Urban impact on water bodies in the Luleå area, northern Sweden, and the role of redox processes

Ralf Rentz and Björn Öhlander

ABSTRACT

Sediment and water from urban water bodies in the Luleå area, northern Sweden, were studied to determine the degree of contamination from metals and PAHs (polycyclic aromatic hydrocarbons). The heavy metals Cd, Cu, Pb and Zn, which are of main concern in urban stormwater, are enriched in all investigated bays. PAH concentrations were also found to be enriched. The water and sediment quality of the investigated water bodies depends on catchment area characteristics and emission impact, from point sources in particular. Water volume and turnover rate in the water bodies with low water levels and no surface runoff during wintertime, and ice covering during winter, contribute to anoxic conditions in the water column and sediments. The present redox conditions in the water bodies predominantly cause fixation of pollutants in the sediment due to formation of sulphides and slow oxidation of organic pollutants. Postglacial land uplift implies continuous changes in the environment, which can lead to changing redox conditions, thereby necessitating new risk assessments.

Key words | redox, sediment, trace metals, urban, water

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INTRODUCTION

Urban impact on water bodies

Water bodies in urban areas fulfil diverse functions. They are natural resources offering food, drinking water and process water for industries (Simmons 1991; Hauer & Lamberti 2006). Water surfaces enhance quality of life for the dwellers and offer them space for recreation and transportation. However, water bodies in urban environments are exposed to emissions from manifold sources. These emissions are integrated in a chain of natural processes affected by human activities. Urban waters are also a medium for sewage transport (Walsh 2000). Pollutants can reach water bodies in urban areas by airborne transport, infiltration and, particularly, by surface runoff.

The diversity of urban environments with residential, commercial and industrial areas, roads and parks affect adjacent water bodies differently. Without passing through any treatment facility, stormwater can have a significant impact on water bodies and groundwater resources as well as on sediments and soils.

Investigations of stormwater treatment that not only consider the question of efficient drainage from urban areas but also minimization of pollution effects became more common in scientific circles in the late-1960s in Sweden. This is reflected by works on stormwater quality by Söderlund & Lehtinen (1970, 1971), who pointed out that stormwater transports toxic substances in larger quantities to receiving water bodies than treated wastewater. Lisper (1974) also concluded that the heavy-metal content in stormwater was as high as in wastewater. Malmqvist (1983) gave a detailed picture of urban stormwater pollutant sources for better prediction and control of stormwater runoff. Recent investigations deal with prediction and simulation of stormwater flows (Björklund et al. 2011), or the efficiency of stormwater treatment systems (Blecken et al. 2009), often related to finding Best Management Practices (BMP).

Human impact and contributions of pollutants from urban areas to the environment have been widely studied (Förstner & Müller 1981; Gocht et al. 2001; Menzie et al. 2002; Brown & Peake 2006). Commonly investigated pollutants in stormwater are metals and polycyclic aromatic hydrocarbons (PAHs), due to the potential risks they pose for living organisms (Wildi et al. 2004; Munch Christensen et al. 2006).

There are as many sources of the pollutants as there are utilizations of their components, and release mechanisms are complex. In urban environments, metals occur in roofing materials, cars, street lamps, crash barriers, gully covers, pipelines, cables, paints, computers, etc. (Brown & Peake 2006). Exposure of these urban constituents to weathering processes makes them a large artificial source of metals. PAHs originate generally from pyrogenic sources, like fossil fuel or wood combustion, and petrogenic sources, such as petroleum products. Also, wear and leaching of asphalt and tyre wear contribute to the PAH content in stormwater (Gonzalez et al. 2000).

The transport capability of stormwater for these pollutants to receiving waters is affected by the particle size of the sediment load. Fine sand fractions, and especially silt and clay fractions, were found to have the highest mass of metals and PAHs (Menzie et al. 2002). The most abundant PAHs in stormwater are phenanthrene, anthracene, fluoranthene and pyrene (Viklander 1998; Lau & Stenstrom 2005). Previous studies of stormwater and gully pot sediments in the Luleå area (Westerlund 2007; Karlsson & Viklander 2008) indicated particle-related transport of metal and organic pollutants with seasonal variations. Pollutants in dissolved form and associated with small suspended particles are not retained effectively in their transport chain from urban surfaces to receiving waters. These pollutants can become enriched in sediments under the right geochemical conditions when reaching standing water bodies. Larger particle sizes have also been found to transport high metal contents (Gonzalez et al. 2000; Brown 2002). The geomorphology and geochemistry of the water bodies and their catchment area determine which and how processes take place in the water bodies. The characteristics of different catchments in the Luleå area may have great impact on geochemical processes in water bodies and sediments.

It is, therefore, of interest to study sediments affected by stormwater and to determine whether water and sediment quality differs from other water bodies with less stormwater impact. The main objectives of this study were to describe the water and sediment status of urban waters in the Luleå area with its shallow bays with brackish water, and to identify important geochemical and geomorphological processes and possible sources of pollution. Other aims were to investigate the role of redox processes for fixation and release of metals in local sediments, and to identify potential risks for dwellers and the environment that may arise from the current environmental status and ongoing processes.

Water bodies in the Luleå area

The town of Luleå, with ~73,000 inhabitants, is situated at the mouth of the Lule River in Norrbotten, Sweden. The river and former shallow bays of the brackish Bothnian Bay are the most characteristic hydrodynamic patterns of Luleå. These bays, called *innerfjärdar*, are the result of postglacial land uplift (8–9 mm per annum), or the construction of artificial banks, often partially enclosed (Lindén et al. 2006). Consequences of the ongoing land uplift are diminishing water surfaces (and volumes) in the shallow bays. Increasing vegetation accompanies silting-up processes in the Luleå *innerfjärdar* (Erixon 1996). To preserve the shallow bays for recreation, they were dammed up at their two connections with the Bothnian Bay (Figure 1). Also, the water level in the Lule River and Bothnian Bay affects the turnover rate and water quality in the shallow bays (Erixon 1996). Luleå's *innerfjärdar* are situated in and around the town of Luleå, and are affected by local catchments which contain urbanized and industrial areas as well as rural and forested areas. They are used for many recreational purposes. Large parts of the catchment areas of the *innerfjärdar* are covered by sea bottom sediments characterized as acid sulphate soils (Erixon 2009).

The bay Skutviken, located close to the centre of Luleå, is enclosed by a road bank constructed in 1962. Skutviken is still connected to the Lule River via a channel. Several stormwater pipes discharge into the bay from a sewer drainage area with industrial and housing areas (Rentz et al. 2011).

Hertsöfjärden is a bay that has been especially affected by the outlets of the steel plant SSAB Tunnplåt AB (formerly
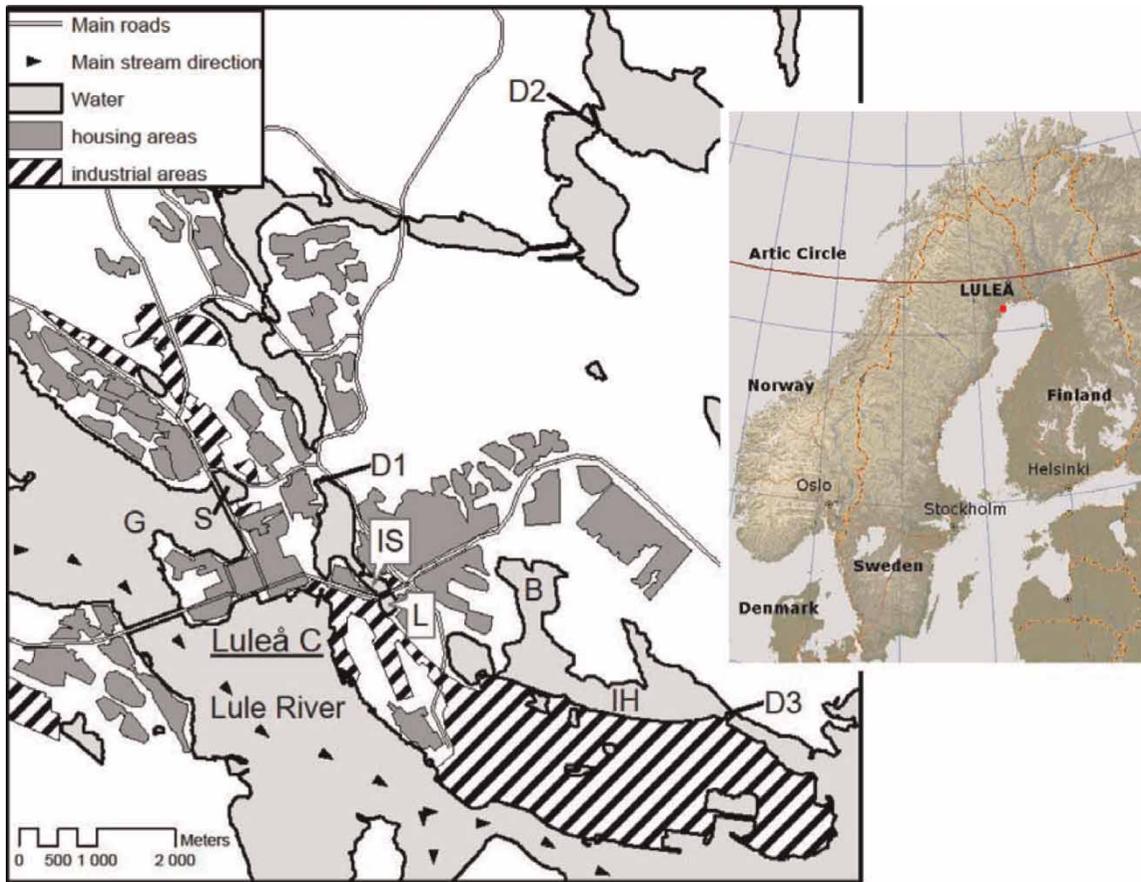
Figure 1 | Water bodies in the Luleå area. S: sample point Skutviken; G: sample point ahead Gültzauudden; IS: sample point Inre Skurholmsfjärden; L: sample point Lövskataviken; B: sample point Bredviken; IH: sample point Inre Hertsöfjärden; D$_{1-3}$: watergates.

Norrbottens Järnverk and SSAB) since the 1940s. Due to plans to build a new steel plant, Stålverk 80, the outer part of the bay was infilled in 1975–76 and an artificial bank divided the bay in two parts. The water in the inner part was dammed up (Timner 1994).

Lövskataviken and Inre Skurholmsfjärden are water bodies in the *innerfjärdar* system in central Luleå. Industrial activities have taken place on their banks for more than 100 years (Olofsson 2002). Petrol stations have been located in the catchment area of Inre Skurholmsfjärden since 1954. The urban catchment area contains industrial and housing areas with parks. A road bank built in the 1960s separates the two water bodies, which are still connected via road culverts (Olofsson 2002).

The Lule River, with its 25,263 km^2 large catchment area, has an annual average discharge of 506 m^3 s^{-1} (SMHI 2010). The Lule River rises in the mountain area in the west, close to the Norwegian border, where vegetation of tundra type occurs. Downstream, coniferous and birch forest dominate, covering 58% of the total catchment area. Lakes and mires are also common, accounting for 11% of the total catchment area. Since the beginning of the 20th century, the river has been regulated and today there are 15 power stations along the river (Drugge 2003).

MATERIALS AND METHODS

Sampling sites

The surface area of Skutviken is ~12 ha, and the mean and maximum depths of the bay are 1.6 and 3.4 m, respectively. The bay is separated from the Lule River by a road bank constructed in 1962, and is connected to the river via a single

channel (8 m in width, 3–4 m in depth, 35 m in length). These physical conditions make the bay similar to other shallow bays in this region. The bay is almost completely enclosed by two heavily trafficked roads with averages of 23,100 and 13,600 vehicles per day (Luleå Kommun 2009). The sewer drainage area contains 0.53 km^2 industrial area and 0.73 km^2 housing area. Since surface runoff and six stormwater channels enter the bay, it almost functions as a large stormwater pond where a large amount of storm-water sediment is trapped, resulting in a reduced sediment supply to the Lule River. All channel outlets are located below the water surface, except during periods of very low water level.

To compare sediment quality, a reference sampling site with less-affected conditions was chosen, situated beside the main streambed of the Lule River in front of the spit Gültzauudden (Figure 1). The sites Hertsöfjärden (Timner 1994), Lövskataviken and Inre Skurholmsfjärden (Olofsson 2002) and the Lule River (Drugge 2003), described in previous studies, were compared with the Skutviken and Gültzauudden sites.

The annual precipitation in the Luleå area is about 500 mm, of which 40–50% falls as snow between November and April/May, and thus is discharged during snowmelt (Hernebring 1996). From November until May the Lule River and the bays close to the city centre are ice-covered.

Previous studies in the Luleå area

Previous studies have examined geochemical characteristics (Table 1) of water bodies in Luleå (Figure 1). Sediment data from Skutviken and Gültzauudden were compared with data from Timner (1994) and Olofsson (2002), who both took sediment samples with a Kajak-corer and analyzed metal contents in sediment and porewater. Timner (1994) found that sediments can bind trace metals coming from the catchment area. Compared with the sediment in the main basin of Inre Hertsöfjärden, the sediment in Bredviken showed a thinner oxidized sediment top layer as a result of less water turnover and ice covering in winter. Parts of the main basin stay ice-free even in wintertime because of the warm water outflow from adjacent industry. The impact of the SSAB steel plant is noted for the main basin in terms of increased concentrations of As, Cd, Co, Hg, Ni, Pb, V,

Table 1 | Used sediment and water data available from different water bodies in the Luleå area

site	Skutviken	Gültzauudden	Lövskataviken	Inre Skurholmsfjärden	Inre Hertsöfjärden	Bredviken	Boden power station
Reference	This paper	This paper	Olofsson (2002)	Olofsson (2002)	Timner (1994)	Timner (1994)	Drugge (2003)
Metals in sediment	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Cu, Ni, Pb, Zn	–
16 PAH in sediment (0–2 cm)	D	D	D	D	–	–	–
LOI in sediment	D	D	D	D	D	D	–
Metals in porewater	Mn, Fe, S, Cd, Cr, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Ni, Pb, Zn	Mn, Fe, S, Cd, Cr, Ni, Pb, Zn	–	Mn, Fe, S, Cd, Cr, Ni, Pb, Zn	–	–
Metals in water	Mn, Fe, S, K, Mg, Na, Si, Al, Ba, Co, Cu, Ca, Mo, Sr, Zn, As, Cd, Cr, Hg, Ni, P, Pb	Mn, Fe, S, K, Mg, Na, Si, Al, Ba, Co, Cu, Ca, Mo, Sr, Zn, As, Cd, Cr, Hg, Ni, P, Pb	–	–	–	–	Mn, Fe, S, K, Mg, Na, Si, Al, Ba, Co, Cu, Ca, Mo, Sr, Zn,

Sediment core depths: Skutviken and Gültzauudden 21 cm, Lövskataviken 30 cm, Inre Skurholmsfjärden 38 cm, Inre Hertsöfjärden 22.5 cm, Bredviken 24.5 cm.
D = determined.

Zn, Fe and Mn in the sediment deposited after 1946. However, also in Bredviken, the values in the sediment top were increased for As, Cd, Cr, Pb, V, Zn and Fe after 1946. A large part of the metal discharge from SSAB, as calculated by Timner (1994), is accumulated in the sediment. Possible secondary movements of Fe, Mn, Zn and other trace elements make it difficult to see changing contamination levels in the sediments and to relate them to the time of sedimentation. Olofsson (2002) showed enrichment of trace metals (As, Cd, Cr, Cu, Hg, Ni, Pb, Zn) and PAHs in the sediments caused by stormwater impact from local industrial areas. For the Lövskataviken sediment, Olofsson (2002) points out that stormwater supply from the industrial areas in the west and south of the bay imports pollutants, as stormwater from rain and melted snow on the road bank. From the road bank, stormwater even reaches Inre Skurholmsfjärden, which is mostly affected by stormwater from an industrial area in the east and an outflow from the housing area Skurholmen. The spreading conditions for the enhanced contents of heavy metals and organic pollutants at Lövskataviken and Inre Skurholmsfjärden are considered to be low, because of the relatively sheltered location of the bays and their low water turnover rates. Owing to the fact that there are adjacent recreation areas, the risk of spreading these pollutants was estimated as low under current conditions. Water data from Skutviken and Gültzauudden were compared with Drugge's (2003) datasets from the Luleå River at Boden power station, ca. 30 km upstream from Luleå, and with data from gully pot catch basins published by Karlsson & Viklander (2008) (Table 2).

Water sampling at Skutviken and Gültzauudden

The surface water was sampled 50 cm below the surface and 50 cm below the ice in winter. Water was pumped by a peristaltic pump (Masterflex® L/S®) into a 25 l polyethylene (PE) container. Membrane filtration (0.22 μm pore size, 142 mm diameter, Millipore® mixed cellulose esters) was carried out in a laboratory within 6 h of sampling. During filtration, each filter was used only up to half of its filtration capacity. This was done to remove discrimination of colloids that is caused by clogging of filters (Morrison & Benoit 2001). The filtrate was collected in a 25 l PE container from which subsamples were taken for analysis. Subsamples

were collected in 60 ml acid-washed PE bottles and refrigerated until further analysis. All used tubing and containers were pre-cleaned with 5% HCl and rinsed with MQ water (Millipore, 18.2 Mohm).

Sediment and porewater sampling at Skutviken and Gültzauudden

The sampling station in Skutviken was located in the deeper parts of the bay with fine-grained sediment. At Skutviken, the water depth was 2.2 m and at Gültzauudden it was 6.1 m. Sediment samples from Skutviken and Gültzauudden were taken in March 2007 from the ice using a Kajak gravity corer with a core tube diameter of 64 mm. The sediment core surfaces were judged to be undisturbed. Cores were sectioned in subsamples (0.5 cm thick for the uppermost 3 and 1 cm thick for the remainder of the core).

For porewater analyses, the sediment samples were put into plastic bags directly after sectioning. All air was pressed out of the bag before it was placed in an Ar-filled container to keep the sediments in an oxygen-free environment until the porewater was extracted within the following 8 h. The porewater was separated by vacuum filtration (0.22 μm Millipore® membrane filters) arranged in an Ar-flushed glove box. The porewater samples were collected in 60 ml acid-washed PE bottles and refrigerated until further analysis.

Near-bottom water was sampled inside the Kajak-corer tube 3 cm above the sediment surface. The water was drawn with a small plastic tube fixed on a syringe and filtered through a 0.22 μm Millipore® membrane filter.

Analyses

The 0.22 μm membrane filtered surface-water samples were analyzed for major and trace elements by inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma sector field mass spectrometry (ICP-SFMS). For instrument operation details, see Rodushkin & Ruth (1997).

The sediment was analyzed for loss on ignition (LOI) and together with porewater for major elements and trace metals. Sediment samples for determination of As, Cd, Co, Hg, Ni, Pb and S were dried at 50 °C digested in a

Table 2 │ Element concentrations ($\mu g\ l^{-1}$) in the filtered phase (<0.22 μm) in the Lule River at Boden power station, Gültzauudden, Skutviken and from three catch basin mixtures in Luleå with different annual average daily traffic (vehicles per day, v d^{-1})

	Boden power station[a]		Luleå						
	Lule River		Gültzauudden		Skutviken		Catch basins[f]		
Element	Winter	Summer	Spring–winter[b]	Summer[c]	Spring–winter[d]	Summer[e]	'1'	'2'	'3'
Mn	3	5.1	6.57	3.4	324	1.6	186	82	365
Fe	71	215	52.9	68	569	165	5,300	60	100
S	647	565	850	1,570	2,660	1,950	3,200	2,800	2,600
K	440	523	<400	735	2,250	977	6,000	3,400	3,900
Mg	582	571	707	1,970	3,190	1,710	2,000	2,800	3,300
Na	1,139	890	1,090	11,700	6,680	6,850	60,000	2,4800	33,600
Si	1,285	1,319	1,370	1,570	3,100	601	–	–	–
Al	8.7	18.6	5.27	9.65	5.49	6.67	738	42	24
Ba	6.4	5.3	6.49	5.53	23.1	8.14	38	48	73
Co	0.01	0.01	0.02	0.02	0.28	0.01	1.2	0.5	2.3
Cu	0.67	0.52	0.44	0.41	0.36	0.64	22	3.1	2.3
Ca	2,785	2,410	3,340	3,050	15,600	6,040	14,600	18,900	22,000
Mo	0.29	0.24	0.21	0.29	0.3	0.31	10	2.4	12
Sr	10.7	9.9	12.1	18.7	53.7	24.7	47	31	58
Zn	2.5	1.2	0.44	0.45	3.42	0.48	82	5.8	14
As	–	–	0.21	<0.4	0.47	0.22	5.1	0.8	3
Cd	–	–	<0.002	<0.002	<0.002	<0.002	0.2	0.02	0.02
Cr	–	–	0.05	0.08	0.11	0.05	4	0.2	0.1
Hg	–	–	<0.002	<0.002	<0.002	<0.002	0.003	0.003	0.003
Ni	–	–	0.26	0.18	0.69	0.36	5.5	1	3.9
P	–	–	1.17	1.1	3.11	4.18	78	16	12
Pb	–	–	0.01	0.02	0.04	0.19	70	0.7	0.3

[a]Weekly sampling from Drugge (2003), Summer: average June to August, Winter: average December to March.
[b]Sampling date: 2007-03-07.
[c]Sampling date: 2007-07-09.
[d]Sampling date: 2007-03-05.
[e]Sampling date: 2007-07-04.
[f]Data from Karlsson et al. (2009), '1' (500 v/d), '2' (13,800 v/d), '3' (25,500 v/d).

microwave oven in closed Teflon bowls with a nitric acid/ water ratio of 1:1. For other elements, 0.125 g dried matter (DM) was melted with 0.375 g LiBO$_2$ and dissolved in HNO$_3$. Metal determinations were made by ICP-AES and inductively coupled plasma mass spectrometry (ICP-MS). To the porewater samples, 1 ml nitric acid (suprapur) was added per 100 ml sample water. Analyses were done with ICP-AES and ICP-SFMS. The following 16 PAHs were analyzed in the sediment: Naphthalene (NAP), Acenaphthylene (ACY), Acenaphthene (ACE), Fluorene (FL), Phenanthrene (PHEN), Anthracene (ANT), Fluoranthene (FLR), Pyrene (PYR), Benzo(a)anthracene (BaA), Chrysene (CHY), Benzo(b)fluoranthene (BbF), Benzo(k)fluoranthene (BkF), Benzo(a)pyrene (BaP), Dibenz(a,h) anthracene (DBA), Benzo(g,h,i)perylene (BPY) and Indeno(1,2,3-cd)pyrene (INP). The PAH sediment samples were leached with acetone–hexan–cyclohexan (1:2:2) and measurements were done with gas chromatography mass spectrometry (GC-MS).

RESULTS AND DISCUSSION

Water column

Dissolved oxygen concentration in the water column at Skutviken varies from summer to winter. The oxygen saturation in the bottom water is close to 0% in wintertime, when the bay is ice-covered. In contrast, the water column is well oxygenated (saturation 85–90%) during the ice-free season (Rentz et al. 2011).

The elemental concentrations of the dissolved phase ($<0.22\,\mu m$) at the three sites (Skutviken, Gültzauudden and the Boden power station on the Lule River) show seasonal and spatial variations. Seasonal variations in the element concentrations are less distinct in the regulated Lule River as compared with the pristine Kalix River (Drugge 2003). It is evident that the water at Gültzauudden is much like the Lule River water (Table 2). In contrast, element concentrations at Skutviken show stronger seasonal variations. Late-winter concentrations of K, Mg, As, Cr, Ni and Sr are twice as high as in summer. The concentrations of Ca are 2.6, Fe 3.4, Si 5, Zn 7, Co 33 and Mn 200 times higher in late-winter than in summer. The concentrations of Na, S, Al, Mo and P do not show much variation. The late-winter concentration of Cu is just half the summer concentration, and for Pb a fifth. Furthermore, Skutviken is characterized by high concentrations of Ca, Fe, K, Na, Co compared with the other sites, especially in late-winter.

Redox conditions and LOI in sediments

The sediment core at Gültzauudden shows the typical concentration profile of freshwater sediments for Mn, Fe and S (Figures 2–4). Oxic conditions in the top of the sediment core imply occurrence of Mn oxyhydroxides (Song & Müller 1999). Decomposition of organic material leads to increasing anoxic conditions with depth, and results in reduction of Mn oxyhydroxides and increased porewater concentration of Mn(II). Anoxic conditions predominate below 4 cm, where the MnO content stabilizes at 0.2%, probably occurring in silicate minerals. From that point, the Mn concentration increases in porewater. This indicates Mn(II) flux upward, resulting in

the oxidation of Mn(II) to Mn(IV) in the oxic parts of the sediment (Wehrli 1991; Davison 1993) (Figure 2). The Mn observations comply with the sediment content and porewater concentration of Fe at Gültzauudden. A Fe_2O_3 peak in the sediment profile is situated below the peak of MnO. The solid Fe_2O_3 peak at a depth of 3 cm depends on the oxic sediment conditions, where Fe occurs as Fe(III) in iron oxyhydroxides. Below 5 cm the solid Fe content declines continuously. When porewater becomes more anoxic with depth, the Fe concentration indicates that reduction of solid Fe(III) to the soluble Fe(II) occurs (Wehrli 1991; Davison 1993) (Figure 3).

At Skutviken, the MnO content in the sediment is much lower than at Gültzauudden in the upper parts of the sediment. It appears that the geochemical conditions where Mn(IV) is reduced to Mn(II) are reached already in the near-bottom water above the sediment surface. During winter, when the bay is ice-covered, the oxygen concentration in the bottom water is $<0.42\,mg/l$ (Rentz et al. 2011). The Mn concentrations in the porewater increase with depth, but never reach as high as the concentrations at Gültzauudden.

The redox conditions at Skutviken permit precipitation of Fe(III) hydroxides at the sediment–water interface, indicated by the presence of a solid Fe_2O_3 maximum at the sediment surface. The anoxic conditions occurring at Gültzauudden at a sediment depth of 3 cm seem in winter to occur already above the sediment column at Skutviken. Therefore, reductive dissolution of Fe hydroxides takes place already at the sediment surface. The decrease in total S in porewater at Skutviken suggests that reduction of SO_4^{2-} occurs immediately below the sediment – water interface (0–2 cm). Precipitation of solid sulphides in the sediment is indicated by the simultaneous increase in solid S (Figure 4).

The sediment profiles for solid Mn at Lövskataviken, Skurholmsfjärden and Bredviken resemble the characteristics at Skutviken with constant low concentrations of MnO over the whole depth. Only at Inre Hertsöfjärden, does an increase of MnO in the uppermost 5 cm in the sediment indicate more oxic conditions in the sediment top. A high concentration of solid Fe(III) already at the sediment surface at Inre Hertsöfjärden suggests that the
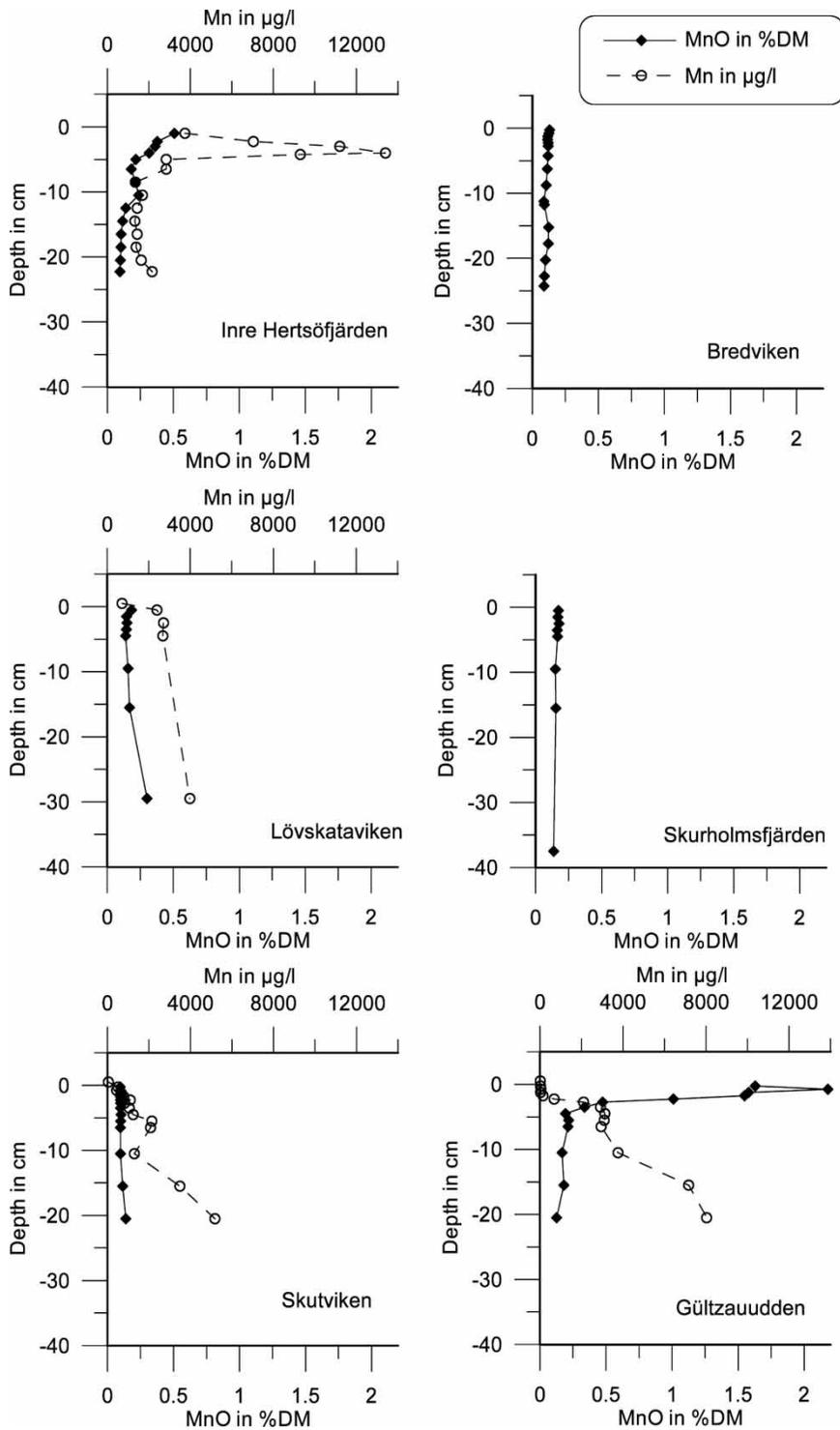
Figure 2 │ MnO in sediment (%DM) and Mn in porewater (μg/l) at Skutviken, Gültzauudden, Lövskataviken, Skurholmsfjärden, Inre Hertsöfjärden and Bredviken. In Figures 2, 3 and 4, the top value for 'porewater' represents the bottom near surface water at Skutviken, Gültzauudden and Lövskataviken. Porewater was not analyzed at Skurholmsfjärden and Bredviken.
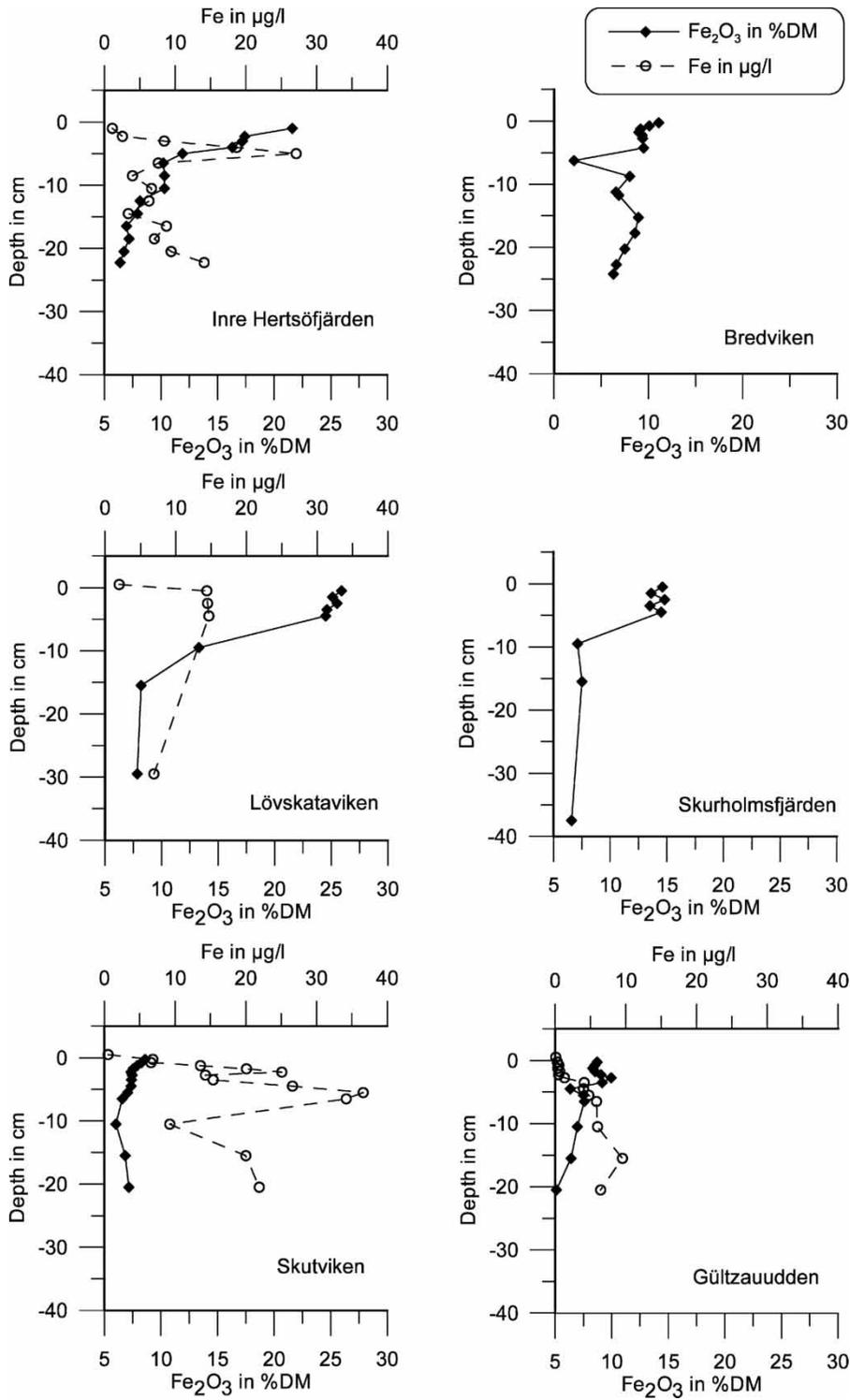
Figure 3 │ Fe$_2$O$_3$ in sediment (%DM) and Fe in porewater (μg/l) at Skutviken, Gültzauudden, Lövskataviken, Skurholmsfjärden, Inre Hertsöfjärden and Bredviken.
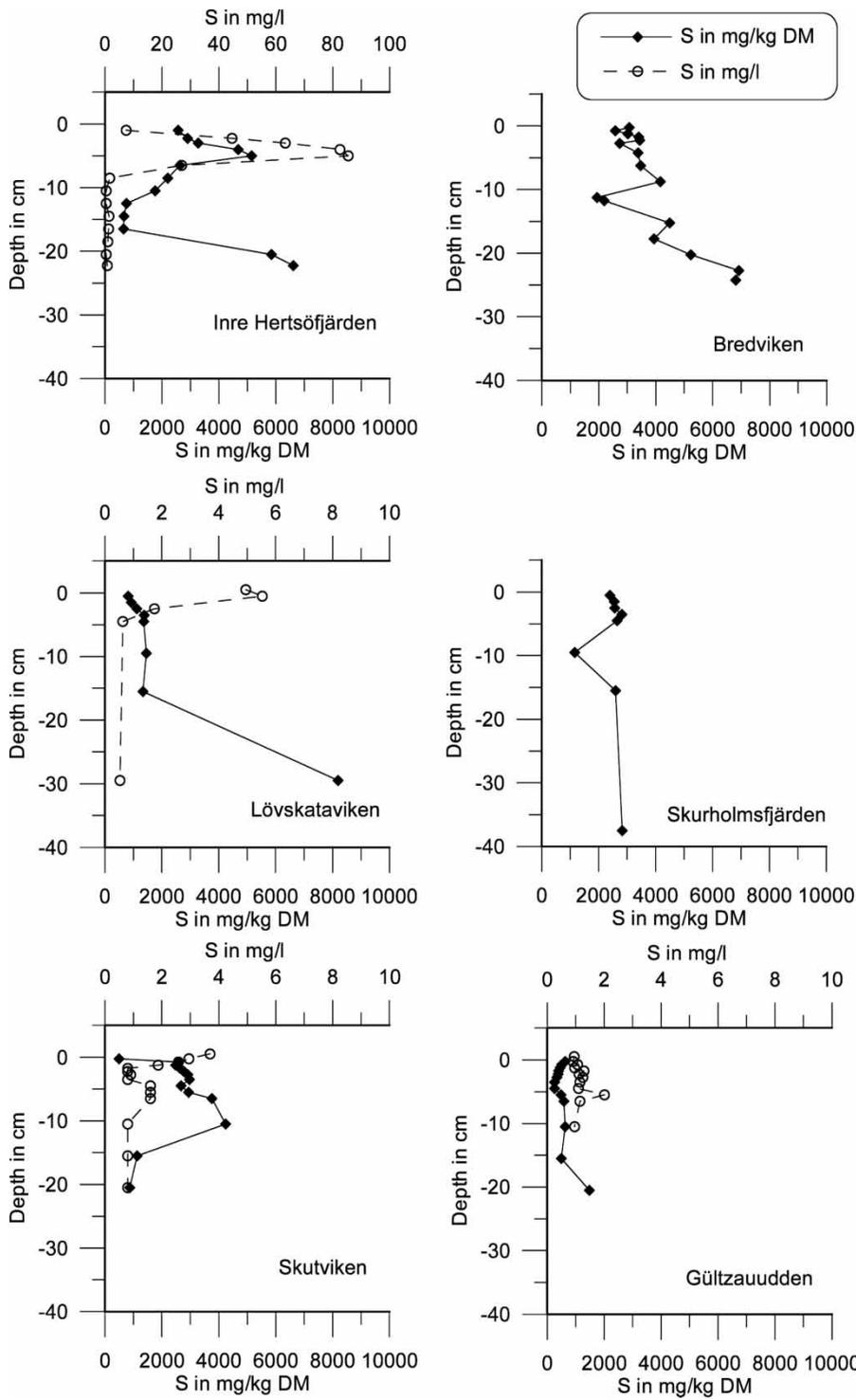
Figure 4 │ S in sediment (mg/kg DM) and S in porewater (mg/l) at Skutviken, Gültzauudden, Lövskataviken, Skurholmsfjärden, Inre Hertsöfjärden and Bredviken.

oxic conditions are low compared with Gültzauudden but higher than at the other sites.

A solid Fe_2O_3 maximum in the sediment top is common for Lövskataviken, Skurholmsfjärden, Inre Hertsöfjärden and Bredviken and corresponds to Skutviken. However, the very high Fe_2O_3 concentrations in the uppermost 5 cm at Lövskataviken, Skurholmsfjärden and Inre Hertsöfjärden are notable. The change from high concentrations to low background concentrations is abrupt at these sites.

At Lövskataviken, the S concentration in the sediment and porewater indicates similar conditions as at Skutviken. Here, the sulfur content in the porewater decreases and the solid sulfur in the sediment increases in the same sediment layer where iron is enriched. Particularly at Lövskataviken, Inre Hertsöfjärden and Bredviken, increasing concentrations of solid S at sediment depths below 15 cm are visible, simultaneously with apparent unchanged low S concentration in the porewater.

The LOI content at all sites is consistently highest in the uppermost section of the sediment columns (Figure 5). After a thin layer with constant, relatively high LOI content, the values decline radically at Skutviken, Inre Skurholmsfjärden, Inre Hertsöfjärden and Bredviken. At Lövskataviken, the LOI content is already relatively low in the top layer compared with the other sites, and shows no strong decrease with depth. At Gültzauudden, the LOI content declines directly from the sediment top, which suggests a minor input of organic material but also relatively high oxygen concentration that helped to decompose organic material. That can be ascribed to continuous circulation in the water column due to the nearby main streambed of the Lule River. Also, at Inre Hertsöfjärden the sediment top seems to be more oxic than at the other sites. The surface water in this bay does not always freeze, since warm water enters the bay via outlets from the nearby industry. The water surface at Lövskataviken, Inre Skurholmsfjärden and Bredviken do freeze regularly, as does Skutviken. Below the ice cover, the oxygen is consumed as a result of decomposition of organic material. Anoxic conditions slow down further decomposition. The content of organic material in the sediment of the shallow bays shows a high input of organic components from the surrounding catchment areas, as indicated by LOI (Figure 5). The low water turnover rate during wintertime at these sites excludes the
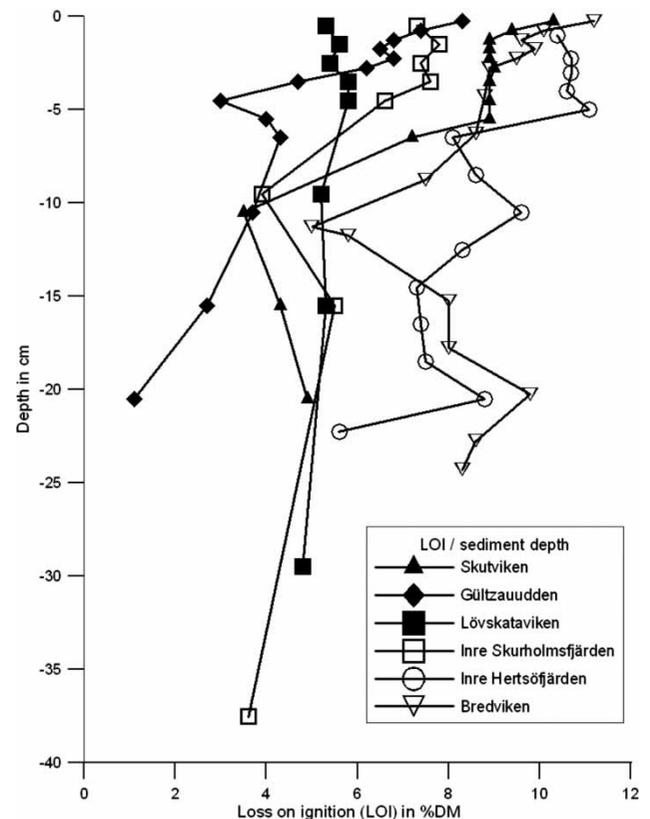

Figure 5 │ Loss on ignition (LOI) versus sediment depth at Skutviken, Gültzauudden, Lövskataviken, Inre Skurholmsfjärden, Inre Hertsöfjärden and Bredviken.

inflow of fresh oxygenated water, which can hamper decomposition.

Metal concentrations in sediments

The average concentrations of the selected metals Cd, Cr, Cu, Ni, Pb, Zn in the upper sediment section (0–4 cm) generally exceed the average concentrations of the deeper section from the same core (Table 3). Only Gültzauudden deviates from the others, since it has the lowest metal concentrations in comparison with the same depth sections at the other sites. Of all sites, Inre Hertsöfjärden exhibits the highest concentrations of all metals except for Ni. Inre Hertsöfjärden shows pollution concentrations for Cd, Ni, and Pb in the range of sediments in central Stockholm (Sternbeck et al. 2003), the Cr and Zn concentrations exceed the averages from central Stockholm by more than three times, and Cu is half the Stockholm average. The Ni concentrations at Inre Skurholmsfjärden and Lövskataviken exceed

Table 3 | Average element concentration (mg/kg DM) in sediment sections 0–4 cm and 4 cm to core end at Skutviken, Gültzauudden, Lövskataviken, Inre Skurholmsfjärden, Inre Hertsöfjärden and Bredviken

Element	Depth in cm	Skutviken	Gültzauudden	Lövskataviken	Inre Skurholmsfjärden	Inre Hertsöfjärden	Bredviken
Cd	0–4	0.7	0.3	0.6	0.8	2	0.7
	4–[a]	0.4	0.3	0.4	0.3	0.8	0.7
Cr	0–4	83	68	80	80	319	122
	4–[a]	87	67	66	62	98	78
Cu	0–4	60	17	56	68	92	37
	4–[a]	37	24	30	30	41	33
Ni	0–4	23	19	47	46	44	34
	4–[a]	22	19	24	25	24	31
Pb	0–4	66	13	39	55	236	69
	4–[a]	47	26	28	20	101	64
Zn	0–4	284	97	302	357	1,733	343
	4–[a]	180	118	166	127	392	283

[a]Core end: Skutviken and Gültzauudden 21 cm, Lövskataviken 30 cm, Inre Skurholmsfjärden 38 cm, Inre Hertsöfjärden 22.5 cm, Bredviken 24.5 cm.

the Stockholm average slightly. Inre Hertsöfjärden is exposed to spill water from a steel plant. To a minor degree, besides urban stormwater, Bredviken is exposed to the same spill water. This can explain the higher Cr concentrations than at Skutviken, Skurholmsfjärden and Lövskataviken. The concentrations at Inre Skurholmsfjärden and Lövskataviken resemble those at Skutviken for Cd and Cu, with less than half the concentration of the Stockholm average. The Cr concentrations are in the range of the central Stockholm sediment. For all sites in Table 3, except Gültzauudden, the catchment areas exhibit possible sources for the enrichment of metals in the sediment. Catch basin mixtures from gully pots in Luleå showed high concentrations of Cd, Cr, Cu, Ni, Pb and Zn, which suggests that traffic and urban stormwater are probable sources at Skutviken, Inre Skurholmsfjärden and Lövskataviken (Karlsson et al. 2009) (Table 2).

PAH in sediments

The high PAH concentrations in the sediment top (Table 4) suggest that the PAH enrichment is generated from sources in the catchment areas of Skutviken, Inre Skurholmsfjärden and Lövskataviken. The concentrations at Inre Skurholmsfjärden exceed those of the other sites, and the sediment at Gültzauudden contains the lowest concentrations for each PAH. The comparison with the Swedish EPA classification

(Swedish EPA 1999) for organic pollutants shows clearly increased concentrations at Inre Skurholmsfjärden, where the light PAHs PHEN, PYR, BaA and CHY reach Class 5, the highest of five contamination classes. At Skutviken only PYR reaches Class 5. However, the total PAH contamination (all 11 PAHs) at Inre Skurholmsfjärden and Skutviken reaches Class 4, the second highest contamination class, while at Lövskataviken total PAH concentrations reach Class 3. Even if the high concentrations of PHEN, PYR, BaA and CHY at Skurholmsfjärden and PYR at Skutviken reach Class 5, the concentrations are distinctly lower than the average from seven sampling stations in central Stockholm (Sternbeck et al. 2003): PHEN 3.5, PYR 3.8, BaA 4.5, and CHY 1.4 times lower.

Future scenarios

The future risk of enriched metal pollutants in the sediments at present is conditional on whether they can be retained in the sediments or mobilized. Mobile dissolved pollutants are made available for uptake by living organisms (Munch Christensen et al. 2006). If the geochemical processes in shallow bays in the Luleå area lead to fixation of metals in anoxic sediments, metal mobility may be impeded as long as these sediments do not become oxygenated. However, anoxic conditions limit PAH degradation due to the fact that biological activity is hampered.

Table 4 | Concentrations (µg kg^{-1} DM) of 16 PAHs in the sediment in 0–2 cm depth at Skutviken and Gültzauudden and 0–4 cm depth at Lövskataviken and Inre Skurholmsfjärden. Eleven PAHs are included by the Swedish EPA guidelines

	Skutviken $n = 1$	Gültzauudden $n = 1$	Lövskataviken $n = 3$	Inre Skurholmsfjärden $n = 3$
Depth in cm	0–2	0–2	0–4	0–4
PHEN[a]	89[f]	22[e]	<80	137[g]
ANT[a]	24[f]	<10	<80	<80
FLR[a]	130[f]	28[e]	102[f]	217[f]
PYR[a]	240[g]	20[e]	106[f]	240[g]
BaA[a]	59[f]	13[e]	<80	120[g]
CHY[a]	69[f]	<10	116[f]	363[g]
BbF[b]	180[f]	10[d]	32[d]	193[f]
BkF[b]	44[e]	<10	28[d]	147[f]
BaP[b]	74[f]	<10	<80	123[f]
BPY[b]	89[e]	<10	<80	180[f]
INP[b]	99[e]	<10	<80	70[e]
Σ 11 PAH	1,097[f]	93[d]	384[e]	1,790[f]
DBA[b]	30	<10	<80	<80
NAP[a]	39	<10	<80	<80
ACY[a]	11	<10	<80	<80
ACE[a]	<10	<10	<80	<80
FL[a]	15	<10	<80	<80
Σ 16 PAH	1,200	93	384	1,790

[a]Light PAH.
[b]Heavy PAH.
Swedish EPA guidelines for 11 PAHs:
[c]Class 1, no content.
[d]Class 2, low content.
[e]Class 3, moderately high.
[f]Class 4, high.
[g]Class 5, very high.

Only three-ring PAHs where found to become degraded under anoxic conditions (Quantin *et al.* 2005). Conditions that benefit the decomposition of PAHs will cause higher risk of secondary release of metal pollutants. Present land uplift (Lindén *et al.* 2006) can implicate future drainage of the buried sediments, which today accumulate on the bottom of coast-near narrow bays. If the submerged soils become oxidized when they are no longer water-covered, release of trapped pollutants occurs. Metal release from sulphate soils of local catchments has led to temporally decreasing water quality (Erixon 2009). Several studies from Finnish areas, concerning sulphate soils and metal release (Åström 1998; Boman *et al.* 2008; Österholm & Åström 2008), indicate the need for investigation of

related risks. In postglacial land uplift areas, ditching of sulphate soils and seasonal variations in precipitation can imply changes of redox conditions in the soil profile (Österholm & Åström 2008; Erixon 2009). Human impact on the water levels, such as damming up the partially enclosed bays, can slow down the long-term processes which result in oxidation of soils and further transport of pollutants. For the year 2004, with low precipitation causing extremely low groundwater levels, Erixon (2009) calculated mass transport of Zn, Ni, Co and Mn from catchment areas with sulphate soils in the Luleå area. The catchment areas of Holmsundet (60 km^2) and Persöfjärden (402 km^2), with a runoff 0.3×10^8 and 1×10^8 m^3 yr^{-1}, respectively, can release 8.5, 3.5,

2.4 and 396 tons of Zn, Ni, Co and Mn per year, respectively. This is more than from the Kalix River (Zn 8.5, Ni 3.2, Co 0.6, Mn 194 ton yr^{-1}) with 23,600 km^2 catchment area and a $100*10^8 \, m^3 \, yr^{-1}$ runoff. The catchment areas of Holmsundet and Persöfjärden contain 50 and 20%, respectively, marine and lacustrine clay sediments. Besides urban stormwater, sulphate soils also have to be considered as an influential factor for disturbance of local water bodies.

CONCLUSIONS

The investigated water bodies in the Luleå area show clear urban impact on sediment quality. The metals Cd, Cu, Pb and Zn, which are of main concern in urban stormwater, are enriched in all investigated bays. Metals can bind to surfaces of sedimenting organic and small inorganic particles. In the sediment they can become part of sulphide formation and are thus fixed in the sediment.

In Skutviken, which is an efficient trap for particulate stormwater pollution, the dissolved and particulate pollutants may be enriched and more concentrated. Concentrations are in general higher during wintertime, which may be due to the reduced inflow of fresh river water and lack of surface runoff, whereby the water turnover in the bay is reduced. The same principle applies to Lövskataviken, Inre Skurholmsfjärden and Bredviken due to their sheltered position. Lövskataviken and Inre Skurholmsfjärden receive stormwater from nearby industrial areas. Inre Skurholmsfjärden is especially contaminated by PAHs, probably from leakage from a former nearby petrol station. For Inre Hertsöfjärden, the impact of the water inflow from the steel plant contributes to the more oxygenated sediment conditions because the warm water prevents the bay from freezing during winter. Even here, pollutant transport to the sediment is a result of the water inflow from the industrial area. All sediment samples comprised mainly particles of the silt and clay fractions, which offer good conditions for bonding on particle surfaces. The high LOI values could be caused by a combination of organic pollutants and natural organic matter. At Skutviken, Bredviken, Lövskataviken and Inre Skurholmsfjärden, decomposition of natural and anthropogenic organic material consumes the oxygen and

causes reduced conditions in the bottom-near water and the sediment during winter.

Water and sediment quality in the Luleå area are dependent on catchment area (size, natural premises and exploitation) and emission impact, especially from point sources. Important factors are water volume and turnover rate in the water bodies with low water levels and no surface runoff in wintertime, and ice covering during winter, which also contributes to anoxic conditions in the water column and sediment. The redox status in the sediments is crucial for release or bonding of pollutants in the sediments. The bays do have the capacity to retain pollutants in their sediment, but there is still a potential risk of release if the redox conditions change. Postglacial land uplift implies continuous changes in the environment, which can lead to changing redox conditions. This will necessitate new risk assessments.

ACKNOWLEDGEMENTS

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