

SWECO Environment Screening Report 2008:5

(Co-)occurrence in different matrices of WFD priority substances

An expanded analysis of data from an earlier screening

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Sammanfattning

Bakgrund och metodik

Inom screeningprogrammet år 2006 hade SWECO i uppdrag från naturvårdsverket att mäta och utvärdera förekomsten av vattendirektivets prioriterade ämnen i ytvatten i Sverige. Mätningar gjordes vid 95 ytvattenlokaler i Sverige (främst limniska men också några få kustnära). De vattenmatriser som prioriterade ämnen mättes i var filtrerat vatten, ofiltrerat vatten samt den lösta, icke fastlagda fraktionen som mättes med passiva provtagare. Studien omfattade ett mycket stort geografisk område (1800 km från nord till syd), i en rad olika typer av ytvattenförekomster i både bakgrundsområden, urbana områden och nära punktutsläpp. Således utgjorde studien och det insamlade datamaterialet ett utmärkt underlag för att utvärdera samförekomst av prioriterade ämnen samt vilka matriser dessa vanligen förekommer i.

Den tidigare screeningrapporten fokuserade inte på detaljerade datautvärderingar utan snarare på att dra slutsatser om vilka som var de viktigaste prioriterade ämnen, de viktigaste källorna till dessa samt om det fanns geografiska skillnader i deras förekomst. Därför har SWECO fått uppdraget att genomföra en mer detaljerad utvärdering av resultaten från 2006 års screening av prioriterade ämnen inom vattendirektivet. Syftet med detta arbete har dels varit att utvärdera i vilka matriser som prioriterade ämnen (främst metaller) förekommer i, och dels att utvärdera samförekomsten mellan alla påträffade prioriterade ämnen.

Utvärderingen baseras på att uppmätta halter har bearbetats med en rad parametriska statistiska metoder såsom korrelationsanalys, regressionsanalys och principal komponent analys. Även icke-parametriska statistiska metoder användes.

Resultat och rekommendation

Följande generella slutsatser kunde dras av datautvärderingen:

- Sambandet mellan halter av nickel i filtrerat vatten (vilket är den gällande matrisen för metaller enligt vattendirektivet) och halter uppmätta med passiva provtagare (DGT) var tillräckligt bra för att sådana provtagare kan användas för övervakning av nickel. För kadmium var motsvarande samband svagare och för bly fanns det inget samband mellan halter uppmätta med passiva provtagare och vattenhalter.
- Skillnaderna mellan halter i vattenprover och halter uppmätta med passiva provtagare (SPMD) för organiska prioriterade ämnen var så pass stora att SPMD inte kan användas för övervakning inom ramen för vattendirektivet när syftet är att fastställa kemisk status. SPMD är dock ett bättre verktyg än

direkt vattenprovtagning för att utröna *vilka* organiska icke-volatila fettlösliga ämnen som förekommer i ytvattnet.

- PAH med 3 – 5 ringar samvarierar mycket tydligt i svenska ytvatten. PAH ämnen samvarierar dock inte med andra prioriterade ämnen.
- I huvudsak så samvarierade inte andra (icke PAH) organiska prioriterade ämnen. Vissa undantag fanns dock, t.ex. för klorbensener.
- De flesta vattenprover hade ingen avvikande sammansättning av prioriterade ämnen. Några provtagningspunkter avvek dock tydligt pga. av höga PAH halter eller pga. av höga metallhalter.

En generell slutsats och rekommendation är att förenklingar och modifieringar av övervakningsprogram av den kemiska ytvattenstatusen till viss del bör baseras på lokala förhållanden. Detta kan t.ex. gälla geokemiska förhållanden, samt vad tidigare övervakning visat och vilka misstänkta föroreningskällor som finns. Dock bör metoden som används för att modifiera och/eller reducera övervakningsprogram baserat på lokala förhållanden, fastställas nationellt eller regionalt .

Summary

Background and methods

Within the screening program of 2006 SWECO has had the assignment from the Swedish Environmental Protection Agency to measure the occurrence of WFD priority Substances in limnic and coastal surface waters of Sweden. Measurements were made at 95 locations in whole water samples, filtered water samples and using passive sampling techniques which measures the free (non associated) concentrations. The data set represented a large number of aquatic sites over a broad geographical range (1800 km) in different surface water matrices which made the data set ideal for further evaluations of both the co-occurrence of priority substances as well as the occurrence in different water matrices.

Since detailed data analysis was not the focus of the previous report, SWECO Environment was contracted by the Swedish Environmental Protection Agency to statistically evaluate the data from the screening study of WFD priority substances performed 2006. The objective of the work was to evaluate which surface water matrices that WFD metals mainly occur in and to evaluate the co-variability of priority substances.

The analysis was done by using various parametric statistical techniques such as correlation, regression, principal component analysis as well as non parametric statistical methods.

Results

Some general conclusions from this study were:

- The relationship between concentrations of nickel in filtered water and concentrations obtained through passive (DGT) sampling is reliable. It may thus be possible to use DGT for monitoring of nickel within the water framework directive. For cadmium the relationship is less clear while it is non-existent for lead. These conclusions are supported by studies in other countries.
- The difference in concentrations of lipophilic organic substances in SPMDs compared to filtered and whole water is so large that SPMDs will not be suitable for compliance monitoring according to the water framework directive.
- There is a very close co-variability between 3 – 5 ring PAH compounds in Swedish surface waters, and PAH compounds do not correlate with other priority substances.
- Most other (non PAH) priority substances did not correlate well with each other.

- Most sampling stations do not separate from each other with regards to their priority substance composition.
- The multivariate analysis also revealed that a few sampling points clearly deviated from the majority of sampling stations due to high concentrations of either PAHs or metals.

One general conclusion is that modifying samplings programs to simplify and modify priority substance monitoring may have to be done on a local level based on geo-chemical conditions, information from prior sampling programmes and the type of diffuse and point sources that may affect a surface water system. How these factors should affect monitoring should perhaps be decided on a national and regional level.

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.

In 2006, the European Commission issued a list of environmental quality standards for concentrations of chemicals in surface water. These standards relate to chemical pollutants identified as 'priority substances' under the European Water Framework Directive (WFD). Within the screening program of 2006 SWECO VIAK has had the assignment from the Swedish Environmental Protection Agency to measure the occurrence of WFD priority Substances in limnic and coastal surface waters of Sweden.

Measurements were made at 95 locations in whole water samples, filtered water samples and using passive sampling techniques which measures the free (non associated) concentrations. The data set obtained was unique since it represented a large number of aquatic sites over a broad geographical range (1800 km) in different surface water matrices. The resulting report

(http://www.naturvardsverket.se/upload/02_tillstandet_i_miljon/Miljoovervakning/rapporter/miljogift/rapport_vattendirektivsamnen.pdf) mainly identified the most problematic substances from a WFD point of view as well as discussing possible sources of these substances and broad geographical patterns.

The large data set and a high variability in many measured parameters make the data set ideal for further evaluations of both the co-occurrence of priority substances as well as implications of occurrence in different matrices. This is reinforced by the fact that the measurements were made relatively close in time (within three weeks) which to some degree eliminates the problem of temporal variations when evaluating geographically widespread data.

Since detailed data analysis was not the focus of the previous report, SWECO Environment has got the assignment from the Swedish Environmental Protection

Agency to statistically evaluate the data from the screening study of WFD substances performed 2006.

1.2 Objectives

In order to facilitate data evaluation, a number of clearly stated objectives were decided upon:

- Evaluate which surface water matrices (associated with large or small particles or non-associated) that WFD substances mainly occur in which also affect the interpretation of future sampling results. This mostly applies to metals which are the substances that consistently occurred in all three phases.
- Evaluate the co-variability of different substances to understand which substances and/or substance groups co-vary. This facilitates planning of monitoring of WFD substances since this type of information can be used to reduce sampling scope by focusing on fewer substances.

2 The screening study of 2006

In this section, the screening of WFD substances in 2006 is presented in order to facilitate an understanding of the data set that is evaluated.

2.1 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 and taking into account the purpose of the screening.

2.1.1 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 were chosen.

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

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 2.1 - Table 2.2

Table 2.1 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.

Limnic (freshwater) sampling stations			
<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

Marine / Coastal sampling stations			
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 2.2 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

2.1.2 Locations

An overview of the sampling stations in Sweden is presented in Figure 2.1. 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.

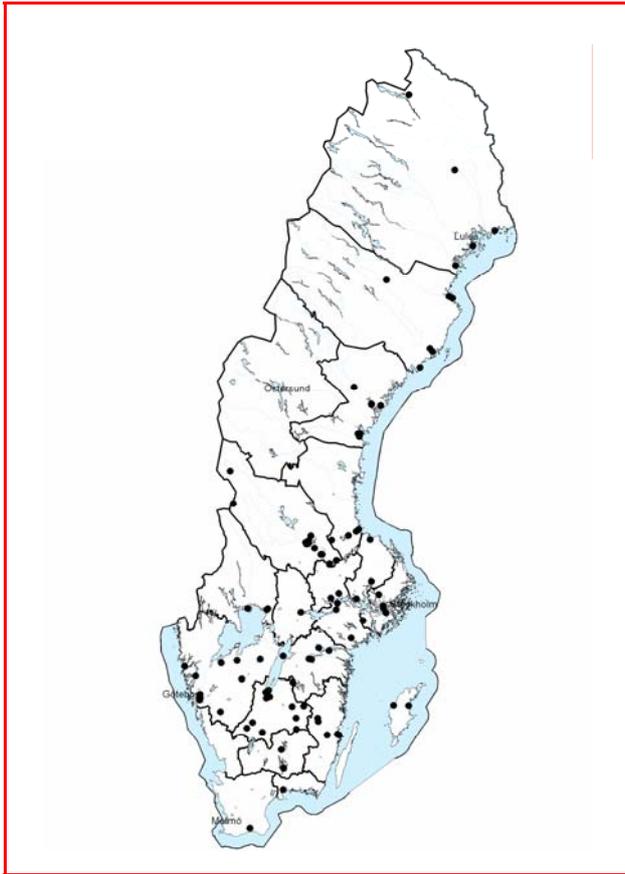


Figure 2.1 Location of sampling points for WFD priority substances in Sweden.

2.2 Sampling

2.2.1 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 2.2); (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. The exception is passive sampling of metals where the last fraction may also contain small inorganic/organic complexes.

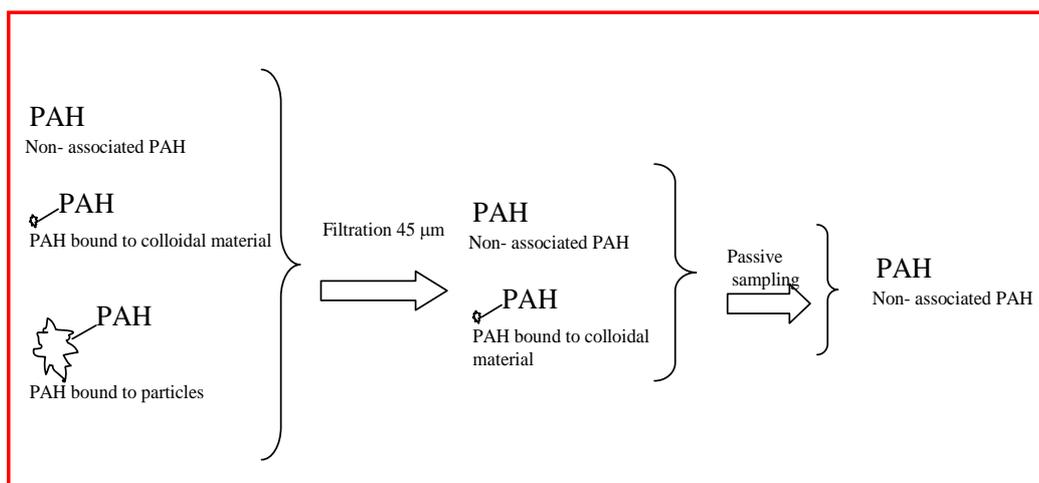


Figure 2.2 Schematic representation of which substance fraction that is sampled. Here exemplified by PAHs, but the principle is valid for all substances sampled.

2.2.2 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. Results from the POCIS sampling will not be presented or evaluated since no substances were found using the POCIS sampler.

2.2.2.1 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 2.3). The sampler consists of a stainless steel canister (Figure 2.6) that holds from one to five spider carriers with membranes.



Figure 2.3 Spider carrier with mounted lipid filled membrane for SPMD sampling.

2.2.2.2 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 2.4) 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 2.2).

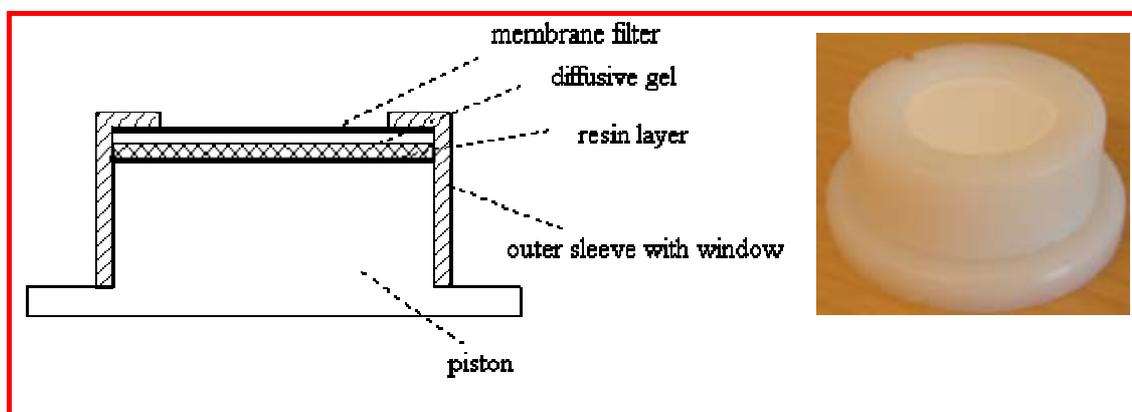


Figure 2.4 Cross section of a DGT passive sampler and a picture of the assembled unit.

2.2.2.3 FIELD DEPLOYMENT OF PASSIVE SAMPLER

The SPMD and POCIS samplers were placed in a perforated metal canister (Figure 2.6). 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 2.5.

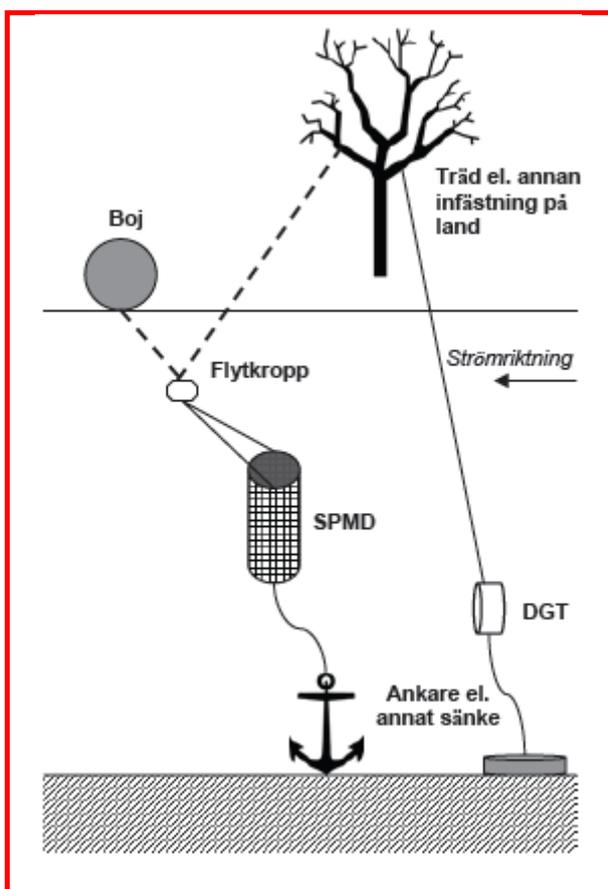


Figure 2.5 Typical deployment setup of passive samplers (in Swedish). From Lindström 2006.

The samplers were deployed for 4 – 6 weeks. The exact time was noted and used in the calculations of the water concentrations (section 0). 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 2.3.2.2)

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 minimize 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 2.6 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 2.6.

2.2.3 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 2.3).

2.3 Measured parameters

2.3.1 Water

In filtered and unfiltered water all the priority substances were analysed..

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 2.2 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 2.2) 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.

2.3.2 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 that were both collected and analyzed in the passive samplers as well as detected in passive samplers are given in table 2.3.

Table 2.3 WFD substances that were measured in passive samplers.

Substance	Passive sampler
Anthracene	SPMD
pentaBDE	SPMD
Cadmium	DGT
Chlorfenvinphos	SPMD
Chlorpyrifos	SPMD
Di(2-ethylhexyl)phthalate (DEHP)	SPMD
Endosulfan	SPMD
Fluoranthene	SPMD
Hexachlorobenzene	SPMD
Hexachlorocyclohexane	SPMD
Lead	DGT
Mercury	DGT
Naphthalene	SPMD
Nickel	DGT
Pentachlorobenzene	SPMD
Pentachlorophenol	SPMD
(Benzo(a)pyrene),	SPMD
(Benzo(b)fluoranthene),	SPMD
(Benzo(g,h,i)perylene),	SPMD
(Benzo(k)fluoranthene),	SPMD
(Indeno(1,2,3-cd)pyrene)	SPMD
Trichlorobenzenes	SPMD
Trifluralin	SPMD

2.3.2.1 CALCULATIONS OF WATER CONCENTRATIONS FROM SPMD MEASUREMENTS

The calculations of water concentrations based on the analyte concentration in the SPMD are dependent on whether the uptake is linear or whether equilibrium conditions control the uptake (Figure 2.7). 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.

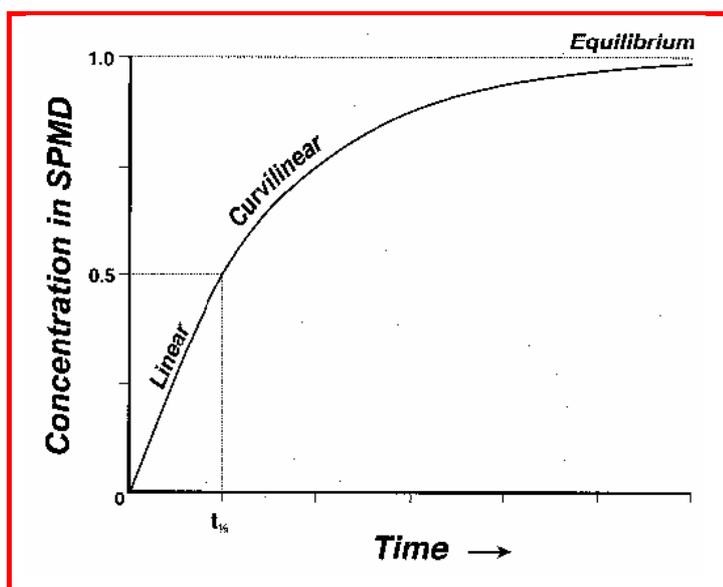


Figure 2.7 The evolution of analyte concentration in the SPMD membrane over time.

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):

$$N = N_0 \exp(-k_e t) \quad (2.1)$$

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

$$k_e = -(\ln(N/N_0))/t \quad (2.2)$$

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.

2.3.2.2 CALCULATIONS OF WATER CONCENTRATIONS FROM DGT MEASUREMENTS

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, Δg 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 Results

Summary statistics on the levels of priority substances in surface water is summarized in Table 3.1. More detailed presentations of the results are given in SWECO VIAK (2006).

Table 3.1 Levels of priority substances in surface waters in Sweden. Only data > LOQ were used in the calculations

Name	Sampling	Unit	AA-EQS	Mean	Median	Percentile					Min	Max
						5:e	25:e	50:e	75:e	95:e		
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(ghi)perylene + indeno(123cd)pyrene	SPMD	pg/l	2000	162	36	15	25	36	68	362	13	4300
Sum benzo(b+k)fluoranthene	SPMD	pg/l	30000	1219	62	15	41	62	158	698	10	38300
Octylphenols	Filtrated	µg/l	0,1	0,022	0,018	0,018	0,018	0,018	0,025	0,030	0,018	0,031
Nonylphenols	Filtrated	µg/l	0,3	0,26	0,21	0,15	0,16	0,21	0,29	0,489	0,15	0,70
Tributyltin compounds	Filtrated	µg/l	0,0002	0,0029	0,0031	0,0016	0,0025	0,0031	0,0034	0,0040	0,0014	0,0041
Trichloromethane	Filtrated	µg/l	2,5	0,20	0,24	0,10	0,1	0,24	0,26	0,28	0,10	0,29
Pentabromodiphenylether	Unfiltered	µg/l	0,0005	0,00035	0,00025	0,00021	0,00022	0,00025	0,00029	0,00083	0,00021	0,0012
Octylphenols	Unfiltered	µg/l	0,1	0,075	0,047	0,018	0,020	0,047	0,10	0,18	0,017	0,21
Nonylphenols	Unfiltered	µg/l	0,3	0,27	0,21	0,11	0,16	0,21	0,28	0,86	0,010	1,11
Tributyltin compounds	Unfiltered	µg/l	0,0002	0,0034	0,0034	0,0030	0,0032	0,0034	0,0037	0,0039	0,0029	0,0039
Trichloromethane	Unfiltered	µg/l	2,5	0,29	0,25	0,15	0,22	0,25	0,31	0,54	0,13	0,66
Hexachlorobutadiene	Unfiltered	µg/l	0,1	0,038	0,013	0,012	0,012	0,013	0,014	0,14	0,012	0,19

4 Statistical evaluations

In the following sections, the statistical evaluations of the screening results are presented divided according to the stated purposes in section 1.2.

4.1 Substances in different matrices and sampling methods

As shown in Table 2.1, WFD substances may occur in any of the three mentioned matrices. Which matrix they occur in has implications for the risks that WFD substances pose to the environment, as well as how future sampling programs are designed.

Substances associated with particles will be much less bioavailable than non-bound pollutant (NRC 2003). The reason is that in most cases and for most exposure pathways, cells are much less prone to take up particles compared to free molecules (NRC 2003, Poet and MacDougal 2002). Even particles bound to colloidal organic material (DOC) will to a certain degree be less bioavailable than non-associated substances (Gallé et al. 2005).

However, the sampling matrices are pre-determined in the water framework directive. In annex X 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.”

Monitoring programmes which ensure compliance with the WFD standards consequently has to use spot sampling techniques to acquire the pollutant levels. A major problem with spot sampling is that it does not take account of variations in pollutant concentrations that occur in the periods between samples. Estimates of pollutants concentrations can be improved by sampling more often, but this can prove time consuming and expensive. Instead, the usage of passive samplers may be possible. These provide time-weighted average (TWA) concentrations of labile (non associated) concentrations in the water phase.

4.1.1 Metals

The phrasing in annex X of the Water Framework Directive 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 in annex X (see also Figure 2.2) it is still close enough that the usage of DGT may be possible. If passive sampling is to be used generally as a national monitoring tool within the water framework directive it is necessary to show that there is a correlation between TWA concentrations and concentrations in filtered water across all the types of waters that may be encountered in Sweden. Thus, the data set obtained in the screening of surface waters in 2006 is especially suited for this purpose because of the broad geographical range. Metals (Cd, Ni and Pb) were the only substances that consistently occurred in the whole water samples, filtered water samples and labile / non associated (sampled with DGT). Consequently it was possible to explore in detail the co-variability between Ni, Cd and Pb in these matrices (Figure 4.1 - Figure 4.3).

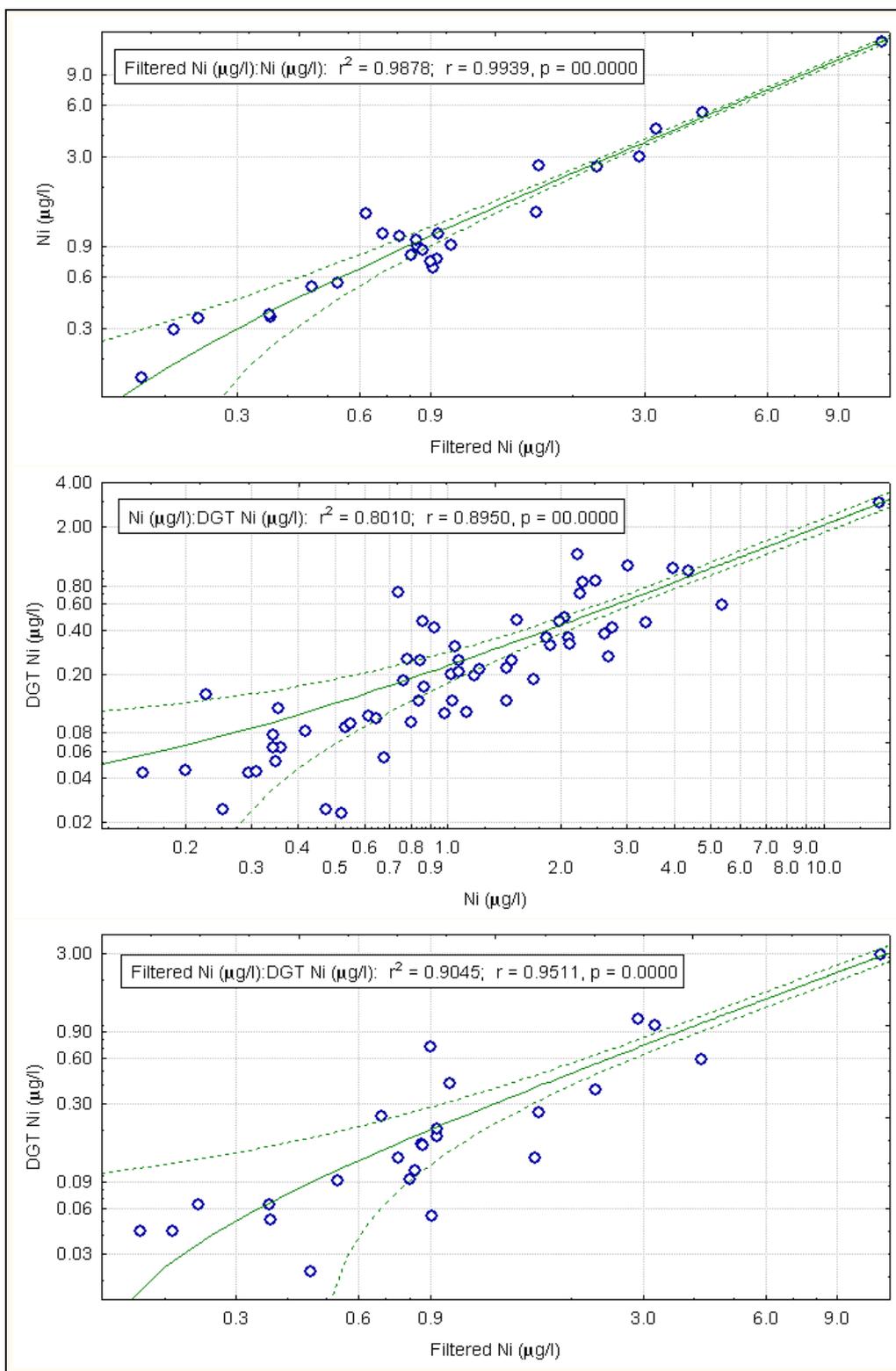


Figure 4.1. Co-variability between nickel measured in different water matrices in surface waters in Sweden. The solid line represents the linear regression line while the dotted line represents the confidence interval which gives information on the expected value of the dependent variable with a 95% probability. All axis scales are logarithmic.

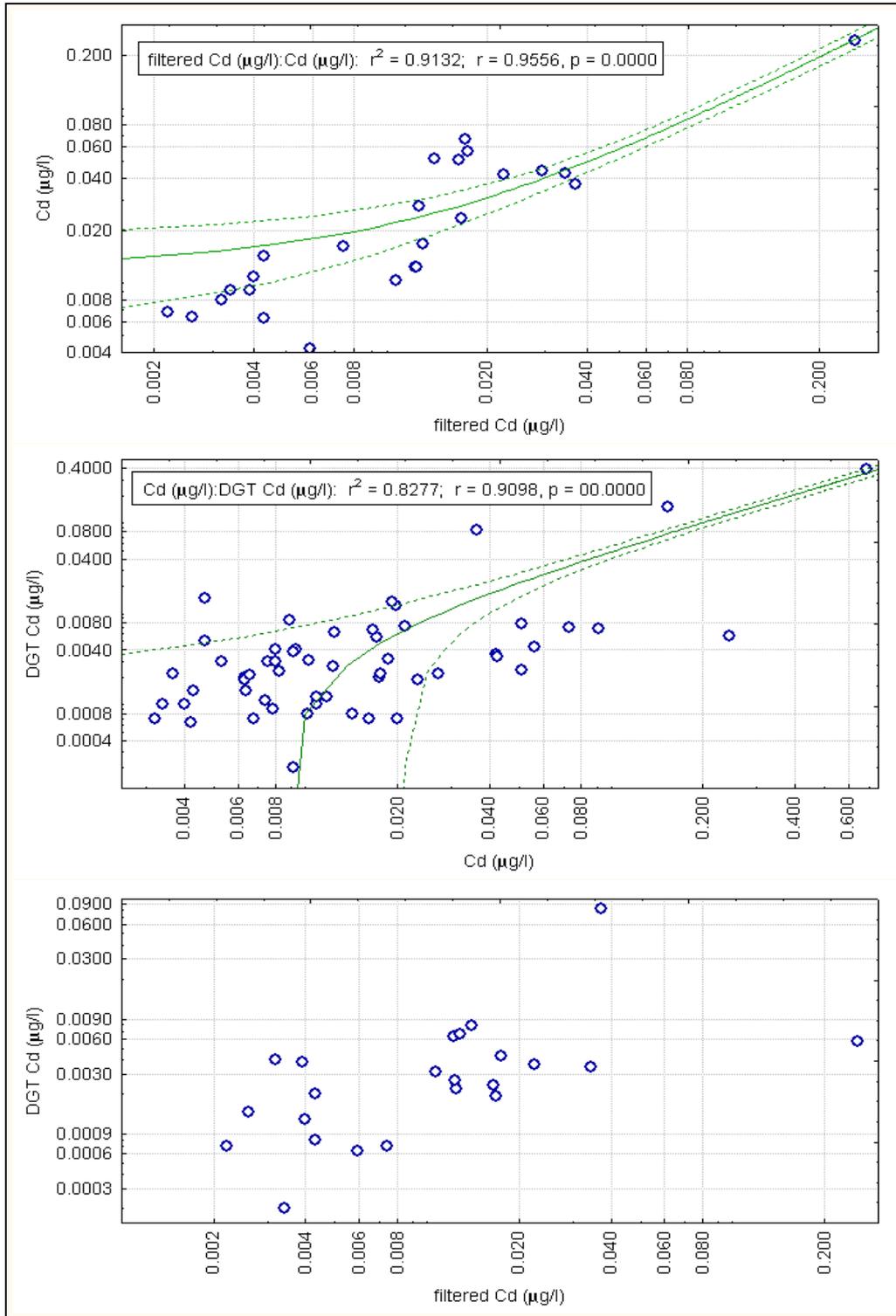


Figure 4.2. Co-variability between nickel measured in different water matrices in surface waters in Sweden. The solid line represents the linear regression line while the dotted line represents the confidence interval which gives information on the expected value of the dependent variable with a 95% probability. All axis scales are logarithmic.

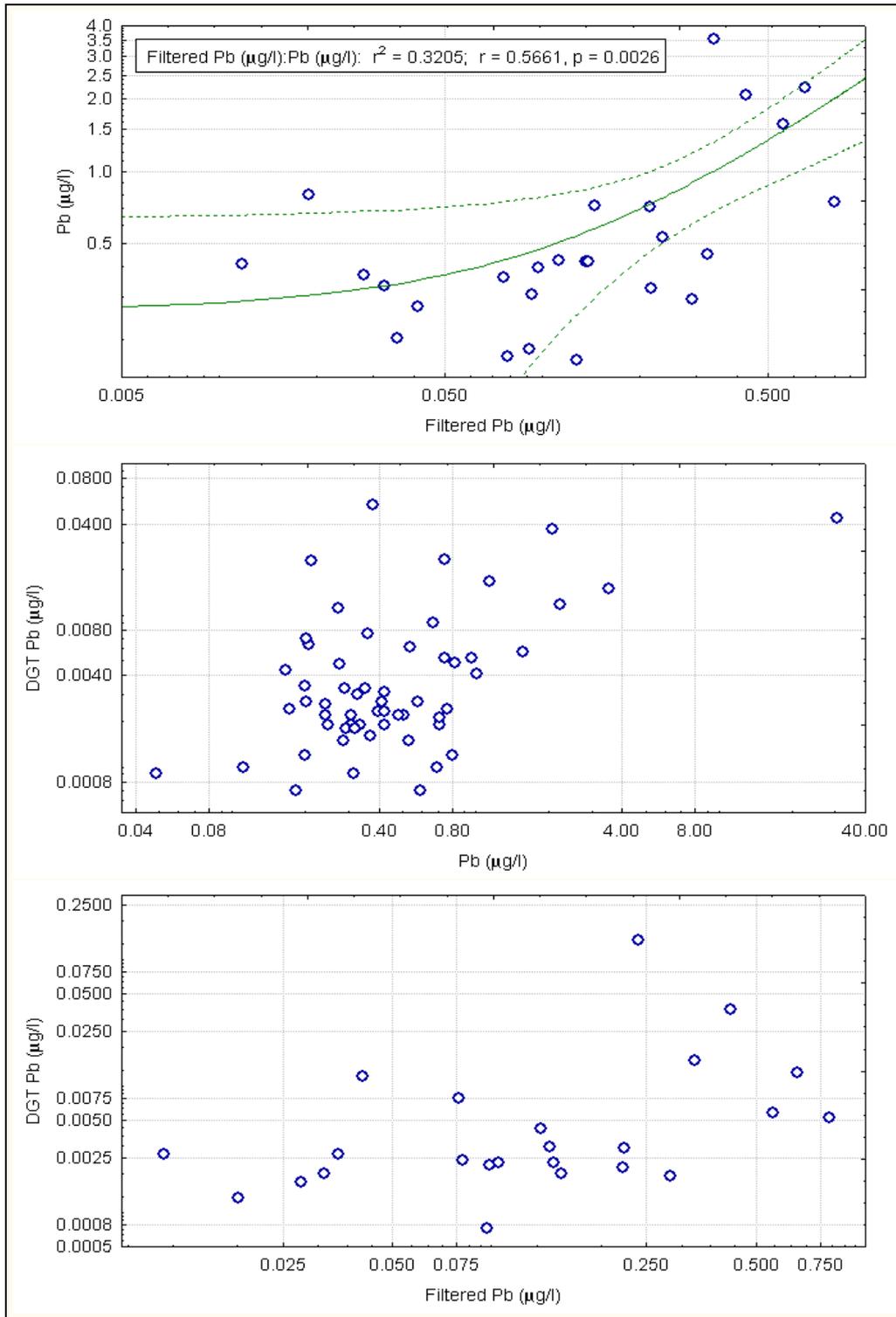


Figure 4.3. Co-variability between lead measured in different water matrices in surface waters in Sweden. The solid line represents the linear regression line while the dotted line represents the confidence interval which gives information on the expected value of the dependent variable with a 95% probability. All axis scales are logarithmic.

Nickel

Nickel sampled with passive samplers clearly co-varied with nickel in filtered water and whole water samples (Figure 4.1). The passive samplers were employed for one month while the water samples were one times samples taken when the passive samplers were deployed. A good correlation between DGT sampling and “one shot” sampling of water indicates:

- that the levels of nickel in surface waters are relatively even over time.
- that there exists a relatively stable equilibrium between dissolved nickel and nickel sorbed to colloidal and larger particles.

Nickel is introduced into the hydrosphere by removal from the atmosphere, by surface run-off, by discharge of industrial and municipal waste, and also following natural erosion of soils and rocks (Inchem 1991). It is consequently a widespread metal with multiple sources which corroborates that levels in surface waters are stable over time. On the other hand, if soils and surface run-off are important sources it would indicate that the levels in surface waters fluctuate with precipitation.

The linear regression equations with nickel in water samples as the dependent variable are:

$$\text{Ni (filtered)} = 0.08 + 0.80 * \text{Ni (whole water)}; r^2=0.91, p<0.00001 \quad (4.1)$$

$$\text{Ni (filtered)} = 0.25 + 3.6 * \text{Ni (DGT)}; r^2=0.99, p<0.00001 \quad (4.2)$$

$$\text{Ni (whole water)} = 0.22 + 3.9 * \text{Ni (DGT)}; r^2=0.89, p<0.00001 \quad (4.3)$$

A recent study aimed to evaluate whether the performance of passive sampling devices (DGT) supports their application in regulatory monitoring of trace metals in surface waters. This was tested through consecutive and overlapping deployments (7–28 days) in the River Meuse (The Netherlands). In order to evaluate the consistency of these TWA labile metal concentrations, they were assessed against total and filtered concentrations measured at relatively high frequency (Allan et al. 2008).

In the Dutch study, the filtered fraction of Nickel as a percentage of the total concentration was 81%. This corroborates very well with the slope of the linear regression (equation 4.1) which indicates that the concentrations in filtered water samples is approximately 80% of the concentration in whole water samples.

Also, water concentrations were 4 – 5 times higher in whole water samples compared to TWA concentrations in the Dutch study. This also corroborates well with the results from the linear regression (equation 4.3) which indicates that the concentration in whole water samples is approximately 4 times higher in whole water samples compared to TWA concentrations obtained through DGT sampling.

Taken together, the present study and the Dutch study indicates that the obtained relationship between concentration of nickel in filtered water, which is the parameter to be measured according to Annex X of the WFD, and TWA concentrations obtained through DGT sampling, is reliable, so that it may be possible to use DGT for monitoring of nickel within the water framework directive. Equation 4.2 could then be used to convert concentrations obtained by DGT to filtered water concentrations. It is also important to notice that the relationship is stronger at higher nickel concentrations (Figure 4.1) which is important for regulatory purposes.

Cadmium

For cadmium, the relationship between TWA concentrations and concentrations in filtered and whole water samples were much less clear (Figure 4.2). Especially, the relationship between filtered water and TWA concentrations were non significant which excludes DGT as a *general* tool for monitoring of cadmium in surface waters. The correlation between TWA concentrations of cadmium and cadmium in filtered water was retested by excluding outliers¹ (defined by those data points whose standard deviation of residuals is $> \pm 3$). This did not improve correlations however.

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. Furthermore, cadmium deposition in southern Sweden originates from coal burning in neighbouring countries (Swedish Chemicals Agency, KEMI 2004). The previous screening report demonstrated geographical patterns of cadmium with no discernible geographic differences in the frequency of elevated levels (SWECO VIAK 2007). Cadmium levels in background stations were at par with other sources which may be explained by acidification of forest soils which have increased the leaching of cadmium to surface waters (Swedish Chemicals Agency, KEMI 2004). Taken together, these results indicate that cadmium levels in surface water could be relatively even over time since many different (diffuse) sources contribute (SWECO VIAK 2007).

Consequently, the reason for the non significant correlation between TWA cadmium concentrations and concentrations in filtered water may not be that the levels in surface waters fluctuate over time. Another reason could be that the fraction taken up in the DGT sampler fluctuates between different types of waters. In the Dutch study there seemed to be a good agreement between the filtered concentrations of Cd and the labile TWA concentrations obtained using DGT (Allan et al. 2008). That study fo-

¹ Outliers are atypical data points which do not appear to follow the characteristic distribution of the rest of the data. These may reflect genuine properties of the underlying phenomenon (variable), or be due to measurement errors or other anomalies. Because of the way in which the regression line is determined outliers have a profound influence on the slope of the regression line and consequently on the value of the correlation coefficient. A single outlier is capable of considerably changing the slope of the regression line and, consequently, the value of the correlation. Outliers may not only artificially increase the value of a correlation coefficient, but they can also decrease the value of a "legitimate" correlation

cused on one river only and it may be that DGT is a valid tool for monitoring of Cd within water bodies with particular geochemical conditions. This has to be tested using passive sampling combined with multiple spot sampling during the deployment time. Such tests could be performed either regionally or in surface waters representing specific geochemical conditions such as hardness.

The linear regression for filtered water concentrations of cadmium versus whole water was:

$$\text{Cd (filtered)} = 0.90 * \text{Cd (whole water)}; r^2=0.90, p<0.00001 \quad (4.4)$$

This relationship was heavily dependent on one very high cadmium concentration. If the high cadmium concentration was excluded together with one more outlier a new regression equation was obtained:

$$\text{Cd (filtered)} = 0.28 * \text{Cd (whole water)}; r^2=0.8, p<0.00004 \quad (4.5)$$

In the Dutch study, the filtered fraction of cadmium as a percentage of the total concentration was 29%. This corroborates very well with the slope of the *modified* linear regression (equation 4.5) which indicates that the concentrations in filtered water samples is approximately 28% of the concentration in whole water samples for cadmium.

Lead

For lead, the relationship between time weighed average concentrations obtained through DGT sampling and concentrations in filtered and whole water samples were the least significant of the WFD metals (Figure 4.3). Especially, the relationship between filtered water and TWA concentrations were non significant which excludes DGT as a general tool for monitoring of lead in surface waters. The correlation between TWA concentrations of lead and lead in filtered water was retested by excluding outliers. This did not improve the correlation however.

In the Dutch study, DGT samplers showed low accumulation of lead and generally large uncertainty on the measured TWA concentrations owing to a very small labile fraction. The main explanation is a possibly a strong association with organic colloids that is not taken up into the passive sampler (Allan et al. 2008). Also, the spread of the spot sampling data was large during the relatively short sampling period (maximum of 28 days) during the Dutch study, which may also explain why spot sampling and DGT sampling did not correlate well.

The linear regression for filtered water concentrations of lead versus whole water was significant but not very strong:

$$\text{Pb (filtered)} = 0.1 + 0.15 * \text{Pb (whole water)}; r^2=0.32, p<0.05 \quad (4.6)$$

In the Dutch study, the filtered fraction of lead as a percentage of the total concentration was 16% (Allan et al. 2008). This corroborates very well with the slope of the linear regression (equation 4.6) which indicates that the concentrations in filtered water samples is approximately 15% of the concentration in whole water samples for lead.

4.1.2 Organic WFD substances

Very few organic WFD substances occurred in more than one sampling matrix. Also, the difference in concentrations of lipophilic organic substances in SPMDs compared to filtered and whole water is so large that SPMDs will not be suitable for compliance monitoring according to the water framework directive. They can however be used as conservative initial measurement tools to assess which lipophilic organic substances that are present in a water body. This information can be used to reduce the scope and costs of chemical analysis of the water samples. For several important organic WFD substances, most noticeably nonylphenol and TBT, no validated passive sampler method exists at present. Efforts to remedy this are however on the way (Arditsoglou and Voutsas 2007, Aguilar-Martínez 2008).

The organic substances that occurred in more than one matrix at more than two sampling points are presented in Figure 4.4. Table 4.1 shows a statistical comparison between the concentrations in different matrices for nonylphenol and pentaBDE.

Table 4.1 Statistical analysis to test whether there are any significant differences between the concentrations in different matrices for nonylphenol and pentabDE.

	<i>Mann whitney U test</i> ²	<i>Wilcoxon matched pair test</i> ³	<i>Sign test</i> ⁴
filtered nonylphenol vs. non-filtered	not significant	not significant	not significant
SPMD pentaBDE vs non-filtered pentaBDE	not significant	significant (Z=2,7; p<0,05)	significant (Z=2,7; p<0,05)

Non parametric statistical tests and significance¹

¹ The more common parametric methods, assume a normal distribution of the data. Since most natural concentration data (including the data from this study) is commonly not normally distributed it is more appropriate to use non-parametric methods. Non-parametric methods do not rely on assumptions that the data are drawn from a given probability distribution and are also more robust for smaller sample sizes than parametric methods.

² Non-parametric test for assessing whether two samples of observations come from the same distribution. The null hypothesis in the Mann-Whitney test is that the two samples are drawn from a single population, and therefore that their probability distributions are equal. The test requires the two samples to be independent, and the observations to be ordinal or continuous measurements

³ The wilcoxon matched pair test is a non-parametric statistical hypothesis test for the case of two related samples or repeated measurements on a single sample

⁴ The test is applicable to situations with two measures for each subject and wants to establish that the two measurements are different. The test can be used to test the hypothesis that there is no difference between the continuous distributions of two random dependent variables.

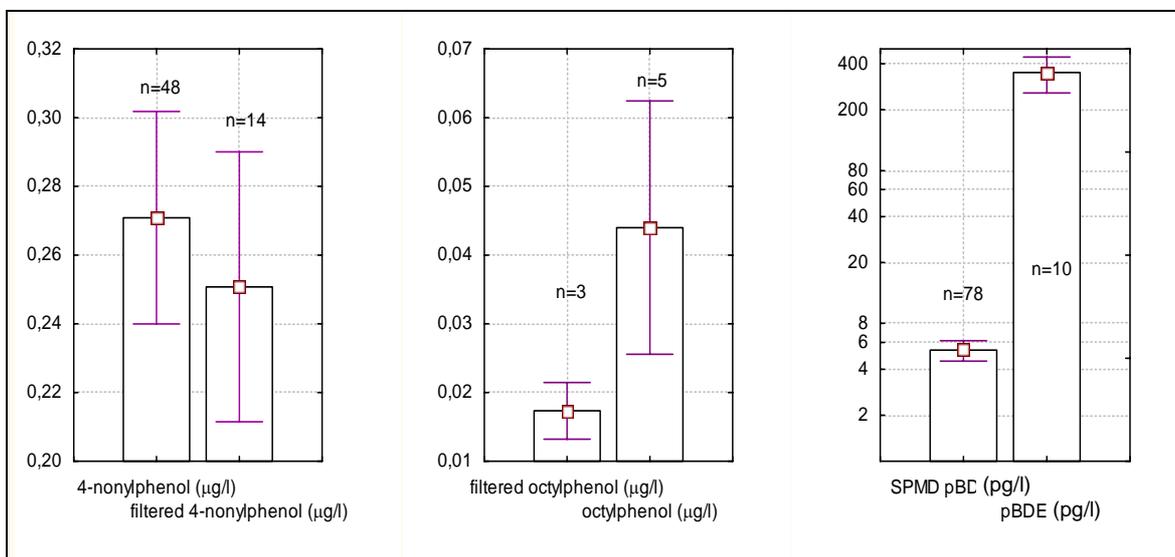


Figure 4.4 A comparison of concentrations of organic substances in different sampling matrices. Bars represent the mean while whiskers represent 0.95*SE (Standard Error). Note the logarithmic scale for pBDE.

4.2 Co-occurrence of WFD substances

Priority substances may have similar or dissimilar uses and/or physicochemical properties, and this will affect their tendency to co-occur. This has implications for future sampling strategies. If, for substances clearly co-occur, monitoring programs may be designed to focus on specific substances that simultaneously represents one or more other substances.

A very efficient way of exploring the co-relationship is to use Principal Component Analysis (PCA) which is a method that can be used to identify co-varying variables in data sets with many variables. In this way, the original variables (=priority substances) are projected into linear combinations of the variables. These linear combinations are denoted principal components.

In this study, the concentration data were log transformed and standardized to the mean 0 and variance 1 before PCA analysis. Only substances and matrices with more than 30 detects were used in the PCA analysis.

The resulting PCA model, explained 60 % of the variation with the first four principal components (Figure 4.5). The resulting PCA plot is shown in Figure 4.6. In the PCA plot, variables close to another tend to co-vary more than variables at larger distances. Also, variables that are close to zero on the (principal component) scale tend to contribute less to the overall variability than those that are further from zero.

The most prominent feature of the multivariate evaluation is the very close co-variability between PAH compounds (Figure 4.6 - Figure 4.7) as well as the fact that PAHs do not co-occur with other compounds (Figure 4.6). The fact that PAH compounds separates from other WFD compounds could be because of different physicochemical properties of PAH compounds. However, many of the organic lipophilic WFD substances have Kow values in the same range as the PAHs. Another more likely explanation is that the PAH substances mainly originate from other sources (hydrocarbon fuels, incineration processes and as components of tar and creosote oils) than the other WFD substances (Rule et al. 2006, Økland et al. 2005).

Within the PAH group there are differences in how well the substances co-vary. PAH substances with more than 3 rings co-vary to a better degree than 3 ring PAHs (Figure 4.7). This is most likely because of a higher water solubility and lower Kow of the 3 ring PAHs. Naphthalene (a 2 ring PAH) occurs separately from the other PAHs. This may be because of much higher water solubility, but it may also be a result of a different usage pattern since naphthalene is used in paint products and surface coating products.

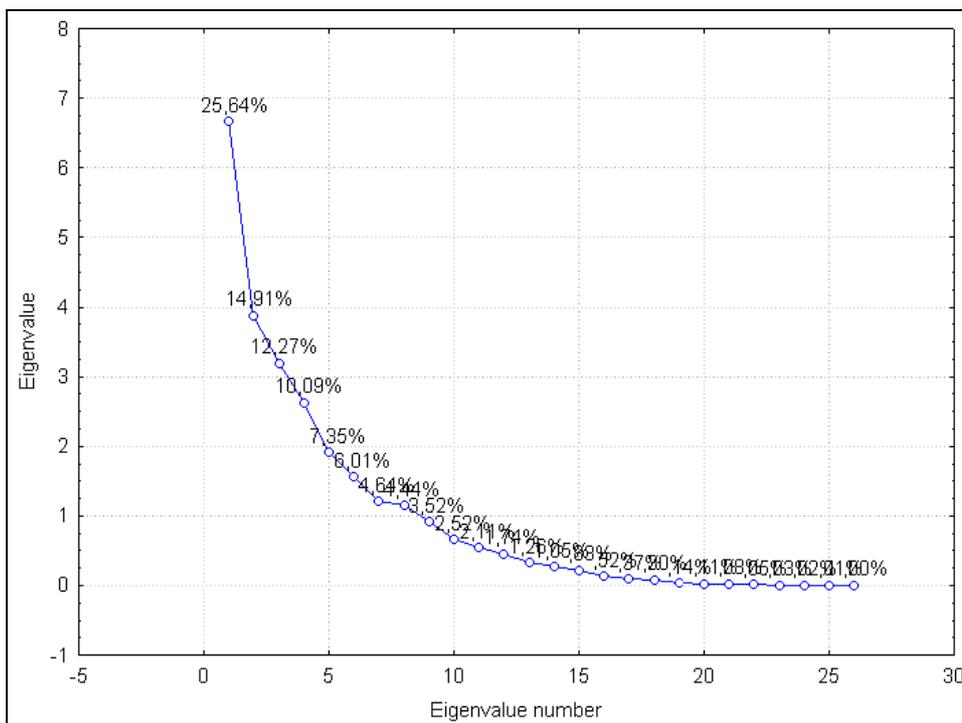


Figure 4.5 Graph showing how much of the total variation in the data set that is explained by each principal component. Eigenvalue number is equal to the principal component number.

PAHs dominate the first principal component while metals and chlorobenzenes dominated PC2 and PC3 respectively (Table 4.2). In general, the co-variability between substances that mostly varies on PC2 was lower than for PAHs (compare Figure 4.7 and Figure 4.8). Some of the patterns seen in Figure 4.8 may be rationally explained. For instance, the apparent co-occurrence between chlorpyrifos and endosulfane is, despite a low number of samples, logical since both are banned or restricted pesticides. The negative correlation between endosulfane and naphthalene (Figure 4.8) is not easily explained, and in general, this kind of analysis has to be done with a degree of scepticism. Patterns of co-variability should be backed up with empirical explanations.

Table 4.2 The degree to which different substance groups explain the three most important principal components.

<i>Substance group</i>	<i>Principal component</i>	<i>Degree to which substance group explains the principal component</i>
PAHs	PC1	95 %
Metals	PC2	70 %
Chlorobenzenes	PC3	70 %

It also has to be stressed that when individually evaluating the correlation between a number of variables, one may find that two variables do co-vary. This may be a purely random event since given enough number of variables two of them will eventually correlate (type I error).

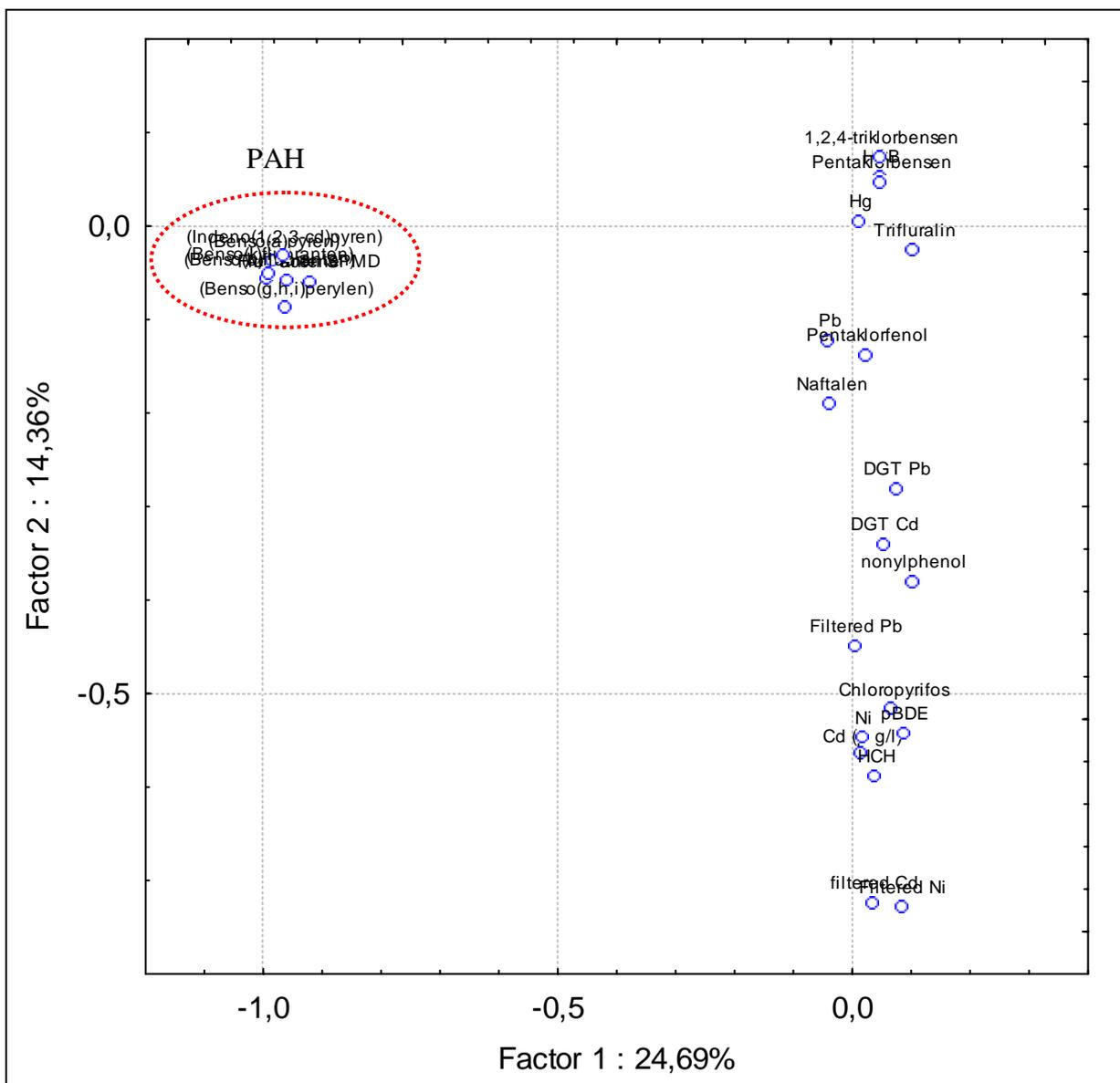


Figure 4.6 PCA plot of the priority substances dataset showing loadings of separate substances along the first two principal components. The first principal component (PC1, x axis) explained 25% of the variation of the levels of substances while the second component (PC2, y axis) explained 14%. PAHs are tightly clustered and separately marked.

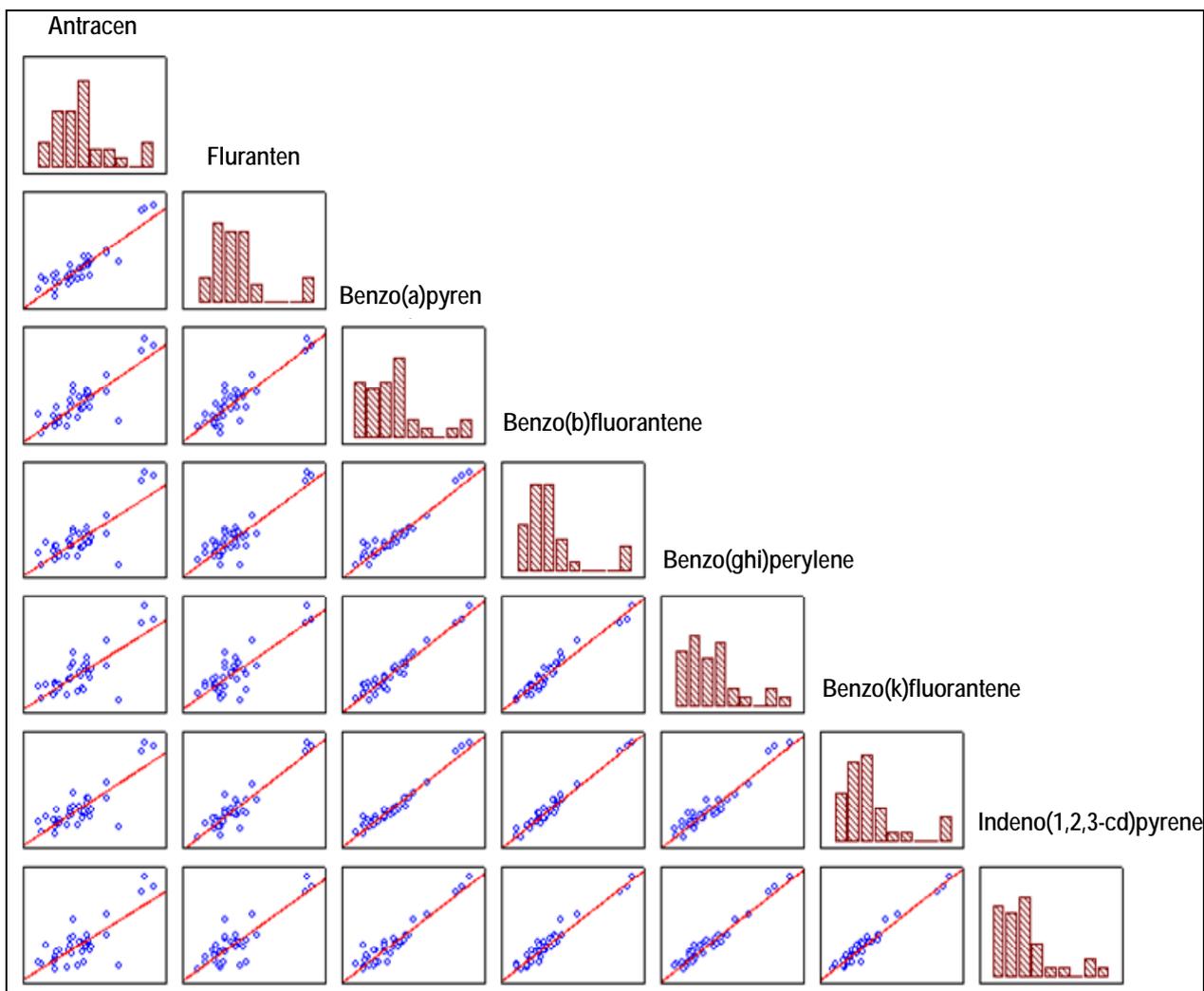


Figure 4.7 Co-variability between PAH substances. All data has been log transformed prior to making the graph. Consequently, the histograms represent log transformed data.

Besides evaluating the general co-occurrence between substances, a PCA analysis can also be used to evaluate how different samplings points deviate with regards to their substance composition. Figure 4.9 shows the projection of the sampling stations on the first two principal components. By comparing this graph with Figure 4.6 it is possible to connect specific sampling points with dominating substances since both the sampling points and the substances are projected on the same principal components.

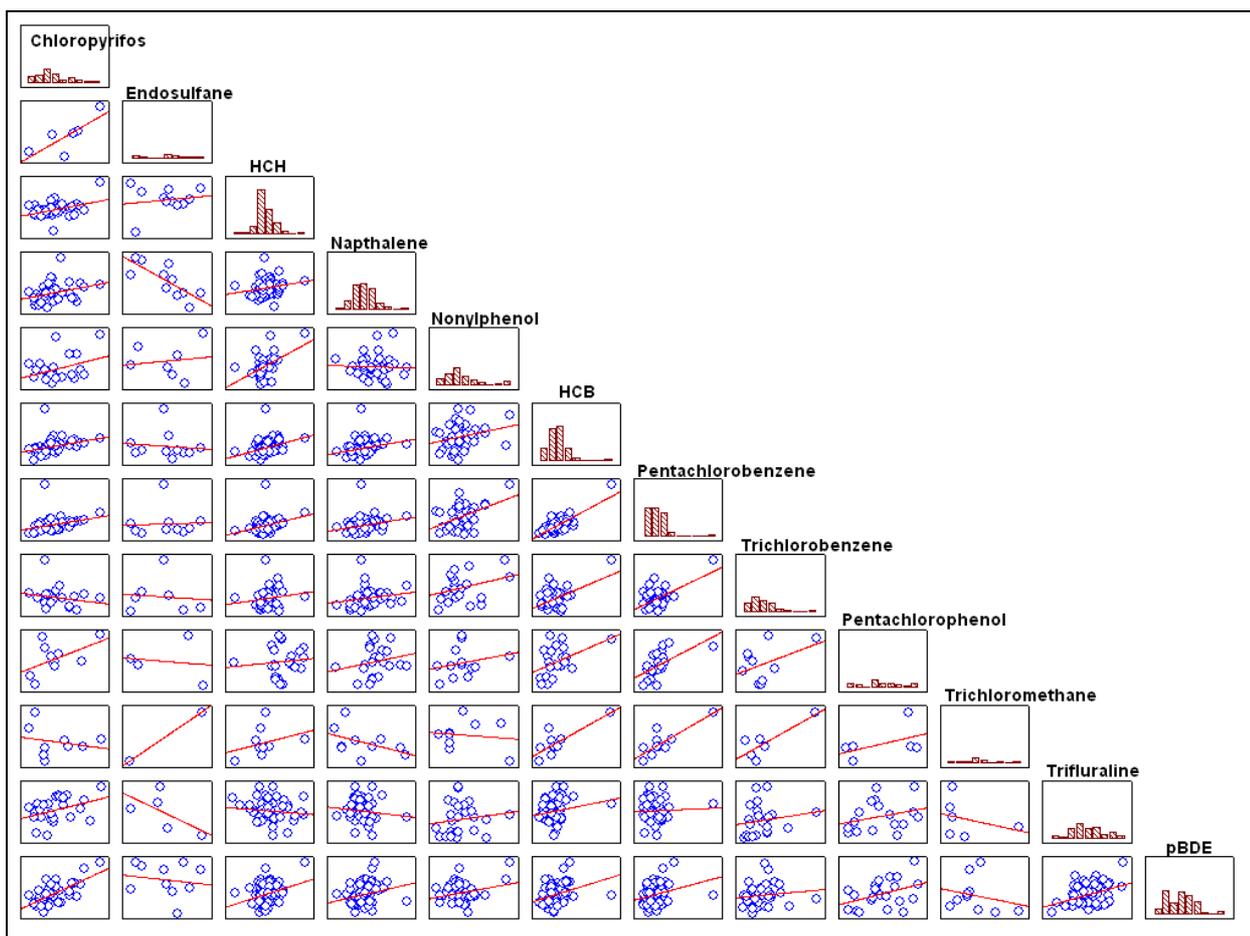


Figure 4.8 Co-variability between non-PAH WFD organic substances. All data has been log transformed prior to making the graph. Consequently, the histograms represent log transformed data.

For example, the sampling points Stockvik, Kaptensudden and Tivoliverket are located on the upper left hand on the principal component graph (Figure 4.9). This is also where the PAHs are situated on the PCA plot, and it turns out that these samples had a higher proportion of PAH substances at relatively high concentrations. Likewise, Svartån Industri and Vormbäcken is dominated by Ni, Cd and Pb while Visby reningsverk is dominated by Ni and nonylphenol.

An important feature of Figure 4.9 is that most sampling stations do not separate from each other. The implication is that, in general, the levels of many WFD substances in Swedish surface waters do not deviate to any large degree from each other. This was also a conclusion from the geographical evaluation of the data (SWECO VIAK 2007) where many substances were found at relatively even concentrations at many sampling stations with some occasional hot spots.

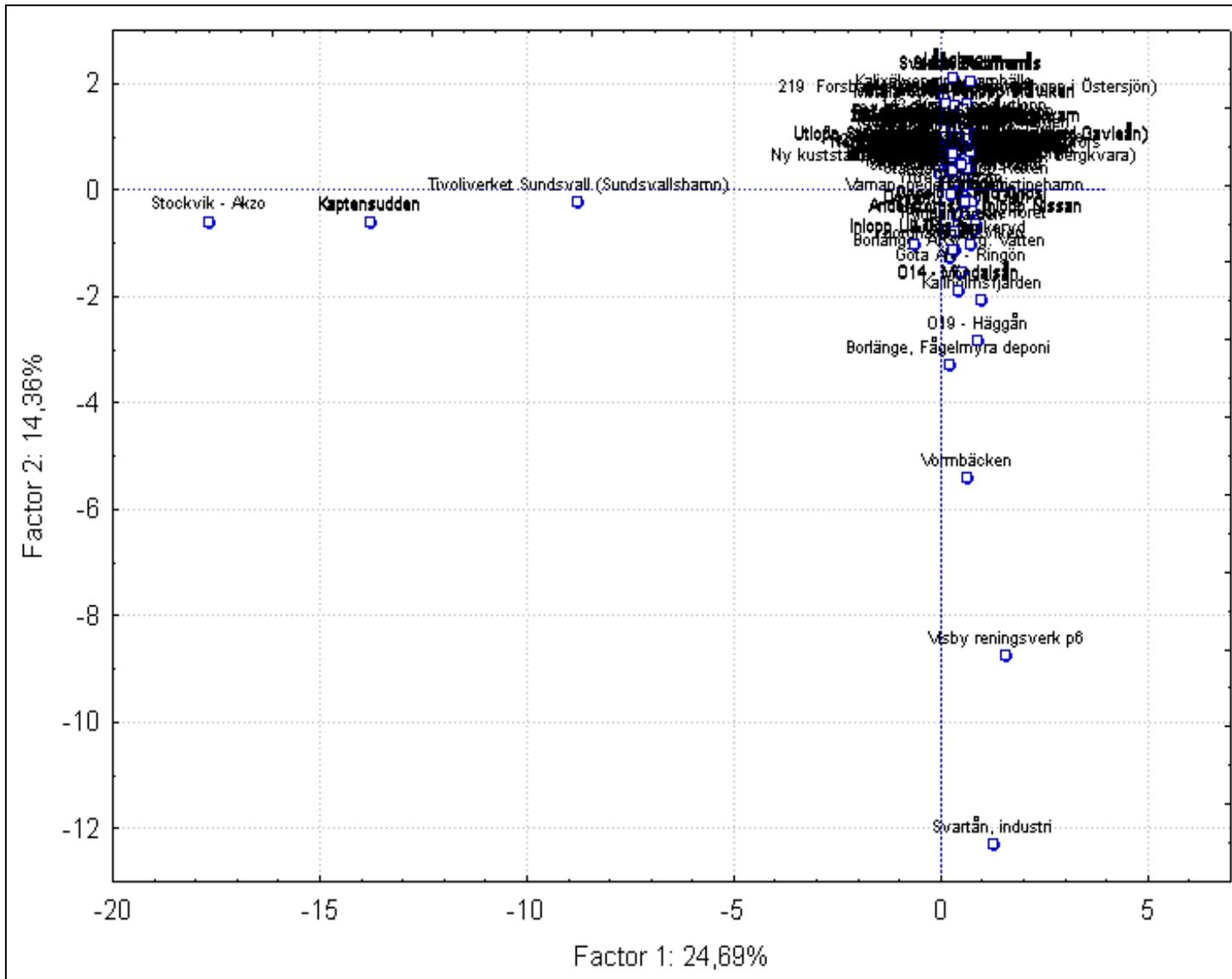


Figure 4.9 Projection of the sampling stations on the first two principal components.

5 Conclusions and recommendations

Some general conclusion from this study are:

- Results from this and other studies indicate that the relationship between concentrations of nickel in filtered water and concentrations obtained through DGT sampling is reliable. It may thus be possible to use DGT for monitoring of nickel within the water framework directive.
- Results from this and other studies indicate that the relationship between concentrations of cadmium in filtered water and concentrations obtained through DGT sampling is not generally reliable. This excludes DGT as a *general* tool for monitoring of cadmium in surface waters. It may be possible to use DGT for monitoring of Cd within water bodies with particular geochemical conditions.
- There was no co-relationship between levels of lead in filtered water and concentrations obtained through DGT sampling. This excludes DGT as a general tool for monitoring of lead in surface waters.
- The difference in water concentrations of lipophilic organic substances measured with SPMDs compared to filtered and whole water is so large that SPMDs will not be suitable for compliance monitoring according to the water framework directive.
- There is a very close co-variability between PAH compounds in Swedish surface waters. The only exception is naphthalene. Also, PAH compounds separates from other WFD compounds. If sampling programs focuses on surface waters with known problem with PAH compounds, it may not be necessary to include all other priority substances. The choice of non-PAH compound to include could be based on a limited sampling using passive samplers.
- In general, the co-variability between non-PAH WFD substances was generally weak with a few exceptions.
- Most sampling stations do not separate from each other with regards to their WFD substance composition. Consequently, in general, the levels of many WFD substances in Swedish surface waters do not deviate to any large degree from each other.

- The multivariate analysis also revealed that a few sampling points clearly deviated from the majority of sampling stations due to high concentrations of either PAHs or metals.

From a cost perspective, there may be a need to simplify and/or modify samplings programs that are aimed at evaluating the chemical status in the water framework directive. A general conclusion from this study is that any modifications may have to be determined on a local level. This involves issues such as the use of different passive samplers as well as the scope of the analytical programme. The factors that may have to be evaluated are both geochemical conditions, information from prior sampling programmes and the type of diffuse and point sources that may affect a surface water system.

At the same time, it is necessary to have a national and regional consensus on how monitoring programs of WFD priority substances can be simplified and modified in order to ensure a cost effective sampling that still fulfil the demands of the water framework directive. The results from this report can be used to support these discussions, and the screening work that has been done under the auspices of the Swedish Environmental Agency decreases the demand for local evaluations of similar kind.

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6 References

Allan, I.J. Knutsson, J. Guigues, N. et al. (2008). Chemcatcher® and DGT passive sampling devices for regulatory monitoring of trace metals in surface water. *Journal of Environmental Monitoring*, 10. 821-829.

Aguilar-Martínez, M.A. et al. (2008) Calibration and use of the Chemcatcher® passive sampler for monitoring organotin compounds in water. *Analytica Chimica Acta*, 618(2). 157-167.

Arditsoglou, A. Voutsas, D. (2007) Passive sampling of selected endocrine disrupting compounds using polar organic chemical integrative samplers. *Environmental Pollution*, 156 (2). 316-324.

Barceló, D. Oubiña, A. Salau, J. Perez, S. (1998) Determination of PAHs in river waters samples by ELISA. *Analytica Chimica Acta*, 376. 49 – 53.

Buoloubassi, I. Saliot, A. (1991) Composition and sources of dissolved and particulate PAH in surface waters from the Rhone Delta. *Marine Pollution Bulletin*, 22(12). 588 – 594.

Chin, Y. Aiken, G. R. O'Loughlin, E. (1994) Binding of pyrene to aquatic and commercial humic substances. The role of molecular weight and aromaticity. *Environmental Science and Technology*, 31(6). 1630 – 1635.

Coquery, M. Morin, A. Bécue, A. Iepot, B. (2005) Priority substances of the European Water Framework Directive: analytical challenges in monitoring water quality. *Trends in analytical Chemistry*, 24(2). 117 – 127.

Gallé, T. Grégoire, C. Wagner, M. Bierl, R. (2005) Bioavailability of HOC depending on the colloidal state of humic substances: A case study with PCB-77 and *Daphnia magna*. *Chemosphere*, 61 (2). 282-292.

Gourlay, G. Miege, C. Noir, A. Ravalet, C. Garric J. Mouchel, J. (2005) How accurately do semi-permeable membrane devices measure the bioavailability of polycyclic aromatic hydrocarbons to *Daphnia magna*. *Chemosphere*, 61. 1734–1739.

Huckins J.N. Petty J.D. and Booij K. (2006). *Monitors of organic chemicals in the environment*. Springer, 223 p.

Inchem (1991) International programme on chemical safety. Environmental health criteria 108. Nickel

KEMI (2004) Strategi för arbetet med kvicksilver, cadmium och bly inom EU och internationellt.

http://www.kemi.se/upload/medier/nyhetsarkiv/aktuellt/Hg_strategi.pdf

KEMI (2006) Delrapport – Tillämpningen av produktvalsprincipen i tillsynen inom kemikalieområdet.

http://www.kemi.se/upload/om_kemi/docs/regeringsuppdrag/rapport_ru_produktilval_20070227.pdf

Laodong, G. Santschi, P. H. Ray, S. M. (2002) Metal partitioning between colloidal and dissolved phases and its relation with bioavailability to American oysters. *Marine environmental research*, 54 (1). 49-64.

Lindström, P. (2006) Miljögifter i ytvatten - en studie av förekomsten av vattendirektivsämnen och andra miljögifter i västsvenska ytvatten. Rapport Länsstyrelsen Västra Götaland.

Loh, C, Ovuka, M. A. (2005) Litteraturstudie av prioriterade ämnen; Information om prioriterade ämnen listade i bilaga 10 till ramdirektivet för vatten. *Enviroplanning*, 1003-02/10/01/rap001.

Mackay, D. Shiu, W. Ma, K. Lee, S. (2006) *Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals, Second Edition*. CRC Press.

Nagy, P. Fekete, J. Sharma, V. (2007) Polycyclic aromatic hydrocarbons (PAHs) in surface waters of Ráckevei-Soroksári Danube Branch. *Journal of Environmental Science and Health, Part A*, 42(3). 231-240.

Naturvårdsverket (2004) Höga halter av miljöfarliga ämnen i miljön? Resultat från Miljöövervakningens Screeningprogram 1996 – 2003. Naturvårdsverket rapport 5449.

National Research Council (NRC) (2003) *Bioavailability of Contaminants in Soils and Sediments; Processes, Tools, and Applications*. National Academies Press, Washington, D.C. 433 p.

Naturvårdsverket (1997) Rapport Riktvärden för förorenad mark - Modellbeskrivning och vägledning. Bilaga 1, Sammanställning av indata till riktvärdesmodellen. REMISSVERSION 2007-10-19.

Poet, T. S. McDougal, J. N. (2002) Skin absorption and human risk assessment. *Chemico-Biological Interactions*, 140. 19-34.

Remberger, M. Kaj, L. Palm, A. Sternbeck, J. Kvernes, E. Brostrom-Lunden, E. (2003) Screening tertiary butylphenols, methylphenols, and long-chain alkylphenols in the Swedish Environment. IVL report B1954.

RPA (1999) Nonylphenol Risk Reduction Strategy, Final Report - September 1999. Prepared for Department of the Environment, Transport and the Regions.

http://www.defra.gov.uk/environment/chemicals/pdf/nonylphenol_rrs.pdf

Rule, K. L. Comber, S.D.W. Ross, D. Thornton, A. Makropoulos, C. K. Rautiu, R. (2006) Sources of priority substances entering an urban wastewater catchment – trace organic chemicals. *Chemosphere*, 63. 581 – 591.

SWECO VIAK (2007). Nationwide screening of WFD of priority substances. SWECO VIAK Screening Report 2007:1.

Sparks, D. (1995) *Environmental Soil Chemistry*. Academic Press, San Diego, 267 p.

Svensson, A. (2002) Miljögifter i avloppsslam- en studie omfattande 19 reningsverk i Västra Götaland. Länsstyrelsen i Västra Götaland Rapport 2002:39.

ter Schure, A. F. H. Larsson, P. Agrell, C. Boon, J. P. (2004) Atmospheric Transport of Polybrominated Diphenyl Ethers and Polychlorinated Biphenyls to the Baltic Sea. *Environmental Science and Technology*, 38(5). 1282-1287.

Tesfalidet, S. (2004) Screening of organotin compounds in the Swedish environment. SNV contract: 219 0102.

Økland, T. E. Wilhelmsen, E. Solevåg, Ø (2005) A study of the priority substances of the Water Framework Directive; Monitoring and need for screening. Norwegian Pollution Control Authority (SFT). TA-2140/2005.