

SWECO Environment Screening Report
2008:7

Temporal variation of WFD priority substances

Client

Swedish Environmental Protection Agency

2009-05-26
SWECO Environment AB
Södra regionen

Niklas Törneman
Project manager

Matilda Johansson
Supporting staff

Klas Andersson
Quality assurance

SWECO
Hans Michelsensgatan 2
Box 286, 201 22 Malmö
Telefon 040-16 70 00
Telefax 040-15 43 47



Contents

Contents	2
Sammanfattning	3
Summary	6
1 Introduction	9
1.1 Background	9
1.2 Objectives	9
2 Water Framework Directive and Priority Substances	10
3 Methods	12
3.1 Study areas	12
3.2 Sampling	15
3.3 Analytical methods	15
3.3.1 Extraction and analysis	15
3.3.2 Quality assurance	16
3.3.3 Additional quality assurance of sampling and analysis of organic tin substances	16
4 Results	18
4.1 Summary statistics water	18
4.2 Summary statistics sediment	25
4.3 Temporal variation	29
5 Discussion	42
5.1 General observations	42
5.2 Temporal variability	43
5.2.1 Limnic surface waters	44
5.2.2 Marine surface waters	47
5.3 Implications for sampling	47
5.4 Sediments	48
5.5 Substances of concern	49
5.6 Limnic vs. marine surface waters	50
5.7 Conclusions and future work	50
6 References	52

Appendix 1 Description of sampling stations

Sammanfattning

Background and methods

År 2006 så lades inom EU fram en rad miljökvalitetsnormer för acceptabla halter av kemikalier i ytvatten. Dessa normer gäller s.k. prioriterade ämnen inom vattendirektivet (i Sverige införlivat i vattenförvaltningsförordningen). En osäkerhet vad gäller övervakning av de prioriterade ämnena är deras haltvariation över året. Inom ramen för Naturvårdsverkets screeningprogram¹ har SWECO Environment fått i uppdrag av Naturvårdsverket att mäta och utvärdera förekomsten av de prioriterade ämnena i limniska och marina/kustnära ytvatten.

Syftet med studien har varit att utröna och utvärdera den årliga variationen från månad till månad, att bedöma vilka effekter årstidsvariationen har på provtagningsstrategier samt att översiktligt bedöma vilka ämnen som är problematiska sett ur perspektivet – ”god kemisk status”.

Screeningen omfattade 8 limniska och 7 marina lokaler. De limniska lokalerna representerade olika typer av miljöer, från opåverkade bakgrundsområden till platser där ytvatten påverkas av diffusa källor eller punktkällor. De marina provtagningspunkterna representerade alla marina havsbassänger som gränsar till Sverige och var mestadels kustnära. Provtagningen skedde månatligen med början i November/December 2007 och ett år framåt. Sedimentprovtagning gjordes vid ett tillfälle i Augusti eller September i ackumulationsbottnar som var så nära som möjligt provtagningspunkten för ytvatten.

Resultat

Studien omfattade 15 provtagningspunkter över hela Sverige. Följaktligen är det inte meningsfullt att utvärdera geografiska mönster. Halterna av prioriterade ämnen var generellt lägre i denna studie jämfört med en tidigare screening av vattendirektivsämnen som omfattade nästan 100 ytvatten över hela Sverige². Orsaken kan vara att den förra studien omfattade relativt fler provtagningspunkter som var tydligt påverkade av utsläpp.

I princip uppnådde ingen av de provtagna vattenförekomsterna god kemisk status. Främst berodde detta på att den årliga medelhalten för TBT och nonylfenol översteg AA-EQS, men även andra ämnen bidrog till avvikelsen från god kemisk status. En orsak till detta var ett konservativt angreppssätt där TBT halten sattes till bestäm-

¹ <http://www.naturvardsverket.se/sv/Tillstandet-i-miljon/Miljoovervakning/Programomraden/Miljogiftssamordning/Screening/>

² http://www.naturvardsverket.se/upload/02_tillstandet_i_miljon/Miljoovervakning/rapporter/miljogift/rapport_vattendirektivsamnen.pdf

ningsgränsen när TBT inte påträffades. Givet att bestämningsgränsen för TBT är fem gånger högre än EQS värdet ger detta ett högt medelvärde även när TBT endast påträffats vid ett fåtal tillfällen. Även om halva bestämningsgränsen för TBT användes så fick de flesta provtagningspunkter/vattenförekomster inte god kemisk status, till store del beroende på att TBT förhållandevis ofta påträffades i halter som 5 – 100 ggr högre än EQS värdet.

Denna och tidigare screeningstudier visar att det ställvis är samma prioriterade ämnen som påträffas. Undantag finns, men det beror då på punktkällor. De mest problematiska prioriterade ämnena i ytvatten vad gäller den kemiska statusen är nonylfenol och TBT följt av (i ingen given ordning) kadmium, bly, nickel och ställvis DEHP. Observera att andra ämnen kan vara problematiska i andra matriser. Ett mycket viktigt exempel är kvicksilver och metylkvicksilver i insjöfisk som utgör ett problem över i stort sett hela landet.

De flesta prioriterade ämnen som var vanligt förekommande uppvisade ofta en kraftig haltvariation från månad till månad (> 5 ggr skillnad mellan högsta och lägsta halt) medan några uppvisar en något mindre haltvariation (se nedanstående tabell). Den höga haltvariationen visar att provtagning vid ett eller två tillfällen per år inte alltid är tillräckligt för att fastställa den kemiska statusen.

	Limniska vattensystem		Marina vattensystem	
	Mindre kraftiga haltvariationer	Mycket kraftiga haltvariationer	Mindre kraftiga haltvariationer	Mycket kraftiga haltvariationer
Nickel*	X		X	
Kadmium		X		X
Bly	X			X
Kvicksilver		X		X
Nonylfenol**	X		X	
TBT		X		X

* tydlig haltminskning i Maj

** högsta halter Maj - Juli

De tydligaste tidstrenderna var att Nickelhalterna minskade tydligt i maj vid nästan alla lokaler samt att nonylfenolhalterna ökade gradvis från maj - augusti för att sedan minska och inte förekomma över bestämningsgränsen efter september/oktober. TBT förekom inte över bestämningsgränsen i någon punkt från juli och framåt i limniska punkter och mycket sällan under hösten i marina punkter.

Alla prioriterade ämnen som förekom i ytvatten påträffades också i sediment. Ytterligare ämnen som var vanliga i sediment men inte (frekvent) i ytvatten var DEHP, vissa

PAH samt oktylfenol. Det föreslagna EQS värdet för fluoranten i sediment (129 µg/kg TS) överskreds vid en majoritet av provtagningspunkterna. Detta indikerar tydligt att fluoranten och PAH ämnen kan komma att bli problematiska vid statusklassificeringen av ytvatten i Sverige.

Limniska vatten påverkades betydligt mer av prioriterade ämnen jämfört med marina ytvatten. Detta beror troligtvis både på spädning i havet samt att många potentiella källor såsom reningsverk, dagvatten, deponier och industrier ofta har limniska ytvatten som recipienter. TBT överskred EQS värdet lika ofta i marina som i limniska vatten vilket visar att detta ämne är problematiskt vad gäller den kemiska statusen inom vattendirektivet i alla typer av ytvattenförekomster.

Generellt rekommenderas att dessa resultat beaktas när övervakningsprogram för vattendirektivsämnen tas fram. Exempelvis kan det vara mer lämpligt med mer frekvent provtagning under våren eftersom sannolikheten att påträffa nonylfenol och TBT är större då.

Några osäkerheter vad gäller prioriterade ämnen i ytvatten och som kan kargöras i kommande studier är:

- Tidsvariationen från vecka till vecka och dag till dag är okänd, och skulle kunna undersökas med en fokuserad provtagning vid ett fåtal lokaler
- Den faktiska förekomsten av TBT är okänd och behöver utredas när rätt provtagnings- och/eller analysmetoder finns tillgängliga
- Bidraget från olika källor till förekomsten av de mer problematiska prioriterade ämnena är till viss del okänd eller i alla fall mycket osäker. Detta kan klargöras via teoretiska massbalansstudier baserat på screeningdata om ytvatten, data från miljöövervakning av nederbörd och kunskap om olika möjliga källor såsom lakvatten, avloppsreningsverk och urbana diffusa källor.

Summary

Background and methods

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 2007, SWECO Environment 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 to investigate the in-year, month to month variations of the levels of WFD substances.

The objectives of the study were to assess the yearly variability of WFD priority substances, assess generally appropriate sampling strategies, and identify problematic priority substances.

The screening involved sampling at 8 limnic and 7 marine locations. Limnic sampling stations represent different type of environments ranging from background locations to sites affected by heavy industry. Marine sampling stations were spread around the Swedish coast and both pelagic and open water locations were represented. Water sampling was done monthly starting November or December 2007 for the different locations. Sediment sampling was done once for each location where an accumulation sea or lake bed could be found as close to the water sampling point as possible.

Results

This study encompassed 15 sampling points in Sweden. Consequently, it was not meaningful to evaluate geographical patterns. The priority substance concentrations were generally lower in this study compared with a study that encompassed almost a hundred surface water sampling points in 2006. This may be because sampling points in this study are not directly influenced by local sources or it may just be a random effect of few sampling points.

Almost all the sampling locations/water bodies did not reach good chemical status because of high yearly average concentrations of TBT and nonylphenol. More sampling stations would have gotten a good chemical status if a less conservative approach had been used for calculating the yearly average of TBT.

A comparison between this study and earlier screening studies of priority substances show that almost the same priority substances occur whenever or wherever the study is performed. Any differences probably depend on the presence of local sources of pollutants. The most pertinent priority substances are consistently nonylphenol and TBT followed by (in no specific order) cadmium, lead, nickel and DEHP. It must be stressed, that these conclusions are only valid for surface waters. Others substances

will probably be of greater importance in other environmental matrices. Mercury (especially methylmercury) in limnic fish is an important example of a substance and matrix that is problematic all over Sweden as regards to the status classification within the water framework directive.

Most of the frequently occurring priority substances exhibited very variable concentrations over the year, while some were less variable (see table below). The substantial variability for many substances demonstrates that sampling of surface waters on one or two occasions per year may not be sufficient to classify the chemical status.

	Limnic waters		Marine waters	
	Less variable concentrations	Very variable concentrations	Less variable concentrations	Very variable concentrations
Nickel*	X		X	
Cadmium		X		X
Lead	X			X
Mercury		X		X
Nonylphenol**	X		X	
TBT		X		X

* dip in May

** increased concentrations in May - July

Some apparent temporal trends were that Nickel had a clear dip in concentrations in May while nonylphenol clearly had the highest concentrations from June – August. TBT was not found at all from July and onward in limnic waters and very seldom during the autumn in marine waters.

All of the priority substances that are common in surface waters were also common in sediments. Some additional compounds such as DEHP, certain PAHs and octylphenol were also common in sediments. There was no co-variability between sediment concentrations and surface water concentrations. The suggested sediment EQS value of 129 µg/kg dw for fluoranthene was exceeded at most of the sampling stations indicating that fluoranthene and PAHs in general may be very problematic substances as regards to the classification of status in the Water Framework Directive.

This study showed that limnic waters in general are more affected by priority substances than marine, which may be a dilution phenomenon and a consequence of potential contaminant sources being more in the vicinity of limnic waters. Elevated TBT levels (above AA-EQS) were as prevalent in marine water systems as in limnic waters systems showing that TBT is an important priority substance in all water systems.

A general recommendation is to take these results into account when planning compliance monitoring of WFD priority substances. As an example, water sampling should perhaps be less frequent during the autumn compared to the spring due to lower levels of TBT, nonylphenol and some metals during the autumn.

Some future uncertainties that may need to be resolved are:

- the weekly and daily temporal variability which would require frequent sampling at a few localities
- the actual occurrence of TBT which would require better analytical methods
- the sources of the most problematic priority substances need to be identified. Which could be done by national mass balance budgets

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 2007 SWECO Environment 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 to investigate the in-year, month to month variations of the levels of WFD substances.

1.2 Objectives

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

- To assess the yearly variability of WFD priority substances in Sweden
- To assess, in general, appropriate sampling frequencies of priority substances
- To assess whether the identification of problematic substances in an earlier national screening still holds

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 33³ 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 concentration 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).

³ 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 Kow	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 - 0.085 (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)
7440-43-9	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		Practically insoluble
470-90-6	Chlorfenvinphos	Pesticide. Not 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
87-68-3	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)*
3412359-6	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, 1806-26-4, 140-66-9	Nonylphenol, 4-para-nonylphenol	Industrial chemical forms through degradation of NP-ethoxylates. Phase-out	0.3	4.2 - 4.7		3 - 11 (pH dependent)
608-93-5	Octylphenol, 4-tert-octylphenol	Industrial chemical forms through degradation of OP-ethoxylates. No restriction	0.1	5.28 (4-ter)		5 (25 °C)
87-86-5	Pentachlorobenzene	Unknown uses	0.007	4.8 - 5.18	SPMD	0.56 (20° C)
50-32-8	Pentachlorophenol, PCP	Pesticide. Banned in 1978	0.4	5.12	SPMD	14
205-99-2	Benzofluoranthene, Benzo(k)fluoranthene	Incomplete combustion	0.05		SPMD	0.0016 - 0.0038 (25 °C)
191-24-2 193-39-5	Benzofluoranthene, Benzo(k)fluoranthene	Incomplete combustion	0.03		SPMD	
122-34-9	Simazine	Incomplete combustion	0.002		SPMD	
688-73-3	Tributyltin, TBT	Pesticide. Banned in 1995	1	2.4	POCIS	5 - 6.2
12002-48-1	Trichlorobenzene	Antifoulant, preservative, stabiliser in plastics. 1993: all ships under 25 m. no new use after 2003	0.0002	3.19 - 3.84		0.1%
67-66-3	Trichloromethane (chloroform)	Industrial chemical. No intended use since 1998	0.4	3.93 - 4.2	SPMD	48 - 100
1582-09-8	Trifluralin	Solvent. Restricted use	2.5	1.97		7500 - 9300
		Pesticide. Banned in 1990	0.03	5.31	SPMD	< 1 (0.184 (20° C)

Table 2.1 Uses, restrictions, Kow and water solubility of WFD priority substances.

3 Methods

3.1 Study areas

The screening involved sampling at 8 limnic and 7 marine locations. Limnic sampling stations represent different type of environments ranging from background locations to sites affected by heavy industry. Marine sampling stations were spread around the Swedish coast and both pelagic and open water locations are represented. The sampling stations are presented with a short description in Table 3.1 below.

Table 3.1 Overview of sampling stations

Sampling station	Anthropogenic influence	Limnic/marine	Type
Abiskojaure	Background	Limnic	Lake
Askö	Diffuse	Marine	Coastal
Fladen	Low	Marine	
Gaviksfjärden	Low	Marine	Coastal
Göta Älv	Urban, Port	Limnic	River
Hasslö	Diffuse, urban	Marine	Arcipelago
Hjulstafjärden	Diffuse, urban	Limnic	Lake
Rånefjärden	Low	Marine	Coastal
Skagerak	Low	Marine	-
Stora Envättern	Low	Limnic	Lake
Storsjön	Urban	Limnic	Lake
The inlet to Vänern at Karlstad	Industry, urban	Limnic	River
The outlet of Vättern to Motala ström	Diffuse, urban	Limnic	Lake
Älvkarleby	Diffuse	Limnic	River
Barsebäck (Öresund)	Diffuse, boat traffic	Marine	Coastal

Information regarding each sampling location is also given in appendix 1. This includes geographical information and photographic presentations, as well as a description of possible substance sources.

An overview of the position of the sampling stations is presented in Figure 3.1. Limnic sampling stations are marked by a green dot and marine stations by a blue.

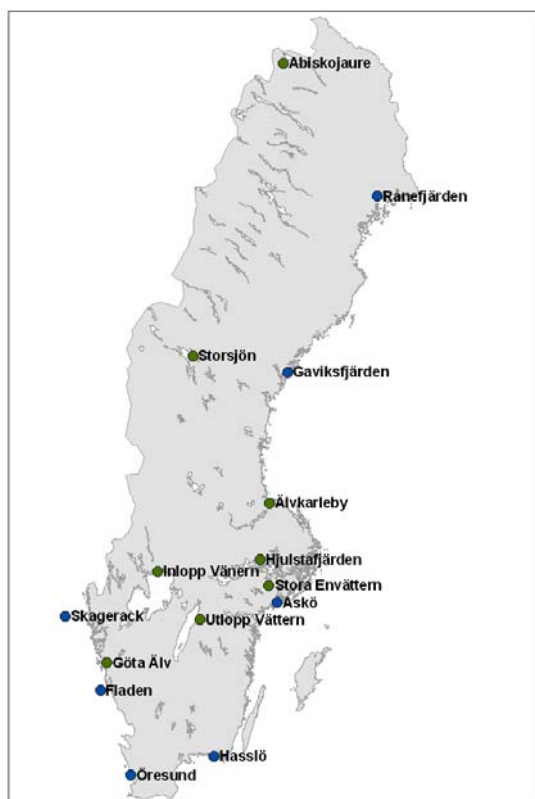


Figure 3.1 Location of sampling points for WFD priority substances in Sweden

Some sampling locations are also presented in Figure 3.2.



Figure 3.2 Some examples of sampling sites of WFD priority substances. Upper: Göta älv, middle left: Abiskojaure, middle right and lower left: Rånefjärden, and lower right: Vänern. Photographers: Mikael Christensson, Anders Eriksson, Anna Palmbo and Sofia Rolén.

3.2 Sampling

Water sampling was done monthly starting November or December 2007 for the different locations. Samples were collected from the surface water approximately 2 – 3 m below the surface.

On each sampling occasion, 6 litres of water was sampled from each site in 1 litre glass flasks. Water for metal analyses was additionally sampled in 125 ml acid rinsed plastic bottles. Samples were kept cold and transported as quickly as possible to the laboratory. At the laboratory samples were kept refrigerated (approx 5 – 8°C) until analysis. Filtration for analysis of dissolved metals was done in the lab.

Sediment sampling was done once for each location. The sediment was taken as close to the water sampling point as possible where an accumulation sea or lake bed could be found. Samples were taken with Ekman grabbers or Gemini corers. Only the top (1-5 cm) sediments were sampled to reflect recent anthropogenic influence. Samples were kept cold during transport and during storage before analysis.

3.3 Analytical methods

3.3.1 Extraction and analysis

ALS Scandinavia AB was responsible for all analytical work both regarding water and sediment samples. All substances were extracted and analyzed according to Table 3.1.

Table 3.1 Analytical methods for extraction and analysis of WFD priority substances.

Compound	Extraction	Derivati- sation	Clean up	Method	Instrument
Water					
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

Compound	Extraction	Derivati- sation	Clean up	Method	Instrument
Hexachlorocyklohexane	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	metha-nol/ethylacetate		SPE	Internal	GC-MS
Tributyltin	EtOH / Na-DDTC, hexane	NaBEt ₄	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 ₃			EPA 200.7 + 200.8	ICP-SFMS
PCB	cyclohexane			EN ISO 6468 F1	GC-MS

3.3.2 Quality assurance

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.

3.3.3 Additional quality assurance of sampling and analysis of organic tin substances

Organic tin substances were frequently found in surface waters in this study. To exclude sampling and/or analytical related reasons for false positives, an additional quality assurance was performed. Firstly, water samples in which organic tin substances had been detected were re-analysed. In all cases, the detected levels were confirmed. Secondly, four samples were sent to another, independent laboratory, for re-analysis. The detected levels were confirmed by the independent laboratory.

Thirdly, the caps used to seal the sampling bottles were analysed for tin to explore the possibility that the caps polluted the sampled water. No tin was found in the caps, excluding these as a source of organic tin to the sampling water.

Finally, the equipment used for water sampling (mostly ruttner samplers) were shaken with clean water (distilled or tap water) after which the water was analyzed. In four cases, monobutyltin (MBT) was detected (2 – 10 ng/l) in the “clean” water that had been in contact with the sampling equipment. In one case, tributyltin (TBT) was detected in the “clean” water. The sampling equipment that seemed to contaminate water samples with TBT originated on a boat that had previously used TBT in the boat paint. This usage was discontinued one year before the sampling took place, and the boat had been sealed with a coating that supposedly prevents TBT leaching from the hull. However, it is possible that the sampling equipment was contaminated with TBT from the boat which could contaminate the sampled water. To prevent this, new sampling equipment was acquired and used in the subsequent sampling.

4 Results

4.1 Summary statistics water

Statistics on the levels of priority substances in surface water is summarized in Table 4.1 - Table 4.2. Figures 4.2 to 4.5 presents the data in more detail together with comparisons to the annual average environmental quality standards (AA-EQS). The layout of these graphs is explained in Figure 4.1. 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 95th or 75th percentile.

In the water samples, some priority substances frequently occurred above the limit of quantification (LOQ), these include:

- Metals (cadmium, mercury, nickel, and lead) in filtrated and non-filtrated samples
- Nonylphenols
- Tributyltin

Some substances were intermittently above the LOQ:

- DEHP
- Polyaromatic hydrocarbons, fluoranten and naphthalene
- Chlorinated solvents, trichloromethane

Most priority substances were consistently below the LOQ:

- Pesticides: alachlor, atrazine, chlorfenvinphos, chlorpyrifos, diuron, endosulphan, isoproturon, simazine, trifluralin
- Polyaromatic hydrocarbons: anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, indeno(1,2,3-cd)pyrene
- Volatile organic substances: benzene, 1,2-dichloroethane
- Brominated diphenylethers
- Chlorinated organic compounds: chloroalkanes (C10-C13), hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, pentachlorobenzene, pentachlorophenol, trichlorobenzenes

Note that in the following graphical representation of the results and the discussion, of temporal trends only those substances which frequently occurred above the LOQ has been included. There are also the substances that most of the rest of the discussion focuses on.

Data on the number of occurrences above the AA-EQS and 10 and 50 percent of the AA-EQS is presented in Table 4.3 - Table 4.4 for all substances occurring at least once above the LOQ. The AA-EQS value for inland surface waters has been used for all limnic sampling stations and the value for other surface waters for all marine sampling stations.

In general, the priority substances were found more frequently and at higher levels in limnic surface waters compared to marine surface waters (Table 4.1 - Table 4.4). Also, more substances were detected in limnic surface waters.

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 Salot 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 be noted that the LOQ for tributyltin is well above the AA-EQS value. For all other substances, the LOQ is equal to, or below the EQS value. It should also be noted that endosulfane and pBDE were always below the very low AA-EQS values of 0.0005 and 0.0002 µg/l.

Table 4.1 Summary statistics of levels of priority substances in marine surface waters. Only data above LOQ were used.

	Min	25 th percentile	Median	75 th percentile	Max	Unit	LOQ	Number of samples > LOQ
Cadmium	0.0042	0.016	0.021	0.028	0.047	µg/l	0.002-0.08	41
Cadmium(filtered)	0.0026	0.013	0.022	0.028	0.052	µg/l	0.002-0.02	44
Mercury	0.0022	0.0026	0.0037	0.0054	0.0071	µg/l	0.002-0.04	19
Mercury(filtered)	0.0022	0.0024	0.0027	0.0046	0.012	µg/l	0.002-0.02	17
Nickel	0.26	0.60	0.73	0.91	34	µg/l	0.2-0.8	74
Nickel(filtered)	0.24	0.60	0.71	0.82	4.5	µg/l	0.2-0.5	73
Lead	0.020	0.15	0.29	0.60	4.9	µg/l	0.01-0.1	71
Lead(filtered)	0.012	0.11	0.18	0.29	43	µg/l	0.01-0.1	54
Nonylphenol	102	129	184	270	1510	ng/l	10	22
Octylphenol	-	-	-	-	20	ng/l	10	1
DEHP	2.9	-	-	-	33	µg/l	1	2
Trichloromethane	0.21	-	0.24	-	0.3	µg/l	0.1-0.2	3
Fluoranthene	-	-	-	-	0.011	µg/l	0.01	1
Tributyltin	1.0	2.0	3.0	5.0	7.0	ng/l	1	20

Table 4.2 Summary statistics of levels of priority substances in limnic surface waters. Only data above LOQ were used.

	Min	25 th percentile	Median	75 th percentile	Max	Unit	LOQ	Number of samples > LOQ
Cadmium	0.0022	0.0060	0.0098	0.013	0.16	µg/l	0.002-0.08	33
Cadmium(filtered)	0.0026	0.0042	0.0052	0.007	0.013	µg/l	0.002-0.02	24
Mercury	0.0022	0.0029	0.0040	0.0043	0.0056	µg/l	0.002-0.04	23
Mercury(filtered)	0.0022	0.0026	0.0029	0.0039	0.0078	µg/l	0.002-0.02	19
Nickel	0.23	0.36	0.53	0.85	793	µg/l	0.2-0.8	91
Nickel(filtered)	0.22	0.33	0.50	0.70	3.3	µg/l	0.2-0.5	91
Lead	0.022	0.19	0.34	0.87	25	µg/l	0.01-0.1	83
Lead(filtered)	0.015	0.076	0.12	0.20	34	µg/l	0.01-0.1	57
Nonylphenol	103	147	199	265	3520	ng/l	10	58
Octylphenol	15	22	28	32	50	ng/l	10	6
DEHP	3	-	3.4	-	3.4	µg/l	1	3
Trichloromethane	0.1	-	-	-	0.19	µg/l	0.1-0.2	2
Fluoranthene	0.023	-	-	-	0.086	µg/l	0.01	2
Naphtalene	0.012	-	-	-	0.012	µg/l	0.01	2
Pyrene	0.014	-	-	-	0.052	µg/l	0.01	2
Tributyltin	1.0	2.0	3.0	4.5	7.0	ng/l	1	23

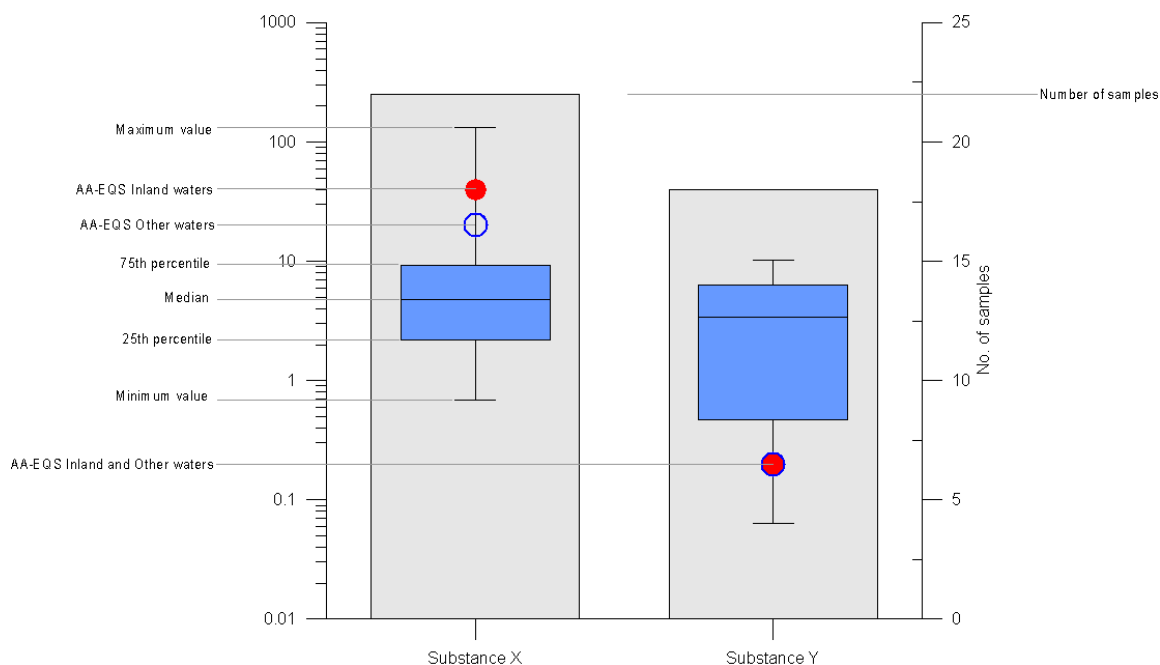


Figure 4.1 Explanation of the graphs summarizing the results from sampling of priority substances

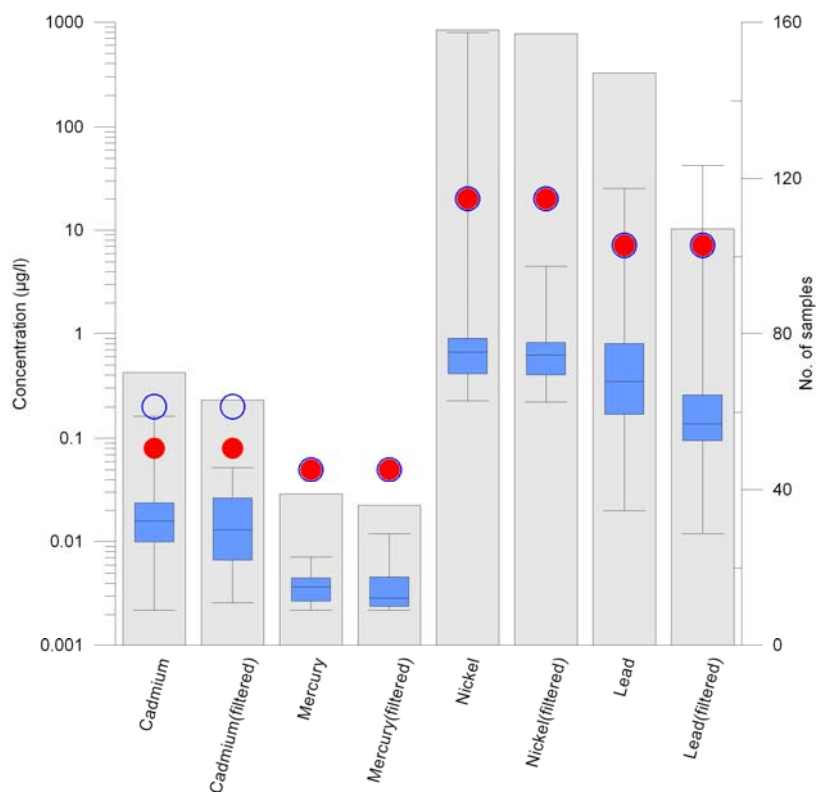


Figure 4.2 Levels of metals in filtrated and non-filtrated water samples. Only data > LOQ were used. Note the logarithmic scale.

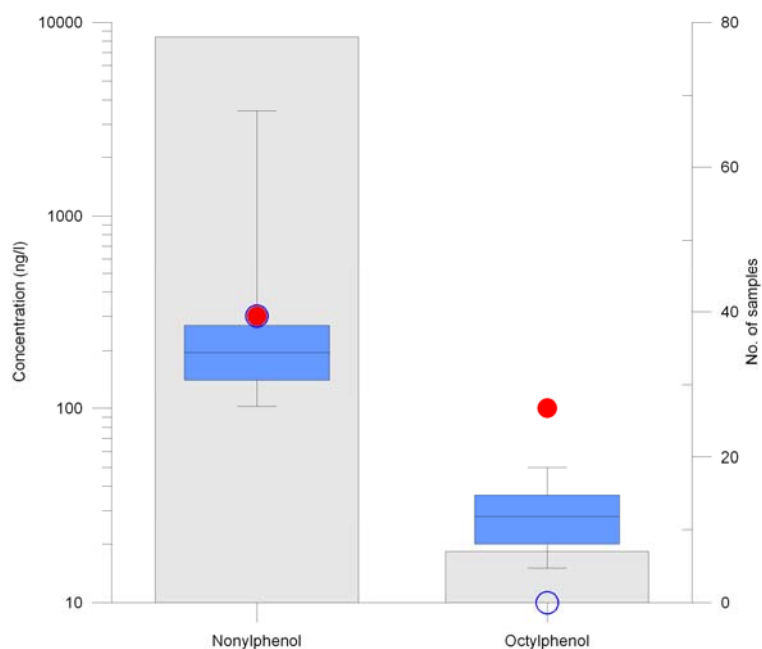


Figure 4.3 Levels of nonyl- and octylphenols in water samples. Only data > LOQ were used. Note the logarithmic scale.

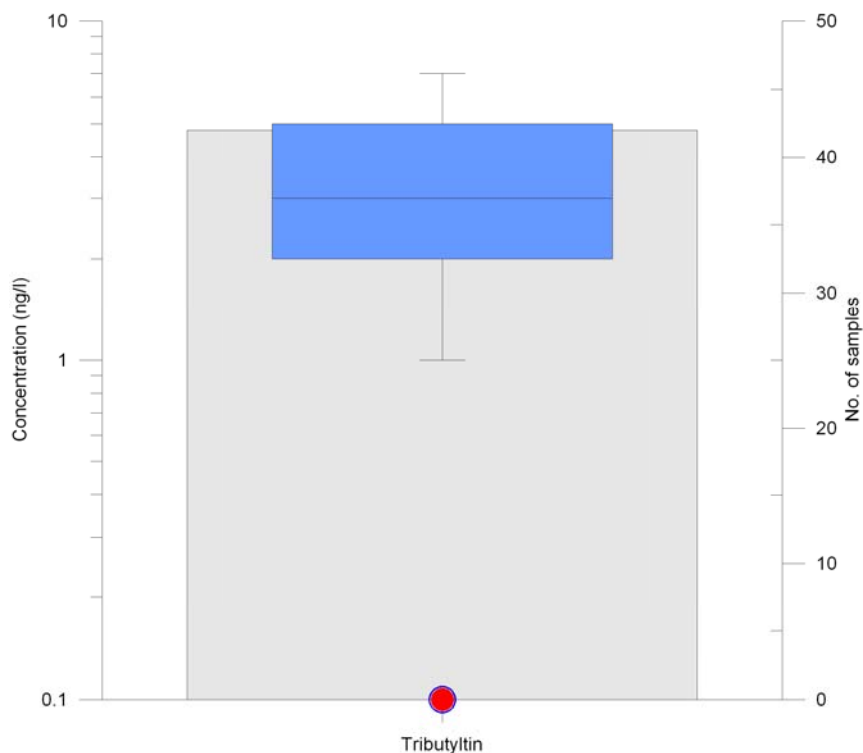


Figure 4.4 Levels of tributyltin in water samples. Only data > LOQ were used. The LOQ for tributyltin was higher (1 ng/l) than the AA-EQS. Note the logarithmic scale.

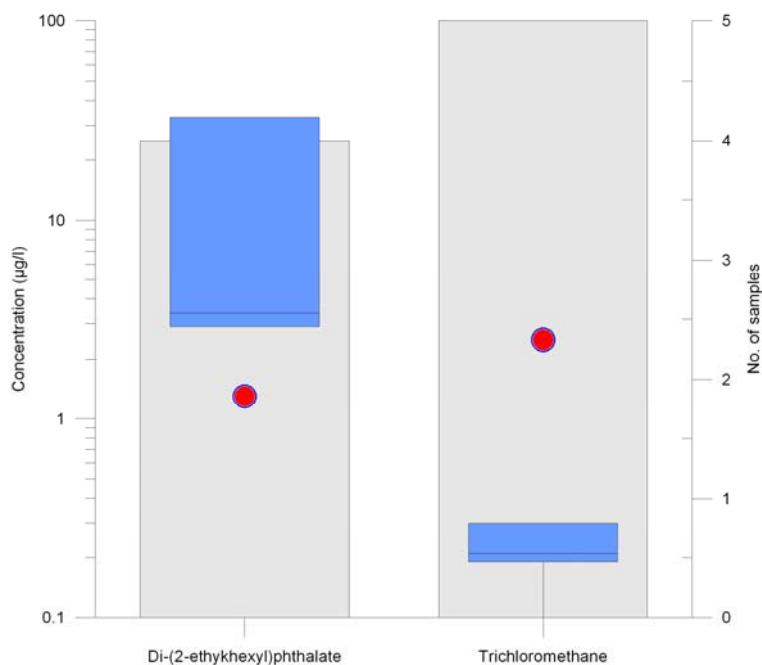


Figure 4.5 Levels of di-(2-ethylhexyl)phthalate (DEHP) and trichloromethane in water samples. Only data > LOQ were used. Note the logarithmic scale.

Table 4.3 Summary information regarding exceedance of EQS in limnic surface waters. Only substances occurring at least once above the LOQ is shown and only data > LOQ were used.

Substance	AA-EQS	No. of samples		AA-EQS
		> 0.1 x AA-EQS	> 0.5 x AA-EQS	
Cadmium	0.08	20	0	1
Cadmium (filtrated)	0.08	4	0	0
Di(2-ethylhexyl)phthalate	1.3	0	0	3
Fluoranthene	0.1	1	1	0
Lead	7.2	15	2	7
Lead (filtrated)	7.2	6	1	2
Mercury	0.05	2	0	0
Mercury (filtrated)	0.05	4	0	0
Naphthalene	2.4	0	0	0
Nickel	20	18	0	1
Nickel (filtrated)	20	9	0	0
Nonylphenol	300	15	31	12
Octylphenol	100	5	0	0
Tributyltin	0.2	0	0	23*
Trichloromethane	2.5	0	0	0

*LOQ>AA-EQS

Table 4.4 Summary information regarding exceedance of EQS in marine surface waters. Only substances occurring at least once above the LOQ is shown and only data > LOQ were used.

Substance	AA-EQS	No. of samples		AA-EQS
		> 0.1 x AA-EQS	> 0.5 x AA-EQS	
Cadmium	0.2	24	0	0
Cadmium (filtrated)	0.2	25	0	0
Di(2-ethylhexyl)phthalate	1.3	0	0	2
Fluoranthene	0.1	1	0	0
Lead	7.2	14	2	0
Lead (filtrated)	7.2	5	0	1
Mercury	0.05	6	0	0
Mercury (filtrated)	0.05	4	0	0
Naphthalene	1.2	0	0	0
Nickel	20	6	0	1
Nickel (filtrated)	20	6	0	0
Nonylphenol	300	9	10	3
Octylphenol	10	0	0	1
Tributyltin	0.2	0	0	20*
Trichloromethane	2.5	0	0	0

*LOQ>AA-EQS

4.2 Summary statistics sediment

Statistics on levels of priority substances in sediments are summarized in Table 4.5. The data is shown in greater detail in Figures 4.6 to 4.9. The layout of these graphs is explained in Figure 4.1 above.

The priority substances that frequently occurred above the LOQ in sediment samples were:

- Metals: cadmium, mercury, nickel, and lead
- Nonylphenols and octylphenols
- DEHP
- Polyaromatic hydrocarbons: anthracene, fluoranthene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(g,h,i)perylene, and indeno(1,2,3-cd)pyrene
- Tributyltin

Some substances were intermittently occurring above the LOQ:

- Polyaromatic hydrocarbons: naphthalene
- Brominated diphenylethers

Most priority substances consistently occurred below the LOQ:

- Pesticides: alachlor, atrazine, chlorfenvinphos, chlorpyrifos, diuron, endosulphan, isoproturon, simazine, and trifluralin
- Volatile organic substances: benzene and 1,2-dichloroethane
- Chlorinated organic compounds: chloroalkanes (C10-C13), hexachlorobenzene, hexachlorobutadiene, hexachlorocyclohexane, pentachlorobenzene, pentachlorophenol, trichlorobenzenes, and trichloromethane

Table 4.5 Summary statistics of levels of priority substances in limnic and marine sediments

	Min	25 th percentile	Median	75 th percentile	Max	LOQ	Unit	Number of samples > LOQ
Cadmium	0.041	0.22	0.39	1.8	3.1		mg/kg dw	12
Mercury	0.073	0.11	0.21	0.40	5.2	0,04	mg/kg dw	7
Nickel	3.8	17	24	33	41		mg/kg dw	12
Lead	10	23	40	53	255		mg/kg dw	12
Nonylphenol	0.012	0.022	0.048	0.063	0.35	0,011	mg/kg dw	6
Octylphenol	0.0011	0.0023	0.0025	0.0028	0.0075	0,003	mg/kg dw	10
BDE 99	0.4	0.42	0.43	0.47	0.5	0,2	µg/kg dw	3
Di-(2-ethylhexyl)phthalate	0.074	0.11	0.46	3.3	87	0,05 – 0,1	mg/kg dw	7
Anthracene	0.055	0.067	0.086	0.1	0.45	0,05	mg/kg dw	5
Benzo(a)pyrene	0.17	0.20	0.24	0.32	1.3	0,05	mg/kg dw	6
Benzo(b)fluoranthene	0.05	0.056	0.2	0.5	1.4	0,05	mg/kg dw	9
Benzo(g,h,i)perylene	0.061	0.12	0.17	0.46	0.91	0,05	mg/kg dw	8
Benzo(k)fluoranthene	0.084	0.097	0.16	0.27	0.65	0,05	mg/kg dw	6
Fluoranthene	0.05	0.061	0.42	0.59	3.5	0,05	mg/kg dw	9
Indeno(123cd)pyrene	0.07	0.12	0.17	0.52	1.2	0,05	mg/kg dw	8
Naphtalene	0.092	0.099	0.11	0.11	0.12	0,05	mg/kg dw	2
Pyrene	0.05	0.31	0.36	0.52	2.2	0,05	mg/kg dw	7
Tributyltin	1.2	2	8.3	20	370	1 - 3	µg/kg dw	9

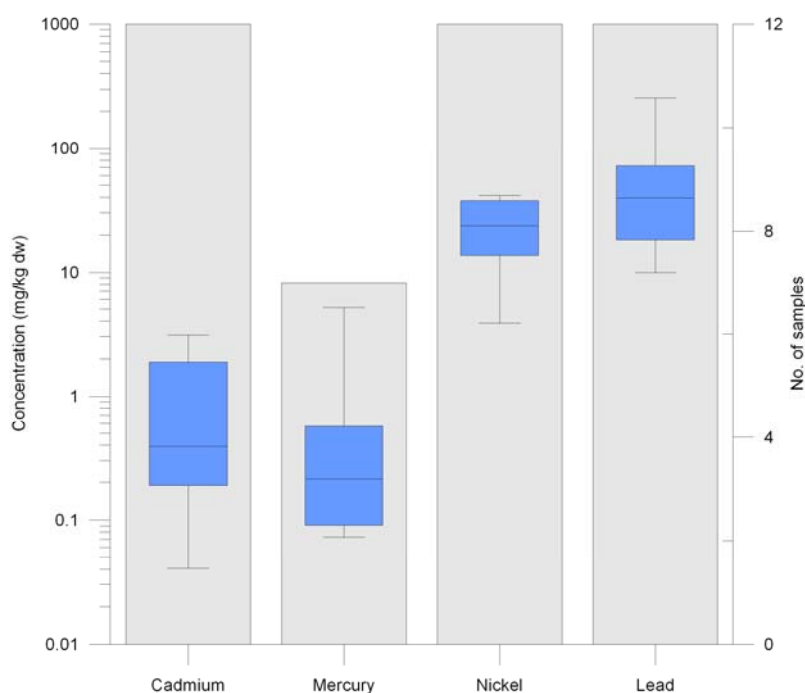


Figure 4.6 Levels of metals in sediments. Only data > LOQ were used. Note the logarithmic scale.

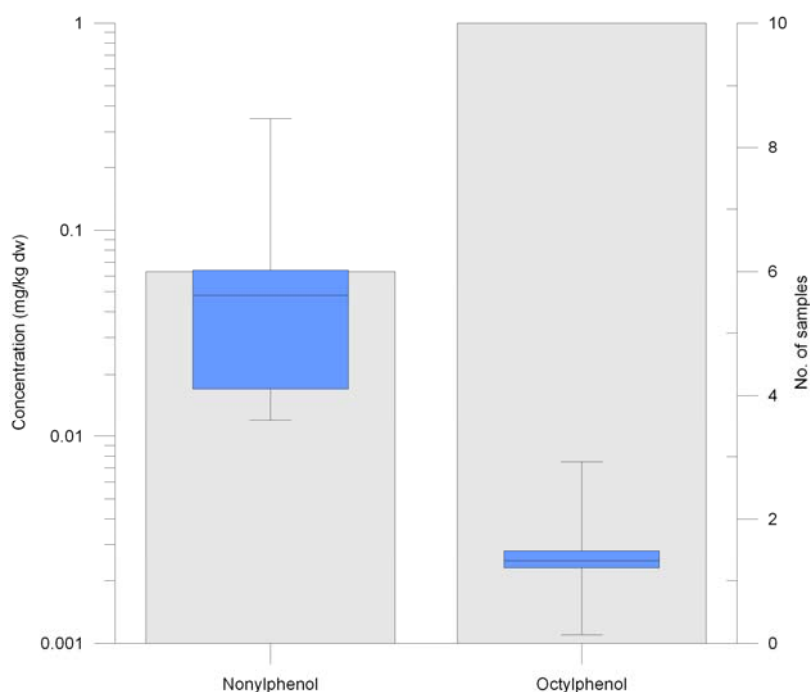


Figure 4.7 Levels of nonylphenols and octylphenols in sediments. Only data > LOQ were used. Note the logarithmic scale.

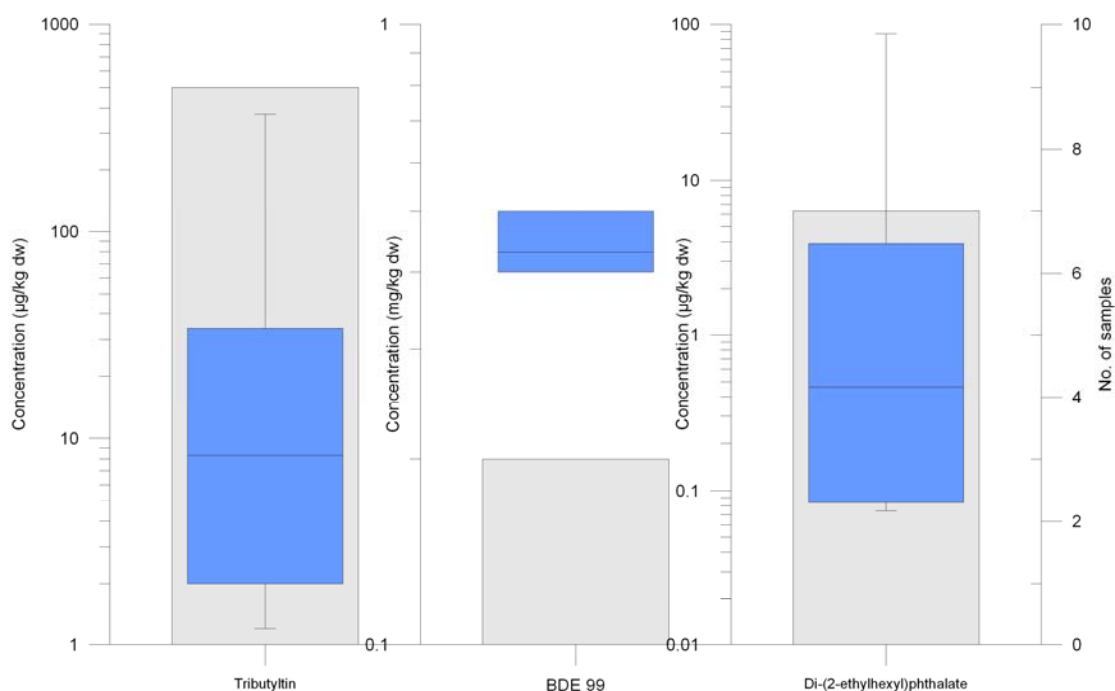


Figure 4.8 Levels of tributyltin, pentabromodiphenyl ether and DEHP in sediments. Only data > LOQ were used. Note the different concentration axes and the logarithmic scale.

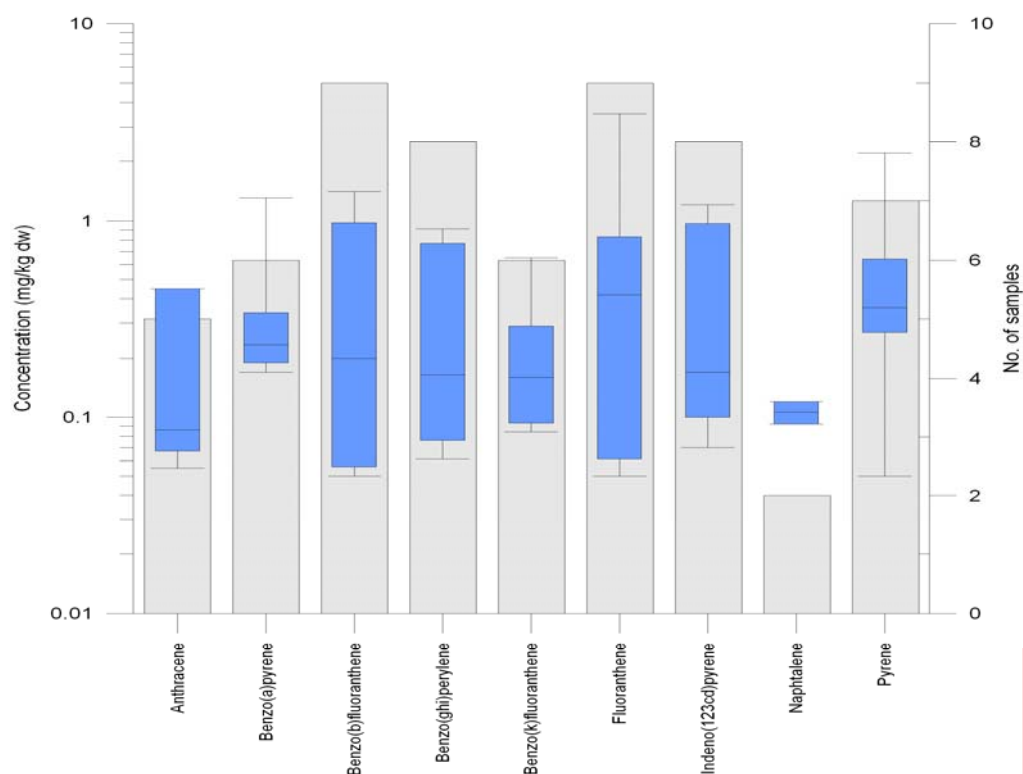


Figure 4.9 Levels of PAHs in sediments. Only data > LOQ were used. Note the different concentration axes and the logarithmic scale.

4.3 Temporal variation

The concentrations over time of selected priority substances are displayed in Figures 4.10 to 4.29 together with the limits of quantification (LOQ) and environmental quality standards (EQS). Concentrations below the LOQ are shown as half the LOQ. Also shown, are the mean concentrations of priority substances in Swedish surface waters obtained from a screening performed in 2006. This study encompassed all priority substances at 95 surface water localities in Sweden (mostly limnic). The mean values were calculated from data above the LOQ only.

Metal concentrations at limnic sampling stations are shown in Figures 4.11 to 4.18 and at marine sampling stations in Figures 4.19 to 4.26. The limits of quantification have varied over the year for some samples which is shown in the figures. Isolated increased or lowered limits are not shown however.

Metal concentrations were generally below EQS values. Cadmium and lead concentrations were intermittently below the limit of quantification, although to a lesser extent in the second half of the year due to lowered LOQ (Figures 4.11 – 4.12 and 4.17 – 4.18).

Lead concentrations in Vänern were consistently above the EQS early in the year. Also, there were generally decreasing concentrations of metals in Vänern over the sampling period. For cadmium, there was a “dip” in the water concentrations from August to September in limnic water. A similar dip occurred for Nickel in limnic waters from May to June. The nickel concentration in the filtrated sample from Vänern, December 2007 is probably not correct, but the value is displayed nevertheless.

The concentrations of tributyltin (TBT) at limnic and marine locations are shown in Figure 4.26 and Figure 4.27 respectively. TBT has been detected above EQS and LOQ at least intermittently at all sites except Rånefjärden. At sites where TBT was not detected, it cannot be established whether the concentrations are above or below the EQS since the LOQ is higher than the EQS. TBT concentrations were above the LOQ more frequently in the beginning of the year. This is especially the case for limnic localities.

Nonylphenol concentrations at limnic locations are shown in Figure 4.28 and at marine locations in Figure 4.29. Concentrations are higher during the summer months both at limnic and marine locations. Concentrations above the EQS are encountered more often at limnic locations.

Arithmetic mean values of measured concentrations were calculated for all substances at all sampling locations to facilitate comparison to the AA-EQS as described in the directive. For values below the LOQ, the LOQ was conservatively used for calculation

of the mean. Mean values for lead, nickel, nonylphenol and TBT were above the AA-EQS at one or more of the limnic sampling stations. Mean values above the AA-EQS at limnic sampling stations is presented in Table 4.6. Mean values for lead and nickel was above the AA-EQS for non-filtrated samples, but below for filtrated samples.

As the LOQ was used in the calculations for all values below the LOQ, mean values for TBT and pentachlorobenzene will always be above the AA-EQS as the LOQ is higher than the AA-EQS. This is also the case for octylphenol and endosulfane in marine surface waters, where the LOQ equals or is close to the AA-EQS. Since pentachlorobenzene and endosulfane was not detected at all in marine water samples they were excluded from Table 4.7.

At one or more of the marine sampling stations mean values for DEHP, octylphenol, (pentachlorobenzene,) and TBT exceeded AA-EQS. Table 4.7.

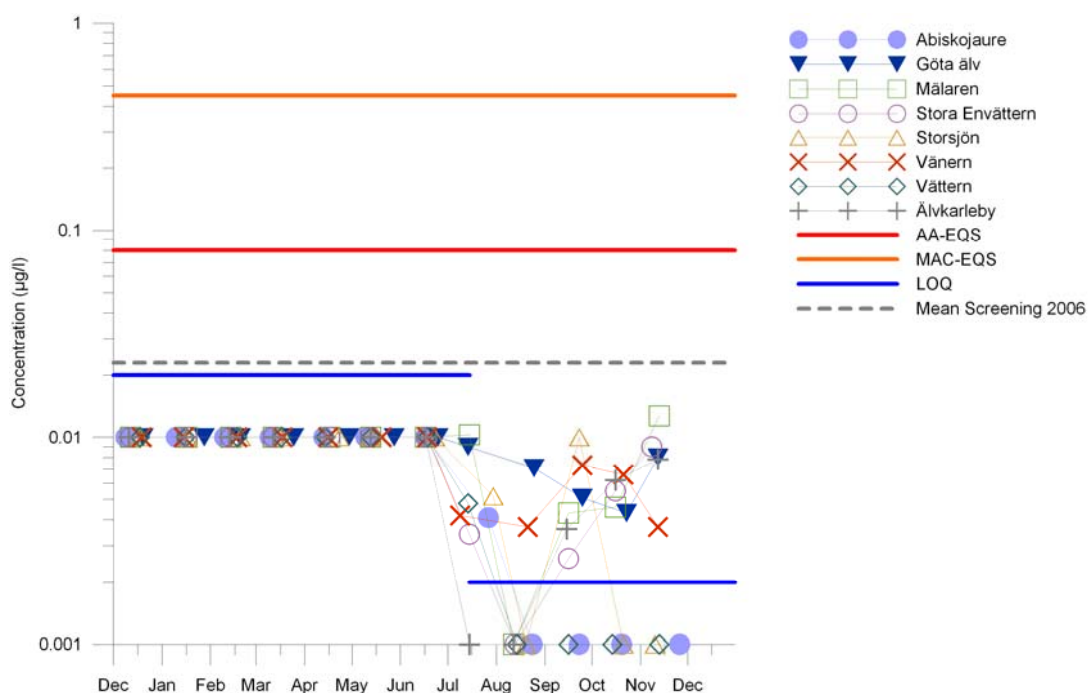


Figure 4.10 Cadmium concentrations in filtered water samples for limnic locations. Note the logarithmic scale.

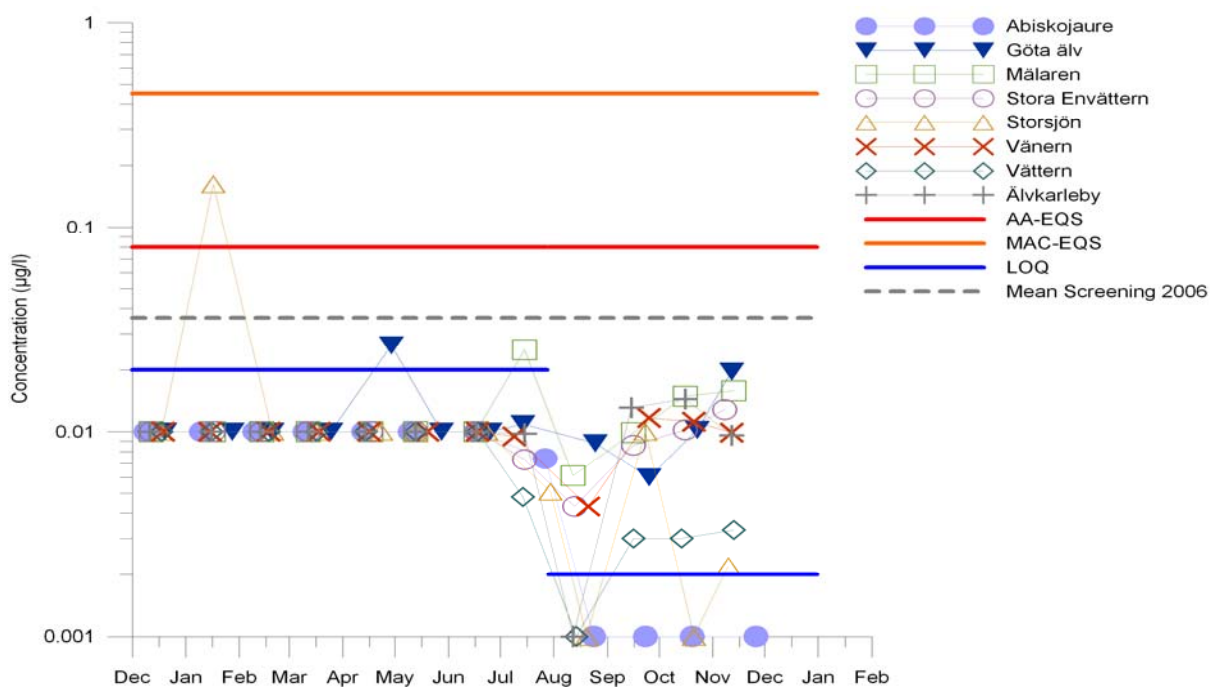


Figure 4.11 Cadmium concentrations in non-filtrated water samples for limnic locations. Note the logarithmic scale.

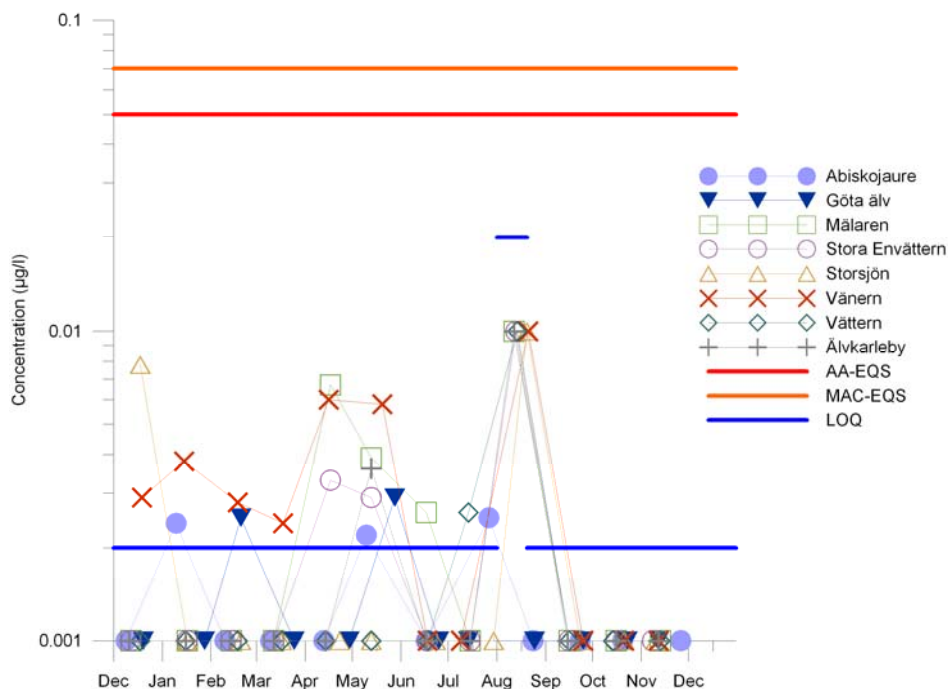


Figure 4.12 Mercury concentrations in filtrated water samples for limnic locations. Note the logarithmic scale. Observe that high value in august are only artefacts (half the LOQ) due to a temporary increased LOQ. Mean value from 2006 is not shown as there were only 5 instances above the LOQ.

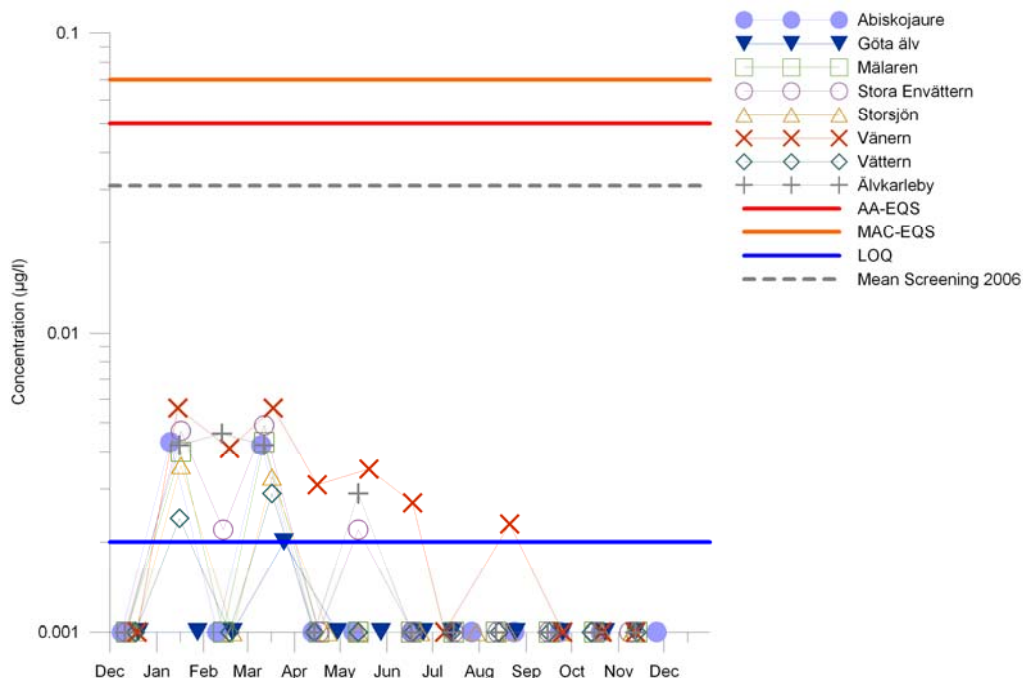


Figure 4.13 Mercury concentrations in non-filtrated water samples for limnic locations. Note the logarithmic scale.

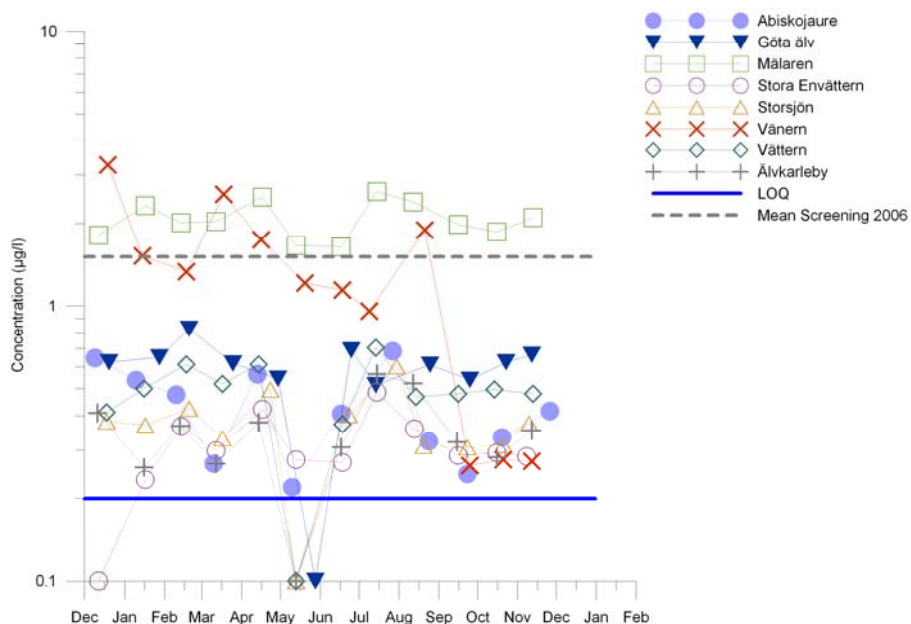


Figure 4.14 Nickel concentrations in filtrated water samples for limnic locations. The EQS for nickel is 20 µg/l. Note the logarithmic scale.

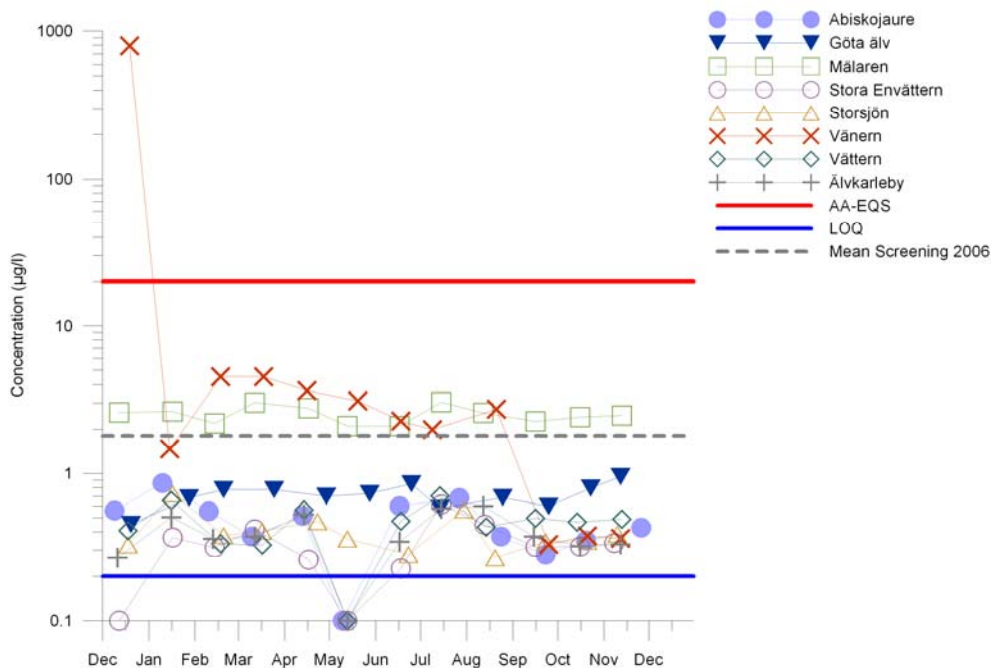


Figure 4.15 Nickel concentrations in non-filtrated water samples for limnic locations. The EQS for nickel is 20 µg/l. Note the logarithmic scale.

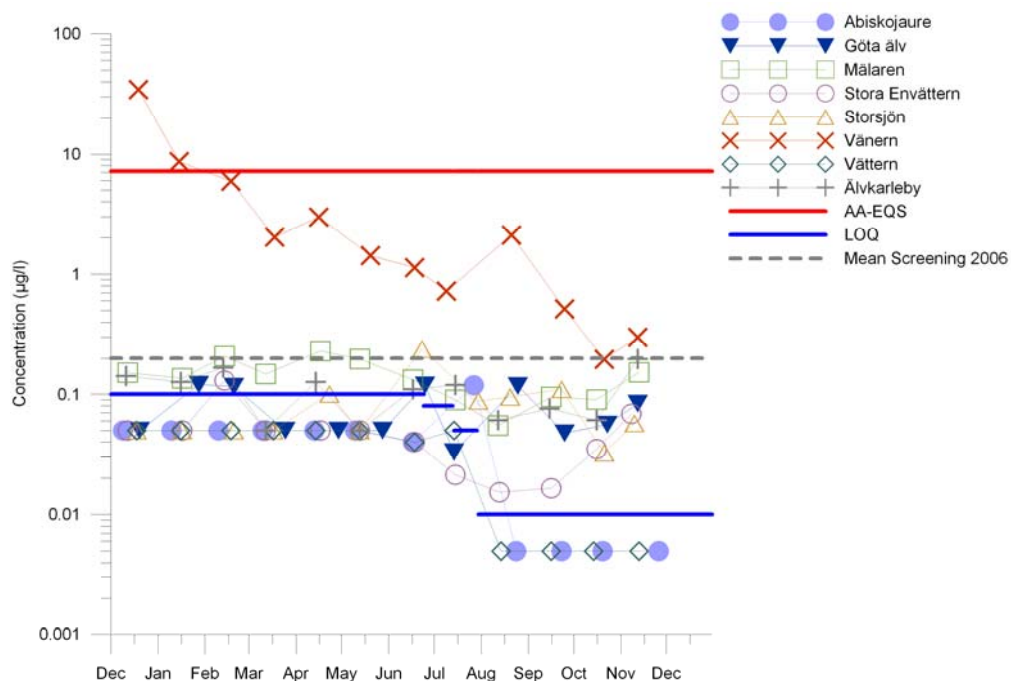


Figure 4.16 Lead concentrations in filtrated water samples for limnic locations. Note the logarithmic scale.

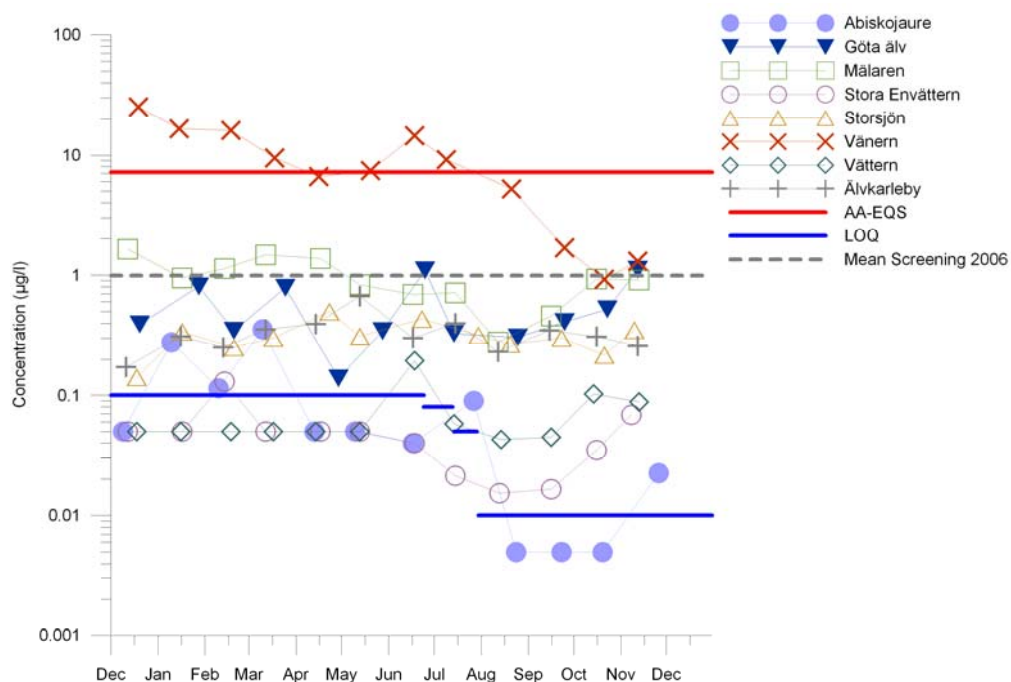


Figure 4.17 Lead concentrations in non-filtrated water samples for limnic locations. Note the logarithmic scale.

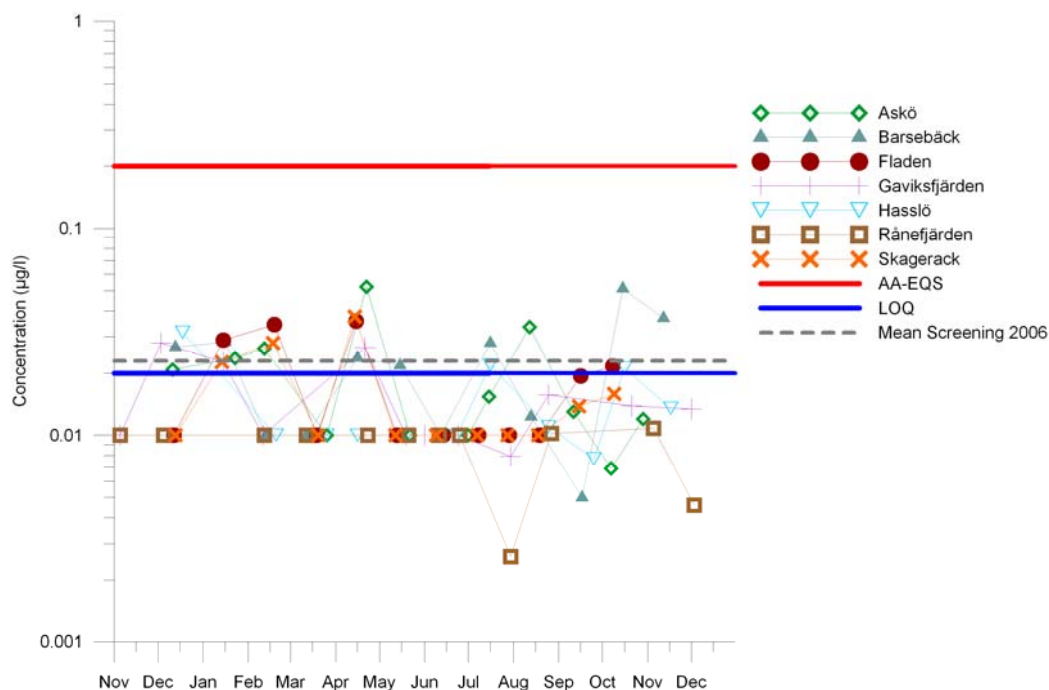


Figure 4.18 Cadmium concentrations in filtered water samples for marine locations. Note the logarithmic scale.

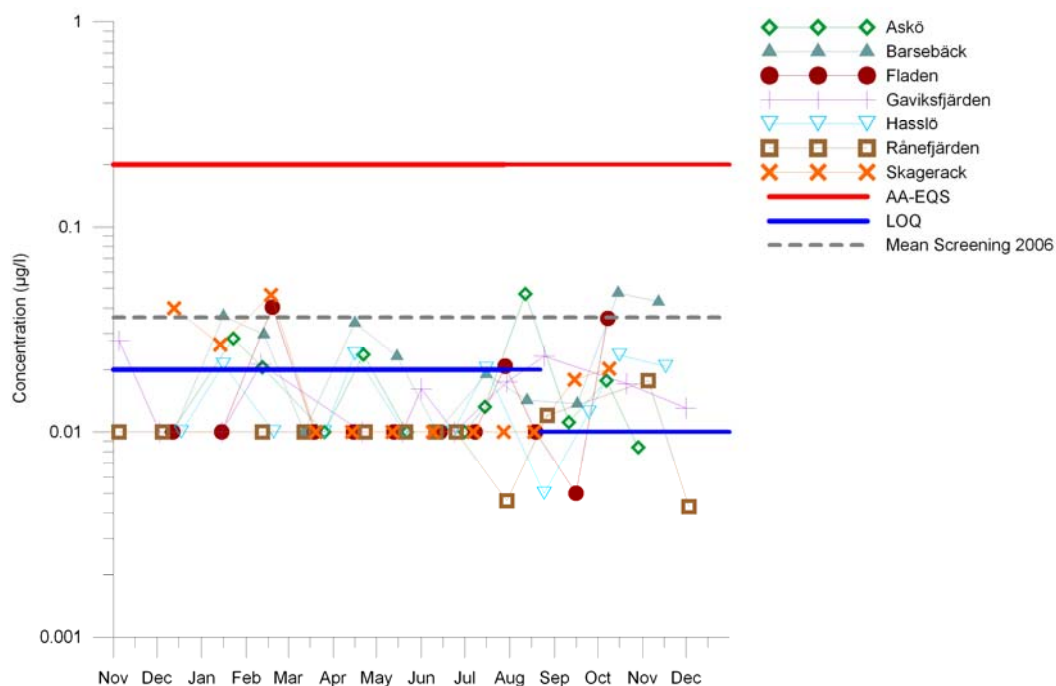


Figure 4.19 Cadmium concentrations in non-filtered water samples for marine locations. Note the logarithmic scale.

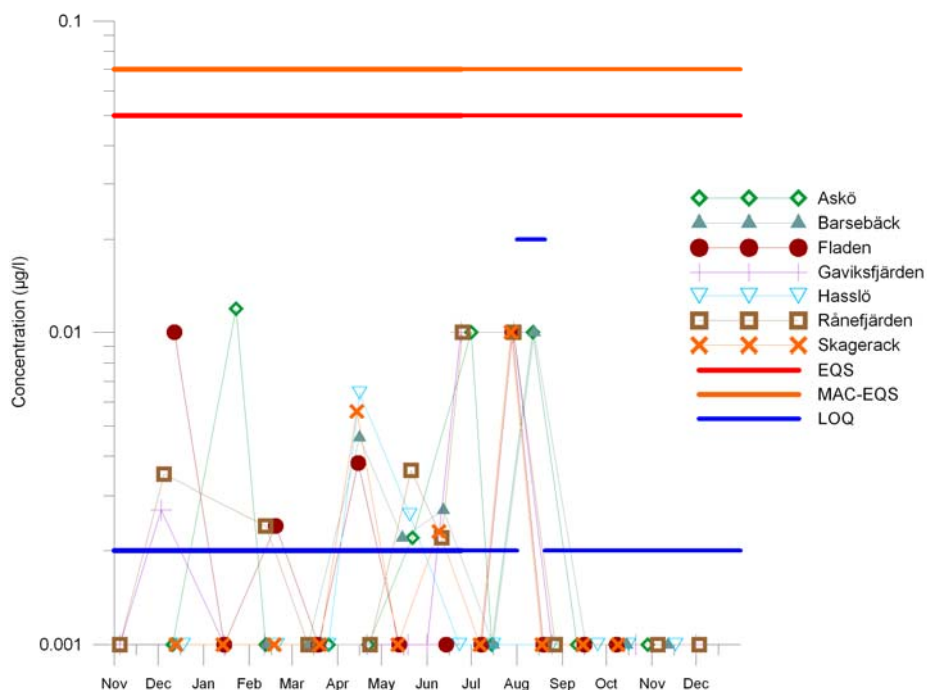


Figure 4.20 Mercury concentrations in filtrated water samples for marine locations. Note the logarithmic scale. Mean value from 2006 is not shown as there were only 5 instances above the LOQ.

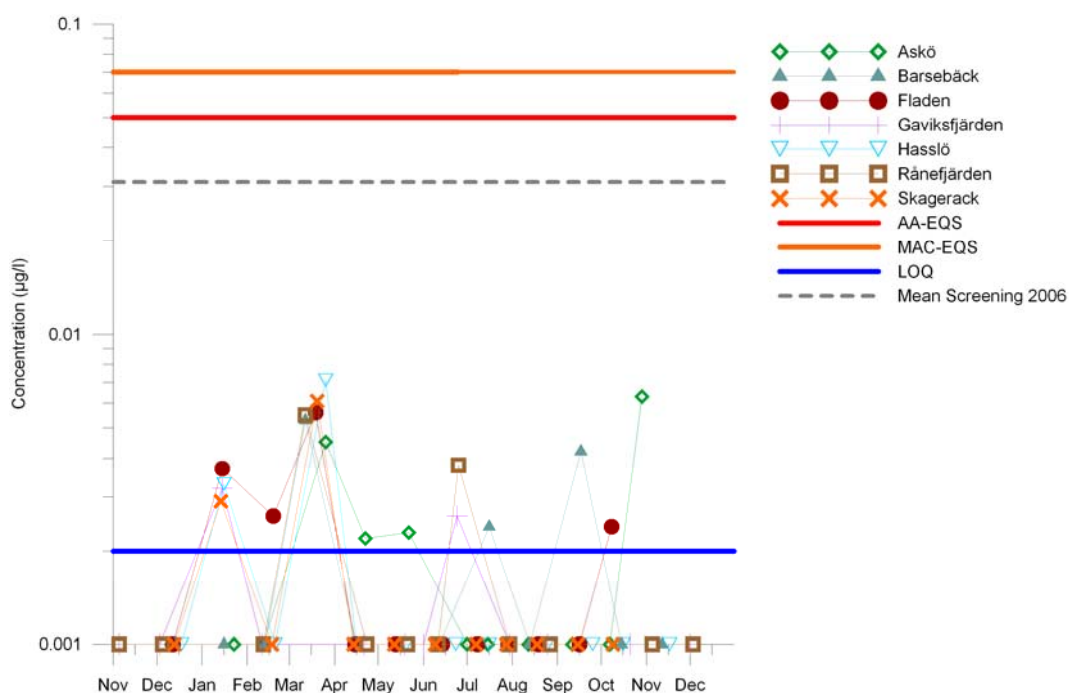


Figure 4.21 Mercury concentrations in non-filtrated water samples for marine locations. Note the logarithmic scale.

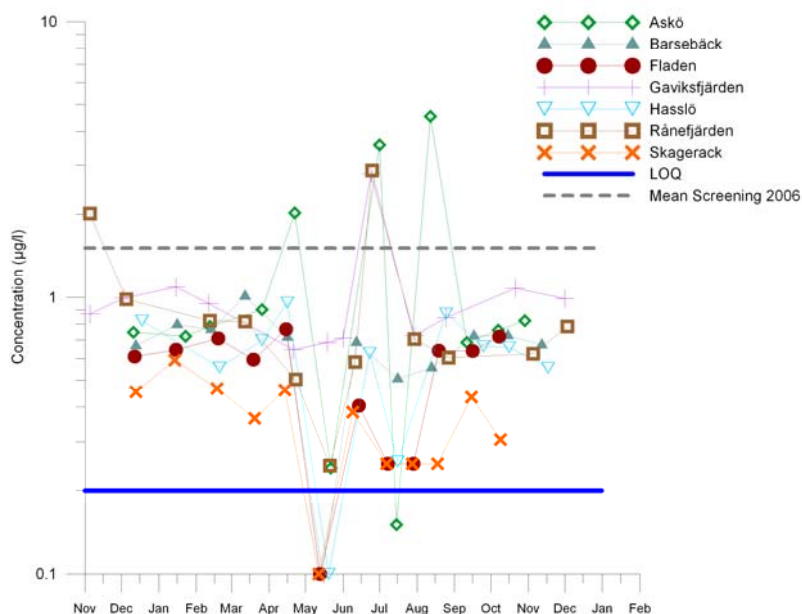


Figure 4.22 Nickel concentrations in filtered water samples for marine locations. The EQS for nickel is 20 µg/l Note the logarithmic scale.

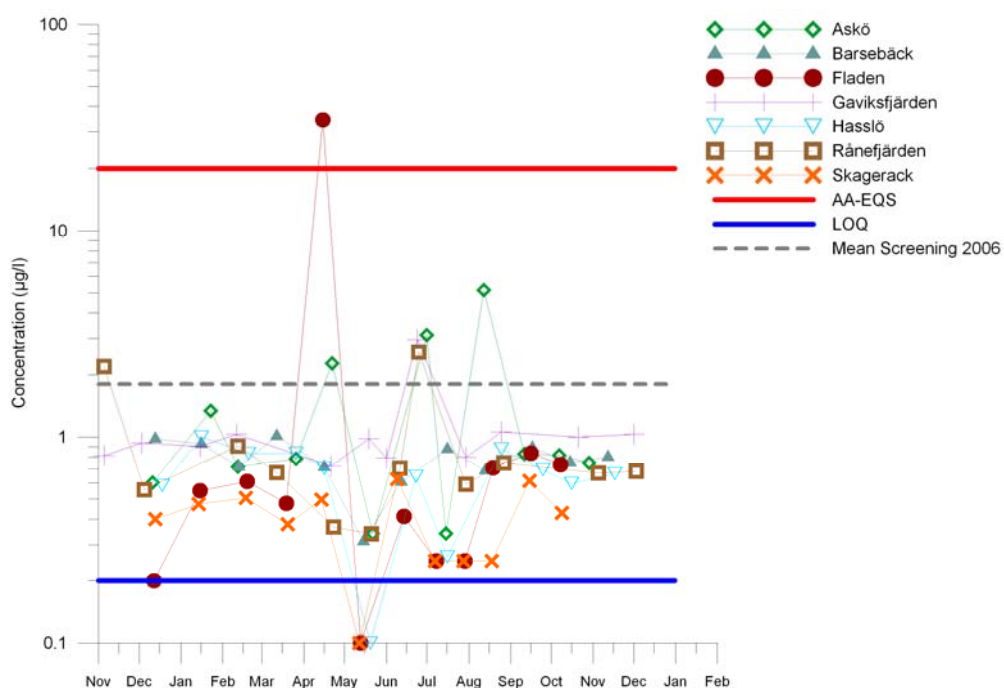


Figure 4.23 Nickel concentrations in non-filtered water samples for marine locations. Note the logarithmic scale.

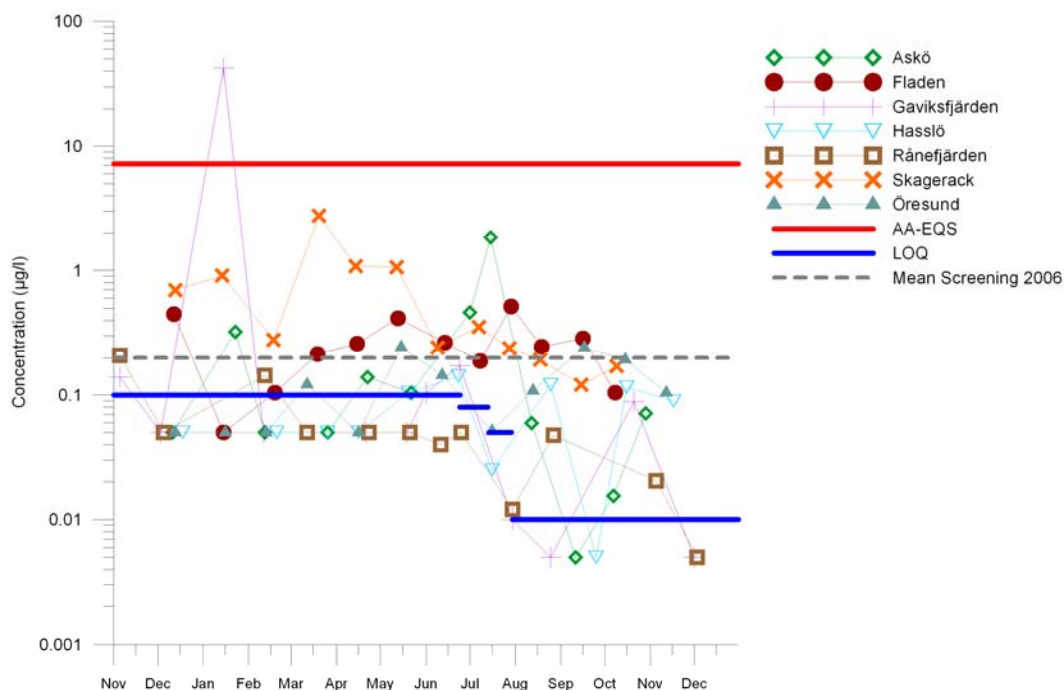


Figure 4.24 Lead concentrations in filtrated water samples for marine locations. Note the logarithmic scale.

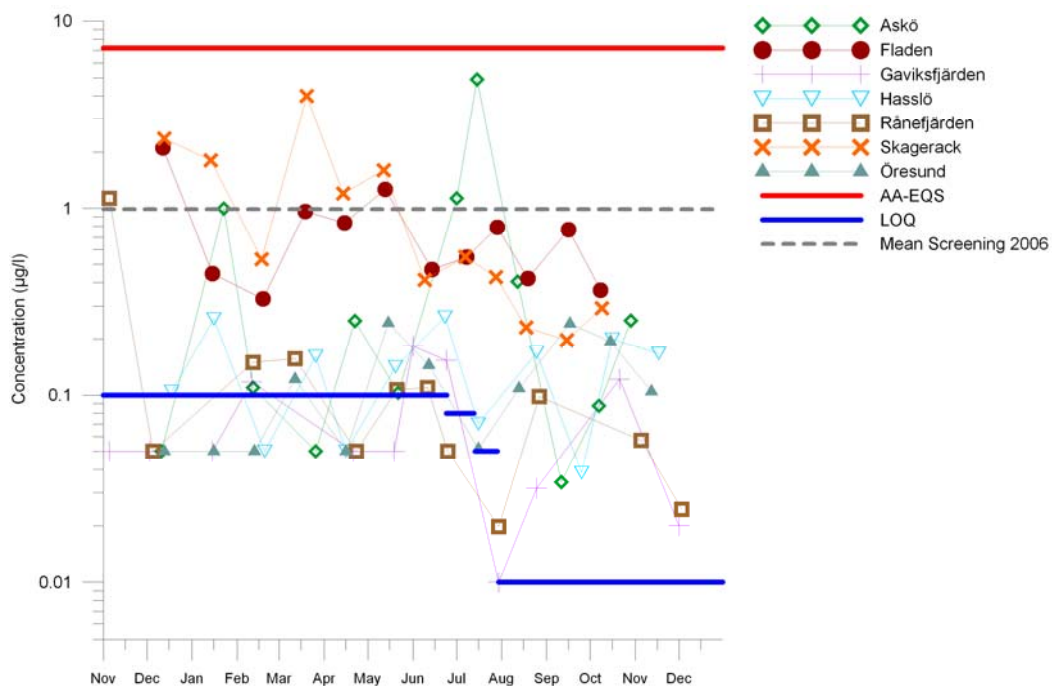


Figure 4.25 Lead concentrations in non-filtrated water samples for marine locations. Note the logarithmic scale.

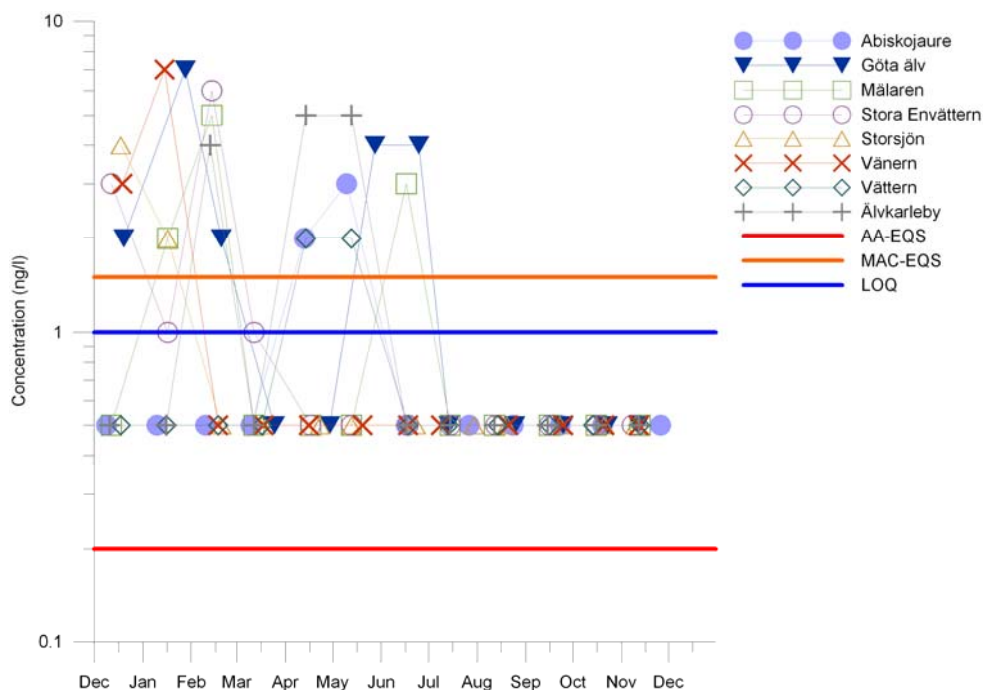


Figure 4.26 Tributyltin concentrations in non-filtrated water samples for limnic locations. Note the logarithmic scale. Mean value from 2006 is not shown as there were only 2 instances above the LOQ.

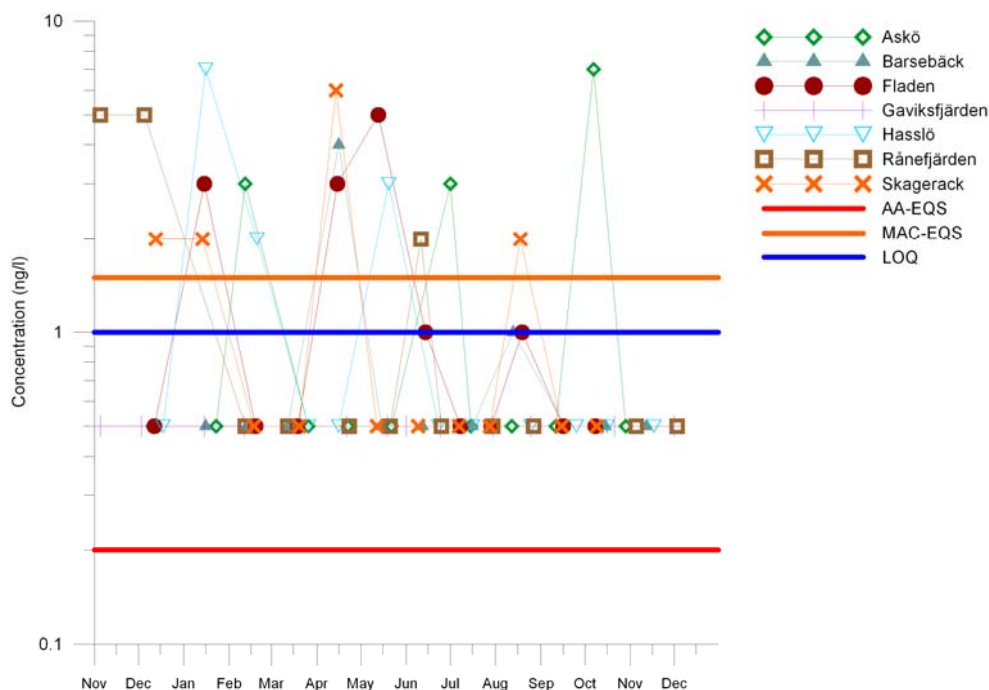


Figure 4.27 Tributyltin concentrations in non-filtrated water samples for marine locations. Note the logarithmic scale. Mean value from 2006 is not shown as there were only 4 instances above the LOQ.

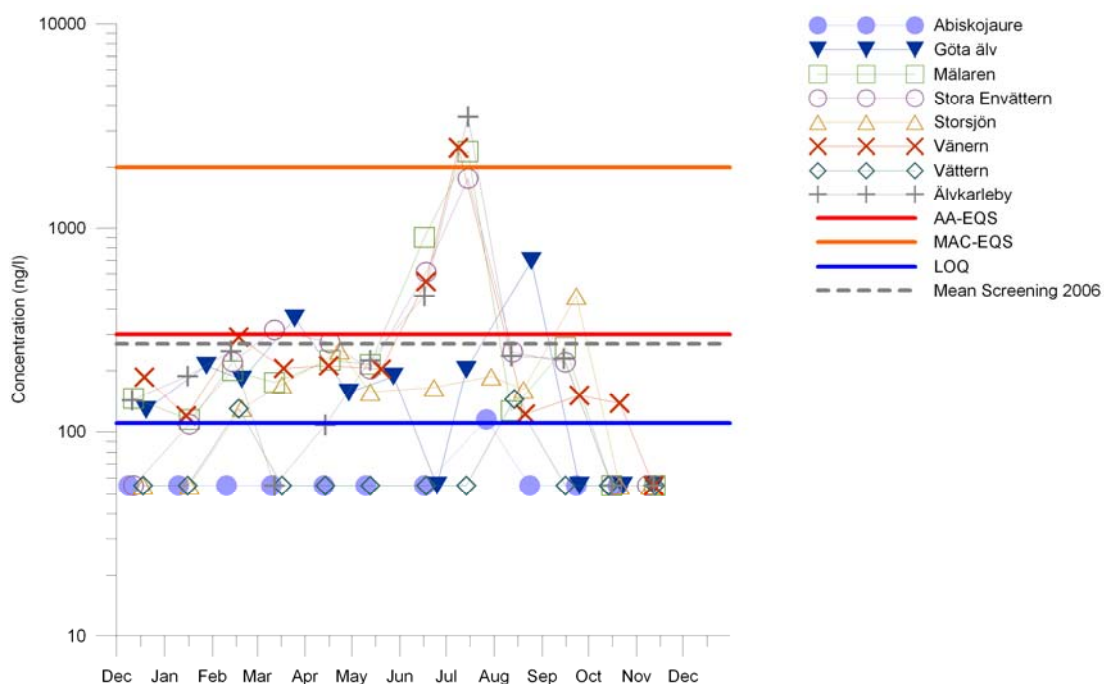


Figure 4.28 Nonylphenol concentrations in non-filtrated water samples for limnic locations. Note the logarithmic scale.

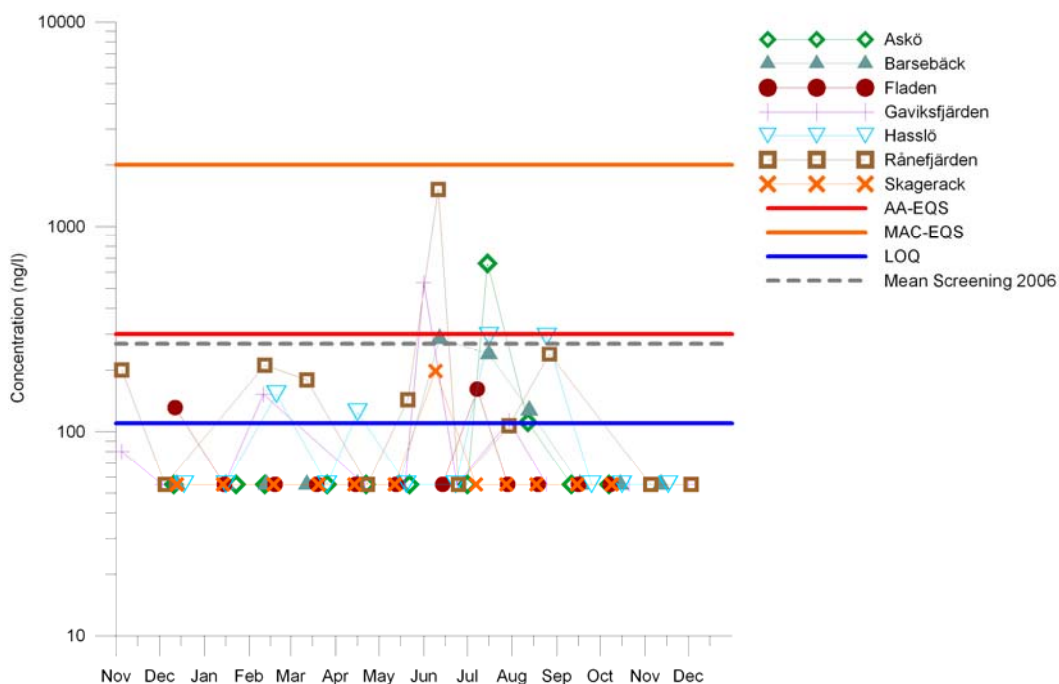


Figure 4.29 Nonylphenol concentrations in non-filtrated water samples for marine locations. Note the logarithmic scale.

Table 4.6 Arithmetic mean of concentrations for substances whose mean exceeded AA-EQS at limnic sampling stations. Note for TBT that the mean values was calculated using the LOQ for non-detects. The LOQ for tributyltin is above the AA-EQS.

	Substance			
	Lead (µg/l) EQS: 7.2	Nickel (µg/l) EQS: 20	Nonylphenol (ng/l) EQS: 300	Tributyltin (ng/l) EQS: 0.2
Abiskojaure				1.3
Göta älv				2.2
Hjulstafjärden			410	1.6
Stora Envättern			350	1.6
Storsjön				1.3
Vänerns inlopp	9.5	68	390	1.7
Vätterns utlopp				1.2
Älvkarleby			470	1.9

Table 4.7 Arithmetic mean of concentrations for substances whose mean exceeded AA-EQS at marine sampling stations. Note for TBT that the mean values was calculated using the LOQ for non-detects. The LOQ for tributyltin is above the AA-EQS.

	Substance	
	DEHP (µg/l) EQS: 1.3	Tributyltin (ng/l) EQS: 0.2
Askö		1.8
Fladen		1.7
Gaviksfjärden		1
Hasslö		1.8
Rånefjärden	3.7	1.8
Skagerack		1.7
Öresund		1.3

5 Discussion

5.1 General observations

This study encompassed 15 sampling points in Sweden. Consequently, it is not meaningful to evaluate geographical patterns. Also, it is difficult to compare levels of priority substances with earlier studies since this will very much be dependent on the choice of sampling points in a geographically limited study such as the present one. It is for example obvious that the priority substance concentrations are generally lower in this study compared with a study that encompassed almost a hundred surface water sampling points in 2006 (compare the mean screening 2006 line with measured concentrations in Figure 4.10 – 4.29). This is despite the fact that the same sampling methods and the same laboratory were used in both studies. One reason may be that more sampling points in this study represented sampling points not directly influenced by local sources. On the other hand, it may just be a random phenomenon, so that the sampling points in this study do not represent a “true” mean in Sweden.

It is more meaningful to compare which priority substances that are reoccurring in different screening studies. Table 5.1 presents such a comparison between the present study, the 2006 screening study of 95 surface waters and a regional screening study of 50 surface waters around Lake Mälaren. The table demonstrates that, in main, the same priority substances occur whenever or wherever the study is performed. The differences probably depend on the presence of local sources of pollutants.

Table 5.1 Priority substances above LOQ in water samples, at any sampling point, in three different screening studies in Sweden.

	Northern Baltic Sea river basin district, October 2008	The present study	Nationwide screening at 95 sampling stations in 2006
PentaBDE			x
Cadmium	x	x	x
C10-13-chloroalkanes			x
Di(2-ethylhexyl)phtalate	x	x	x
Diuron	x		
Fluoranthene		x	
Hexachlorobutadiene			x
Lead	x	x	x
Mercury	x	x	x
Nickel	x	x	x
Nonylphenol		x	x
Oktylphenol	x	x	x
Benso(b)fluoranthene	x		

	Northern Baltic Sea river basin district, October 2008	The present study	Nationwide screening at 95 sampling stations in 2006
Indeno(1,2,3-cd)perylene	x		
Tributyltin	x	x	x
Trichloromethane	x	x	x

One important observation is that a few substances seldom occur in surface waters. However, when they are found, the concentrations are clearly elevated. The most obvious example is DEHP which was above LOQ on four occasions and also above the AA-EQS on the same four occasions. Another example is octylphenol.

5.2 Temporal variability

The temporal variability in concentrations of priority substances may depend on a number of factors. The temporal variability in the load of pollutants from different sources such as industrial activities and waste water municipal plants is probably important. One other reason for differing concentrations may be physiochemical conditions. It is for example well known that the water solubility of nonylphenol is dependent on the pH of the surface water.

It may also depend on the amount of water in the surface water system. If the sources of contaminants remain constant, the amount of water in the system will influence the dilution of substances and subsequently concentrations. These parameters are in themselves influenced by a number of variables. The water flow in surface water may for example, be influenced by the rainfall intensity and snow melt periods as well as properties of the catchment area. Furthermore, many variables will exert their effects on surface water concentrations independently of each other. Consequently it is very difficult to understand and explain causes of observed temporal variability.

Some generalizations regarding water flow are nevertheless possible. A period of high water flow due to snow melt occurs in May – July in northern Sweden. In southern Sweden, high flow periods usually occur in April and in December – January with the highest flow in April. Since most of the precipitation in southern Sweden occurs as rainfall, the water levels and water flows are much more even compared to northern Sweden where as much as 50% of yearly precipitation may consist of snow.

A general temporal trend was that the levels of priority substances seemed to be lower during the autumn and winter (September to December). There is however no general mechanism that can explain such a pattern. The above mentioned water flow patterns would, as an example, imply lower concentrations during December – January in southern Sweden and May – July in northern Sweden due to dilution.

5.2.1 Limnic surface waters

Cadmium was below the limit of quantification during the first half of the sampling period. When the LOQ was lowered, a pattern was revealed with no major temporal variability. A low temporal variability may indicate that cadmium originates from precipitation, groundwater or surface waters since this would lessen any dilution effects. This may be plausible because cadmium occurs as a contamination in phosphate fertilizers applied to soil, in deposition originating from coal burning in neighbouring countries. It is also suspected that the acidification of forest soils have increased the leaching of cadmium to surface waters (Swedish Chemicals Agency, KEMI 2004). The earlier screening study in 2006 (SWECO VIAK 2006) showed a geographical pattern of cadmium with no discernible geographic differences in the frequency of elevated levels, and levels in background stations at par with other sources.

Mercury exhibited very variable concentrations with no clear temporal pattern apart from levels being below LOQ from October to December. Low levels at the end of the year all over Sweden do not imply a dilution effect since water levels/flows are not at their lowest during this time. This would instead imply a declining source during October – December.

Nickel exhibited relatively even concentrations over the year at each sampling point. The only exception was a clear dip in concentration from May – June. This would be expected as a dilution effect in the northern sampling stations (Abiksojaure and Storsjön for example) where the snow melt increase water levels and flow during this period. Flow pattern do not explain the dip in the southern sampling stations however.

Lead exhibited relatively even concentrations at each sampling point. Low temporal variability may indicate that lead originates from precipitation, groundwater or surface waters since this would lessen any dilution effects. Lead is still a major component in run-off water and is considered a widespread compound with many anthropogenic sources.

TBT exhibited a very variable temporal pattern. Even given the fact that the LOQ was five times lower than the EQS value it is noticeable that levels could vary by a factor of 5 – 6 at one sampling location. TBT was not found at all from July and onward in Limnic waters, a pattern that remain unexplained. It does not coincide with any clear flow patterns in Sweden. TBT in limnic systems partly originates from sewage treatment plants (Svensson 2002) and the temporal pattern may reflect temporal variability in the outflow of TBT from these.

Levels of *nonylphenol* were relatively even over time except for a clearly defined increase in concentrations that occurred from June - August for most sampling stations with a slight delay until September for other sampling stations.

Since nonylphenol seem to be one of the more problematic priority substances it is of interest to elucidate the observed temporal pattern in more detail. Figure 5.1 displays both the temporal and geographical pattern of nonylphenol concentrations at the sampling stations. It is apparent from figure 5.1 that the increase in nonylphenol levels does not seem correlate with geographical position. A clear tendency is rather that surface waters with high concentrations early in the year (January – February) also have the highest maximum concentrations. These surface waters also reach their peak concentrations earlier.

The main source of nonylphenol is most likely municipal sewage treatment plants (STPs) (Svensson 2002). The observed temporal pattern may be explained by the fact that the recipient of the STPs has their lowest flow in June – September so that the observed pattern is dependent on the dilution between outflow concentrations from STPs and flows in recipients. The sampling stations with the highest nonylphenol concentrations should consequently receive a relatively high load from STPs. The stations with lower concentrations that also lag in their peak concentration may have generally lower load of nonylphenol because of a lower influence from STPs. As water from the more influenced surface waters reach these surface waters, the levels still increase albeit to lower levels and somewhat later in the year.

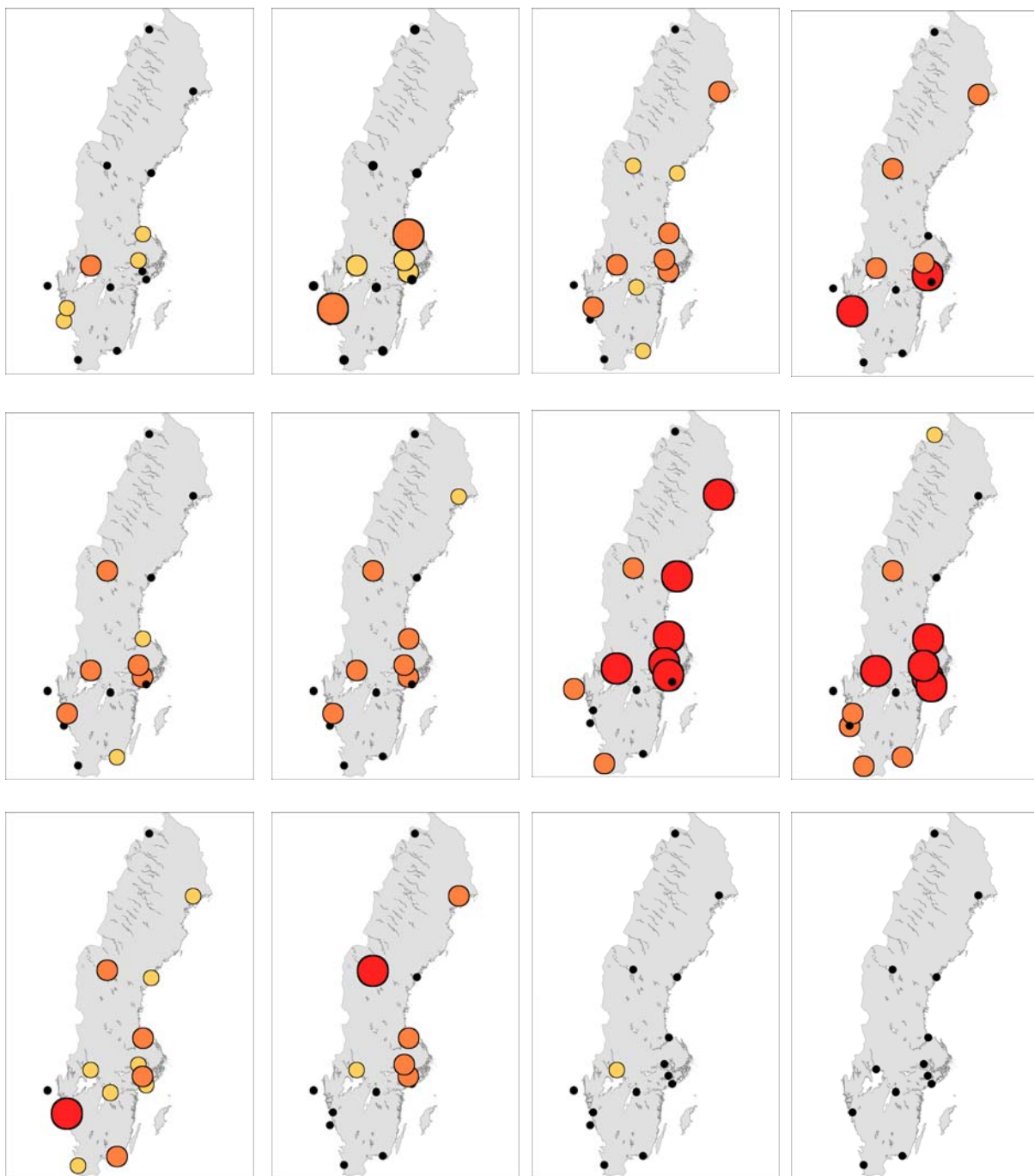


Figure 5.1 Monthly variation of nonylphenol concentrations from december 2007 (upper left) to november 2008 (lower right). Red > 300 ng/l, orange 150 – 300 ng/l, yellow < 150 ng/l, and black < LOQ (110 ng/l). The AA-EQS for nonylphenol is 300 ng/l

5.2.2 Marine surface waters

Cadmium and *mercury* levels were relatively variable, with no discernable temporal pattern in marine waters. The concentrations of *lead* were also relatively even over the year with slightly decreasing concentration at some sampling stations during the autumn.

Nickel levels were relatively even at each sampling station over the year, with a very clear dip in concentrations in May. This dip coincides with the dip at Limnic sampling stations, implying either that Limnic waters are the main source to marine waters or that both marine and Limnic waters have the same source. There was no discernible difference in the degree of the dip in concentrations dependent on geographical position and/or distance to shore.

TBT exhibited a very variable temporal pattern in marine surface waters. Even given the fact that the LOQ was five times lower than the EQS value it is noticeable that levels could vary by a factor of 5 – 6 at one sampling location. One difference from limnic waters was that TBT was found on a few occasions during the autumn. It is very probable that TBT in marine waters have boat paint as an important source which may not be the case in limnic waters, and this may explain the why TBT was found in marine surface waters during the autumn.

Nonylphenol was less frequently above the LOQ in marine waters, but the increase in concentrations from June - August was still evident as in Limnic waters. This implies either that limnic waters are the main source to marine waters or that both marine and limnic waters have the same source.

5.3 Implications for sampling

Table 5.2 summarizes information on the relative variability of the most frequently occurring priority substances. Those substances that are classified as having a less variable temporal distribution may not need to be monitored with the same frequency as those with a more variable temporal distribution. For nonylphenol it seems that sampling may only be necessary from May – August since all sampling stations had their highest levels during this period. For nickel, sampling should be avoided in May when the lowest concentrations occur.

To decrease the variability, passive samplers can be used to get time integrated concentrations representative during one month for example. An evaluation of the screening study of 2006 showed that this could be an appropriate methodology for nickel and cadmium, but not for other substances.

A problem with using these data for assessing general sampling strategies are that occasionally surface waters will deviate due to the presence of point sources. Lead at the outlet to lake Vänern is one obvious example (figure 4.16 – 4.17) where a unknown source causes locally elevated lead concentrations during the year. This source has not been identified. Before a long term monitoring programme of priority substances is initiated, it may thus be necessary to measure all priority substances on a few occasions to identify any outlying substances that need to be monitored more regularly.

Table 5.2 Generalizations regarding the month to month variability of the most frequently occurring priority substances.

	Limnic waters		Marine waters	
	Less variable concentrations	Very variable concentrations	Less variable concentrations	Very variable concentrations
Nickel*	X		X	
Cadmium		X		X
Lead	X			X
Mercury		X		X
Nonylphenol**	X		X	
TBT		X		X

* dip in May

** increased concentrations in May - July

5.4 Sediments

All of the frequently occurring priority substances in surface waters were also frequent in sediments. However, octylphenol, DEHP and most notably PAHs frequently occurred in sediment but not in surface waters. This most likely reflects physiochemical properties of these compounds that cause them to be much more prone to exist in the sediment phase and not surface waters. Octylphenol for example has a much higher affinity for organic carbon compared to nonylphenol which may explain the difference in surface water vs sediment occurrence for two such similar substances.

A statistical analysis (not shown here) using principal component analysis and correlation analysis demonstrated that there was no relationship between sediment concentrations of these compounds and surface water concentrations. This demonstrates that the source of priority substances in surface waters is most probably not sediments. In very shallow waters systems it may be different since sediment resuspension will affect a larger part of the water column.

A limit value of 129 µg/kg dw for fluoranthene in sediment has been suggested by the Swedish EPA (Naturvårdsverket 2009). This value was exceeded at most of the sampling stations (table 4.5) indicating that fluoranthene and PAHs in general may be very

problematic substances as regards to the classification of status in the Water Framework Directive. The results imply that the suggested level of 129 µg/kg is close to or above the national average background levels, although further studies are needed before conclusions on this matter can be made.

5.5 Substances of concern

As has been the case in earlier monitoring and screening of surface waters, TBT and nonylphenol remains the most problematic priority substances. In the screening study of 2006, cadmium very frequently occurred at elevated concentrations which were not the case in this study. Instead, lead was the most problematic compound. This was only because lead concentrations at one sampling point was highly elevated during the whole sampling period. This demonstrated once again the importance of being careful with drawing general conclusions from national studies regarding which substances that may be most problematic on a local level. On a national level, the screening studies are valuable tools to assess which are the most problematic priority substances, but this has to be confirmed by local sampling.

It must be stressed, that these conclusions are only valid for surface waters. Others substances will probably be of greater importance in other environmental matrices. Mercury (especially methylmercury) in limnic fish is an important example of a substance and matrix that is problematic all over Sweden as regards to the status classification within the water framework directive.

5.6 Chemical status of surface waters

Most sampling point/water bodies in this study could not be classified as having a good chemical status. In all cases this was due to the fact that the yearly arithmetic mean exceeded the AA-EQS value.

In a few instances the reason was a conservative approach for TBT where the LOQ (=which is 5 times higher than the AA-EQS) was chosen as the concentration when TBT was not detected. This is deemed an acceptable approach because of the common occurrence of TBT in general and the need to put a focus on the problem of TBT in surface waters. In most instances, even using half the LOQ of TBT would still mean that the yearly average exceeded the AA-EQS values. Also, other substances caused the chemical status to deviate from good, most notably nonylphenol.

The most heavily affected sampling point, the inlet to Lake Vänern (Skoghallsådran), was clearly the sampling point that was most negatively influenced by chemicals since the yearly average of four substances exceeded the AA-EQS. For Nickel this was a result of one value being very high while all the others were below AA-EQS.

5.7 Limnic vs. marine surface waters

The AA-EQS value was exceeded 55 times in limnic surface waters and 26 times in marine surface waters. Also, 12 substances were found at levels above LOQ in limnic waters and 9 in marine waters. This shows that limnic waters in general are more affected by priority substances. Important reason are probably dilution in the marine waters systems and the fact that many of the point sources such as waster water treatment plants, urban run-off, landfills and industries have limnic water systems as their primary recipients. It is also interesting that TBT exceeded its EQS value with the same frequency in marine waters and limnic waters, which contradicts a general view that TBT is mostly a marine problem. TBT originating from waste water treatment plants may be as big a problem as TBT originating from marine boat paints.

5.8 Conclusions and future work

The main conclusions from this study are:

- Almost all the sampling locations and water bodies did not reach good chemical status because of high yearly average concentrations of TBT and nonylphenol. More sampling stations would have gotten a good chemical status if a less conservative approach had been used for calculating the yearly average of TBT.
- The substantial variability for many substances demonstrate that sampling of surface waters on one or two occasions per year may not be sufficient to classify the chemical status.
- In general, the most frequently occurring priority substances exhibit substantial month by month variability during one year.
- A few priority substances exhibited less variability over part of the year, most noticeable nickel and nonylphenol.
- Nickel had a clear dip in concentrations in May while nonylphenol clearly had the highest concentrations from June – August.
- TBT was not found at all from July and onward in Limnic waters, and very seldom during the autumn in marine waters.
- TBT and nonylphenol remains the most important priority substances, although this may deviate locally because of point sources.
- Cadmium, lead, nickel and DEHP may also be important substances, depending on local conditions.
- All of the priority substances that are common in surface waters were also common in sediments. Some additional compounds such as DEHP, certain PAHs and octylphenol were common in sediments but not ion water.

- There were no co-variability between sediment concentrations and surface water concentrations.
- Exceedance of EQS values was much more prevalent in limnic surface waters compared to marine. Also, more substances were found in limnic water systems.
- Elevated TBT levels (above AA-EQS) were as prevalent in marine water systems as in limnic water systems.

A general recommendation is to take these results into account when planning compliance monitoring of WFD priority substances. As an example, water sampling should perhaps be less frequent during the autumn compared to the spring due to lower levels of TBT, nonylphenol and some metals during the autumn.

Future work could focus on the following:

- The weekly and daily temporal variability needs to be assessed at a few representative sampling locations to better understand how representative one sample per month are of the total load. This could be combined with flow measurement to calculate the actual load.
- Screening studies focusing only on nonylphenol and TBT using better analytical methods (for TBT) and/or passive samplers should be performed to answer questions regarding the sources of these compound, their behavior in the surface water environment and the actual risks that these possess. These should be combined with measurements in fish and sediments.
- The water framework directive demands that action is taken to reduce the concentration of priority substances exceeding EQS values. To do this, the sources need to be identified. This could be done by developing National mass balance budgets of nonylphenol, TBT and possibly other priority substances. By comparing inputs from possible sources with the amounts found in surface waters, it will be possible to systematically identify possible sources and evaluate if there are any sources that has not been identified. The source term in this context can be local sources, diffuse urban sources as well as diffuse pollution from deposition and soil leaching.

6 References

- Barceló, D. Oubiña, A. Salau, J. Perez, S. (1998) Determination of PAHs in river waters samples by ELISA. *Analytica Chimica Acta*, 376. 49 – 53.
- Bruen, M. Johnston, P. Quinn, M. K. Desta, M. Higgins, N. Bradley, C. Burns, S. (2006) Impact Assessment of Highway Drainage on Surface Water Quality. Irish Environmental protection Agency. 2000-MS-13-M2.
- 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.
- 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.
- 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
- 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.

Naturvårdsverket (2009) Förslag till implementering av direktiv 2008/105/EG om miljökvalitetsnormer inom vattenpolitikens område - Redovisning av ett regeringsuppdrag. Utkast för remiss 2009-04-24.

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.

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

Andersson, Å. Sörne, L. (2007) Substansflödesanalys av alkylfenoler och alkylfenoletoxilater i Stockholms stad 2004. Stockholms Stad. ISSN 1653-9168

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.