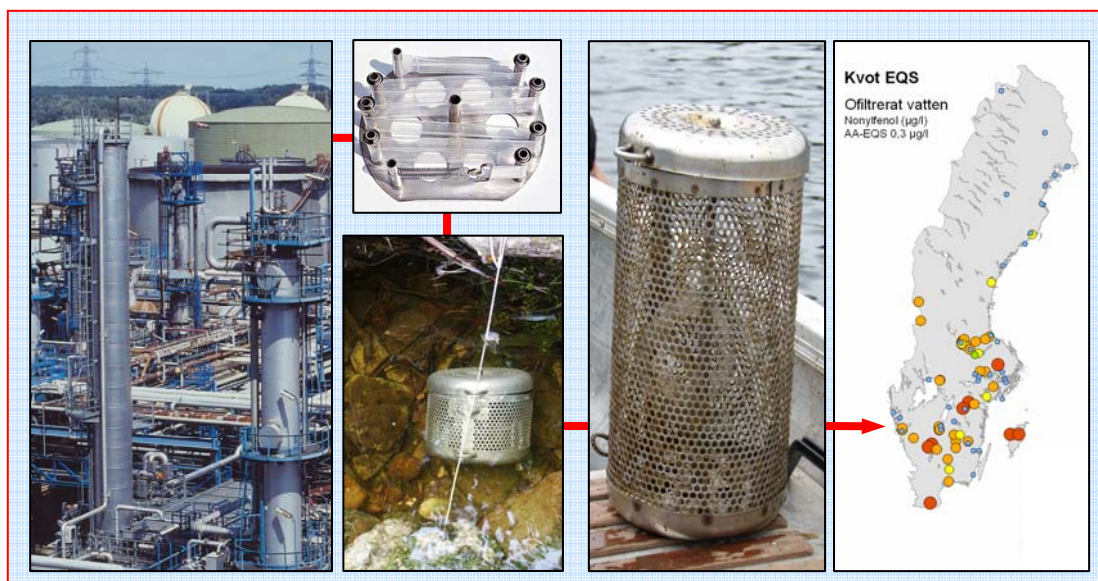


SWECO VIAK Screening Report 2007:1

# Nationwide screening of WFD priority substances

Client

Swedish Environmental Protection Agency



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# Sammanfattning

## Bakgrund och metodik

Inom screeningprogrammet 2006 har SWECO VIAK på uppdrag av Naturvårdsverket utfört mätningar för att kartlägga förekomsten av vattendirektivets prioriterade ämnen i limniska och kustnära ytvatten i Sverige. Syftena med studien var:

- att bedöma vilka av de prioriterade ämnena som är mest förekommande i Sverige samt huruvida det förekommer regionala skillnader i halterna av dessa
- att utvärdera användandet av passiva provtagare vid mätningar av prioriterade ämnen
- att undersöka vilka som är de viktigaste källorna till prioriterade ämnen i Sverige

Screeningen omfattade provtagning på 92 platser över hela Sverige. De flesta provpunkter var påverkade av någon av följande utsläppskällor: 1) punktkällor inklusive industrier, 2) diffusa källor inklusive dagvatten, 3) avfallsanläggningar 4) reningsverk. Ett flertal vattenprov togs också i opåverkade bakgrundsområden.

Kemiska analyser utfördes både på ofiltrerat och filtrerat (45 µm) vatten. Dessutom användes passiva provtagare med vars hjälp månadsmedelhalten i vatten kunde bestämmas.

Tre typer av passiva provtagare användes i projektet: 1) semipermeabla membran provtagare (SPMD) för provtagning av opolära organiska ämnen, 2) "Diffusive Gradient in Thin Film" (DGT) för metaller och 3) "Polar Organic Chemical Integrative Sampler" (POCIS) för polära/hydrofila organiska ämnen. I filtrerade och ofiltrerade vattenprover analyserades alla 33 prioriterade ämnen tillsammans med fysikaliska/kemiska parametrar. I de passiva provtagarna analyserades 23 prioriterade ämnen.

## Resultat

Många av de prioriterade ämnena förekom under bestämningsgränsen eller i låga halter över hela Sverige utan något urskiljbart geografiskt mönster.

Följande ämnen förekom i låga koncentrationer eller under bestämningsgränsen över hela Sverige men sporadiskt även i höga koncentrationer nära eller över EQS-värdet: *Kvicksilver, endosulfan, vissa PAH ämnen, tributyltenn, hexaklorbutadiene samt oktyl-fenol.*

Följande prioriterade ämnen förekom i låga koncentrationer i norra Sverige men mer frekvent i högre koncentrationer i södra Sverige:

*Bly, nickel, kvicksilver, endosulfan, pentabrominerade difenyletrar (pBDE) och nonyl-fenol.*

Kadmium förekom i förhöjda koncentrationer över hela Sverige utan något tydligt geografiskt mönster.

Vattendistriktet var påverkade av prioriterade ämnen enligt följande ordning: Västerhavet > Södra Östersjön > Norra Östersjön > Bottenhavet > Bottenviken.

Följande ämnen bedöms utifrån denna studie vara de prioriterade ämnen som bör uppmärksammas mest:

**4-Nonylfenol** förekom frekvent i nivåer över EQS-värdet. AA-EQS-värdet överskreds i 12 % av provpunkterna och förhöjda halter hittades i 50 % av provpunkterna. Det geografiska mönstret för nonylfenol med låga halter i norra Sverige och högre i landets södra delar indikerar att nonylfenolhalten följer befolkningstätheten och de urbana områdenas utbredning i Sverige.

**Kadmium**-halterna var förhöjda i många prover utan att överskrida EQS-värdet lika många gånger som för nonylfenol. AA-EQS-värdet överskreds i ungefär 5 % av provpunkterna medan förhöjda halter påvisades i 57 %. Det kunde inte påvisas några tydliga geografiska skillnader i frekvensen av förhöjda halter. Detta tyder på att kadmium är ett allmänt förekommande ämne som härstammar från olika källor.

**Tributyltenn (TBT)**. För TBT var bestämningsgränsen mellan 5 och 10 gånger högre än AA-EQS värdet vilket har gjort tolkningen av resultaten osäker. Om en signifikant sänkning skulle kunna göras av bestämningsgränsen är det inte omöjligt att fler provpunkter skulle visa sig ha TBT-halter över EQS värdet. Ytterligare nationell screening av TBT med mer utvecklade analytiska metoder kan därför vara befogat.

Även andra ämnen förekom sporadiskt nära EQS-värdet. Mest framträdande av dessa var bly och nickel.

När det gäller de passiva provtagarna bedömdes DGT vara potentiellt lämplig för provtagning av de prioriterade metallerna. Användandet SPMD och POCIS överensstämmer för närvarande inte med riktlinjerna för provtagning i vattendirektivet men kan initialt användas som hjälpmedel för att välja vilka prioriterade ämnen som skall analyseras i övervakningsprogram.

Framtida studier med fokus på att hitta orsakerna till de förhöjda nivåerna av prioriterade ämnen samt åtgärder för att minska deras emissioner vore av intresse. Det finns också ett behov att ta fram och implementera analytiska metoder som ger en bestämningsgräns för TBT som är lägre än AA-EQS värdet och därefter genomföra vidare screening av TBT. Framtida screening av vattendirektivsämnen bör förslagsvis fokusera mer på provtagning nära utsläppskällor som inte ingick i denna studie, tätare lokala provtagningar i påverkade vattensystem, ökad provtagning nära möjliga föroreningskällor och fler provtagningar i bakgrundsområden för att avgöra huruvida olika prioriterade ämnen härrör från lokala/regionala källor eller från global transport.

# Summary

## Background and methods

Within the screening program of 2006 SWEKO VIAK has had the assignment from the Swedish Environmental Protection Agency to measure the occurrence of Water Framework Directive Priority Substances in limnic and coastal surface waters of Sweden. The main objectives were to:

- assess which of the priority substances that are of the highest concern in Sweden and whether there are regional differences in the levels of these substances
- assess the practicality of using passive sampling for monitoring of priority substances
- assess which are the most important sources of priority substances.

The screening involved sampling all across Sweden at 92 sampling points. Most of the Limnic and marine/coastal sampling stations were influenced by any of the following discharge sources: 1) industrial plants and other point sources, 2) urban runoff and other diffuse sources, 3) landfills, 4) sewage treatment plants. A number of sampling points in unaffected background areas were also used.

In order to assess whether priority substances were mainly associated with particles and whether passive sampling could be an appropriate method for sampling of priority substances unfiltered water, filtered water (45 µm) and passive samplers were used.

Three types of passive samplers were used: 1) Semi Permeable Membrane Devices (SPMD) for sampling of non-polar organic compounds, 2) Diffusive Gradient in Thin film (DGT) for sampling metals and 3) Polar Organic Chemical Integrative Sampler (POCIS) for sampling of polar/hydrophilic organic compounds.

In filtered and unfiltered water all 33 priority substances were analysed as was physio-chemical parameters. 23 priority substances were collected and analysed in the passive samplers.

## Results

The results showed that many priority substances consistently occurred below the limit of quantification (LOQ) or at low levels all over Sweden with no discernible geographical difference.

One subset of priority substances had generally low concentration all over Sweden with sporadically high concentrations even close to or above EQS:

*Mercury, endosulfane, some PAHs, Trichloromethane, tributyltin, hexachlorobutadiene, pentabrominated diphenyl ether and oktylphenol*

Some priority substances occurred at low levels in the Northern part of Sweden while occurring more frequently at higher concentrations in Southern Sweden:

*Lead, nickel, mercury, endosulfane, trichloromethane, hexachlorobutadiene, pentabrominated diphenyl ether and nonylphenol*

Finally, *cadmium* occurred at elevated concentrations all over Sweden without any apparent geographical pattern.

The most affected national water districts were in order of priority substance influence: Västerhavet > Södra Östersjön > Norre östersjön > Bottenhavet > Bottenviken.

The following substances were identified as of being of primary concern in Sweden with regards to the water framework directive:

**4-Nonylphenol** frequently occurred at levels above the EQS value. The AA-EQS value was exceeded in 12% of the sampled waters while elevated levels was found in 50% of the sampled waters. The geographical patterns of nonylphenol with low levels in northern Sweden and high levels in southern Sweden indicated that nonylphenol levels coincide with population density and urban areas in Sweden.

**Cadmium** levels were often elevated although not exceeding the EQS value as often as nonylphenol. The AA-EQS was exceeded in ca. 5% of the surface waters while elevated levels occurred in 57% of the sampled waters. There were no discernible geographic differences in the frequency of elevated levels indicating that cadmium is an omnipresent pollutant originating from different sources.

**Tributyltin (TBT).** Since the LOQ of TBT was approximately 5 – 10 times higher than the AA-EQS the interpretations of the results were uncertain. If the LOQ could be lowered significantly it can not be excluded that more sampling stations with TBT levels above the EQS would be discovered. Further national screening of TBT in surface waters using more developed analytical techniques may thus be warranted.

Other substances occasionally exceeded the EQS value or were close to the EQS value while not exceeding it. Most noticeable of these were **lead** and **nickel**.

The DGT was tentatively deemed to be suitable for monitoring of priority metals. The usage of SPMD and POCIS does not concur with the directions in water framework directive but could possibly be of help when choosing priority substances to include in monitoring programs.

Future studies focusing on the reason for the elevated levels of priority substances and possible measures to reduce their emissions are of importance. There is also a need to implement analytical methods for TBT that has a LOQ < EQS and to re-screen TBT. Future screening of WFD substances should perhaps focus on discharges not to a large degree included in this investigation, a higher density of local sampling points in affected water systems, increased sampling closer to possible sources and more sampling at background stations to delineate whether different priority substances originates from local/regional or national/international sources.

# 1 Introduction

## 1.1 Background

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.).

To maximize the information gained from the screening program measurements are made in many matrices at many sites, but with few samples per site. The Swedish EPA is responsible for the screening at the national level and selects the chemicals that are to be included. County Administrative Board's choose to participate in regional screening studies whose function is to increase the density of sampling point at a regional level. Consequently, the Administrative Board in each county select regionally important sample points.

Within the screening program of 2006 SWECO VIAK has had the assignment from the Swedish Environmental Protection Agency to measure the occurrence of Water Framework Directive Priority Substances in limnic and coastal surface waters of Sweden.

## 1.2 Objectives

Given the large scope of the study, and in order to facilitate data evaluation, a number of clearly stated objectives were decided upon:

- To assess whether priority substances are present in Swedish surface waters.
- To assess which of the priority substances that constitutes the most significant problems (i.e. those substances which are found at levels close to their EQS values)
- To assess whether there are regional differences with regard to the levels of priority substances found
- To assess whether passive sampling of priority substances is an appropriate technology
- To assess which are the most important sources (i.e. point discharge, diffuse discharge and/or the type of activity emitting priority substances) of priority substances.



## 2 Water Framework Directive and Priority Substances

The Water Framework Directive (WFD) is a European Union directive which commits member states to making all water bodies (surface, estuarine and groundwater) of good qualitative and quantitative status by 2015 (Annex X, decision 2455/2001/EC). Within the directive 33<sup>1</sup> substances have been selected on the basis of their risk to the aquatic environment, or to human health via the aquatic environment. Note that they only apply to surface water and not to ground water. 13 of the priority substances are classified as hazardous priority substances, which mean that all emission and release of those must cease within the next 20 years.

For each of these substances, an environmental quality standard (EQS) has been established. The EQS are limits to the degree of concentration, i.e. the quantity in water of the substances concerned must not exceed certain thresholds. The proposal sets out two types of standard:

1. AA-EQS - the average quantity of the substance concerned calculated over a one-year period. The purpose of this standard is to ensure the long-term quality of the aquatic environment;
2. MAC-EQS - the maximum allowable concentration of the substance measured. The purpose of this second standard is to limit peaks of pollution.

The proposed quality standards are differentiated for inland surface waters and transitional, coastal and territorial waters.

Member States must ensure compliance with these standards. They must also verify that the concentrations of substances concerned do not increase in sediments or in organisms living in surface water.

The list of priority substances is presented in Table 2.1, together with some short information on their usage, regulation, and chemical properties. (Loh and Ovuka 2005 and Økland et al. 2005).

It should be noted that the list of priority substances and their associated EQS values is not static and changes and/or amendments are at present being discussed. This also means the EQS values have not yet been incorporated into national law.

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<sup>1</sup> There are at present 33 priority substances for surface water included in the water framework directive. Of these, PAHs is actually a substance group with 5 individual PAHs included in the directive. This gives a total of 37 substances to be measured. There are however only 35 EQS AA-EQS values because the concentration of the PAHs benzo(b)fluoranthene and benzo(k)fluoranthene are summed and compared to one EQS value. This is also the case for the sum of benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene.



CAS-no	Name	Uses or emission sources and national regulation	AA-EQS (µg/l)	Log K <sub>ow</sub>	Passive sample	Water solubility (mg/l)
15972-60-8	Atrachlor	Pesticide. Not approved use since 1978	0.3	3.7	POCIS	18.07 (25 °C)
120-12-7	Anthracene	Incomplete combustion.	0.1	4.20 - 4.63	SPMD	0.032 - 0.086 (20 °C)
1912-24-9	Atrazine	Pesticide. Banned in 1989	0.6	2.2 - 2.5	POCIS	33 - 70
71-43-2	Benzene	Incomplete combustion, component in petroleum products. Restricted use	10	2.13	SPMD	1800 (25 °C)
32534-81-9	Pentabrominated diphenyl ethers, PBDE #47, 99, 100	Flame retardant. Phase-out banned from Aug 2004	0.0005	5.03 - 8.09	SPMD	< 0.01 (20C)
7400-43-9	Cadmium, Cd	Numerous. Restricted use	0.08-0.25	-	DGT	Insoluble, some compounds are soluble
85535-84-8	C10-13-chloroalkanes, SCCA	Lubricant, cutting fluid. Phase-out	0.4	4.39 - 8.69	POCIS	Practically insoluble
470-90-6	Chlorfenvinphos	Pesticide. No approved use since 2001	0.1	4.15	POCIS	3.022 (25 °C)
2921-88-2	Chlorpyrifos	Pesticide. Restricted use	0.03	4.66	SPMD	0.357 (25 °C)
107-06-2	1,2-Dichloroethane	Solvent. Restricted use	10	1.48		8690
1975-09-02	Dichloromethane	Solvent in medical industry. Banned 1993 in consumer products. 1996 for prod. use	20	1.3 (calculated)		13700 (20 °C)
111-81-7	Di(2-ethylhexyl)phthalate, DEHP	Plasticiser. 1999: restricted children's toys	1.3	4.88 - 7.6		0.3 - 0.4, lower in salt water. DEHP will adsorb to particles in water (especially salt water), even though solubility is low.
330-54-1	Duron	Pesticide. Banned in 1993	0.2	2.67	POCIS	36.4 (25 °C)
1115-29-7, 959-98-8	Endosulfan	Pesticide. Banned in 1996	0.005	3.5	SPMD	0.32 - 0.52
206-44-0	Fluoranthene	Incomplete combustion.	0.1	4.7	SPMD	0.265 (20 °C)
1118-74-1	Hexachlorobenzene, HCB	Biocide: unintended formation. No intended use since 1980	0.01	3.03 - 6.92	SPMD	0.005 - 0.006
87-86-3	Hexachlorobutadiene, HCBD	Industrial chemical by product from chlorinated solvent production. No restriction	0.1	3.74 - 4.78		2 - 4
608-73-1	Hexachlorocyclohexanes, HCHs	Pesticide. Banned	0.02	3.81/3.78/4.14*	SPMD	2 (28 °C)/0.2 (25 °C)/31.4 (25 °C)*
34123-59-6	Isoproturon	Pesticide. Restricted use	0.3	2.84		143.8
7439-92-1	Lead, Pb	Numerous. Phase-out	7.2	-	DGT	Insoluble, some compounds may be soluble
7439-97-6	Mercury, Hg	Numerous. Phase-out	0.05	-		Insoluble to 0.0639
91-20-3	Naphthalene	Incomplete combustion	2.4	3.01 - 3.7	SPMD	30 (20 °C)
7440-02-0	Nickel, Ni	Numerous	20	-	DGT	Insoluble (some compounds are soluble)
25154-52-3, 104-40-5	Nonylphenol, 4-para-nonylphenol	Industrial chemical: forms through degradation of NP-ethoxylates. Phase-out	0.3	4.2 - 4.7		3 - 11 (pH dependent)
1806-26-4, 140-66-9	Octylphenol, 4-tert-octylphenol	Industrial chemical: forms through degradation of OP-ethoxylates. No restriction	0.1	5.28 (4-ter)		5 (25 °C)
608-93-5	Pentachlorobenzene	Unknown uses	0.007	4.8 - 5.18	SPMD	0.56 (20 °C)
87-86-5	Pentachlorophenol, PCP	Pesticide. Banned in 1978	0.4	5.12	SPMD	14
50-32-8	Benzo(a)pyrene	Incomplete combustion	0.05		SPMD	0.0016 - 0.0038 (25 °C)
205-99-2	Benzo(b)fluoranthene, Benzo(k)fluoranthene	Incomplete combustion	0.03		SPMD	
191-24-2 193-39-5	Benzo(g,h,i)perylene, Indeno(1,2,3-cd)pyrene	Incomplete combustion	0.002		SPMD	
122-34-9	Simazine	Pesticide. Banned in 1995	1	2.4	POCIS	5 - 6.2
688-73-3	Tributyltin, TBT	Antifoulant, preservative: stabiliser in plastics. 1993: all ships under 25 m. no new use after 2003	0.0002	3.19 - 3.84		0.1%
12002-48-1	Trichlorobenzene	Industrial chemical. No intended use since 1998	0.4	3.93 - 4.2	SPMD	48 - 100
67-66-3	Trichloromethane (chloroform)	Solvent. Restricted use	2.5	1.97		7500 - 9300
1582-09-8	Trifluralin	Pesticide. Banned in 1990	0.03	5.31	SPMD	< 1.0/0.184 (20 °C)

*Table 2.1 Uses, restrictions, K<sub>ow</sub> and water solubility of WFD priority substances.*

## 3 Methods

### 3.1 Study areas

The screening involved sampling all across Sweden at 92 sampling points. In general regional and local authorities chose the sampling point given regional priorities, strategic considerations (section 3.1.1), and taking into account the purpose of the screening (section 1.2).

#### 3.1.1 Strategy

Based on the stated objectives, sampling stations impinged by anthropogenic activities should preferably be influenced by any of the following discharge sources:

- point sources
- diffuse sources
- industrial plants
- urban run off water
- landfills
- sewage treatment

Furthermore both limnic and marine/coastal sampling points should, if possible, be included. Because of the higher cost associated with marine sampling only a few true coastal sampling points could be chosen.

For comparative reasons and in order to assess whether long range atmospheric transport was of importance sampling points in unaffected background areas were also necessary.

Based on these considerations, regional and local authorities choose a number of sampling points, whose characteristics together with information on the type of sampling is presented in Table 3.1 and table 3.2. Further detailed information regarding each sampling station is given in appendix 1 (in Swedish).

*Table 3.1 Overview of sampling stations divided by type of sampling and type of discharge that may affect the sampling station. Some sampling station may receive discharge from both diffuse sources and point sources. Sampling stations in major rivers that are placed at the outflow to the sea are considered to be both limnic and coastal sampling points.*

<b>Limnic (freshwater) sampling stations</b>			
<i>Sampling parameter</i>	<i>Unaffected (back-ground)</i>	<i>discharge from diffuse sources</i>	<i>Discharge from point sources</i>
Unfiltered water	5	45	46
Filtered water	2	14	11
DGT	5	41	34
POCIS	5	44	40
SPMD	6	41	40
Physiochemical	3	44	36

<b>Marine / Coastal sampling stations</b>			
Unfiltered water	2	5	5
Filtered water	2	5	4
DGT	1	8	8
POCIS	2	8	7
SPMD	2	8	8
Physiochemical	2	8	8

*Table 3.2 Overview of sampling stations divided by the type of discharge that may affect the sampling stations. Some sampling stations may receive discharge from several of the listed sources.*

<i>Operation/activity that may influence the sampling station</i>	<i>Number of sampling stations</i>
Unaffected	9
Discharge from diffuse sources	60
Discharge from point sources	63
Run off water	64
Agricultural	15
Forestry	6
Landfills	9
Mining	2
Pulp and paper	8
Chemical plants	2
Metals industry	9
Saw mills	3
Sewage treatment	22
Mixed industry, sewage treatment, etc..	39

### 3.1.2 Locations

Information regarding each sampling location is given in appendix 1 (in Swedish). This includes

- Geographical information (including maps)
- Motivation for choice of sampling point (including possible discharge sources reaching the sampling point)
- WFD priority substances expected
- Results from earlier monitoring

An overview of the sampling stations in Sweden is presented in Figure 3.1. As can be seen, there is a higher concentration of sampling points in Southern Sweden. In the northern part of Sweden, most sampling points are situated along the coast where the large rivers flow out to the Baltic Sea. In general, the sampling density coincides with the population density, the only exception being the lack of sampling points in the southernmost part of Sweden.

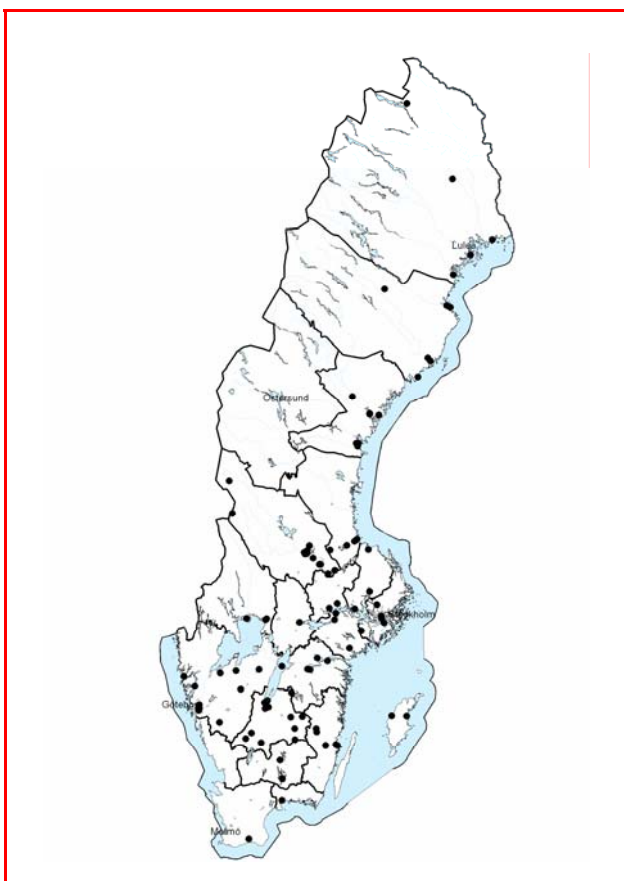


Figure 3.1 Location of sampling points for WFD priority substances in Sweden.

Some examples of sampling locations are given in Figure 3.2.



*Figure 3.2 Some examples of sampling sites of WFD priority substances. Upper left: Krageholmssjön, the unaffected background lake in southern Sweden. Upper right: Gothemsån a locality on Gotland, the island/county on the East Coast of Sweden. Lower left: A sampling point in central Stockholm with the city hall in the background. Lower right, a coastal sampling point in Northern Sweden outside a major pulp and paper industry.*

## 3.2 Sampling

### 3.2.1 Sampled fractions

In order to assess whether priority substances were mainly associated with particles and whether passive sampling could be an appropriate method for sampling of priority substances three matrices were sampled and analysed:

1. unfiltered water
2. water filtered through a 45 µm filter
3. passive samplers

Using this approach, three different substance fractions were sampled in the water (Figure 3.3); (1) The unfiltered water contains free substances and all those associated with particles and colloidal particles; (2) The filtrated water contains free substances and all those associated with colloidal particles; (3) Only free unassociated substances will pass through the passive sampling membrane.

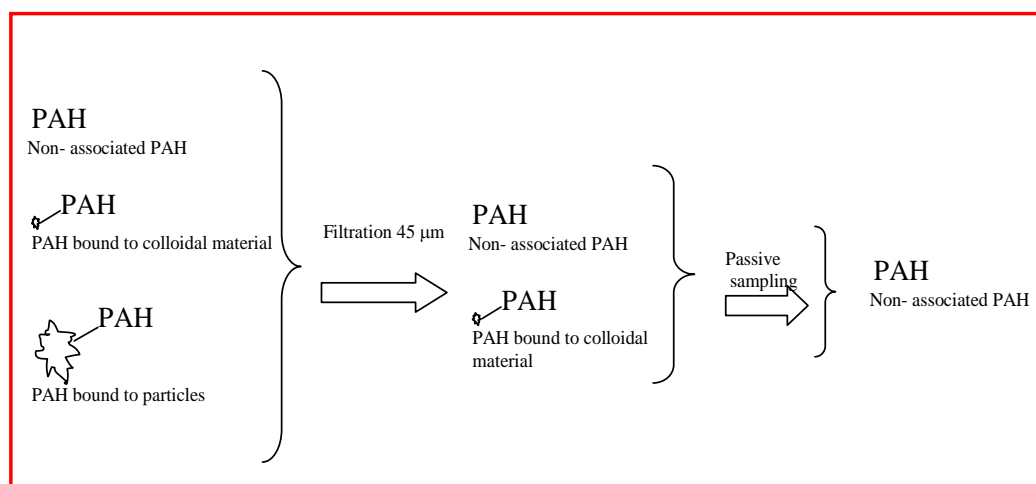


Figure 3.3 Schematic representation of which substance fraction that is sampled. Here exemplified by PAHs, but the principle is valid for all substances sampled.

### 3.2.2 Passive sampling

Passive sampling offers several advantages over conventional sampling. The sampler is in place for a longer period of time (often days or weeks), accumulating the analytes. The result is an average of the concentration during this time, which eliminates the risk of non-detection of, for example, occasional peaks in emitted pollutants. It is also the case that to a large degree only the bioavailable fraction, i.e. the part that can be taken up by organisms, is sampled in a passive sampler.

Three types of passive samplers were used in the present study, SPMD, DGT and POCIS.

#### 3.2.2.1 PASSIVE SAMPLING USING SPMD

Semi Permeable Membrane Devices (SPMD) is a passive sampling method for non-polar organic compounds such as PAH, PCB, and dioxins. The sampling method is based on a membrane that contains a lipid which easily dissolves hydrophobic substances (i.e. substances that dissolve in an organic phase like fat but only to a very small degree in water).

The length of the sampling period is variable, but is often about one month. During this time organic pollutants in dissolved or gas phase diffuse through the membrane and accumulate in the lipid. This uptake mimics the accumulation of organic pollutants in, for example, fish. The organic compounds are then extracted from the membrane for subsequent chemical analysis.

From the analytical result, concentrations in the sampled medium can be calculated. Concentrations of lipid-soluble substances in water are often so low that direct chemical analysis is difficult, but the passive sampler provides substantial preconcentration and thus enables more reliable analyses. Due to the large capacity of the lipid, a relatively long time (often >1 month) will elapse before the sampler is saturated, i.e. before a state of equilibrium has been attained between sampler and water.

The lipid filled membrane is mounted in a so-called spider carrier (Figure 3.4). The sampler consists of a stainless steel canister (Figure 3.8) that holds from one to five spider carriers with membranes.



Figure 3.4 Spider carrier with mounted lipid filled membrane for SPMD sampling.



### 3.2.2.2 PASSIVE SAMPLING USING DGT

Diffusive Gradient in Thin film (DGT) passive samplers are used to sample metals in the water. The simple plastic sampler used (Figure 3.5) contains a layer of binding agent (resin) impregnated in a hydrogel to accumulate the solutes. The binding-layer is overlain by a diffusive layer of hydrogel and a filter. Metal ions in the water diffuse through the filter and the gel, and finally accumulate in the ion exchange resin.

The longer the sampling time, the larger the amount of ions accumulated. In uncontaminated water, the equipment can be left in place for several months. The ions are then eluted from the resin with an acid, and can be determined by ICP-AES or ICP-MS. Temperature is an important parameter controlling the rate of diffusion. Since diffusion controls the uptake in DTG samplers (see equation 3.5) it is often necessary to measure the temperature during deployment and uptake, especially if large variations in temperature is expected during the deployment period. If the water temperature is known, the concentration of each metal in the water can then be easily calculated. Since diffusion does not control uptake in SPMD and POCIS samplers they will not be affected by temperature.

When sampling metals using DGT, particle-bound and strongly complexed metals will be excluded in a manner which corresponds to their non-availability for biota. Consequently DGT is not directly comparable to either total or dissolved concentrations in ordinary water samples (Figure 3.3).

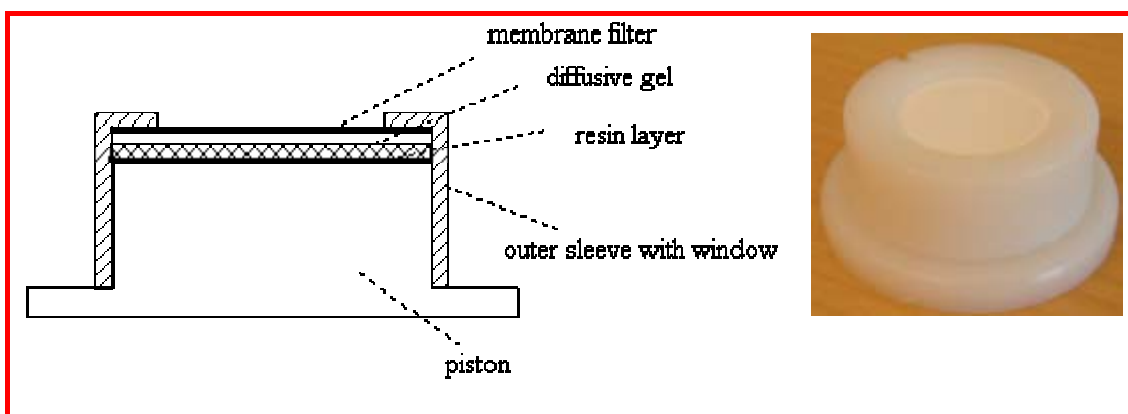


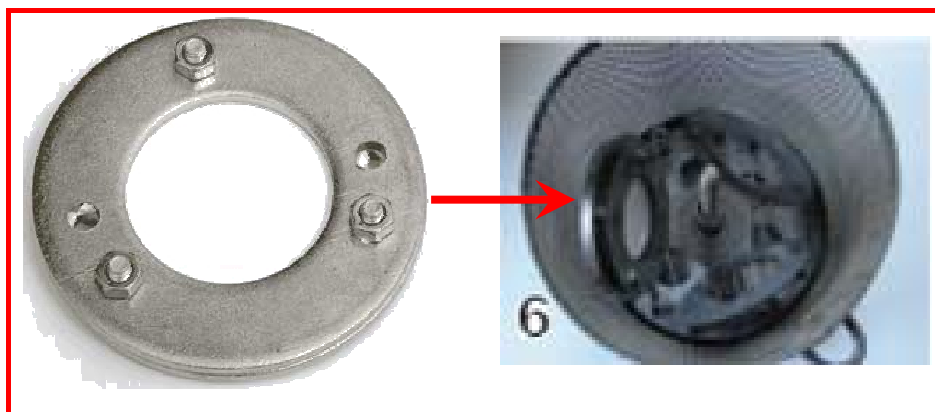
Figure 3.5 Cross section of a DGT passive sampler and a picture of the assembled unit.

### 3.2.2.3 PASSIVE SAMPLING USING POCIS

Polar Organic Chemical Integrative Sampler (POCIS) is a passive sampling device for polar organic compounds in water. Many hydrophilic (i.e. easily dissolved in water) pesticides belong to this category.

The sampler consists of a solid sorbent (powder), enclosed between two membrane layers that are mounted in a pair of stainless steel washers (Figure 3.6). From one to

three samplers can be placed in a steel canister (Figure 3.6). Notice that the same steel canister is used for SPMD and POCIS. Polar compounds diffuse through the membranes and are accumulated by the sorbent. Following extraction, the analysis is carried out by standard methods, and the concentrations in the sampled water can be calculated.



*Figure 3.6 POCIS sampler on the left placed in a steel canister on the right.*

#### 3.2.2.4 FIELD DEPLOYMENT OF PASSIVE SAMPLER

The SPMD and POCIS samplers were placed in a perforated metal canister (Figure 3.8). If the water was deep, the metal canister was kept at the appropriate level below surface using a buoy. The DGT sampler was tied to a nylon fishing line. A typical setup is shown in Figure 3.7.

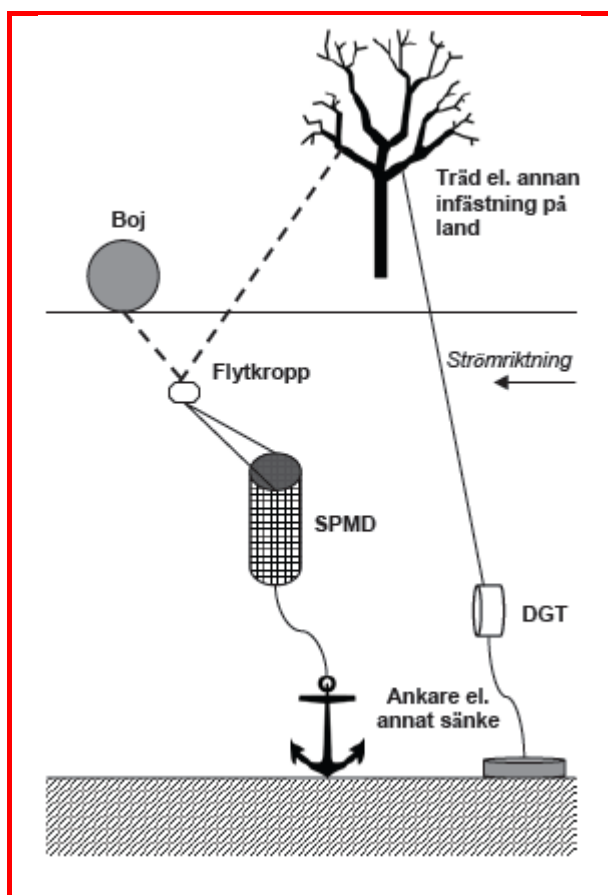


Figure 3.7 Typical deployment setup of passive samplers (in Swedish). From Lindström 2006.

The samplers were deployed for 4 – 6 weeks. The exact time was noted and used in the calculations of the water concentrations (section 3.4.2.3). The water temperature was measured at the time of deployment and when the samplers were removed. In some cases, if a major temperature difference was expected, the water temperature was measured on more occasions using a temperature logger. The water temperature was used to adjust the diffusion coefficient for metals when calculating the water concentrations (section 3.5.2)

All sampling personnel received detailed instruction that governed the deployment and removal of the passive samplers. This included:

- The deployment and removal was to be executed as fast as possible since the uptake of analytes starts immediately after the transport containers have been opened.
- Disposable gloves were to be used during deployment and removal to minimise contamination.
- For the deployment of DGTs a minimum flow rate in the surface water was recommended.

- DGTs were to be deployed upstream of the SPMD and POCIS sampler since the metal canister containing the SPMD and POCIS could otherwise influence the DGT.
- If trees or other objects did not shadow the sampling point, the samplers were to be deployed a minimum of 50 cm below the water surface to minimize photo-oxidation of accumulated analytes.



*Figure 3.8 Upper left: Metal canister containing the POCIS and SPMD sampler. Upper right: Deployed metal canister. Middle left: Buoy keeping the deployed metal canister floating below the water surface with a floating pamphlet describing the sampling and why it should not be removed. Middle right: Buoy keeping the deployed metal canister floating below the water surface. Lower: SPMD membrane removed from spindle holder after the sampling period and being transferred to a clean transport container.*

- If soft sediments were present at the site, the samplers were to be deployed a minimum of 50 cm above the sediment surface to minimize the influence of contaminants in the sediment.

Some pictures from the deployment and uptake of passive samplers are given in Figure 3.8.

### 3.2.3 Water sampling

Water sampling commenced when the passive samplers were initially deployed in the field. For analysis of priority substances and additional substances, 6 litres of water was sampled from each site for filtered and unfiltered water respectively. The water was sampled into acid rinsed and pre combusted 1 l glass flasks and were immediately transported to the laboratory where they were kept refrigerated (approx 5 – 8 °C). In addition water was also sampled into ½ litre plastic bottles for analysis of physico-chemical parameters (section 3.3).

## 3.3 Measured parameters

### 3.3.1 Water

In filtered and unfiltered water all the priority substances in Table 2.1 was analysed. In addition, the following substances were also analysed:

- PAH substances; Besides the priority PAHs (see Table 2.1) all other 16 EPA PAHs were analysed
- Tin organic compounds; Besides tributyltin nine other alkylated tin compounds were analysed
- Polybrominated flame retardants; Besides pentabromodiphenylether (pBDE), all other common polybrominated diphenylethers (PBDEs) were also analysed
- As a general indicator of anthropogenic influence, 7 PCBs were also analysed.

However, the additional substances were not included in the evaluation and analysis of the results.

To support the interpretation of data and explain observed differences between unfiltered water and passive samplers some physiochemical parameters were also analysed; The colloidal particles referred to in Figure 3.3 consists mainly of dissolved organic carbon (DOC) which is an important carrier of many substances in water (Chin et al. 1997). Substances bound to DOC will not be taken up in the passive samplers (Figure 3.3) and DOC was therefore measured in most water samples. The ultraviolet absorption at 245 nm (ABS 245) of a water sample is a good indicator of both the DOC content (Chin et al. 1997) and of the DOC aromaticity (i.e. the occurrence of aromatic rings). It is believed that ABS 245 correlates well with the tendency of substances to

associate to the DOC molecules (Chin et al. 1997) and was therefore measured in most water samples. pH was also measured as part of the physiochemical package.

### 3.3.2 Passive samplers

All priority substances could not be collected in the passive samplers because of a lack of experimentally derived uptake coefficients that could be used to calculate water concentrations. The substances collected and analyzed in the passive samplers are given in Table 2.1.

At some sampling stations dioxins and/or a suite of 10 additional metals were sampled in the SPMD and DGT respectively. These results are not included in the present study.

## 3.4 Analytical methods

### 3.4.1 Extraction and analysis

AGS Analytica AB was responsible for all analytical work both regarding the passive samplers and the water samples. All substances were extracted and analyzed according to Table 3.3.

Compound	Extraction	Derivatisa- tion	Clean up	Method	Instrument
<b>Water</b>					
Alachlor	n-hexane			Internal	GC-MS
Antracene	cyclohexane			Internal	GC-MS
Atrazin	metha- nol/ethylacetate		SPE	Internal	GC-MS
Benzene	n/a			DIN 38407-F9	HS-GC-MS
pBDE	Toluen		silica gel + alumina oxide	Internal	GC-MS
Chloroparaffins	Toluen		silica gel + alumina oxide	Internal	GC-MS
Klorfenivos	n-hexane			Internal	GC-MS
Klorpyrifos	n-hexane			Internal	GC-MS
1.2-dichloroethane	n/a			DIN EN ISO 10301 F4	HS-GC-MS
Dichloromethane	n/a			DIN EN ISO 10301 F4	HS-GC-MS
DEHP	n-hexane			Internal	GC-MS
Diuron	Acetonitrile		SPE	Internal	HPLC-DAD
Endosulfane	n-hexane			DIN 38407 F2	GC-MS
Fluorantene	cyclohexane			Internal	GC-MS
Hexachlorobenzene	cyclohexane			DIN EN ISO 6468 F1	GC-MS
Hexachlorobutadiene	n/a			Internal	HS-GC-MS
Hexachlorocyclohexane	n-hexane			DIN 38407 F2	GC-MS
Isoproturon	Acetonitrile		SPE	Internal	HPLC-DAD
Naphtalene	cyclohexane			Internal	GC-MS
4-n-nonylphenol	n-hexane, pH>10	MSTFA		Internal	GC-MS
4-nonylphenol	n-hexane, pH>10	MSTFA		Internal	GC-MS
4-n-oktylphenol	n-hexane, pH>10	MSTFA		Internal	GC-MS

4-t-oktylphenol	n-hexane, pH>10	MSTFA		Internal	GC-MS
Pentachlorobenzene	cyclohexane			DIN EN ISO 6468 F1	GC-MS
Pentachlorophenol	tetrahydrofurane, pH=2	MSTFA	SPE	Macherey-Nagel 1993-11	GC-MS
PAH	cyclohexane			Internal	GC-MS
Simazin	methanol/ethylacetate		SPE	Internal	GC-MS
Tributyltin	EtOH / Na-DDTC, hexane	NaBEt <sub>4</sub>	aluminia-oxide	Internal	GC-AED
Trichlorobenzenes	cyclohexane			DIN EN ISO 6468 F1	GC-MS
Trichloromethane	n/a			DIN EN ISO 10301 F4	HS-GC-MS
Trifluralin	n-hexane				GC-MS
Metals	HNO <sub>3</sub>			EPA 200.7 + 200.8	ICP-SFMS
PCB	cyclohexane			EN ISO 6468 F1	GC-MS
<b>SPMD</b>					
PAH	n-hexane		silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS
pBDE	n-hexane		silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS
OCP	n-hexane		silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS
PCB	n-hexane		silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS
Chlorobenzenes	n-hexane		silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS
Chlorophenols	n-hexane	MSTFA	silicagel/H <sub>2</sub> SO <sub>4</sub>	Internal	GC-MS-MS
<b>DGT</b>					
Metaller	HNO <sub>3</sub>			EPA 200.7 + 200.8	ICP-SFMS
<b>POCIS</b>					
Alachlor	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD
Atrazine	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD
Klorfenivos	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD
Isoproturon	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD
Diuron	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD
Simazin	methanol/toluene/dichloromethane (10:10:80)			Alvarez et al*	HPLC-DAD

\* Environmental Toxicology and Chemistry Vol 23 1640-1648 2004

Table 3.3 Analytical methods for extraction and analysis of WFD priority substances.



### 3.4.2 Quality assurance

#### 3.4.2.1 GENERAL

A blank sample that followed the entire analytical process was added to every series of samples. To control the extraction efficiency, internal standards were added prior to sample extraction. Certified reference materials (CRM) were used when commercially available. When such standards were unavailable synthetic standards were used. To control the reproducibility within the laboratory, one sample in every batch was run in duplicate. The entire analytical procedure followed EN ISO/IEC 17025.

#### 3.4.2.2 INTERNAL STANDARDS IN PASSIVE SAMPLERS

In order to assess an analyte's in situ SPMD-water exchange kinetics, performance compounds (PRCs) were added to the SPMD triolein (Huckins m.fl 2006). The use of the PRC method accounts for the effects of membrane biofouling, flow-turbulence, and temperature differences.

To use this approach PRCs that do not occur in the environment has to be used. In this study PCB congeners 3, 8, 37, 54, octachloronaphthalene, deuterium (D10) labelled acenaphthene, fluorene and phenanthrene and D12 chrysene was used.

PRC dissipation is governed by (Huckins m.fl 2006):

$$N = N_0 \exp(-k_e t) \quad (3.1)$$

where  $N_0$  is the amount present at  $t=0$ . If  $N$  and  $N_0$  are measured, the PRC release rate constant ( $k_e$ ) can be estimated using

$$k_e = -(\ln(N/N_0))/t \quad (3.2)$$

When the  $k_e$  and SPMD-water partition coefficient of the PRC are known, its  $R_s$  (sampling rate) can be calculated. More precisely, we assume that the PRC  $R_s$  is representative of the in situ sampling rates of target compounds with similar physicochemical properties as the PRC.

#### 3.4.2.3 QUALITY DATA CHECK OF NONYLPHENOLS

Nonylphenols were consistently quantified at higher levels (closer to their EQS values) compared to other substances. In order to confirm the reported results an additional quality check of the data was undertaken.

As a first step all raw-data, including blank values, were re-validated. No discrepancies were found during this step.

To further ascertain the reported results, some samples where sufficient sample volume remained were re-analysed. In total, 7 samples were re-analysed and all previously reported results were confirmed. The conclusion of the investigation was that the results reported were indeed correct.

## 3.5 Calculations of concentrations in water

### 3.5.1 SPMD

The calculations of water concentrations based on the analyte concentration in the passive sampler are dependent on whether the uptake is linear or whether equilibrium conditions control the uptake (Figure 3.9). If the uptake is linear the following equation applies:

$$C_W = (C_{SPMD} \cdot M_{SPMD}) / (R_s \cdot t) \quad (3.3)$$

where  $C_W$  is the analyte concentration in water (g / l),  $C_{SPMD}$  is the analyte concentration in the SPMD membrane (g / l),  $M_{SPMD}$  is the mass of the SPMD membrane,  $R_s$  is the uptake rate (l / d) and  $t$  is the sampling time in the field.  $R_s$  has been determined in the laboratory for the priority substances sampled.

If the uptake is governed by equilibrium conditions, the following equation applies:

$$C_W = C_{SPMD-E} / K_{SPMD} \quad (3.4)$$

where  $C_{SPMD-E}$  is the measured equilibrium concentration in the membrane and  $K_{SPMD}$  is the analyte equilibrium rate constant between water and the SPMD membrane.

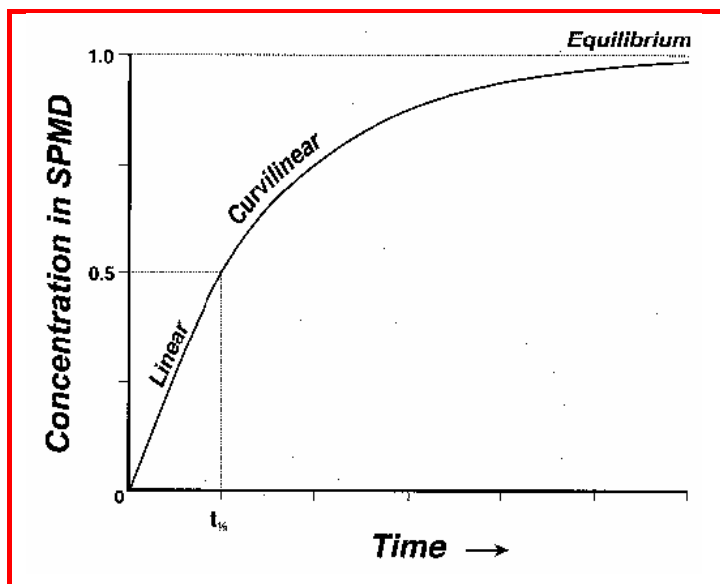


Figure 3.9 The evolvement of analyte concentration in the SPMD membrane over time.

### 3.5.2 DGT

The water concentrations of metal measured by DGT ( $C_W$ ) can be calculated using the following Equation:

$$C_w = M \cdot \Delta g / (D_t \cdot A) \quad (3.5)$$

where M is the mass of metal in the resin gel,  $\Delta g$  is the thickness of the diffusive gel plus the thickness of the filter membrane, D is the diffusion coefficient of metal in the gel, t is deployment time and A is the exposure area (of the DGT).

### 3.5.3 POCIS

The water concentration of substances taken up in the POCIS sampler is calculated by:

$$C_w = C_{POCIS} / (R_s \cdot t) \quad (3.6)$$

Where  $C_w$  is the estimated water concentration,  $C_{POCIS}$  is the total mass of the analyte in the POCIS sample extract,  $R_s$  is the sampling rate in 1/d, and t is the deployment time in days.  $R_s$  has been determined in the laboratory for the priority substances sampled.

# 4 Results

## 4.1 Summary statistics

Summary statistics on the levels of priority substances in surface water<sup>2</sup> is summarized in Table 4.1 and presented in more detail together with comparisons to the EQS values in Figure 4.2 - 4.8. Figure 4.1 explains the layout of these graphs. These graphs are intended to facilitate the understanding of the variability of the measured concentrations in relation to the AA-EQS values. For instance, it is easy to discern if the AA-EQS value is above the maximum measured concentration or whether it falls within the 95<sup>th</sup> or 75<sup>th</sup> percentile.

Note, that in the following text all values/concentrations pertaining to the passive samplers refer to the *calculated* water concentrations according to equation 3.3 – 3.6.

Table 4.2– 4.3 summarize the degree to which the priority substances exceeded the limit of quantification and the EQS values.

The yearly average EQS value (AA EQS) for inland surface water is consistently used in this report because it is more convenient to use one EQS value for comparisons and because the AA EQS value is the most conservative. Also, in most cases there is little difference between the EQS values of different water bodies. The regional county boards will however use the correct EQS values for regulatory purposes when evaluating the results.

Some priority substances consistently occur below the limit of quantification (LOQ) in both water and passive samplers. These include:

- Pesticides: alaklor, atrazine, chlorfenviphos, diuron, isoproturon, simazine
- Volatile organic substances: benzene, dichloromethane, 1,2-dichloroethane
- C10 – C13 chloroalkanes
- Di(2-ethylhexyl)-phtalate

Some substances that were not sampled in passive samplers were intermittently above LOQ in water:

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<sup>2</sup> Two sampling points from the regional county of Dalarna consisted of untreated ground water rather than surface water. The levels of WFD substances in these samples were below the detection limit except for nickel, cadmium and lead that occurred at low concentrations. These results are included in the statistics of figure 4.3 and table 4.2 – 4.3. The inclusion does however not have any discernible effects on the statistical results or the evaluation of the data.

- pentaBDE
- Octylphenol
- Tributyltin
- trichloromethane

The substances most commonly occurring above the limit of quantification were:

- metals in filtrated and non filtrated water and in DGT
- all organic priority substances sampled in SPMD
- nonylphenol in filtrated and non filtrated water

PAHs, which are among the most ubiquitous priority substances, were only detected in a few water samples. Other studies of PAHs in surface waters using methods with lower LOQs generally found PAH concentrations below the LOQs of this study (Barcelo et al. 1998, Bouloubassi and Saliot 1991, Nagy et al. 2007,). This reflects the fact that these compounds are much more likely to be found in sediments and fish (McKay et al. 2006). It is also the case that analysis of PAHs in water samples close to the detection limit (0.01 µg/l) is somewhat problematic as shown by a trans-European inter laboratory testing of WFD priority substances (Coquery et al. 2005).

It should also be noted that the LOQ for tributyltin is well above the AA-EQS value (Table 4.3).

Name	Sampling	Unit	AA-EQS	Mean	Median	5:e	25:e	Percentile 50:e	75:e	95:e	Min	Max
Nickel	DGT	µg/l	20	0.34	0.20	0.024	0.098	0.20	0.39	1.07	0.0061	2.94
Lead	DGT	µg/l	7.2	0.010	0.0027	0.00095	0.0018	0.0027	0.0064	0.046	0.00070	0.13
Cadmium	DGT	µg/l	0.08	0.012	0.0024	0.00060	0.0011	0.0024	0.0057	0.018	0.00020	0.39
Lead	Unfiltered	µg/l	7.2	0.99	0.42	0.16	0.28	0.42	0.71	2.08	0.048	31
Nickel	Unfiltered	µg/l	20	1.80	0.91	0.23	0.53	0.91	1.95	4.55	0.089	25
Mercury	Unfiltered	µg/l	0.05	0.031	0.0036	0.0025	0.0028	0.0036	0.0057	0.14	0.0023	0.52
Cadmium	Unfiltered	µg/l	0.08	0.036	0.012	0.0041	0.0074	0.012	0.030	0.10	0.0032	0.69
Lead	Filtrated	µg/l	7.2	0.20	0.13	0.021	0.077	0.13	0.28	0.63	0.012	0.80
Nickel	Filtrated	µg/l	20	1.51	0.86	0.22	0.58	0.86	1.32	3.88	0.18	12
Mercury	Filtrated	µg/l	0.05	0.0039	0.0038	0.0029	0.0034	0.0038	0.0046	0.0048	0.0028	0.0049
Cadmium	Filtrated	µg/l	0.08	0.023	0.012	0.0027	0.004	0.012	0.017	0.037	0.0022	0.26
Hexachlorobenzene	SPMD	pg/l	10000	64	9.20	2.20	5.40	9.20	16	39	1.50	4100
Chlorpyrifos	SPMD	pg/l	30000	15	5	1.49	3.00	5.00	11	50	1.00	200
Pentachlorobenzene	SPMD	pg/l	7000	60	11	3.66	6.23	11	18	33	3.20	3400
Pentachlorophenol	SPMD	pg/l	400000	11	6.10	1.35	4.30	6.1	14	35	1.30	42
Trifluralin	SPMD	pg/l	30000	7.85	5.20	2.06	3.33	5.20	9.30	18	0.86	36
Sum trichlorobenzene	SPMD	pg/l	400000	293	125	62	83	125	198	449	47	5230
Sum endosulfan	SPMD	pg/l	5000	983	742	160	456	742	1257	2454	148	2825
Sum pentabrominated diphenyl ethers	SPMD	pg/l	500	5.33	3.33	1.20	1.67	3.33	6.00	12	0.68	57
Sum hexachlorocyclohexanes	SPMD	pg/l	20000	379	324	185	243	324	438	614	69	2146
Anthracene	SPMD	pg/l	100000	630	68	13	30	68	198	1655	4.00	15000
Benzo(a)pyrene	SPMD	pg/l	50000	441	26	7	13	26	90	2516	6.00	9200
Fluoranthene	SPMD	pg/l	100000	10820	590	139	360	590	1150	6700	35	320000
Naphthalene	SPMD	pg/l	2400000	1790	1450	633	985	1450	2000	3500	280	17000
Sum benzo(g,h,i)perylene + indeno(123cd)pyrene	SPMD	pg/l	2000	162	36	15	25	36	68	362	13	4300
Octylphenols	SPMD	pg/l	30000	1219	62	15	41	62	158	698	10	38300
Nonylphenols	Filtrated	µg/l	0.1	0.022	0.018	0.018	0.018	0.018	0.025	0.030	0.018	0.031
Tributyltin compounds	Filtrated	µg/l	0.3	0.26	0.21	0.15	0.16	0.21	0.29	0.489	0.15	0.70
Trichloromethane	Filtrated	µg/l	0.0002	0.020	0.0031	0.0016	0.0025	0.0031	0.0034	0.0040	0.0014	0.0041
Pentabromodiphenylether	Filtrated	µg/l	2.5	0.20	0.24	0.10	0.1	0.24	0.26	0.28	0.10	0.29
Octylphenols	Unfiltered	µg/l	0.0005	0.00035	0.00025	0.00021	0.00022	0.00025	0.00029	0.00083	0.00021	0.0012
Nonylphenols	Unfiltered	µg/l	0.1	0.075	0.047	0.018	0.020	0.047	0.10	0.18	0.017	0.21
Tributyltin compounds	Unfiltered	µg/l	0.3	0.27	0.21	0.11	0.16	0.21	0.28	0.86	0.010	1.11
Trichloromethane	Unfiltered	µg/l	0.0002	0.0034	0.0034	0.0030	0.0032	0.0034	0.0037	0.0039	0.0029	0.0039
Hexachlorobutadiene	Unfiltered	µg/l	2.5	0.29	0.25	0.15	0.22	0.25	0.31	0.54	0.13	0.66
	Unfiltered	µg/l	0.1	0.038	0.013	0.012	0.012	0.013	0.014	0.14	0.012	0.19

Table 4.1 Levels of priority substances in surface waters in Sweden. Only data > LOQ were used in the calculations

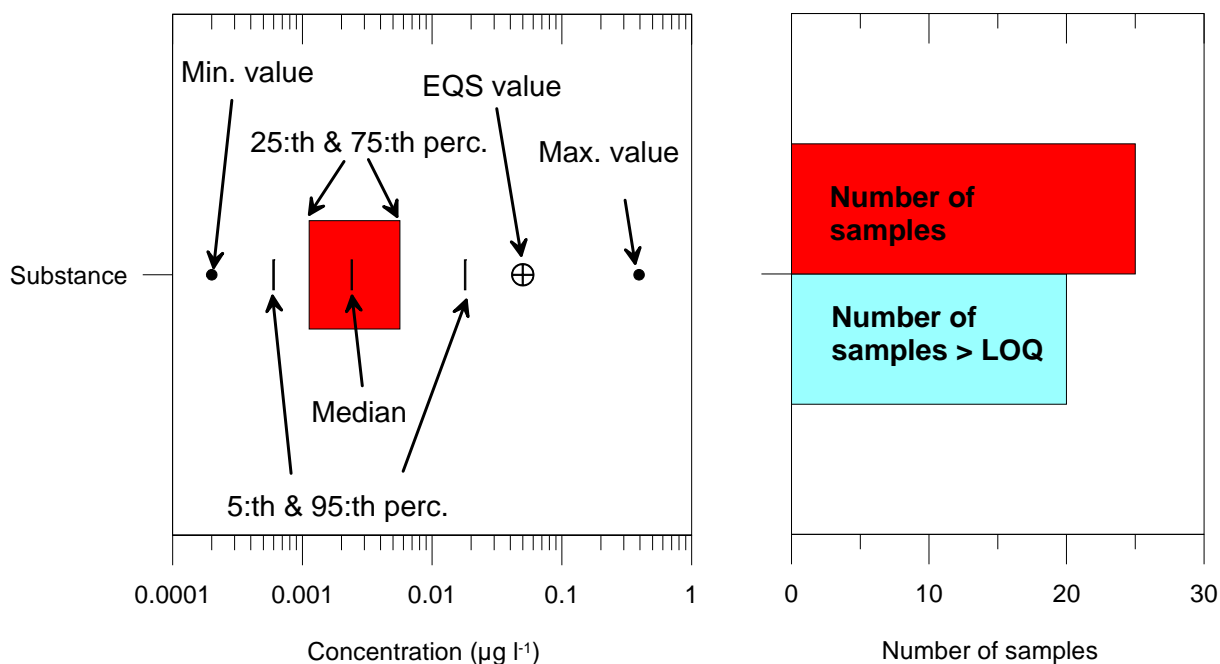


Figure 4.1 Explanation of the graphs summarizing the results from sampling of priority substances.

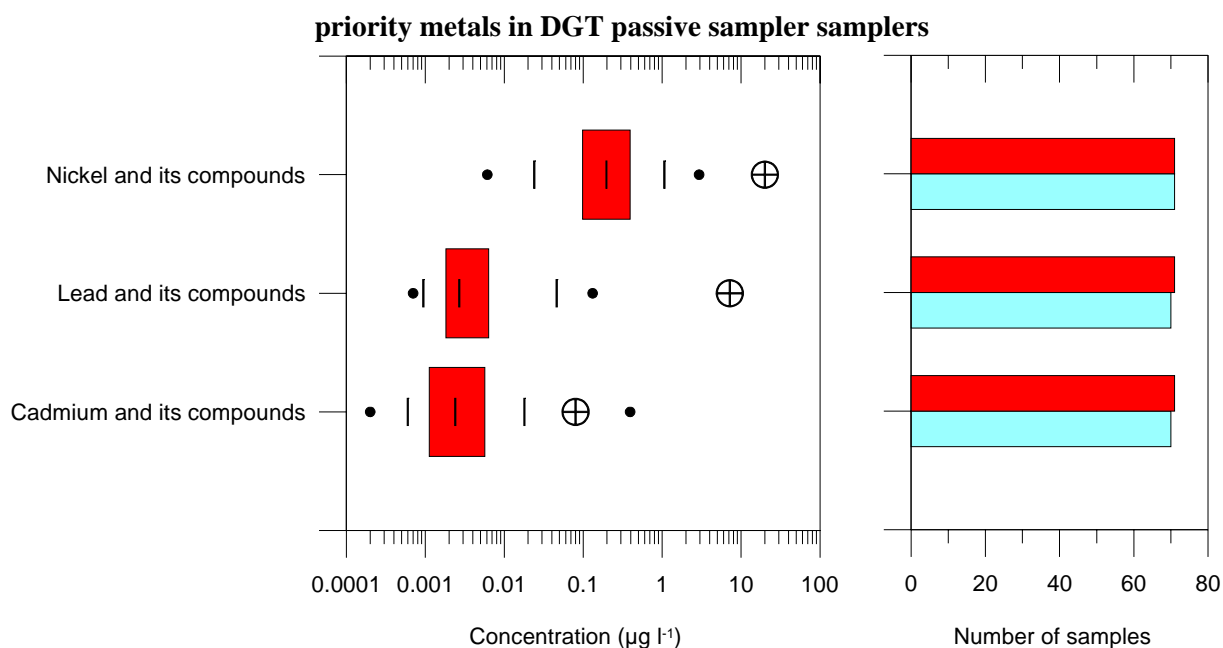


Figure 4.2 Levels of metal priority substances in surface waters in Sweden. Water concentrations calculated from *passive samplers (DGT)* according to equation 3.5. Note the logarithmic scale. Only data > LOQ was used.



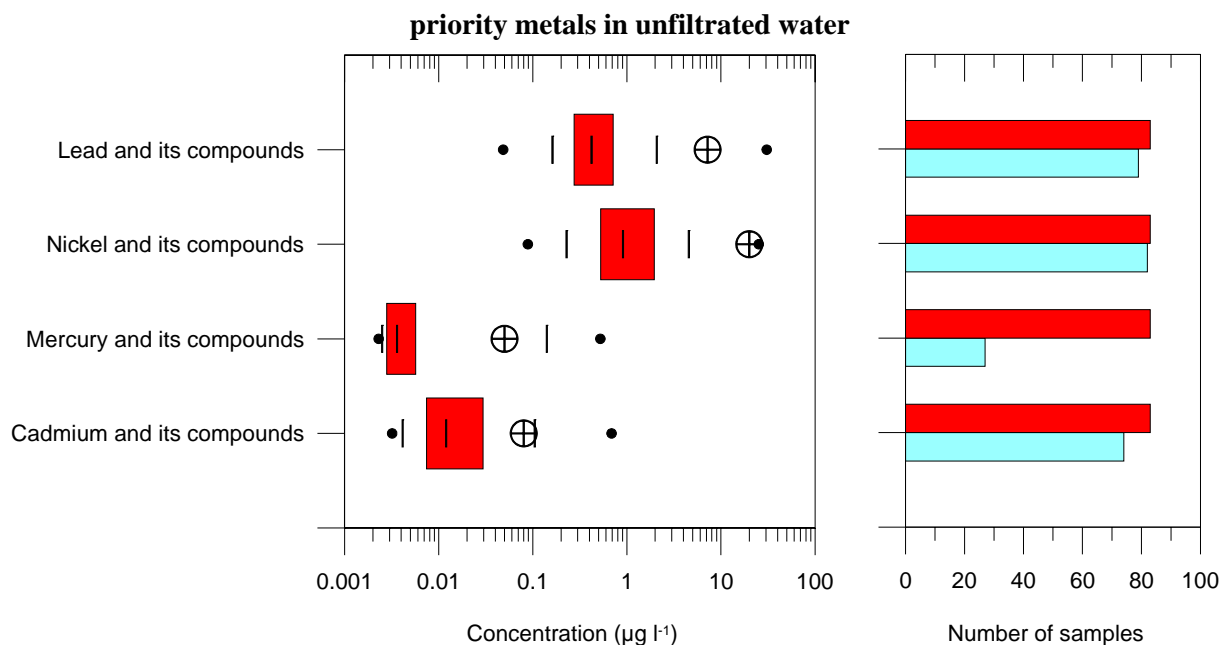


Figure 4.3 Levels of metal priority substances in **unfiltered** surface waters in Sweden. Note the logarithmic scale. Only data > LOQ were used.

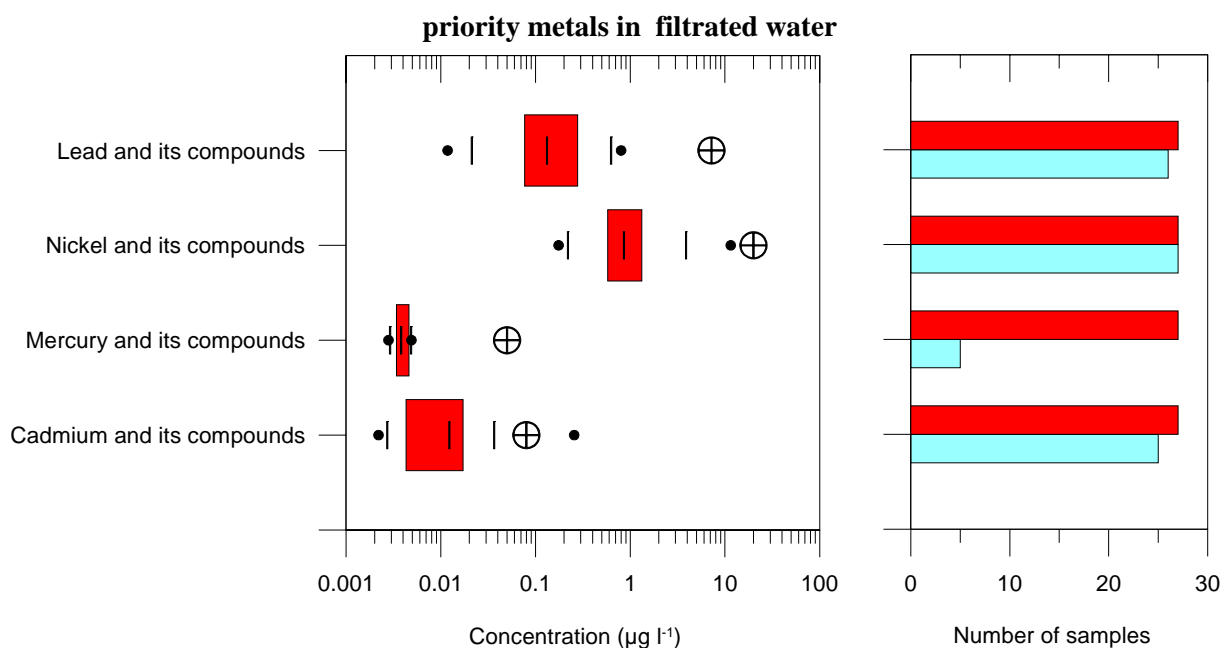
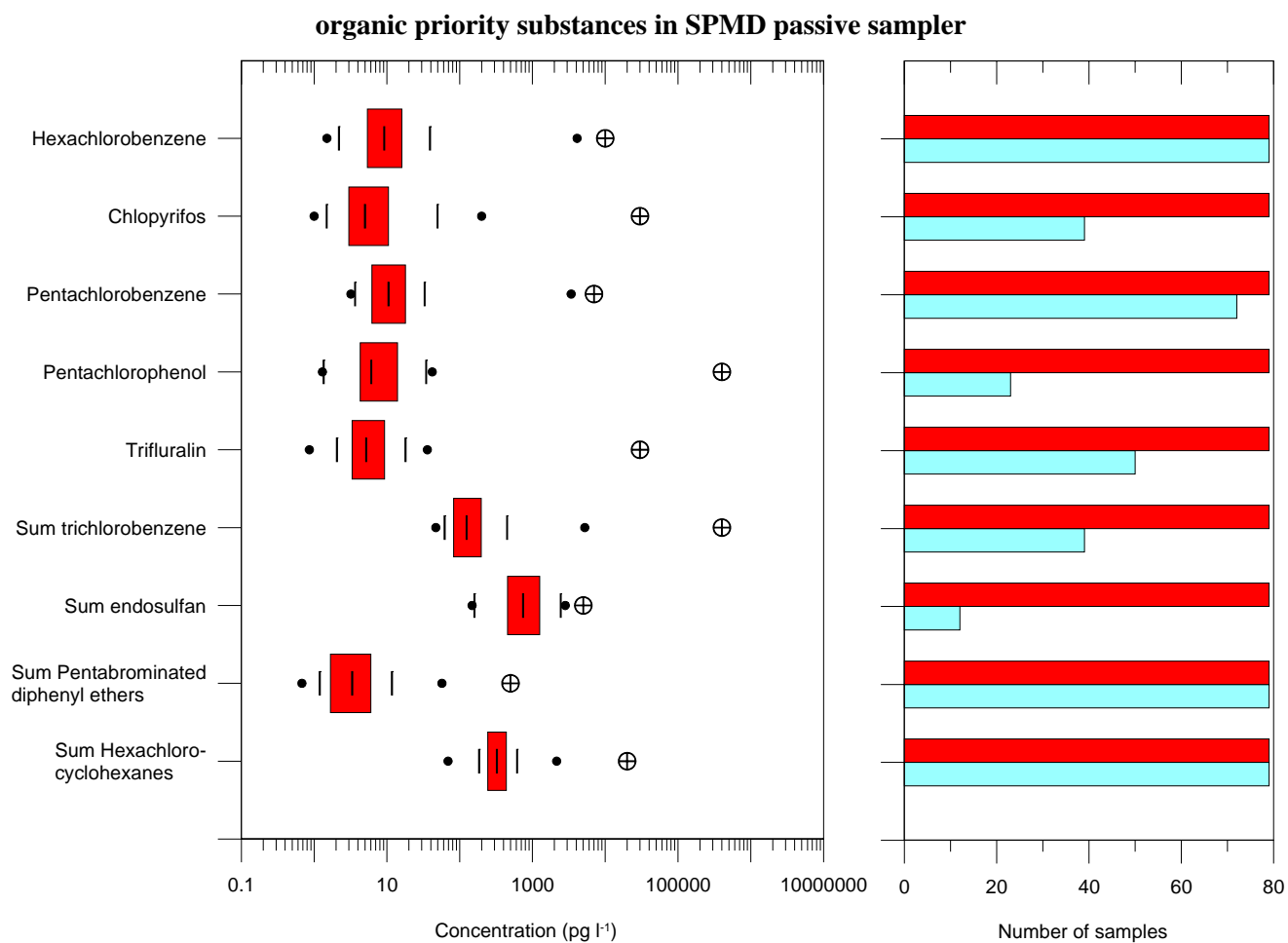
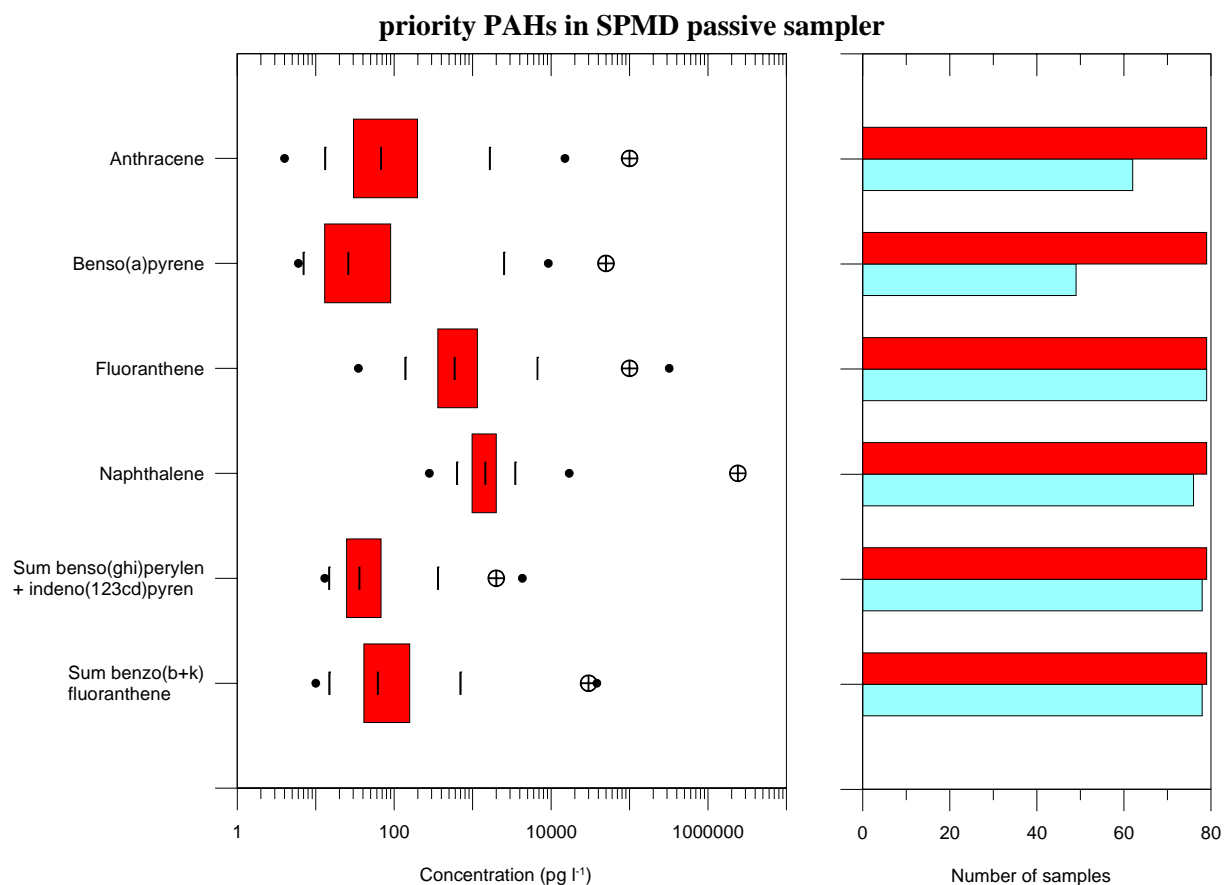


Figure 4.4 Levels of metal priority substances in **filtered** surface waters in Sweden. Note the logarithmic scale. Only data > LOQ were used.



*Figure 4.5 Levels of quantified organic priority substances in surface waters in Sweden. Water concentrations calculated from **passive samplers (SPMD)** according to equation 3.3 – 3.4..*

*Note the logarithmic scale. Only data > LOQ was used.*



*Figure 4.6 Levels of priority PAHs in surface waters in Sweden. Water concentrations calculated from **passive samplers (SPMD)** according to equation 3.3 – 3.4. Note the logarithmic scale. Only data > LOQ was used.*

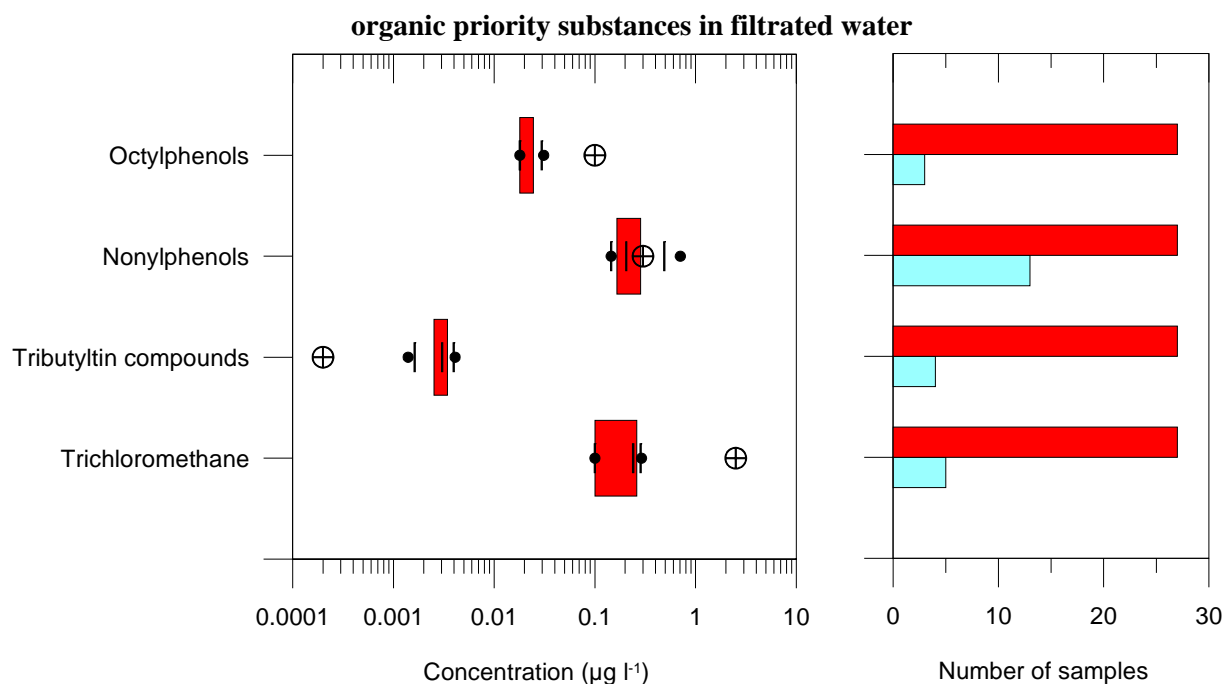


Figure 4.7 Levels of quantified organic priority substances in *filtrated* surface waters in Sweden. Note the logarithmic scale. Only data > LOQ was used.

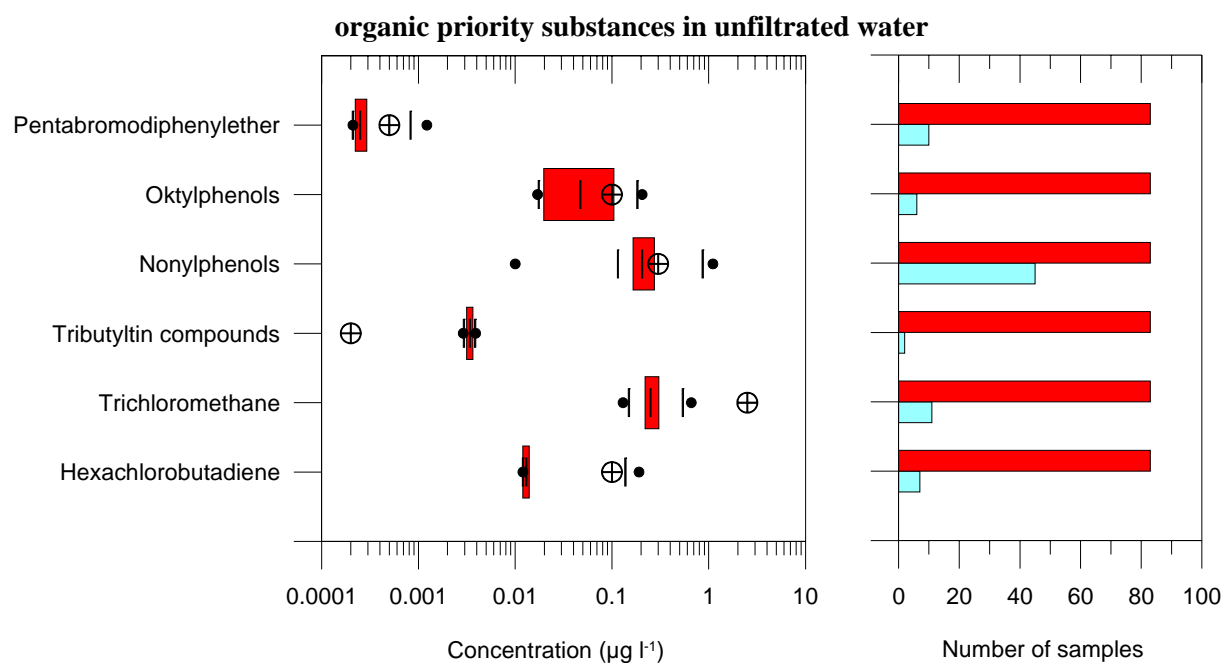


Figure 4.8 Levels of quantified organic priority substances in *unfiltrated* surface waters in Sweden. Note the logarithmic scale. Only data > LOQ was used.

Substance	Measured in no. samplers			AA-EQS (µg/l)	No. samples > AA-EQS			Limit of quantification, LOQ (µg/l)			No. samples > LOQ		
	unfiltered water	filtered water	passive samplers		unfiltered water	filtered water	passive samplers	unfiltered water	filtered water	passive samplers	unfiltered water	filtered water	passive samplers
Aklor	83	27	79	0.3	0	0	0	0.01	0.01	0.0005 - 0.001	0	0	1
Anthracene	83	27	79	0.1	0	0	0	0.01	0.01	9E-6 - 9.6E-5	0	0	62
Atrazine	83	27	79	0.6	0	0	0	0.01-0.03	0.01	0.0006-0.009	0	0	1
Benzene	83	27		10	0	0		0.2			0	0	
Pentabrominated diphenyl ethers	83	27		0.0005	1	0	0	0.00015			10	0	79
Cadmium	83	27	71	0.08-0.25	6*	1**	3***	0.002-0.05		0.0003	74	25	70
C10-13-chloroalkanes	83	27		0.4	0	0		0.2			1	0	
Chlorfenvinphos	83	27	79	0.1	0	0	0	0.02		0.001-0.004	0	0	2
Chlorpyrifos	83	27	79	0.03	0	0	0	0.02		6.9E-7 - 1.3E-5	0	0	39
1,2-Dichloroethane	83	27		10	0	0		1			0	0	
Dichloromethane	83	27		20	0	0		0.2			0	0	
Di(2-ethylhexyl)-phthalate	83	27		1.3	1	0		1			1	0	
Diuron	83	27	79	0.2	0	0	0	0.01-0.05	0.01	0.003-0.007	0	0	0
Endosulfan	83	27	79	0.005	0	0	0	0.01		1.25E-4 - 5.8E-4	0	0	12
Fluoranthene	83	27	79	0.1	0	0	3	0.01		NA	0	1	79
Hexachlorobenzene	83	27	79	0.01	0	0	0	0.01		NA	0	0	79
Hexachlorobutadiene	83	27		0.1	1	0		0.01			7	0	
Hexachlorocyclohexanes	83	27	79	0.02	0	0	0	0.015		NA	0	0	79
Isoproturon	83	27	79	0.3	0	0	0	0.01-0.05	0.01	0.002-0.004	0	0	1
Lead	83	27	71	7.2	1	0	0	0.002-0.6	0.6	0.001	79	26	70
Mercury	83	27		0.05	2	0		0.002-0.02			27	5	
Naphthalene	83	27	79	2.4	0	0	0	0.01		0.00085	1	0	76

NA - not applicable, always above LOQ

\* 5 samples > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

\*\* 1 sample > guideline value class 5: 0.25 (µg/l)

\*\*\* 1 sample > guideline value class 1: 0.08 (µg/l). sample > guideline value class 4: 0.15 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

Table 4.2 Summary information regarding the exceedance of EQS values and limits of quantification, substance a – n.

Substance	Measured in no. samples			AA-EQS (µg/l)	No. samples > AA EQS			Limit of quantification, LOQ (µg/l)			No. samples > LOQ		
	unfiltered water	filtered water	passive samplers		unfiltered water	filtered water	passive samplers	unfiltered water	filtered water	passive samplers	unfiltered water	filtered water	passive samplers
Nickel	83	27	71	20	1	0	0	0.6	0.055	NA	82	27	71
Nonylphenol	83	27		0.3	10	3					45	13	
Octylphenol	83	27		0.1	2	0		0.01			6	3	
Pentachlorobenzene	83	27	79	0.007	0	0	0	0.01		1.6E-6 - 6.6E-6	0	0	72
Pentachlorophenol	83	27	79	0.4	0	0	0	0.1		8.9E-8 - 2E-5	0	0	23
Benso(a)pyrene	83	27	79	0.05	0	0	0	0.01		4E-6 - 2.1E-5	0	0	49
Benzo(b+h)fluoranthene	83	27	79	0.03	0	0	1	0.01		0.000011	0	0	78
Benzo(ghi)perylene + Indeno(123cd)pyrene	83	27	79	0.002	0	0	2	0.01		0.000006	0	0	78
Simazine	83	27	79	1	0	0	0	0.01-0.03	0.01	0.0007-0.002	0	0	1
Tributyltin	83	27		0.0002	2	4		0.001			2	4	
Trichlorobenzene	83	27	79	0.4	0	0	0	0.015		3.4E-5 - 1.18E-4	0	0	39
Trichloromethane	83	27		2.5	0	0		0.1-0.2	0.1		11	5	
Trifluralin	83	27	79	0.03	0	0	0	0.01		6.9E-7 - 9.3E-6	0	0	50

NA - not applicable, always above LOQ

\* 5 samples > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

\*\* 1 sample > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 4: 0.15 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

\*\*\* 1 sample > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 4: 0.15 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

NA - not applicable, always above LOQ

\* 5 samples > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

\*\* 1 sample > guideline value class 5: 0.25 (µg/l)

\*\*\* 1 sample > guideline value class 1: 0.08 (µg/l). 1 sample > guideline value class 4: 0.15 (µg/l). 1 sample > guideline value class 5: 0.25 (µg/l)

Table 4.3 Summary information regarding the exceedance of EQS values and limits of quantification.

## 4.2 Geographical distribution

The geographical distribution of measured (for passive samplers calculated) levels of priority substances in Sweden is given in appendix 2.

Since, for the purpose of this report, it is more interesting to elucidate how measured concentrations relate to the EQS values, the map figures (Figure 4.9 – 4.16) presents the ratio between measured concentrations in surface waters<sup>3</sup> and AA-EQS values. For clarity, only those substances where more than 3 sampling points are above LOQ are presented in these maps. In appendix 3, the same maps are presented in a larger format. The EQS value for Cadmium is dependent on the water hardness. In the present report the measured concentrations were compared to the lowest AA-EQS value representing the lowest hardness (class 1, < 40 mg CaCO<sub>3</sub>/l). For regulatory purposes a more site specific determination of water hardness may be necessary.

Some general geographical patterns worth noticing are:

### 1. Consistently below LOQ

Some priority substances consistently occur below LOQ all over Sweden. These include:

- Pesticides: alaklor, atrazine, chlorfenviphos, diuron, isoproturon, simazine
- Volatile organic substances: benzene, dichloromethane, 1,2-dichloroethane
- C10 – C13 chloroalkanes
- Di(2-ethylhexyl)-phtalate

### 2. Consistently low levels

Some priority substances consistently occur at low levels all over Sweden with no discernible geographical differences. These include:

- Pesticides: chloropyrifos and trifuralin (Figure 4.10).
- Chlorinated semi volatile substances (Figure 4.11)
- Some PAHs (Figure 4.12)

### 3. Generally low levels that sporadically are close to or exceeds EQS

Some substances have generally low concentration all over Sweden with sporadically high concentrations even close to or above EQS. This pattern indicates that the sampling station is influenced by a local source of these contaminants. Priority substances with this pattern include:

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<sup>3</sup> Two sampling points from the regional county of Dalarna consisted of untreated ground water rather than surface water. The levels of WFD substances in these samples were below the detection limit except for nickel, cadmium and lead that occurred at low concentrations. These results are included in the map figures below. This is not entirely correct since there are at present no EQS values for groundwater. The inclusion does however not affect the general interpretation of the data.



- mercury (Figure 4.15)
- endosulfan (Figure 4.10)
- some PAHs (Figure 4.12)
- trichloromethane (Figure 4.13)
- tributyltin (Figure 4.13)
- hexachlorobutadiene (Figure 4.14)
- pentabrominated diphenyl ether (Figure 4.14)
- oktylphenol (Figure 4.16)

It should however be noted that for some substances (i.e. tributyltin, pentaBDE, PAHs) the LOQ is close to or above the EQS value. Consequently, a non-detect does not preclude that these substances are close to or above the EQS value.

#### **4. Higher levels in southern Sweden**

Some priority substances occurs at low levels in the Northern part of Sweden while occurring more frequently at higher concentrations, even close to or above EQS, in Southern Sweden. Priority substances with this pattern include:

- Lead (Figure 4.9)
- Nickel (Figure 4.9)
- Mercury (Figure 4.15)
- endosulfan (Figure 4.10)
- trichloromethane (Figure 4.13)
- hexachlorobutadiene (Figure 4.14)
- pentabrominated diphenyl ether (Figure 4.14)
- nonylphenol (Figure 4.16)

#### **5. High levels regardless of latitude - Cadmium**

Cadmium (Figure 4.9) occurs at elevated concentrations all over Sweden without any apparent geographical pattern.

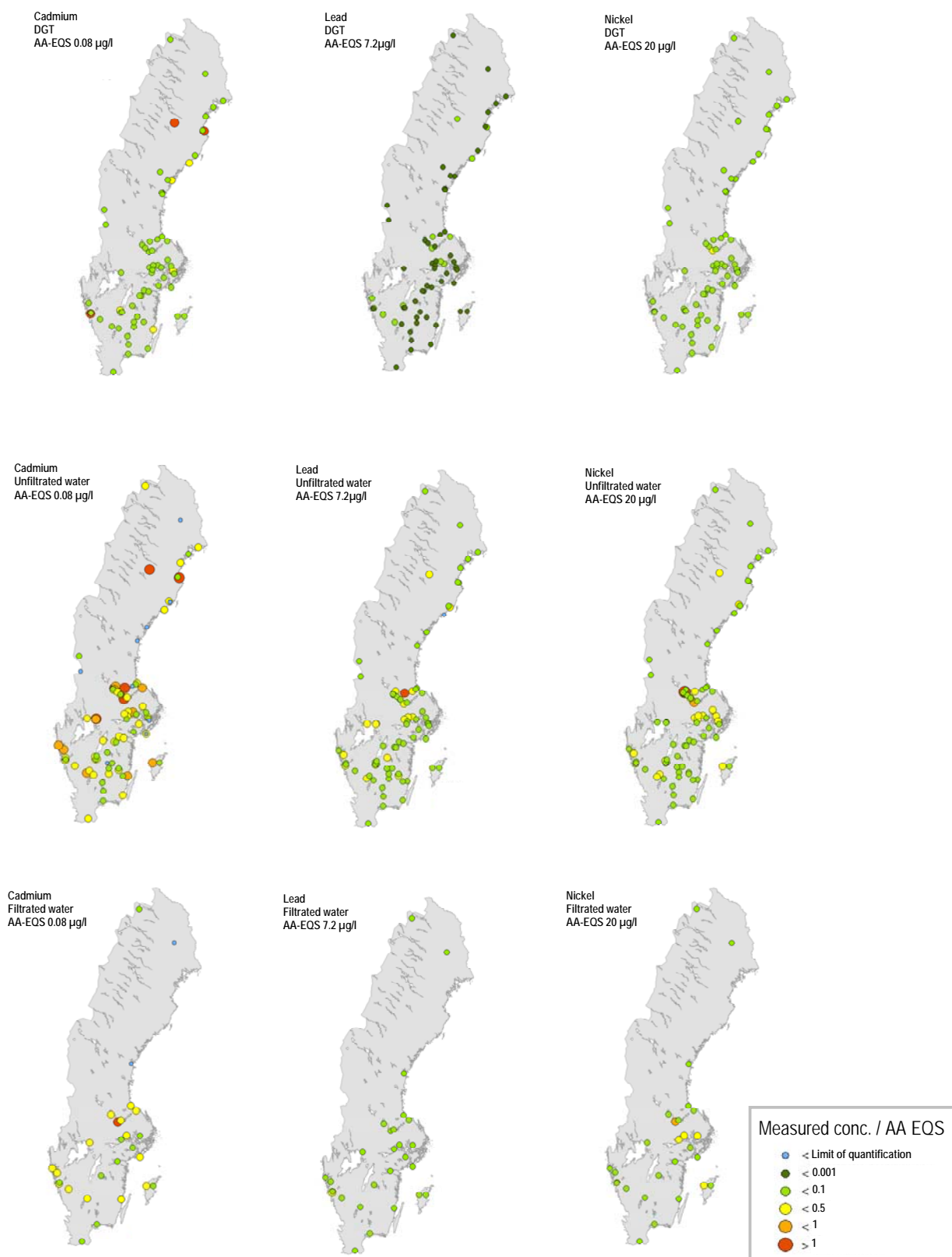


Figure 4.9 Geographical distribution of the ratio between measured (for DGT samplers calculated according to equation 3.5) priority metal concentrations and EQS values.

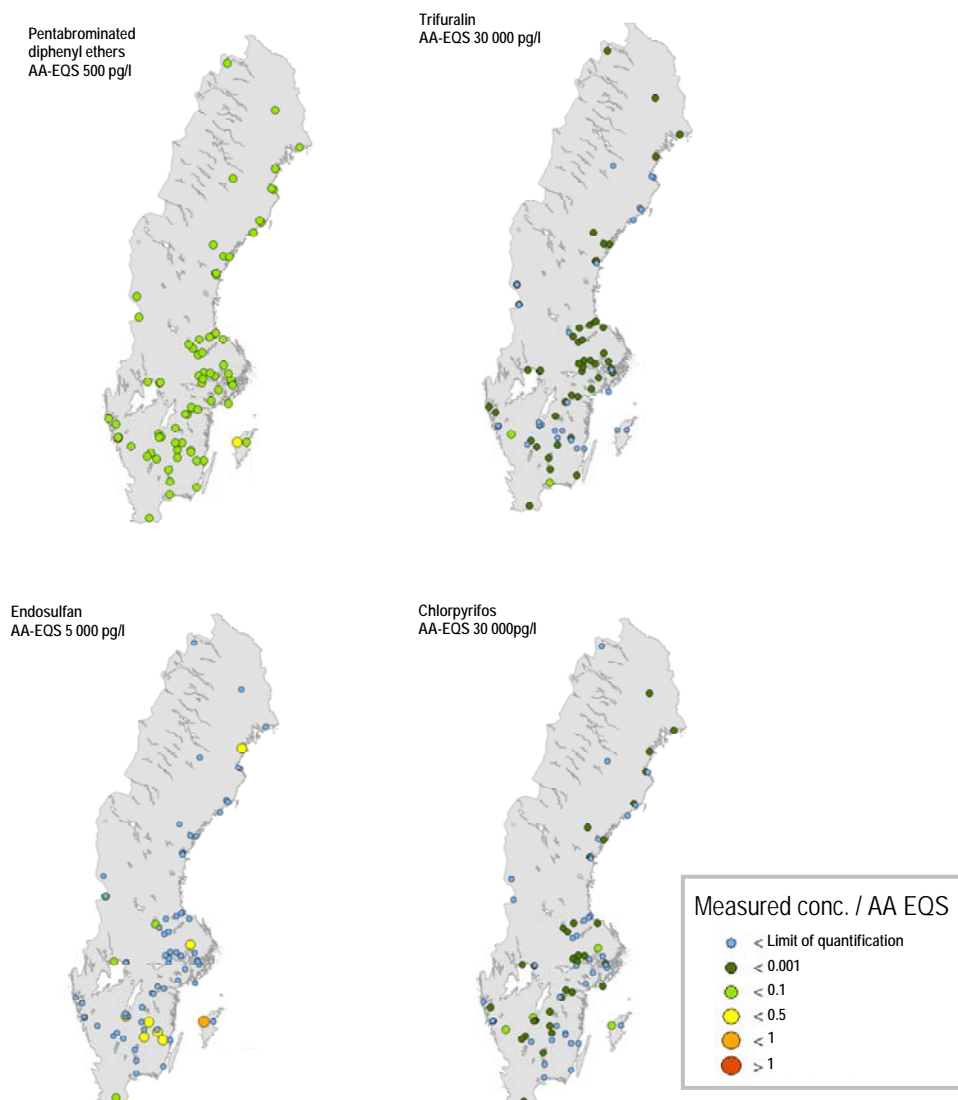
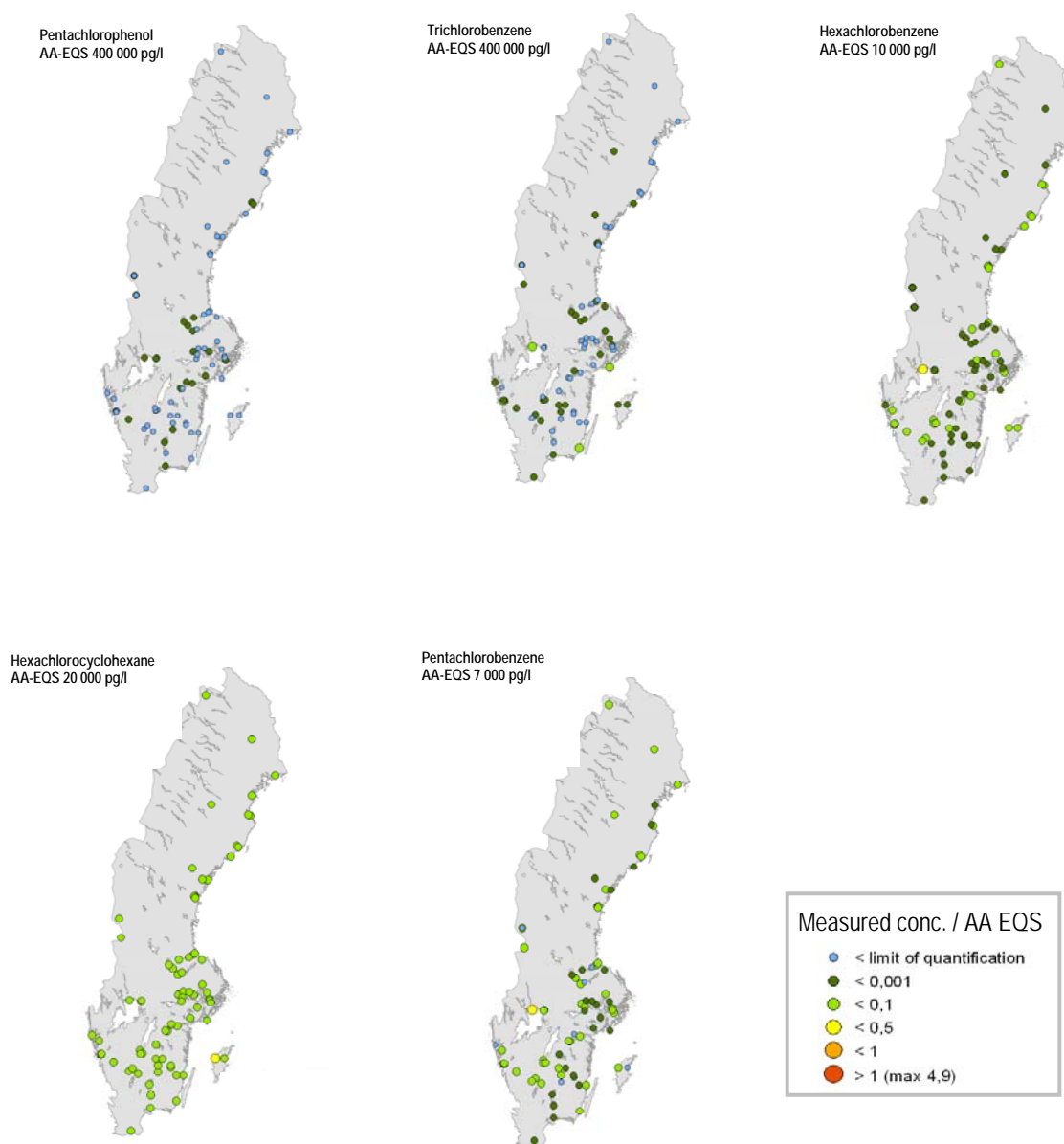


Figure 4.10 Geographical distribution of the ratio between measured concentrations of organic priority substances priority and EQS values. All maps represent water concentrations calculated from passive samplers (SPMD) according to equation 3.3 – 3.4.



*Figure 4.11 Geographical distribution of the ratio between measured concentrations of chlorinated priority substances priority and EQS values. All maps represent water concentrations calculated from passive samplers (SPMD) according to equation 3.3 – 3.4. .*

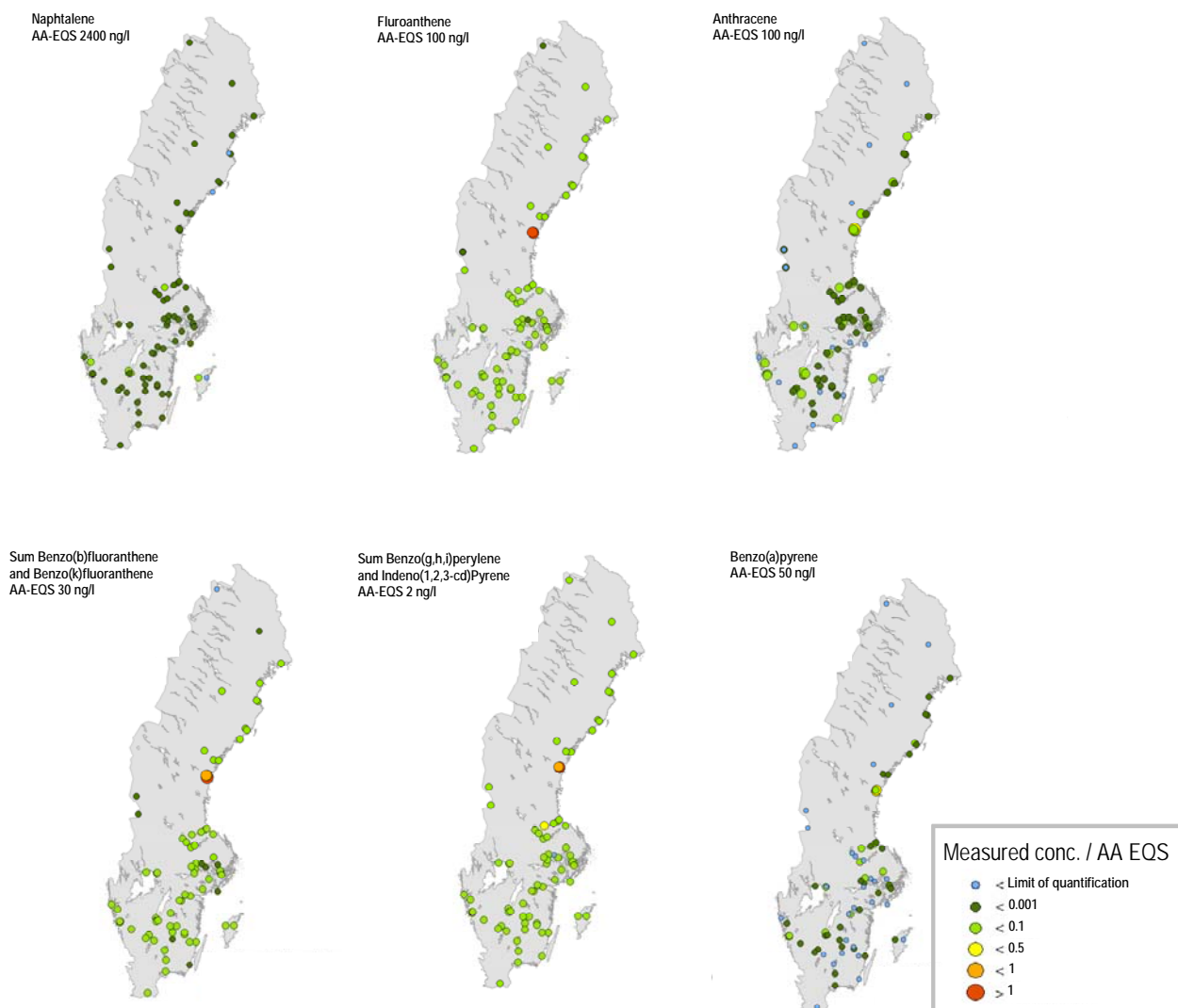


Figure 4.12 Geographical distribution of the ratio between measured priority PAH concentrations and EQS values. All maps represent water concentrations calculated from passive samplers (SPMD) according to equation 3.3 – 3.4..

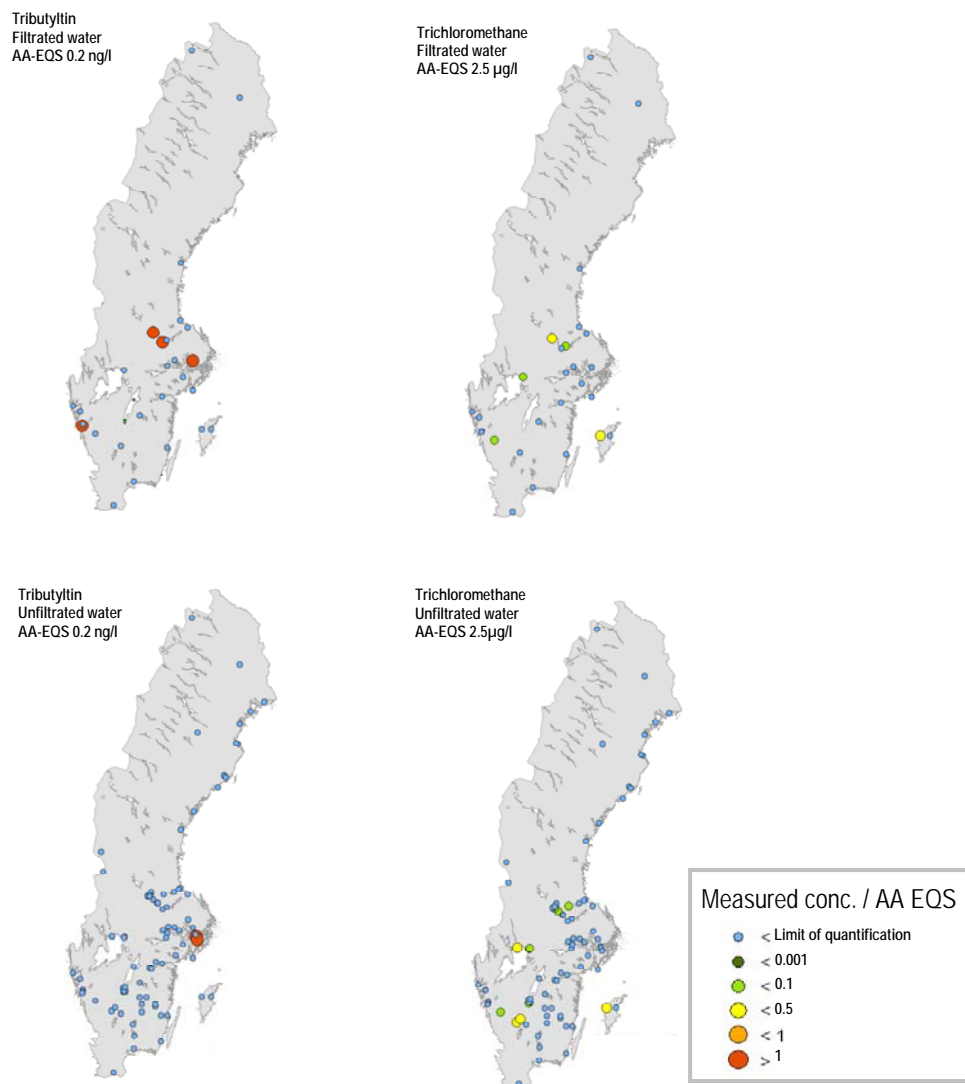


Figure 4.13 Geographical distribution of the ratio between EQS values and measured concentrations of tributyltin and trichloromethane.

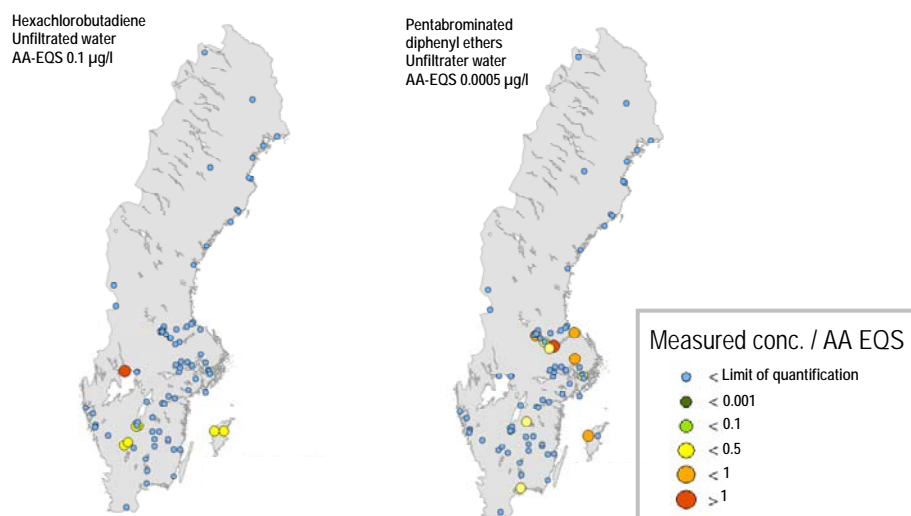


Figure 4.14 Geographical distribution of the ratio between EQS values and measured concentrations of hexachlorobutadiene and pentaBDE.

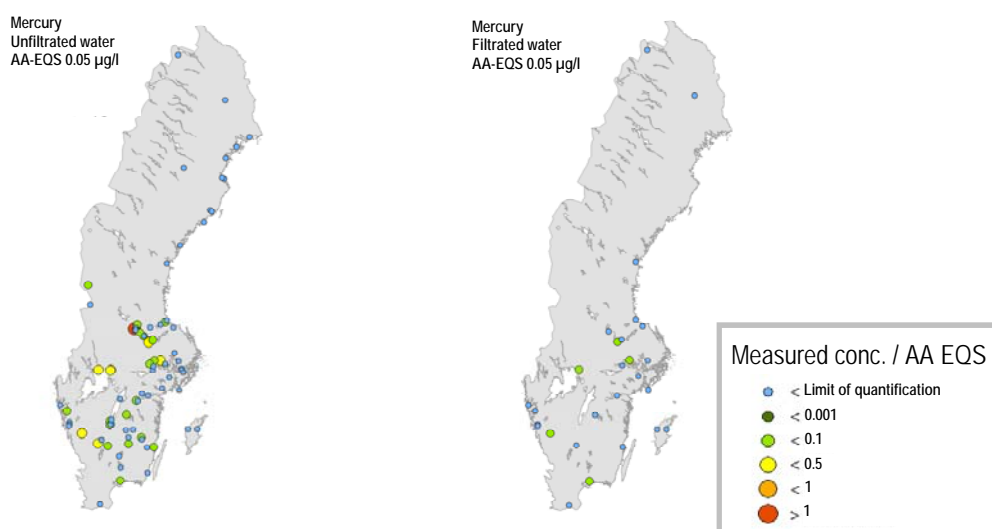


Figure 4.15 Geographical distribution of the ratio between measured mercury concentrations and EQS values in filtered and unfiltered water.

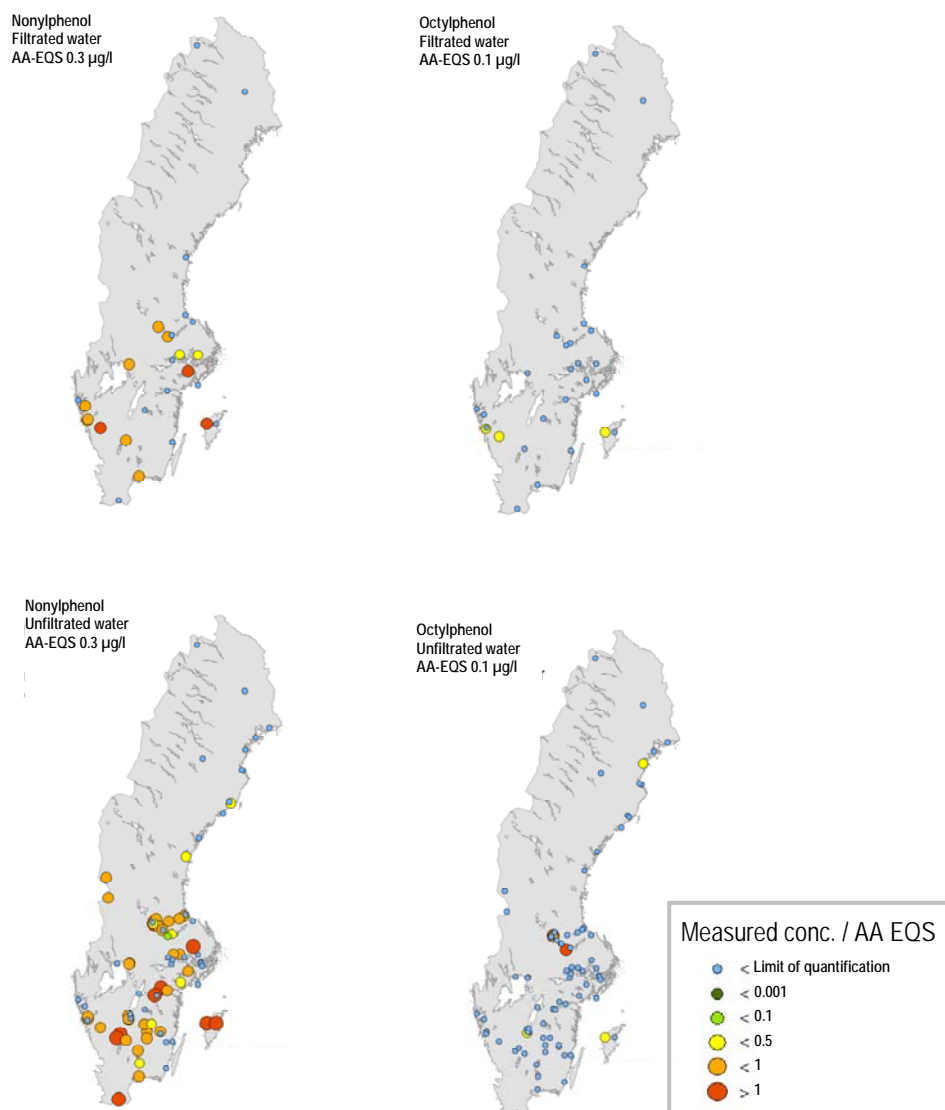


Figure 4.16 Geographical distribution of the ratio between EQS values and measured concentrations of nonylphenol and octylphenol.



## 4.3 Discharge sources

The actual concentrations of priority substances are of less concern when evaluating how different types of discharges affect the sampling points. It is more relevant to compare the concentrations to some measure that indicates environmental consequences. Within the context of this report, the AA-EQS values are used.

Consequently, to calculate the influence ( $I$ ) of the discharge type ( $DT$ ) on the degree to which a sampling point is affected by a priority substance ( $PS$ ) the ratio between the priority substance median concentration ( $\tilde{C}$ ) of all sampling points being affected by a discharge type and the EQS value for that priority substance was calculated:

$$I = \frac{\tilde{C}_{PS,DT}}{EQS_{PS}} \quad 4.1$$

The calculated value for each priority substance and discharge is presented in Table 4.4. A value of 1 in Table 4.4 indicates that the median concentration for a particular substance at all sampling point being influenced by a discharge type is equal to the EQS value for that substance.

Substance	Discharge type			Discharge source						
	Un-affected	Diffuse load	Point sources	Urban load	Agri-culture	Forestry	Industry	Land-fill	Sewage treatment	Mix; indu- stry, sewa- ge..
<b>Unfiltrated water</b>										
Trichlorormethane	<i>0.10</i>	0.1	0.1	0.1	<i>0.1</i>	<LOQ	0.2	<i>0.1</i>	0.09	0.1
Tributyltin	<LOQ	1.7	2.0	1.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cadmium	0.2	0.1	0.2	0.1	0.1	0.1	0.2	0.2	0.1	0.2
Mercury	0.1	0.08	0.07	0.07	0.08	<LOQ	0.09	0.08	0.06	0.06
Nickel	0.04	0.04	0.05	0.05	0.07	0.02	0.05	0.04	0.04	0.05
Lead	0.05	0.06	0.08	0.06	0.04	0.03	0.06	0.07	0.04	0.07
Octylphenol	<LOQ	0.2	0.5	0.2	<LOQ	0.2	0.7	0.7	0.2	0.7
Nonylphenol	0.7	0.6	0.7	0.7	0.7	2.6	0.7	0.7	1.0	0.7
Pentabrominated diphenyl ethers	<LOQ	<LOQ	0.5	0.5	0.5	<LOQ	0.5	<LOQ	0.5	0.5
<b>Filtrated water</b>										
Trichlorormethane	<LOQ	0.1	0.1	0.1	<i>0.1</i>	<LOQ	0.6	<LOQ	<i>0.1</i>	0.1
Tributyltin	<LOQ	1.6	2.1	1.6	<i>1.5</i>	<LOQ	<LOQ	<LOQ	<LOQ	1.6
Cadmium	0.05	0.2	0.2	0.1	0.07	<LOQ	0.2	0.05	0.1	0.2
Mercury	<LOQ	0.08	0.08	0.08	0.1	<LOQ	0.07	<LOQ	<i>0.07</i>	0.07
Nickel	0.02	0.04	0.05	0.04	<i>0.05</i>	<i>0.01</i>	0.05	0.04	0.04	0.05
Lead	0.04	0.02	0.03	0.01	0.01	<i>0.01</i>	0.02	0.00	0.01	0.02
Octylphenol	<LOQ	<LOQ	0.2	0.2	<LOQ	<LOQ	<LOQ	<LOQ	0.3	0.2
Nonylphenol	<i>1.2</i>	0.7	0.7	0.7	0.6	<LOQ	0.6	<LOQ	0.7	0.7
<b>DGT</b>										
Cadmium	0.06	0.03	0.04	0.03	0.02	0.02	0.03	0.03	0.03	0.04
Lead	0.0003	0.0004	0.0006	0.0004	0.0003	0.0001	0.0004	0.0003	0.0003	0.0005
Nickel	0.003	0.01	0.01	0.01	0.01	0.005	0.010	0.007	0.007	0.009
<b>SPMD</b>										
Naphtalene	0.0004	0.0006	0.0007	0.0006	0.0004	0.0008	0.0006	0.0006	0.0006	0.0007
Antracene	0.0001	0.0008	0.0009	0.0008	0.0005	0.001	0.0008	0.002	0.001	0.0009
Fluoranthene	0.003	0.007	0.0110	0.007	0.003	0.006	0.006	0.007	0.007	0.008
Benzo(a)pyrene	0.0004	0.0008	0.0008	0.0008	0.001	0.0002	0.0004	0.002	0.0007	0.0008
Pentachlorobenzene	0.001	0.002	0.002	0.002	0.001	0.001	0.001	0.001	0.001	0.002
Hexachlorobenzene	0.0007	0.0009	0.0012	0.001	0.0006	0.0006	0.0006	0.0009	0.001	0.001
Pentachlororphenol	0.00004	0.00001	0.00001	0.00001	0.00001	0.00003	0.00001	0.00001	0.00001	0.00001
Chlorpyrifos	<i>0.0001</i>	0.0001	0.0002	0.0002	0.0005	0.0002	0.0002	0.0002	0.0002	0.0002
Trifluralin	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0002	0.0004	0.0001	0.0002
Penatbrominated diphenyl ethers	0.006	0.007	0.007	0.007	0.006	0.004	0.006	0.01	0.007	0.01
Endosulfan	<i>0.2</i>	0.08	0.2	0.2	<i>0.4</i>	<i>0.1</i>	0.1	<i>0.1</i>	0.3	0.1
Trichlorobenzene	0.0002	0.0004	0.0004	0.0003	0.0002	<i>0.0007</i>	0.0004	0.0006	0.0004	0.0004
Benzo(b) + Benzo(k) fluoranthene	0.001	0.002	0.0043	0.003	0.002	0.001	0.002	0.003	0.003	0.004
Benzo(g,h,i) + Benzo(1,2,3-cd)	0.02	0.02	0.03	0.02	0.02	0.01	0.02	0.03	0.02	0.03
<b>Median</b>	<b>0.01</b>	<b>0.02</b>	<b>0.04</b>	<b>0.03</b>	<b>0.02</b>	<b>0.01</b>	<b>0.02</b>	<b>0.01</b>	<b>0.02</b>	<b>0.03</b>

Table 4.4 How discharge sources affects the levels of priority substances. Priority substance influence is estimated by dividing the median concentration (of sampling points receiving a specific type of discharge) with the EQS value. Only substances that have been detected are included. A value in italic relies on only one measurement. <LOQ indicates that no values for that substance and discharge source were above the LOQ.

## 5 Discussion

### 5.1 The presence of priority substances in Swedish surface waters

It is noticeable that a majority of the priority substances are present in surface waters from northern to southern Sweden. Especially metals and some lipophilic semi volatile substances sampled in the SPMDs were present at all sampling points including the northernmost and southernmost unaffected background reference sampling stations (the sampling points furthest north and south in the map figure) as well as in reference stations in the middle and western part of Sweden. Hexachlorobenzene is a good example of one such substance (Figure 4.11).

The usage of some of the organic substances occurring all over Sweden have been restricted for a long time while others have a limited use (pentachlorobenzene, pentachlorophenol, hexachlorocyclohexane, hexachlorobenzene, trifluralin, chlorpyrifos; Table 2.1) indicating that the levels found are the result of historical pollution.

Other substances (i.e. PAHs and metals) have been emitted from anthropogenic sources for a long time and are still in use and the levels seen are likely the result of both historical pollution and emission from ongoing activities. Notice the special case of cadmium (section 5.2).

Some of the substances found at the highest levels (i.e. nonylphenols and pentaBDE) are phase-out substances that have a relatively modern origin and it can not be ruled out that the levels seen in surface waters is dominated by ongoing emissions.

### 5.2 Priority substances of concern

There is no generally accepted definition of what comprises an elevated surface water concentration. However, in the following discussion and especially in Table 5.1 a measured surface water concentration of  $0.1 \times \text{AA-EQS}$  was designated as an *elevated* concentration. This is an *ad hoc* designation and it may be that another definition ( $0.25 \times \text{AA-EQS}$  for example) would change the interpretation of the results, although a cursory data evaluation did not indicate that this is the case. It should also be noted that concentrations  $> 0.1 \times \text{AA-EQS}$  does not automatically denote a level that gives rise to any concern or need for regulatory measures.

Considering the frequency by which a substance exceeds its AA-EQS value (Table 5.1) and the relationship between the percentiles and the EQS value (Figure 4.2 - 4.8) the following substances were identified as of being of concern in Sweden with regards to the water framework directive:

## 1. Nonylphenol

Nonylphenol is used in the manufacturing of plastics, paints and rubber as a stabilizer (Andersson och Sörne 2007). The main use is however as a precursor for the production of nonylphenoethoxilates. Nonylphenoethoxilates are easily degraded to nonylphenol both in sewage treatment plants and in the natural environment and it is likely that the nonylphenol levels seen in the environment are a result of biodegradation of nonylphenoethoxilates (RPA 1999). Nonylphenoethoxilates are used in a large number of industrial and household products as emulsifiers, dispersants, wetting agents, detergents and defoamers. Some usage examples are pesticide products, in the pulp and paper industry, in household and industrial cleaning products, in metal cleaning processes, in paints and glues, in cosmetics and other personal care products (shampoo etc.) and in the manufacturing of various polymers (Remberger et al. 2003, RPA 1999).

Nonylphenol frequently occurred at levels close to or above the EQS value (Figure 4.16, Table 5.1). Both in filtered and in non-filtered water the 75<sup>th</sup> percentile of nonylphenol concentrations coincided with the AA-EQS value (Figure 4.7 – 4.8). This figure is based on only samples where nonylphenol was detected. Taking into account all samples, the AA-EQS value was exceeded in 12% of both filtered and non-filtered water while elevated levels ( $>0.1 \times \text{AA-EQS}$ ) was found in 50% of the sampled waters (Table 5.1). Note that the pattern of elevated levels was the same in both filtered water and non-filtered water showing that both are appropriate for monitoring of nonylphenols.

The geographical patterns of nonylphenol with low levels in northern Sweden and high levels in southern Sweden (Figure 4.16) indicate that nonylphenol levels coincide with population density and urban areas in Sweden.

At most unaffected sampling locations the nonylphenol levels were below the quantification limit, the exception being the southernmost background locality and one sampling point receiving discharge from forestry (Table 4.4). Other than this, the data indicates that sewage treatment plants is an important source of nonylphenols to surface waters which correlates with the fact that nonylphenol is a common contaminant in sludge in Sweden (Svensson 2002) and also with the fact that nonylphenol levels in outgoing water from sewage treatment plants are occasionally high (Naturvårdsverket 2005). A number of other sources also seem to be important (Table 4.4) and nonylphenol is probably the most widespread of all priority substances. A good indication of this is the high levels found in the Baltic sea outside the island / County of Gotland. To summarize, the data indicate that even though restrictions on the use of nonylphenols have been implemented its emissions to surface waters may continue.

## 2. Cadmium

Cadmium is used in batteries (especially Ni-Cd batteries), for pigments, coatings and plating, and as a stabilizer in plastics. Cadmium also occurs as a contamination in

phosphate fertilizers applied in Sweden. Cadmium deposition in southern Sweden also originates from coal burning in neighbouring countries (Swedish Chemicals Agency, KEMI 2004).

Cadmium levels were often elevated although not exceeding the EQS value as often as nonylphenol (Figure 4.9) The map figures indicate that cadmium is a priority substance of concern while the statistical evaluation indicate that the AA-EQS is reached or exceeded in ca. 5% of the types of surface waters sampled (Figure 4.2 – 4.4, Table 5.1). The chosen EQS value for Cadmium represented the lowest hardness class and consequently the results may be somewhat misleading, especially if the water hardness is above 100 mg CaCO<sub>3</sub>/l (hardness class 4 according to the water framework directive).

The geographical patterns of cadmium with no discernible geographic differences in the frequency of elevated levels (Figure 4.9) indicate that cadmium is an omnipresent pollutant originating from different sources. Table 4.4 also indicates that no specific source dominates.

Cadmium levels in background stations are at par with other sources (Table 4.4). It is suspected that the acidification of forest soils have increased the leaching of cadmium to surface waters which may explain the observed geographical pattern (Swedish Chemicals Agency, KEMI 2004).

### 3. Tributyltin

Tributyltin (TBT) has been extensively used as an additive in antifouling paints, preservatives, fungicides and biocides (Tessalidet 2004). TBT-paints are used on vessel hulls to prevent growth of organisms. In the early 1990s the use of TBT in antifouling paints on boats shorter than 25 m was prohibited by law through the EU directive 89/677/EC. The IMO (International Maritime Organisation) has implemented rules that aim at phasing out TBT in larger vessels no later than 2008 (Swedish Chemicals Agency, KEMI 2006).

Since the LOQ of TBT is approximately 5 – 10 times higher than the AA-EQS value the interpretation of the results are uncertain. The detected TBT levels were up to 5 times higher than the AA-EQS (actual concentrations are shown in appendix 2). If the LOQ could be lowered significantly it can not be excluded that more sampling stations with TBT levels above the EQS would be discovered. Further national screening of TBT in surface waters using more developed analytical techniques may thus be warranted.

TBT is a well known contaminant occurring at relatively high levels in sea and harbour sediments in Sweden (Naturvårdsverket 2005). The levels in freshwater sediments are less known but considering that TBT has been used on vessels trafficking inland waters for a long time it can not be excluded that freshwater sediments are sources of TBTs to limnic surface waters. TBT is also common in sludge in Swedish

sewage treatment plants (Svensson 2002) and this may constitute one important source to surface waters in Sweden.

#### 4. Other substances

Other substances occasionally exceeded the EQS value or were close to the EQS value while not exceeding it (Table 5.1). Most notable are lead, nickel and pentaBDE.

Despite the fact that the water samples were taken on one occasion a number of priority substances were still in the range of 10 – 90% of AA-EQS (Table 5.1). Because of the scope of this study where both passive samplers and water samples were analyzed, the AA-EQS value was used for comparative purposes. Since the highest levels were mostly found in the water samples the MAC-EQS would perhaps been more appropriate. This would have increased the EQS most notably for nonylphenol, hexachlorobutadiene and tributyltin, but also for cadmium and mercury in Table 5.1.

*Table 5.1 Priority substances occurring at elevated levels in Sweden.*

Priority substance	Most commonly high levels in	Geographic pattern	Percentage of all samples > AA-EQS*	Percentage of all samples > 0.1×AA-EQS*
Nonylphenol	Unfiltrated water	Higher in southern Sweden	12%	50%
Cadmium	Unfiltrated water	Elevated levels all over Sweden	7%	57%
Tributyltin	Filtrated water	Not applicable	14%	14%
Lead	Unfiltrated water	Higher levels in southern Sweden	1%	18%
Nickel	Unfiltrated water	Higher levels in southern Sweden	1%	17%
pentaBDE	Unfiltrated water	Higher levels in southern Sweden	1%	12%
Mercury	Unfiltrated water	No geographic pattern	0%	10%
Endosulfan	SPMD	Higher levels in southern Sweden	0%	10%
oktylphenol (water),	Water	No geographic pattern	1%	7%
Hexachlorobutadiene	Unfiltrated water	Higher levels in southern Sweden	1%	8%

\* Percentage calculated on the media (i.e. filtrated, unfiltrated or passive sampler) that the substance was most commonly elevated in

## 5.3 Regional differences

As described in section 4.2 two overall geographical patterns dominated the occurrence of priority substances in Sweden:

1. Regardless of the levels of priority substances no geographical differences are apparent between different parts of Sweden.
2. Higher levels in southern Sweden

The interpretation of geographical patterns is complicated by the lower number of sampling points in northern Sweden. Nonetheless, for some substances (most noticeably nonylphenol), it is clear that the levels found are substantially higher in the more populated southern part of Sweden.

Such a pattern would be expected simply based on the higher population density and prevalence of urban areas in southern Sweden. However, most of the sampling points in northern Sweden were placed in surface waters that potentially receive priority substances from a number of sources (including urban areas, sewage treatment plants, industrial facilities etc.). Some of these sampling points were downstream and at the outlet (to the Baltic sea) of the major rivers in northern Sweden and the observed pattern could be a result of a higher dilution in these rivers compared to the smaller water system in Southern Sweden.

Sweden has adopted five national water districts in order to implement the water framework directive (<http://www.vattenmyndigheterna.se/vattenmyndigheten/>). A comparison of these water districts with regards to the quotient between the levels of priority substances and the AA-EQS values is presented in Figure 5.1.

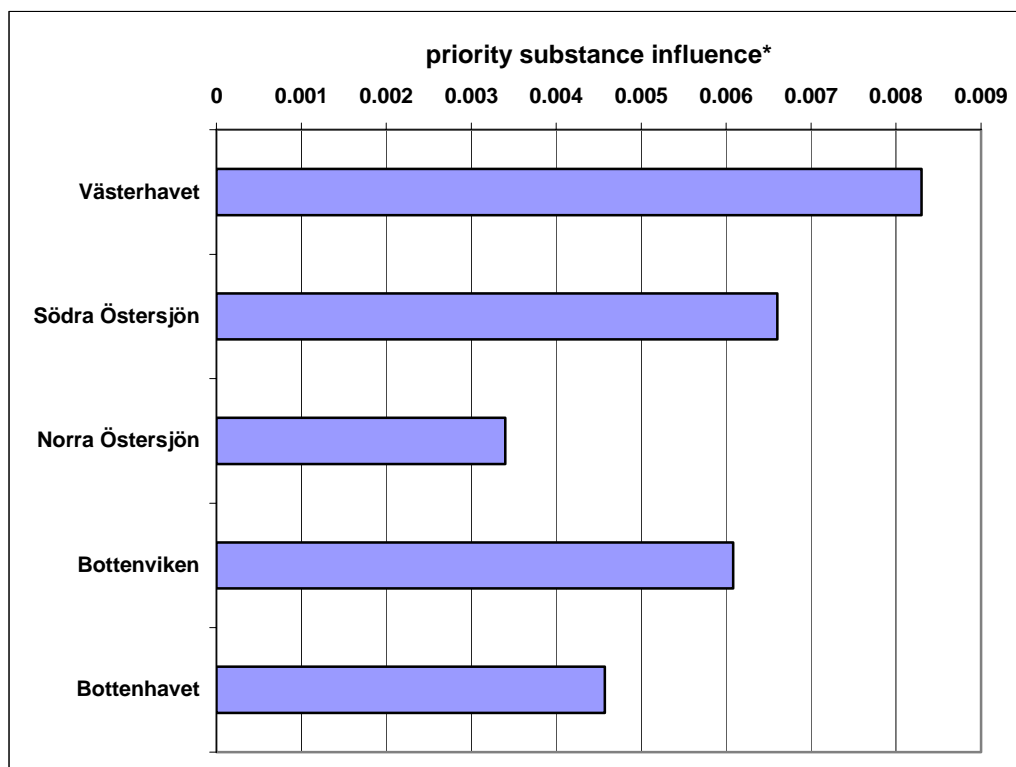


Figure 5.1 Influence of priority substances on all sampling points within different national water districts. \*Influence is here defined as the median of the ratio between the levels of all priority substances and the EQS value (equation 4.1).

As expected, there is a higher influence of priority substances on the southern water districts (Västerhavet and Södra Östersjön) compared to the water districts of northern Sweden (Norra Östersjön, Bottenviken and Bottenhavet). The difference between northern and southern Sweden seem to be lower than the EQS ratio maps indicate (Figure 4.9 - Figure 4.16). The reason is that the northern water districts had a high prevalence of concentrations < LOQ and priority substance influence in Figure 5.1 was only calculated when concentrations were above LOQ.

## 5.4 Sampling of priority substances

In annex X of the water framework directive it is stated that:

“With the exception of cadmium, lead, mercury and nickel (hereinafter “metals”) the Environmental Quality Standards (EQS) set up in this Annex are expressed as total concentrations in the whole water sample. In the case of metals the EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment.”



This would expressively exclude the use of passive samplers for the monitoring of priority substances.

A possible exception is the use of DGT for sampling of metals. Even though passive sampling of metals does not exactly equal the definition of dissolved concentrations given above (see also Figure 3.3) it is still close enough that the usage of DGT may be possible. When evaluating the data it seems that levels of metals in filtrated water were somewhat higher than in the DGT samplers (appendix 2, Figure 4.9, Figure 4.2, Figure 4.4). In order to fully compare these methods the water sampling should have been done periodically during the DGT deployment time. Nevertheless, the advantage of using a passive sampler and the small differences between DGT and filtrated water in this study warrants that the usage of DGT for sampling of priority metals should be considered.

A number of semivolatile organics substances (i.e. PAHs, chlorobenzenes, pentachlorophenol, hexachlorocyclohexane, endosulfane, trifuralin and chlorpyrifos) were detected in the SPMDs but not in the water samples. Even though SPMD sampling is not appropriate for sampling according to Annex X it is an appropriate method purely from a monitoring point of view.

On those few occasions where PAHs in SPMDs exceeded the EQS value (Figure 4.12) it was not detected in the water samples most likely because the one-time water sampling did not encompass a period of high PAH levels in the water. Another advantage with the SPMD is that for some of the substances (i.e. pentachlorobenzene, benzo(ghi)perylene + indeno(123cd)pyrene, endosulfane) the LOQ for water is higher than the AA-EQS which is not the case for SPMD. Finally, the substances sampled by the SPMD closely resemble the bioavailable fraction of contaminants in surface waters (Gourlay et al. 2005).

## 5.5 Sources of priority substances

Figure 5.2 visualizes how sampling point receiving discharges from different sources are influenced by priority substances. Influence is here defined as the ratio between levels of priority substances and their EQS values. The data is the same as that presented in the last line of Table 4.4. The data should be viewed with some caution since it is influenced by the choice of sampling points. There are for example only a few sampling points affected by landfills and a number of sampling points are influenced by several of the sources in the figure.

As expected, there is a decreasing influence from point sources and diffuse sources to unaffected background localities. It is also interesting to note that undefined urban load, probably with run off water as an integral component, seem to be the one of the most important sources of priority substances. The importance of urban run offs for

the levels of priority substances have been observed both in Ireland (Bruen et al. 2006) and England (Rule et al. 2006).

The sampling points designated as being influenced by “a mixture of industries, sewage treatment etc” (Table 3.2) also scored high on the level of priority substance influence. The reason was mostly that these sampling points were influenced by a larger number of different priority substances. This would be expected on the basis that a more differentiated mix of polluting activities would give rise to a larger set of different priority substances.

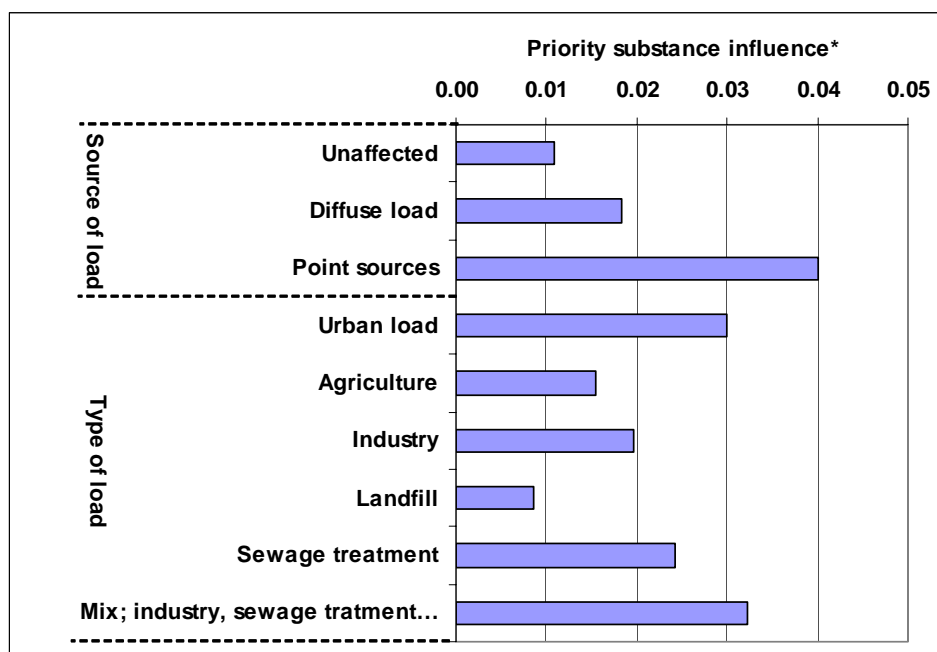


Figure 5.2 Influence of priority substances of sampling points possibly receiving discharge from different sources. \*Influence is here defined as the median of the ratio between the levels of all priority substances and the EQS value (equation 4.1). Notice that the values presented here are taken from the last line in Table 4.4

## 5.6 Conclusions and future work

This investigation has revealed that most priority substances generally occur at low levels at both unaffected and affected sampling stations with only some local sporadic levels > EQS. A few substances, most noticeably nonylphenol, cadmium and possibly TBT, pose a bigger problem from a WFD perspective. Thus, studies focusing on the reason for the elevated levels of these substances and possible measures to reduce their emissions are of importance. Of special importance in this regard is to clarify whether substances that seem to be elevated on a national level are the responsibility of regional or local authorities or if measures are to be focused on a national / international level. One way to clarify the importance of local/regional sources versus transnational

atmospheric transport would be sampling and analysis of air and rain samples from northern to southern Scandinavia.

From an environmental monitoring perspective there is an obvious need to implement analytical methods for TBT that has a LOQ < EQS. Once this is in place there is a need for a new national screening of TBT in surface water to clarify whether this is a substance of concern in this regard. Methods-wise there is also a need to clarify whether passive sampling should be a part of the monitoring of priority substances (section 5.4). One alternative could be to use passive sampling to identify those priority substances that may be of concern and thereafter using traditional sampling methods (that adheres to the directions given in the water framework directive) for those substances.

Future screening of WFD substances should perhaps focus on surface waters receiving discharge that were not to a large degree included in this investigation (landfills for instance). Also, in some instances there may be a need for a higher density of local sampling points in water systems that were profoundly influenced by priority substances although the question remains whether this should be a focus of national screening or local monitoring

Increased focus on screening of priority substances closer to possible sources could also be of interest. The most obvious example are sludge, waste water (at the outlet of polluting activities) and run off water. Given the surprisingly high levels of priority substances in the sampling points designated as background areas there is a need for more sampling at background stations to delineate whether different priority substances originates from local / regional or national / international sources.

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