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Broad substance screening of stormwater runoff

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Bakgrund och metodik

De flesta undersökningar av dagvatten och dagvattensediment fokuserar på traditionella ämnen som metaller, PAHer samt olje- och bränsle relaterade ämnen. Studier som använder riktade analytiska metoder (dvs. man letar efter specifika ämnen) har dock påvisat att ett mycket stort antal andra ämnen kan förekomma i dagvattensystem. 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 dagvatten och dagvattensediment. Screeningsstudien har således som primärt syfte att genomföra en fullödig karaktärisering av dagvatten och dagvattensediment.

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 de olika dagvattensystemen. För att både flyktiga och icke flyktiga organiska ämnen skulle innefattas av studien, valdes *både* vatten och dagvattensediment (från botten av dagvattenbrunnar eller dagvattendammar) ut för provtagning och analys från varje provpunkt.

GC-MS metoder användes för detektion av okända ämnen i såkallat "scan" läge där masspektrometern förutsättningslöst skannar av så många påträffade molekyler (jonfragment) som möjligt med syfte att identifiera dessa. De massspektrometiska 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 och vatten. Det tydligaste mönstret var att mestadels så påträffades "vanliga" ämnen såsom metaller, PAHer samt olje- och bränslerelaterade ämnen snarare är nya okända organiska ämnen som studien syftade till att hitta. Generellt så påträffades dessutom fler ämnen i dagvattensediment än i vatten
.

	Dagvatten		Dagvattensediment	
	Antal ämnen	Antal gånger påträffat	Antal ämnen	Antal gånger påträffat
Metaller	11	102	12	95
Bränsle- och oljerelaterade organiska ämnen	3	8	5	13
PAH ämnen	11	16	17	74
Flyktiga organiska ämnen	7	7	0	0
Andra organiska ämnen	4	4	10*	13

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 dagvattenmatriserna.

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:

- Methyl isopropyl fenantren är en PAH som bildas vid förbränning av växter. Ämnet är exempelvis vanligt i kreosot.
- Tetrametyl fenantren har troligtvis sitt ursprung i olje- och bränslerelaterade ämnen
- Aceton är ett vanligt lösningsmedel både industriellt och i produkter som återfinns i hemmet.
- Benzyl butyl ftalat är en mjukgörare som vid tidigare screeningstudier har enbart har mätts och återfunnits i luftprover.
- BDE 99 är en viktig del i flamskyddsmedlet pentaBDE som är ett prioriterat ämne i vattendirektivet och som numera har fasats ut
- Dimetyl sulfid (DMS) används för dammbekämpning i stålindustrin samt vid petrokemisk tillverkning. Det är även ett ämne som bildas naturligt av växtplankton i ytvatten.
- Bis-metyletylbifenyl har troligtvis sitt ursprung i olje- och bränslerelaterade produkter.
- Thujon är ett naturligt förekommande ämne i växter
- Dekalin är ett lösningsmedel som återfinns bl.a i lacker, lackbaserade färger samt i poleringsmedel.
- Alfa-pinen är ett naturligt förekommande ämne i barrväxter.

Ett fåtal av dessa ämnen identifierades som potentiella screeningsämnen, även om sådana beslut kräver ytterligare utvärderingar om t.ex ämnenas farlighet och spridningsmönster:

- Benzyl butyl ftalat
- Dimetyl sulfid (DMS), även om ämnet kan ha ett naturligt ursprung.
- Dekalin

Summary

Background and methods

Most studies of stormwater runoff focuses on oil and fuel related compounds, and the total extent of the chemical content of stormwater runoff 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 stormwater runoff. The aims of the project was mainly to assess the unprejudiced content of inorganic and organic substances in run off water and storm water and, if possible, to discover substances that has not been found in stormwater runoff before

Since the objective involved finding as many substances as possible in stormwater runoff, the sampling points chosen were heavily influenced by contaminant source and varied in the types of contaminant sources that may reach them. To represent both semivolatile and volatile substances both stormwater as well as sediment from the bottom of the stormwater wells or stormwater dams were sampled and analyzed at each sampling station.

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 sediment and storm water. In general, more substances were found in the stormwater sediments compared to the water samples.

	Stormwater		Stormwater sediment	
	No of substances	No of detects	No of substances	No of detects
Metals	11	102	12	95
Oil and fuel related hydrocarbons	3	8	5	13
PAHs	11	16	17	74
Volatile organic substances	7	7	0	0
Other organic substances	4	4	10*	13

Most of the organic substances found in both runoff water and stormwater sediments in this study were those commonly expected in stormwater runoff systems such as metals, PAHs and oil- and fuel related substances. A few other seldom measured organic substances were also found in water and sediment samples.

- <u>Methyl isopropyl phenanthrene</u> is a PAH originating from plants products and commonly present in coal tar and effluents from paper mills.
- <u>Tetramethyl-phenanthrene</u> is most likely derived from petroleum fuels.
- <u>Acetone</u> is an organic industrial solvent that is also commonly used in households products.
- <u>Benzyl butyl phthalate</u> is a plasticizer that has been included in one earlier study within the Swedish screening program. In that study it was measured only in air samples where it was also found
- <u>BDE 99</u> is an important part of the flame retardant mixture pentaBDE whose production has been.
- <u>Dimethyl sulfide (DMS)</u> is used to control dusting in steel mills and commonly in petrochemical production processes.
- <u>Bis-methylethylbiphenyl</u> most likely originates from vehicle fuels.
- <u>Thujone</u> is a natural compound in a large number of plants species.
- <u>Decalin</u> is used as an industrial solvent.
- <u>Alpha-pinene</u> is natural compound mainly found in coniferous trees.

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 more specialized analytical techniques. A few organic substances were identified as being of tentative interest for further screening studies:

- Benzyl-Butyl-phthalate
- Dimethylsulfide (DMS), even though this is also a naturally produced biogenic compound
- Decalin

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 stormwater runoff focuses on oil and fuel related hydrocarbons (Menzie et al. 2002). Recently, some studies has shown that stormwater runoff may contain a number emerging substances (industrial and household chemicals as well as pharmaceuticals) from various sources including traffic and diffuse pollution from industrial activities (Boxal and Maltby 1995, Buus Madsen and Nielsen 2008, Hoenicke et al. 2007), although the full extent of the chemical content of stormwater runoff has never been fully investigated.

This could be remedied 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 performed in Denmark (Buus Madsen and Nielsen 2008a, 2008b) and other countries (Menzie et al. 2002). 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 stormwater runoff when using a targeted analytical approach.

An alternative strategy is to use broad analytical screening 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 stormwater runoff.

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 storm water systems.

- If possible, to discover substances that has not been found in stormwater runoff 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 stormwater runoff and not on evaluating substances

3. The sampling program is not designed for making any risk assessments (i.e. no measurements in surface waters)

2 Methodology

2.1 Sampling strategy and study areas

Since the objective involved finding as many substances as possible in stormwater runoff, 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 stormwater runoff used in this study.

Sampling location	Possible source of contamination
Tibbledammen	General urban influence
Örjadiket	Industrial area, chemical industry, manufacturing industry
Car park	Traffic, general urban influence
Akzo	Chemical industry
Pulp mill	Pulp mill
Äspered	Landfill, industrial area
Malmö residential area 1	Residential living influence
Malmö residential area 2	Residential living influence
Sorbusdammen	General urban influence, mainly traffic
Storm water dam	Traffic, agricultural area

The matrices chosen at each sampling stations was both stormwater as well as sediment from the bottom of the stormwater wells or stormwater dams (hereafter denoted stormwater sediment). The reason for this strategy was the assumption that more volatile/water soluble compounds would mainly be found in the water phase while less

water soluble substances with a high affinity for organic carbon and solids would be found in the sediments. This strategy was consequently aimed at covering as many substances as possible.

2.2 Sampling

Collection of storm water was usually done using spot sampling approach with a peristaltic pump or a grab catcher. The exception was water from Tibbledammen which was sampled using a flow proportional approach; At the inlet to the dam, a container was placed containing the sampling equipment. The sampling of the water was controlled by a water flow meter which was connected to a sampling pump. The flow meter gives a signal to the pump to collect a small amount of water when an appropriate amount of water has passed. The water was collected in a 20 l pre-burned glass bottle that was placed in a refrigerator (5 ^{0}C) within the container. Water was sampled for 3 weeks.

Sediment sampling was done once for each location. Samples were taken with Ekman grabbers or Gemini corers (stormwater dams) or a specially designed grab catcher that can extend for up to 3 m to take sediment samples from the bottom of wells. Samples were kept cold during transport and during storage before analysis.

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

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mode, specific ion fragments are entered, which will be the only one detected by the mass spectrometer. The advantage of SIM is 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 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 concentrations. 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 ^{o}C. The concentrations was determined through calibration with elemental standards.

3 Results

All substances found and the analysis methods used are summarized in table Table 3.1
- Table 3.10 for each sample point. A statistical evaluation is presented in Table 3.11 -
Table 3.12.

Table 3.1 Results of GC-MS screening of stormwater run off and stormwater sediment from Tibbledammen

Sampling station	Tibbledammen, Stockholm					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Semivolatile			**GC-MS EI Semivolatile**		
	GC-MS EI Volatile					
	GC-MS NCI			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Inorganics						
Aluminium	340	µg/l	ICP-MS			
Arsenic				7,6	mg/kg dw	ICP-MS
Barium	16	µg/l	ICP-MS			
Cadmium	0,064	µg/l	ICP-MS	0,13	mg/kg dw	ICP-MS
Calcium	27	mg/l	ICP-MS			
Chromium	9,7	µg/l	ICP-MS	57	mg/kg dw	ICP-MS
Cobalt	0,17	µg/l	ICP-MS	16	mg/kg dw	ICP-MS
Copper	8,0	µg/l	ICP-MS	28	mg/kg dw	ICP-MS
Iron	0,32	mg/l	ICP-MS			
Lead	0,50	µg/l	ICP-MS	21	mg/kg dw	ICP-MS
Molybdenum	1,3	µg/l	ICP-MS			
Nickel	2,1	µg/l	ICP-MS	38	mg/kg dw	ICP-MS
Strontium	66	µg/l	ICP-MS			
Vanadium				67	mg/kg dw	ICP-MS
Zinc	36	µg/l	ICP-MS	120	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35	0,094	mg/l	GC-MS EI			
Other organic substances						
DEHP Di-(2-ethyl-hexyl) phtha-late	0,1	mg/l	GC-MS EI			
BDE 99	n.q		GC-MS NCI			
mixture of halogenated com-pounds	n.q		GC-MS NCI			
two non-halogenated com-pounds with sulphur				n.q		GC-MS NCI
two high-halogenated com-pounds				n.q		GC-MS NCI

Table 3.2 Results of GC-MS screening of stormwater runoff and stormwater sediment from Örjadiket

Sampling station	Örjadiket, Landskrona					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Semivolatile			GC-MS EI Semivolatile		
	GC-MS EI Volatile			GC-MS EI Volatile		
	GC-MS NCI			GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Inorganics						
Aluminium	340	µg/l	ICP-MS			
Arsenic	1,2	µg/l	ICP-MS	42	mg/kg dw	ICP-MS
Barium	24	µg/l	ICP-MS	130	mg/kg dw	ICP-MS
Cadmium	0,061	µg/l	ICP-MS	1,8	mg/kg dw	ICP-MS
Calcium	33	mg/l	ICP-MS			
Chromium	2,5	µg/l	ICP-MS	40	mg/kg dw	ICP-MS
Cobalt	1,1	µg/l	ICP-MS	8,3	mg/kg dw	ICP-MS
Copper	7,2	µg/l	ICP-MS	80	mg/kg dw	ICP-MS
Iron	0,95	mg/l	ICP-MS			
Lead	26	µg/l	ICP-MS	310	mg/kg dw	ICP-MS
Mercury	0,0045	µg/l	ICP-MS	0,071	mg/kg dw	ICP-MS
Molybdenum	2,4	µg/l	ICP-MS			
Nickel	3,6	µg/l	ICP-MS	27	mg/kg dw	ICP-MS
Strontium	107	µg/l	ICP-MS			
Vanadium				35	mg/kg dw	ICP-MS
Zinc	78	µg/l	ICP-MS	650	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C10-C12				98	mg/kg dw	GC-MS EI
Aliphatic hydrocarbons >C12-C16				320	mg/kg dw	GC-MS EI
Aliphatic hydrocarbons >C16-C35	1,2	mg/l	GC-MS EI	1300	mg/kg dw	GC-MS EI
Aromatic hydrocarbons						
Aromatic hydrocarbons >C8-C10				3,8	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Naphthalene				0,17	mg/kg dw	GC-MS EI
Fluorene				0,13	mg/kg dw	GC-MS EI
Phenanthrene	0,42	µg/l	GC-MS EI	0,49	mg/kg dw	GC-MS EI
Anthracene				0,13	mg/kg dw	GC-MS EI
Fluoranthen	1,0	µg/l	GC-MS EI	1,0	mg/kg dw	GC-MS EI
Pyrene	0,92	µg/l	GC-MS EI	1,0	mg/kg dw	GC-MS EI

Sampling station	Örjadiket, Landskrona					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Semivolatile			**GC-MS EI Semivolatile**		
	GC-MS EI Volatile			**GC-MS EI Volatile**		
	GC-MS NCI			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Benz(a)anthracene	0,32	µg/l	GC-MS EI	0,38	mg/kg dw	GC-MS EI
Chrysene	0,84	µg/l	GC-MS EI	0,73	mg/kg dw	GC-MS EI
Benz(b)fluoranthene	0,80	µg/l	GC-MS EI	0,69	mg/kg dw	GC-MS EI
Benz(k)fluoranthene	0,17	µg/l	GC-MS EI	0,22	mg/kg dw	GC-MS EI
Benz(a)pyrene	0,27	µg/l	GC-MS EI	0,32	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene	0,29	µg/l	GC-MS EI	0,39	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene	0,26	µg/l	GC-MS EI	0,26	mg/kg dw	GC-MS EI
Other organic substances						
DEHP Di-(2-ethyl-hexyl) phtha-late				30	mg/kg dw	GC-MS EI
Decalin				5	mg/kg dw	GC-MS EI

Table 3.3 Results of GC-MS screening of stormwater runoff and stormwater sediment at a car park in Malmö

Sampling station	Car park, Malmö					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Volatile.			**GC-MS EI Semivolatile**		
				GC-MS NCI		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Inorganics						
Aluminium	250	µg/l	ICP-MS			
Arsenic	1,2	µg/l	ICP-MS	6,6	mg/kg dw	ICP-MS
Barium	36	µg/l	ICP-MS	210	mg/kg dw	ICP-MS
Cadmium	0,033	µg/l	ICP-MS	0,32	mg/kg dw	ICP-MS
Calcium	15	mg/l	ICP-MS			
Chromium	1,1	µg/l	ICP-MS	110	mg/kg dw	ICP-MS
Cobalt	3,6	µg/l	ICP-MS	7,9	mg/kg dw	ICP-MS
Copper	14	µg/l	ICP-MS	81	mg/kg dw	ICP-MS
Iron	0,68	mg/l	ICP-MS			
Lead	2,9	µg/l	ICP-MS	82	mg/kg dw	ICP-MS
Mercury	0,0028	µg/l	ICP-MS	0,064	mg/kg dw	ICP-MS
Molybdenum	2,3	µg/l	ICP-MS			
Nickel	2,4	µg/l	ICP-MS	57	mg/kg dw	ICP-MS

Sampling station	Car park, Malmö					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Volatile.			GC-MS EI Semivolatile		
				GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Strontium	54	µg/l	ICP-MS			
Vanadium				56	mg/kg dw	ICP-MS
Zinc	80	µg/l	ICP-MS	680	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35				1700	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Phenanthrene				0,52	mg/kg dw	GC-MS EI
Fluoranthen				1,0	mg/kg dw	GC-MS EI
Pyrene				1,1	mg/kg dw	GC-MS EI
Benz(a)anthracene				0,30	mg/kg dw	GC-MS EI
Chrysene				0,54	mg/kg dw	GC-MS EI
Benz(b)fluoranthene				0,87	mg/kg dw	GC-MS EI
Benz(k)fluoranthene				0,22	mg/kg dw	GC-MS EI
Benz(a)pyrene				0,34	mg/kg dw	GC-MS EI
Dibenz(a,h)anthracene				0,070	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene				0,52	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene				0,32	mg/kg dw	GC-MS EI
Other organic substances						
DEHP Di-(2-ethyl-hexyl) phthalate				40	mg/kg dw	GC-MS EI

Table 3.4 Results of GC-MS screening of stormwater runoff from a chemical factory

Sampling station	Chemical factory		
	Storm Water		
Performed analyses	ICP-MS		
	GC-MS EI Semivolatile		
	GC-MS EI Volatile		
Substance	Value	Unit	Method
Inorganics			
Aluminium	1030	µg/l	ICP-MS
Arsenic	1,9	µg/l	ICP-MS
Barium	21	µg/l	ICP-MS
Cadmium	0,019	µg/l	ICP-MS

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Sampling station	Chemical factory		
	Storm Water		
Performed analyses	ICP-MS		
	GC-MS EI Semivolatile		
	GC-MS EI Volatile		
Substance	Value	Unit	Method
Calcium	13	mg/l	ICP-MS
Chromium	0,89	µg/l	ICP-MS
Cobalt	0,21	µg/l	ICP-MS
Copper	3,3	µg/l	ICP-MS
Iron	0,4	mg/l	ICP-MS
Lead	0,82	µg/l	ICP-MS
Mercury	1,4	µg/l	ICP-MS
Molybdenum	1,3	µg/l	ICP-MS
Nickel	3,0	µg/l	ICP-MS
Strontium	27	µg/l	ICP-MS
Zinc	26	µg/l	ICP-MS
Aliphatic hydrocarbons			
Aliphatic hydrocarbons >C16-C35	0,048	mg/l	GC-MS EI
Polyaromatic hydrocarbons			
Chrysene	0,11	µg/l	GC-MS EI
Benz(a)pyrene	0,15	µg/l	GC-MS EI
Chlorinated hydrocarbons			
Trichloromethane	6,6	µg/l	GC-MS EI
1,2-dichloroethane	36	µg/l	GC-MS EI
Cis-1,2-dichloroethene	110	µg/l	GC-MS EI
Trans-1,2-dichloroethene	17	µg/l	GC-MS EI
Trichloroethene	71	µg/l	GC-MS EI
Tetrachloroethene	58	µg/l	GC-MS EI

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Table 3.5 Results of GC-MS screening of stormwater runoff and stormwater sediment at a pulp mill

Sampling station	Pulp mill, Northern Sweden					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Semivolatile			**GC-MS EI Volatile**		
	GC-MS EI Volatile			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Inorganics						
Aluminium	70	µg/l	ICP-MS			
Arsenic	0,45	µg/l	ICP-MS	5,2	mg/kg dw	ICP-MS
Barium	17	µg/l	ICP-MS	110	mg/kg dw	ICP-MS
Cadmium	0,04	µg/l	ICP-MS	0,38	mg/kg dw	ICP-MS
Calcium	16	mg/l	ICP-MS			
Chromium	0,31	µg/l	ICP-MS	40	mg/kg dw	ICP-MS
Cobalt	0,25	µg/l	ICP-MS	10	mg/kg dw	ICP-MS
Copper	6,3	µg/l	ICP-MS	130	mg/kg dw	ICP-MS
Iron	0,37	mg/l	ICP-MS			
Lead	0,29	µg/l	ICP-MS	50	mg/kg dw	ICP-MS
Mercury				6,4	mg/kg dw	ICP-MS
Molybdenum	0,21	µg/l	ICP-MS			
Nickel	4,6	µg/l	ICP-MS	46	mg/kg dw	ICP-MS
Strontium	67	µg/l	ICP-MS			
Vanadium				38	mg/kg dw	ICP-MS
Zinc	60	µg/l	ICP-MS	340	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35	0,13	mg/l	GC-MS EI	520	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Naphtalene				0,10	mg/kg dw	GC-MS EI
Phenanthrene				0,20	mg/kg dw	GC-MS EI
Fluoranthen				0,35	mg/kg dw	GC-MS EI
Pyrene				0,35	mg/kg dw	GC-MS EI
Benz(a)anthracene				0,15	mg/kg dw	GC-MS EI
Chrysene				0,37	mg/kg dw	GC-MS EI
Benz(b)fluoranthene				0,26	mg/kg dw	GC-MS EI
Benz(k)fluoranthene				0,070	mg/kg dw	GC-MS EI
Benz(a)pyrene				0,15	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene				0,14	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene				0,11	mg/kg dw	GC-MS EI
Hydrated, methylated isopropyl phenanthrene	5	µg/l	GC-MS EI	4	mg/kg dw	GC-MS EI
Tetramethyl-phenanthrene				10	mg/kg dw	GC-MS EI
Polychlorinated bifenyl						
PCBs				max	µg/kg dw	GC-MS NCI

Sampling station	Pulp mill, Northern Sweden					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Semivolatile			GC-MS EI Volatile		
	GC-MS EI Volatile			GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
PCB, summa				1000* <1	mg/kg dw	GC-MS EI
Other organic substances						
Bis-methylethylbiphenyl				4	mg/kg dw	GC-MS EI
DEHP Di-(2-ethyl-hexyl) phthalate				10	mg/kg dw	GC-MS EI

* 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 3.6 Results of GC-MS screening of stormwater runoff and stormwater sediment at Äsperöd in Gothenburg

Sampling station	Äspered, Göteborg					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Semivolatile			GC-MS EI Volatile		
	GC-MS EI Volatile			GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Inorganics						
Aluminium	2150	µg/l	ICP-MS			
Arsenic	2,1	µg/l	ICP-MS	0,63	mg/kg dw	ICP-MS
Barium	38	µg/l	ICP-MS	36	mg/kg dw	ICP-MS
Cadmium	0,063	µg/l	ICP-MS	0,015	mg/kg dw	ICP-MS
Calcium	18	mg/l	ICP-MS			
Chromium	7,8	µg/l	ICP-MS	8,2	mg/kg dw	ICP-MS
Cobalt	3,7	µg/l	ICP-MS	3,4	mg/kg dw	ICP-MS
Copper	23	µg/l	ICP-MS	28	mg/kg dw	ICP-MS
Iron	6,5	mg/l	ICP-MS			
Lead	8,7	µg/l	ICP-MS	10	mg/kg dw	ICP-MS
Molybdenum	1,6	µg/l	ICP-MS			
Nickel	15	µg/l	ICP-MS	5,5	mg/kg dw	ICP-MS
Strontium	66	µg/l	ICP-MS			
Vanadium				15	mg/kg dw	ICP-MS
Zinc	54	µg/l	ICP-MS	57	mg/kg dw	ICP-MS

Sampling station	Äspered, Göteborg					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Semivolatile			**GC-MS EI Volatile**		
	GC-MS EI Volatile			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C10-C12	0,012	mg/l	GC-MS EI			
Aliphatic hydrocarbons >C12-C16	0,15	mg/l	GC-MS EI			
Aliphatic hydrocarbons >C16-C35	0,83	mg/l	GC-MS EI	31	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Pyrene	0,14	µg/l	GC-MS EI			
Benz(a)anthracene	0,10	µg/l	GC-MS EI			

Table 3.7 Results of GC-MS screening of stormwater runoff and stormwater sediment at a residential area in Malmö

Sampling station	Residential area no 1, Malmö					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
				GC-MS EI Volatile		
	GC-MS EI Volatile			**GC-MS EI Semivolatile**		
	GC-MS NCI			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Inorganics						
Aluminium	200	µg/l	ICP-MS			
Arsenic	0,61	µg/l	ICP-MS	3,1	mg/kg dw	ICP-MS
Barium	50	µg/l	ICP-MS	110	mg/kg dw	ICP-MS
Cadmium	0,029	µg/l	ICP-MS	0,50	mg/kg dw	ICP-MS
Calcium	19	mg/l	ICP-MS			
Chromium	0,71	µg/l	ICP-MS	26	mg/kg dw	ICP-MS
Cobalt	0,80	µg/l	ICP-MS	7,6	mg/kg dw	ICP-MS
Copper	6,7	µg/l	ICP-MS	93	mg/kg dw	ICP-MS
Iron	0,33	mg/l	ICP-MS			
Lead	2,9	µg/l	ICP-MS	62	mg/kg dw	ICP-MS
Mercury	0,0051	µg/l	ICP-MS	0,11	mg/kg dw	ICP-MS
Molybdenum	0,94	µg/l	ICP-MS			
Nickel	1,2	µg/l	ICP-MS	20	mg/kg dw	ICP-MS
Strontium	43	µg/l	ICP-MS			
Vanadium				65	mg/kg dw	ICP-MS
Zinc	40	µg/l	ICP-MS	420	mg/kg dw	ICP-MS

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Sampling station	Residential area no 1, Malmö					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
				GC-MS EI Volatile		
	GC-MS EI Volatile			GC-MS EI Semivolatile		
	GC-MS NCI			GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35				1900	mg/kg dw	GC-MS EI
Aromatic hydrocarbons >C8-C10						
Toluene				0,91	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Naphthalene				0,15	mg/kg dw	GC-MS EI
Acenaphtylene				0,38	mg/kg dw	GC-MS EI
Phenanthrene				1,1	mg/kg dw	GC-MS EI
Anthracene				0,60	mg/kg dw	GC-MS EI
Fluoranthen				2,8	mg/kg dw	GC-MS EI
Pyrene				2,2	mg/kg dw	GC-MS EI
Benz(a)anthracene				0,90	mg/kg dw	GC-MS EI
Chrysene				2,3	mg/kg dw	GC-MS EI
Benz(b)fluoranthene				3,7	mg/kg dw	GC-MS EI
Benz(k)fluoranthene				0,80	mg/kg dw	GC-MS EI
Benz(a)pyrene				0,82	mg/kg dw	GC-MS EI
Dibenz(a,h)anthracene				0,20	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene				1,5	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene				1,3	mg/kg dw	GC-MS EI
Chlorinated hydrocarbons						
Chlorobenzenes, sum				<1	mg/kg dw	GC-MS EI
Hexachlorobenzene				Max 400*	µg/kg dw	GC-MS NCI
Organic sulfides						
Dimethyl sulfide				1	mg/kg dw	GC-MS EI
Other organic substances						
Alpha-pinene				1	mg/kg dw	GC-MS EI

* 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 3.8 Results of GC-MS screening of stormwater runoff and stormwater sediment at a residential area in Malmö

Sampling station	Residential area no 2, Malmö					
	Storm water			Strom water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Volatile.			GC-MS EI Semivolatile		
				GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Inorganics						
Aluminium	56	µg/l	ICP-MS			
Arsenic	0,33	µg/l	ICP-MS	0,75	mg/kg dw	ICP-MS
Barium	15	µg/l	ICP-MS	56	mg/kg dw	ICP-MS
Cadmium	0,016	µg/l	ICP-MS	0,29	mg/kg dw	ICP-MS
Calcium	15	mg/l	ICP-MS			
Chromium	0,33	µg/l	ICP-MS	16	mg/kg dw	ICP-MS
Cobalt	0,33	µg/l	ICP-MS	5,8	mg/kg dw	ICP-MS
Copper	3,6	µg/l	ICP-MS	710	mg/kg dw	ICP-MS
Iron	0,26	mg/l	ICP-MS			
Lead	0,98	µg/l	ICP-MS	44	mg/kg dw	ICP-MS
Mercury				0,095	mg/kg dw	ICP-MS
Molybdenum	0,37	µg/l	ICP-MS			
Nickel	0,69	µg/l	ICP-MS	14	mg/kg dw	ICP-MS
Strontium	36	µg/l	ICP-MS			
Vanadium				29	mg/kg dw	ICP-MS
Zinc	11	µg/l	ICP-MS	190	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35				560	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Phenanthrene				0,14	mg/kg dw	GC-MS EI
Fluoranthen				0,31	mg/kg dw	GC-MS EI
Pyrene				0,26	mg/kg dw	GC-MS EI
Benz(a)anthracene				0,15	mg/kg dw	GC-MS EI
Chrysene				0,23	mg/kg dw	GC-MS EI
Benz(b)fluoranthene				0,38	mg/kg dw	GC-MS EI
Benz(k)fluoranthene				0,10	mg/kg dw	GC-MS EI
Benz(a)pyrene				0,15	mg/kg dw	GC-MS EI
Benzo(g,h,i)perylene				0,19	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene				0,17	mg/kg dw	GC-MS EI
Other organic substances						
Thujone				9	mg/kg dw	GC-MS EI

Table 3.9 Results of GC-MS screening of stormwater runoff and stormwater sediment in the Suobus dam

Sampling station	Sorbus dam, Stockholm					
	Storm water			Storm water sediment		
Performed analyses	ICP-MS			ICP-MS		
	GC-MS EI Semivolatile			GC-MS EI		
	GC-MS EI Volatile.			GC-MS NCI		
Substance	Value	Unit	Method	Value	Unit	Method
Inorganics						
Aluminium	540	µg/l	ICP-MS			
Arsenic				2,4	mg/kg dw	ICP-MS
Barium	84	µg/l	ICP-MS		mg/kg dw	ICP-MS
Cadmium	0,088	µg/l	ICP-MS	0,37	mg/kg dw	ICP-MS
Calcium	43	mg/l	ICP-MS			
Chromium	1,7	µg/l	ICP-MS	65	mg/kg dw	ICP-MS
Cobalt	6,1	µg/l	ICP-MS	25	mg/kg dw	ICP-MS
Copper	13	µg/l	ICP-MS	140	mg/kg dw	ICP-MS
Iron	1,3	mg/l	ICP-MS			
Lead	1,4	µg/l	ICP-MS	51	mg/kg dw	ICP-MS
Mercury				0,10	mg/kg dw	ICP-MS
Molybdenum	4,6	µg/l	ICP-MS			
Nickel	3,4	µg/l	ICP-MS	29	mg/kg dw	ICP-MS
Strontium	160	µg/l	ICP-MS			
Vanadium			ICP-MS	89	mg/kg dw	ICP-MS
Zinc	78	µg/l	ICP-MS	700	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C12-C16				140	mg/kg dw	GC-MS EI
Aliphatic hydrocarbons >C16-C35	0,13	mg/l	GC-MS EI	2400	mg/kg dw	GC-MS EI
Polyaromatic hydrocarbons						
Naphtalene				0,24	mg/kg dw	GC-MS EI
Fluorene				0,22	mg/kg dw	GC-MS EI
Phenanthrene				1,2	mg/kg dw	GC-MS EI
Anthracene				0,15	mg/kg dw	GC-MS EI
Fluoranthen				1,7	mg/kg dw	GC-MS EI
Pyrene				2,0	mg/kg dw	GC-MS EI
Benz(a)anthracene	0,13	µg/l	GC-MS EI	0,84	mg/kg dw	GC-MS EI
Chrysene				0,95	mg/kg dw	GC-MS EI
Benz(b)fluoranthene				1,2	mg/kg dw	GC-MS EI
Benz(k)fluoranthene				0,31	mg/kg dw	GC-MS EI
Benz(a)pyrene				0,71	mg/kg dw	GC-MS EI

Sampling station	Sorbus dam, Stockholm					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Semivolatile			**GC-MS EI**		
	GC-MS EI Volatile.			**GC-MS NCI**		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Benzo(g,h,i)perylene				1,1	mg/kg dw	GC-MS EI
Indeno(1,2,3-cd)pyrene				0,34	mg/kg dw	GC-MS EI
Other organic substances						
Acetone	14	µg/l	GC-MS EI			
Benzyl-Butyl-phthalate	3	µg/l	GC-MS EI			

Table 3.10 Results of GC-MS screening of stormwater runoff and stormwater sediment in a storm water runoff dam in Lomma.

Sampling station	Storm water dam, Lomma					
	Storm water			**Storm water sediment**		
Performed analyses	**ICP-MS**			**ICP-MS**		
	GC-MS EI Volatile.			**GC-MS EI Semivolatile**		
				GC-MS NCI		
Substance	**Value**	**Unit**	**Method**	**Value**	**Unit**	**Method**
Inorganics						
Aluminium	34	µg/l	ICP-MS			
Arsenic	0,53	µg/l	ICP-MS	5,0	mg/kg dw	ICP-MS
Barium	63	µg/l	ICP-MS	65	mg/kg dw	ICP-MS
Cadmium	0,0051	µg/l	ICP-MS	0,11	mg/kg dw	ICP-MS
Calcium	100	mg/l	ICP-MS			
Chromium	0,34	µg/l	ICP-MS	29	mg/kg dw	ICP-MS
Cobalt	0,11	µg/l	ICP-MS	6,6	mg/kg dw	ICP-MS
Copper	1,7	µg/l	ICP-MS	9,4	mg/kg dw	ICP-MS
Iron	0,055	mg/l	ICP-MS			
Lead	0,52	µg/l	ICP-MS	12	mg/kg dw	ICP-MS
Mercury				0,048	mg/kg dw	ICP-MS
Molybdenum	0,71	µg/l	ICP-MS			
Nickel	0,96	µg/l	ICP-MS	18	mg/kg dw	ICP-MS
Strontium	540	µg/l	ICP-MS			
Vanadium				31	mg/kg dw	ICP-MS
Zinc	5,7	µg/l	ICP-MS	42	mg/kg dw	ICP-MS
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35				23	mg/kg dw	GC-MS EI

Table 3.11 Statistics on the substances found in stormwater.

Substance	Storm water					
	Measured in no. samples	Median	25th percentile	75th percentile	90th percentile	Unit
Inorganics						
Aluminium	10	300	100	490	1100	µg/l
Barium	10	30	18	47	65	µg/l
Cadmium	10	0,035	0,022	0,060	0,065	µg/l
Calcium	10	18	15	32	48	mg/l
Chromium	10	1,0	0,43	2,3	8,0	µg/l
Cobalt	10	0,57	0,22	3,0	3,9	µg/l
Copper	10	6,9	4,3	12	15	µg/l
Iron	10	0,39	0,32	0,88	1,8	mg/l
Lead	10	1,2	0,59	2,9	10	µg/l
Molybdenum	10	1,3	0,76	2,1	2,6	µg/l
Nickel	10	2,7	1,5	3,6	5,7	µg/l
Strontium	10	66	46	97	200	µg/l
Zinc	10	47	29	73	78	µg/l
Arsenic	8	0,91	0,51	1,8	2,0	µg/l
Mercury	4	0,0048	0,0041	0,35	0,98	µg/l
Aliphatic hydrocarbons						
Aliphatic hydrocarbons >C16-C35	6	0,13	0,10	0,66	1,0	mg/l
Aliphatic hydrocarbons >C10-C12	1	0,012	0,012	0,012	0,012	mg/l
Aliphatic hydrocarbons >C12-C16	1	0,15	0,15	0,15	0,15	mg/l
Polyaromatic hydrocarbons						
Benz(a)anthracene	3	0,13	0,12	0,23	0,28	µg/l
Benz(a)pyrene	2	0,21	0,18	0,24	0,26	µg/l
Chrysene	2	0,48	0,29	0,66	0,77	µg/l
Pyrene	2	0,53	0,34	0,73	0,84	µg/l
Benz(b)fluoranthene	1	0,8	0,8	0,8	0,8	µg/l
Benz(k)fluoranthene	1	0,17	0,17	0,17	0,17	µg/l
Benzo(g,h,i)perylene	1	0,29	0,29	0,29	0,29	µg/l
Fluoranthen	1	1,0	1,0	1,0	1,0	µg/l
Indeno(1,2,3-cd)pyrene	1	0,26	0,26	0,26	0,26	µg/l
Phenanthrene	1	0,42	0,42	0,42	0,42	µg/l

Storm water					
Substance	**Measured in no. samples**	**Median**	**25th percentile**	**75th percentile**	**90th percentile**	**Unit**
Hydrated, methylated isopropyl phenanthrene	1	5	5	5	5	µg/l
Volatile hydrocarbons						
1,2-dichloroethane	1	36	36	36	36	µg/l
Cis-1,2-dichloroethene	1	110	110	110	110	µg/l
Tetrachloroethene	1	58	58	58	58	µg/l
Trans-1,2-dichloroethene	1	17	17	17	17	µg/l
Acetone	1	14	14	14	14	µg/l
Trichloroethene	1	71	71	71	71	µg/l
Trichloromethane	1	6,6	6,6	6,6	6,6	µg/l
Other organic substances						
Benzyl-Butyl-phthalate	1	3	3	3	3	µg/l
DEHP Di-(2-ethyl-hexyl) phthalate	1	0,1	0,1	0,1	0,1	mg/l
BDE 99	1					
mixture of halogenated compounds	1					

Table 3.12 Statistics on the substances found in stormwater sediments.

Storm water sediment					
Substance	**Measured in no. samples**	**Median**	**25th percentile**	**75th percentile**	**90th percentile**	**Unit**
Inorganics						
Arsenic	9	5,0	2,4	6,6	14,5	mg/kg dw
Cadmium	9	0,32	0,13	0,38	0,76	mg/kg dw
Chromium	9	40	26	57	74	mg/kg dw
Cobalt	9	7,9	6,6	10	17	mg/kg dw
Copper§	9	81	28	130	250	mg/kg dw
Lead	9	50	21	62	127	mg/kg dw
Nickel	9	27	18	38	48	mg/kg dw
Vanadium	9	38	31	65	72	mg/kg dw
Zinc	9	340	120	650	680	mg/kg dw
Barium	7	110	60	120	162	mg/kg dw
Mercury	7	0,10	0,067	0,11	2,6	mg/kg dw
Aliphatic hydrocarbons						

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| Storm water sediment | | | | | |
Substance	Measured in no. samples	Median	25th percentile	75th percentile	90th percentile	Unit
Aliphatic hydrocarbons >C16-C35	8	930	400	1800	2100	mg/kg dw
Aliphatic hydrocarbons >C12-C16	2	230	190	280	300	mg/kg dw
Aliphatic hydrocarbons >C10-C12	1	98	98	98	98	mg/kg dw
Aromatic hydrocarbons >C8-C10						
Toluene	1	0,91	0,91	0,91	0,91	mg/kg dw
Aromatic hydrocarbons >C8-C10	1	3,8	3,8	3,8	3,8	mg/kg dw
Polyaromatic hydrocarbons						
Phenanthrene	6	0,51	0,27	0,96	1,2	mg/kg dw
Fluoranthen	6	1,0	0,51	1,5	2,3	mg/kg dw
Pyrene	6	1,1	0,51	1,8	2,1	mg/kg dw
Benz(a)anthracene	6	0,34	0,19	0,73	0,87	mg/kg dw
Chrysene	6	0,64	0,41	0,90	1,6	mg/kg dw
Benz(b)fluoranthene	6	0,78	0,46	1,1	2,5	mg/kg dw
Benz(k)fluoranthene	6	0,22	0,13	0,29	0,56	mg/kg dw
Benz(a)pyrene	6	0,33	0,19	0,62	0,77	mg/kg dw
Benzo(g,h,i)perylene	6	0,46	0,24	0,96	1,3	mg/kg dw
Indeno(1,2,3-cd)pyrene	6	0,29	0,193	0,34	0,82	mg/kg dw
Naphtalene	4	0,16	0,14	0,19	0,22	mg/kg dw
Anthracene	3	0,15	0,14	0,38	0,51	mg/kg dw
Fluorene	2	0,18	0,15	0,20	0,21	mg/kg dw
Dibenz(a,h)anthracene	2	0,14	0,10	0,17	0,19	mg/kg dw
Acenaphtylene	1	0,38	0,38	0,38	0,38	mg/kg dw
Tetramethyl-phenanthrene	1	10	10	10	10	mg/kg dw
Hydrated, methylated isopropyl phenanthrene	1	5	5	5	5	mg/kg dw
Other substances						
PCBs	1	1	1	1	1	mg/kg dw
Dimethyl sulfide	1	1	1	1	1	mg/kg dw
DEHP Di-(2-ethyl-hexyl) phthalate	3	30	20	35	38	mg/kg dw
Bis-methylethylbiphenyl	1	4	4	4	4	mg/kg dw
Thujone	1	9	9	9	9	mg/kg dw
Decalin	1	5	5	5	5	mg/kg dw
Alpha-pinene	1	1	1	1	1	mg/kg dw

Storm water sediment						
Substance	Measured in no. samples	Median	25th percentile	75th percentile	90th percentile	Unit
two non-halogenated compounds w sulfur	1					
two high-halogenated compounds	1					
Hexachlorobenzene	1	1	1	1	1	mg/kg dw

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4 Discussion

Table 4.1 presents a condensed summary of which substance groups that were found in sediment and storm water. In general, more substances were found in the stormwater sediments compared to the water samples. This is not surprising given that most substances have low water solubilities and a tendency to adhere to solid particles. The only exception was volatile organic substances that only occurred in the water samples. These results should be interpreted remembering that semivolatile extraction was mostly used for sediments samples and volatile extraction was mostly used for water samples. Still, in ten out of twenty samples a separate analysis was made of both the semivolatile and volatile fraction.

If the objective of investigating runoff stormwater is to identify new organic substances, it may be that both matrices has to be investigated, because several of the non traditional substances were identified in water and not in sediments, although *most* were found in sediments.

Most of the organic substances found in both runoff water and stormwater sediments in this study were those commonly expected in stormwater runoff systems (Rule et al. 2006) such as metals, PAHs and oil- and fuel related substances (Table 4.1). 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 techniques used and the fact that earlier studies have found emerging type contaminants in stormwater runoff (Boxal and Maltby 1995, Buus Madsen and Nielsen 2008, Hoenicke et al. 2007). Other studies indicate the opposite. In GC MS screening studies of road retention/infiltration ponds in France it was shown that the main component of the organic fraction stemmed from petroleum derived products like diesel fuel and motor oil (Duranda et al. 2004). Also, some studies have concluded that stormwater runoff does not have any toxic effects (Waara and Färm 2008) while others show that at least 20% of the investigated stormwater samples had severe ecotoxicological effects (Marsalek et al. 1999).

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

	Stormwater		Stormwater sediment	
	No of substances	No of detects	No of substances	No of detects
Metals	11	102	12	95
Oil and fuel related hydrocarbons	3	8	5	13
PAHs	11	16	17	74
Volatile organic substances	7	7	0	0
Other organic substances	4	4	10*	13

Two of which remained unidentified

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 and groundwater. 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
- butylbensylpthalate
- dicyclohexylpthalate
- di-n-propylpthalate

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- 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 < 100 µg/kg.

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 biologically produced by conifer trees. It is also present in effluents from wood pulp and paper mills (Meriläinen 2007) which agrees to this substance being found in stormwater run off and sediments from a paper mill industry.

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).

Acetone

Acetone is an organic solvent that is miscible with water, and most organic solvents. It is as an important solvent with more than 3 billion kilograms produced annually (mainly as a precursor within the chemical industry (Sifniades and levy 2005). It is also commonly used in households as the active ingredient in nail polish remover, paint thinner and sanitary cleaner.

Acetone was found in a stormwater dam receiving runoff from traffic. The reason for finding acetone in such an environment is consequently unclear, especially since the levels were clearly elevated (14 µg/l).

Benzyl butyl phthalate

Benzyl butyl phthalate is an ester of phthalic acid, benzyl alcohol and n-butanol. It is mostly used as a plasticizer for polyvinyl chloride, polyvinyl acetate, rubbers, cellulose plastics and polyurethane. End application include PVC floorings and wall coverings, expanded leather, PVC foams, films, sealing and adhesive systems based on

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polyurethane or polysulphide, PVAc based adhesives and paint binders. In 2006 there were 724 tonnes registered[1] in 112 products in Sweden.

Benzyl butyl phthalate has previously been found within the Swedish screening programme (Cousins et al. 2005) but only in air samples. Within that study benzyl butyl phthalate had the highest maximum concentrations in air of the eight phthalates investigated (Cousins et al. 2005). The dam in which the substance was found in this study only have traffic and urban deposition as contaminant sources and the presence in the water of this dam indicated diffuse urban pollution. Since it has not previously been investigated in other matrixes than air, it may be of interest to include this substance in further screening studies.

BDE 99 (PentaBDE)

BDE 99 constitutes approximately 50% of the commercial pentaBDE mixture (United Nations Environment Programme 2007). Commercial pentaBDE has been used as a flame retardant in polyurethane foam. The annual worldwide usage was approximately 7,500 tonnes in 2001, of which Europe accounted for 150 tonnes (United Nations Environment Programme 2007). From 2007 and onwards, the production of pentaBDE has been discontinued in Europe, Japan, Canada, Australia and USA (United Nations Environment Programme 2007).

PentaBDE is released to the environment by emissions from manufacture of pentaBDE-containing products and from the products themselves. The substance was found in the runoff water of a dam that receives urban runoff from a multitude of sources in a suburb to Stockholm. This agrees to a possible release from pentaBDE containing products, given that the substance in no longer used in production.

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 produced naturally by phytoplankton in very large amounts globally.

DMS was found in stormwater sediments from the bottom of a stormwater well in the road at a residential area in Malmö. The usage indicates a petrochemical source (vehicle fuels and exhaust). It is a compound that has been found when using GC-MS EI

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[1] The product registry is a national database on more than 120 000 chemical products and biotechnical organisms. The information about these are provided 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.

screenings to look for unknown substances in site remediation projects in Sweden (Swedish - "efterbehandlingsprojekt"). It has not been included in screening studies previously, and it may be warranted to evaluate as a possible future screening substance. On the other hand, it is also a naturally produced compound which is common in the marine environment.

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).

Thujone

Thujone is a ketone and a monoterpene with a menthol odour. It is a natural compound that originates from a large number of different plants species.

Decalin

Decalin (Decahydronaphthalene) is a bicyclic organic compound. It is used as an industrial solvent, primarily for many resins and in paints lacquers and polishing substances. In 2006 there were 25 tonnes registered in 5 products in Sweden. The product categories were not given in the product registry, but a internet search showed that the substances is for example used in hobby paints sold in Sweden. It has to be noted that the product registry does not cover substances that are imported as an integral part of a product sold in Sweden. Consequently, the product registry will tend to underestimate the amount of a substance that occurs in Sweden.

Decalin was found in a stormwater drainage ditch that dewaters a large industrial area with mostly small scale industries and workshops. This agrees with a possible use of the substance in paints and as a solvent. Decalin has not been included in screening studies previously, and it may be warranted to evaluate as a possible future screening substance.

Alpha-pinene

Alpha-pinene is a terpene class containing a reactive four-membered ring. It is mainly found in many species of coniferous trees, most notably pine, and in herbs such as rosemary.

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. Stormwater and stormwater sediments is a very complicated matrix whose organic composition is usually dominated by oil and fuel related substances (Duranda et al. 2004). This is

evidenced by the fact that the aliphatic C16 – C35 fraction was very common in stormwater sediment and in water samples (Table 3.11 - Table 3.12). 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 in the sample creates a so called oil peak that tends to dominate and hide the presence of other compounds. A typical such peak can be found for Örjadiket (see page 10 in appendix 2 – Örjadiket, Landskrona). 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 to 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 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)..

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).

5 Conclusions and recommendations

The study has shown that fuel and petroleum related compounds dominate in stormwater runoff and stormwater sediments. There is a possibility that organic substances has not been identified due to the complex sample matrix in combination with the analytical techniques used. A follow up screening study could remedy this. Such a screening 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.

A few organic substances were identified in the present study that could be of interest for further screening studies:

- Benzyl-Butyl-phthalate was found in urban storm water. Since it has not previously been investigated in other matrixes than air, it may be of interest to include this substance in further screening studies.

- Dimethylsulfide (DMS) was found in stormwater sediments from the bottom of a stormwater well in the road at a residential area in Malmö. It is a compound that has been found in few site remediation projects in Sweden (Swedish - "efterbehandlingsprojekt"), but it has not been included in screening studies previously. Consequently, it may be warranted to evaluate DMS as a possible screening substance. On the other hand, this compound is produced naturally by phytoplankton in large amounts.

- Decalin was found in a stormwater drainage ditch that dewaters a large industrial area with mostly small scale industries and workshops. The substance is used in paints and as a solvent, and has not been included in screening studies previously. It may be warranted to evaluate decalin as a possible screening substance.

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