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Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2008

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1 Introduction

This report gives a summary of the monitoring activities within the national Swedish contaminant programme in marine biota. It is the result from the joint efforts of: the *Department of Applied Environmental Science* at Stockholm University (analyses of organochlorines), the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences (analyses of heavy metals), *Department of Chemistry* at Umeå University (analyses of PCDD/PCDF) and the *Department* of *Contaminant Research* at the Swedish Museum of Natural History (co-ordination, sample collection administration, sample preparation, recording of biological variables, storage of frozen biological tissues in the Environmental Specimen Bank for retrospective studies, data preparation and statistical evaluation). The monitoring programme is financiated by the *Environmental Protection Agency* (EPA) in Sweden.

The data of concern in this report represent the bioavailable part of the investigated contaminants i.e. the part that has virtually passed through the biological membranes and may cause toxic effects. The objectives of the monitoring program in marine biota could be summarised as follows:

- to estimate the levels and the normal variation of various contaminants in marine biota from several representative sites, uninfluenced by local sources, along the Swedish coasts. The goal is to describe the general contaminant load and to supply reference values for regional and local monitoring programmes

- to monitor long term time trends and to estimate the rate of found changes.
quantified objective: to detect an annual change of 10% within a time period of 10 years with a power of 80% at a significance level of 5%.

- to estimate the response in marine biota of measures taken to reduce the discharges of various contaminants
quantified objective: to detect a 50% decrease within a time period of 10 years with a power of 80% at a significance level of 5%.

- to detect incidents of regional influence or widespread incidents of 'Chernobyl'-character and to act as watchdog monitoring to detect renewed usage of banned contaminants.
quantified objective: to detect an increase of 200% a single year with a power of 80% at a significance level of 5%.

- to indicate large scale spatial differences
quantified objective: to detect differences of a factor 2 between sites with a power of 80% at a significance level of 5%.

- to explore the development and regional differences of the composition and pattern of e.g. PCB's, HCH's and DDT's as well as the ratios between various contaminants.

- the time series are also relevant for human consumption since important commercial fish species like herring and cod are sampled. A co-operation with the Swedish Food Administration is established. Sampling is also co-ordinated with SSI (Swedish Radiation Protection Authority) for analysing radionuclides in fish and blue mussels (HELCOM, 1992).

- all analysed, and a large number of additional specimens, of the annually systematically collected material are stored frozen in *the Environmental Specimen Bank.*. This invaluable material enables future retrospective studies of contaminants impossible to analyse today as well as control analyses of suspected analytical errors.

- although the programme is focused on contaminant concentration in biota, also the development of biological variables like e.g. condition factor (CF), liver somatic index (LSI) and fat content are monitored at all sites. At a few sites, integrated monitoring with fish physiology and population are running in co-operation with the University of Gothenburg and the Swedish Board of Fisheries.

- experiences from the national programme with several time series of over 25 years can be used in the design of regional and local monitoring programmes.

- the perfectly unique material of high quality and long time series is further used to explore relationships among biological variables and contaminant concentrations in various tissues; the effects of changes in sampling strategy, the estimates of variance components and the influence on the concept of power *etc*.

- the accessibility of high quality data collected and analysed in a consistent manner is an indispensable prerequisite to evaluate the validity of hypothesis and models concerning the fate and distribution of various contaminants. It could furthermore be used as input of ‘real’ data in the ongoing model building activities concerning marine ecosystems in general and in the Baltic and North Sea environment in particular.

- the contaminant programme in marine biota constitute an integrated part of the national monitoring activities in the marine environment as well as of the international programmes within ICES, OSPARCOM and HELCOM.

The present report displays the timeseries of analysed contaminants in biota and summarises the results from the statistical treatment. It does *not* in general give the background or explanations to significant changes found in the timeseries. Increasing concentrations thus, urge for intensified studies.

Short comments are given for temporal trends as well as for spatial variation and, for some contaminants, differences in geometric mean concentration between various species caught at the same site. Sometimes notes of seasonal variation and differences in concentration between tissues in the same species are given. This information could say something about the relative appropriateness of the sampled matrix and be of help in designing monitoring programmes. In the temporal trend part, an extract of the relevant findings is summarised in the 'conclusion'-paragraph. It should be stressed though, that geographical differences may not reflect antropogenic influence but may be due to factors like productivity, temperature, salinity etc.

The report is continuously updated. The date of the latest update is reported at the beginning of each chapter. The creation date of each figure is written in the lower left corner.

2 Summary 2006/07

A short summary of the results up to year 2006/07 is given below. Graphical presentations, tables and details are given in the following chapters.

- The condition of herring in the Baltic is *decreasing*, together with the fat content in herring muscle, in all autumn and spring time series except at Ängskärsklubb (autumn and spring). During recent years this decrease has stopped at Landsort and Utlängan and the condition and fat content have improved somewhat.

- Due to a change of method for metal analysis in 2004, values after 2003 are not presented. The new method is under investigation, since the values are uncertain.

- Lead concentrations in herring, cod and perch livers are *decreasing*, in almost all time series, both on the Swedish west coast and in the Baltic.

- The increasing trends of cadmium concentrations in herring liver from the Baltic Proper and from the Bothnian Sea reported for the period 1980 to 1997 seems to have *ceased*.

- Cadmium concentrations in blue mussels from the Baltic Proper are about *5 times higher* than the suggested background levels for the North Sea and 3 times higher than in blue mussels from the Swedish west coast.

- HCH's are *decreasing* at almost all sites with time series long enough to permit a statistical trend analysis.

- HCB is *decreasing* in herring, cod and guillemot from the Baltic Proper and also in herring and cod at the Swedish west coast. However, some relatively *high concentrations* have been detected in the last years, and it looks like the decrease is levelling out.

- There was a significant decrease of TCDD/TCDF in guillemot eggs from St Karlsö between 1970 and the middle of the 80-ies, after which the decrease has levelled out. In herring there is no decrease in TCDD-equivalents during the investigated time period 1990-2006. At Harufjärden even a significant increase in lipid weight concentrations has been recorded.

3 Sampling

3.1 Sampling area

The sampling area is generally defined by a central co-ordinate surrounded by a circle of 3 nautical miles. The exact sampling location should be registered at collection. General demands on sampling sites within the national contaminant monitoring programme are defined in chap. 5.

3.2 Collected specimens

For many species adult specimens are less stationary than sub-adults and represent a more recent picture of the contaminant load since many contaminants accumulates over time. To increase comparability between years, young specimens are generally collected. However, the size of the individual specimens has to be big enough to allow individual chemical analysis. Thus the size and age of the specimens vary between species and sites (see chap. 4). To avoid possible contribution of between-year variance due to sex differences the same sex (females) is analysed each year in most timeseries. In the past both sexes were used and thus, at least for the oldest time series, both sexes appear. To achieve the requested number of individual specimens of the prescribed age range and sex, about 50 - 100 specimens are collected at each site.

Only healthy looking specimens with undamaged skin are selected.

The collected specimens are placed individually in polyethene plastic bags, deep frozen as soon as possible and transported to the sample preparation laboratory.

Collected specimens, not used for the annual contaminant monitoring programme are stored in the Environmental Specimen Bank (see Odsjö 1993 for further information). These specimens are thoroughly registered and biological information and notes of availabe amount of tissue together with a precise location in the cold-store are accessible from a database. These specimens are thus available for retrospective analyses or for control purposes.

3.3 Number of samples and sampling frequency

In general 10-12 individual specimens from the Baltic sites (reported to HELCOM) and 25 from the Swedish westcoast sites (reported to OSPARCOM) are analysed annually from each site/species. For guillemot eggs and perch, 10 individual specimens are analysed. Organochlorines in blue mussels are analysed in pooled samples containing about 20 individual specimens in each pool. Since 1996, samples from 12 individual specimens are analysed which is proposed in the revised guidelines for HELCOM and OSPARCOM.

The sampling recommendation prescribes a narrow age range for sampled species. In a few cases it has not been possible to achieve the required number of individuals within that range. In order to reduce the between-year variation due to sample differences in age composition, only specimens within the range of age classes given in brackets after species name in the figures, are selected in this presentation.

Sampling is carried out annually in all timeseries. A lower frequency would result in a considerable loss in statistical and interpretational power.

3.4 Sampling season

Sampling of the various fish species and blue mussels is carried out in autumn, outside the spawning season. However, from two sites; Ängskärsklubb and Utlängan, herring is also sampled in spring. The two spring series started already in 1972. In the beginning only organochlorines where analysed but since 1996 metals have been analysed on a yearly basis. This provides a possibility to study seasonal differences and, when possible, to adjust for these differences and improve the resolution of the time series. It also gives an opportunity study possible changes in the frequencies of spring and autumn spawners.

Guillemot eggs are collected in the beginning-middle of May. A second laid egg (due to a lost first egg) should not be collected and are avoided by sampling early laid eggs (see 4.6).

3.5 Sample preparation and registered variables

A short description of the various sampling matrices and the type of variables that are registered are given below. See TemaNord (1995) for further details.

3.5.1 Fish

For each specimen total body weight, total length, body length, sex, age (see chap. 4 for various age determination methods depending on species), reproductive stage, state of nutrition, liver weight and sample weight are registered.

Muscle samples are taken from the middle dorsal muscle layer. The epidermis and subcutaneous fatty tissue are carefully removed. Samples of 10 g muscle tissue are prepared for organochlorine and 1.5 g for mercury analysis.

The liver is completely removed and weighted in the sample container. Samples of 0.5 – 1g are prepared for metal analyses.

3.5.2 Blue mussel

For each specimen total shell length, shell and soft body weight are registered. Trace metals are analysed in individual mussels whereas samples for organochlorine determination are analysed in pools of about 20 specimens.

3.5.3 Guillemot egg

Length, width and total weight are recorded. Egg contents are blown out. Embryo tissue is separated from the yolk and white that are homogenised.

Weight of the empty and dried eggshell is recorded. The eggshell thickness is measured at the blowing hole using a modified micrometer.

2 g of the homogenised egg content is prepared for mercury analyses and another to 2 g for the other analysed metals. 10 g is prepared for analyses of organochlorines.

3.6 Data registration

Data are stored in a flat ASCII file in a hierarchical fashion where each individual specimen represents one level. Each measured value is coded and the codes are defined in a code list

(Persson, *et al.*, 2008). The primary data files are processed through a quality control program. Suspected values are checked and corrected if appropriate. Data are retrieved from the primary file into a table format suitable for further import to database or statistical programs.

4 Sample matrices

The sample database provides the basic information for this report and contains data of contaminant concentrations in biota from individual specimens of various species.

Table 4. Number of individual specimen of various species sampled for analysis of contaminants within the base program

Species	N of individual specimen	%
Herring	4600	51
Cod	1032	11
Perch	744	8
Eelpout	466	5
Dab	346	3
Flounder	340	3
Guillemot	567	6
Blue mussel	798	9
Total	8893	

4.1 Herring (*Clupea harengus*)

Herring is a pelagic species that feeds mainly on zooplankton. It becomes sexually mature at about 2-3 years in the Baltic and at about 3-4 years at the Swedish west coast. It is the most dominating commercial fish species in the Baltic. It is important not only for human consumption but essential also for several other predators in the marine environment.

Herring is the most commonly used indicator species for monitoring contaminants in biota within the BMP (Baltic Monitoring Programme) in the HELCOM convention area and is sampled by Finland, Estonia, Poland and Sweden.

Herring muscle tissue is fat and thus very appropriate for analysis of fat-soluble contaminants i.e. hydrocarbons.

Herring samples are collected each year from six sites along the Swedish coasts: Harufjärden (Bothnian Bay), Ängskärsklubb (Bothnian Sea), Landsort (northern Baltic Proper), Utlängan (southern Baltic Proper), Fladen (Kattegatt) and at Väderöarna (Skagerack). Since 2005 herring from Örefjärden (Bothnian Bay) has also been collected.

Herring liver tissue is analysed for lead, cadmium, copper and zinc. 1995 analyses of chromium and nickel were added to the programme. Herring muscle tissue is analysed for mercury, organochlorines (DDT's, PCB's, HCH's, HCB, PCDD/PCDF), polybrominated flameretardants and perflourinated substances. Herring muscle from spring caught specimens from Ängskärsklubb and Utlängan are analysed for organochlorines and from 1996 also for the metals mentioned above. Herring samples from various sites within the marine monitoring programme have also been analysed for dioxins/dibenzofurans, co-planar CB’s, polybrominated diphenyl ethers (Sellström, 1996) and fat composition in pilot studies. Monitoring of Cs-135 is also carried out on herring from these sites by the Swedish Radiation Protection Institute.

The herring specimens are age determined by scales. The analysed specimens are females between 2 - 5 years. Total body weight, liver weight, total length and maturity of gonads is also recorded.

Table 4.2. The range of weeks when collection of samples has been carried out in all (or almost all) years at a specific location and the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total length, liver weight and liver and muscle dry weight are also given.

	Sampling week	age (year)	body weight (g)	length (cm)	liver weight (g)	liver dry weight (%)	muscle dry weight (%)
Harufjärden	38-42	3-4	28-31	16-17	0.32-0.39	20-35	22-23
Ängskärsklubb	38-42	3-5	33-42	17-18	0.38-0.56	20-35	21-23
- " - spring	20-24	2-5	25-33	16-17	0.31-0.54	19-23	20-22
Landsort	41-48	3-5	38-50	18-20	0.46-0.66	20-32	22-24
Karlskrona	41-46	2-4	38-48	17-19	0.36-0.51	22-35	23-25
- " - spring	18-23	2-3	51-65	19-22	0.30-0.55	17-20	18-20
Fladen	35-45	2-3	47-61	19-20	0.55-0.70	22-38	25-27
Väderöarna	38-40	2-3	50-90	18-24	0.40-1.0	27-39	24-35

The growth rate varies considerably at the different sites, see Table 4.3 below.

Table 4.3. Average length at the age of three and age at the length of 16 cm at the various sites

	Average length (cm) at 3 years	Average age (years) at 16 cm
Harufjärden	15.91	3.07
Ängskärsklubb	16.87	2.24
- " - spring	16.79	2.42
Landsort	17.28	2.17
Karlskrona	18.20	1.19
Fladen	20.32	0.82
Väderöarna	21.73	0.53

4.2 Cod (*Gadus morhua*)

The Baltic cod lives below the halocline feeding on bottom organisms. It becomes sexually mature when 2-6 years old in Swedish waters. The spawning takes place during the period May - August (occasionally spawning specimens could be found in March or September). The cod requires a salinity of at least 11 PSU and an oxygen content of at least 2 ml/l (Nissling, 1995) for the spawning to be successful. The population shows great fluctuations and has decreased dramatically during the period 1984-1993. Cod fishing for human consumption is economically important.

Cod is among the 'first choice species' recommended within the JAMP (Joint Assessment and Monitoring Programme) and BMP (Baltic Monitoring Programme).

Cod is collected in the autumn from two sites: south east of Gotland and from Fladen at the Swedish west coast. Cods are age determined by otoliths. Specimens of both sexes, between 3-4 years from Gotland and between 2-4 years from Fladen, are analysed.

The cod liver is fat and organic contaminants are often found in relatively high concentrations. For that reason, it is a very appropriate matrix for screening for 'new' contaminants.

Cod liver tissue is analysed for lead, cadmium, copper and zinc as well as for organochlorines. 1995 analyses of chromium and nickel were added. Cod muscle tissue is analysed for mercury.

Before 1989, 20 individual samples from south east of Gotland and 25 samples from Kattegatt were analysed for organochlorines. Between 1989-1993 one pooled sample from each site, each year was analysed. Since 1994, 10 individual cod samples are analysed at the two sites each year.

Table 4.4. The range of weeks when collection of samples has been carried out in all (or almost all) years at a specific location, the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total length, liver weight and liver dry weight are also given.

	Sampling week	age (year)	body weight (g)	Length (cm)	liver weight (g)	liver dry weight (%)
SE Gotland	35-39	3-4	310-455	32-35	16-41	53-63
Fladen	37-42	2-3	240-345	29-33	4-10	33-44

4.3 Dab (*Limanda limanda*)

Dab is a bottom living species feeding on crustaceans, mussels, worms, echinoderms and small fishes. The males become sexually mature between 2-4 years and the females between 3-5 years. The spawning takes place during the period April – June shallow coastal waters. The dab tends to migrate to deeper water in late autumn.

Dab is among the 'first choice species' recommended within the JAMP (Joint Assessment and Monitoring Programme).

Because of reduced analytical capacity, organochlorines in dab were annually analysed in one pooled sample from 1989 to 1995. Since 1995 samples of dab are no longer analysed but are still collected and stored in the Environmental Specimen Bank.

Dab is collected from Kattegatt (Fladen) in the autumn. Liver tissue samples have been analysed for lead, cadmium, copper and zinc and muscle tissue samples for organochlorines and mercury. The dab specimens are age determined by otoliths. Specimens between 3-5 years have been analysed.

Table 4.5. The range of weeks when collection of samples has been carried out in all (or almost all) years, the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are also given.

	Sampling week	age (year)	body weight (g)	length (cm)	liver weight (g)	liver dry weight (%)
Fladen	37-44	2-6	50-250	15-30	0.5-2	20-40

4.4 Flounder (*Platichtys flesus*)

Flounder is a bottom living species feeding on crustaceans, mussels, worms, echinoderms and small fishes. The males in the Skagerack become sexually mature between 3-4 years of age and the females one year later. The spawning in the Skagerack takes place during the period January – April in shallow coastal waters. The flounder tends to migrate to deeper waters in late autumn.

Flounder is among the 'second choice species' recommended within the JAMP (Joint Assessment and Monitoring Programme).

Because of reduced analytical capacity, organochlorines in flounder were annually analysed in one pooled sample from 1989 to 1995. Since 1995 samples of flounder are no longer analysed but are still collected and stored in the Environmental Specimen Bank.

Flounder is collected from the Skagerack (Väderöarna) in the autumn. Liver tissue samples have been analysed for lead, cadmium, copper and zinc and muscle tissue samples for organochlorines and mercury. The flounder specimens are age determined by otoliths. Specimens between 4-6 years have been analysed.

Table 4.6. The range of weeks when collection of samples has been carried out in all (or almost all) years, the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are also given.

	Sampling week	age (year)	body weight (g)	length (cm)	liver weight (g)	liver dry weight (%)
Väderöarna	37-44	3-6	100-400	20-35	1-5	18-30

4.5 Blue mussel (*Mytilus edulis*)

Blue mussels are one of the most common used organisms for monitoring contaminants in biota. Adult mussels are sessile and hence it is easier to define the area the samples represent, compared to fish.

Blue mussel is among the ‘first choice species’ recommended within the JAMP (Joint Assessment and Monitoring Programme).

Blue mussels are collected from the Kattegatt (Fladen, Nidingen), from the Skagerack (Väderöarna) and from Kvädöfjärden in the Baltic Proper. The mussels are sampled in the autumn. Sampling depth varies between the sampling sites.

Soft body tissue is analysed for lead, cadmium, copper, zinc, mercury and organochlorines. In 1995 analyses of chromium and nickel were added. From 1995 samples from Kvädö-fjärden were included in the analysis. Hitherto, samples from this site had only been collected and stored (since 1981). Organochlorines in blue mussels are analysed in pooled samples from each site and year whereas the trace metals are analysed in 25 individual samples per year and site (15 from 1996).

Table 4.7. The range of weeks when collection of samples has been carried out in all (or almost all) years at a specific location, the shell length interval selected in the presented time series below. The 95% confidence intervals for the yearly means of soft body weight and shell weight are also given.

	Sampling week	Sampling depth (m)	shell length (cm)	shell weight (g)	soft body weight (g)
Kvädöfjärden	38-43	2-10	2-3	0.4-0.6	1-2
Fladen, Nidingen	37-51	0.5	5-8	5-25	2-10
Väderöarna	42-51	2	6-10	10-30	5-25

4.6 Guillemot (*Uria aalge*)

Guillemots are appropriate for monitoring of contaminants in the Baltic Sea since most of them do not migrate further than to the southern parts of the Baltic proper during the winter season. They feeds mainly on sprat (*Sprattus sprattus)* and herring (*Clupea harengus*). The guillemot breed for the first time at the age of 4-5 years and the egg is hatched after about 32 days.

The egg content is fat (11-13%) and thus very appropriate for analysis of fat-soluble contaminants i.e. hydrocarbons.

Normally the guillemot lay just a single egg but if this egg is lost, it may lay another. It has been shown that late laid eggs of guillemot contain significantly higher concentrations of organochlorines compared to early laid eggs (Bignert *et al.*, 1995). In this presentation only early laid eggs are included except for dioxins where the results from all collected eggs are included. 10 guillemot eggs, collected between week 19-21(22), are analysed each year.

Guillemot egg contents from St Karlsö are analysed for mercury and organochlorines. From 1996, the concentrations of Pb, Cd, Ni, Cr, Cu and Zn are also analysed. The timeserver has also been analysed for PCC (Wideqvist *et al.* 1993), dioxins/dibenzofurans, perflourinated compounds (Holmström *et al.*, 2005) and polybrominated compounds (Sellström, 1996). Various shell parameters e.g. shell weight, thickness and thickness index is also monitored. The weights of several hundreds of fledglings are normally recorded each year at St Karlsö. Eggs have also been collected for some years from Bonden in the northern parts of the Bothnian Sea but so far only results (organochlorines) for 1991 are available.

4.7 Perch (*Perca fluviatilis*)

Perch is an omnivorous, opportunistic feeding predatory fish. Male perch become sexually mature between 2-4 years and the females between 3-6 years of age. The spawning takes place during the period April - June when the water temperature reaches about 7-8 degrees. Perch muscle tissue is lean and contains only about 0.8% fat.

Integrated monitoring with fish physiology and population development is running on perch in co-operation with the University of Gothenburg and the Swedish Board of Fisheries. Perch is also used as an indicator species for contaminant monitoring within the national monitoring programme of contaminants in freshwater biota.

Perch muscle tissue samples from two coastal sites, Holmöarna and Kvädöfjärden in the Baltic, are analysed for organochlorines and mercury. In 1995 analyses of lead, cadmium, chromium, nickel, copper and zinc in perch liver were added to the programme.

Table 4.8. The range of weeks when collection of samples has been carried out in all (or almost all) years at a specific location, the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are also given.

Perch	**Sampling week**	**age (year)**	**body weight (g)**	**length (cm)**	**liver weight (g)**
Holmöarna	33-42	3-5	77-88	17-21	0.86-1.5
Kvädöfjärden	31-40	3-5	56-67	15-20	0.50-0.73

4.8 Eelpout, viviparous blenny (*Zoarces viviparus*)

The eelpout is considered as a more or less stationary species living close to the bottom, feeding on insect larvae, molluscs, crustaceans, worms, hard roe and small fishes. It becomes sexually mature when 2 years old at a length of 16 - 18 cm. The spawning takes place during August - September. After 3-4 weeks the eggs hatch inside the mothers body where the fry stay for about three months. The possibility to measure the number of eggs, fertilized eggs, the size of the larvae and the embryonic development makes the species suitable for integrated studies of contaminants and reproduction (Jacobsson *et al.,* 1993). Integrated monitoring with fish physiology and population development is running on eelpout in co-operation with the University of Gothenburg and the Swedish Board of Fisheries.

Eelpout specimens have been collected from Väderöarna in the Skagerack since 1988. In this time series analyses of various PCB congeners are available. Since 1995, eelpout is also collected from Holmöarna and Kvädöfjärden. Liver tissue is analysed for lead, cadmium, chromium, nickel, copper and zinc whereas muscle tissue is analysed for mercury and organochlorines.

Table 4.9. The range of weeks when collection of samples has been carried out in all (or almost all) years at a specific location, the age classes selected in the presented time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver and muscle dry weight are also given.

	Sampling week	**age (year)**	**total weight (g)**	**length (cm)**	**liver weight (g)**	**liver dry weight (%)**	**muscle dry weight (%)**
Holmöarna	47	3-6	21-26	18-20	0.20-0.50	13-26	17-21
Kvädöfjärden	46	3-6	28-39	19-22	0.20-0.60	18-25	17-20
Väderöarna	(36), 45-47	3-6	35-70	20-25	0.40-1.00	14-32	18-20

5 Sampling sites

The location and names of the sample sites are presented in Figure 5. The sampling sites are located in areas regarded as locally uncontaminated and, as far as possible, uninfluenced by major river outlets or ferry routes and not too close to heavy populated areas.

The Swedish sampling stations are included in the net of HELCOM stations in the Baltic and in the Oslo and Paris Commissions' Joint Monitoring Programme (OSPAR, JMP) station net in the North Sea. Finland has one site in the Bothnian Bay, four sites in the Bothnian Sea and three in the Gulf of Finland i.e. altogether eight sites from which data is reported to HELCOM. Poland has three sites along the Polish coast. Denmark submits trace metal data from three sites. Data of contaminants in biota from Russia, Estonia, Latvia, Lithuania or Germany has not yet been assessed within HELCOM. Within JMP time series of various contaminants in biota are reported from Belgium (3 sites, both OC's and heavy metals), Denmark (2, heavy metals), France (7, heavy metals), Germany (22, both), Iceland (12), The Netherlands (12), Norway (41), Spain (7), Sweden (2) and UK (2).

During 2007 the monitoring programme has been expanded, herring from 10 new sites have been added. Name and location of these sites are found at the map below.

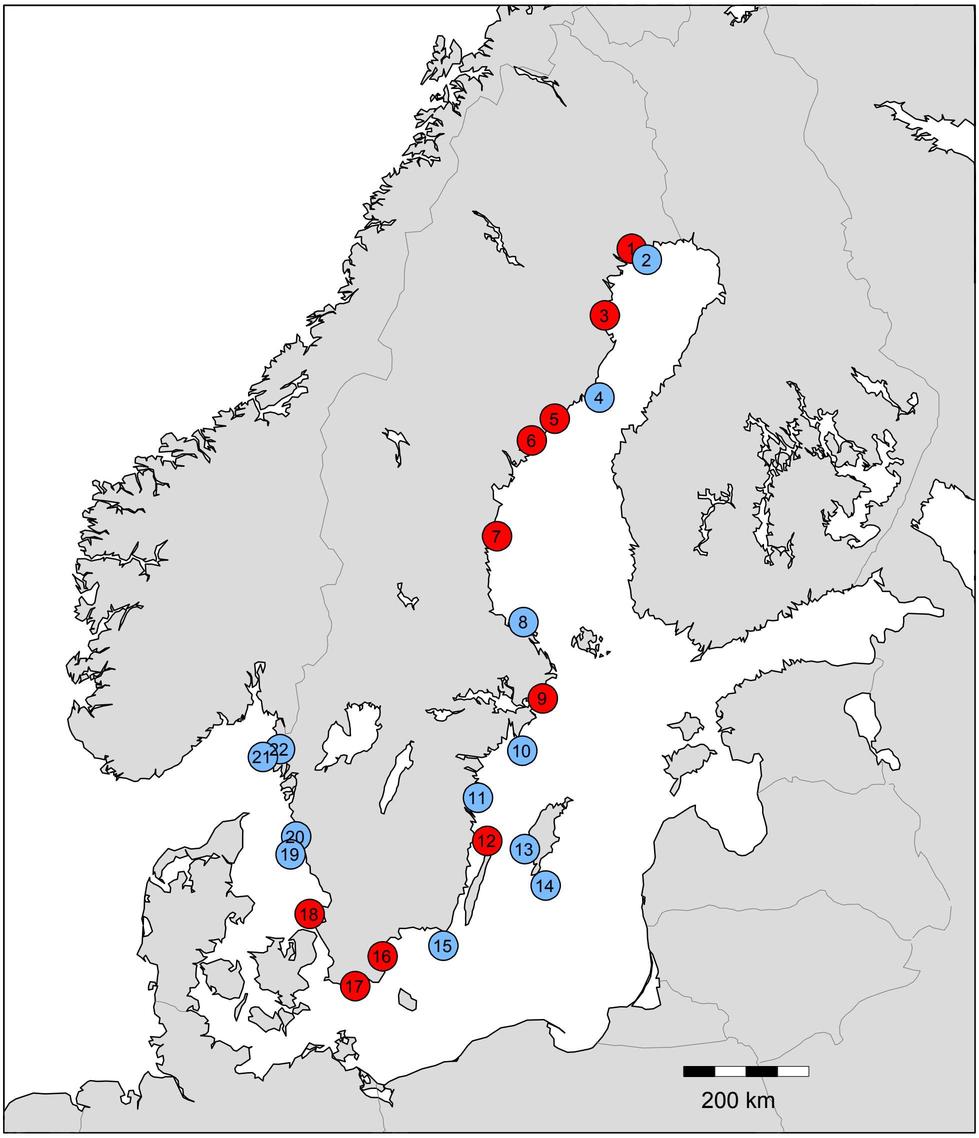

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Figure 5. Sampling sites within the National Monitoring Programme in Marine. 1) Rånefjärden, 2) Harufjärden, 3) Kinnbäcksfjärden, 4) Holmöarna, 5) Örefjärden, 6) Gaviksfjärden, 7) Långvindsfjärden, 8) Ängskärsklubb, 9) Lagnö, 10) Landsort, 11) Kvädöfjärden, 12) Byxelkrok, 13) St.Karlsö, 14) SE Gotland, 15) Utlängan, 16) V. Hanöbukten, 17) Abbekås, 18) Kullen, 19) Fladen, 20) Nidingen, 21) Väderöarna, 22) Fjällbacka

5.1 Harufjärden, Bothnian Bay, north

Co-ordinates: 65 35’ N, 22 53’ E within a radius of 3’, ICES 60H2 93
County: Norrbotten

Surface salinity: <3 PSU
Average air temperature: January: -10° / April: -1° / July: 15° / October: 2°

Sampling matrix: Baltic herring, autumn
Start: 1978 DDT/PCB, 1980 Hg, 1982 Pb/Cd/Cu/Zn, 1988 HCH’s/HCB, 1995 Cr/Ni

5.2 Örefjärden, Bothnian Bay, north

Co-ordinates: 63 25' N, 19 24' E within a radius of 3'County: Norrbotten

Average air temperature: January: -10° / April: -1° / July: 15° / October: 2°

Sampling matrix: Baltic herring, autumn
Start: 2005 PFC

5.3 Holmöarna, Bothnian Bay, south, coastal site

Co-ordinates: 63 41' N, 20 53' E, ICES 56H0 County: Västerbotten

Surface salinity: c 4 PSU
Average air temperature: January: -5° / April: 0° / July: 15° / October: 4°

Start year for various contaminants and species:

Contaminant/ Species	PCB/DDT	HCH/HCB	Hg	Pb/Cd/Cu/Zn	Cr/Ni
Perch	1980	19(89)95	19(91)95	1995	1995
Eelpout	1995	1995	1995	1995	1995

Both species are collected during the autumn.

At Holmöarna the contaminant monitoring is integrated with fish population and -physiology monitoring, carried out by the Swedish Board of Fisheries and the University of Gothenburg.

5.4 Bonden, northern Bothnian Sea

Co-ordinates: 63 25' N, 20 02' E, ICES 55H0 County: Västerbotten

Surface salinity: c 5 PSU
Average air temperature: January: -5° / April: 0° / July: 15° / October: 4°

Sampling matrix: Guillemot egg, summer
Start: 1991 DDT/PCB

The collection of egg samples has been more or less sporadic however, since the population development has been low.

5.5 Ängskärsklubb, Bothnian Sea

Co-ordinates: 60 44' N, 17 52' E, ICES 50G7 83 County: Gävleborg / Uppsala

Surface salinity: c 6 PSU
Average air temperature: January: -3° / April: 2° / July: 15° / October: 6°

Sampling matrix: Baltic herring, spring/autumn
Start, spring: 1972 DDT/PCB, 1972-75 Hg, 1988 HCH's/HCB
Start, autumn: 1978 DDT/PCB, 1980 Hg, 1982 Pb/Cd/Cu/Zn, 1988 HCH's/HCB, 1995 Cr/Ni

In 1996 collection and analyses of herring samples from four other sites in the region were financiated by the county board of Gävleborgs län. This investigation is valuable to estimate the representativeness of the well established sample site at Ängskärsklubb. It also gives information on small scale geographical variation in general.

5.6 Landsort, Baltic Proper, north

Co-ordinates: 58 42' N, 18 04' E, ICES 46G8 23 County: Stockholm / Södermanland

Surface salinity: c 6-7 PSU
Average air temperature: January: -1° / April: 3° / July: 16° / October: 7°

Sampling matrix: Baltic herring, autumn
Start: 1978 DDT/PCB, 1981 Hg, 1982 Pb/Cd/Cu/Zn; 1988, HCH's/HCB; 1995 Cr/Ni

Herring samples have also been collected to analyse the metallothionein concentration and to compare the fat composition in old versus young herring specimen.

5.7 Kvädöfjärden, Baltic Proper, coastal site

Co-ordinates: 58 2' N, 16 46' E, ICES 45G6 County: Östergötland / Kalmar

Surface salinity: c 6-7 PSU
Average air temperature: January: -1° / April: 4° / July: 17° / October: 7°

Start year for various contaminants and species:

Contaminant/ Species	PCB/DDT	HCH/HCB	Hg	Pb/Cd/Cu/Zn	Cr/Ni
Perch	1980	19(84)90	1981	1995	1995
Blue mussel	1995	1995	1995	1995	1995
Eelpout	1995	1995	1995	1995	1995

All species are collected during the autumn.

At Kvädöfjärden the contaminant monitoring is integrated with fish population and -physiology monitoring, carried out by the Swedish Board of Fisheries and the University of Gothenburg.

Neuman *et al.* (1988) report decreasing Secchi depths during the invested period; somewhat below 6 m 1980 to somewhat above 4 m in the middle of the eighties.

5.8 St Karlsö, Baltic Proper

Co-ordinates: 57 11' N, 17 59' E, ICES 43G7 County: Gotland

St Karlsö is situated about 7 km west of the island Gotland and about 80 km east of the Swedish Baltic coast.

Surface salinity: c 7 PSU
Average air temperature: January: 0° / April: 3° / July: 16° / October: 8°

Sampling matrix: Guillemot egg, May
Start: 1968 DDT/PCB, 1969 Hg, 1988 HCH's/HCB

5.9 South east of Gotland, Baltic Proper

Co-ordinates: 56 53’ N / 18 38’ E, ICES 42G8 43 County: Gotland

Surface salinity: c 7-8 PSU
Average air temperature: January: 0° / April: 3° / July: 16° / October: 8°

Sampling matrix: Cod, autumn
Start: 1980 DDT/PCB/Hg, 1982 Pb/Cd/Cu/Zn, 1988 HCH’s/HCB, 1995 Cr/Ni

5.10 Utlängan, Karlskrona archipelago, Baltic Proper, south

Co-ordinates: 55 57’ N, 15 47’ E, ICES 40G5 73 County: Blekinge

Surface salinity: c 8 PSU
Average air temperature: January: 0° / April: 4° / July: 16° / October: 8°

Start year for analysis of various contaminants in herring spring/autumn:

Contaminant/ Species	PCB/DDT	HCH/HCB	Hg	Pb/Cd/Cu/Zn	Cr/Ni
Herring, spring	1972	1988	1972-75,95	1995	1995
Autumn	1979	1988	1981	1982	1995

In 1997 collection and analyses of herring samples from one site rather close to the reference site and two sites in Hanöbukten were financiated by the Environmental Protection Agency. This investigation is valuable to estimate the representativeness of the well-established sample site at Utlängan. It will also give information on small-scale geographical variation in general.

5.11 Fladen, Kattegatt, Swedish west coast

Co-ordinates: 57 14’ N / 11 50’ E, ICES 43G1 83, JMP J34 County: Halland

Surface salinity: c 20-25 PSU
Average air temperature: January: 0° / April: 5° / July: 16° / October: 8°

Start year for various contaminants and species:

Contaminant/ Species	PCB/DDT	HCH/HCB	Hg	Pb/Cd/Cu/Zn	Cr/Ni
Herring	1980	1988	1981	1981	1995
Cod	1979	1988	1979	1981	1995
Dab	1981	1988	1981	1981	-
Blue mussel	1984	1988	1981	1981	1995

All species are collected during the autumn.

Since 1987 blue mussels have been collected at Nidingen about 10 km NNE of Fladen.

5.12 Väderöarna, Skagerack, Swedish west coast

Co-ordinates: 58 31' N, 10 54' E ICES 46G0 93, JMP J33
County: Göteborgs- o Bohus

Surface salinity: c 25-30 PSU
Average air temperature: January: 0° / April: 5° / July: 16° / October: 8°

Start year for various contaminants and species:

Contaminant/ Species	PCB/ DDT	HCH/ HCB	Hg	Pb/Cd/ Cu/Zn	Cr/Ni
Herring	1995	1995	1995	1995	1995
Eelpout	1995	1995	1995	1995	1995
Flounder	1980	1988	1980	1981	-
Blue mussel	1984	1988	1980	1981	1995

Eelpout and blue mussels are collected at Musön, Fjällbacka at the coast (about10 km east of Väderöarna). All species are collected during the autumn.

6 Analytical methods

6.1 Trace metals

The analyses of trace metals are carried out at the Department of Environmental Assessment at Swedish University of Agricultural Sciences. Analytical methods for metals in liver are described by Borg *et al.*,1981, for mercury by May & Stoeppler, 1984, and Lindsted & Skare,1971. The laboratory participates in the periodic QUASIMEME intercallibration rounds. It has also participated in the programme for sampling quality control, QUASH

CRM's used for mercury are:
DORM-2: 1994-1997
and for the other metals:
DOLT-1: 1990-1991, DOLT-2: 1993-1997 and Bovine Liver B.L 1577b: 1997, TORT-2: 1997

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

6.2 Organochlorines and brominated flame retardants

The analyses of organochlorines and brominated flame retardants are carried out at the Laboratory for Analytical Environmental Chemistry at the Institute of Applied Environmental Research (ITM) at Stockholm University. The analytical methods applied are described elsewhere. The organochlorines are presently determined by high resolution gas chromatography (Jensen *et al.*, 1983, Eriksson *et al.*, 1994). The brominated substances are analysed by GC connected to a mass spectrometer operating in the electron capture /negative ion mode (Sellström et al.,1998). This year a screening study concerning the higher brominated substances BDE 196, 197, 203, 205, 206, 207 and 209 has been carried out. The analyse is similar to the one for the lower brominated ones except for the use of a shorter column, 15m, with a thinner phase, 0.1µm.

6.2.1 Quality assurance

The Quality control for organochlorines has continuously improved the last ten years and resulted in an accreditation 1999. Assessment is performed once a year by the accreditation body SWEDAC and was last done in the autumn of 2007. The laboratory is fulfilling the obligation in SS-EN ICO/IEC 17025.The accreditation is valid for CB 28, 52, 101, 118, 153, 138, 180, DDEpp, DDDpp, DDTpp, HCB and a- b- y-HCH in biological tissues. So far the brominated flame retardants (BFRs) are not accredited but the analysis of BDE 47, 99,100, 153, 154 and HBCD are in many ways performed with the same quality aspects as the organochlorines.

The Quality Assurance program is built on the Quality Manual, SOPs and supplements. The annual audit includes a review of the qualifications of the staff, internal quality audit (vertical), SOPs, internal quality controls, filing system, proficiency testing, up-to-date record of the training of the staff (to be able to perform their assigned tasks), accredited methods and audit of the quality program.

6.2.2 Standards

The original of all standards are certified with known purity and precision. The concentrations are calculated for each individual congener. In April 2005 a new PBDE-standard as well as HBCD-standard were introduced. The standards were made from solutions where the concentrations of each compound had lower uncertainty (± 5%) compared with the old standards (± 10%).

6.2.3 Detection limits and the uncertainly in the measurements

The uncertainty in the measurement is found to follow the theory stated by Horwitz in 1982. With increasing level follows decreasing relative standard deviation (Horwitz et al., 1989). These relative standard deviations are calculated from 6094 PCB and pesticides values from control samples during 13 years. The uncertainly in the measurements is expressed as two relative standard deviations and is less the 36% in the interval 0.04-0.5 ng/g, less then 22% in the interval 0.5-5 ng/g and less then 16% when higher then 5 ng/g.
The uncertainly in the measurements for BFRs is expressed in the same way as for the PCBs, and are in the same range (20-36%) in the interval 0,005-5 ng/g. The standard deviation for the five BDEs and HBCD are calculated from 1068 values from control samples.

Detection limits and other comments are reported under each contaminant description.

6.2.4 Validation

To have the possibility to control impurities in solvents, equipments and glasswares, one blank sample is extracted together with each batch of environmental samples.

Coeluation of congeners in GC analysis is dependent upon instrumental conditions such as column type, length, internal diameter, film thickness and oven temperature etc. Some potentially coeluting PCB congeners on a column with the commonly used phase DB-5 are CB-28/-31, CB-52/-46/-49, CB-101/-84/-90, CB-118/-123/-149,CB-138/-158/-163, CB-153/-132/-105 and CB-180/-193 (Schantz et al., 1993). To minimize those problems a column with a more polar phase is used in parallell. Coeluation with other PCBs then the seven can then be avoided on at least one column, with the exception for CB-138, which coelutes with CB-163 (Larsen et al., 1990). Therefore CB-138 is reported as CB-138+163.

In order to verify possibly coelutions with HCHs, DDTpp and DDDpp one representative sample extract are also treated with potassium hydroxide after the treatment with sulphuric acid. The two extracts are analysed and the chromatograms compared. No remaining peaks at the same retention time as the analytes indicates no coelutions.
When introducing a new matrix one of the samples is re-extracted with a mixture of more polar solvents for control of no remaining contaminants in the matrix residual. Samples

from new matrixes and samples from already established matrixes from new sampling location are also examined for suitable internal standard.
From 2005 to 2008 ITM will take part in the EU project NORMAN where. One of the issues of the project is to provide protocols for validation for harmonisation and dissemination of chemical monitoring methods and a first version of this protocol is now on the website www.norman-network.net.

6.2.5 Reference Material

Two laboratory reference materials (LRM) are used as extraction controls, chosen with respect to their lipid content and level of organic contaminants. The controls consist of herring respectively salmon muscle, homogenised in a household mixer and stored in aliquots of 10 gram of herring respectively 3 gram of salmon in air tight bags of aluminium laminate at -80°C. At every extraction event one extraction control is extracted as well.

From 1998 CRM 349, cod lever oil was analysed twice a year for PCBs. During 2003 the laboratory changed to CRM 682 and 718, mussel (whole body) respectively herring (muscle), being better representants since they cover the whole extraction procedure. One of those samples are analysed once a year. Until now no CRM exist for BFRs.

6.2.6 Intercalibration and certifications

Concerning PCBs and pesticides, the laboratory has participated in the periodic QUASIMEME intercalibration exercise since 1993, with two rounds every year, each one containing two samples**.** 521 of the 546 values that the laboratory has produced during the years have been satisfactory according to QUASIMEME, meaning they have falling within +/- 2 sd of the assigned value. In 2000, the laboratory participated in the first interlaboratory study ever performed for BFR and since 2001 the BFRs are incorporated in the QUASIMEME scheme. From the beginning there was one yearly exercise but after 2006 this was changed to two exercises per year. The laboratory has performed with good results for these studies until this year. The reason for this less good performance is that the access to the instrument has been limited, with not enough time for cleaning and pre-tests**.** However, the prerequisite for 2008 is better since a new instrument has been bought. Still, as a total, 52 of the 65 values the laboratory has produced during the years have been satisfactory according to QUASIMEME.
The laboratory has since 1998 participating in three certification exercises, concerning PCBs, pesticides and BFRs. In two of this the laboratory was involved as a co-organizer. As a total, 494 of the 534 reported values were accepted and could be used as a part of the certification. The laboratory has also participated in the programme for sampling quality control, QUASH.

6.3 Dioxins, dibenzofurans and dioxinlike PCB´s

The analyses of dioxins and dioxin-like PCBs are carried out at the Department of Chemistry, Umeå University. The extraction method is described by Wiberg *et al.*,1998, the clean-up method by Danielsson *et al.* 2005, and the instrumental analysis (GC-HRMS) by Liljelind *et al.* 2003. The laboratory participates in the annual FOOD intercallibration rounds, and include a laboratory reference material (salmon tissue) with each set of samples.

6.4 Perfluorinated substances

The analyses of perfluorinated substances are carried out at the Analytical Environmental Chemistry Unit at the Department of Applied Environmental Science (ITM), University of Stockholm.

6.4.1 Sample preparation and instrumental analysis

A sample aliquot of 0.2 to 1 g homogenized tissue was transferred to a polypropylene (PP)-centrifuge tube, and spiked with 5 ng each of the mass-labelled internal standards $^{13}C_4$-perfluorooctanoic acid ($^{13}C_4$-PFOA) and ammonium $^{18}O_2$-perfluorooctane sulfonate ($^{18}O_2$-PFOS). The samples were extracted twice with 5 mL of acetonitrile in an ultrasonic bath. Following centrifugation, the supernatant extract was removed and the combined acetonitrile phases were concentrated to 1 mL under a stream of nitrogen. The concentrated extract underwent dispersive clean-up on graphitized carbon and acetic acid. Approximately 0.5 mL of the cleaned-up extract was added to 0.5 mL of aqueous ammonium acetate. Precipitation occurred and the extract was centrifuged before the clear supernatant was transferred to an autoinjector vial for instrumental analysis and the volume standards BTPA and bPFDcA were added.

Aliquots of the final extracts were injected automatically on a high performance liquid chromatography system (HPLC; Alliance 2695, Waters) coupled to a tandem mass spectrometer (MS-MS; Quattro II, Micromass). Compound separation was achieved on an Ace 3 C_{18} column (150 x 2.1 mm, 3 µm particles, Advanced Chromatography Technologies) with a binary gradient of ammonium acetate buffered methanol and water. The mass spectrometer was operated in negative electrospray ionization mode with the following optimized parameters: Capillary voltage, 2.5 kV; drying and nebuliser gas flow (N_2), 300 and 20 L/h, respectively; desolvation and source temperature, 150 and 120 °C, respectively. Quantification was performed in selected reaction monitoring chromatograms using the internal standard method. $^{13}C_4$-PFOA and $^{13}C_4$-PFOS were employed as internal standards for perfluorocarboxylates (PFCAs) and perfluorosulfonates incl. PFOSA (PFSs), respectively.

6.4.2 Quality control

The extraction method employed in the present study (with the exception of the concentration step) has previously been validated for biological matrices and showed excellent analyte recoveries ranging between 90 and 110% for PFCAs from C_6 to C_{14} (Powley and Buck, 2005). Including extract concentration, we presently determined recoveries between 70 and 90% for C_6- to C_{10}-PFCAs and 65–70% for C_{11}-C_{14} PFCAs. Extraction efficiencies for perfluorosulfonates (PFSs), including perfluorooctane sulfonamide (PFOSA), were determined to 70–95%. Furthermore, mean method recoveries of the mass labelled compounds $^{18}O_2$-PFOS and $^{13}C_4$-PFOA were 82% and 80%, respectively. Method quantification limits (MQLs) for all analytes were determined on the basis of blank extraction experiments and ranged between 0.06 and1.6 ng/g wet weight (w.w.) for the different compounds. One herring liver sample was analysed in triplicate in 2006. The obtained values varied 16% for PFOSA and <10% for all other detected analytes (perfluorononanoate (PFNA), -decanoate (PFDcA), -undecanoate (PFUnA), -dodecanoate

(PFDoA), -tridecanoate (PFTriA), perfluorohexane sulfonate (PFHxS), PFOS). A fish tissue sample used in an international inter-laboratory comparison (ILC) study in 2005 (van Leeuwen et al., 2005) was analyzed along with the samples in 2006. The obtained concentrations deviated from the median concentration from the ILC study by 67% for PFOSA (however, median and mean of the ILC differed by more than a factor of 2), 37% for PFDoA and less than 22% for all other compounds quantified in the ILC (i.e., perfluorohexanoate (PFHxA), -heptanoate (PFHpA), PFOA, PFNA, PFDcA, PFUnA, perfluorobutane sulfonate (PFBS), PFHxS and PFOS). ,

7 Statistical treatment, graphical presentation

7.1 Trend detection

One of the main purposes of the monitoring programme is to detect trends. The trend detection is carried out in three steps.

7.1.1 Log-linear regression analyses

Log-linear regression analyses are performed for the *entire investigated time period* and also for the *recent ten years* for longer time series.

The slope of the line describes the yearly percentual change. A slope of 5% implies that the concentration is halved in 14 years whereas 10% corresponds to a similar reduction in 7 years and 2% in 35 years. See table 7.1 below.

Table 7.1. The approximate number of years required to double or half the initial concentration assuming a continuous annual change of 1, 2, 3, 4, 5, 7, 10, 15 or 20% a year.

	1%	2%	3%	4%	5%	7%	10%	12%	15%	20%
Increase	70	35	24	18	14	10	7	6	5	4
Decrease	69	35	23	17	14	10	7	6	4	3

7.1.2 Non-parametric trend test

The regression analysis presupposes, among other things, that the regression line gives a good description of the trend. The leverage effect of points in the end of the line is also a well-known fact. An exaggerated slope, caused 'by chance' by a single or a few points in the end of the line, increases the risk of a false significant result when no real trend exist. A non-parametric alternative to the regression analysis is the Mann-Kendall trend test (Gilbert, 1987, Helsel & Hirsch,1995, Swertz,1995). This test has generally lower power than the regression analysis and does not take differences in magnitude of the concentrations into account; it only counts the number of consecutive years where the concentration increases or decreases compared with the year before. If the regression analysis yields a significant result but not the Mann-Kendall test, the explanation could be either that the latter test has lower power or that the influence of endpoints in the time series has become unwarrantable great on the slope. Hence, the eighth line reports Kendall's 'τ', and the corresponding p-value. The Kendall's 'τ' ranges from 0 to 1 like the traditional correlation coefficient 'r' but will generally be lower. 'Strong' linear correlations of 0.9 or above corresponds to τ-values of about 0.7 or above (Helsel and Hirsch, 1995, p. 212). This test was recommended by the Swedish EPA for use in water quality monitoring programmes with annual samples, in an evaluation comparing several other trend tests (Loftis *et al.* 1989).

7.1.3 Non-linear trend components

An alternative to the regression line in order to describe the development over time is a kind of smoothed line. The smoother applied here is a simple 3-point running mean smoother fitted to the annual geometric mean values. In cases where the regression line is badly fitted the smoothed line may be more appropriate. The significance of this line is tested by means of an Analysis of Variance where the variance explained by the smoother and by the regression line is compared with the total variance. This procedure is used at assessments at ICES and is described by Nicholson *et al.*, 1995.

7.2 Adjustments for covariables

It has been shown that metal concentrations in cod liver are influenced by fat content (Grimås *et. al.*, 1985). Consequently the metal concentrations in cod liver are adjusted for fat content. In some occasions (when the average fat content differs between years) this is of major importance and might change the direction of the slope and decrease the between-year variation considerable. For the same reasons, mercury concentrations are adjusted for body weight and organochlorines in spring caught herring muscle tissue are adjusted for fat content (Bignert *et. al*., 1993) where appropriate (indicated in the header text of the figures).

7.3 Outliers and values below the detection limit

Observations further from the regression line than what is expected from the residual variance around the line is subjected to special concern. These deviations may be caused by an atypical occurrence of something in the physical environment, a changed pollution load or errors in the sampling or analytical procedure. The procedure to detect suspected outliers in this presentation is described by Hoaglin and Welsch (1978). It makes use of the *leverage coefficients* and the *standardised residuals*. The standardised residuals are tested against a $t_{.05}$ distribution with n-2 degrees of freedom. When calculating the *i*th standardised residual the current observation is left out implying that the *i*th observation does not influence the slope nor the variance around the regression line. The suspected outliers are merely indicated in the figures and are included in the statistical calculations except in a few cases, pointed out in the figures.

Values reported below the detection limit is substituted using the ‘robust’ method suggested by Helsel & Hirsch (1995) p 362, assuming a log-normal distribution within a year.

7.4 Legend to the plots

The analytical results from each of the investigated elements are displayed in figures. A selection of sites and species are presented in plots, time series shorter than 4 years.

The plot displays the geometric mean concentration of each year (circles) together with the individual analyses (small dots) and the 95% confidence intervals of the geometric means.

The overall geometric mean value for the time series is depicted as a horizontal, thin line.

The trend is presented by one or two regression lines (plotted if $p < 0.10$, two-sided regression analysis); one for the whole time period in red and one for the last ten years in pink (if the time series is longer than ten years). Ten years is often too short a period to statistically detect a trend unless it is of considerable magnitude. Nevertheless the ten year regression line will indicate a possible change in the direction of a trend. Furthermore, the residual variance around the line compared to the residual variance for the entire period will indicate if the sensitivity have increased as a result of e.g. an improved sampling technique or that problems in the chemical analysis have disappeared.

A smoother is applied to test for non-linear trend components (see 7.1.3). The smoothed line in blue is plotted if $p < 0.10$. A broken line or a dashed line segment indicates a gap in the time series with a missing year.

The log-linear regression lines fitted through the geometric mean concentrations follow smooth exponential functions.

A cross inside a circle, indicate a suspected outlier, see 7.3. The suspected outliers are merely indicated in the figures and are included in the statistical calculations except in a few cases, pointed out in the figures.

Each plot has a header with species name, age class and sampling locality. Age class may be replaced bye shell length for blue mussels. Sampling locality is in a few cases in a coded form to save space; C1=herring, Harufjärden, C2=herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, C6=herring, Fladen, V2=spring caught herring, Ängskärsklubb, V4=spring caught herring, Karlskrona archipelago, U8=guillemot egg, St Karlsö, G5=cod south east of Gotland, G6=cod, Fladen, P2=perch, Kvädöfjärden, M6=blue mussel, Fladen/Nidingen, M3=blue mussel, Väderöarna, L6=dab, Fladen, P3=flounder, Väderöarna. Below the header of each plot the results from several statistical calculations are reported:

n(tot)= The first line reports the total number of analyses included together with the number of years (**n(yrs)=**).

m= The overall geometric mean value together with its 95% confidence interval is reported on the second line of the plot (N.B. d.f.= n of years - 1).

slope= reports the slope, expressed as the yearly percentual change together with its 95% confidence interval.

sd(lr)= reports the square root of the residual variance around the regression line, as a measure of between-year variation, together with the *lowest detectable change* in the current time series with a power of 80%, one-sided test, $\alpha=0.05$. The last figure on this line is the estimated *number of years* required to detect an annual change of 5% with a power of 80%, one-sided test, $\alpha=0.05$.

power= reports the power to detect a log-linear trend in the time series (Nicholson & Fryer, 1991). The first figure represent the power to detect an annual change of 5% with the number of years in the current time series. The second figure is the power estimated as if the slope where 5% a year and the number of years were ten. The third figure is the *lowest detectable change* (given in percent per year) for a ten year period with the current between year variation at a power of 80%. The results of the power analyses from the various time series are summarised in chapter 9.

r^2= reports the coefficient of determination (r^2) together with a p-value for a two-sided test (H_0: slope = 0) i.e. a significant value is interpreted as a true change, provided that the assumptions of the regression analysis is fulfilled.

y(96)= reports the concentration estimated from the regression line for the last year together with a 95% confidence interval, e.g. y(96)=2.55(2.17,3.01) is the estimated concentration of year 1996 where the residual variance around the regression line is used to calculate the confidence interval. Provided that the regression line is relevant to describe the trend, the residual variance might be more appropriate than the within-year variance in this respect.

tao= reports Kendall's '**τ**', and the corresponding p-value.

sd(sm)= reports the square root of the residual variance around the smoothed line. The significance of this line could be tested by means of an Analysis of Variance (see 7.1.3). The p-value is reported for this test. A significant result will indicate a non-linear trend component.

Below these nine lines are additional lines with information concerning the regression of the last ten years.

In some few cases where an extreme outlying observation may hazard the confidence in the regression line, the ordinary regression line is replaced by the 'Kendall-Theil Robust line', see Helsel and Hirsch (1995) page 266. In these cases only the 'Theil'-slope and Kendall's '**τ**' are reported.

7.5 Legend to the three dimensional maps

The height of the bars represents a geometric mean of the last 5 years. The coloured bars indicate 5 class levels. The levels are only provisional at this stage but are to the greatest part based on recalculated EU-EQS values to various species and tissues. Blue and green (1,2) represent the best classes, and yellow, orange and red (3,4,5) represent levels of concern. For more information concerning the levels see (Bignert & Nyberg, 2007)

8 The power of the programme

Before starting to interpret the result from the statistical analyses of the time series it is essential to know with what power temporal changes can be detected (i.e. the chance to reveal true trends with the investigated matrices). It is crucial to know whether a negative result of a trend test indicate a stable situation or if the monitoring programme is too poor to detect even serious changes in the contaminant load to the environment. One approach to this problem is to estimate the power of the time series based on the 'random' between-year variation. Alternatively the lowest detectable trend could be estimated at a fixed power to represent the sensitiveness of the time series.

The first task would thus be to estimate the 'random' between-year variation. In the results presented below this variation is calculated using the residual distance from a log-linear regression line. In many cases the log-linear line, fitted to the current observations, seems to be an acceptable 'neutral' representation of the true development of the time series. In cases where a significant 'non-linear' trend has been detected (see above), the regression line may not serve this purpose; hence the sensitiveness- or power-results based on such time series are marked with an asterix in the tables below. These results are also excluded from estimations of median performances.

Another problem is that a single outlier could ruin the estimation of the between-year variation. As an example, the time series of lead concentrations in fish liver seem to suffer from occasional outliers, especially in the beginning of the investigated period 1981-1984. The estimated median sensitiveness of these series is 12.5% a year. If a few outliers, identified by means of objective statistical criteria's, are deleted, the calculated median sensitiveness improves to 5.8%. In the presented results suspected outliers are included which means that the power and sensitiveness might be underestimated.

Due to a change of method for metal analysis in 2004, values after 2003 are not presented. The new method is under investigation, since the values are uncertain.

Table 8.1. reports the number of years that various contaminants have been analysed and detected from the monitored sites. Generally the monitoring of trace metals has continued for about 20-25 years, PCB and DDT for about 25 years (spring caught herring and guillemot egg however, more than 30 years) and HCH and HCB only about 15 years.

Table 8.1. Number of years that various contaminants have been analysed and detected. C1=herring, Harufjärden, C2=herring, Ängskärsklubb, V2=spring caught herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, V4=spring caught herring, Karlskrona archipelago, C6=herring, Fladen, C7=herring, Väderöarna, G5=cod south east of Gotland, G6=cod, Fladen, P1=perch, Holmöarna, P2=perch, Kvädöfjärden, Z1=eelpout, Holmöarna, Z2=eelpout, Kvädöfjärden, Z3, eelpout, Väderöarna, M2= blue mussel, Kvädöfjärden, M6=blue mussel, Fladen/Nidingen, M3=blue mussel, Väderöarna, L6=dab, Fladen, P3=flounder, Väderöarna, U8=guillemot egg, St Karlsö.

	C1	C2	V2	C3	C4	V4	C6	C7	G5	G6	P1	P2	Z1	Z2	Z3	M2	M6	M3	L6	P3	U8
Hg	26	26	15	27	27	14	27	11	28	28	12	24	11	12	12	11	24	26	14	15	34
Pb*	21	22	8	23	23	5	23	9	23	23	9	8	7	9	8	9	21	22	14	14	8
Cd*	22	22	8	23	23	7	23	9	23	23	9	9	7	9	8	9	21	22	14	14	8
Ni*	9	9	8	9	9	7	9	9	9	9	8	8	7	9	8	9	9	9	-	-	8
Cr*	9	9	8	9	9	7	9	9	9	9	9	8	7	8	8	9	9	9	-	-	8
Cu*	22	22	8	23	23	7	23	9	23	23	9	8	7	9	8	9	21	22	14	14	8
Zn*	21	21	8	22	22	7	22	9	22	22	9	8	7	9	8	9	21	21	13	13	8
sPCB	27	27	34	28	27	32	27	-	27	26	20	23	-	-	-	-	20	21	13	15	36
CB-153	18	18	19	20	19	18	19	11	18	17	13	19	10	12	12	12	19	18	5	6	20
sDDT	27	27	34	28	27	32	27	11	26	26	21	26	10	12	12	12	23	26	14	15	36
α-HCH	11	16	16	20	19	17	14	7	18	18	5	14	6	8	4	12	14	14	6	6	17
β-HCH	10	16	19	20	19	18	10	1	18	11	4	3	6	11	2	10	9	5	-	-	20
γ-HCH	13	15	17	20	19	18	14	7	18	16	5	9	5	8	8	12	16	15	6	6	13
HCB	18	17	19	19	19	18	19	10	18	17	13	15	10	12	12	12	9	10	6	6	21

* values until 2003

Table 8.2 reports the number of years required to detect an annual change of 5% with a power of 80 %. The power is to a great extent dependent of the length of the time series and the possibility to statistically verify an annual change of 5% at a power of 80% generally requires 10-15 years.

Table 8.2. Number of years required to detect an annual change of 5% with a power of 80 %. C1=herring, Harufjärden, C2=herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, C6=herring, Fladen, V2=spring caught herring, Ängskärsklubb, V4=spring caught herring, Karlskrona archipelago, U8=guillemot egg, St Karlsö, G5=cod south east of Gotland, G6=cod, Fladen, P1=Holmöarna, P2=perch, Kvädöfjärden, M6=blue mussel, Fladen, M3=blue mussel, Väderöarna, L6=dab, Fladen, P3=flounder, Väderöarna.

Mercury

Based on geometric means on a fresh weight basis

	C1	C2	C3	C4	C6	U8	G5	G6	P2	M6	M3	Median
Hg	16	25	*18	*19	15	*13	*14	*14	*18	*16	*19	16

Other trace metals

Based on geometric means on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3	P2	Median
Pb	16	17	17	19	18	20	20	26	24	14	11
Cd	19	17	*17	15	14	*16	*21	*13	*16	18	17
Cu	15	12	*15	14	*15	16	20	13	*14	14	15
Zn	*13	11	11	*10	9	16	12	*14	*17	15	13

Organochlorines

Based on geometric means on a lipid weight basis

	C1	C2	C3	C4	C6	V2	V4	U8	G5	G6	P1	P2	M6	M3	Median
sPCB	*17	15	16	15	14	18	15	12	*17	*22	*18	*20	*16	*19	16
sDDT	*20	17	16	16	20	19	15	*17	16	*18	*21	23	24	*22	19
DDE	*21	16	17	17	18	19	16	*17	16	*18	*19	*24	20	19	18
α-HCH	10	14	12	8	7	9	*10	15	10	*13	8	16	13	18	11
β-HCH	10	*14	13	13	28	11	*14	*12	10	26	-	-	23	17	13
γ-HCH	*11	16	12	10	*16	11	*12	32	10	18	15	*19	*17	*18	15.5
HCB	14	20	*19	19	15	18	16	*14	17	18	15	22	16	20	17

* indicates a significant non-linear trend component

In table 8.3 the lowest trend possible to detect within a 10-year period with a power of 80 % is presented both for the entire time series and for the latest 10-year period. The table shows that the sensitiveness for Pb and Cd is approximately the same (10%-20%) whereas for Zn and Cu it is somewhat better (5-10% For PCB, sDDT and HCB the estimated sensitiveness is about 10-13%. The time series of DDD and DDT is somewhat poorer mainly due to extremely low concentrations that in some matrices fall below the detection limit. For the HCH's the estimated median sensitiveness is between 7% and 10%. Biological variables like the condition index for herring, cod and perch show a sensitiveness of about 1-2%.

Table 8.3. Lowest detectable trend within a 10-year period with a power of 80% for various variables in various matrices at various sites. The top row for every substance gives the figure based on the residual variance for the whole period, whereas the bottom row gives the figure for the last ten years of the time series. If no figure is given here this indicates that the time series show a significant non-linear trend component. To calculate power for these time series is not relevant.

Mercury

Based on geometric means on a fresh weight basis

	C1	C2	C3	C4	C6	G5	G6	P2	U8	M6	M3	Median
Hg	10	24	-	-	9.7		-	-	-	-	-	9.3
	12	21	-	-	9.8		-	-	-	-	-	12.5

Other trace metals

Based on geometric means on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3	Median
Pb	11	12	11	15	14	16	15	24	22	12
	12	14	14	12	8.1	21	12	13	23	5.3
Cd	15	12	-	9.9	8.6	-	-	-	-	9.4
	17	11	-	10	7.4	-	-	-	-	10
Cu	9.3	6.9	-	7.9	-	10	15	6.9	-	9.2
	8.9	7.7	-	6.2	-	13	18	7.3	-	9.7
Zn	-	5.4	5.8	-	4.1	11	6.5	-	-	7.25
	-	7.3	4.2	-	5.1	15	5.3	-	-	8.85

Organochlorines

Based on geometric means on a lipid weight basis

	C1	C2	V2	C3	C4	V4	C6	G5	G6	P1	P2	U8	M6	M3	Med
sPCB	-	9.6	13	10	9.5	9.5	8.6	-	-	-	-	6.5	-	-	10
	-	5.5	15	7.5	12	10	8.2	-	-	-	-	7.0	-	-	9.7
sDDT	-	12	15	10	11	9.6	16	10	-	-	20	-	21	-	13
	-	14	15	8.1	13	10	17	12	-	-	20	-	23	-	13
DDE	-	11	15	12	11	10	13	11	-	-	-	-	16	14	13
	-	9.6	17	8.4	12	11	15	11	-	-	-	-	14	11	11
α-HCH	4.8	7.9	3.9	5.9	3.1	-	2.7	4.3		3.0	10	9.5	7.8	13	7.9
β-HCH	5.0	-	5.1	6.9	7.3	-	29	5.0	25	-	-	-	20	11	7.4
γ-HCH	-	10	5.7	6.5	4.7	-	-	4.9	13	9.3	-	35	-	-	9.65
HCB	8.6	16	13	-	15	10	9.5	12	13	8.9	18	-	10	16	13

Biological variables

	C1	C2	V2	C3	C4	V4	C6	G5	G6	P1	P2	Me.
Cond	1.6	2.2	-	2.3	-	1.6	2.0	-	-	1.6	1.2	1.7
	1.3	0.9	-	1.4	-	2.0	1.7	-	-	1.0	1.6	1.55
Fat	8.1	9.6	-	-	10	9.5	11	-	18	2.4	-	9.9
	5.5	5.7	-	-	10	7.5	5.7	-	10	2.6	-	6.65

Table 8.4 reports the power to detect an annual change of 5% covering the monitoring period, i.e. the length of the time series varies depending on site and investigated contaminant. For the long time series the estimated power is close to100% in most cases. For the shorter time series of HCH's and HCB however, about 80-100%. For the series of α- and γ-HCH though, the decreasing rate has been considerable (about 15-20% a year) leading to statistically significant results from most sites.

Table 8.4. Power to detect an annual change of 5% covering the entire monitoring period. The length of the time series varies depending on site and investigated contaminant. In cases where considerable increased power has been achieved during the recent ten years period, this value has been used. * indicates a significant non-linear trend.

Mercury

Based on annual geometric mean concentrations on a fresh weight basis

	C1	C2	C3	C4	C6	G5	G6	P2	U8	M6	M3
Hg	1.0	.85	*1.0	*1.0	1.0	*1.0	*1.0	*1.0	*1.0	*1.0	*1.0

Other trace metals

Based on annual geometric mean concentrations on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3
Pb	.99	1.0	1.0	.97	.99	.96	.96	.55	.69
Cd	.95	.99	*1.0	*1.0	1.0	*1.0	*.93	*1.0	*1.0
Cu	1.0	1.0	*1.0	1.0	*1.0	1.0	.96	*1.0	*1.0
Zn	*1.0	1.0	*1.0	*1.0	1.0	1.0	1.0	*1.0	*.99

Organochlorines

Based on annual geometric mean concentrations on a lipid weight basis

	C1	C2	V2	C3	C4	V4	C6	G5	G6	P1	P2	U8	M6	M3
sPCB	*1.0	1.0	1.0	1.0	1.0	1.0	1.0	*1.0	*.97	*.94	*.95	1.0	*.99	*.95
sDDT	*1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	*1.0	*.85	.94	*1.0	.78	*.97
DDE	*.99	1.0	1.0	1.0	1.0	1.0	1.0	1.0	*1.0	*.93	*.83	*1.0	.86	.95
α-HCH	.93	.97	1.0	1.0	1.0	*1.0	1.0	1.0	*1.0	.25	.68	.94	.89	.46
β-HCH	.81	*.98	1.0	1.0	1.0	*.99	.08	1.0	.11			*1.0	.09	.07
γ-HCH	*.97	.78	*1.0	1.0	1.0	*1.0	*.63	1.0	.65	.07	*.13	.10	*.77	*.60
HCB	.99	.59	.92	*.84	*.81	.96	.99	.89	.74	.69	.35	*1.0	.22	.15

9 Condition

Updated 08.03.31

The stoutness of fish, i.e. weight against length is a common measure of the ‘degree of well-being’ of an individual or a population.

In this report the commonly used ‘condition factor’, K, (Vibert & Lagler, 1961) is used:

$$K = 100 \; W / L^3$$

where the weight (W) is given in grams and the length (L) in centimetres.

9.1 Temporal variation

Significant decreasing trends for the condition factor of herring are observed from Harufjärden, Landsort and Utlängan (autumn and spring) while it increases at Ängskärsklubb in spring caught herring for the whole time series and in autumn caught herring during the last ten years. The increase at Ängskärsklubb may be explained by an unintentional increase of the average age over time in the collected samples.

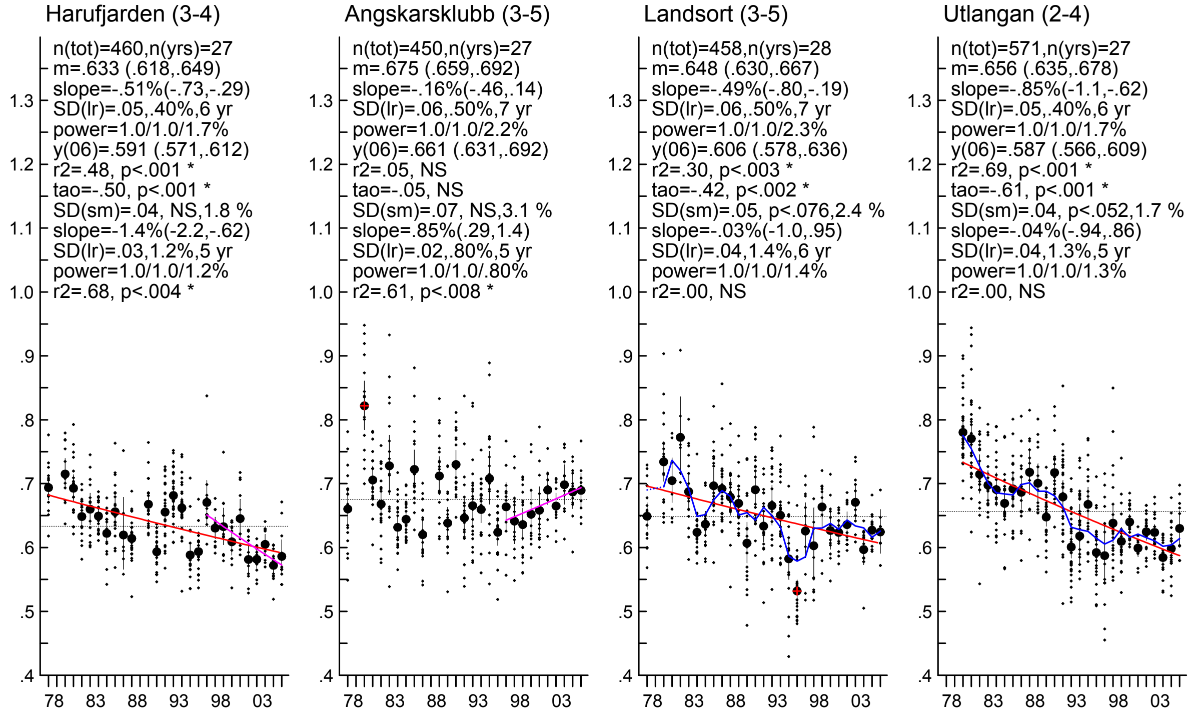
The condition factor estimated for cod show significant upward trends at both Gotland and Fladen over the whole investigated period, but for the recent 5-10 years indications of a decreasing trend is observed at both locations. The observed increase might be explained by the simultaneous decrease in population density during the investigated period.

Significantly decreasing trends for the conditionfactor are observed at Holmöarna for perch and eelpout.

9.2 Spatial variation

The average condition factor, estimated over a period of over 20 years is slightly lower in herring sampled at Harufjärden in the northern parts of the Bothnian Bay compared to samples from Fladen and Väderöarna at the Swedish west coast.

Condition factor, herring



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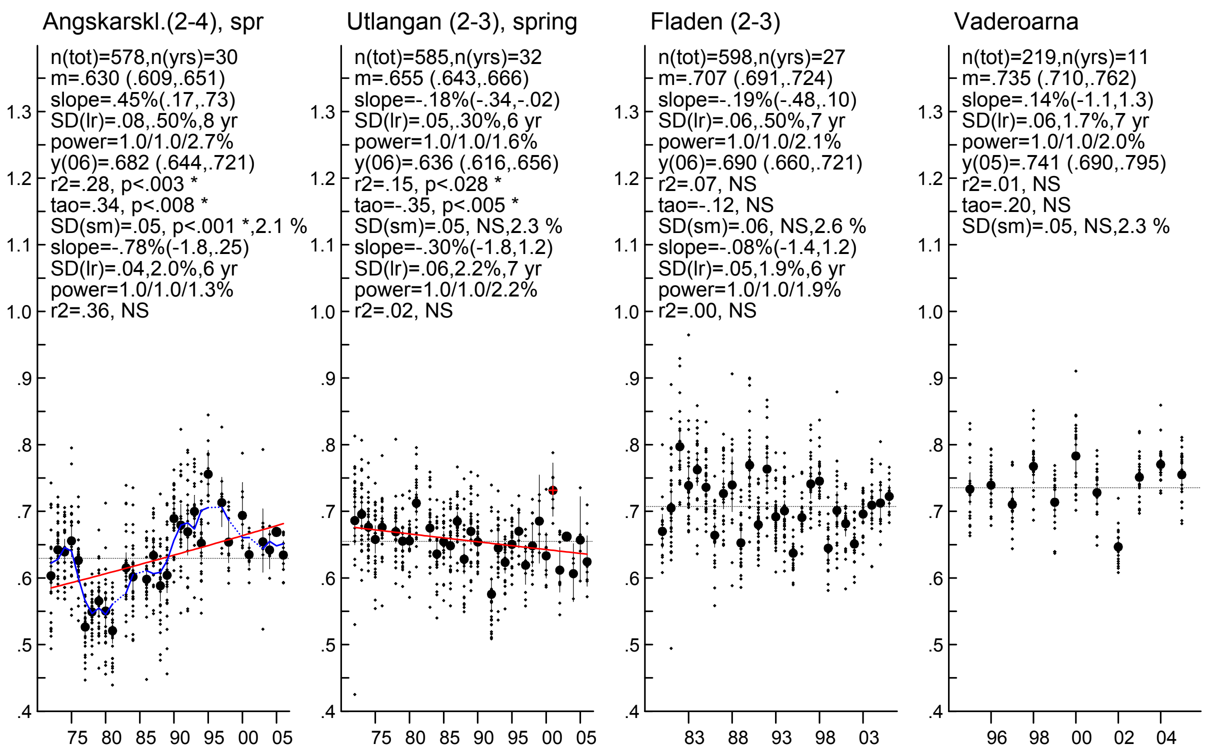
Condition factor, herring



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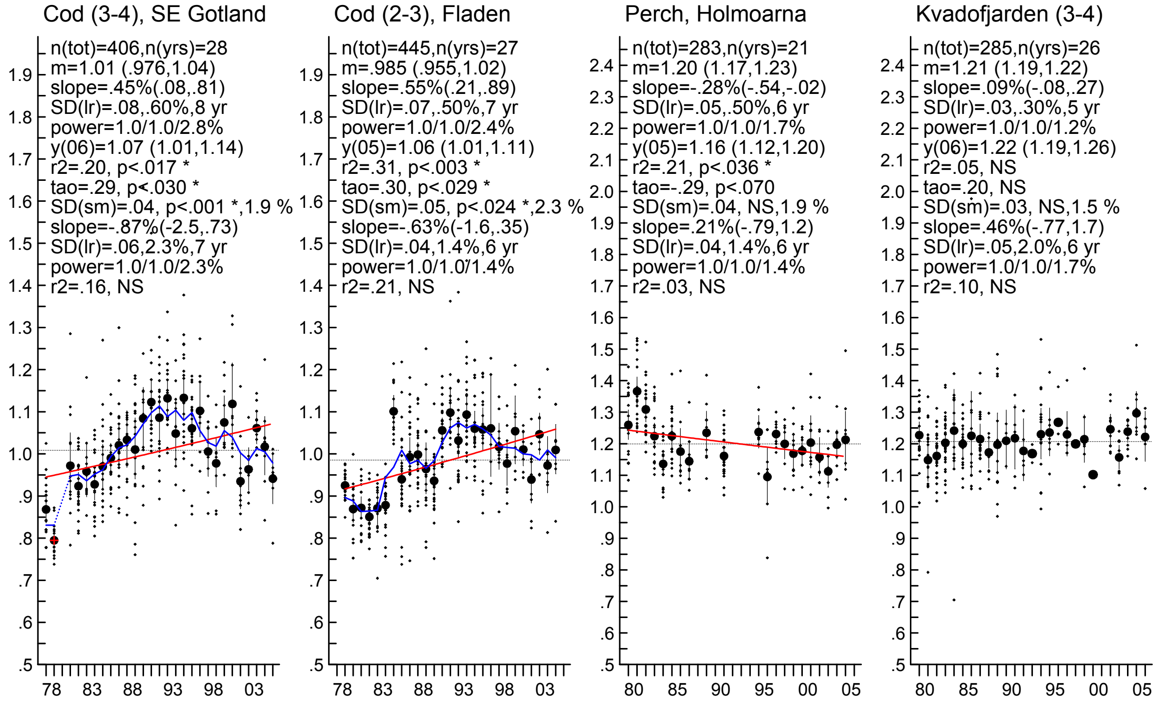
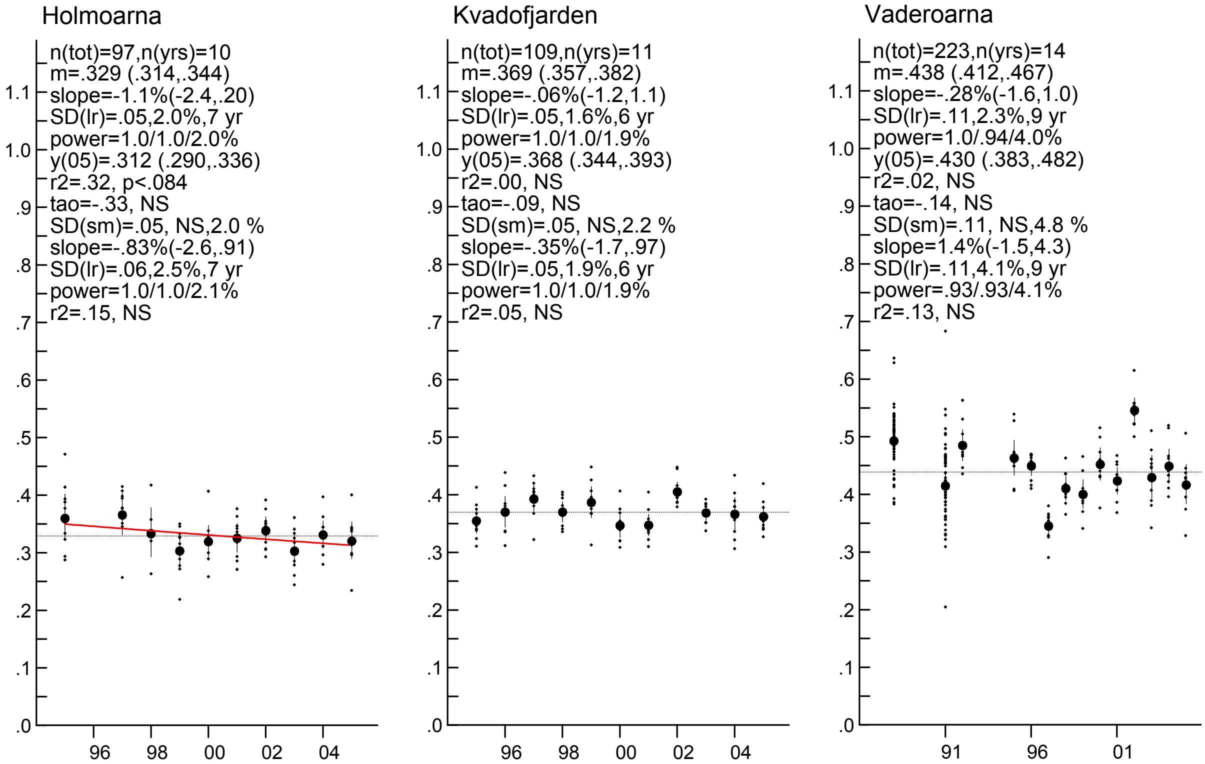
Condition factor, cod and perch



- 07.03.02 08:34, CONDGP

Condition factor, eelpout



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10 Fat content

Updated 08.03.28

The fat content is determined in samples that are analysed for organochlorines i.e. herring, eelpout (dab and flounder) muscle, cod liver and blue mussel soft body. A strong negative correlation between concentrations of organochlorines (expressed on a fat weight basis) and fat content in spring caught herring has been shown (Bignert *et al.* 1993) but also between the concentration of various metals and fat content in cod liver (Grimås *et al*. 1985). The analysed concentrations of these contaminants are hence adjusted for varying fat content.

In general, an extremely low fat content, due to e.g. starvation, may cause elevated concentrations of organo chlorines expressed on a fat weight basis.

The sample fat content is determined after extraction with acetone and hexane with 10% ether without heating (Jensen *et al*. 1983) in the present investigation.

The result of the fat determination may vary considerable depending on the extraction method used.

In herring muscle tissue, the subcutaneous fat layer is removed before the samples are prepared. Analyses of fat content including skin and subcutaneous fat shows at least 1.5 times higher fat content.

10.1 Temporal variation

In the Baltic, *decreasing* trends of fat in herring muscle tissue are indicated from Harufjärden, Landsort and Utlängan (autumn and spring). The fast decrease at Landsort and Utlängan (autumn) seems to have ceased during the past decade (with an exception of last year when the fat content was down to really low levels, less than 2%).

Overall increasing trends in fat content are found in cod liver from south east of Gotland and Fladen, but during the past ten years the fat content has decreased in cod liver south east of Gotland. The fluctuating fat content in cod has to be considered when evaluating the time series of trace metals in cod liver (see above).

Decreasing trends of fat content in perch muscle are indicated at both Holmöarna and Kvädöfjärden in the Baltic. Eelpout from Holmöarna in the Baltic proper and Väderöarna on the west coast is also showing a decline in fat content.

The time series of blue mussel from Väderöarna shows a decrease in fat content during the past ten years.

10.2 Spatial variation

Today, the fat content in autumn caught herring from the Baltic is rather similar in muscle tissue from all investigated sites. In the beginning of the eighties however, the samples from Ängskärsklubb in the Bothnian Sea and Harufjärden in the Bothnian Bay were lower compared to samples from the Baltic Proper.

The fat content in herring from Skagerack varier and can sometimes be about twice as high compared to herring muscle from the Baltic and the Kattegatt. This is not surprising since Atlantic herring muscle tissue may contain more than 20% fat.

The fat content in cod liver is highly variable even between specimens caught at the same time at the same place. The geometric mean fat content over time in samples from SE of Gotland is more than 2.5 times higher compared to cod livers from the Kattegatt. This difference is significant.

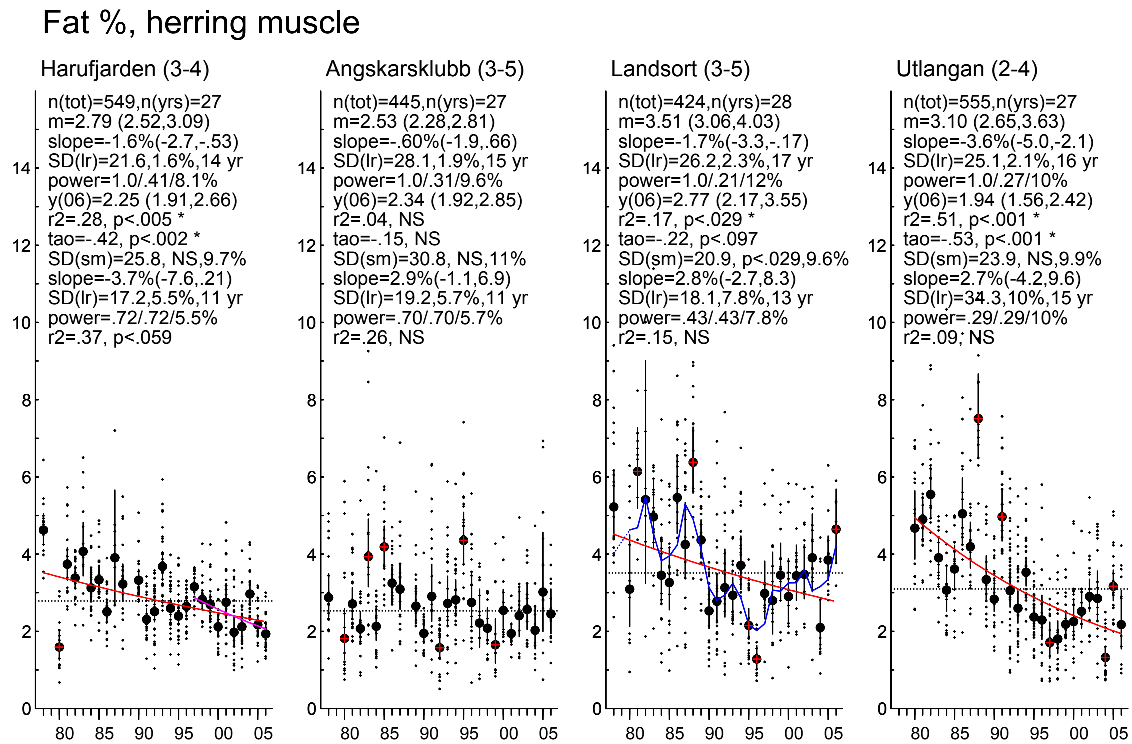
10.3 Seasonal variation

Fat content in spring caught herring from Ängskärsklubb show approximately the same mean value) as herring from the same site caught in the autumn whereas herring from Karlskrona archipelago caught in the autumn show about 30% higher mean fat content compared to spring caught herring from the same area.

Table 10.1. Geometric mean **fat** content (%) in various matrices with a 95% confidence interval. Total number of analysed individual specimens and number years are also reported. Last years values are estimated from trend if p<0.1 or from the mean if no trend is present.

Matrix	age	n	N yrs	Year	trend (95% ci)	last year (95% ci)
Herring muscle						
Harufj. autumn	3-4	549	27	78-06	-1.6 (-2.7,-.53)*	2.3 (1.9-2.7)
Ängskärskl. aut.	3-5	445	27	78-06		2.3 (1.9-2.9)
” spring	2-5	624	34	72-07		2.7 (2.3-3.3)
Landsort	3-5	424	28	78-06	-1.7 (-3.3,-.17)*	2.8 (2.2-3.6)
Utlängan, aut.	2-4	555	27	80-06	-3.6 (-5.0, -2.1)*	1.9 (1.6-2.4)
” spring	2-3	573	32	72-06	-2.1 (-3.0, -1.2)*	1.5 (1.3-1.8)
Fladen	2-3	593	27	80-06		3.8 (3.1-4.8)
Väderöarna		219	11	95-05		5.2 (4.0-6.7)
Cod liver						
SE Gotland	3-4	391	27	80-06	2.4 (1.5, 3.3)*	73 (64-84)
Fladen	2-3	430	27	80-06	2.4 (-0.02, 4.9)*	25 (17-36)
Perch muscle						
Holmöarna		270	21	80-06	-.96 (-1.3,-0.61)*	.67 (.63-.70)
Kvädöfjärden		289	25	80-06	-1.0 (-1.6,-0.50)*	.62 (.57-.67)
Eelpout muscle						
Holmöarna		95	10	95-06	-5.3 (-9.5, -1.2)*	.55 (.43-.72)
Kvädöfjärden		112	12	95-06		.60 (.48-.74
Väderöarna		234	15	88-06	-3.5 (-6.9,-11)*	.54 (.40-.74)
Dab muscle						
Fladen	3-6	158	13	81-94	-3.7 (-5.2,-2.2)*	.61 (.54-.68)
Flounder muscle						
Väderöarna	4-6	190	15	80-94	-3.4 (-5.7, -1.0)*	.60 (.50-.73)
Blue mussel						
Fladen		84	24	81-06		.88 (.58-1.3)
Väderöarna		91	26	80-06		1.5 (1.1-2.0)
Kvädöfjärden		60	12	95-06		1.5 (1.1-2.0)
Guillemot egg						
St. Karlsö		391	37	69-07		12 (11-13)

* significant trend, p < 0.05



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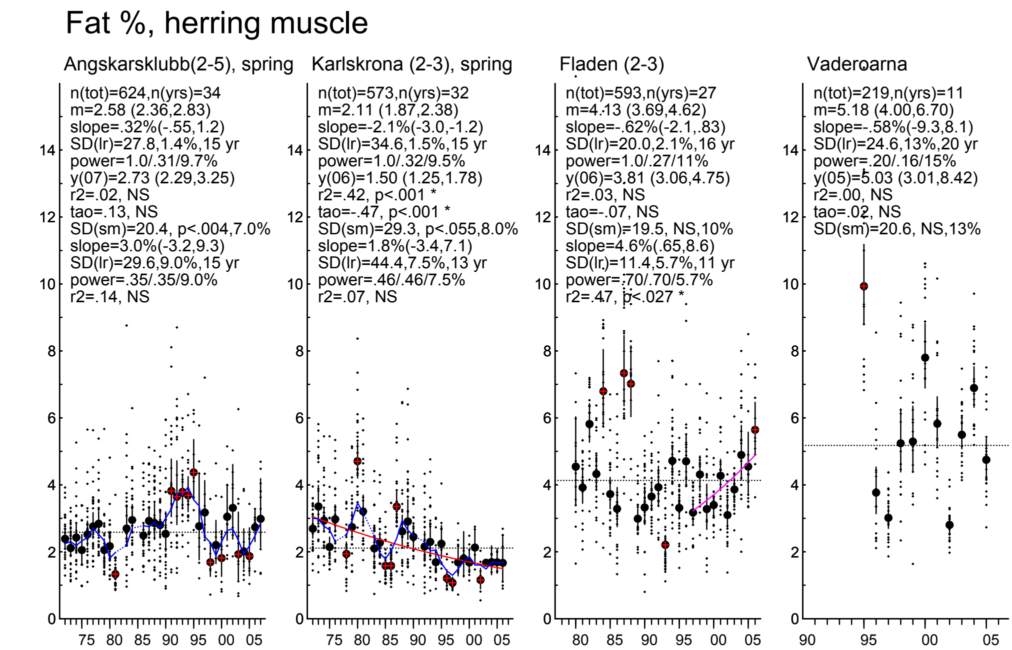

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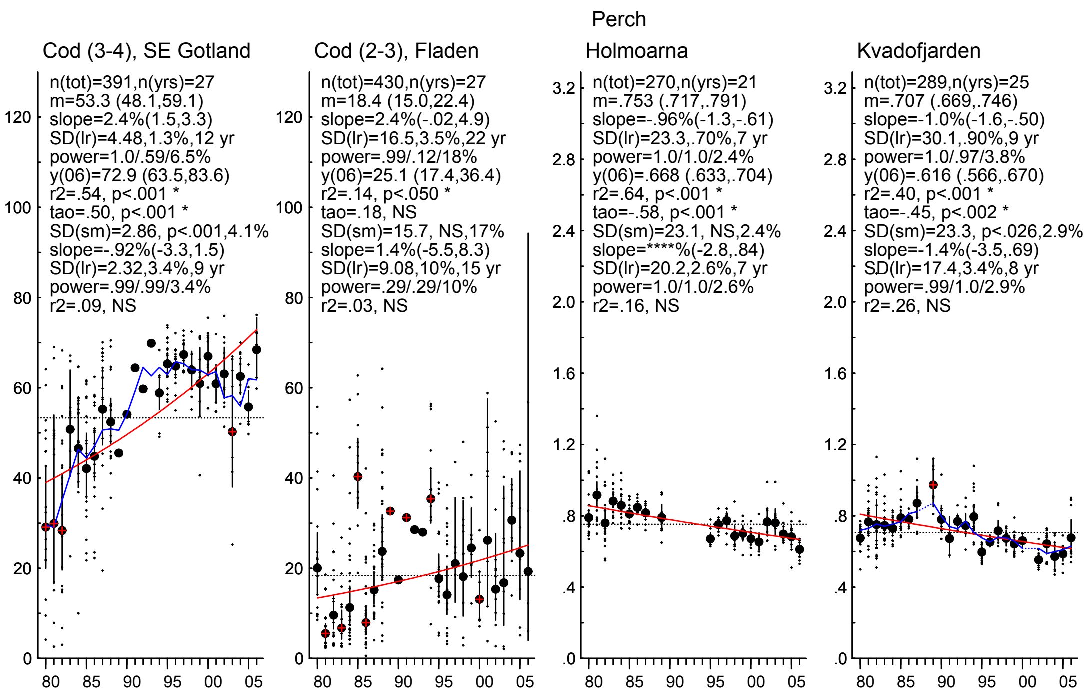
Fat %, cod liver and perch muscle



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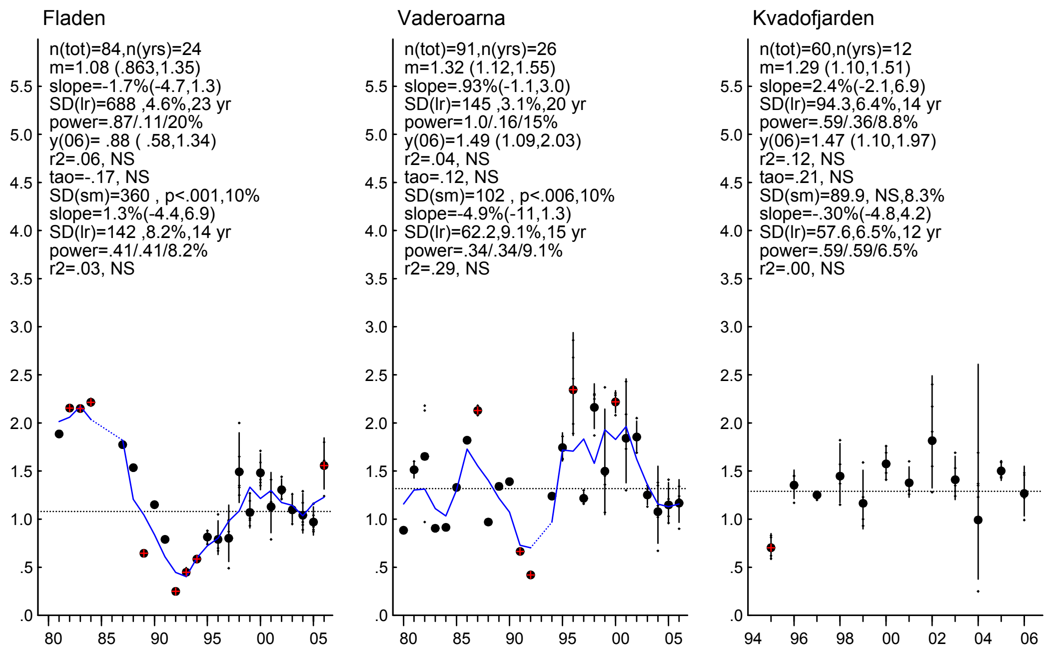
Fat %, blue mussel soft body



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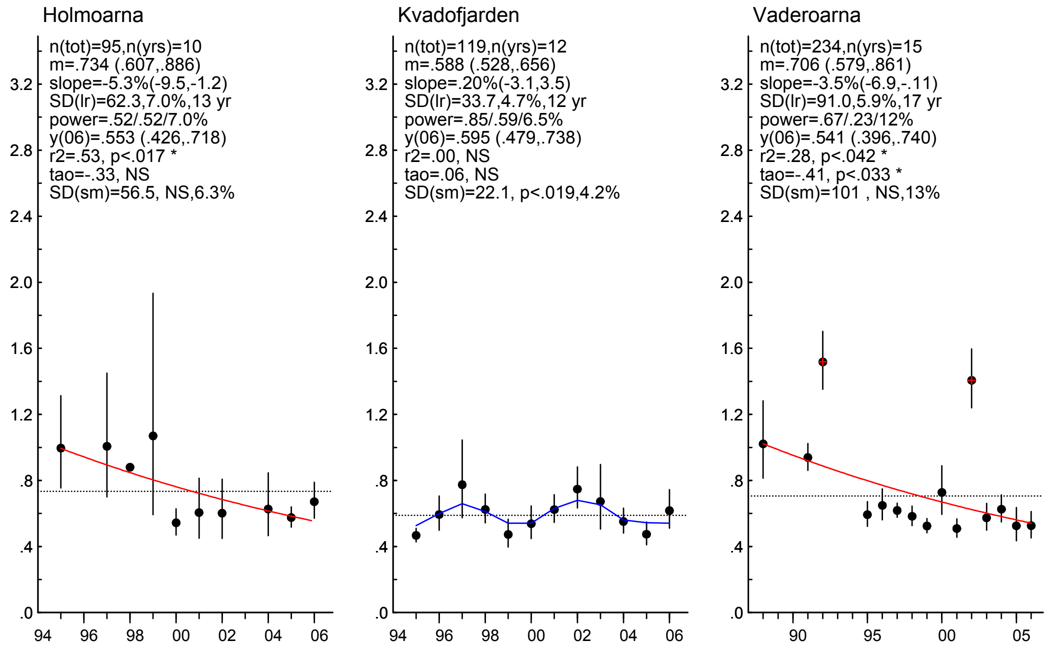
Fat %, Eelpout



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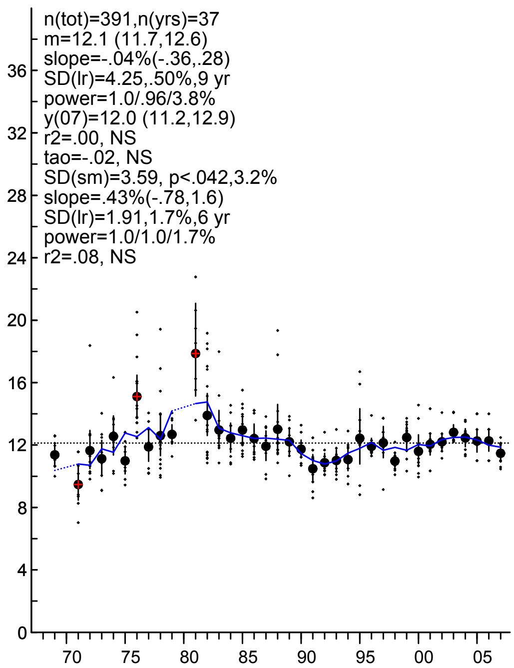
Fat %, guillemot egg, early laid



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11 Mercury

Updated 08.03.28

Mercury is one of the *mandatory* contaminants that should be analysed and reported within both the OSPARCOM and HELCOM conventions.

The concentration of mercury in fish muscle and blue mussel soft body is determined using a 'Mercury Monitor LCD 3200' detector at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences. The detection limit is estimated to approximately 10 ng/g dry weight.

Table 11.1. Mean divergence from standard value of analysed CRM (Certified Reference Material). The last column shows the mean deviation from the standard, including the sign.

Year	CRM	n	%	%
94	DORM-2	16	4.6	-0.2
95	DORM-2	38	3.6	-0.6
96	DORM-2	20	3.9	2.6
97	DORM-2	4	5.0	-0.3

The uncertainty of a single analytical value is estimated to be between 3-5% in average. The deviation of the mean value (including the sign) of the analysed CRM samples, from the standard value is less than 3%.

In 1992, new analytical equipment was introduced and great efforts have been made to intercallibrate the new method by reanalysing old samples both dried extracts and samples from the Environmental Specimen Bank.

11.1 Temporal variation

11.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the mercury discharges are to be reduced by 70% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of the discharges of mercury to air and water by 50% by 1995 with 1987 as a base year.

The use of mercury in the paper pulp industries has been banned in Sweden since 1966.

According to a governmental proposition (1993/94:163) the aim is that all mercury usage should have ceased the year 2000 in Sweden.

11.1.2 This investigation

There is no common general trend for mercury in herring muscle for the investigated time series. The time series from Landsort show a significant increasing trend of about 2% per year for the whole time period, but during the last ten years the concentrations have decreased. Mercury was monitored in spring caught herring from Ängskärsklubb and Karlskrona for four years in the beginning of the seventies, and these series were continued in 1996. Both series show a significant decrease. Both time series from the Swedish west coast (Fladen and Väderöarna) show a significant increase of between 1 and 6%

The time series from Ängskärsklubb in the Bothnian Sea shows a very large between-year variation. Although the sampling site at Ängskärsklubb is located rather far off the coast, the mercury concentration in the herring samples could be influenced by local discharges. Ängskärsklubb may thus not be representative of the Bothnian Sea. During 1995-1996 the estimated mean concentration in herring muscle from Ängskärsklubb were on the same level as measured in comparable samples from Landsort. However, in 1997 and 1999 the geometric mean concentrations increased to the same level that was recorded in the beginning of the eighties.

The number of years required to detect an annual change of 5% varied between 13 to 19 (25 for Ängskärsklubb) years for the herring time series. The power to detect a 5% annual change is close to 100% for most of the long herring and cod series. The large between-year variation in Ängskärsklubb lowers the power of that specific time series to about 85%.

Perch muscle samples from Kvädöfjärden in the Baltic Proper show a significant decreasing trend.

Cod from SE of Gotland show a significant increasing linear trend.

Mercury concentration in eelpout showed a significant increasing trend at Väderöarna.

The mercury concentration in blue mussels from Kvädöfjärden in the Baltic Proper has increased significantly during the last ten years. A similar pattern can also be seen in blue mussels from Väderöarna and Fladen on the Swedish west coast.

Guillemot eggs from St Karlsö in the Baltic proper show a significant decreasing trend of about 1.5% a year in mercury concentration. It should be noted that the mercury analyses in this time series have been carried out in a retrospective study i.e. all analyses have been performed at one occasion at the same laboratory.

11.1.3 Conclusion

The results concerning the development of mercury concentration in the investigated matrices are not consistent. The mercury concentration in guillemot egg decreases whereas the concentration in herring from the northern Baltic Proper seems to increase or fluctuate. The future development of mercury has to be studied carefully and possible analytical problems thoroughly investigated.

11.2 Spatial variation

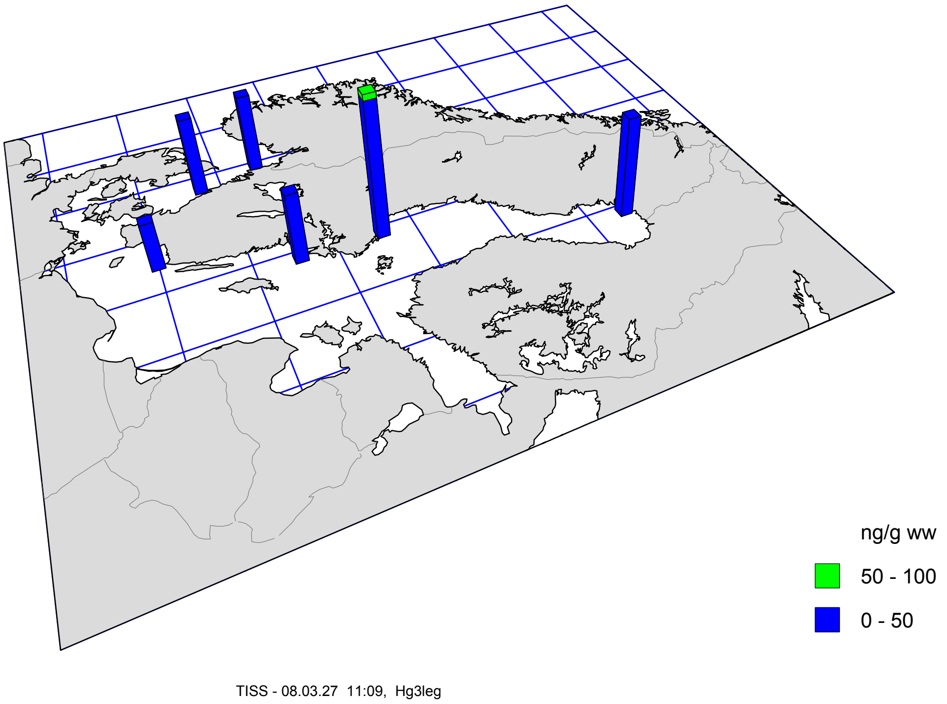


Figure 11.1. Spatial variation in concentration (w.w.) of mercury in herring liver.

Herring muscle from Ängskärsklubb show the highest mercury concentrations of all herring samples. This might be due to local discharges. Samples collected during the eighties from Ängskärsklubb are thus most probably not representative of the Bothnian Sea, regarding the mercury concentration. In the beginning of the eighties the mercury concentrations in herring from Ängskärsklubb ranged from 60-180 ng/g. Finnish mercury analyses of herring muscle samples between 1980-83 from the eastern part of the Bothnian Sea show concentrations around 20 ng/g (ICES, 1995), i.e. the same level as the results from Ängskärsklubb in 1994-1996.

Among the other herring sites, Harufjärden show the highest mercury concentration over time, significantly higher than Landsort, Utlängan and Fladen. The time series from Utlängan in the southern Baltic proper shows the lowest mercury concentrations in the Baltic with a geometric mean concentration about 17 ng/ g.

Cod muscle tissue from Fladen in the Kattegatt (56 ng/g) show significantly higher concentrations than samples from south east of Gotland (40 ng/g). Finnish data of mercury in cod from the Bothnian Sea and from the mouth of the Gulf of Finland show concentrations in the same range as the Swedish data from Gotland (ICES, 1995). The mercury concentration in cod muscle from Fladen is however within the same range as in cod muscle from the same age class from reference stations along the Norwegian coast (Green & Rönningen, 1994) analysed at NIVA.

Perch muscle samples from Holmöarna in the Quark show significantly higher concentrations (64 ng/g) compared to perch samples from Kvädöfjärden (24 ng/g) at the coast of the Baltic Proper. The estimated geometric mean concentration for Holmöarna 2006 is about 3 times higher than for Kvädöfjärden 2006.

The mercury concentration in flounder from the Skagerack show values in the same range as Danish flounder samples from the Belt Sea but significantly lower compared to Danish flounder samples from the Sound (ICES, 1995).

Mercury in blue mussels from Fladen in Kattegatt and Väderöarna in Skagerack show no spatial variation. The overall mean concentration in blue mussel samples from the two sites, exceed the upper limit of the range of 'present background concentrations in pristine areas within the OSPAR Convention Area' proposed to be between 5-10 ng/g wet weight (ICES, 1997).

The estimated mean concentrations for 2006 in herring and cod muscle (accept for cod from Fladen (56 ng/g), perch and eelpout from Holmöarna (64 and 72 ng/g respectively) and eelpout from Kvädöfjärden (76 ng/g)); all fall inside the range proposed as the 'present background concentrations in pristine areas within the OSPAR Convention Area' (10-50 ng/g fresh weight in round fish, ICES, 1997).

11.3 Seasonal variation

No significant differences in mercury concentrations were found between spring and autumn caught herring from Ängskärsklubb and Karlskrona.

11.4 Species differences

Significant differences in mean mercury concentration (ng/g w.w.), in fish muscle and blue mussel soft body, were found between various species at the Swedish west coast.

Holmöarna: Eelpout(82) > Perch(65)
Kvädöfjärden: Eelpout(77) > Blue mussel(25) - Perch(24)
Fladen: Cod(53) > Herring(30) > Blue mussel(14)
Väderöarna: Eelpout(44) - Herring(34) - > Blue mussel(15)

The mercury concentration in blue mussel is in general lower than in fish muscle. The levels found in guillemot eggs are 3 to 20 times higher compared to the levels in fish muscle.

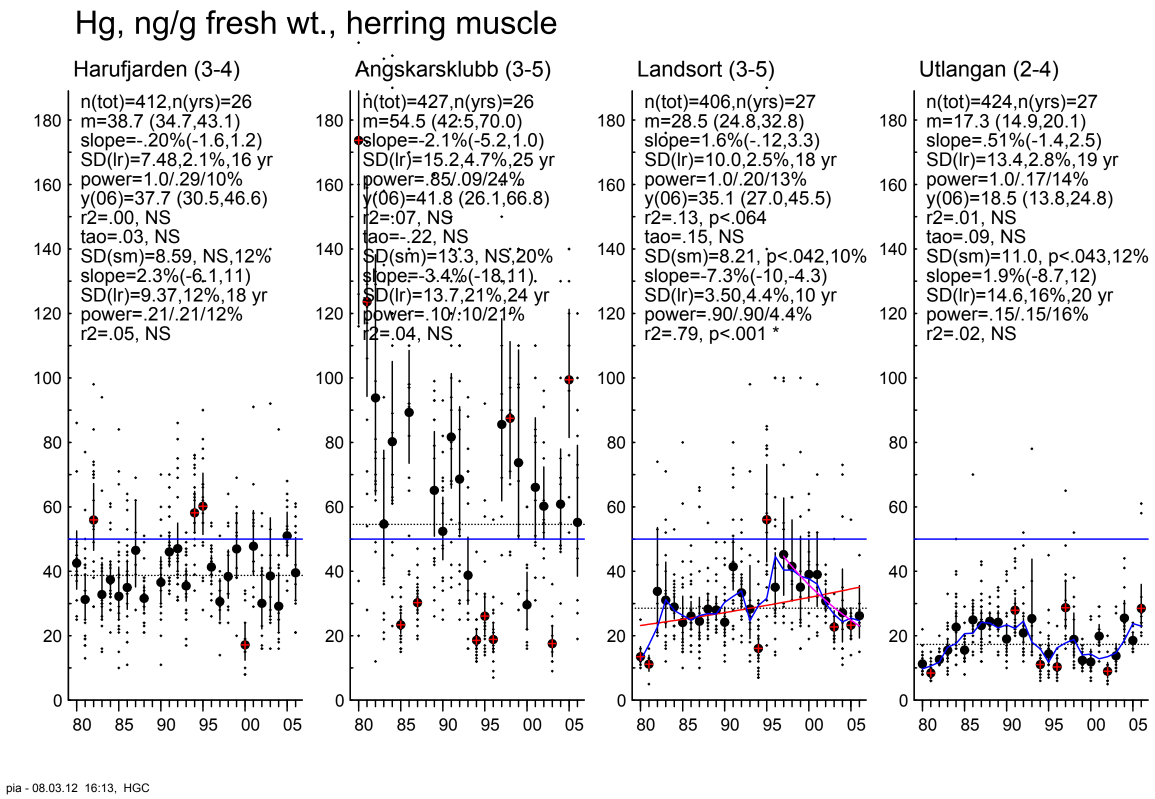
The concentration in fish muscle from the various sites all fall below the suggested limit (by the Swedish National Food Administration – SNFA) for human consumption (500 ng/g fresh weight) by a factor 6-25. However, the suggested limit for children's food is 50 ng/g, which is close to the overall mean concentration in fish muscle from most of the investigated sites (SLVFS, 1993). The limit within the European Community for several fish species is set to 500 ng/g fresh weight (EG, 2001).

Table 11.2. Estimated geometric mean concentrations of **mercury** (ng/g **fresh weight**) for the last sampled year in various matrices and sites during the investigated time period. The trend is reported, if p<0.1. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

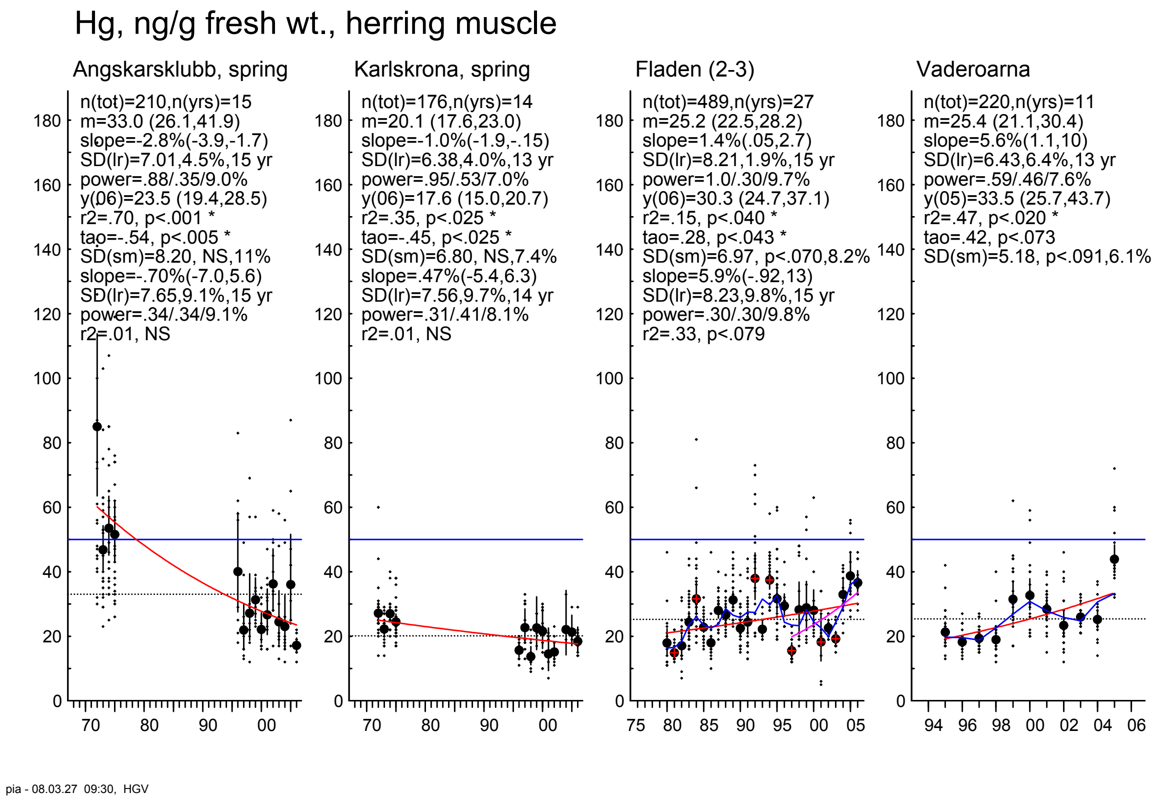
Matrix	age	n	n yrs	year	trend (95% ci)	last year (95% ci)
Herring muscle						
Harufj. autumn	3-4	412	26	80-06		39 (35-43)
Ängskärskl. aut.	3-5	427	26	80-06		55 (43-70)
” spring		210	15	72-75,96-06	-2.8 (-3.9,-1.7)*	24 (19-29)
Landsort	3-5	406	27	80-06	1.6 (-.12, 3.3)	35 (27-46)
Utlängan, aut.	2-4	424	27	80-06		17 (15-20)
” spring		176	14	72-75,96-06	-1.0 (-1.9,-0.15)*	18 (15-21)
Fladen	2-3	489	27	80-06	1.4 (0.05, 2.7)*	30 (25-37)
Väderöarna		220	11	95-05	5.6 (1.1, 10)*	34 (26-44)
Cod muscle						
SE Gotland	3-4	402	28	79-06	2.2 (1.1, 3.3)*	40 (34-48)
Fladen	2-3	447	28	79-06		53 (49-58)
Perch muscle						
Holmöarna	3-6	134	12	91,95-06		65 (55-76)
Kvädöfjärden	3-6	236	24	81-06	-3.3 (-5.2, -1.4)*	24 (18-32)
Eelpout muscle						
Holmöarna		107	11	95-06		82 (70-96)
Kvädöfjärden		119	12	95-06		77 (65-91)
Väderöarna		120	12	95-06	10 (3.1, 17)*	44 (28-68)
Dab muscle						
Fladen	3-6	278	14	81-94		78 (52-115)
Flounder muscle						
Väderöarna	4-6	248	14	81-94		46 (25-83)
Blue mussel	shell 1					
Fladen		473	24	81-06		14 (13-16)
Väderöarna		499	26	80-06		15 (13-17)
Kvädöfjärden		107	11	95-05	9.6 (3.5, 16)*	25 (18-37)
Guillemot egg						
St. Karlsö		255	34	69-06	-1.5 (-2.3, -.82)	260 (230-310)

confidence interval based on only two-three years d.f = n of obs. -1, in all other cases d.f.= n of years -1

* significant trend, p < 0.05



The blue lines indicate the suggested limit in children food by SNFA.



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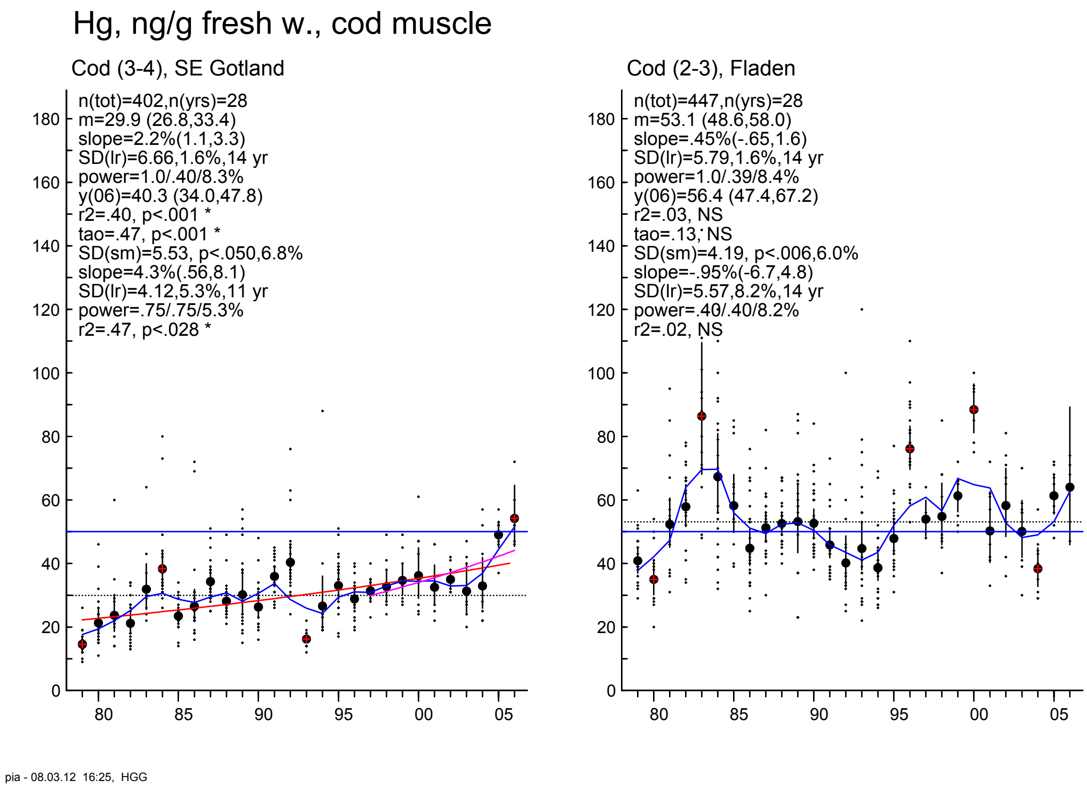
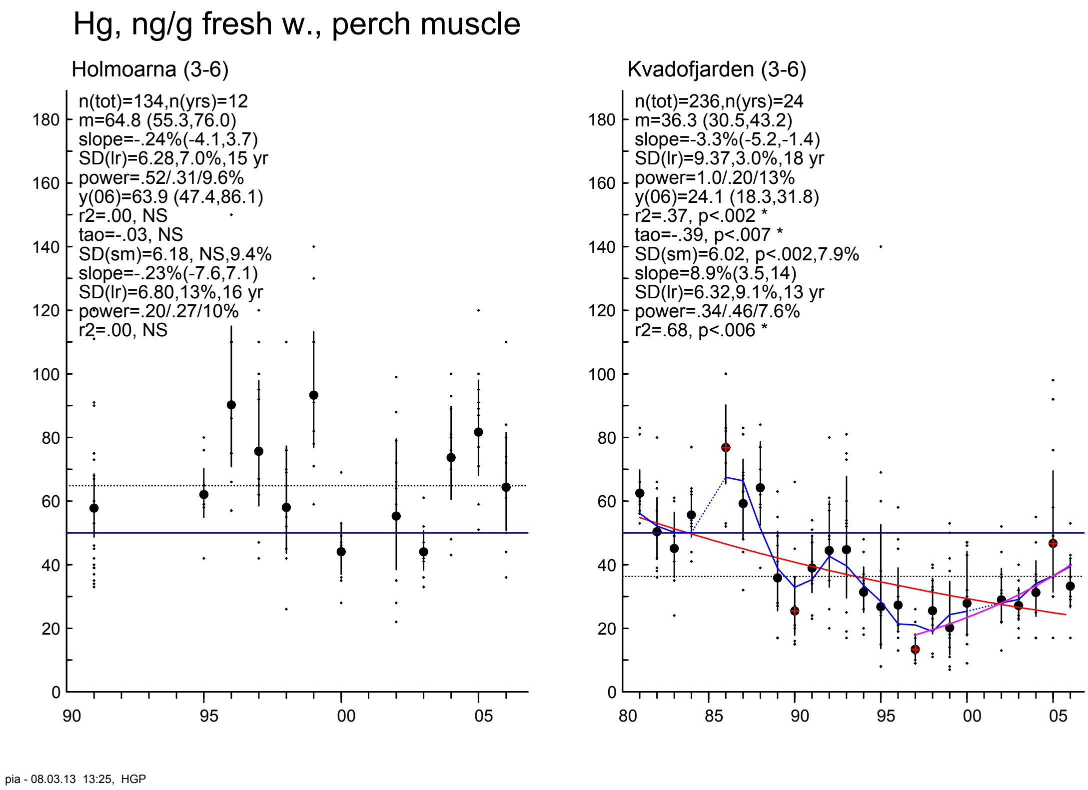


The blue lines indicate the suggested limit in children food by SNFA.



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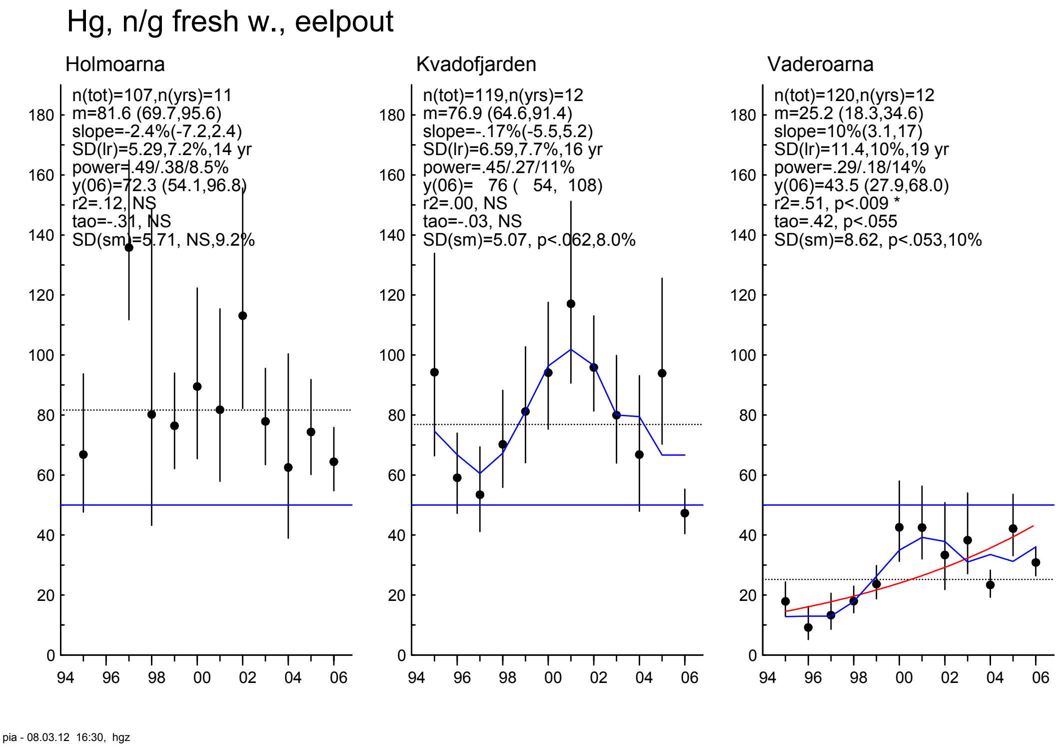
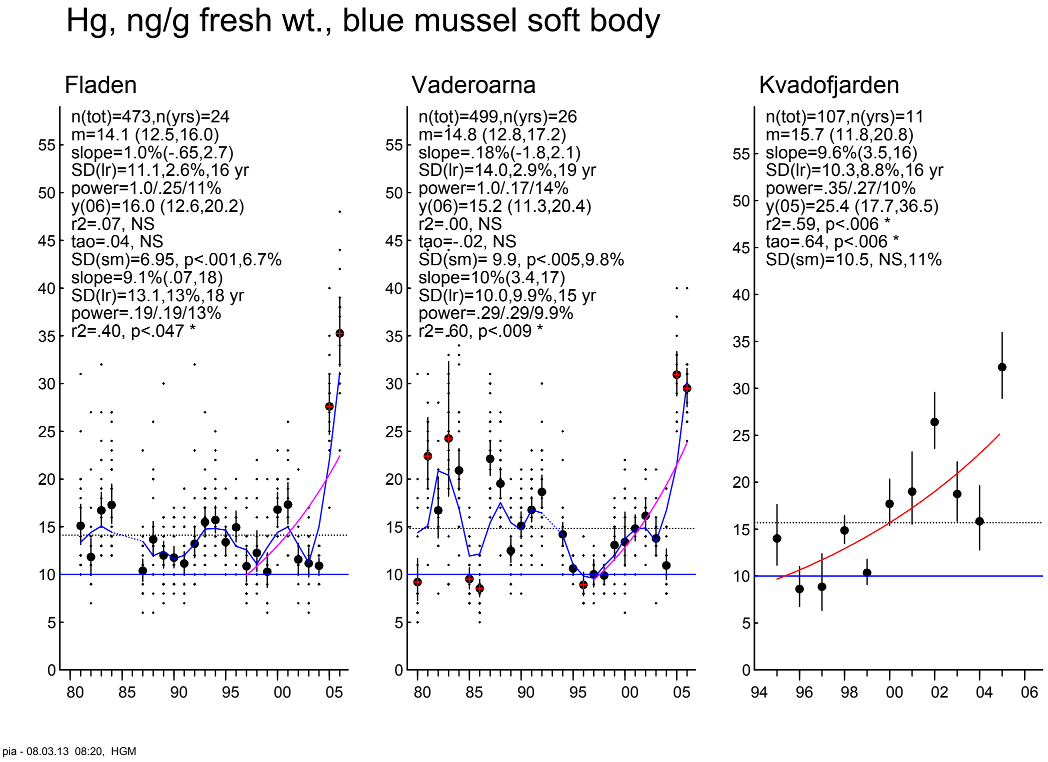
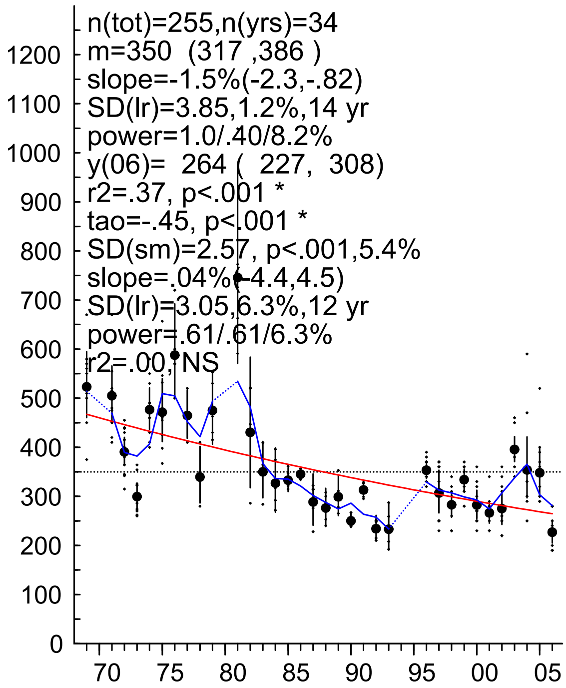


The blue lines indicate the suggested limit in children food by SNFA.



The blue lines indicate background concentration in OSPAR areas.

Hg, ng/g fresh w., guillemot eggs, early laid



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12 Lead

Updatated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

The toxic effects of lead involve several organ system and biochemical activities and the major risk is its toxicity to the nervous system. The risk is highest for Children and unborn, partly because of higher permeability of the blood-brain barrier (Klaassen & Rozman, 1991).

Lead is known to concentrate in liver tissue but to an even greater extent in the bone matrix. Approximately 90% of the total amount of lead in humans are found in the skeleton (Klaassen & Rozman, 1991). The lead concentration in liver from Baltic herring is about 4 times higher (wet wt.) than the concentration reported for the edible parts of herring. For cod, the concentration in liver is about 2.5 times higher and for perch about 2 times. Concentrations in edible parts are reported by Jorhem and Sundström, 1993.

Lead is one of the *mandatory* contaminants that should be analysed and reported within both the OSPARCOM and HELCOM conventions.

The concentration of lead in fish liver and blue mussel soft body is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences. The detection limit is estimated to approximately 10 ng/g dry weight which implies that the concentrations in herring, flounder and dab are approximately 10-20 times above the detection limit.

The estimated residual variance is higher in the beginning of the time series. 1982 seems to be lower than the surrounding years in all series but one, indicating an analytical problem.

Table 12.1. Mean divergence from standard value of analysed CRM (Certified Reference Material). The last column shows the mean deviation from the standard, including the sign.

Year	CRM	n	%	%
90	DOLT-1	12	14	-6.1
91	DOLT-1	12	13	-8.1
93	DOLT-2	17	7.4	-1.7
94	DOLT-2	12	6.9	3.6
95	DOLT-2	3	4.5	1.5
97	SLRS-3	9	9.0	1.8

The uncertainty of a single analytical value is thus estimated to be between 5-15%. The mean deviation (including the sign) of the analysed CRM samples, from the standard value is between 1-10%.

12.1 Temporal variation

12.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the lead discharges are to be reduced by 70% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of the discharges of lead to air and water by 50% by 1995 with 1987 as a base year.

12.1.2 Other investigations

Jorhem and Sundström (1993) found about *75% lower levels of lead* in fish samples (Baltic herring, cod and pike) from the period 1983-90 compared to a previous study from the period 1973-82 (Jorhem *et al.* 1984).

12.1.3 This investigation

At Harufjärden, Ängskärsklubb (autumn), Landsort, Utlängan and Fladen, the investigated time series in herring liver show significant decreasing trends.

The number of years required to detect an annual change of 5% varied between 9 to 19 years for the herring time series with a power to detect a 5% annual change ranging from 0.19 (shorter series) to 1.0 (longer series). An annual change greater than 10% would likely be detected.

Lead concentrations in cod liver (after adjusting for varying fat content) showed decreasing trends from SE Gotland and Fladen.

Lead concentrations in the shorter time series of perch liver showed decreasing trends from Kvädöfjärden but not for Holmöarna.

The short time series (8 years) of lead in guillemot eggs show a significant decreasing trend.

The lead concentration in blue mussel soft body from Fladen showed a significant decreasing trend and the short time series from Kvädöfjärden a significant increasing trend.

12.1.4 Conclusion

The decrease of lead in most matrices at most sampling sites probably reflects a general decrease of lead in the environment.

12.2 Spatial variation

The lead concentration in blue mussels from the Swedish west coast is not significantly higher compared to blue mussel samples of similar length from a reference site at Kobbefjord, Greenland (Riget *et al* 1993). Mussel samples from all three sites show mean levels below the 'background concentration at diffuse loading' in blue mussels for lead of <5 µg/g dry weight, proposed by Knutzen and Skie (1992).

12.3 Species differences

Significant differences in mean lead concentration (µg/g dry weight), in fish liver and blue mussel soft body, were found between the species marked with '>':

Holmöarna: Eelpout(0.14) > Perch(0.04)
Kvädöfjärden: Blue mussel (4.3) > Eelpout(0.18) > Perch(0.033)
Fladen: Blue mussel(0.86) > Herring(0.08) > Cod(0.04)
Väderöarna: Blue mussel(1.1) > Eelpout(0.14) > Herring(0.044)

The lead concentration in blue mussel soft body tissue is thus generally much higher than concentration in fish liver. The concentration in eelpout liver is about three to five times higher than perch liver in the analysed samples.

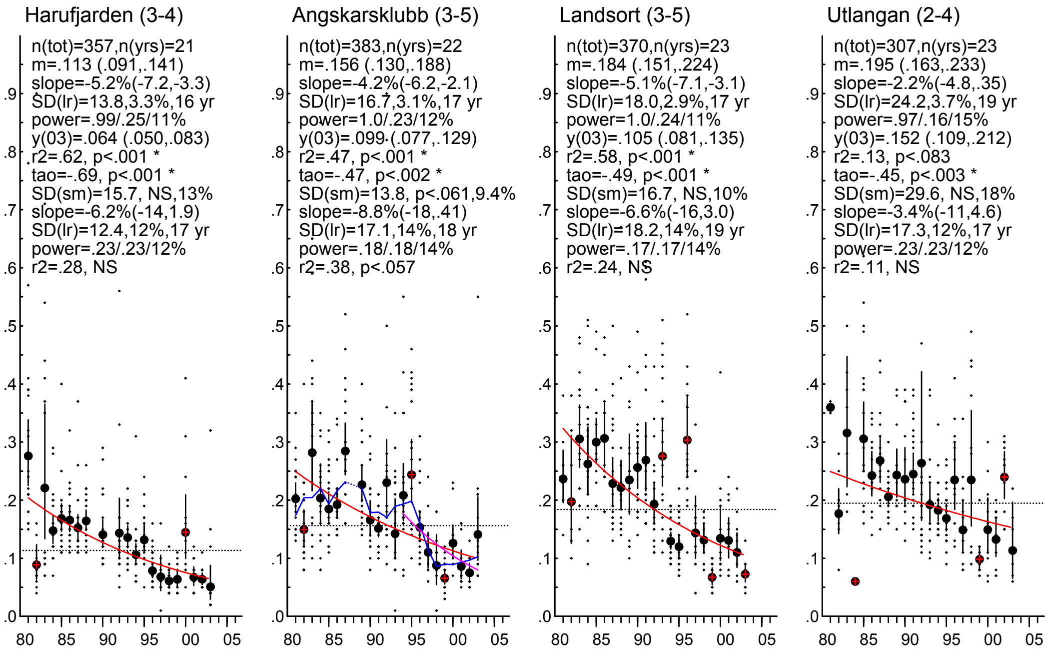
The recommended limit for children's food is set by the Swedish Food Administration to 50 ng/g fresh weight (SLVFS, 1993). Within the European Community the limit in fish muscle is set to 0.2 ug/g and in mussels to 1.5 ug/g. (EG, 2002).

Table 12.2. Estimated geometric mean concentrations of **lead** (ug/g **dry weight**) for the last sampled year in various matrices and sites during the investigated time period. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend (95% ci)	last year (95% ci)
Herring liver						
Harufj. autumn	3-4	357	21	81-03	-5.2(-7.2, -3.3)*	0.064 (.050-.083)
Ängskärskl. aut.	3-5	383	22	81-03	-4.2 (-6.2, -2.1)*	.099 (.077-.13)
” spring	3-6	80	8	96-03		.18 (.15-.21)
Landsort	3-5	370	23	81-03	-5.1 (-7.1,-3.1)*	.11 (.081-.14)
Utlängan, aut.	2-4	307	23	81-03	-2.2 (-4.8, .35)	.15 (.11-.21)
” spring	0 -4	47	5	96-03		.19 (.17-.21)
Fladen	2-3	443	23	81-03	-4.2 (-6.6, -1.8)*	.080 (.059, 0.11)
Väderöarna	2-4	180	9	95-03		.056 (.044-.072)
Cod liver						
SE Gotland	3-4	339	23	81-03	-7.2 (-9.9,-4.5)*	.021 (.014-.030)
Fladen	2-4	425	23	81-03	-5.1 (-7.8,-2.4)*	.040 (.029-.057)
Perch liver						
Holmöarna	0-7	90	9	95-03		.048 (.035-.065)
Kvädöfjärden	3-7	80	8	95-03	-10 (-17,-3.0)*	.033 (.023-.047)
Eelpout liver						
Holmöarna		67	7	95-03		.16 (.12-.20)
Kvädöfjärden		89	9	95-03		.19 (.17-.21)
Väderöarna		79	8	95-03		.13 (.10-.17)
Dab liver						
Fladen	3-6	257	14	81-94	.77 (-3.0, 4.6)*	221 (165-296)
Flounder liver						
Väderöarna	4-6	239	14	81-94	-0.06 (-5.4,5.3)*	173 (115-260)
Blue mussel	shell l					
Fladen	5-8	396	21	81-03	-4.4 (-8.6-.12)*	.86(.51-1.5)
Väderöarna	6-10	412	22	81-03		1.4 (1.1-1.8)
Kvädöfjärden		88	9	95-03	19 (1.3, 36)*	4.3 (1.9-9.8)
Guillemot egg						
St. Karlsö		80	8	96-03	-13 (-18,-8.7)*	.030 (.025-.037)

* significant trend, $p < 0.05$

Pb, ug/g dry w., herring liver



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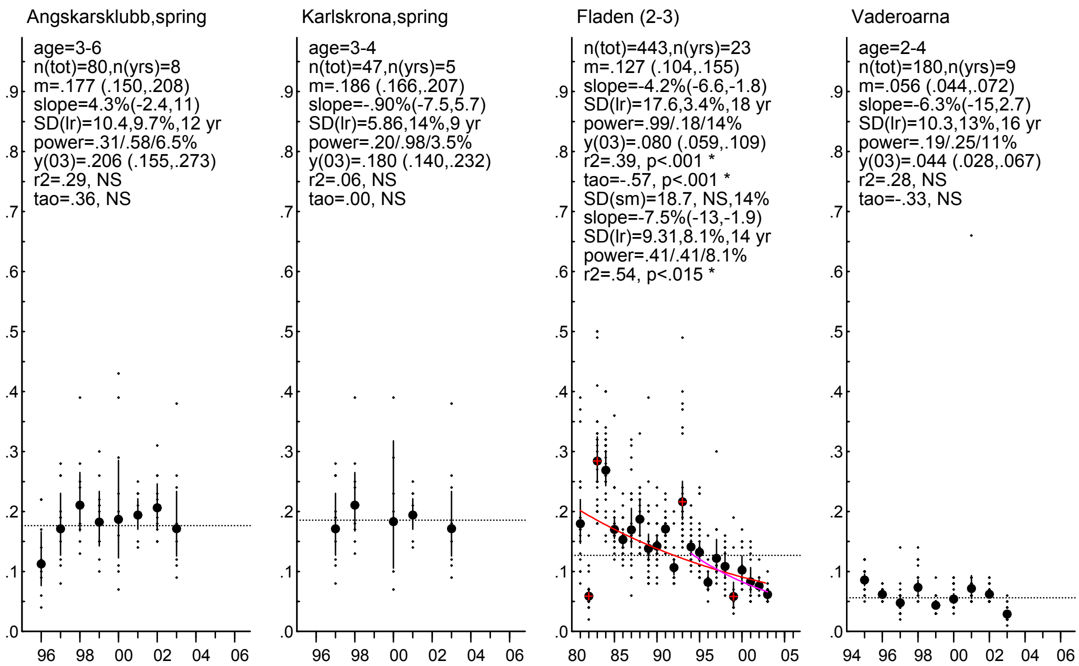
Pb, ug/g dry weight, herring liver



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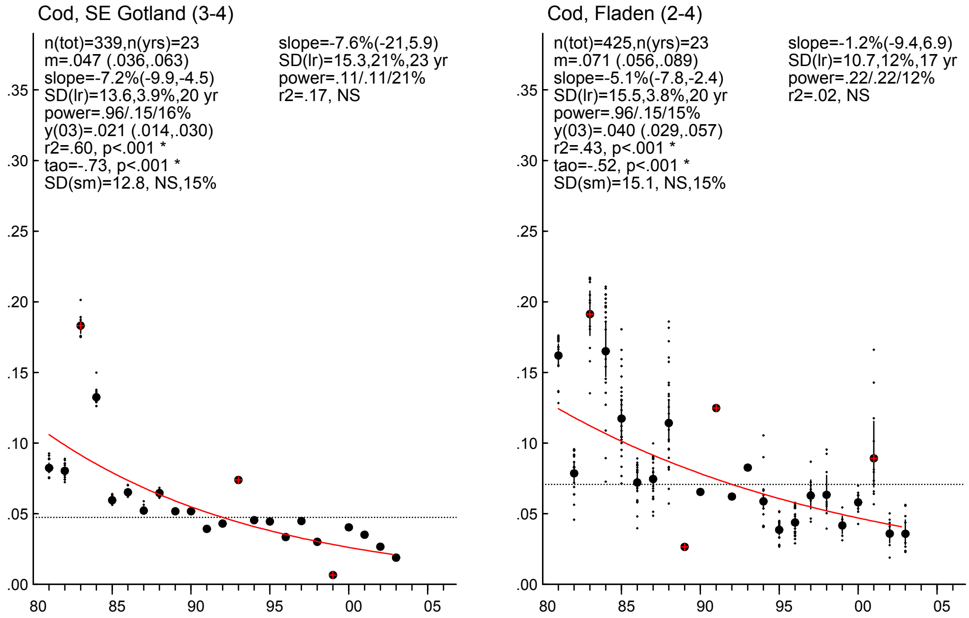
Pb, ug/g dry w., cod liver

Fat adjusted geometric means



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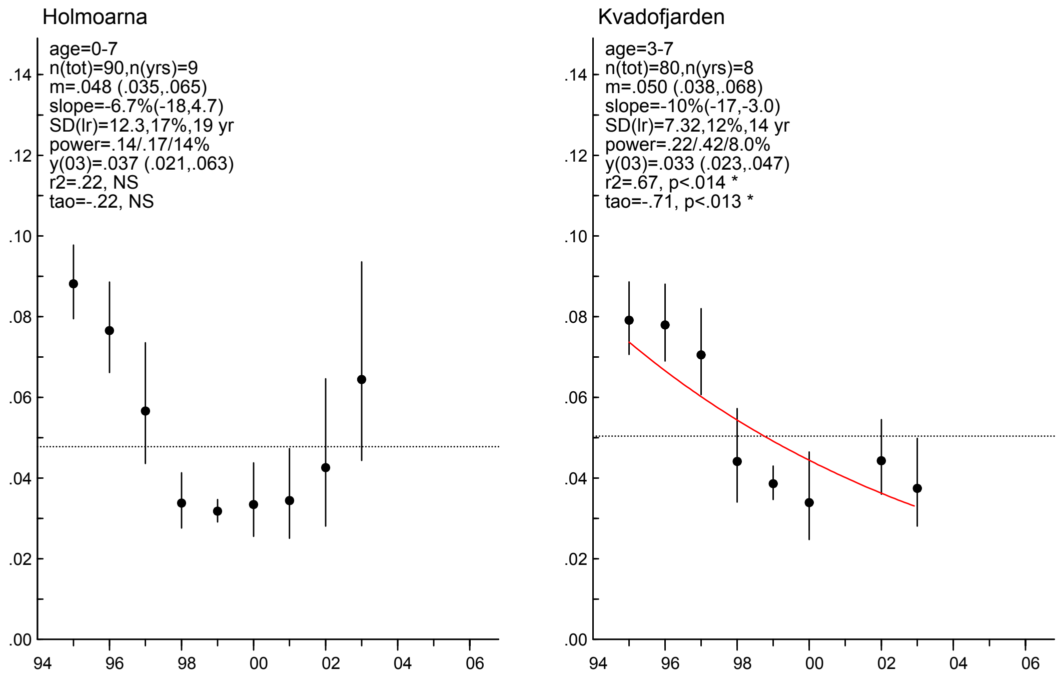
Pb, ug/g dry w. perch



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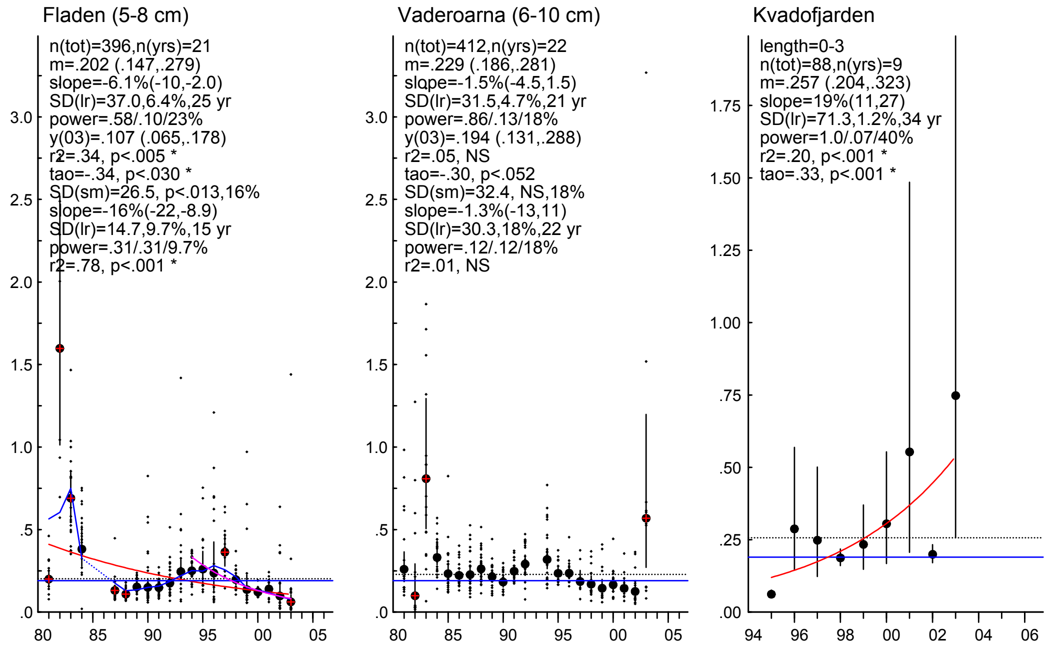
Pb, ug/g wet w., blue mussel softbody

Shell lengths in brackets



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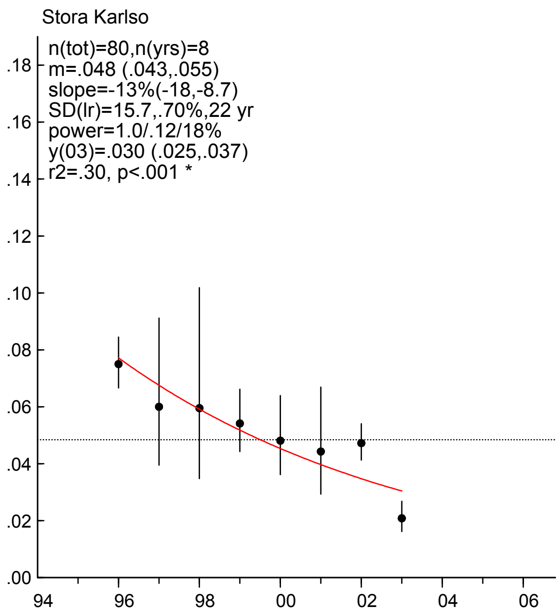
The blue lines indicate background concentration in OSPAR areas.

Pb, ug/g dry w. Guillemot egg



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13 Cadmium

Updated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

Cadmium is an important metal in many industrial applications. It has been excessively used until the end of the seventies, in electroplating or galvanising because of its noncorrosive properties. It is has also been used (and is still used to some extent) as a cathode material for nickel-cadmium batteries and as a colour pigment for paints and plastics. Its industrial use has however decreased considerable during recent years. In 1982, Sweden as the first country in the world introduced a principal ban for certain industrial applications. Cadmium does also reach the environment as a by-product of zinc and lead mining and smelting and as an undesired element in fertilisers.

Cadmium is one of the *mandatory* contaminants that should be analysed and reported within both the OSPARCOM and the HELCOM conventions.

The time series of cadmium concentration in fish liver and blue mussel soft body, presented below, start 1981. It is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences. The detection limit is estimated to approximately 5 ng/g dry weight.

Table 13.1. Mean divergence from standard value of analysed CRM (Certified Reference Material). The last column shows the mean deviation from the standard, including the sign.

Year	CRM	n	%	%
90	Dolt-1	4	6.3	6.3
91	Dolt-1	15	4.0	-0.5
93	Dolt-2	20	4.1	0.5
94	Dolt-2	21	3.3	1.7
95	Dolt-2	22	2.7	-0.1
96	Dolt-2	24	5.5	2.4
97	Dolt-2	6	4.9	-2.4

The uncertainty of a single analytical value is thus estimated to be around ±5% on average and has not changed over time. The mean deviation (including the sign) of around 20 samples from the standard value is (except for 1990) less than 2.5% and shows no systematic deviation. Although the concentration of cadmium in Dolt2 is about 10 to 15 times higher compared to the levels in the investigated herring livers, there is no reason, sofar, to believe that the impact from analytical errors on the evaluation of the time series is important.

13.1 Temporal variation

13.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the cadmium discharges are to be reduced by 70% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of the discharges of cadmium to air and water by 50% by 1995 with 1987 as a base year.

The Swedish Parliament has agreed on a general reduction of cadmium discharges aiming at a reduction of 70% between 1985 and 1995. Further, that all use of cadmium that implies a risk of discharges to the environment, in a longer term perspective, will cease (prop 1990/91:90, JoU 30, rskr.343).

In 1982, the use of cadmium in electroplating and as a thermal stabilisor was banned in Sweden.

A fee on batteries containing cadmium was introduced 1987 in Sweden. This fee was raised considerably in 1991.

The content of cadmium in fertilisers was restricted to 100g/ton phosphorus, 1993.01.01 in Sweden.

13.1.2 Input

The discharges of cadmium to the environment in Sweden have been estimated to have decreased with approximately 45% between 1985 and 1990 while the airborne cadmium load during the same period is estimated to have decreased with approximately 15% (SNV, Rapport 4135). The river discharges to the Baltic from Sweden have decreased considerably during the recent decades while from Poland, Russia and the Baltic countries the discharges are still very high. The estimated cadmium burden (in tons) 1990 from Sweden compared to all countries was, to; the Bothnian Bay and the Bothnian Sea, 2/17; the Baltic proper 0.41/110; the Kattegatt, 0.5/6(Widell, 1990,1992).

13.1.3 Proposed processes

a) Decreased contaminant load may cause a corresponding decrease in the amount bioavaillable cadmium.

b) Bengtsson (1975) among others, suggested that decreasing salinity increase the bioavailability of cadmium. Studies by Danielsson *et al.*(1983), Mart *et al.*(1985) and Nolting (1986) show that cadmium is desorbed from particulate material during transition from fresh to more saline water. Hence, plankton may gain in adsorption capacity as salinity decrease. Decreasing levels of salinity during the period have been reported from several stations in the Baltic (Bergström & Matthäus, 1995) but also in the Bothnian Bay. Herring feeding on plankton may thus be exposed to increasing levels of bioavaillable cadmium (Harms, 1995).

c) Increased mobility of Cd-ions due to acidification may cause an increased cadmium concentration in the run off (e.g. Borg *et al*, 1989).

d) Cadmium can be bound to metallothionein (MT) (da Silva and Williams, 1994). It is further known that various compounds can induce (and possibly also inhibit) the formation of MT in fish liver (Bouquegneau *et al.,* 1975). A change in the amount of MT, due to induction, inhibition or ceased induction or inhibition, might thus change the metal concentration in the analysed liver tissue.

13.1.4 Other investigations

Concentrations of dissolved and particulate cadmium were determined in seawater from several sites in the Baltic proper for nine years during the time period 1980 to 1993 (Pohl, 1994, Schneider & Pohl, 1995). The material was separated into two regions. A *decrease* of approximately 7% per year was found in the Mecklenburg Bight/Arkona Sea and in surface waters of the Bornholm Sea/Gotland Sea. The time series are however based on data from various seasons and the analytical technique has changed over time.

Cadmium concentration analysed in herring muscle between 1979 to 1993 from three Finnish sites: western and eastern Gulf of Finland and southern Bothnian Bay show *decreasing* trends of between 10 to 12% a year (ICES, 1995). However, the analysed cadmium concentrations are close to, and for several years below, the detection limit.

Cadmium concentration in herring muscle has also been reported from three sites along the Polish coast between 1974-1988 (Protasowicki *et al*. 1975) and during 1991-1993 (Polak-Juszczak and Domagala, 1994) where the mean values indicate a decrease. Polish data of Cd concentrations analysed in herring muscle and liver from three sites were also reported to HELCOM and assessed by ICES but were found too short to disclose any trends (ICES, 1995).

A general remark for extra cautiousness is appropriate when interpreting analyses of low concentrations near the detection level as in water or muscle samples. An improved analytic technique may lead to decreasing concentrations due to less risk of sample contamination.

13.1.5 This investigation

Cadmium concentrations in herring liver from Utlängan (autumn) in the Baltic proper show a significant *increasing* log-linear trend. The total increase in cadmium concentration during 1981-95 at Ängskärsklubb, Landsort and Utlängan is about 2.5 times. During recent years the increases have levelled out and also turned to a decrease at least at Landsort and Ängskärsklubb.
Cadmium concentrations in cod liver samples (adjusted for varying fat content) from south east of Gotland and Fladen show significant *decreasing* trends .

Cadmium concentrations in eelpout samples from Holmöarna, Kvädöfjärden and Väderöarna all show significant increasing trends (the between year variation at Holmöarna and Kvädöfjärden is large though).

The number of years required to detect an annual change of 5% varied between 10 to 19 years for the herring time series with a power to detect a 5% annual change ranging from 0.46 to 1.0. (Since it is not appropriate to fit a log-linear trend at Ängskärsklubb and Utlängan, these sites were excluded from the power calculations.)

The geometric mean concentration of cadmium in dab liver was extremely high in 1988, about 5 times the overall mean concentration.

13.1.6 Conclusion

The rapid increase of cadmium concentrations at Ängskärsklubb and Landsort seems to have stopped and is now turning downward

Cadmium is concentrated in internal organs, i.e. liver, why the concentration in muscle tissue is very low. Analysed values for perch and herring muscle are 0.5 and 4 ng/g dry weight respectively (unpublished data). The average cadmium concentration in potatoes (in a sample of 8, during 1987-1990) was reported to 17 ng/g (Jorhem and Sundström, 1993). The cadmium concentrations of 0.5 to 4 ng/g indicates that there is no immediate risk for human consumption, since the EU limit suggested for human consumption of fish is 50 ng/g fresh weight (EG nr 221/2002).

13.2 Spatial variation

13.2.1 Other investigations

Cadmium analysed in kidney cortex from juvenile harbour seals showed significantly lower values in samples from the Baltic compared to comparable samples from the west coast (Frank *et al.* 1992)

13.2.2 This investigation

The overall mean Cd-concentrations in herring liver from the Baltic show significantly higher cadmium concentrations compared to Fladen in the Kattegatt and Väderöarna in the Skagerack at the Swedish west coast. All sampling sites in the Baltic show significantly higher levels, estimated 2000, compared to Fladen. The geometric mean concentration in herring liver, for the period 1981-2003, from Harufjärden (Bothnian Bay) and Ladsort (Baltic proper) show about 3 repectively 3.5 times higher values compared to samples from the Kattegatt.

Eelpout livers from Holmöarna in the southern Bothnian Bay and Kvädöfjärden in the Baltic Proper show about 3 to 4 times higher geometric mean Cd-concentrations (dry weight) compared to samples from Väderöarna in the Skagerack.

Blue mussels from Kvädöfjärden, analysed 1995-03, show about 3 times higher concentrations compared to blue mussel samples from the Swedish west coast. The samples from the Swedish west coast show mean levels similar to what is found in blue mussels from the Belgian coast (Vyncke *et al.* 1999) and do not exceed the 'high background concentration at diffuse loading' for cadmium in blue mussels of <2 µg/g dry weight, proposed by Knutzen and Skie (1992) whereas the samples from Kvädöfjärden does. All blue mussel samples exceed the range of 'present background concentrations in pristine areas within the OSPAR Convention Area' proposed to 0.070-0.11 µg/g wet weight (ICES, 1997). The estimated geometric mean concentration from Kvädöfjärden exceeds this concentration by about 4 times.

Cadmium concentrations in cod livers from Fladen in the Kattegatt, are significantly higher (about 3 times on a dry weight basis and about 2 times on a fresh weight basis) compared to samples from south east of Gotland. This may be explained by the fact that the average fat content in cod liver from Gotland is about 2.5 times higher compared to the samples from the Kattegatt. The Swedish data from SE of Gotland are in the same range as Finnish data of cod liver from the Gulf of Finland and the Bothnian Sea.

Herring liver from Fladen in the Kattegatt show significantly higher concentrations compared to Väderöarna in the Skagerack.

13.3 Species differences

Significant differences in mean cadmium concentration (µg/g dry weight), in fish liver and blue mussel soft body, were found between the species marked with '>' :

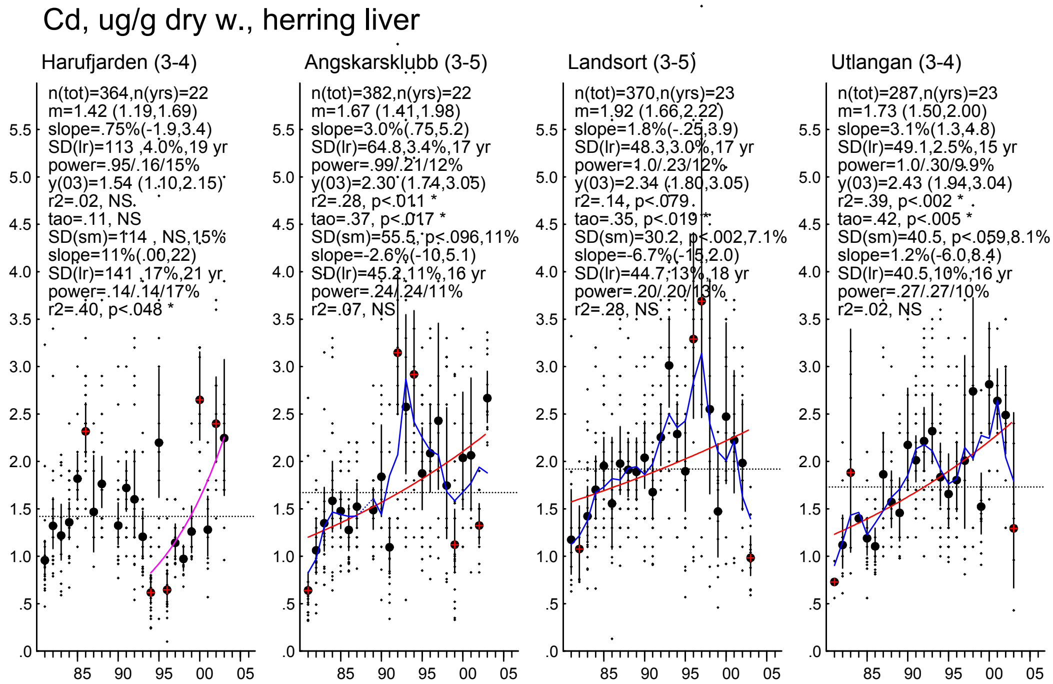
Holmöarna: Eelpout(1.8) > Perch(0.47)
Kvädöfjärden: Blue mussel(4.3) > Eelpout(2.1) > Perch(0.60)
Fladen: Blue mussel(0.96) > Herring(0.54) > Cod(0.12)
Väderöarna: Blue mussel(1.1) > Herring(0.33) - Eelpout(0.49)

The cadmium concentration in blue mussel soft body tissue is thus about 2 to 9 times the concentration found in fish liver and the concentration in eelpout liver is about twice as high as in perch liver in the analysed samples. The concentration found in guillemot egg is extremely low, at least 500 times lower (dry weight) compared to herring liver.

Table 13.2. Geometric mean concentrations of **cadmium** (µg/g **dry weight**) in various matrices and sites during the whole investigated time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend (95% ci)	last year (95% ci)
Herring liver						
Harufj. autumn	3-4	364	22	81-03		1.4 (1.2-1.7)
Ängskärskl. aut.	3-5	382	22	81-03	3.0 (.75, 5.2)*	2.3 (1.7-3.1)
” spring	3-6	80	8	96-03		3.9 (3.3-4.7)
Landsort	3-5	370	23	81-03	1.8 (-.25, 3.9)	2.3 (1.8-3.1)
Utlängan, aut.	3-4	287	23	81-03	3.1 (1.3, 4.8)*	2.4 (1.9-3.0)
” spring	0-4	70	7	96-03		2.4 (2.1-2.7)
Fladen	2-3	443	23	3		.54 (.48-.59)
Väderöarna	2-4	180	9	95-03		.33 (.29-.38)
Cod liver						
SE Gotland	3-4	343	23	81-03	-6.4 (-8.3,-4.5)*	.027 (.021-.035)
Fladen	2-4	426	23	81-03	-3.5 (-6-4,-.60)*	.12 (.079-.17)
Perch liver						
Holmöarna	0-7	90	9	95-03		.47 (.35-.62)
Kvädöfjärden		90	9	95-03		.60 (.47-.77)
Eelpout liver						
Holmöarna		67	7	95-03	11 (4.7, 17)*	1.8 (1.4-2.3)
Kvädöfjärden	2-9	89	9	95-03	10 (4.7, 16)*	2.1 (1.6-2.7)
Väderöarna	3-8	79	8	95-03	11 (5.6, 17)	.49 (.38-.63)
Dab liver						
Fladen	3-6	257	14	81-94	3.7 (-4.8,12)*	0.81 (.42-1.5)
Flounder liver						
Väderöarna	4-6	239	14	81-94	1.7 (-3.7,7.0)*	0.53 (.35-.80)
Blue mussel	shell 1					
Fladen	5-8	396	21	81-03	-1.3 (-2.7, .19)	.96 (.80-1.2)
Väderöarna	6-10	413	22	81-03		1.1 (.94-1.2)
Kvädöfjärden	0-3	88	9	95-03		4.3 (3.8-4.8)
Guillemot egg						
St. Karlsö		78	8	96-03	-16 (-25,-7.1)*	.001 (.001-.002)

* significant trend, $p < 0.05$



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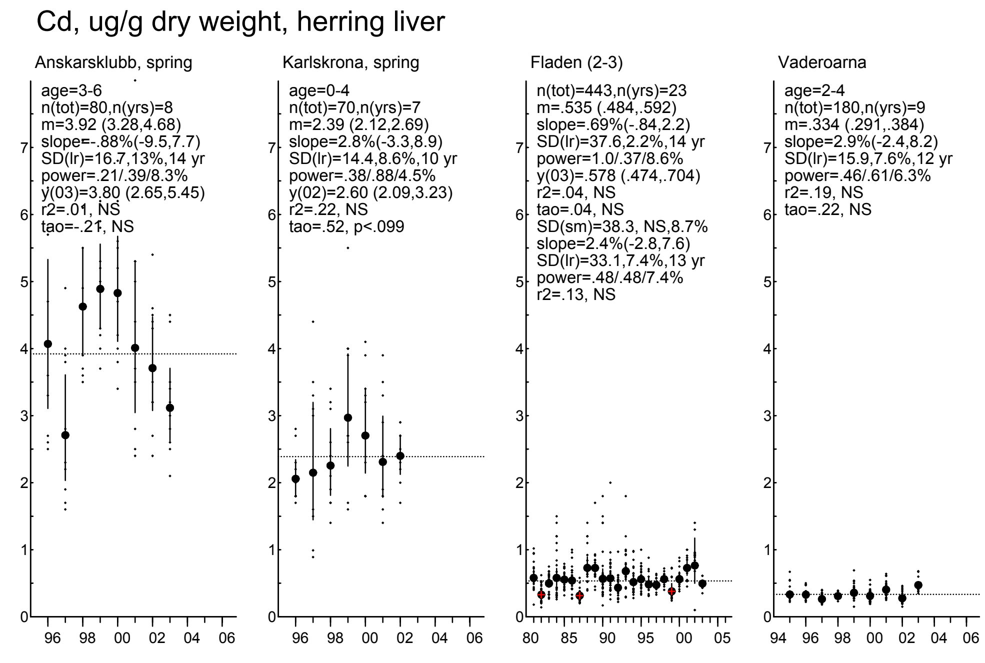

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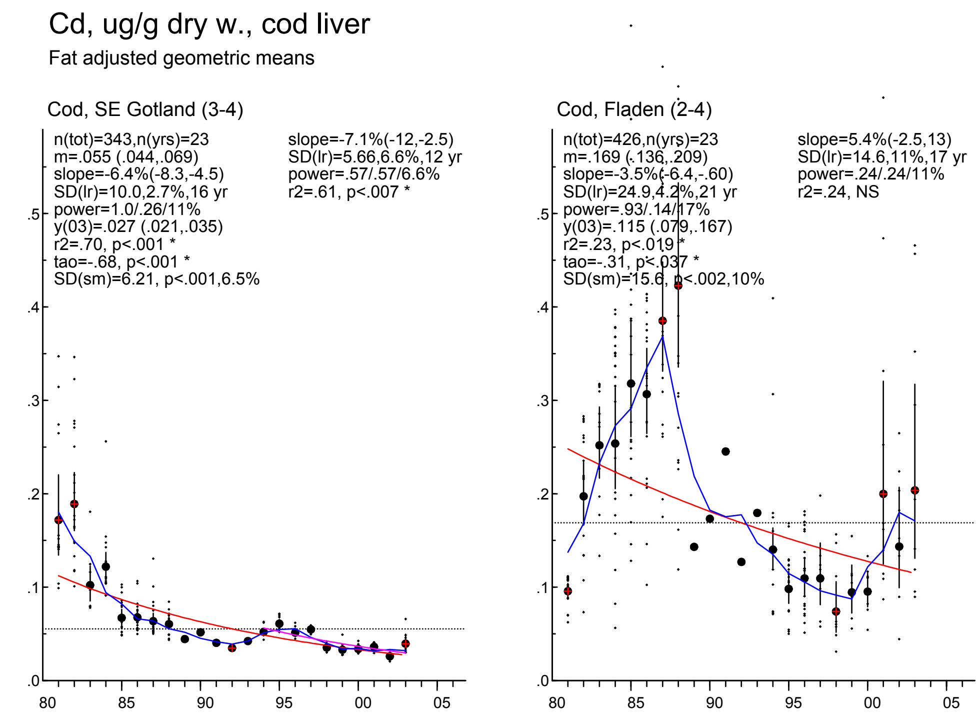

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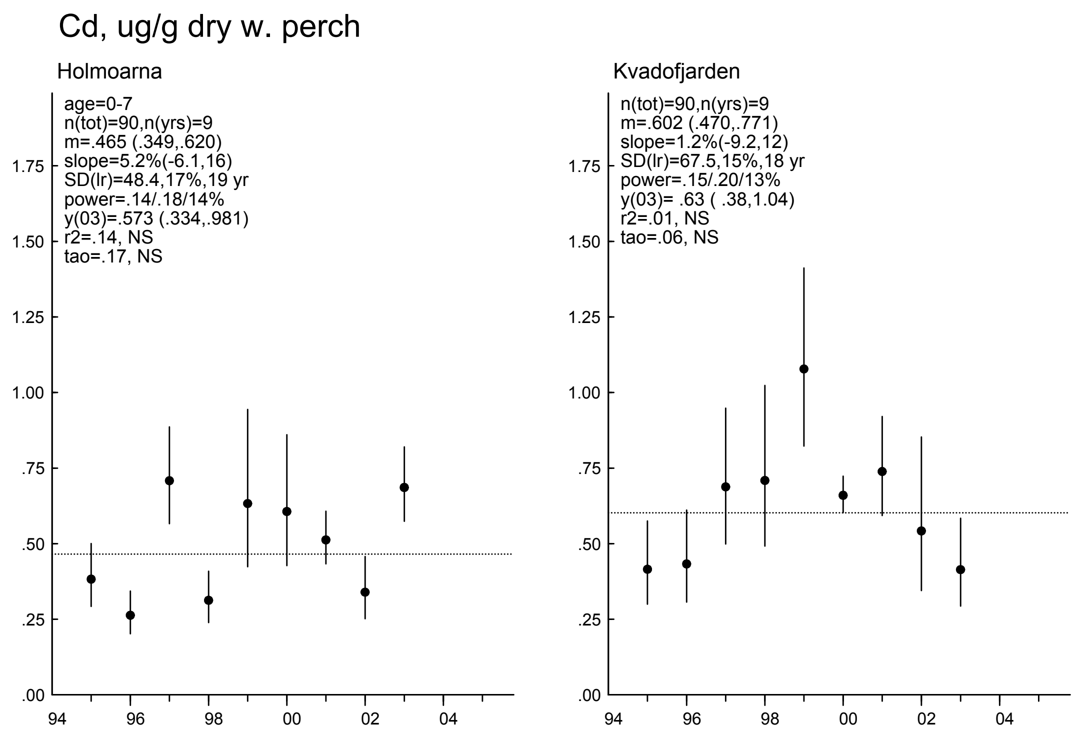

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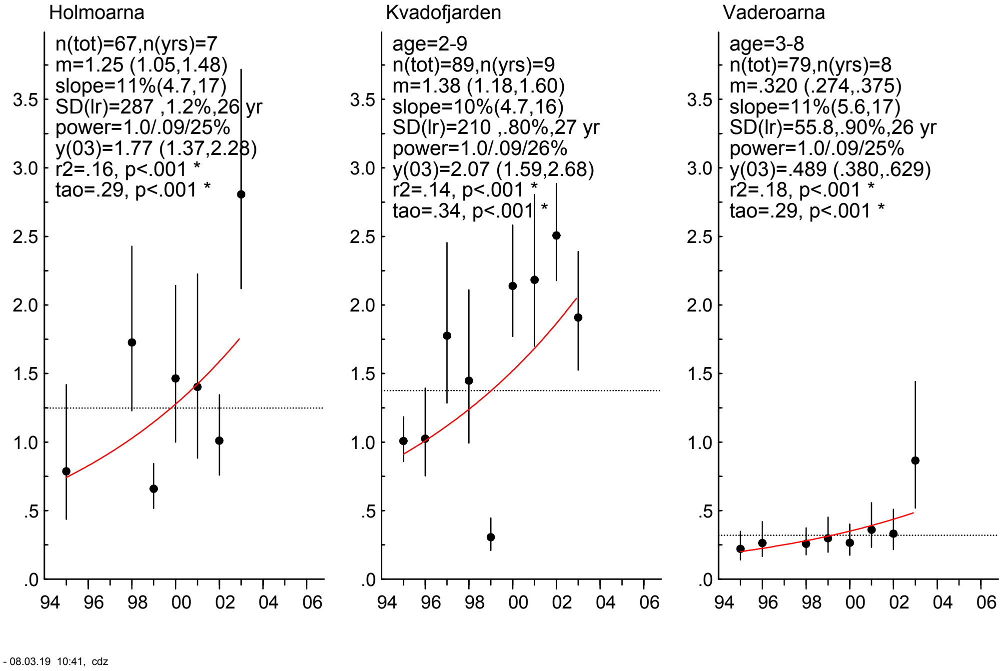
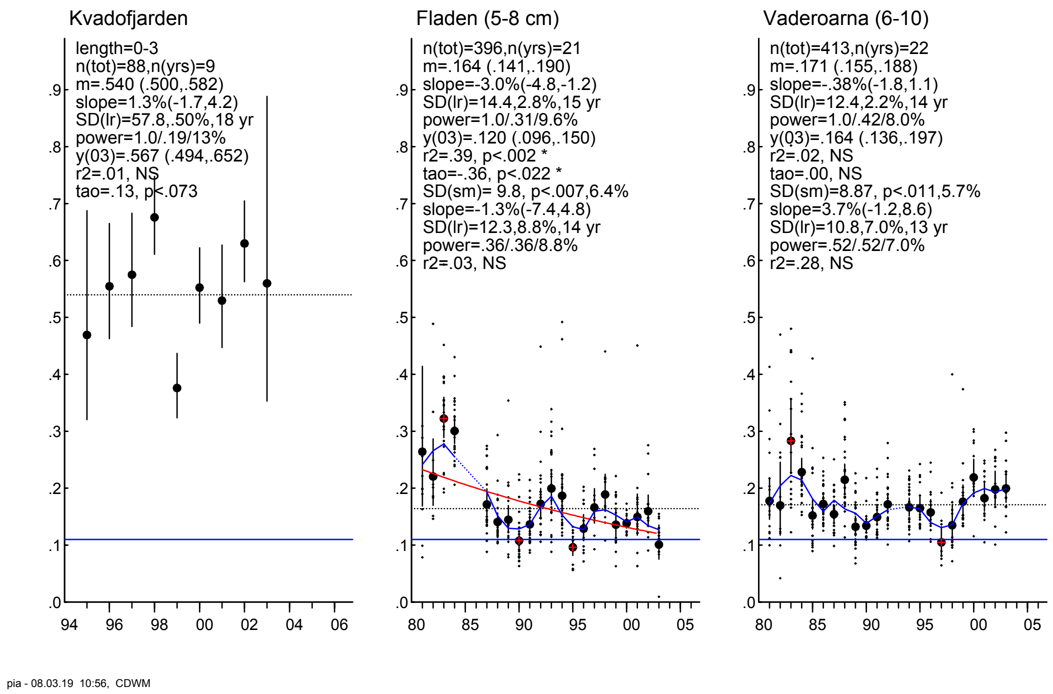
Cd, ug/g dry w., Eelpout



Cd, ug/g wet w., blue mussel softbody

Shell lengths in brackets



The blue lines indicate background concentration in OSPAR areas.

14 Nickel

Updated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

The concentration of nickel in fish liver is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences. The detection limit is estimated to approximately 0.1 μg/g dry weight.

The analysis started on samples collected 1995.

14.1 Temporal variation

The time series of herring from Landsort, Fladen and Väderöarna, cod liver from SE Gotland and Fladen, perch liver from Holmöarna and eelpout from Kvädöfjärden and Väderöarna, all show significant decreasing trends.

Nickel has only been analysed since 1995 (eight years) and therefore the possibilities to detect time trends are limited. For herring the number of years required to detect an annual change of 5 % varies between 13 to 26 years. The power to detect an annual change of 5 % range from 0.08 to 0.36.

14.2 Spatial variation

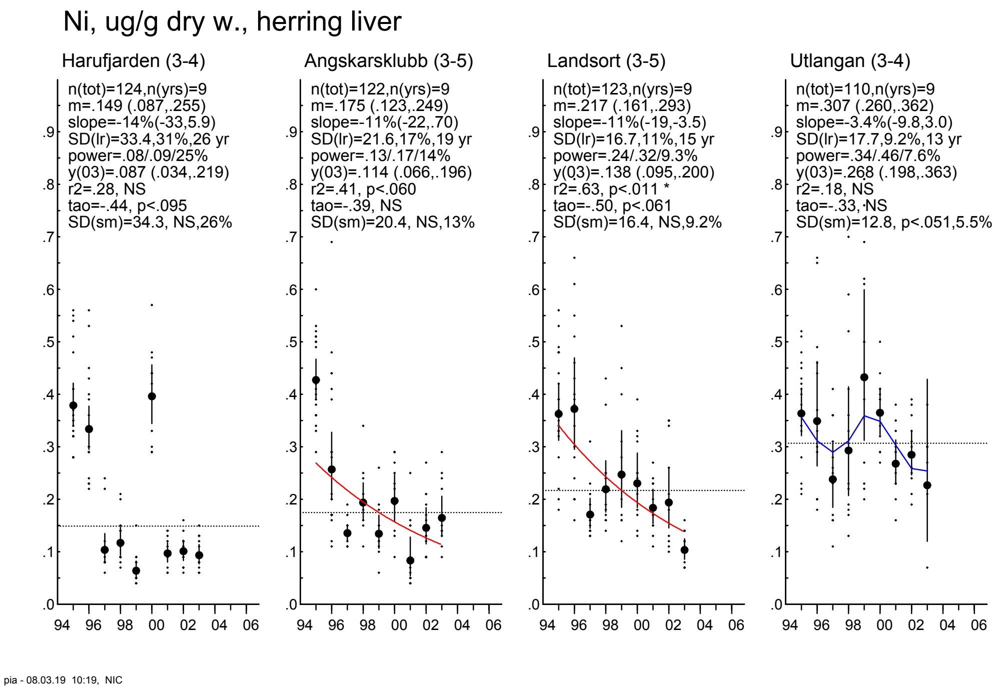
Significantly lower nickel concentrations were observed in herring liver from Väderöarna compared to the samples from Landsort and Karlskrona archipelago.

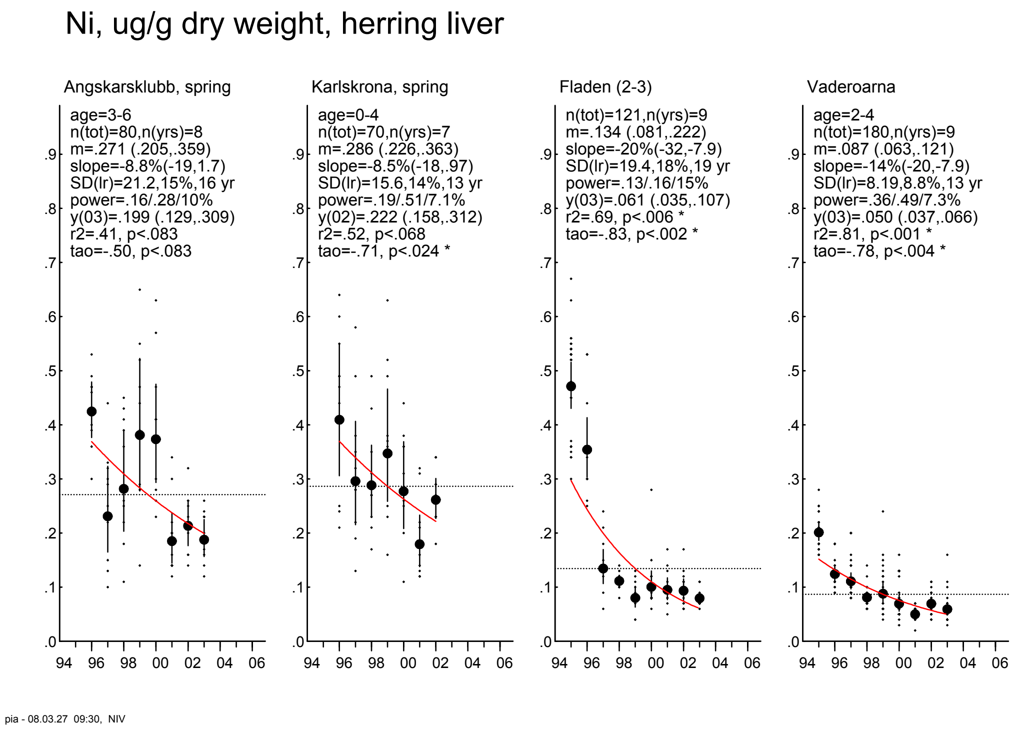
Mussels from all three sites show mean levels below the upper limit of the 'high background concentration at diffuse loading' in blue mussels for nickel of <5 μg/g dry weight, proposed by Knutzen and Skie (1992).

Table 14.1. Geometric mean concentrations of **nickel** (μg/g **dry weight**) in various matrices and sites during the time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend % (95% ci)	last year(95% ci)
Herring liver						
Harufj. autumn	3-4	124	9	95-03		.15 (.087-.26)
Ängskärskl. aut.	3-5	122	9	95-03	-11 (-22, 0.7)	.11 (.066-.20)
” spring	3-6	80	8	96-03	-8.8 (-19, 1.7)	.20 (.13-.31)
Landsort	3-5	123	9	95-03	-11 (-19,-3.5)*	.14 (.095-.20)
Utlängan, aut.	3-4	110	9	95-03		.31 (.26-.36)
” spring	0-4	70	7	96-03	-8.5 (-18, .97)	.22 (.16-.31)
Fladen	2-3	121	9	95-03	-20 (-32,-7.9)*	.061 (.035-.11)
Väderöarna	2-4	180	9	95-03	-14 (-20,-7.9)*	.05 (.037-.066)
Cod liver						
SE Gotland	0-6	110	9	95-03	-8.8 (-16,-2)*	.065 (.047-.090)
Fladen	0-5	110	9	95-03	-9.5 (-19,-.07)*	.12 (.077-.19)
Perch liver						
Holmöarna	4-7	76	8	95-03	-20 (-48,-1.5)*	.045 (.018-.11)
Kvädöfjärden	3-6	79	8	95-03	-16 (-36, 3.9)	.054 (.020-.15)
Eelpout liver						
Holmöarna	3-6	19	7	95-03		.19 (.10-.34)
Kvädöfjärden	2-6	66	9	95-03	-16 (-25,-7.2)*	.11 (.072-.17)
Väderöarna	3-5	71	8	95-03	-16 (-26,-5.1)*	.14 (.086-.22)
Blue mussel	shell 1					
Kvädöfjärden		88	9	95-03		2.8 (2.4-3.2)
Fladen		139	9	95-03		2.2 (1.8-2.6)
Väderöarna		130	9	95-03		1.1 (.91-1.4)
Guillemot egg						
St. Karlsö		80	8	96-03		.076 (.048-.12)

- significant trend, $p < 0.05$




Ni, ug/g dry weight, herring liver
Angskarsklubb, spring
age=3-6
n(tot)=80,n(yrs)=8
m=.271 (.205,.359)
slope=-8.8%(-19,1.7)
SD(lr)=21.2,15%,16 yr
power=.16/.28/10%
y(03)=.199 (.129,.309)
r2=.41, p<.083
tao=-.50, p<.083
Karlskrona, spring
age=0-4
n(tot)=70,n(yrs)=7
m=.286 (.226,.363)
slope=-8.5%(-18,.97)
SD(lr)=15.6,14%,13 yr
power=.19/.51/7.1%
y(02)=.222 (.158,.312)
r2=.52, p<.068
tao=-.71, p<.024 *
Fladen (2-3)
n(tot)=121,n(yrs)=9
m=.134 (.081,.222)
slope=-20%(-32,-7.9)
SD(lr)=19.4,18%,19 yr
power=.13/.16/15%
y(03)=.061 (.035,.107)
r2=.69, p<.006 *
tao=-.83, p<.002 *
Vaderoarna
age=2-4
n(tot)=180,n(yrs)=9
m=.087 (.063,.121)
slope=-14%(-20,-7.9)
SD(lr)=8.19,8.8%,13 yr
power=.36/.49/7.3%
y(03)=.050 (.037,.066)
r2=.81, p<.001 *
tao=-.78, p<.004 *
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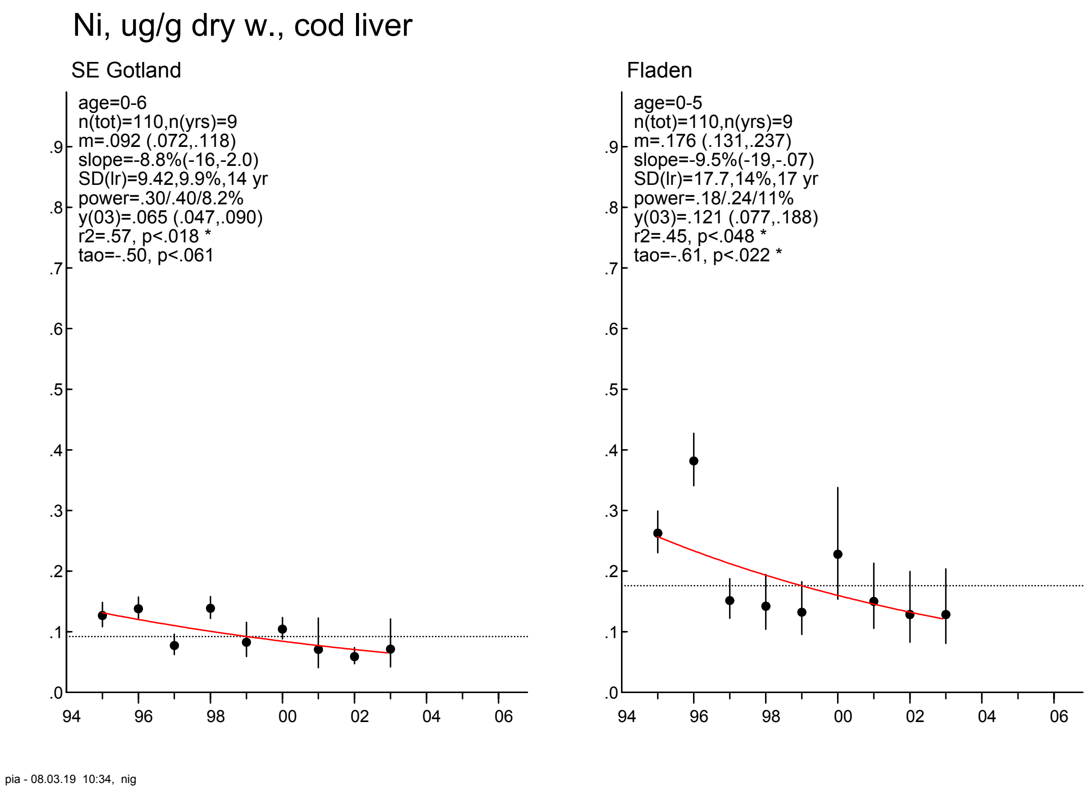
Ni, ug/g dry w., cod liver
SE Gotland
age=0-6
n(tot)=110,n(yrs)=9
m=.092 (.072,.118)
slope=-8.8%(-16,-2.0)
SD(lr)=9.42,9.9%,14 yr
power=.30/.40/8.2%
y(03)=.065 (.047,.090)
r2=.57, p<.018 *
tao=-.50, p<.061
Fladen
age=0-5
n(tot)=110,n(yrs)=9
m=.176 (.131,.237)
slope=-9.5%(-19,-.07)
SD(lr)=17.7,14%,17 yr
power=.18/.24/11%
y(03)=.121 (.077,.188)
r2=.45, p<.048 *
tao=-.61, p<.022 *
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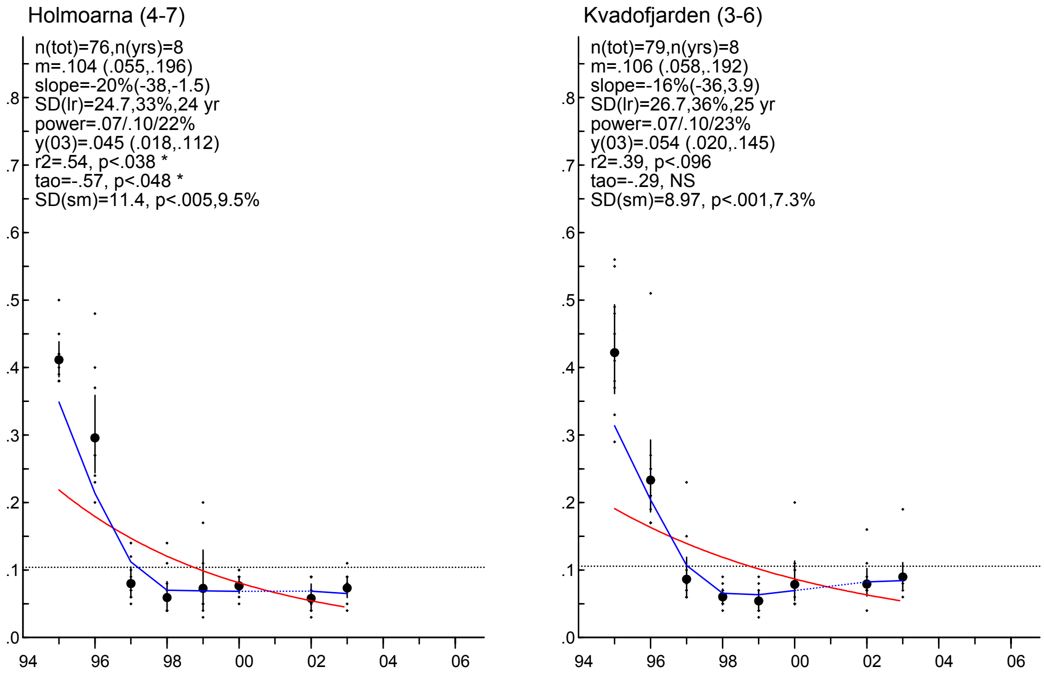
Ni, ug/g dry w., perch liver



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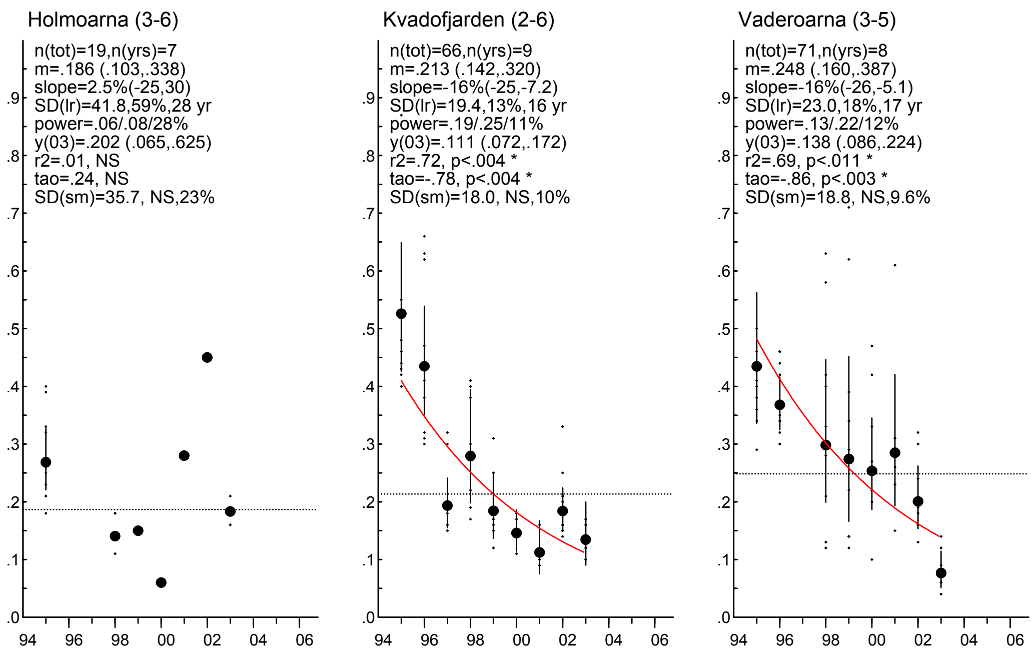
Ni, ug/g dry w., eelpout liver



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15 Chromium

Updated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

The concentration of chromium in fish liver is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences. The detection limit is estimated to approximately 0.1 μg/g dry weight.

The analysis started on samples collected 1995.

15.1 Temporal variation

Chromium decrease significantly in herring from Ängskärsklubb (autumn), Utlängan (autumn), Karlskona (spring), Fladen and Väderöarna, in cod and blue mussels from Fladen, in perch from Holmöarna and in guillemot eggs.

The required minimum years to detect an annual change of 5 % varies between 10 and 33 years for herring. The power to detect an annual change of 5 % ranges between 0.06 and 0.64.

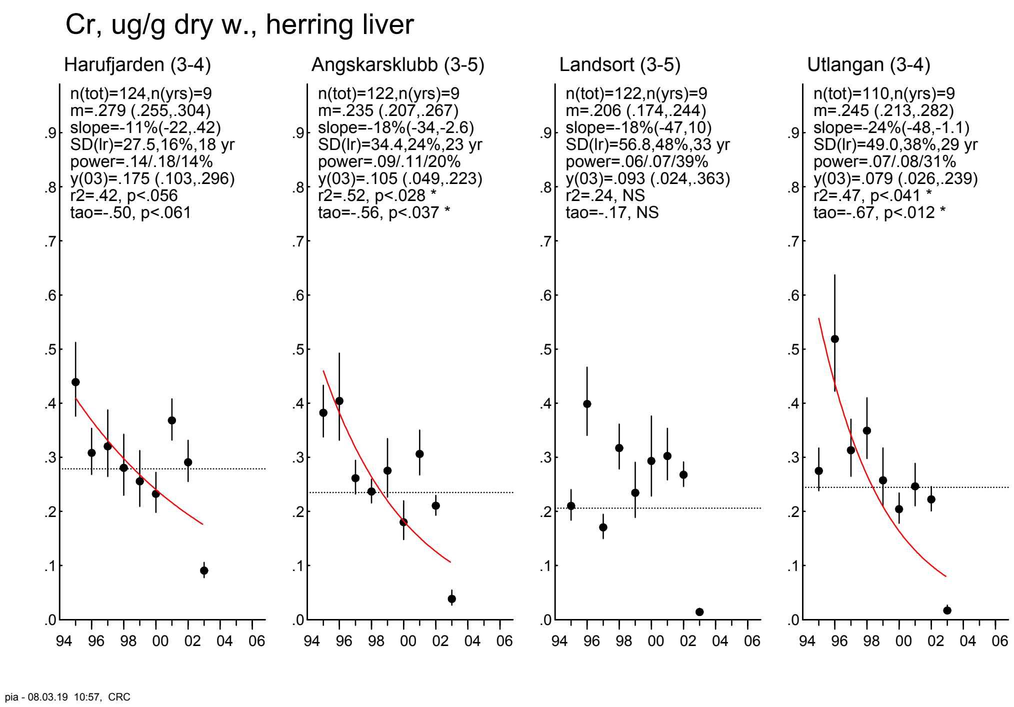
15.2 Spatial variation

The chromium concentration in blue mussel samples from the Kattegatt varies between years and shows a geometric mean concentration in the same range as mussels from the Baltic Proper. These concentrations are about 2-3 times higher compared to samples from the Skagerack and close to or above the 'high background concentration at diffuse loading' in blue mussels for chromium of <3 μg/g dry weight, proposed by Knutzen and Skie (1992). The samples from the Skagerack are well below this value.

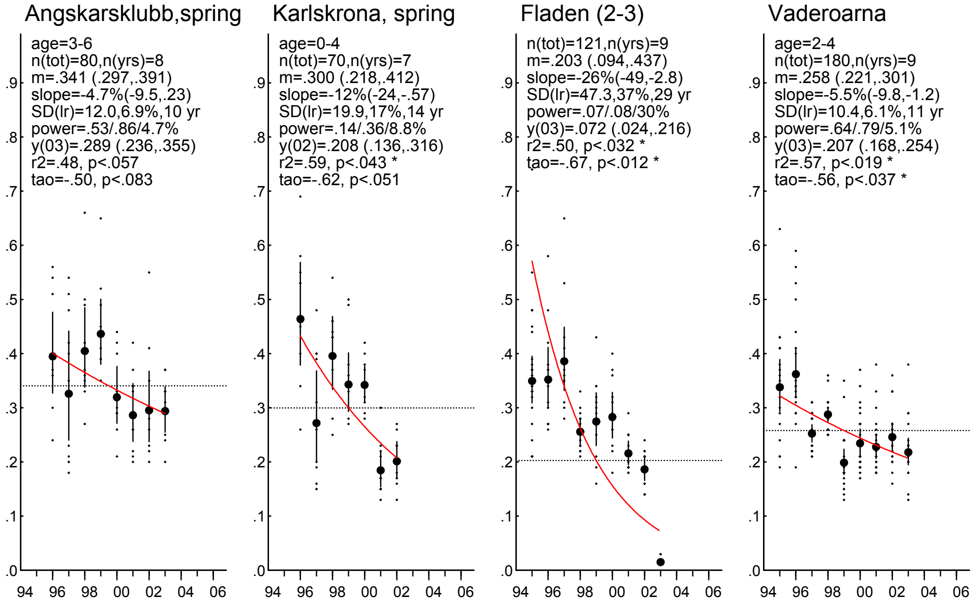
Table 15.1. Geometric mean concentrations of **chromium** (µg/g **dry weight**) in various matrices and sites during the time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend % (95% ci)	last year (95% ci)
Herring liver						
Harufj. autumn	3-4	124	9	95-03	-11 (-22, .42)	.18 (.10-.30)
Ängskärskl.aut.	3-5	122	9	95-03	-18 (-34,-2.6)*	.11 (.049-.22)
” spring	3-6	80	8	96-03	-4.7 (-9.5, .23)	.29 (.24-.36)
Landsort	3-5	122	9	95-03		.21 (.17-.24)
Utlängan, aut.	3-4	110	9	95-03	-24 (-48,-1.1)*	.079 (.026-.24)
” spring	0-4	70	7	96-03	-12 (-24,-.57)*	.21 (.14-.32)
Fladen	2-3	121	9	95-03	-26 (-49,-2.8)*	.072 (.024-.22)
Väderöarna	2-4	180	9	95-03	-5.5 (-9.8,-1.2)*	.21 (.17-.25)
Cod liver						
SE Gotland	3-4	107	9	95-03		.08 (.039-.16)
Fladen	2-4	106	9	95-03	-18 (-39, 2.4)	.067 (.025-.18)
Perch liver						
Holmöarna		90	9	95-03	-8.9 (-15,-2.9)*	.10 (.077-.14)
Kvädöfjärden	3-6	79	8	95-03		.15 (.067-.33)
Eelpout liver						
Holmöarna	5-9	53	7	95-03		.27 (.12-.64)
Kvädöfjärden	2-6	56	8	95-03		.41 (.37-.46)
Väderöarna	3-5	71	8	95-03		.36 (.25-.51)
Blue mussel	shell 1					
Kvädöfjärden		88	9	95-03		2.3 (1.7-2.7)
Fladen		139	9	95-03	-24 (-37,-12)*	.82 (.46-1.5)
Väderöarna		130	9	95-03		.89 (.73-1.1)
Guillemot egg						
St. Karlsö		80	8	95-03	-18 (-23,-13)	.12 (.097-.15)

* significant trend, $p < 0.05$



Cr, ug/g dry weight, herring liver



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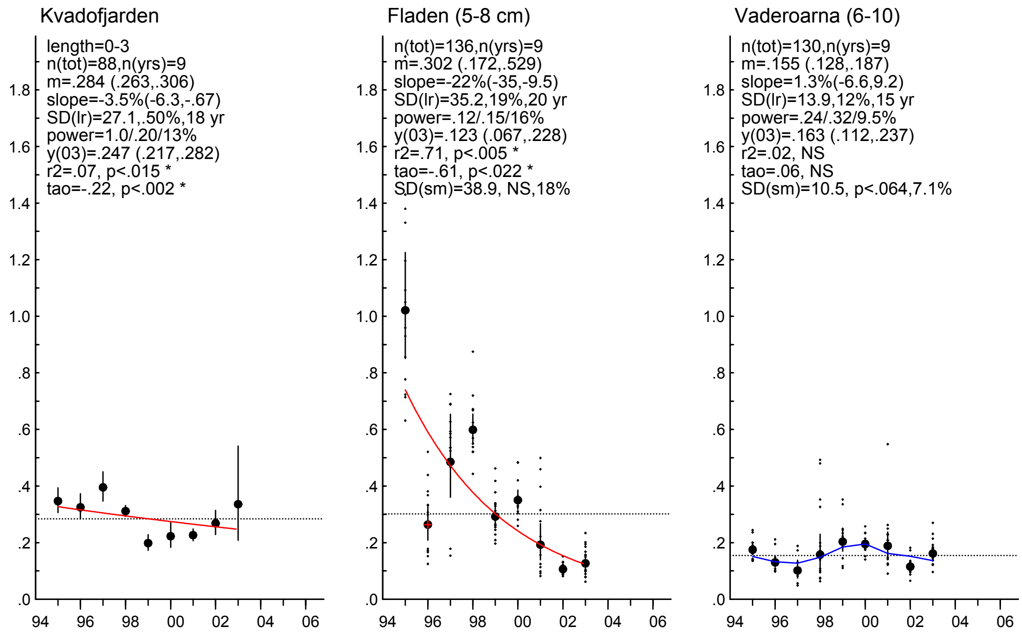
Cr, ug/g wet w., blue mussel softbody

Shell lengths in brackets



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16 Copper

Updated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

The concentration of copper in fish liver is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences.

Copper is a nutritionally essential metal and the concentration is regulated by homeostatic mechanisms. The free copper is effectively controlled by metallothionein synthesis (da Silva and Williams, 1994) induced by copper it self or by other substances. Although copper is not believed to *accumulate* with continued exposure, changes found in biological tissues may still reflect changes in concentration of the ambient water.

The copper concentration in *liver* from Baltic herring is about 4.5 times higher than the concentration reported from the edible parts of herring. For cod the concentration in the liver is about 40-60 times higher and for perch about 12-14 times. Concentrations in edible parts are reported by Jorhem and Sundström, 1993.

The concentration of copper in fish liver and blue mussel soft body is determined using an atomic absorption spectrophotometer with graphite furnace. The detection limit is estimated to approximately 10 ng/g dry weight.

16.1 Temporal variation

16.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the copper discharges are to be reduced by 50% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of the discharges of copper to air and water by 50% by 1995 with 1987 as a base year.

16.1.2 This investigation

A significant upward trend of copper in herring was found at Utlängan and significantly decreasing trends at Fladen for herring and blue mussels.

The number of years required to detect an annual change of 5% varied between 12 to 15 years for the herring time series at a power of 80%.

16.2 Spatial variation

No significant differences in mean copper concentration in herring between the sampling sites were found.

The copper concentration in blue mussels from the Swedish west coast is not significantly different compared to blue mussel samples of similar length from a reference site at Kobbefjord, Greenland (Riget *et al* 1993). Mussel samples from all three sites show mean levels below the 'high background concentration at diffuse loading' in blue mussels for copper of <10 µg/g dry weight, proposed by Knutzen and Skie (1992).

16.3 Species differences

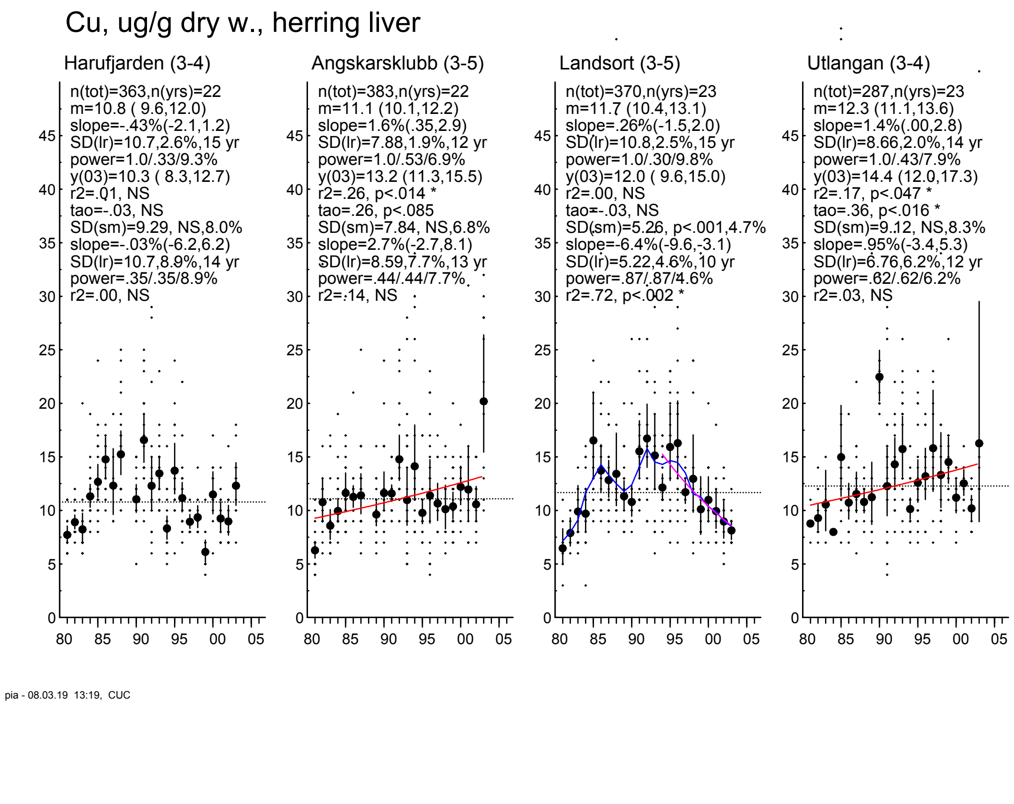
Significant differences in mean copper concentration, in fish liver and blue mussel soft body, were found between the species marked with '>':

Kvädöfjärden: Eelpout(22) > Perch(13) > Blue mussel (7.9)
Fladen: Cod(17) > Herring(10) > Blue mussel(5.4)
Väderöarna: Eelpout(31) > Herring(9.2) > Blue mussel(5.2)

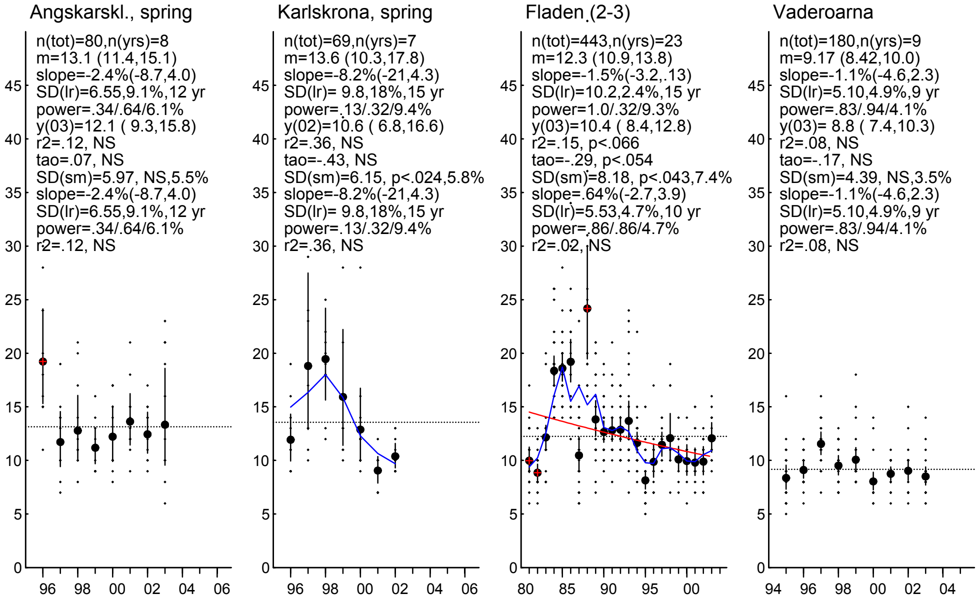
Table 16.1. Geometric mean concentrations of **copper** (μg/g **dry weight**) in various matrices and sites during the time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend	last year
Herring liver						
Harufj. autumn	3-4	363	22	81-03		11 (9.6-12)
Ängskärskl. aut.	3-5	383	22	81-03	1.6 (.35, 2.9)	13 (11-16)
” spring		80	8	96-03		13 (11-15)
Landsort	3-5	370	23	81-03		12 (10-13)
Utlängan, aut.	3-4	287	23	81-03	1.4 (.00, 2.8)*	14 (12-17)
” spring		69	7	96-03		14 (10-18)
Fladen	2-3	443	23	81-03	-1.5 (-3.2, 0.13)	10 (8.4-13)
Väderöarna		180	9	95-03		9.2 (8.4-10)
Cod liver						
SE Gotland	3-4	343	23	81-03		16 (15-18)
Fladen	2-4	425	23	81-03		17 (14-21)
Perch liver						
Holmöarna	0-7	90	9	95-03		11 (8.6-13)
Kvädöfjärden	3-7	80	8	95-03		13 (10-15)
Eelpout liver						
Holmöarna	3-*	67	7	95-03		12 (10-13)
Kvädöfjärden	2-9	89	9	95-03		22 (20-25)
Väderöarna	3-8	79	8	95-03		31 (28-35)
Dab liver						
Fladen	3-5	257	14	81-94		18 (14-23)
Flounder liver						
Väderöarna	4-6	239	14	81-94		51 (35-74)
Blue mussel	sh. l					
Fladen	5-8	396	21	81-03	-1.1 (-2.2, .03)	5.4 (4.7-6.2)
Väderöarna	6-10	413	22	81-03		5.2 (4.9-5.6)
Kvädöfjärden		88	9	95-03		7.9 (7.2-8.7)
Guillemot egg						
St. Karlsö		80	8	96-03		2.9 (2.7-3.2)

* significant trend, $p < 0.05$



Cu, ug/g dry w., herring (liver)



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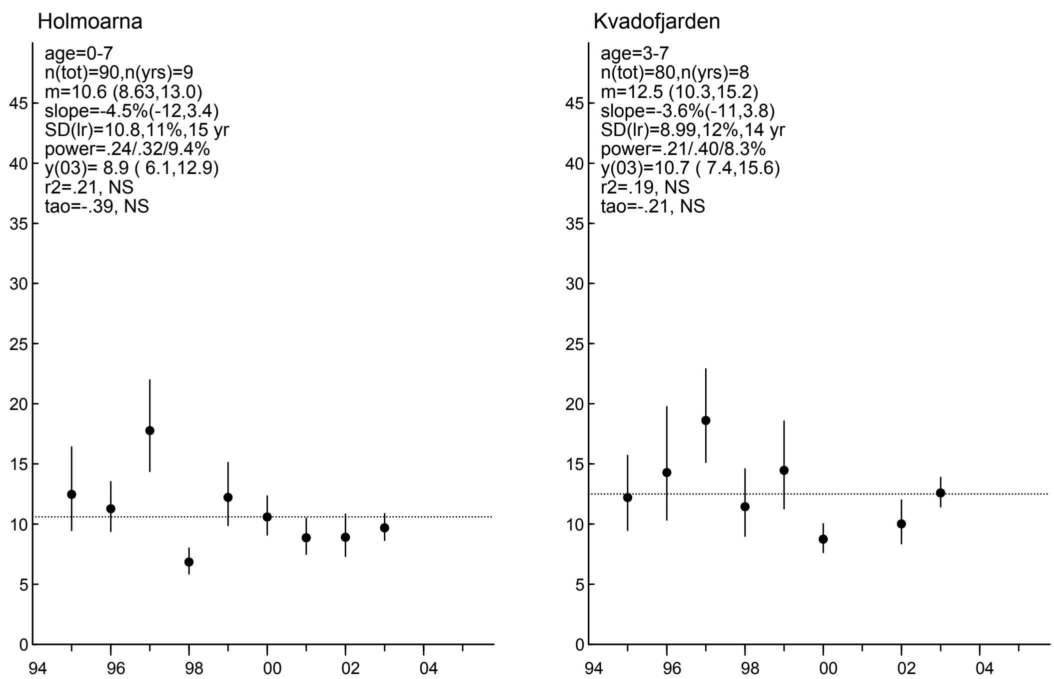
Cu, ug/g dry w., perch liver



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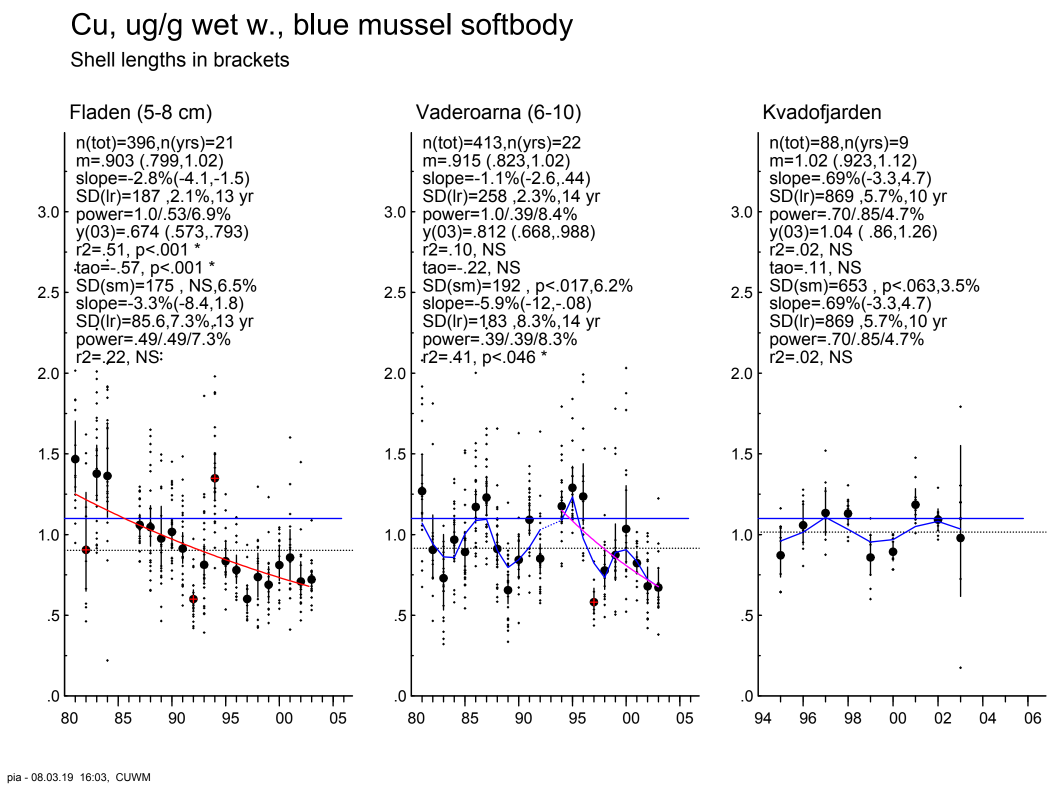


The blue lines indicate background concentration in OSPAR areas.

17 Zinc

Updated 08.03.28

Due to a change of method for metal analysis in 2004, values after 2003 are not presented in this section. The new method is under investigation, since the values are uncertain.

The time series of zinc concentration in fish liver and blue mussel soft body, presented below, start 1981. It is determined using an atomic absorption spectrophotometer with graphite furnace at the *Department of Environmental Assessment* at Swedish University of Agricultural Sciences

Zinc is a nutritionally essential metal and the concentration is regulated by homeostatic mechanisms. Hence, zinc is not believed to *accumulate* with continued exposure but changes found in biological tissues may still reflect changes in concentration of the ambient water.

The zinc concentration in liver from Baltic herring is about 1.5 times higher than the concentration reported from the edible parts of herring. For cod the concentration in the liver is about 6 - 8 times higher and for perch about 3.5 times. Concentrations in edible parts are reported by Jorhem and Sundström, 1993.

The concentration of zinc in fish liver and blue mussel soft body is determined using an atomic absorption spectrophotometer with graphite furnace. The detection limit is estimated to approximately 100 ng/g dry weight.

17.1 Temporal variation

17.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the zinc discharges are to be reduced by 50% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of the discharges of zinc to air and water by 50% by 1995 with 1987 as a base year.

17.1.2 This investigation

Significant downward trends are shown in herring liver from Landsort (the past ten years) and in guillemot eggs during the whole analysed time period. Significant upward trends are found for herring from Harufjärden and Fladen for the whole period and also for Utlängan the last ten years.

The number of years required to detect an annual change of 5% varied between 9 to 13 years for the herring time series with a power to detect a 5% annual change ranging from

0.43 for the shorter time series to 1.0 for the longer ones. (Since it is not appropriate to fit a log-linear trend at Harufjärden and Utlängan, these sites were excluded from the power calculations.)

17.2 Spatial variation

No significant differences in mean zinc concentration are observed in herring among the sampling sites in the Baltic Sea and the Swedish west coast.

The zinc concentration in cod liver from Fladen is significantly higher than in cod liver from the site SE of Gotland. This may be explained by the significantly lower fat content in cod liver from Fladen since zinc concentration is negatively correlated with fat content.

The zinc concentration in blue mussels from the Swedish west coast is not significantly different compared to blue mussel samples of similar length from a reference site at Kobbefjord, Greenland (Riget *et. al* 1993). The zinc concentrations in blue mussels from all the three investigated sites are below the proposed background concentrations for the North Sea (ICES, 1997)

17.3 Differences among various species

Significant differences in mean zinc concentration, in fish liver and blue mussel soft body, were found between the species marked with '>':

Holmöarna: Eelpout(158) > Perch(102)
Kvädöfjärden: Eelpout(189) > Perch(114)
Fladen: Blue mussel(112) - Herring(105) > Cod(71)
Väderöarna: Blue mussel (108) - Herring(107)

17.4 Seasonal variation

The concentrations in spring caught herring from Ängskärsklubb and Utlängan is considerable higher compared to samples from the same areas in the autumn (table 17.1).

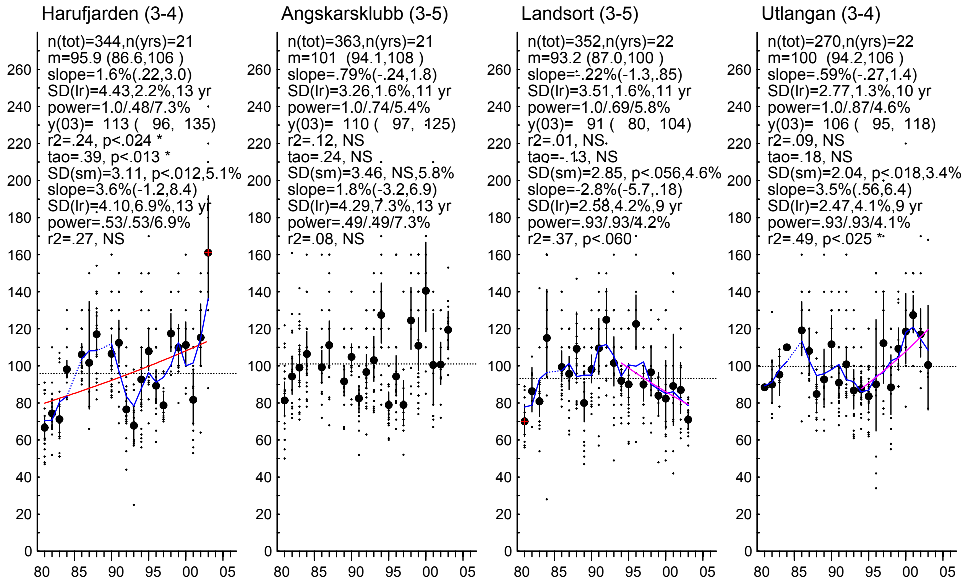
Table 17.1. Geometric mean concentrations of **zinc** (µg/g **dry weight**) in various matrices and sites during the time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend (95% ci)	last year
Herring liver						
Harufj. autumn	3-4	344	21	81-03	1.6 (.22, 3.0)*	110 (96-140)
Ängskärskl. aut.	3-5	363	21	81-03		100 (94-110)
” spring	3-6	80	8	96-03		150 (130-170)
Landsort	3-5	352	22	81-03		93 (87-100)
Utlängan, aut.	3-4	270	22	81-03		100 (94-110)
” spring	0-4	70	7	96-03		130 (100-150)
Fladen		418	22	81-03	1.0 (.25, 1.8)*	110 (95-120)
Väderöarna	2-4	180	9	95-03		110 (94-120)
Cod liver						
SE Gotland	3-4	325	22	81-03		34 (30-39)
Fladen	2-4	403	22	81-03		71 (66-77)
Perch liver						
Holmöarna	0-7	90	9	95-03		100 (90-120)
Kvädöfjärden	3-7	80	8	95-03		110 (92-140)
Eelpout liver						
Holmöarna		67	7	95-03		160 (130-190)
Kvädöfjärden	2-9	89	9	95-03		190 (150-240)
Väderöarna	3-8	79	8	95-03		220 (180-270)
Dab liver						
Fladen	3-5	234	13	81-94		88 (77-101)
Flounder liver						
Väderöarna	4-6	232	13	81-94		183 (149-223)
Blue mussel	sh. l					
Fladen	5-8	396	21	81-03		110 (100-130)
Väderöarna	6-10	391	21	81-03		110 (94-120)
Kvädöfjärden		88	9	95-03		130 (120-150)
Guillemot egg						
St. Karlsö		80	8	96-03	-2.8 (-5.3,-.33)*	43 (38-47)

NL = non-linear trend components

* significant trend, $p < 0.05$

Zn, ug/g dry w., herring liver



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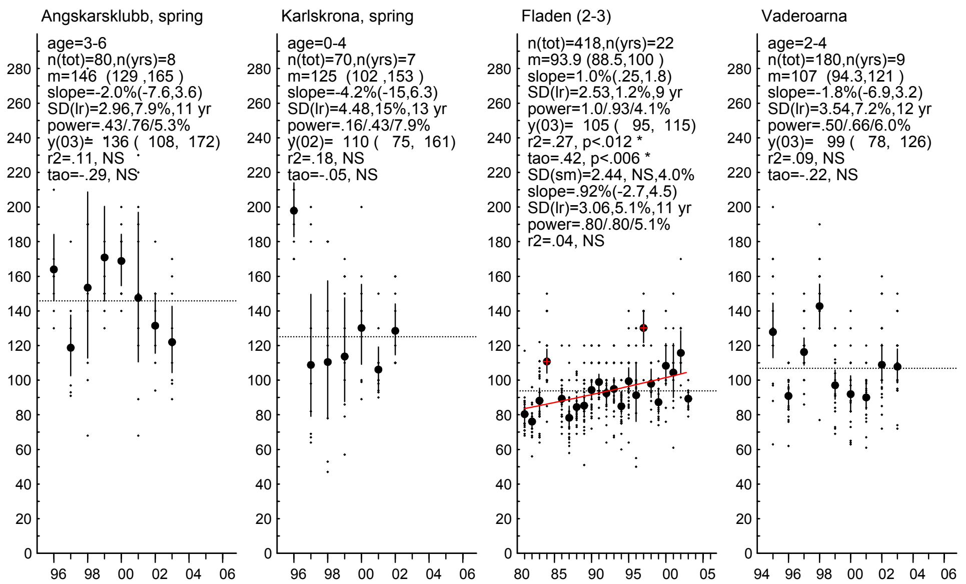
Zn, ug/g dry weight, herring liver



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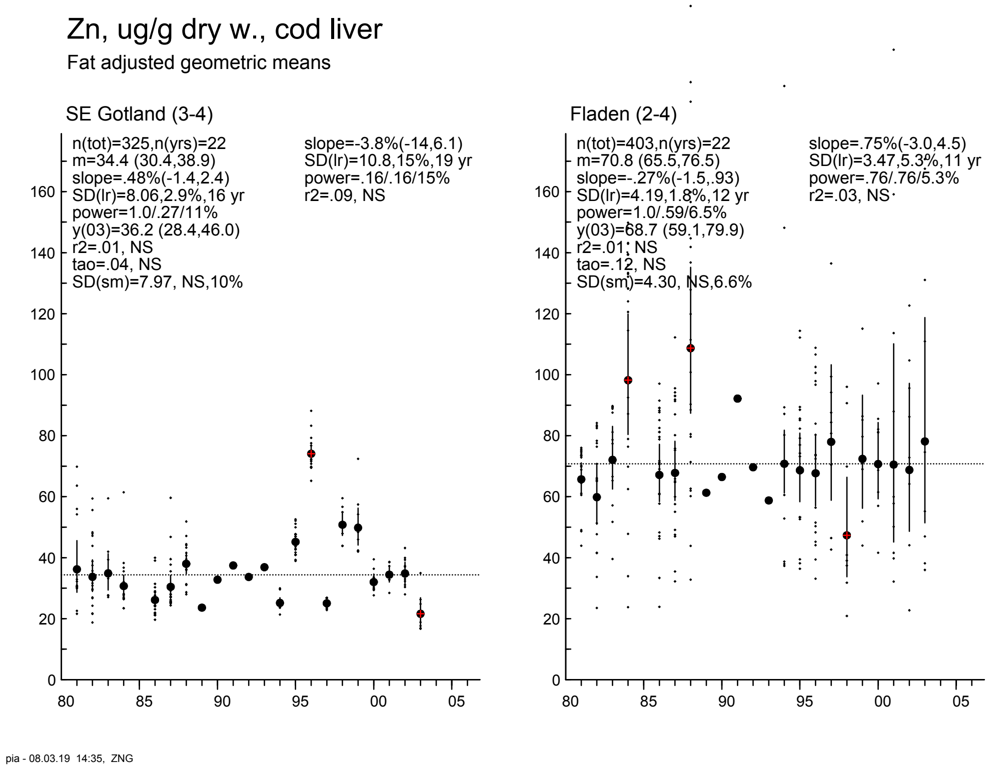
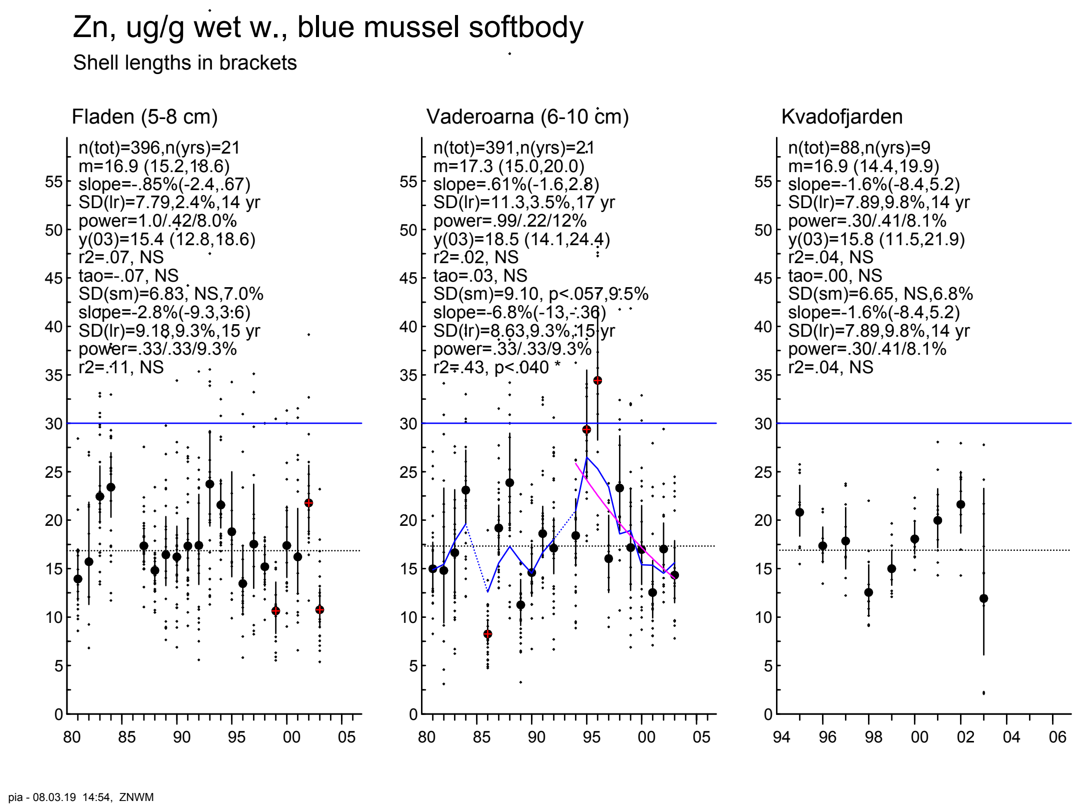




The blue lines indicate background concentration in OSPAR areas.

18 PCB's, Polychlorinated biphenyles

Updated 08.03.27

PCB's have been used in a wide variety of manufacturing processes especially as plasticizers and as insulators and fire retardants. It is widely distributed in the environment through inappropriate handling of waste material or e.g. leakage from large condensers and hydraulic systems. Their toxicological effects e.g. on reproduction in mink is well documented (Aulerich *et al.* 1977, Jensen *et al.* 1977 and Bleavins *et al*. 1980).

The number of possible congeners is 209, having one to ten chlorines. Twenty of these have non-ortho chlorine substitutions and so can attain a planar structure similar to the highly toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (McKinney *et al.* 1985, Serico *et al.* 1991).

Seven CB-congeners (CB-28, CB-52, CB-101, CB-118, CB-138, CB-153 and CB-180) are listed as *mandatory* contaminants that should be analysed and reported within both the OSPARCOM and the HELCOM conventions. In the proposed revised guidelines for OSPARCOM (1996) the congeners CB-105 and CB-156 are added to this list.

The concentration of the PCB's in fish muscle, cod liver, blue mussel soft body and guillemot egg is determined using a gas chromatograph (GC) equipped with an electron capture detector.

Before 1988, PCB's were analysed by a packed column GC and the total sum of PCB was estimated from 14 peaks after calibration with Aroclor 1254 (Jensen et al. 1983). During 1988, analyses on capillary column were introduced, admitting analysis of individual congeners (Eriksson *et al*., 1994).

Although the relative abundance of the various CB-congeners is considered to be fairly constant, both geographical differences and temporal changes in the ratios between the investigated congeners can be shown, see below.

Coeluation of congeners in GC analysis is dependent upon instrumental conditions such as column type, length, internal diameter, film thickness and oven temperature etc. Some potentially coeluting PCB congeners are CB-28/-31, CB-52/-49, CB-101/-90, CB-138/-163/-164 and CB-153/-132/-105 (Schantz et al.,1993). During recent years it has been discovered that congener CB-163, and possibly also CB-164, has interfered with CB-138 (see also Roos et al. 1990). This implies that the reported concentration of CB-138 also includes a minor contribution from CB-163 and possibly also from CB-164.

The sum of PCB's (sPCB), presented in this report, is estimated from the concentration of peak 10 (PCB10) in the chromatogram from packed column chromatography using the ratio, R_1=PCB10/sPCB. PCB10 constitute approximately 11-14%, of the total amount of PCB in herring, 13-15% in cod, 16-17% in perch, 12 % in blue mussel and 18% in guillemot egg. Thus, the ratio varies between matrices but is very stable within the same matrix at the same sampling site - the coefficient of variation is found, with few exceptions, to be between 3.5 - 6%, see CV_1 in table 18.1 From 1989 and forward, PCB10 concentrations have been estimated using the ratio, R_2=(CB-138 + CB-163)/PCB10. CB-138 + CB-163 constitute about 60-80% of PCB10 and 7-12% of the total sum of PCB's in herring. The mean ratios are given in table 18.1, below.

The sum of PCB's is until 1988 estimated according to:

$sPCB = PCB10 / R_1$

and after 1988:

$sPCB = (CB\text{-}138+CB\text{-}163) /(R_1 \cdot R_2)$

Table 18.1. Mean ratios between peak 10 and the total sum of PCB's, from packed column gas chromatography (GC) (R_1) and mean ratios between CB-138+CB-163 (capillary GC) and PCB10 (R_2). Also the number of analyses (n) and the Coefficient of Variation (CV) for the two ratios are given.

	n_1	R_1	CV_1	n_2	R_2	C.I.	CV_2	$R_1 \cdot R_2$
Herring								
Harufjärden	169	.14	4.0	19	.73	.67-.76	9.1	.098
Ängskärsklubb	188	.14	5.1	20	.83	.79-.88	11	.12
" spring	397	.13	5.1	25	.79	.75-.82	11	.10
Landsort	159	.12	5.2	29	.61	.59-.63	7.4	.070
Utlängan	94	.12	5.4	20	.65	.62-.68	9.8	.075
" spring	371	.12	5.3	10	.67	.64-.69	5.4	.080
Fladen	191	.13	5.3	25	.82	.79-.86	10	.11
Cod								
Gotland	152	.14	4.0	11	.69	.65-.72	7.3	.093
Fladen	176	.15	5.9	10	.85	.81-.89	6.9	.13
Perch								
Holmöarna	140	.17	5.3					
Kvädöfjärden	108	.16	6.0					
Dab								
Fladen	153	.18	5.9	10	.71		18	.13
Flounder								
Väderöarna	137	.13	9.8	5	.74		11	.096
Blue mussel								
Fladen	5	.12	11.	1	.74		-	.087
Väderöarna	9	.12	5.6	1	.95		-	.11
Guillemot								
St. Karlsö	211	.18	3.5	30	.77	.74-.80	9.8	.14

Table 18.2. Approximate detection limit (capillary column, GC) for the analysed CB-congeners

Congener	ng/g, fat weight
CB-28 (2,4,4'-tri CB)	4
CB-52 (2,2',5,5'-tetra CB)	4
CB-101 (2,2',4,5,5'-penta CB)	4
CB-118 (2,3',4,4',5-penta CB)	5
CB-138 (2,2',3,4,4',5-hexa CB)	6
CB-153 (2,2',4,4',5,5'-hexa CB)	5
CB-180 (2,2',3,4,4',5,5'-hepta CB	4

18.1 Temporal variation

18.1.1 Conventions, aims and restrictions

The Helsinki Convention (HELCOM) revised 1992 especially names PCB for which special bans and restrictions on transport, trade, handling, use and disposal are imposed. The Minister Declaration from 1988, within HELCOM, calls for a reduction of stable organic substances by 50% by 1995 with 1987 as a base year.

The Minister Declaration from 1996, within HELCOM, and the declaration in Esbjerg 1995, calls for measures for toxic, persistent, bioaccumulating substances to have ceased completely in the year 2020.

The use of PCB was banned in Sweden in 1973, except for sealed systems. In 1978, all new use of PCB was forbidden.

18.1.2 This investigation

The concentration of sPCB (sum of PCB's estimated from CB-138 or peak 10 from packed column chromatography) in herring muscle from all herring sites in the Baltic and at the west coast show significant decreasing trends during the time period 1978/80-2006. The average rate varies between -5 and -10% per year. A similar significant decrease within the same range (5 and 10% a year) was also found in the two time series of spring caught herring, 1972-2007. This implies a total decrease of about 70% at Ängskärsklubb and about 90% at Karlskrona, of the PCB-concentration in herring muscle, since the beginning of the seventies.

An extremely high concentration of PCB's was recorded at Landsort 1996. This could most probably be explained by the very low fat content in herring this year.

The two cod time series from south east of Gotland in the Baltic Proper and Fladen at the west coast show significant decreasing trends.

Also in the time series of perch the sPCB concentrations have decreased as well as in blue mussel from the west coast and in guillemot eggs (1969-2006). The latter trend corresponds to a total decrease of almost 90% since the beginning of the seventies.

The number of years required to detect an annual change of 5% varied between 14 to 22 years for the herring and cod time series.

18.1.3 Conclusion

The concentration of PCB has decreased approximately with 5-10% per year, in herring and cod from the Baltic Sea and Kattegatt as well as in guillemot eggs and perch from the Baltic Sea, since the end of the seventies.

18.2 Spatial variation

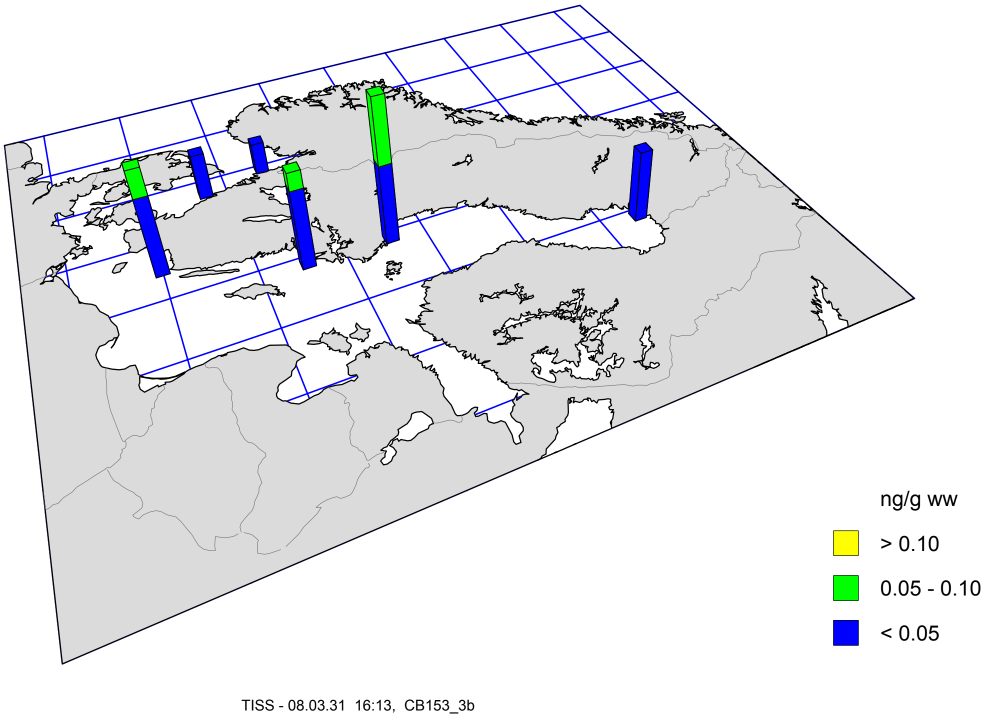


Figure 18.1. Spatial variation in concentration (w.w.) of sPCB in herring muscle.

Herring muscle from Ängskärsklubb in the Bothnian Sea and Landsort and Utlängan in the Baltic Proper show elevated concentrations of PCB compared to Harufjärden in the Bothnian Bay and Fladen and Väderöarna.

The estimated concentration of CB-153 (wet weight) for year 2006 from Harufjärden in the Bothnian Bay show similar or in fact lower concentrations, about 1 ng/g wet weight, compared to Fladen in the Kattegatt and Väderöarna in the Skagerack, and significantly lower than herring samples from the Bothnian Sea and the Baltic Proper (2-4 ng/g w.w.). However, no significant difference was found between CB-153 (wet weight) concentrations analysed in cod liver from south east of Gotland and the Kattegatt.

The ratio CB-118/CB-153 is significantly lower at Ängskärsklubb compared to all the other sites. Herring from Landsort has the highest ratio.

The concentration of CB-153 is higher in herring muscle from Ängskärsklubb and Karlskrona than in herring from Fladen and Väderöarna.

Table 18.3. Geometric mean concentrations of **sPCB** (µg/g **lipid weight**) in various matrices and sites during the time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	**age**	**n**	**n yrs**	**year**	**trend (95% ci)**	**last year (95% ci)**
Herring msc.						
Harufj. autumn	3-4	371	27	78-06	-8.9 (-10,-7.5)*	.20 (.16-.25)
Ängskärskl. aut.	3-5	346	27	78-06	-7.9 (-9.1,-6.6)*	.37 (.31-.46)
” spring	2-5	623	34	72-07	-5.1 (-6.2,-3.9)*	1.1 (0.9-1.4)
Landsort	3-5	372	28	78-06	-5.4 (-6.7,-4.1)*	.69 (.56-.84)
Utlängan, aut.	3-4	288	27	80-06	-5.4 (-6.7,-4.1)*	.57 (.47-.69)
” spring	2-4	605	32	72-06	-9.8 (-11,-8.9)*	.71 (.59-.84)
Fladen	2-3	457	27	80-06	-7.4 (-8.6,-6.2)*	.17 (.14-.21)
Cod liver						
SE Gotland	3-4	296	27	80-06	-6.4 (-8.0,-4.8)*	.0.96 (.75-1.2)
Fladen	2-3	312	26	80-06	-6.4 (-8.9,-4.0)*	1.3 (.87-1.8)
Perch muscle						
Holmöarna	4-7	259	20	80-06	-8.8 (-11,-6.9)*	.26 (.19-.35)
Kvädöfjärden	3-4	213	23	80-06	-10 (-13,-8.0)*	.10 (.07-.15)
Dab muscle						
Fladen	3-6	158	13	81-94	-4.6 (-12,2.8)	0.72 (.40-1.3)
Flounder msc						
Väderöarna	4-6	143	15	80-94	-2.8 (-7.4,1.8)	1.7 (1.2-2.6)
Blue mussel						
Fladen		73	20	84-06	-6.5 (-8.6,-4.4)*	.25(.20-.32)
Väderöarna		74	21	84-06	-7.6 (-10,-5.1)*	.25 (.18-.35)
Guillemot egg						
St. Karlsö		380	36	69-07	-8.9 (-9.4,-8.3)*	13 (12-15)

* significant trend, $p < 0.05$

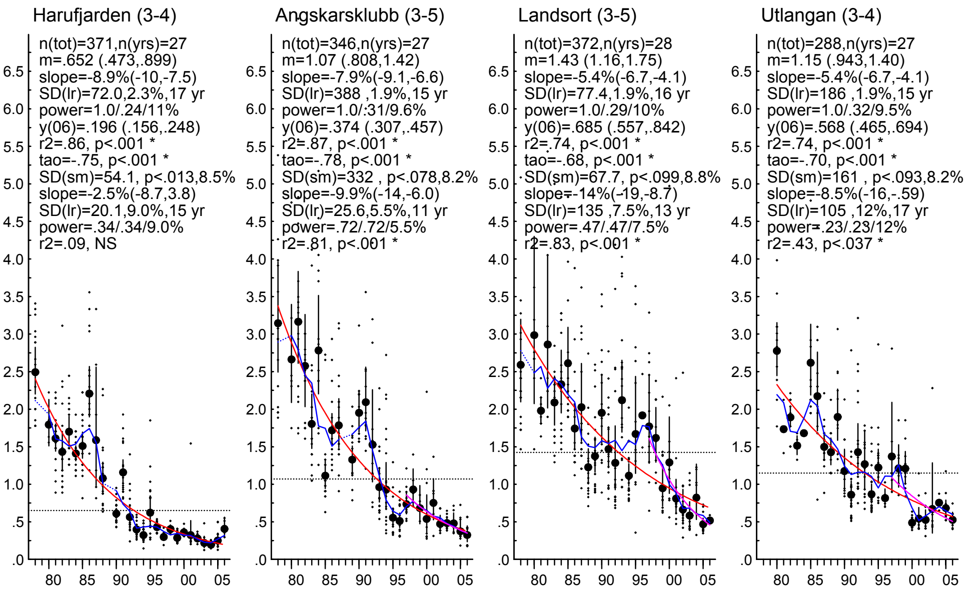
Table 18.4. Geometric mean concentrations of **CB-153** (**ug/g lipid weight**) in various matrices and sites during 1987-1995/96 and estimated mean concentration for the last year.

Matrix	age	n tot	n yrs	year	trend	last yr
Herring msc.						
Harufj. autumn	3-4	254	18	87-06	-3.6 (-7.0,-0.12)	.038 (.027-.054)
Ängskärskl. aut.	3-5	275	18	89-06	-6.4 (-9.4,-3.4)*	.075 (.056-.10)
” spring		259	19	89-07		.22 (.17-.27)
Landsort	3-5	292	20	87-06	-4.6 (-8.3,-.93)*	.070 (.046-.11)
Utlängan, aut.	3-4	256	19	88-06		.095 (.078-.11)
” spring		244	18	87-06	-5.6 (-8.2 -2.9)*	.11 (.085-.15)
Fladen	2-3	312	19	88-06	-6.1 (-8.4,-3.8)*	.027 (.021-.034)
Väderöarna		219	11	95-05		.023 (.019-.029)
Cod liver						
SE Gotland	3-4	144	18	89-06	-2.0 (-4.4, 0.34)	.16 (.12-.20)
Fladen	2-3	136	17	89-06		.44 (.36-.54)
Perch muscle						
Holmöarna		129	13	89,95-06	-11 (-17, -4.7)*	.043 (.029-.065)
Kvädöfjärden		191	19	84,89-06	-8.0 (-12, -3.8)*	.025 (.016-.038)
Eelpout muscle						
Holmöarna		94	10	95,97-06		.15 (.10-.23)
Kvädöfjärden		119	12	95-06	-12 (-19, -5.4)*	.094 (.061-.15)
Väderöarna		119	12	95-06		.28 (.19-.39)
Dab muscle						
Fladen	3-6	5	5	89-94		-
Flounder msc						
Väderöarna	4-6	6	6	89-94		-
Blue mussel **						
Fladen		74	19	88-06	-6.7 (-8.4,-5.0)*	.030 (.025-.036)
Väderöarna		71	18	88-06	-6.5 (-9.8,-3.2)*	.030 (.021-.042)
Kvädöfjärden		60	12	95-06		.063 (.059-.068)
Guillemot egg						
St. Karlsö		198	20	88-07	-6.9 (-8.3,-5.5)*	2.3 (2.0-2.7)

* significant trend, $p < 0.05$

** Pooled samples

sPCB, ug/g lipid w., herring muscle



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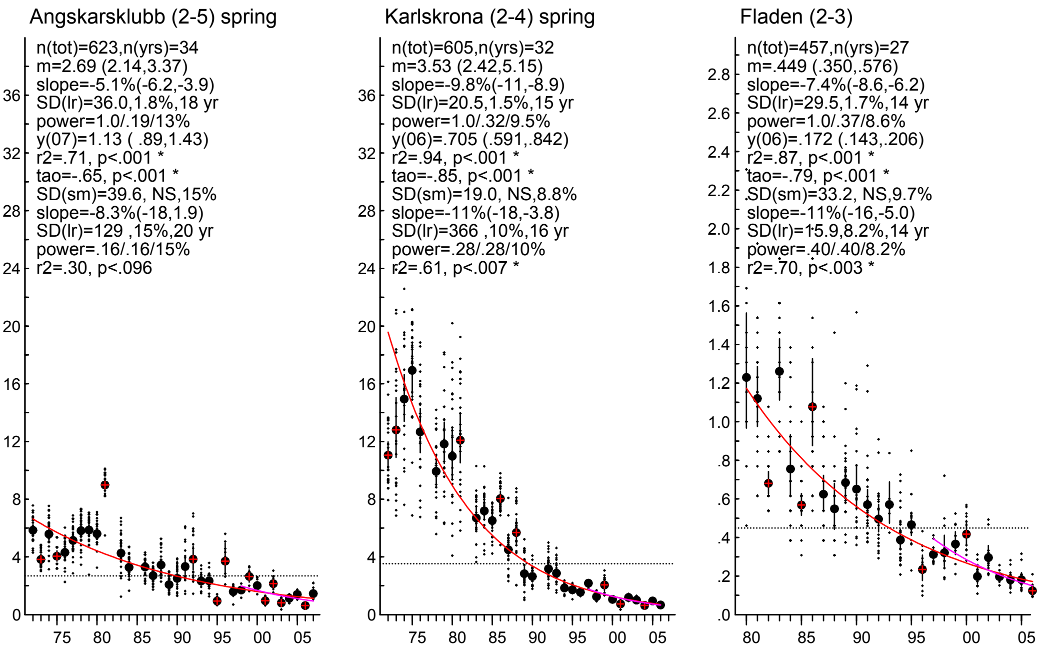
sPCB, ug/g lipid w., herring muscle

Fat adjusted geometric means (spring)



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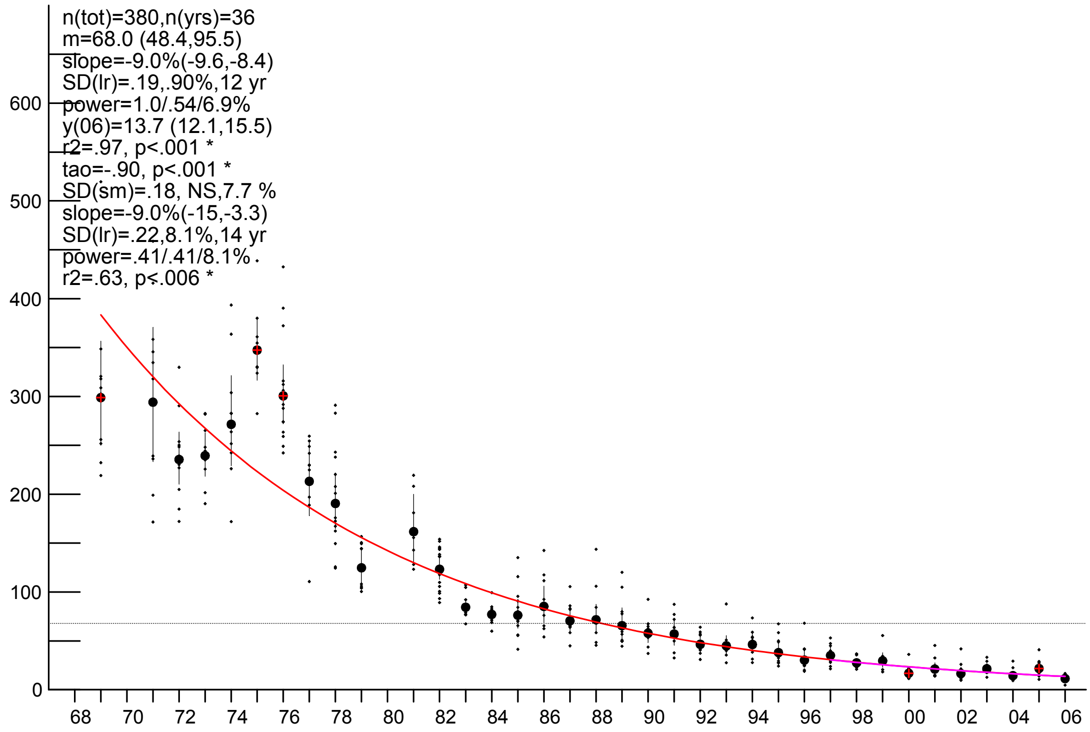
sPCB, ug/g lipid w., Guillemot eggs, early laid. St Karlso



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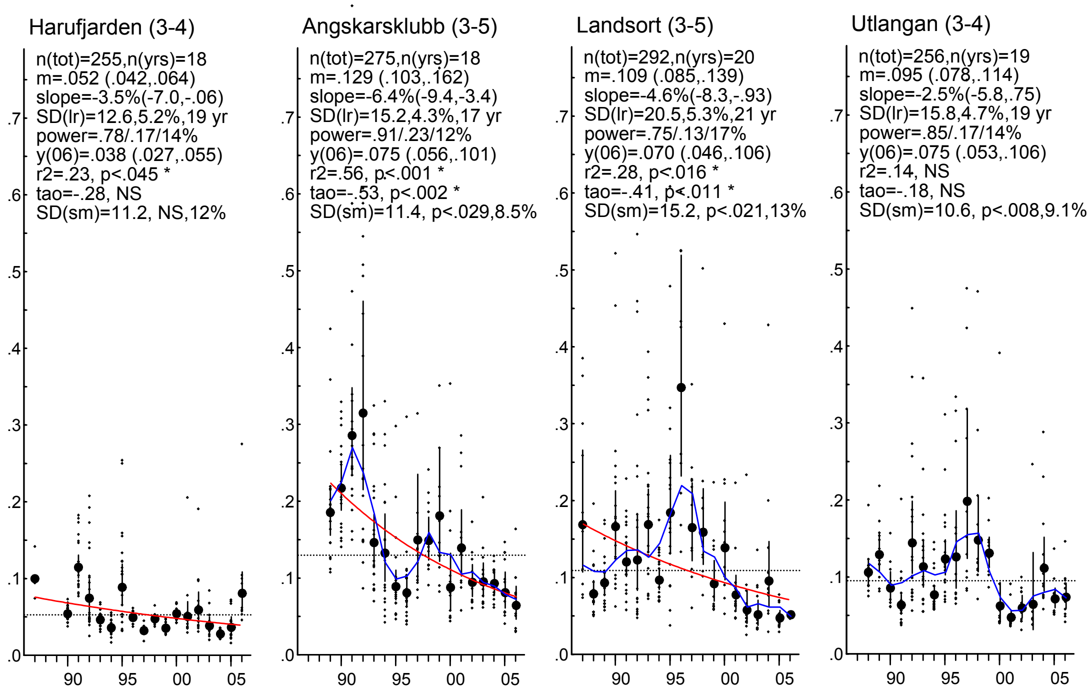
CB-153, ug/g lipid w., herring muscle



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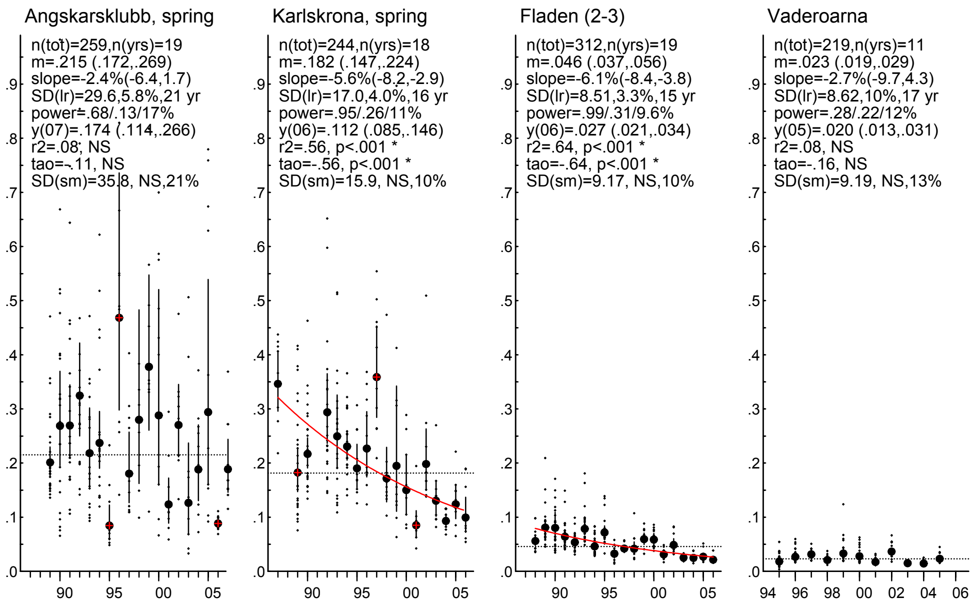
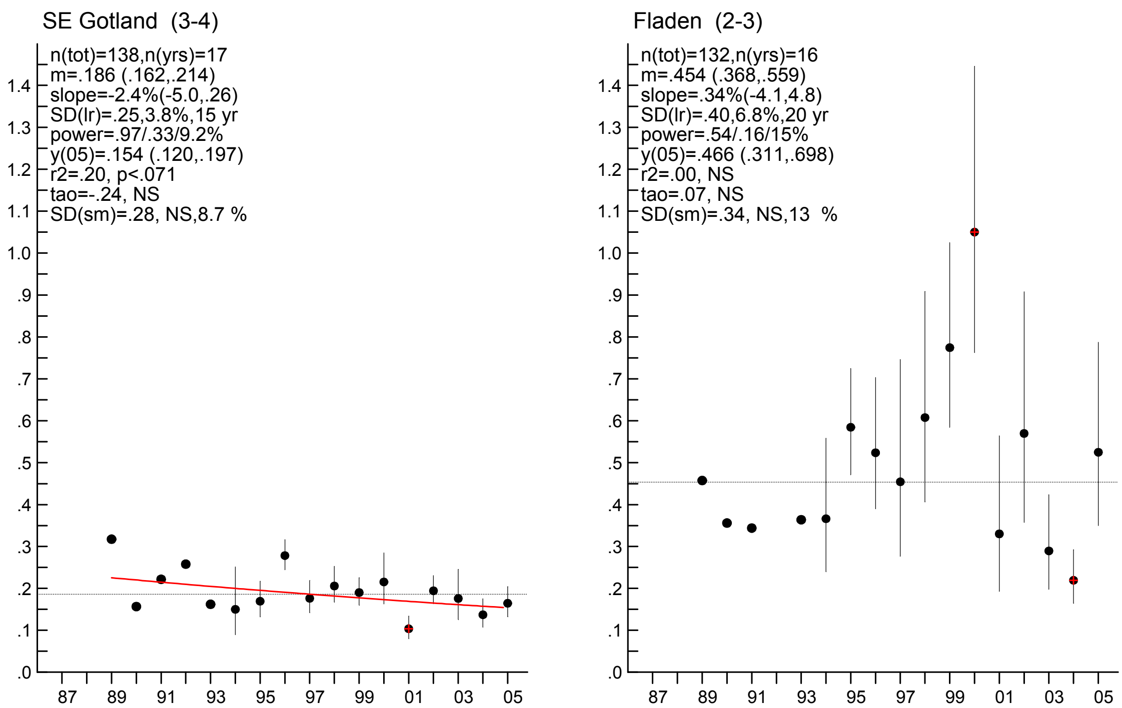
CB-153, ug/g lipid w., herring muscle



pia - 08.03.27 09:26, 153V

CB-153, ug/g lipid w., cod liver



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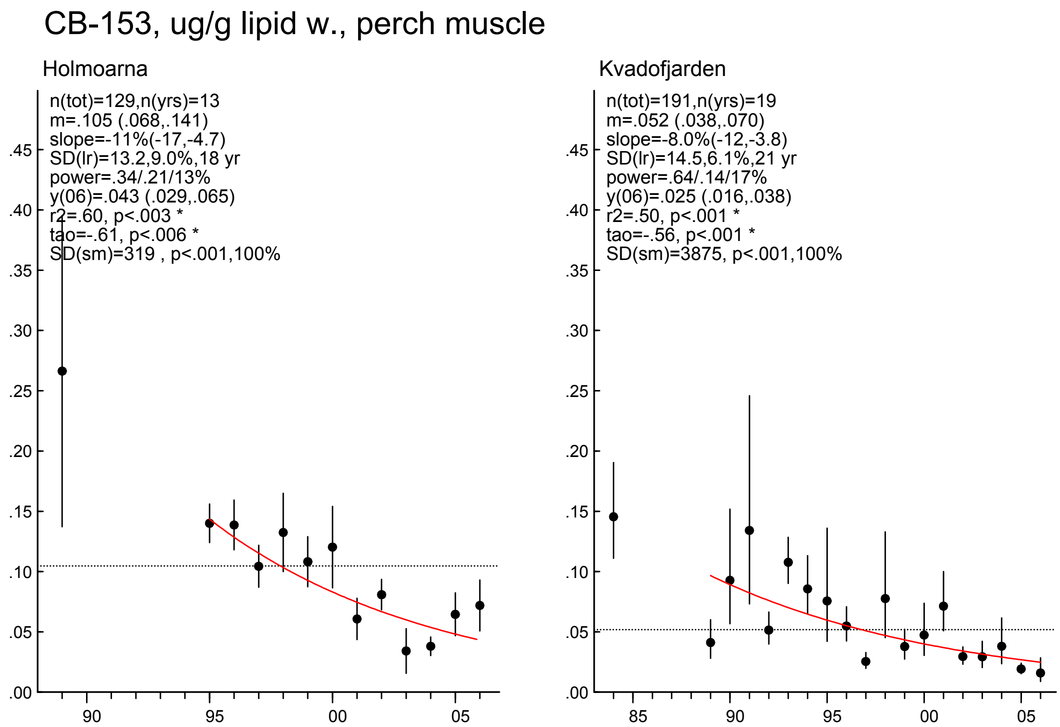

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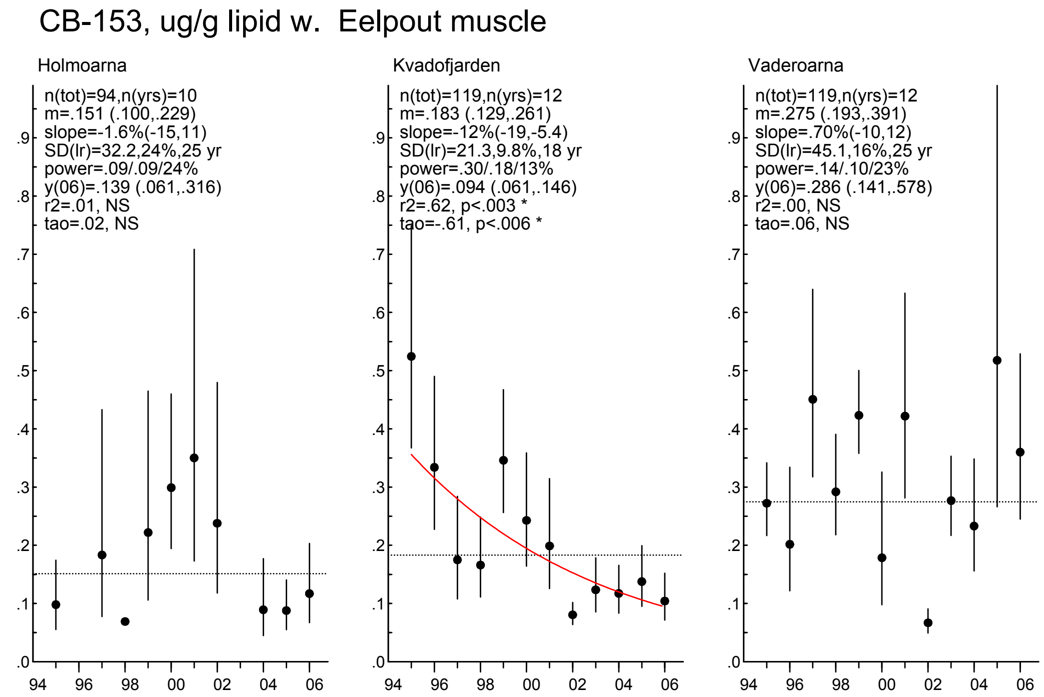

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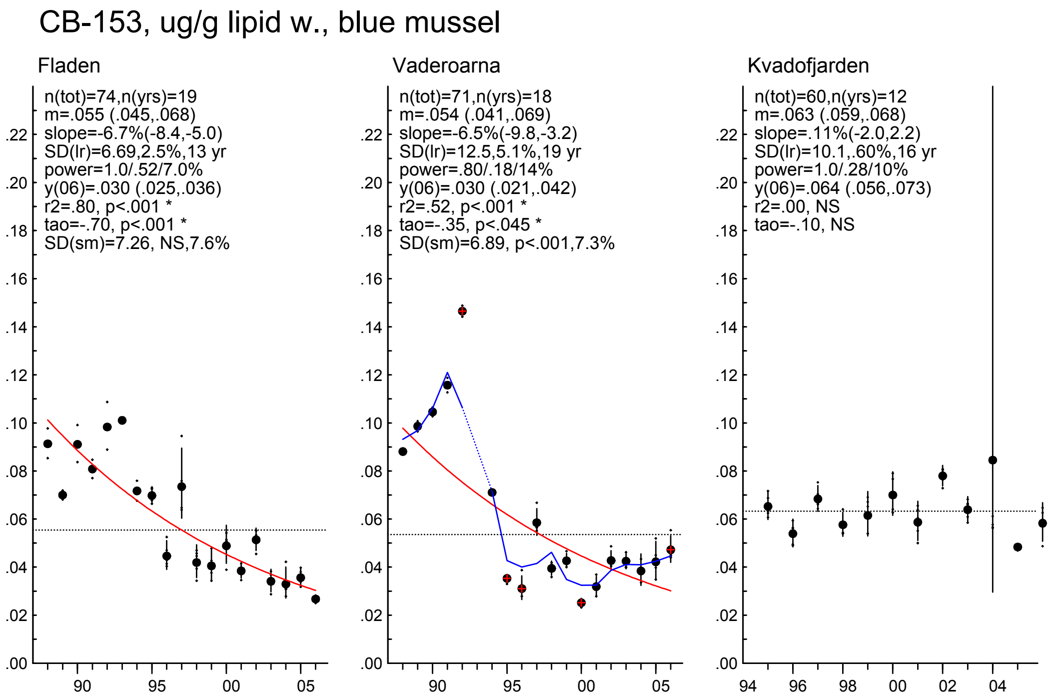

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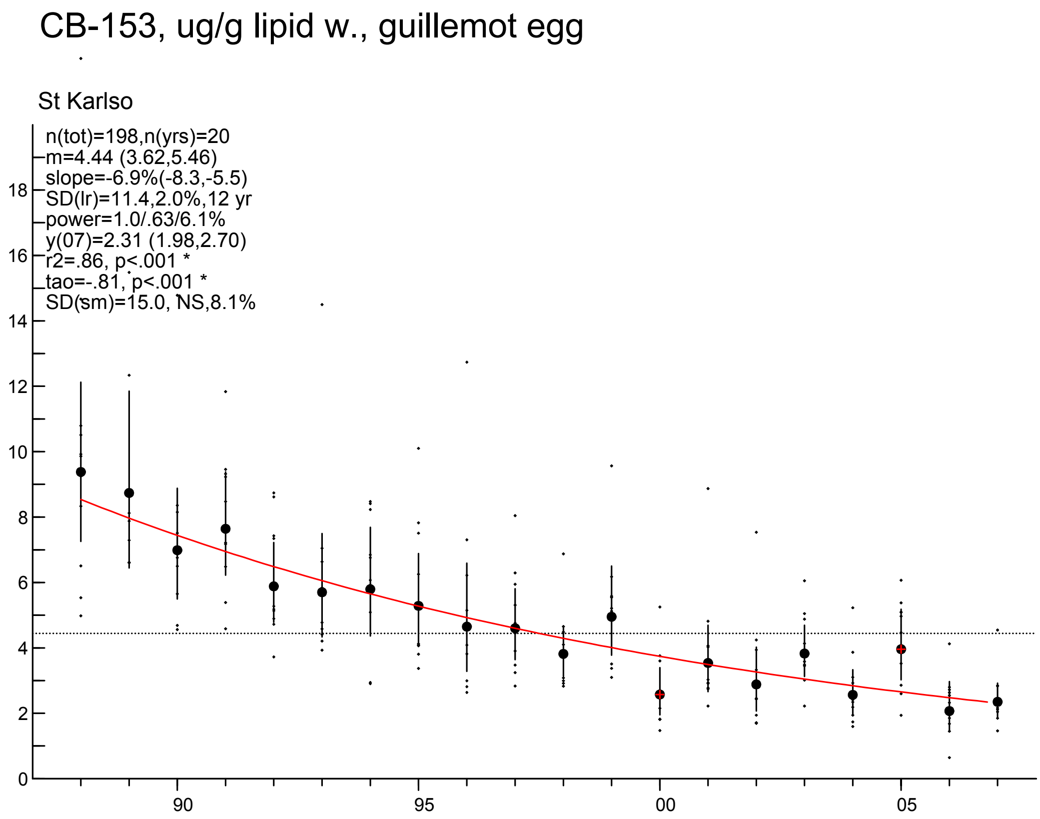

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19 DDT's, Dichlorodiphenylethanes

Updated 08.03.28

The concentration of DDT's in fish muscle and blue mussel soft body is determined using a gas chromatograph (GC) equipped with an electron capture detector.

Before 1988 DDT's (DDT, DDE, DDD) were analysed on a *packed* column GC. During 1988, analyses on *capillary* column were introduced. The two methods give slightly different results for the various DDT-compounds. In table 19.1 the mean ratio: 'capillary column results' / 'packed column results' from various sites and matrices are presented. When the concentrations are close to the detection limit (D.L.) for packed column GC the results seem to be underestimated. This is particularly true for the estimated sum of DDT's (sDDT) since DDT and DDD may fall below D.L. and hence only DDE will constitute the sum. To avoid this bias at low levels, only samples with DDE concentrations above 0.2 µg/g have been selected to calculate the ratios given below. Only analyses where DDE, DDD and DDT were all present in levels above D.L. are included in the sDDT ratio (in the time series of sDDT, presented below, however, also sums where one of the three is below D.L. is included). When it has been possible to estimate these ratios, they are in general close to 1. There are a few exceptions; at Landsort both the DDE and DDT ratios are lower than 1, indicating overestimated concentrations from the packed column, possible due to interference with other compounds in the DDE and DDT peaks in the packed column chromatogramme. At Fladen the DDE ratio is significantly above 1 indicating underestimated DDE concentration from the packed column GC.

In the time series presented below the ratio of 1 has been used.

Table 19.1. Ratios of DDE, DDT, DDD and sDDT analysed on a capillary column versus the same samples analysed on a packed column gas chromatography (GC) and the corresponding 95% confidence interval.

	n	DDE	95% C.I..	n	DDT	95% C.I..	n	DDD	95% C..I.	n	sDDT	95% C.I.
Herring muscle												
Harufjärden	6	1.1	.99-1.2	6	.96	.89-1.0	4	1.5	1.1-2.0	4	1.1	.98-1.2
Ängskärsklubb	16	1.1	1.0-1.2	-	-	-	15	.63	.55-.70	-	-	-
Spring	24	1.0	1.0-1.1	1	.62	-	21	.77	.68-.85	1	.75	-
Landsort	28	.79	.76-.82	28	.75	.67-.81	28	.87	.77-.96	27	.79	.77-.82
Utlängan	20	1.1	1.0-1.1	20	1.0	.98-1.1	20	1.1	1.1-1.2	20	1.1	1.0-1.1
Spring	20	1.1	1.1-1.1	10	.81	.74-.88	10	1.1	1.0-1.1	10	1.0	.98-1.1
Fladen	6	1.4	1.3-1.4	5	.90	.77-1.0	6	1.1	.94-1.3	4	1.2	1.1-1.3
Cod liver												
SE Gotland	6	1.0	.95-1.1	-	-	-	-	-	-			
Fladen	8	1.1	1.0-1.1	-	-	-	-	-	-			
Dab muscle												
Fladen	9	1.0	.92-1.1									
Flounder muscle												
Väderöarna		1.0	.86-1.2									
Guillemot egg												
St. Karlsö	30	1.2	1.1-1.2	-	-	-	-	-	-			

The detection limit (capillary column, GC) is estimated to approximately 7 ng/g fat weight for DDE, 4 ng/g for DDD and 3 ng/g for DDT.

19.1 Temporal variation

19.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the DDT discharges are to be reduced by 50% between 1985 and 1995, using 1985 as a base year.

The Helsinki Convention (HELCOM) revised 1992 especially names the DDTs for which special bans and restrictions on transport, trade, handling, use and disposal are imposed. The Minister Declaration from 1988, within HELCOM, calls for a reduction of stable organic substances by 50% by 1995 with 1987 as a base year.

In Sweden, DDT was partially banned as a pesticide in 1970, and completely banned in 1975 due to its persistence and environmental impact.

19.1.2 This investigation

sDDT concentrations in herring muscle from all investigated sites and in cod ,perch and blue mussels from the Kattegatt and Skagerack decreased significantly during the time period 1980-2006. The rate varies between 6 and 12% a year. The time series of guillemot eggs (1969-2007) show a significant trend of -10% a year.

DDT concentrations in herring muscle and cod liver from all sites show significant decreasing trends (11-17%) during the time period 1978(80)-2006. The discharge of fresh DDT during 1983-84 (Bignert *et al*, 1990) is clearly noticeable in the time series from Landsort and Utlängan in the Baltic proper and Fladen at the Swedish west coast.

The number of years required to detect an annual change of 5% for DDE in herring varied between 16 to 21 years. The variation of DDE is somewhat less between years in general compared to DDT and DDD. When comparing the power of the time series of DDT's with other contaminants it should be noted that the DDT incident 1983-84 deteriorate the power of the time series calculated from the log-linear regression lines.

The ratio of DDT/sDDT is decreasing significantly at all herring sites except for Väderöarna where there is not enough data points to detect a possible change.

19.1.3 Conclusion

The concentration of DDT's has decreased at a rate of approximately 6-12% per year (in herring), in the Baltic as well as in the Kattegatt, since the end of the seventies. The DDT has generally decreased faster than the sum of DDT’s.

19.2 Spatial variation

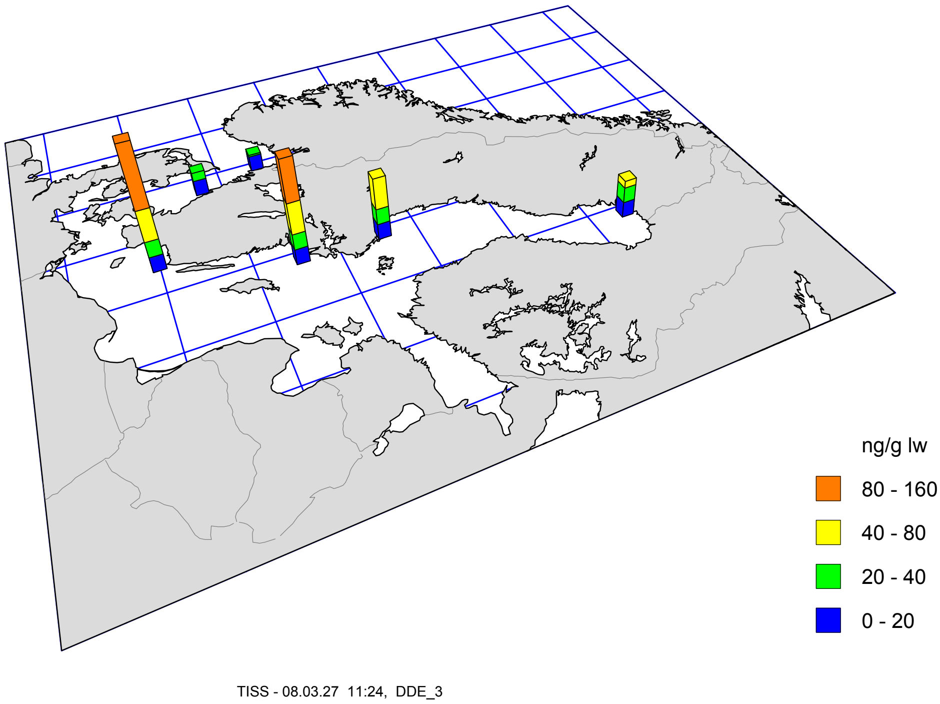


Figure 19.1. Spatial variation in concentration (w.w.) of DDE in herring muscle.

The highest concentraions of sDDT in herring are found at Landsort and Utlängan in the Baltic proper, significantly higher than from Harufjärden (Bothnian bay) and Fladen (Swedish west coast).

The sDDT concentrations in cod from the Baltic Proper (southeast of Gotland) are about twice as high, compared to cod from Fladen at the Swedish west coast.

Table 19.2. Estimated geometric mean concentrations of **sDDT** (µg/g **lipid** weight) in various matrices and sites for the last sampled year.

Matrix	age	n tot	n yrs	year	trend	last yr
Herring msc.						
Harufj. autumn	3-4	420	27	78-06	-11 (-13,-8.7)*	.038 (.027-.052)
Ängskärskl. aut.	3-5	445	27	78-06	-9.5 (-11,-8.0)*	.083 (.065-.11)
” spring	2-5	623	34	72-07	-7.1 (-8.4,-5.8)*	.29 (.23-.38)
Landsort	3-5	424	28	78-06	-7.5 (-8.9,-6.2)*	.21 (.17-.26)
Utlängan, aut.	3-4	339	27	80-06	-6.5 (-8.0,-5.0)*	.26 (.21-.33)
” spring	2-3	573	32	72-06	-12 (-13, -11)*	.32 (.26-.38)
Fladen	2-3	487	27	80-06	-11 (-13-9.1)*	.028 (.020-.039)
Väderöarna		219	11	95-05	-11 (-19-3.4)*	.021 (.013-.033)
Cod liver						
SE Gotland	3-4	277	26	80-06	-7.6 (-9.1,-6.2)*	.42 (.33-.52)
Fladen	2-3	312	26	80-06	-6.4 (-8.3,-4.6)*	.20 (.15-.27)
Perch muscle						
Holmöarna		270	21	80-06	-11 (-13,-8.2)*	.035 (.024-.049)
Kvädöfjärden		331	26	80-06	-11 (-13,-8.1)*	.030 (.020-.045)
Eelpout muscle						
Holmöarna		93	10	95-06		.15 (.11-.22)

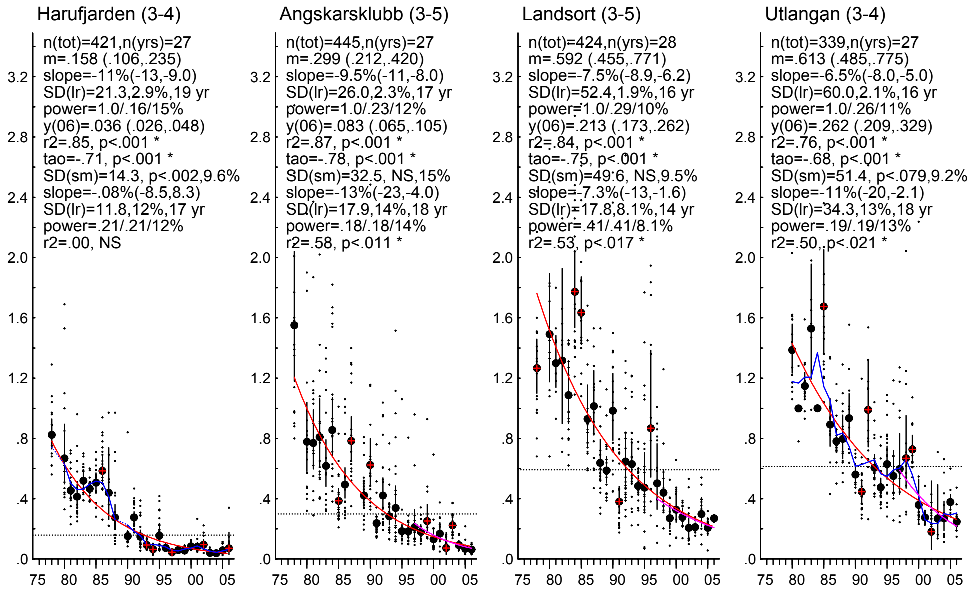
Kvädöfjärden		118	12	95-06	-14 (-23,-4.8)*	.11 (.059-.19)
Väderöarna		117	12	95-06		.10 (.076-.14)
Dab muscle						
Fladen	3-5	184	14	81-94		.12 (.062-.23)
Flounder msc						
Väderöarna	4-6	163	15	80-94		.11 (.060-.20)
Blue mussel						
Fladen		79	23	81-06	-9.1 (-12,-6.0)*	.017 (.011-.027)
Väderöarna		106	26	80-06	-9.7 (-12,-7.2)*	.014 (.009-.020)
Kvädöfjärden		60	12	95-06		.10 (.092-.12)
Guillemot egg						
St. Karlsö		380	36	69-07	-9.8 (-11,-8.8)*	10 (8.1-12)

* significant trend, $p < 0.05$

Table 19.3. The estimated proportion of DDT, DDE, DDD, DDT (%) in various matrices and sites.

Matrix	age	n yrs	year	DDT	DDE	DDD
Herring msc.						
Harufj. autumn	3-4		78-95	33	60	7
Ängskärskl. aut.	3-5		78-95	17	64	18
Landsort	3-5		78-95	17	51	32
Utlängan, aut.	2-4		80-95	19	49	32
Fladen	2-3		80-95	22	55	23
Cod liver						
SE Gotland	3-4		80-95	17	56	27
Fladen	2-4		80-95	10	76	14
Perch muscle						
Holmöarna			80-95	5	82	13
Kvädöfjärden	3-5		80-95	6	85	9
Blue mussel						
Fladen			81-95	17	63	20
Väderöarna			80-95	18	65	17

sDDT, ug/g lipid w., herring muscle



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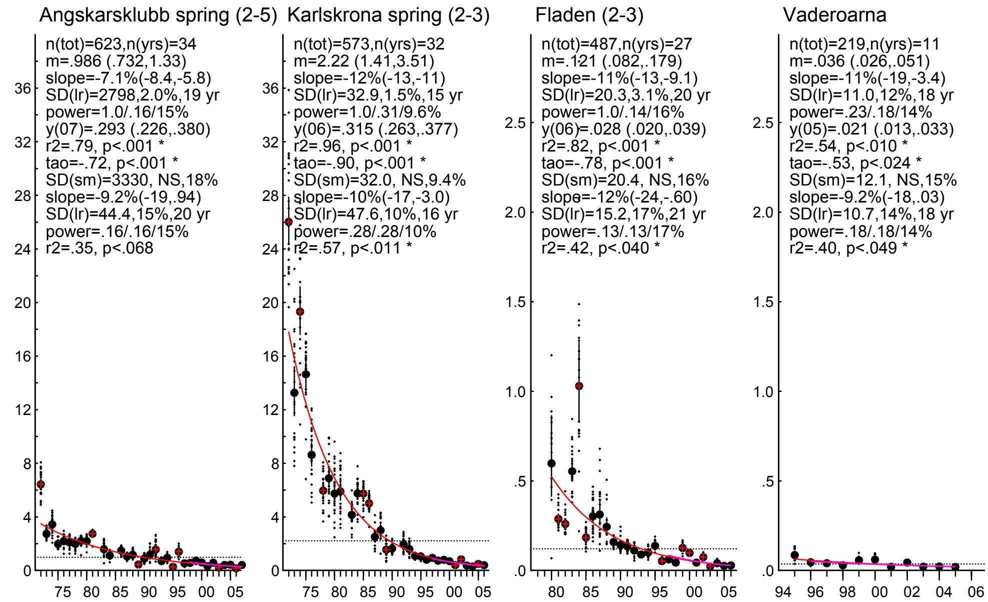
sDDT, ug/g lipid w., herring muscle

Fat adjusted spring herring samples



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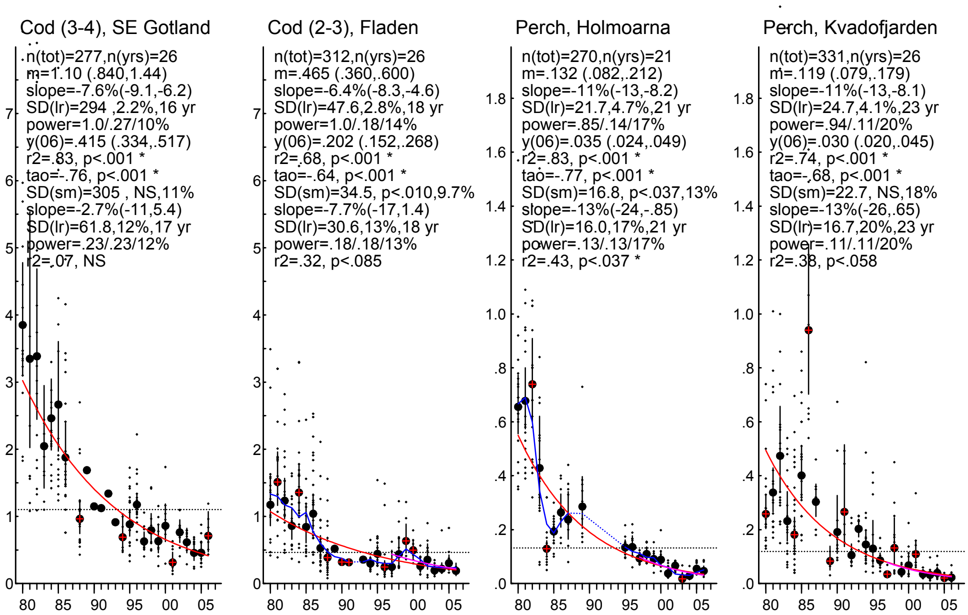
sDDT, ug/g lipid w., cod liver and perch muscle



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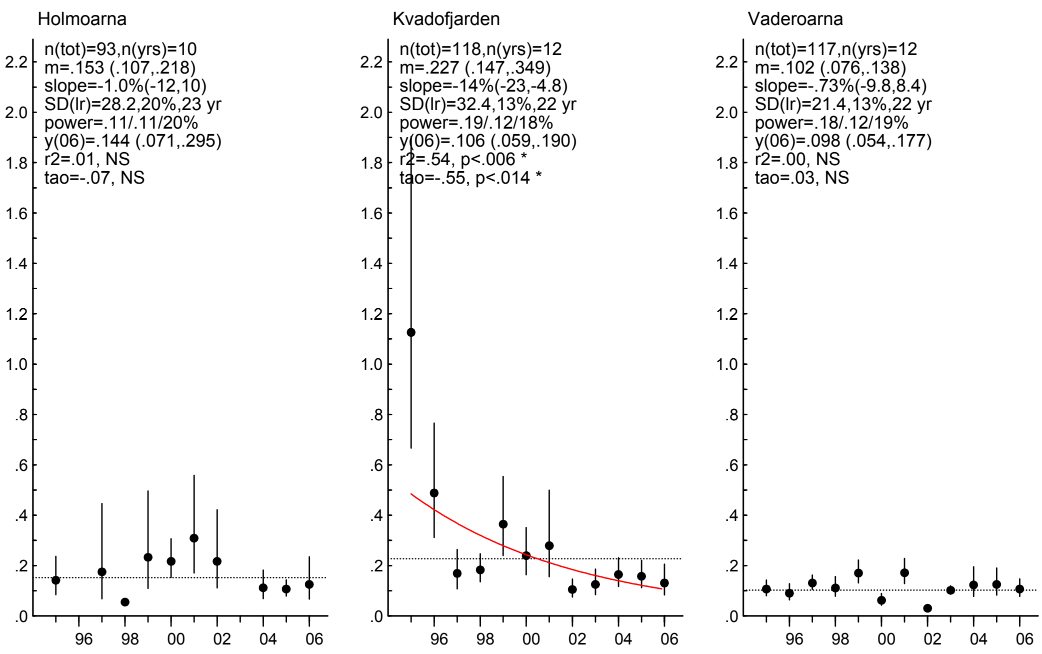
sDDT, ug/g lipid w., Eelpout



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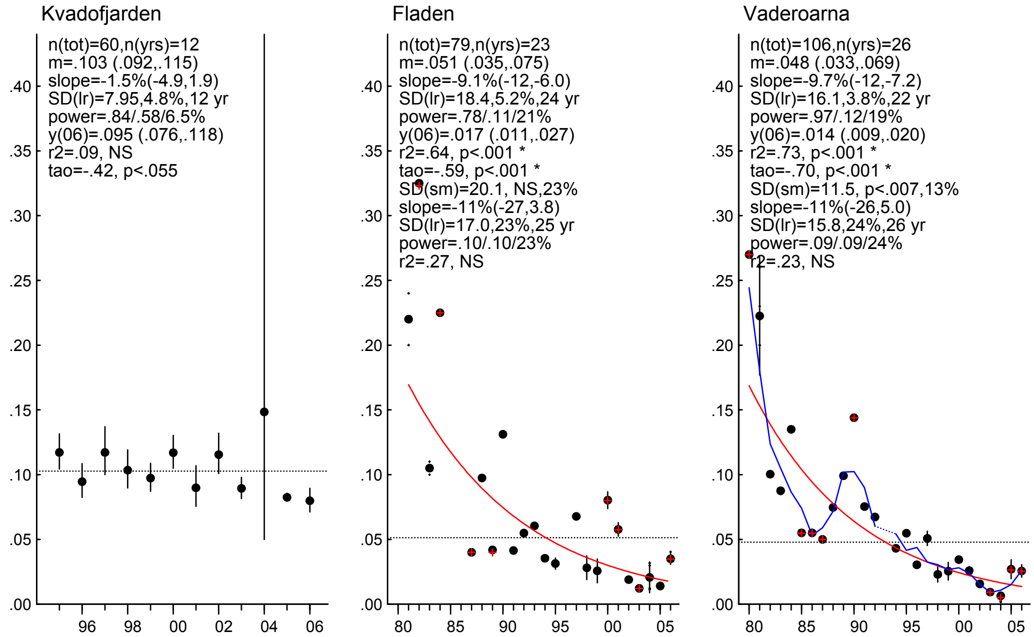
sDDT, ug/g lipid w., blue mussel



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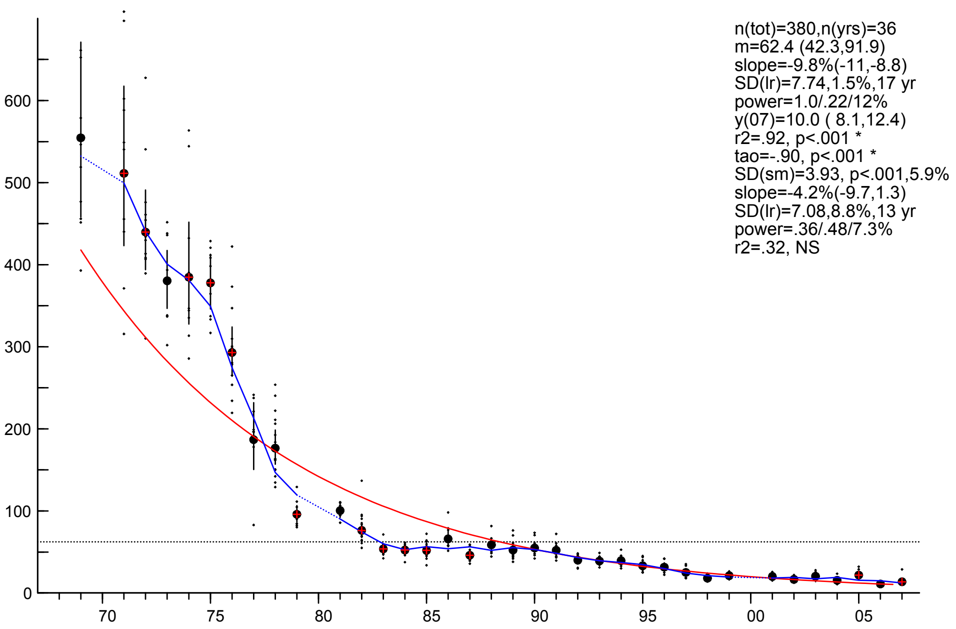
sDDT, ug/g lipid w., guillemot egg, early laid



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20 HCH's, Hexachlorocyclohexanes

Updated 08.03.28

Technical HCH contains various isomers: 60-75% α-HCH, 15% γ-HCH (lindane), 7-10% β-HCH, δ-HCH 7%, ε-HCH 1-2% and came into general use in 1950 (Gaul, 1992). The γ-isomer is the most toxic isomer of the HCH's, 500 to 1000 times as active as the α-isomer (White-Stevens, 1971). The use of technical HCH stopped in the countries around the Baltic between 1970-1980. Since 1980, use of lindane in Europe has been allowed only as an insecticide. It was still used to a great extent in France and Italy 1990 (Yi-Fan *et al.* 1996)

The isomers: α-HCH, ß-HCH and γ-HCH i.e. Lindane have been analysed in muscle tissue for various fish species (liver tissue for cod), blue mussel soft body and guillemot eggs since 1988, see table below. Samples from 1987 at Harufjärden and Landsort have been retrospectively analysed. The concentrations of ß-HCH are in many cases close to the detection limit, which implies analytical problems.

The detection limit is estimated to approximately 2 ng/g fat weight for α-HCH, 3 ng/g for β-HCH and 3 ng/g for γ-HCH.

20.1 Temporal variation

20.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the discharges of HCHs are to be reduced by 50% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of stable organic substances by 50% by 1995 with 1987 as a base year.

In Sweden, the use of lindane was severely restricted 1970, subsequently prohibited for use in agriculture 1978 because of its suspected carcinogenic properties and persistence. Remaining use was banned 1988/89.

20.1.2 This investigation

The variance for concentrations of α-HCH in herring muscle is generally low. Decreasing trends of about 13-20%. are found for herring from all sites The concentrations in cod liver are also decreasing significantly both in the time series from south east of Gotland and Fladen (in Kattegatt at the Swedish west coast).Concentrations of α-HCH are also decreasing in perch from Kvädöfjärden and Holmöarna and in guillemot eggs.

The number of years required to detect an annual change of 5% is about 10-13 years for cod and varies between 7 to 14 years for the herring time series.

Concentrations of β-HCH are generally decreasing, and are now approaching the detection limit. This makes the substance less fitted for use in this kind of study. The concentrations of ß-HCH in some matrices are however still detectable and show significant decreasing trends, for example in herring from Ängskärsklubb, Landsort and Utlängan, in cod from SE Gotland and in guillemot eggs.

The concentration of lindane (γ-HCH) has decreased significantly in all analysed matrices at all sampling sites except for guillemot eggs (St Karlsö) and herring from Väderöarna. The decrease is in the magnitude of 10 to 16% for herring, perch, and blue mussel and 15 to 20% for cod and eelpout. .

The ratio α-HCH/lindane in herring, show significant decreasing trends from Harufjärden, Landsort and Utlängan.

20.1.3 Conclusion

In general, the concentration of HCH's seems to have decreased at a rate of about 10% or more per year, in various species from the Baltic as well as at the Swedish west coast, since the end of the eighties. From ten time series on herring, cod and guillemot eggs for the period 1987-95, a median decrease of 65 % (38-88%) could be estimated. α-HCH is in general decreasing faster than lindane.

Measures taken to fulfil the aim of the North Sea Conference and the HELCOM Convention of a 50% reduction of the discharges of HCHs, 1995 with 1985 and 1987 respectively as base years, thus seems to have had a measurable effect in biota.

20.2 Spatial variation

Somewhat higher concentrations of HCH's are found in the herring samples from the Baltic Proper compared to the Bothnian Bay and the Kattegatt even after the rapid decrease mentioned above, see tables 20.1 and 20.2.

The ratio lindane/α-HCH is higher in the Kattegatt compared to the Baltic in both herring and cod. This could reflect that in the former east-bloc countries mainly technical HCH were used whereas the use of lindane (γ-HCH) was more common in western countries.

20.3 Seasonal variation

Unlike the PCB's, the DDT's and HCB, *the HCH's* show *no* significant seasonal difference in concentrations between herring caught in the spring and in the autumn.

Table 20.1. Geometric mean concentrations of **a-HCH** (ug/g **lipid** weight) in various matrices and sites during the studied time period and the estimated mean concentration for the last year. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend (95% ci)	Last year (95% ci)
Herring msc.						
Harufj. autumn	3-4	168	11	87, 90-99#	-16 (-19,-13)*	.**
Ängskärskl. aut.	3-5	243	16	89-04#	-20 (-23,-17)*	**
” spring	2-4	197	16	89-07	-18(-19,-17)*	.003 (.003-.003)
Landsort	3-5	289	20	87-06	-18 (-19,-16)*	.004 (.004,.005)
Utlängan, aut.	3-4	248	19	88-06	-18 (-19,-17)*	.004 (.003-.004)
” spring	2-3	209	17	87-06	-18 (-20,-17)*	.004 (.003-.004)
Fladen	2-3	243	14	88-01#	-16 (-17,-15)*	**
Väderöarna		107	7	95-99, 03#	-13 (-17, -9.6)*	**
Cod liver						
SE Gotland		155	18	89-06	-20 (-21,-18)*	.004 (.004-.004)
Fladen		130	18	89-06	-16 (-18,-14)	.002 (.001-.002)
Perch muscle						
Holmöarna		43	5	89,95-98#	-16 (-20,-12)*	**
Kvädöfjärden		116	14	84, 89-01,06	-19 (-22,-16)*	.001 (.001-.002)
Eelpout						
Holmöarna		34	6	95,97,99-02#	-16 (-26, -6.1)*	**
Kvädöfjärden		48	8	95-02#	-16 (-21, -9.8)*	**
Väderöarna		30	4	95,96,98,05		.004 (.001-.013)
Blue mussel						
Kvädöfjärden		60	12	95-06	-15 (-18,-13)*	.005 (.004-.006)
Fladen		48	14	88-01#	-15 (-18,-12)*	**
Väderöarna		48	14	88-04#	-13 (-17,-9.6)*	**
Guillemot egg						
St. Karlsö		158	17	88-07	-14 (-17,-12)*	.003 (.002-.004)

All values at or below detection limit during recent years

* significant trend, $p < 0.05$

** No estimated value because of concentrations at or below detection limit

Table 20.2. Geometric mean concentrations of **γ-HCH** (Lindane) (ug/g **lipid** weight) in various matrices and sites during the studied time period and the estimated mean concentration for the last year. The age interval for fish is also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n yrs	year	trend (95% ci)	Last year (95% ci)
Herring msc.						
Harufj. autumn	3-4	183	13	87, 90-01#	-10 (-13,-7.7)*	**
Ängskärskl. aut.	3-5	229	15	89-03#	-16 (-19, -12)*	**
” spring	2-5	214	17	89-05#	-14 (-16, -12)*	**
Landsort	3-5	285	20	87-06	-13 (-14, -12)*	.005 (.005-006)
Utlängan, aut.	2-4	278	19	88-06	-14 (-15, -13)*	.005 (.004-.006)
” spring	2-3	204	18	87-06	-16 (-17, -14)*	.005 (.004-.005)
Fladen	2-3	252	14	88-01#	-9.9 (-14,-5.6)*	**
Väderöarna		120	7	95-01#		**
Cod liver						
SE Gotland	3-4	140	18	89-06	-15 (-16, -13)*	.005 (.004-.006)
Fladen	2-3	106	16	89-06	-18 (-21, -14)*	.002 (.002-.003)
Perch muscle						
Holmöarna		41	5	89,95-98#	-14 (-26, -3.1)*	**
Kvädöfjärden		72	9	89, 94-01#	-11 (-20, -2.9)*	**
Eelpout						
Holmöarna		30	5	95,97,99, 01-02#	-17 (-32, -3.2)*	**
Kvädöfjärden		60	8	95-02#	-18 (-21, -15)*	**
Väderöarna		69	8	95-02,05#	-20 (-28, -12)*	**
Blue mussel						
Kvädöfjärden		57	12	95-06	-16 (-20, -12)*	.004 (.003-.006)
Fladen		53	16	81, 83, 88-01#	-9.5 (-12, -6.5)*	**
Väderöarna		50	15	83, 88-04#	-12 (-16, -8.5)*	**
Guillemot egg						
St. Karlsö		96	13	88-91,93-97,00-01,07		.006 (.003-.011)

all values below detection limit during recent years

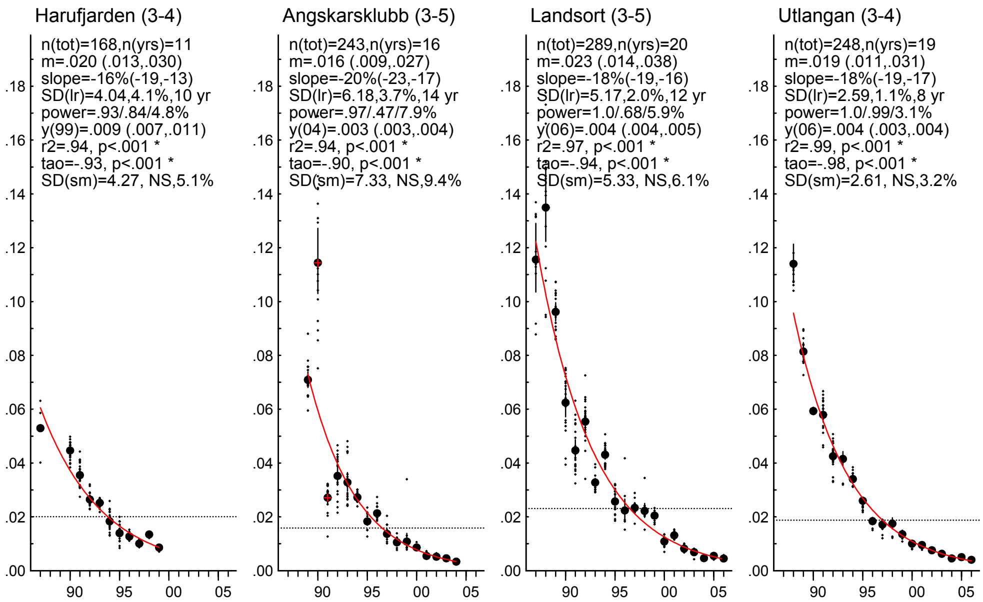
* significant trend, $p < 0.05$

** no estimated value because of concentrations at or below detection limit

Table 20.3. The estimated proportion of α-, β-, γ- HCH (%) in various matrices and sites.

Matrix	age	n yrs	year	α	β	γ
Herring msc.						
Harufj. autumn	3-4	7	87, 90-95	57	16	27
Ängskärskl. aut.	3-5	7	89-95	49	22	28
” spring	2-5	7	89-95	48	26	26
Landsort	3-5	9	87-95	47	25	28
Utlängan, aut.	2-4	8	88-95	43	27	30
” spring	2-3	7	87-95	43	24	33
Fladen	2-3	7	87-95	37	10	53
Cod liver						
SE Gotland	3-4	7	87-95	45	28	27
Fladen	2-4	7	87-95	37	11	52
Blue mussel						
Fladen		10	81-95	32	11	57
Väderöarna		8	83-95	31	9	60

a-HCH, ug/g lipid w., herring muscle



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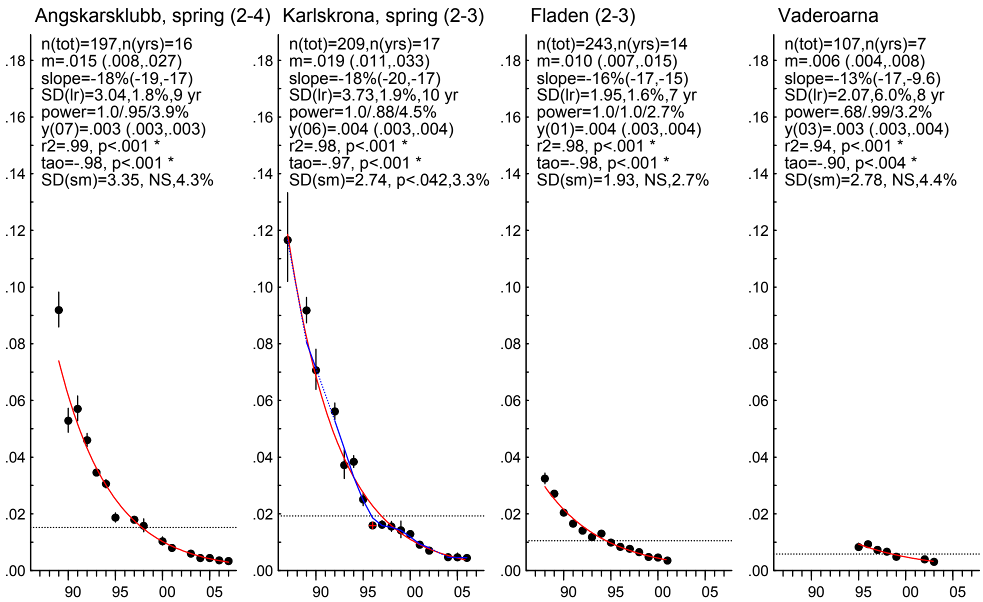
a-HCH, ug/g lipid w., herring



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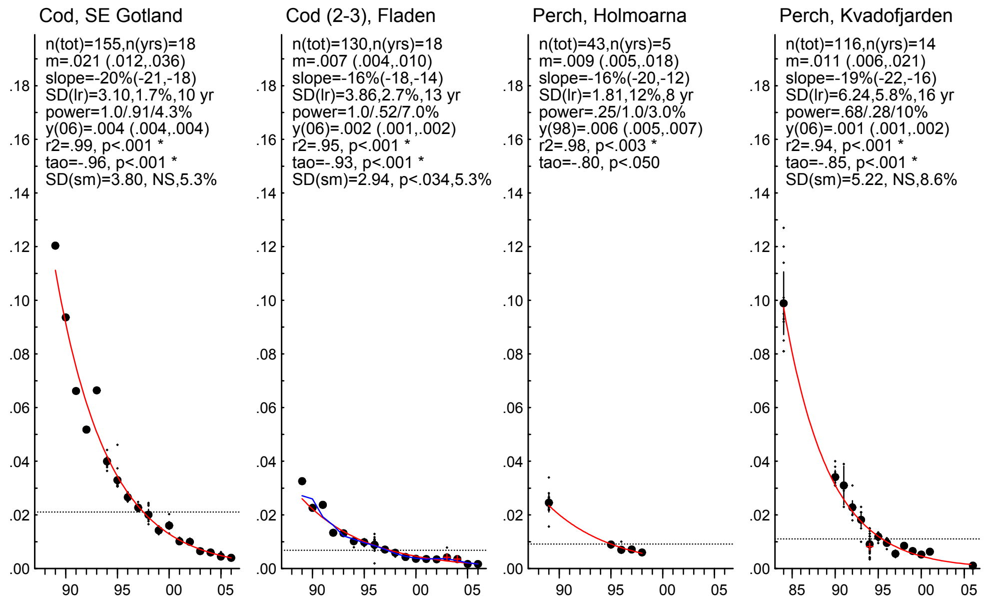
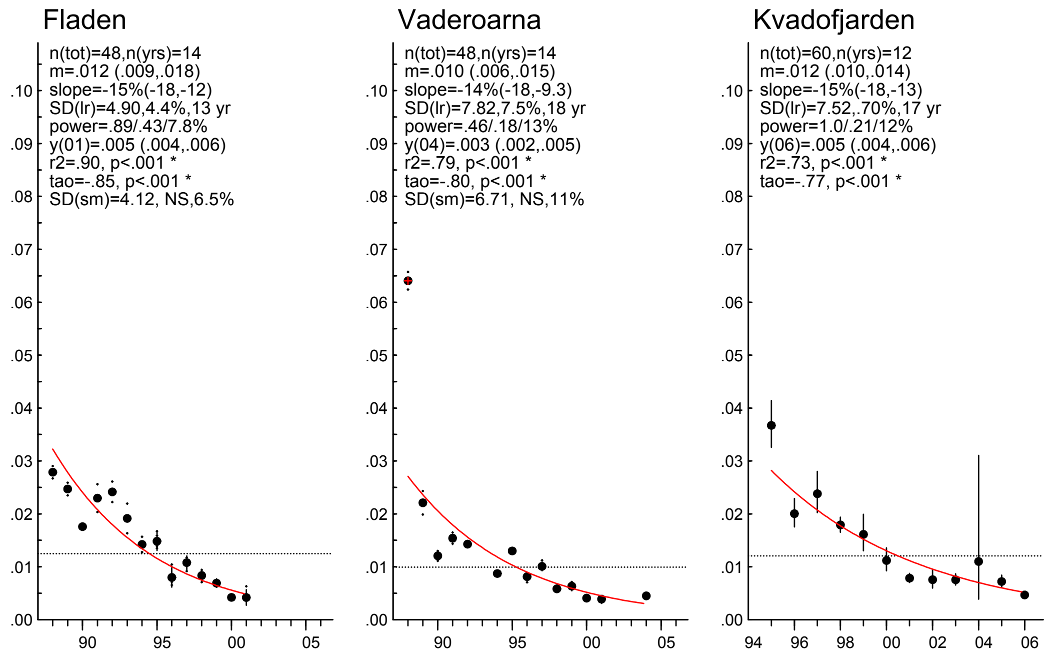
a-HCH, ug/g lipid w., cod liver and perch muscle

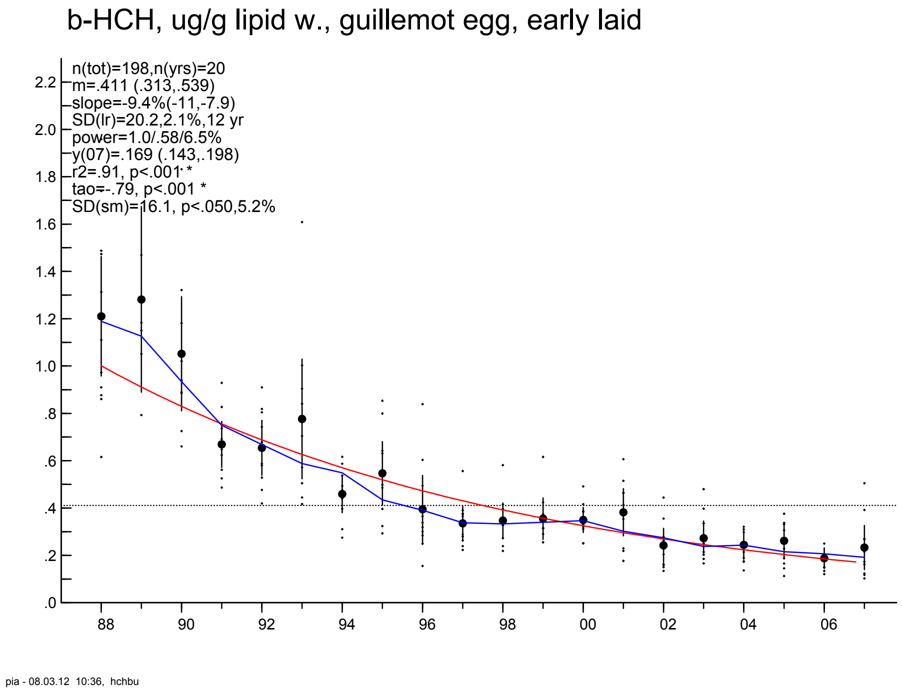


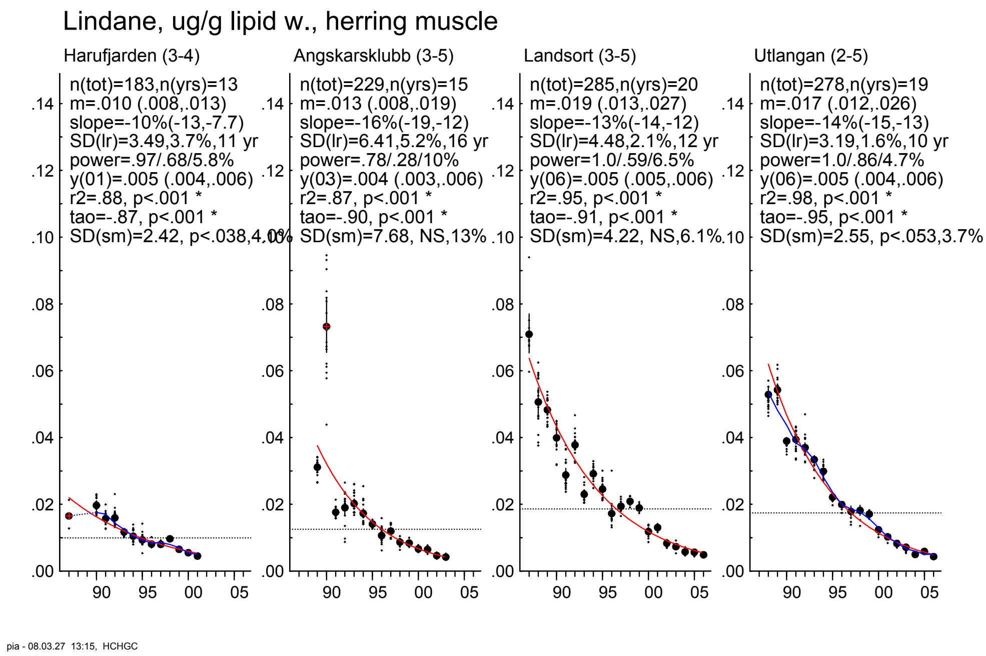
pia - 08.03.12 10:00, HCHAGP

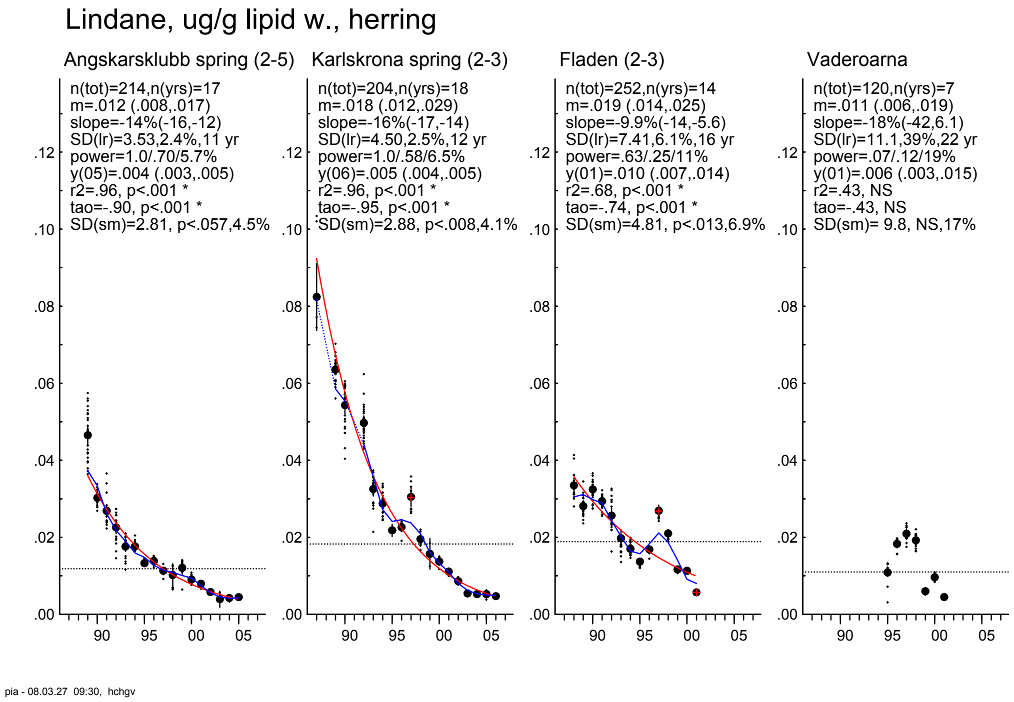
a-HCH, ug/g lipid w., blue mussel



pia - 08.03.12 10:06, HCHAM


b-HCH, ug/g lipid w., guillemot egg, early laid
n(tot)=198,n(yrs)=20
m=.411 (.313,.539)
slope=-9.4%(-11,-7.9)
SD(lr)=20.2,2.1%,12 yr
power=1.0/.58/6.5%
y(07)=.169 (.143,.198)
r2=.91, p<.001 *
tao=-.79, p<.001 *
SD(sm)=16.1, p<.050,5.2%
pia - 08.03.12 10:36, hchbu


Lindane, ug/g lipid w., herring muscle
Harufjarden (3-4)
n(tot)=183,n(yrs)=13
m=.010 (.008,.013)
slope=-10%(-13,-7.7)
SD(lr)=3.49,3.7%,11 yr
power=.97/.68/5.8%
y(01)=.005 (.004,.006)
r2=.88, p<.001 *
tao=-.87, p<.001 *
SD(sm)=2.42, p<.038,4.0%
Angskarsklubb (3-5)
n(tot)=229,n(yrs)=15
m=.013 (.008,.019)
slope=-16%(-19,-12)
SD(lr)=6.41,5.2%,16 yr
power=.78/.28/10%
y(03)=.004 (.003,.006)
r2=.87, p<.001 *
tao=-.90, p<.001 *
SD(sm)=7.68, NS,13%
Landsort (3-5)
n(tot)=285,n(yrs)=20
m=.019 (.013,.027)
slope=-13%(-14,-12)
SD(lr)=4.48,2.1%,12 yr
power=1.0/.59/6.5%
y(06)=.005 (.005,.006)
r2=.95, p<.001 *
tao=-.91, p<.001 *
SD(sm)=4.22, NS,6.1%
Utlangan (2-5)
n(tot)=278,n(yrs)=19
m=.017 (.012,.026)
slope=-14%(-15,-13)
SD(lr)=3.19,1.6%,10 yr
power=1.0/.86/4.7%
y(06)=.005 (.004,.006)
r2=.98, p<.001 *
tao=-.95, p<.001 *
SD(sm)=2.55, p<.053,3.7%
pia - 08.03.27 13:15, HCHGC


Lindane, ug/g lipid w., herring
Angskarsklubb spring (2-5)
n(tot)=214,n(yrs)=17
m=.012 (.008,.017)
slope=-14%(-16,-12)
SD(lr)=3.53,2.4%,11 yr
power=1.0/.70/5.7%
y(05)=.004 (.003,.005)
r2=.96, p<.001 *
tao=-.90, p<.001 *
SD(sm)=2.81, p<.057,4.5%
Karlskrona spring (2-3)
n(tot)=204,n(yrs)=18
m=.018 (.012,.029)
slope=-16%(-17,-14)
SD(lr)=4.50,2.5%,12 yr
power=1.0/.58/6.5%
y(06)=.005 (.004,.005)
r2=.96, p<.001 *
tao=-.95, p<.001 *
SD(sm)=2.88, p<.008,4.1%
Fladen (2-3)
n(tot)=252,n(yrs)=14
m=.019 (.014,.025)
slope=-9.9%(-14,-5.6)
SD(lr)=7.41,6.1%,16 yr
power=.63/.25/11%
y(01)=.010 (.007,.014)
r2=.68, p<.001 *
tao=-.74, p<.001 *
SD(sm)=4.81, p<.013,6.9%
Vaderoarna
n(tot)=120,n(yrs)=7
m=.011 (.006,.019)
slope=-18%(-42,6.1)
SD(lr)=11.1,39%,22 yr
power=.07/.12/19%
y(01)=.006 (.003,.015)
r2=.43, NS
tao=-.43, NS
SD(sm)= 9.8, NS,17%
.12
.10
.08
.06
.04
.02
.00
90
95
00
05
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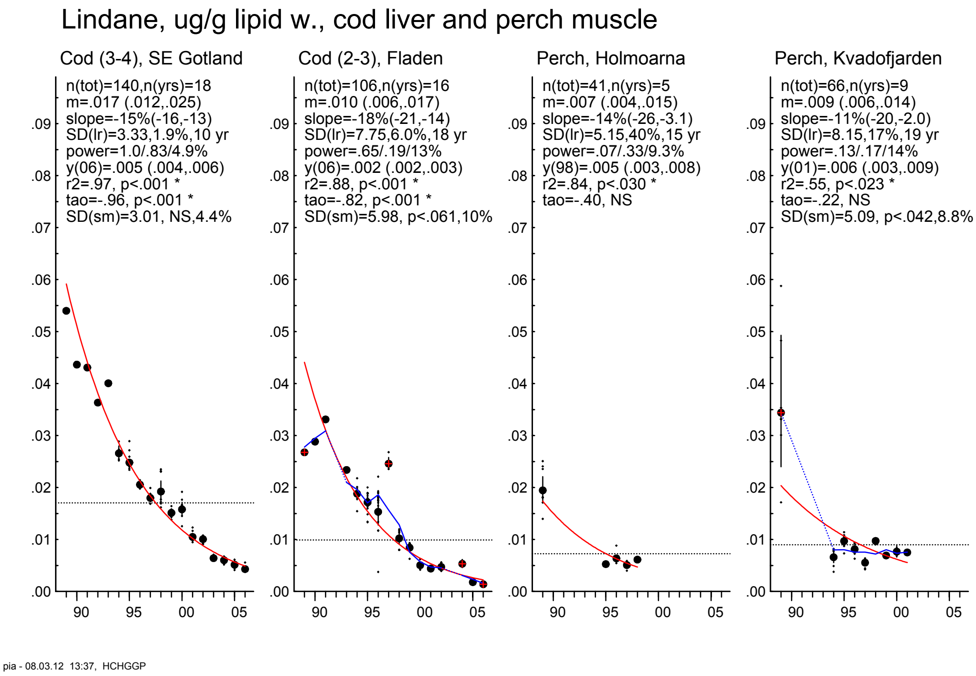
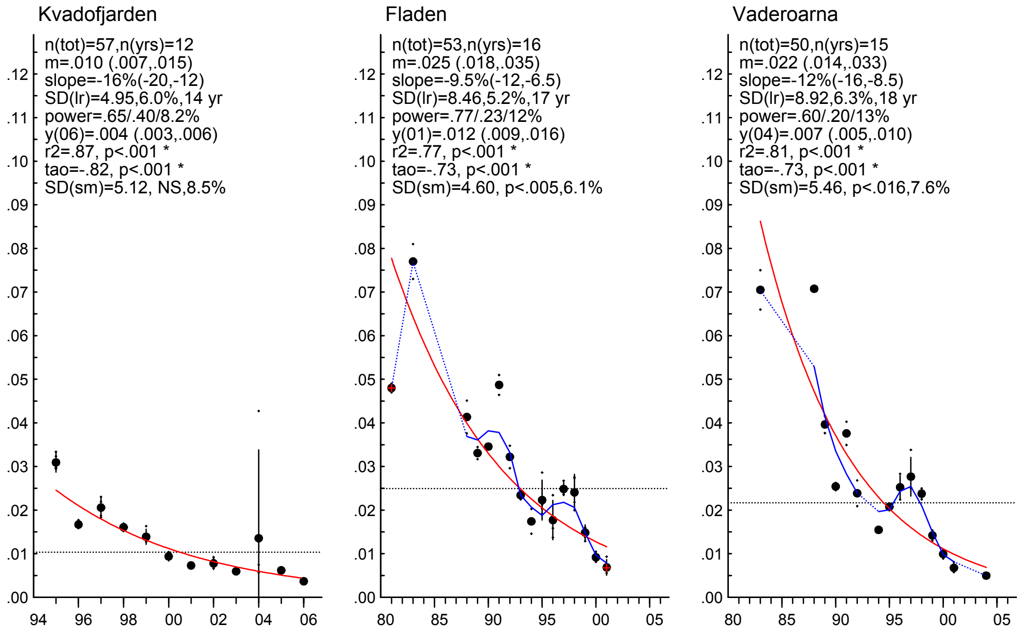

Lindane, ug/g lipid w., cod liver and perch muscle
Cod (3-4), SE Gotland
n(tot)=140,n(yrs)=18
m=.017 (.012,.025)
slope=-15%(-16,-13)
SD(lr)=3.33,1.9%,10 yr
power=1.0/.83/4.9%
y(06)=.005 (.004,.006)
r2=.97, p<.001 *
tao=-.96, p<.001 *
SD(sm)=3.01, NS,4.4%
Cod (2-3), Fladen
n(tot)=106,n(yrs)=16
m=.010 (.006,.017)
slope=-18%(-21,-14)
SD(lr)=7.75,6.0%,18 yr
power=.65/.19/13%
y(06)=.002 (.002,.003)
r2=.88, p<.001 *
tao=-.82, p<.001 *
SD(sm)=5.98, p<.061,10%
Perch, Holmoarna
n(tot)=41,n(yrs)=5
m=.007 (.004,.015)
slope=-14%(-26,-3.1)
SD(lr)=5.15,40%,15 yr
power=.07/.33/9.3%
y(98)=.005 (.003,.008)
r2=.84, p<.030 *
tao=-.40, NS
Perch, Kvadofjarden
n(tot)=66,n(yrs)=9
m=.009 (.006,.014)
slope=-11%(-20,-2.0)
SD(lr)=8.15,17%,19 yr
power=.13/.17/14%
y(01)=.006 (.003,.009)
r2=.55, p<.023 *
tao=-.22, NS
SD(sm)=5.09, p<.042,8.8%
.09
.08
.07
.06
.05
.04
.03
.02
.01
.00
90
95
00
05
pia - 08.03.12 13:37, HCHGGP

Lindane, ug/g lipid w., blue mussel



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21 HCB, Hexachlorobenzene

Updated 08.03.28

The use of the highly persistent HCB as a fungicide is banned in the Baltic countries and although it may still reach the environment as a by-product of many chlorinating processes e.g. pentachlorophenol and vinyl chloride monomer production, we have reasons to expect a decrease in biological samples from the Baltic.

HCB has been analysed in various species, see table below, since 1988. At Harufjärden and Landsort samples from 1987 have been retrospectively analysed.

The detection limit is estimated to approximately 1 ng/g fat weight.

21.1 Temporal variation

21.1.1 Conventions, aims and restrictions

The North Sea Conference (1984, 1987, 1990) that covers all routes of pollution to the North Sea, states that the HCB discharges are to be reduced by 50% between 1985 and 1995, using 1985 as a base year.

The Minister Declaration from 1988, within HELCOM, calls for a reduction of stable organic substances by 50% by 1995 with 1987 as a base year.

HCB was withdrawn from market 1980 in Sweden, because of its carcinogenic effects on experimental animals and it persistence.

21.1.2 This investigation

In the Baltic proper there are significant decreases in concentrations of HCB in all analysed fish species and in guillemot eggs . Decreasing trends are also found on the Swedish west coast, in herring and cod from Fladen and blue mussels from Väderöarna.

In blue mussels from the Swedish west coast the concentrations are very low. Since the year 2000 values are at or below detection limit and hence blue mussels are not considered to be a good matrice for monitoring of HCB´s in this region.

The number of years required to detect an annual change of 5% varied between 14 to 20 years for the herring time series.

21.1.3 Conclusion

The concentration of HCB in herring, cod, dab and guillemot egg has decreased at a rate of about 5-10% per year from the Baltic Proper since 1988. The aim of the North Sea Conference and the HELCOM Convention of a 50% reduction of HCB, 1995 with 1985 and 1987 respectively as a base year thus seems to be fulfilled.

21.2 Spatial variation

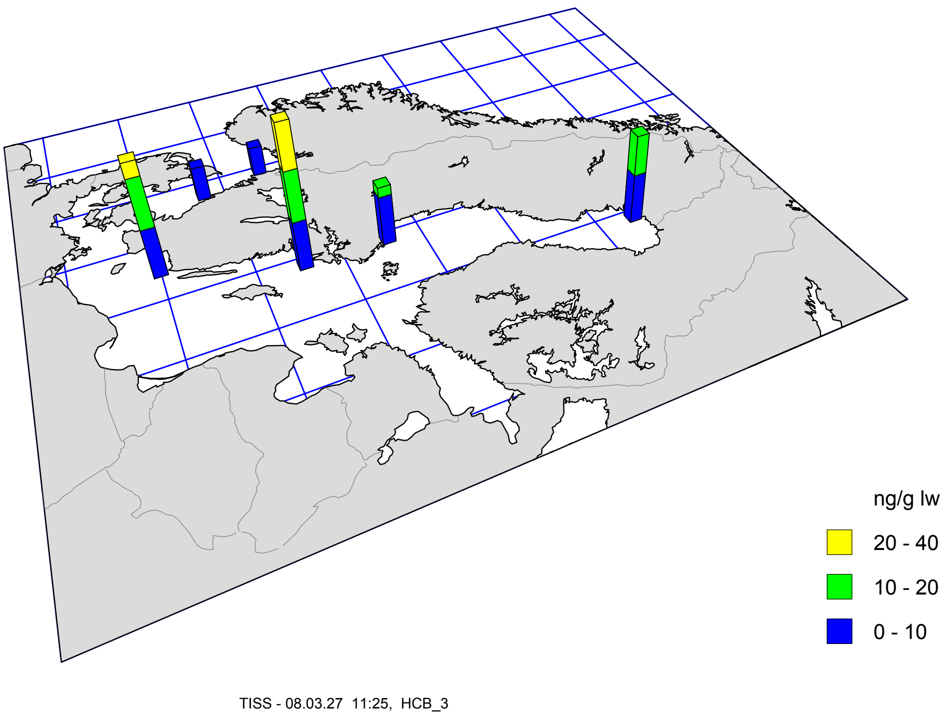


Figure 21.1. Spatial variation in concentration (w.w.) of HCB in herring muscle.

Herring muscle from Landsort and Utlängan in the Baltic Proper represent the highest HCB concentrations of the herring samples, significantly higher compared to the other sites in the late eighties. However, since the concentrations have decreased considerably in the samples from the Baltic Proper and the variance from the Bothnian Bay and the Baltic Sea are large, no significant differences can be shown in the estimated concentrations for 2006 in the autumn caught herring from the various sites in the Baltic and the Kattegatt, although the estimated concentrations from 2006 is almost twice as high in the Baltic compared to the west coast.

The results from eelpout and blue mussel samples from Kvädöfjärden that were analysed for HCB for the first time 1995, *indicate about twice as high concentrations or more in the Baltic compared to the Kattegatt and the Skagerack*. This difference is significant for blue mussels and for eelpout when comparing Holmöarna and Väderöarna.

21.3 Differences among various species

At some of the sampling sites, specimens of various species are collected within the same area. HCB is analysed in fish muscle tissue except for cod where the liver is used whereas whole soft body is analysed in blue mussels. The concentrations found are listed in decreasing order. Differences in geometric mean HCB concentration among the species samples from the same area are marked with '>':

Holmöarna: Eelpout(16) > Perch(7)
Kvädöfjärden: Eelpout(10) > Perch(6)- Blue mussel(6)
Fladen: Cod(10) - Herring(7) >Blue mussel(2.5)
Väderöarna: Eelpout(9) - Herring(8) > Blue mussel(2)

The lowest concentrations are found in blue mussels whereas the highest are found in guillemot eggs.

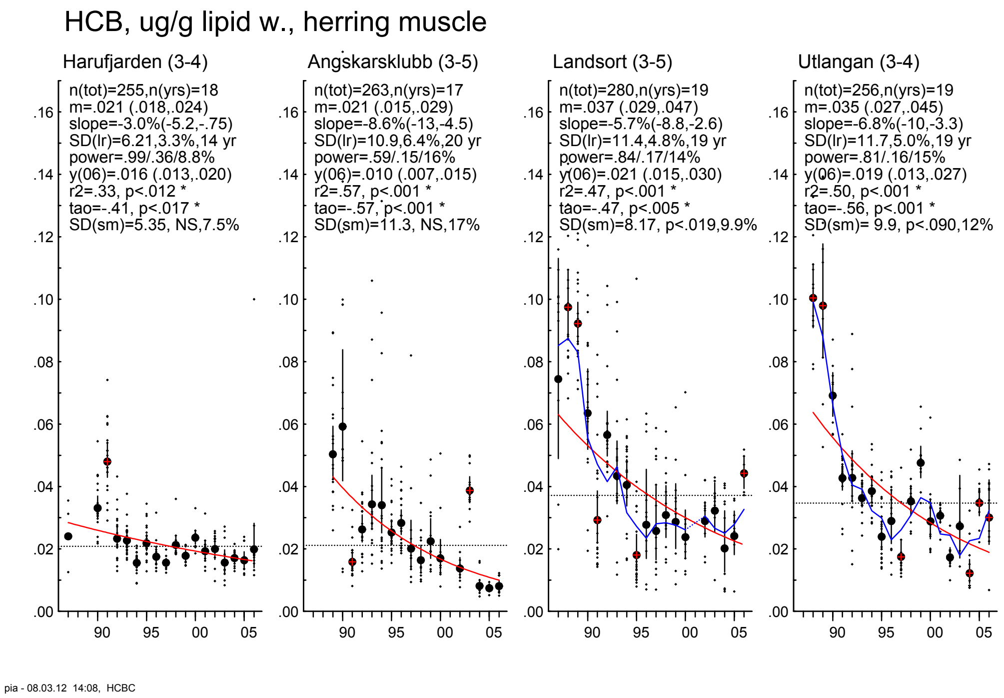
21.4 Seasonal variation

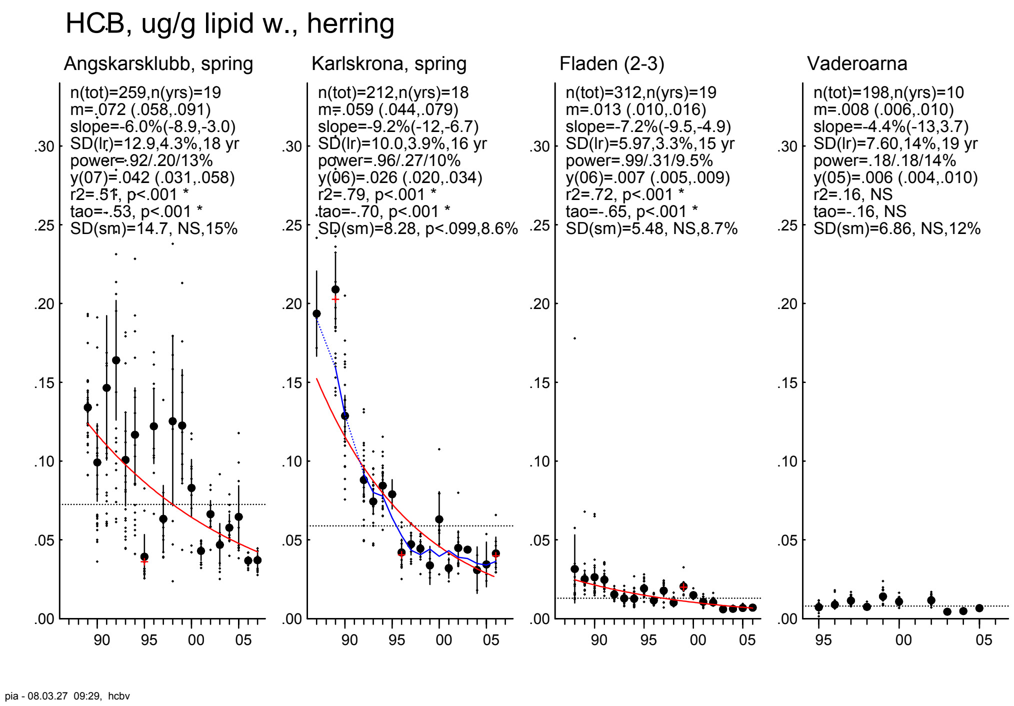
Herring caught in the spring show 2-3 times higher HCB-concentrations on a lipid weight basis compared to samples collected in the autumn.

Table 21.1. Estimated geometric mean concentrations of **HCB** (ug/g **lipid** weight) in various matrices and sites for the last sampled year.

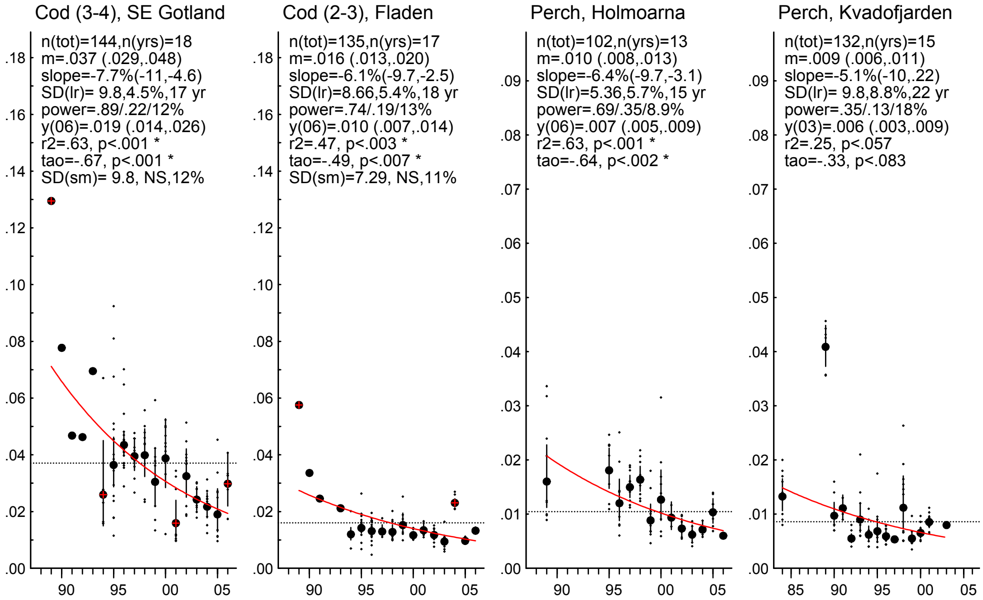
Matrix	age	n	n yrs	year	trend	last yr
Herring msc.						
Harufj. autumn	3-4	254	18	87-06	-3.2 (-5.4,-1.0)*	.016 (.013-.020)
Ängskärskl. aut.	3-5	263	17	89-06	-8.6 (-13,-4.5)*	.010 (.007-.015)
” spring		259	19	89-07	-6.0 (-8.9, -3.0)*	.042 (.031-.058)
Landsort	3-5	280	19	87-06	-5.7 (-8.8-2.6)*	.021 (.015-.030)
Utlängan, aut.	3-4	256	19	88-06	-6.8 (-10,-3.3)*	.019 (.013-.027)
” spring		212	18	87-06	-9.2 (-12,-6.7)*	.026 (.020-.034)
Fladen	2-3	312	19	88-06	-7.2 (-9.5,-4.9)*	.007 (.005-.009)
Väderöarna		198	10	95-05		.008 (.006-.010)
Cod liver						
SE Gotland	3-4	144	18	89-06	-7.7 (-11,-4.6)*	.019(.014-.026)
Fladen	2-3	135	17	89-06	-6.1 (-9.7,-2.5)*	.010 (.007-.014)
Perch muscle						
Holmöarna		102	13	89,95-06	-6.4 (-9.7, -3.1)*	.007 (.005-.009)
Kvädöfjärden		132	15	84,89-00,03#	-5.1 (-10, -.22)*	**
Eelpout muscle						
Holmöarna		93	10	95-06	-11 (-21, -0.47)*	.016 (.008-.031)
Kvädöfjärden		111	12	95-06	-4.5 (-8.7,-.19)*	.010 (.008-.013)
Väderöarna		96	12	95-06		.009 (.008-.010)
Dab muscle						
Fladen	3-5	6	6	89-94		.004 (.003-.006)
Flounder msc						
Väderöarna	4-6	6	6	89-94		.004 (.001-.028)
Blue mussel						
Fladen		32	9	88-00#		**
Väderöarna		31	10	88-00#	-7.9 (-16,-.05)*	**
Kvädöfjärden		57	12	95-06		.006 (.005-.008)
Guillemot egg						
St. Karlsö		208	21	79,88-07	-6.5 (-8.4,-4.6)*	.62 (.50-.76)

all values below detection limit during recent years
* significant trend, p < 0.05
** no estimated value because of concentrations at or below detection limit





HCB, ug/g lipid w., cod liver and perch muscle



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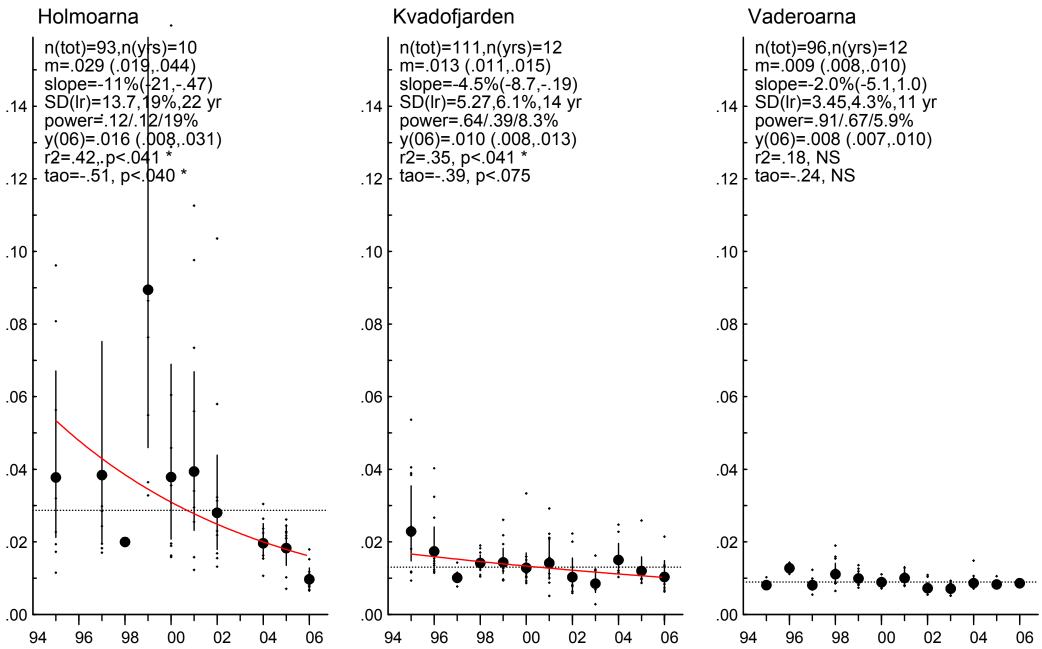
HCB, ug/g lipid w., eelpout



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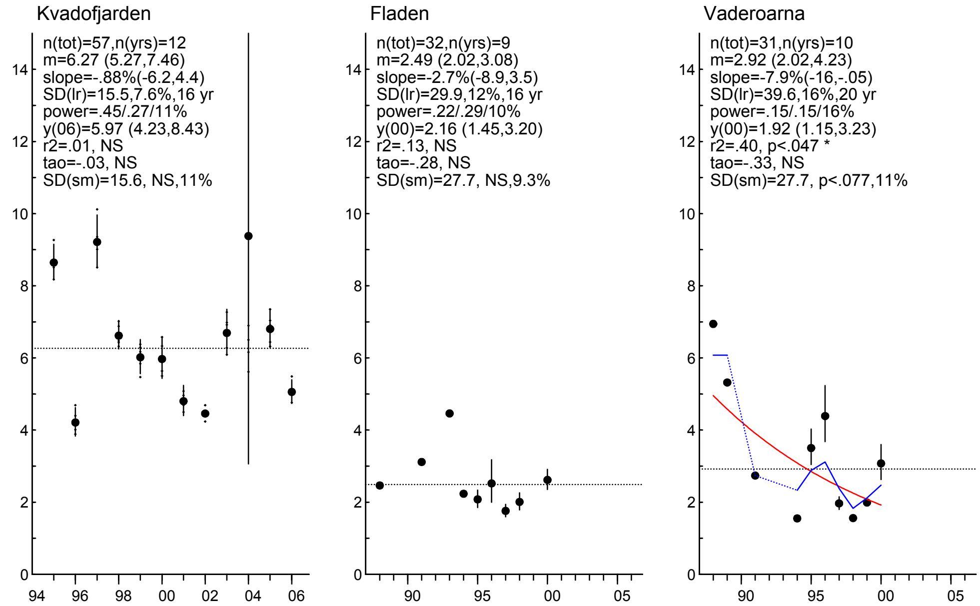
HCB, ng/g lipid w., blue mussel



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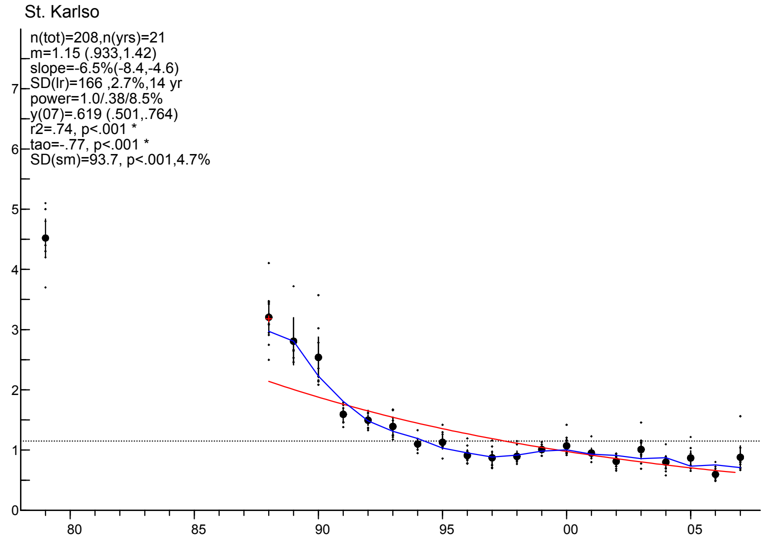
HCB, ug/g lipid w., guillemot egg, early laid



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22 PCDD/PCDF, Polychlorinated Dioxins and Dibenzofurans

Updated 08.03.31

Dioxins are unintentionally created during combustion of organic materials. They are highly toxic and carcinogenic.

Dioxins in guillemot eggs from St. Karlsö have been retrospectively analysed in a time series back to 1968. Herring muscle tissue has also been analysed during recent years.

22.1 Conventions aims and restrictions

Dioxins are comprised by the objective of HELCOM's strategy for hazardous substances, that is to continuously reduce discharges, emissions and losses of hazardous substances, with a goal of their eventual cessation by the year 2020. The ultimate aim is to achieve concentrations in the environment near background values for naturally occurring substances and close to zero for man-made synthetic substances. This objective was adopted in 1998 and dioxin has been selected as one of the priority substances for immediate action.

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international agreement, requiring measures for reducing or preventing releases of dioxins to the environment

22.2 Temporal variation

22.2.1 This investigation

The dioxin content of fat fish from the Baltic often exceeds the prescribed maximum limit (4 WHO-PCDD/F pg/g or 8 WHO-PCDD/F-PCBTEQ pg/g fresh weight) within the European Union, and therefore Sweden and Finland are currently only allowed to sell on the domestic market or to non member states (EC 2375/2001, EC 201/2002, EC 199/2006, EC 1881/2006). However, the TEQ levels in herring (mean = 0.39-0.81 TEQ pg/g fresh weight) from the reference sites in this investigation do not exceed the prescribed maximum.

In guillemot eggs significant decreasing trends are observed for TCDD, TCDF and TCDD-equivalents during the whole period. However there is a difference over time between PCDD and PCDF. PCDF does not show the same decrasing trend during the recent 10 years as PCDD. This might explain the ceased trend for TCDD-equivalents during the last 20 years. The number of years required to detect an annual change of 5% varied between 12 and 18 years in the time series of guillemot.

There are no significant changes in concentration over time in herring muscle. The number of years required to detect an annual change of 5% varied between 17 and 18 years for these time series.

22.3 Spatial variation

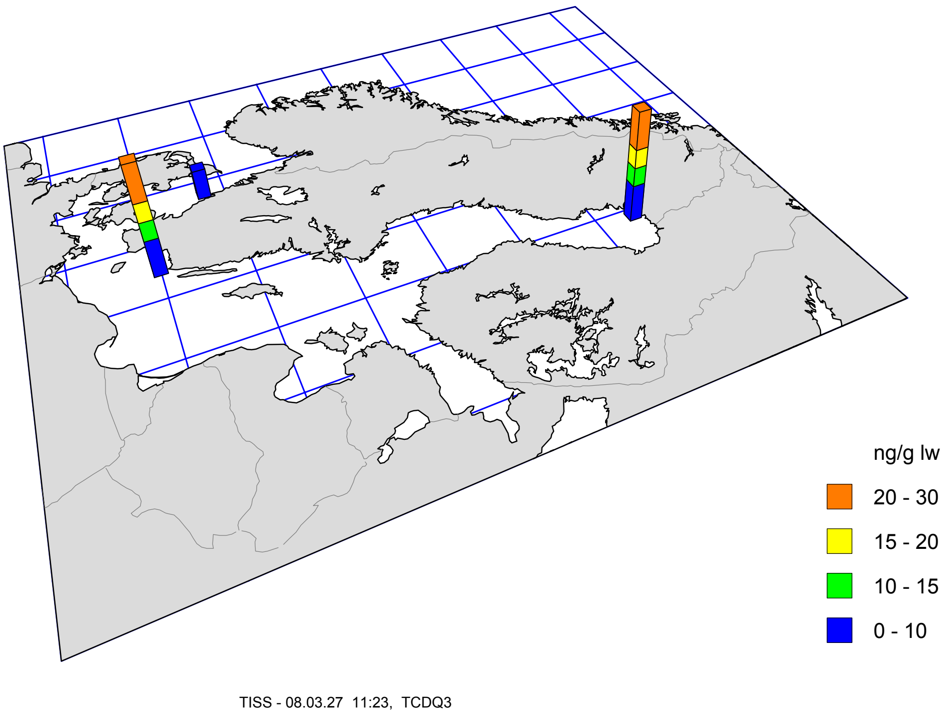


Figure 22.1. Spatial variation in concentration (w.w.) of TCDD-equivalents in herring muscle.

The TCDD-eqv are elevated in herring muscle from Harufjärden (Bothnian Sea) and Utlängan (Baltic Proper) compared to the Swedish west coast, (2 times as high on a fresh weight basis)

Table 22.1. Geometric mean concentrations of **TCDD-eqv.** (pg/g **lipid** weight) in various matrices and sites during 1988/1990-2006 and estimated mean concentration 2006.

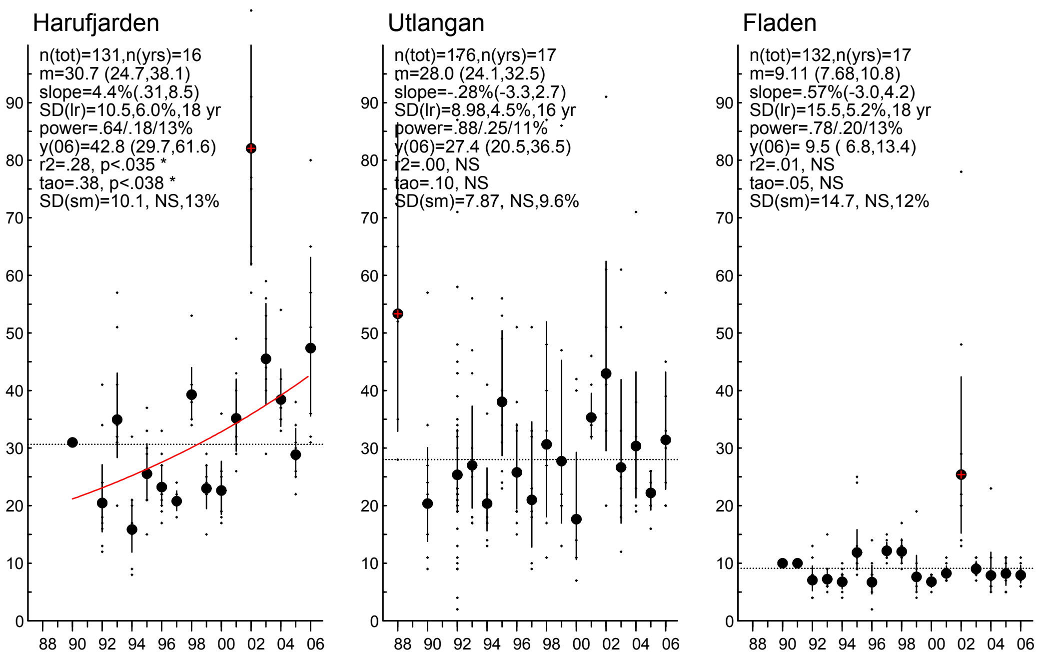
Matrix	age	n tot	n yrs	year	trend	Mean (last year if trend)
Herring msc.						
Harufj. autumn		131	16	90-06	4.4 (-.31, 85)*	43 (30-62)
Utlängan		176	17	88, 90, 92-06		28 (24-33)
Fladen		132	17	90-06		9.1 (7.7-11)
Guillemot egg						
St. Karlsö		161	36	68-06	-3.1 (-3.8, -2.3)*	.84 (.73-0.98)

* significant trend, p < 0.05

Table 22.2. Geometric mean concentrations of **TCDD-eqv.** (pg/g **fresh** weight) in various matrices and sites during 1988/1990-2006 and estimated mean concentration 2006.

Matrix	age	n tot	n yrs	year	trend	Mean (last year if trend)
Herring msc.						
Harufj. autumn		131	16	90-06		.81 (.65-.99)
Utlängan		170	16	90, 92-06		.72 (.59-.87)
Fladen		132	17	90-06		.39 (.32-.47)

TCDD-equivalents, pg/g fat, herring muscle



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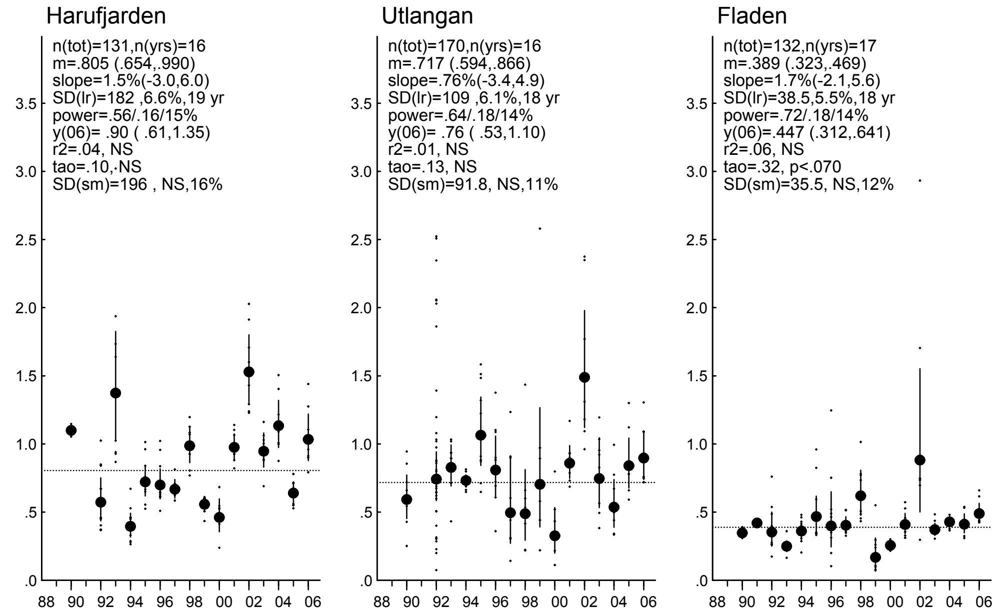
TCDD-equivalents, pg/g fresh wt, herring muscle



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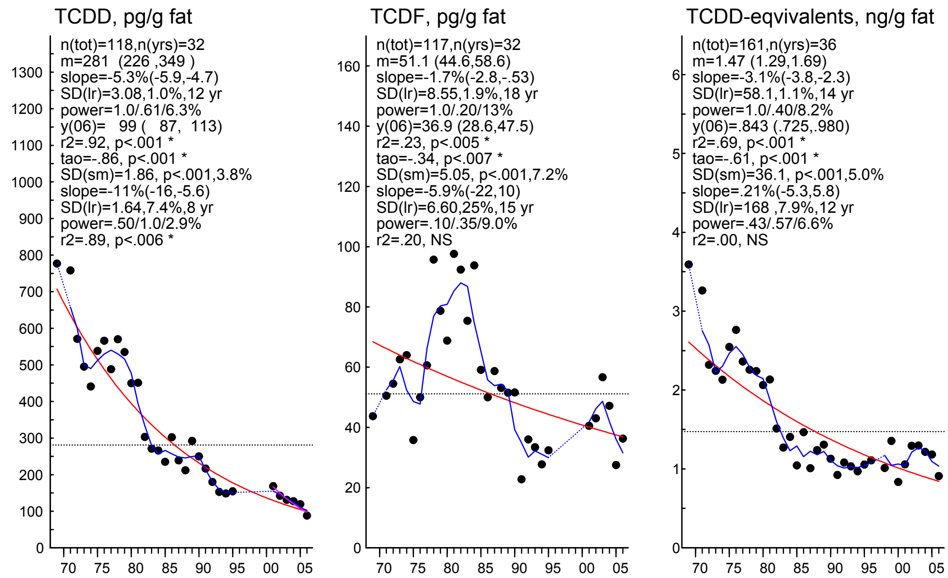
PCDD/PCDF in guillemot egg



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23 Polybrominated flame retardants

Updated 08.03.28

Polybrominated flame retardants in guillemot eggs from St. Karlsö have been retrospectively analysed in a time series back to 1968. Herring muscle tissue has also been analysed during recent years.

23.1 Temporal variation

23.1.1 This investigation

Significant increasing concentrations of BDE-47, BDE-99 and BDE-100, in guillemot eggs, from the late sixties until the early nineties are followed by decreasing values during the recent.period.
Decreasing concentrations of BDE-47 can also be observed in herring from Ängskärsklubb and Väderöarna and in cod and herring from Fladen.
For HBCD a significant increase of is shown.The concentrations of HBCD are increasing in guillemot eggs with about 3% per year. Increasing values are also observed in herring from Landsort, but not at the other herring sites.
The time series for herring and cod are relatively short (5 to 8 years) which decreases the possibility to detect trends. The number of years required to detect an annual change of 5%, in the concentration of BDE-47, is 11 to 18 years for herring and cod (except for herring caught at Ängskärsklubb in spring).

23.2 Spatial variation

Yet only five to eight years of analysis (1999-2006) are presented (Figure 23.2). The figures indicate elevated concentrations of some of the substances at Karlskrona in the southern Baltic Proper. The number of analyses are still too few to make any firm conclusions, but in general the PBDE’s and HBCD seems to be more evenly distributed among sites compared to e.g. PCB.

Table 23.1. Geometric mean concentrations of **BDE-47** (ng/g **lipid** weight) in various matrices and sites during monitoring period and estimated mean concentration 2006.

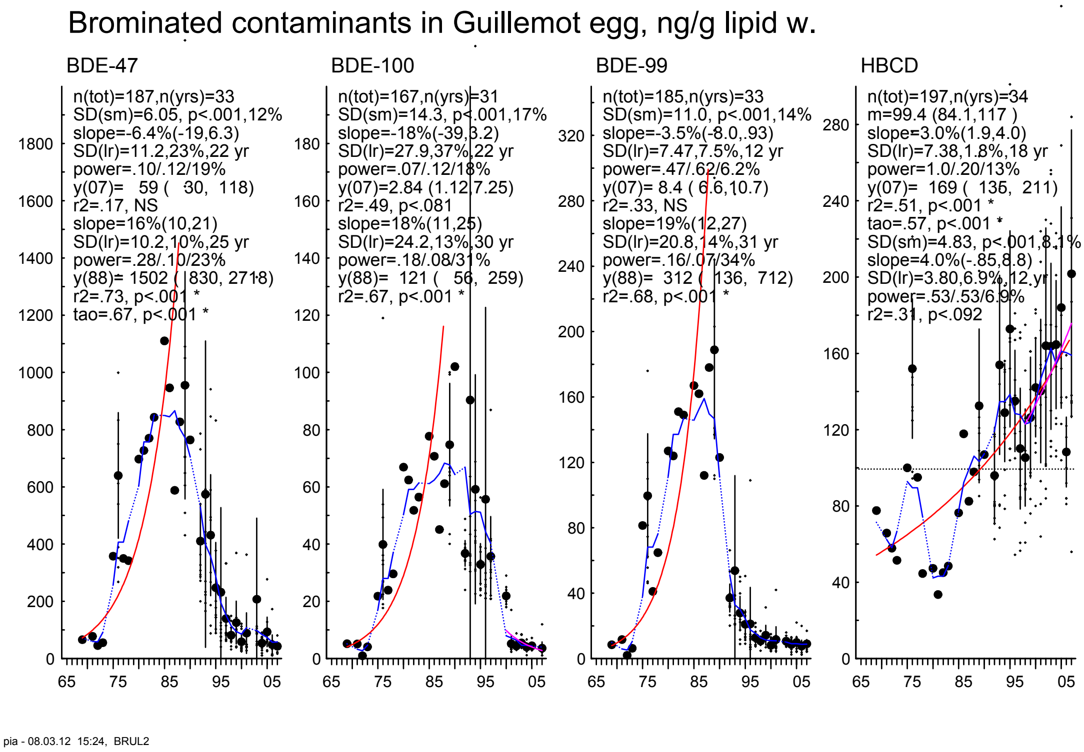
Matrix	age	n tot	n yrs	year	trend	Mean (last year if trend)
Herring msc.						
Harufj.		95	8	99-06		7.3 (5.7-9.4)
Ängskärsklubb autum		96	8	99-06	-15 (-23,-7.1)*	3.5 (2.5-4.9)
Ängskärsklubb spring		57	6	02-07		15 (8.3-28)
Landsort		91	8	99-06		7.5 (5.5-10)
Utlängan autumn		90	8	99-06	-8.3 (-19,2.2)	6.9 (4.5-11)
Utlängan spring		48	5	03-07		13 (8.3-21)
Fladen		96	8	99-06	-18 (-24,-12)*	2.3 (1.8-3.0)
Väderöarna		140	7	99-05	-20 (-33,-7.3)*	2.7 (1.7-4.3)
Cod liver						
SE Gotland		77	8	99-06		20 (16-24)
Fladen		73	8	99-06	-20 (-33,-6.3)*	14 (7.7-24)
Guillemot egg						
St. Karlsö		187	33	68-07		59 (30-120)

* significant trend, $p < 0.05$

Table 23.2. Geometric mean concentrations of **HBCD** (ng/g **lipid** weight) in various matrices and sites during monitoring period and estimated mean concentration 2006.

Matrix	age	n tot	n yrs	year	trend	Mean (last year if trend)
Herring msc.						
Harufj.		95	8	99-06		8.0 (4.7-14)
Ängskärsklubb autum		96	8	99-06		4.4 (2.6-7.5)
Landsort		91	8	99-06	5.8 (-1.3,13)	16 (12-21)
Utlängan autumn		89	8	99-06		17 (12-25)
Cod liver						
SE Gotland		90	9	99-06		4.3 (.36-53)
Fladen		58	6	99-06		1.4 (.031-58)
Guillemot egg						
St. Karlsö		197	34	68-07	3.0 (1.9,4.0)*	170 (140-210)

* significant trend, $p < 0.05$



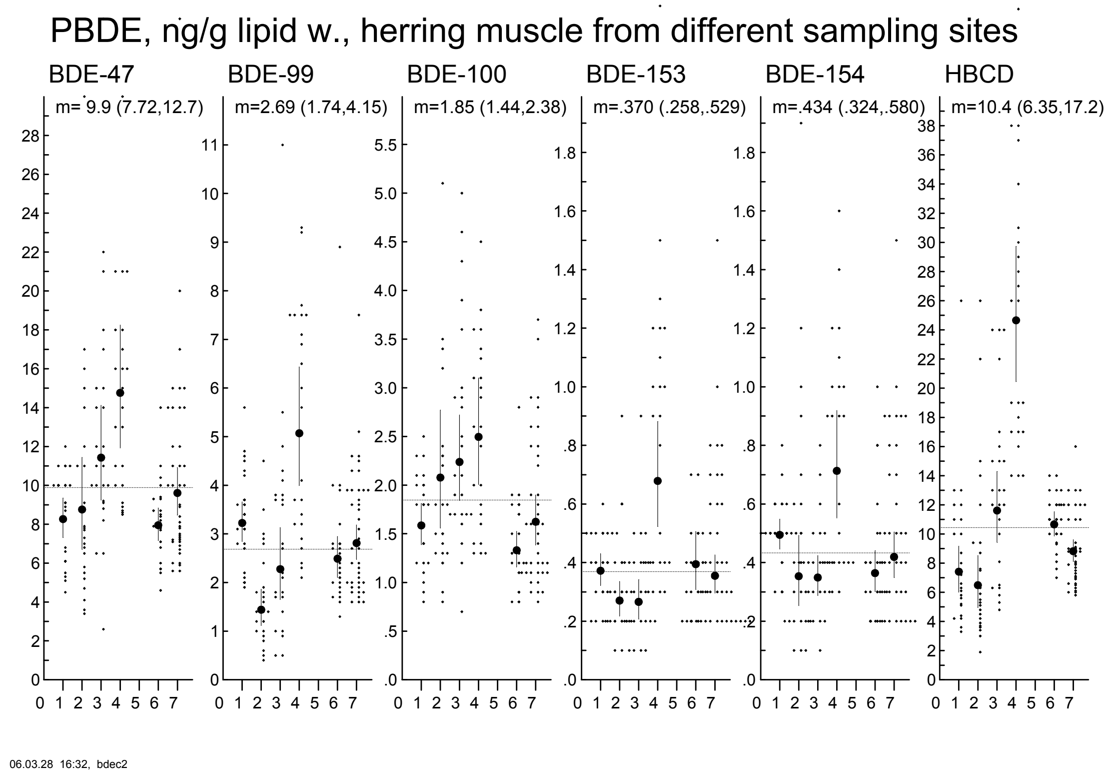
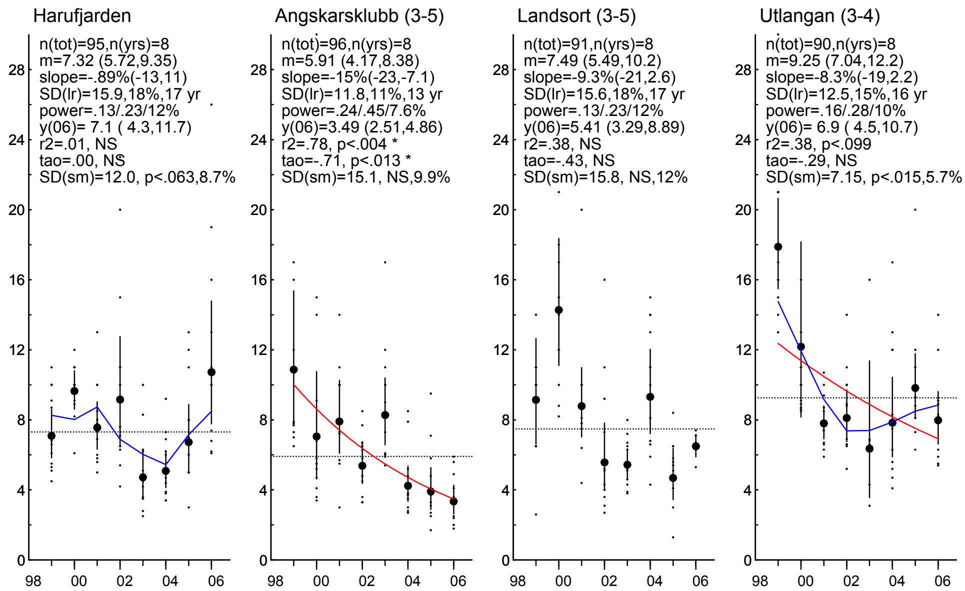


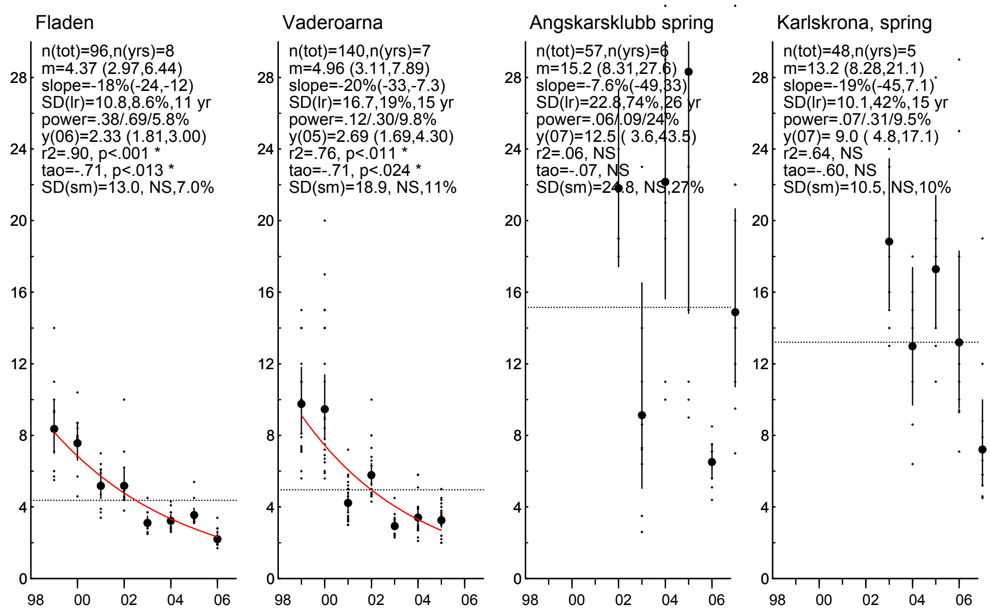
Figure 23.2: Spatial variation of some polybrominated flame retardants. 1=Harufjärden (Bothnian Bay), 2=Ängskärsklubb (S. Gulf of Bothnia), 3=Landsort (N. Baltic Proper), 4=Karlskrona (S.Baltic Proper), 6=Fladen (Kattegatt), 7=Väderöarna (Skagerack)

BDE-47, ng/g lipid w., herring muscle



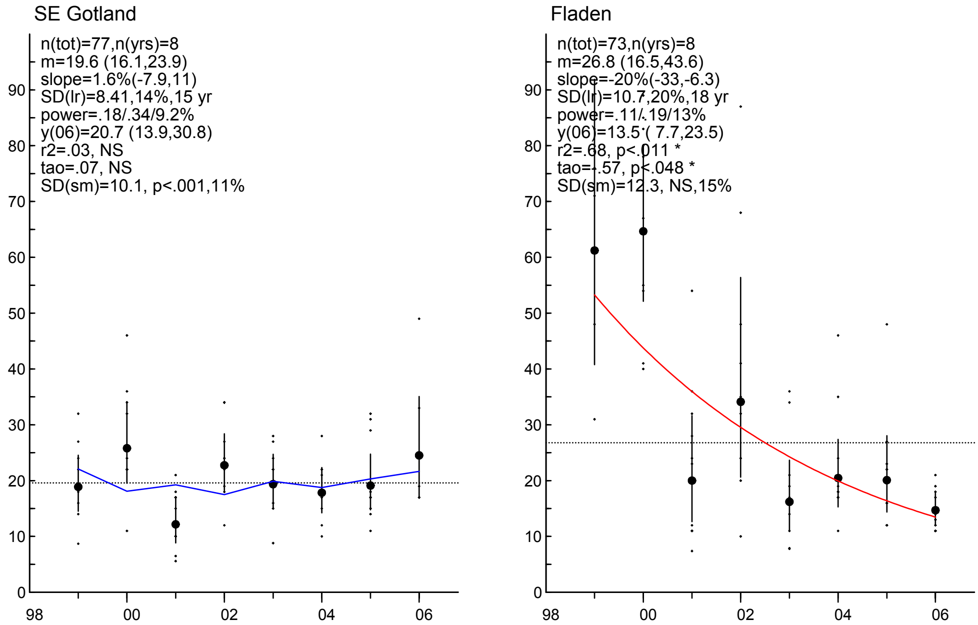
pia - 08.03.26 09:50, bde47c

BDE-47, ng/g lipid w., herring muscle



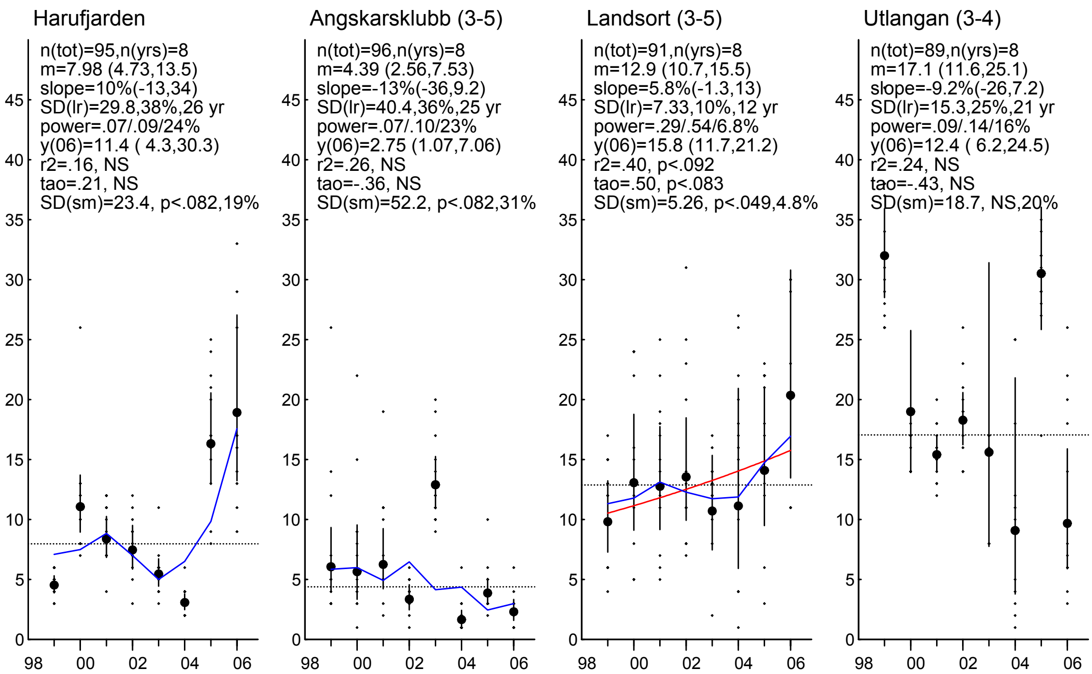
pia - 08.03.27 09:27, bde47v

BDE-47, ng/g lipid w., cod liver



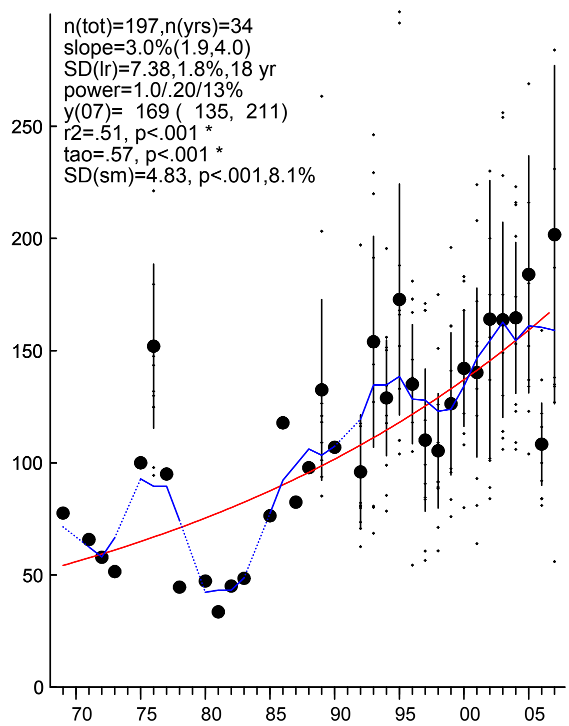
pia - 08.03.26 09:50, bde47g

HBCD, ng/g lipid w., herring muscle



pia - 08.03.26 09:51, hbcdc

HBCD in Guillemot egg, ng/g lipid w.



pia - 08.03.12 15:48, HBCDU

24 PAHs, Polyaromatic Hydrocarbons

Updated 07.03.31

Polyaromatic Hydrocarbons have been retrospectively analysed in blue mussels from Kvädöfjärden in a time series from 1987 to 1999. PAHs are since 2003 analysed from three blue mussels locations, Kvädöfjärden in the Baltic and Fladen and Väderöarna at the Swedish west coast. The PAHs analysed are: Naphthalene, Acenaphtene, Fluorene, Phenantrene, Antracene, Flouranthene, Pyrene, Benso(a)antracene, Chrysene, Benso(b)fluoranthene, Benso(k)fluoranthene, Benso(a)pyrene, Dibenso(a,h)antracene, Benso(g,h,i)perylene and Indeno(1,2,3-cd)pyrene.

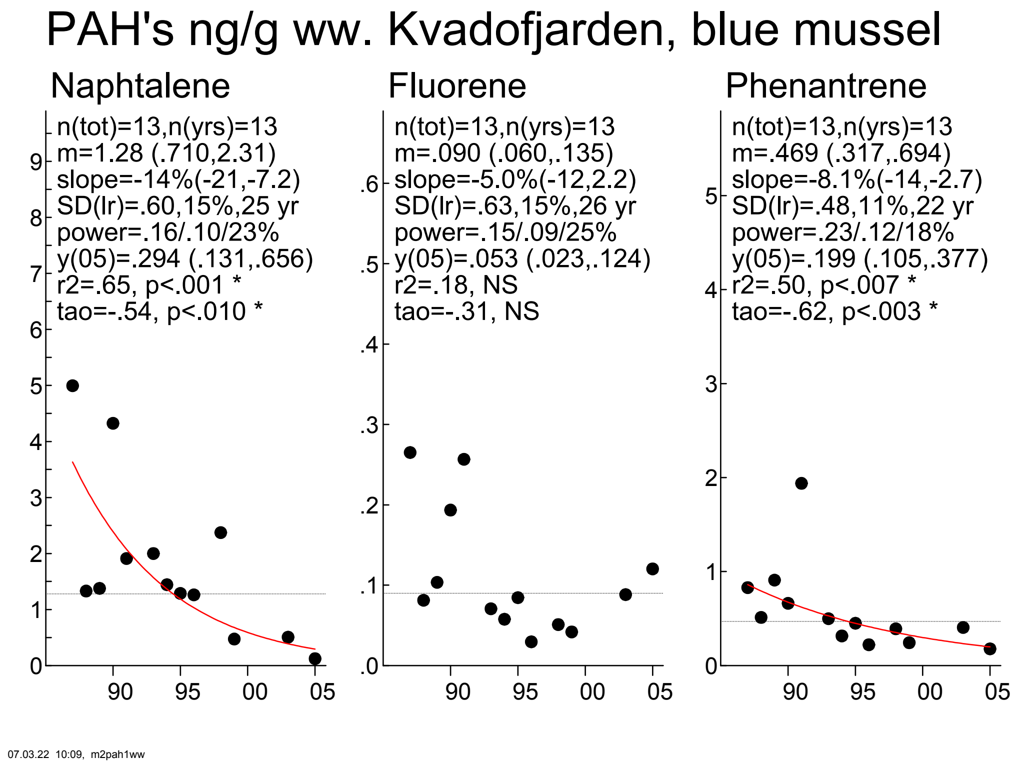
24.1 Temporal variation

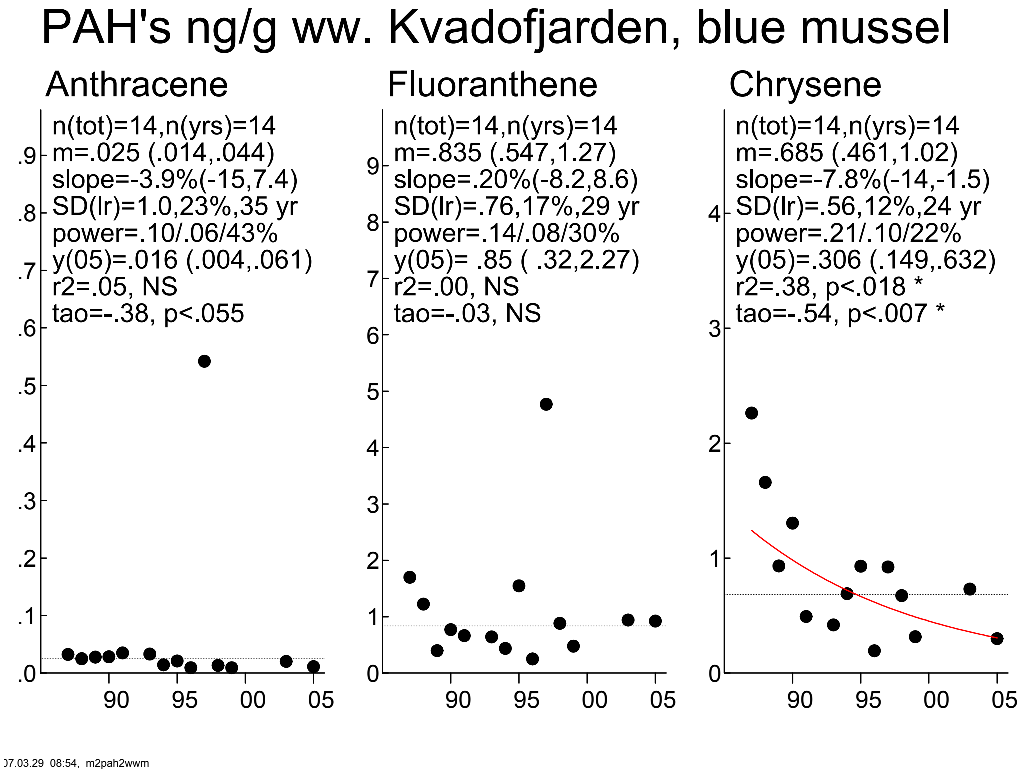
24.1.1 This investigation

Significant decreasing trends are found in the time series for the majority of the PAHs (Naphthalene, Phenantrene, Anthracene, Chrysene, Benso(k)fluoranthene, Indeno(1,2,3-cd)pyrene, Dibenso(a,h)anthracene and Benso(g,h,i)perylene) in blue mussel from Kvädöfjärden. Acenaphtene was almost never found over the detection limit, 86% of the analyses were below and for Benso(a)antracene 7% were below. Anthracene and Fluoranthene are extremely high in concentration in 1997 and these results are considered to be extreme outliers. Below both the time trends are shown (with and without extreme outliers) and the power and number of years required to detect a trend are greatly improved when the outliers are excluded.

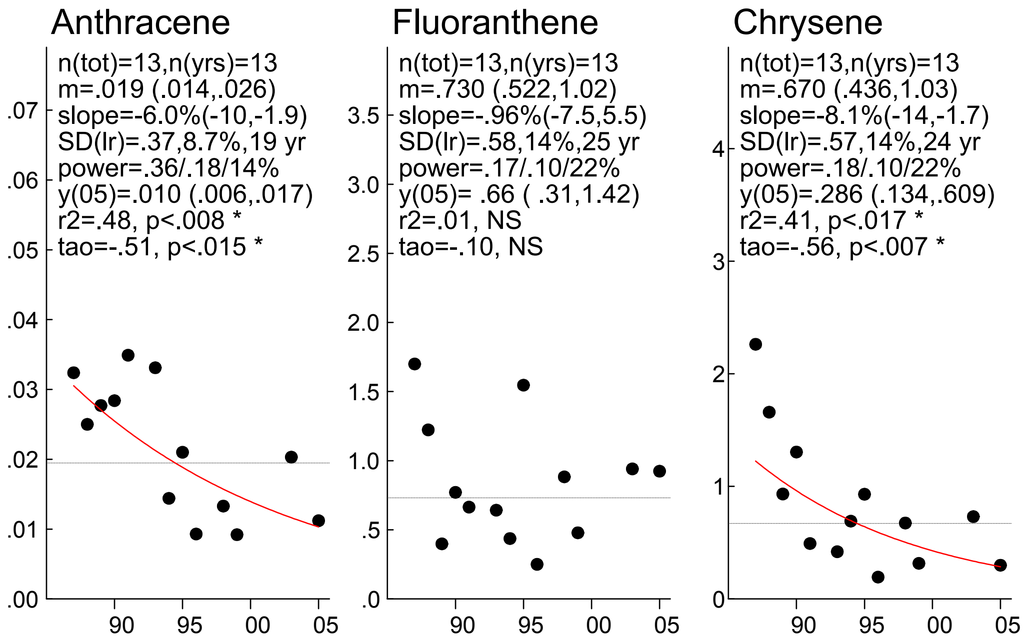
Tabell 24.1. Number of analysis (in %) below LOQ and number of years to detect a trend of 5% with a power of 80% for PAHs in blue mussel in Kvädöfjärden.

Substance	% below LOQ	n years to detect a trend of 5%
Naphtalene	0	25
Acenaphtene	86	46
Fluorene	0	26
Phenantrene	0	22
Anthracene	0	19
Fluoranthene	0	25
Pyrene	0	23
Benso(a)antracene	7	29
Chrysene	0	24
Benso(b)fluoranthene	0	27
Benso(k)fluoranthene	0	25
Benso(a)pyrene	0	27
Dibenso(a,h)anthracene	0	25
Benso(g,h,i)perylene	0	25
Indeno(1,2,3-cd)pyrene	0	24


PAH's ng/g ww. Kvadofjarden, blue mussel
Naphtalene
n(tot)=13,n(yrs)=13
m=1.28 (.710,2.31)
slope=-14%(-21,-7.2)
SD(lr)=.60,15%,25 yr
power=.16/.10/23%
y(05)=.294 (.131,.656)
r2=.65, p<.001 *
tao=-.54, p<.010 *
Fluorene
n(tot)=13,n(yrs)=13
m=.090 (.060,.135)
slope=-5.0%(-12,2.2)
SD(lr)=.63,15%,26 yr
power=.15/.09/25%
y(05)=.053 (.023,.124)
r2=.18, NS
tao=-.31, NS
Phenantrene
n(tot)=13,n(yrs)=13
m=.469 (.317,.694)
slope=-8.1%(-14,-2.7)
SD(lr)=.48,11%,22 yr
power=.23/.12/18%
y(05)=.199 (.105,.377)
r2=.50, p<.007 *
tao=-.62, p<.003 *
90 95 00 05
07.03.22 10:09, m2pah1ww

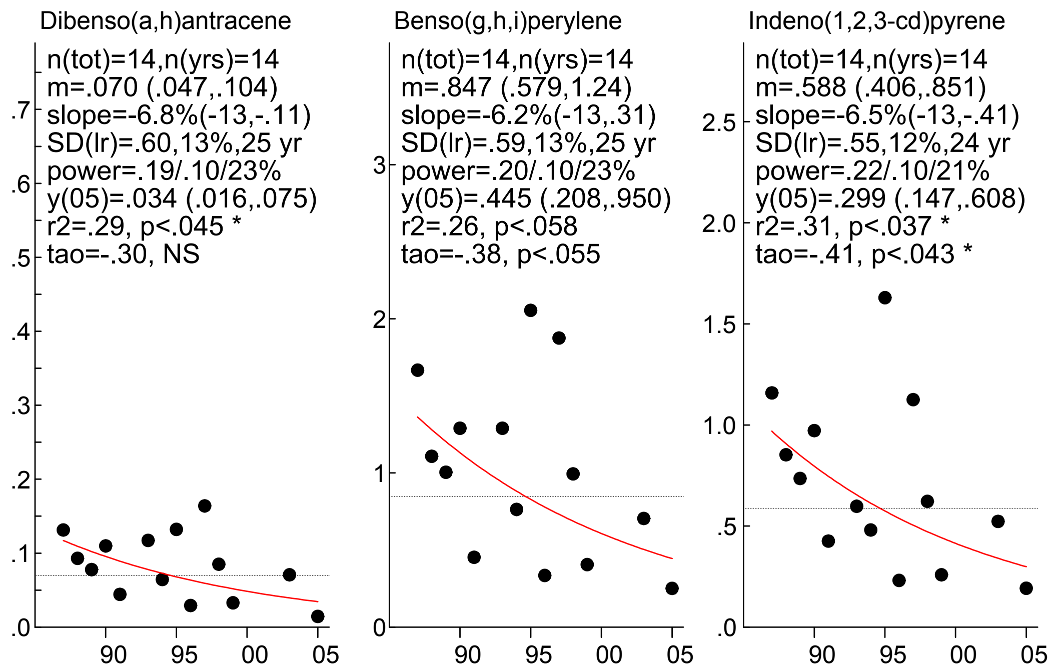

PAH's ng/g ww. Kvadofjarden, blue mussel
Anthracene
n(tot)=14,n(yrs)=14
m=.025 (.014,.044)
slope=-3.9%(-15,7.4)
SD(lr)=1.0,23%,35 yr
power=.10/.06/43%
y(05)=.016 (.004,.061)
r2=.05, NS
tao=-.38, p<.055
Fluoranthene
n(tot)=14,n(yrs)=14
m=.835 (.547,1.27)
slope=.20%(-8.2,8.6)
SD(lr)=.76,17%,29 yr
power=.14/.08/30%
y(05)= .85 (.32,2.27)
r2=.00, NS
tao=-.03, NS
Chrysene
n(tot)=14,n(yrs)=14
m=.685 (.461,1.02)
slope=-7.8%(-14,-1.5)
SD(lr)=.56,12%,24 yr
power=.21/.10/22%
y(05)=.306 (.149,.632)
r2=.38, p<.018 *
tao=-.54, p<.007 *
90 95 00 05
07.03.29 08:54, m2pah2wwm

PAH's ng/g ww. Kvadofjarden, blue mussel (1997 excl)

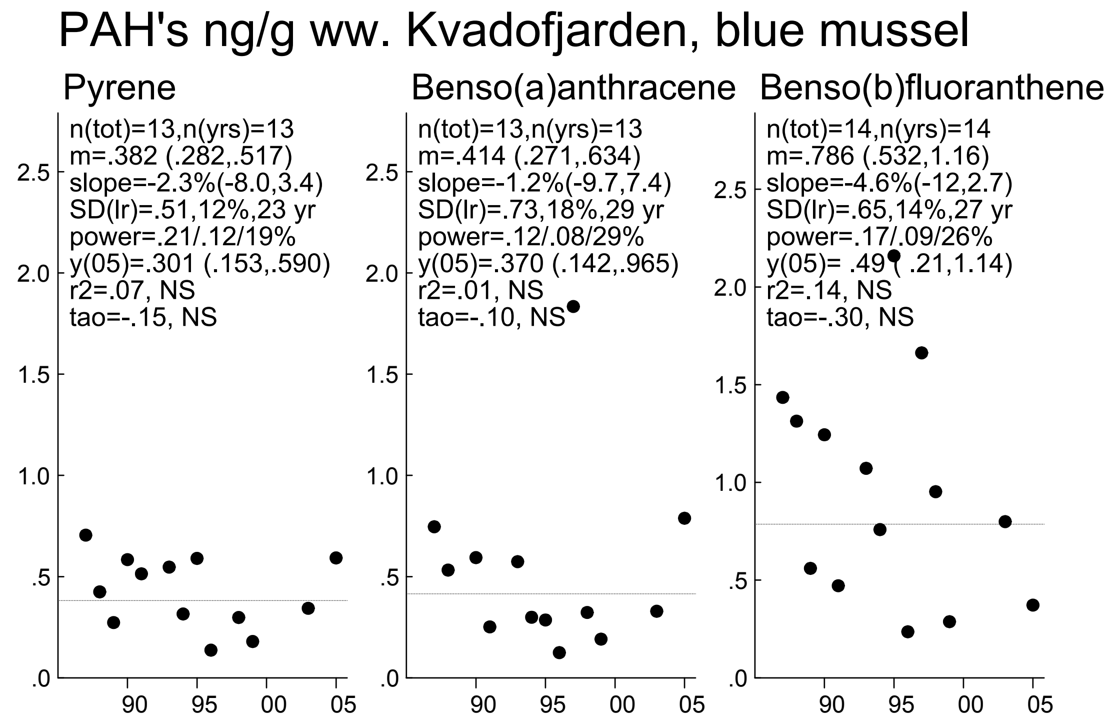


pia - 07.03.22 10:20, m2pah2wwe

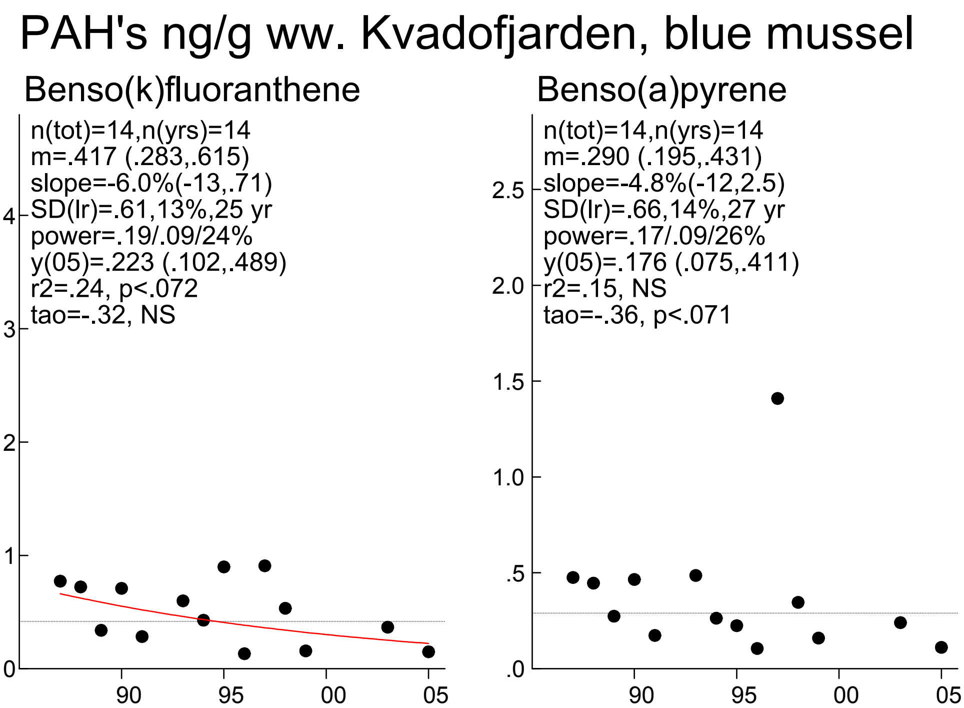
PAH's ng/g ww. Kvadofjarden, blue mussel



07.03.22 13:34, m2pah5ww



a - 07.03.22 09:21, m2pah3ww



07.03.22 13:22, m2pah4ww

25 Perfluorinated substances

Updated 07.06.01

Perfluorinated substances have been used industrially and commercially since the beginning of the1950s and it was not until recently (2000) that the main producer, 3M, started to phase out their production of the main compound of concern, perfluorooctane sulfonate (PFOS) and PFOS-related chemicals (Key et al., 1997 and Holmström et al., 2005).

PFOS has been retrospectively analysed in guillemot eggs from St. Karlsö in a time serie starting 1968. Additionally, a selection of perfluorinated substances has been analysed in herring liver tissue during the last years. These comprised perfluorinated carboxylates (PFCAs): perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDcA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorotridecanoate (PFTriA), perfluorotetradecanoate (PFTeA), perfluoropentadecanoate (PFPeDA) as well as perfluorinated sulfonates (PFSs): perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), PFOS, perfluorodecane sulfonate (PFDcS), perfluorooctane sulfonamide (PFOSA) and 6:2 fluorotelomer sulfonate (6:2 FTS).

25.1 Temporal variation

25.1.1 This investigation

A significant increasing trend is observed for PFOS in guillemot eggs with 7-11% per year, which is equal to an increase to 25-30 times higher levels in the early 2000s as compared to the late 1960ties. Due to change of the analytical method between 2003 and 2004 and relatively high inter-annual variations, the future trend for PFOS concentrations in the Baltic marine environment cannot be predicted. Further monitoring will reveal if the phase out by 3M will make a difference for the PFOS concentrations in biota.

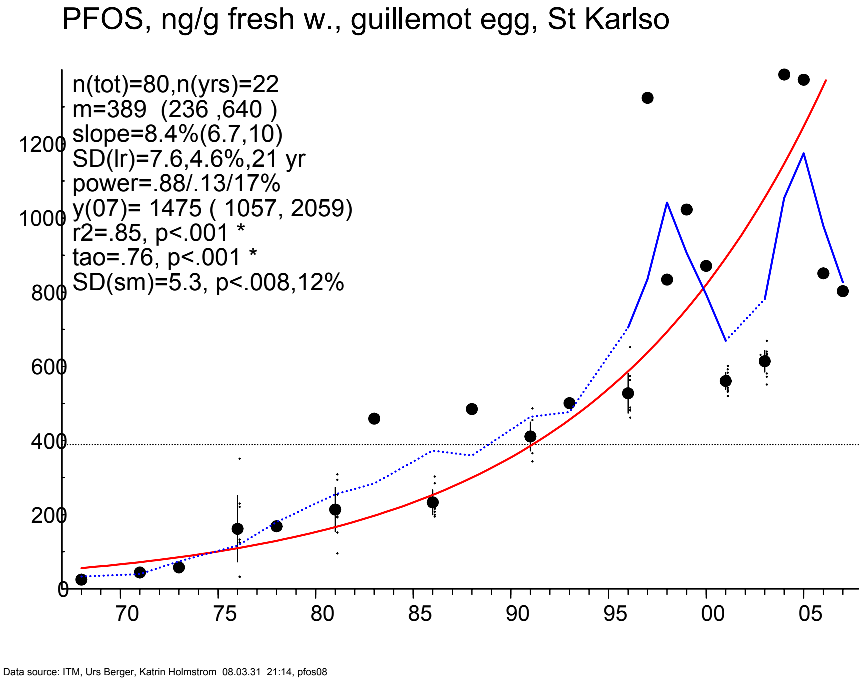


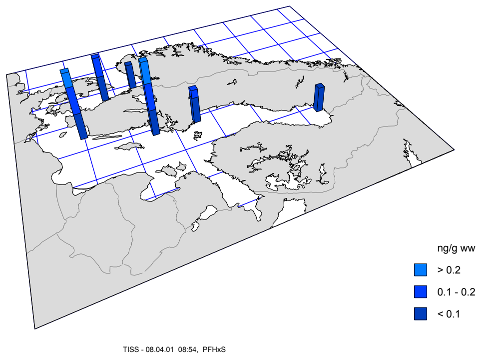
Figure 25.1 Temporal trend of PFOS concentrations in guillemot eggs (ng/g w.w.). The mean annual PFOS value shown as red dot in the figure of the time series is based on pooled samples or mean values of individual samples.

25.2 Spatial variation

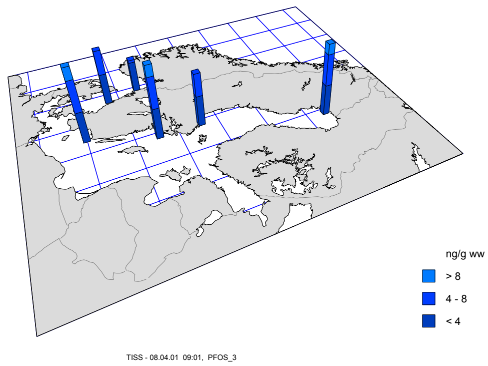
25.2.1 This investigation

So far only two years (2005-06) of analysis in herring liver are available (pooled samples, 10 fish in each). Therefore, the obtained results have to be interpreted carefully. However, it has been shown that the individual variation of perfluorinated substances is relatively small compared to classical POPs (Verreault et al., in press). The spatial variations of 7 perfluorinated substances (3 PFSs in Figure 25.2: PFHxS, PFOS and PFOSA; 4 PFCAs in Figure 25.3: PFNA, PFDcA, PFUnA and PFTriA) are presented below. The selection was based on number of results above LOQ.

A)



B)



C)

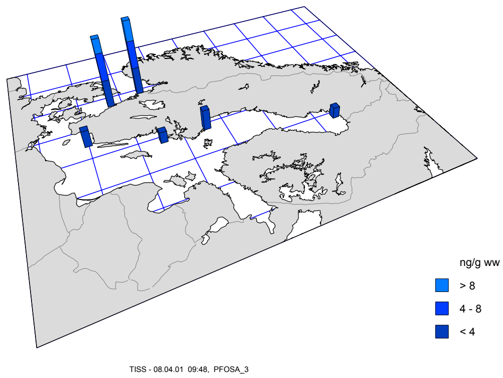
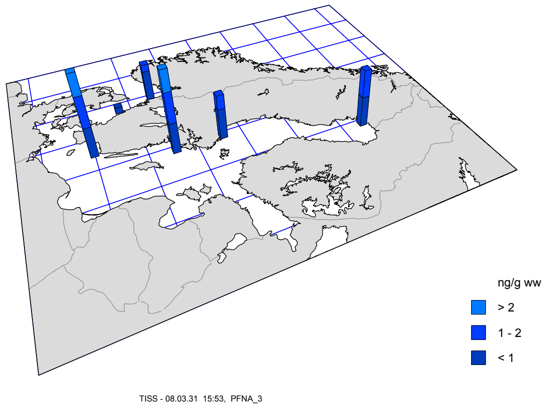


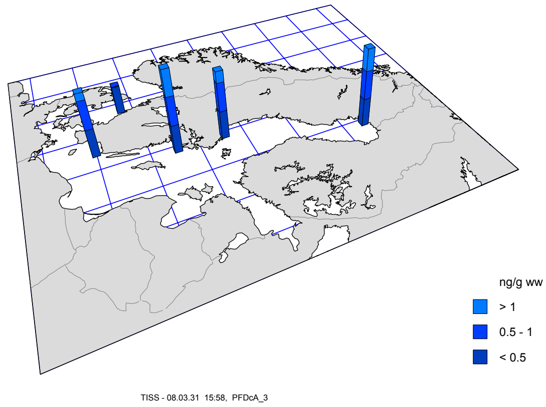
Figure 25.2 Spatial variation in concentration (w.w.) of **A)** PFHxS, **B)** PFOS and **C)** PFOSA in herring liver. Highest concentration of PFHxS) and PFOS were 0.22 ng/g and 7.85 ng/g, respectively. Highest concentration of PFOSA (14.2 ng/g) was found at Fladen in the Kattegatt.

PFHxS and PFOS show a very similar spatial pattern, but PFOS concentrations were approximately 45 times higher than PFHxS levels. This was as expected, since PFHxS has not been produced intentionally, but only occurred as by-product in technical PFOS. Furthermore, the distribution of PFOS and PFHxS is quite homogenous along the Swedish coast, which is a result of the extraordinary persistency of these compounds and the long history of use (three decades). The somewhat higher levels in the south might reflect the higher population density and associated current emissions from consumer products still containing technical PFOS. PFOSA, however, is not persistent, but a precursor compound to PFOS. The high concentrations at the west coast reflect a current source probably located around the North Sea. The relatively short environmental half-life of PFOSA does not allow it to diffuse into the Baltic, due to the low water exchange between the two seas. Degradation of PFOSA to PFOS might also contribute to the higher PFOS levels in Southern Sweden compared to the north. Taken into account that liver generally contains about 5 times higher concentrations than fish muscle, PFOS levels in herring liver are in agreement with levels found in other fish species from the Baltic (Swedish Environmental Protection Agency, 2007). PFOS concentrations in guillemot eggs from 2005, however, are about 200 times higher than in herring liver (herring being the main prey of guillemot), showing the high retention of this compound in guillemot and the transport potential to the forming egg.

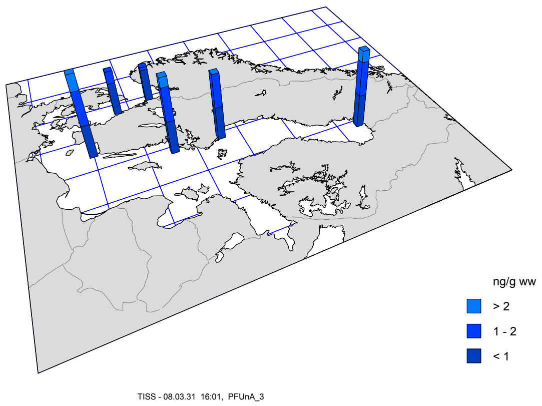
A)



B)



C)



D)

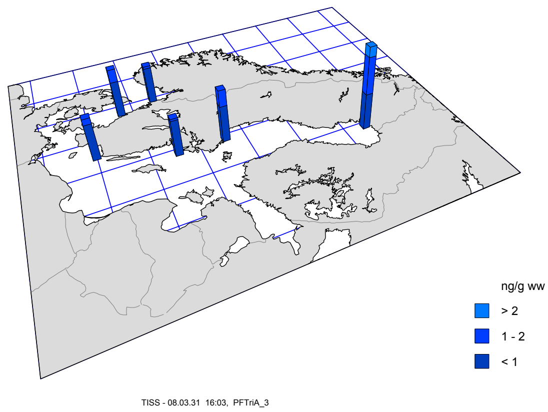


Figure 25.3 Spatial variation in PFCA concentrations (w.w.) of **A)** PFNA, **B)** PFDcA, **C)** PFUnA and **D)** PFTriA in herring liver. Highest concentrations of PFNA (2.57 ng/g) and PFDcA (3.91 ng/g) were found at Örefjärden (close to Holmöarna) in the Bothnian Bay and lowest (0.26 and 0.59 ng/g, respectively) at Fladen in the Kattegatt, whereas the levels at Väderöarna were below LOQ for both PFNA and PFDcA. Highest concentrations of PFUnA (2.59 ng/g) and PFTriA (2.16 ng/g) were found at Harufjärden in the Bothnian Bay and lowest (0.56 and 0.72 ng/g, respectively) at Väderöarna in the Skagerack.

PFCAs in the environment can have two types of sources, direct sources (from manufacturing and use of PFCAs) and indirect sources (from degradation of volatile precursor compounds) (Prevedouros et al., 2006). PFNA is intentially produced and therefore probably originates mainly from direct sources (production and use of consumer products containing PFNA, such as PTFE products) and waterborne transport to remote locations. This may partly explain the spatial variations of PFNA in this study, as sewage treatment plant effluents from industry or larger cities could represent hot-spots. In contrast, PFUnA and PFTriA are unintentionally produced substances, and their presence in the environment is probably due to both direct sources (impurities in PFOA and PFNA productions) and indirect sources (atmospheric transport and degradation of precursors). The fact that the odd-chained PFUnA and PFTriA are higher concentrated than PFDoA and the homogenous spatial distribution of these compounds supports the theory that indirect sources are important for these long-chain PFCAs. Also levels and compound patterns of

PFCAs are in good agreement with concentrations in other Baltic fish (Swedish Environmental Protection Agency, 2007).

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