

Miljögifter och metaller i biologiskt material från marin miljö

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> Programområde Hav

Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota

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Compiled by

Anders Bignert

Contaminant Research Group at the Swedish Museum of Natural History

Lillemor Asplund

Institute of Applied Environmental Research at the University of Stockholm

Anders Wilander

Centre for Environmental Monitoring at the University of Agriculture

Chemical analysis:

Organochlorines

Institute of Applied Environmental Research at the University of Stockholm

Trace metals

Centre for Environmental Monitoring at the University of Agriculture

PCDD/PCDF

Institute of Environmental Chemistry at the University of Umeå

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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 *Institute of Applied Environmental Research* at Stockholm University (analyses of organochlorines), the *Centre for Environmental Monitoring* at the University of Agriculture (analyses of heavy metals) and the *Contaminant Research Group* at the Swedish Museum of Natural History (co-ordination, sample collection administration, sample preparation, recording of biological variables, minor additional analyses of organochlorines, 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* 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 biological 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 status and to serve as 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, liver somatic index (LSI) and fat content are monitored at all sites. At some few sites, integrated monitoring with fish physiology and population are running in co-operation with the Swedish Fishery Board.
- experiences from the national program with several time series of over 20 years can be used in the design of regional and local monitoring programmes.
- the perfectly unique material of high quality, long time series is further used to explore relationships among biological variables and contaminants 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 2002/03

A short summary of the results up to year 2002/03 is given below. Graphical presentations, tables and details are given in the following chapters. A summary of the estimated concentrations up to 2002/03 is given in table 23.3.

- The condition of herring in the Baltic is *decreasing* in almost all autumn time series. At the same time fat content is decreasing in herring from Harufjärden, Landsort and Utlängan (autumn and spring).
- Lead concentrations in herring, cod and perch livers are *decreasing* in almost all time series from both the Swedish west coast and 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 *stopped*. In herring from Ängskärsklubb a significant decrease can be seen for the last ten years, and in the time series from Landsort there is also indications of this decrease.
- 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 the mussel samples from Fladen and Väderöarna.
- HCH's are *decreasing* at almost all sites with a time serie 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 westcoast. However, some relatively *high concentrations* have been detected in the last years, and it looks like the decrease is levelling out.
- TCDD-equivalents have *not decreased* in herring at Harufjärden, Karlskrona and Fladen during the investigated timeperiod 1990-1999. There is a significant decrease of these substances in guillemot eggs from St Karlsö between 1970 and the middle of the 80-ies after that, the decrease has levelled out.

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. 4.

3.2 Collected specimens

For many species adult specimens are less stationary than sub-adults. 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. 3). 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 being collected.

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 togeter 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 20 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 50 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 sampling 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 certainly result in a considerably 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 <u>also</u> sampled in spring. These two series started already 1972 and are analysed only for organochlorines. This also implies that for these two sites it is possible to study seasonal differences and, where it is possible to adjust for these differences, that the time resolution is considerably improved.

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 3.6).

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.

Fish

For each specimen total body weight, total length, body length, sex, age (see chap. 3 for various age determination methods depending on species), reproductive stage, state of nutrition, liver weight and sample weight are registered.

The epidermis and subcutaneous fatty tissue are carefully removed. Muscle samples are taken from the middle dorsal muscle layer. 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.

Blue mussel

For each specimen total shell length, shell and soft body weight are registered. Samples for trace metals are analysed individually whereas samples for organochlorine determination are analysed in pools of about 50 specimen.

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 egg shell thickness are 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 rest of the analysed metals. 10 g is prepared for the 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 are coded and the codes are defined in a codelist (Persson, 1998). 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. In some cases, additional samples from special investigations have been used as reference values in the report.

	N of	
Species	individual	
	specimen	%
Herring	4078	48
Cod	950	11
Perch	685	8
Eelpout	350	4
Dab	345	4
Flounder	339	4
Guillemot	525	6
Blue mussel	1145	14
Total	8417	

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 westcoast. 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 fatsoluble 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 (Skagerrak).

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 and organochlorines (DDT's, PCB's, HCH's and HCB). 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 dioxines/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 are also recorded.

Table 4.1.1. 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 timeseries 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	body weight	length	liver weight	liver dry weight	muscle dry weight
	WEEK	(year)	(g)	(cm)	(g)	(%)	(%)
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 4.1.2 below.

Table 4.1.2. Average length at the age of three and age at the length of 16 cm at the various sites

	Average length (cm)	Average age (years) at 16
	at 3 years	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 is living below the halocline feeding on bottom organisms. It becomes sexually mature between 2-6 years in Swedish waters. The spawning takes place during the period May - August (occasionally spawning specimens could be found in Mars 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 westcoast. The cod specimens 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 also a very appropriate matrix for screening for 'new' contaminants.

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

Table 4.2.1. 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 timeseries 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	age	body	length	liver	liver dry
	week		weight		weight	weight
		(year)	(g)	(cm)	(g)	(%)
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)

The 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. 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).

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

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

Table 4.3.1. 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 timeseries 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	body weight	length	liver weight	liver dry weight
		(year)	(g)	(cm)	(g)	(%)
Fladen	37-44	2-6	50-250	15-30	0.5-2	20-40

4.4 Flounder (Platichtys flesus)

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

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

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

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

Table 4.4.1. 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 timeseries 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	body weight	length	liver weight	liver dry weight
		(year)	(g)	(cm)	(g)	(%)
Väderöarna	37-44	3-6	100-400	20-35	1-5	18-30

4.5 Blue mussel (Mytilus edulis)

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 Kattegat (Fladen, Nidingen), from the Skagerrak (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 samples are analysed for lead, cadmium, copper, zinc, mercury and organochlorines. In 1995 analyses of chromium and nickel were added. From 1995 samples from Kvädöfjärden 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 4.5.1. 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 timeseries below. The 95% confidence intervals for the yearly means of soft body weight and shell weight are also given.

	Sampling week	Sampling depth	shell length	shell weight	soft body weight
		(m)	(cm)	(g)	(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*)

Most of the guillemots do not migrate further than to the southern parts of the Baltic proper during the winter season. It feeds mainly on sprat (*Sprattus sprattus*) and herring (*Clupea harengus*). The guillemot breeds 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 egg. 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 timeserie has also been analysed for PCC (Wideqvist *et al.* 1993), dioxins/dibenzofurans and polybrominated compounds (Sellström, 1996). Various shell parameters e.g. shell weight, thickness and thickness index is also beeing monitored. Also the weight of several hundreds of fledglings are normally recorded each year at St Karlsö. Eggs are also beeing collected for some years from Bonden in the northern parts of the Bothnian Sea but so far only results (organochlorines) from 1991 are available.

4.7 Perch (Perca fluviatilis)

The perch males become sexually mature between 2-4 years and the females between 3-6 years. 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 Swedish Fishery Board. 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, cupper and zinc in perch liver were added to the programme.

Table 4.7.1. 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 timeseries 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	body weight	length	liver weight
		(year)	(g)	(cm)	(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 Swedish Fishery Board.

Eelpout specimens have been collected from Väderöarna in the Skagerrak 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, cupper and zinc whereas muscle tissue is analysed for mercury and organochlorines.

Table 4.8.1. 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 timeseries 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	total weight	length	liver weight	liver dry weight	muscle dry weight
		(year)	(g)	(cm)	(g)	(%)	(%)
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 1. The sampling sites are located in areas regarded as locally uncontaminated and, as much as possible, uninfluenced by major river outlets or ferry routes and not too close to heavy populated areas.

The Swedish sampling stations are parts 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).

Angskarsklubb

Vaderoarna

Kvadofjarden

St.Karlso
SE Gotland

Utlangan

Figure 1. Sampling sites within the National Monitoring Programme in Marine Biota

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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 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	НСН/НСВ	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 Fishery Board.

5.3 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.

5.4 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 countyboard 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.

5.5 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

At Landsort a pilot investigation has started to study the contribution of small-scale time and spatial variation to the total within- and between-year variation.

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

5.6 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 Fishery Board.

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.

5.7 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

5.8 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

5.9 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 Environmentaal 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.

5.10 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.

5.11 Väderöarna, Skagerrak, 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/	PCB/	HCH/	Hg	Pb/Cd/	Cr/Ni
Species	DDT	HCB		Cu/Zn	
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 (c 10 km east of Väderöarna). All species are collected during the autumn.

6 Analytical methods

Trace metals

The analyses of trace metals are carried out at the Centre for Environmental Monitoring at the University of Agriculture. Analytical metods 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

Organochlorines and brominated flame retardants

The analyses of organochlorines are carried out at the Laboratory for Analytical Environmental Chemistry at the Institute of Applied Environmental Research (ITM) at the University of Stockholm. 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)

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 2003. 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.

Standards

The original of all standards are certified with known purity and precision. The concentrations are calculated for each individual congener.

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 4000 PCB and pesticides

values from control samples during 10 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 600 values from control samples.

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

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 but new sampling location are also examined for suitable internal standard.

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 switched to CRM 682 and 718, mussel (whole body) respectively herring (muscle), as being better representants since they cover the whole extraction procedure. Each of those samples are analysed twice a year. Until now no CRM exist for BFRs.

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. 370 values of the 376 values that the laboratory has produced during the years have been within statistical control, meaning they have falling within +/- 3 sd of the assigned value and have not been falling outside +/- 2 sd two values after each

other. 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. The laboratory has performed with good results for these first two studies.

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.

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 is performed both for the *entire investigated time period* and for time series longer than ten years, also for the *recent ten years*.

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 continous 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 analyses presupposes, among other thing, 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 timeserie has become unwarrantable great on the slope. Hence, the eighth line reports Kendall's 't', 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 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 would be some 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 the liver 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 too far from the regression line considering from what could be 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 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. Each site/species is represented by a separate plot except for 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 timeserie 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 timeserie 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 indicate a gap in the time serie 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 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:

 $\mathbf{n(tot)}$ = The first line reports the total number of analyses included together with the number of years ($\mathbf{n(yrs)}$ =).

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 timeserie with a power of 80%, one-sided test, α =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, α =0.05.

power= reports the power to detect a log-linear trend in the timeserie (Nicholson & Fryer, 1991). The first figure represent the power to detect an annual change of 5% with the number of years in the current timeserie. 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.

 \mathbf{r}^2 = reports the coefficient of determination (\mathbf{r}^2) together with a p-value for a two-sided test (\mathbf{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.

8 The power of the programme

Before starting to interprete the result from the statistical analyses of the time series it is essential to know with what power temporal changes could be detected (i.e. the chance to reveal true trends with the investiged matrices). It is of course 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 would be 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 serie.

The first task would thus be to estimate the 'random' between-year variation. In the results presented below this varation 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 serie. 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 seems 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 criteras, are deleted, the calculated median sensitiveness improved to 5.8%. In the presented results also suspected outliers are included which means that the power and sensitiveness are underestimated.

Table 9.1. 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 15 years, PCB and DDT for about 17 years (spring caught herring and guillemot egg however, more than 20 years) and HCH and HCB only about 7-8 years.

Table 9.1. 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	Z 1	Z2	Z3	M2	M6	M3	L6	P3	U8
Hg	22	22	12	23	23	11	23	8	24	24	9	9	7	8	8	8	20	22	14	15	30
Pb	20	21	8	22	22	7	22	8	22	22	8	7	6	8	7	8	20	20	14	14	7
Cd	21	21	8	22	22	7	22	8	22	22	8	7	6	8	7	8	20	20	14	14	7
Ni	8	8	8	8	8	7	8	8	8	8	8	8	6	8	7	7	8	8	-	-	7
Cr	8	8	8	8	8	7	8	8	8	8	8	8	6	8	7	7	8	8	-	-	7
Cu	21	21	8	22	22	7	22	8	22	22	8	8	6	8	7	8	20	20	14	14	7
Zn	20	20	8	21	21	8	21	8	21	21	8	7	6	8	7	8	20	20	13	13	7
sPCB	23	23	30	24	23	29	23	-	23	21	17	20	-	-	-	-	20	20	13	15	33
CB-153	14	14	15	16	15	15	15	8	14	13	10	16	7	8	8	7	15	14	5	6	16
sDDT	23	23	30	24	23	29	23	8	22	22	18	23	7	8	8	8	19	22	14	15	33
α-НСН	11	14	12	16	15	14	14	6	14	14	5	13	5	6	4	8	14	13	6	6	13
β-НСН	10	12	15	16	15	15	10	1	-	-	-	-	-	-	-	-	-	-	-	_	16
ү-НСН	11	14	15	16	15	15	14	7	14	13	5	9	3	5	6	8	16	14	6	6	11
HCB	14	13	15	15	15	15	15	7	14	13	10	14	7	8	8	8	9	10	6	6	17

Table 9.2 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 timeserie and the possibility to statistically verify an annual change of 5% at a power of 80% generally requires 10-15 years.

Table 9.2. 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	L6	Р3	Median
Hg	16	*25	17	*19	15	*13	14	*14	15	11	*17	16	*23	15

Other trace metals

Based on geometric means on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3	L6	P3	Median
Pb	17	*17	16	20	17	20	21	*25	22	13	11	17
Cd	19	*18	*14	14	14	*17	*21	*15	*14	*22	*15	15
Cu	15	11	*15	14	*15	15	19	13	*14	11	16	14.5
Zn	*12	11	11	*10	9	15	15	*14	*17	7	8	11

Organochlorines

Based on geometric means on a lipid weight basis

	C1	C2	C3	C4	C6	V2	V4	U8	G5	G6	P1	P2	M6	M3	L6	P3	Median
sPCB	16	16	15	15	14	18	15	*12	17	*22	*18	*21	*16	*18	20	15	15.5
sDDT	*19	16	16	*17	21	19	15	17	16	*19	*21	24	24	*19	*24	*20	17
DDE	*21	16	18	17	18	19	16	*16	16	*18	31	25	21	19	13	20	18
α-НСН	11	16	13	9	8	10	11	15	10	10	8	14	13	18	18	16	12
β-НСН	10	15	13	12	25	10	14	12	11	23	-	-	24	17	-	-	13.5
ү-НСН	11	16	12	8	*16	11	*12	21	9	17	15	15	*17	*18	22	19	15
HCB	15	17	17	18	15	19	16	*14	18	*16	15	22	16	20	11	*32	17

^{*} indicates a significant non-linear trend component

In table 9.3 the lowest trend possible to detect within a 10 year period with a power of 80 % is presented both for the entire time serie and for the latest 10 year period. The table shows that the sensitiveness for lead has improved and is considerable better for the last 10 years compared to the entire timeseries. It further indicates that the sensitivenes for Pb, Cd and Cu is approximately the same (6-8%) whereas for zinc it is somewhat better (4-5%). For PCB, sDDT and HCB the estimated sensitiveness is about 8-10%. The timeseries 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 around 4-5%. Biological variables like the condition index for herring, cod and perch show a sensitiveness of about 1-2% and guillemot shell thickness 1%.

Table 9.3. 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 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	С3	C4	C6	G5	G6	P2	U8	M6	M3	L6	Р3	Median
Hg	11	23	12	-	9.7	8.3	-	10	-	6.8	-	11	-	10.5
_	13	21	13	-	9.8	6.2	-	9.3	-	7.3	-	9.9	-	9.85

Other trace metals

Based on geometric means on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3	L6	Р3	Median
Pb	11	-	11	15	14	16	17	24	19	8.1	12	14.5
	12	-	15	11	9.3	21	12	13	7.0	6.9	5.3	11.5
Cd	15	-	-	8.3	8.7	-	-	-	9.4	-	-	9.05
	18	-	-	7.6	8.0	-	-	-	6.3	-	-	7.8
Cu	9.4	5.9	-	8.0	-	9.2	15	7.1	-	6.6	11	8.6
	8.5	4.1	-	5.8	-	12	15	7.5	-	5.3	11	8.0
Zn	-	5.5	5.5	-	4.0	9.3	9.1	-	-	3.7	5.5	5.5
		7.3	3.8	-	4.5	14	7.1	-	-	2.7	3.1	4.5

Organochlorines

Based on geometric means on a lipid weight basis

	C1	C2	V2	C3	C4	V4	C6	G5	G6	P1	P2	U8	M6	M3	L6	Р3	Med
sPCB	10	11	13	9.2	9.7	9.7	8.7	12	-	13	-	-	-	-	15	11	11
	8.6	10	19	11	12	9.7	10	11	-	11	-	-	-	-	15	9.3	11
sDDT	-	11	15	11	11	9.5	17	10	-	17	22	-	21	-	-	-	13
	-	11	20	9.6	13	8.7	16	12	-	14	22	-	20	-	-	-	13.5
DDE	-	10	15	12	12	10	14	11	-	33	23	-	17	14	9.1	-	13
	-	9.5	22	12	13	9.5	17	11	-	8.9	20	-	14	9.1	7.4	-	11.5
α-НСН	5.7	10	4.9	7.3	3.6	5.3	3.2	4.7	4.6	3.0	8.8	9.9	7.8	13	-	10	5.5
β-НСН	4.5	9.5	4.9	7.4	6.5	-	22	5.7	19			6.6	22	11			7.4
ү-НСН	5.7	11	5.9	6.3	-	-	11	3.7	-	9.3	14	17	-	-	-	13	9.3
HCB	9.8	12	14	12	-	10	9.2	13	-	9.3	18		10	16	5.7	-	11

Biological variables

	C1	C2	V2	C3	C4	V4	C6	G5	G6	P1	P2	U8	M6	M3	L6	Р3	Me.
Cond	1.7	2.3	-	-	1.7	1.7	2.2	-	-	1.7	1.2						1.7
	1.9	1.4	-	-	1.6	2.0	2.0	-	-	1.5	1.5						1.6
Fat	8.6	10	-	12	10	9.9	11	-	19	2.5	-	3.5	-	-	2.9	5.3	9.95
	6.2	8.4	-	12	8.5	9.7	9.7	-	11	2.5	-	1.5	-	-	2.9	6.5	8.45

Table 9.4 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 timeseries the estimated power is between 80-100% in most cases. For the shorter timeseries of HCH's and HCB however, only about 50%. 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 9.4. 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 have been used. A * indicates that a significant non-linear trend have caused a low value.

Mercury

Based on annual geometric mean concentrations on a fresh weight basis

	C1	C2	C3	C4	C6	G5	G6	P2	U8	M6	M3	L6	P3
Hg	1.0	.65	1.0	*.98	1.0	1.0	*1.0	.22	*1.0	1.0	*.99	.62	*.39

Other trace metals

Based on annual geometric mean concentrations on a dry weight basis

	C1	C2	C3	C4	C6	G5	G6	M6	M3	L6	Р3
Pb	.98	*.99	1.0	.94	.98	.92	.89	.49	.69	.86	.77
Cd	.92	*.98	*1.0	1.0	1.0	*1.0	*.87	*1.0	1.0	*.31	*.59
Cu	1.0	1.0	*1.0	1.0	*1.0	1.0	.95	1.0	*1.0	.96	.67
Zn	*1.0	1.0	1.0	*1.0	1.0	1.0	1.0	*1.0	*.98	.99	.97

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	L6	Р3
sPCB	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	*.82	.82	*.83	*1.0	*.88	*.80	.36	.70
sDDT	*.98	1.0	1.0	1.0	*1.0	1.0	.92	1.0	*.96	.61	.76	*1.0	.51	*.95	*.31	*.36
DDE	*.94	1.0	1.0	1.0	1.0	1.0	.99	1.0	*.98	.22	.58	*1.0	.54	.70	.58	*.19
α-НСН	.83	.70	.98	.99	1.0	1.0	1.0	1.0	1.0	.25	.71	.71	.89	.40	.13	.15
β-НСН	.88	.53	1.0	.99	.99	.91	.10	.99	.08			1.0	.07	.07	-	-
ү-НСН	.83	.64	1.0	1.0	1.0	*.99	*.63	1.0	*.48	.07	.14	.23	*.77	*.51	*.12	.13
HCB	.72	.47	.52	.64	*.58	.79	.86	.50	*.54	.33	.29	*.99	.22	.15	.23	*.10

9 Condition

Updated 04.04.08

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:

$$K = 100 \text{ W} / \text{L}^3$$

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

Temporal variation

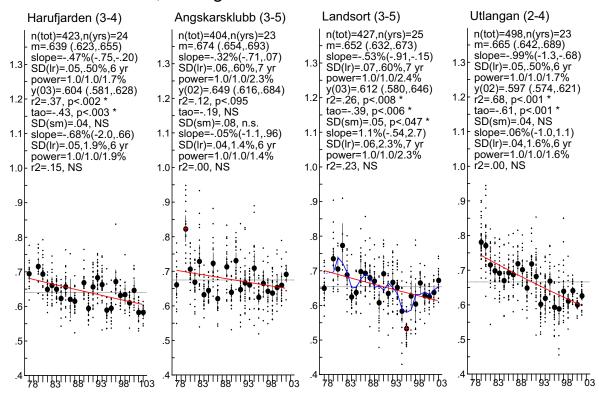
Significant decreasing trends for the condition factor of herring are observed from Harufjärden (-0.47%) Landsort (-0.53%) and Utlängan autumn (-0.99%) while it increases at Ängskärsklubb in spring caught herring (+0.56%). The increase at Ängskärsklubb may be explained by an unintentional increase of the average age over time in the collected samples from Ängskärsklubb.

The condition factor estimated for cod show significant upward trends at both Gotland (0.65%) and Fladen (0.68%) over the whole investigated period, but for the recent 5-10 years indications of a decreasing trend is observed at Fladen. The observed increase might be explained by the simultaneous decrease in population density during the investigated period.

Spatial variation

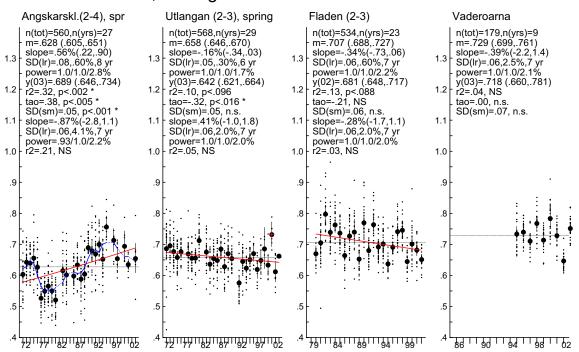
The average condition factor, estimated over a period of over 20 years, showed slightly but significantly lower values in herring sampled at Harufjärden in the northern parts of the Bothnian Bay compared to samples from Fladen and Väderöarna at the Swedish westcoast.

Condition factor, herring



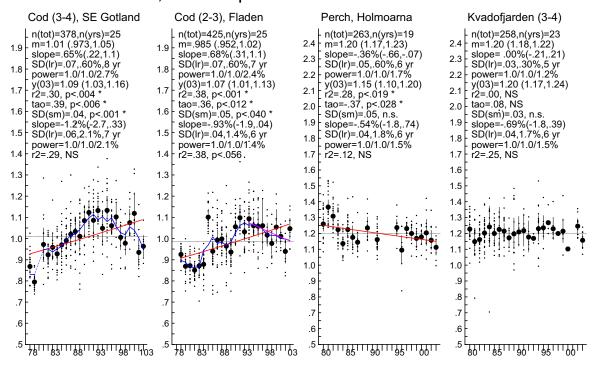
pia - 04.03.23 12:17, CONDC

Condition factor, herring



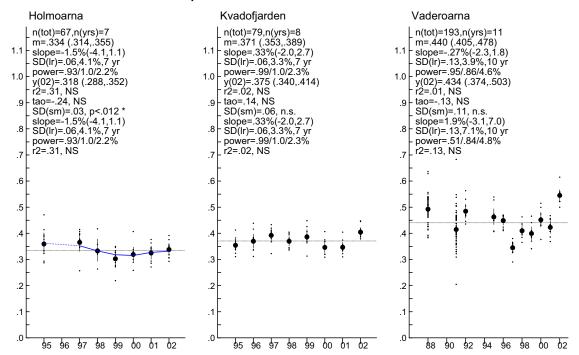
pia - 04.03.22 10:17, CONDV

Condition factor, cod and perch



pia - 04.03.22 10:08, CONDGP

Condition factor, eelpout



pia - 04.03.16 15:10, CONDZ

10 Fat content

Updated 04.04.08

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 showed (Bignert *et al.* 1993) but also between the concentration of various metals and fat content in cod liver (Grimås *et al.* 1985). The analysed concentration 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 organochlorines expressed on a fat weight basis.

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

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. In herring muscle tissue, the subcutaneous fat layer is removed before the samples are prepared.

Temporal variation

In the Baltic, *decreasing* trends in herring muscle tissue are indicated from Harufjärden (-1.4%), Landsort (-2.8%), Utlängan autumn (-4.4%) and spring (-2.3%). The fast decrease to really low levels at Landsort has now ceased and the fat content is back to around 3%. A decreasing trend can also be seen in herring from Fladen on the Swedish west coast (-2.0%).

An increasing trend in fat content are found in cod liver from south east of Gotland (3.3%). The fluctuating fat content in cod liver has to be considered when evaluating the time series of trace metals in cod liver (see above).

Decreasing trends of fat content of perch muscle are indicated at both Holmöarna (-0.89%) and Kvädöfjärden (-0.93%) in the Baltic. Eelpout from Holmöarna (-9.3%) is also showing a decline in fat content.

The time series of blue mussel from Kvädöfjärden shows an increase in fat content of +8.6% per year.

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 eightes 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 the Skagerrak is variable and can sometimes be about twice as high compared to herring muscle from the Baltic and the Kattegatt. This is not suprising since Atlantic herring muscle tissue may contain more than 20% fat.

The fat content in cod liver is highly variable even between specimen 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.

Seasonal variation

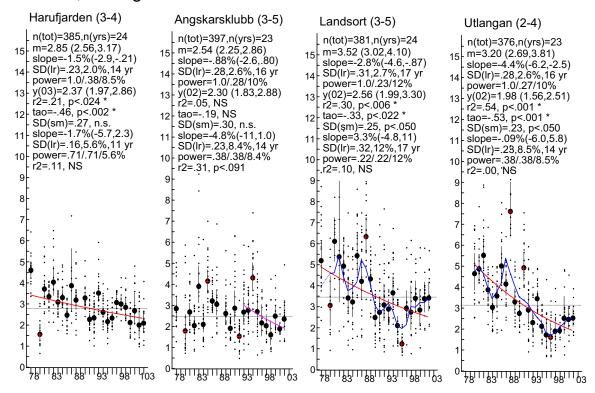
Fat content in spring caught herring from Ängskärsklubb show the same mean value (2.6%) as herring from the same site caught in the autumn whereas herring from Karlskrona archipelago caught in the autumn show about 50% higher mean fat content compared to spring caught herring from the same area.

Table 11.1. 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	Year	trend (95% ci)	last year (95% ci)
			yrs			
Herring muscle						
Harufj. autumn	3-4	373	23	78-02	-1.4 (-2.9, .01)*	2.9 (2.6-3.2)
Ängskärskl. aut.	3-5	397	23	78-02		2.5 (2.3-2.9)
" spring	2-4	587	30	72-03		2.6 (2.4-2.9)
Landsort	3-5	381	24	78-02	-2.8 (-4.6,87)*	3.5 (3.0-4.1)
Utlängan, aut.	2-4	376	23	80-02	-4.4 (-6.2, -2.5)*	3.2 (2.7-3.8)
" spring	2-3	556	29	72-02	-2.3 (-3.4, -1.2)*	2.2 (1.9-2.5)
Fladen	2-3	439	23	80-02	-2.0 (-4.0,13)*	3.9 (3.4-4.5)
Väderöarna		159	8	95-02		5.0 (3.5-7.3)
Cod liver						
SE Gotland	3-4	262	23	80-02	3.3 (2.3, 4.4)*	52 (47-59)
Fladen	2-3	278	22	80-02		17 (14-22)
Perch muscle						
Holmöarna	3-6	240	18	80-03	89 (-1.3,46)*	0.77 (.7381)
Kvädöfjärden	3-6	168	18	80-03	93 (-1.8,04)*	0.73 (.6778)
Eelpout muscle						_
Holmöarna	3-6	65	7	95-02	-9.3 (-18,62)*	.79 (.60-1.0)
Kvädöfjärden	2-6	79	8	95-02		.60 (.5170)
Väderöarna	3-5	130	9	88-02		.70 (.5490)
Dab muscle						_
Fladen	3-6	158	13	81-94	-3.7 (-5.2,-2.2)*	0.61 (.5468)
Flounder muscle						
Väderöarna	4-6	190	15	80-94	-3.4 (-5.7, -1.0)*	0.60 (.5073)
Blue mussel	shell 1					
Fladen	5-8	64	20	81-02		1.1 (.81-1.4)
Väderöarna	6-10	71	22	80-02		1.4 (1.1-1.6)
Kvädöfjärden	2-3	40	8	95-02	8.6 (.90, 16)*	1.3 (1.0-1.6)
Guillemot egg						
St. Karlsö		351	33	69-03		12.1 (11.7-12.6)

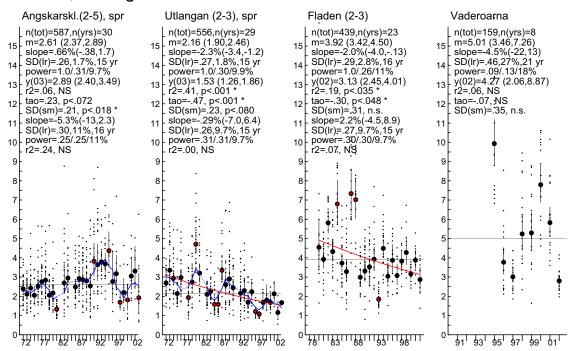
^{*} significant trend, p < 0.05

Fat %, herring muscle



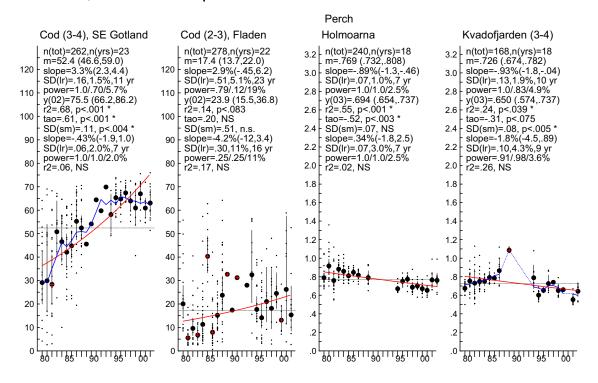
pia - 04.03.23 12:18, FATC

Fat %, herring muscle



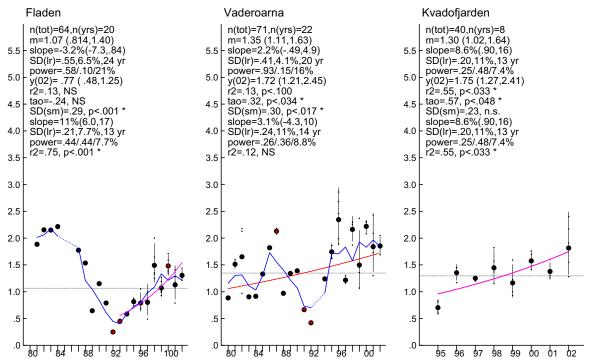
pia - 04.03.16 15:12, FATV

Fat %, cod liver and perch muscle



pia - 04.03.16 15:14, FATGP

Fat %, blue mussel soft body



pia - 04.03.22 10:10, FATM

11 Mercury

Updated 04.04.08

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 *Centre for Environmental Monitoring* at the University of Agriculture. The detection limit is estimated to approximately 10 ng/g dry weight.

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	%	%
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 thus estimated to be between 3-5% on 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 paid to intercallibrate the new method by reanalysing old samples both dried extracts and samples from the Environmental Specimen Bank.

Temporal variation

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.

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 (3.3%). Mercury was monitored in spring caught herring from Ängskärsklubb and Karlskrona for four years in the beginning of the seveties, and these series were taken up again in 1996. Both series show a significant decrease, -2.8% and -1.4% respectively.

The timeseries 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 our 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. Hower, in 1997 and 1999 the geometric mean concentrations increased to the same level that was recorded in the beginning of the eigthies.

The number of years required to detect an annual change of 5% varied between 12 to 19 (25 for Ängskärsklubb) years for the herring timeseries. The power to detect a 5% annual change is about 95% or more for the long herring and cod series. The large between year variation in Ängskärsklubb lowers the power of that specific time series to about 65%.

Perch muscle samples from Kvädöfjärden in the Baltic Proper show a significant decreasing trend of 4.7 % a year.

Cod from from SE of Gotland show a significant increasing linear trend of 1.9% a year. The trend for the last ten years is an increase of 5.7%.

Blue mussels from Kvädöfjärden in the Baltic Proper shows a significant increasing trend of 12% per year.

Guillemot eggs from St Karlsö in the Baltic proper show a significant decreasing trend of about 2% a year in mercury concentration. It should be noted that the mercury analyses in this timeseries have been carried out in a retrospective study i.e. all analyses have been performed at one occasion at the same laboratory.

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.

Spatial variation

Herring muscle from Ängskärsklubb show the highest mercury concentrations of all herring samples. This, we believe, is due to local discharges. Samples collected during the eighties from Ängskärsklubb is 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. However, since the

concentrations have increased at Landsort, the estimated levels for 2000 are approximately the same for Harufjärden, Ängskärsklubb, Landsort and Fladen all the sites mentioned above. The timeserie 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 Kattegat (c 50 ng/g) show significantly higher concentrations than samples from south east of Gotland (c 25-30 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 not higher than cod muscle samples in 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 compared to perch samples from Kvädöfjärden at the coast of the Baltic Proper. The estimated geometric mean concentration for Holmöarna 2000 is about 2-3 times higher than for Kvädöfjärden.

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 Kvädöfjärden in the Baltic Proper, from Fladen in Kattegatt and Väderöarna in Skagerack show no spatial variation (only six years of samples from Kvädöfjärden has been analysed so far). The overall mean concentration in blue mussel samples from all three sites, exceed, but only to a minor degree, 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 2001 in herring and cod muscle, 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). It should be noted, though, that the concentrations in Fladen has exceeded the proposed range a few times in the recent years.

Seasonal variation

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

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 westcoast.

Holmöarna: Eelpout(67) > Perch(63)

Kvädöfjärden: Eelpout(81) > Perch(37) > Blue mussel(14) Fladen: Dab(80) > Cod(50) > Herring(24) > Blue mussel(12)

Väderöarna: Flounder(38) > Herring(24) > Eelpout(22) > Blue mussel(13)

The mercury concentration found in blue mussel is in general lower than in fish muscle. The levels found in guillemot eggs were 4 to 20 times higher compared to the levels found in fish muscle.

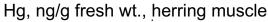
The levels found in fish muscle from the various sites all fall below the suggested limit for human consumption (500 ng/g fresh weight) by a factor 6-25. However, the suggested limit for childrens food is 50 ng/g, which is close to the overall mean concentration i fish muscle from the investigated sites.

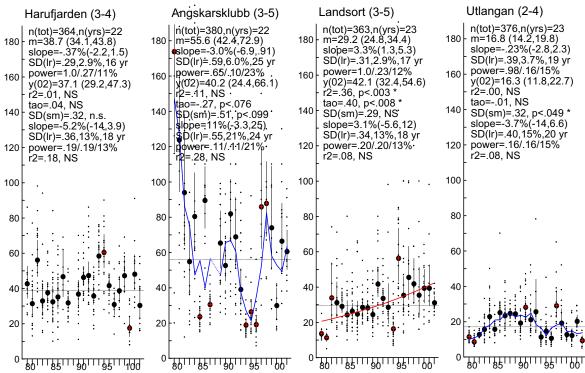
Table 12.2. Estimated geometric mean concentrations of **mercury** (ng/g fresh weight) for the last sampled year in various matrices and sites during the investigated time period. The trend is reported, if p<0.1. The age interval for fish, and the length interval for blue mussels are also presented together with the total number of analyses and the number of years of the various time-series.

Matrix	age	n	n	year	trend (95% ci)	last year (95% ci)
			yrs			
Herring muscle						
Harufj. autumn	3-4	364	22	80-02		39 (34-44)
Ängskärskl. aut.	3-5	380	22	80-02		56 (42-73)
" spring	2-4	180	12	72-75,96-03	-2.8(-3.9, -1.6)*	36 (27-47)
Landsort	3-5	363	23	80-02	3.3 (1.3-5.3)*	29 (25-34)
Utlängan, aut.	2-4	376	23	80-02		17 (14-20)
" spring	2-3	159	11	72-75,96-02	-1.4 (-2.5,37)*	20 (17-24)
Fladen	2-3	441	23	80-02		24 (22-27)
Väderöarna		160	8	95-02		24 (19-29)
Cod muscle						
SE Gotland	3-4	368	24	79-02	1.9 (.54, 3.3)*	28 (26-32)
Fladen	2-3	413	24	79-02		53 (48-59)
Perch muscle						
Holmöarna	3-6	104	9	91,95-02		63 (51-77)
Kvädöfjärden		235	21	81-02	-4.7 (-6.9, -2.4)*	37 (31-45)
Eelpout muscle						
Holmöarna	3-6	67	7	95-02		90 (71-112)
Kvädöfjärden	2-6	79	8	95-02		81 (65-101)
Väderöarna	3-5	80	8	95-02	19 (6.2, 31)*	22 (14-35)
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	5-8	376	20	81-02		12 (11-13)
Väderöarna	6-10	417	22	80-02		13 (11-15)
Kvädöfjärden	2-3	77	8	95-02	12 (1.3, 23)*	14 (10-20)
Guillemot egg						
St. Karlsö		214	30	69-02	-2.0 (-2.8, -1.2)*	353 (317-393)

 $^{\#\} confidence\ interval\ based\ on\ only\ two-three\ years\ d.f=n\ of\ obs.\ -1,\ in\ all\ other\ cases\ d.f.=n\ of\ years\ -1$

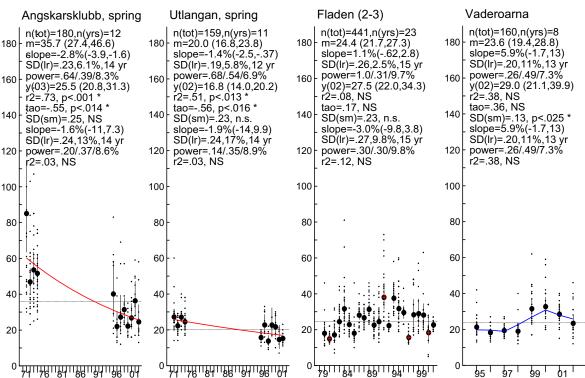
^{*} significant trend, p < 0.05





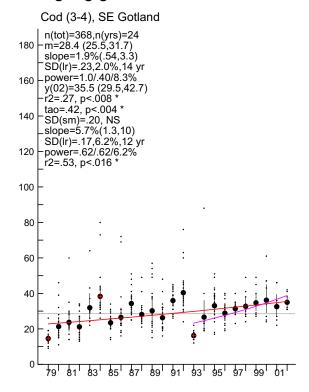
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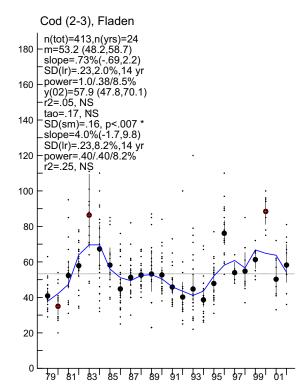
Hg, ng/g fresh wt., herring muscle



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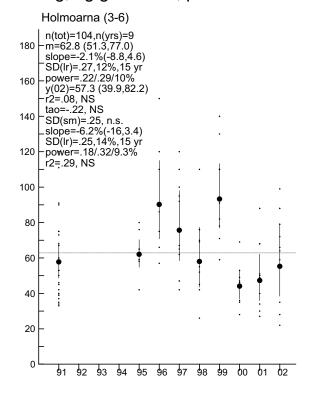
Hg, ng/g fresh w., cod muscle

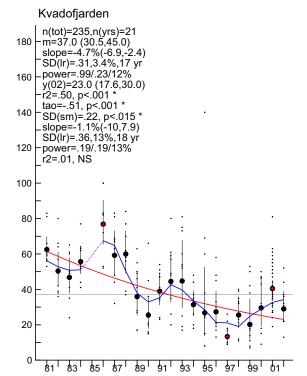




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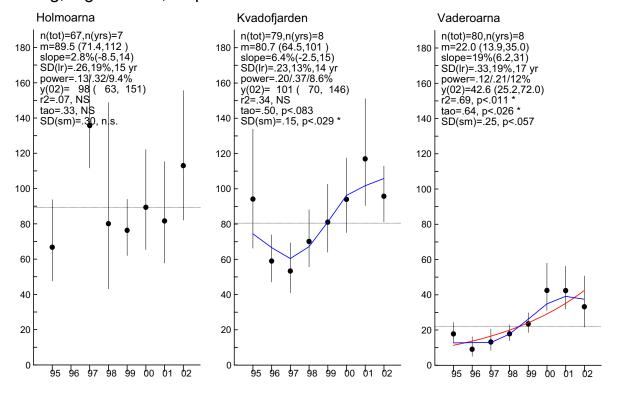
Hg, ng/g fresh w., perch muscle





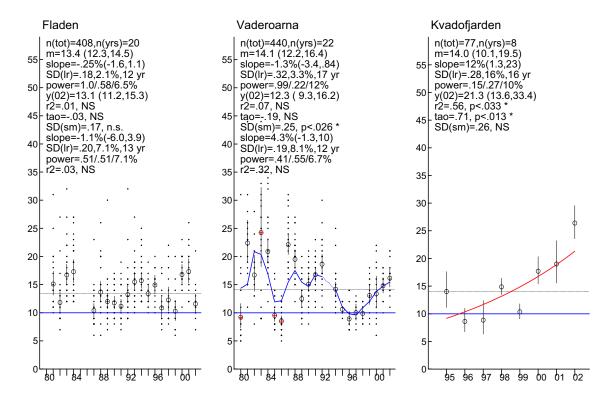
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Hg, n/g fresh w., eelpout



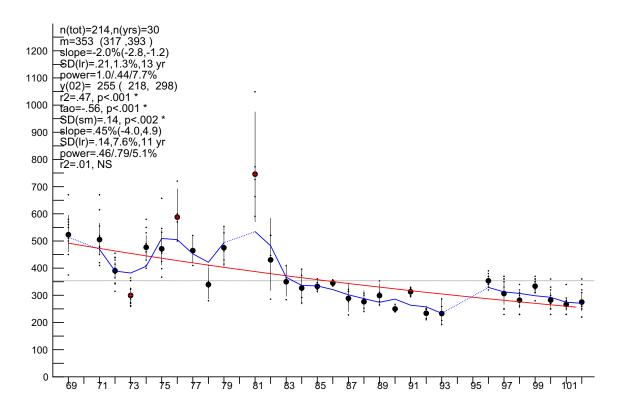
pia - 04.03.18 13:39, HGZ

Hg, ng/g fresh wt., blue mussel soft body



pia - 04.04.06 13:59, HGM1

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



pia - 04.03.16 15:29, HGU1

The toxic effects of lead involve several organ system and biochemical activities but the major risk is its toxicity to the nervous system. The most susceptible are the children and in particular the unborn fetus, 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 lead in man is 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 the 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 *Centre for Environmental Monitoring* at the University of Agriculture. 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 timeseries. 1982 seems to be lower than the surrounding years in all series but one, indicating an analytical problem.

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	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%.

Temporal variation

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.

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).

This investigation

At Harufjärden (-5.0%), Ängskärsklubb (autumn, -4.6%), Landsort (-4.6%) and Fladen (-3.9%), the investigated timeseries in herring liver show significant decreasing trends.

The number of years required to detect an annual change of 5% varied between 12 to 20 years for the herring timeseries 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 (-7%) and Fladen (about -4.9%).

Lead concentrations in the shorter timeseries of perch liver showed decreasing trends from Holmöarna (-13%) and Kvädöfjärden (-12%).

The short time serie (7 years) of lead in guillemot eggs show a significant decreasing trend (-7.9%).

The lead concentration in blue mussel softbodies from Fladen showed a significant decreasing trend of -5.3%. In Väderöarna the concentrations show a significant decreasing trend of -2.9% Both series also show decreasing trends for the last ten years; -11% and -10%, respectively.

Conclusion

There are convincing evidence that lead has decreased in the environment. The coastal perch samples show a faster decline, however not reflected in the eelpout samples. Concentrations in blue mussels are much higher than in fish (see below).

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 well below the 'background concentration at diffuse loading' in blue mussels for lead of $<5 \,\mu\text{g/g}$ dry weight, proposed by Knutzen and Skie (1992).

Species differences

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

Holmöarna: Eelpout(0.16) > Perch(0.09)

Kvädöfjärden: Blue mussel(0.49) > Eelpout(0.22) > Perch(0.08)Fladen: Blue mussel(1.5) > Dab(0.21) - Herring(0.16) > Cod(0.09)

Väderöarna: Blue mussel(1.6) > Flounder(0.17) - Eelpout(0.10) - Herring(0.09)

The lead concentration in blue mussel soft body tissue is thus generally about 7 to 18 times the concentration found in fish liver from the Swedish west coast and the concentration in eelpout liver is about twice as high as in perch liver in the analysed samples. Blue mussel samples from Kvädöfjärden show about twice as high concentration as in eelpout liver from the same site.

Table 13.2. Estimated geometric 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.

various tille-serie	3.					
Matrix	age	n	n yrs	year	trend (95% ci)	last year (95% ci)
Herring liver						
Harufj. autumn	3-4	332	20	81-02	-5.0(-7.2, -2.8)*	.119 (.096147)
Ängskärskl. aut.	3-5	371	21	81-02	-4.6 (-6.8, -2.5)*	.157 (.129141)
" spring	3-6	80	8	96-03		.177 (.150208)
Landsort	3-5	358	22	81-02	-4.6 (-6.7,-2.5)*	.192 (.160231)
Utlängan, aut.	3-4	280	22	81-02		.201 (.167241)
" spring	2-4	70	7	96-02		.160 (.131196)
Fladen	2-3	431	22	81-02	-3.9 (-6.4,-1.3)*	.131 (.108159)
Väderöarna	2-4	160	8	95-02		.061 (.051074)
Cod liver						
SE Gotland	3-4	326	22	81-02	-7.0 (-10,-4.1)*	.049 (.037065)
Fladen	2-4	400	22	81-02	-4.9 (-8.0,-1.7)*	.075 (.059095)
Perch liver						· · · · · ·
Holmöarna	3-7	80	8	95-02	-13 (-23,-2.3)*	.046 (.033065)
Kvädöfjärden	3-7	70	7	95-02	-12(-22,-2.2)*	.053 (.038073)
Eelpout liver						<u> </u>
Holmöarna	3-6	57	6	95-02		.175 (.157195)
Kvädöfjärden	2-6	79	8	95-02		.197 (.178218)
Väderöarna	3-5	70	7	95-02		.131 (.096177)
Dab liver						<u> </u>
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 1				, ,	,
Fladen	5-8	377	20	81-02		1.42 (1.05-1.92)
Väderöarna	6-10	397	21	81-02	-3.7 (-7.1,37)*	1.35 (1.06-1.72)
Kvädöfjärden	2-3	78	8	95-02	, , ,	1.74 (1.03-2.93)
Guillemot egg						, , , , , , , , , , , , , , , , , , , ,
St. Karlsö		70	7	96-02	-7.9 (-13, -2.4)*	.055 (.049061)
					· · · · · /	`

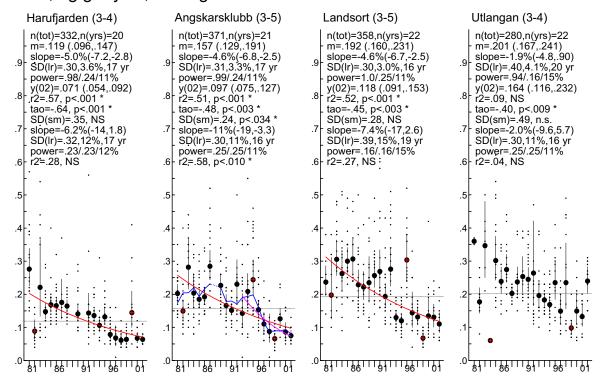
^{*} significant trend, p < 0.05

Table 13.3. Geometric concentrations of **lead** (ng/g fresh weight) in various matrices and sites during the time period 1980-1995/97 and the estimated mean concentration for the last year - 1995/97. 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	320	19	81-01	-4.8 (-6.9,-2.6)*	23 (18-29)
Ängskärskl. aut.	3-5	359	20	81-01	-4.2 (-6.4, 2.0)*	28 (22-37)
" spring	4-6	50	5	96-00		35 (26-46)
Landsort	3-5	346	21	81-01	-5.8 (-7.8,-3.7)*	30 (23-37)
Utlängan, aut.	3-4	268	21	81-01		54 (44-67)
" spring	2-4	69	7	96-02		33 (26-43)
Fladen	2-3	407	20	81-00	-3.2 (-6.2,19)*	31 (22-44)
Väderöarna	2-3	120	6	95-00		18 (1-26)
Cod liver						
SE Gotland	3-4	297	19	81-99	-8.3 (-13,-4.1)*	.014 (.009022)
Fladen	2-4	370	19	81-99	-5.9 (-9.4,-2.3)*	.017 (.012025)
Perch liver						
Holmöarna	4-7	70	7	95-01	-19 (-30,-8.3)*	.006 (.004008)
Kvädöfjärden	3-6	95	7	95-01	-15 (-24,-6.2)*	.007 (.005010)
Eelpout liver						
Holmöarna	3-6	47	5	95-01		.032 (.029036)
Kvädöfjärden	2-9	69	7	95-01		.038 (.034042)
Väderöarna	3-6	60	6	95-01		.026 (.023029)
Dab liver						
Fladen	3-6	257	14	81-94		
Flounder liver						
Väderöarna	4-6	239	14	81-94		
Blue mussel	shell 1					
Fladen	5-8	362	19	81-01	-5.0 (-9.8,16)*	.140 (.082240)
Väderöarna	6-10	382	20	81-01		.225 (.185274)
Kvädöfjärden	2-3	58	6	95-00		.195 (.156244)
Guillemot egg						. , , , , , , , , , , , , , , , , , , ,
St. Karlsö		60	6	96-01		12 (11-13)

^{*} significant trend, p < 0.05

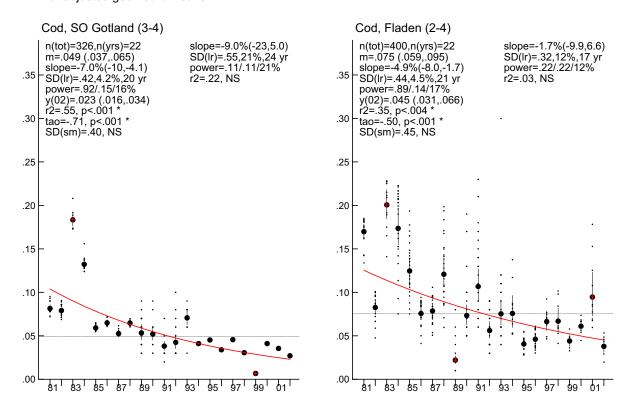
Pb, ug/g dry w., herring liver



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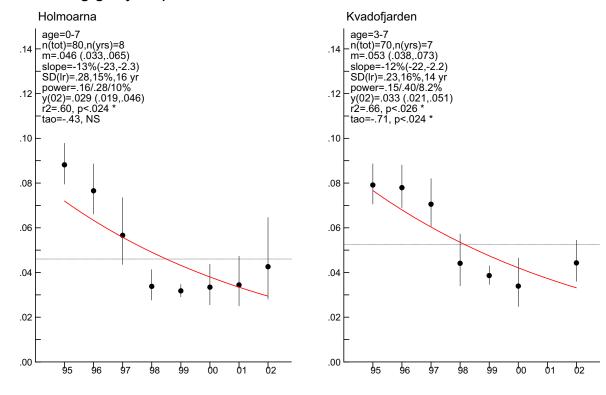
Pb, ug/g dry w., cod liver

Fat adjusted geometric means



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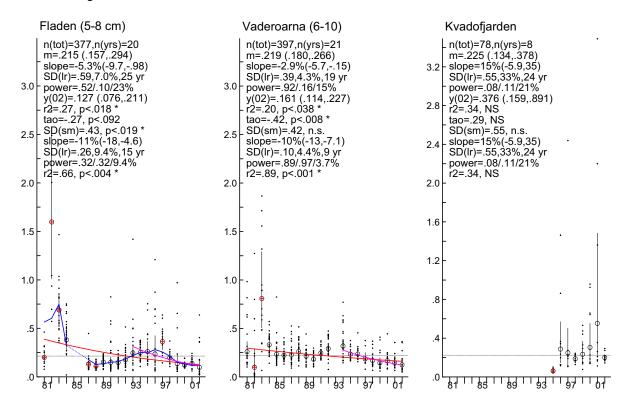
Pb, ug/g dry w. perch



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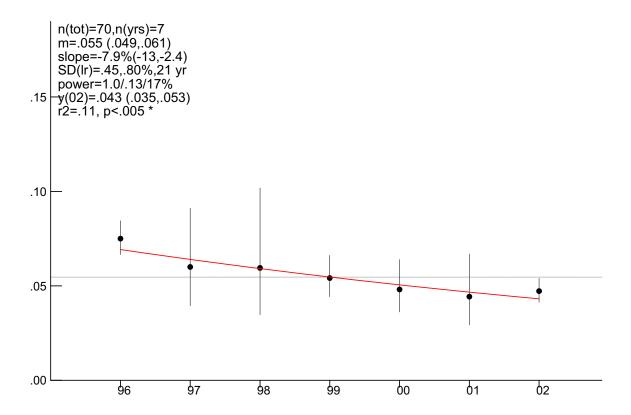
Pb, ug/g wet w., blue mussel softbody

Shell lengths in brackets



pia - 04.03.23 10:25, PBWM2

Pb, ug/g dry w. Guillemot egg



pia - 04.03.16 15:34, pbu

13 Cadmium

Updated: 04.04.08

Cadmium is an important metal in many industrial applications. Its 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 timeseries 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 *Centre for Environmental Monitoring* at the University of Agriculture. The detection limit is estimated to approximately 5 ng/g dry weight.

Table 14.1. 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 $\pm 5\%$ 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 show 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 timeseries is important.

Temporal variation

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.

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).

Proposed processes

- a) Decreased contaminant load may cause a corresponding decrease in the amount bioavailable 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 (?, 19??). Herring feeding on plankton may thus be exposed to increasing levels of bioavailable 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.

Other investigations

Concentrations of dissolved and particulate cadmium were determined in sea water 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 timeseries 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.

This investigation

Cadmium concentrations in herring liver from Ängskärsklubb in the Bothnian Sea, Landsort and Utlängan in the Baltic proper show significant *increasing* log-linear trends, between 2.8 and 3.9% a year, whereas samples from Harufjärden in the Bothnian Bay and Fladen in the Kattegat do not. The total increase in cadmium concentration during the recent 15 years (1981-95) at Ängskärsklubb, Landsort and Utlängan is about 2.5 times. During recent years the concentrations at Ängskärsklubb have decreased somewhat.

Cadmium concentrations in cod liver samples (adjusted for varying fat content) from south east of Gotland and Fladen, however, show significant *decreasing* trends of –7.2% and –4.2%, respectively.

Cadmium concentrations in eelpout samples from Kvädöfjärden in the Baltic Proper show a significant increasing trend of 11%.

The timeseries of dab liver show an extreme geometric mean cadmium concentration in 1988, about 5 times the overall mean concentration.

The number of years required to detect an annual change of 5% varied between 10 to 19 years for the herring timeseries with a power to detect a 5% annual change ranging from 0.21 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.)

Conclusion

The rapid increase of cadmium concentrations at Ängskärsklubb seems to have stopped and is now turning back, still the concentrations are generally higher compared to the beginning of the investigated period.

Assuming that the concentration in muscle tissue is about 25% of the concentration measured in liver tissue the above, the concentrations in herring *muscle* is reaching about 16 ng/g on a fresh weight basis. The average cadmium concentration in potatoes (in a sample of 8, during 1987-1990) was reported to 17 ng/g (Jorhem and Sundström, 1993). Although the estimated concentration of 16 ng/g is only approximate there is thus, no immediate risk for human consumption.

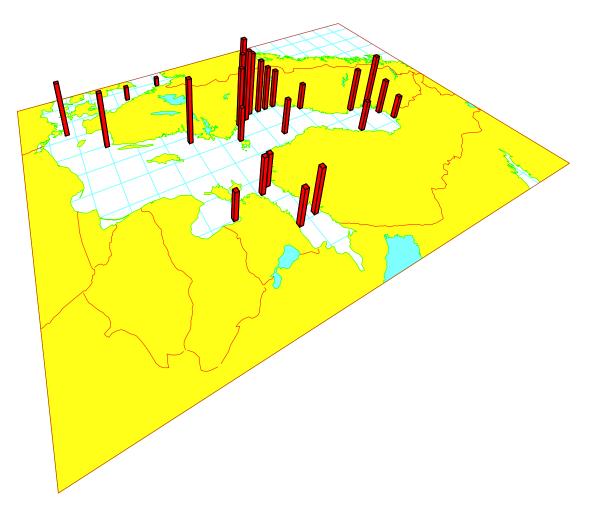


Figure 14.1. Spatial variation in concentration (w.w.) of cadmium in herring liver. Highest concentration (0.91 μ g/g) found along the Swedish coast of the Bothnian Sea and lowest (0.16 μ g/g) in the Kattegat. Even lower concentrations found in the Skagerrack (0.10 μ g/g).

Spatial variation

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)

This investigation

The overall mean *Cd-concentrations in herring liver from the Baltic show significantly higher cadmium concentrations compared to* Fladen in *the Kattegat* and Väderöarna in the Skagerakk 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 from the Bothnian Bay for the period 1981-2002, show about 3.5 times higher values compared to similar samples from the Kattegatt and samples from Landsort show 4 times higher values compared to those from the Kattegatt.

Eelpout livers from Holmöarna in the southern Bothnian Bay and Kvädöfjärden in the Baltic Proper show about 4 to 5 times higher geometric mean Cd-concentrations (dry weight) compared to samples from Väderöarna in the Skagerrak.

Blue mussels from Kvädöfjärden, analysed 1995-02, show about 3 – 4 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 as the sample 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.

Cod livers from Fladen in the Kattegat though, show significantly higher cadmium concentrations (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 however 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 some few 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 similar samples from Väderöarna in the Skagerakk.

Species differences

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

Holmöarna: Eelpout(1.1) > Perch(0.44)

Kvädöfjärden: Blue mussel(4.2) > Eelpout(1.3) > Perch(0.65)Fladen: Blue mussel(1.1) > Dab(0.61) - Herring(0.54) > Cod(0.17)

Väderöarna: Blue mussel(1.1)- Flounder(0.50) > Herring(0.32) - Eelpout(0.28)

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 14.2. Geometric concentrations of **cadmium** (μ g/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	352	21	81-02		1.4 (1.2-1.7)
Ängskärskl. aut.	3-5	370	21	81-02	2.8 (.35,5.2)*	1.6 (1.4, 1.9)
" spring	3-6	80	8	96-03		3.9 (3.3-4.7)
Landsort	3-5	358	22	81-02	2.9 (1.2,4.6)*	2.0 (1.7-2.3)
Utlängan, aut.	3-4	281	22	81-02	3.9 (2.3,5.5)*	1.8 (1.5,2.0)
" spring	3-4	70	7	96-02		2.4 (2.1-2.7)
Fladen	2-3	431	22	81-02		0.54 (0.48-0.60)
Väderöarna	2-4	160	8	95-02		0.32 (0.29-0.36)
Cod liver						
SE Gotland	3-4	330	22	81-02	-7.2 (-9.4,-5.0)*	0.057 (.044073)
Fladen	2-3	401	22	81-02	-4.2 (-7.4,-1.0)*	0.174 (.138219)
Perch liver						
Holmöarna	3-7	80	8	95-02		0.44 (.3360)
Kvädöfjärden	3-7	105	8	95-02		.65 (.4986)
Eelpout liver						
Holmöarna	3-6	56	6	95-02		1.1 (.91-1.3)
Kvädöfjärden	2-9	79	8	95-02	11 (4.2, 18)*	1.3 (1.1-1.6)
Väderöarna	3-6	70	7	95-02		0.28 (.2533)
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 (.3580)
Blue mussel	shell 1					
Fladen	5-8	377	20	81-02		1.1 (1.0-1.2)
Väderöarna	6-10	398	21	81-02		1.1 (0.93-1.2)
Kvädöfjärden	2-3	78	8	95-02		4.2 (3.7-4.7)
Guillemot egg						
St. Karlsö		69	7	96-02		.003 (.002003)

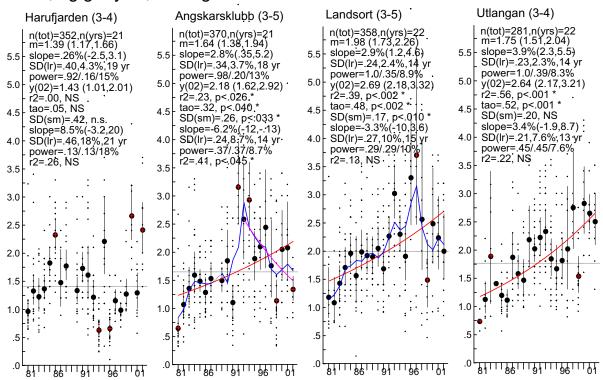
^{*} significant trend, p < 0.05

Table 14.3. Geometric concentrations of **cadmium** (μ g/g **fresh** 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	340	20	81-01		.40 (.3447)
Ängskärskl. Aut.	3-5	358	20	81-01	3.7 (1.6,5.8)*	.63 (.5081)
" spring	5-6	50	5	96-00		0.84 (.62-1.1)
Landsort	3-5	346	21	81-01	2.2 (.58,3.9)*	.66 (.5579)
Utlängan, aut.	2-4	269	21	81-01	3.4 (1.4,5.5)*	.66 (.5284)
" spring	2-4	69	7	96-02		0.50 (.4258)
Fladen	2-3	407	20	81-00		0.16 (0.1418)
Väderöarna	2-3	120	6	95-00		0.10 (.08212)
Cod liver						
SE Gotland	3-4	301	19	81-99	-7.6 (-10, -4.8)*	.019 (.014025)
Fladen	2-4	371	19	81-99	-5.6 (-9.3,-1.9)*	.041 (.027060)
Perch liver						
Holmöarna	3-7	70	7	95-01		.097 (.08611)
Kvädöfjärden	3-7	60	6	95-00	15 (-1.7,31)*	.14 (.1216)
Eelpout liver						
Holmöarna	3-6	47	5	95-00		.20 (.1725)
Kvädöfjärden	2-9	69	7	95-00		.24 (.2029)
Väderöarna	3-5	60	6	95-01		.054 (.046062)
Dab liver						
Fladen	3-6	257	14	81-94	2.8 (-4.0,9.6)	0.23 (.1338)
Flounder liver						
Väderöarna	4-6	239	14	81-94	0.64 (-5.9,7.2)	0.12 (.07419)
Blue mussel	shell 1				·	· · · · · · · · · · · · · · · · · · ·
Fladen	5-8	362	19	81-01	-3.1 (-5.2,99)*	.126 (.09916)
Väderöarna	6-10	383	20	81-01		0.17 (.1519)
Kvädöfjärden	2-3	58	6	95-00		0.52 (.4857)
Guillemot egg						ng/g
St. Karlsö		59	6	96-01		0.79 (0.61-1.0)

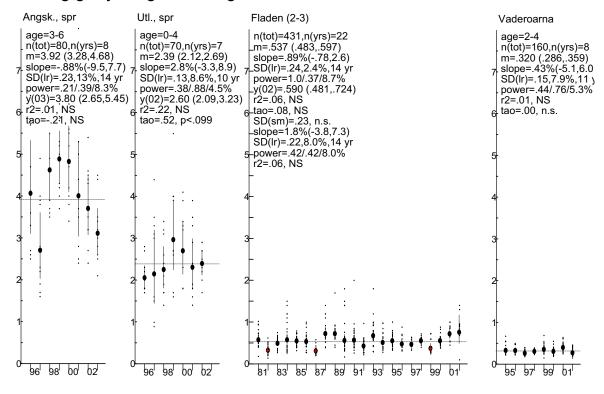
^{*} significant trend, p < 0.05

Cd, ug/g dry w., herring liver



Contaminant Research Group /NRM, Dep.Env.Assess./SLU 04.03.16 15:47, CDC

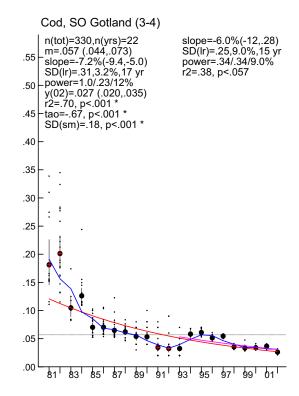
Cd, ug/g dry weight, herring liver

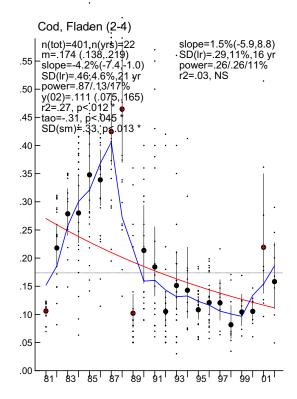


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Cd, ug/g dry w., cod liver

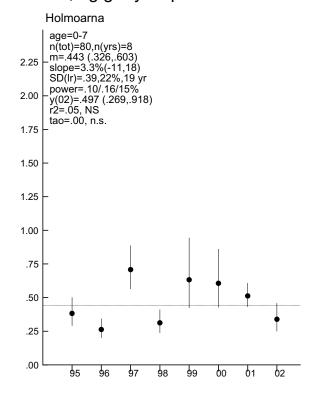
Fat adjusted geometric means

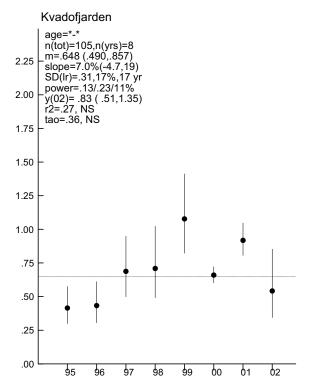




pia - 04.03.16 15:49, CDG

Cd, ug/g dry w. perch

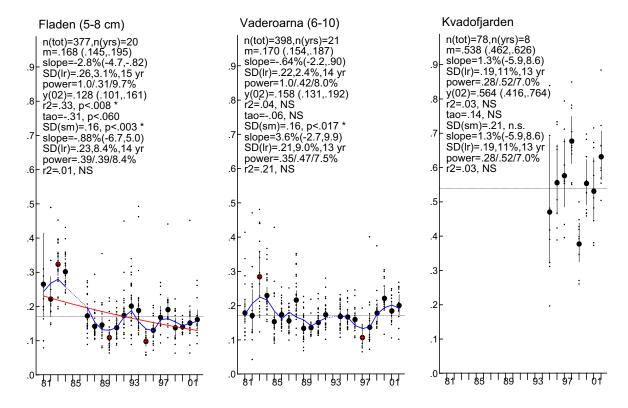




pia - 04.03.24 14:17, CDP

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

Shell lengths in brackets



pia - 04.03.23 10:26, CDWM1

14 Nickel

Updated 04.04.08

The concentration of nickel in fish liver is determined using an atomic absorption spectrophotometer with graphite furnace at the *Centre for Environmental Monitoring* at the University of Agriculture. The detection limit is estimated to approximately 0.1 μ g/g dry weight.

The analysis started on samples collected 1995.

Temporal variation

The timeseries of herring from Ängskärsklubb(-15%), Fladen(-23%) and Väderöarna(-16%), cod liver from SE gotland (-9.9%), perch liver from Holmöarna(-26%) and Kvädöfjärden(-21%) and eelpout from Kvädöfjärden(-18%) and Väderöarna(-9.2%), all show significant decreasing trends.

Spatial variation

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

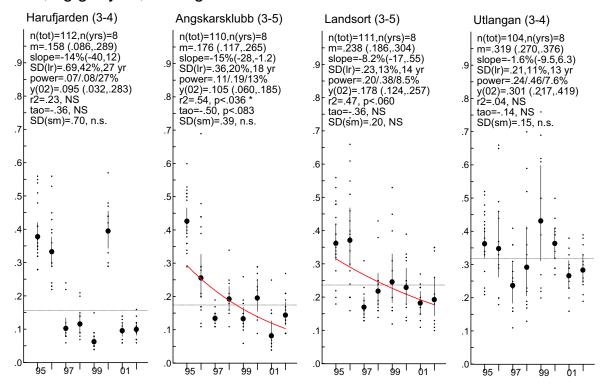
Mussel samples from all three sites show mean levels below the upper limit of the 'high background concentration at diffuse loading' in blue mussels for nickel of $<5 \mu g/g$ dry weight, proposed by Knutzen and Skie (1992).

Table 15.1. Geometric concentrations of **nickel** (μ g/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	112	8	95-02		.16 (.08629)
Ängskärskl. Aut.	3-5	110	8	95-02	-15 (-28, -1.2)*	.18 (.1227)
" spring	3-6	80	8	96-03		.27 (.2136)
Landsort	3-5	111	8	95-02		.24 (.1930)
Utlängan, aut.	3-4	104	8	95-02		.32 (.2738)
" spring	3-5	70	7	96-02		.29 (.2336)
Fladen	2-3	109	8	95-02	-23 (-38,-7.7)*	.14 (.08225)
Väderöarna	2-4	160	8	95-02	-16 (-23,-8.5)*	.091 (.06413)
Cod liver						
SE Gotland	3-6	100	8	95-02	-9.9 (-19,91)*	0.10 (.07313)
Fladen	2-5	100	8	95-02		0.18 (.1325)
Perch liver						
Holmöarna	4-7	79	8	95-02	-26 (-45,-7.4)*	.098 (.051-0.19)
Kvädöfjärden	3-6	105	8	95-02	-21 (-41,21)*	.10 (.057-0.19)
Eelpout liver						
Holmöarna	3-6	17	6	95-02		0.19 (.08939)
Kvädöfjärden	2-6	62	8	95-02	-18 (-30,-6.7)*	0.23 (.1535)
Väderöarna	3-5	64	7	95-02	-9.2 (-13,-5.2)*	0.29 (.2337)
Blue mussel	shell 1					
Kvädöfjärden	2-3	78	8	95-02		2.7 (2.4-2.9)
Fladen	5-8	119	8	95-02		2.2 (1.8-2.6)
Väderöarna	6-10	115	8	95-02		1.1 (.86-1.4)
Guillemot egg						• /
St. Karlsö		70	7	96-02		0.078 (.04513)

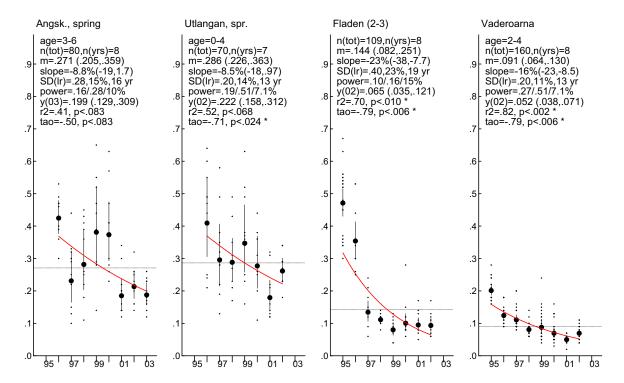
^{*} significant trend, p \leq 0.05

Ni, ug/g dry w., herring liver



pia - 04.03.16 15:56, NIC

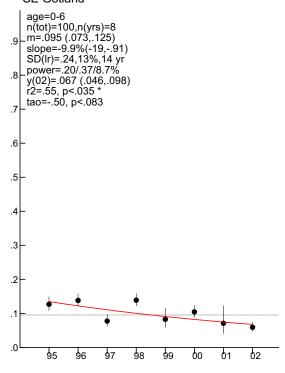
Ni, ug/g dry weight, herring liver



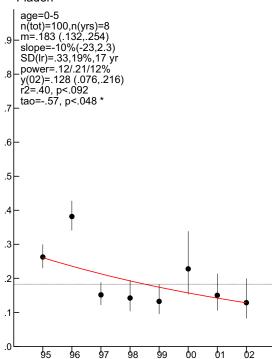
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Ni, ug/g dry w., cod liver





Fladen



pia - 04.03.16 15:57, nig

Ni, ug/g dry w., perch liver

Holmoarna (4-7)

Kvadofjarden (3-6)

n(tot)=105,n(yrs)=8
-m=.104 (.057,.189)
slope=-21%(-41,-.21)
-SD(lr)=.55,32%,24 yr
power=.08/.11/21%
y(02)=.050 (.021,.119)
-r2=.50, p<.047*
tao=-.43, NS
-SD(sm)=.20, p<.002*

.6
.5
.1
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95 96 97 98 99 00 01 02

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.0

95

96

97

98

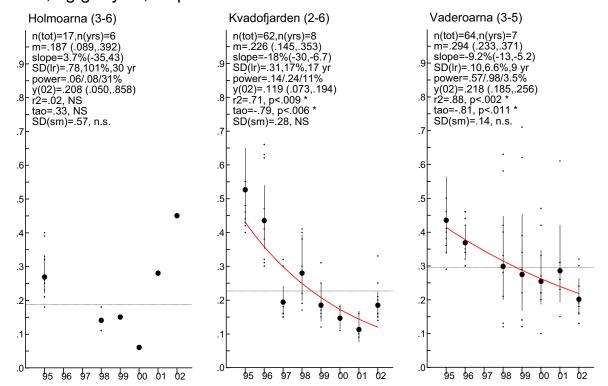
99

90

01

62

Ni, ug/g dry w., eelpout liver



pia - 04.03.18 13:42, NIZ

15 Chromium

Updated 04.04.08

The concentration of chromium in fish liver is determined using an atomic absorption spectrophotometer with graphite furnace at the *Centre for Environmental Monitoring* at the University of Agriculture. The detection limit is estimated to approximately $0.1~\mu g/g$ dry weight.

The analysis started on samples collected 1995.

Temporal variation

The timeseries of herring liver from Utlängan, spring(-12%), Fladen(-9.2%), Väderöarna (-6.1%), perch liver from Holmöarna(-12%) and Kvädöfjärden (-9.2%) and blue mussel from Kvädöfjärden (-7.9%) and Fladen(-26%) show significant decreasing trends. However, a significant upward trend is detected for eelpout liver from Kvädöfjärden (4.8%).

Spatial variation

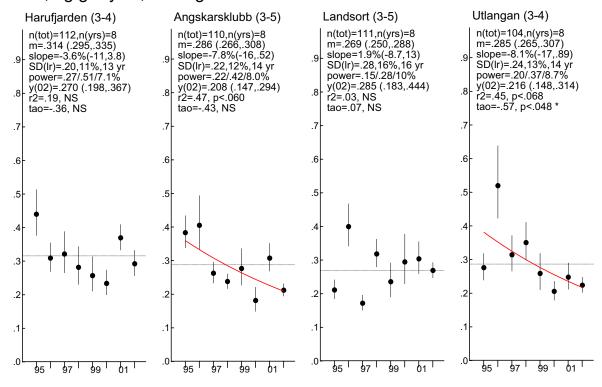
The chromium concentration in blue mussel samples from the Kattegatt varies between years and shows a geometric mean concentration in the same range as mussels from the Baltic Proper. These concentrations are about 2-3 times higher compared to samples from the Skagerrak and close to or above the 'high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

Table 16.1. Geometric concentrations of **chromium** (μ g/g **dry** weight) in various matrices and sites during the time period 1995-1997 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	112	8	95-02		.31 (.3034)
Ängskärskl. Aut.	3-5	110	8	95-02		.29 (.2731)
" spring	5-6	80	8	96-03		.34 (.3039)
Landsort	3-5	111	8	95-02		.27 (.2529)
Utlängan, aut.	3-4	104	8	95-02		.29 (.2731)
" spring	3-5	70	7	96-02	-12 (-24,57)*	.30 (.2241)
Fladen	2-3	109	8	95-02	-9.2 (-14, -4.5)*	.28 (.2335)
Väderöarna	2-3	160	8	95-02	-6.1 (-12,44)*	.26 (.2231)
Cod liver						
SE Gotland	3-4	99	8	95-02		.10 (.06017)
Fladen	2-3	96	8	95-02		.18 (.1423)
Perch liver						
Holmöarna	4-7	80	8	95-02	-12 (-17, -7.7)*	.15 (.1119)
Kvädöfjärden	3-6	109	8	95-02	-9.2 (-14, -4.5)*	.28 (.2335)
Eelpout liver						
Holmöarna	3-6	43	6	95-02		.37 (.2459)
Kvädöfjärden	2-6	52	7	95-02	4.8 (1.0, 8.6)*	.42 (.3748)
Väderöarna	3-5	64	7	95-02		.37 (.2556)
Blue mussel	shell 1					
Kvädöfjärden	2-3	78	8	95-02	-7.9 (-13, -2.6)*	2.2 (1.8-2.6)
Fladen	5-8	119	8	95-02	-26 (-42, -9.8)*	2.4 (1.3-4.5)
Väderöarna	6-10	115	8	95-02		.85 (.69-1.0)
Guillemot egg						. , , , , , , , , , , , , , , , , , , ,
St. Karlsö		70	7	95-02	-4.2 (-7.3, -1.2)*	.28 (.2629)

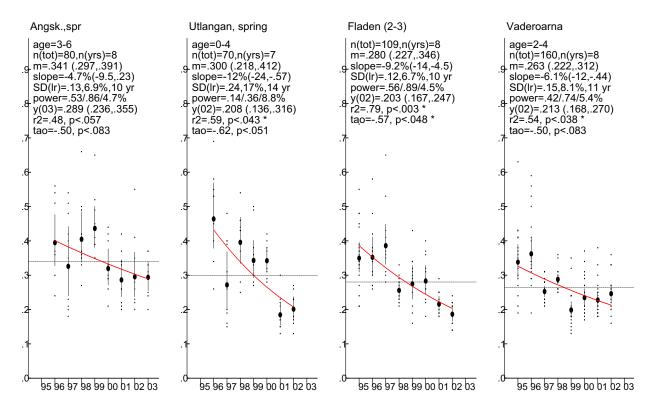
^{*} significant trend, p < 0.05

Cr, ug/g dry w., herring liver



pia - 04.03.16 16:04, CRC

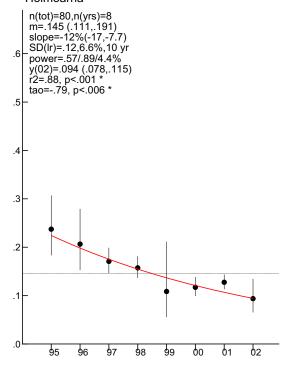
Cr, ug/g dry weight, herring liver



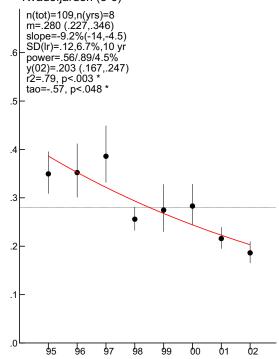
pia - 04.03.16 16:04, CRV

Cr, ug/g dry w. perch

Holmoarna



Kvadofjarden (3-6)



pia - 04.03.16 16:05, crp

16 Copper

Updated 04.04.08

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.

Temporal variation

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.

This investigation

None of the time series show increasing trends in copper concentrations. A significant decreasing trend can be seen in the time series for blue mussel from Fladen (-2.9%).

The number of years required to detect an annual change of 5% varied between 10 to 15 years for the herring timeseries with a power to detect a 5% annual change ranging from 0.13 to 1.0.

Spatial variation

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

The copper concentration in blue mussels from the Swedish westcoast 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 $<10 \,\mu\text{g/g}$ dry weight, proposed by Knutzen and Skie (1992).

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(12)

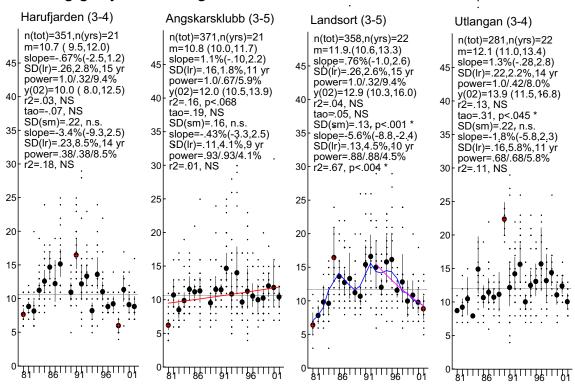
Fladen: Dab(19) > Cod(17) > Herring(12) > Blue mussel(6.0)

Väderöarna: Flounder(34) > Eelpout(29) > Herring(9.3) > Blue mussel(5.2)

Table 17.1. Geometric concentrations of **copper** (μ g/g **dry** weight) in various matrices and sites during the time period 1980-1997 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.

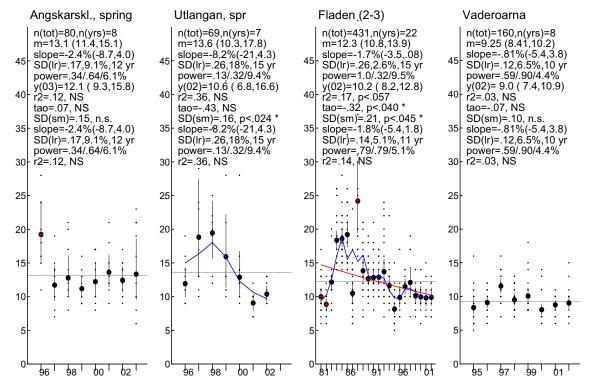
Matrix	age	n	n yrs	year	trend	last year
						-
Harufj. Autumn	3-4	351	21	81-02		11 (10-12)
Ängskärskl. aut.	3-5	371	21	81-02		11 (10-12)
" spring	5-6	80	8	96-03		13 (11-15)
Landsort	3-5	358	22	81-02		12 (11-13)
Utlängan, aut.	3-4	281	22	81-02		12 (11-13)
" spring	2-4	69	7	96-02		14 (10-18)
Fladen	2-3	431	22	81-02		12 (11-14)
Väderöarna	2-3	160	8	95-02		9 (8-10)
Cod liver						
SE Gotland	3-4	330	22	81-02		17 (15-19)
Fladen	2-4	400	22	81-02		17 (14-21)
Perch liver						
Holmöarna	3-7	80	8	95-02		11 (8-14)
Kvädöfjärden	3-6	105	8	95-02		12 (9-15)
Eelpout liver						
Holmöarna	3-6	56	6	95-02		11 (10-12)
Kvädöfjärden	2-9	79	8	95-02		22 (20-25)
Väderöarna	3-6	70	7	95-02		29 (26-32)
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	377	20	81-02	-1.1 (-2.3, .12)	6.0 (5.6-6.5)
Väderöarna	6-10	398	21	81-02		5.2 (4.9-5.6)
Kvädöfjärden	2-3	78	8	95-02		7.8 (7.1-8.6)
Guillemot egg						. ,
St. Karlsö		70	7	96-02		2.9 (2.6-3.2)

Cu, ug/g dry w., herring liver



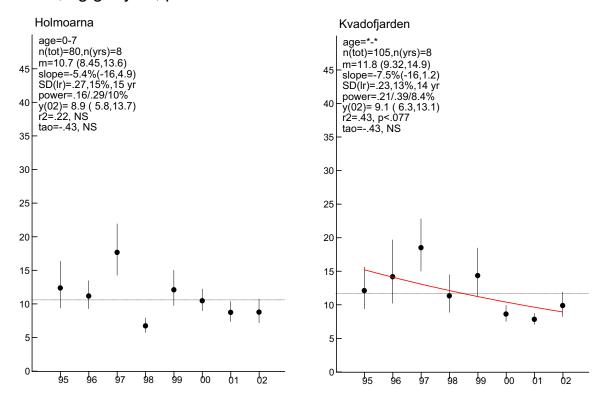
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Cu, ug/g dry w., herring liver



pia - 04.03.16 16:14, cuv

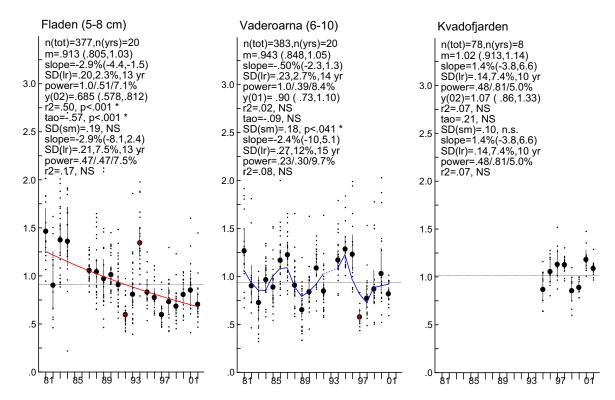
Cu, ug/g dry w., perch liver



pia - 04.03.16 16:14, CUP

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

Shell lengths in brackets



pia - 04.03.16 16:15, CUWM1

17 Zinc

Updated 04.04.08

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.

Temporal variation

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.

This investigation

Herring liver from Fladen show a significant *upward* trend of 1.2%. A significant increasing trend of 4.5% has also been shown for herring liver from Utlängan for the last ten years. Significant *decreasing* trends are shown in guillemot eggs (-5.6%), and in blue mussels from Väderöarna in the last ten years (-7.4%).

The number of years required to detect an annual change of 5% varied between 9 to 13 years for the herring timeseries with a power to detect a 5% annual change ranging from 0.16 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 was excluded from the power calculations.)

Spatial variation

No significant differences in mean zinc concentration in herring among the four sampling sites in the Baltic and the Swedish westcoast.

The zinc concentration in cod liver from Fladen is significantly higher than in cod liver from the site SE of Gotland. This may however 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 westcoast 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)

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(136) > Perch(76) Kvädöfjärden: Eelpout(191) > Perch(71)

Fladen: Blue mussel(115) > Herring(89) - Dab(80) - Cod(72) Väderöarna: Flounder(168) > Herring(128) - Blue mussel(109)

The zinc concentration seems to be about twice as high or more in eelpout as in perch.

Seasonal variation

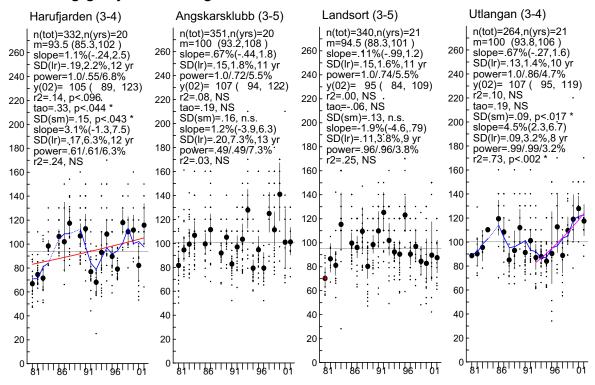
The concentrations in spring caught herring from Ängskärsklubb and Utlängan is considerable higher compared to samples from the same areas in the autumn (table 18.1).

Table 18.1. Geometric concentrations of **zinc** (μ g/g **dry** weight) in various matrices and sites during the time period 1980-1999/2000 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	year	trend (95% ci)	last year
			yrs			
Herring liver						
Harufj. Autumn	3-4	332	20	81-02		94 (85-102)
Ängskärskl. aut.	3-5	351	20	81-02		100 (93-108)
" spring	3-6	80	8	96-03		146 (129-165)
Landsort	3-5	340	21	81-02		95 (88-101)
Utlängan, aut.	3-4	264	21	81-02		100 (94-106)
" spring	2-4	70	7	96-02		125 (102-153)
Fladen	2-3	406	21	81-02	1.2 (.43, 2.0)	94 (89-100)
Väderöarna	2-4	160	8	95-02		107 (92-123)
Cod liver						
SE Gotland	3-4	312	21	81-02		35 (32-40)
Fladen	2-4	378	21	81-02		74 (66-83)
Perch liver						
Holmöarna	3-7	80	8	95-02		99 (88-111)
Kvädöfjärden	3-7	70	7	95-02		117 (92-149)
Eelpout liver						
Holmöarna	3-8	56	6	95-02		163 (134-200)
Kvädöfjärden	2-9	79	8	95-02		183 (144-233)
Väderöarna	3-6	70	7	95-02		213 (172-264)
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	377	20	81-02		114 (102-128)
Väderöarna	6-10	376	20	81-02		108 (93-124)
Kvädöfjärden	2-3	78	8	95-02		137 (120-156)
Guillemot egg						·
St. Karlsö		70	7	96-02	-5.6 (-8.7, -2.5)	46 (43-49)

NL = non-linear trend components

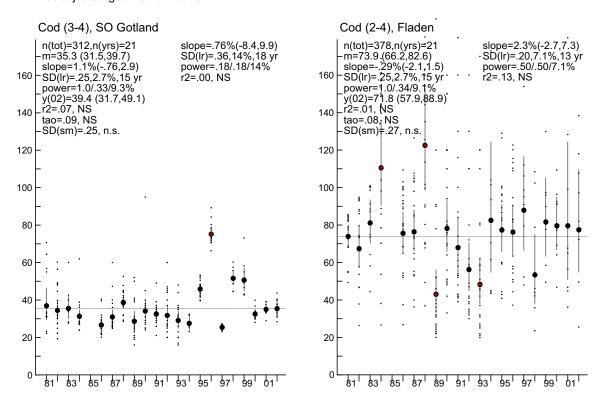
Zn, ug/g dry w., herring liver



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Zn, ug/g dry w., cod liver

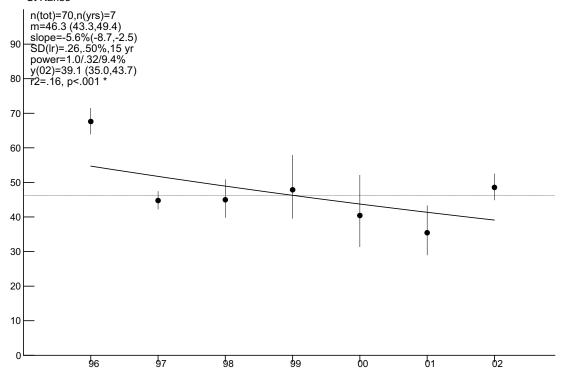
Fat adjusted geometric means



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Zn, ug/g dry w. Guillemot

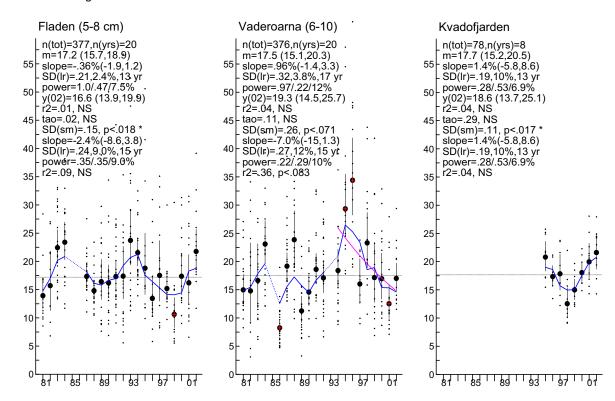




pia - 04.03.16 16:20, ZNU

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

Shell lengths in brackets



pia - 04.03.23 10:32, ZNWM1

18 PCB's, Polychlorinated biphenyles

Updated 04.04.08

The PCB's has been used in a wide variety of manufacturing processes especially as plasticizers and as insulators and fire retardents. 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 are 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, blue mussel soft body and guillemot egg is determined using a gas chromatograph (GC) equipped with an electron capture detector.

Before 1988, PCB were analysed by a <u>packed</u> column GC and the total sum of PCB were estimated from 14 peaks after calibration with Aroclor 1254 (Jensen et al. 1983). During 1988, analyses on <u>capillary</u> 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 CV₁ 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 hence estimated until 1988:

 $sPCB = PCB10 / R_1$ and after 1988: $sPCB = (CB-138+CB-163) / (R_1 \cdot R_2)$

Table 19.1. 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	.6776	9.1	.098
Ängskärsklubb	188	.14	5.1	20	.83	.7988	11	.12
" spring	397	.13	5.1	25	.79	.7582	11	.10
Landsort	159	.12	5.2	29	.61	.5963	7.4	.070
Utlängan	94	.12	5.4	20	.65	.6268	9.8	.075
" spring	371	.12	5.3	10	.67	.6469	5.4	.080
Fladen	191	.13	5.3	25	.82	.7986	10	.11
Cod								
Gotland	152	.14	4.0	11	.69	.6572	7.3	.093
Fladen	176	.15	5.9	10	.85	.8189	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	.7480	9.8	.14

Table 19.2. 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

Temporal variation

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, bioackumulating 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.

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 westcoast show significant decreasing trends during the time period 1978/80-2002. The average rate varies between 4 and 10% per year. A similar significant decrease within the same range (4 and 10% a year) was also found in the two timeseries of spring caught herring, 1972-2003. 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 recorded at Landsort 1996. This could most probably be explained by the very low fat content this year.

The two *cod* timeseries from south east of Gotland in the Baltic Proper and Fladen at the west coast, show significant decreasing trends at the rate of 7.5 and 6.1% per year respectively (1980-2002).

Also in the timeseries of *perch* the sPCB concentrations decreased about 8 to 10% a year as well as in *guillemot eggs* (1969-2003), about 9% a year. This 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 timeseries.

Conclusion

The concentration of PCB is decreasing at a rate of approximately 4 - 10% per year in herring and cod from the Baltic as well as from the Kattegat and in guillemot eggs and perch from the Baltic since the end of the seventies.

Spatial variation

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 2000 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 Skagerakk, and significantly lower than herring samples from the Bothnian Sea and the Baltic Proper (2-4 ng/g ww). 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-101/CB-153 is significantly lower at Ängskärsklubb compared to all the other sites. Utlängan is showing 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 19.3. Geometric concentrations of **sPCB** (μ g/g **lipid weight**) in various matrices and sites during the time period 1980-1997 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	318	23	78-02	-9.7(-11,-8.0)*	0.76 (.55-1.1)
Ängskärskl. aut.	3-5	282	23	78-02	-7.6 (-9.3,-5.8)*	1.25 (.95-1.6)
" spring	2-5	586	30	72-03	-4.8 (-6.2,-3.4)*	3.01 (2.4-3.7)
Landsort	3-5	320	24	78-02	-4.1 (-5.7,-2.6)*	1.63 (1.4-1.9)
Utlängan, aut.	2-4	240	23	80-02	-5.9 (-7.6,-4.1)*	1.23 (1.0-1.52)
" spring	2-3	575	29	72-03	-9.7 (-11,-8.6)*	4.09 (2.8-5.9)
Fladen	2-3	408	23	80-02	-6.7 (-8.2,-5.1)*	0.53 (.4366)
Cod liver						
SE Gotland	3-4	262	23	80-02	-7.5 (-9.6,-5.5)*	2.42 (1.9-3.1)
Fladen	2-3	278	22	80-02	-6.1 (-9.3,-2.8)*	3.37 (2.5-4.5)
Perch muscle						
Holmöarna	4-7	239	18	80-03	-8.3 (-11,-6.1)*	0.95 (.65-1.4)
Kvädöfjärden	3-4	193	21	80-02	-9.8 (-13,-6.9)*	0.49 (.3371)
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	shell 1					
Fladen	5-8	58	17	84-02	-6.0 (-9.1,-3.0)*	0.56 (.4570)
Väderöarna	6-10	60	18	84-02	-10 (-14,-7.2)*	0.62 (.4488)
Guillemot egg			•		_	_
St. Karlsö		350	33	69-03	-9.0 (-9.7,-8.4)*	78 (56-108)

^{*} significant trend, p < 0.05

Table 19.4. Geometric concentrations of **CB-153** (**ng/g lipid weight**) in various matrices and sites during 1987-1995/96 and estimated mean concentration for the last year.

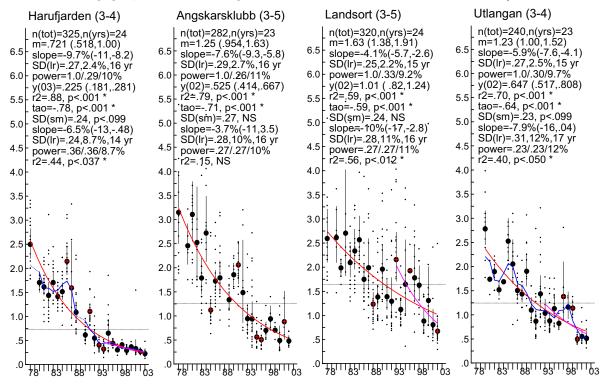
Matrix age n tot year trend last yr n yrs Herring msc. Harufj. autumn 87-02 .056 (.044-.070) 3-4 207 14 89-02 -6.1 (-11,***)* Ängskärskl. aut. 3-5 227 14 .147 (.115-.188) " spring 2-4 219 15 89-03 .228 (.177-.292) 3-5 87-02 .127 (.100-.160) Landsort 249 16 Utlängan, aut. 2-4 214 15 88-02 .100 (.079-.125) spring 2-3 214 15 87-03 -4.6 (-8.2, -1.0)* .203 (.165-.249) -3.9 (-7.2,-.54)* Fladen 2-3 264 15 88-02 .054 (.046-.064) 95-02 Väderöarna 159 8 .026 (.020-.033) Cod liver SE Gotland 3-4 110 14 89-02 .193 (.164-.227) Fladen 2-3 102 13 89-02 .491 (.398-.606) Perch muscle 99 Holmöarna 10 89,95-03 -15 (-24, -5.8)* .099 (.066-.147) Kvädöfjärden 3-5 186 16 84,89-03 -5.9 (-12, -.02)* .061 (.046-.082) **Eelpout muscle** 7 95,97-02 Holmöarna 65 .183 (.106-.316) 3-6 2-6 Kvädöfjärden 79 8 95-02 -17 (-33, -.31)* .226 (.140-.365) 95-02 Väderöarna 3-5 79 8 .250 (.147-.426) Dab muscle Fladen 3-6 5 5 89-94 Flounder msc Väderöarna 89-94 4-6 6 6 Blue mussel \$ Fladen 54 15 88-02 -6.1 (-8.9,-3.4)* .064 (.053-.077) Väderöarna 52 14 88-02 -10 (-15,-5.5)* .057 (.041-.079) Kvädöfjärden 40 95-02 2.2 (.33, 4.0)* .064 (.061-.067) 8 Guillemot egg 158 St. Karlsö 16 88-03 -7.2 (-9.0,-5.5)* 5.06 (4.15-6.17)

^{\$} Pooled samples

Table 19.5. Geometric concentrations of **CB-153** (ng/g **fresh weight**) in various matrices and sites during 1987-1995-00 and estimated mean concentration for the last year.

Matrix	age	n tot	n	year	mean	last yr
			yrs			
Herring msc.						
Harufj. autumn	3-4	183	12	87-00	1.6 (1.2,2.1)	.91 (.65-1.3)
Ängskärskl. aut.	3-5	204	12	89-00	3.7 (3.0-4.7)	2.4 (1.8-3.2)
" spring	2-5	187	12	89-00	7.2 (5.6,9.1)	6.2 (3.9,9.9)
Landsort	3-5	225	14	87-00	4.2 (3.8,4.7)	3.8 (3.1,4.6)
Utlängan, aut.	3-4	191	13	88-00	3.0 (2.4,3.8)	2.0 (1.4,2.9)
" spring	2-3	195	13	87-01	4.2 (3.2-5.6)	2.4 (1.8-3.2)
Fladen	2-3	249	13	88-00	2.1 (1.7,2.5)	1.5 (1.1,2.1)
Väderöarna		119	6	95-00	1.4 (1.0-2.0)#	1.7 (.81-3.5)#
Cod liver						
SE Gotland	3-4	91	12	89-00	124 (108-144)	131 (99-173)
Fladen	2-3	84	11	89-00	109 (88-134)	126 (86-184)
Perch muscle					, ,	•
Holmöarna		70	7	89,95-00	.94 (.70-1.2)	0.69 (.6080)
Kvädöfjärden	3-5	131	13	84,89-00	0.48 (.3566)	0.29 (.1945)
Eelpout						
Holmöarna		35	4	95, 97-99	1.3 (.93,1.8)	
Kvädöfjärden		49	5	95-99	1.6 (1.4,1.9)	
Väderöarna		49	5	95-99	1.8 (1.6,2.1)	
Blue mussle					` ,	
Holmöarna		30	6	95-00	.76 (.68,.85)	1.0 (.89,1.2)
Kvädöfjärden		44	13	95-00	.55 (.42,.73)	.46 (.72,.78)
Väderöarna		42	12	95-00	.80 (.66,.96)	.60 (46,.80)
Guillemot egg						. , ,
St. Karlsö		79	8	79,88-95	782	541

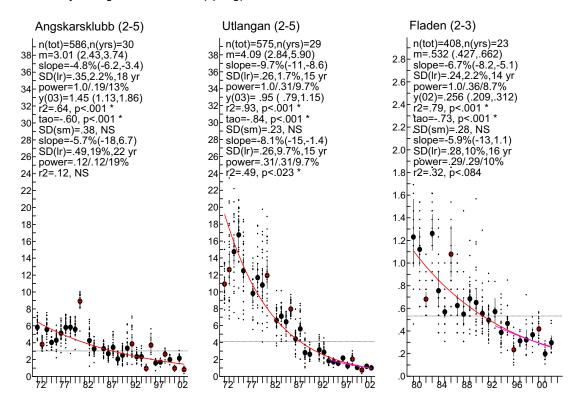
sPCB, ug/g lipid w., herring muscle



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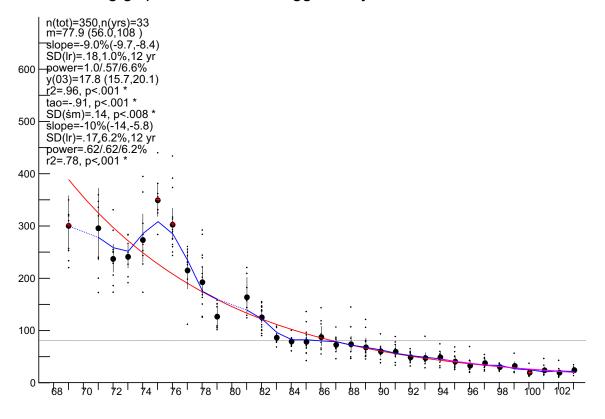
sPCB, ug/g lipid w., herring muscle, spring caught

Fat adjusted geometric means (spring)



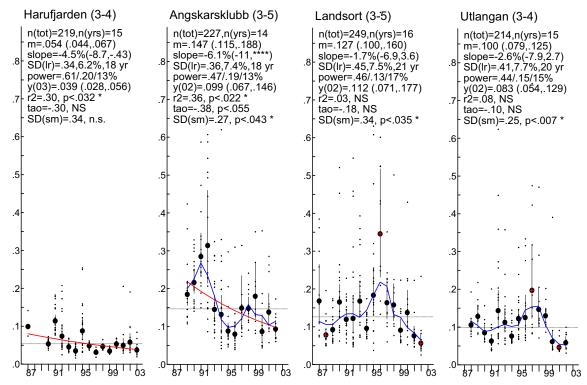
pia - 04.03.16 16:35, PSSV

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



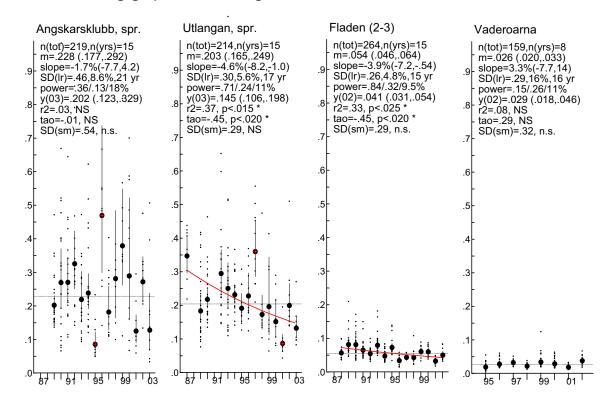
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CB-153, ug/g lipid w., herring muscle



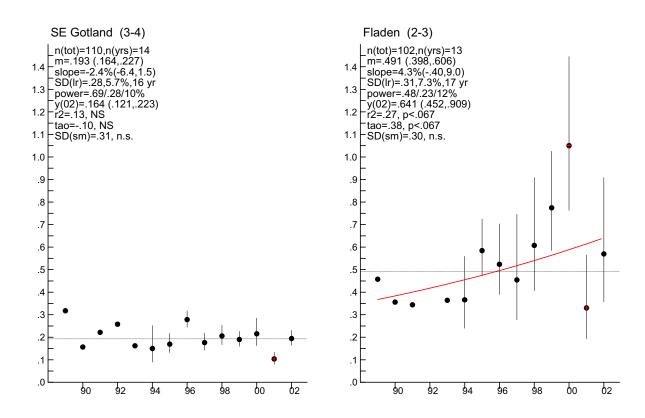
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CB-153, ug/g lipid w., herring muscle



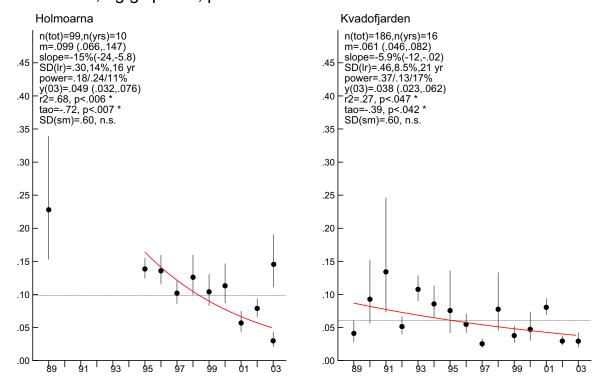
pia - 04.03.16 16:39, 153V

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



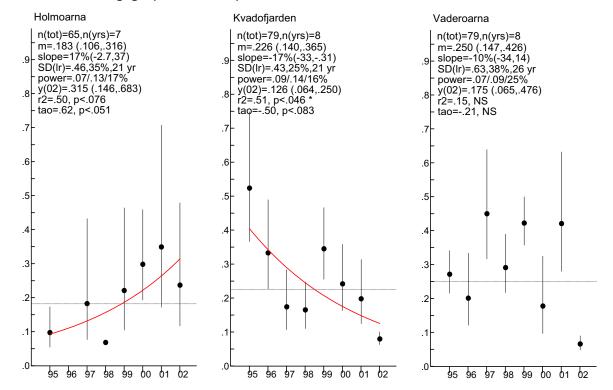
pia - 04.03.16 16:39, 153G

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



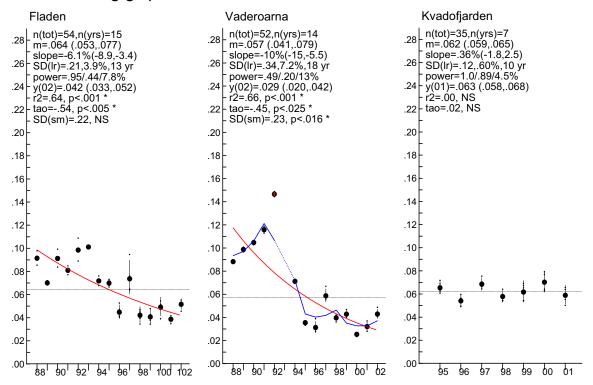
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CB-153, ug/g lipid w. Eelpout muscle



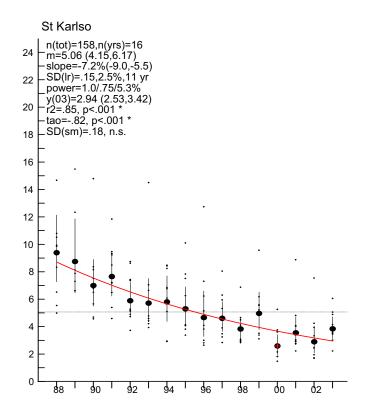
pia - 04.03.16 16:43, 153Z

CB-153, ug/g lipid w., blue mussel



pia - 04.03.16 16:51, 153M

CB-153, ug/g lipid w., guillemot egg



pia - 04.03.16 16:51, 153u

19 DDT's, dichlorodiphenylethanes

Updated 04.04.08

The concentration of the 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 the 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 seems 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 timeseries of sDDT, presented below, however, even sums where one of the three is below D.L. is included). Where it has been possible to estimate these ratios, there 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 timeseries presented below the ratio of 1 has been used.

Table 20.1. 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% conidence intervall.

unarysed on a pack	n	DDE	95% C.I	n		95% C.I	n	DDD	95% CI.	n	sDD T	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	.5570	-	-	-
Spring	24	1.0	1.0-1.1	1	.62	_	21	.77	.6885	1	.75	_
Landsort	28	.79	.7682	28	.75	.6781	28	.87	.7796	27	.79	.7782
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	.7488	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.

Temporal variation

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.

This investigation

sDDT concentrations in *herring* muscle from all investigated herring sites (except for Väderöarna where the time series is still short) and also in *cod* and *perch* and in *blue mussels* from the Kattegatt and Skagerak show significant decreasing trends during the time period 1980-2002. The rate varies between 6 and 12% a year. The timeserie of *guillemot eggs* (1969-2001) show a significant trend of about 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)-2001. The discharge of fresh DDT during 1983-84 (Bignert *et al*, 1990) is clearly noticeable in the timeseries 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 for the herring timeseries. The series of DDE show somewhat less between year variation in general compared to DDT and DDD. When comparing the power of the DDT's with other contaminants it should be noted that the DDT incident 1983-84 deteriorate the power of the timeseries 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.

Conclusion

The concentration of DDT's is decreasing at a rate of approximately 2-13% per year in the Baltic as well as in the Kattegat since the end of the seventies. The DDT is in general decreasing faster than the sum of DDT's.

Spatial variation

Herring muscle from Landsort and Utlängan in the Baltic proper show the highest sDDT concentrations of the herring samples, significantly higher than from Harufjärden and Fladen. The estimated geometric mean sDDT concentrations 2000 at Harufjärden in the Bothnian Bay and Fladen at the Swedish westcoast show no significant difference.

Also cod from the Baltic Proper (southeast of Gotland) show significantly higher sDDT concentrations, about twice as high, compared to cod from Fladen at the Swedish westcoast.

Table 20.2. Estimated geometric concentrations of **sDDT** (μ g/g **lipid** weight) in various matrices and sites for

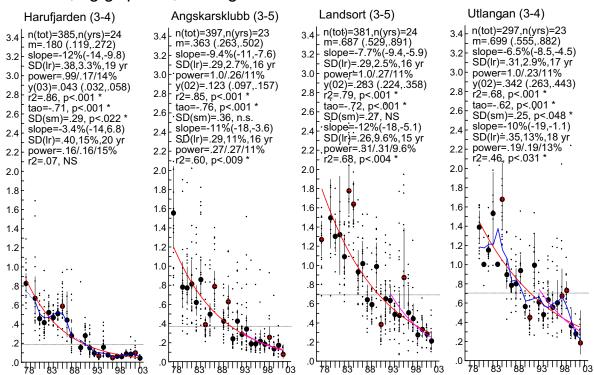
the last sampled year.

the last sampled ye	ar.					
Matrix	age	n tot	n yrs	year	trend	last yr
Herring msc.						
Harufj. autumn	3-4	373	23	78-02	-12 (-14,-9.5)*	.192 (.128290)
Ängskärskl. aut.	3-5	397	23	78-02	-9.4 (-11,-7.6)*	.363 (.263502)
" spring	2-5	586	30	72-03	-7.1 (-8.7,-5.6)*	1.14 (.847-1.52)
Landsort	3-5	381	24	78-02	-7.7 (-9.4,-5.9)*	.687 (.529891)
Utlängan, aut.	2-4	297	23	80-02	-6.5 (-8.5,-4.5)*	.699 (.555882)
" spring	2-3	556	29	72-03	-12 (-13,-11)*	2.65 (1.69-4.15)
Fladen	2-3	439	23	80-02	-11 (-14,-7.7)*	.157 (.109226)
Väderöarna		159	8	95-02		.044 (.030066)
Cod liver						
SE Gotland	3-4	243	22	80-02	-8.6 (-10,-6.8)*	1.25 (.936-1.67)
Fladen	2-3	278	22	80-02	-6.5 (-9.0,-3.9)*	.531 (.409689)
Perch muscle					•	· , , , , , , , , , , , , , , , , , , ,
Holmöarna		240	18	80-03	-11 (-14,-8.1)*	.160 (.097262)
Kvädöfjärden	3-5	326	23	80-03	-9.7 (-13,-6.2)*	.146 (.100215)
Eelpout muscle					, , , ,	
Holmöarna	3-6	65	7	95-02		.173 (.103290)
Kvädöfjärden	2-6	79	8	95-02	-21 (-42, .08)*	.285 (.155525)
Väderöarna	3-5	79	8	95-02		.097 (.060157)
Dab muscle						. , , , , , , , , , , , , , , , , , , ,
Fladen	3-5	184	14	81-94		.12 (.06223)
Flounder msc						
Väderöarna	4-6	163	15	80-94		.11 (.06020)
Blue mussel						`
Fladen		59	19	81-02	-8.7 (-13,-4.5)*	.065 (.045095)
Väderöarna		71	22	80-02	-9.1 (-12,-6.5)	.060 (.044084)
Kvädöfjärden		40	8	95-02	` ' '	.106 (.097116)
Guillemot egg						`
St. Karlsö		350	33	69-03	-10 (-12,-9.4)	71.4 (48.4-105)
					, ,	

Table 20.3. 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

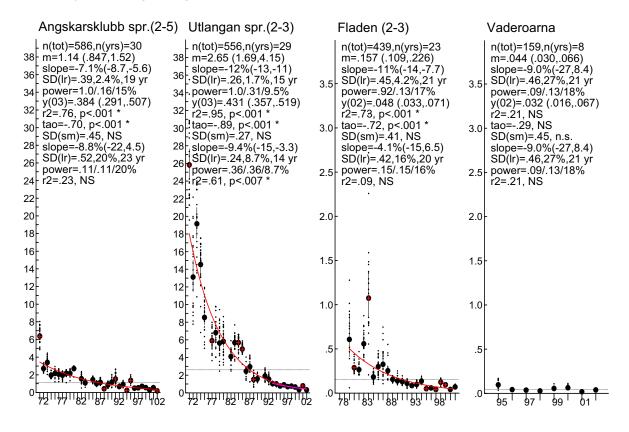
sDDT, ug/g lipid w., herring muscle



pia - 04.03.23 12:23, DSSC

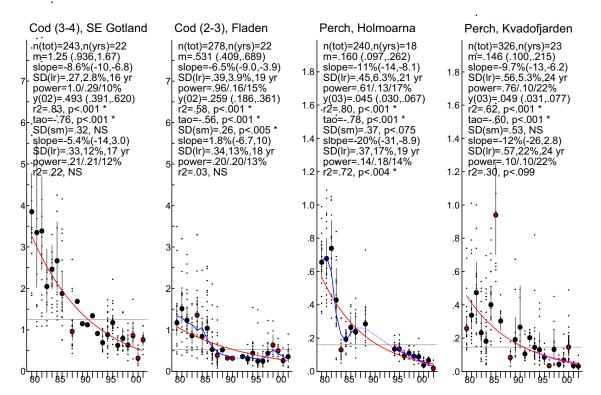
sDDT, ug/g lipid w., herring muscle

Fat adjusted spring herring samples



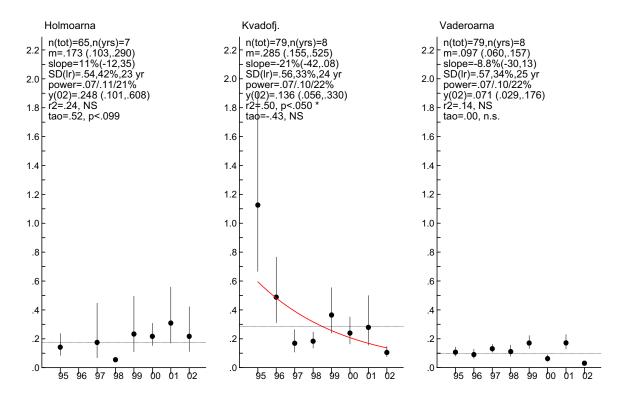
pia - 04.03.16 16:58, dssv

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



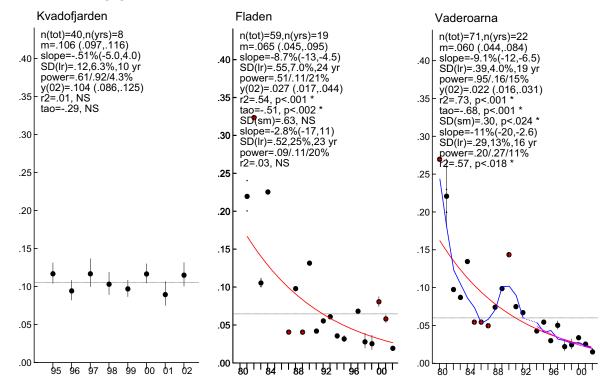
pia - 04.03.16 16:59, DSSGP

sDDT, ug/g lipid w., Eelpout



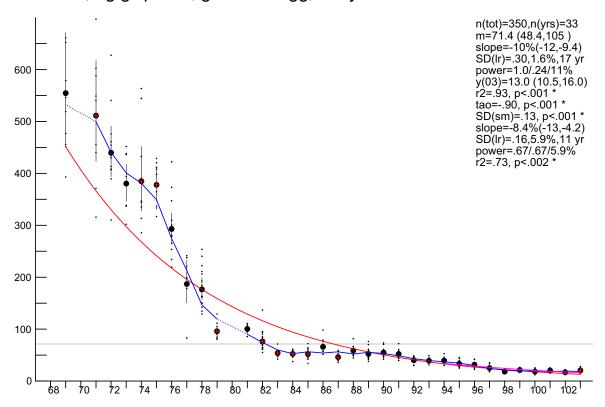
pia - 04.03.16 16:59, DSSZ

sDDT, ug/g lipid w., blue mussel



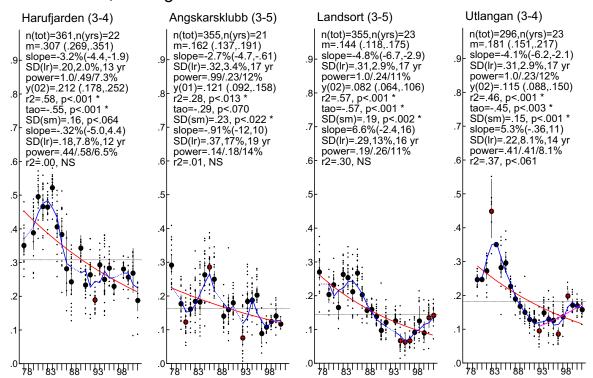
pia - 04.03.19 13:46, DSSM

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



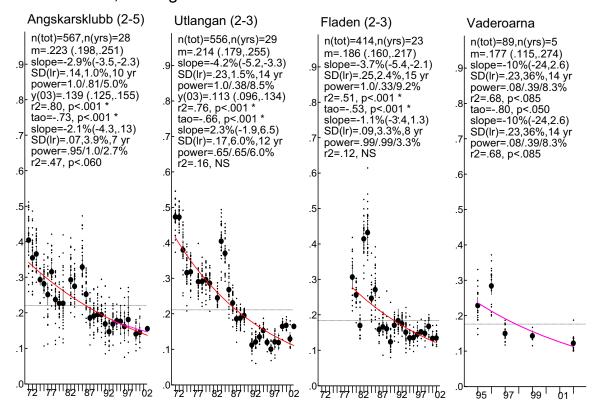
pia - 04.03.16 17:01, DSSU

DDT/sDDT, herring muscle



pia - 04.03.16 17:02, DTSC

DDT/sDDT, herring muscle



pia - 04.03.16 17:03, dtsv

20 HCH's, Hexachlorocyclohexanes

Updated 04.04.08

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, β -HCH and γ -HCH i.e. Lindane are analysed in muscle tissue for various fish species and in blue mussel soft body since 1988, see table below. Samples from 1987 at Harufjärden and Landsort have been retrospectively analysed. The concentrations of β -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.

Temporal variation

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.

This investigation

The concentrations of α -HCH in herring muscle show low variance in general. Decreasing trends are found from all sites about 13-21%. Also in cod liver the concentrations are decreasing significantly both in the timeserie from south east of Gotland (-19%) and from Fladen in Kattegat (-17%) at the Swedish west coast and in perch from Kvädöfjärden (-17%) and Holmöarna (-16%). The timeserie of α -HCH in guillemot eggs show a similar significant decrease of -17% a year.

The number of years required to detect an annual change of 5% is about 10 years for the cod and varies between 8 to 16 years for the herring time series.

The concentration of β -HCH in blue mussels and in perch, dab and flounder muscle as well as in other matrices from some of the sites are very close to the detection limit, causing increasing random between-year variation and uncertain trend analysis.

Concentrations of β -HCH are generally showing decreasing trends, and are now approaching the detection limit. This makes the substance less fitted for use in this kind of study. The concentrations of β -HCH in some matrices are however still detectable and show significant decreasing trends, for example herring from the sites Ängskärsklubb (-7.8%), Landsort (-6.1%) and Utlängan (-8.2%), and cod from SE Gotland -8.4(%). Guillemot eggs show a significant decrease of about 11% a year.

The concentration of lindane (γ -HCH) in herring muscle show decreasing trends from Harufjärden, Ängskärsklubb (spring and autumn), Landsort and Utlängan (spring and autumn) with an annual decrease between 9-16% in the Baltic, and at Fladen at a rate of approximately -10%. Also in cod liver from south east of Gotland show a significant decreasing trend (-13%) and Fladen (-16%) as well as the blue mussel series from the Baltic (-19%), the Kattegat (-9.5%) and the Skagerrak (-11%). The concentrations of γ -HCH in perch from Kvädöfjärden show a similar significant decrease of about -11% a year and also in guillemot egg of about -11% a year.

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

Conclusion

In general, the concentration of HCH's seems to decrease at a rate of about 10% or more per year in various species from the Baltic as well as at the Swedish westcoast since the end of the eighties. From ten timeseries 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 (except for herring in the Kattegatt).

Measures taken to fulfill 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.

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 Kattegat even after the rapid decrease mentioned above, see tables 21.1 and 21.3.

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 technial HCH were used whereas the use of lindane (γ -HCH) was more common in western countries.

Seasonal variation

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

Table 21.1. Geometric concentrations of a-HCH (ng/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)*	.009 (.007011)
Ängskärskl. aut.	3-5	226	14	89-02	-21 (-25,-17)*	.019 (.012033)
" spring	2-5	183	12	89-02	-19 (-20,-17)*	.024 (.014041)
Landsort	3-5	249	16	87-02	-17 (-19,-15)*	.033 (.021,.052)
Utlängan, aut.	2-4	214	15	88-02	-18 (-20,-17)*	.027 (.017043)
" spring	2-3	194	14	87-02	-19 (-21,-17)*	.026 (.016044)
Fladen	2-3	243	14	88-01	-16 (-17,-15)*	.004 (.003004)
Väderöarna		99	6	95-99, 02	-13 (-18, -6.8)*	.006 (.005009)
Cod liver						
SE Gotland	3-4	115	14	89-02	-19 (-21,-17)*	.032 (.020050)
Fladen	2-3	101	14	89-02	-17 (-19,-16)	.009 (.006014)
Perch muscle						
Holmöarna	4-7	43	5	89,95-98	-16 (-20,-12)*	.006 (.005007)
Kvädöfjärden	3-6	120	13	89, 94-01	-17 (-20,-14)*	.005 (.004006)
Eelpout						
Holmöarna		34	6	95,97,99-02	-16 (-26, -6.1)*	9.6 (5.95-15.5)
Kvädöfjärden		48	8	95-02	-16 (-21, -9.8)*	9.9 (7.01-13.9)
Väderöarna		21	3	95,96,98		5.5 (3.1-9.6)
Blue mussel	shell 1					
Kvädöfjärden		40	8	95-02	-22 (-24,-19)*	.016 (.013018)
Fladen	5-8	48	14	88-01	-15 (-18,-12)*	.012 (.009018)
Väderöarna	6-10	47	13	88-01	-16 (-21,-10)*	.011 (.007017)
Guillemot egg						
St. Karlsö		137	14	88-03	-17 (-20,-13)	.021 (.013035)

^{*} significant trend, p < 0.05

Table 21.2. Geometric concentrations of a-HCH (ug/g fresh 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.						
Harufjärden	3-4	180	12	87, 89-00	-20 (-25,-15)*	.17 (.1223)
Ängskärsklubb	3-5	204	12	89-00	-21 (-27,-14)*	.19 (.1228)
Landsort	3-5	225	14	87-00	-21 (-28,-14)*	.31 (.18,.54)
Utlängan.	2-4	191	13	88-00	-26 (-32,-20)*	.18 (.1227)
Fladen	2-3	240	13	88-00	-17 (-23,-11)*	.147 (.1022)
Väderöarna		97	5	95-99		.005 (.004007)

Table 21.3. Geometric 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 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	900	n	n yrs	vear	trend (95% ci)	Last year (95% ci)
	age	- 11	п ут 5	yeai	ti enu (93/0 ci)	Last year (93 /0 Cl)
Herring msc.	2.4			07 00 00	0.0 (1.0 7.0) #	011 (000 014)
Harufj. autumn	3-4	171	11	87, 90-99	-8.9 (-12,-5.8)*	.011 (.009014)
Ängskärskl. aut.	3-5	225	14	89-02	-16 (-20,-12)*	.014 (.009020)
" spring	2-5	206	15	89-03	-14 (-16,-12)*	.014 (.009019)
Landsort	3-5	249	16	87-02	-12 (-14,-9.5)*	.025 (.018,.034)
Utlängan, aut.	2-4	214	15	88-02	-12 (-13,-11)*	.025 (.018034)
" spring	2-3	195	15	87-03	-15 (-17,-13)*	.024 (.015036)
Fladen	2-3	252	14	88-01	-9.9 (-14,-5.6)*	.019 (.014025)
Väderöarna		120	7	95-01		.011 (.006019)
Cod liver						
SE Gotland	3-4	110	14	89-02	-13 (-14,-11)*	.024(.017032)
Fladen	2-3	91	13	89-02	-16 (-20, -11)*	.014 (.009,.021)
Perch muscle						
Holmöarna	4-7	41	5	89,95-98#	-14 (-26, -3.1)*	.007 (.004015)
Kvädöfjärden	3-6	72	9	89, 94-01	-11 (-20, -2.9)*	.009 (.006013)
Eelpout						
Holmöarna		30	5	95,97,99, 01-02	-17 (-32, -3.2)*	.009 (.005018)
Kvädöfjärden		60	8	95-02	-18 (-21, -15)*	.013 (.009018)
Blue mussel	shell 1					_
Kvädöfjärden		40	8	95-02	-19 (-26, -13)*	.014 (.009021)
Fladen	5-8	53	16	81, 83, 88-01	-9.5 (-12, -6.5)*	.025 (.018035)
Väderöarna	6-10	49	14	83, 88-01	-11 (-15, -7.1)*	.024 (.016035)
Guillemot egg						
St. Karlsö		91	11	88-91, 93-97, 00-	-11 (-19,-2.0)*	.014 (.009023)
				01#	, ,	,

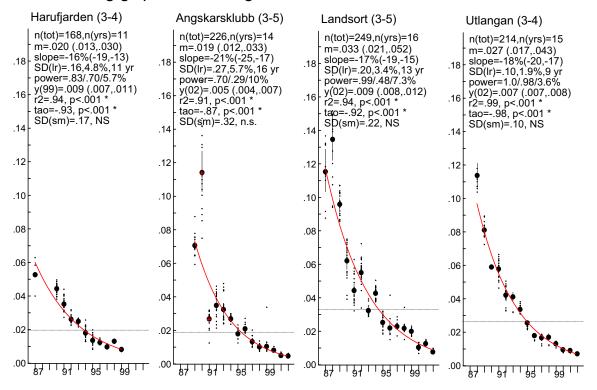
[#] all values below detection limit during recent years

Table 21.4. 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

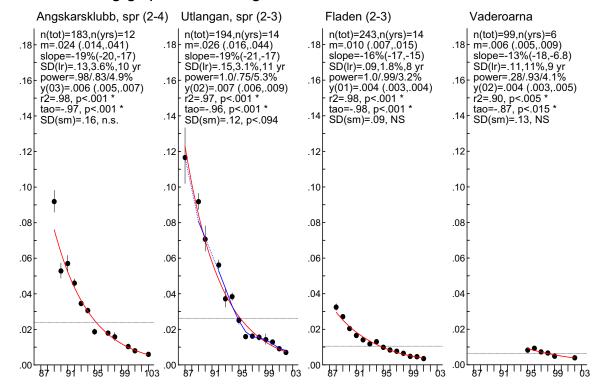
^{*} significant trend, p < 0.05

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



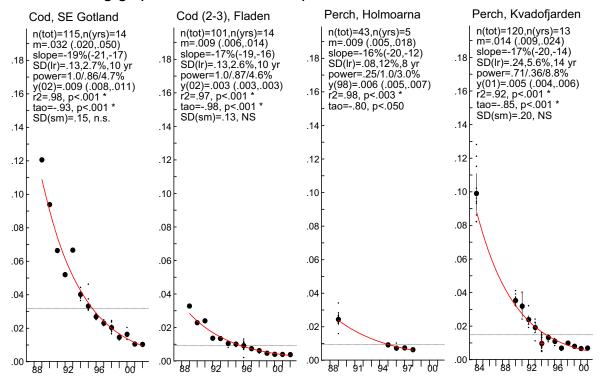
pia - 04.03.16 17:14, HCHAC

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



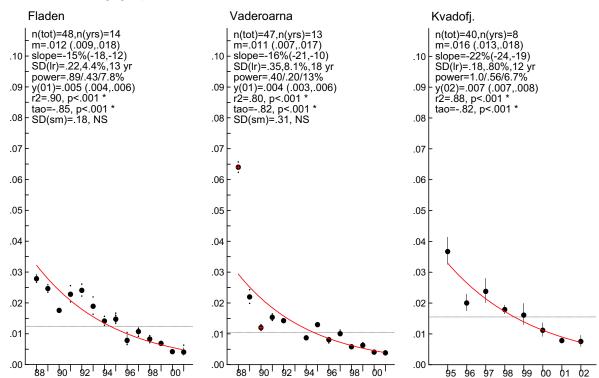
pia - 04.03.16 17:15, hchav

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



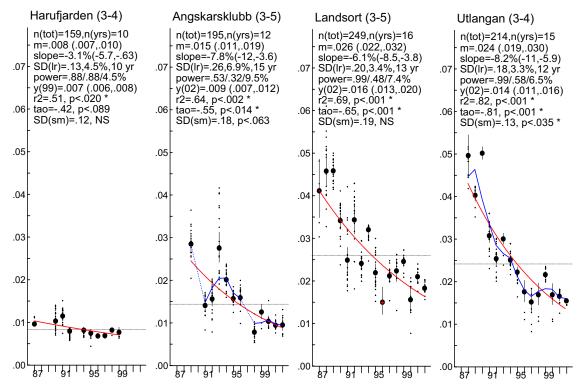
pia - 04.03.16 17:16, HCHAGP

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



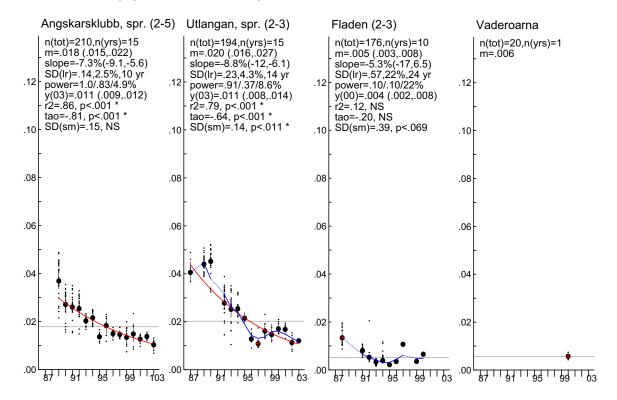
pia - 04.03.19 13:48, HCHAM

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



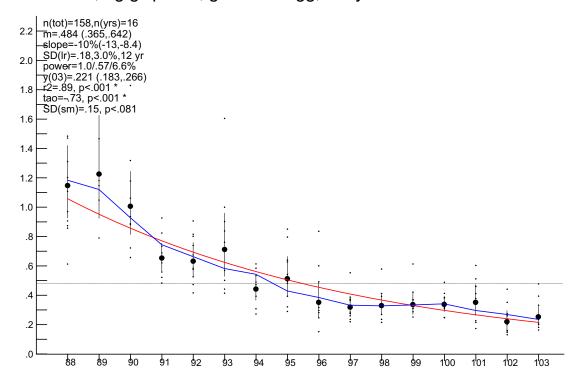
pia - 04.03.16 17:18, HCHBC

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



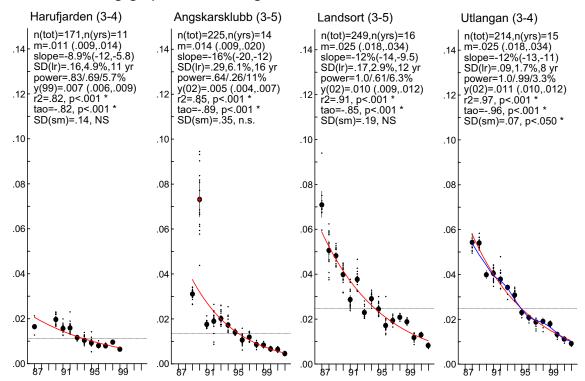
pia - 04.03.16 17:19, hchby

b-HCH, ug/g lipid w., guillemot egg, early laid



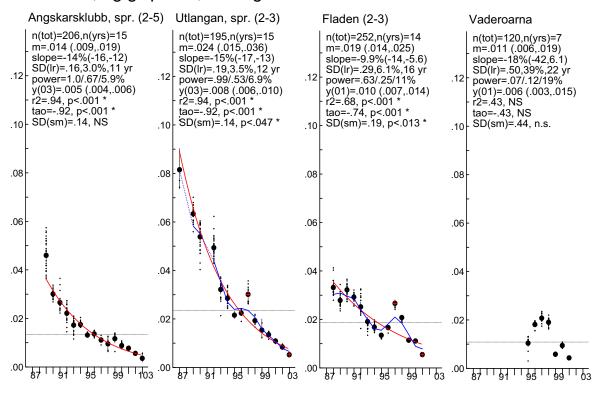
pia - 04.03.17 10:55, hchbu

Lindane, ug/g lipid w., herring muscle



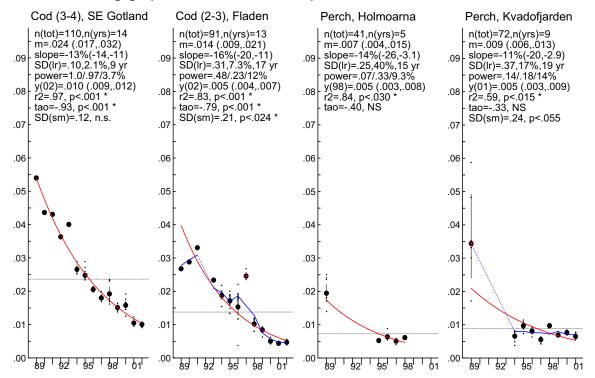
pia - 04.03.17 10:56, HCHGC

Lindane, ug/g lipid w., herring



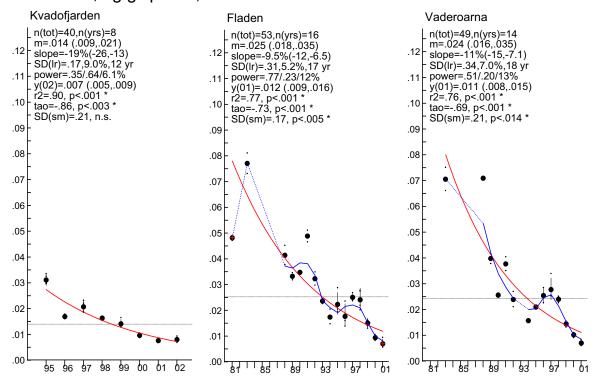
pia - 04.03.17 10:57, hchgv

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



pia - 04.03.17 10:58, HCHGGP

Lindane, ug/g lipid w., blue mussel



pia - 04.03.19 13:50, HCHGM

21 HCB, Hexachlorobenzene

Updated 04.04.08

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 is analysed in various species, see table below, since 1988. Samples from 1987 at Harufjärden and Landsort have been retrospectively analysed.

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

Temporal variation

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.

This investigation

Significant decreasing trends in herring muscle are shown from Ängskärsklubb (spring, -5.7% and autumn, -8.2%) Landsort (-9.1%), Utlängan (spring, -11% and autumn, -9.1%) and in cod south east of Gotland (-9.1%) and guillemot egg from St Karlsö (-7.8%) in the Baltic proper. Both series for perch are also showing declining trends (Holmöarna –6.8% and Kvädöfjärden –6.0%). Decreasing trends are also found in samples from the Kattegatt; herring (-5.2%) and cod (-9.5%).

In blue mussels from the Swedish westcoast the concentrations are very low (about 3-4 ng/g lipid w.) i.e. close to and for some years below the detection limit and hence blue mussel is less useful for monitoring HCB in this region. Blue mussels from Fladen show a steep decreasing trend in fat content which might explain the non decreasing trend in HCB in blue mussels from Fladen.

The number of years required to detect an annual change of 5% varied between 13 to 19 years for the herring timeseries.

Conclusion

The concentration of HCB in herring, cod, dab and guillemot egg seems to decrease 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.

Spatial variation

Herring muscle from Landsort and Utlängan in the Baltic Proper shows 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 differencies can be shown in the estimated concentrations for 2000 in the autumn caught herring from the various sites in the Baltic and the Kattegatt, although the estimated concentrations from 2000 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 Skagerrak*. This difference is significant for blue mussels and for eelpout if Holmöarna and Väderöarna are compared.

Differences among various species

At some of the samling 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. The whole soft body in blue mussels is analysed. 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(38) > Perch(12)

Kvädöfjärden: Eelpout(14) > Perch(9) > Blue mussel(6) Fladen: Cod(17) - Herring(16) > Dab(8) > Blue mussel(3)

Väderöarna: Flounder(9) - Eelpout(9) - Herring(10) > Blue mussel(3)

The blue mussels are showing the lowest values compared to other species from the same area. Guillemot egg contains about 20 - 600 times higher concentrations of HCB compared to the other investigated matrices.

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.

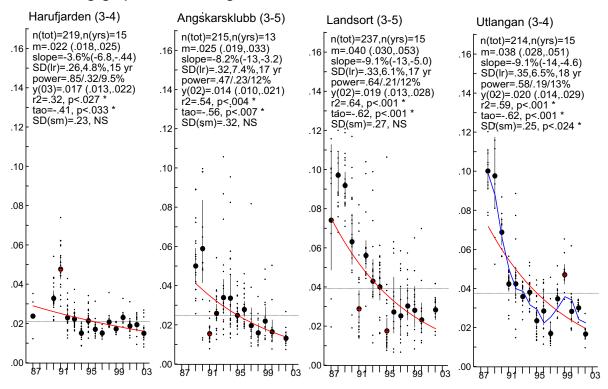
Table 22.1. Estimated geometric concentrations of **HCB** (ng/g **lipid** weight) in various matrices and sites for the last sampled year.

Matrix	age	n	n yrs	year	trend	last yr
Herring msc.	<u> </u>		11 J15	y cui	ii cii u	iuse y i
Harufj. autumn	3-4	207	14	87-02		.022 (.019026)
Ängskärskl. aut.	3-5	215	13	89-02	-8.2 (-13, -3.2)*	.025 (.019033)
" spring	2-4	219	15	89-03	-5.7 (-10,84)*	.082 (.064104)
Landsort	3-5	237	15	87-02	-9.1 (-13,-5.0)*	.040 (.030053)
Utlängan, aut.	2-4	214	15	88-02	-9.1 (-14,-4.6)*	.038 (.028051)
" spring	2-3	195	15	87-03	-11 (-14,-7.5)*	.066 (.047091)
Fladen	2-3	264	15	88-02	-5.2 (-8.5,-2.0)*	.016 (.013019)
Väderöarna		139	7	95-02		.010 (.008012)
Cod liver						
SE Gotland	3-4	110	14	89-02	-9.1 (-14,-4.1)*	.042 (.032057)
Fladen	2-3	101	13	89-02	-9.5 (-14,-5.1)*	.017 (.013023)
Perch muscle						,
Holmöarna		88	10	89,95-03	-6.8 (-12, -2.1)*	.012 (.009015)
Kvädöfjärden	3-5	105	14	84,89-00,03	-6.0 (-12,32)*	.009 (.006012)
Eelpout muscle						
Holmöarna	3-6	65	7	95-02		.038 (.025057)
Kvädöfjärden	2-6	77	8	95-02		.014 (.011018)
Väderöarna	3-5	74	8	95-02		.009 (.008011)
Dab muscle						
Fladen	3-5	6	6	89-94		4 (3-6)
Flounder msc						
Väderöarna	4-6	6	6	89-94		4 (1-28)
Blue mussel						
Fladen		32	9	88-00		2.5 (2.0-3.1)
Väderöarna		31	10	88-00	-7.9 (-16,05)*	2.9 (2.0-4.2)
Kvädöfjärden		37	8	95-02		6.0 (4.7-7.7)
Guillemot egg						
St. Karlsö		168	17	79,88-03	-7.8 (-9.7,-5.8)*	1.37 (1.05-1.80)

Table 22.2. Geometric concentrations of **HCB** (ng/g **fresh** weight) in various matrices and sites during 1987-1996 and estimated mean concentration for the last analysed year.

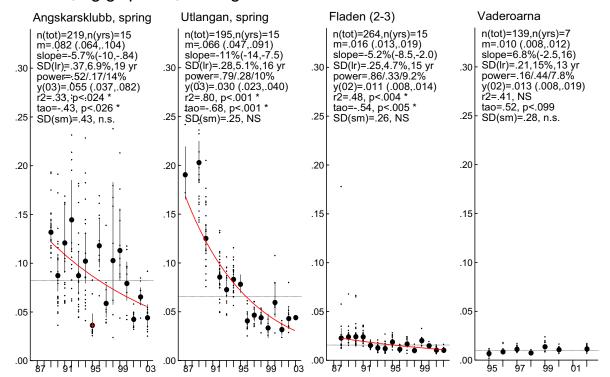
Matrix	age	n tot	n yrs	year	trend	last yr
Herring msc.			-			•
Harufj. autumn	3-4	183	12	87-00	-7.2 (-12, -2.5)	0.42 (.3158)
Ängskärskl. aut.	3-5	204	12	89-00	-8.7 (-16,91)	0.40 (.2467)
" spring	2-4	150	8	89-97		2.1 (1.04.2)
Landsort	3-5	223	14	87-00	-15 (-23, -6.3)	0.48 (.2690)
Utlängan, aut.	3-4	191	13	88-00	-18 (-27, -8.6)	0.39 (.2174)
" spring	2-3	145	8	87-96		0.80 (.49-1.3)
Fladen	2-3	240	13	88-00	-6.0 (-13, .95)	0.42 (.2568)
Väderöarna		119	6	95-00		0.51 (.4656)
Cod liver						
SE Gotland	3-4	31	7	89-95		20 (11-38)
Fladen	2-3	33	6	89-95		2.8 (1.4-5.6)
Perch muscle						
Holmöarna		20	2	89,95		-
Kvädöfjärden	3-5	64	8	84,89-95		.049 (.02012)
Eelpout muscle						
Holmöarna	3-6	35	4	95-98		0.40 (.2858)
Kvädöfjärden	2-6	49	5	95-99		0.088 (.07610)
Väderöarna	3-5	49	5	95-99		0.058 (.053064)
Dab muscle						
Fladen	3-5			89-94		.02
Flounder msc						
Väderöarna	4-6			89-94		.02
Blue mussel						
Fladen				88-95		.02
Väderöarna				88-95		.03
Kvädöfjärden		30	6	95-00		0.080 (.071089)
Guillemot egg						
St. Karlsö				79,88-97		104

HCB, ug/g lipid w., herring muscle



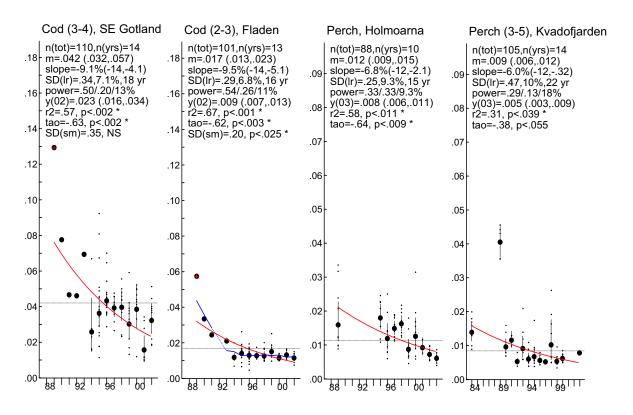
pia - 04.03.23 12:27, HCBC

HCB, ug/g lipid w., herring



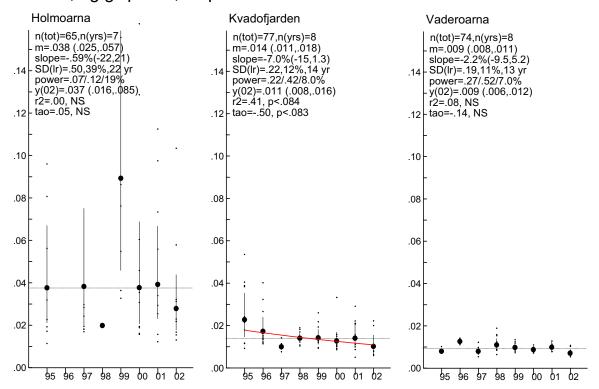
pia - 04.03.17 11:01, hcbv

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



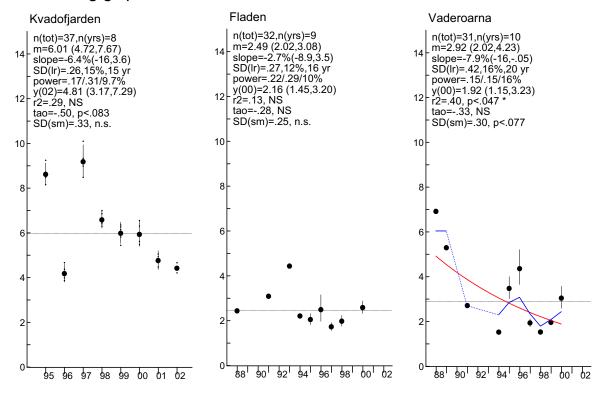
pia - 04.03.08 10:48, HCBGP

HCB, ug/g lipid w., eelpout



pia - 04.03.08 10:49, HCBZ

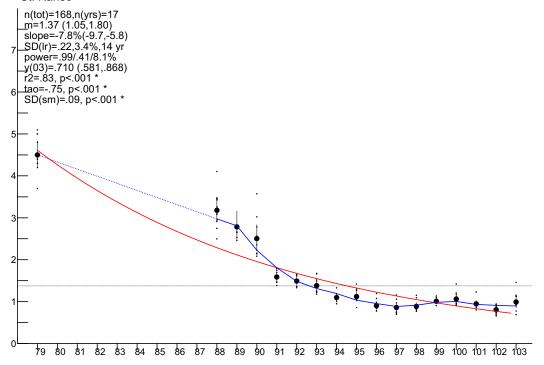
HCB, ng/g lipid w., blue mussel



pia - 04.03.19 13:51, HCBM

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

St. Karlso



pia - 04.03.08 10:50, hcbu

22 PCDD/PCDF,

Polychlorinated Dioxines and Dibenzofuranes

Updated 04.04.08

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

Temporal variation

This investigation

In guillemot eggs significant decreasing trends are observed for TCDD, TCDF and TCDD-equivalents. The development over time is quite different for TCDD and TCDF, see Figure below. TCDD-equivalents has not continued to decrease significantly during the recent 10 years. The number of years required to detect an annual change of 5% varied between 10 and 14 years for the last ten years.

No significant changes can be seen in herring muscle. The number of years required to detect an annual change of 5% varied between 15-16 years for these time series.

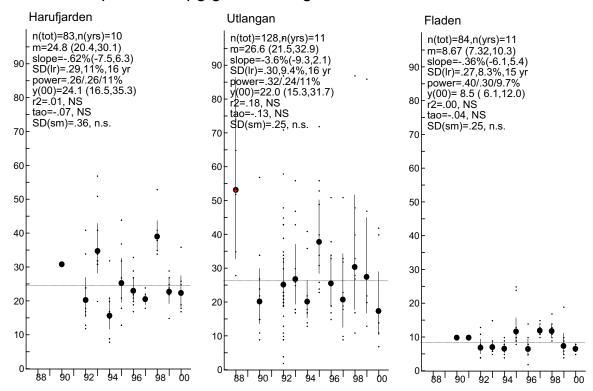
Table 23.1. Geometric concentrations of **TCCD-eqv.** (pg/g **lipid** weight) in various matrices and sites during 1988/1990-1998 and estimated mean concentration 1998.

Matrix	age	n tot	n yrs	year	trend	Mean
Herring msc.						
Harufj. autumn		83	10	90-00		24.8 (20.4-30.1)
Utlängan		128	11	88-00		26.6 (21.5-32.9)
Fladen		84	11	90-00		8.67 (7.32,10.3)

Table 23.2. Geometric concentrations of **TCCD-eqv.** (pg/g **fresh** weight) in various matrices and sites during 1988/1990-1998 and estimated mean concentration 1998.

Matrix	age	n tot	n yrs	year	trend	Mean (last year if
						trend)
Herring msc.						
Harufj. autumn		75	9	90-99		.74 (.5599)
Utlängan		114	9	88-99		.70 (.5885)
Fladen		76	10	90-99		.36 (.28,.46)

TCDD-equivalents, pg/g fat, herring muscle



pia - 04.03.08 10:50, tcddec

24 Polybrominated flame retardants

Updated 04.04.08

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

Temporal variation

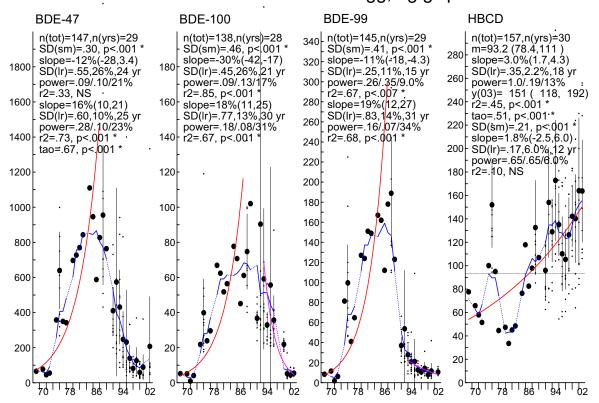
This investigation

Significant increasing trends followed by decreasing trends during the recent 10-year period are observed for BDE-47, BDE-99 and BDE-100. For HBCD a significant increase of about 3% per year is shown.

Spatial variation

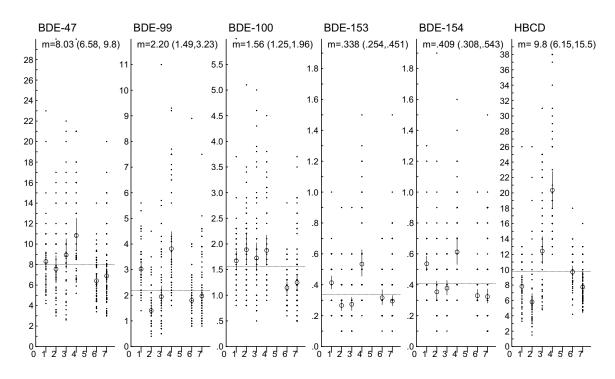
Yet only four years of analysis (1999-2002) is presented (Figure 24.2). The Figure indicates elevated concentrations of some of the substances at Karlskrona in the southern Baltic Proper. The number of analyses is still too few to make any firm conclusions, though. In general the PBDE's and HBCD seems to be more evenly distributed compared to e.g. PCB.

Brominated contaminants in Guillemot egg, ng/g lipid w.



pia - 04.03.17 11:02, BRUL2

PBDE, ug/g lipid w., herring muscle from different sampling sites



pia - 04.03.23 12:07, bdec2

Figure 24.2: 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 (Skagerakk)

25 Summary tables

Table 25.1. Estimated mean values for biological variables, for the last years analysis. In order to get a robust estimate of the current concentrations levels in each time series, the concentration values are based on the current trend rather than the individual year. If no significant trend (p<0.10) is found the geometric mean concentration and the corresponding 95% confidence interval is reported. C1=herring, Harufjärden, C2=herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, C6=herring, Fladen, C7=herring, Väderöarna, V2=spring caught herring, Ängskärsklubb, V4=spring caught herring, Karlskrona archipelago, G5=cod south east of Gotland, G6=cod, Fladen, P2=perch, Kvädöfjärden, Z1=eelpout, Holmöarna, Z2=eelpout, Kvädöfjärden, Z3=eelpout, Väderöarna, M2=blue mussel, Kvädöfjärden, M6=blue mussel, Fladen, M3=blue mussel, Väderöarna, U8=guillemot egg, St Karlsö.

Biological variables

	Tot. weight	Tot. length	liver	fat%	liver dry %	muscle dry
	g	cm	weight			%
C1, 01	25	16	0.28	3.0	30	22
C2, 01	34	17	0.42	2.0	24	20
C3, 01	30	17	0.45	3.6	25	22
C4, 01	31	17	0.32	2.6	28	23
C6, 01	55	20	0.62	3.9	40	22
C7, 01	63	21	0.78	6.0	34	27
V2, 01	29	17	0.33	3.2	20	21
V4, 01	39	17	0.51	2.5	22	21
G5, 01	436	34	22	61	68	20
G6, 01	293	31	6.5	64	64	19
P1, 00	80	19	0.55	13	32	20
P2, 00	49	16	0.36	0.67	21	19
Z1, 01	37	22	0.38	0.54	19	17
Z2, 01	47	24	0.65	0.47	18	17
Z3, 01	43	22	0.47	0.73	19	17

Table 25.1. Estimated mean values for biological variables, in herring from other investigations not included in the ordinary Swedish Monitoring Programme in Marine Biota. The geometric mean concentration and the corresponding 95% confidence interval are reported. Hapa = Haparanda archipelago (BD), Pite = Pite archipelago (BD), Skel = Skelleftebukten (AC), Trys = Trysunda (AC), Juni = Juniskär (AC), Lövg = NO Lövgrund (X), Egge = NO Eggegrund (X), Jätt = SV Jättholmarna (X), Höli = Hölick (X), Bank = 10' N Västra Banken (X), Stor = N Storjungfrun (X).

Biological variables

	Tot. weight	liver weight	fat%
Hapa, 96	37 (33-40)	.47 (.4055)	1.8 (1.5-2.2)
Pite, 96	35 (34-37)	.40 (.3645)	2.0 (1.5-2.7)
Skel, 96	38 (34-41)	.47 (.4154)	2.3 (1.6-3.4)
Trys, 96	34 (32-35)	.37 (.3143)	3.9 (3.3-4.6)
Junis, 96	67 (61-72)	.77 (.5598)	6.3 (5.5-7.2)
Lövg, 96	37 (34-40)	.42 (.3548)	2.9 (1.9-4.5)
Egge, 96	40 (34-45)	.36 (.3141)	4.3 (3.1-5.8)
Jätt, 96	42 (37-47)	.58 (.4770)	3.6 (2.2-5.8)
Höli, 96	48 (43-53)	.51 (.3864)	6.5 (5.0-8.5)
Bank, 96	45 (41-49)	.49 (.3266)	- -
Stor , 96	47 (40-54)	.52 (.4360)	-

Table 25.1. Estimated geometric mean concentrations, **dry weight**, for the last years analysis. In order to get a robust estimate of the current concentrations levels in each time series, the concentration values are based on the current trend rather than the individual year. If no significant trend (p<0.10) is found the geometric mean concentration and the corresponding 95% confidence interval is reported. C1=herring, Harufjärden, C2=herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, C6=herring, Fladen, C7=herring, Väderöarna, V2=spring caught herring, Ängskärsklubb, V4=spring caught herring, Karlskrona archipelago, 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, M3=blue mussel, Väderöarna, U8=guillemot egg, St Karlsö.

-	Pb	Cd	Ni	Cr	Cu	Zn
	μg/g dw.	μg/g dw.	μg/g dw.	μg/g dw.	μg/g dw.	μg/g dw.
C1, 02	0.119	1.39	0.158	0.314	10.7	93.5
,	(.096147)	(1.17-1-66)	(.086289)	(.295335)	(9.5-12.0)	(85.3-102)
C2, 02	0.157	1.64	0.176	0.286	10.8	100
,	(.129191)	(1.38-1.94)	(.117265)	(.266308)	(10.0-11.7)	(93.2-108)
C3, 02	0.192	1.98	0.238	0.269	11.9	94.5
,	(.160231)	(1.73-2.26)	(.186304)	(.250288)	(10.6-13.3)	(88.3-101)
C4, 02	0.201	1.75	0.319	0.285	12.1	100
,	(.167241)	(1.51-2.04)	(.270376)	(.265307)	(11.0-13.4)	(93.8-106)
C6, 02	0.131	0.537	0.144	.280	12.3	94.1
,	(.108159)	(.483597)	(.082251)	(.227346)	(10.8-13.9)	(88.5-100)
C7, 02	0.061	0.320	0.091	0.263	9.25	107
•	(.051074)	(.286359)	(.064130)	(.222312)	(8.41-10.2)	(92.4-123)
V2, 03	0.177	3.92	0.271	.341	13.1	146
,	(.150208)	(3.28-4.68)	(.205359)	(.297391)	(11.4-15.1)	(129-165)
V4, 02	.160	2.39	0.286	0.300	13.6	125
,	(.131196)	(2.12-2.69)	(.226363)	(.218412)	(10.3-17.8)	(102-153)
G5, 02	0.049	0.057	0.095	0.102	16.8	35.3
	(.037065)	(.044073)	(.073125)	(.060172)	(15.1-18.7)	(31.5-39.7)
G6, 02	0.075	0.174	0.183	0.178	17.4	73.9
	(.059095)	(.138219)	(.132254)	(.137232)	(14.4-20.9)	(66.2-82.6)
P1, 02	0.046	0.443	0.098	0.145	10.7	98.8
	(.033065)	(.326603)	(.051192)	(.111191)	(8.45-13.6)	(88.0-111)
P2, 02	0.053	0.648	0.104	0.280	11.8	117
	(.038073)	(.490857)	(.057189)	(.227346)	(9.32-14.9)	(92.3-149)
Z1, 02	0.175	1.08	0.187	0.374	10.9	163
	(.157195)	(.909-1.28)	(.089392)	(.238589)	(9.7-12.4)	(134-200)
Z2, 02	0.197	1.32	0.226	0.418	22.3	183
	(.178218)	(1.12-1.56)	(.145353)	(.367476)	(20.1-24.9)	(144-233)
Z3, 02	0.131	0.282	0.294	0.373	28.7	213
	(.096177)	(.245325)	(.233371)	(.248563)	(25.7-32.1)	(172-264)
M2, 02	1.74	4.16	2.66	2.16	7.78	137
	(1.03-2.93)	(3.69-4.70)	(2.43-2.92)	(1.78-2.63)	(7.06-8.57)	(120-156)
M6, 02	1.42	1.11	2.15	2.42	6.04	114
	(1.05-1.92)	(1.01-1.23)	1.75-2.64)	(1.30-4.52)	(5.57-6.54)	(102-128)
M3, 02	1.35	1.05	1.10	0.850	5.22	108
	(1.06-1.72)	(.925-1.18)	(.862 - 1.40)	(.694-1.04)	(4.86-5.60)	(93.4-124)
U8, 02	0.055	0.003	0.078	0.276	2.91	46.3
	(.049061)	(.002003)	(.045134)	(.258294)	(2.61-3.24)	(43.3-49.4)

Table 25.1. Estimated geometric mean concentrations, **fresh weight**, for the last years analysis. In order to get a robust estimate of the current concentrations levels in each time series, the concentration values are based on the current trend rather than the individual year. If no significant trend (p<0.10) is found the geometric mean concentration. The corresponding 95% confidence interval is also reported. C1=herring, Harufjärden, C2=herring, Ängskärsklubb, C3=herring, Landsort, C4=herring, Utlängan, C6=herring, Fladen, C7=herring, Väderöarna, V2=spring caught herring, Ängskärsklubb, V4=spring caught herring, Karlskrona archipelago, G5=cod south east of Gotland, G6=cod, Fladen, P2=perch, Kvädöfjärden, Z1=eelpout, Holmöarna, Z2=eelpout, Kvädöfjärden, Z3=eelpout, Väderöarna, M2=blue mussel, Kvädöfjärden, M6=blue mussel, Fladen, M3=blue mussel, Väderöarna, U8=guillemot egg, St Karlsö.

	Hg	Pb	Cd	Ni	Cr	Cu	Zn
	ng/g ww	ng/g ww	μg/g ww	ng/g ww	ng/g ww	μg/g ww	μg/g ww
C1, 01	39	23*	.40	50	94	3.2	27
	34-45	18-29	.3447	27-95	88-101	2.9-3.5	25-30
C2, 01	39*	28*	.63#	25*	80	3.2#	26
	23-65	22-37	.5081	13-48	74-87	2.8-3.7	24-29
C3, 01	43#	30*	.66#	61	66	3.2	25
	33-56	23-37	.5579	48-77	61-71	2.9-3.5	23-27
C4, 01	17	540	.66#	83	75	3.3	27
	15-20	44-67	.5284	67-103	70-81	3.0-3.7	25-29
C6, 01	24	50	.16			4.0	26
	22-28	37-69	.1319			3.4-4.8	24-28
C7, 01	31#	22	.11		86	2.7	38
	23-42	8.5-58	.05620		75-98	1.6-4.3	15-100
V2, 02	26*	39	.81	51	68	2.5	30
	21-33	33-46	.53-1.3	34-76	61-76	2.2-2.9	23-39
V4, 01	18*	33	.50#	59	62	2.8	26
	14-21	26-43	.4258	48-73	56-68	2.1-3.9	23-30
G5, 01	35#	14*	.018*	65	65	9.9	21
	29-42	9-22	.014025	47-89	36-119	8.8-11	18-24
G6, 01	53	17*	.041*	73	72	6.6	27
	48-59	12-25	.027060	53-99	53-98	5.5-8.0	25-29
P1, 00	67	6*	.097	8*	22*	2.3	20
	52-86	4-8	.08611	4-20	18-27	1.7-3.2	18-23
P2, 00	21*	7*	.14	24*	53#	2.5	24
	17-28	5-10	.1216	20-30	46-62	1.7-3.5	17-32
Z1, 01	86	32	.20	35	80	1.5*	31
	67-111	29-36	.1725	29-41	58-110	1.3-1.9	28-34
Z2 , 01	79	38	.24	51	79	4.3	36
	31-102	34-42	.2029	44-60	70-89	3.8-4.8	33-39
Z3, 01	41#	26	.054	63	72	5.8	43
	23-73	23-29	.046062	55-72	46-113	5.0-6.6	40-47
M2,00	12	195	.52#	334	289*	.98	17
	8.7-16	156-244	.4857	305-365	267-314	.86-1.1	14-20
M6, 01	14	140*	.13*	308	397	0.70*	17
	12-15	82-240	.09916	250-380	236-667	.5984	16-19
M3, 01	14	225	.17	205	161	0.94	18
	12-16	185-274	.1519	164-255	127-203	.85-1.1	15-21
U8, 98	257*	12*	.79 ng/g	22	78	0.83	9.8*
	219-302	11-13	.61-1.0	19-26	72-83	.7988	7.5-13

^{*} negative trend (p<0.05), # upward trend (p<0.05)

Table 25.1. Estimated geometric mean concentrations, **dry weight**, in herring from other investigations not included in the ordinary Swedish Monitoring Programme in Marine Biota. The geometric mean concentration and the corresponding 95% confidence interval are reported. Hapa = Haparanda archipelago (BD), Pite = Pite archipelago (BD), Skel = Skelleftebukten (AC), Trys = Trysunda (AC), Juni = Juniskär (AC), Lövg = NO Lövgrund (X), Egge = NO Eggegrund (X), Jätt = SV Jättholmarna (X), Höli = Hölick (X), Bank = 10' N Västra Banken (X), Stor = N Storjungfrun (X).

	Pb	Cd	Ni	Cr	Cu	Zn
	μg/g dw.					
Нара,	.080	1.1	.12	.25	12	105
96	.05512	.77-1.5	.09017	.2131	9.7-14	90-120
Pite,	.18	2.6	.21	.33	16	130
96	.1325	2.2-3.1	.1432	.2839	13-21	120-150
Skel,	.16	2.0	.17	.29	13	135
96	.1123	1.5-2.8	.1420	.2435	10-17	110-170
Trys,	.20	1.2	.19	.41	8.2	80
96	.1527	.57-2.4	.1426	.3153	6.0-11	67-95
Junis,	.13	1.6	.74	.37	9.0	87
96	.09119	1.2-2.1	.55-1.0	.2946	7.4-11	77-99
Lövg,	.10	3.9	.27	.36	15	98
96	.07313	3.2-4.8	.1937	.2945	11-21	85-110
Egge,	.17	3.3	.25	.40	21	100
96	.1125	2.2-5.2	.1446	.2759	13-32	87-120
Jätt,	.074	1.9	.20	.44	18	82
96	.05610	1.1-3.2	.1922	.3359	12-27	73-91
Höli,	.095	2.1	.26	.36	11	64
96	.08211	1.5-3.0	.2131	.2748	9.2-12	56-74
Bank,	.20	2.9	.19	.41	13	100
96	.1232	2.2-3.9	.1426	.3054	8.3-20	80-130
Stor,	.20	2.6	.20	.37	11	93
96	.1136	1.9-3.6	.1427	.2654	4.09-28	62-140

Table 25.1. Geometric mean concentrations, **fresh weight**, in herring (mercury in muscle other metals in liver) from other investigations not included in the ordinary Swedish Monitoring Programme in Marine Biota. The geometric mean concentration and the corresponding 95% confidence interval are reported. Hapa = Haparanda archipelago (BD), Pite = Pite archipelago (BD), Skel = Skelleftebukten (AC), Trys = Trysunda (AC), Juni = Juniskär (AC), Lövg = NO Lövgrund (X), Egge = NO Eggegrund (X), Jätt = SV Jättholmarna (X), Höli = Hölick (X), Bank = 10' N Västra Banken (X), Stor = N Storjungfrun (X).

	Hg	Pb	Cd	Ni	Cr	Cu	Zn
	ng/g ww	ng/g ww	μg/g ww.	ng/g ww.	ng/g ww.	μg/g ww.	μg/g ww.
Нара,	83	20	.26	31	63	2.9	26
96	72-97	14-27	.1935	22-42	55-71	2.5-3.2	23-29
Pite,	41	43	.62	50	78	3.9	31
96	31-55	33-56	.5569	35-71	68-90	3.3-4.7	28-35
Skel,	49	39	.49	41	69	3.3	33
96	29-85	29-52	.3666	32-51	62-78	2.8-3.8	28-37
Trys,	22	54	.30	49	110	2.1	21
96	15-33	43-67	.1563	38-64	88-130	1.7-2.7	19-23
Junis,	26	36	.44	207	100	2.5	24
96	22-31	27-49	.3457	153-279	85-120	2.2-2.9	22-26
Lövg,	21	23	.91	62	84	3.5	23
96	14-31	18-30	.80-1.0	47-81	72-98	2.7-4.5	20-25
Egge,	32	38	.76	58	92	4.7	24
96	19-54	22-64	.55-1.1	33-99	65-130	3.2-6.9	21-26
Jätt,	25	20	.51	53	120	4.8	22
96	13-45	16-24	.3378	42-67	97-140	3.4-6.9	19-24
Höli,	16	28	.61	74	110	3.1	19
96	12-21	24-32	.4193	65-85	81-140	2.7-3.5	17-21
Bank,	-	54	.80	52	110	3.5	28
96		35-84	.60-1.1	37-74	88-140	2.3-5.3	23-33
Stor,	-	55	.72	54	100	2.9	26
96		38-80	.5790	41-71	83-130	1.4-6.2	21-31

Organo chlorines, lipid weight

Organo	CB-153	sDDT	γ-НСН	НСВ
	μg/g lw.	μg/g lw.	η-ΠΟΠ μg/g lw.	μg/g lw.
C1, 02	<u>μg/g IW.</u> 0.056	0.192	.011	.022
C1, 02	(.044070)	(.128290)	(.009014)	(.019026)
C2 02	0.147	0.363	.014	.025
C2, 02				
C2 02	(.115188) 0.127	(.263502) 0.687	(.009020) .025	(.019033) .040
C3, 02				
C4 02	(.100160)	(.529891) 0.699	(.018034)	(.030053)
C4, 02	0.100		.025	.038
C(02	(.079125)	(.555882)	(.018034)	(.028051)
C6, 02	0.054	0.157	.019	.016
G= 04	(.046064)	(.109226)	(.014025)	(.013019)
C7, 02	0.026	0.044	.011	.010
	(.020033)	(.030066)	(.006019)	(.008012)
V2, 03	0.228	1.14	.014	.082
	(.177292)	(.847-1.52)	(.009019)	(.064104)
V4, 03	0.203	2.65	.024	.066
	(.165249)	(1.69-4.15)	(.015036)	(.047091)
G5, 02	0.193	1.25	.024	.042
	(.164227)	(.936-1.67)	(.017032)	(.032057)
G6, 02	0.491	0.531	.014	.017
	(.398606)	(.409689)	(.009021)	(.013023)
P1, 03	0.099	0.160	.007	.012
	(.066147)	(.097262)	(.004015)	(.009015)
P2, 03	0.061	0.146	.009	.009
	(.046082)	(.100215)	(.006013)	(.006012)
Z1, 02	0.183	0.173	.009	.038
	(.106316)	(.103290)	(.005018)	(.025057)
Z2 , 02	0.226	0.285	.013	.014
	(.140365)	(.155525)	(.009018)	(.011018)
Z3, 02	0.250	0.097	.011	.009
	(.147426)	(.060157)	(.007017)	(.008011)
M2, 02	0.064	0.106	.014	6.01
	(.061067)	(.097116)	(.009021)	(4.72-7.67)
M6, 02	0.064	0.065	.025	2.49
•	(.053077)	(.045095)	(.018035)	(2.02-3.08)
M3, 02	0.057	0.060	.024	2.92
,	(.041079)	(.044084)	(.016035)	(2.02-4.23)
U8, 03	5.06	71.4	.014	1.37
- ,	(4.15-6.17)	(48.4-105)	(.009023)	1.05-1.80

Table 25.3. Estimated geometric mean concentrations, **fat weight**, in herring muscle tissue from other investigations not included in the ordinary Swedish Monitoring Programme in Marine Biota. The geometric mean concentration and the corresponding 95% confidence interval are reported. Hapa = Haparanda archipelago (BD), Pite = Pite archipelago (BD), Skel = Skelleftebukten (AC), Trys = Trysunda (AC), Juni = Juniskär (AC), Lövg = NO Lövgrund (X), Egge = NO Eggegrund (X), Jätt = SV Jättholmarna (X), Höli = Hölick (X).

Organochlorines

CB-153	DDE	a-HCH	g-HCH	НСВ	TNCL
μg/g lw	μg/g lw	ng/g lw	ng/g lw	ng/g lw	ng/g lw
.13	.13	12	11	25	26
.08022	.07323	11-13	9.9-12	18-34	17-40
.18	.20	17	11	40	44
.1227	.1234	16-17	10-12	31-52	32-61
.19	.20	19	13	37	39
.09536	.1040	17-21	12-13	26-52	23-67
.099	.15	24	15	47	27
.06814	.1022	24-25	15-16	37-59	19-37
.19	.39	20	11	55	59
.1426	.2953	19-21	11-12	51-60	46-76
.18	.31	19	13	47	41
.1325	.2244	16-22	12-14	37-60	31-53
.15	.22	18	12	44	32
.1120	.1828	16-21	12-13	38-52	24-42
.13	.24	23	13	56	37
.06925	.1248	15-35	10-17	31-100	22-62
.078	.14	20	12	43	25
.064095	.1019	19-20	12-12	41-45	20-31
	μg/g lw .13 .08022 .18 .1227 .19 .09536 .099 .06814 .19 .1426 .18 .1325 .15 .1120 .13 .06925 .078	μg/g lw μg/g lw .13 .13 .08022 .07323 .18 .20 .1227 .1234 .19 .20 .09536 .1040 .099 .15 .06814 .1022 .19 .39 .1426 .2953 .18 .31 .1325 .2244 .15 .22 .1120 .1828 .13 .24 .06925 .1248 .078 .14	μg/g lw μg/g lw ng/g lw .13 .13 12 .08022 .07323 11-13 .18 .20 17 .1227 .1234 16-17 .19 .20 19 .09536 .1040 17-21 .099 .15 24 .06814 .1022 24-25 .19 .39 20 .1426 .2953 19-21 .18 .31 19 .1325 .2244 16-22 .15 .22 18 .1120 .1828 16-21 .13 .24 23 .06925 .1248 15-35 .078 .14 20	μg/g lw μg/g lw ng/g lw ng/g lw .13 .13 12 11 .08022 .07323 11-13 9.9-12 .18 .20 17 11 .1227 .1234 16-17 10-12 .19 .20 19 13 .09536 .1040 17-21 12-13 .099 .15 24 15 .06814 .1022 24-25 15-16 .19 .39 20 11 .1426 .2953 19-21 11-12 .18 .31 19 13 .1325 .2244 16-22 12-14 .15 .22 18 12 .1120 .1828 16-21 12-13 .13 .24 23 13 .06925 .1248 15-35 10-17 .078 .14 20 12	μg/g lw μg/g lw ng/g lw ng/g lw ng/g lw .13 .13 12 11 25 .08022 .07323 11-13 9.9-12 18-34 .18 .20 17 11 40 .1227 .1234 16-17 10-12 31-52 .19 .20 19 13 37 .09536 .1040 17-21 12-13 26-52 .099 .15 24 15 47 .06814 .1022 24-25 15-16 37-59 .19 .39 20 11 55 .1426 .2953 19-21 11-12 51-60 .18 .31 19 13 47 .1325 .2244 16-22 12-14 37-60 .15 .22 18 12 44 .1120 .1828 16-21 12-13 38-52 .13 .24 23

Organochlorines, fresh weights

9180110	CB-153	а-НСН	д-НСН
	ng/g ww	ng/g ww	ng/g ww
Hapa,	2.4	.22	.20
96			
Pite,	3.6	.34	.22
96			
Skel,	4.3	.44	.29
96			
Trys,	3.9	.95	.60
96			
Junis,	12	1.2	.72
96			
Lövg,	5.2	.55	.38
96			
Egge,	6.2	.78	.53
96			
Jätt,	4.8	.82	.48
96			
Höli,	5.0	1.3	.78
96			

Table 25.4. The 5, 50(median), 90, 95% percentile for concentrations of various contaminants and trace metals in fish tissue from the Baltic, collected in the autumn from 1994 and onwards.

Mercury

Levels in ng/g on a fresh weight basis, muscle tissue

Herring		n= 280		Perch	n= 70		Eelpout		n= 40			
	5%	50%	90%	95%	5%	50%	90%	95%	5%	50%	90%	95%
Hg	9	28	75	92	9	45	109	120	30	64	110	130

Other trace metals

Levels in $\mu g/g$ on a dry weight basis, liver tissue.

	Herring				Perch				Eelpout						
	n	5%	50%	90%	95%	n	5%	50%	90%	95%	n	5%	50%	90%	95%
Pb	280	0.060	0.14	0.25	0.33	60	0.041	0.080	0.10	0.11	30	0.10	0.21	0.37	0.46
Cd	280	0.51	1.9	4.4	5.3	60	0.19	0.49	0.90	1.0	30	0.35	1.0	1.4	2.0
Cu	280	7.0	11	21	24	60	7.0	14	24	26	30	7.6	17	47	54
Zn	280	62	92	140	160	60	65	100	130	150	30	97	170	229	244
Ni	200	0.11	0.33	0.51	0.56	60	0.060	0.25	0.48	0.51	30	0.20	0.41	0.66	0.89
Cr	200	0.17	0.33	0.58	0.65	60	0.11	0.21	0.29	0.34	20	0.14	0.29	0.47	0.83

Organo chlorines

Levels in $\mu g/g$ on a lipid weight basis, muscle tissue

	Herring									
	n	5%	50%	90%	95%	n	5%	50%	90%	95%
DDE	234	0.030	0.19	0.55	0.71	80	0.026	0.077	0.15	0.31
DDD	234	.0043	0.054	0.24	0.29	67	0.0038	0.012	0.034	0.062
DDT	233	0.013	0.043	0.099	0.13	66	0.0044	0.019	0.046	0.061
sDDT	228	0.052	0.30	0.82	1.1	80	0.031	0.10	0.22	0.37
у-НСН	228	.0077	0.016	0.030	.031	70	0.0044	0.0061	0.0096	0.011
а-НСН	231	0.011	0.022	0.038	.043	79	0.0043	0.0079	0.013	0.013
HCB	234	0.012	0.024	0.047	.055	70	0.0042	0.0079	0.020	0.023
CB-153	240	0.031	0.088	0.26	0.33	70	0.020	0.087	0.16	0.18
CB-118	240	.0099	0.031	0.11	0.13	70	0.0083	0.027	0.054	0.062

		Eelpout	t		
	n	5%	50%	90%	95%
DDE	30	0.037	0.35	1.5	2.1
DDD	28	.0061	0.029	0.18	0.23
DDT	30	0.019	0.077	0.19	0.23
sDDT	30	0.060	0.44	1.9	2.6
γ-НСН	30	0.013	0.019	.025	.026
a-HCH	30	0.013	0.017	.021	.022
HCB	30	0.011	0.022	.078	0.11
CB-153	50	0.039	0.26	0.74	1.0
CB-118	50	.0059	0.052	0.24	0.34

Table 25.5. The 5, 50(median), 90, 95% percentile for concentrations of various contaminants and trace metals in herring along the Swedish coast (the Baltic and the Swedish west coast), collected in the autumn from 1994 and onwards.

Mercury

Levels in ng/g on a fresh weight basis, muscle tissue

	Herring	n= 414		
	5%	50%	90%	95%
Hg	9	26	64	78

Other trace metals

Levels in $\mu g/g$ on a dry weight basis, liver tissue.

	Herring								
	n	5%	50%	90%	95%				
Pb	402	0.050	0.14	0.23	0.29				
Cd	402	0.27	1.2	3.7	4.8				
Cu	402	7.0	11	19	23				
Zn	402	63	95	140	159				
Ni	297	0.090	0.30	0.53	0.56				
Cr	297	0.18	0.33	0.55	0.63				

Organo chlorines

Levels in µg/g on a lipid weight basis, muscle tissue

Levels in pg/g on a lipite weight casts, masere th										
Herring										
	n	5%	50%	90%	95%					
DDE	342	0.013	0.11	0.44	0.64					
DDD	342	0.0034	0.027	0.21	0.27					
DDT	342	0.0048	0.028	0.090	0.11					
sDDT	336	0.027	0.16	0.74	1.0					
у-НСН	336	0.0072	0.016	0.028	.030					
a-HCH	339	0.0079	0.018	0.034	.040					
HCB	342	0.0058	0.019	0.043	.052					
CB-153	336	0.019	0.070	0.23	0.31					
CB-118	336	0.0077	0.024	0.085	0.12					

26 References

Alsberg T., Balk L., Nylund K., de Wit C., Bignert A., Olsson M., Odsjö T. 1993. Persistent Organic Pollutants and the Environment. Swedish Environmental Protection Agency, report 4246.

Bengtsson B-E. 1975. Accumulation in cadmium in some aquatic animals from the Baltic Sea. In: 3rd Soviet-Swedish Symp. on the Baltic Sea pollution, Stockholm. NBL-report.

Bergström S. and Matthäus W. 1996. Meteorological and hydrographical conditions. In: 3rd Periodic Assessement of the State of the Marine Environment of the Baltic Sea, 1989-93. HELCOM, No 64B.

Bignert A., Odsjö T. & Olsson M. 1990. Övervakning av miljögifter i levande organismer. Rapport från verksamheten 1989. Naturvårdsverket rapport 3805.

Bignert A., Göthberg A., Jensen S., Litzén K., Odsjö T., Olsson M. and Reutergårdh L. 1993. The need for adequate biological sampling in ecotoxicological investigations: a retrospective study of twenty years pollution monitoring. The Science of the Total Environment, 128 (1993) 121-139.

Bignert A. 1994. Sensitivity to detect trends in timeseries of contaminant concentrations in marine biota along the Swedish coasts. ICES, annual report from WGSAEM. C.M.1994/ENV:6.

Bignert A, Litzen K, Odsjö T, Olsson M, Persson W & Reutergårdh L. 1995. Time-related factors influence the concentration of sDDT, PCBs and shell parameters in eggs of Baltic Guillemot (Uria aalge), 1861-1989. Environmental pollution 89(1995).

Borg. H., Edin A., Holm K., Sköld E. 1981. Determination of metals in fish livers by flameless atomic absorption spectroscopy. Water research Vol.15. pp.1291-1295.

Borg H., Andersson P. and Johansson K. 1988. Influence of Acidification on Metal Fluxes in Swedish Forest Lakes. The Science of the Total Environment, 87/88 (1989) 241-253.

Bouquegneau J. M., Gerdy Ch. and Disteche A. 1975. Fish mercury-binding thionein related to adaption mechanism. FEBS Lett. 55:173-177.

Danielsson, L-G., Magnusson B., Westerlund S. and Kerong Z. 1983. Trace metals in the Göta River estuary. Estuar. Coast. Shelf Sci., 17, 73-85.

Eriksson U., Johansson A., Litzén K., Häggberg L., Winberg A., Zakrisson S. 1994. Analysmetod för bestämning av klorerade organiska miljögifter i biologiskt material. ITM rapport 18.

Esmen N. & Hammond Y. 1977. Log-Normality of Environmental Sampling Data. J Environ Sci Health A12(1&2):29-41.

Frank A., Galgan V., Roos A., Olsson M., Petersson L.R. and Bignert A. 1992. Metal Concentrations in Seals from Swedish Waters. Ambio Vol.21 No 8. p. 529-538.

Fryer R. & M.D. Nicholson. 1991. Summarising Trends with Locally-Weighted Running-Line Smoothers. Report of the Working Group on Statistical Aspects of Trend Monitoring. ICES C.M.1991.

Gaul H. 1992. Temporal and spatial trends of organic micropollutants in the sea water of the Baltic Sea, the North Sea, and the Northeast Atlantic. ICES mar. Sci. Symp., 195:110-126.

Gilbert R.O. 1987. Statistical Methods for Environmental Pollution Monitoring. Van Nostrand Reinhold, New York.

Green N.W. and Rönningen. 1994. Contaminants in shellfish and fish 1981-92. Joint Monitoring Programme (JMP) Norwegian biota data. NIVA 1995, report no. 585/94

Grimås U., A. Göthberg, M. Notter, M. Olsson and L. Reutergårdh. 1985. Fat Amount - A Factor to Consider in Monitoring Studies of Heavy Metals in Cod Liver. Ambio

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Helsel, D.R. & R.M. Hirsch. 1995. Statistical Methods in Water Resources, Studies in Environmental Sciences 49. Elsevier, Amsterdam.

Hoaglin D.C. & R.E. Welsch. 1978. The hat matrix in regression and ANOVA. Amer. Stat. 32:17-22.

HELCOM. Baltic Sea environment Proceedings nr 61, Radioactivity in the Baltic Sea 1984-1991 (ISSN 0357-2994).

ICES. 1995. Report of the ICES/HELCOM Workshop on Temporal Trend Assessment of Data on Contaminants in Biota from the Baltic Sea. ICES CM 1995/ENV:10, Ref.:E.

ICES. 1997. Report of the OSPAR/ICES Workshop on the overall evaluation and update of background/reference concentrations for nutrients and for contaminants in sea water, biota and sediment. SIME 97/7/2-E. Ostend 3-7 February 1997.

Jacobsson A., Neuman E. and Olsson M. 1993. The viviparous blenny as an indicator of effects of toxic substances. Fiskeriverket, Kustrapport 1993:6.

Jensen, S., Reutergårdh, L. and Jansson, B. 1983. Analytical methods for measuring organochlorines and methyl mercury by gas chromatography. FAO Fish. Technical paper, 212, 21-33.

Jorhem L., Mattsson P. and Slorach S. 1984. Lead, cadmium, zinc and certain other metals in foods on the Swedish market. Vår Föda (Suppl. 3) 36, 135 - 208.

Jorhem L. and Sundström B. 1993. Levels of Lead, Cadmium, Zinc, Copper, Nickel, Chromium, Manganese and Cobalt in Foods on the Swedish Market, 1983 - 1990. Journal of Food Composition and Analysis 6, 223-241.

Klaassen C.D. and Rozman K. 1991. Absorption, Distribution and Exretion of Toxicants. <u>In:</u> Casarett and Doull's Toxicology - The Basic Science of Poisons. Pergamon Press.

Knutzen J. and Skei J. 1992. Preliminary proposals for classification of marine environmental quality respecting micropollutants in water, sediments and selected organisms. Norwegian Institute for Water Research, Report O-862602/O-89266, 22 p.

Lindsted G. and Skare I. 1971. Microdetermination of mercury in biological samples. Analyst, Vol.96, pp. 223-229.

Loftis J.C., Ward R.C., Phillips R.D. 1989. An Evaluation of Trend Detection Techniques for Use in Water Quality Monitoring Programs. EPA/600/3-89/037. 139 p.

Mart L., Nürnberg H.W. and Rützel H. 1985. Levels of heavy metals in the tidal Elbe and its estuary and the heavy metal input into the sea. Sci. Total Environm. 44, 35-49.

May K. and Stoeppler M. 1984. Pretreatment studies with biological and environmental materials. Fresenius Anal.Chem 317:248-251.

Neuman E. 1988.

Nicholson M.D. & R. Fryer. 1991. The Power of the ICES Cooperative Monitoring Programme to Detect Linear Trends and Incidents. In: Anon. Report of the Working Group on Statistical Aspects of Trend Monitoring. ICES Doc CM 1991.

Nicholson M.D., R. Fryer and J.R.Larsen. 1995. A Robust Method for Analysing Contaminant Trend Monitoring Data. Techniques in Marine Environmental Sciences. ICES.

Nissling A. 1995. Salinity and oxygen requirements for successful spawning of Baltic cod, Gadus morhua. Phd Thesis. Dept of Systems Ecology, Stockholm University.

Nolting R.F. 1986. Copper, zinc, cadmium, nickel, iron and manganese in the Southern Bight of the North Sea. Mar. Pollut. Bull., 17, 113-117.

Notter M. 1993. Metallerna och miljön. MIST. Naturvårdsverket. Rapport 4135.

Odsjö T. 1993. The Swedish Environmental Specimen Bank with reference to the National Contaminant Monitoring Programme in Sweden. The Science of the Total Environment, 139/140; 147-156.

Pohl, C. 1994. Monitoring of trace metals in the Baltic Sea 1992 - 1993. Institut fur Ostseeforschung Warnemunde.

Polak-Juszczak L. and Domagala M. 1994. Levels of Heavy Metals in Baltic Fish in 1991-1993. Bulletin of the Sea Fisheries Institute.

Protasowicki M., Kurpios M. and Ciereszko W. 1993. Changes in Levels of Hg, Cd, Pb, Cu, Zn, DDT, PCB in selected commercial fish of the Baltic in 1974-1988. International Baltic Monitoring Programme. Inst. Ochr. Srod., Warszawa

Riget F., Johansen P. og Asmund G. 1993. Naturlig variation af kobber, cadmium, bly og zink i blæretang og blåmussling ved Nuuk. Teknisk rapport. Grfnlands Miljfundersfgelser.

Roos A., Kienhuis P., Traag W. and Tuistra W. 1989. Problems encountered in the determination of 2,3,4-2',4',5' hexachlorobiphenyl (CB-138) in environmental samples. Intern. J. Env. Anal. Chem., 36:155.

Schantz M.M., Parris R.M., Kurz J., Ballschmiter K. and Wise S.A. 1993. Comparison of methods for the gas-chromatographic determination of PCB congeners and chlorinated pesticides in marine reference materials. Fresenius Z. Anal. Chem., 346:766-78.

Schneider, B. and Pohl, C. 1995. Time series of dissolved cadmium at a coastal station in the western Baltic Sea. Submitted to J. Mar. Sys.

Sellström, U. 1996. Polybrominated diphenyl ethers in the Swedish environment. ITM-Report. Stockholm University.

da Silva F. and Williams R.J.P. 1994. The Biological Chemistry of the Elements. The Inorganic Chemistry of Life. Clarendon Press. Oxford.

Swertz O. 1995. Trend assessment using the Mann-Kendall test. Report of the Working Group on Statistical Aspects of Trend Monitoring. ICES CM 1995/D:2.

TemaNord 1995:543. Manual for Nordic Environmental Specimen Banking.

Vibert R. and Lagler K.F. 1961. Peches continentales, biologie et amenagement. 1 vol., 720 p Paris Dunod.

Vyncke W., Roose P., Guns M., van Hoeyweghen P. 1999. Trace metals in blue mussels from the Belgian coast (1979-1997). OSPAR, ASMO (1) 99/4/Info.2-E.

Widell A. 1990. Pollution load compilation. SNV.

Widell A. 1992. Correction to Pollution load compilation 1990. SNV.

Wideqvist U., Jansson B., Reutergårdh L., Olsson M., Odsjö T., Uvemo U-B. 1993. Temporal Trends of PCC in Guillemot Eggs from the Baltic. Chemospere, Vol.27, No 10.

White-Stevens R. 1971. Pesticides in the Environment. Marcel Dekker, New York. 270 pp.

Yi-Fan L., McMillan A. and Scholtz M.T. 1996. Global HCH Usage 1° x 1° Longitude/Latitude Resolution. Environ. Sci. Technol. 1996, 30, 325-3533.