distribution of metal concentrations in the Gräsanoja dataset, and the differences between catchments dominated by unbuilt areas and low density residential areas in the areal dataset (Fig. 33) reveal the independent positive impact that low density residential areas have on metal concentrations.

The results of the present study suggest that high density urban areas exert the highest contamination effect on the sediments. Although this finding is in line with the general understanding of increasing metal concentrations with increasing urbanization intensity, it has rarely been statistically shown for stream sediments. Quantitative studies on the influence of different urban land use types on trace metal contamination of stream or stormwater pond sediments are rare (although see Parker 2000; Karouna-Renier & Sparling 2001; Liebens 2001; Andrews & Sutherland 2004). These studies show that the evidence on the differences between different urban land use types has not been very strong and consistent. Although highest metal concentrations have been reported for commercial areas in stormwater pond and stream sediments (Liebens 2001; Andrews & Sutherland 2004), other studies have failed to show such differences (Parker et al. 2000; Karouna-Renier & Sparling 2001). Although the dense urban land use types differed from the low density residential areas in this study, the lack of clear differences between the dense urban land use types further demonstrates the difficulty of discriminating the impacts of different land use types. The diversity of different results shows that point sources, local circumstances and differences in human activity (such as street cleansing operations) greatly affect the relationships between sediment metal concentrations and land use. Correspondingly, Baker (2003) has stated that also the correlations between land use and water chemistry are often site-specific. The prediction of highest metal concentrations based on land
use information is therefore difficult among relatively densely built catchments.

12.4.4. Spatial arrangement of urban areas

The land use of the entire upstream catchment appeared to be related to the sediment metal concentrations in the areal dataset. On the other hand, land use of the immediate upstream catchment correlated relatively weakly with sediment metal concentrations in both datasets, which shows that the potential metal loads entering the stream close to the sampling site were not particularly well reflected in the sediment chemistry. These results show that metal input from different land use classes has impacts on the stream sediment metal concentrations relatively far downstream. This results from the long range transport of dissolved and particulate bound metals. The result does not indicate exactly, how far the most obvious impact is detectable. The most distant areas are, however, likely to exert a lower influence on the sediment when compared with areas located closer to the sampling site, since part of the metals are stored in the stream bed as sediment is transported downstream (Miller 1997).

The local riparian zone has an equally strong relationship with the metal concentrations compared to the immediate upstream catchment in the Gräsanoja dataset. The riparian zone filters sediment and associated metals when a shallow water layer flows slowly through the vegetated buffer zone (Barling & Moore 1994; Schueler 2000). Therefore, the high percentage of impervious surfaces in the riparian zone decreases the capability of the buffer zone to remove metals and also increases direct metal loads discharging to the stream. The efficiency of riparian zone in decreasing metal loads from stormwater has been questioned by Schueler (2000). He claims that in urban areas 90% of the surface runoff is converted to channels before it reaches the buffer zone. Consequently, a high proportion of the runoff bypasses the bufferzone. The positive correlations between metals and TIA of the riparian zone were not statistically significant. Therefore, the results did not confirm the importance of the riparian zone, but the results do suggest that the riparian areas may impact upon the transport of metals. Therefore, a more detailed study on the linkage between the land use of the buffer zone and the metal contamination should be conducted in future.

The impact of the spatial distribution of land use on stream sediment chemistry has not been studied previously. However, Comeleo et al. (1996) found that the metal levels of estuarine sediments were best predicted by local land use (less than 10 km from the sampling site). Also for water quality there exist several scale studies but it remains unclear whether the land use of the riparian or local zone exerts a greater impact on water quality than land use of the entire catchment (Johnson et al. 1997; Sliva & Williams 2001; Sponseller et al. 2001; Baker 2003). In this study the local upstream catchment was delineated using the hydrological pathways of sediment and pollutants, which is likely to increase the correspondence between local land use and metals compared to previous studies. However, the results suggest that the entire upstream catchment is more important than the local zone. In current literature catchment scale approach to sediment management is also strongly emphasized (Owens 2008; White & Apitz 2008). The stream network and adjacent hillslopes function as an open system, where major changes in one part impacts upon other parts (Owens 2008). The present results confirm the importance of the entire upstream catchment when the catchment size is up to a few square kilometres. Throughout the land use metrics correlations with land use were higher in the areal dataset when compared with the Gräsanoja dataset, which shows that, the fairly homogeneous land use of the small catchments controls metal concentrations more strongly than the more heterogeneous larger catch-
12.4.5. Point sources

Concentrations of individual metals were elevated at some sites, which may indicate the influence of point sources or some other site-specific factors. Such sites were at least those classified as outliers based on high positive residuals (when the metals were modelled using land use and sediment composition as explanatory variables). These sites appeared to be impacted by other sources than merely the diffuse urban pollution, which is supposed to determine the metal concentrations of the bulk of the study sites. At least one site stood out as an outlier for each metal. The reasons for the elevated concentrations are difficult to interpret case by case, but many of the sites received discharges from industrial areas (sites 37, 33B, G1, 900, 94). Another reason may be the proximity of a major highway which was not included in the contributing catchment (site 21).

In the Gräsanoja dataset, examination of the spatial distribution of metal concentrations revealed evidence of point sources at some additional sites. The acid extractable Pb concentrations were enriched at several sites in small tributaries along the Turunväylä highway (sites 11, 12, 14 and 15). Erosion of soils previously contaminated by Pb probably caused substantial Pb enrichment in these sediments. The pollution impact was, however, mostly local, since the high concentrations were not strongly reflected in the sediments of the main channel. For Cd, one site (45) showed highly elevated concentration compared to other sites in the Gräsanoja dataset. This Cd “hot spot” is most probably related to some point source of Cd. However, low metal concentrations around the old solid waste landfill in the Stream Gräsanoja catchment shows that, when the leachate waters are conveyed to wastewater treatment plant the adverse effects of an old landfill can be effectively eliminated and elevated metal concentrations do not occur in bed sediments. The results of the sediment assessment do not, however, rule out the possibility of momentary peaks of dissolved trace metals.

The elevated Cu and Zn concentrations at the estuary (site 39) are probably due to the higher pH of the water at the estuary (7.9) when compared with freshwater sites (pH 7.3–7.7). According to Förstner and Wittman (1981) high pH of the environment increases the adsorption of metals. The increased content of organic matter, silt and clay also suggest increased flocculation and settling in the saline environment (Webster 1995; Birch et al. 2000; Johannesson et al. 2003). High ionic strength and Cl-concentration of the water inhibit the Cd adsorption (Palheiros et al. 1989). This apparently overcomes the effect of higher pH in the estuary, and consequently Cd concentrations are lower in the estuarine sediments when compared with fluvial environments.

Horowitz et al. (2008) reported that contribution of nonpoint-sources to sediment bound trace metals of streamwater in Atlanta were more important than point-sources. In the present study, metal concentrations were moderately determined by diffuse pollution. However, metal concentrations showed considerable residual variation particularly among the urban sites, when the land use was accounted for. The variation may be related to point sources or some unmeasured environmental factor (such as some element of sediment composition).

12.4.6. Easily reducible metal and land use

The easily reducible metals appeared to reflect the land use of the catchment more strongly than the acid extractable metals in the Gräsanoja dataset. Different from the acid extractable metals, the correlations between general urbanization indicators (urban%, dense urban%, TIA) and metals were
moderately high within the urban sites. The correlations with land use type percentages were slightly weaker, but the commercial and traffic areas appeared to have the strongest positive relationship with metal concentrations.

As described earlier, the easily reducible metal concentrations, particularly of Cu and Pb, were substantially controlled by the sediment composition and the competition between different binding forms of metals. Even so, the easily reducible metals appear to be sensitive indicators of metal loading from urban settlement.

12.4.7. Predicting metal concentrations

The predictive regression models showed that land use explained only 10-24% of the standardized metal concentration data of urban sites used to construct the models. For the validation data coefficients of determination were even lower. The strong variation of observed metal concentrations around the predicted concentration (Fig. 37) showed that, the models cannot be used to estimate the concentrations of individual sites. However, some broad spatial or temporal trends may be estimated using the information of the catchment urbanization. Better models can be obtained, if the sediment composition is incorporated in the model instead of using general standardization methods, as the average bias of the land use-sediment-metal models were slightly lower than that of the land use-metal models. However, this method necessitates the collection of representative sediment chemistry data from the study area.

The predictive ability of the regression models decreased considerably when cross-validation was performed. Thus, the models were unstable, and the removal of one tenth of the data lead to differences in the variables selected to the models. The instability is related to the small size of the data, as well as to the heterogeneity of the data (very high concentrations at some sites compared to the rest of the samples). For more accurate predictions of metal concentrations a larger calibration data is needed, in addition to some estimate of the possible of point sources.

The logistic regression models showed that the occurrence of very high metal concentrations can be predicted to some degree. The models performed moderately for the complete dataset, but the predictive statistics for the cross-validation were mostly poor (Zn performed moderately-well). However, the logistic regression models for Cu and Zn appeared to make some distinction between the present and absent sites even during the cross-validation stage. The proportion of sites where the sediment quality guidelines were exceeded could be increased by collecting samples only from the sites predicted to be present (i.e. containing a high concentration of metals). Thus, if only the presence of high concentrations in an area is to be confirmed, screening of the sites according to land use reduces the costs of the study.

12.4.8. The role of land use

It appears that the impact of urbanization on trace metals was clearly evident when the baseline sites were compared with the urban sites in both datasets. Thus, the trace metal concentrations (particularly Cu, Zn and Pb) showed considerably higher concentrations in all of the urban land use types than at the baseline sites (in the areal dataset). The shift from fairly sparse residential areas dominated by single-family houses to dense urban areas with apartment buildings and commercial or institutional districts increased the average metal concentrations considerably. However, differences between different land use types in dense urban areas cannot be easily distinguished. The variations between rather similar catchments can be almost as much as the variation in the median concentrations between different ends of the urban continuum. Thus, dominating land use poorly predicts the concentrations at individual sites, and the land use of the catchment cannot be used as an indication of the potential need for stormwater treatment or
stream restoration. The dense urban areas and industrial areas appear to have the most potential for high metal concentrations, but enriched sites were also observed in low density residential catchments.

The correlations between land use metrics and trace metal concentrations confirmed the relationship between contamination and the degree of urbanization within the urban sites of the areal dataset. However, the majority of the correlations between land use variables and trace metal concentrations were non-significant or showed only relatively low significance levels. This was partly due to the corrections performed to decrease the errors caused by multiple statistical tests. If the correlations were tested only for the most commonly used indicators of urbanization (TIA, EIA), then considerably higher significance levels would have been obtained. The use of the corrected significance levels means, however, that only a very small proportion of the significant correlations between the metals and the indicators of urbanization were caused by change. The purpose of this study was to explore the nature of the relationships between land use and metal contamination. Therefore the results were not interpreted on a pass/fail basis according to the significance levels. Instead, the sizes of the correlation coefficients were also considered (see Cabin & Mitchell 2000; Moran 2003).

Despite the significance of the results, the correlation coefficients between the land use metrics and trace metal concentrations were at most moderate. This reflects the importance of other factors, such as sediment composition (which could not be totally accounted for by normalization) and point sources. In the Gräsanoja dataset, the p-values were low due to the low number of independent observations. This did not have a strong impact on the interpretation of the results, because most of the correlation coefficients between land use and metals were too low to indicate any meaningful relationships. Thus, the proportions of different land use types and other land use metrics had a substantially stronger relationship with trace metals in the small catchments of the areal dataset when compared with the larger catchment of the Stream Gräsanoja.

The idea of linkages between land use and metals is based on the assumption that most of the metals are derived from diffuse pollution arising from various urban sources. Consequently, abundant point sources may reduce this correspondence. In this study, the similarity of the spatial variations of the studied metals indicates that similar diffuse sources were dominantly responsible for metal concentration variations. However, the highest concentrations of metals did not occur at the same locations, and hence point sources were likely to occur in the urbanized catchments. Accordingly, this decreased the correspondence between metals and land use metrics. More detailed studies, especially with a smaller spatial resolution, are needed to confirm the sources of the highest metal concentrations.

Moreover, complexity of sediment and metal transport, and the spatial differences in erosion may complicate the spatial patterns of metal concentrations (Karouna-Renier & Sparling 2001). The influence of sediment characteristics was taken into account in this study, but other processes such as catchment hydrology and flow conditions, the design of stormwater sewerage system or biogeochemical changes may mask land use effects. Charlesworth and Lees (2001) went so far as to claim that the sediment may finally reflect the processes which formed it rather than the original sediment material, because the sediment goes through alterations on the way downstream from urban surfaces to stream sediments.

The results emphasize the importance of the entire upstream catchment to the metal concentrations in the stream sediment. Thus, urban development at the watershed areas could have an impact on the chemical quality of the sediments and water of the downstream stream reaches. The results of this study concerning the land use impact on trace metals might be at least partly trans-
ferable to other small urban catchments with a fairly similar, mainly residential history of urban development. The extrapolation of results obtained from small areas to larger catchments is, however, more problematic due to the increase of the possibility of disturbing factors (increasing noise) (Ongley 1987). The results could serve as an information source for land use planners and environmental administrators in minimizing the detrimental effects of urban development on nature. Ongley (1987) claims that medium sized study catchments (tens to several hundred km2) are needed in order to make interventions involving general questions of land use and to offer information for the development of land use policies. In Finland, however, urban areas are relatively small in extent, and the impact of urbanization is likely to be most pronounced in small water bodies. The contamination of most urban water bodies may, thus, be best controlled by regulating and steering the local land use.

12.5. Spatial and temporal variation

12.5.1. Analytical and fine-scale spatial variation

The fine-scale variations of metal concentrations within a site were small when compared to other investigations (Birch et al 2000, 2001; Walling et al. 2003). Furthermore, the small-scale variations of sediment properties were on average under 25%, a limit considered to indicate significant differences by Fisher et al. (2004). However, the magnitude of small-scale variation in relation to regional and local concentration differences is more important than the absolute value of small-scale variation. Thus, the fine-scale variations of trace metals within the replicate sites were very low compared to variations between the replicate sites, and between all sites of the Gräsanoja dataset. This suggests that fine-scale variations do not have a considerable impact on the interpretation of spatial variations of metal concentrations (Birch et al. 2001). However, the ability to distinguish the differences of metal concentrations between sampling sites also depends upon the contaminant gradient (Birch et al. 2001). In the lower reaches of the main channel metal gradients were low, and the differences between sites were affected by fine-scale variation. However, regional comparisons of metal concentrations have primarily a meaningful interpretation in the Gräsanoja dataset. In addition to the acid extractable metals, the easily reducible metal patterns also seemed to be unaffected by the fine-scale spatial variations.

The fine-scale spatial variation of replicate samples includes variation of metal concentrations at the sampling site and variance associated with sample pre-treatment and analytical process itself (Birch et al. 2001). The results show that the sampling site selection within an area of a few square meters, and the pre-treatment methods (sieving, settling and freezing) were not involved with substantial variation between the samples (c.f. Barbanti & Bothner 1993; Miserocchi et al. 2000). The fine scale-variations were only slightly higher than the analytical variance, which demonstrates that the pre-treatment methods and concentration determination provided reproducible results. However, both analytical and fine-scale spatial variances were high (more than 20%) at some sites particularly for Pb, which shows that moderately low concentrations differences between single sites may be affected by errors related to the selection of the sampling site or the analytical process.

In previous studies, high fine-scale variability even between sites separated by a few metres have been observed (van der Perk & van Gaans 1997), which is in contrast to the present results. Typical reasons for the fine-scale variability include locally varying sedimentational conditions and sediment composition, particularly organic matter content and the relative variations of fine particles and coarse diluting material (Wilber & Hunter 1979; Miller 1997; van der Perk & van Gaans 1997; Ciszewski 1998; Ladd et
al. 1998; Rhoads and Cahill 1999; Birch et al. 2000, 2001; Walling et al. 2003). In this study the control of sediment composition on trace metals was also relatively strong. However, due to the small number of replicate sites the results are not conclusive. Since the replicates represented similar morphological settings (low energy environments), the fine-scale variations of sediment composition and metals were low. Higher fine-scale variability of both sediment composition and metals could be expected between different geomorphological units or different parts of the cross-section.

12.5.2. Temporal variation

The variations of metal concentrations between two low flow periods were studied in order to assess the influence of temporal variation over the period of a sampling campaign on the results of the study. Sediment dynamics is one of the most important factors affecting temporal variations of metals. It is strongly dependent upon the hydrological conditions which influence runoff characteristics and erosion intensity in the catchment. During high flow, the fine grained settled sediments are resuspended and the bottom sediment is fairly coarse (Jain et al. 2005; Taylor et al. 2008). During dry periods and slow flow velocities fine grained sediments and associated trace metals accumulate on the bottoms of the streams. The samples were collected during low-flow periods, but temporal variations of metal concentrations were more than 15% for all other metals than Cd. The observed variations were, however, comparable to seasonal variation between low-flow periods in consecutive years reported elsewhere (Axtmann & Luoma 1991; Birch et al. 2000; Walling et al. 2003). Even higher average variation (10-50%) tends to be associated with more differing hydrological conditions (Birch et al. 2001).

The reasons for temporal variation are often difficult to identify (Rhoads & Cahill 1999; Birch et al. 2000, 2001; Walling et al. 2003). The metal concentrations between the two sampling occasions did not increase or decrease consistently, although Cu and Zn concentrations were mostly higher in the samples taken in October than September. The variations of metals were controlled by the sediment composition, TOC in particular. In addition, the variations were likely to be related to local factors, such as changes in the sediment sources through time, and consequently variations of the influx of contaminants or diluting sediment material (Wei & Morrison 1993; Foster & Charlesworth 1996; Rhoads & Cahill 1999; Walling et al. 2003).

Temporal variations of metals were substantially higher than the fine-scale variations. The results indicated that moderate spatial differences between sites can be a consequence of temporal variations in metal concentrations. Thus, relatively low variations between neighbouring sites should not be interpreted from sediment data due to the possibility of analytical, fine-scale spatial or especially temporal variations. However, concentration trends or broad-scale patterns are not affected by sources of variation. The temporal variation tends to decrease the statistical relationships between regional patterns of metals and environmental factors, but does not induce bias. In addition, the identification of sites showing very high concentrations, i.e. “hotspots”, were not impeded by the temporal variation between low-flow periods.

The temporal variability can occur at different scales from hours, to months (seasonal) and years (climatic change) as a response to the scale of major flow variations (Birch et al. 2001; Jain et al. 2005). High flows (flood peaks) are generally recorded several times a year in southern Finland (see Kotola & Nurminen 2003; Ruth 2004), and the surficial sediments in the sampling sites of this study have rarely time to sustain for months or years. Therefore, the sediment samples are likely to reflect the properties of suspended sediment transported by relatively recent storm events.
12.5.3. Spatial autocorrelation of metals

Metal concentrations showed moderate spatial dependency, which implies that the metal concentrations of closely located sites are similar. The residuals of the sediment composition models show no substantial autocorrelation which indicates that sediment composition is primarily responsible for the observed spatial autocorrelation pattern. Consequently, true local autocorrelation, related to the dispersion of metals independently of the environmental factors appears to be fairly low.

In other studies high metal concentrations have been encountered close to metal sources such as mining activity or large urban centres, with a pattern of downstream decreasing concentrations (Axtmann & Luoma 1991; Heiny & Tate 1997; Callender & Rice 2000). Possible reasons for this spatial autocorrelation pattern include hydraulic sorting, dilution by uncontaminated sediment and losses along the channel as metals are deposited (Axtmann & Luoma 1991; Miller 1997; van der Perk & van Gaans 1997). In fluvial environment, water transport further tends to lengthen the extent of spatial autocorrelation (Dent & Grimm 1999).

Unfortunately, few quantitative studies exist on the spatial autocorrelation of metals in stream sediments (for exceptions, see van der Perk & van Gaans 1997; Ladd et al. 1998), and none for urban settings. One can assume that spatial autocorrelation occurs downstream of metal sources, which include stormwater outlets or industrial discharges. This kind of behavior has been observed qualitatively by several authors (e.g. Wei & Morrison 1993; Bubb & Lester 1994; van der Perk & van Gaans 1997; Rhoads & Cahill 1999), but only downstream of individual metal sources. In this study, the transport and dilution pattern of metals in stream sediments were approached using spatial statistics. The purpose of the approach was to determine, whether the metal concentrations in adjacent locations are dependent on each other in urbanized areas, where metal discharges are not dominated by one but several smaller sources (e.g. stormwater outlets). Sampling intervals of 200 meters turned out to be too high to record the strength and extent of local spatial autocorrelation in the Stream Gräsanoja using spatial statistics. The concentrations are, thus, likely to decrease rapidly due to dilution by bank and surface erosion. Van der Perk and van Gaans (1997) also observed no spatial dependency of metals at finer spatial scales. Ladd et al. (1998) on the other hand found spatial autocorrelation between sites separated by 50 meters or less. Consequently, based on the results of this study and reading of literature, the spatial autocorrelation of metals in fluvial system receiving metals from several moderate sources does not extend to hundreds of meters distance in flat terrain. A smaller sampling interval would allow the determination of finer scale spatial patterns.

The small extent of local spatial autocorrelation suggests that there is no local dependency between adjacent sites and that the sediment samples collected using 200 metre sampling intervals would be spatially independent of each other. However, the transport of metals appears to play a major role in controlling the metal concentrations at broader scale. This was demonstrated by the importance of the entire upstream catchment in determining the metal concentrations. Consequently, each observation does not represent an independent sample and bring a full degree of freedom in statistical analysis (Lichstein et al. 2002; Wagner & Fortin 2005). As a result, correlations appear to be more significant than they actually are (Lennon 2000). Therefore, the extent of spatial autocorrelation was estimated from the spatial correlograms of the metal concentrations, so that the number of independent observations could be determined. Finally, the correlations between metals and sediment composition or land use metrics were calculated using a reduced number of degrees of freedom, as suggested by Diniz-Filho et al. (2003) and Wagner and Fortin.
Determination of spatial patterns is dependent on the distance and connectivity measures used (Ganio et al. 2005; Peterson et al. 2006; Ver Hoef et al. 2006). The fluvial systems pose challenges when determining the spatial autocorrelation. Hydrological distances, which means the downward distance between two sites which are functionally connected, i.e. water must flow from one site to another, were used in this study. However, the connection between two sites is not necessarily solely determined by the absolute distance along the network. Sites located on a small tributary may have a weaker impact on the downstream sites when compared with sites located on larger tributaries (see Peterson et al. 2006). Models that take water flow into account have already been developed, but further research in this field is still required (Peterson et al. 2006; Ver Hoef et al. 2006). In future, more appropriate hydrological geostatistical models may provide more functional spatial patterns in fluvial systems.

12.6. Trace metals in the water phase and SPM

The partitioning between dissolved and particulate phases showed the typical sequence of Pb being the most attached to the particulates (see Salomons & Förstner 1984). The particulate proportions of Zn, Cd and Cu were relatively low during the low-flow period, but increased during the high-flow period (c.f. Blake et al. 2003). During the snow-melt period Cd was also nearly completely bound to the particulate phase. The relatively low pH-values of the first stages of the snow-melt period did not evidently cause a decrease in the solid partitioning of metals. The high particulate proportions suggest that a major fraction of the metals transported by the streams during high-flow events could theoretically be removed from the water utilizing stormwater treatment systems. However, these systems should be able to retain even the finest particles to work efficiently on the suspended matter.

Most of the SPM metal concentrations showed a statistically significant difference between the baseline sites and urban sites during both sampling periods, whereas the total metal concentrations in water did not show any difference between land use categories during the low-flow period. In addition, all of the SPM metal concentrations were strongly related with the imperviousness of the catchment during the high-flow period. Hence, the suspended particles seem to reflect the land use of the catchment considerably better than the total metal concentrations in water. The correlations of metals with land use percentages were low during the low-flow stage. Therefore, the low-flow SPM metal concentrations are likely to reflect the differences between urban and non-urban land use, but do not indicate the degree of urbanization more specifically.

The temporal trends of SPM metal concentrations are very diverse (Williamson 1985; Carter et al. 2003, 2006; DeCarlo et al. 2004; Bibby & Webster-Brown 2005; Horowitz et al. 2008), and the various patterns may reflect differences in storm events, land use and other catchments characteristics. Often, the metal concentrations of hydrological events are lower than base-flow concentrations due to the dilution effect, and higher grain-size of the sediment being transported (Carter et al. 2006; Horowitz et al. 2008). However, in urban catchments the dilution effect is weaker, since there is less potential for erosion of uncontaminated areas, and the metal concentrations of SPM may remain relatively constant throughout the storm (Carter et al. 2006). The results of this study also suggest that the SPM metal concentrations may be higher during snow-melt induced high-flow periods in urban catchments when compared with baseflow conditions. The SPM metal concentrations were not related with the amount of suspended sediment during high flow, which indicates that no substantial dilution by eroded surface soils occurred during the sampling period.
Controversial opinions of the role of bed sediments as indicators of suspended sediment metal concentrations of different flow regimes have been presented. Horowitz et al. (1999, 2008) have considered bed sediment to correspond with the base-flow suspended sediment, whereas other researchers have found a correspondence between metals in bed sediments and SPM collected during storm events (Rhoads & Cahill 1999; Owens et al. 2001). In this study, metal concentrations of SPM appeared to be related to the bed sediment metal concentrations during both hydrological conditions. However, the high-flow concentrations had a closer association with the sedimentary concentrations. Catchments were poorly hydraulically connected with the stream in dry periods, and it is unlikely that considerable amounts of particulate metals were transported to the stream from urban areas at the time of the sampling. The interaction between the bed-sediments and low-flow SPM may be related to the remobilization of bed sediments (see Salant et al. 2007).

Here the bed sediment samples were collected in summer base-flow conditions, when the amount of fine sediments accumulated on the stream bed is usually considered to be highest (Walling et al. 1998; Collins & Walling 2007). The upper fluffly layers (SFGL) of the sediment have probably accumulated during base-flow mainly via deposition of aqueous flocs. Previously, SFGLs have been observed to reach thicknesses of 5-20 mm (Carling & Reader 1982; Droppo & Stone 1994a). At the majority of the sites, the sediment beneath the SFGL layer presumably accumulated during normal conditions and the falling limb of the previous storm event. Wood and Armitage (1999) described the succession of fine sediment deposition on the bed of a small stream in the UK. They observed that the marginal deposits were the first to accumulate on the declining limb of the hydrograph, while the other deposits (depressions, macrophyte deposits, lee-side deposits and SFGL) were created later during normal and low flow conditions. It is likely that accumulation of the sampled bed sediments has taken place over a relatively long time period, although the results suggested a close correspondence between the bed sediments and storm-flow SPM.

The metal concentrations of the water phase were only weakly associated with the degree of urbanization. The low-flow concentrations had no relationship with land use for any of the aqueous metal concentrations. During the high-flow stage there was a distinction between the total metal concentrations of the urban and non-urban sites, but no linkages between metal concentrations and land use could be distinguished within the urban sites. The total metal concentrations were dependent upon the concentration of suspended sediment, which indicates that the use of aqueous metal concentrations in contamination monitoring may suffer from the problems associated with temporal variation of suspended matter during a storm event. Correspondingly, temporal metal concentration variations of an order of magnitude have been recently observed in stormwater during a storm event in Helsinki (Karvinen 2009). The samples of this study were collected when the snow cover was gradually thawing. Therefore, the suspended sediment concentrations and consequently also the aqueous metal concentrations, were relatively stable over time. When sampling is carried out during individual storm events, it may be difficult to obtain as stable metal concentrations for extensive spatial comparisons.

The dissolved Cu and Zn concentrations of high-flow samples appeared to be related to the degree of urbanization. This indicates that the higher input of metals from urban surfaces is also reflected as high dissolved concentrations. During low-flow conditions, when practically no water is discharger to streams from urban surfaces, the dissolved metals did not reflect the land use of the catchment.

Dissolved Pb displayed a negative relationship with urbanization indicators during
the snow-melt period, which was very surprising, since it indicates that dissolved Pb is dominantly derived from non-urban areas. This behavior may be related, in addition to the influence of pH, to water characteristics, particularly the abundance of complexing agents. However, the reason for the negative correlation between Pb and urbanization remained unclear. Due to the low percentage of dissolved Pb, this unexpected pattern does not play a dominant role in determining the behavior of total Pb concentrations.

The particulate metal concentrations were not closely correlated with urbanization of the catchment, and are consequently not particularly suitable for contamination monitoring. Dissolved Cu showed a closer relationship with land use during the high-flow period. However, the concentrations of some metals (e.g. Pb) were often very low in the dissolved phase, which may increase the impact of analytical errors on the results. Thus, the concentrations of different sites would not be entirely comparable to each other.

In fluvial environments metal contamination assessment studies are often performed by collecting water samples, and consequently analyzing dissolved or total metal concentrations (Nurmi 1998; Gromaire-Mertz et al. 1999; Davis et al. 2001; Ruth 2004). The sediment concentrations of bed sediments and SPM are rarely considered. The results of this study show, however, that metals in bed sediment and suspended particles are better correlated with the intensity of urbanization than metals in the aqueous phase. Consequently, by using these matrixes for metal contamination assessment, the ability to detect the most important contaminant sources could be improved at least in urban environments, where metals are predominantly transported in the particulate phase. Bed sediment samples ought to be collected during low-flow periods, when the temporal variations are relatively low. The use of bed sediments is, however, constrained by the availability of suitable sediment at the site of investigation. Sampling of exceptionally coarse sediment due to lack of fine-grained deposits may lead to major underestimation of anthropogenic metal contamination.

Sampling of SPM should preferentially take place during high-flow periods. It is, however, essential to confirm the benefits of bed sediment and SPM, by performing more detailed studies on the temporal variations of metal concentrations in these matrixes. For example, the impact of dilution on SPM metal concentrations over the course of a short rain event might be crucial in determining the suitability of SPM for source detection studies.

12.7. Implications for water pollution studies

12.7.1. Objectives of sediment assessment

Sediment assessment may serve a number of different objectives from specific problem oriented investigations to national or international water quality measurement programmes. The usefulness and the requirements concerning the sampling, analytical techniques and data analysis of sediment assessment depend fundamentally on the aims of the study (see Förstner 2004). The following classification of the objectives of water quality measurements that also apply to sediments has been presented: survey, surveillance and monitoring (Water quality surveys 1978). A fourth category, spatial and temporal prognosis, was later attached to the classification by Förstner (2004) and Förstner and Heise (2006). Surveying is an intensive investigation which aims to gathering information of a specific sediment/water quality problem. Surveillance also serves a specific purpose related to the control or management but is continuous in nature. In addition, surveillance studies often focus on detecting sources and tracing pathways of contaminants (Förstner & Heise 2006). Monitoring is 'a continuous, standardized measurement and observation of the envi-
ronment’ (Water quality surveys 1978) with specific emphasis on anthropogenic changes and the suitability of water quality for future use (Förstner 2004). Monitoring often involves the determination of bioavailability of contaminants and the ecological status of the watershed utilizing a tiered approach (Förstner 2004). Spatial and temporal prognosis aims to assess the risks related to soil or sediment erosion or chemical mobilization currently or in the future (Förstner & Heise 2006).

The sediment assessments usually involve different chemical, biological, physical analyses and/or modelling. The determination of sediment metal concentrations often serves as a first stage of the risk assessment associated with sediment contaminants (Chapman & Mann 1999; Förstner 2004). However, metal concentrations and the identification of metal sources may even be the central issue of many survey and surveillance type sediment investigations. The main focus of the following discussion is on the application of sediment chemistry analysis to detection of metal sources in the fluvial environment.

Different environmental factors can increase the uncertainties related to assessment of sediment metal concentrations. These uncertainties can be partly reduced by careful selection of proper methods, but the chain of different procedures involved in measuring sediment metal concentrations depends on the purpose of the study. Therefore, different requirements and recommendations may be proposed concerning the sampling (sampling site selection, sampling interval etc.), pre-treatment (sieving, drying), analytical techniques (including digestion), data presentation or interpretation of the results. When the purpose of the study is to detect metal sources, interference may be caused by sediment composition, temporal variations of metal loading and transport of metals. Minimizing the impact of these factors on the results reduces the uncertainties related with the interpretation of metal sources.

12.7.2. Accounting for variations in sediment composition

Sediment composition is one of the most often cited factors that obscure the metal patterns at the regional, local and temporal scales (Arakel 1995; Ladd et al. 1998; Kersten & Smedes 2002; Walling et al. 2003). The influence of sediment properties and components that most strongly affect the trace metal binding capacity of the sediment (surface area, metal oxides, organic matter, clay mineralogy) increases with decreasing grain size (Horowitz & Elrick 1988). In this study, it was also assumed, that grain-size variations arising from different hydraulic conditions (both regionally and locally) essentially control the metal concentrations of fluvial sediments. Thus, the sediment samples were collected from depositional areas where the sediments are primarily fine-grained. The depositional zones usually show highest metal concentrations, and low natural variability (Ciszewski 1998; Ladd et al. 1998; Rhoads & Cahill 1999). These are of high importance especially in detecting anomalies, as high natural variability of sediment quality prevents the meaningful interpretation of regional differences (Birch et al. 2000). The fine-grained sediment is also important for the biota, since they offer most of the food (organic matter) for sediment dwelling organisms (Förstner 2004).

According to Ladd et al. (1998) the approach, where sediments of only one type, for example depositional zone, are sampled, is appropriate when the aim is to detect the maximum concentrations of metals. When the goal is to describe the overall quality of the sediment or bioaccumulation of metals, or estimate transport and storage of metals, more complex sampling strategies should be implemented which aim to produce samples that represent the variety of sediment types in the stream (Ladd et al. 1998; Walling et al. 2003; Förstner & Heise 2006).

Secondly, the remaining grain-size variations were reduced by sieving of the sediment to separate the clay and silt (mud) frac-
tions from the sand fraction. The purpose of this granulometric normalization approach is to distinguish between natural variability and human induced pollution (Kersten & Smedes 2002). The usefulness of sieving procedure in tracing pollution sources is slightly controversial, because the finest sediment particles are most strongly affected by erosion and transport processes (Wilber & Hunter 1979). In spite of that, sieving has been successfully applied to reduce metal variation (e.g. Birch et al. 2001), and it has been suggested as a standard approach for sediment quality assessments (Horowitz & Elrick 1988; Arakel 1995).

The results of the present study show that the grain-size separation succeeded well in decreasing the fine-scale variation of metals. The resulting variation of the mud fraction was very low, and did not appear to mask any metal concentration differences between sites. In the sand fraction, both analytical and fine-scale spatial variations were greater, which suggests that more pronounced uncertainty is associated with the results, although the errors did not appear to disguise the occurrence of metal “hotspots”. In addition, the dependence of metal concentrations on sediment composition appeared to be stronger in the sand fraction. Thus, the sieving procedure decreased the control of sediment composition on metals, although the correlations between metals and land use did not show considerable differences between the size-fractions. The most serious drawback of granulometric normalization is that the method is very time-consuming and laborious. Therefore, despite the evident benefits of the grain-size separation, it remains unclear, whether the bulk sediment could also be used for cost-efficient tracing of metal sources. Hence, future investigations would benefit from a pilot study undertaken to assess the extent of fine-scale variation of metals and the influence of sediment composition on metals in the bulk sediment.

Next, in the series of different procedures aimed at reducing the influence of sediment composition and enhancing the possibility to detect anomalies is the choice of the proper extraction method. In this study, partial dissolution (nitric acid extraction assisted by microwave) was used as the standard approach, but the usefulness of the easily reducible phase for metal source detection was also examined. The partial dissolution is often considered more sensitive to anthropogenic effects compared to total digestion (Arakel 1995; Vallius & Lehto 1998), although Sutherland et al. (2001) found only limited differences between the total leach and the nitrogen acid digestion. The acid extractable metal concentrations do not reflect the effects of the minerals as strongly as the total leach, as most of the silicate minerals and associated metals remain undissolved (Vallius & Lehto 1998), although the partial dissolution used dissolves most of biotite and clay minerals and some of plagioclase in addition to the organic matter and oxides (Hämäläinen et al. 1997, Lahermo et al. 1996). The results of the present study show that, for the purpose of source identification, partial dissolution appears to be appropriate since the metal concentrations obtained reflect relatively well the land use of the areas surrounding the streams, and moderate correlations were also found between metals and land use metrics in the areal dataset.

The higher enrichment factors of the easily reducible metals compared to acid extractable concentrations suggested that metals of the most mobile phase are more strongly affected by human actions compared to the more strongly bound metals. This conclusion is based on the assumption that the standardized concentrations above the reference values are of anthropogenic origin (Irabien & Velasco 1999). A major part of the variations above the reference concentrations is likely to be attributable to land use differences, since the metal concentrations correlated relatively strongly with the land use metrics. The correlations were even somewhat higher compared to the acid extractable metals. The results thus indicated that the metals in the most mobile phase are particularly sensitive indicators of anthropo-
genic metal contamination. This parallels the findings of Förstner and Müller (1981), who reported that, the metals released to aquatic systems by human actions are associated with relatively labile phases (cation exchangeable positions and easily reducible compounds). However, the extent of fine-scale spatial and particularly temporal variations showed that the uncertainties related to individual measurements were higher when compared with the acid extractable concentrations. Nitric acid digestion assisted by microwave is a standardized, well controlled procedure (Vallius & Lehto 1998), and the obtained concentrations can be compared to reference values and concentrations of other studies, which further support the applicability of the digestion.

The various extraction methods evidently have their own benefits and drawbacks. Tack and Verloo (1995) recommended non-selective leaches that are easier to apply when compared with (multiple) selective extractions. Furthermore, Sutherland et al. (2001) considered weak non-selective extractants to be the best indicators of anthropogenic contamination. However, the future availability of reference materials for different digestions should further guide the selection of methods to be applied. Based on this study the acid extraction offers a relatively useful, reliable and rapid method for surveillance investigations focused on anthropogenic metal pollution (c.f. Wilson et al. 2006).

Despite the granulometric normalization applied, the acid extractable metal concentrations of the mud fraction showed fairly strong dependence on sediment composition. Since the sieving approach mainly reduces the grain-size effects, variations of organic matter content and mineralogy remain after sieving (Kersten & Smedes 2002; Walling et al. 2003). So far, the effect of different grain-size properties driven by different hydraulic conditions has been considered as the major confounding factor for the interpretation of sediment chemistry data (Combest 1991; Bubb & Lester 1994; Kersten & Smedes 2002). In contrast, the results obtained in the present study indicate, that in sieved sediments collected from depositional zones the effect of organic matter may exceed that of pure granulometric variations.

The importance of the effects of sediment characteristics on metal variations in this study supports the conclusion presented by Kersten & Smedes (2002), that a two-tiered normalization, using both sieving and geochemical normalization is necessary. There exist several alternative methods for geochemical normalization (Fe, Co, organic matter, clay content) (Loring 1991; Schiff & Weisberg 1999; Matthai & Birch 2001; Kersten & Smedes 2002), most commonly the normalization is achieved using conservative elements such as Al or Li that represent proxies for clay mineral content (Schropp et al. 1990; Rubio et al. 2000; Misrocchi et al. 2000; Aloupi & Angelidis 2001; Kersten & Smedes 2002). The use of organic matter as a normalizer has been criticized for two reasons. Firstly, it is not conservative but takes part in diagenetic processes in sediments (Kersten & Smedes 2002). Secondly, it has various sources and can originate from pollution sources, such as wastewater discharges or black carbon particles in urban areas (Leivuori 1998; Lin & Chen 1998; Matthai et al. 1998; Kersten & Smedes 2002). In this study, however, organic matter appeared to be the most significant control on metals, and the impact of common sources between metals and organic matter were considered as being less important. Therefore, the sediments were normalized to organic matter and clay content, which succeeded in removing most of the effects of sediment composition. However, the regression models between metal and land use showed that, the variations in metal concentrations could be accounted for better when the sediment composition was included in the models, and the parameters were estimated specifically for this data. However, the influence of sediment composition varied slightly even between the two datasets of this study. This corresponds with the view that the effect of
sediment composition is somewhat area-specific (Horowitz & Elrick 1988).

12.7.3 The influence of metal transport and temporal variations on sediment sampling and interpretation of the results

The results obtained here suggest that metal concentrations are rapidly diluted in the downstream direction in urban fluvial systems. As a result of the small extent of local spatial autocorrelation, some moderate point source inputs may be missed if the sediment samples are collected a few hundreds of metres apart. Therefore, for a detailed survey of the metal sources, the use of a smaller sampling interval is recommended. Strong fine scale variations of metals are usually overcome by collecting composite samples (Ladd et al. 1998; Salminen et al. 1998). Thus, a site may comprise a stretch of 100-500 metres of the stream. Multiple subsamples are collected from several depositional zones along the stream within the site, and the subsamples are composited to decrease the natural variability of metal concentrations. The results of the present study show, however, that for the identification of anomalous concentrations in small urban streams, sediment sampling sites should be limited in size. Due to the spatial pattern of metal transport (autocorrelation), the collection of composite samples may effectively impede the detection of metal sources (see also Karouna-Renier & Sparling 2001). The reliability of the results is better increased by collecting replicate samples at very fine scale and by analyzing the spatial autocorrelation structure from distances of metres to several hundred meters. Compositing is usually selected based on the lower costs associated with the approach. However, results of the fine scale variation and spatial autocorrelation structure analyzed in a pilot study can be used to direct the main sampling campaignmore cost-effectively (Arakel 1995; Birch et al. 2001). Alternatively the fine scale variation may be studied at the end of the investigation as suggested by Birch et al. (2001).

The regional variations of sediment properties appear to be relatively unaffected by temporal variations between the two periods which represent base flow conditions. Low flow conditions are likely to reflect the maximum metal concentrations (see Birch et al. 2001) which are appropriate for investigations aiming at tracing metal sources. Higher temporal variability would be expected between variable hydrological conditions and different seasons (Förstner & Wittman 1981; Walling et al. 2003). These variations need to be determined in order to obtain a comprehensive view of the comparability of sediment samples collected at different times (Walling et al. 2003).

There are no clear standards of the appropriate sampling interval but usually water samples are collected more frequently than sediment samples (Förstner 1989). Stronkhorst et al. (2004) suggested that once every 1 to 3 years is enough for monitoring purposes under the demands of the European Water Framework Directive. However, Rhoads and Cahill (1999) and Birch et al. (2001) concluded that due to high temporal variability in the urban fluvial environment, assessment of metal contamination may require temporal sediment monitoring over several years. Thus, site-specific risk assessment and decisions on sediment management options in urban fluvial environments should probably be conducted based upon information of temporal (at least seasonal and short term) variations. However, one sampling campaign may serve the needs of preliminary catchment-scale site prioritization.

12.7.4. Applicability of sediment for aquatic pollution monitoring

In this study, metal concentrations of different matrixes were correlated with the land use metrics in the following order: high flow particulate << high flow dissolved < low flow bed sediments < high-flow SPM. Thus, the suspended sediments may, at best, provide
better indication of contamination when compared to bed sediments, but the effects of varying flow conditions may weaken their advantage in contamination assessment. The results suggest, however, that sediments are appropriate for pollution monitoring especially with a focus on detecting metal sources in fluvial environments, when sediment compositional effects are taken into account. Enrichment factors or easily reducible metal concentrations offer additional insights into the degree of contamination due to anthropogenic effects.

The benefit of sediment assessment is that ‘the sampling does not need to be restricted to a limited number of infrequent high flow events’ (Owens et al. 2001). However, sediment quality assessment is not as straightforward as that for water, since many site-specific parameters, such as sediment composition, influence the pollutant concentrations and their bioavailability (see Förstner 2004).

The ecological consequences of contamination have recently been a focal aspect of sediment assessment (Apitz 2006). This trend will continue particularly due to the ecological goals included in the European WFD (Apitz 2006). However, neither the metal concentrations of the partial leach or enrichment factors over baseline provide an indication of where adverse effects on biota or human health could occur (Thomson et al. 1984; Burton 2002). Following the emphasis on the ecological quality of waterbodies, sediment does not play a key role in the new European water framework directive despite the calls for including the role of sediment and sustainable sediment management as an integrated part of WFD and river basin management (Crane 2003; Brils 2004). Sediment should not be treated in isolation, but rather as a factor that impacts the ecological quality of a waterbody and may be an obstacle to receiving good ecological status (Stronkhorst et al. 2004). WFD with its daughter directive on the environmental quality standards in the field of water policy (EC 2008) offer a mechanism to monitor sediment quality, but monitoring is not demanded from the member states. Compliance monitoring to check if the preset quality standards are met is not yet appropriate because no environmental quality standards have been set for sediment at the EU scale (Stronkhorst et al. 2004). The implementation and setting of European EQS for sediment are obstructed by the additional costs associated with sediment monitoring, and to the lack of correspondence between observed toxicity and EQSs (Stronkhorst et al. 2004; Karvonen 2006). Recognizing the misfit between toxicity and sediment chemistry, proposals have been made to use the sediment EQS as a screening tool in the first tier of a risk assessment rather than as a legally enforceable pass/fail limit in EU (Apitz & Power 2002; Crane 2003).

The use of sediment seems to be a fairly simple, reliable and a relatively cost-effective way to gather information for spatial and trend monitoring (c.f. Metals in lakes and watercourses 2000; Brils 2004). Sediment assessment appears to be particularly valuable for surveillance investigations or synoptic surveys of metal pollution in urban areas, when a large or dense spatial coverage is essential. Thus, a general view of the metal concentrations and their variation may be obtained. In addition, the sites may be screened for more detailed analyses (e.g. extent of contamination or biological status). The bed sediments might offer a more stable and time-integrated estimate of the actual contaminant concentrations when compared with water samples. Stronkhorst et al. (2004) and Casper (2008) even recommend that analysis of sediment contaminant concentrations could serve the purposes of the WFD at relevant locations by aiding in the monitoring of the progressive reduction of contamination. Standardization of the sampling and pre-treatment procedures in addition to the development of some sediment quality guidelines would further increase the usefulness of the sediment approach.
13. Conclusions

Trace metal contamination of urban streams in the Helsinki Metropolitan region, Finland, was examined in this study utilizing the information provided by bed sediment chemistry. In addition, the effects of the most important controls, namely sediment composition and land use, were analysed statistically (Fig. 43). The variations of metal concentrations at different scales were also quantified in order to increase the understanding of the influence of natural factors and processes on metal concentrations. The results were finally evaluated to determine the applicability of sediment assessment in aquatic contamination monitoring. Based on the findings, five main conclusions can be drawn:

1. Streams draining small suburban catchments in the Helsinki Metropolitan region are typically moderately contaminated based on sediment chemistry assessment. At the majority of the sites metal concentrations were clearly above the baseline but did not appear to pose an immediate threat to the biota. At some sites, however, high metal concentrations showed potential for harmful effects. At these sites a risk assessment involving the whole sediment mass and biological methods should be carried out to verify the pollution status of the sediments. In the catchment of the Stream Gräsanoja the most contaminated sites were located in the headwater reaches. Hence, it would be relatively easy to control the highest metal discharges using local stormwater treatment facilities. Furthermore, owing to their location in the small headwater reaches, the concentration “hotspots” are unlikely to initiate large scale pollution.

The influence of sediment composition on metal concentration variations is comparable to that of land use, and it can interfere with the detection of anthropogenic contamination patterns. Organic matter was the dominant sedimentary control on metals, although metals

![Figure 43: Factors controlling the variations of trace metal concentrations (outside the outer circle). The nested circles describe the contribution of different scale variation components on the regional variation of metals: the fine-scale spatial variation, temporal variations within the sampling period and the between site variations.](image-url)
were not operationally bound to organic compounds. Scavenging of metals to the sediment appeared to be strongly dependent upon the amount of flocs which consisted of organic matter and mineral components. Signals of abundant soil aggregates were observed in sediments with low metal concentrations. Consequently, organic matter appears to have a strong indirect influence on the metal binding capacity of the sediment. Hence, despite the critical views presented previously, it appears that sediment metal concentrations should be normalized to organic matter content, that is if substantial contributions from sewage can be ruled out.

3. While diffuse sources from urban land use lead to moderate increases of metal concentrations with increasing urbanization, point sources or some other site-specific factors appear to be responsible for the highest metal concentrations. Especially the concentrations that indicate a probable threat to the biota could not be explained by land use. From the environmental perspective, future studies should focus on assessing the reasons for these high concentrations.

The results further indicated that the highest metal concentrations were not linked with any particular dense urban land use type, although many of the industrial sites showed very high metal concentrations. The impacts of buildings and transport areas appeared to be equally strong. These findings contradict many of the loading estimates and water quality studies carried out with relatively few study catchments. It seems evident that different approaches to estimating metal sources can improve the current knowledge of the factors responsible for urban contamination. The advantage of sediments studies in particular is the high number of catchments that can be included. In future, fingerprinting studies involving stable isotope measurements may offer a novel method to assess the contributions of different sources in stream sediments. The information of the general increase of metal concentrations with increasing urbanization can be utilized in land use planning or large scale environmental management projects. However, the results show that questions concerning more detailed issues, for example in stormwater treatment or stream restoration decisions, require site-specific metal concentration analyses.

In the fine-grained depositional sediments metal concentrations are dominantly determined by regional patterns, in that the fine-scale spatial or temporal (between two low-flow periods) variations do not appear to hamper the detection of significant metal concentration patterns. The problems caused by natural spatial and temporal processes can evidently be reduced by the sampling and sediment analysis methods used here, and the sediment approach is according to the present results, applicable to metal contamination studies. However, further studies should be aimed at capturing the temporal and spatial variations of metal concentrations. The temporal variations of metal concentrations in depositional surface sediments are still poorly understood, and it is vital to investigate the variations of sediment composition and metal concentrations a) between different seasons b) between separate low-flow periods and c) in the short term, focusing on the building up of metal concentrations following a storm-event. Studies involved with
the spatial variations of sedimentary metals would be most beneficial at scales ranging from tens of metres to a few hundred meters. The results of this study suggest that the major increase in spatial variation occurs within this range for depositional sediments.

5. The stream bed sediments and suspended particles show potential for wider use in spatial and temporal contamination monitoring in urbanized areas. When single samples are collected, these matrices appear to reflect land use better than the commonly used total metal concentrations of the water phase. Sediment and suspended sediment chemistry analysis provide methods for cost-effective and rather reliable contamination assessment when continuous water quality measurements are not available. Such general estimates of metal contamination may be needed, for example, as a basis for stormwater management strategies or as screening level information for further contamination assessment in urban areas. The sediment approach might also improve the quality of temporal environmental monitoring data when only coarse temporal resolution is needed. However, the lack of sediment quality guidelines hampers the use of sediment assessment in official monitoring tasks. Thus, development of sediment quality guidelines would increase the applicability of sediment chemistry data in the future by enabling compliance monitoring.

The statistical approach adopted here in analysing the metal-land use relationships has provided new insights into the nature of the relationships between different land use parameters and trace metal concentrations. So far, the urban metal pollution investigations have mostly yielded information of the metal loads from a limited number of study sites and catchments. The spatial coverage of water quality studies is restricted by the high amount of data needed to obtain reliable results. In spite of the relatively high number of studies, the general understanding of the relationships is rather vague (e.g. Baker 2003; Tiefenthaler et al. 2008). In particular, the variation of metal contamination within certain land use types or within equally urbanized catchments cannot be determined if the number of studied catchments is low. This is certainly the case in Finland, where studies on aquatic metal contamination in urbanized areas are scarce. Therefore, although some of the present results support the general perceptions, the quantitative results of a large number of independent catchments obtained here essentially contribute to the knowledge of the patterns and variations of stream sediment metal concentrations in urbanized areas. This information may be highly valuable in future, since stormwater and the development of stormwater management strategies are increasingly important issues for municipalities.

Finally, the application of sediment analyses does not mean that all water quality analyses could be replaced. Actual loading estimates and information of short term variations provided by continuous measurements have their own advantages. In addition, aquatic pollutants may in some situations remain in dissolved form, which necessitates the measurement of dissolved metal concentrations. However, the potential benefits of the sediment approach are substantial. Stream bed sediments appear to be suitable for contamination monitoring, particularly for the detection of spatial patterns and sources of trace metals. Large spatial coverage would be useful in many environmental monitoring tasks, but the availability of resources limits the number of catchments that can be studied by water quality analyses. In these situations sediment analyses would be particularly valuable, and could be applied more frequently. The resources allocated to more detailed research
on the sediment approach in contamination monitoring may lead to reduced costs of environmental monitoring in the future, if water quality analyses can be replaced by sediment analyses.

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I received storm sewer maps from the study region, and I warmly thank all persons who assisted in providing these maps. Special thanks go to Heidi Kauppinen (Helsinki Water), Juha Hermunen and Juhani Moilanen (City of Espoo), Eero Heiskanen (City of Kauniainen) and Ulla-Maija Rimpiläinen (City of Vantaa).

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References


Åström, M. & N. Corin (2000). Abundance, sources and speciation of trace elements in
humus-rich streams affected by acid sulphate soils. *Aquatic Geochemistry* 6, 367-383.


Basic map 1:20 000, sheet 204301. Perus-CD. National Land Survey of Finland, Helsinki.
Basic map 1:20 000, sheet 204307. Perus-CD. National Land Survey of Finland, Helsinki.
Bedrock map 1:100 000, sheet 2032 Siuntio. National Land Survey of Finland, Helsinki.
Bedrock map 1:100 000, sheet 2034 Helsinki. National Land Survey of Finland, Helsinki.
Bedrock map 1:100 000, sheet 2043 Kerava. National Land Survey of Finland, Helsinki.


Bibby, R. L. & J. G. Webster-Brown (2005). Characterisation of urban catchment suspended particulate matter (Auckland region, New Zealand); a comparison with non-urban


ISO 17294-2. Water quality -- Application of inductively coupled plasma mass spectrometry


Owens, P. N., D. E. Walling, J. Carton, A. A. Meharg, J. Wright & G. J. L. Leeks


Tack, F. M. G. & M.G. Verloo (1995). Chemical speciation and fractionation in soil and


Turer, D., J. B. Maynard & J. J. Sansalone (2001). Heavy metal contamination in soils of


Appendix 1. Locations and elevations of the sampling sites in addition to the dominating land use and surficial sediment types of the catchments (areal dataset) (Map of quaternary deposits 1:20 000, sheets 203211, 203212, 203403, 203406, 203409, 204110, 204301, 204304 and 204307). HDR=high density residential, LDR= low density residential.

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<td>Clay and silt</td>
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</tr>
<tr>
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<td></td>
<td>24°58'48.2&quot;E 60°14'19.4&quot;N</td>
<td>29</td>
<td>0.77</td>
<td>HDR</td>
<td></td>
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<tr>
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<td>Varisto</td>
<td>24°48'52&quot;E 60°16'32&quot;N</td>
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<td>0.97</td>
<td>Clay and silt</td>
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<tr>
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<td></td>
<td>24°48'52.2&quot;E 60°16'32.4&quot;N</td>
<td>29</td>
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<td>HDR</td>
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</tr>
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<td>903</td>
<td>Tammisto</td>
<td>24°58'52&quot;E 60°16'46&quot;N</td>
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<td>Clay and silt</td>
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<td>24°58'52.2&quot;E 60°16'46.4&quot;N</td>
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<td>HDR</td>
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<td>904</td>
<td>Tattarimyou</td>
<td>25°3'11&quot;E 60°15'36&quot;N</td>
<td>16</td>
<td>0.14</td>
<td>Clay and silt</td>
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<tr>
<td></td>
<td></td>
<td>25°3'11.2&quot;E 60°15'36.4&quot;N</td>
<td>29</td>
<td>0.77</td>
<td>HDR</td>
<td></td>
</tr>
<tr>
<td>905</td>
<td>Petikko</td>
<td>24°49'34&quot;E 60°17'19&quot;N</td>
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<td>Clay and silt</td>
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<td>24°49'34.2&quot;E 60°17'19.4&quot;N</td>
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<td>0.77</td>
<td>HDR</td>
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<tr>
<td>906</td>
<td>Kaivoksela (East)</td>
<td>24°52'57&quot;E 60°16'11&quot;N</td>
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<td>Clay and silt</td>
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<tr>
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<td>0.77</td>
<td>HDR</td>
<td></td>
</tr>
<tr>
<td>940</td>
<td>Juvannalmi (East)</td>
<td>24°45'22&quot;E 60°16'55&quot;N</td>
<td>30</td>
<td>0.39</td>
<td>Bedrock outcrops</td>
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<tr>
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<td></td>
<td>24°45'22.2&quot;E 60°16'55.4&quot;N</td>
<td>29</td>
<td>0.77</td>
<td>HDR</td>
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</tr>
<tr>
<td>96</td>
<td>Paloheinä (North)</td>
<td>24°55'31&quot;E 60°15'24&quot;N</td>
<td>20</td>
<td>0.84</td>
<td>Clay and silt</td>
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<tr>
<td></td>
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<td>24°55'31.2&quot;E 60°15'24.4&quot;N</td>
<td>29</td>
<td>0.77</td>
<td>HDR</td>
<td></td>
</tr>
<tr>
<td>960</td>
<td>Paloheinä (East)</td>
<td>24°55'40&quot;E 60°15'25&quot;N</td>
<td>20</td>
<td>0.30</td>
<td>Clay and silt</td>
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</tr>
<tr>
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<td>24°55'40.2&quot;E 60°15'25.4&quot;N</td>
<td>29</td>
<td>0.77</td>
<td>HDR</td>
<td></td>
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</table>
Appendix 2. Correlations between metals and sediment components in the sediments of the Stream Gräsanoja and its tributaries. Degrees of freedom for the calculation of the p-value=22 (24 independent samples, separated by more than 0.75 km)

<table>
<thead>
<tr>
<th></th>
<th>(\log_{10}\text{Cu})</th>
<th>(\log_{10}\text{Zn})</th>
<th>(\log_{10}\text{Pb})</th>
<th>(\log_{10}\text{Cd})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>0.49</td>
<td>0.48</td>
<td>0.22</td>
<td>0.59</td>
</tr>
<tr>
<td>Am. Fe-oxides</td>
<td>0.02</td>
<td>0.10</td>
<td>0.25</td>
<td>0.27</td>
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<tr>
<td>Fe-oxides</td>
<td>-0.03</td>
<td>0.06</td>
<td>-0.24</td>
<td>0.11</td>
</tr>
<tr>
<td>Mn-oxides</td>
<td>0.00</td>
<td>0.16</td>
<td>-0.24</td>
<td>-0.12</td>
</tr>
<tr>
<td>Clay-%</td>
<td>0.08</td>
<td>0.06</td>
<td>-0.05</td>
<td>-0.10</td>
</tr>
<tr>
<td>Coarse silt-%</td>
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<td>-0.24</td>
<td>-0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>Al</td>
<td>0.09</td>
<td>-0.04</td>
<td>-0.11</td>
<td>0.00</td>
</tr>
<tr>
<td>Li</td>
<td>0.40</td>
<td>0.31</td>
<td>0.21</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Appendix 3. Correlations between metals and sediment components in the areal dataset.

<table>
<thead>
<tr>
<th></th>
<th>(\log_{10}\text{Cu})</th>
<th>(\log_{10}\text{Zn})</th>
<th>(\log_{10}\text{Pb})</th>
<th>(\log_{10}\text{Cd})</th>
</tr>
</thead>
<tbody>
<tr>
<td>TOC</td>
<td>0.51***</td>
<td>0.55***</td>
<td>0.60***</td>
<td>0.44***</td>
</tr>
<tr>
<td>(\log_{10}\text{Clay-%})</td>
<td>-0.41**</td>
<td>-0.37**</td>
<td>-0.44***</td>
<td>-0.35**</td>
</tr>
<tr>
<td>(\log_{10}\text{Fe})</td>
<td>0.04</td>
<td>0.14</td>
<td>0.11</td>
<td>0.17</td>
</tr>
<tr>
<td>Al</td>
<td>-0.10</td>
<td>-0.02</td>
<td>-0.14</td>
<td>0.00</td>
</tr>
<tr>
<td>Li</td>
<td>-0.24</td>
<td>-0.01</td>
<td>-0.21</td>
<td>0.06</td>
</tr>
<tr>
<td>(\log_{10}\text{Mn})</td>
<td>-0.08</td>
<td>-0.16</td>
<td>-0.05</td>
<td>-0.01</td>
</tr>
</tbody>
</table>

Appendix 4. Correlations between SPM metal concentrations (µg/g) and land use parameters within the urban sites of the areal dataset. Land use percentages were arcsine-transformed, metal concentrations \(\log_{10}\)-transformed and traffic and population densities sqrt-transformed.

<table>
<thead>
<tr>
<th></th>
<th>Low-flow period</th>
<th>High-flow period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{Cu}_{\text{SPM}})</td>
<td>(\text{Zn}_{\text{SPM}})</td>
</tr>
<tr>
<td>Urban</td>
<td>0.07</td>
<td>0.10</td>
</tr>
<tr>
<td>Dense urban</td>
<td>0.22</td>
<td>0.04</td>
</tr>
<tr>
<td>TIA</td>
<td>0.05</td>
<td>-0.04</td>
</tr>
<tr>
<td>EIA</td>
<td>0.10</td>
<td>-0.04</td>
</tr>
<tr>
<td>Low density residential</td>
<td>-0.16</td>
<td>0.05</td>
</tr>
<tr>
<td>High density residential</td>
<td>0.30</td>
<td>0.19</td>
</tr>
<tr>
<td>Institutional</td>
<td>0.24</td>
<td>0.10</td>
</tr>
<tr>
<td>Commercial &amp; traffic</td>
<td>0.17</td>
<td>0.17</td>
</tr>
<tr>
<td>Industrial</td>
<td>-0.20</td>
<td>-0.31</td>
</tr>
</tbody>
</table>
Appendix 5. Correlations between metal concentrations in the particulate phase (µg/l) and land use parameters within the urban sites of the areal dataset. Land use percentages were arcsine-transformed, metal concentrations log₁₀-transformed and traffic and population densities sqrt-transformed.

<table>
<thead>
<tr>
<th></th>
<th>Low-flow period</th>
<th>High-flow period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu&lt;sub&gt;SPM&lt;/sub&gt;</td>
<td>Zn&lt;sub&gt;SPM&lt;/sub&gt;</td>
</tr>
<tr>
<td>Urban</td>
<td>0.06</td>
<td>0.11</td>
</tr>
<tr>
<td>Dense urban</td>
<td>0.08</td>
<td>-0.08</td>
</tr>
<tr>
<td>TIA</td>
<td>0.03</td>
<td>-0.05</td>
</tr>
<tr>
<td>EIA</td>
<td>0.00</td>
<td>-0.11</td>
</tr>
<tr>
<td>Low density residential</td>
<td>-0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>High density residential</td>
<td>0.07</td>
<td>-0.02</td>
</tr>
<tr>
<td>TIA</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>EIA</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>Commercial &amp; traffic</td>
<td>-0.03</td>
<td>-0.05</td>
</tr>
<tr>
<td>Industrial</td>
<td>-0.02</td>
<td>-0.09</td>
</tr>
</tbody>
</table>

Appendix 6. Correlations between metal concentrations in the dissolved phase (µg/l) and land use parameters within the urban sites of the areal dataset. Land use percentages were arcsine-transformed, metal concentrations log₁₀-transformed and traffic and population densities sqrt-transformed.

<table>
<thead>
<tr>
<th></th>
<th>Low-flow period</th>
<th>High-flow period</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cu&lt;sub&gt;SPM&lt;/sub&gt;</td>
<td>Zn&lt;sub&gt;SPM&lt;/sub&gt;</td>
</tr>
<tr>
<td>Urban</td>
<td>0.07</td>
<td>0.19</td>
</tr>
<tr>
<td>Dense urban</td>
<td>0.12</td>
<td>0.16</td>
</tr>
<tr>
<td>TIA</td>
<td>0.09</td>
<td>0.11</td>
</tr>
<tr>
<td>EIA</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>Low density residential</td>
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<td>-0.05</td>
</tr>
<tr>
<td>High density residential</td>
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</tr>
<tr>
<td>Institutional</td>
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<tr>
<td>Commercial &amp; traffic</td>
<td>-0.10</td>
<td>-0.10</td>
</tr>
<tr>
<td>Industrial</td>
<td>0.06</td>
<td>0.13</td>
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</table>