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Broad substance screening of sediments

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Sammanfattning

Bakgrund och metodik

De flesta undersökningar av sediment fokuserar på traditionella ämnen som metaller, PAH ämnen samt olje- och bränsle relaterade ämnen. Studier som använder riktade analytiska metoder (dvs. man letar efter specifika ämnen) har påvisat att ett mycket stort antal andra ämnen kan förekomma i sediment. Sådana riktade studier är dock inte förutsättningslösa utan baseras på medvetna val av vilka ämnen som man vill undersöka. Denna screeningsstudie fokuserar istället på att använda förutsättningslösa analytiska metoder som letar efter ”alla” ämnen som förekommer i sediment. Screeningsstudien har således som primärt syfte att genomföra en fullödlig karaktärisering av sediment.

För att täcka in ett så stort antal föroreningar som möjligt valdes så hårt förorenade punkter som möjligt ut, som samtidigt karaktäriserades av att helt olika typer av föroreningskällor påverkade sedimenten.

GC-MS metoder användes för detektion av okända ämnen i så kallat ”scan” läge där masspektrometern förutsättningslöst skannar av så många påträffade molekyler (jonfragment) som möjligt med syfte att identifiera dessa. De masspektrometiska metoder som användes var EI (Electron Impact) och NCI (Negative Chemical Ionization).

Resultat och rekommendation

Nedanstående tabell redovisar mycket översiktligt vilka ämnesgrupper som påträffades i sediment. Det tydligaste mönstret var att mestadels så påträffades ”vanliga” ämnen såsom metaller, PAH ämnen samt olje- och bränslerelaterade ämnen snarare är nya okända organiska ämnen som studien syftade till att hitta.

	Antal ämnen	Antal ganger påträffat
Metaller	11	126
Bränsle- och oljerelaterade organiska ämnen	1	10
PAH ämnen	19	87
Andra organiska ämnen	6	8

Orsaken till dessa resultat kan ha varit:

1. Besvärliga provmatriser med mycket olja som döljer förekomsten av andra antropogena ämnen.
2. De analytiska tekniker som användes.

3. Att andra ämnen *de facto* inte förekom i sedimenten.

För att svara på frågan om resultaten i denna studie var representativa eller om ämnen missades så är en möjlighet en uppföljande screeningsstudie där andra analytiska extraktions och detektionsmetoder används.

Några ”icke traditionella” ämnen påträffades dock::

Metylisopropylfenantren är en PAH som bildas vid förbränning av växter. Ämnet är exempelvis vanligt i kreosot. I denna studie påträffades ämnet i sediment som var påverkade av pappersindustrier, sågverk samt äldre industriområden.

Tetrametylfenantren är troligtvis ett olje- och bränslerelaterat ämne. Ämnet förekom utanför en sågverksindustri varifrån utsläpp av hydraulolja skett till sedimenten där provet togs.

Dimetyl sulfid (DMS) används för dammbekämpning i stålindustrin samt vid petrokemisk tillverkning. Det är även ett ämne som bildas naturligt av växtplankton i ytvatten. Den naturliga bildningen är troligtvis orsaken till att ämnet återfanns i marina sediment (en hamn).

Bis-metylylbifenyl har troligtvis sitt ursprung i olje- och bränslerelaterade produkter

Klornaftalener har använts i produkter för isolering av elektriska kablar, impregneringsmedel för trä, plast- och gummitillsatser och i smörjmedel. Ämnena är potentiella PBT ämnen och deras användning är numera förbjuden. Ämnena återfanns i sediment som påverkas av stora industriområden med lång historisk verksamhet.

Av dessa ämnen identifierade klornaftalener som potentiella screeningämnen givet deras persistens och storskaliga historiska användning.

Summary

Background and methods

Most studies of sediments focuses on oil and fuel related compounds as well as metals, and the total extent of the chemical content of sediments has usually not been fully investigated. This could be remedied by extensive targeted analysis programs which involve a conscious choice of which substances to include which also introduces biases. An alternative strategy is to use broad analytical screenings methods that do not target any specific substances. This study focuses on using such methods to obtain unprejudiced information about the content of substances in marine and limnic sediments. The aims of the project was mainly to assess the unprejudiced content of inorganic and organic substances in sediments and, if possible, to discover substances that has not been found in sediments before

Since the objective involved finding as many substances as possible in sediments, the sampling points chosen were heavily influenced by varying types of contaminant sources.

The analytical strategies for organic substances were to use mass spectrometric methods primarily in scan mode which is useful for determining unknown compounds in a sample. Both Electron Impact (EI) and Negative Chemical Ionization (NCI) GC-MS methods were used. ICP-MS. ICP-MS (Inductively coupled plasma mass spectrometry) was used for the analysis of inorganic compounds.

Results

The table below presents a condensed summary of which substance groups that were found in sediments.

	No of substances	No of detects
Metals	11	126
Oil and fuel related hydrocarbons	1	10
PAHs	19	87
Other organic substances	6	8

In general, most of the organic substances found in sediments were those commonly expected such as metals, PAHs and oil- and fuel related substances. A few other seldom measured organic substances were also found in sediment samples.

Methyl isopropyl phenanthrene is a PAH originating from plants products and commonly present in coal tar and effluents from paper mills. The substance was found in sediments affected by a sawmill and in sediment adjacent to chemical manufacturing industries as well as wood industries.

Tetramethyl phenanthrene is most likely derived from petroleum fuels. It was found in sediments affected by a sawmill that had caused lubricant oil pollution of the sediment were the sample was taken.

Dimethyl sulfide (DMS) is used to control dusting in steel mills, and in a range of organic syntheses. It is also commonly used in petrochemical production processes. Dimethylsulfide is also a naturally produced biogenic gas essential for the Earth's biogeochemical cycles. DMS was found in sediments from a marine harbour where it probably originates from natural sources.

Bis-methylethylbiphenyl most likely originates from vehicle fuels.

Hepta and octachloro naphthalene (polychlorinated naphthalenes - PCN) are used for electrical wire coatings, wood preservatives, as rubber and plastic additives, for capacitor dielectrics and in lubricants. The production and usage has been prohibited and discontinued. The substances was found in sediments affected by multiple chemical industries and may reflect historical usage at the site.

The only substances that may be warranted for a future screening study is Hepta and Octachloro naphthalene given the high historical usage and PBT properties.

A follow up screenings study could be used to clarify whether the results from this study are representative or an artefact of the complex matrix and analysis methods used. Such a study would use even more specialized analytical techniques.

1 Introduction

1.1 Background and aims

At present there is a lack of knowledge regarding the emission, distribution and exposure for many of the chemicals emitted to the environment. The aim of the screening program financed by the Swedish Environmental Protection Agency is to alleviate this lack of knowledge by estimating the occurrence of different chemicals in the environment in relevant matrices (soil, water etc.).

Most studies of sediments are targeted on specific substances and usually also on traditional anthropogenic substances such as PCBs, PAHs, Metals and oil and fuel related substances (Hwang et al. 2009). A number of studies has targeted more unconventional emerging contaminants in sediments such as household, pharmaceutical and industrial chemicals (Arikan et al. 2008, Bradely et al. 2007, Kim and Carlson 2005), although the full extent of the chemical content of sediments samples has never been fully investigated.

This is problematic given that sediments are the final reservoirs for many (most) substances originating in the technosphere (Fernex et al. 2001, Dewulf and DeVisscher 1996), especially those substances that do not degrade easily (Bradely et al. 2007).

More complete characterizations of sediments could be done by extensive targeted analysis programs focusing on a large number of different substances groups. This has been done in a limited manner (Arikan et al. 2008) although there are inherent limitations since a conscious choice of substances by definition also excludes substances that are not chosen.

An alternative strategy is to use broad analytical screenings methods to that do not target any specific substances. This study focuses on using such methods to obtain unprejudiced information about the content of substances in marine and limnic sediments.

1.2 Objectives

In order to facilitate data evaluation, some clearly stated objectives were decided upon:

- To assess the unprejudiced content of inorganic and organic substances in limnic and marine sediments
- If possible to discover substances that has not been found in limnic and marine sediments in Sweden before

This study does not encompass a risk assessment of the substances found. The reason is:

1. The concentrations obtained using the analytical techniques in this study are at best semi quantitative
2. The study focuses on finding “new” substances in sediments and not on evaluating these substances

2 Methodology

2.1 Sampling strategy and study areas

Since the objective was to find as many substances as possible in sediments, the sampling points chosen were:

1. Heavily influenced by contaminant sources.
2. Varied in the types of contaminant sources that may reach them.

The sampling points that were chosen based on these premises are briefly presented in Table 2.1 and more fully presented in appendix 1.

Table 2.1 Sampling points for sediments used in this study.

Sampling location	Possible source of contamination
Sawmill	Sawmill industry
Mölnåsaån	Mainly traffic and urban influence
Casco	Chemical industry and municipal sewage plant
Höje å	Municipal sewage plant
Vänern, Skoghäll	Chemical industry
Sege å	Traffic, industry (production of coatings and a couple of smaller industries), agricultural drainage area.
Holmsund harbour (basin)	Oil terminal, container terminal. Close to pulp mill and wood impregnation.
Holmsund harbour (UKV)	Oil terminal, container terminal. Close to pulp mill and wood impregnation.
Göta älv	Urban influence (Gothenburg city), traffic, marina, an industrial drainage area.
Malmö harbour	Container terminal, ferry-traffic, former industrial area.
Gävle harbour	Container terminal, ore-handling, scrap and coal storage.
Marina, Borstahusen	Marina, small fishing port.

2.2 Sampling

Sediment sampling was done once for each location. Samples were taken with Ekman grabbers or Gemini corers. Only the top 5-8 centimetres were mixed and analysed.

The reason was that:

1. The samples should reflect relatively modern anthropogenic influence
2. The samples should not be too big which could cause dilution of unevenly distributed chemicals within the sample

2.3 Analytical methods

2.3.1 Overview

Different gas chromatographic mass spectrometer (GC-MS) techniques were used for the analytical work. In a GC-MS system, a gas chromatograph initially separates the molecules in a sample depending on differences in chemical properties of the molecules. The mass spectrometer downstream of the GC captures and detects the molecules. The mass spectrometer does this by breaking each molecule into ionized fragments and detecting these fragments using their mass to charge ratio.

The analytical strategies for organic substances were to use mass spectrometric methods primarily in a scan mode which is useful in determining unknown compounds in a sample. When collecting data in a scan mode, a range of ionized mass fragments is screened. The determination of what range to use is controlled by the anticipated substances in the samples as well as the solvents used and possible interferences. Additionally if a large scan range is used, then the sensitivity of the instrument is decreased. The reason is that a wide range of mass fragments means that there will be fewer scans per second since each scan will have to detect a larger range.

Scan mode provides more information than the other common scan method, selective Ion Monitoring (SIM) when it comes to confirming compounds in a sample. In SIM mode, specific ion fragments are entered, which will be the only one detected by the mass spectrometer. The advantages of SIM are that the detection limit is lower since the instrument is only looking at a small number of fragments during each scan which means that more scans can take place each second. Also, matrix interferences are typically lower because of the very limited mass range.

After the molecules travel through the gas chromatograph, and enter the mass spectrometer, they are ionized into fragments using various methods. The ionization technique chosen is independent of using a Scan or SIM method. The most common form of ionization is electron ionization (EI) where the molecules are bombarded with free electrons which cause a "hard" ionization that fragments the molecule. An alternate

method is chemical ionization which typically cause a 'soft' ionization of the molecules (i.e. a lower fragmentation than the hard ionization of EI).

Quantification of a detected and identified molecule is dependent on the use of standards. These are very much alike the compound of interest and are injected into the sample in known amounts. By looking at the size of a peak of the known standard, and comparing with the size of the chromatographic peak of the compound of interest, quantification is possible. When using scan mode to look for unknown substances in a sample, full quantification it is not possible, since it has to be known in advance which standards to add to the samples. In this study another technique was used whereby eight different standards representing molecules of different size and behavior were injected into the sample. Using these, it was possible to approximately quantify the substances (semi quantification).

2.3.2 GC-MS EI

GC-MS methods with electron ionization were used for all samples. When semivolatile substances (such as PAHs, PCBs, PBDEs and HCHs) were in focus, an accelerated solvent extraction (ASE) method was used with acetone/pentane in a 1:1 ratio as the solvent. The pentane phase was injected into the GC and electron ionization was used to fragment the molecules in the mass spectrometer. When more volatile substances were in focus (such as benzenes, toluenes, and chlorinated aliphatics) a head space techniques was used which forces the volatile compounds into a gas phase, where after the gas phase is introduced into the GC. In both cases, full scan mode was used.

2.3.3 GC-MS-NCI methods

GC-MS methods with negative chemical ionization is a very sensitive technique for detecting low levels of almost all halogenated organic substances. This is also a less standardized technique which makes it more costly and consequently it was used on a limited number of samples that were considered to be either more polluted than other samples or atypical in the type of compounds that could be expected (i.e. if a unique source of substances could be suspected).

The GC-MS NCI was performed in a SIM/SCAN mode which enables an initial broad search after compounds and a more focused identification of interesting mass fragments. Quantification of molecules using the NCI method is problematic because the response factors (i.e. the intensity of a signal for a given mass fragment) varies to a large degree. Consequently, as a complement, gas chromatography combined with Electron Capture Detection (ECD) was used for semiquantification.

2.3.4 ICP-MS

ICP-MS (Inductively coupled plasma mass spectrometry) was used for the analysis of inorganic compounds. ICP-MS is a kind of mass spectrometry that is very sensitive and capable for the determination of a range of inorganic substances at low concentra-

tions. The ICP-MS allows determination of elements with atomic mass in ranges from 7 to 250 (Li to U). Unlike atomic absorption spectroscopy, which can only measure a single element at a time ICP-MS has the capability to scan for all elements simultaneously. The technique is based on pairing inductively coupled plasma as a method of producing ions (ionization) with a mass spectrometer as a method of separating and detecting the ions.

Before analysis the samples were treated with nitrous acid (HNO_3). The acid sample solution was pumped through a loop into a plasma chamber in the ICP instrument with a temperature of 8000 °C. The concentrations was determined through calibration with elemental standards.

3 Results

All substances found and the analysis methods used are summarized in Table 3.1 - Table 3.12 for each sample point. A statistical evaluation is presented in Table 3.13.

Table 3.1 Results from GC-MS and ICP MS analysis of sediments being influenced by sawmill effluents

Sawmill, Middle part of Sweden			
Limnic			
ICP MS			
GC-MS EI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	0,53	mg/kg dw	ICP MS
Barium	55	mg/kg dw	ICP MS
Cadmium	0,64	mg/kg dw	ICP MS
Chromium	1,6	mg/kg dw	ICP MS
Cobalt	0,35	mg/kg dw	ICP MS
Copper	9,1	mg/kg dw	ICP MS
Lead	25	mg/kg dw	ICP MS
Mercury	0,059	mg/kg dw	ICP MS
Nickel	2,7	mg/kg dw	ICP MS
Vanadium	2,5	mg/kg dw	ICP MS
Zinc	98	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	540	mg/kg dw	GC-MS EI
<i>Aromatic hydrocarbons >C8-C10</i>			
Alkylated, hydrated naphthalene	30	mg/kg dw	GC-MS EI
Oxygen containing aromatic	200	mg/kg dw	GC-MS EI
Hydrated, methylated isopropyl phenanthrene	200	mg/kg dw	GC-MS EI
Bis-Methylethyl-biphenyl	500	mg/kg dw	GC-MS EI
Tetramethyl phenantrene	1000	mg/kg dw	GC-MS EI
<i>Polyaromatic hydrocarbons</i>			
Benz(a)anthracene	0,11	mg/kg dw	GC-MS EI
Chrysene	0,080	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,13	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,16	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,18	mg/kg dw	GC-MS EI
Dibenz(a,h)anthracene	0,19	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	0,12	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,17	mg/kg dw	GC-MS EI

Table 3.2 Results from GC-MS and ICP MS analysis of sediments in Mölndalsån

Mölndalsån, Göteborg			
Limnic			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	0,25	mg/kg dw	ICP MS
Chromium	4,2	mg/kg dw	ICP MS
Cobalt	1,8	mg/kg dw	ICP MS
Copper	3,2	mg/kg dw	ICP MS
Lead	5,7	mg/kg dw	ICP MS
Nickel	2,5	mg/kg dw	ICP MS
Vanadium	8,5	mg/kg dw	ICP MS
Zinc	17	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	27	mg/kg dw	GC-MS EI

Table 3.3 Results from GC-MS and ICP MS analysis of sediments being influenced by effluents from a chemical manufacturing plant

Chemical manufacturing plant			
Limnic			
ICP MS			
GC-MS EI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	1,8	mg/kg dw	ICP MS
Barium	190	mg/kg dw	ICP MS
Cadmium	0,14	mg/kg dw	ICP MS
Chromium	26	mg/kg dw	ICP MS
Cobalt	13	mg/kg dw	ICP MS
Copper	11	mg/kg dw	ICP MS
Lead	20	mg/kg dw	ICP MS
Nickel	16	mg/kg dw	ICP MS
Vanadium	49,0	mg/kg dw	ICP MS
Zinc	100	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	79	mg/kg dw	GC-MS EI

Table 3.4 Results from GC-MS and ICP MS analysis of sediments in Höje Å.

Höje å, Lund			
Limnic			
ICP MS			
GC-MS EI Semivolatile			
GC-MS EI Volatile			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	4,0	mg/kg dw	ICP MS
Barium	110	mg/kg dw	ICP MS
Cadmium	0,36	mg/kg dw	ICP MS
Chromium	18	mg/kg dw	ICP MS
Cobalt	6,2	mg/kg dw	ICP MS
Copper	17	mg/kg dw	ICP MS
Lead	17	mg/kg dw	ICP MS
Nickel	14	mg/kg dw	ICP MS
Vanadium	21	mg/kg dw	ICP MS
Zinc	110	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	57	mg/kg dw	GC-MS EI
<i>Polyaromatic hydrocarbons</i>			
Benz(a)anthracene	0,070	mg/kg dw	GC-MS EI
Chrysene	0,070	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,090	mg/kg dw	GC-MS EI

Table 3.5 Results from GC-MS and ICP MS analysis of sediments in Skoghallsådran before it flows into the Lake Vänern.

Vänern, Skoghall			
Limnic			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	14	mg/kg dw	ICP MS
Barium	96	mg/kg dw	ICP MS
Cadmium	0,38	mg/kg dw	ICP MS
Chromium	27	mg/kg dw	ICP MS
Cobalt	4,2	mg/kg dw	ICP MS
Copper	420	mg/kg dw	ICP MS
Lead	40	mg/kg dw	ICP MS
Mercury	16	mg/kg dw	ICP MS
Nickel	27	mg/kg dw	ICP MS
Vanadium	25	mg/kg dw	ICP MS
Zinc	180	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	300	mg/kg dw	GC-MS EI
<i>Aromatic hydrocarbons >C8-C10</i>			
Hydrated, methylated isopropyl phenanthrene	40	mg/kg dw	GC-MS EI
Bis-Methylethyl-biphenyl	20	mg/kg dw	GC-MS EI
Tetramethyl phenantrene	80	mg/kg dw	GC-MS EI
<i>Polyaromatic hydrocarbons</i>			
Naphtalene	0,27	mg/kg dw	GC-MS EI
Acenaphtene	0,10	mg/kg dw	GC-MS EI
Fluorene	0,14	mg/kg dw	GC-MS EI
Phenanthrene	0,66	mg/kg dw	GC-MS EI
Anthracene	0,13	mg/kg dw	GC-MS EI
Fluoranthene	0,88	mg/kg dw	GC-MS EI
Pyrene	0,69	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,35	mg/kg dw	GC-MS EI
Chrysene	0,37	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,47	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,17	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,30	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	0,16	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,17	mg/kg dw	GC-MS EI
<i>Chlorinated hydrocarbons</i>			

Chlorobenzenes, sum	2,0	mg/kg dw	GC-MS EI
Hexachlorobenzene	max 200*	µg/kg dw	GC-MS NCI
Hepta and Octachloro naphtalene **			GC-MS NCI

Polychlorinated bifenyyl

PCB, summa	<1	mg/kg dw	GC-MS EI
PCB209 (+other PCBs)	max 100*	µg/kg dw	GC-MS NCI

* Semi-quantification was not possible to perform in "NCI-mode" since the response factors vary too much between different substances. Another GC-MS screening performed in EI-mode i.e. electronic ionization, where the response factors are more stable, gave the estimated concentrations. Certain substances were only detected in NCI-mode since the EI screening is less sensitive than the NCI screening.

** Identification uncertain.

Table 3.6 Results from GC-MS and ICP MS analysis of sediments in Sege å.

Sege å, Malmö			
Limnic			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	15	mg/kg dw	ICP MS
Barium	140	mg/kg dw	ICP MS
Cadmium	1,2	mg/kg dw	ICP MS
Chromium	32	mg/kg dw	ICP MS
Cobalt	8,6	mg/kg dw	ICP MS
Copper	90	mg/kg dw	ICP MS
Lead	63	mg/kg dw	ICP MS
Mercury	0,15	mg/kg dw	ICP MS
Nickel	23	mg/kg dw	ICP MS
Vanadium	42	mg/kg dw	ICP MS
Zinc	380	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	340	mg/kg dw	GC-MS EI
<i>Polyaromatic hydrocarbons</i>			
Phenanthrene	0,20	mg/kg dw	GC-MS EI
Fluoranthene	0,47	mg/kg dw	GC-MS EI
Pyrene	0,44	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,24	mg/kg dw	GC-MS EI
Chrysene	0,28	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,51	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,12	mg/kg dw	GC-MS EI

Benz(a)pyrene	0,19	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	0,28	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,19	mg/kg dw	GC-MS EI

Table 3.7 Results from GC-MS and ICP MS analysis of sediments in Holmsund harbour

Holmsund harbour, Umeå (Basin)			
Marine			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	4,6	mg/kg dw	ICP MS
Barium	40	mg/kg dw	ICP MS
Cadmium	0,13	mg/kg dw	ICP MS
Chromium	22	mg/kg dw	ICP MS
Cobalt	4,5	mg/kg dw	ICP MS
Copper	38	mg/kg dw	ICP MS
Lead	29	mg/kg dw	ICP MS
Nickel	12	mg/kg dw	ICP MS
Vanadium	16	mg/kg dw	ICP MS
Zinc	63	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	27	mg/kg dw	GC-MS EI
<i>Polyaromatic hydrocarbons</i>			
Phenanthrene	0,12	mg/kg dw	GC-MS EI
Anthracene	0,12	mg/kg dw	GC-MS EI
Fluoranthene	0,18	mg/kg dw	GC-MS EI
Pyrene	0,14	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,12	mg/kg dw	GC-MS EI
Chrysene	0,10	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,12	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,050	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,090	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,060	mg/kg dw	GC-MS EI

Table 3.8 Results from GC-MS and ICP MS analysis of sediments in Holmsund Harbour

Holmsund harbour, Umeå (UKV 2)			
Marine			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	3,7	mg/kg dw	ICP MS
Barium	31	mg/kg dw	ICP MS
Cadmium	0,080	mg/kg dw	ICP MS
Chromium	15	mg/kg dw	ICP MS
Cobalt	4,0	mg/kg dw	ICP MS
Copper	9,1	mg/kg dw	ICP MS
Lead	6,5	mg/kg dw	ICP MS
Mercury	0,040	mg/kg dw	ICP MS
Nickel	9,8	mg/kg dw	ICP MS
Vanadium	15	mg/kg dw	ICP MS
Zinc	42	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	<20	mg/kg dw	GC-MS EI

Table 3.9 Results from GC-MS and ICP MS analysis of sediments in Göta Älv.

Göta älv			
Limnic			
ICP MS			
GC-MS EI Semivolatile			
GC-MS EI Volatile			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	5,0	mg/kg dw	ICP MS
Barium	68	mg/kg dw	ICP MS
Cadmium	0,39	mg/kg dw	ICP MS
Chromium	33	mg/kg dw	ICP MS
Cobalt	8,4	mg/kg dw	ICP MS
Copper	130	mg/kg dw	ICP MS
Lead	43	mg/kg dw	ICP MS
Mercury	0,40	mg/kg dw	ICP MS
Nickel	17	mg/kg dw	ICP MS
Vanadium	40	mg/kg dw	ICP MS
Zinc	220	mg/kg dw	ICP MS
<i>Aliphatic hydrocarbons</i>			
Aliphatic hydrocarbons >C16-C35	150	mg/kg dw	GC-MS EI

Polyaromatic hydrocarbons

Naphtalene	0,23	mg/kg dw	GC-MS EI
Phenanthrene	0,25	mg/kg dw	GC-MS EI
Fluoranthen	0,41	mg/kg dw	GC-MS EI
Pyrene	0,37	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,28	mg/kg dw	GC-MS EI
Chrysene	0,3	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,36	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,12	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,25	mg/kg dw	GC-MS EI
Dibenz(a,h)anthracene	0,06	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	0,2	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,6	mg/kg dw	GC-MS EI

Table 3.10 Results from GC-MS and ICP MS analysis of sediments in Malmö Harbour

Malmö harbour			
Marine			
ICP MS			
GC-MS EI Semivolatile			
GC-MS EI Volatile			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	6,0	mg/kg dw	ICP MS
Barium	47	mg/kg dw	ICP MS
Cadmium	0,51	mg/kg dw	ICP MS
Chromium	22	mg/kg dw	ICP MS
Cobalt	3,5	mg/kg dw	ICP MS
Copper	49	mg/kg dw	ICP MS
Lead	56	mg/kg dw	ICP MS
Mercury	0,27	mg/kg dw	ICP MS
Nickel	10	mg/kg dw	ICP MS
Vanadium	17	mg/kg dw	ICP MS
Zinc	150	mg/kg dw	ICP MS

Aliphatic hydrocarbons

Aliphatic hydrocarbons >C16-C35	44	mg/kg dw	GC-MS EI
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Polyaromatic hydrocarbons

Fluoranthen	0,18	mg/kg dw	GC-MS EI
Pyrene	0,16	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,13	mg/kg dw	GC-MS EI
Chrysene	0,10	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,18	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,060	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,10	mg/kg dw	GC-MS EI

Indeno(1,2,3-cd)pyrene 0,070 mg/kg dw GC-MS EI

Organic sulfides

Dimethyl sulfide 0,2 mg/kg dw GC-MS EI

Table 3.11 Results from GC-MS and ICP MS analysis of sediments in Gävle Harbour

Gävle harbour			
Marine			
ICP MS			
GC-MS EI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	3,0	mg/kg dw	ICP MS
Barium	38	mg/kg dw	ICP MS
Cadmium	0,65	mg/kg dw	ICP MS
Chromium	18	mg/kg dw	ICP MS
Cobalt	4,6	mg/kg dw	ICP MS
Copper	18	mg/kg dw	ICP MS
Lead	66	mg/kg dw	ICP MS
Mercury	0,14	mg/kg dw	ICP MS
Nickel	9,2	mg/kg dw	ICP MS
Vanadium	17	mg/kg dw	ICP MS
Zinc	190	mg/kg dw	ICP MS

Table 3.12 Results from GC-MS and ICP MS analysis of sediments in the Borstahusen Marina.

Marina, Borstahusen			
Marine			
ICP MS			
GC-MS EI			
GC-MS NCI			
Substance	Value	Unit	Method
<i>Metals</i>			
Arsenic	6,3	mg/kg dw	ICP MS
Barium	160	mg/kg dw	ICP MS
Cadmium	0,37	mg/kg dw	ICP MS
Chromium	23	mg/kg dw	ICP MS
Cobalt	2,9	mg/kg dw	ICP MS
Copper	550	mg/kg dw	ICP MS
Lead	130	mg/kg dw	ICP MS
Mercury	4,1	mg/kg dw	ICP MS
Nickel	7,9	mg/kg dw	ICP MS
Vanadium	15	mg/kg dw	ICP MS
Zinc	370	mg/kg dw	ICP MS

Aliphatic hydrocarbons

Aliphatic hydrocarbons >C16-C35	110	mg/kg dw	GC-MS EI
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Aromatic hydrocarbons >C8-C10

Alkylated, hydrated naphthalene	2	mg/kg dw	GC-MS EI
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Polyaromatic hydrocarbons

Naphtalene	0,10	mg/kg dw	GC-MS EI
Acenaphthylene	0,49	mg/kg dw	GC-MS EI
Acenaphtene	0,12	mg/kg dw	GC-MS EI
Fluorene	0,41	mg/kg dw	GC-MS EI
Phenanthrene	3,6	mg/kg dw	GC-MS EI
Anthracene	0,67	mg/kg dw	GC-MS EI
Fluoranthene	6,4	mg/kg dw	GC-MS EI
Pyrene	4,3	mg/kg dw	GC-MS EI
Benz(a)anthracene	2,4	mg/kg dw	GC-MS EI
Chrysene	2,8	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	3,5	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	1,3	mg/kg dw	GC-MS EI
Benz(a)pyrene	2,3	mg/kg dw	GC-MS EI
Dibenz(a,h)anthracene	0,37	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	1,3	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	1,5	mg/kg dw	GC-MS EI

Polychlorinated biphenyl

PCB, summa	<1	mg/kg dw	GC-MS EI
PCBs	max 50**	µg/kg dw	GC-MS-NCI

* Semi-quantification was not possible to perform in "NCI-mode" since the response factors vary too much between different substances. Another GC-MS screening performed in EI-mode i.e. electronic ionization, where the response factors are more stable, gave the estimated concentrations. Certain substances were only detected in NCI-mode since the EI screening is less sensitive than the NCI screening.

Table 3.13 Statistical evaluation of the substances found in sediments

Substance	Measured in no. Samples	Median	25th percentile	75th percentile	90th percentile	Unit
<i>Metals</i>						
Arsenic	12	4,3	2,7	6,1	14	mg/kg dw
Chromium	12	22	17	26	32	mg/kg dw
Cobalt	12	4,4	3,4	6,8	8,6	mg/kg dw
Copper	12	28	11	100	420	mg/kg dw
Lead	12	35	19	58	66	mg/kg dw
Nickel	12	11	8,9	16	23	mg/kg dw
Vanadium	12	17	15	29	42	mg/kg dw
Zinc	12	130	89	198	370	mg/kg dw
Barium	11	68	44	125	163	mg/kg dw
Cadmium	11	0,38	0,25	0,58	0,71	mg/kg dw
Mercury	8	0,21	0,12	1,3	8,9	mg/kg dw
<i>Aliphatic hydrocarbons</i>						
Aliphatic hydrocarbons >C16-C35	10	95	47	263	308	mg/kg dw
<i>Aromatic hydrocarbons</i>						
Bis-Methylethyl-biphenyl	2	260	140	380	20	mg/kg dw
Oxygen containing aromatic	1	200	200	200		mg/kg dw
<i>Polyaromatic hydrocarbons</i>						
Benz(a)anthracene	8	0,19	0,12	0,30	1,2	mg/kg dw
Chrysene	8	0,19	0,095	0,32	1,3	mg/kg dw
Benz(b)fluoranthene	8	0,27	0,13	0,48	1,7	mg/kg dw
Benz(k)fluoranthene	7	0,12	0,09	0,17	0,74	mg/kg dw
Benz(a)pyrene	7	0,19	0,14	0,28	1,3	mg/kg dw
Indeno(1,2,3-cd)pyrene	7	0,17	0,12	0,40	1,1	mg/kg dw
Fluoranthene	6	0,44	0,24	0,78	3,6	mg/kg dw
Pyrene	6	0,41	0,21	0,63	2,5	mg/kg dw
Phenanthrene	5	0,25	0,2	0,66	2,4	mg/kg dw
Benzo(g,h,i)perylene	5	0,20	0,16	0,28	0,99	mg/kg dw

Substance	Measured in no. Samples	Median	25th percentile	75th percentile	90th percentile	Unit
Naphthalene	3	0,23	0,17	0,25	0,26	mg/kg dw
Anthracene	3	0,13	0,13	0,40	0,56	mg/kg dw
Dibenz(a,h)anthracene	3	0,19	0,13	0,28	0,34	mg/kg dw
Acenaphthene	2	0,11	0,11	0,12	0,12	mg/kg dw
Fluorene	2	0,28	0,21	0,34	0,38	mg/kg dw
Acenaphthylene	1	0,49	0,49	0,49	0,49	mg/kg dw
Alkylated, hydrated naphthalene	2	16	9	23	2	mg/kg dw
Hydrated, methylated isopropyl phenanthrene	2	120	80	160	40	mg/kg dw
Tetramethyl phenantrene	2	540	310	770	80	mg/kg dw
<i>Chlorinated hydrocarbons</i>						
Chlorobenzenes, sum	1	2,0	2,0	2,0	2,0	mg/kg dw
Hexachlorobenzene	1					
<i>Polychlorinated biphenyl</i>						
PCB, summa	2					
<i>Organic sulfides</i>						
Dimethyl sulfide	1	0,2	0,2	0,2	0,2	mg/kg dw

4 Discussion

One general observation is that there was no clear trend in the type or number of substances that were detected. For instance, the harbour sediments (Gävle, Malmö and Umeå) did not differ in any obvious way from other types of sediments in their content. The results are affected by the fact that the extraction and analysis focused on semivolatile substances. This strategy was chosen because semivolatile substances have low water solubilities and a tendency to adhere to solid particles. But even in those cases when volatile substances were also included (Höje Å, Göta Älv, and Malmö Harbour – Table 3.4, Table 3.9, Table 3.10) there was clearly not more substances found. The exception was dimethylsulfide in Malmö Harbour which is included in the semivolatile analysis.

Most studies of sediments are targeted on specific substances and usually also on traditional anthropogenic substances such as PCBs, PAHs, Metals and oil and fuel related substances (Hwang et al. 2009). A number of studies has targeted more unconventional emerging contaminants in sediments such as household, pharmaceutical and industrial chemicals (Arikan et al. 2008, Bradely et al. 2007, Kim and Carlson 2005), although the full extent of the chemical content of sediments samples has never been fully investigated.

This is problematic given that sediments are the final reservoirs for many (most) substances originating in the technosphere (Fernex et al. 2001, Dewulf and DeVisscher 1996), especially those substances that do not degrade easily (Bradley et al. 2007). Consequently, sediments are potentially good indicators of a large number of substances from the technosphere that reach the environment.

More complete characterizations of sediments could be done by extensive targeted analysis programs focusing on a large number of different substances groups. This has not been fully done, but some efforts in that direction have been carried out (Arikan et al. 2008, Bradely et al. 2007, Kim and Carlson 2005). However, using this approach involves a conscious choice of which substances to include which may be based on professional judgment as well as literature surveys. It is however, impossible to keep track of all the > 100 000 thousands of substances that occurs in the technosphere and consequently, it is likely that some or many substances are never identified in sediments when using a targeted analytical approach.

Most of the organic substances found in sediments are those included in standard analyses of environmental matrices (Hwang et al. 2009) namely metals, PAHs and oil- and fuel related substances (**Fel! Hittar inte referenskälla.**). It was tentatively expected that additional substances, apart from the more common ones, should have been found given both the varying types of contaminant sources, the analytical tech-

niques used and the fact that earlier studies have found emerging type contaminants in sediment (Arikan et al. 2008, Bradely et al. 2007, Kim and Carlson 2005). Another reason to expect more substances is that sediments can be the final reservoir for many (most) substances originating in the technosphere (Fernex et al. 2001, Dewulf and DeVisscher 1996), especially those substances that do not degrade easily (Buffer et al. 2001).

Table 4.1 A summary of the results from GC-MS screening of sediments

	No of substances	No of detects
Metals	11	126
Oil and fuel related hydrocarbons	1	10
PAHs	19	87
Other organic substances	6	8

Other studies indicate the opposite. In GC MS screening studies of limnic sediments affected by urban sources, it was shown that, despite looking for a multitude of different substances, it was mainly the well known metals and hydrocarbons stemming from petroleum derived products like diesel fuel and motor oil that dominated (Agarth et al. 2001). Also, some studies have concluded that urban sediments does have negative ecotoxicological, effects (Muller et al. 2002) while others have concluded that they do not (Billworth et al. 1998). The reason for differences in the occurrence of substances in sediments may not only be the types of anthropogenic sources affecting a surface water but also if environmental conditions (redox conditions, organic matter content, nutrients etc.) are amenable for natural (bio)degradation (Alexander 1996).

The reason for a lack of detection of additional non traditional organic substances remains unknown, but it may be due to analytical reasons (see section 4.1) and/or an *actual* lack of such additional substances. The answer to this question would be dependent on a follow up study using partly other/better analytical techniques.

Within the field of site remediation, the GC-MS EI techniques and associated extraction methods that was used in the present study, are commonly used to obtain unprejudiced information about the composition of organic compounds in soil, groundwater and sediments both in Sweden and in other countries. The sites in question are both active industrial sites and old industrial sites without industrial activities at present.

The techniques have been relatively successful at obtaining information about the content of unknown organic substances at such sites. As an example, a large industrial

site in Sweden was analyzed using the GC-MS techniques of this study. This revealed the present of a large number of organic substances in soil and groundwater:

- 1,2 dichloropropane
- diethoxyethane
- Trimethylcyclohexanemethanol
- alfa pinen
- etylhexaneacid
- hexadecane acid
- octadecane acid
- propylphenanthrene
- tetrametylphenanthrene
- diethylsulfide
- ethanol
- acetone
- methylacetate
- butanone
- hexane
- pentanone
- heptane
- dipropylethyldioxane
- methylethylketone
- formaldehyde
- diethanolamine
- triethanolamine
- propylenglykol
- butylbensylphthalate
- dicyclohexylphthalate
- di-n-propylphthalate
- propylphenol
- pentanethioles

This demonstrates that the techniques used are able to obtain information on a large number of different organic compounds. Also, the samples from the industrial site often contained appreciable amounts of oil related compounds. Despite this, other compounds were also found. One reason for the difference in results between the present study and the industrial site may be generally higher concentrations at the industrial site, although some of the substances in the above list were found at levels < 50 µg/kg.

The industrial site is situated adjacent to marine surface waters. The sediments were analyzed using the methods of this study as well as several targeted analytical techniques. Despite the large number of substances present in groundwater and soil of the

industrial site, very few compounds were found in the sediments. Those that were found, were among the more persistent of those that occurred in soil and groundwater..

The following section shortly discusses the few non traditional organic substances that were found in the water and sediment samples.

Methylated isopropyl phenanthrene

Methyl isopropyl phenanthrene is a polycyclic aromatic hydrocarbon present in coal tar. It is derived by heat degradation of diterpenoids that are biologically produced by conifer trees. It is also present in effluents from wood pulp and paper mills (Meriläinen 2007). These sources agree with the fact that the substance was found in sediments affected by a sawmill where creosote has been used. It was also found in Skoghallsådran, a small subsidiary of Klarälven adjacent to chemical manufacturing industries as well as wood industries. This substance was also found in a screening of runoff and stormwater, indicating that it is a relatively common PAH derivative in the environment.

Tetramethyl-phenanthrene

This is most likely a substance that is derived from petroleum fuels. It has been shown to be a common component in the petroleum organic fraction of sediments from road retention/infiltration ponds in France (Duranda et al. 2004). The substance was found in sediments affected by a sawmill from which lubricant oil had been released to the sediments. It is interesting to note that the levels of traditional PAHs at this site was low while the levels of the more non-traditional PAHs and fuel related substances were at least 100 times higher.

Dimethyl sulfide

Dimethyl sulfide (DMS) is an water-insoluble organosulfur compound that has a characteristic disagreeable odor (Glindemann et al. 2006). DMS is used to control dusting in steel mills, and in a range of organic syntheses. It is also commonly used in petrochemical production processes to inhibit the formation of coke and carbon monoxide.

Dimethylsulfide is also a naturally produced biogenic gas essential for the Earth's biogeochemical cycles. Certain species of phytoplankton, synthesize the molecule dimethylsulfoniopropionate (DMSP) which is the precursor to DMS. When phytoplankton cells are damaged they release their contents into the seawater. Bacteria and phytoplankton are thereafter involved in degrading the released algal DMSP to DMS (<http://www.csa.com/discoveryguides/dimethyl/overview.php> - retrieved 2009-06-10). There is still a large uncertainty in the absolute flux of DMS from the global oceans but estimates range from 13 to 37 Tg S per year (Kettle and Andreae 2000)

DMS was found in sediments from Malmö harbour (Table 3.10) which is affected by numerous industrial activities as well as shipping traffic. However, it is most likely

that DMS in a sea environment originates from natural sources and it is consequently not interesting from a screening point of view.

Bis-methylethylbiphenyl

Despite extensive literature searches, no information regarding this specific substance has been obtained. It is however most likely that this compound originates from vehicle fuels since a group of very similar compounds are common components of petroleum mixtures (Yew and Mair 1966).

Hepta and Octachloro naphthalene

Polychlorinated naphthalene (PCN) are made by chemically reacting chlorine with naphthalene. Commercial PCNs are mixtures of 75 chlorinated naphthalene congeners plus by-products and are often described by the total fraction of chlorine. Some PCNs make effective insulating coatings for electrical wires. Others have been used as wood preservatives, as rubber and plastic additives, for capacitor dielectrics and in lubricants. Since the middle of the 1980s, the worldwide production of these compounds has mostly ceased, with the exception of some Eastern European countries and a production of a synthetic rubber (Neoprene FB) in Northern Ireland using pentachloronaphthalene. Most PCNs persist in the environment, and are considered potential PBT compounds. After more than 80 years of use and total production of several hundred million kilograms, PCN residues are widespread.

Hepta and Octachloro naphthalene was found in sediments of Skoghallsådran, a small subsidiary of Klarälven adjacent to chemical manufacturing industries as well as wood industries. The source remains unclear but the discontinued usage as well as the fact that the substances do not appear in the Swedish product registry¹ indicates historical pollution of sediments and/or adjacent groundwater and soils. If the substance has not been included in earlier screening studies, it may be warranted with a future screening study of this substances given its high historical usage and PBT properties.

4.1 Analytical methods

One reason for the lack of detection of more unknown organic substances may be the complicated matrix in combination with the analytical methods chosen. Sediments are usually very complicated matrixes whose organic composition is usually dominated by oil and fuel related substances as well as natural hydrocarbons from biological material in various degrees of decomposition (humus – Decker et al. 1994). The common occurrence of fuel related compounds is evidenced by the fact that the aliphatic C16 –

¹ The product registry is a national database on more than 120 000 chemical products and biotechnical organisms. The information about these are provide by approximately 2 500 organisations that are required to do so by law. A notification to the product registry has to be done if a legal entity produces, packages, distributes, redistributes or imports certain chemical products if the yearly volume exceeds 100 kg per product.

C35 fraction was very common in the sediment samples (Table 3.13). This is a marker compound for oil related hydrocarbons which in reality represents a very complex mixture of up to > 1000 of different hydrocarbon moieties. The biggest problem from the point of view of detecting emerging contaminants is that the presence of oil- and fuel related hydrocarbons as well as humic substances in the sample creates so called matrix disturbance that tends to dominate and hide the presence of other compounds. A typical such oil related disturbance can be found for the sediment outside of a saw-mill (see page 10 in appendix 2 – Sawmill). To elucidate the identity of unknown organic substances in such a complex matrix, may demand other extraction methods and possibly even more refined analytical detection methods;

The extraction methods used in this study may have been somewhat too rough in the sense that they extract all organic substances that can be classified as either volatile and/or semivolatile. In a sense this is correct since the aim of this study was to find as many new organic substances as possible. If a more selective extraction is used, this strategy is no longer fully practiced. On the other hand, more refined extraction techniques have been used to detect a large number of emerging contaminants in complex matrix samples such as industrial wastewater effluents (Gomez et al. 2009). However, these studies tend to find unknown/unexpected compound to a lesser degree than those using focused extraction. As an example, a study using one extraction technique (SPE) to cover all substances followed by GC-MS in scan mode, found more than 300 substances in leachates from a Swedish landfill. Most of these could be denoted as non-traditional emerging substances (Paxeus 2000).

One possible way of using more refined extraction is to use solid-phase extraction (SPE). This is a separation process that uses the affinity of solutes dissolved or suspended for a solid through which the sample is passed to separate a mixture into desired and undesired components. The result is that either the desired analytes of interest or undesired impurities in the sample are retained on the stationary phase. The solid phase can be chosen so as to exclude certain types of compounds (such as oil related ones). A variant of this technique is solid phase microextraction (SPME) which has been used when identifying >500 different emerging-type organic contaminants in landfill leachates which is also a very complex matrix (Benfenati m.fl. 2004, Benfenati m.fl. 2003, Jimenez m.fl. 2002) and in sediment samples (reference)

The other possible remedy for identifying unknown substances in a very complex matrix is to use even more advanced analytical separation and detection methods. One such method could be the use of tandem mass spectrometry (MS/MS) which is a very powerful technique to quantify low levels of target compounds in the presence of a high sample matrix background. Another possibility is the use of two dimensional gas chromatography in which all the eluted compounds from a first separation are successively submitted to a new separation using different selectivity parameters. This tech-

nique has been used with some success for municipal sludge and effluents (Semard et al. 2008) as well as sediment samples (Agardh et al. 2002).

5 Conclusions and recommendations

The study has shown that metals and fuel and petroleum related compounds dominate in limnic and marine sediments that are influenced by anthropogenic sources. There is a possibility that organic substances have not been identified due to the complex sample matrix in combination with the analytical techniques used. A follow up screenings study could remedy this. Such a screenings could be designed to first use a number of different analytical extraction and detection methods on a few samples with a complex chemical composition. The best methodology could then be applied to 10 – 15 additional samples, possibly from the same locations as in this study, in order to make comparisons between the results.

The only detected non traditional organic substance that may be warranted for a future screening study is Hepta and Octachloro naphthalene given its high historical usage and PBT properties. None of the additional organic substances in this study were deemed of interest for a follow up screening, with the possible exception of methyl isopropyl phenanthrene. It may be that this is a common PAH compound that is not part of the commonly used PAH analytical packages used in regulatory monitoring in Sweden.

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