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Övervakning av metaller och organiska miljögifter i marin biota, 2014

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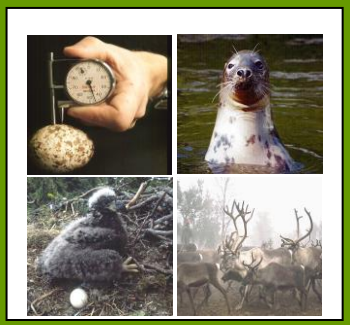

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Summary
The report summarises the monitoring activities within the National Swedish Contaminant Programme in marine biota.

Time series of analysed contaminants (heavy metals, organochlorines, brominated flame retardants, perfluorinated substances and polycyclic aromatic hydrocarbons) in biota are presented together with summaries of the results from the statistical treatment. The data represent the bioavailable portion of the investigated contaminants i.e. the portion that has effectively passed through biological membranes and may cause toxic effects. The report does not in general give background or explanations to significant changes found in the time series. Thus, increasing concentrations highlight the need for intensified studies.

There was no general trend in heavy metal concentrations except for lead that is generally decreasing over the study period (in time series of sufficient length), supposedly due to the elimination of lead in gasoline.

Generally, decreasing trends were observed for organochlorines (DDT's, PCB's, HCH's, HCB), also including TCDD-equivalents over the whole study period, but not during the last decades. The chlorinated compounds generally show higher concentrations in the Bothnian Sea and/or Baltic Proper when compared to the Bothnian Bay and the Swedish west coast.

Increasing trends of brominated flame retardants in guillemot eggs from late 1960s until early 1990s for polybrominated diphenyl ethers as BDE-47, -99 and -100 and until mid-2000s for HBCDD but with decreasing concentrations during the more recent time period. The PBDEs and HBCDD show higher

concentrations in the Baltic Sea compared to the Swedish west coast.

A consistently increasing trend of PFOS in guillemot eggs has been observed throughout the whole time period, however, during the most recent ten years a change of direction is indicated.

Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2014

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1 Introduction

This report summarises the monitoring activities within the National Swedish Contaminant Programme in marine biota. It is the result of joint efforts from the *Department of Applied Environmental Science* at Stockholm University (analyses of heavy metals, organochlorines, brominated flame retardants and perfluorinated substances), the *Department of Chemistry* at Umeå University (analyses of PCDD/PCDF), *IVL – Swedish Environmental Research Institute* (analyses of polycyclic aromatic hydrocarbons) and the *Department of Contaminant Research* at the Swedish Museum of Natural History (co-ordination, sample collection administration, sample preparation, recording of biological variables, storage of frozen biological tissues in the Environmental Specimen Bank for retrospective studies, data preparation and statistical evaluation). The monitoring programme is financed by the *Swedish Environmental Protection Agency* (EPA).

Data in this report represent the bioavailable portion of the investigated contaminants i.e. the portion that has effectively passed through biological membranes and may cause toxic effects. The objectives of the monitoring program in marine biota are as follows:

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

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

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

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

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

- To explore developmental and regional differences in the composition and pattern of e.g. PCBs, HCHs, DDTs, PCDD/F, PBDE/HBCDD, PAHs and PFCs as well as the ratios between various contaminants.

- Because important commercial fish species like herring and cod are sampled, the time series are also relevant for human consumption of these species from Sweden. A cooperation with the Swedish Food Administration is established. Sampling is also co-ordinated with SSM (Swedish Radiation Safety Authority) for analysing radionuclides in fish and blue mussels (HELCOM, 1992).

- All analysed samples, and numerous additional specimens, of annual systematically collected material, are stored frozen in the *Environmental Specimen Bank.* This material enables future retrospective studies of contaminants that are impossible to analyse today, as well as to control analyses of suspected analytical errors.

- Although the programme is focused on contaminant concentration in biota, it also investigates the development of biological variables, e.g. condition factor (CF), liver somatic index (LSI) and fat content, which are monitored at all sites. At a few sites, integrated monitoring of fish physiology and population are run in cooperation with the University of Gothenburg and SLU AQUA the former Swedish Board of Fisheries.

- Experience from the national programme, which has several time series of greater than 40 years, can be used in the design of regional and local monitoring programmes.

- The unique, high quality material and long time series is further used to explore relationships between biological variables and contaminant concentrations in various tissues, e.g. 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 for evaluating the validity of hypotheses 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 constitutes an integrated part of the national monitoring activities in the marine environment, as well as of the international programmes within ICES, OSPARCOM, HELCOM and EU.

The present report displays the time series of analysed contaminants in biota and summarises results from the statistical treatment. It does *not* in general give background or explanations to significant changes found in the time series. Thus, increasing concentrations highlight the need 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 may indicate the relative appropriateness of the sampled matrix and be of help in designing future monitoring programmes. In the temporal trend section, an extract of the relevant findings is summarised in the 'conclusion' paragraph. However, it should be stressed that geographical differences may not reflect anthropogenic influences, but may instead be due to factors such as productivity, temperature, salinity etc.

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

2 Summary 2012

The environmental toxicants examined in this report can be classified into five groups – heavy metals, chlorinated compounds, brominated flame retardants, polyaromatic hydrocarbons and perfluorinated compounds. Each of these contaminants has been examined from various sites for up to six different fish species, in blue mussels, and in guillemot eggs, for varying lengths of time. The following summary examines overall trends, spatial and temporal, for the five groups.

Condition and Fat Content
Condition and fat content in different species tended to follow the same pattern at the same sites, with a few exceptions. Most of the fish species generally displayed a decreasing trend in both condition and fat content at most sites examined. Exceptions to this were increases in condition factor seen in cod liver at Fladenand for herring at Ängskärsklubb in spring. There were also some sites where no log linear trend were seen.

Heavy Metals
Due to a change in methods for metal analysis (not Hg) in 2004, values between 2003 and 2007 should be interpreted with care. From 2009 metals are analyzed at ITM, Stockholm University.

Generally, higher mercury concentrations are found in the Bothnian Bay, but also from one station in the southern parts of Bothnian Sea and one in the northern parts of Baltic Sea, compared to other parts of the Swedish coastline. The time series show varying concentrations over the study period. The longer time series in guillemot egg and spring-caught herring from the southern Bothnian Sea and southern Baltic Proper show significant decreases of mercury. On the other hand, increasing trends are seen in e.g. cod muscle, but the concentrations are fairly low compared to measured concentrations in perch from fresh water and coastal sites. However, in most cases, these concentrations are above the target level of 20 ng/g wet weight.

Lead is generally decreasing over the study period (in time series of sufficient length), supposedly due to the elimination of lead in gasoline. Elevated lead concentrations between 2003 and 2007 (e.g. Harufjärden) should be viewed with caution (see above regarding change in analysis methods).

Cadmium concentrations show varying non-linear trends over the monitored period. It is worth noting that despite several measures taken to reduce discharges of cadmium, generally the most recent concentrations are similar to concentrations measured 30 years ago in the longer time series.

The reported nickel concentrations show no consistent decreasing trends. Some series begin with two elevated values that exert a strong leverage effect on the regression line and may give a false impression of decreasing trends. Chromium generally shows decreasing trends, possibly explained by a shift in analytical method. The essential trace metals, copper and zinc, show no consistent trends during the monitored period.

Generally higher concentrations of arsenic and silver are found along the west coast compared to other parts of the Sweadish coast line. However for silver a few stations in the Bothnian Sea and Bothnian Bay show comparable concentrations to the west coast stations.

Chlorinated Compounds

Generally, a decreasing trend was observed for all compounds (DDT's, PCB's, HCH's, HCB) in all species examined, with a few exceptions, such as no change in TCDD-equivalents being seen in herring muscle (except at Änskärsklubb where very high concentrations at the beginning of the sampling period were seen and also at the west coast station Fladen). The longer time-series in guillemot also show a marked decrease from the start in the late 1960s until about 1985 from where no change can be seen in TCDD-equivalent concentrations.

The chlorinated compounds generally show higher concentrations in the Bothnian Sea and/or Baltic Proper when compared to the Bothnian Bay and the Swedish west coast.

Brominated Flame Retardants

Elevated levels of HBCDD are seen in sites from Baltic Proper. In addition, lower concentrations of all investigated PBDEs and HBCDD are seen on the Swedish west coast compared to the east coast. Temporally, significant increases in BDE-47, 99 and 100 have been seen in guillemot eggs since the late 1960s until the early 1990s, where concentrations then began to show decreases. Also, the concentration of HBCDD in guillemot eggs show a decrease during the most recent ten years. For fish and blue mussels, BDE-47, BDE-99 and BDE-153 decreased at some sites and showed no trend at other sites. The concentration of HBCDD in fish and blue mussels showed inconsistent trends.

PAHs

Only blue mussels have been examined for spatial differences in PAH concentrations. Concentration of sPAH was found to be higher from Kvädöfjärden in the Baltic Proper compared to stations at the west coast, but individual PAHs showed varying spatial patterns. Over time, acenaphthalene was rarely found above the detection limit. Significant decreasing trends were observed for sPAH, chrysene, fluoranthene and pyrene at Fjällbacka; for naphthalene at Kvädöfjärden; and for pyrene at Fladen. Significant increasing trends were seen for benzo(a)anthracene at Kvädöfjärden and in the last 10 years for fluorene at Nidingen.

PFASs

PFHxS and PFOS show a similar spatial pattern, but PFOS concentrations were approximately 25 times higher than PFHxS levels. The distribution of PFOS is quite homogenous along the Swedish coast but with somewhat higher concentrations in the Baltic Proper. PFOS concentrations in guillemot eggs are about 100-200 times higher than in herring liver. An ovarall increasing trend of PFOS in guillemot eggs has been observed throughout the whole time period, however, during the most recent ten years, a change of direction is detected.

Organotin compounds

The majority of the analysed tinorganic compounds showed concentrations below LOQ. However TBT and DPhT showed concentrations above LOQ at all stations with highest reported concentrations in fish from Örefjärden in the northern part of Bothnian Sea.

3 Sampling

3.1 Sampling area

Sampling areas are defined by a central coordinate surrounded by a circumference of three nautical miles. The exact sampling location is registered at collection. General demands on sampling sites within the national contaminant monitoring programme are defined in chapter five.

3.2 Collected specimens

For many species, sub-adults represent a more recent picture of the contaminant load than adults since many contaminants bioaccumulate. To increase comparability between years, young specimens are generally collected. However, the size of individual specimens has to be big enough to allow individual chemical analysis. Thus, the size and age of specimens vary between species and sites (see chapter four). To avoid possible influences of between-year variance due to sex differences, the same sex (female) is analysed each year in most time series. 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 and sex range, about 50 - 100 specimens are collected at each site. Only healthy looking specimens with undamaged skin are selected.

The collected specimens are placed individually in polyethylene plastic bags, 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 (ESB) (see Odsjö 1993 for further information). These specimens are registered. Biological information and notes of the availabe amount of tissue, together with a precise location in the ESB, are accessable 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 for most substances, 10 - 12 individual specimens from the old Baltic sites (reported to the Helsinki Convention (HELCOM)) and the old Swedish west coast sites (reported to OSPARCOM) are analysed annually from each site for each species. At the new Baltic and west coast sites and also for the spring caught herring, 2 pools of 12 individuals are analysed from each site for each species. For guillemot eggs and perch (old sites), 10 individual specimens are analysed. Organochlorines in blue mussels are analysed in pooled samples containing approximately 20 individuals in each pool. Since 1996, samples from 12 individual specimens are analysed, which is proposed in the revised guidelines for HELCOM and OSPARCOM.

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

Sampling is carried out annually for all time series. Less frequent sampling would result in a considerable loss in statistical and interpretational power.

3.4 Sampling season

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

Guillemot eggs are collected in the beginning to the middle of May. Due to a lost first egg, a second egg is often laid. These second eggs should not be collected. To avoid this, only early laid eggs are sampled (see section 4.6).

3.5 Sample preparation and registered variables

A short description of the various sampling matrices and the type of variables that are registered are given below. See TemaNord (1995) for further details. The sampling and sample preparations are all performed according to the manual for collection, preparation and storage of fish (SMNH, 2012).

3.5.1 Fish

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

Muscle samples are taken from the middle dorsal muscle layer. The epidermis and subcutaneous fatty tissue are carefully removed. Samples of 10 g muscle tissue are prepared for organochlorine/bromine analysis, 20 g for analysis of PCDD/F and 1.5 g for mercury analysis.

The liver is completely removed and weighed. Samples of 0.5 – 1 g are prepared for metal analyses, and 0.5 g for analysis of perfluorinated substances.

3.5.2 Blue mussels

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

3.5.3 Guillemot egg

Length, width and total weight are recorded. Egg contents are removed (blown out). The eggs are collected soon after they are laid, hence the embryos are small and the total egg content is homogenized.

Weight of the empty, dried eggshell is recorded. Egg shell thickness is me
asured at the blowing hole using a modified micrometer.

Two grams of the homogenised egg content is prepared for mercury analyses, and another 2 g for the other analysed metals. Ten grams is prepared for analyses of organochlorines/bromines, 30 g for analysis of PCDD/F and 1 g for perfluorinated substances.

3.6 Data registration

Data are stored in a flat ASCII file in a hierarchical fashion, where each individual specimen represents one level. Each measured value is coded and the codes are defined in a code list (Danielsson, Gustavsson and Nyberg, 2011). The primary data files are processed

through a quality control program. Suspect values are checked and corrected if necessary. Data are retrieved from the primary file into a table format suitable for 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 different species (table 4.1).

Table 4.1. Number of specimens for various species sampled for analysis of contaminants within the base program.

Species	N of individual specimen	%
Herring	6288	49
Cod	1130	9
Perch	1044	8
Eelpout	566	4
Dab	350	3
Flounder	340	3
Guillemot	620	5
Common Tern	30	0.2
Eurasian Oystercatcher	30	0.2
Blue mussel	2350	18
Total	12748	100

4.1 Herring (*Clupea harengus*)

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

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

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

Herring samples are collected each year from seventeen sites along the Swedish coasts: Råne fjärden, Harufjärden, Kinnbäcksfjärden (Bothnian Bay), Holmöarna, Örefjärden, Gaviksfjärden, Långvindsfjärden, Ängskärsklubb (Bothnian Sea), Lagnö, Landsort (northern Baltic Proper), Byxelkrok, Abbekås, Hanöbukten, Utlängan (southern Baltic Proper), Kullen, Fladen (Kattegat) and at Väderöarna (Skagerrak). Herring are also collected from two sites in the open sea, the Baltic Proper and the Bothnian Sea, (by SLU AQUA).

Herring liver tissue is analysed for lead, cadmium, copper, zinc and perflourinated substances. In 1995, analyses of chromium and nickel were added to the programme. Herring muscle tissue is analysed for mercury, organochlorines (DDTs, PCBs, HCHs, HCB and PCDD/PCDF) and polybrominated flame retardants. Herring muscle from spring-caught specimens from Ängskärsklubb and Utlängan are analysed for organochlorines and polybrominated flame retardants. From 1996, herring tissue has also been analysed for the

above mentioned metals. Herring samples from various sites within the marine monitoring programme have been analysed for dioxins/dibenzofurans, co-planar CBs, 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 age of the herring specimens is determined using their scales. The analysed specimens are females, between 2 - 5 years. Total body weight, liver weight, total length and maturity of gonads are recorded (Table 4.2). Growth rate varies considerably at the different sites (Table 4.3).

Table 4.2. Weeks when sample collections have been carried out in all (or most) years at the old locations; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total length, liver weight and liver and muscle dry weight are given.

	Sampling week	**age (year)**	**body weight (g)**	**length (cm)**	**liver weight (g)**	**liver dry weight (%)**	**muscle dry weight (%)**
Harufjärden	38-42	3-4	28-31	16-17	0.32-0.39	20-35	22-23
Ängskärsklubb	38-42	3-5	33-42	17-18	0.38-0.56	20-35	21-23
- spring	20-24	2-5	25-33	16-17	0.31-0.54	19-23	20-22
Landsort	41-48	3-5	38-50	18-20	0.46-0.66	20-32	22-24
Utlängan	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

Table 4.3. Average length at the age 3 years, and age at 16 cm length at the old sites.

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

4.2 Cod (*Gadus morhua*)

The Baltic cod lives below the halocline, feeding on bottom organisms. In Swedish waters, it becomes sexually mature between 2 - 6 years old. Spawning takes place during May - August (occasionally spawning specimens can be found in March or September). Cod require a salinity of at least 11 PSU, and an oxygen content of at least 2 ml/l (Nissling, 1995) to successfully spawn. The population shows great fluctuations and decreased dramatically between 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.

Cod is collected in autumn from two sites - southeast of Gotland, and from Fladen on the Swedish west coast. Cod age is determined using otoliths. Specimens of both sexes, between 3 - 4 years from Gotland, and between 2 - 4 years from Fladen, are analysed (Table 4.4).

Table 4.4. Weeks when sample collections have been carried out in all (or most) years at a specific location; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total length, liver weight and liver dry weight are given.

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

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

Cod liver tissue is analysed for lead, cadmium, copper and zinc, as well as for organo-chlorines. In 1995, analyses of chromium and nickel were added, and in 1999, analysis for brominated substances and HBCDD were added. Cod muscle tissue is analysed for mercury.

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

4.3 Perch (*Perca fluviatilis*)

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

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

Perch muscle tissue samples from two coastal sites, Holmöarna and Kvädöfjärden in the Baltic (Table 4.5), are analysed for organochlorines and mercury. In 1995, analyses of lead, cadmium, chromium, nickel, copper and zinc in perch liver were added to the programme, and in 2006 PCDD/Fs were added.

Table 4.5. Weeks when sample collections have been carried out in all (or most) years at the old sites; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are given.

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

4.4 Eelpout, viviparous blenny (*Zoarces viviparus*)

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

Eelpout specimens have been collected from Fjällbacka in the Skagerrak since 1988. In this time series, analyses of various PCB congeners are available. Since 1995, eelpout have also been collected from Holmöarna and Kvädöfjärden (Table 4.6). Liver tissue is analysed for lead, cadmium, chromium, nickel, copper and zinc, whereas muscle tissue is analysed for mercury and organochlorines. Contaminant analysis in eelpout from Holmöarna ended in 2007.

Table 4.6. Weeks when sample collections have been carried out in all (or most) years at a specific location; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver and muscle dry weight are given.

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

4.5 Dab (*Limanda limanda*)

Dab is a bottom living species feeding on crustaceans, mussels, worms, echinoderms and small fish. Males become sexually mature between 2 - 4 years, and females between 3 - 5 years. Spawning takes place during April – June in shallow coastal waters. Dab tend to migrate to deeper water in late autumn.

Dab is among the 'first choice species' recommended within the JAMP.

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

Dab is collected from the Kattegat (Fladen) in autumn. Liver tissue samples have been analysed for lead, cadmium, copper and zinc, and muscle tissue samples for organo-chlorines and mercury. Dab age is determined using otoliths. Specimens between 3 - 5 years have been analysed (Table 4.7).

Table 4.7. Weeks when sample collections have been carried out in all (or most) years; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are given.

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

4.6 Flounder (*Platichtys flesus*)

Flounder is a bottom-dwelling species that feeds on crustaceans, mussels, worms, echinoderms and small fish. In the Skagerrak, males become sexually mature between 3 - 4 years of age, and females one year later. Spawning in the Skagerrak takes place during January – April in shallow coastal waters. Flounder tend to migrate to deeper waters in late autumn.

Flounder is among the 'second choice species' recommended within the JAMP.

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

Flounder is collected from the Skagerrak (Väderöarna) in autumn. Liver tissue samples have been analysed for lead, cadmium, copper and zinc, and muscle tissue samples for organochlorines and mercury. Flounder age is determined using otoliths. Specimens between 4 - 6 years of age have been analysed (Table 4.8).

Table 4.8. Weeks when sample collections have been carried out in all (or most) years; selected age classes are presented in the time series below. The 95% confidence intervals for the yearly means of total body weight, total body length, liver weight and liver dry weight are also given.

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

4.7 Blue mussels (*Mytilus edulis*)

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

Blue mussels are among the 'first choice species' recommended within the JAMP.

Blue mussels are collected from the Kattegat (Fladen, Nidingen), the Skagerrak (Fjällbacka) and Kvädöfjärden in the Baltic Proper. The mussels are sampled in autumn. Sampling depth varies between the sampling sites (Table 4.9).

Soft body tissue is analysed for lead, cadmium, copper, zinc, mercury and organochlorines. In 1995 analyses of chromium and nickel were added, and in 2000 analysis of brominated substances were added. From 1995, samples from Kvädöfjärden were included in the analysis. Since 1981, samples from this site had only been collected and stored. Organochlorines in blue mussels are analysed in pooled samples from each site and year, whereas trace metals are analysed in 25 individual samples per year and site (15 from 1996). PAHs have been analysed retrospectively (start 1984/87) in mussels from all three localities and, since 2003, are analysed on a yearly basis in pooled samples (Table 4.9).

Table 4.9. Weeks when collection of samples have been carried out in all (or most) years at a specific location; selected shell length interval are presented in the time series below. The 95% confidence intervals for the yearly means of soft body weight and shell weight are given.

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

4.8 Guillemot (*Uria aalge*)

Guillemots are suitable for monitoring contaminants in the Baltic Sea as most do not migrate further than the southern parts of the Baltic Proper during the winter season. They feed mainly on sprat (*Sprattus sprattus)* and herring (*Clupea harengus*). Guillemot breed for the first time at 4 - 5 years of age. Eggs hatch after about 32 days.

The egg content is high in fat (11 - 13%), 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, another may be laid. It has been shown that guillemot eggs that are laid late tend to contain significantly higher concentrations of organochlorines compared to eggs laid early (Bignert et al. 1995). Ten guillemot eggs, collected between weeks 19 – 21 (22), are analysed each year. In this report, only early laid eggs are included, except for dioxins, where the results from all collected eggs are included.

Guillemot egg contents from St Karlsö are analysed for mercury, organochlorines, perflourinated compounds (Holmström et al. 2005) and polybrominated compounds (Sellström 1996). From 1996, the concentrations of lead, cadmium, nickel, chromium, copper and zinc have also been analysed. The time series has also been analysed for PCC (Wideqvist et al. 1993). Various shell parameters, for example shell weight, thickness and thickness index, are also monitored. The weight of several hundred fledglings is normally recorded each year at St Karlsö. Eggs have also been collected for some years from Bonden in the northern Bothnian Sea, but so far only results (organochlorines) from 1991 are available.

4.9 Common Tern *(Sterna hirundo)*

Common tern is a seabird with a circumpolar distribution and can be found breeding in most of Europe, Asia and North America. It is migratory and winters further south in coastal tropical and subtropical regions. The tern inhabits Sweden from May to September.

Common tern is considered to be an income breeder, i. e. substances forming the eggs do largely originate from nutrients incorporated by the female in the two weeks of courtship feeding by the male mate immediately before egg-laying (Wendeln & Becker 1996, Wendeln 1997). In the breeding season, foraging of Common Terns takes place in comparatively small distances mostly within 10 km of the breeding colony (Becker et al. 1993). Common tern feed mainly on small fish and crustaceans taken by plunge-diving and is considered a top-predator in the marine food-chain.

The breeding period ranges from April to June. Up to three eggs may be laid, and the eggs hatch in around 21–22 days.

Common tern egg contents from Tjärnö are analysed for metals, organochlorines, perflourinated compounds and polybrominated compounds. Various shell parameters, for example shell weight, thickness and thickness index, are also monitored.

4.10 Eurasian Oystercatcher *(Haematopus ostralegus)*

Eurasian Oystercatcher is a wader and breeds in Western Europe, Central Eurasia, and the north eastern parts of Asia. Most populations of this species are fully migratory. The European population breeds mainly in northern Europe, but in winter the birds can be found in North Africa and southern parts of Europe. The Swedish population migrates between late August and mid March to other parts of the North Sea region.
Compared with the terns, the Oystercatcher is more a capital breeder, producing eggs also from substances stored in the body over longer time periods. The species is a resident breeder over large parts of the North Sea area (Koffijberg et al. 2006).The species is chiefly coastal outside of the breeding season, and primarily found at estuarine mudflats, saltmarshes and sandy and rocky shores. Foraging in estuaries, polychaetes and crustaceans are the main parts of the diet, however, molluscs (e.g. mussels, limpets and whelks) are most important on rocky shores. Prey such as earthworms and insect larvae may form an important part of the diet when inland foraging. In the breeding season, foraging of Oystercatcher takes place in comparatively small distances mostly less than 5 km of the breeding colony (Becker et al. 1993).
The species breeds from April to July, 2-4 eggs are laid.

Eurasian Oystercatcher egg contents from Tjärnö are analysed for metals, organochlorines, perflourinated compounds and polybrominated compounds. Various shell parameters, for example shell weight, thickness and thickness index, are also monitored.

5 Sampling sites

The location and names of the sample sites are shown in figure 5.1. The sampling sites are located in areas regarded as locally uncontaminated and, as far as possible, uninfluenced by major river outlets or ferry routes and not too close to heavily populated areas.

The Swedish sampling stations are included in the net of HELCOM stations in the Baltic and the Oslo and Paris Commissions' Joint Monitoring Programme (OSPAR, JMP) station net in the North Sea. Denmark (plaice), Estonia (herring, perch), Finland (herring), Germany (perch, cod, herring), Latvia (perch), Lithuania (herring, cod, flounder) and Poland (herring) all report contaminant data within HELCOM. Within the JMP, the time series of various contaminants in biota are reported from Belgium, Denmark, France, Germany, Iceland, The Netherlands, Norway, Spain, Sweden, Ireland and UK. All of the countries within HELCOM and OSPAR submit the data directly to ICES.

During 2007, the National Swedish marine monitoring programme has been expanded, and herring from 10 new sites have been added. Name and location of these sites are found in figure 5.1. From 2007 onwards, herring has also been collected by SLU AQUA from a number of sites in the open sea (Baltic). Two sites, one from the Baltic Proper and one from the Bothnian Sea (fish from 2008 onwards) have been analysed for various contaminants within the national monitoring programme.

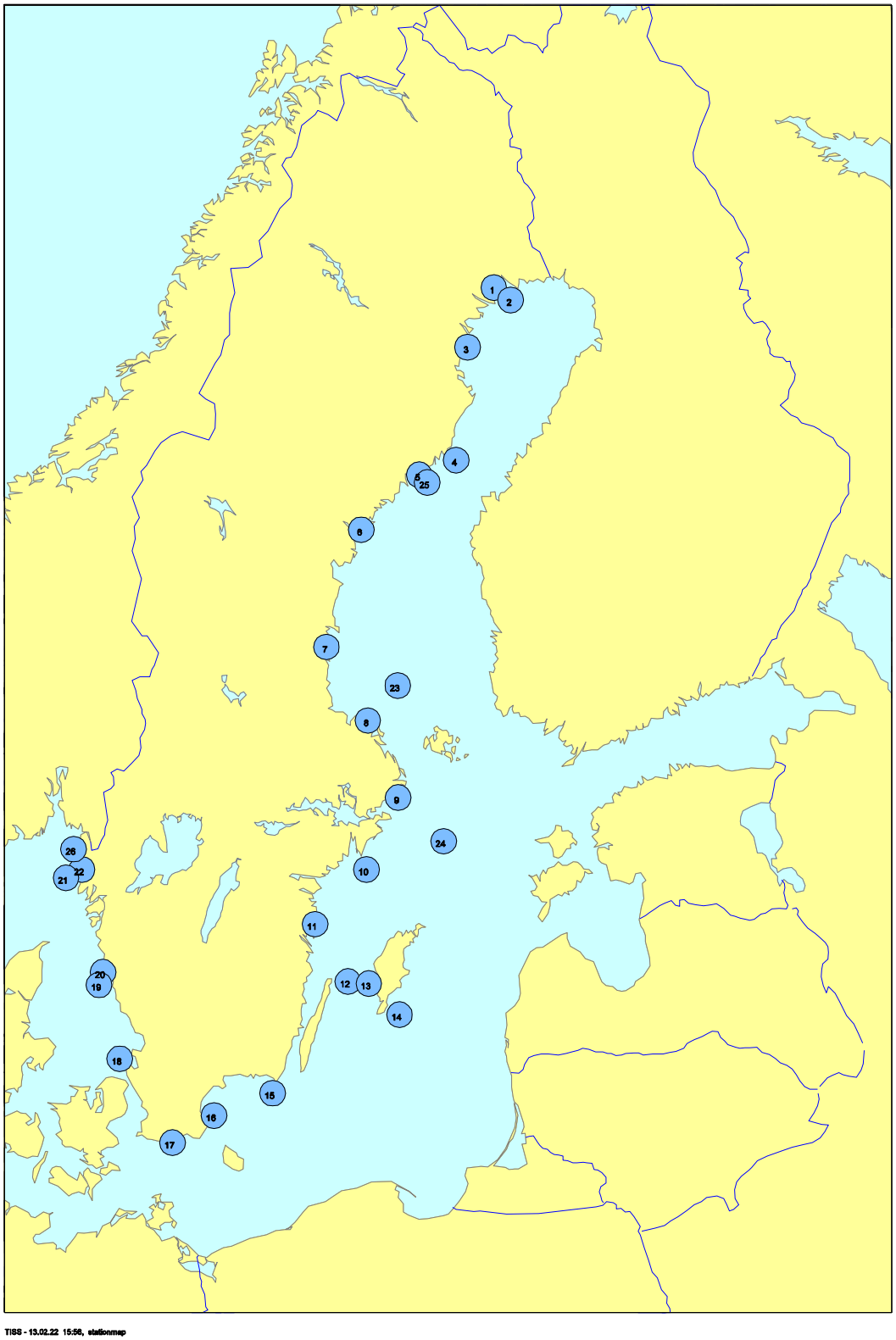


Figure 5.1. Sampling sites within the National Swedish Marine Monitoring Programme; 1) Råne fjärden, 2) Harufjärden, 3) Kinnbäcksfjärden, 4) Holmöarna, 5) Örefjärden, 6) Gaviksfjärden, 7) Långvindsfjärden, 8) Ängskärsklubb, 9) Lagnö, 10) Landsort, 11) Kvädöfjärden, 12) Byxelkrok, 13) St. Karlsö, 14) SE Gotland, 15) Utlängan, 16) V. Hanöbukten, 17) Abbekås, 18) Kullen, 19) Fladen, 20) Nidingen, 21) Väderöarna, 22) Fjällbacka, 23) Bothnian Sea offshore site, 24) Baltic Proper offshore site, 25) Bonden, 26) Tjärnö.

5.1 Ånefjärden, Bothnian Bay, north

Co-ordinates: 65° 45'N, 22° 25'E within a radius of 3', ICES 60H2 93
County: Norrbottens län

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

Sampling matrix: Baltic herring and perch (only sampling), autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs.

5.2 Harufjärden, Bothnian Bay, north

Co-ordinates: 65° 35'N, 22° 53'E within a radius of 3', ICES 60H2 93
County: Norrbottens län

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 HCHs/HCB; 1990 PCDD/F; 1995 Cr/Ni; 1998 PBDE/HBCDD; 2005 PFAS; 2007 Ag/As

5.3 Kinnbäcksfjärden, Bothnian Bay

Co-ordinates: 65° 03'N, 21° 29'E within a radius of 3', ICES 58H1
County: Norrbottens län

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

Sampling matrix: Baltic herring and perch (only sampling), autumn
Start: 2008 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs.

5.4 Holmöarna, Bothnian Bay, south, coastal site

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

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

Table 5.1. Start year for various contaminants for perch and eelpout.

Contaminant/ Species	PCB/ DDT	HCH/HCB	Hg	Pb/Cd/Cu/Zn	Cr/Ni	PCDD/F	Ag/As
Perch	1980	19(89)95	19(91)95	1995	1995	2007	2007
Eelpout	1995	1995	1995	1995	1995		

Both species are collected during autumn. Since 2007, Baltic herring has also been sampled for DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs.

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

5.5 Örefjärden, Bothnian Bay, south

Co-ordinates: 63° 31'N, 19° 50'E within a radius of 3', ICES 55G9
County: Västernorrlands län

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

Sampling matrix: Baltic herring (only sampling) and perch, autumn
Start: 2008 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, PCDD/F and HCHs/HCB.

5.6 Gaviksfjärden, Bothnian Bay, south

Co-ordinates: 62° 52'N, 18° 14'E within a radius of 3', ICES 54G8
County: Västernorrlands län

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

Sampling matrix: Baltic herring and perch (only sampling), autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

5.7 Långvindsfjärden, Bothnian Sea

Co-ordinates: 61° 27'N, 17° 10'E within a radius of 3', ICES 52G7
County: Gävleborgs län

Average air temperature: January: -3° / April: 2° / July: 15° / October: 6°

Sampling matrix: Baltic herring and perch (only sampling), autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

5.8 Ängskärsklubb, Bothnian Sea

Co-ordinates: 60° 32'N, 18° 09'E, ICES 50G7 83
County: Gävleborgs län/Uppsala län

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 HCHs/HCB; 1979 PCDD/F; 1995 Pb/Cd/Cu/Zn Cr/Ni; 2005 PFASs; 2007 Ag/As

Start, autumn: 1978 DDT/PCB; 1980 Hg; 1982 Pb/Cd/Cu/Zn; 1988 HCHs/HCB; 1995 Cr/Ni; 1994 PBDE/HBCDD; 1979 PCDD/F; 2005 PFC;Ag/As

In 1996, collection and analyses of herring samples from four other sites in the region were financed by the county board of Gävleborgs län. This investigation is valuable to estimate how

representative the well established sample site at Ängskärsklubb is. It also gives information on small scale geographical variation in general.

5.9 Lagnö, Baltic Proper, north

Co-ordinates: 59° 34'N, 18° 50'E, ICES 47G8
County: Stockholms län

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

Sampling matrix: Baltic herring and perch (only sampling), autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

5.10 Landsort, Baltic Proper, north

Co-ordinates: 58° 42'N, 18° 04'E, ICES 46G8 23
County: Stockholms län/Södermanlands län

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 HCHs/HCB; 1995 Cr/Ni; 1995 PBDE/HBCDD; 2005 PCDD/F and PFASs ; 2007 Ag/As

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

5.11 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°

Table 5.2. Start year for various contaminants for perch, blue mussels and eelpout.

Contaminant/ Species	PCB/ DDT	HCH/ HCB	Hg	Pb/Cd/ Cu/Zn	Cr/Ni	PAH	PBDE/ HBCDD	PCDD /F	Ag/As
Perch	1980	19(84)90	1981	1995	1995			2007	2007
Blue mussel	1995	1995	1995	1995	1995	1987	2000		2007
Eelpout	1995	1995	1995	1995	1995				2007

All species are collected during autumn.

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

Neuman et al. (1988) reports decreasing Secchi depths during the investigated period, from just below 6 m in 1980, to just above 4 m in the mid-1980s.

5.12 Byxelkrok, Baltic Proper

Co-ordinates: 57° 19'N, 17° 30'E, ICES 43G7
County: Kalmar län

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

Sampling matrix: Baltic herring, autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

5.13 St Karlsö, Baltic Proper

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

St Karlsö is situated about 7 km west of the island of 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, PBDE/HBCDD, PFAS; 1969 Hg, PCDD/F; 1988 HCHs/HCB; 1995 Pb/Cd/Cu/Zn/Cr/Ni; 2007 Ag/As

5.14 Southeast 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/ PBDE/HBCDD; 1982 Pb/Cd/Cu/Zn; 1988 HCHs/HCB; 1995 Cr/Ni; 2007 Ag/As

5.15 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°

Table 5.3. Start year for analysis of various contaminants for herring in spring and autumn.

Contaminant/ Species	PCB/ DDT	HCH/ HCB	Hg	Pb/Cd/ Cu/Zn	Cr/Ni	PBDE/ HBCDD	PCDD/ F	PFAS	Ag/As
Herring, spring	1972	1988	1972-75,95	1995	1995	2000	2000	2005	2007
Autumn	1979	1988	1981	1982	1995	2000	2000	2005	2007

In 1997, collection and analyses of herring samples from one site rather close to the reference site, and two sites in Hanöbukten, were financed by the Swedish EPA. This investigation is valuable to

estimate how representative the well-established sample site at Utlängan is. It will also give information on small-scale geographical variation in general.

5.16 Västra Hanöbukten, Baltic Proper, south

Co-ordinates: 55° 45'N, 14° 17'E, ICES 40G4
County: Skåne

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

Sampling matrix: Baltic herring, autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs; 2007 Ag/As

5.17 Abbekås, Baltic Proper, south

Co-ordinates: 55° 18'N, 13° 36'E, ICES 39G3
County: Skåne

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

Sampling matrix: Baltic herring, autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs; 2007 Ag/As

5.18 Kullen, Kattegat, Swedish west coast

Co-ordinates: 56° 19'N, 12° 23'E, ICES 41G2
County: Skåne

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

Sampling matrix: Herring, autumn
Start: 2007 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs, 2007 Ag/As

5.19 Fladen, Kattegat, 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°

Table 5.4. Start year for various contaminants for herring, cod, dab and blue mussels.

Contaminant/ Species	PCB/ DDT	HCH/ HCB	Hg	Pb/Cd/ Cu/Zn	Cr/Ni	PAH	PBDE/ HBCDD	PCDD/ F	PFAS	Ag/As
Herring	1980	1988	1981	1981	1995		1999	1997	2005	2007
Cod	1979	1988	1979	1981	1995		1999			2007
Dab	1981	1988	1981	1981	-					
Blue mussel	1984	1988	1981	1981	1995	1985	2000			2007

All species are collected during autumn.

5.20 Nidingen, Kattegat, Swedish west coast

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

5.21 Väderöarna, Skagerrak, Swedish west coast

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

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

Table 5.5. Start year for various contaminants for herring, eelpout, flounder and blue mussels.

Contaminant/ Species	PCB/ DDT	HCH/ HCB	Hg	Pb/Cd/ Cu/Zn	Cr/Ni	PAH	PBDE/ HBCDD	PCDD/ F	PFAS	Ag/As
Herring	1995	1995	1995	1995	1995		1999	2007	2005	2007
Eelpout	1995	1995	1995	1995	1995					2007
Flounder	1980	1988	1980	1981	-					
Blue mussel	1984	1988	1980	1981	1995	1985	2000			2007

All species are collected during autumn.

5.22 Fjällbacka, Skagerrak, Swedish west coast

Eelpout and blue mussels are collected at Musön and Fjällbacka on the Swedish west coast, about 10 km east of Väderöarna.

5.23 Bothnian Sea, offshore site

Co-ordinates: 60° 57 N, 18° 57'E, ICES 51G9

Average air temperature: January: -3° / April: 2° / July: 15° / October: 6°

Sampling matrix: Herring, autumn
Start: 2008 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

5.24 Baltic Proper north, offshore site

Co-ordinates: 59° 60'N, 19° 52'E, ICES 46H0

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

Sampling matrix: Herring, autumn
Start: 2008 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs.

5.25 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 (only rotten eggs), summer
Start: 1991 DDT/PCB

The collection of egg samples has been sporadic because of low population growth.

5.26 Tjärnö, Swedish west coast

Co-ordinates: 58° 52'N, 11° 02'E
County: Bohus län

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

Sampling matrix: Common tern and Oystercatcher egg; May
Start: 2011 DDT/PCB, Hg, Pb/Cd/Cu/Zn/Cr/Ni/Ag/As, HCHs/HCB, PBDE/HBCDD, PCDD/F and PFASs

6 Analytical methods

6.1 Trace metals

Prior to 2007, metal analyses were carried out at the Department of Environmental Assessment at the Swedish University of Agricultural Sciences (SLU). Due to some inconsistencies in results, the results from the years 2003 up to 2006 should be looked upon with caution. From 2007, the analyses were carried out at the Department of Applied Environmental Science (ITM) at Stockholm University (SU).

Prior to 2007, heavy metal concentrations, except mercury, in fish liver and blue mussel soft body, were determined using an atomic absorption spectrophotometer with a graphite furnace at SLU. The quantification limit was estimated to approximately 100 ng/g dry weight for zinc, approximately 10 ng/g dry weight for lead and copper, approximately 5 ng/g dry weight for cadmium and approximately 0.1 μg/g dry weight for nickel and chromium, which implies that the concentrations in herring, flounder and dab are approximately 10 - 20 times above the quantification limit.

Since 2007, ITM has determined heavy metal concentrations in fish liver and fish muscle (mercury), blue mussel soft body and guillemot egg. Analytical methods for metals in liver are performed according to the Swedish standards SS-EN 13805 (Foodstuffs – Determination of trace elements – Pressure digestion) and SS-EN ISO 17294-2 (Water quality – Application of inductively coupled plasma mass spectrometry (ICP-MS) – Part 2: Determination of 62 elements), and for mercury according to the US EPA Method 7473 (mercury in solids and solutions by thermal decomposition, amalgamation and atomic absorption spectrophotometry). The laboratory participates in the periodic QUASIMEME intercalibration rounds.

CRMs (certified reference material) used for mercury are:
DORM-2 and DORM-3 (dogfish muscle)
For all other metals, CRMs used are:
DOLT-3 (dogfish liver)
TORT-2 (lobster hepatopancreas)
NIST 1566 (oyster tissue).

Due to the change in laboratory and hence analysis methods, an intercalibration has been conducted to provide comparable results for the time series between laboratories.

Results from metal analysis have been compared between the laboratories. For herring from Utlängan, Väderöarna and Fladen, cod from SE Gotland and Fladen and guillemot egg from St. Karlsö the same individuals have been compared. For blue mussel from Nidingen, perch from Kvädöfjärden and herring from Landsort the comparisons are made on samples from same catch but not the same individuals (due to lack of sufficient sample material). No intercalibration has been made for eelpout.

The metal concentrations analysed by SLU have, in the time series, been recalculated by the ratios between laboratories in cases where these were significantly separated from 1, presented in table 6.1, to make the SLU-data comparable with the results from ITM. No comparison between the laboratories has been done for eelpout. No recalculation has been made for eelpout.

Table 6.1. Ratios of metal concentrations analysed by SLU versus ITM with corresponding standard error. p-values below 0.05 indicates that the mean ratio is significantly different from 1.

Herring	**n**	**Ratio, SLU/ITM**	**Std.Err.**	**p**
Hg	9	0.92	0.16	NS
Pb	**40**	**1.40**	**0.12**	**<0.01**
Cd	**40**	**1.14**	**0.06**	**<0.05**
Cu	**40**	**0.89**	**0.03**	**<0.01**
Zn	**40**	**1.13**	**0.03**	**<0.01**
Ni	**36**	**1.97**	**0.20**	**<0.01**
Cr	**30**	**2.01**	**0.30**	**<0.01**
Cod				
Hg	**9**	**1.19**	**0.07**	**<0.05**
Pb	**15**	**3.06**	**0.76**	**<0.05**
Cd	**19**	**1.85**	**0.18**	**<0.01**
Cu	**19**	**1.35**	**0.15**	**<0.05**
Zn	19	1.30	0.20	NS
Ni	11	1.38	0.27	NS
Cr	11	1.42	0.87	NS
Perch				
Hg	9	0.95	0.06	NS
Pb	**9**	**2.31**	**0.19**	**<0.01**
Cd	**9**	**1.50**	**0.21**	**<0.05**
Cu	**9**	**1.35**	**0.12**	**<0.05**
Zn	9	1.21	0.11	NS
Ni	1	0.76	-	-
Cr	2	8.95	1.05	NS
Mussel				
Hg	10	1.01	0.15	NS
Pb	10	1.30	0.20	NS
Cd	**10**	**0.74**	**0.07**	**<0.01**
Cu	**10**	**0.74**	**0.05**	**<0.01**
Zn	10	0.98	0.08	NS
Ni	7	0.96	0.15	NS
Cr	**7**	**2.48**	**0.47**	**<0.05**
Guillemot egg				
Hg	**9**	**1.25**	**0.07**	**<0.01**
Pb	0		-	-
Cd	0		-	-
Cu	9	0.95	0.04	NS
Zn	9	1.15	0.11	NS
Ni	0		-	-
Cr	**8**	**9.19**	**2.05**	**<0.01**

Table 6.2. Herring, cod and perch mean ratios of metal concentrations analysed by SLU versus ITM.

mean fish ratios	n	Ratio SLU/ITM
Hg	27	1.02
Pb	64	2.26
Cd	68	1.50
Cu	68	1.20
Zn	68	1.21
Ni	48	1.67
Cr	41	1.71

6.2 Organochlorines and brominated flame retardants

The analyses of organochlorines and brominated flame retardants are carried out at the Institute of Applied Environmental Science (ITM) at Stockholm University. Specific analytical methods applied are described in the respective chapters where applicable. Before 1988, organochlorines were analysed by a packed column gas chromatography (GC). During 1988, analysis on a capillary column was introduced, allowing analysis of individual congeners (Eriksson et al. 1994). The extraction method originates from the method described by Jensen et al. (1983) where wet tissues are extracted with a mixture of polar and non-polar solvents. The organochlorines are analysed on a gas chromatograph (GC) equipped with a μ-electron capture detector (Eriksson et al. 1994). The BFRs are analysed by a GC connected to a mass spectrometer operating in electron capture negative ionization mode (NICI) (Sellström et al. 1998).

6.2.1 Quality assurance

Quality control for organochlorines has continuously improved over the last 20 years, resulting in accreditation in 1999. Assessment is performed once a year by the accreditation body SWEDAC. The laboratory is fulfilling the obligations in SS-EN ICO/IEC 17025:2005. The accreditation is valid for CB28, 52, 101, 118, 153, 138, 180, HCB, *p,p'*-DDE, *p,p'*-DDD, *p,p'*-DDT and α, β- and γ–HCH in biological tissues. So far the 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 based on the Quality Manual, standard operation procedures (SOPs) and supplements. The annual audit includes a review of the SOPs, reference materials, proficiency testing, filing system, qualifications of the staff, up-to-date record of the training of the staff (to be able to perform their assigned tasks), accredited methods and audit of the quality program.

6.2.2 Standards

The original of all standards are well documented with known purity and certified concentration with uncertainty for the solutions.

6.2.3 Selectivity

To have the possibility to control impurities in solvents, equipments and glassware, one blank sample is extracted together with each batch of environmental samples.
Coelution of PCB congeners and pesticides in GC analysis is dependent upon instrumental conditions such as column type, length, internal diameter, film thickness and oven temperature. To minimize possible coelutions, two 60 m columns are used in parallel, the commonly used 5 % phenyl-methylsilicone phase and the more polar 14 %

cyanopropylphenyl-methylsilicone phase. The only remaining known coelution is for CB-138, which coelutes with CB-163 (Larsen et al. 1990). Therefore CB-138 is reported as CB138+163. PBDE and HBCD are analysed on a 30 m DB-5 MS column, monitoring m/z 79 and 81.
When introducing a new matrix one of the samples is re-extracted with a mixture of more polar solvents for control of no remaining contaminants in the matrix residual.

Samples from new matrixes and samples from already established matrixes from new sampling locations are also examined for suitable internal standards.

6.2.4 Reference Material

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

The certified reference material CRM 718 (herring muscle) is analysed for PCB once a year.

6.2.5 Proficiency testing

Concerning PCBs and pesticides, the laboratory has participated in the periodic QUASIMEME proficiency testing since 1993, with two rounds every year, each one containing two samples. Around 95% of all reported values have been satisfactory according to QUASIMEME, meaning they have been within +/- 2 standard deviations of the assigned value. In 2000, the laboratory participated in the first interlaboratory study ever performed for PBDEs and HBCD, contaminants that since 2001 are incorporated in the QUASIMEME proficiency testing scheme. Around 80% of the values the laboratory has produced during the years have been satisfactory according to QUASIMEME.

6.2.6 Quantification limits and uncertainty in the measurements

Calculation of the uncertainty in the measurement is based on the Nordtest Report TR 537 “Handbook for calculation of measurement uncertainty in environmental laboratories”, where the within-laboratory reproducibility is combined with estimate of the method and laboratory bias. The within-laboratory reproducibility is calculated from LRM from more than 8000 PCB- and pesticide values during a period of nearly 20 years and around 2000 BDE- and HBCD values during nearly 15 years. The bias is estimated from proficiency testing of more than 8 samples during at least 4 years. The bias for PBDE is used also for HBCD since no reliable proficiency testing (or certified reference material) exists today. Finally, the expanded uncertainty is calculated, using a coverage factor of 2 to reach approximately 95% confidence level (table 6.3). The reproducibility for the PCBs and pesticides follows the theory stated by Horwitz where the relative standard deviation increase when the concentration level decrease (Horwitz and Albert, 2006). The reproducibility for the PBDEs and HBCD follows a function where the relative standard deviations increase first at the very lowest concentration.

Table 6.3. Expanded uncertainty (%) at different concentrations

	CB28,101,118, 153,138,180,HCB	CB52	HCH α, β, γ	ppDDE ppDDD	ppDDT		PBDEs	HBCD
ng/g lw	%	%	%	%		ng/g lw	%	%
2-50	36	49	40	43		0.2-1	73	
4-50					52	> 2	58	
> 50	29	30	34	31	38	2-25		103
						> 25		64

The quantification limit is estimated to approximately 2 ng/g fat weight for all analysed PCBs, α, β, γ–HCH, HCB, pp-DDE and pp-DDD and 4 ng/g fat weight for pp-DDT. For all analysed PBDEs the quantification limit is estimated to approximately 0.2 ng/g fat weight and for HBCDD 2 ng/g.

6.3 Dioxins, dibenzofurans and dioxin-like PCBs

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

6.4 Polycyclic Aromatic Hydrocarbons

The analysis of PAHs are carried out at IVL, the Swedish Environmental Research Institute. The extraction and analysis of the samples were performed according to IVLs accredited method for PAHs.

The biota samples were spiked with recovery standard, homogenised in acetone and extracted in an ultrasonic bath. The extract was safeguarded and the samples were extracted once more with acetone and twice with pentane/ether. The extracts were combined and the organic compounds were extracted to an organic phase by liquid/liquid extraction with water and pentane, and further concentrated under nitrogen.

The samples were hydrolysed and pre-treatment procedures, such as fractionation of the organic compounds on silica, were performed as additional "clean-up" procedures. Laboratory blanks followed the same procedures as samples in the analytical work.

Determination of PAH components was carried out using a high performance liquid chromatograph (HPLC, type Varian Prostar 240, M410) with a 5 µm C_{18}-column (Chromosphere PAH 100* 3 mm, Chrompack). A linear gradient elution program was used, starting with acetonitrile/water 50:50 and ending with 100% acetonitrile (Rathburne HPLC-grade) at a flow rate of 1 ml min^{-1}. A fluorescence detector (Varian Prostar 363) with a wavelength program optimised for each PAH was used for quantification. The peak heights were registered with a chromatographic system from Varian (Star). The concentrations of 16 different PAH compounds were calculated by comparison to a certified standard, NIST, SRM 1647.

All of the standards used (both internal standard and quantification standards) are certified with known purity and precision.

6.5 Organotin compounds

Analysis of organotin compounds were carried out at IVL Swedish Environmental Research Institute.

Two freeze dried samples internal standards (monoheptyltin, diheptyltin) and 10 ml hydrobromic acid (50%) were added. The mixture was extracted twice with 20 ml dichloromethane in an ultrasonic bath and on a shaker. The organic extract was reduced in volume by evaporation under a stream of nitrogen and the solvent changed to 2 ml hexane: methanol 1:1. 40 µl 25% sodium tetraethylborate in tetrahydrofuran was added and was allowed to react for 2h at 90°C. After cooling, water was added and the hexane phase (together with an additional hexane extract) was reduced in volume and was cleaned up on an alumina column with hexane as solvent.

A six point calibration curve was prepared by diluting Organotin mix 8 stock solution (LGC Promochem) to which fresh solutions of monophenyltin trichloride and diphenyltin dichloride in methanol had been added. After ethylation using sodium tetraethylborate water was added and the ethylates extracted with hexane.

Instrumental analysis was carried out using a 7890A gas chromatograph connected to a 7004A triple quadrupole mass spectrometer (Agilent) used in electron ionization and multiple reaction monitoring (MRM) mode. For most compounds two MRMs were recorded, one as a quantifier and the other as a qualifier to increase specificity. Certified reference materials are used to check the performance of the method.

6.6 Perfluoroalkyl substances

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

6.6.1 Sample preparation and instrumental analysis

A sample aliquot of approximately 1.0 g (0.5 g for bird eggs) homogenized tissue in a polypropylene (PP)-centrifuge tube was spiked with 1.0 ng (10 ng for bird eggs) each of a

suite of mass-labelled internal standards (^{18}O- or ^{13}C-labelled perfluoroalkyl sulfonates and carboxylic acids). The samples were extracted twice with 5 mL of acetonitrile in an ultrasonic bath. Following centrifugation, the supernatant extract was removed and the combined acetonitrile phases were concentrated to 1 mL under a stream of nitrogen. The concentrated extract underwent dispersive clean-up on graphitised carbon and acetic acid. A volume of 0.5 mL of the cleaned-up extract was added to 0.5 mL of aqueous ammonium acetate. Precipitation occurred and the extract was centrifuged before the clear supernatant was transferred to an autoinjector vial for instrumental analysis and the volume standards M8PFOA and M8PFOS were added.

Aliquots of the final extracts were injected automatically on an ultra performance liquid chromatography (UPLC) system (Acquity, Waters) coupled to a tandem mass spectrometer (MS-MS; Xevo TQS, Waters). Compound separation was achieved on a BEH C18 UPLC column (1.7 µm particles, 50 × 2.1 mm, Waters) with a binary gradient of ammonium acetate buffered acetonitrile and water. The mass spectrometer was operated in negative electrospray ionisation mode. Quantification was performed in selected reaction monitoring chromatograms using the internal standard method.

6.6.2 Quality control

The extraction method employed in the present study (with the exception of the concentration step) has previously been validated for biological matrices and showed excellent analyte recoveries ranging between 90 and 110% for PFCAs from C6 to C14 (Powley & Buck 2005). Including extract concentrations, we determined recoveries between 70 and 90% for C6- to C10-PFCAs and 65 – 70% for C11-C15 PFCAs. Extraction efficiencies for perfluorosulfonates (PFSAs), including perfluorooctane sulfonamide (FOSA), were determined to 70 – 95%. Method quantification limits (MQLs) for all analytes were determined on the basis of blank extraction experiments and ranged between 0.02 and 1.0 ng/g wet weight for the different compounds. A fish tissue sample used in an international inter-laboratory comparison (ILC) study in 2007 (van Leeuwen et al. 2009) was analysed as control sample along with all sample batches. The obtained concentrations were in good agreement with the mean concentrations from the ILC study for all seven compounds quantified in the ILC.

7 Statistical treatment, graphical presentation

7.1 Trend detection

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

7.1.1 Log-linear regression analyses

Log-linear regression analyses are performed for the *entire investigated time period* and also for the *most recent 10 years* for the longer time series.

The slope of the line describes the yearly percentage change. A slope of 5% implies that the concentration is halved in 14 years, whereas a slope of 10% corresponds to a similar reduction in 7 years, and 2% in 35 years. (Table 7.1).

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

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

7.1.2 Non-parametric trend test

The regression analysis assumes, among other things, that the regression line gives a good description of the trend. The leverage affect of points at the end of the line is also a well-known fact. An exaggerated slope, caused 'by chance' by a single or a few points at 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 generally has lower power than the regression analysis, and does not take into account differences in magnitude of concentrations; 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 the Mann-Kendall test does not, the explanation could be either that the latter test had lower power, or that the influence of end points in the time series has become unjustifiably high on the slope. Hence, the eighth line reports Kendall's '**τ**', and the corresponding p-value. The Kendall's '**τ**' range from 0 to 1 like the traditional correlation coefficient 'r', but will generally be lower. 'Strong' linear correlations of 0.9 or above correspond to τ-values of about 0.7 or above (Helsel & Hirsch 1995, p. 212). This test was recommended by the US Environmental Protection Agency (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

In order to describe development over time, an alternative to the regression line is a type 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 a poor fit, the smoothed line may be more appropriate. The significance of this line is tested by means of an Analysis of Variance, where the variance is explained by the smoother line, and the regression line is compared with the total variance. This procedure has been used in assessments at ICES and is described by Nicholson et al. (1995).

7.2 Adjustments for covariables

It has been shown that metal concentrations in cod liver are influenced by fat content (Grimås et al. 1985). Consequently, the metal concentrations in cod liver are adjusted for fat content. On 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 considerably. For the same reasons, 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 quantification limit

Observations further from the regression line than expected from the residual variance around the line are subject to special concern. These deviations may be caused by an atypical occurrence of something in the physical environment, a change in pollution load, or errors in the sampling or analytical procedure. The procedure used to detect suspected outliers in this report 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 or the variance around the regression line. The suspected outliers are merely indicated in the figures and are included in the statistical calculations except in a few cases, as indicated in the figures.

Values reported that are below the quantification limit are substituted using the reported LOQ divided by the square root of 2.

In time series where all values in one year are below LOQ, a gray bar show the maximum LOQ and a dot represent the geometric mean value estimated from the individual LOQs divided by the square root of 2. In earlier years the LOQ were not reported. In these cases when at least one analysis showed a concentration above LOQ, a blue bar represents the minimum value above LOQ. The dot in these cases is estimated from the minimum value divided by 2

7.4 Plot Legends

The analytical results from each of the investigated elements are displayed in figures. A selection of sites and species are presented in the plots; no time series are shorter than four years.

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

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

The trend for the whole time period is presented by a regression line (plotted if $p < 0.10$, two-sided regression analysis); $p < 0.05$ is presented by a red line and $0.05 < p < 0.10$ is presented by a dashed blue line. The trend for the last ten years is plotted if $p < 0.2$ and $p < 0.05$ is presented by a red line and $0.05 < p < 0.2$ is presented by a dashed light blue line. Ten years is often a too short 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 has increased as a result of, for example, improved sampling techniques or that problems in the chemical analysis have disappeared.

A smoother is applied to test for non-linear trend components (see section 7.1.3). The smoothed line is plotted if $p < 0.10$, as a red line if $p < 0.05$ and as a dashed blue line if $p > 0.05$ but < 0.10. A broken line segment indicates a gap in the time series with a missing year.

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

A cross inside a circle, indicates a suspected outlier (see section 7.3). Suspected outliers are indicated in the figures and are included in the statistical calculations, except in a few cases, and pointed out in the figures.

Each plot has a header with species name, age class and sampling locality. Age class may be replaced by shell length for blue mussels. Below the header of each plot the results from several statistical calculations are reported:

Tv=…,**lp% or dp%=**… **Tv** is the target level (see Chapter 10) calculated on a lipid weight base (**lp%=**) or on dry weight base (**dp%=**), original target value was given on a wet weight basis.

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

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

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

CV(lr)= reports the coefficient of variation around the regression line as a measure of between-year variation, together with the lowest detectable change in the current time series with a power of 80%, one-sided test, $\alpha=0.05$. The last figure on this line is the estimated number of years required to detect an annual change of 10% with a power of 80%, one-sided test, $\alpha=0.05$.

power= reports the power to detect a log-linear trend in the time series (Nicholson & Fryer, 1991). The first figure represents the power to detect an annual change of 10% with the number of years in the current time series. The second figure is the power estimated as if the slope were 10% 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 nine.

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

Y(10)= reports the concentration estimated from the regression line for the last year together with a 95% confidence interval, e.g. y(10)=2.55(2.17,3.01) is the estimated concentration for the year 2010, 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.

CV(sm)= reports the coefficient of variation around the smoothed line. The significance of this line could be tested by means of an Analysis of Variance (see section 7.1.3). The p-value is reported for this test. A significant result will indicate a non-linear trend component. After the p-value, the minimum trend (%/year), likely to be detected, at a power of 80%, during a period of 10 years, should a log-linear trend occur, is shown. This estimate is compensated for by the loss of degrees of freedom, considering the smoother.

Below these nine lines are additional lines with information concerning the regression of the last 10 years.

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

7.5 Legend for the three dimensional maps

The height of the bars represents the arithmetic mean for the last three years, or less if results are not available. The bars are split into three sections of equal size (that each represents the same concentration).

8 The power of the programme

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

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

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

The number of years that various contaminants have been analysed and detected from the monitored sites is reported in tables for the respective compounds. Generally the monitoring of trace metals has continued for about 25 - 30 years; PCB and DDT for about 25 - 30 years (spring-caught herring and guillemot egg however, for more than 35 years; HCH, HCB and PCDD/PCDF for about 20 years; PBDE/HBCDD for about 10 years; and PFCs only for about 5 years).

In each chapter, there is a table in the end giving information regarding the results but also the power of the analysis. In the tables, YRQ represents the number of years required to detect an annual change of 10% with a power of 80%. Power is to a great extent dependent on the length of the time series. The possibility to statistically verify an annual change of 10% at a power of 80% generally requires 8-12 years for the organic substances. Furthermore, in the tables LDT represents the smallest trend able to be detected within a 10 year period with a power of 80 %.

The power to detect an annual change of 10% covering the monitoring period, i.e. the length of the time series, varies depending on site and investigated contaminant (table 8.4). For the long time series, the estimated power is in most cases close to100%. For the shorter time series of BDE-47 and HBCDD, estimated power is about 30-100%.

Table 8.1. Power to detect an annual change of 10% covering the entire monitoring period. The length of the time series varies depending on site and investigated contaminant. Where a considerable increase in power has been achieved during the most recent 10 year period, this value has been used instead.

Metals. Based on annual geometric mean concentrations on a dry weight basis except for Hg expressed on a wet weight basis.

	Harufjärden, herring	Ängskärsklubb, herring	Ängskärsklubb (spring), herring	Landsort herring	Utlängan herring	Utlängan (spring), herring	Fladen, herring	Väderöarna, herring	Holmöarna, perch	Kvädöfjärden, perch	SE Gotland, cod	Fladen, cod	Holmöarna, eelpout	Kvädöfjärden, eelpout	Fjällbacka, eelpout	Kvädöfjärden, mussel	Nidingen, mussel	Fjällbacka, mussel	St. Karlsö, guillemot
Hg	1.0	1.0	1.0	*1.0	*1.0	1.0	1.0	*1.0	1.0	*1.0	*1.0	*1.0	0.99	1.0	*1.0	*1.0	*1.0	*1.0	*1.0
Pb	*1.0	1.0	0.86	1.0	1.0	0.99	1.0	1.0	0.98	0.99	*1.0	1.0	0.17	0.97	1.0	0.96	*1.0	1.0	*0.74
Cd	1.0	*1.0	0.98	*1.0	*1.0	1.0	1.0	1.0	1.0	*1.0	*1.0	1.0	0.72	0.95	1.0	1.0	*1.0	*1.0	-
Cu	*1.0	1.0	1.0	*1.0	1.0	1.0	*1.0	1.0	1.0	1.0	1.0	1.0	0.80	*1.0	1.0	*1.0	1.0	1.0	*1.0
Zn	*1.0	*1.0	1.0	*1.0	*1.0	1.0	*1.0	1.0	*1.0	*1.0	1.0	1.0	0.99	1.0	1.0	*1.0	1.0	1.0	*1.0

Organochlorines, bromines, fluorines. Based on annual geometric mean concentrations on a lipid weight basis, fresh weight for PFOS

	Harufjärden, herring	Ängskärsklubb, herring	Ängskärsklubb (spring), herring	Landsort herring	Utlängan herring	Utlängan (spring), herring	Fladen, herring	Väderöarna, herring	Holmöarna, perch	Kvädöfjärden, perch	SE Gotland, cod	Fladen, cod	Holmöarna, eelpout	Kvädöfjärden, eelpout	Fjällbacka, eelpout	Kvädöfjärden, mussel	Nidingen, mussel	Fjällbacka, mussel	St. Karlsö, guillemot
CB-153	1.0	*1.0	1.0	*1.0	*1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	*0.32	1.0	0.99	1.0	1.0	*1.0	1.0
DDE	*1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	*1.0	*1.0	1.0	*1.0	0.50	0.98	1.0	1.0	1.0	*1.0	*1.0
a-HCH	*1.0	*1.0	*1.0	1.0	*1.0	*1.0	*1.0	1.0	1.0	*1.0	1.0	1.0	-	-	-	1.0	*1.0	*1.0	*1.0
HCB	*1.0	1.0	1.0	1.0	1.0	1.0	*1.0	1.0	1.0	1.0	1.0	*1.0	0.46	0.99	1.0	1.0	1.0	*1.0	*1.0
TCDD-eqv	1.0	1.0	-	-	1.0	-	1.0	-	-	-	-	-	-	-	-	-	-	-	*1.0
BDE-47	0.96	0.96	0.29	1.0	1.0	0.50	1.0	0.99	-	-	1.0	0.91	-	-	-	*0.95	0.99	1.0	*1.0
HBCDD	0.81	0.66	0.36	1.0	0.91	0.76	0.95	.80	-	-	1.0	0.54	-	-	-	0.34	0.53	0.81	*1.0
PFOS	.*0.37	0.21	-	0.35	0.45	-	*0.91	0.13	-	-	-	-	-	-	-	-	-	-	*1.0

* indicates a significant non-linear trend component

9 Pollutant regulation: conventions and legislation

9.1 The Stockholm Convention on Persistent Organic Pollutants

The Stockholm Convention on Persistent Organic Pollutants (POPs) is an international agreement requiring measures for reducing or preventing release of dangerous substances into the environment. The Stockholm Convention was adopted in 2001 and entered into force in 2004. The convention deals with organic compounds that are persistent and remain in the environment for a long time, have a potential for long-range transport, bioaccumulate in fatty tissue in organisms and have adverse effects on human health or the environment. Initially, 12 chemicals were included in the treaty in 2001 (aldrin, chlordane, DDT, dieldrin, endrin, heptachlor, mirex, toxaphene, PCB, hexachlorobenzene, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans). In May 2009, an amendment was adopted into the convention, and nine additional chemicals were listed as POPs (hexa-/heptabromdiphenyl-ether, tetra-/pentabromodiphenylether, chlordecone, hexabromobiphenyl, lindane, α- and β –hexachlorocyklohexane, pentachlorobenzen and PFOS). In May 2011 an amandement was adopted into the convention and technical endosulfan and its related isomers were added to the list with specific exemptions. Five more substances have been nominated to be included on the list, and are currently under review by the Persistent Organic Pollutants Review Committee (short-chained chlorinated paraffins, hexabromocyclododecane, chlorinated naphtalenes, hexachlorobutadiene, and pentachlorophenol) (www.pops.int).

9.2 The Helsinki Convention

The Helsinki Convention is the Convention on the Protection of the Marine Environment of the Baltic Sea. It was signed in 1992 by all the states bordering the Baltic Sea, entered into force in 2000, and is governed by the Helsinki Comission (HELCOM). The main focus of the convention is to protect the marine environment of the Baltic Sea from all sources of pollution, with the future vision being a healthy Baltic Sea. The Baltic Sea Action Plan (BSAP) is a program within HELCOM that aims to restore a good ecological status of the marine environment by 2021. Joint monitoring of pollutants in the Baltic Sea is important to evaluate the status of the Baltic Sea. Data from the Swedish national monitoring program is reported to HELCOM every year via the International Council for the Exploration of the Sea (ICES) (www.helcom.fi).

9.3 The Oslo Paris Convention

The convention for the protection of the marine environment of the North-East Atlantic (The Oslo Paris Convention, OSPAR) was adopted in 1992 after a meeting of The Oslo and The Paris Commissions, and entered into force in 1998. Within OSPAR, six different working areas have been identified that address the main areas of concern (the Biodiversity and Ecosystem Strategy, the Eutrophication Strategy, the Hazardous Substances Strategy, the Offshore Industry Strategy, the Radioactive Substances Strategy and a Strategy for the

Joint Assessment and Monitoring Programme). The OSPAR Hazardous Substances Strategy works to prevent pollution of the marine environment. The aim is to achieve levels near background concentrations for naturally occurring substances, and close to zero for man-made synthetic substances. The hazardous substances work is implemented by OSPAR's Hazardous Substances Committee, which is working to achieve this goal by 2020. Within OSPAR, hazardous substances are defined as substances that are persistent, bio accumulative and toxic (PBT). OSPAR has a list of chemicals of priority concern, and a list of chemicals of possible concern. These lists are continuously being updated as knowledge on the substances is improved. Data from the Swedish national monitoring program is reported to OSPAR every year through ICES (www.ospar.org).

9.4 The Convention on Long-Range Trans boundary Air Pollution

The Convention on Long Range Trans boundary Air Pollution (CLRTAP) was initiated in 1972 at a United Nations Conference on the Human Environment in Stockholm. After the scientific findings that acidification in Swedish lakes was caused by sulphur emission from continental Europe, the necessity for international measures to reduce emissions to air that had environmental effects far from the source, was addressed. In 1979 the convention was signed in Geneva, and entered into force in 1983. Initially, the convention focused on sulphuric compounds causing acidification, but later eight protocols were added for other groups of substances e.g. nitrogen oxides, volatile organic compunds (VOCs) and persistent organic pollutants (POPs) (http://www.unece.org/env/lrtap/lrtap_h1.htm)

9.5 EU chemical legislation

9.5.1 REACH

REACH is the EU chemicals policy that entered into force on the 1st of June 2007 (EC 1907/2006). REACH stands for Registration, Evaluation, Authorization and Restriction of Chemical Substances. The policy places more responsibility on industry, and importers and users have to gather information about their chemicals which they then report to the European Chemicals Agency (ECHA) based in Helsinki. ECHA manages REACH by gathering information and keeps databases of chemicals used in the EU. (http://ec.europa.eu/environment/chemicals/reach/reach_intro.htm).

9.5.2 RoHS directive

The Directive on the Restriction of Hazardous Substances (RoHS) was adopted in February 2003. The RoHs directive reduces the use of six chemical substances in electrical or electronic products that were released on the market after July 2006. These substances are mercury, cadmium, lead, chromium VI, polybrominated biphenyls and polybrominated diphenyl ethers. The maximum allowed amount of these substances (based on weight) is 0.01% for cadmium, and 0.1% for the other substances. (http://www.kemi.se/templates/Page____3794.aspx).

9.5.3 Water Framework Directive

The Water Framework Directive (WFD) aims to achieve good ecological and chemical status of all surface waters and ground water bodies in the EU by 2015. WFD was adopted in October 2000, and deals with fresh water as well as coastal-zone and estuary waters. Within the WFD, a list of 33 prioritized substances has been established, and later eight additional substances were added. To evaluate if "good chemical status" has been achieved, threshold values or Environmental Quality Standards (EQS) have been established for the listed substances (see chapter 10). It is the responsibility of each member state to assess and report if the goal has been fulfilled. (http://ec.europa.eu/environment/water/water-framework/index_en.html).

9.5.4 Marine Strategy Framework Directive

The Marine Strategy Framework Directive (MSFD) was adopted in 2008 with the aim of achieving good environmental status in all European marine waters by 2020. Two of eleven descriptors that have been identified for good environmental status deal with contaminants. These are "contaminants and pollution effects" and "contaminants in fish and other sea food". The implementation for Swedish waters will be based on the regional international conventions of OSPAR and HELCOM.
(http://ec.europa.eu/environment/water/index_en.htm).

9.6 Swedish chemical legislation

One of the 16 Swedish environmental quality objectives is "A non-toxic environment", which means that concentrations of non-naturally occurring substances should be close to zero, and naturally occurring substances should be close to background concentrations. Their impact on human health and ecosystems should be negligible (http://www.miljomal.se/4-Giftfri-miljo/Definition/). The agency responsible for coordinating this work is the Swedish Chemicals Agency (KEMI). The Swedish chemical legislation is following the EU legislations. Much of the national legislations that existed before June 2007 were replaced by REACH.
(http://www.kemi.se/templates/Page____3064.aspx).

10 Target levels for chemical status assessment

Good Environmental Status (GES), in accordance with the Marine Strategy Framework Directive 2008/56/EC (MSFD), is defined as "concentrations of contaminants at levels not giving rise to pollution effects". GES is determined from quality assessments based on target levels representing a threshold that should not be exceeded. Established to protect sensitive organisms from the harmful effects of hazardous substances, target levels have been developed within several groups or conventions; Environmental Quality Standards (EQS) developed within the EC to evaluate GES, and the Environmental Assessment Criteria (EAC), developed within OSPAR. In addition to EQSs and EACs, chemical status can also be assessed from the point of human consumption. Maximum levels for contaminants in food are set in Commission Regulation (EC, No 1881/2006).

The Environmental Quality Standards Directive (2013/39/EU) lays Environmental Quality Standards (EQSs) and for priority substances and certain other pollutants, as provided for in Article 16 of the WFD, with the aim of achieving good surface water chemical status. The objective is to protect pelagic and benthic freshwater and marine ecosystems, as well as human beings from adverse impacts of chemical contaminants. The annual average concentration (AA-EQS) refers to the annual arithmetic mean concentration providing protection against chronic exposure and cover short-term chemical effects in biota. The methodological framework used in deriving these EQSs is described in CIS (2011). Substance EQS Data Sheets (SDS) contains background information regarding the development of EQS (available at the CIRCABC webpage). Here, data from ecotoxicological studies are compiled to Specific Quality Standards (QS), derived for water, sediment, biota (QS_{biota}), which is set to protect for secondary poisoning in predators, and human health (QS_{hh}). To date, EQS_{biota} is available for 11 out of 45 substances.

Within the OSPAR convention, Environmental Assessment Criteria (EAC) has been developed for interpretation of chemical monitoring data in sediments and biota (OSPAR CEMP 2009). Concentrations below the EACs are considered to present no significant risk to the environment and may be considered as related to the EQSs.

In this report, primarily internationally agreed target levels such as EQS, EAC or EC recommendations for foodstuffs are used. If reliable target levels have been produced with specific regard to Swedish environmental conditions, these are considered (e.g. HCH and BDEs). Only one type of target level is applied within each substance group (e.g. we do not mix EQS and EACs depending on availability of different PCB or PAH congeners). Concentration of substances lacking internationally agreed target levels are presented without evaluation against target levels (e.g Cr, Cu, Zn, As, Ag, Al, Sn, Bi).

Table 10.1. Target levels for various environmental pollutants.

Group of substance		Target levels		
		Fish (µg/kg ww)	Mussels (µg/kg dw)	Background reference
Metals	Cadmium	160		QS_{biota}
	Lead	1000		QS_{biota}
	Mercury	20		EQS
	Nickel	730		QS_{biota}
PAHs	Fluoranthene	-	110 (EAC)/ 30 ww (EQS)	
	Anthracene		290 (EAC)	
	Naphtalene		340 (EAC)	
	Phenantrene	-	1700 (EAC)	
	Pyrene		100 (EAC)	
	Benzo(a)anthracene		80 (EAC)	
	Benzo(a)pyrene	-	600 (EAC)/ 5 ww (EQS)	
	Benzo(b)flouranthene	-		
	Benzo(k)flouranthene	-		
	Benzo(ghi)perylene	-	110 (EAC)	
	Indenol(1,2,3-cd)-pyrene	-		
Pesticides	DDE (p,p')	5		EAC
	HCH (incl. lindane)	2.6/26		IVL
PCBs	CB-28	64 lw		EAC
	CB-52	108 lw		EAC
	CB-101	120 lw		EAC
	CB-105			EAC
	CB-118	24 lw		EAC
	CB-138	316 lw		EAC
	CB-153	1600 lw		EAC
	CB-156			EAC
	CB-180	480 lw		EAC
Other	BDEs (congeners 28, 47, 99, 100, 153, and 154)	0.0085		EQS_{biota}
	HBCDD	167		EQS_{biota}
	ΣPCDDs+PCDFs	0.0035		EQS_{biota}
	HCB	10		EQS_{biota}
	PFOS	9.1		EQS_{biota}

10.1 Metals

10.1.1 Cadmium

There is no EQS or EAC developed for cadmium. The QS_{biota} is set at 0.16 mg/kg prey tissue wet weight and evaluates whole fish concentrations in a freshwater system. The QS_{hh} is set at 0.1 – 1.0 mg/kg in edible parts of fish. The EC foodstuff regulation sets a maximum level for muscle meat at 0.05 mg/kg wet weight. The directive states that where fish are intended to be eaten whole, the maximum level shall apply to the whole fish.

Selected target level: QS_{biota}

10.1.2 Lead

There is no EQS or EAC developed for lead. The QS_{biota} is set at 1000 µg/kg prey tissue wet weight and evaluates whole fish concentrations. The QS_{hh} is set at limit values of 200 – 1000 µg/kg fishery product wet weight. The EC foodstuff regulation sets a maximum level for lead in muscle meat of fish at 0.3 mg/kg wet weight. The directive states that where fish are intended to be eaten whole, the maximum level shall apply to the whole fish.

Selected target level: QS_{biota}

10.1.3 Mercury

The EQS_{biota} for mercury is set at 20 µg/kg (methyl-Hg) prey tissue wet weight to protect against secondary poisoning. There is no EAC developed for mercury. The EC foodstuff regulation sets a maximum level for mercury at 0.5 mg/kg wet weight. The directive states that where fish are intended to be eaten whole, the maximum level shall apply to the whole fish.

Selected target level: EQS_{biota}

10.1.4 Nickel

There is no EQS or EAC developed for nickel. The QS_{biota} is set at 0.73 mg/kg prey tissue wet weight. The QS_{hh} is set at 0.67 mg/kg fishery product wet weight. There is no EC foodstuff regulation developed for nickel.

Selected target level: QS_{biota}

10.2 PAHs

There are EQSs set for Fluoroanthene (30 ug/kg ww) and Benzo(a)pyrene (5 ug/kg ww) in mussels. The EACs developed for PAHs in mussels expressed as µg/kg dry weight are; fluoranthene: 110, anthracene. 290, naphthalene: 340, phenantrene: 1700, pyrene: 100, benzo(a)anthracene: 80, benzo(a)pyrene: 600, benzo(ghi)perylene: 110. The EC foodstuff

regulation sets a maximum level for benzo(a)pyrene in bivalve molluscs at 10.0 µg/kg wet weight.

Selected target level: EAC

10.3 Pesticides

10.3.1 DDTs, (DDT, DDE and DDD)

There are no EQS or EC foodstuff regulation developed for any of the DDTs. The EAC developed for DDE is set at 0.005 mg/kg wet weight.

Selected target level: EAC

10.3.2 HCH

There are no EQS or EC foodstuff regulation developed for HCHs. The EACs developed for γHCH in fish liver is set at 11 µg/kg lipid weight. With regard to Swedish levels of organic carbon in the sediments and factors for bioconcentration (BCF) and biomagnification (BMF), the Swedish Environmental Research Institute (IVL) have performed translations between EQS for surface water to biota (Lilja et al. 2010). The IVL target level is set for the sum of HCH (including lindane) at 26 µg/kg wet weight in a limnic environment and 2.6 µg/kg wet weight in a marine environment.

Selected target level: IVL

10.4 PAHs

The EACs developed for PAHs in mussels expressed as µg/kg dry weight are; fluoranthene: 110, anthracene. 290, naphthalene: 340, phenantrene: 1700, pyrene: 100, benzo(a)anthracene: 80, benzo(a)pyrene: 600, benzo(ghi)perylene: 110. The EC foodstuff regulation sets a maximum level for benzo(a)pyrene in bivalve molluscs at 10.0 µg/kg wet weight.

Selected target level: EAC

10.5 PCBs

The draft EQS for concentrations of CBs is based on biota and is set at 0.003 µg/kg wet weight. The EQS is based on effects in organisms exposed to Aroclor 1254 which contains the PCBs CB-28, CB-52, CB-101, CB-118, CB-138, CB-153, and CB-180 in a proportion superior to 90%. The EAC developed for PCBs is expressed as µg/kg lipid weight: CB-28: 64, CB-52: 108, CB-101: 120, CB-118:24, CB-138: 316, CB-153: 1600, CB-180: 480.The EC foodstuff regulation developed for concentrations of PCBs in muscle meat of fish is set for the sum of CB-28, CB-52, CB-101, CB-138, CB-153, CB-180 (ICES - 6) at 75 ng/g wet weight.

Selected target level: EAC

10.6 Brominated flame retardants

10.6.1 BDEs

The EQSbiota for concentrations of sumBDEs is set at 0.0085 µg/kg wet weight. There are no EAC or EC foodstuff regulation developed for BDEs. The EQSbiota is based on QS set for human health.

Selected target level: EQSbiota

10.6.2 HBCDD

The EQSbiota for concentrations of HBCDD is based on secondary poisoning of predators and set at 167 µg/kg fresh weight. There are no EAC or EC foodstuff regulation developed for HBCDD.

Selected target level: EQSbiota

10.7 Other

10.7.1 Dioxins, furans and dioxin-like PCBs.

The EQSbiota for concentrations of dioxins, furans and dioxinlike PCBs is based on the EC foodstuff regulation and set at 0.0065 µgWHO05-TEQ /kg ww. The QS set for human health was identified as the critical EQS because of the consensus regarding the value used in existing food legislation and because there is a greater uncertainty regarding the values calculated for QS sec. pois. The EC foodstuff regulation for only dioxins and furans is 0.0035 µgWHO05-TEQ /kg ww.

Selected target level: EQSbiota

10.7.2 HCB

The EQSbiota for HCB is based on human health and set at 10 µg/kg fishery product wet weight. There is no EC foodstuff regulation developed for HCB.

Selected target level: EQSbiota

10.7.3 PFOS

The EQSbiota for concentrations of PFOS is based on human health and set at 0.0091 mg/kg wet weight. There are no EAC or EC foodstuff regulation developed for PFOS.

Selected target level: EQSbiota

11 Condition

Updated 14.02.28

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

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

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

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

11.1 Spatial variation

Average condition factor, estimated over a period of more than 30 years, were at similar levels in herring sampled in the Baltic Sea. The lowest result was reported for herring samples from Harufjärden (Fig. 11.1) in the northern parts of the Bothnian Bay. Herring from Fladen and Väderöarna on the Swedish west coast (Fig. 11.2) were at higher levels compared to samples from the Baltic Sea. The same pattern was seen for eelpout with higher condition factor at the Swedish west coast (Fjällbacka) compared to the Baltic sampling sites (Fig. 11.4).

11.2 Temporal variation

Significant *decreasing* trends in herring condition factor were observed from Harufjärden, Landsort and Utlängan (autumn and spring) (Fig. 11.1, 11.2). At Ängskärsklubb, it *increased* in spring-caught herring for the whole time series. The increase at Ängskärsklubb may be explained by an unintentional increase in average age over time in the collected samples (Fig. 11.2).

The condition factor estimated for cod showed a significant *increasing* trend at Fladen over the whole period examined (Fig. 11.3). The observed increase might be explained by the simultaneous decrease in population density during the period examined.

Significantly *decreasing* trends in both perch and eelpout condition factor were observed at Holmöarna (0.30% and 1.1 % respectively) (Fig. 11.3, 11.4).

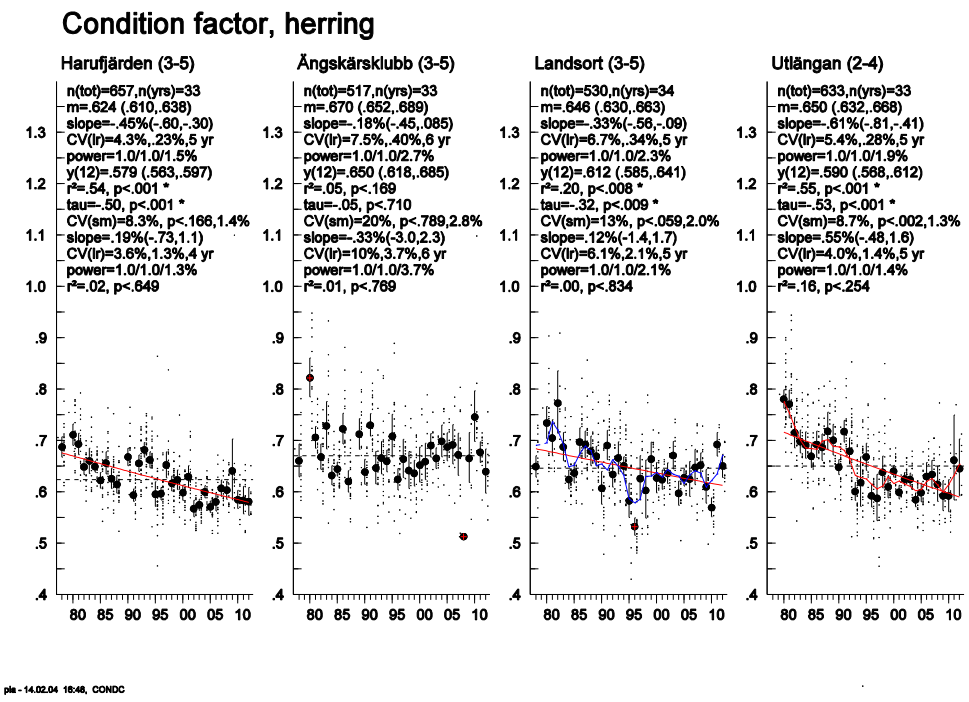


Figure 11.1. Condition factor for herring from Harufjärden, Ängskärsklubb, Landsort, and Utlängan (time series starting in 1978).

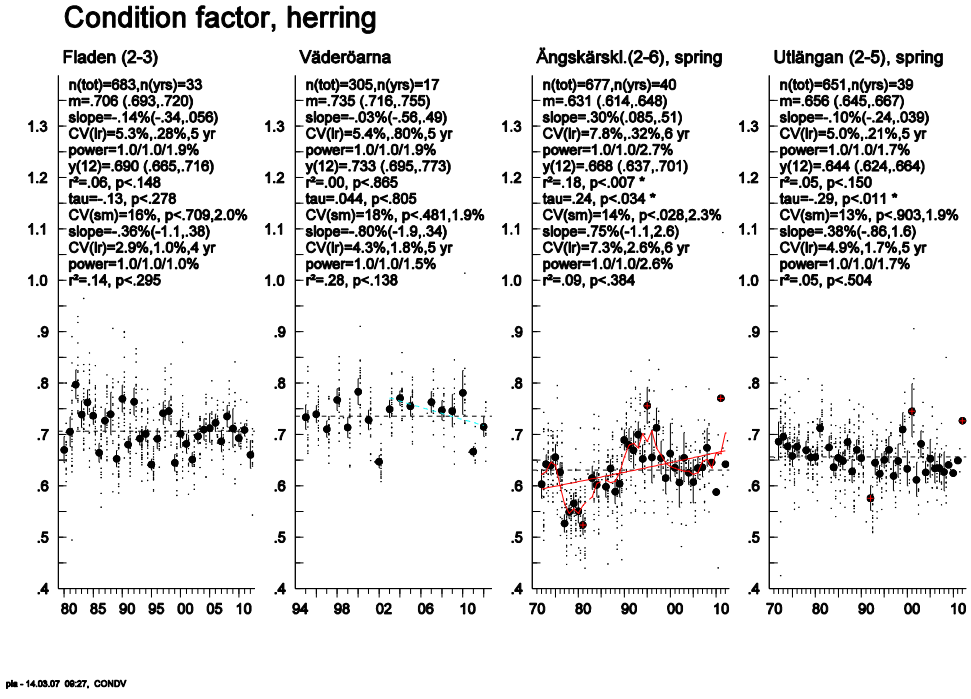


Figure 11.2. Condition factor for herring from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1994 respectively.

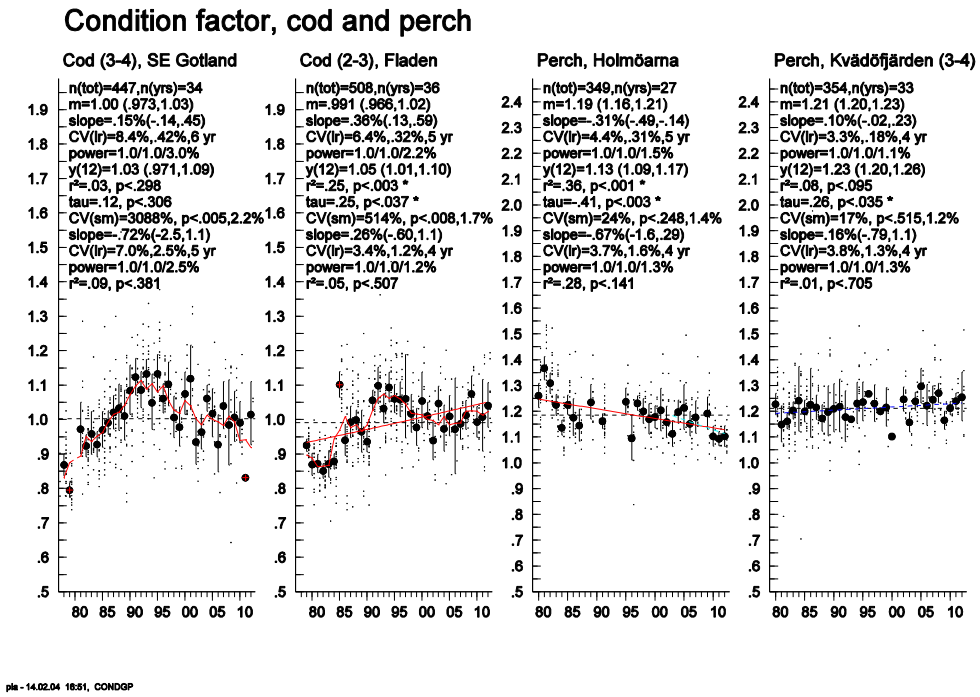


Figure 11.3. Condition factor for cod and perch from southeast Gotland and Fladen (cod); and Holmöarna and Kvädöfjärden (perch) (time series starting in 1978 and 1980 respectively).

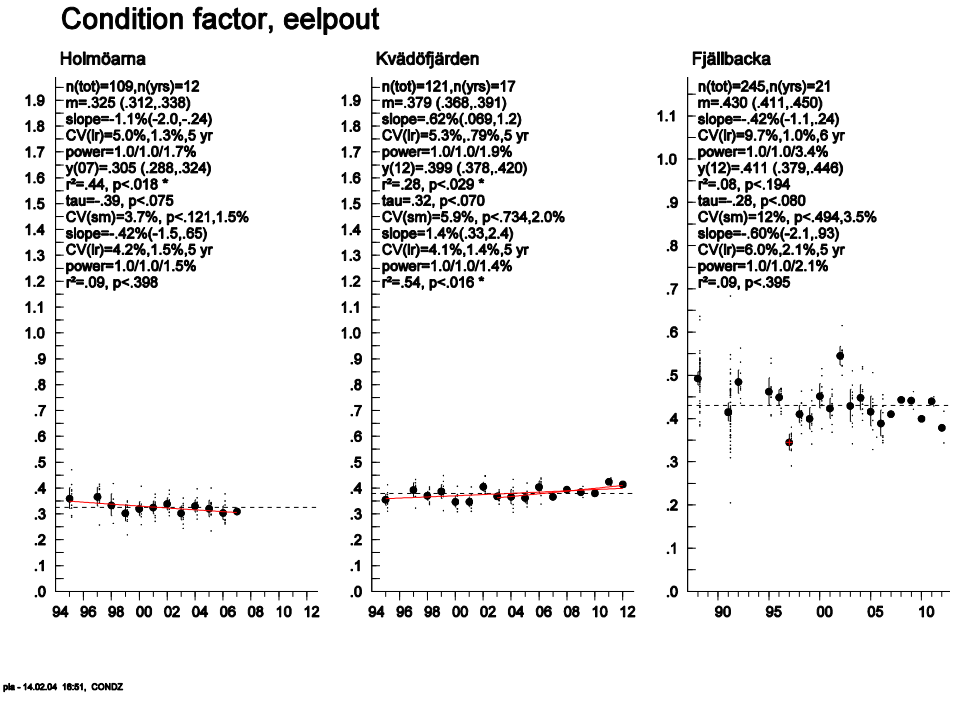


Figure 11.4. Condition factor for eelpout from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995, 1995 and 1988 respectively).

11.3 Conclusion

Average condition factor, estimated over the whole monitoring period, showed similar levels in herring from the Baltic Sea but slightly higher levels at the west coast. The same result was found for eelpout with higher condition factor at the west coast compared to the Baltic Sea.

The condition factor in herring seemed to decrease over time in the Baltic Sea, with exception for samples caught at Ängskärsklubb, while no trend was seen for herring at the west coast.

Table 11.1. Trend (in %) for condition factor assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001l. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's condition values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	657	33	78-12	-.45(-.60,-.30)	.0000 ---	5	1.5	.579 (.563,.597)
Harufjärden(3-5)		10	03-12	.19(-.73,1.1)	0.6495	4	1.27	
Ängskärsklubb(3-5)	517	33	78-12	-.18(-.45,.085)	0.1692	6	2.66	.670 (.652,.689) m
Ängskärsklubb(3-5)		10	03-12	-.33(-3.0,2.3)	0.7689	6	3.7	
Landsort(3-5)	530	34	78-12	-.33(-.56,-.09)	.0080 --	5	2.35	.612 (.585,.641)
Landsort(3-5)		10	03-12	.12(-1.4,1.7)	0.8345	5	2.15	
Utlängan(2-4)	633	33	80-12	-.61(-.81,-.41)	.0000 ---	5	1.89	.590 (.568,.612)
Utlängan(2-4)		10	03-12	.55(-.48,1.6)	0.2542	5	1.42	
Ängskärsklubb spring(2-6)	677	39	72-12	.30(.085,.51)	.0070 ++	6	2.78	.668 (.637,.701)
Ängskärsklubb spring(2-6)		10	03-12	.75(-1.1,2.6)	0.3837	6	2.61	
Utlängan spring(2-4)	651	38	72-12	-.10(-.24,.039)	0.1499	5	1.77	.656 (.645,.667) m
Utlängan spring(2-4)		10	03-12	.38(-.86,1.6)	0.5040	5	1.73	
Fladen(2-3)	683	33	80-12	-.14(-.34,.056)	0.1478	5	1.9	.706 (.693,.720) m
Fladen(2-3)		10	03-12	-.36(-1.1,.38)	0.2948	4	1.04	
Väderöarna	305	17	95-12	-.03(-.56,.49)	0.8651	5	1.92	.735 (.716,.755) m
Väderöarna		9	03-12	-.80(-1.9,.34)	0.1377	5	1.52	
Eelpout muscle								
Holmöarna	109	12	95-07	-1.1(-2.0,-.24)	0.0176	5	1.75	.305 (.288,.324)
Holmöarna		10	98-07	-.42(-1.5,.65)	0.3977	5	1.48	
Kvädöfjärden	121	17	95-12	.62(.069,1.2)	.0287 +	5	1.88	.399 (.378,.420)
Kvädöfjärden		10	03-12	1.4(.33,2.4)	.0156 +	5	1.45	
Fjällbacka	245	21	88-12	-.42(-1.1,.24)	0.1937	6	3.44	.430 (.411,.450) m
Fjällbacka		10	03-12	-.60(-2.1,.93)	0.3952	5	2.13	
Cod liver								
SE Gotland(3-4)	447	34	78-12	.15(-.14,.45)	0.298	6	2.97	1.00 (.973,1.03) m
SE Gotland(3-4)		10	03-12	-.72(-2.5,1.1)	0.3805	5	2.48	
Fladen(2-3)	508	34	79-12	.36(.13,.59)	.0029 ++	5	2.24	1.05 (1.01,1.10)
Fladen(2-3)		10	03-12	.26(-.60,1.1)	0.507	4	1.19	
Perch muscle								
Holmöarna	349	27	80-12	-.31(-.49,-.14)	.0010 --	5	1.54	1.13 (1.09,1.17)
Holmöarna		9	03-12	-.67(-1.6,.29)	0.1409	4	1.3	
Kvädöfjärden	354	32	80-12	.10(-.02,.23)	0.0952	4	1.15	1.23 (1.20,1.26)
Kvädöfjärden		10	03-12	.16(-.79,1.1)	0.7047	4	1.32	

12 Fat content

Updated 14.02.28

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

In general, an extremely low fat content, due to for example starvation, may cause elevated concentrations of organochlorines expressed on a fat weight basis.

The sample fat content is determined after extraction with acetone and hexane with 10% ether without heating (Jensen et al. 1983) in the present investigation. Results of the fat determination may vary considerably depending on the extraction method used.

In herring muscle tissue, the subcutaneous fat layer was removed before samples were prepared. Analyses of fat content, including skin and subcutaneous fat, showed a fat content at least 1.5 times higher than samples without skin.

12.1 Spatial variation

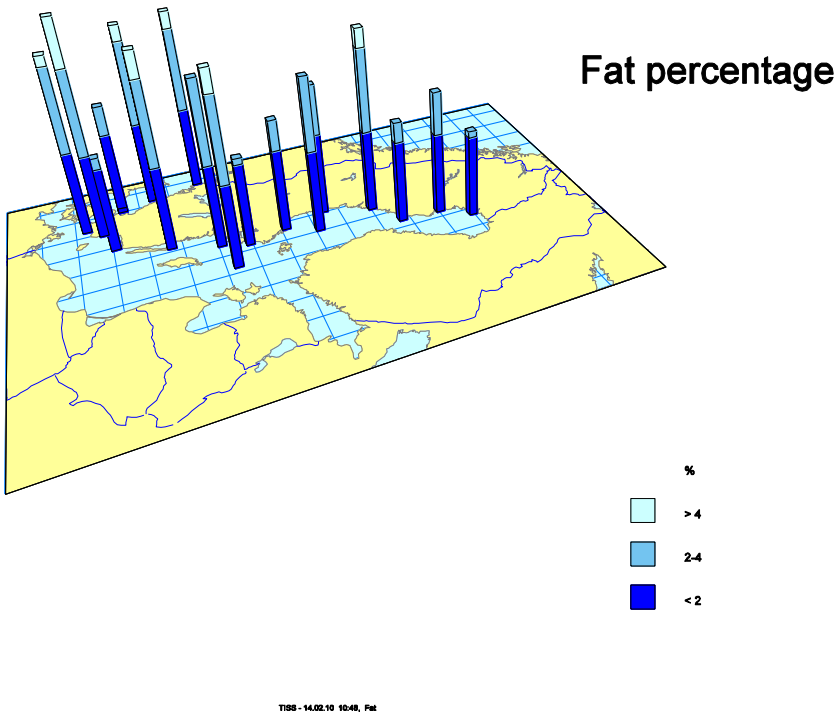


Figure 12.1. Spatial variation in fat percentage in herring muscle.

The fat content in autumn-caught herring is somewhat higher in the southern Baltic proper and on the west coast (around 4-6 %) compared to the rest of the Baltic (around 2-3 %) (Fig. 12.1). The highest fat content was found in herring from Abbekås while the lowest fat content was found in herring from Harufjärden (Fig. 12.1).

The fat content in cod liver was highly variable even between specimens caught at the same time at the same site. Geometric mean fat content over time in samples from southeast of Gotland was more than 2.5 times higher compared to cod livers from the Kattegat.

12.2 Temporal variation

In the Baltic, significant decreasing trends in fat content were observed in herring muscle tissue from Harufjärden and Utlängan (autumn and spring) (Fig. 12.2, 12.3). The fat content in herring from Utlängan (autumn) was exceptionally low, less than 2%, during the last six years with exception for the most recent year.
Increased fat content were found in cod liver from the southeast of Gotland seen over the whole monitored time period with the highest levels during the 1990s (Fig. 12.4). Fluctuating fat content in cod has to be considered when evaluating the time series of trace metals in cod liver.
Significant decreasing trends of fat content in perch muscle were observed at both Holmöarna and Kvädöfjärden in the Baltic (Fig. 12.4). No linear trend is seen for fat content in blue mussels (Fig. 12. 5). Eelpout from Holmöarna in the Baltic proper and Fjällbacka on the west coast also show significant declines in fat content over the whole time period (Fig. 12.6). No linear trend is seen for fat content in guillemot eggs (Fig. 12.7).

12.3 Seasonal variation

Fat content in spring-caught herring from Ängskärsklubb showed approximately the same mean value as herring from the same site caught in the autumn, whereas herring from Utlängan archipelago caught in the autumn generally, seen over the whole monitored period, had about 40% higher mean fat content compared to spring-caught herring from the same area (table 12.1).

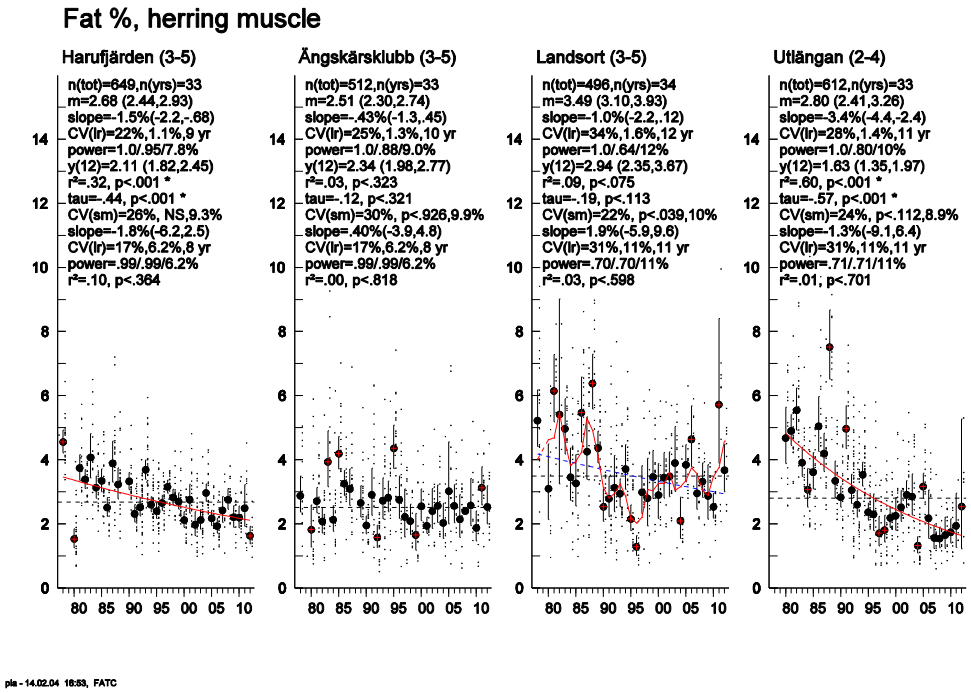


Figure 12.2. Fat percentage in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978 and 1980 respectively).

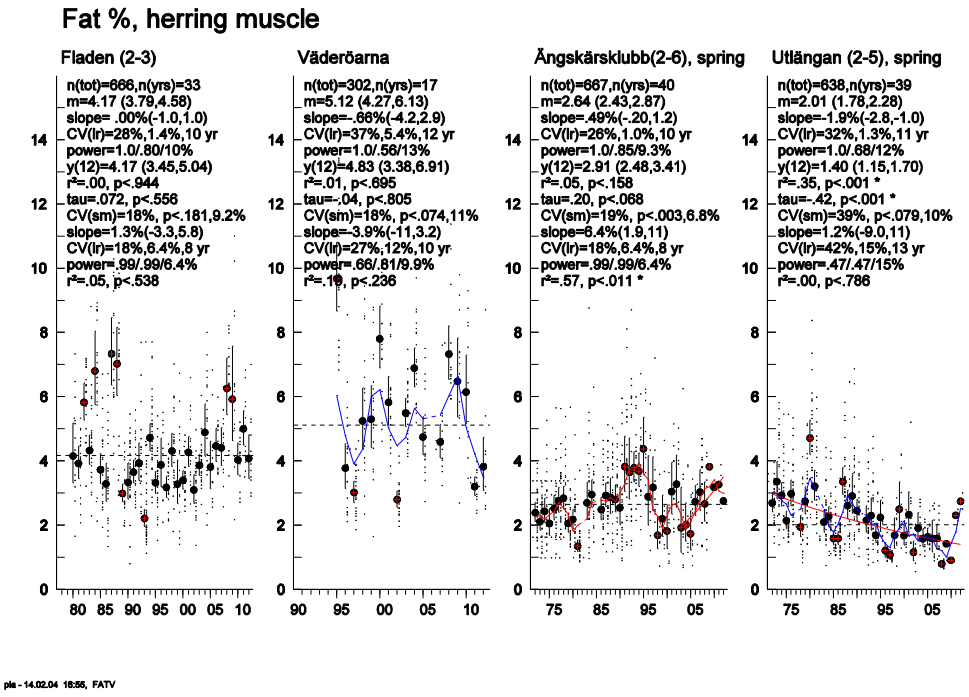


Figure 12.3. Fat percentage in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1995 respectively).

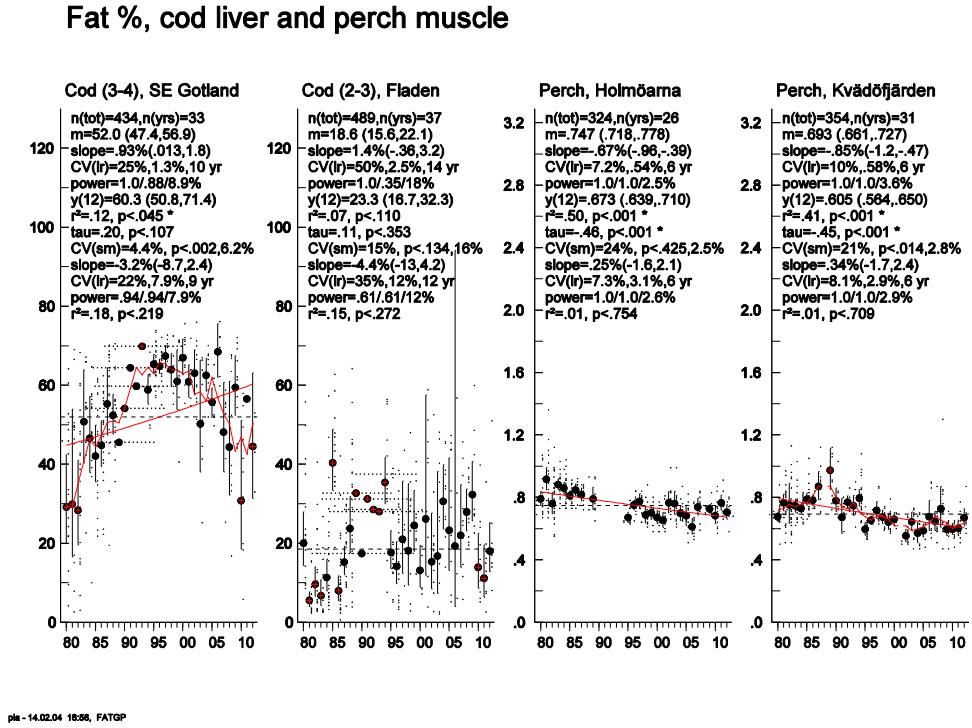


Figure 12.4. Fat percentage for cod liver from southeast Gotland and Fladen (time series starting 1980), and perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1980)

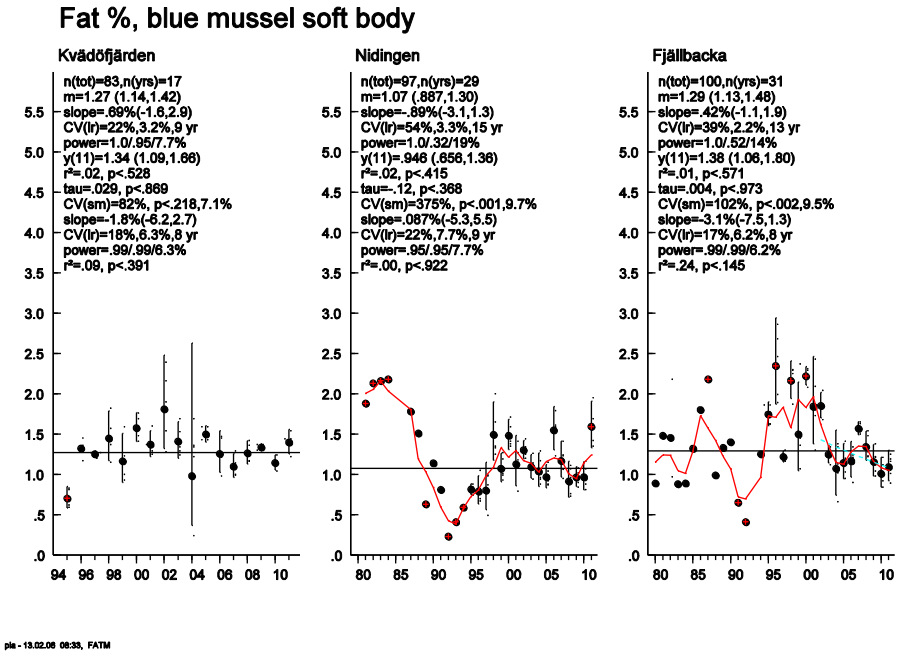


Figure 12.5. Fat percentage for blue mussel soft body from Nidingen, Väderöarna and Kvädöfjärden (time series starting in 1981, 1980, and 1995 respectively).

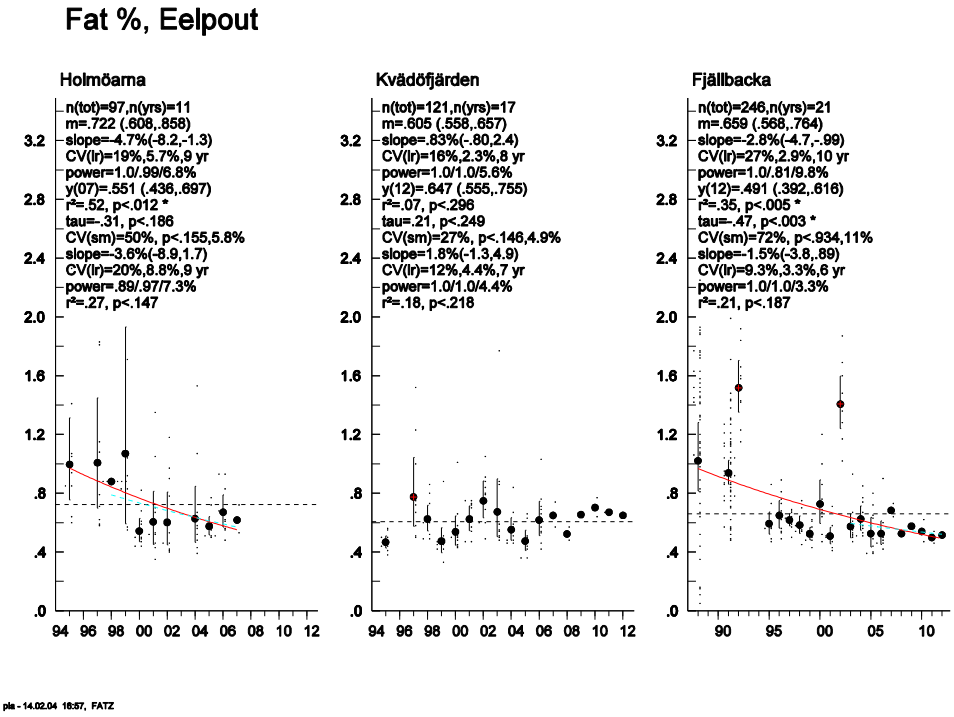


Figure 12.6. Fat percentage in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995, 1995 and 1988 respectively).

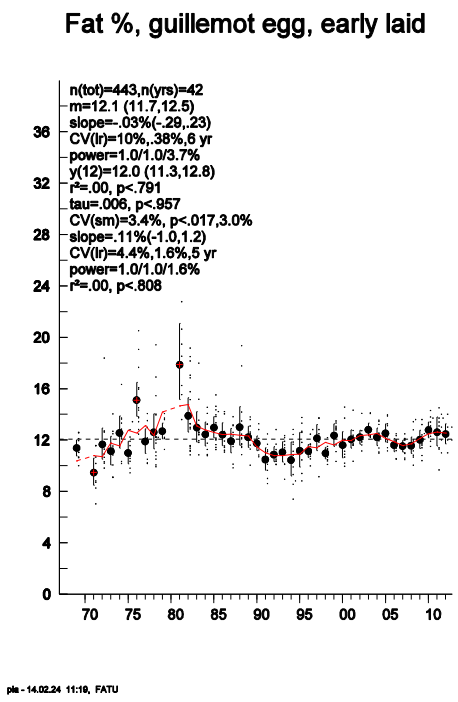


Figure 12.7. Fat percentage in guillemot eggs from Stora Karlsö (time series starting in 1969).

12.4 Conclusion

The fat content was slightly higher in herring from the southern Baltic Sea and at the west coast. In general, decreses in fat content, over the whole monitored period, were seen for herring and perch from the Baltic Sea, except for Ängskärsklubb.

Table 12.1. Trend (in %) for concentration of fat (%) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's fat concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	649	33	78-12	-1.5(-2.2,-.68)	.0006 ---	9	7.77	2.11 (1.82,2.45)
Harufjärden(3-5)	484	10	03-12	-1.8(-6.2,2.5)	0.3645	8	6.2	2.89 (2.30,3.63)
Ängskärsklubb(3-5)	512	33	78-12	-.43(-1.3,.45)	0.3232	10	8.95	2.51 (2.30,2.74) m
Ängskärsklubb(3-5)		10	03-12	.40(-3.9,4.8)	0.818	8	6.15	
Landsort(3-5)	496	34	78-12	-1.0(-2.2,.12)	0.0749	12	12.1	2.94 (2.35,3.67)
Landsort(3-5)		10	03-12	1.9(-5.9,9.6)	0.5983	11	11.3	
Utlängan(2-4)	612	33	80-12	-3.4(-4.4,-2.4)	.0000 ---	11	10	1.63 (1.35,1.97)
Utlängan(2-4)		10	03-12	-1.3(-9.1,6.4)	0.7012	11	11.2	
Ängskärsklubb spring(2-6)	667	39	72-12	.49(-.20,1.2)	0.1582	10	9.31	2.64 (2.43,2.87) m
Ängskärsklubb spring(2-6)		10	03-12	6.4(1.9,11)	.0113 +	8	6.41	
Fladen(2-3)	666	33	80-12	.00(-1.0,1.0)	0.9443	10	10	4.17 (3.79,4.58) m
Fladen(2-3)		10	03-12	1.3(-3.3,5.8)	0.5383	8	6.44	
Väderöarna	302	17	95-12	-.66(-4.2,2.9)	0.695	12	13.4	5.12 (4.27,6.13) m
Väderöarna		9	03-12	-3.9(-11,3.2)	0.2363	10	9.9	
Utlängan spring(2-4)	638	38	72-12	-1.9(-2.8,-1.0)	.0001 ---	11	11.5	1.40 (1.15,1.70)
Utlängan spring(2-4)		10	03-12	1.2(-9.0,11)	0.7856	13	14.9	
Cod liver								
SE Gotland(3-4)	434	33	80-12	.93(.013,1.8)	.0446 +	10	8.9	60.3 (50.8,71.4)
SE Gotland(3-4)		10	03-12	-3.2(-8.7,2.4)	0.2193	9	7.91	
Fladen(2-3)	489	33	80-12	1.4(-.36,3.2)	0.1099	14	18	18.6 (15.6,22.1) m
Fladen(2-3)		10	03-12	-4.4(-13,4.2)	0.2718	12	12.5	
Perch muscle								
Holmöarna	324	26	80-12	-.67(-.96,-.39)	.0001 ---	6	2.53	.673 (.639,.710)
Holmöarna		9	03-12	.25(-1.6,2.1)	0.7543	6	2.57	
Kvädöfjärden	354	31	80-12	-.85(-1.2,-.47)	.0001 ---	6	3.58	.605 (.564,.650)
Kvädöfjärden		10	03-12	.34(-1.7,2.4)	0.7092	6	2.86	
Blue mussel								
Nidingen	102	30	81-12	-.38(-2.5,1.8)	0.7152	15	21.8	1.10 (.909,1.33) m
Nidingen		10	03-12	4.6(-2.2,11)	0.1561	10	10.3	
Fjällbacka	105	32	80-12	.39(-1.0,1.8)	0.5784	13	14.8	1.29 (1.13,1.47) m
Fjällbacka		10	03-12	-.17(-3.6,3.3)	0.878	7	4.99	
Kvädöfjärden	88	18	95-12	.62(-1.4,2.6)	0.5272	9	7.76	1.27 (1.15,1.41) m
Kvädöfjärden		10	03-12	.42(-3.0,3.9)	0.7761	7	4.97	
Eelpout muscle								

Holmöarna	97	11	95-07	-4.7(-8.2,-1.3)	0.0125	9	6.75	.551 (.436,.697)
Holmöarna		9	98-07	-3.6(-8.9,1.7)	0.1465	9	7.3	
Kvädöfjärden	121	17	95-12	.83(-.80,2.4)	0.2964	8	5.63	.605 (.558,.657) m
Kvädöfjärden		10	03-12	1.8(-1.3,4.9)	0.2182	7	4.39	
Fjällbacka	246	21	88-12	-2.8(-4.7,-.99)	.0045 --	10	9.8	.491 (.392,.616)
Fjällbacka		10	03-12	-1.5(-3.8,.89)	0.1867	6	3.29	
Guillemot egg								
Stora Karlsö	443	42	69-12	-.03(-.29,.23)	0.7915	6	3.74	12.1 (11.7,12.5) m
Stora Karlsö		10	03-12	.11(-1.0,1.2)	0.8085	5	1.57	

13 Mercury - Hg

Updated 14.02.28

13.1 Introduction

13.1.1 Usage, Production and Sources

Mercury exists naturally in the environment in a number of chemical and physical forms. The main inorganic forms include Hg^0 (metallic), Hg_2^{++} (mercurous), and Hg^{++} (mercuric). Organic forms include CH_3HgCH_3 (dimethylmercury) and CH_3Hg+ (monomethylmercury) (Suzuki et al. 1991).

Some of the more well-known uses of mercury include thermometers, barometers, sphygmomanometers (blood pressure cuffs), float valves (e.g. ball cock in flushing system of toilets), some electrical switches, amalgam for dental restoration, batteries, fluorescent lamps, anti-lock braking systems (ABS) in some 4WD vehicles and airbag sensors in some vehicle models. It can also be found in beauty products, such as mascara, as thiomersal. For a comprehensive list of mercury usage in everyday life, see Huber (1998). Highly toxic and bioaccumulatory methylmercury compounds were previously used as fungicides or were unwanted byproducts of the chemical industry (Clarkson 1992).

Natural sources of mercury include volcanoes, forest fires, fossil fuels, petroleum and cinnabar ore, which is mined primarily in Spain and Italy, although shortages of this rare metal have encouraged mining in other countries (Calvert 2007). There are numerous atmospheric anthropogenic sources of mercury, such as fossil fuel combustion, mining, smelting and solid waste combustion, and soil and water anthropogenic sources, such as agricultural application of fertilisers, industrial wastewater disposal, landfills, the manufacture of cement and metals, and through other industrial processes. In Sweden, a south to north gradient exists in atmospheric mercury concentration, due to the south being closer to source points in Europe (Wängberg & Munthe 2001). However, mercury use has almost ceased in Sweden (AMAP/UNEP 2008).

13.1.2 Environmental Fate

Mercury concentration in fish is highly correlated with water pH, with acidic conditions favouring mercury methylation; increased water temperature is known to increase methylation rates (Doetzel 2007). Sulfate reducing bacteria has been shown to be a controlling factor of mercury methylation in estuarine sediments (Choi & Bartha 1994). Fish biology also influences mercury levels, with age, size and diet affecting bioaccumulation rates (Doetzel 2007).

13.1.3 Toxic Effects

Mercury bioaccumulates (Clarkson 1992). Methylmercury is the form of most concern to human health and ecosystem processes. Methylmercury combines with the amino acid cysteine to form a structure similar to another amino acid, methionine, which penetrates all mammalian cells and easily crosses the blood-brain barrier, from whence the central nervous system can be affected (Suzuki et al. 1991, Huber 1998). High exposure can affect brain development, with young children and infants the most at risk (Doetzel 2007), as methylmercury disturbs cell division and therefore development (Huber 1998).

The severity of symptoms after mercury exposure depends upon exposure level. Symptoms related to severe exposure are well documented after two major disasters of methylmercury contamination in Iraq in 1972, and Japan in 1957 (for a brief overview see Amin-Zaki et al. 1974; Rustam & Hadmi 1974; Clarkson 1992; Huber 1998). Symptoms are related to type of exposure. For example, inhalation of elemental mercury vapours results in respiratory problems, followed by neurological disturbance and general systemic effects. However, one of the most common routes of mercury exposure is via ingestion of methylmercury (Ratcliffe et al. 1996), often through consumption of contaminated fish (Huber 1998), the risk of which can be greater for *in utero* children in pregnant women (Koren & Bend 2010). Exposure becomes problematic if contaminated fish (or other contaminated substances) are eaten often, and neurological effects in both adults and children *in utero* can be seen (Ratcliffe et al. 1996).

Wildlife in all environments are affected by mercury accumulation; however animals in aquatic systems appear to show more intense bioaccumulation/biomagnification effects than terrestrial species (Huber 1998). Bioaccumulation usually occurs through diet (Huber 1998). A biomagnification effect is seen in fish at higher trophic levels (i.e. piscivorous fish) compared to those at lower trophic levels (da Silva et al. 2005). In the 1960s, the usage of methylmercury compounds as fungicides on seed grains led to the realisation that this compound was an ecological poison, because large bird species that preyed on smaller birds that in turn had eaten these grains, suffered from severe population declines (Clarkson 1992). While methylmercury accumulates in fish muscle, highest concentrations are generally seen in the blood, spleen, kidney and liver; in mammals and birds, highest concentrations are typically seen in the feathers and fur (Huber 1998). Embryos and very young animals tend to be the most affected by mercury damage due to its ability to interfere with cell division processes (Huber 1998).

13.1.4 Conventions, aims and restrictions

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

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

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

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

13.1.5 Target Levels

The target level (TL) used for Hg in the time series for fish is 20 µg/kg wet weight. The original target level is set for concentrations of mercury in whole-fish and the data presented in this report is measured in muscle and therefor the target level is recalculated in the time series. The recalculation of the TL for whole-fish is based on a study that compared concentrations of Hg in the muscle and whole-fish of herring and perch (Boalt et al., 2011). The whole-fish:muscle ratio was 0.86 and 0.72 for herring and perch respectively (Boalt et al., 2011).

For further information on TL and selection of target level see chapter 10.

In Swedish top layer soils (mor), the highest mercury concentrations are seen in the south, decreasing towards the north, with considerable local variation. Mercury concentrations vary regionally, with means from 0.5 mg/kg to 0.2 mg/kg. Natural background levels in mor/top layer soils are estimated to be 0.07 mg/kg, based on concentrations seen from the least affected northern areas. Natural background mercury concentrations in pike are estimated to be 0.2 mg/kg (European Communities 2002). Mercury concentrations in the ocean ranges from 0.7 – 1.1 pmol/L, with no difference between surface and deeper waters (Berlin et al. 2007). A decrease in mercury concentrations in surface waters of the Baltic Proper have been observed since 2000 (Pohl & Hennings 2006).

13.2 Methods

13.2.1 Analytical Information

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

The Department of Applied Environmental Science (ITM) at Stockholm University has determined the concentration of mercury in fish muscle and blue mussel soft body since 2007. Prior to 2007, the concentration of mercury in fish muscle and blue mussel soft body was determined using a ‘Mercury Monitor LCD 3200’ detector at the Department of Environmental Assessment at the Swedish University of Agricultural Sciences (SLU). The quantification limit is estimated to approximately 10 ng/g dry weight.

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

Please note that since 2007, the analytical laboratory for metals changed from SLU to ITM at SU. See chapter 6 section 6.1 for further details.

13.3 Results

13.3.1 Spatial Variation

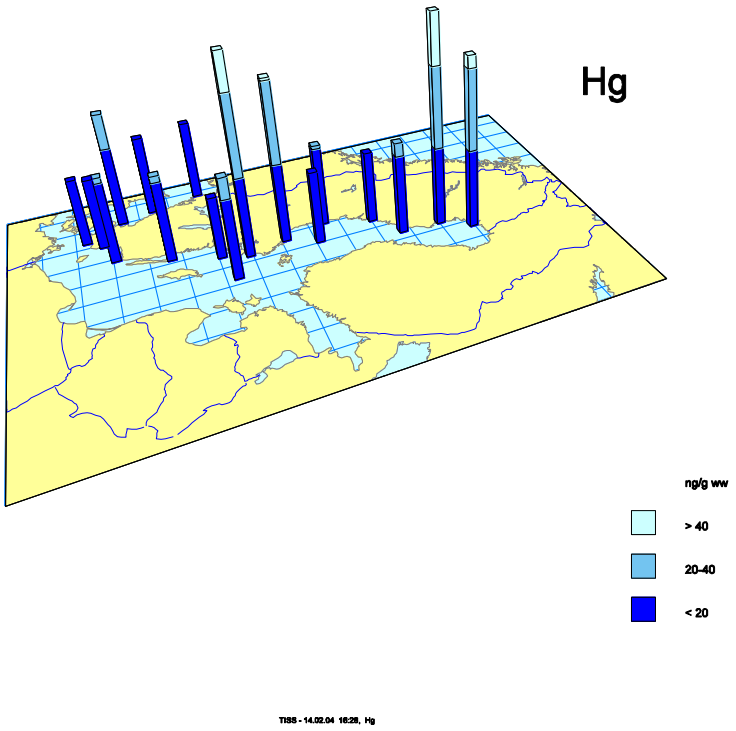


Figure 13.1. Spatial variation in mercury concentrations (ng/g wet weight) in herring muscle.

Herring muscle from Kinnbäcksfjärden shows the highest mercury concentrations of all herring samples 2010-2012 and Landsort shows the lowest concentration (Fig. 13.1).

In the time series, the herring from Ängskärsklubb show the highest mercury concentration (except for the last few years) (Fig 13.2). This might be due to local discharge levels. Samples collected during the 1980s from Ängskärsklubb are therefore most probably not representative of mercury concentration in the Bothnian Sea. At the beginning of the 1980s, mercury concentrations in herring from Ängskärsklubb ranged from 60 - 180 ng/g.

Among the other long time-trend herring sites, Harufjärden showed the highest mercury concentration over time, being significantly higher than Landsort, Utlängan and Fladen. The time series from Utlängan in the southern Baltic Proper showed the lowest mercury concentrations in the Baltic with a geometric mean concentration of approximately 18 ng/g (Fig 13.2).

Cod muscle tissue from Fladen in the Kattegat (59 ng/g) showed higher concentrations than samples from southeast of Gotland (44 ng/g) (Fig 13.5).Seen over the whole time-period perch muscle samples from Holmöarna in the Bothnian Sea showed significantly higher

concentrations compared to perch samples from Kvädöfjärden on the coast of the Baltic Proper (Fig 13.4). The estimated geometric mean concentration for Holmöarna 2012 was about two times higher than for Kvädöfjärden in 2011.

Mercury concentration in flounder from the Skagerrak showed 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 concentrations in blue mussels from Nidingen in the Kattegat and Fjällbacka in Skagerrak showed no spatial variation (Fig. 13.7). The overall mean concentration in blue mussel samples from the two sites exceeded the upper limit 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 2012 in herring and cod muscle (except for cod from Fladen (56 ng/g), perch and eelpout from Holmöarna (57 and 64 ng/g respectively) and eelpout from Kvädöfjärden (54 ng/g), all fall inside the proposed range of 'present background concentrations in pristine areas within the OSPAR Convention Area' (10 - 50 ng/g fresh weight in round fish (ICES, 1997)).

13.3.2 Temporal variation

There is no common general trend for mercury in herring muscle for the investigated time series (Fig. 13.2, 13.3). Mercury was monitored in spring-caught herring from Ängskärsklubb and Utlängan for four years at the beginning of the 1970s (Fig. 13.3). These series were continued in 1996. There was a significant decrease of 2.1 % for autumn-caught herring from Ängskärsklubb and 2.3% for spring-caught herring (Fig. 13.2 and 13.3). The time series from Landsort show a significant decrease of 8.5% during the last ten years (Fig. 13.2).

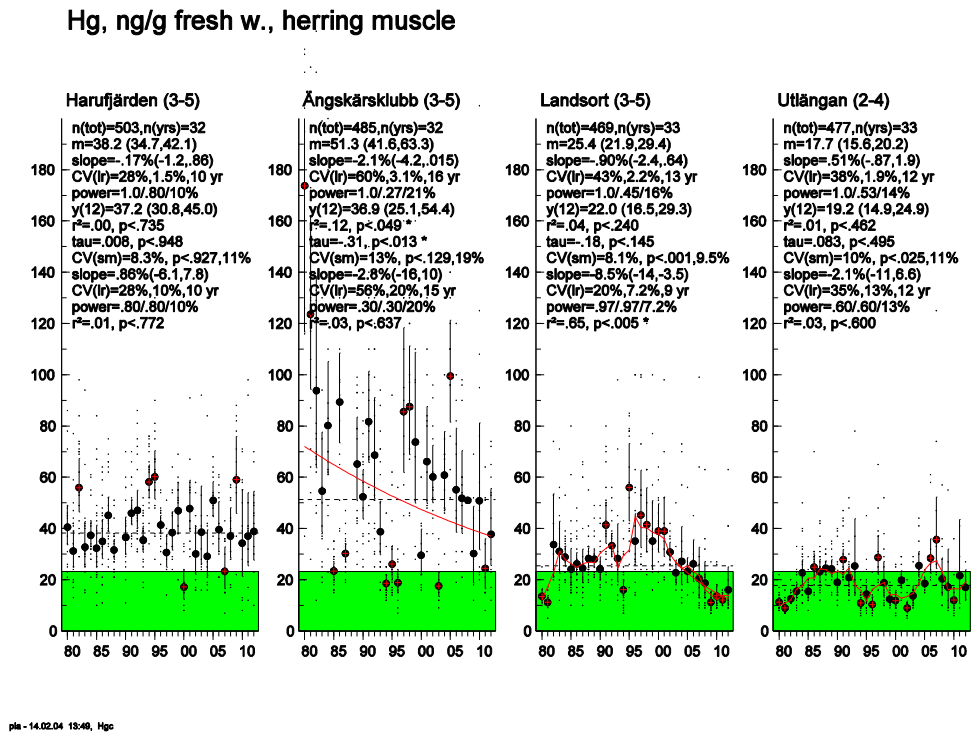


Figure 13.2. Mercury concentrations (ng/g fresh weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting 1980). The green line denotes the suggested target value for mercury in fish.

The time series from Ängskärsklubb in the Bothnian Sea shows a very large between-year variation. Although the sampling site at Ängskärsklubb is located relatively far off the coast, mercury concentration in 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 was on par with that measured in comparable samples from Landsort. However, in 1997 and 1999, the geometric mean concentrations increased to the same level as that recorded at the beginning of the 1980s.

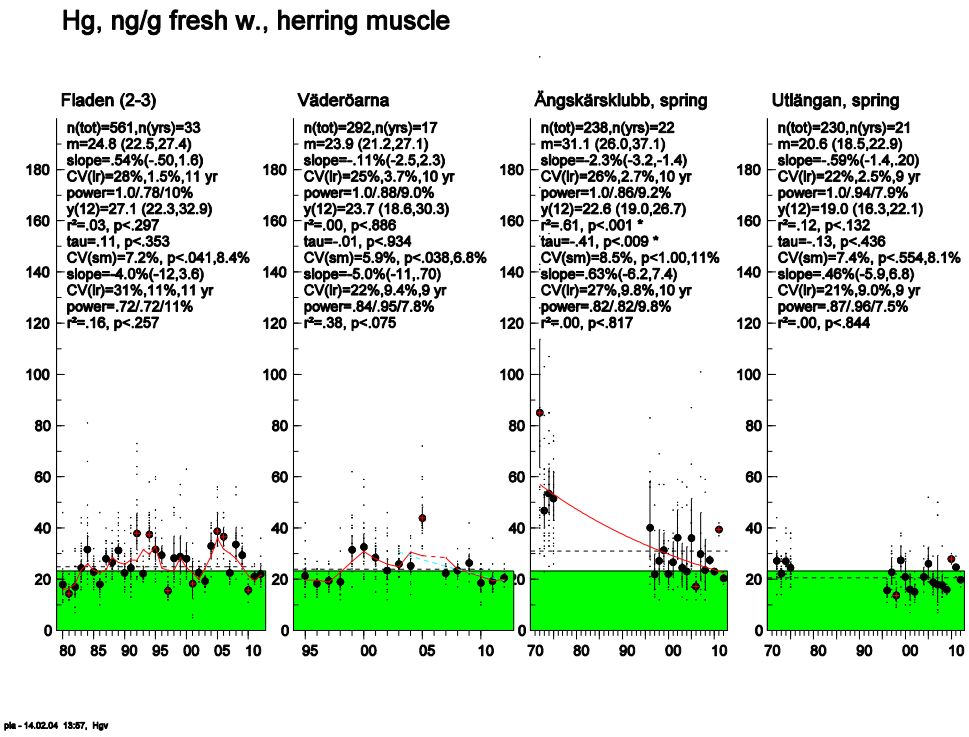


Figure 13.3. Mercury concentrations (ng/g fresh weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1970, 1980 and 1995 respectively). The green area denotes the levels below the suggested target value for mercury in fish.

The number of years required to detect an annual change of 10% varied between 9-13 (16 for Ängskärsklubb) years for the herring time series. The power to detect a 10% annual change was close to 1.0 for most of the time series.

Perch muscle samples from Kvädöfjärden in the Baltic Proper show a significant increasing trend for the last ten years, whereas no significant trend is seen at Holmöarna (Fig. 13.4).

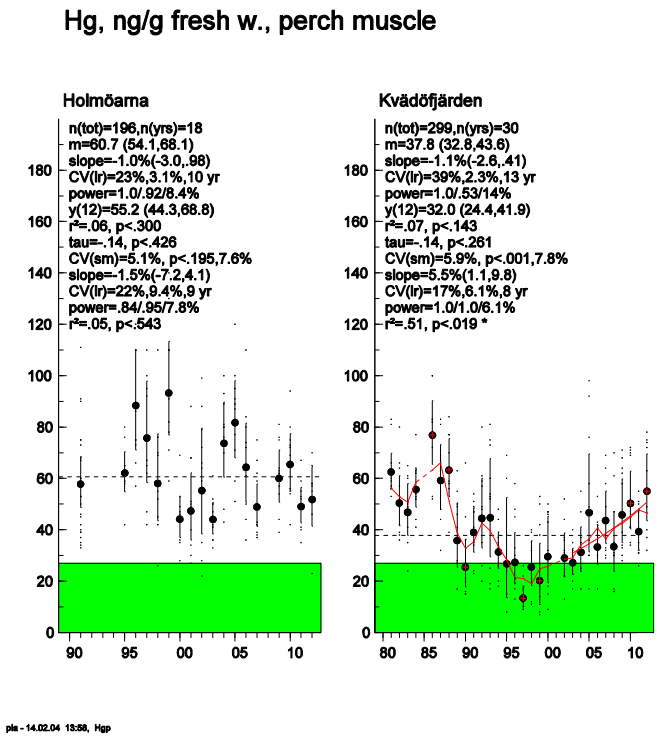


Figure 13.4. Mercury concentrations (ng/g fresh weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1991 and 1981 respectively). The green area denotes the levels below the suggestedtarget value for mercury in fish.

Cod from both Fladen and southeast of Gotland shows significant increasing trends of 1 and 3% respectively (Fig. 13.5).

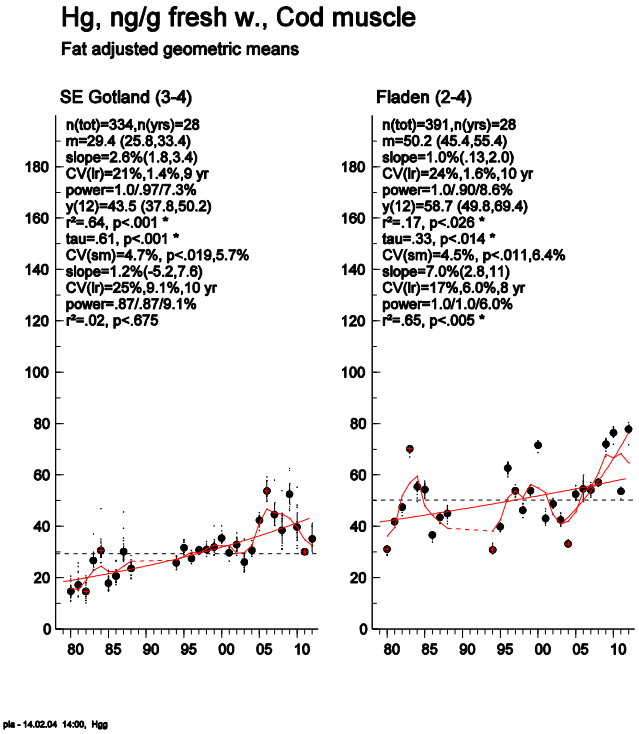


Figure 13.5. Mercury concentrations (ng/g fresh weight) in cod muscle from southeast Gotland and Fladen (time series starting in 1979).

Mercury concentration in eelpout shows significant decreasing trends at Kvädöfjärden, both for the whole time period but also during the last ten years, and at Holmöarna a significant decreasing trend isobserved during the last ten years (Fig. 13.6).

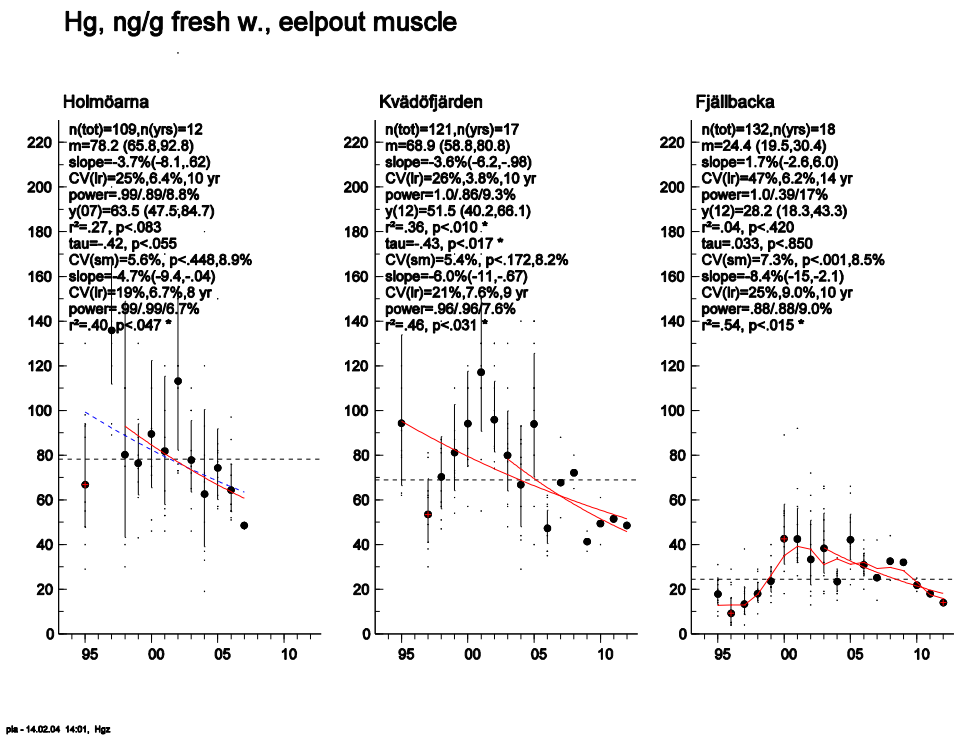


Figure 13.6. Mercury concentrations (ng/g fresh weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

Mercury concentrations in blue mussels show no linear trend for any of the sites for the whole time period (Fig. 13.7).

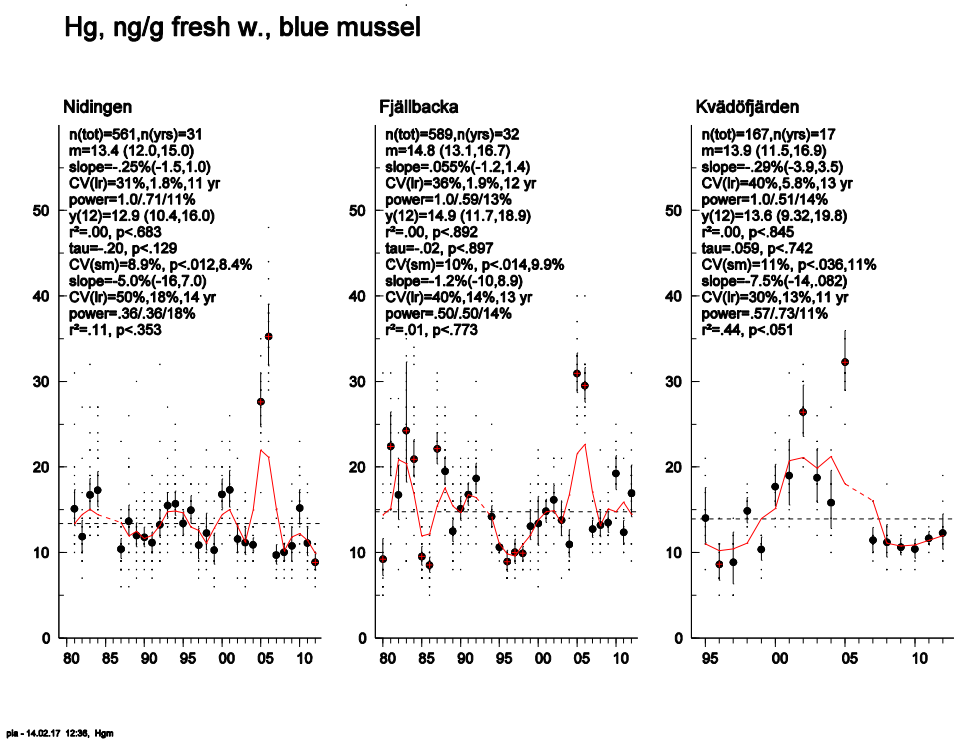


Figure 13.7. Mercury concentrations (ng/g fresh weight) in blue mussel soft body tissue from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1981, 1980 and 1995 respectively).

Guillemot eggs from Stora Karlsö in the Baltic proper show a significant decrease in mercury concentration of about 1.8% a year (Fig 13.8). It should be noted that the mercury analysis in this time series has been carried out in a retrospective study i.e. all analyses were performed at one occasion at the same laboratory up until 2007.

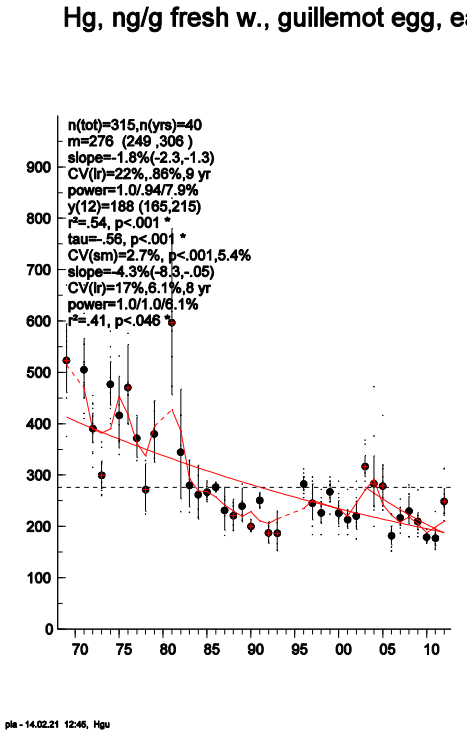


Figure 13.8. Mercury concentrations (ng/g fresh weight) in guillemot eggs (early laid) from St. Karlsö (time series starting in 1969).

13.3.3 Species Differences

Differences in mean mercury concentrations (ng/g wet weight) between species. Differences were found in fish muscle and blue mussel soft body between species on the Swedish west coast (table 13.1).

Holmöarna: Eelpout (64) - Perch (60)
Kvädöfjärden: Eelpout (51) > Perch (38) > Blue mussel (14)
Fladen/Nidingen: Cod (56) > Herring (25) > Blue mussel (13)
Väderöarna/Fjällbacka: Eelpout (24) – Herring (24) - > Blue mussel(15)

The mercury concentrations in blue mussel were, for all sites, lower than in fish muscle. The levels found in guillemot eggs were 3 - 20 times higher compared to levels in fish muscle.

No significant differences in mercury concentrations were found between spring- and autumn-caught herring from Utlängan, but the concentrations at Ängskärsklubb differed; autumn 37 > spring 23.

13.3.4 Comparison to threshold

The suggested target level for Hg based on ECs EQS of 20 ng/g wet weight was exceeded in 50% of the herring time series; Harufjärden, Ängskärsklubb autumn and spring, and Utlängan spring. Furthermore, the concentration of Hg was also exceeded in both perch time series.

13.4 Conclusion

Within the current research data, there is considerable spatial variation in mercury concentrations between sites within species. Finnish mercury analyses of herring muscle samples between 1980 - 83 from the eastern part of the Bothnian Sea showed concentrations around 20 ng/g (ICES, 1995), i.e. the same level as results from Ängskärsklubb in 1994 - 1996.

Finnish data of mercury levels in cod from the Bothnian Sea and the mouth of the Gulf of Finland showed concentrations in the same range as the Swedish data from Gotland (ICES, 1995). However, the mercury concentration in cod muscle from Fladen was within the same range as in cod muscle from the same age class from reference stations along the Norwegian coast (Green & Rönningen, 1994) analysed at the Norwegian Institute for Water Research (NIVA).

The results concerning changes in mercury concentrations in the investigated matrices are inconsistent. Mercury concentrations in guillemot eggs decreased, whereas the concentrations in herring from the majority of the stationsfluctuated. In most cases, the observed trends do not meet the North Sea Conference or HELCOM aims for mercury reduction. Future changes in mercury concentrations have to be studied carefully, and possible analytical problems thoroughly investigated.

Generally, mercury concentrations are above the suggested target level for concentrations in fish for the protection of predators against secondary poisoning of 20 ng/g wet weight, but below 100 ng/g wet weight.

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

Perttilä et al. (1982) examined heavy metal concentrations in herring muscle (from specimens aged 1 – 4 years), caught from the Gulf of Finland in 1981. Mercury concentrations were highest in older specimens (0.044 mg/kg). Mercury levels in perch muscle from specimens caught in the Pomeranian Bay and Szczecin Lagoon were examined seasonally between 1996 – 1997. Concentrations ranged from 0.028 – 0.120 $\mu g/g^{-1}$ wet weight (Szefer et al. 2003). Mercury content in guillemot feathers from the Baltic, the Kattegat, the Faroe Islands and Greenland was measured, and found to be higher in the Baltic and Kattegat (Appelquist et al. 1985). Mercury concentration was examined in the eggs of a number of Norwegian seabirds, including guillemot, in 1983. In guillemot eggs, levels ranged from 0.08 – 0.13$\mu g/g^{-1}$ (Barrett et al. 1985).

Table 13.1. Trend (in %) for **mercury** (ng/g fresh weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's mercury concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	503	32	80-12	-.17(-1.2,.86)	0.7346	10	10	38.2 (34.7,42.1) m
Harufjärden(3-5)		10	03-12	.86(-6.1,7.8)	0.7716	10	10	
Ängskärsklubb(3-5)	485	32	80-12	-2.1(-4.2,.015)	0.0491	16	21.4	36.9 (25.1,54.4)
Ängskärsklubb(3-5)		10	03-12	-2.8(-16,10)	0.6371	15	19.9	
Landsort(3-5)	469	33	80-12	-.90(-2.4,.64)	0.2401	13	15.5	25.4 (21.9,29.4) m
Landsort(3-5)		10	03-12	-8.5(-14,-3.5)	.0048 --	9	7.2	
Utlängan(2-4)	477	33	80-12	.51(-.87,1.9)	0.4624	12	13.8	17.7 (15.6,20.2) m
Utlängan(2-4)		10	03-12	-2.1(-11,6.6)	0.6	12	12.7	
Ängskärsklubb spring	238	21	72-12	-2.3(-3.2,-1.4)	.0000 ---	10	9.15	22.6 (19.0,26.7)
Ängskärsklubb spring		10	03-12	.63(-6.2,7.4)	0.8172	10	9.8	
Utlängan spring	230	20	72-12	-.59(-1.4,.20)	0.1325	9	7.93	20.6 (18.5,22.9) m
Utlängan spring		9	04-12	.46(-5.9,6.8)	0.844	9	7.47	
Fladen(2-3)	561	33	80-12	.54(-.50,1.6)	0.297	11	10.2	24.8 (22.5,27.4) m
Fladen(2-3)		10	03-12	-4.0(-12,3.6)	0.2569	11	11	
Väderöarna	292	17	95-12	-.11(-2.5,2.3)	0.8865	10	8.99	23.9 (21.2,27.1) m
Väderöarna		9	03-12	-5.0(-11,.70)	0.0747	9	7.8	
Perch muscle								
Holmöarna	196	18	91-12	-1.0(-3.0,.98)	0.3002	10	8.35	60.7 (54.1,68.1) m
Holmöarna		9	03-12	-1.5(-7.2,4.1)	0.5432	9	7.81	
Kvädöfjärden	299	30	81-12	-1.1(-2.6,.41)	0.1428	13	13.9	37.8 (32.8,43.6) m
Kvädöfjärden		10	03-12	5.5(1.1,9.8)	.0191 +	8	6.13	
Cod liver								
SE Gotland(3-4)	334	28	80-12	2.6(1.8,3.4)	.0000 +++	9	7.34	43.5 (37.8,50.2)
SE Gotland(3-4)		10	03-12	1.2(-5.2,7.6)	0.6749	10	9.12	
Fladen(2-4)	391	28	80-12	1.0(.13,2.0)	.0257 +	10	8.61	58.7 (49.8,69.4)
Fladen(2-4)		10	03-12	7.0(2.8,11)	.0050 ++	8	5.96	
Eelpout muscle								
Holmöarna	109	12	95-07	-3.7(-8.1,.62)	0.0826	10	8.83	63.5 (47.5,84.7)
Holmöarna		10	98-07	-4.7(-9.4,-.04)	0.0469	8	6.67	
Kvädöfjärden	121	17	95-12	-3.6(-6.2,-.98)	0.0101	10	9.26	51.5 (40.2,66.1)
Kvädöfjärden		10	03-12	-6.0(-11,-.67)	0.0309	9	7.57	
Fjällbacka	132	18	95-12	1.7(-2.6,6.0)	0.4202	14	16.9	24.4 (19.5,30.4) m
Fjällbacka		10	03-12	-8.4(-15,-2.1)	0.0148	10	8.98	
Holmöarna	109	12	95-07	-3.7(-8.1,.62)	0.0826	10	8.83	63.5 (47.5,84.7)

Holmöarna		10	98-07	-4.7(-9.4,-.04)	-0.0469	8	6.67	
Blue mussel								
Nidingen	561	30	81-12	-.25(-1.5,.99)	0.6829	11	11.8	13.4 (12.0,15.0) m
Nidingen		10	03-12	-5.1(-17,6.8)	0.3526	14	19.5	
Fjällbacka	589	32	80-12	.055(-1.2,1.3)	0.892	12	13.7	14.8 (13.1,16.7) m
Fjällbacka		10	03-12	-1.2(-11,8.6)	0.7731	13	15.4	
Kvädöfjärden	167	17	95-12	-.29(-4.0,3.4)	0.8447	13	15.3	13.9 (11.5,16.9) m
Kvädöfjärden		9	03-12	-7.8(-16,.082)	0.0505	11	11.5	
Guillemot egg								
St.Karlsö	315	40	69-12	-1.8(-2.4,-1.3)	0.0000 ---	9	8.23	188 (165,215)
St.Karlsö		10	03-12	-4.4(-8.7,-.05)	0.0464 -	8	6.27	

14 Lead - Pb

Updatated 14.02.28

14.1 Introduction

14.1.1 Usage, Production and Sources

Lead is produced in many isoptopes, but only three are stable. There are four natural isotopes, ^{204}Pb, ^{206}Pb, ^{207}Pb and ^{208}Pb. ^{204}Pb is slightly radioactive, and has a half-life of 22.2 years. In nature, lead is usually found in ore with zinc, silver or copper. Atmospheric sources of lead in Sweden show a south to north gradient, due to northward atmospheric transport from sources located in other parts of Europe (Renberg et al. 2000). The main sources of lead pollution in Sweden comes from ammunition, lead petrol emissions and associated contamination in road side soils (although leaded gasoline was eliminated in 1994 in Sweden (Faiz et al. 1996)), lead pigments, cables and batteries. There are also point sources (e.g. metal works) that have resulted in high local pollution (Bergbäck et al. 1992), e.g. a secondary lead smelter in Landskrona where lead from car batteries is recycled (Farago et al. 1999).

There are numerous other uses for lead, including, but not limited to, lead in car batteries, in the ballast keel of sailboats, scuba diving weight belts, fishing sinkers, firearms (bullets and shot), colouring elements in paints and ceramic glazes, PVC plastics, lead sheeting used for sound proofing, lining chemical treatment baths, storage vessels, weathering, roofing, cladding, organ pipes, soldering, electrodes, high voltage power cables, tennis racquets, statues, sculptures, anti-knocking additive in aviation fuel, leaded gasoline, solar energy cells and infrared detectors and coffins. Houses built prior to 1980 are at a higher risk of having been painted with lead-based paints. Many cities did (and some still do) use lead water and sewage pipes. Lead can leach out of the water pipes into drinking water. Lead arsenate was the most commonly used insecticide in deciduous fruit tree orchards prior to the introduction of DDT in 1947. High lead levels are still found in some top soils in the USA (Peryea & Creger 1993; Peryea & Kammereck 1995).

14.1.2 Environmental Fate

Increased acidity levels appear to contribute to increased lead bioavailability in soils (Jin et al. 2005). In lakes, the level of lead in fish body tissues is often greater in low-alkalinity waters compared to lakes with a higher pH (Spry & Wiener 1991). These results indicate that pH may influence lead bioavailability in water systems and sediments.

14.1.3 Toxic Effects

Lead is a non-essential element (Tewari et al. 1987) and a known neurotoxin, damaging the nervous system and causing brain and blood disorders. The toxic effects of lead involve several organ systems and biochemical activities. The risk is highest for children and those *in utero*, partly because of high permeability of the blood-brain barrier and placenta (Klaassen & Rozman, 1991). Some neurophysiological development effects can be seen in children even at low levels of lead exposure (Gidlow 2004).

Lead is known to bioaccumulate in soft tissue, but to a much greater extent in the bone matrix. Approximately 90% of the total amount of lead in humans is found in the skeleton

(Klaassen & Rozman, 1991). Between 90% to 95% of lead that is found in blood is isolated in the red blood cells where haemoglobin synthesis can be inhibited, and subsequently symptoms such as anaemia are seen (Gidlow 2004). In females, lead is a known abortifacient, but problems in male reproduction are equivocal (Gidlow 2004).

In animals, absorbed lead enters the blood and soft tissues, but is eventually redistributed to the bones. In birds, lead shot is a common cause for lead poisoning (Cook & Trainer 1966; Pattee et al. 1981), and there have been reports of fishing sinkers causing bird deaths (Locke et al. 1981). In Sweden, bird death from lead poisoning is more common in swans, geese and ducks, but has also been reported in woodpeckers (Mörner & Petersson 1999). Lead levels were found to be highest in woodpecker liver and kidney (Mörner & Petersson 1999).

14.1.4 Conventions, Aims and Restrictions

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

14.1.5 Target Levels

The target level (TL) used for Pb in the time series for herring and perch is 1000 µg/kg wet weight in whole-fish. For further information on TL and selection of target level see chapter 10. The original TL has been recalculated to dry weight in liver for each time series to fit the presented data. The recalculation of the TL for whole-fish is based on a study that compared concentrations of Pb in the liver and whole-fish of herring and perch (Boalt et al., 2011). The whole-fish:liver ratio was 4.58 and 12.18 for herring and perch respectively. (Boalt et al., 2011) and the recalculation to dry weight is based on the dry weight in each time series. The recalculated target level (Tv) together with the dry percentage (dp) is shown above the statistical information in each time series.

The recommended limit for children's food is set by the Swedish National Food Administration (SNFA) at 50 ng/g fresh weight (SLVFS, 1993).

14.2 Methods

14.2.1 Analytical Information

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

The concentration of heavy metals, except mercury, in fish liver and blue mussel soft body was determined using an atomic absorption spectrophotometer with a graphite furnace at the Department of Environmental Assessment at the Swedish University of Agricultural Sciences (SLU) up until 2003. The quantification limit is estimated to approximately 100 ng/g dry weight for zinc, approximately 10 ng/g dry weight, which implies that the concentrations in herring, flounder and dab are approximately 10 - 20 times above the quantification limit.

Please note that since 2007, the analytical laboratory for metals changed from SLU to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

14.3 Results

14.3.1 Spatial variation

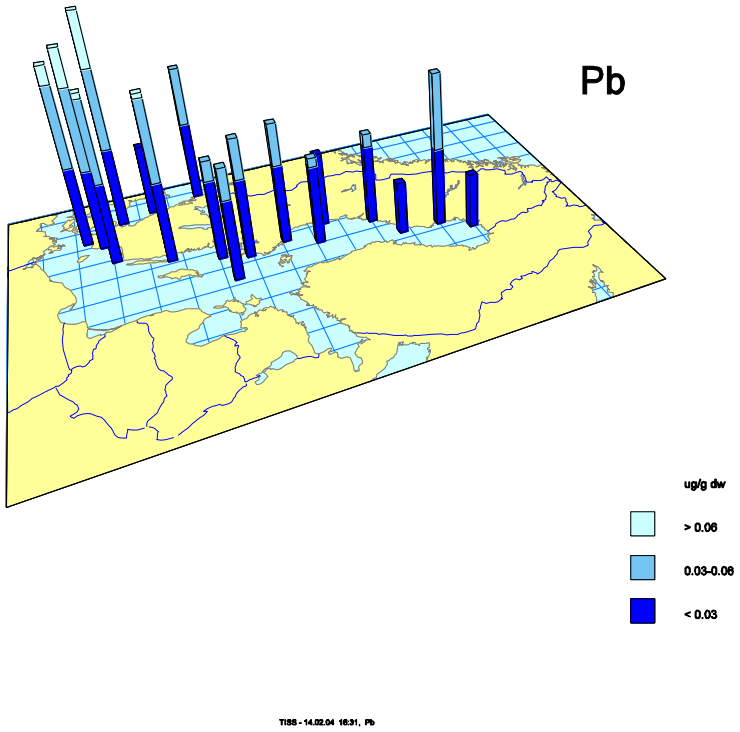


Figure 14.1. Spatial variation in lead concentrations (ug/g dry weight) in herring liver.

Kullen on the Swedish west coast has the highest concentrations of lead in herring liver 2010-2012. High levels are also observed in the South Baltic Proper (Fig 14.1).

The lead concentrations in blue mussels from the Swedish west coast were 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 (Kvädöfjärden, Nidingen, Fjällbacka) showed mean levels below the 'background concentration at diffuse loading' in blue mussels for lead of <5 µg/g dry weight, proposed by Knutzen and Skie (1992).

14.3.2 Temporal variation

At Harufjärden, Ängskärsklubb (autumn), Landsort, Utlängan (autumn) and Fladen, the investigated time series in herring liver show significant decreasing trends (Fig. 14.2, 14.3).

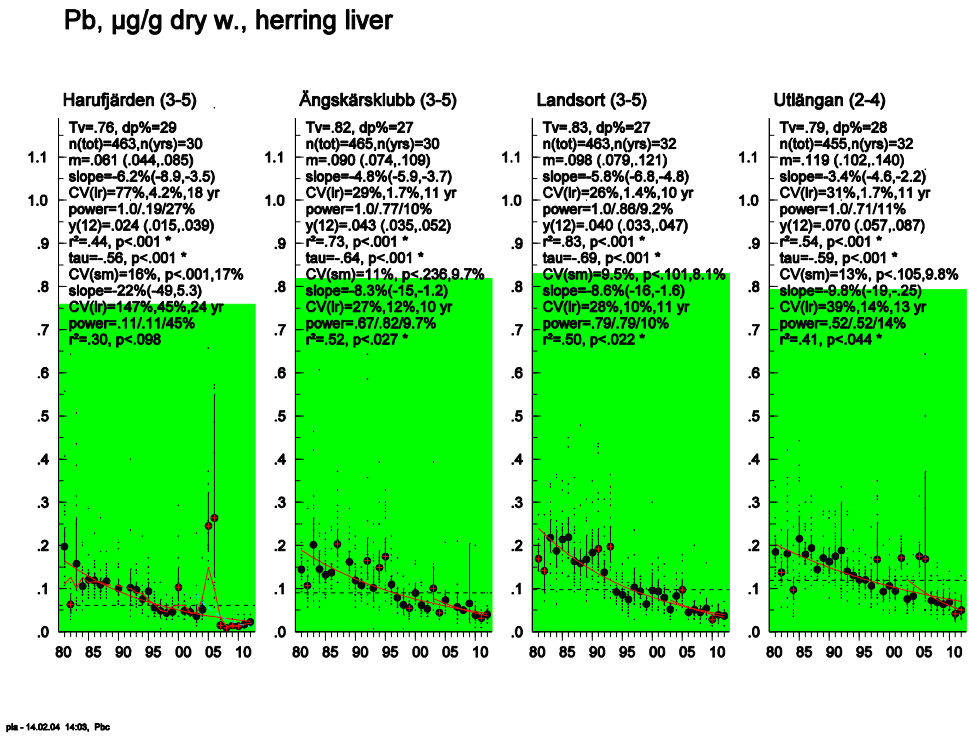
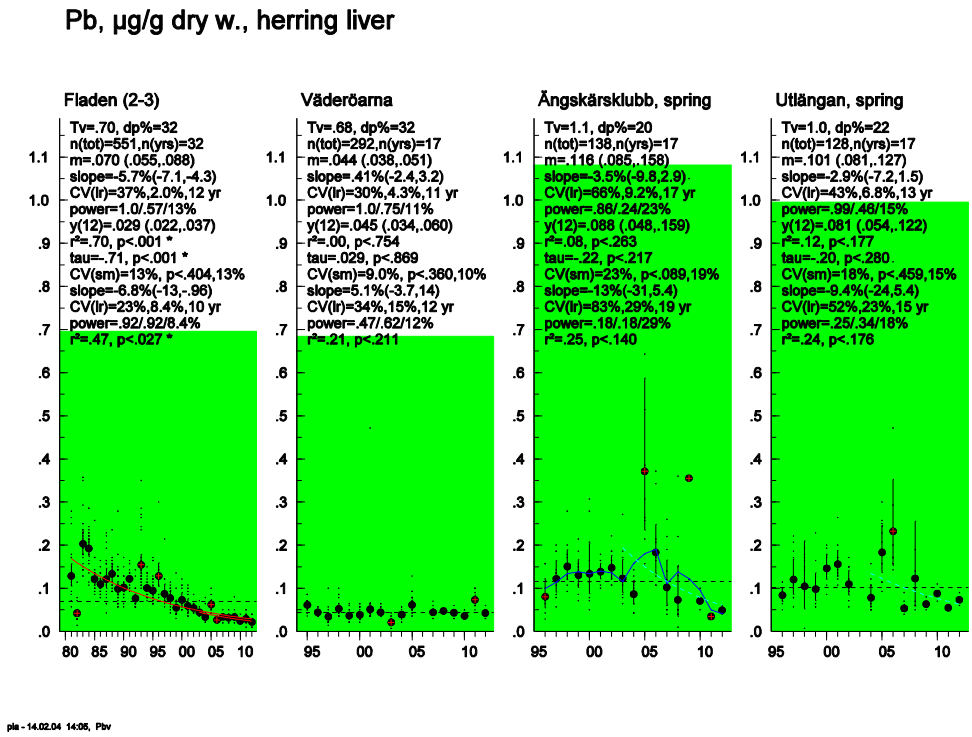


Figure 14.2 (above) and **14.3** (below). Lead concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981)(above); and Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1997, 1981 and 1995 respectively). The green area denotes the levels below the suggested target value for lead in fish.



The number of years required to detect an annual change of 10% varied between 10 - 18 years for the herring time series, with a power to detect a 10% annual change ranging from 0.88 (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) show significant decreasing trends over the whole time period from southeast of Gotland and Fladen (Fig. 14.4), however, at Fladen a significant increasing trend is observed during the last ten years.

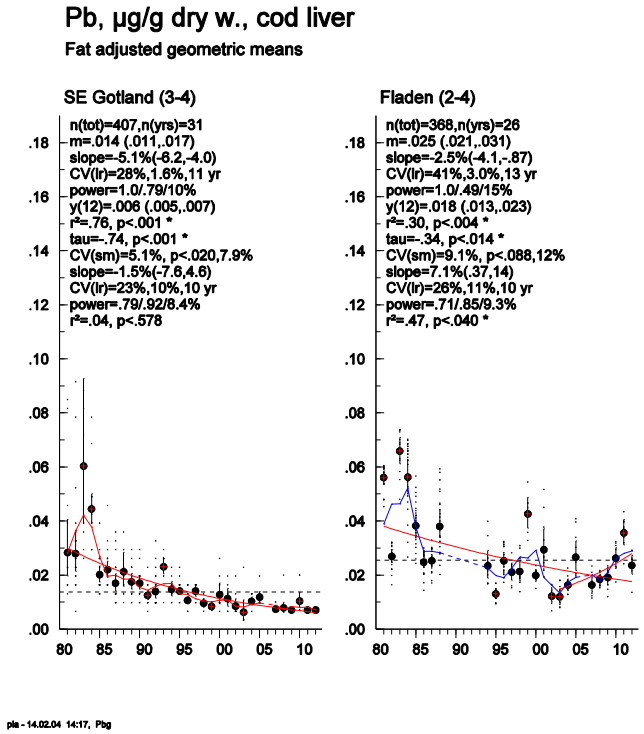


Figure 14.4. Lead concentrations (µg/g dry weight) in cod liver from southeast Gotland and Fladen (time series starting in1981).

Lead concentrations in the shorter time series of perch liver show significant decreasing trends from both Kvädöfjärden and Holmöarna (Fig. 14. 5).

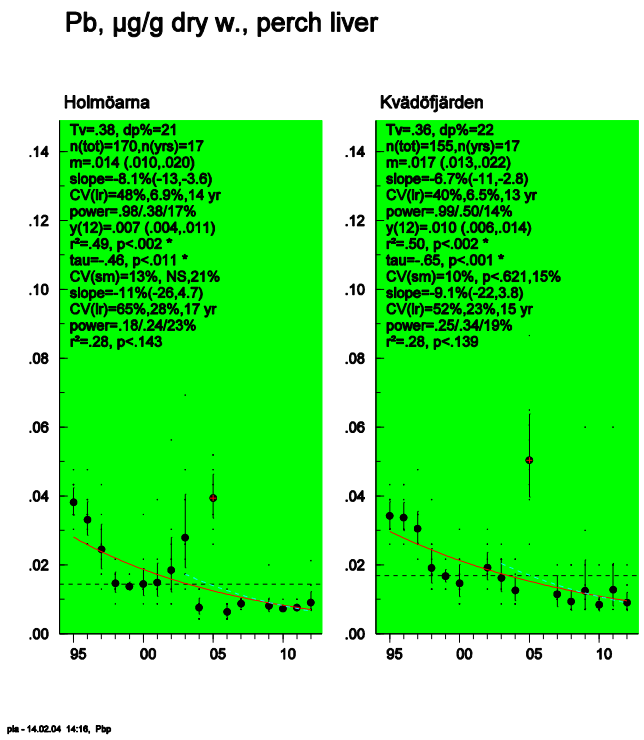


Figure 14.5. Lead concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjären (time series starting in1995). The green area denotes the levels below the suggested target value for lead in fish.

The lead concentration in eelpout liver show significant decreasing trends at Kvädöfjärden and Fjällbacka and at Holmöarna a decreasing trend is indicated (Fig. 13.6).

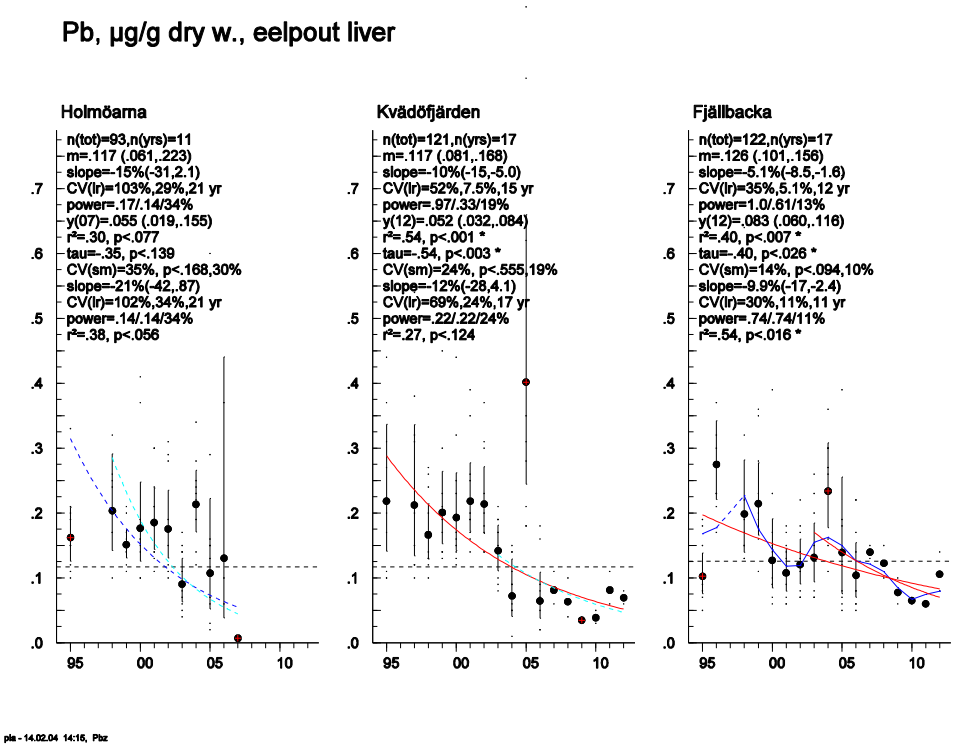


Figure 13.6. Lead concentrations (ug/g dry weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

The lead concentrations in blue mussel soft body from Nidingen show a significant decreasing trend (Fig. 14.7). During the ten most recent years Fjällbacka show a significant decreasing trend and Kvädöfjärden an indicated decreasing trend. These results should be interpreted with caution since problems with the analysis of lead in the beginning of 2000 might influence the trends.

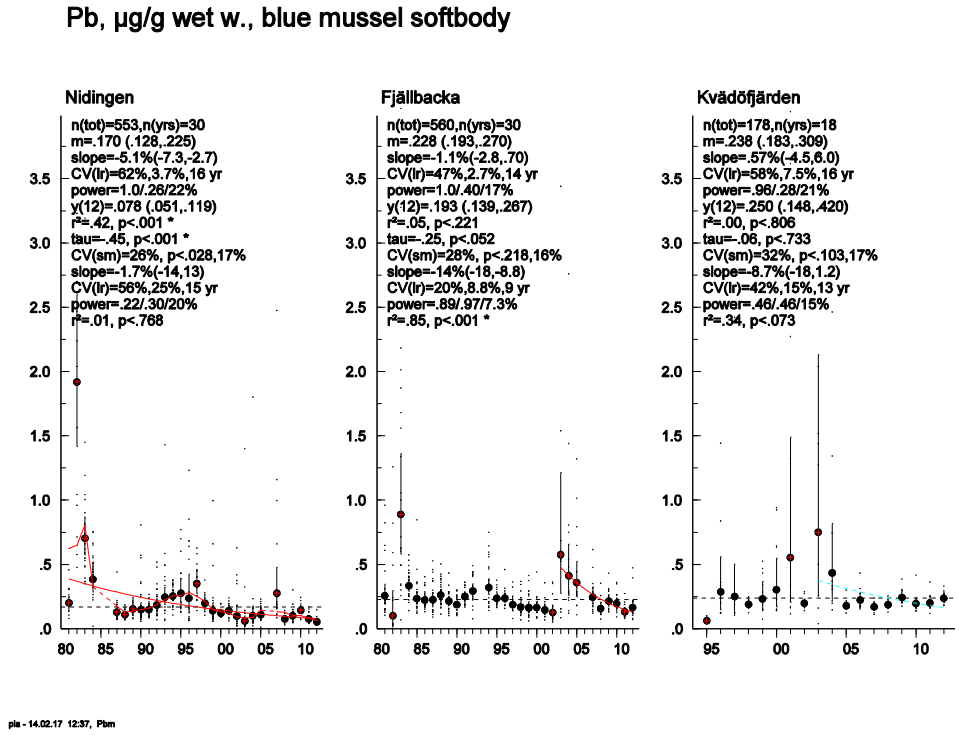


Figure 14.7. Lead concentrations (µg/g wet weight) in blue mussel soft body tissue from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1981, 1981 and 1995 respectively).

The time series of lead in guillemot eggs shows a significant decreasing trend of 12% per year (Fig. 14.8).

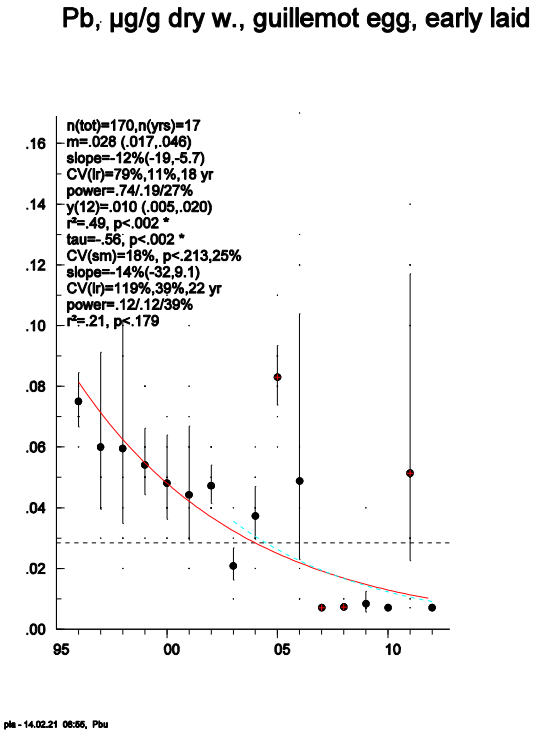


Figure 14.8. Lead concentrations (µg/g dry weight) in guillemot eggs from Stora Karlsö (time series starting in 1996).

14.3.3 Species differences

Differences in mean lead concentration (µg/g dry weight) between species.

Holmöarna: Eelpout (0.055) > Perch (0.007)
Kvädöfjärden: Blue mussel (2.0) > Eelpout (0. 052) > Perch (0. 010)
Fladen/Nidingen: Blue mussel (0.41) > Herring (0. 029) > Cod (0. 018)
Väderöarna/Fjällbacka: Blue mussel (1.5) > Eelpout (0. 083) > Herring (0.044)

The lead concentration in blue mussel soft body tissue was generally higher than concentrations in fish liver. The concentration in eelpout liver was about five to seven times higher than perch liver in the analysed samples. There was no difference in lead concentration between spring and autumn-caught herring from Utlängan, while at Ängskärsklubb spring samples had twice as high concentrations compared to autumn samples.

14.3.4 Comparison to threshold

In all herring and perch time series, Pb concentrations are below the suggested target level based on QS_{biota} of 1ug/g wet weight. This has to be interpreted carefully as the recalculation between levels of lead in whole-body and liver is based on only one study.

14.4 Conclusion

On a spatial scale, lead levels in herring muscle from individuals aged from 1 – 6 years old sampled in the Gulf of Finland in 1981, were found to vary little, from 0.04 – 0.06 mg/kg (Perttilä et al. 1982). No difference was seen in lead concentrations of blue mussels examined between three sites; these lead concentrations were not significantly different to results seen from similar sized blue mussels sampled from a reference site in Kobbefjord, Greenland (Riget et al. 1993).

Over time, lead concentrations have decreased in most species at most sites. This probably reflects a general decrease of lead in the environment, supposedly due to elimination of leaded gasoline. Jorhem and Sundström (1993) found lead levels to be about 75% lower in fish samples (Baltic herring, cod and pike) from 1983 – 1990, compared with a previous study from 1973 - 1982 (Jorhem et al. 1984).

The lead concentrations are all below the suggested target level based on maximum levels in prey tissue, 1000 ng/g wet weight. The recommended limit for children's food, as set by the Swedish National Food Administration, is 50 ng/g wet weight. Current concentrations of lead in herring liver from the examined sites are lower than this. However, it is important to bear in mind that concentrations of Pb in herring liver are lower than whole-fish concentration

Table 14.1. Trend (in %) for **lead** (µg/g dry weight, wet weight for blue mussels) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's lead concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	463	30	81-12	-6.2(-8.9,-3.5)	.0001 ---	18	26.8	.024 (.015,.039)
Harufjärden(3-5)		10	03-12	-22(-49,5.3)	0.0979	24	45.2	
Ängskärsklubb(3-5)	465	30	81-12	-4.8(-5.9,-3.7)	.0000 ---	11	10.4	.043 (.035,.052)
Ängskärsklubb(3-5)		9	03-12	-8.3(-15,-1.2)	0.027	10	9.7	
Landsort(3-5)	463	32	81-12	-5.8(-6.8,-4.8)	.0000 ---	10	9.17	.040 (.033,.047)
Landsort(3-5)		10	03-12	-8.6(-16,-1.6)	0.0219	11	10.1	
Utlängan(2-4)	455	32	81-12	-3.4(-4.6,-2.2)	.0000 ---	11	11.2	.070 (.057,.087)
Utlängan(2-4)		10	03-12	-9.8(-19,-.25)	0.0441	13	14	
Ängskärsklubb spring	138	17	96-12	-3.5(-9.8,2.9)	0.2625	17	23.3	.116 (.085,.158) m
Ängskärsklubb spring		10	03-12	-13(-31,5.4)	0.1402	19	28.6	
Utlängan spring	128	16	96-12	-2.9(-7.2,1.5)	0.1772	13	15.3	.101 (.081,.127) m
Utlängan spring		9	04-12	-9.4(-24,5.4)	0.1756	15	18.5	
Fladen(2-3)	551	32	81-12	-5.7(-7.1,-4.3)	.0000 ---	12	13.2	.029 (.022,.037)
Fladen(2-3)		10	03-12	-6.8(-13,-.96)	0.0269	10	8.35	
Väderöarna	292	17	95-12	.41(-2.4,3.2)	0.7538	11	10.6	.044 (.038,.051) m
Väderöarna		9	03-12	5.1(-3.7,14)	0.2105	12	12.4	
Perch muscle								
Holmöarna	170	17	95-12	-8.1(-13,-3.6)	.0017 --	14	17.2	.007 (.004,.011)
Holmöarna		9	03-12	-11(-26,4.7)	0.1428	17	22.9	
Kvädöfjärden	155	16	95-12	-6.7(-11,-2.8)	.0023 --	13	14.5	.010 (.006,.014)
Kvädöfjärden		9	03-12	-9.1(-22,3.8)	0.1385	15	18.6	
Cod liver								
SE Gotland(3-4)	407	31	81-12	-5.1(-6.2,-4.0)	.0000 ---	11	10.1	.006 (.005,.007)
SE Gotland(3-4)		9	03-12	-1.5(-7.6,4.6)	0.5784	10	8.39	
Fladen(2-4)	368	26	81-12	-2.5(-4.1,-.87)	.0041 --	13	14.6	.018 (.013,.023)
Fladen(2-4)		9	03-12	7.1(.37,14)	.0403 +	10	9.3	
Eelpout muscle								
Holmöarna	93	11	95-07	-15(-31,2.1)	0.0768	21	34.5	.055 (.019,.155)
Holmöarna		10	98-07	-21(-42,.87)	0.0561	21	34.3	
Kvädöfjärden	121	17	95-12	-10(-15,-5.0)	.0008 ---	15	18.6	.052 (.032,.084)
Kvädöfjärden		10	03-12	-12(-28,4.1)	0.1237	17	24.4	
Fjällbacka	122	17	95-12	-5.1(-8.5,-1.6)	.0065 --	12	12.6	.083 (.060,.116)
Fjällbacka		10	03-12	-9.9(-17,-2.4)	0.0155	11	10.8	

Blue mussel								
Nidingen	553	29	81-12	-5.2(-7.6,-2.8)	.0002 ---	16	24.7	.078 (.051,.119)
Nidingen		9	03-12	-1.7(-16,12)	0.768	15	22.2	
Fjällbacka	560	30	81-12	-1.1(-2.9,.70)	0.2208	14	18.2	.228 (.193,.270) m
Fjällbacka		9	03-12	-15(-20,-9.2)	.0005 ---	9	7.59	
Kvädöfjärden	178	18	95-12	.56(-4.7,5.8)	0.8058	16	23.1	.238 (.183,.309) m
Kvädöfjärden		10	03-12	-9.1(-19,1.2)	0.073	13	16.3	
Guillemot egg								
St.Karlsö	170	17	95-12	-13(-20,5.8)	0.0017--	18	31.5	.010 (.005,.020)
St.Karlsö		10	03-12	-15(-39,8.7)	0.1794	22	47.4	

15 Cadmium – Cd

Updatated 14.02.28

The time series of cadmium concentrations in fish liver and blue mussel soft body started in 1981.

15.1 Introduction

15.1.1 Usage, Production and Sources

Cadmium is a chemical element widely used in many industrial processes and products. Within the EU, the main use of cadmium is for the production of rechargable nickel-cadmium batteries and for metal plating and alloys. It is also used as a colour pigment in paints and a stabiliser in plastics. Cadmium is an impurity in phosphate rock used to manufacture fertilisers.

Natural processes, such as volcanic emissions and weathering of cadmium-bearing rocks release cadmium to both air and water. Anthropogenic sources include metal production, burning of fossil fuels, incorrect waste disposal (mainly Ni-Cd batteries) and transportation. Phosphate fertilisers used to be the main source of cadmium to agricultural land in Sweden, however, the applied amount has successively decreased since 1993 due to regulatory restrictions of the cadmium content in fertilisers. The main sources of cadmium to the Baltic Sea are point sources and riverine runoff (HELCOM 2010). Atmospheric deposition accounts for ca. 15%. According to HELCOM (2010), the waterborne input of cadmium to the Baltic Sea has decreased 91% and the atmospheric deposition 46% between 1990-2007. Despite this significant overall reduction, no decrease in the cadmium load from Swedish rivers to the Baltic Sea has been observed in the last 15 years (Naturvårdsverket 2007).

15.1.2 Environmental Fate

The environmental fate of cadmium depends largely on the surrounding conditions, e.g. pH, redox condition, salinity and presence of organic matter, which influence its chemical form. In water, cadmium exists as dissolved ions and soluble or insoluble complexes. Soluble cadmium is relatively mobile in water and in soil. Under oxic conditions, cadmium primarily adsorb to organic matter and form oxide/hydroxide complexes, while the formation of less soluble Cd-sulfides is dominating under reducing conditions. Cadmium tend to partition to sediments and the levels in sediment are often at least an order of magnitude higher than in the overlying water column. In soils it may be very mobile, particularly under acidic conditions, and the amount of cadmium transported from land to sea via rivers is often strongly correlated with the annual run-off.

Increasing salinity generally increase the soluble fraction of Cd. This is due to a combination of an increased formation of soluble chloride-complexes and by competition with Ca^{2+} for adsorption sites on suspended particles. However, the bioavailable fraction (i.e. the free Cd^{2+} ion) decreases with increasing salinity, since the Cd-chloride complexes are not available for uptake.

15.1.3 Toxic Effects

Cadmium is highly toxic to aquatic organisms. It can bioaccumulate and be transferred through the food chain. Cadmium does not undergo any direct metabolisation but can bind

to specific metal-binding proteins, e.g. metallothionein, preventing it from exerting its toxicity. Relatively large amounts of cadmium can be retained in the body bound to metallothionein. Chronic exposure results in the accumulation of cadmium in the kidney and liver. Kidney damage is the main toxic effect of chronic exposure to cadmium.

The most common source of cadmium for humans is via cigarette smoke (Godt et al. 2006). There is also a low risk of being exposed to cadmium via oral and dermal pathways (Godt et al. 2006). Cadmium is generally found in the liver or kidneys, 30% of the cadmium body burden is found in the kidneys. The kidneys are the main organ for long term cadmium accumulation in humans, leading to renal tube dysfunction (Godt et al. 2006). Bone tissues are secondarily affected. At very high exposure rates, effects on the respiratory system (e.g. emphysema) are known, while the nervous system in developing animals appears to be sensitive (Godt et al. 2006). There have been some effects on reproduction, and some proof of carcinogenic effects. Cadmium transported in blood plasma becomes bound to albumin and is then preferentially taken up by the liver, where metallothionein is synthesised. The placenta is only a partial barrier to foetal exposure. Cadmium is excreted in faeces and urine (Godt et al. 2006).

15.1.4 Conventions, Aims and Restrictions

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

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

The Swedish Parliament has agreed on a general reduction of cadmium discharge, aiming at a reduction of 70% between 1985 and 1995, and further, that all use of cadmium that implies a risk of discharge 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 stabiliser was banned in Sweden.

In 1987, a fee on batteries containing cadmium was introduced in Sweden. This fee was raised considerably in 1991.

In 1993, the content of cadmium in fertilisers was restricted to 100g/ton of phosphorus in Sweden.

15.1.5 Target Levels

The target level (TL) used for Cd in the time series for herring and perch is 160 ug/kg wet weight in whole-fish. For further information on TL and selection of target level see chapter 10. Since most data presented here are ug Cd per dry weight liver, the original TL has been recalculated for comparison. The recalculation of the TL for whole-fish is based on a study that compared concentrations of Cd in the liver and whole-fish of herring and perch (Boalt et al., 2011). The whole-fish:liver ratio was 0.11 and 0.16 for herring and perch respectively (Boalt et al., 2011) and the recalculation to dry weight is based on the dry weight in each time series. The recalculated target level (Tv) together with the dry weight percentage (dp) is shown above the statistical information in each time series.

15.2 Methods

15.2.1 Analytical Information

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

Please note that since 2007, the analytical laboratory for metals changed from the Swedish University of Agricultural Sciences (SLU) to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

15.3 Results

15.3.1 Spatial variation

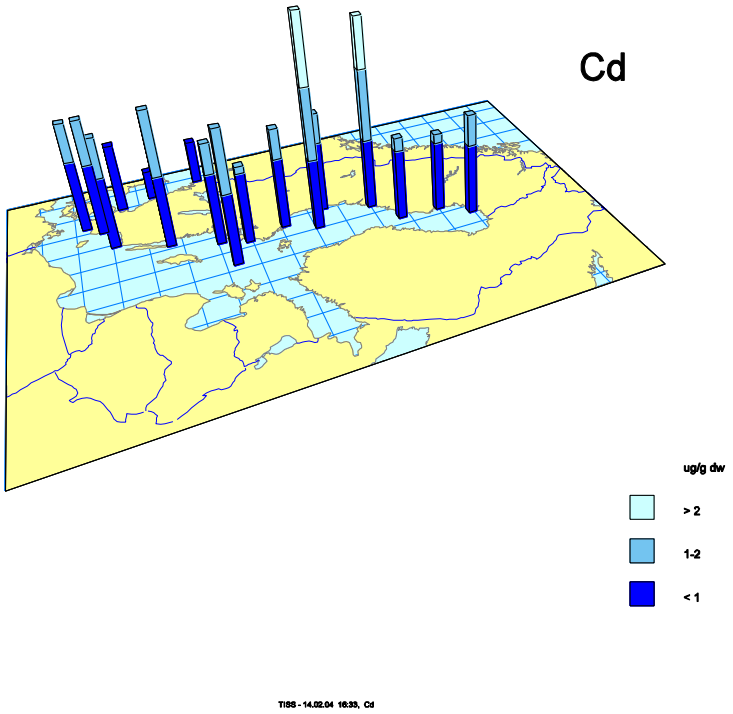


Figure 15.1. Spatial variation in cadmium concentrations (ug/g dry weight) in herring liver.

The Bothnian Sea and the Baltic Proper showed higher levels of cadmium in herring liver compared to the Bothnian Bayand the Swedish west coast. The highest level was observed at Baltic proper offshore followed by Gaviksfjärden, and the lowest concentration was found at Fladen on the Swedish west coast (Fig 15.1).

Overall, mean cadmium concentrations in herring liver from the Baltic showed significantly higher concentrations when compared to Fladen in the Kattegat and Väderöarna in the Skagerakk on the Swedish west coast (table. 15.1). The geometric mean concentration in herring liver for 1981 - 2012 from Landsort and Utlängan (the Baltic Proper) show approximately 4 times higher values, compared to samples from the Kattegat and Skagerrak (table 15.1).

Eelpout livers from Holmöarna in the southern Bothnian Bay and Kvädöfjärden in the Baltic Proper, showed six and four times higher geometric mean cadmium concentrations respectively, (1995-2012) compared to samples from Fjällbacka in the Skagerrak (table 15.1).

Blue mussels from Kvädöfjärden, analysed between 199-2012, showed about two to three times higher concentrations compared to blue mussel samples from the Swedish west coast (table 15.1). The samples from the Swedish west coast showed mean levels similar to that found in blue mussels from the Belgian coast (Vyncke et al. 1999) and did not exceed the 'high background concentration at diffuse loading' for cadmium in blue mussels (<2 µg/g dry weight) proposed by Knutzen and Skie (1992), whereas the samples from Kvädöfjärden did. All blue mussel samples exceeded the range of 'present background concentrations in pristine areas within the OSPAR Convention Area' proposed at 0.070-0.11 µg/g wet weight (ICES 1997). The estimated geometric mean concentration from Kvädöfjärden exceeded this concentration by about five times.

Cadmium concentrations in cod livers from Fladen in the Kattegat were significantly higher (about three times higher on a dry weight basis) compared to samples from southeast of Gotland. This may be explained by the average fat content in cod liver from Gotland being about 2.5 times higher compared to samples from the Kattegat. The Swedish data from southeast of Gotland were in the same range as Finnish data of cod liver from the Gulf of Finland and the Bothnian Sea.

15.3.2 Temporal variation

Total cadmium concentrations increased about 2 to 3 times during 1981 - 1995 at Ängskärsklubb, Landsort and Utlängan. In more recent years, these increases have levelled out and the levels today for most herring sites are lower than during the mid 1990s (Fig. 15.2). However, the opposite is seen at Väderöarna with a significant increasing trendbetween 1995-2012 (Fig 15.3).
The number of years required to detect an annual change of 10% varied between 9 - 14years for the herring time series, with a power to detect a 10% annual change ranging from 0.98 to 1.0.

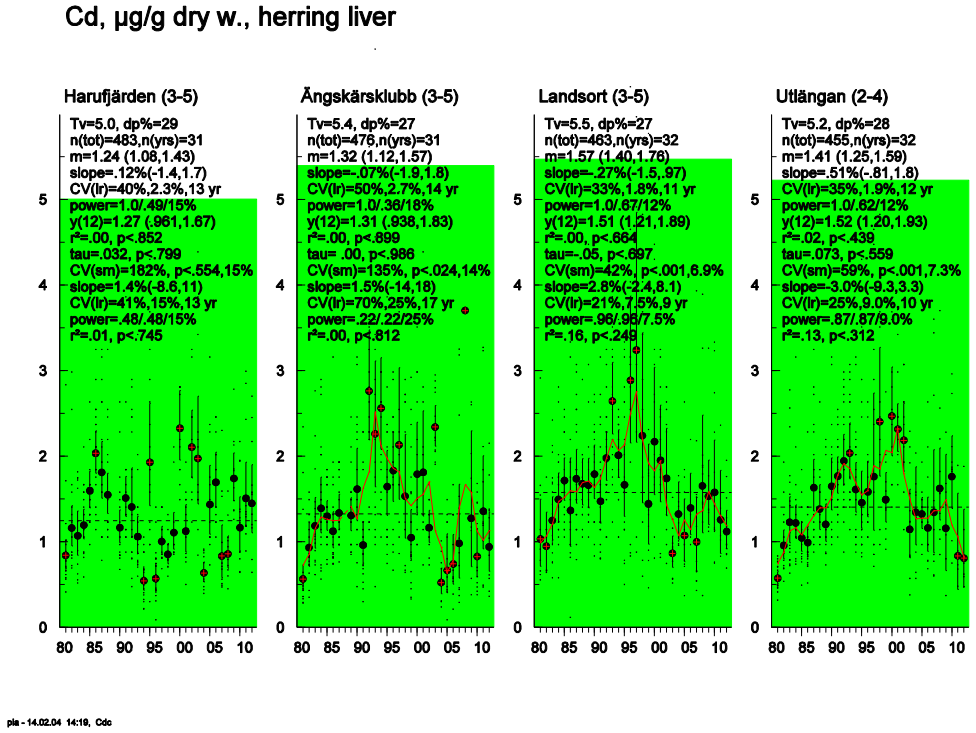


Figure 15.2. Cadmium concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981). The green area denotes the levels below the suggested target value for cadmium in fish.

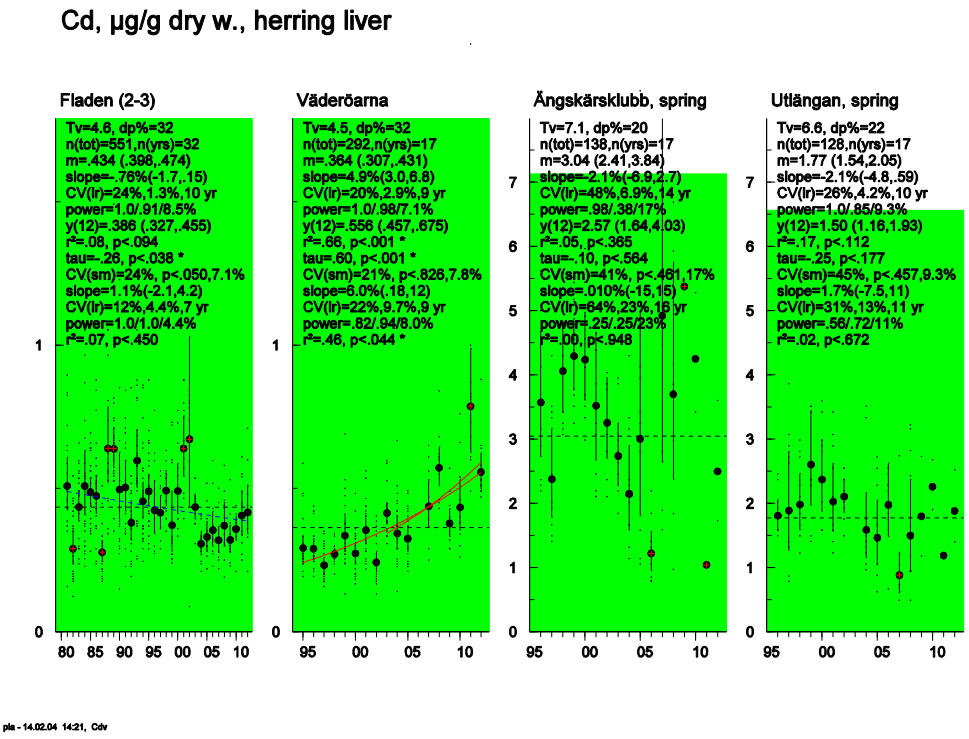


Figure 15.3. Cadmium concentrations (µg/g dry weight) in herring liver from Ängskärsklubb (spring), Utlängan, Fladen and Väderöarna (time series starting in 1995, 1995, 1980 and 1995, respectively). The green area denotes the levels below the suggested target value for cadmium in fish

A significant decreasing trend was seen for cadmium concentrations in cod liver samples (adjusted for varying fat content) from south east of Gotland and also an indicated decrease for samples from Fladen (Fig. 15.4).

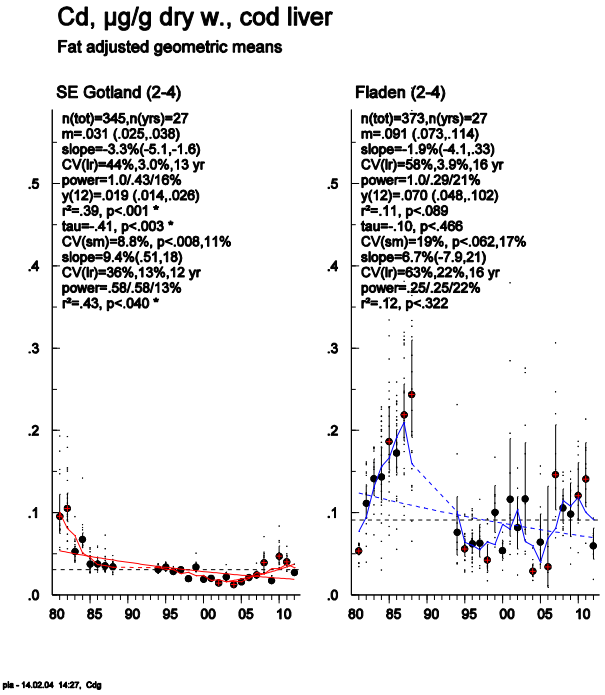


Figure 15.4. Cadmium concentrations (µg/g dry weight) in cod liver from southeast Gotland and Fladen (time series starting in 1980).

Cadmium concentrations in perch liver samples showed no linear trend at any of the sites (Fig. 15.5).

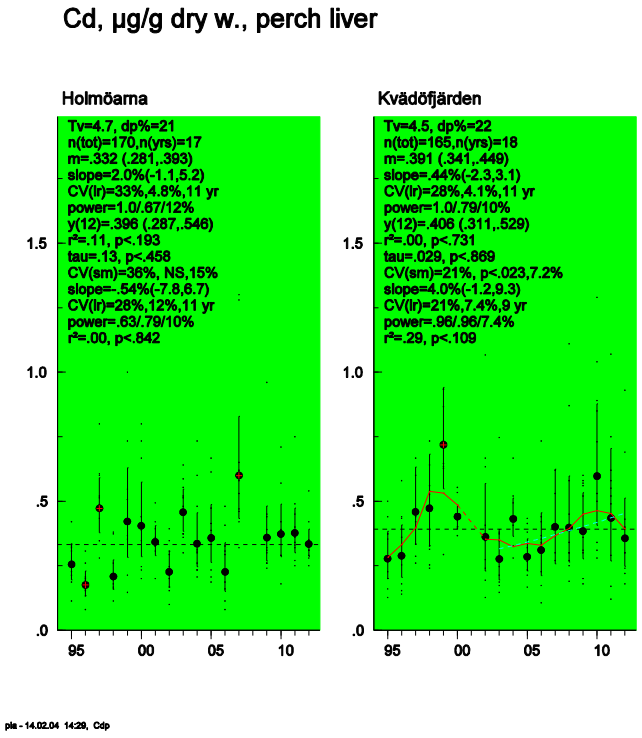


Figure 15.5. Cadmium concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995). The green area denotes the levels below the suggested target value for cadmium in fish.

Cadmium concentrations in eelpout samples from Holmöarna showed a significant increasing trend, however, the between-year variation at Holmöarna is large (Fig. 15.6). A significant decreasing trend for cadmium was observed at Kvädöfjärden during the ten last years (Fig. 15.6).

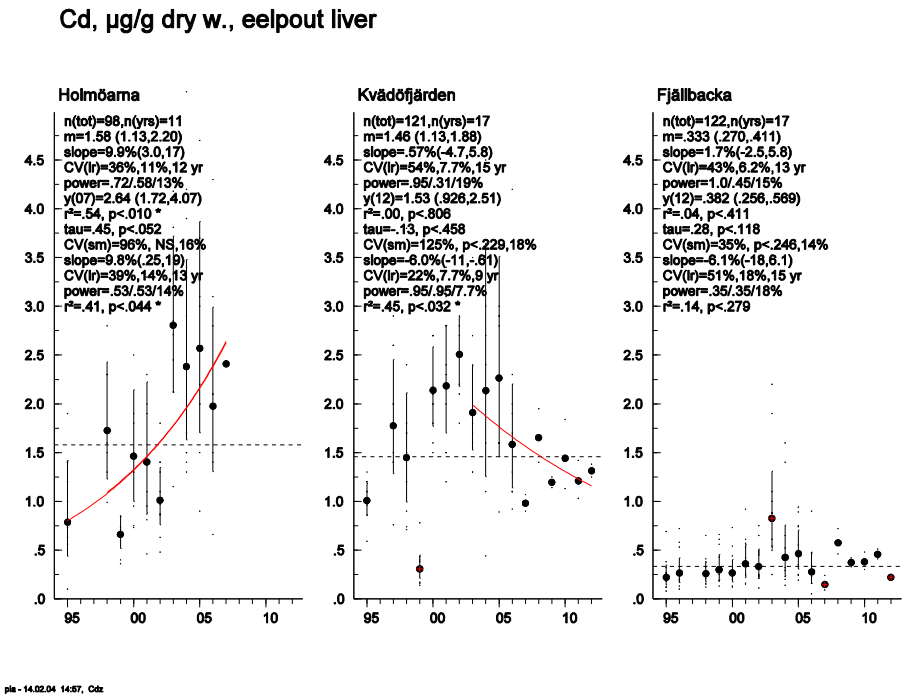


Figure 15.6. Cadmium concentrations (µg/g dry weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

Cadmium concentrations in blue mussel soft body tissue show significant decreasing trends at Nidingen, Fjällbacka, and Kvädöfjärden for the whole time period (Fig. 15.7).

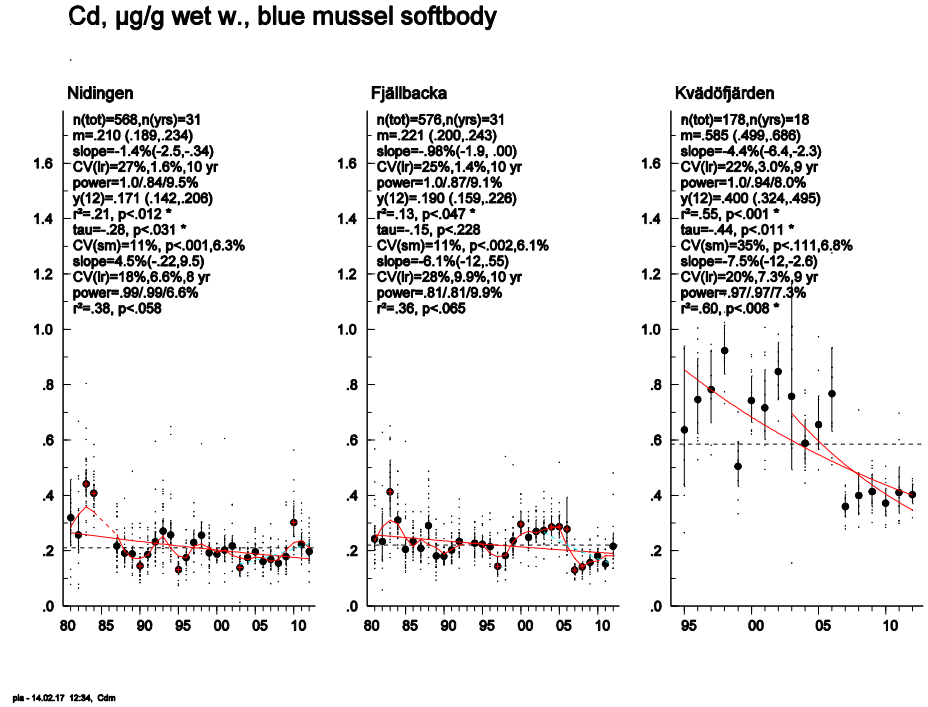


Figure 15.7. Cadmium concentrations (µg/g wet weight) in blue mussel soft body tissue from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1981, 1981 and 1995 respectively).

15.3.3 Species differences

Differences in mean cadmium concentration (μg/g dry weight) between species.

Holmöarna: Eelpout (2.6) > Perch (0. 33)
Kvädöfjärden: Blue mussel (3.3) > Eelpout (1.5) > Perch (0.39)
Fladen/Nidingen: Blue mussel (0.9) > Herring (0.39) > Cod (0.070)
Väderöarna/Fjällbacka: Blue mussel (1.3) >Herring (0. 55) – Eelpout (0.33)

Cadmium concentration in blue mussel soft body tissue is about two to ten times higher than the concentration found in fish liver. The concentration in eelpout liver is three to six times higher than in perch liver in the analysed samples. The concentration found in guillemot eggs was between 40-300 times lower (0.009 ug/g dry weight) when compared to herring liver.

15.4 Conclusion

Generally, cadmium concentration was higher in samples taken on the Baltic coast compared to samples from the Swedish west coast, with the exception of cod.
With regards to temporal variation, the rapid increase in cadmium concentrations observed at Ängskärsklubb and Landsort appears to have stopped, and this trend has now reversed.

Cadmium is concentrated in internal organs, i.e. the liver, whereas the concentration in muscle tissues is very low. Analysed values for perch and herring muscle are 0.8 and 4 ng/g dry weight respectively (Strandmark et al. 2008). Cadmium concentrations of 0.8 - 4 ng/g indicates that there is no immediate risk for human consumption, since the suggested EU limit for human consumption of fish is 160 ng/g fresh weight.

A general remark for extra caution is appropriate when interpreting analyses of low concentrations near the quantification level, as in water or muscle samples. An improved analysis technique may lead to decreasing concentrations due to a decreased risk of sample contamination.

The cadmium concentrations in herring and in perch are all below the suggested target level.

15.4.1 Comparison to threshold

In all herring and perch time series, Cd concentrations are below the suggested target level based on the QS_{biota} of 0.16 ug/g wet weight. This has to be interpreted carefully as the recalculation between levels of cadmium in whole-body and liver is based on only one study.

Table 15.1. Trend (in %) for **cadmium** (µg/g dry weight, wet weight for blue mussels) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's cadmium concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	483	31	81-12	.12(-1.4,1.7)	0.852	13	14.5	1.24 (1.08,1.43) m
Harufjärden(3-5)		10	03-12	1.4(-8.6,11)	0.7449	13	14.7	
Ängskärsklubb(3-5)	476	31	81-12	-.07(-1.9,1.8)	0.8986	14	17.9	1.32 (1.12,1.57) m
Ängskärsklubb(3-5)		10	03-12	1.5(-14,18)	0.8116	17	24.6	
Landsort(3-5)	463	32	81-12	-.27(-1.5,.97)	0.6636	11	11.7	1.57 (1.40,1.76) m
Landsort(3-5)		10	03-12	2.8(-2.4,8.1)	0.2491	9	7.51	
Utlängan(2-4)	455	32	81-12	.51(-.81,1.8)	0.4392	12	12.5	1.41 (1.25,1.59) m
Utlängan(2-4)		10	03-12	-3.0(-9.3,3.3)	0.3119	10	9.04	
Ängskärsklubb spring	138	17	96-12	-2.1(-6.9,2.7)	0.3646	14	17.2	3.04 (2.41,3.84) m
Ängskärsklubb spring		10	03-12	.010(-15,15)	0.9476	16	22.7	
Utlängan spring	128	16	96-12	-2.1(-4.8,.59)	0.1115	10	9.31	1.77 (1.54,2.05) m
Utlängan spring		9	04-12	1.7(-7.5,11)	0.6721	11	11.1	
Fladen(2-3)	551	32	81-12	-.76(-1.7,.15)	0.0945	10	8.5	.386 (.327,.455)
Fladen(2-3)		10	03-12	1.1(-2.1,4.2)	0.4496	7	4.42	
Väderöarna	292	17	95-12	4.9(3.0,6.8)	.0001 +++	9	7.12	.556 (.457,.675)
Väderöarna		9	03-12	6.0(.18,12)	.0439 +	9	8.03	
Cod liver								
SE Gotland (3-4)	345	27	81-12	-3.3(-5.1,-1.6)	.0006---	13	17.1	.019(.014,.026)
SE Gotland (3-4)		10	03-12	9.4(.51,18)	.0395+	12	13.8	
Fladen (2-4)	373	27	81-12	-1.9(-4.1,.33)	.0893	16	22.8	.070(.048,.102)
Fladen (2-4)		10	03-12	6.7(-7.9,21)	.3221	16	24.9	
Perch muscle								
Holmöarna	170	17	95-12	2.0(-1.1,5.2)	0.1925	11	11.7	.332 (.281,.393) m
Holmöarna		9	03-12	-.54(-7.8,6.7)	0.8419	11	10.2	
Kvädöfjärden	165	17	95-12	.44(-2.3,3.1)	0.7308	11	10.1	.391 (.341,.449) m
Kvädöfjärden		10	03-12	4.0(-1.2,9.3)	0.1094	9	7.43	
Eelpout muscle								
Holmöarna	98	11	95-07	9.9(3.0,17)	.0098 ++	12	13.1	2.64 (1.72,4.07)

Holmöarna		10	98-07	9.8(.25,19)	.0441 +	13	13.9	
Kvädöfjärden	121	17	95-12	.57(-4.7,5.8)	0.8059	15	19.4	1.46 (1.13,1.88) m
Kvädöfjärden		10	03-12	-6.0(-11,-.61)	-0.0323	9	7.7	
Fjällbacka	122	17	95-12	1.7(-2.5,5.8)	0.4109	13	15.4	.333 (.270,.411) m
Fjällbacka		10	03-12	-6.1(-18,6.1)	0.2793	15	18.2	
Blue mussel								
Nidingen	568	30	81-12	-1.4(-2.5,-.34)	-0.0115	10	10	.171 (.142,.206)
Nidingen		10	03-12	4.4(-.22,9.1)	0.0575	8	6.81	
Fjällbacka	576	31	81-12	-.98(-2.0, .00)	-0.0471	10	9.5	.190 (.159,.226)
Fjällbacka		10	03-12	-6.3(-13,.55)	0.0649	10	10.4	
Kvädöfjärden	178	18	95-12	-4.5(-6.6,-2.3)	.0005 ---	9	8.34	.400 (.324,.495)
Kvädöfjärden		10	03-12	-7.8(-13,-2.6)	.0082 --	9	7.56	
Guillemot egg								
St.Karlsö	80	8	96-11	-.27(-5.6,5.0)	0.8714	12	13.4	.009 (.007,.012) m
St.Karlsö		5	05-11	7.1(-16,30)	0.3963	12	13.7	

16 Nickel - Ni

Updated 14.02.28

The analysis of nickel concentration in fish liver started on samples collected in 1995.

16.1.1 Usage, Production and Sources

The most common ores of nickel include pentlandite, pyrrhotite, and garnierite. In addition, nickel also occurs as an impurity in ores of iron, copper, cobalt, and other metals.
Natural nickel is a mixture of five isotopes, i.e. 58Ni, 60Ni, 61Ni, 62Ni, and 64Ni. Seven radioactive isotopes of nickel are also known; however, only 63Ni of the radioactive isotopes is used in industry for the detection of explosives, and in certain kinds of electronic devices, such as surge protectors.

The most important use of nickel is in manufacturing of a variety of alloys including stainless steel (Cempel and Nikel 2006). Moreover, nickel is also very popular in the battery industry; nickel-cadmium and nickel-metal hydride batteries are the main line products. Nickel is also used in a great variety of appliances, including hand-held power tools, compact disc players, pocket recorders, camcorders, cordless and cellular telephones, scanner radios, and laptop computers. Nickel is also used in electroplating.

16.1.2 Environmental Fate

Nickel can be released to the environment both by natural sources and anthropogenic activities. Weathering of rocks and soils, volcanic emissions, forest fires are the main natural sources of atmospheric nickel. Anthropogenic activities producing nickel include combustion of fossil fuel, incineration of waste, using stainless steel utensils, smoking tobacco (Cempel and Nikel 2006). Domestic wastewater effluents and non-ferrous metal smelters are responsible for the nickel contamination in aquatic ecosystems (Cempel and Nikel 2006). In water, nickel can deposit to sediments or uptake by biota. Nickel typically accumulates in the surface soils once deposit from industrial and agricultural activities (Scott-Fordsmand 1997).

16.1.3 Toxic Effects

Nickel is one of the essential metals for the function of several animals, organisms, and plants. Toxicity can occur either when the amount of Ni in the body is abundant or deficient. Nickel has not been recognized as a nutritional element for humans. Therefore, exposure to nickel compounds can have adverse effects on human health. Human exposure to Ni is primarily through ingestion of contaminated drinking water or food and inhalation (Cempel and Nikel 2006). Allergic skin reactions by nickel has been reported as one of the most common causes of allergic contact dermatitis (Andrea 2005). Erythema, eczema and

lichenification can be produced once skin is in contact with nickel. Nickel compounds have been exhibited as carcinogenic in some animals and modes of human exposure (Kasprzak et al. 2003; WHO 1991). The ability to enter cells determines its carcinogenic properties. High water-soluble nickel compounds have less carcinogenic potency than some certain water-soluble nickel compounds (Cempel and Nikel 2006). Recent studies have reported the ability of nickel to enhance lipid peroxidation in the liver, kidney, lung, bone marrow and serum (Cempel and Nikel 2006; Denkhaus and Salnikow 2002).

16.1.4 Target Levels

The target level (TL) for nickel is 730 µg/kg wet weight for whole-fish. For further information on TL and selection of target level see chapter 10. The concentrations of Ni presented in this report are in liver and there are no conversion factors available for recalculation to whole-fish at present, therefore the TL is not presented in the timeseries for Ni.

16.2 Methods

16.2.1 Analytical Information

Please note that since 2007, the analytical laboratory for metals changed from the Swedish University of Agricultural Sciences (SLU) to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

16.3 Results

16.3.1 Spatial variation

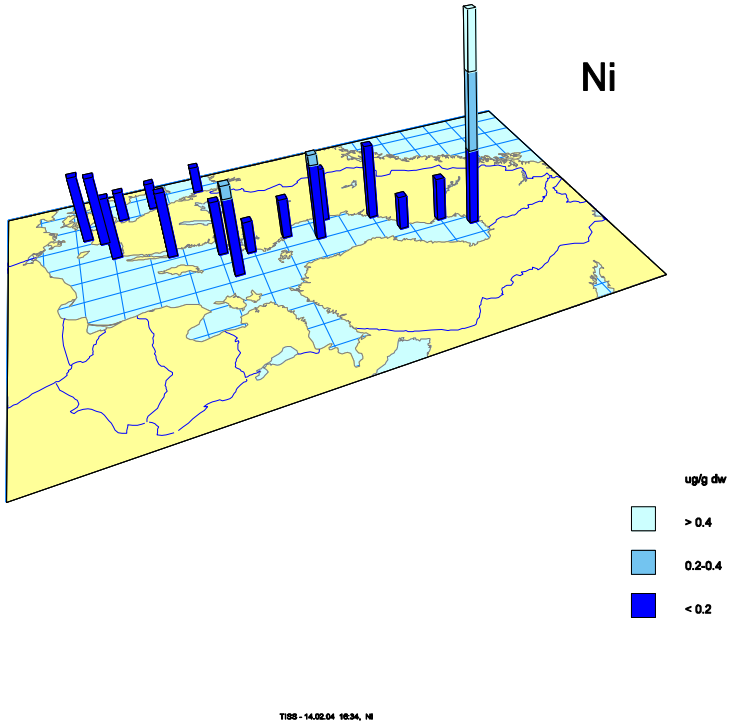


Figure 16.1. Spatial variation in nickel concentrations (µg/g dry weight) in herring liver.

Significantly lower nickel concentrations were observed in herring liver from Fladen and Väderöarna compared to samples from the Baltic sites (except for Lagnö, Kinnnbäcksfjärden, and Örefjärden). The overall highest concentration was observed at Harufjärden (Fig. 16.1). However, this high concentration is probably a result of one outlier from 2011, which had a concentration almost 25 times higher compared to all the other samples.

Mussels from all three sites showed mean levels below the upper limit of the 'high background concentration at diffuse loading' in blue mussels for nickel of <5 µg/g dry weight, proposed by Knutzen and Skie (1992) (table 16.1).

16.3.2 Temporal variation

The cod liver time series from southeast of Gotland and Fladen (Fig. 16.4), eelpout from Kvädöfjärden (Fig. 16.6), and guillemot from Stora Karlsö (Fig.16.8), all show significant decreasing trends for the whole time period. Significant increasing trends for the last ten years were observed for herring at Harufjärden, Landsort, Väderöarna, and Utlängan (spring) (Fig. 16.2, 3).

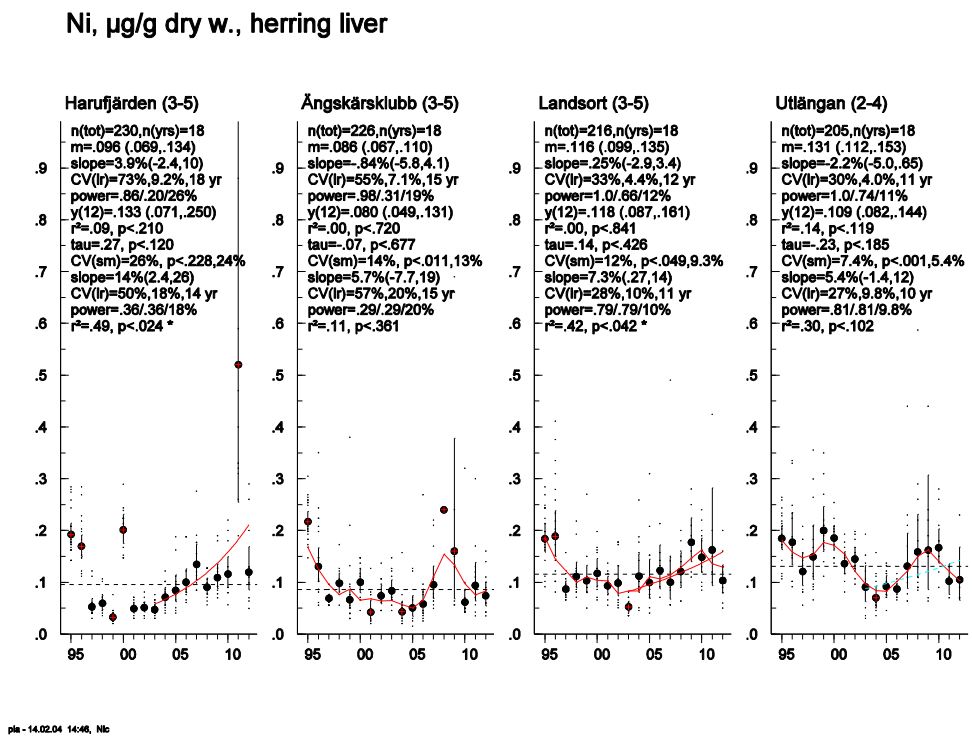
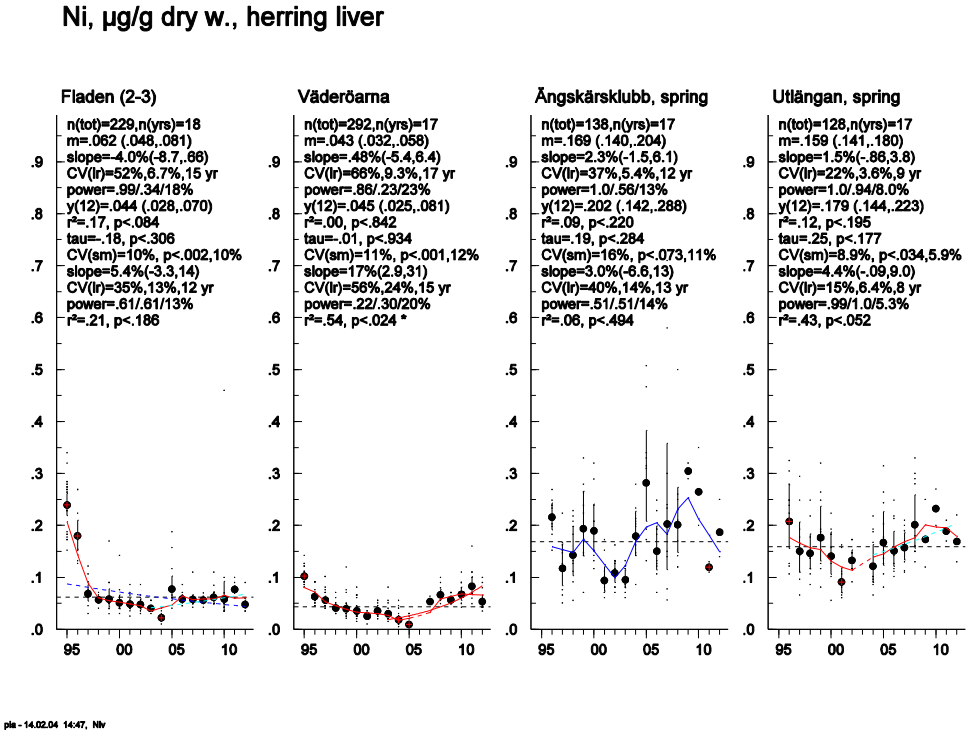


Figure 16.2 (above) and **16.3** (below). Nickel concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1995) (above); and Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1996, 1995 and 1995 respectively).



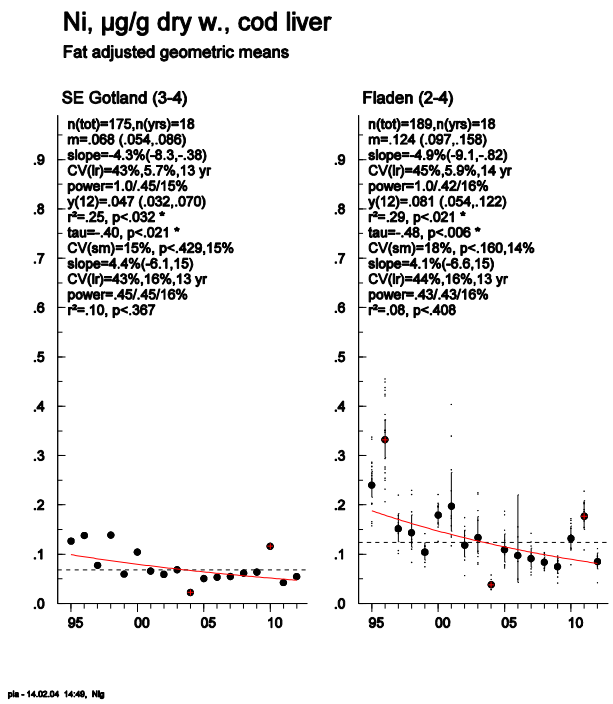


Figure 16.4. Nickel concentrations (µg/g dry weight) in cod liver from southeast Gotland and Fladen (time series starting in 1995).

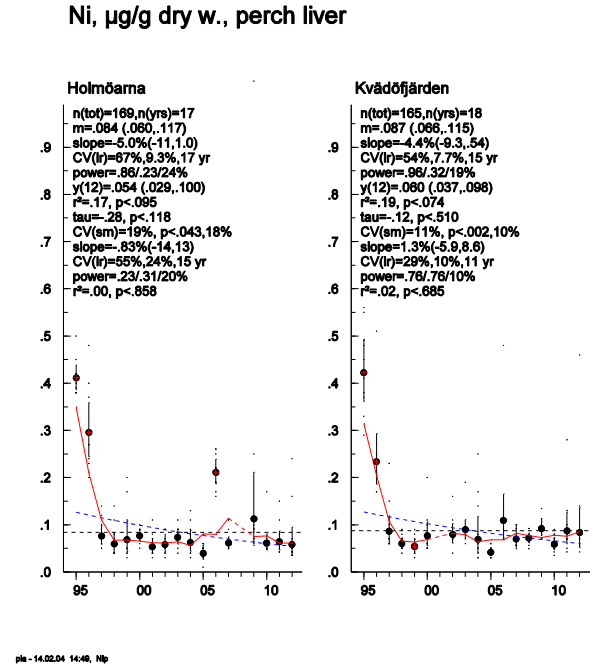


Figure 16.5. Nickel concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

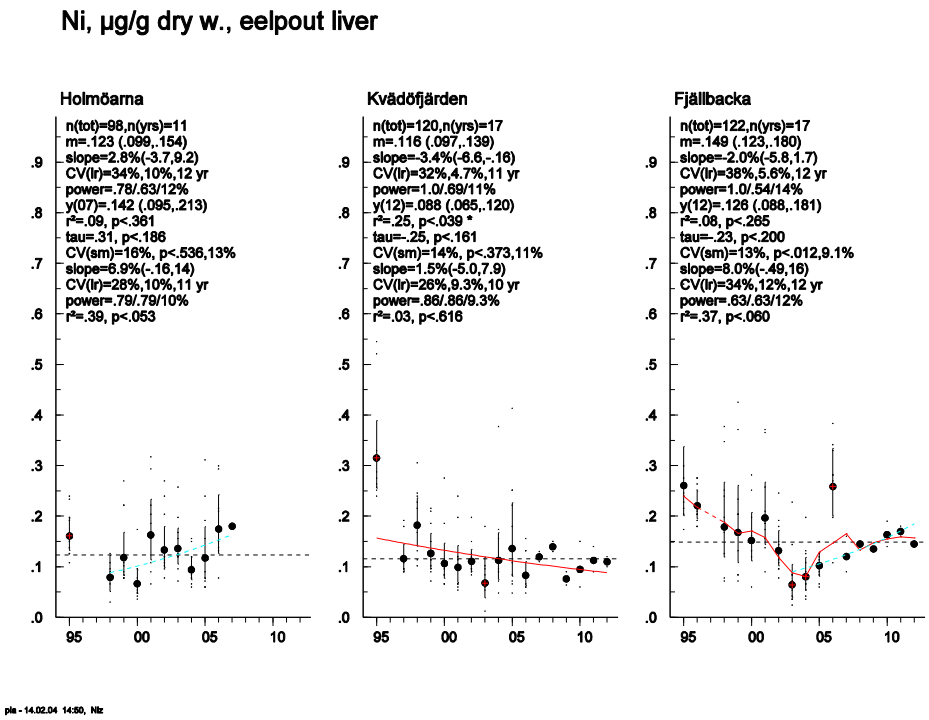


Figure 16.6. Nickel concentrations (µg/g dry weight) in eelpout liver from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

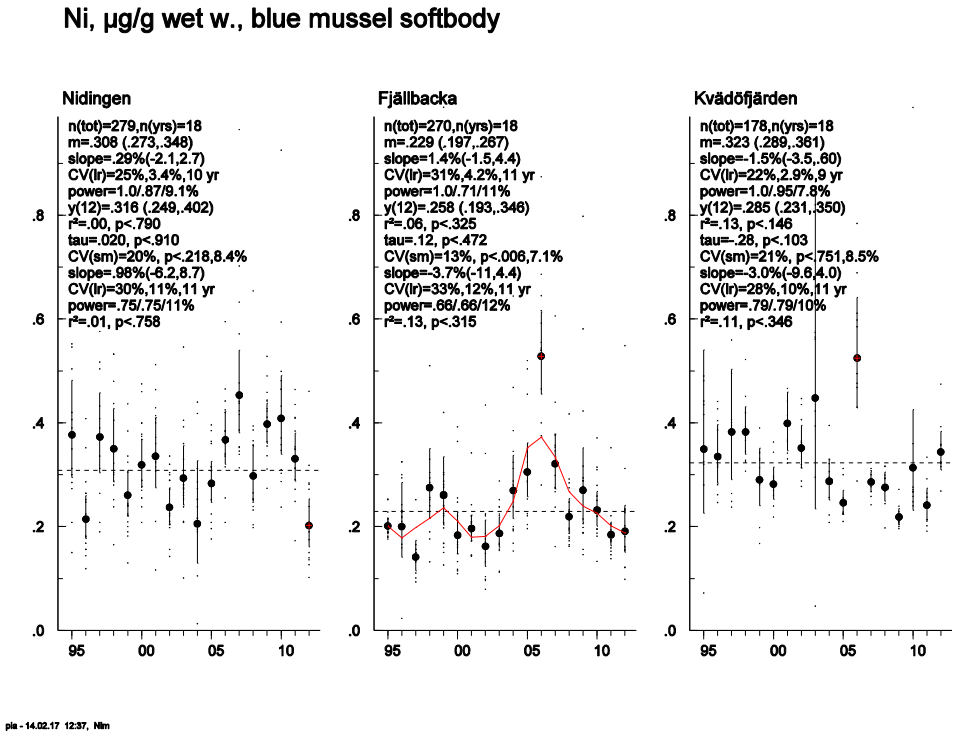


Figure 16.7. Nickel concentrations (µg/g wet weight) in blue mussel soft body tissue from Kvädöfjärden, Nidingen, and Fjällbacka (time series starting in 1995).

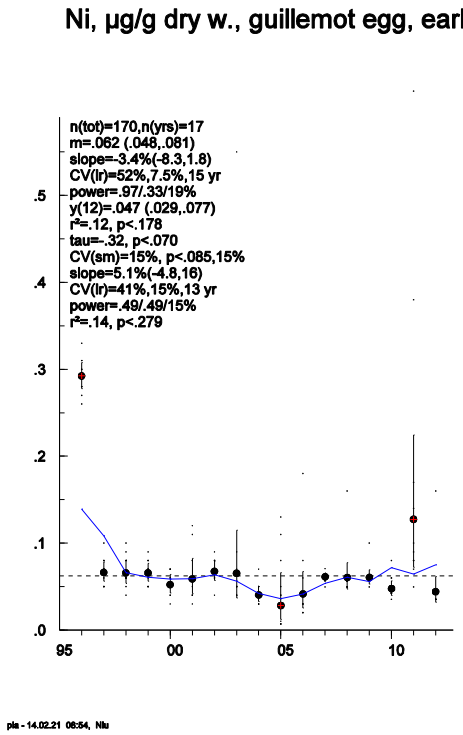


Figure 16.8. Nickel concentrations (µg/g dry weight) in guillemot eggs Stora Karlsö (time series starting in 1996).

The number of years required in the herring series to detect an annual change of 10 % varies between 9 - 18 years. The power to detect an annual change of 10 % ranges from 0.86 - 1.0.

16.3.3 Conclusion

Nickel concentrations in herring liver are lower on the west coast compared to the east coast of Sweden. Blue mussels examined from all three sites were below the upper limit of the 'high background concentration at diffuse loading' in blue mussels for nickel of <5 µg/g dry weight, proposed by Knutzen and Skie (1992).

No general increasing or decreasing trend was observed for nickel.

Table 16.1. Trend (in %) for **nickel** (µg/g dry weight, wet weight for blue mussels) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's nickel concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	230	18	95-12	3.9(-2.4,10)	0.2101	18	25.7	.096 (.069,.134) m
Harufjärden(3-5)		10	03-12	14(2.4,26)	.0238 +	14	17.9	
Ängskärsklubb(3-5)	226	18	95-12	-.84(-5.8,4.1)	0.7199	15	19.5	.086 (.067,.110) m
Ängskärsklubb(3-5)		10	03-12	5.7(-7.7,19)	0.3611	15	20.2	
Landsort(3-5)	216	18	95-12	.25(-2.9,3.4)	0.8408	12	11.9	.116 (.099,.135) m
Landsort(3-5)		10	03-12	7.3(.27,14)	.0422 +	11	10.1	
Utlängan(2-4)	205	18	95-12	-2.2(-5.0,.65)	0.1188	11	10.8	.131 (.112,.153) m
Utlängan(2-4)		10	03-12	5.4(-1.4,12)	0.102	10	9.8	
Ängskärsklubb spring	138	17	96-12	2.3(-1.5,6.1)	0.2199	12	13.3	.169 (.140,.204) m
Ängskärsklubb spring		10	03-12	3.0(-6.6,13)	0.4943	13	14.2	
Utlängan spring	128	16	96-12	1.5(-.86,3.8)	0.1945	9	7.98	.159 (.141,.180) m
Utlängan spring		9	04-12	4.4(-.09,9.0)	0.0522	8	5.3	
Fladen(2-3)	189	18	95-12	-4.9(-9.1,-.82)	0.0208	14	16.1	.081 (.054,.122)
Fladen(2-3)		10	03-12	4.1(-6.6,15)	0.4081	13	15.8	
Väderöarna	292	17	95-12	.48(-5.4,6.4)	0.8416	17	23.5	.043 (.032,.058) m
Väderöarna		9	03-12	17(2.9,31)	.0237 +	15	19.9	
Perch muscle								
Holmöarna	169	17	95-12	-5.0(-11,1.0)	0.0949	17	23.5	.054 (.029,.100)
Holmöarna		9	03-12	-.83(-14,13)	0.8581	15	19.6	
Kvädöfjärden	165	17	95-12	-4.4(-9.3,.54)	0.0745	15	19.2	.060 (.037,.098)
Kvädöfjärden		10	03-12	1.3(-5.9,8.6)	0.6849	11	10.5	
Cod liver								
SE Gotland(3-4)	175	18	95-12	-4.3(-8.3,-.38)	0.0323	13	15.5	.047 (.032,.070)
SE Gotland(3-4)		10	03-12	4.4(-6.1,15)	0.3669	13	15.5	
Eelpout muscle								
Holmöarna	98	11	95-07	2.8(-3.7,9.2)	0.3606	12	12.2	.123 (.099,.154) m
Holmöarna		10	98-07	6.9(-.16,14)	0.0526	11	10.2	
Kvädöfjärden	120	17	95-12	-3.4(-6.6,-.16)	0.0392	11	11.5	.088 (.065,.120)
Kvädöfjärden		10	03-12	1.5(-5.0,7.9)	0.6158	10	9.27	
Fjällbacka	122	17	95-12	-2.0(-5.8,1.7)	0.2653	12	13.7	.149 (.123,.180) m
Fjällbacka		10	03-12	8.0(-.49,16)	0.0599	12	12.3	
Blue mussel								
Nidingen	279	18	95-12	.29(-2.1,2.7)	0.79	10	9.6	.308 (.273,.348) m
Nidingen		10	03-12	.98(-6.4,8.3)	0.7583	11	11.2	

Fjällbacka	270	18	95-12	1.4(-1.5,4.3)	0.3252	11	11.9	.229 (.197,.267) m
Fjällbacka		10	03-12	-3.8(-12,4.3)	0.3151	11	12.5	
Kvädöfjärden	178	18	95-12	-1.5(-3.6,.60)	0.1465	9	8.16	.323 (.289,.361) m
Kvädöfjärden		10	03-12	-3.1(-10,4.0)	0.3459	11	10.6	
Guillemot egg								
St.Karlsö	170	17	96-12	-3.4(-8.6,1.8)	0.1779	15	20.6	.062 (.048,.081) m
St.Karlsö		10	03-12	5.0(-4.9,15)	0.2791	13	15.8	

17 Chromium - Cr

Updated 14.02.28

The analysis of chromium concentration in fish liver started on samples collected in 1995.

17.1 Introduction

17.1.1 Usage, Production and Sources

The abundance of chromium in the Earth's crust is about 100 to 300 ppm in rock (Domy 2001). Chromium does not occur as a free element. Rocks or sediments present a wide range of chromium concentration whereas natural water contains quite small amounts (Richard and Bourg 1991). Most chromium is produced from chromite, or chrome iron ore (FeCr2O4). Chromium is used in the manufacturing of stainless steels, electroplating, leather tanning, pigments for inks and paints.

There are four naturally occurring isotopes of chromium: 50Cr, 52Cr, 53Cr, 54Cr and seven known radioactive isotopes (Eisler, 1986). Oxidation states of chromium can vary from Cr (0) to Cr (VI), in which Cr (III) and Cr (VI) are the most stable and important species for natural aquatic systems (Richard and Bourg 1991). Aqueous chromium presents as Cr3+ state under reducing environments and pH lower than 3.6, while Cr (VI) is only presented in oxidizing conditions (Richard and Bourg 1991).

17.1.2 Environmental Fate

Chromium can be transported between various environmental media and once present in the environment, it can be taken up by humans and other biota. Chromium is introduced to the environment mainly through anthropogenic activities than through weathering processes (Eisler 1986). Chromium alloy, metal production, coal combustion, municipal incinerators, cement production, and cooling towers are responsible for the major atmospheric emissions of Cr (Towill et al. 1978). The transformation and transport of chromium in the atmosphere are in association with aerosols. Chromium is removed from the atmosphere by both wet and dry deposition and reintroduced via resuspension of chromium-containing soil particles. In the aquatic environment, the major sources of chromium are atmospheric deposition, industrial activities (i.e. electroplating, metal finishing industries and waste water treatment plants), and weathering of natural rocks (Kimbrough et al. 1999). Chromium leaks to soil and sediment mainly from human activities, i.e. using chromium in phosphate fertilizers, chromium plating bath, ferrochromium slag (de Lopez Camelo et al. 1997).

17.1.3 Toxic Effects

The toxicity of chromium is regulated by its oxidation state, irrespective of its total concentration. Chromium (III) appears to be a nutrient for some plants and animals, including humans; however, Cr (VI) has been reported to be toxic to bacteria, plants, and animals (Richard and Bourg 1991). Environmental properties, i.e. hardness, temperature,

pH, and salinity of water, in combination with biological factors, i.e. species, life stage, sensitivities of local population, determines the toxicity of chromium to aquatic biota (de Lopez Camelo et al. 1997). In addition, interaction effects of chromium with other contaminants, duration of exposure, and chemical form of Cr are also important factors. In general, Cr (III) is less toxic than Cr (VI) due to its high oxidizing potential and its easier membrane permeability (Eisler 1986; Richard and Bourg 1991). For sensitive aquatic biota, LC50 of Cr(III) were from 2000 to 3200 ppb while Cr(VI) ranged from 445 to 2000 ppb (Eisler 1986). Chromium is a trace element that has significant biological effects to the human body. Small amounts of chromium are necessary for plants and animals to metabolize glucose and synthesize amino acid and nucleic acid (Richard and Bourg 1991). Chromium deficiency leads to diabetes-like symptoms in humans (Towill et al. 1978). At high level, chromium can cause nausea, skin ulcerations or lung cancer depending on exposure pathway and amounts of uptake.

17.1.4 Conventions, Aim, and restriction

The maximum chromium concentration in drinking water, recommended by the Commission of European Communities, the World Health Organization or the U.S. Environmental Protection Agency, is 50 µg/l (Richard and Bourg 1991).

17.1.5 Target levels

No national target level for biota is agreed upon for Cr.

17.2 Methods

17.2.1 Analytical Information

Please note that since 2007, the analytical laboratory for metals changed from the Swedish University of Agricultural Sciences (SLU) to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

17.3 Results

17.3.1 Spatial variation

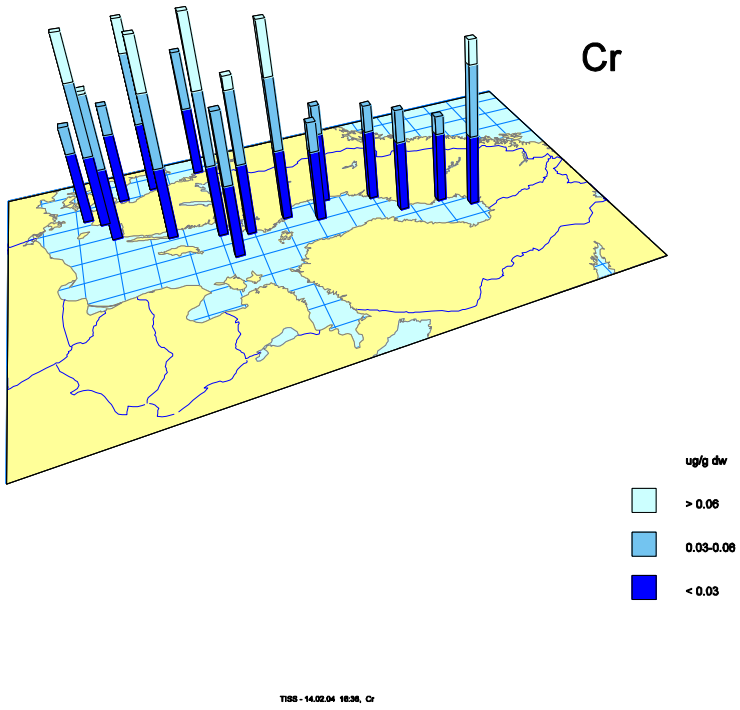


Figure 17.1. Spatial variation in chromium concentrations (ug/g dry weight) in herring liver.

The concentration of chromium in herring liver is quite even along the Swedish coast, but is somewhat lower in the Bothnian Sea (except from Ängskärsklubb). The highest concentration was observed at Landsort in the Baltic Proper, followed by Ängskärsklubb in the south Bothnian Sea (Fig 17.1).

Chromium concentrations in blue mussel samples are at similar levels at both stations on the west coast and just slightly higher in Baltic Proper (Fig. 17.7). These concentrations are generally below the 'high background concentration at diffuse loading' in blue mussels for chromium of <3 µg/g dry weight, proposed by Knutzen and Skie (1992).

17.3.2 Temporal variation

Chromium decreased significantly in all herring time series (Fig. 17.2, 17.3), in cod from Fladen and southeast of Gotland (Fig. 17.5), in perch from Holmöarna and Kvädöfjärden (Fig. 17.4), and in eelpout from Holmöarna, Kvädöfjärden and Fjällbacka (Fig. 17.6) seen over the whole monitored period. In blue mussels on the other hand, chromium increased significantly at Fjällbacka and Kvädöfjärden over the whole time period and during the last ten years at Nidingen (Fig. 17.7). During the last ten years an increase in chromium concentration is seen for guillemot eggs (Fig. 17. 8) but also in herring from Ängskärsklubb, Landsort, Utlängan och Fladen.

The results of chromium concentrations should be interpreted with caution. In a major part of the time trends, clear shifts in concentration levels are visible between 2002 and 2003. This shift might be explained by changed methods for analysis.

The required minimum years to detect an annual change of 10 % varies between 14 - 23 years for herring. The power to detect an annual change of 10 % ranges between 0.48 - 0.98.

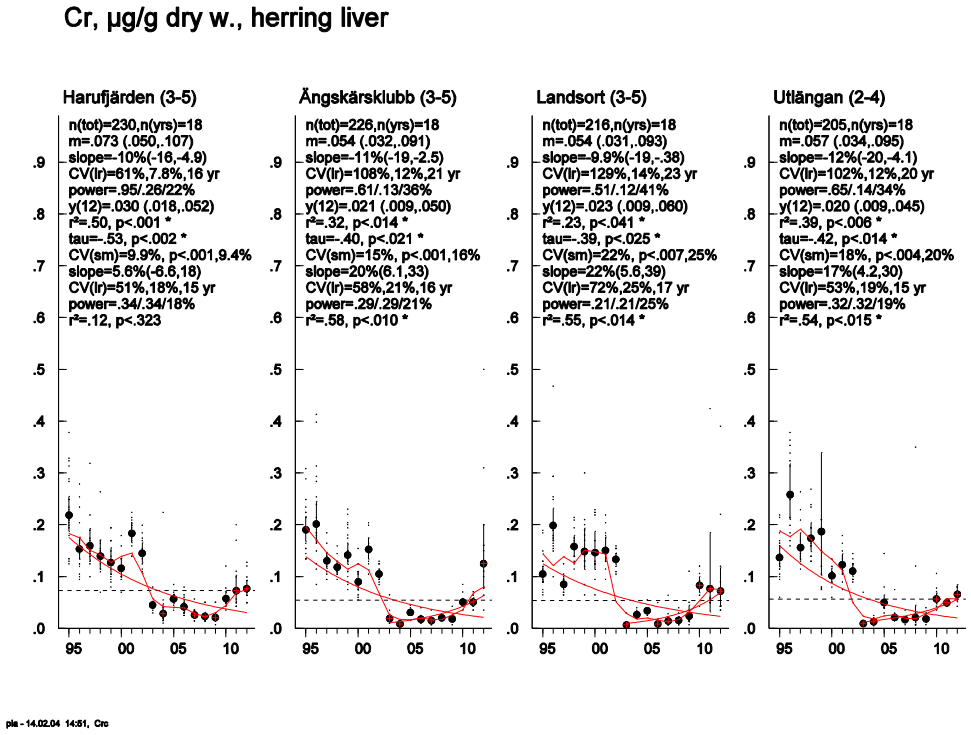


Figure 17.2. Chromium concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1995).

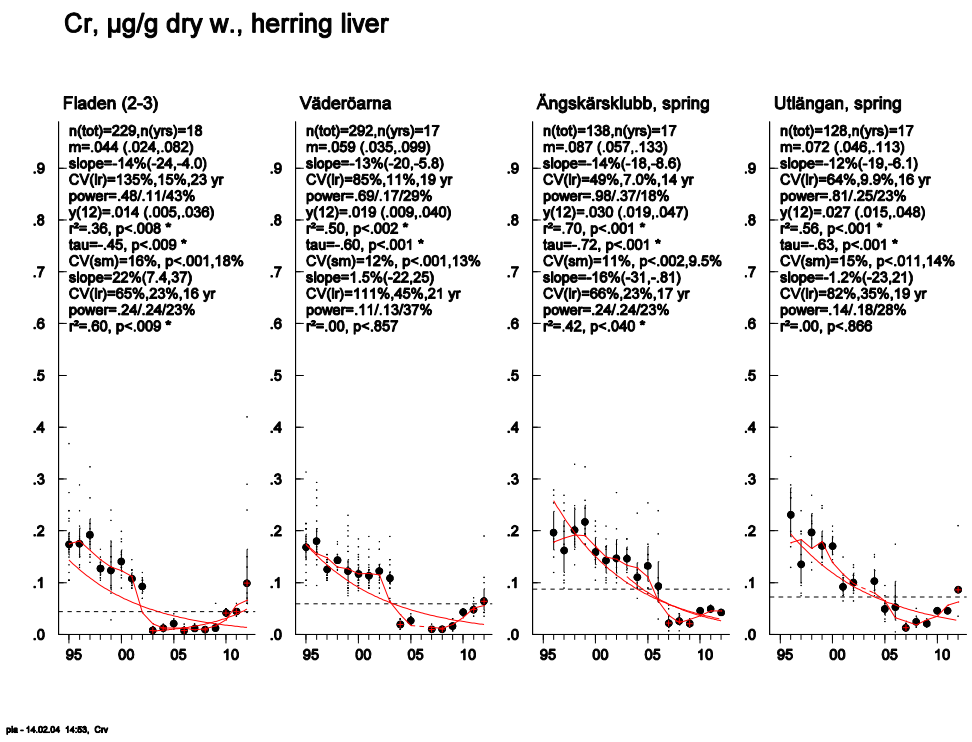


Figure 17.3. Chromium concentrations (µg/g dry weight) in herring liver from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1996, 1995 and 1995 respectively).

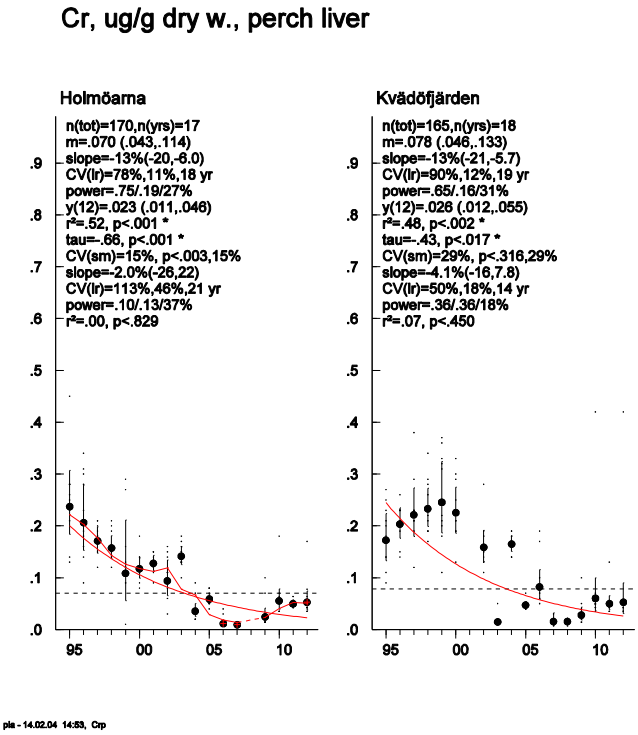


Fig. 17.4. Chromium concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

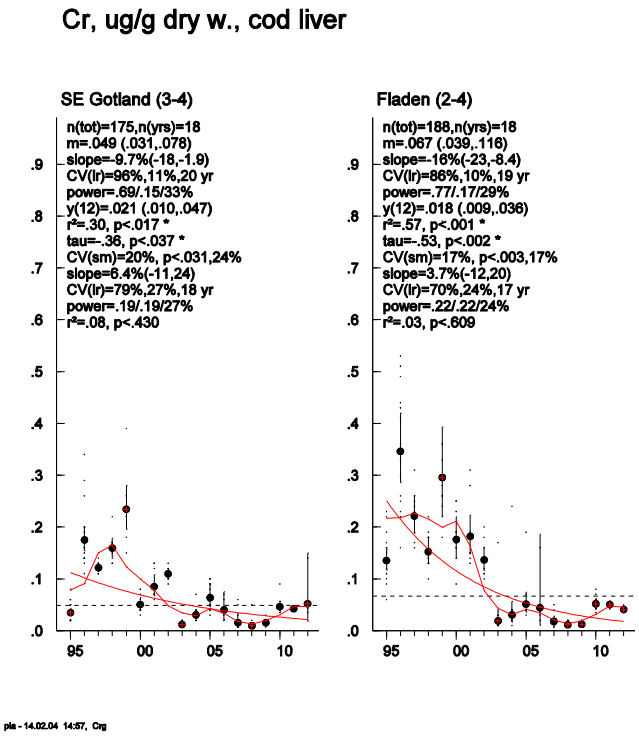


Fig. 17.5. Chromium concentrations (µg/g dry weight) in cod liver from southeast of Gotland and Fladen (time series starting in 1995).

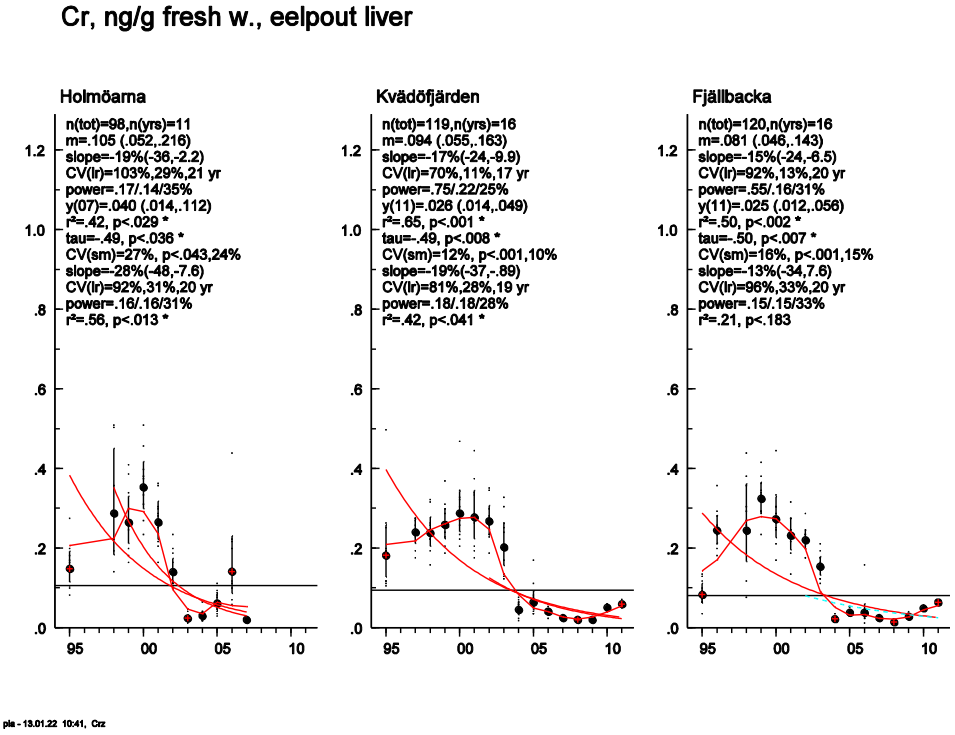


Fig. 17.6. Chromium concentrations (µg/g dry weight) in eelpout liver from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

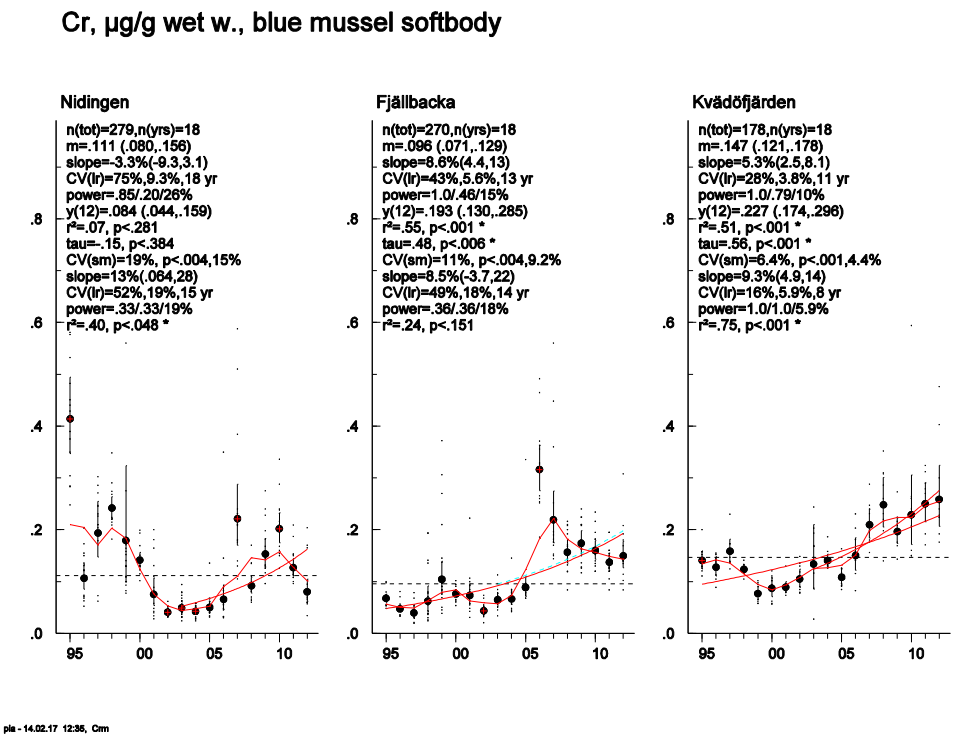


Figure 17.7. Chromium concentrations (µg/g wet weight) in blue mussel soft body from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1995).

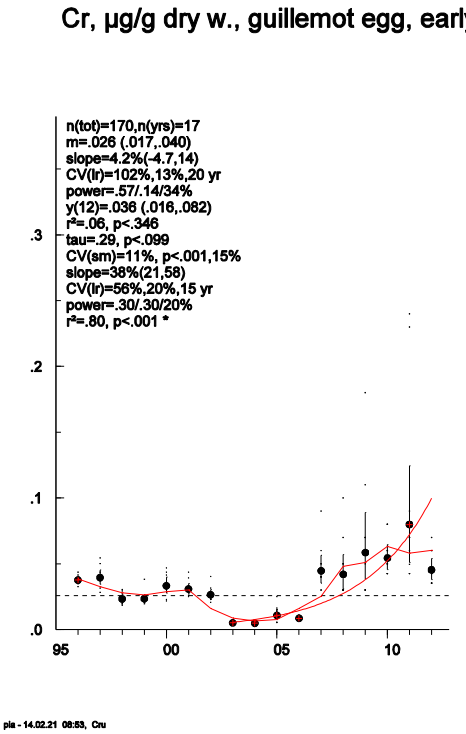


Figure 17.8. Chromium concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996)

17.4 Conclusion

Concentrations of chromium show similar levels along the Swedish coast. Visible for both fish and blue mussel.

An overall decrease of chromium concentration over time was seen across the time series for fishsince the start 1995. However for the blue mussels and the ten most recent years for guillemot eggs and herring from Ängskärsklubb, Landsort, Utlänan and Fladen the trend show increasing concentrations.

The results should be viewed with caution since the a change in method might influence the interpretation of the trends.

Table 17.1. Trend (in %) for **chromium** (µg/g dry weight, wet weight for blue mussels) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's cromium concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	230	18	95-12	-10(-16,-4.9)	.0010 --	16	21.7	.030 (.018,.052)
Harufjärden(3-5)		10	03-12	5.6(-6.6,18)	0.3226	15	18.3	
Ängskärsklubb(3-5)	226	18	95-12	-11(-19,-2.5)	0.0136	21	35.8	.021 (.009,.050)
Ängskärsklubb(3-5)		10	03-12	20(6.1,33)	.0102 +	16	20.5	
Landsort(3-5)	216	18	95-12	-9.9(-19,-.38)	0.0407	23	41.1	.023 (.009,.060)
Landsort(3-5)		10	03-12	22(5.6,39)	.0145 +	17	25.4	
Utlängan(2-4)	205	18	95-12	-12(-20,-4.1)	.0055 --	20	34.1	.020 (.009,.045)
Utlängan(2-4)		10	03-12	17(4.2,30)	.0152 +	15	19	
Ängskärsklubb spring	138	17	96-12	-14(-18,-8.6)	.0000 ---	14	17.6	.030 (.019,.047)
Ängskärsklubb spring		10	03-12	-16(-31,-.81)	0.0401	17	23.3	
Utlängan spring	128	16	96-12	-12(-19,-6.1)	.0008 ---	16	22.5	.027 (.015,.048)
Utlängan spring		9	04-12	-1.2(-23,21)	0.8664	19	28.4	
Fladen(2-3)	229	18	95-12	-14(-24,-4.0)	.0084 --	23	42.7	.014 (.005,.036)
Fladen(2-3)		10	03-12	22(7.4,37)	.0087 ++	16	22.9	
Väderöarna	292	17	95-12	-13(-20,-5.8)	.0017 --	19	29.3	.019 (.009,.040)
Väderöarna		9	03-12	1.5(-22,25)	0.8567	21	36.6	
Perch muscle								
Holmöarna	170	17	95-12	-13(-20,-6.0)	.0012 --	18	27	.023 (.011,.046)
Holmöarna		9	03-12	-2.0(-26,22)	0.8293	21	37.2	
Kvädöfjärden	165	17	95-12	-13(-21,-5.7)	.0020 --	19	30.7	.026 (.012,.055)
Kvädöfjärden		10	03-12	-4.1(-16,7.8)	0.4502	14	17.8	
Cod liver								
SE Gotland(3-4)	175	18	95-12	-9.7(-18,-1.9)	0.0169	20	32.6	.021 (.010,.047)
SE Gotland(3-4)		10	03-12	6.4(-11,24)	0.43	18	27.5	
Fladen(2-4)	188	18	95-12	-16(-23,-8.4)	.0003 ---	19	29.5	.018 (.009,.036)
Fladen(2-4)		10	03-12	3.7(-12,20)	0.6093	17	24.5	
Eelpout muscle								
Holmöarna	98	11	95-07	-19(-36,-2.2)	0.0295	21	34.6	.040 (.014,.112)
Holmöarna		10	98-07	-28(-48,-7.6)	0.0127	20	31.5	
Kvädöfjärden	119	16	95-11	-17(-24,-9.9)	0.0002	17	24.5	.026 (.014,.049)
Kvädöfjärden		10	02-11	-19(-37,-.89)	0.0406	19	28.2	
Fjällbacka	120	16	95-11	-15(-24,-6.5)	0.0023	20	31.3	.025 (.012,.056)
Fjällbacka		10	02-11		N.S.	20	32.6	
Blue mussel								

Nidingen	279	18	95-12	-3.4(-9.8,3.0)	0.281	18	29.9	.111 (.080,.156) m
Nidingen		10	03-12	13(.064,25)	.0476 +	15	20.6	
Fjällbacka	270	18	95-12	8.2(4.3,12)	.0005 +++	13	16.5	.193 (.130,.285)
Fjällbacka		10	03-12	8.1(-3.7,20)	0.1506	14	19.4	
Kvädöfjärden	178	18	95-12	5.1(2.5,7.8)	.0009 +++	11	10.7	.227 (.174,.296)
Kvädöfjärden		10	03-12	8.9(4.8,13)	.0012 ++	8	6.04	
Guillemot egg								
St.Karlsö	170	17	96-12	4.1(-4.8,13)	0.3459	20	40.6	.026 (.017,.040) m
St.Karlsö		10	03-12	32(19,45)	.0006 +++	15	21.9	

18 Copper - Cu

Updated 14.02.28

18.1 Introduction

18.1.1 Usage, Production and Sources

Copper is a nutritionally essential metal, and the concentration is regulated by homeostatic mechanisms. Free copper is effectively controlled by metallothionein synthesis (da Silva & Williams 1994) induced by copper itself 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.

Copper occurs naturally in rocks, soil, water, sediment and at low levels in air. In its natural (metallic) form, copper can be found in electrical wiring and some water pipes, for example, plumbing, building wire, telecommunications, automotive electrical wiring and air conditioning systems (Dorsey et al. 2004). Copper compounds can be found in alloys such as brass and bronze. Other anthropogenic sources include road run off (Rice et al. 2002) and mining of copper ore. Copper compounds can be commonly found in use in agriculture as fungicides, as wood, leather and fabric preservative, or for water treatment (Dorsey et al. 2004).

18.1.2 Conventions, Aims and Restrictions

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

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

18.1.3 Target Levels

No national target level for biota is agreed upon for Cu.

Average copper concentrations in the earth's crust is 50 ppm (Dorsey et al. 2004). The 'background concentration at diffuse loading' in blue mussels for copper is <10 μg/g dry weight, proposed by Knutzen and Skie (1992).

18.2 Methods

18.2.1 Analytical Information

Please note that since 2007, the analytical laboratory for metals changed from the Swedish University of Agricultural Sciences (SLU) to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

18.3 Results

18.3.1 Spatial variation

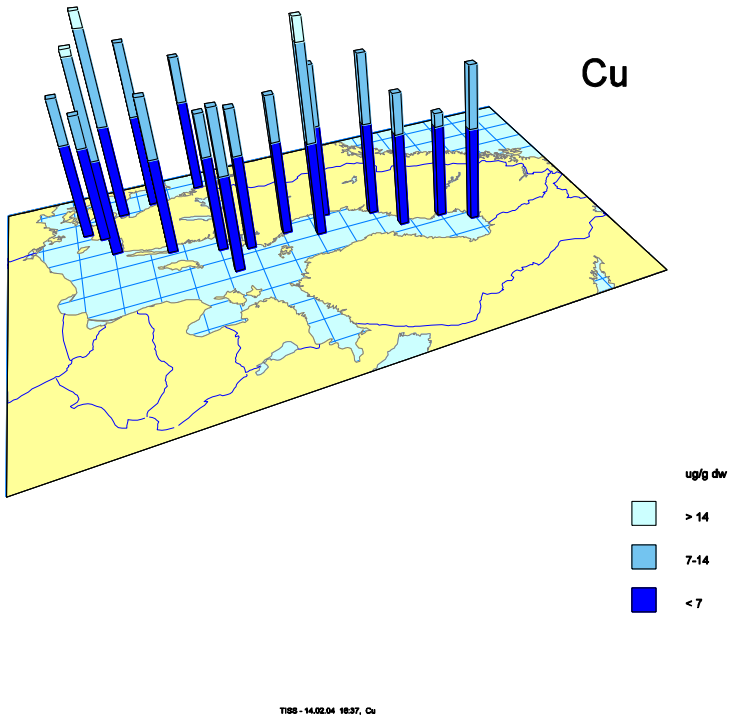


Figure 18.1. Spatial variation in copper concentrations (ug/g dry weight) in herring liver.

No general differences in mean copper concentrations were found in herring along the Swedish coast. The highest concentrations (around 15 ug/g dw) were found at the Bothnian sea offshore site, Utlängan, and Kullen (Fig 18.1).

Eelpout from Fjällbacka had almost three times as high copper concentrations compared to eelpout from Kvädöfjärden (Fig. 18.6).

Blue mussels from the west coast had slightly lower copper concentrations compared to mussels from Kvädöfjärden. The copper concentrations in blue mussels from the Swedish west coast was at comparable levels to blue mussel samples of similar length from a

reference site at Kobbefjord, Greenland (Riget et al. 1993) and showed mean levels below the 'high background concentration at diffuse loading' in blue mussels for copper of <10 µg/g dry weight, proposed by Knutzen and Skie (1992). However, for blue mussels from Kvädöfjärden the copper concentration was 10 µg/g dry weight.

18.3.2 Temporal variation

Decresing trends of copper concentrations were seen for herring from Fladen (Fig. 18.3) and eelpout from Kvädöfjärden (Fig. 18.6). No other general trend was seen for copper concentration in fish.However for blue mussels, all stations (Nidingen, Fjällbacka and Kvädöfjärden) showed significantly decreasing trends (Fig. 18.7).

The number of years required to detect an annual change of 10% varied between 7 - 12 years for the herring time series at a power of 80%.

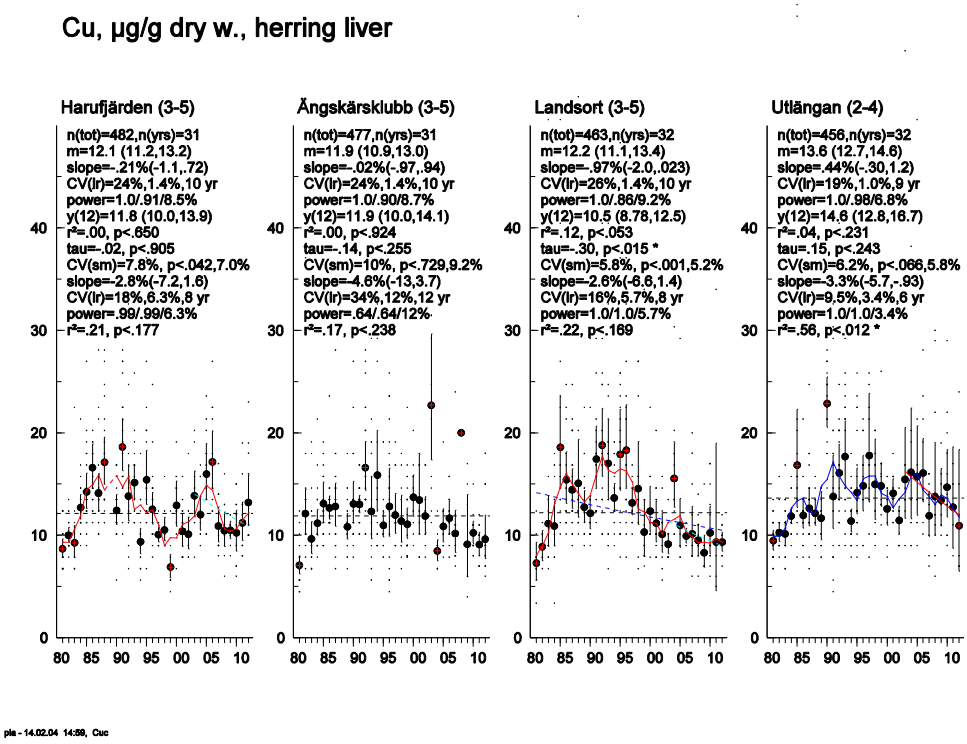


Figure 18.2. Copper concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981).

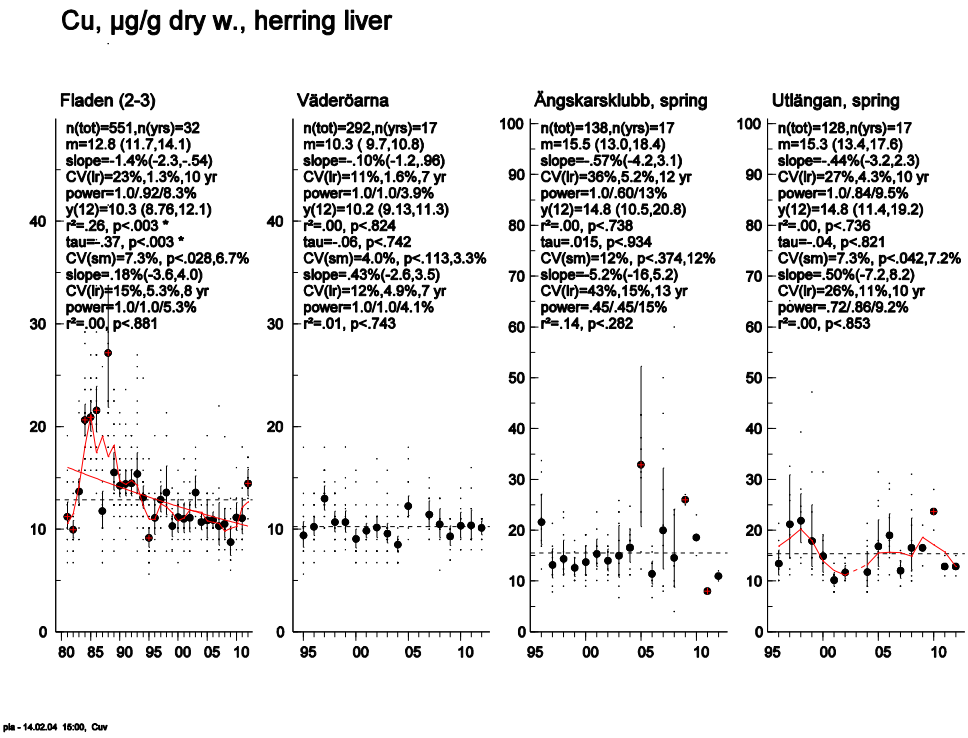


Figure 18.3. Copper concentrations (µg/g dry weight) in herring liver from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1996, 1981 and 1995 respectively).

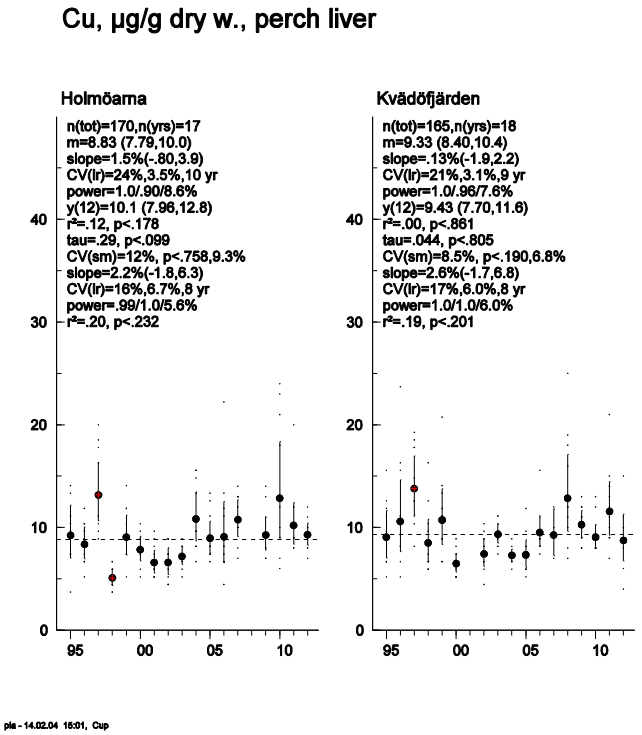


Figure 18.4. Copper concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

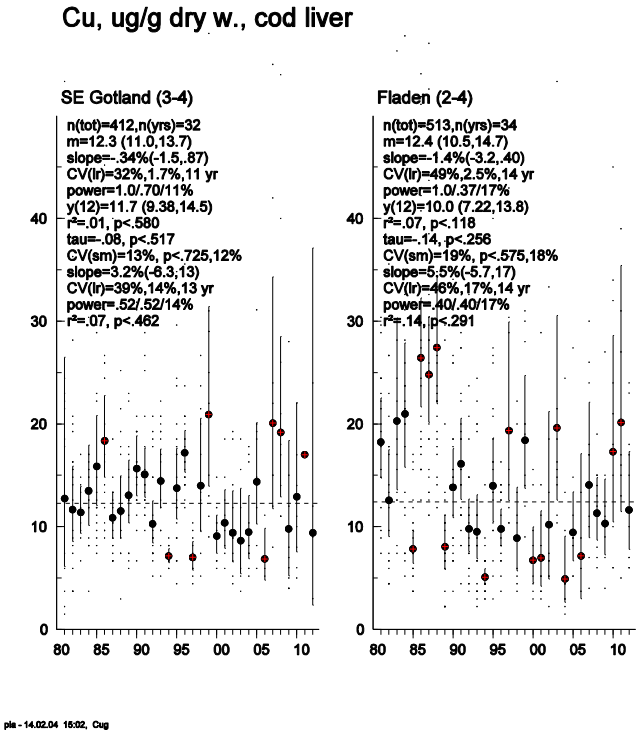


Fig. 18.5. Copper concentrations (µg/g dry weight) in cod liver from southeast of Gotland and Fladen (time series starting in 1980).

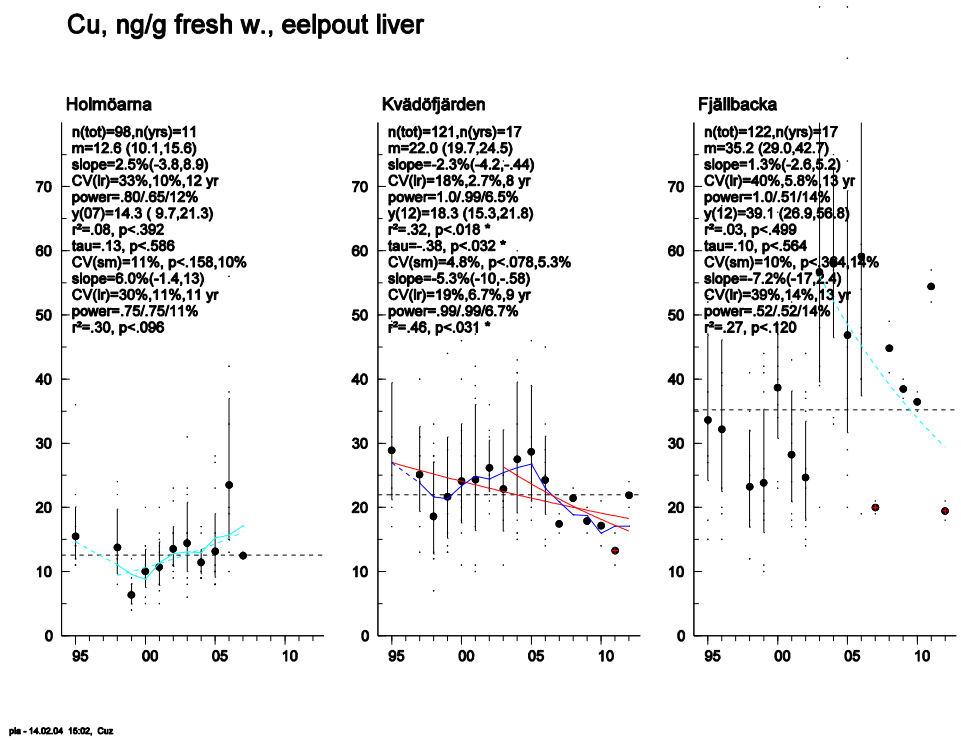


Fig. 18.6. Copper concentrations (µg/g dry weight) in eelpout liver from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

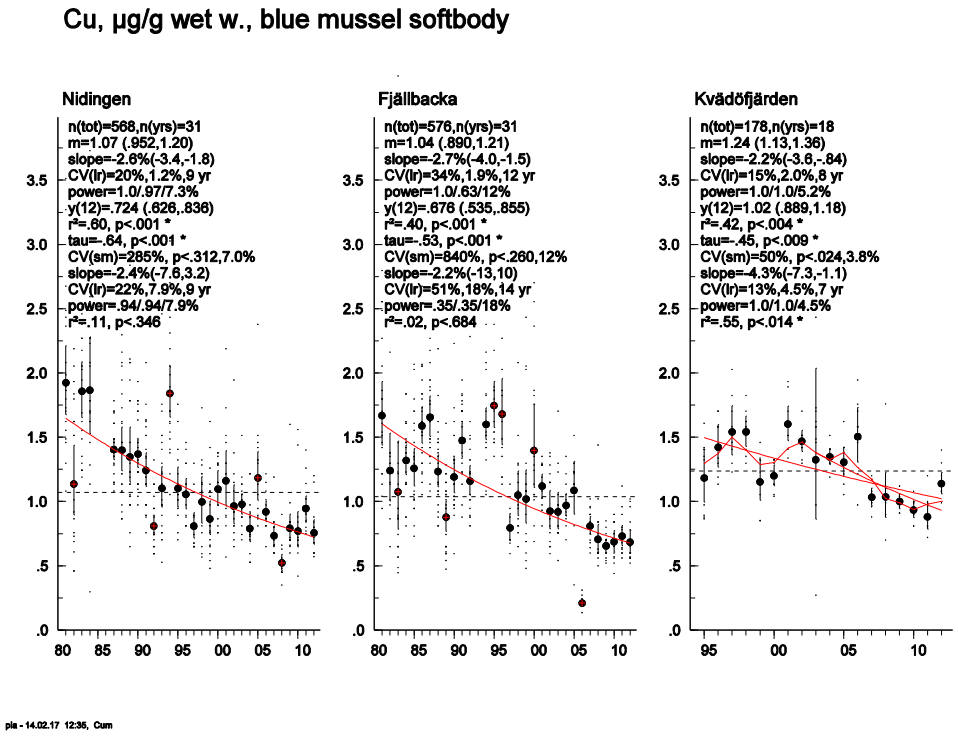


Figure 18.7. Copper concentrations (µg/g wet weight) in blue mussel soft body from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1981, 1981 and 1995 respectively).

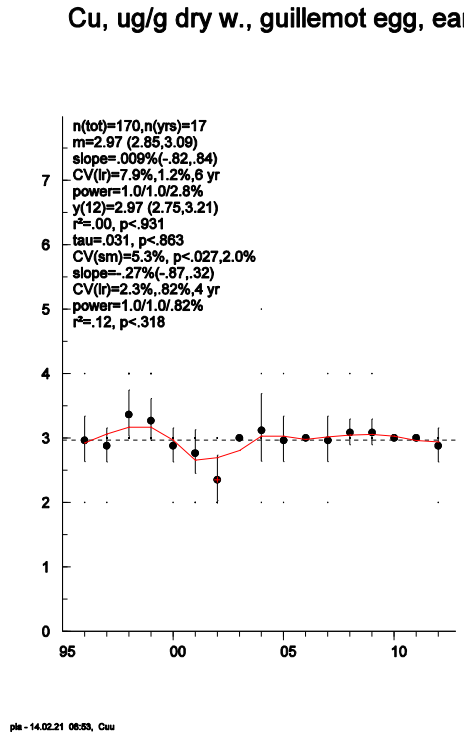


Figure 18.8. Copper concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996).

18.3.3 Species differences

Differences in mean copper concentrations (µg/g dry weight) between species.

Holmöarna: Eelpout (12.6) > Perch (8.83)
Kvädöfjärden: Eelpout (18.3) > Perch (9.33) - Blue mussel (8.2)
Fladen/Nidingen: Herring (10.3) –_Cod (12.4) > Blue mussel (3.9)
Väderöarna/Fjällbacka: Eelpout (35.2) > Herring (10.3) > Blue mussel (4.5)

The concetrations in blue mussels are lower than fish liver samples at all stations. The concentration of copper is almost three times as high in eelpout from Fjällbacka compared to Holmöarna and Kvädöfjärden. There is no difference in copper concentration between spring and autumn-caught herring from Utlängan and Ängskärsklubb.

18.4 Conclusion

There was no significant spatial variation in copper concentrations in herring liver. Copper concentrations in blue mussels showed no significant difference to blue mussels examined in Kobbefjord, Greenland (Riget et al. 1993).

In general, most time trend series do not show any log-linear trends over the monitored period. However the blue mussels, with decreasing copper concentrations at all three stations and herring from Fladen and eelpout from Kvädöfjärden with decreasing concentrations are the exceptions from this general view.
Copper concentrations in *liver* from Baltic herring are about 4.5 times higher than the concentrations reported from the edible parts of herring. For cod, the concentrations in liver are about 40 - 60 times higher, and for perch about 12 - 14 times. Concentrations in edible parts are reported by Jorhem and Sundström (1993).

Table 18.1. Trend (in %) for **copper** (µg/g dry weight, wet weight for blue mussels) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's copper concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	482	31	81-12	-.21(-1.1,.72)	0.6499	10	8.54	12.1 (11.2,13.2) m
Harufjärden(3-5)		10	03-12	-2.8(-7.2,1.6)	0.1768	8	6.25	
Ängskärsklubb(3-5)	477	31	81-12	-.02(-.97,.94)	0.9242	10	8.7	11.9 (10.9,13.0) m
Ängskärsklubb(3-5)		10	03-12	-4.6(-13,3.7)	0.2377	12	12.1	
Landsort(3-5)	463	32	81-12	-.97(-2.0,.023)	0.0526	10	9.21	10.5 (8.78,12.5)
Landsort(3-5)		10	03-12	-2.6(-6.6,1.4)	0.1686	8	5.68	
Utlängan(2-4)	456	32	81-12	.44(-.30,1.2)	0.2313	9	6.81	13.6 (12.7,14.6) m
Utlängan(2-4)		10	03-12	-3.3(-5.7,-.93)	0.0125	6	3.36	
Ängskärsklubb spring	138	17	96-12	-.57(-4.2,3.1)	0.7376	12	12.8	15.5 (13.0,18.4) m
Ängskärsklubb spring		10	03-12	-5.2(-16,5.2)	0.2819	13	15.4	
Utlängan spring	128	16	96-12	-.44(-3.2,2.3)	0.7364	10	9.5	15.3 (13.4,17.6) m
Utlängan spring		9	04-12	.50(-7.2,8.2)	0.8534	10	9.17	
Fladen(2-3)	551	32	81-12	-1.4(-2.3,-.54)	.0028 --	10	8.31	10.3 (8.76,12.1)
Fladen(2-3)		10	03-12	.18(-3.6,4.0)	0.8813	8	5.34	
Väderöarna	292	17	95-12	-.10(-1.2,.96)	0.8241	7	3.86	10.3 (9.7,10.8) m
Väderöarna		9	03-12	.43(-2.6,3.5)	0.7434	7	4.08	
Perch muscle								
Holmöarna	170	17	95-12	1.5(-.80,3.9)	0.1778	10	8.58	8.83 (7.79,10.0) m
Holmöarna		9	03-12	2.2(-1.8,6.3)	0.2322	8	5.56	
Kvädöfjärden	165	17	95-12	.13(-1.9,2.2)	0.8615	9	7.6	9.33 (8.40,10.4) m
Kvädöfjärden		10	03-12	2.6(-1.7,6.8)	0.2006	8	6.04	
Cod liver								
SE Gotland(3-4)	412	32	81-12	-.34(-1.5,.87)	0.58	11	11.3	12.3 (11.0,13.7) m
SE Gotland(3-4)		10	03-12	3.2(-6.3,13)	0.4621	13	14	
Fladen(2-4)	513	32	81-12	-1.4(-3.2,.40)	0.1177	14	17.4	12.4 (10.5,14.7) m
Fladen(2-4)		10	03-12	5.5(-5.7,17)	0.2906	14	16.6	
Eelpout muscle								
Holmöarna	98	11	95-07	2.5(-3.8,8.9)	0.3915	12	11.9	12.6 (10.1,15.6) m
Holmöarna		10	98-07	6.0(-1.4,13)	0.0958	11	10.7	
Kvädöfjärden	121	17	95-12	-2.3(-4.2,-.44)	0.0181	8	6.5	18.3 (15.3,21.8)
Kvädöfjärden		10	03-12	-5.3(-10,-.58)	0.0312	9	6.71	
Fjällbacka	122	17	95-12	1.3(-2.6,5.2)	0.4992	13	14.3	35.2 (29.0,42.7) m
Fjällbacka		10	03-12	-7.2(-17,2.4)	0.1196	13	14	
Blue mussel								

Nidingen	568	30	81-12	-2.7(-3.5,-1.8)	.0000 ---	9	7.59	.724 (.626,.836)
Nidingen		10	03-12	-2.4(-8.0,3.1)	0.3455	9	8.21	
Fjällbacka	576	31	81-12	-2.8(-4.1,-1.5)	.0002 ---	12	13.1	.676 (.535,.855)
Fjällbacka		10	03-12	-2.2(-14,9.9)	0.684	14	19.8	
Kvädöfjärden	178	18	95-12	-2.2(-3.6,-.84)	.0037 --	8	5.35	1.02 (.889,1.18)
Kvädöfjärden		10	03-12	-4.4(-7.6,-1.2)	0.0138	7	4.63	
Guillemot egg								
St.Karlsö	170	17	96-12	.009(-.82,.84)	0.9311	6	2.83	2.97 (2.85,3.09) m
St.Karlsö		10	03-12	-.28(-.87,.32)	0.318	4	0.823	

19 Zinc - Zn

Updated 14.02.28

The zinc concentration time series in fish liver and blue mussel soft body, presented below, started in 1981.

19.1 Introduction

19.1.1 Usage, Production and Sources

Zinc is a nutritionally essential metal naturally present in some foods. It is a biological requirement for many animals and plants (Zinc factsheet 2011). Zinc concentration is regulated by homeostatic mechanisms. Hence, it is not believed to *accumulate* with continued exposure, but changes found in biological tissues may still reflect changes in concentrations of the ambient water. Zinc occurs naturally in the environment, but most zinc comes from human activities such as mining, steel production and coal burning. In its pure form, anthropogenic sources of zinc can include its use in galvanising steel and iron to prevent rust and corrosion; it is mixed with other metals to form alloys such as brass and bronze; and it is used to make dry cell batteries (Draggan 2008). Zinc compounds are used in industries e.g. for making white paints and ceramics, producing rubber, preserving wood and dyeing fabrics (Draggan 2008). Tyre tread material contains approximately 1% weight of zinc. Wear of tyres on road surfaces can contribute a small amount of zinc to the environment (Councell et al. 2004). Some sunscreens use zinc oxide nanoparticles (Osmond & McCall 2010); other zinc compounds can be found in for example, deodorants, nappy rash cream and anti-dandruff shampoo (Draggan 2008).

19.1.2 Environmental Fate

Zinc is present in water, air and soil. In air, zinc is present mostly as small particles that fall to the earth and drain into waterways with precipitation. Most of this zinc ends up settling in sediment at the bottom of water bodies; however some zinc can remain bound to the soil. Dissolved zinc in water can increase acidity levels (Draggan 2008).

19.1.3 Conventions, Aims and Restrictions

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

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

19.1.4 Target level

No national target level for biota is agreed upon for Zn.

19.2 Methods

19.2.1 Analytical Information

Please note that since 2007, the analytical laboratory for metals changed from the Swedish University of Agricultural Sciences (SLU) to the Department of Applied Environmental Science (ITM) at Stockholm University. See chapter 6 section 6.1 for further details.

19.3 Results

19.3.1 Spatial variation

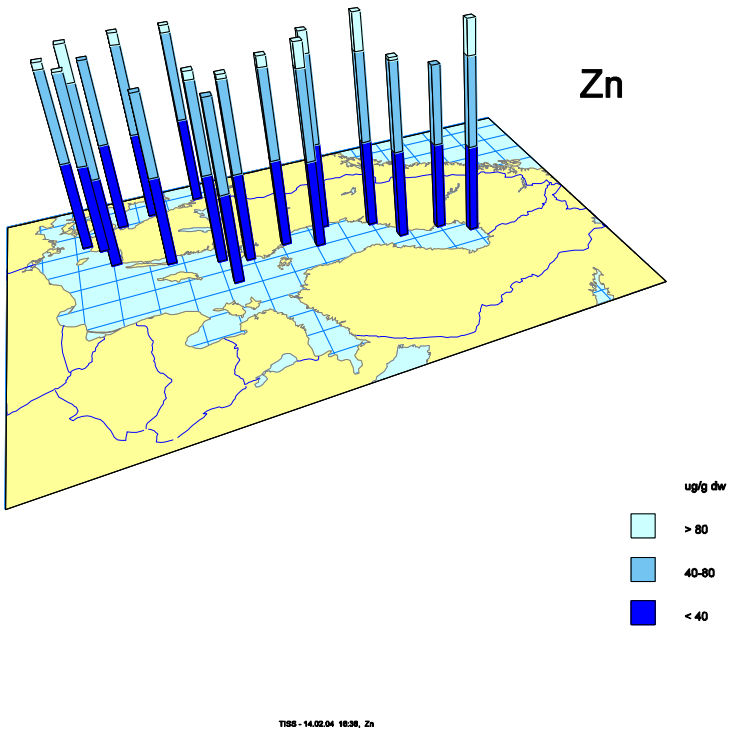


Figure 19.1. Spatial variation in zinc concentrations (ug/g dry weight) in herring liver.

In herring, no differences in mean zink concentrations were found between the sampling sites in the years 2010-2012 The highest concentration of zink was found at Gaviksfjärden (Fig 19.1).

Zinc concentration in cod liver from Fladen was twice as high as in cod liver from southeast of Gotland (table 19.1). The significantly lower fat content in cod liver from Fladen may explain this, since zinc concentrations are negatively correlated with fat content.

Zinc concentrations in blue mussels from all three investigated sites were below the proposed background concentrations for the North Sea (ICES, 1997) (table 19.1).

19.3.2 Temporal Variation

Significant decreasing trends were seen in herring liver from Ängskärsklubb (spring) (Fig. 19.3), cod liver from Fladen (Fig. 19. 5) and in blue mussel soft body tissue from Nidingen and Kvädöfjärden (Fig. 19.7).for the whole monitored period.
Significantly increasing trends were seen for herring from Utlängan for the whole monitored period and for herring from Landsort and Fladen during the 10 most recent years (Fig. 19.2 and 19.3).

The number of years required to detect an annual change of 10% varied between 7 - 9 years for the herring time series, with a power of 1.0 to detect a 10% annual change for all of the herring time series.

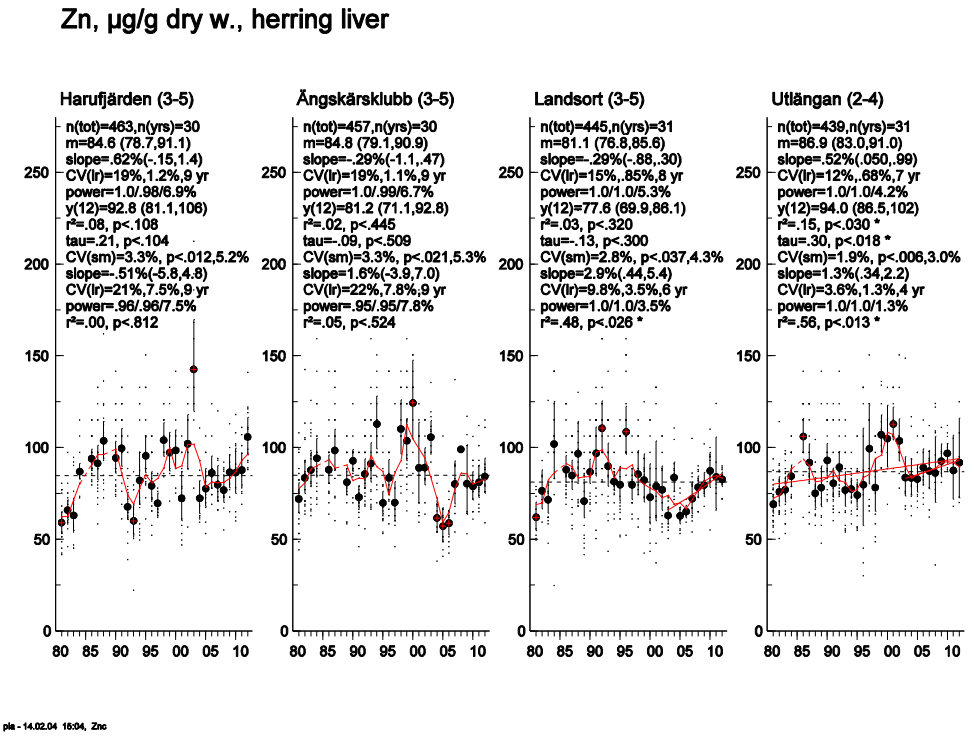


Figure 19.2. Zinc concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981).

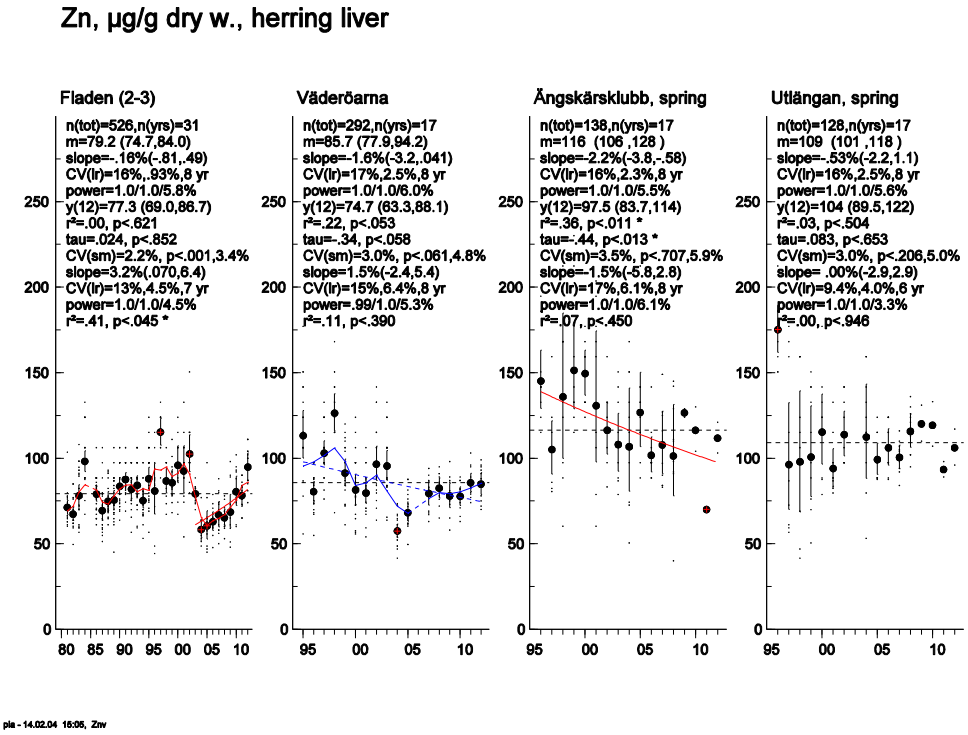


Figure 19.3. Zinc concentrations (µg/g dry weight) in herring liver from Ängskärsklubb (spring), Utlängan (spring), Fladen and Fjällbacka (time series starting in 1996, 1996, 1981 and 1995 respectively).

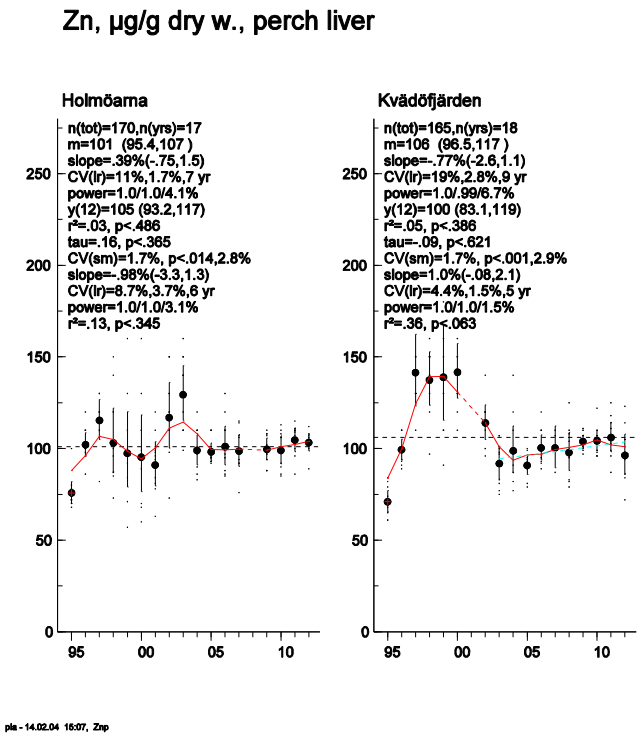


Fig. 19.4. Zinc concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

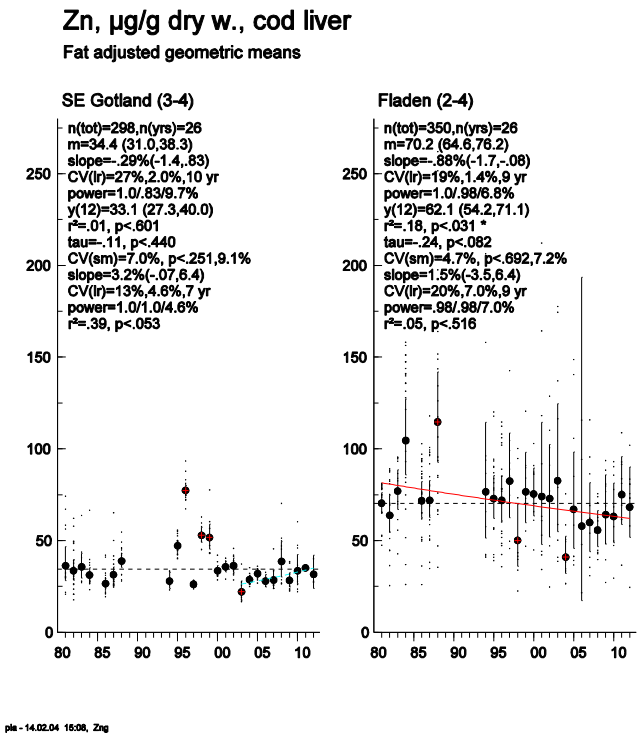


Figure 19.5. Zinc concentrations (µg/g dry weight) in cod liver from southeast Gotland and Fladen (time series starting in1981).

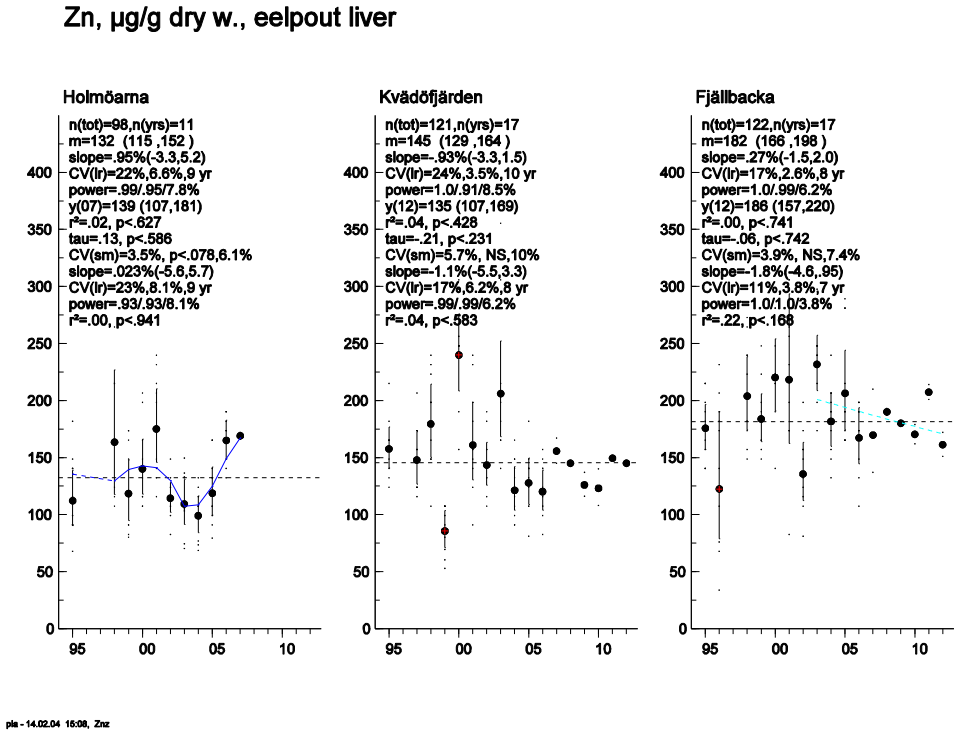


Fig. 19.6. Zinc concentrations (µg/g dry weight) in eelpout liver from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

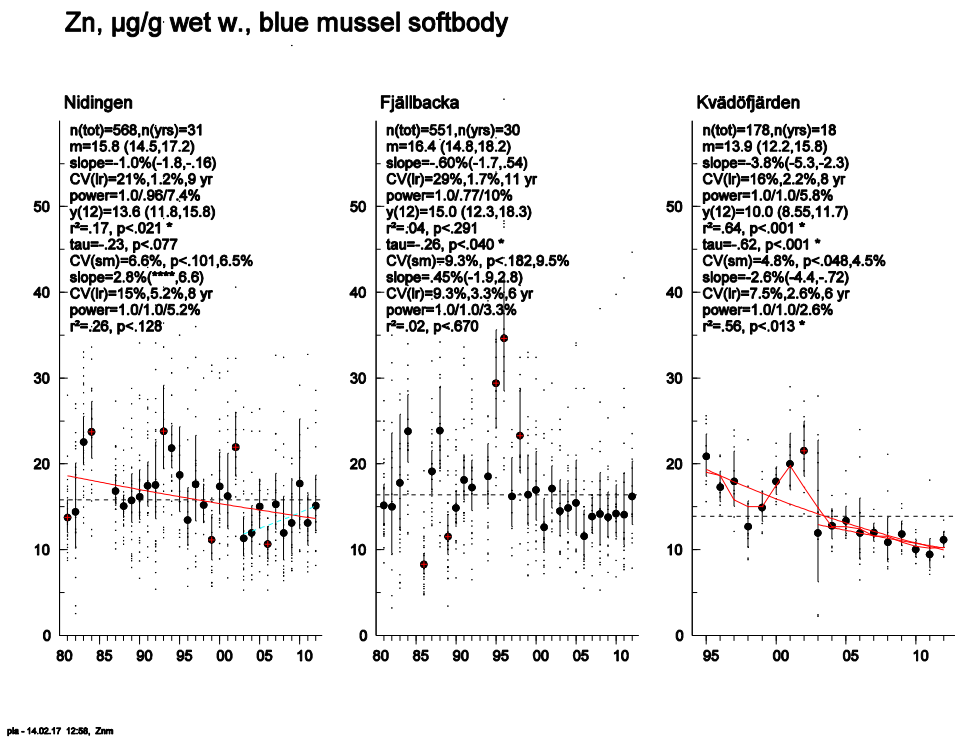


Figure 19.7 Zinc concentrations (µg/g wet weight) in blue mussel soft body from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1981, 1981 and 1995 respectively).

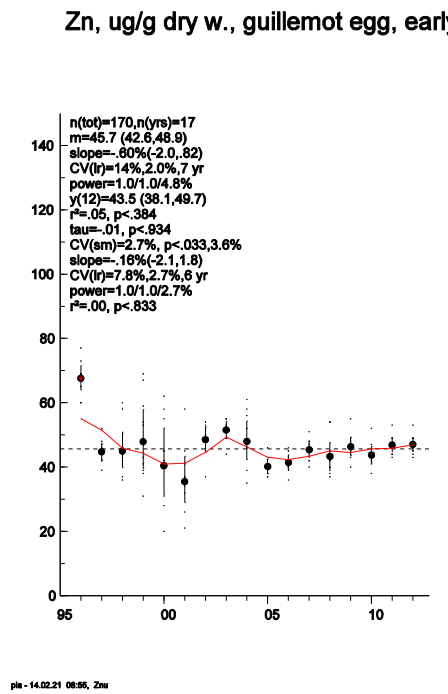


Figure 19.8 Zinc concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996).

19.3.3 Species Differences

Differences in mean zinc concentrations (µg/g dry weight) between different species.

Holmöarna: Eelpout (132) > Perch (101)
Kvädöfjärden: Eelpout (145) > Perch (106) > Blue mussel (80)
Fladen/Nidingen: Blue mussel (73) - Herring (79.2) – Cod (62.1)
Väderöarna/Fjällbacka: Eelpout (182) > Blue mussel (110) > Herring (74.7)

The concentrations in spring-caught herring from Ängskärsklubb and Utlängan were somewhat higher compared to samples from the same areas in the autumn (table 19.1).

19.4 Conclusion

No significant differences in zinc concentrations were observed in herring between sampling sites in the Baltic Sea and the Swedish west coast. Zinc concentrations in liver from Baltic herring are about 1.5 times higher than that reported from the edible parts of herring. For cod, the concentrations in the liver are about 6 - 8 times higher, and for perch about 3.5 times. Concentrations in edible parts are reported by Jorhem and Sundström (1993).

Zinc concentration in blue mussels from the Swedish west coast was not significantly different compared to blue mussel samples of similar length from a reference site at Kobbefjord, Greenland (Riget et al. 1993).

Over time, zinc concentrations have been inconsistent between fish species, with some significant increases and decreases seen between sites.

Table 19.1. Trend (in %) for **zinc** (µg/g dry weight, wet weight for blue mussels)) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's zink concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	463	30	81-12	.62(-.15,1.4)	0.1076	9	6.87	84.6 (78.7,91.1) m
Harufjärden(3-5)		10	03-12	-.51(-5.8,4.8)	0.8124	9	7.53	
Ängskärsklubb(3-5)	457	30	81-12	-.29(-1.1,.47)	0.4446	9	6.72	84.8 (79.1,90.9) m
Ängskärsklubb(3-5)		10	03-12	1.6(-3.9,7.0)	0.5242	9	7.77	
Landsort(3-5)	445	31	81-12	-.29(-.88,.30)	0.3202	8	5.26	81.1 (76.8,85.6) m
Landsort(3-5)		10	03-12	2.9(.44,5.4)	.0258 +	6	3.47	
Utlängan(2-4)	439	31	81-12	.52(.050,.99)	.0298 +	7	4.16	94.0 (86.5,102)
Utlängan(2-4)		10	03-12	1.3(.34,2.2)	.0130 +	4	1.26	
Ängskärsklubb spring	138	17	96-12	-2.2(-3.8,-.58)	0.011	8	5.54	97.5 (83.7,114)
Ängskärsklubb spring		10	03-12	-1.5(-5.8,2.8)	0.4496	8	6.11	
Utlängan spring	128	16	96-12	-.53(-2.2,1.1)	0.5041	8	5.55	109 (101 ,118) m
Utlängan spring		9	04-12	.00(-2.9,2.9)	0.9464	6	3.33	
Fladen(2-3)	526	31	81-12	-.16(-.81,.49)	0.6211	8	5.78	79.2 (74.7,84.0) m
Fladen(2-3)		10	03-12	3.2(.070,6.4)	.0448 +	7	4.45	
Väderöarna	292	17	95-12	-1.6(-3.2,.041)	0.053	8	6.01	74.7 (63.3,88.1)
Väderöarna		9	03-12	1.5(-2.4,5.4)	0.3905	8	5.29	
Perch muscle								
Holmöarna	170	17	95-12	.39(-.75,1.5)	0.4864	7	4.07	101 (95.4,107) m
Holmöarna		9	03-12	-.98(-3.3,1.3)	0.3448	6	3.09	
Kvädöfjärden	165	17	95-12	-.77(-2.6,1.1)	0.386	9	6.71	106 (96.5,117) m
Kvädöfjärden		10	03-12	1.0(-.08,2.1)	0.063	5	1.54	
Cod liver								
SE Gotland(3-4)	298	26	81-12	-.29(-1.4,.83)	0.6007	10	9.7	34.4 (31.0,38.3) m
SE Gotland(3-4)		10	03-12	3.2(-.07,6.4)	0.0527	7	4.56	
Fladen(2-4)	350	26	81-12	-.88(-1.7,-.08)	0.0314	9	6.81	62.1 (54.2,71.1)
Fladen(2-4)		10	03-12	1.5(-3.5,6.4)	0.516	9	7.04	
Eelpout muscle								
Holmöarna	98	11	95-07	.95(-3.3,5.2)	0.627	9	7.78	132 (115 ,152) m
Holmöarna		10	98-07	.023(-5.6,5.7)	0.9405	9	8.08	
Kvädöfjärden	121	17	95-12	-.93(-3.3,1.5)	0.4279	10	8.47	145 (129 ,164) m
Kvädöfjärden		10	03-12	-1.1(-5.5,3.3)	0.5827	8	6.19	
Fjällbacka	122	17	95-12	.27(-1.5,2.0)	0.7412	8	6.21	182 (166 ,198) m
Fjällbacka		10	03-12	-1.8(-4.6,.95)	0.1682	7	3.85	
Blue mussel								

Nidingen	568	30	81-12	-1.0(-1.9,-.16)	0.0207	9	7.72	13.6 (11.8,15.8)
Nidingen		10	03-12	2.7(-1.0,6.4)	0.1281	8	5.37	
Fjällbacka	551	30	81-12	-.60(-1.7,.54)	0.2913	11	10.9	16.4 (14.8,18.2) m
Fjällbacka		10	03-12	.45(-1.9,2.8)	0.6701	6	3.33	
Kvädöfjärden	178	18	95-12	-3.9(-5.4,-2.3)	.0001 ---	8	5.95	10.0 (8.55,11.7)
Kvädöfjärden		10	03-12	-2.6(-4.5,-.72)	0.0128	6	2.69	
Guillemot egg								
St.Karlsö	170	17	96-12	-.60(-2.0,.82)	0.3835	7	4.94	45.7 (42.6,48.9) m
St.Karlsö		10	03-12	-.16(-2.1,1.8)	0.8333	6	2.78	

20 Arsenic - As

Updated 14.02.28

20.1 Introduction

20.1.1 Uses, Production and Sources

Arsenic is a natural component of the earth's crust, and found in all environmental media (WHO 2001). Major anthropogenic sources of environmental arsenic contamination are via industrial smelters, coal-fired power plants and production and use of arsenic pesticides and herbicides (Eisler 1994). An estimation of world arsenic production showed that copper chrome arsenate (CCA) used in timber treatment accounts for most arsenic use; however, this source has recently decreased due to new arsenic compound regulations, which has seen the industry sector turn to arsenic-free preparations (KEMI).

Elemental arsenic is produced by reduction of arsenic trioxide (As_2O_3) with charcoal, which in turn is produced as a by-product of metal smelting operations, especially in copper smelting (WHO 2001) (Eisler 2007). Sweden was the world's leading producer of arsenic trioxide, with ore from the Boliden area containing the highest levels of arsenic (Eisler 2007) (SGU). Dumped chemical munitions from the end of World War II possibly contribute to increased arsenic levels in the Baltic Sea, Skagerakk and Kattegat environment (HELCOM 2010) (OSPAR 2005) (Garnaga et al. 2006).

Marine organisms tend to contain much higher levels of arsenic compared to terrestrial and freshwater organisms. This is due to a low phosphate concentration resulting in a high arsenate:phosphate ratio. The main type of arsenic accumulated in marine organisms is a water-soluble form called arsenobetaine (WHO 2001). This form has a low toxicity and is quickly excreted via urine (SGU 2005) (Eisler 2007).

20.1.2 Toxic Effects

Acute, sub-acute and chronic arsenic effects can involve a number of organ systems, including the respiratory, gastrointestinal, cardiovascular, nervous, and haematopoietic systems and disturbance of liver function, which has been observed in both humans and animals after chronic exposure. Evidence of affects on the heart has been found in humans (WHO 1981).

In general, inorganic arsenic is more toxic than organic arsenic to aquatic biota, with trivalent species being more toxic than pentavalent. The toxic effects are modified by numerous biological factors such as water temperature, pH, organic content, phosphate concentration, suspended solids and the presence of other substances and toxicants (Eisler 1994). Arsenic from water bioaccumulates in aquatic organisms, but there has been no evidence of biomagnification in the food web (Eisler 1994) (SGU 2005).

20.1.3 Conventions, Aims and Restrictions

Restrictions on the use of arsenic as a wood preservative are described in Annex XVII of the EU Regulation (EC) 1907/2006 on the Registration, Evaluation and

Authorisation of Chemicals (REACH).

COMMISSION DIRECTIVE 2006/139/EC (20th December 2006) amending Council Directive 76/769/EEC in regards to restrictions on the marketing and use of arsenic compounds for the purpose of adapting Annex I to technical progress, states that arsenic compounds may not be used in the EU as substances and constituents of preparations intended for, amongst other things, the preservation of wood. Wood treated with arsenic compounds may not be sold on the EU market.

20.1.4 Target Levels

No national target level for biota is agreed upon for As.

Concentrations in water are usually < 10 µg/l (WHO 2001). Average levels of arsenic in seawater at a salinity of 35 ppm is 2.6 - 3 µg. (SGU 2005). Dissolved arsenic in seawater collected in 1983 from the Baltic Sea was on average 0.76 µg/l, with a range from 0.45 - 1.11 µg/l (Stoeppler et al. 1986).

Within Sweden the natural mean levels of arsenic in sediment is 10 mg/kg dry weight, with variations of 5 - 20 mg/kg dry weight (SGU 2005).

In a study of marine species from the coast of Bohus, the mean concentration of arsenic measured in blue mussels was 10 mg/kg, with a range from 0.39 - 19 dry weight; in eelpout, the mean concentration was 11 mg/kg, with a range from 9 – 13 mg/kg; and in cod liver, the mean concentration was 19 mg/kg with a range from 5 – 37 mg/kg.

20.2 Methods

20.2.1 Analytical Information

Arsenic has only been analysed for a few years within the national Swedish monitoring programme (2007 onwards). See chapter 6 section 6.1 for further details.

20.3 Results

20.3.1 Spatial Variation

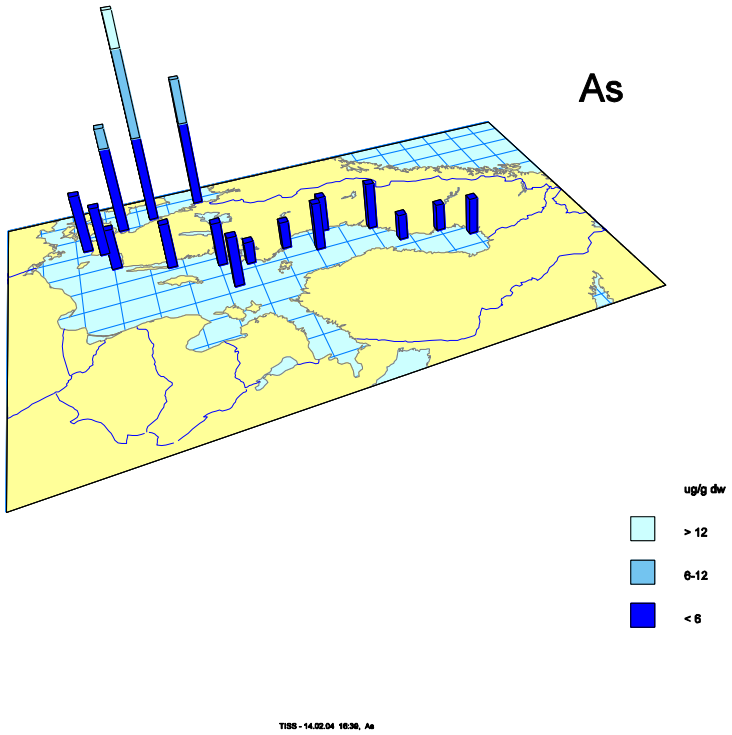


Figure 20.1. Spatial variation in arsenic concentrations (µg/g dry weight) in herring liver.

The concentration of arsenic in herring liver from the Swedish west coast is higher than the concentration in herring liver from the Baltic. The highest concentration in 2010-2012 was observed at Fladen (Fig. 20.1).

20.4 Conclusion

The concentration of arsenic in herring liver seems to be higher at the Swedish west coast than in the Baltic, but this result has to be treated with caution since arsenic only has been analysed for four years. This could possibly be explained by the difference in salinity between the Baltic and the North Sea. A study with several fish species showed that arsenic concentrations are positively correlated with salinity for fish taken from the Baltic Sea and North Sea (Larsen & Francesconi 2003).

21 Silver - Ag

Updated 14.02.28

21.1 Introduction

21.1.1 Uses, Production and Sources

Silver is a noble metal (resistant to corrosion and oxidation) that occurs naturally, especially in sulfide-rich ores and in combination with other noble metals and copper, lead and zinc (Eisler 1996) (IVL 2007). The main source of silver today is as a by-product in copper and lead smelting. In Sweden, silver is extracted in a copper mine near Gällivare, a lead mine at Arjeplog, and mines close to Skellefteå (IVL 2007).

Anthropogenic sources of silver comes mainly from smelting operations, the manufacture and disposal of certain photographic and electrical supplies, coal combustion and cloud seeding (WHO 2002). Silver is used for jewelry, ornaments, tableware, utensils and currency (Eisler 1996) (IVL 2007) (WHO 2004). Electronics, batteries and solders containing silver may appear as solid waste either deposited in landfills or burnt in waste incinerators. Dispersal of residues in the environment may occur via leakage or emissions to the air (IVL 2007).

In medicine, silver is used for its bactericidal properties. Soluble silver compounds are used as antiseptic and bacteriostatic agents, as disinfectants (WHO 2004); and as antiseptic and antiodour agents in products such as washing machines, refrigerators, socks and shoes (IVL 2007). Metallic silver is used in amalgam dental fillings alloyed with mercury and small amounts of other metals (IVL 2007).

Silver concentrations in biota have been found to be higher near sewage outfalls, electroplating plants, mine waste and silver-iodide-seeded areas, than from more distant sites (Eisler 1997).

21.1.2 Toxic Effects

Silver has no known biological function in living organisms (IVL 2007). It occurs naturally in several oxidation states. The most common states are elemental silver Ag^{o} and the monovalent ion Ag^{+}. Soluble silver salts are generally more toxic than insoluble salts. Silver as ionic Ag^{+} is one of the most toxic metals known to aquatic organisms in laboratory studies (Eisler 1996) (IVL). The availability of free silver in the marine environment is, however, strongly controlled by salinity due to the affinity of silver to chloride ions (Eisler 1996) (WHO 2002). Silver also has an affinity for suspended particles (Gill et al. 1994). Free silver ion concentrations can range from 47 % when there is a low content of chloride ions and suspended solids, to 0.01 % in marine systems (Gill et al. 1994). In fish, silver has been found to induce the metal-binding protein metallothionein

(IVL 2007). In seawater the key mechanism of acute toxicity appears to involve osmoregulatory failure (Hogstrand & Wood 1998).

21.1.3 Conventions, Aims and Restrictions

Silver and all of the chemical compounds that emit silver or silver ions, should be regarded as a biocide product if its purpose is to prevent growth of bacteria. Silver used as a biocide product is restricted by the European directive 98/8/EC concerning the placing of biocidal products on the market.

21.1.4 Target Levels

No national target level for biota is agreed upon for Ag.

The tolerable daily intake of silver for humans has been set at 5 µg/kg body weight (IRIS 1991). WHO recommendations for protection of groundwater reports a critical concentration of 50 µg/l (WHO 2004).

Silver is comparably rare in the earth's crust. The crustal abundance is estimated at 0.07 mg/kg, predominantly concentrated in basalt (Eisler 1996). Average concentrations of silver in natural waters are 0.2 – 0.3 µg/l (WHO 2004).

In Sweden, the analyses of background concentrations of silver have shown concentrations of 0.07 mg/kg in the fine particulate fraction of moraine, and 0.2 mg/kg in the fine fraction of sediment soils (SGU 2006). In analysed lake sediments, measured concentrations were 0.16 – 0.66 mg/kg dry weight (Grahn et al. 2006), and 5 – 22 mg/kg dry weight (IVL 2007). Background concentrations of silver in fish muscle from lakes have been measured as <0.21 µg/kg fresh weight (IVL 2007).

21.2 Methods

21.2.1 Analytical Information

Silver has only been analysed for a few years within the national Swedish monitoring programme (2007 onwards). See chapter 6 section 6.1 for further details.

21.3 Results

21.3.1 Spatial Variation

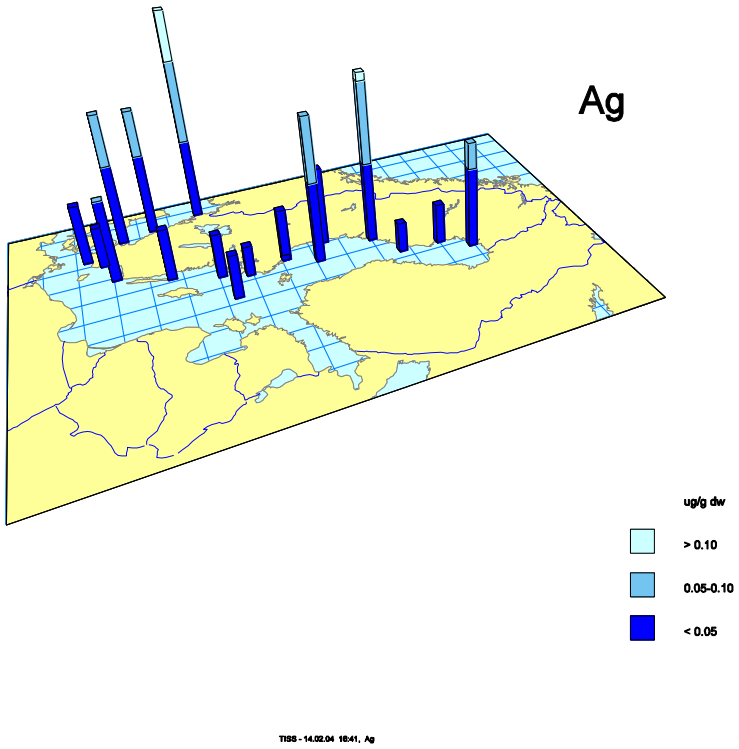


Figure 21.1. Spatial variation in silver concentrations (ug/g dry weight) in herring liver.

The concentrations of silver in herring liver from the Bothnian Sea, Bothnian Bay, and the Swedish west coast is for the majority of the sampling sites higher than in herring liver from the Baltic Proper. The highest concentration of silver was found at Väderöarna on the Swedish west coast followed by Gaviksfjärden in the Bothnian Sea (Fig. 21.1).

21.4 Conclusion

The level of silver in herring along the Swedish coast seems to be somewhat lower in the Baltic Proper compared to the other parts. This result has to be treated with caution since silver only has been analysed for four years.

22 PCBs, Polychlorinated biphenyles

Updated 14.02.28

22.1 Introduction

22.1.1 Usage

PCBs have been used in a wide variety of manufacturing processes, especially as plasticizers, insulators and fire retardants. They are widely distributed in the environment due to inappropriate handling of waste material, or for example, leakage from large condensers and hydraulic systems. In Sweden, restrictions against the use of PCBs were introduced in the beginning of 1970's.

The number of possible congeners is 209, as it has one to ten chlorine atoms. Twenty of these congeners 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).

22.1.2 Toxicological Effects

The toxicological effects of PCBs on, for example, reproduction in mink, is well documented (Aulerich et al. 1977; Jensen et al. 1977; Bleavins et al. 1980). PCBs degrade very slowly and they are fat and oil soluble, which leads to bioaccumulation in biota to high concentrations (Newman & Unger, 2003).

22.1.3 Conventions, Aims and Restrictions

In 1992, HELCOM revised the PCBs for which special bans and restrictions on transport, trade, handling, use and disposal were imposed. The Minister Declaration from 1988, within HELCOM, calls for a reduction of stable organic substances by 50% by 1995, with 1987 as the base year.

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

PCB is one of the initial 12 Persistent Organic Pollutants (POPs) included in The Stockholm Convention on POPs, an international agreement requiring measures for reducing or preventing release of dangerous substances into the environment. The Stockholm Convention was adopted in 2001 and entered into force in 2004.
In 1973, the uses of PCBs were banned in Sweden, except for sealed systems. In 1978, all new use of PCBs were forbidden.

22.1.4 Target Levels

The target level used for CB-153 in the time series for fish is 1600 µg/kg lipid weight and for CB-118 24 µg/kg lipid weight. For further information on target levels and selection of target level see chapter 10.

22.2 Methods

22.2.1 Analytical Information

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 that list.

See chapter 6, sections 6.2 for further information on analysis methods for PCBs.

The concentration of PCBs in fish muscle, cod liver, blue mussel soft body and guillemot eggs were determined using a gas chromatograph (GC) equipped with an electron capture detector.

Before 1988, PCBs were analysed by a packed column GC. The total sum of PCBs was estimated from 14 peaks after calibration with Aroclor 1254 (Jensen et al. 1983). During 1988, analysis on a capillary column was introduced, allowing analysis of individual congeners (Eriksson et al. 1994). The approximate quantification limit for the capillary column for the analysed congeners is shown in table 22.1.

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

It has been discovered that congener CB-163, and possibly also CB-164, interfers with CB-138 (see also Roos et al. 1989). 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 PCBs (sPCB) presented in this report were estimated from the concentration of peak 10 (PCB10) in the chromatogram from packed column chromatography, using the ratio R_1=PCB10/sPCB. PCB10 constitutes approximately 11 - 14% of the total amount of PCB in herring; 13 - 15% in cod; 16 - 17% in perch; 12 % in blue mussels; and 18% in guillemot eggs. Thus, the ratio varies between matrices but is very stable within the same matrix at the same sampling site - the coefficient of variation is found, with few exceptions, to be between 3.5 - 6% (see CV_1 in table 22.1). From 1989 onwards, PCB10 concentrations were 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 PCBs in herring. Mean ratios are given in table 22.2.

The sum of PCBs until 1988 was estimated according to:

$$sPCB = PCB10 / R_1$$

and after 1988:

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

Table 22.1. Mean ratios between peak 10 and the total sum of PCBs from packed column gas chromatography (GC) (R_1), and mean ratios between CB-138+CB-163 (capillary GC) and PCB10 (R_2). The number of analyses (n) and the Coefficient of Variation (CV) for the two ratios are given.

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

Table 22.2. Approximate quantification 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

22.3 Results

22.3.1 Spatial variation

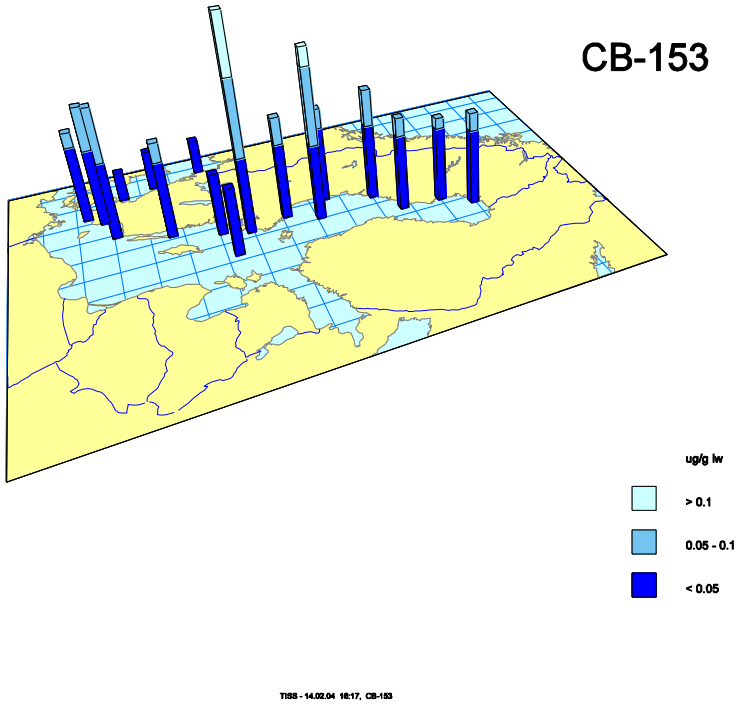


Figure 22.1. Spatial variation in concentrations (µg/g lipid weight) of CB-153 in herring muscle.

Herring muscle from the Bothnian Sea offshore site and Lagnö show elevated concentrations of CB-153 compared to concentrations in the Bothnian Bay and at the Swedish west coast (lipid weight) (Figure 22.1), Lagnö had the overall highest concentration. The ratio of CB-118:CB-153 is significantly lower at Ängskärsklubb compared to all of the other sites. Herring from Landsort has the highest ratio.

A significant difference was found between CB-153 (lipid weight) concentrations analysed in cod liver from southeast of Gotland and Fladen in the Kattegat, where Fladen had almost three times as high concentration compared to Gotland (Fig. 22.8)

Eelpout from Fjällbacka (Swedish west coast) had around three times as high concentration of CB-153 compared to eelpout from Kvädöfjärden (Baltic proper) (Fig. 22. 10).

Blue mussels from Kvädöfjärden had more than twice as high concentration compared to blue mussels from the Swedish west coast (Nidingen and Fjällbacka) (Fig. 22.11).

22.3.2 Temporal variation

sPCB concentration (lipid weight) decreased over time across all species examined, with most of these trends being significant (table 22.3). The same decreasing trend is seen for most species examined for CB-153 over time (table 22.4). The concentration of sPCB (the sum of PCBs estimated from CB-138 or peak 10 from packed column chromatography) in herring muscle from all herring sites in the Baltic and on the west coast, show significant decreases between 1978/80 – 2012 (Fig. 22.2, 22.3). The average decrease varies between -5 and -7% per year. A similar significant decrease within the same range (5-9% per year) is also seen in the two time series of spring-caught herring between 1972-2012 (Fig. 22.3). This implies a total decrease of PCB concentrations in herring muscle of about 70% at Ängskärsklubb and 90% at Utlängan since the beginning of the 1970s.

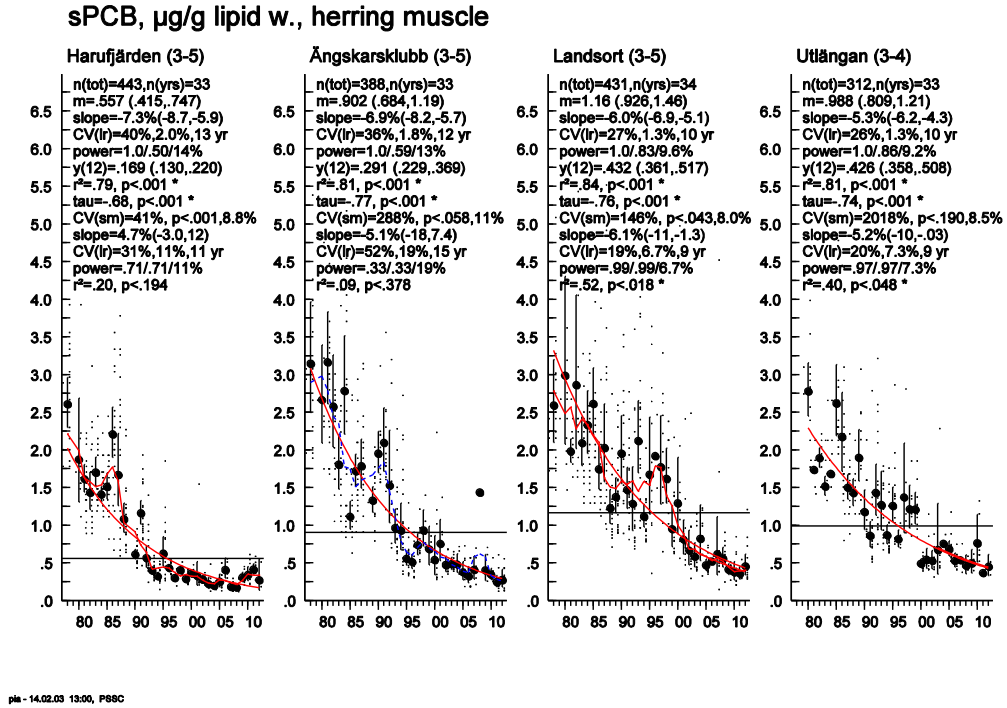


Figure 22.2. sPCB concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978, 1978, 1978 and 1980 respectively).

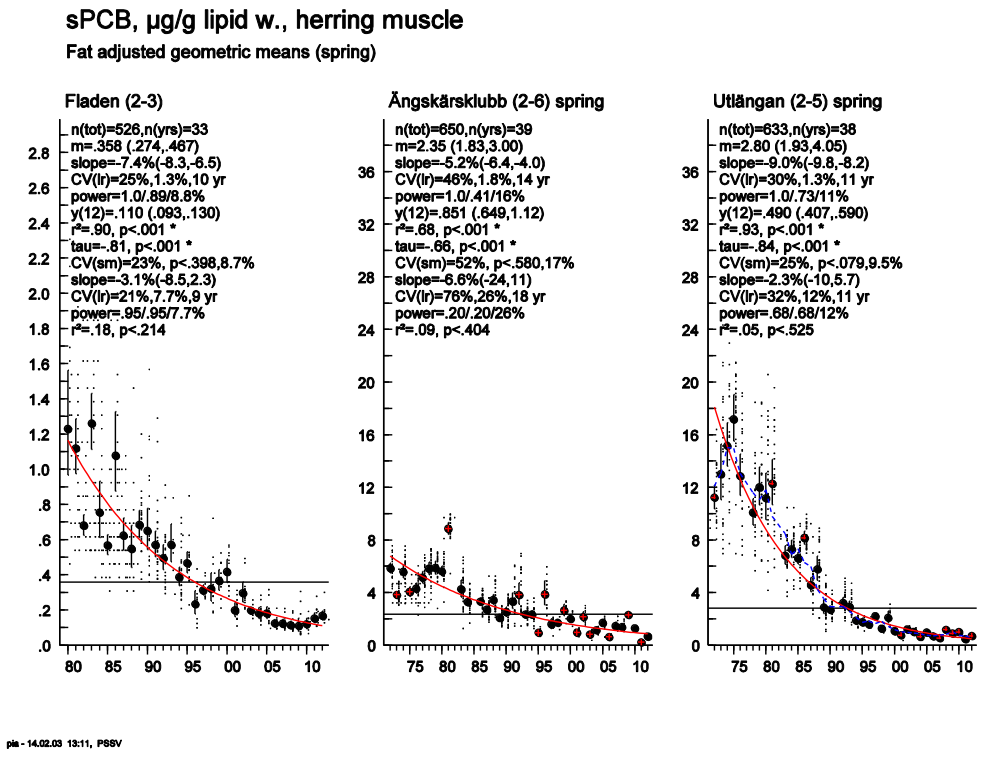


Figure 22.3. sPCB concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), and Fladen (time series starting in 1972, 1972 and 1980 respectively).

Significant decreasing trends for sPCB are observed in blue mussels from the Swedish west coast (Fig. 22.4) and guillemot eggs (1969 - 2011) (Fig. 22.5). The latter trend corresponds to a total decrease of almost 90% since the beginning of the 1970s.

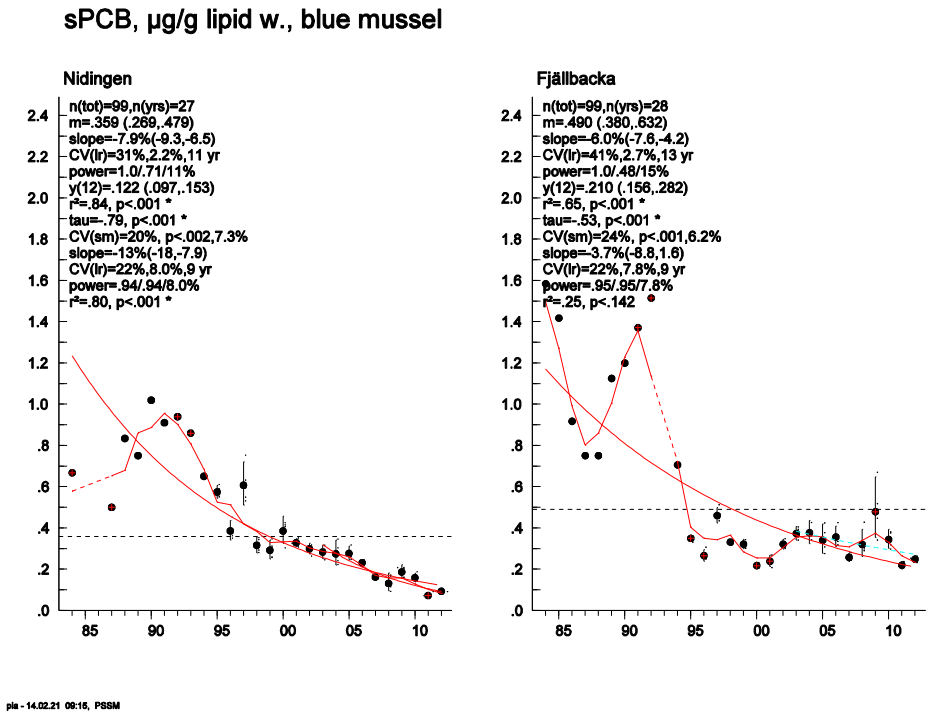


Figure 22.4. sPCB concentrations (µg/g lipid weight) in blue mussels from Nidingen and Fjällbacka (time series starting in 1984).

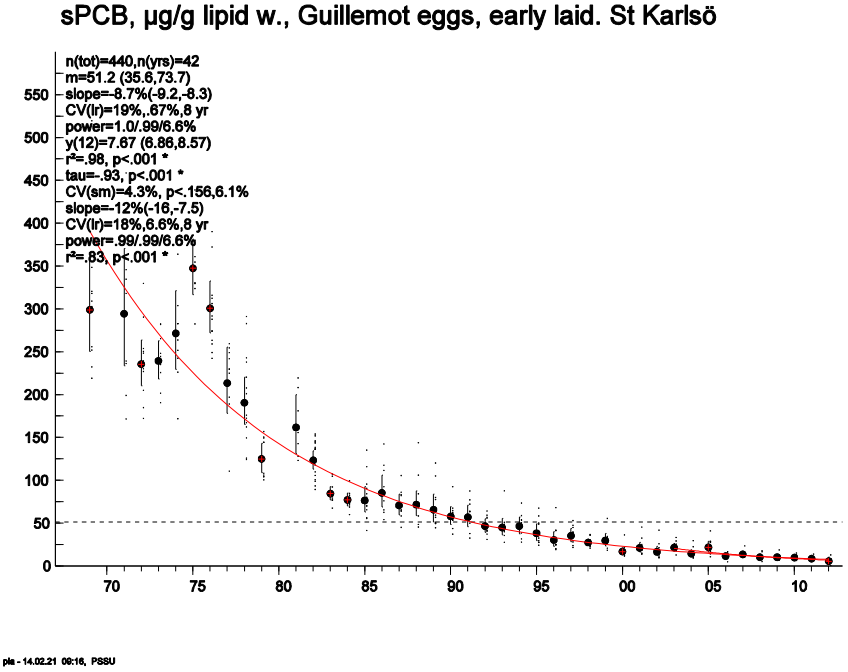


Figure 22.5. sPCB concentrations (µg/g lipid weight) in guillemot eggs from St. Karlsö (time series starting in 1969).

CB-153 shows a similar decreasing trend in herring muscle as sPCB at all sites, except for Väderöarna, where no trend is observed (Fig. 22.6, 22.7). Extremely high PCB concentrations are recorded from Landsort in 1996 (Fig. 22.6). This can probably be explained by the very low fat content in herring in that year.

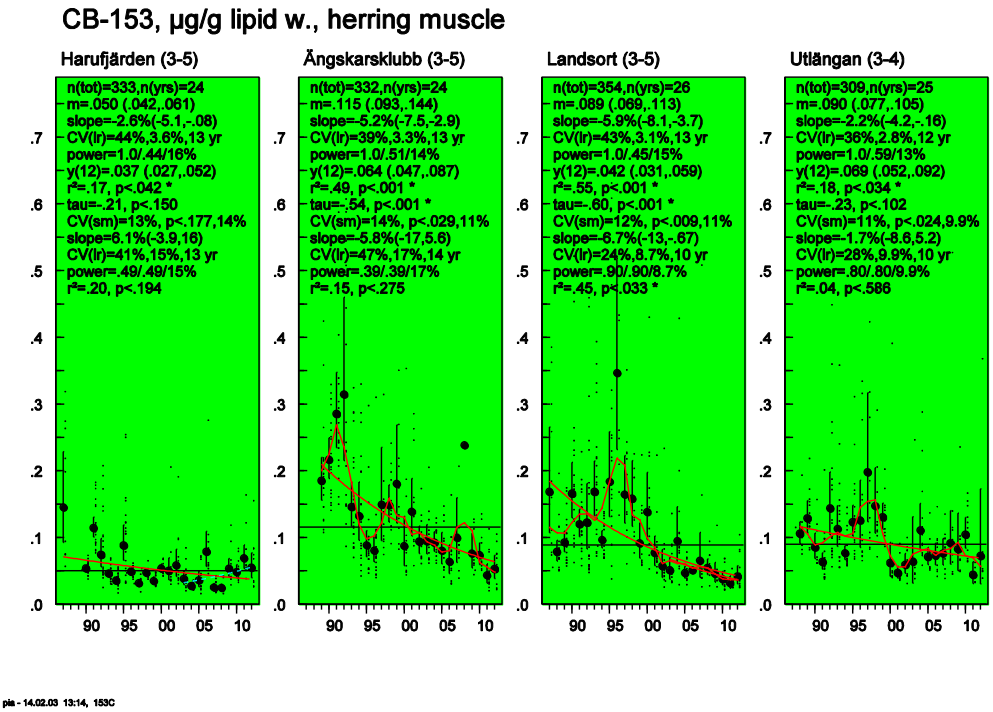


Figure 22.6.CB-153 concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for CB-153 in fish.

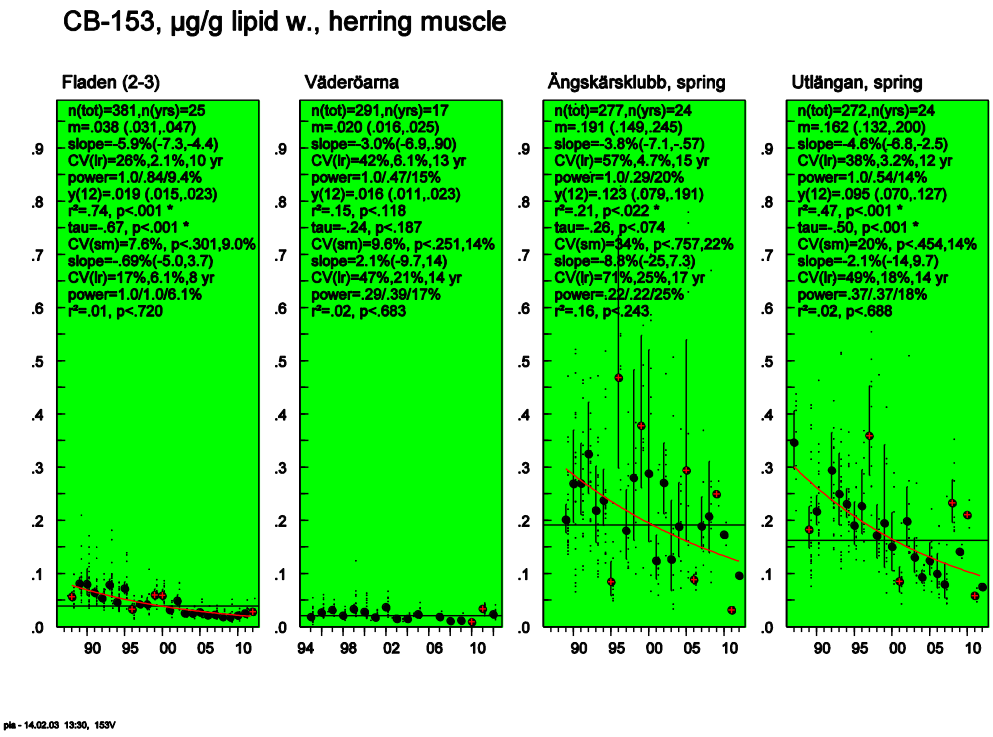


Figure 22.7. CB-153 concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for CB-153 in fish.

The cod time series from southeast of Gotland in the Baltic Proper and Fladen on the west coast show significant decreasing trends for sPCB. Unlike this, no decreasing trend is observed for CB-153 in the cod time series and at Fladen there is even an increase during the ten most recent yers.(Fig. 22.8). In the perch CB-153 time series, concentrations have decreased significantly at both Holmöarna and Kvädöfjärden (Fig. 22.9). CB-153 shows a significant decreasing trend at Kvädöfjärden for eelpout muscle (Fig. 22.10).

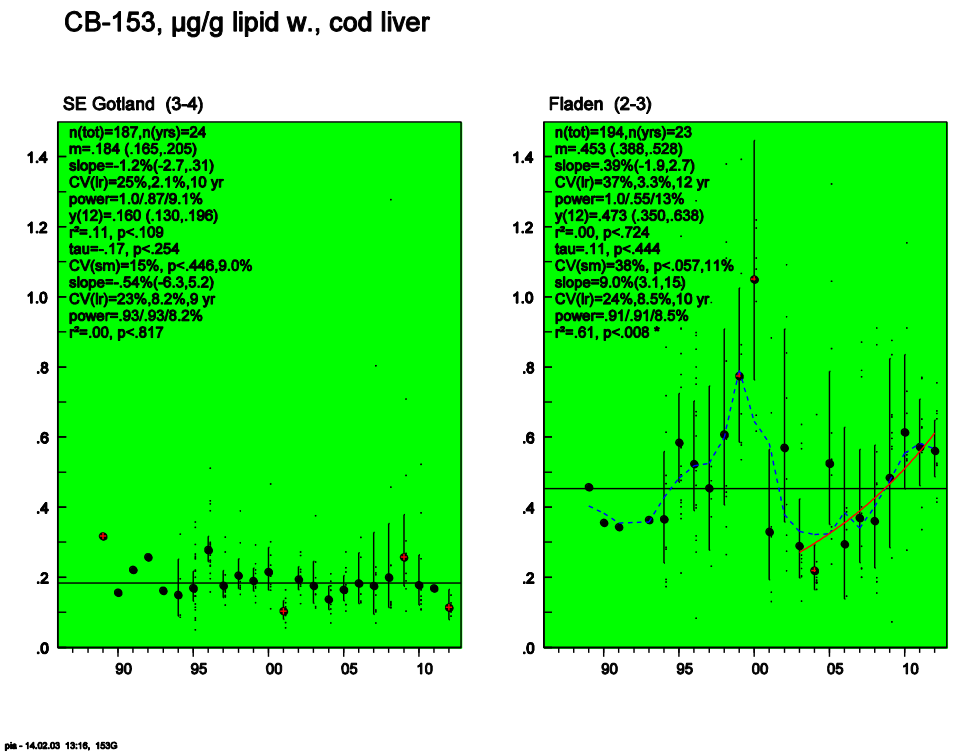


Figure 22.8. CB-153 concentrations (µg/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1989. The green area denotes the levels below the suggested target value for CB-118 in fish.

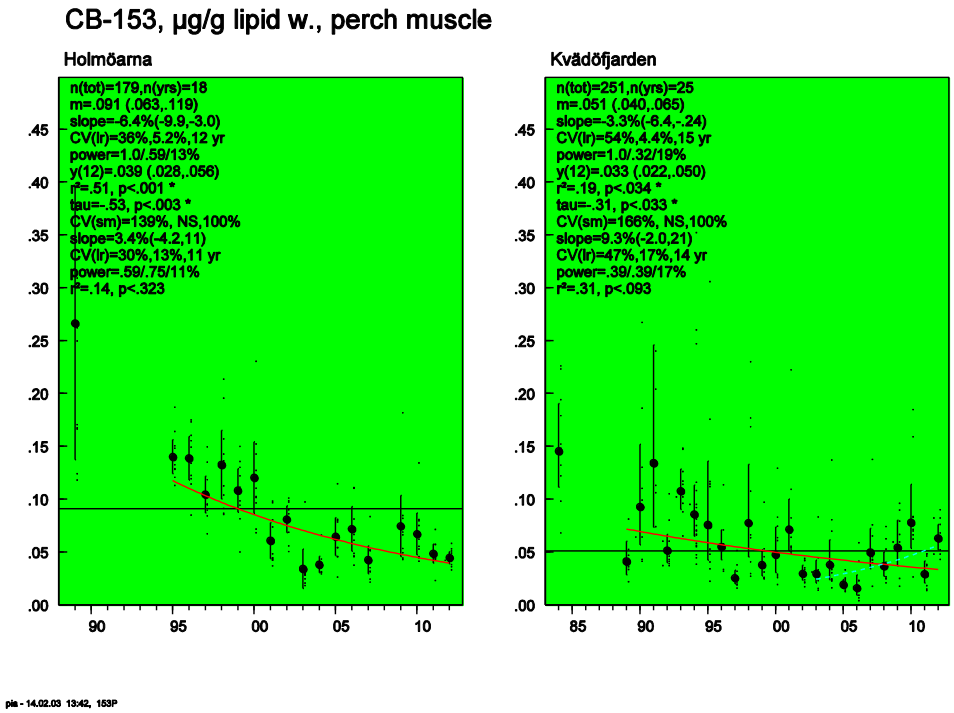


Figure 22.9. CB-153 concentrations (µg/g lipid weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 and 1984 respectively). The green area denotes the levels below the suggestedtarget value for CB-153 in fish.

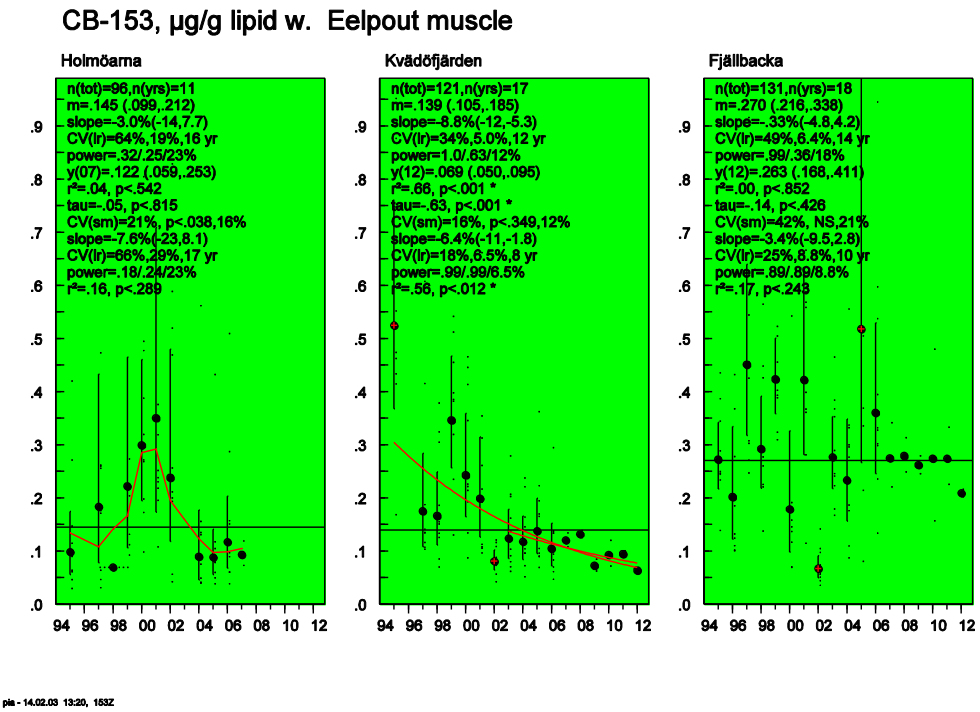


Figure 22.10. CB-153 concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for CB-153 in fish.

Significant decreasing trends are seen for CB-153 in blue mussels at all sites (Fig. 22.11).

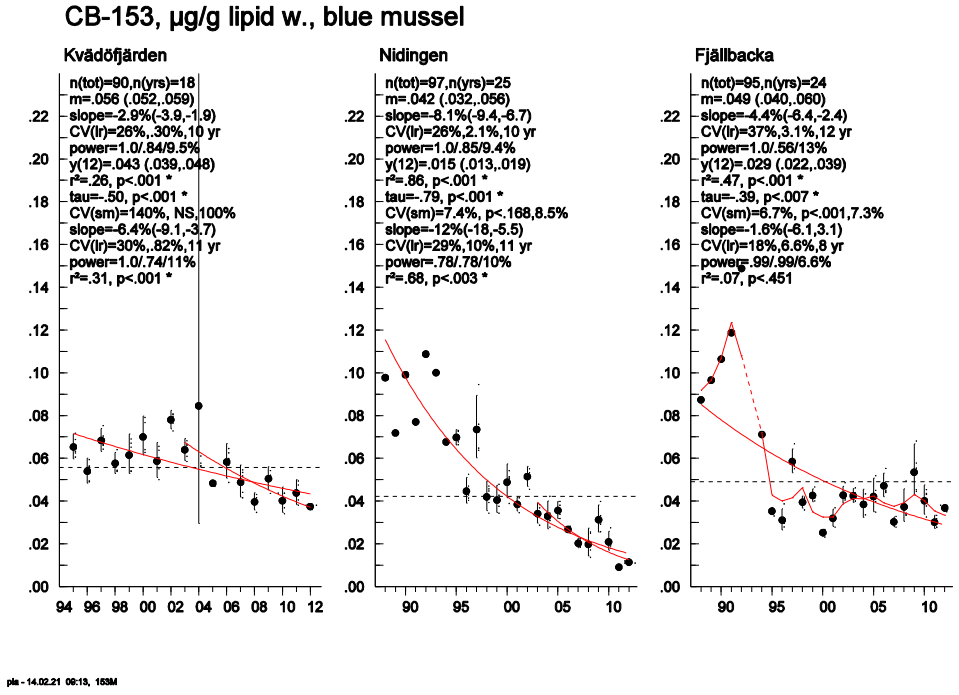


Figure 22.11. CB-153 concentrations (µg/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1988, 1988 and 1995 respectively).

A decreasing trend in CB-153 in guillemot eggs is seen over the whole time period and for the most recent ten years (Fig. 22.12).

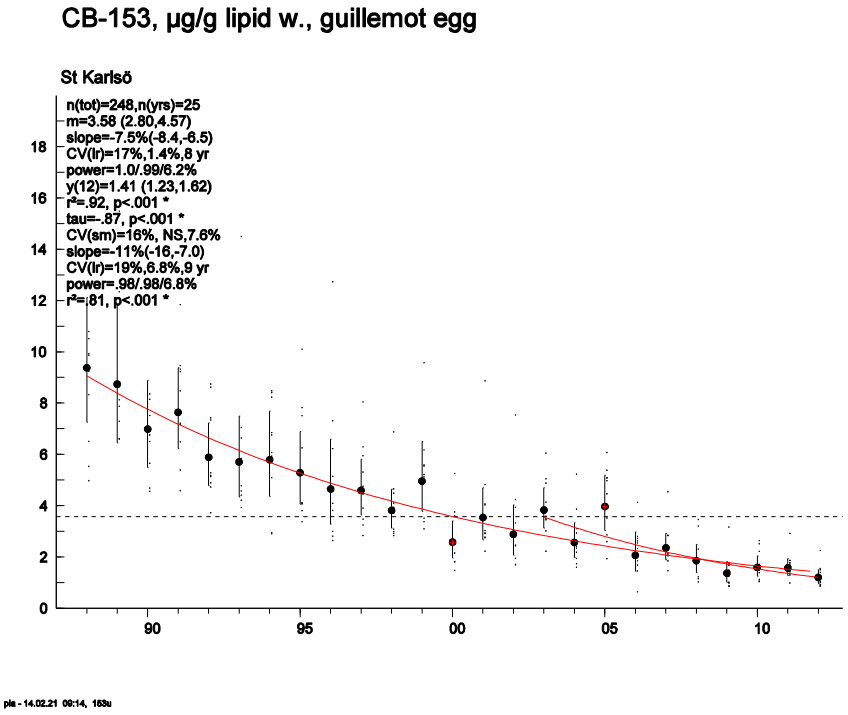


Figure 22.12. CB-153 concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1988).

The number of years required to detect an annual change of 10% for CB-153 varies between 10 - 16 years for the herring, perch, mussel, and cod time series.

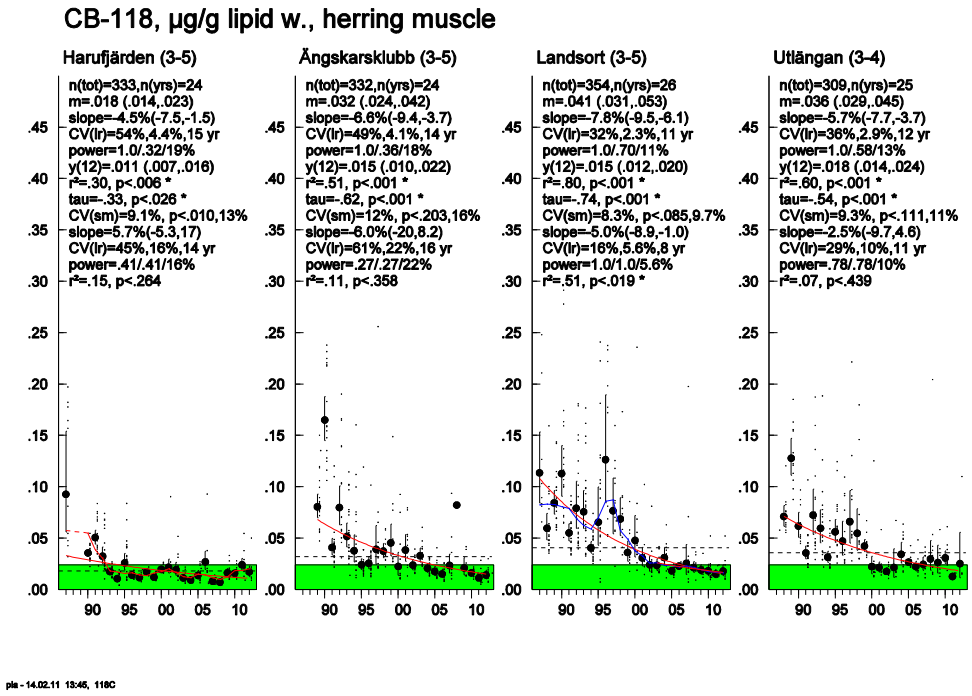


Figure 22.13. CB-118 concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for CB-118 in fish.

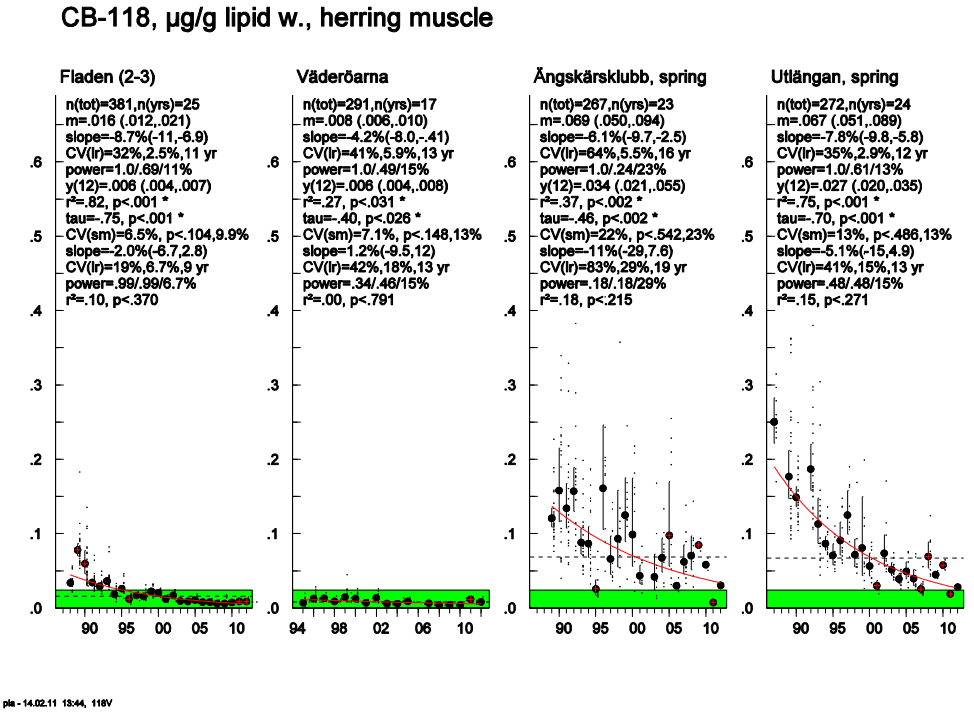


Figure 22.14. CB-118 concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for CB-118 in fish.

All herring time series show decreasing trends of CB-118 with annual decreases between 4.2-8.7% per year (Fig. 22.13-14).

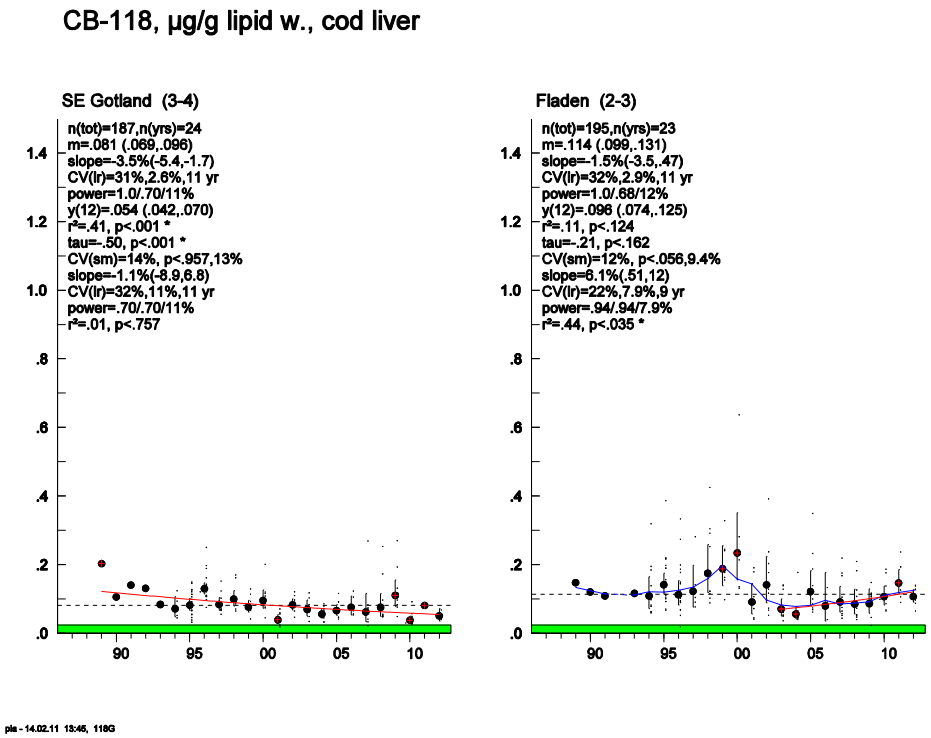


Figure 22.15. CB-118 concentrations (µg/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1989. The green area denotes the levels below the suggested target value for CB-118 in fish.

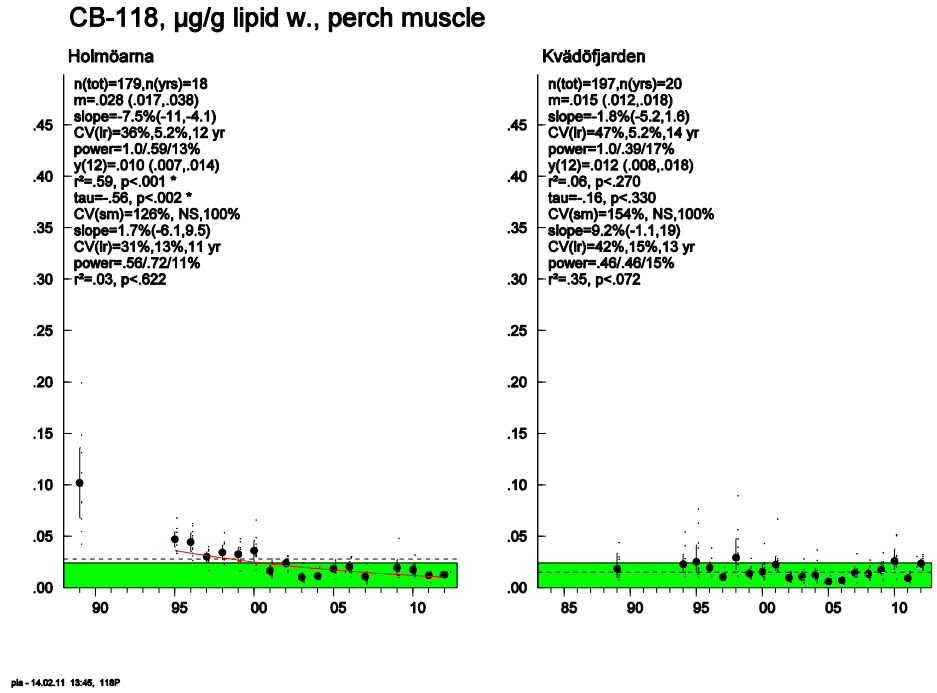


Figure 22.16. CB-118 concentrations (µg/g lipid weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 and 1984 respectively). The green area denotes the levels below the suggestedtarget value for CB-118 in fish.

Cod liver showed a decreasing trend for CB-118 at southeast of Gotland but at fladen an increase was seen for the ten most recent years (Fig. 22.15). The perch series showed a decreasing trend for CB-118 at Holmöarna (Fig. 22.16). Decreasing concentrations over time was also seen in eelpout from Kvädöfjärden (Fig. 22.17).

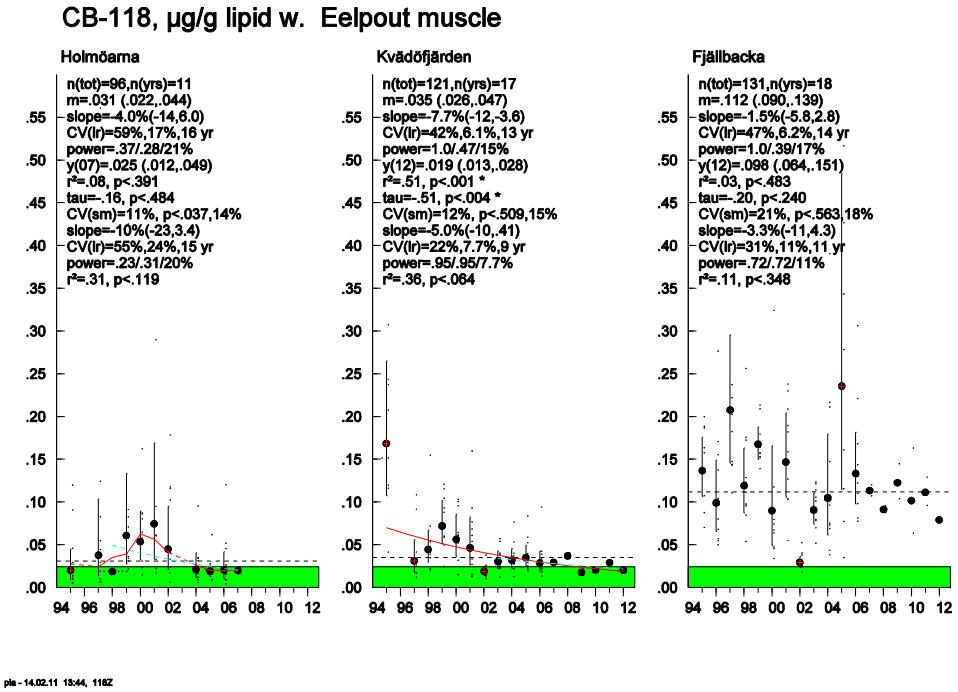


Figure 22.17. CB-118 concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for CB-118 in fish.

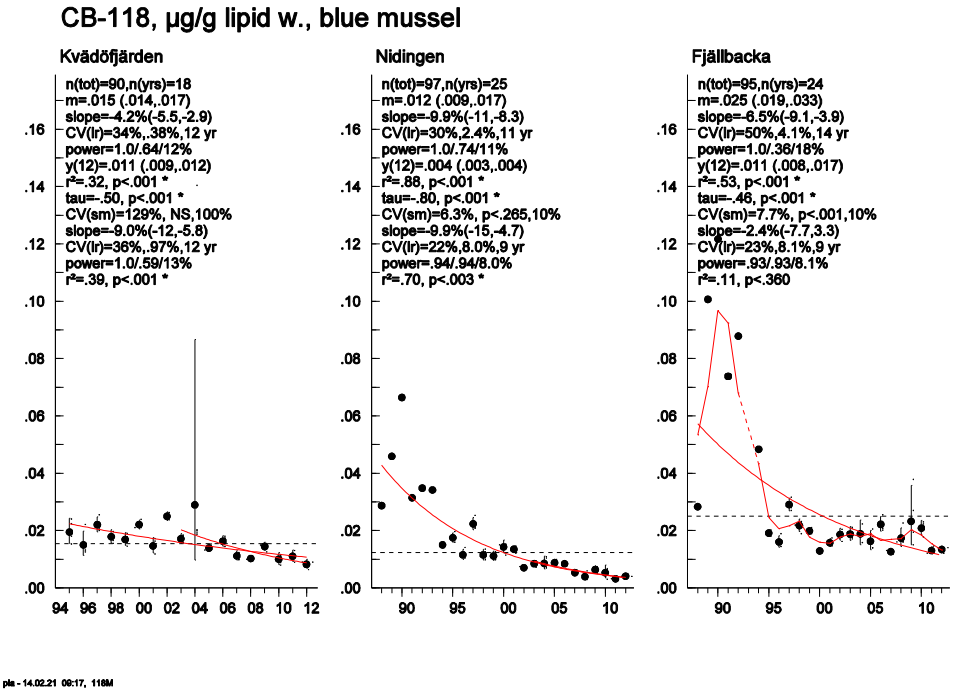


Figure 22.18. CB-118 concentrations (µg/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1988, 1988 and 1995 respectively).

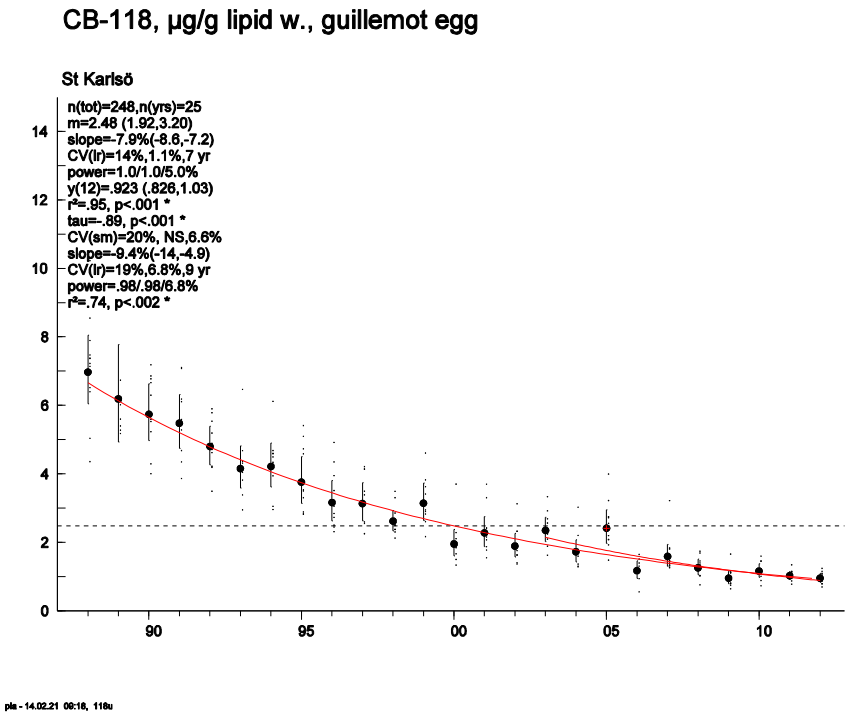


Figure 22.19. CB-118 concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1988).

All blue mussel time series (Fig. 22.18) and the guillemot egg series (Fig. 22.19) showed decreasing trends of CB-118 over time.

22.3.3 Comparison to threshold

In all fish species from all areas, CB-153 concentration is below the suggested target level based on the OSPAR EAC (Environmental Assessment Criteria) of 1.6 ug/g lipid weight. For CB-118, concentrations in eelpout from Fjällbacka, in cod and in spring caught herring are above the OSPAR EAC (Environmental Assessment Criteria) of 0.024 ug/g lipid weight. Concentrations of CB-118 in eelpout from the Baltic sites, perch and autumn caught herring are close to or at the target level.

22.4 Conclusion

PCB concentrations varied between species and sites; however temporally, the concentration of PCBs has decreased by approximately 5 - 10% per year in herring and cod from the Baltic Sea and the Kattegat, as well as from guillemot eggs and perch from the Baltic Sea since the end of the 1970s.

In all areas, CB-153 concentrations are below the suggested target level in fish. Levels of CB-118 in fish are close to or above the suggrested target level in all areas.

Table 22.3 Trend (in %) for **sPCB** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's sPCB concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	443	33	78-12	-7.3(-8.7,-5.9)	.0000 ---	13	15.4	.169 (.130,.220)
Harufjärden(3-5)		10	03-12	4.7(-3.0,12)	0.1938	11	11.8	
Ängskärsklubb(3-5)	388	33	78-12	-6.9(-8.2,-5.7)	.0000 ---	12	13.7	.291 (.230,.369)
Ängskärsklubb(3-5)		10	03-12	-5.1(-18,7.4)	0.3778	15	20.5	
Landsort(3-5)	431	34	78-12	-6.0(-6.9,-5.1)	.0000 ---	10	10.1	.432 (.361,.517)
Landsort(3-5)		10	03-12	-6.1(-11,-1.3)	0.0176	9	6.9	
Utlängan(3-4)	312	33	80-12	-5.3(-6.2,-4.3)	.0000 ---	10	9.6	.426 (.358,.508)
Utlängan(3-4)		10	03-12	-5.2(-10,-.03)	0.0475	9	7.56	
Ängskärsklubb spring(2-6)	650	39	72-12	-5.1(-6.3,-4.0)	.0000 ---	14	17.8	.861 (.657,1.13)
Ängskärsklubb spring(2-6)		10	03-12	-5.9(-23,11)	0.4544	18	30.1	
Utlängan spring(2-4)	633	38	72-12	-9.0(-9.8,-8.1)	.0000 ---	11	11.8	.498 (.411,.602)
Utlängan spring(2-4)		10	03-12	-1.4(-9.5,6.7)	0.6983	11	12.5	
Fladen(2-3)	526	33	80-12	-7.4(-8.3,-6.5)	.0000 ---	10	9.22	.110 (.093,.130)
Fladen(2-3)		10	03-12	-3.1(-8.5,2.3)	0.2144	9	7.98	
Blue mussel								
Nidingen	99	27	84-12	-8.3(-9.8,-6.8)	.0000 ---	11	11.8	.122 (.097,.153)
Nidingen		10	03-12	-14(-20,-8.3)	.0005 ---	9	8.36	
Fjällbacka	99	28	84-12	-6.1(-8.0,-4.3)	.0000 ---	13	15.9	.210 (.156,.282)
Fjällbacka		10	03-12	-3.8(-9.3,1.6)	0.1423	9	8.06	
Guillemot egg								
Stora Karlsö	440	42	69-12	-9.1(-9.6,-8.7)	.0000 ---	8	6.83	7.67 (6.86,8.57)
Stora Karlsö		10	03-12	-12(-17,-7.8)	.0003 ---	8	6.82	

Table 22.4. Trend (in %) for **CB-153** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's CB-153 concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	333	24	87-12	-2.6(-5.1,-.08)	0.0418	13	16.9	.037 (.027,.052)
Harufjärden(3-5)		10	03-12	6.1(-3.9,16)	0.1937	13	15.8	
Ängskärsklubb(3-5)	332	24	89-12	-5.2(-7.5,-2.9)	.0002 ---	13	15.2	.064 (.047,.087)
Ängskärsklubb(3-5)		10	03-12	-5.8(-17,5.6)	0.2746	14	18.4	
Landsort(3-5)	354	26	87-12	-7.8(-9.5,-6.1)	.0000 ---	11	12	.015 (.012,.020)
Landsort(3-5)		10	03-12	-6.7(-13,-.67)	0.0327	10	9.07	
Utlängan(3-4)	309	25	88-12	-2.2(-4.2,-.16)	0.0337	12	13.8	.069 (.052,.092)
Utlängan(3-4)		10	03-12	-1.7(-8.6,5.2)	0.5861	10	10.5	
Väderöarna	291	17	95-12	-3.0(-6.9,.90)	0.1181	13	16.2	.020 (.016,.025) m
Väderöarna		9	03-12	2.1(-9.7,14)	0.6831	14	18.4	
Ängskärsklubb spring(2-6)	277	24	89-12	-3.8(-7.1,-.57)	0.0223	15	22.6	.123 (.079,.191)
Ängskärsklubb spring(2-6)		10	03-12	-8.8(-25,7.3)	0.2435	17	28.1	
Utlängan spring(2-4)	272	24	87-12	-4.6(-6.8,-2.5)	.0002 ---	12	14.7	.095 (.070,.127)
Utlängan spring(2-4)		10	03-12	-2.1(-14,9.7)	0.6877	14	19.2	
Fladen(2-3)	381	25	88-12	-5.9(-7.3,-4.4)	.0000 ---	10	9.9	.019 (.015,.023)
Fladen(2-3)		10	03-12	-.69(-5.0,3.7)	0.7203	8	6.33	
Perch muscle								
Holmöarna	179	17	95-12	-6.4(-9.9,-3.0)	.0013 --	12	13.7	.039 (.028,.056)
Holmöarna		9	03-12	3.4(-4.2,11)	0.3228	11	11.3	
Kvädöfjärden	251	24	89-12	-3.3(-6.4,-.24)	0.034	15	21.1	.033 (.022,.050)
Kvädöfjärden		10	03-12	9.3(-2.0,21)	0.0927	14	18.4	
Cod liver								
SE Gotland(3-4)	187	24	89-12	-1.2(-2.7,.31)	0.1087	10	9.5	.184 (.165,.205) m
SE Gotland(3-4)		10	03-12	-.54(-6.3,5.2)	0.8167	9	8.56	
Fladen(2-3)	194	23	89-12	.39(-1.9,2.7)	0.7241	12	14.4	.453 (.388,.528) m
Fladen(2-3)		10	03-12	9.0(3.1,15)	.0078 ++	10	8.84	
Eelpout muscle								
Holmöarna	96	11	95-07	-3.0(-14,7.7)	0.5416	16	25.3	.145 (.099,.212) m
Holmöarna		9	98-07	-7.6(-23,8.1)	0.2893	17	26.2	
Kvädöfjärden	121	17	95-12	-8.8(-12,-5.3)	.0001 ---	12	13.1	.069 (.050,.095)
Kvädöfjärden		10	03-12	-6.4(-11,-1.8)	0.0123	8	6.72	
Fjällbacka	131	18	95-12	-.33(-4.8,4.2)	0.8524	14	19.2	.270 (.216,.338) m
Fjällbacka		10	03-12	-3.4(-9.5,2.8)	0.2428	10	9.2	
Blue mussel								
Nidingen	97	25	88-12	-8.4(-9.9,-6.9)	.0000 ---	10	9.9	.015 (.013,.019)
Nidingen		10	03-12	-13(-20,-5.6)	.0034 --	11	10.9	
Fjällbacka	95	24	88-12	-4.5(-6.6,-2.4)	.0002 ---	12	14.3	.029 (.022,.039)
Fjällbacka		10	03-12	-2.4(-8.0,3.3)	0.3598	9	8.4	
Kvädöfjärden	90	18	95-12	-3.0(-4.7,-1.2)	.0022--	8	6.60	.043 (.037,.051)
Kvädöfjärden		10	03-12	-6.7(-11,-2.7)	.0050 --	8	5.8	
Guillemot egg								
Stora Karlsö	248	25	88-12	-7.7(-8.7,-6.8)	.0000 ---	8	6.36	1.41 (1.23,1.62)
Stora Karlsö		10	03-12	-12(-17,-7.2)	.0005 ---	9	7.08	

Table 22.5. Trend (in %) for **CB-118** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's CB-118 concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	333	24	87-12	-4.5(-7.5,-1.5)	.0055 --	15	21.1	.011 (.007,.016)
Harufjärden		10	03-12	5.7(-5.3,17)	0.2643	14	17.6	
Ängskärsklubb(3-5)	332	24	89-12	-6.6(-9.4,-3.7)	.0001 ---	14	19.3	.015 (.010,.022)
Ängskärsklubb(3-5)		10	03-12	-6.0(-20,8.2)	0.3582	16	24.1	
Landsort(3-5)		10	03-12	-5.0(-8.9,-1.0)	0.0194	8	5.71	
Utlängan(3-4)	309	25	88-12	-5.7(-7.7,-3.7)	.0000 ---	12	14	.018 (.014,.024)
Utlängan(3-4)		10	03-12	-2.5(-9.7,4.6)	0.4387	11	10.8	
Väderöarna	291	17	95-12	-4.2(-8.0,-.41)	0.0309	13	15.7	.006 (.004,.008)
Väderöarna		9	03-12	1.2(-9.5,12)	0.7909	13	16.3	
Ängskärsklubb spring(2-6)	267	23	89-12	-6.1(-9.7,-2.5)	.0022 --	16	25.5	.034 (.021,.055)
Ängskärsklubb spring(2-6)		10	03-12	-11(-29,7.6)	0.2147	19	33	
Utlängan spring(2-4)	272	24	87-12	-7.8(-9.8,-5.8)	.0000 ---	12	13.4	.027 (.020,.035)
Utlängan spring(2-4)		10	03-12	-5.1(-15,4.9)	0.2714	13	15.9	
Fladen(2-3)	381	25	88-12	-8.7(-11,-6.9)	.0000 ---	11	12.1	.006 (.004,.007)
Fladen(2-3)		10	03-12	-2.0(-6.7,2.8)	0.3702	9	6.91	
Cod liver								
SE Gotland(3-4)	187	24	89-12	-3.5(-5.4,-1.7)	.0008 ---	11	11.9	.054 (.042,.070)
SE Gotland(3-4)		10	03-12	-1.1(-8.9,6.8)	0.7569	11	12	
Fladen(2-3)	195	23	89-12	-1.5(-3.5,.47)	0.1242	11	12.3	.114 (.099,.131) m
Fladen(2-3)		10	03-12	6.1(.51,12)	.0348 +	9	8.22	
Perch muscle								
Holmöarna	179	17	95-12	-7.5(-11,-4.1)	.0004 ---	12	13.7	.010 (.007,.014)
Holmöarna		9	03-12	1.7(-6.1,9.5)	0.6222	11	11.7	
Kvädöfjärden	197	20	89-12	-1.8(-5.2,1.6)	0.2699	14	18.2	.015 (.012,.018) m
Kvädöfjärden		10	03-12	9.2(-1.1,19)	0.0717	13	16.4	
Eelpout muscle								
Holmöarna	96	11	95-07	-4.0(-14,6.0)	0.3913	16	23.2	.031 (.022,.044) m
Holmöarna		9	98-07	-10(-23,3.4)	0.1195	15	21.7	
Kvädöfjärden	121	17	95-12	-7.7(-12,-3.6)	.0013 --	13	16.2	.019 (.013,.028)
Kvädöfjärden		10	03-12	-5.0(-10,.41)	0.0637	9	8.03	
Fjällbacka	131	18	95-12	-1.5(-5.8,2.8)	0.4832	14	18.5	.112 (.090,.139) m
Fjällbacka		10	03-12	-3.3(-11,4.3)	0.3483	11	11.7	
Blue mussel								
Nidingen	97	25	88-12	-10(-12,-8.7)	.0000 ---	11	11.3	.004 (.003,.004)

Nidingen		10	03-12	-10(-16,-4.9)	.0027 --	9	8.32	
Fjällbacka	95	24	88-12	-6.7(-9.5,-4.0)	.0001 ---	14	19.6	.011 (.008,.017)
Kvädöfjärden	90	18	95-12	-4.3(-6.8,-1.8)	.0021 --	10	9.9	.011 (.008,.014)
Kvädöfjärden		10	03-12	-9.4(-15,-3.4)	.0068 --	10	8.93	
Guillemot egg								
Stora Karlsö	248	25	88-12	-8.2(-9.0,-7.4)	.0000 ---	7	5.07	.923 (.826,1.03)
Stora Karlsö		10	03-12	-9.9(-15,-5.0)	.0016 --	9	7.08	

23 DDTs, Dichlorodiphenylethanes

Updated 14.01.28

23.1 Introduction

23.1.1 Usage

DDT and its metabolites (DDE and DDD) are organochlorine insecticides. DDT is mainly known for its usage as vector control during the second World War. However, thereafter it has been used widely for control of agricultural pests, vector diseases (e.g. Malaria), ectoparasites of farm animals and insects in domestic and industrial premises (Walker et al. 200, Li & Macdonald 2005).

23.1.2 Toxicological effects

DDT is a very persistent organochlorine and it has a high fat solubility. This leads to bioaccumulation in the food web. One of the most known effects of DDT is eggshell thinning in predatory bird eggs (Peakall & Lincer 1996, Helander et al. 2002), even at very low doses. The white-tailed sea eagle was almost extinct due to DDT pollution in the Baltic (Olsson & Reutergårdh 1986).

23.1.3 Conventions, Aims and Restrictions

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

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

DDT is one of the initial 12 Persistent Organic Pollutants (POPs) included in The Stockholm Convention on POPs, an international agreement requiring measures for reducing or preventing release of dangerous substances into the environment.

The Stockholm Convention was adopted in 2001 and entered into force in 2004.
In Sweden, DDT was partially banned as a pesticide in 1970, and completely banned in 1975 due to its persistence and environmental impact.

23.1.4 Target Levels

The target level (TL) used for DDE in the time series for fish is 5 µg/kg wet weight. For further information on TL and selection of target level see chapter 10. The original TL has been recalculated for each time series based on the lipid percentage. The recalculated target level (Tv) together with the lipid percentage (lp) is shown above the statistical information in each time series.

23.2 Methods

23.2.1 Analytical Information

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

See chapter 6, section 6.2 for further information on analysis methods for DDTs.

Before 1988, DDTs (DDT, DDE, DDD) were analysed on a packed column GC. During 1988, analysis on a capillary column was introduced. The two methods give slightly different results for the various DDT-compounds. In table 23.1, the mean ratio 'capillary column results'/'packed column results' from various sites and matrices are presented. When the concentrations are close to the quantification limit (DL) for the packed column GC, the results seem to be under-estimated. This is particularly true for the estimated sum of DDTs (sDDT), since DDT and DDD may fall below DL, hence only DDE will constitute the sum. To avoid this bias at low levels, only samples with DDE concentrations above 0.2 µg/g were selected to calculate the ratios below. Only analyses where DDE, DDD and DDT were all present in levels above DL were included in the sDDT ratio. When it was possible to estimate these ratios, they were in general close to one. There were a few exceptions - at Landsort both the DDE and DDT ratios were lower than one, indicating over-estimated concentrations from the packed column possibly due to interference with other compounds in the DDE and DDT peaks in the packed column chromatogram. At Fladen, the DDE ratio was significantly above one, indicating under-estimated DDE concentrations from the packed column GC.

In the time series presented below, DDE is shown for herring, cod, perch, eelpout, blue mussels, and guillemot.

Table 23.1. Ratios of DDE, DDT, DDD and sDDT analysed on a capillary column, versus the same samples analysed on a packed column gas chromatography (GC), and the corresponding 95% confidence intervals.

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

The quantification 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.

23.3 Results

23.3.1 Spatial variation

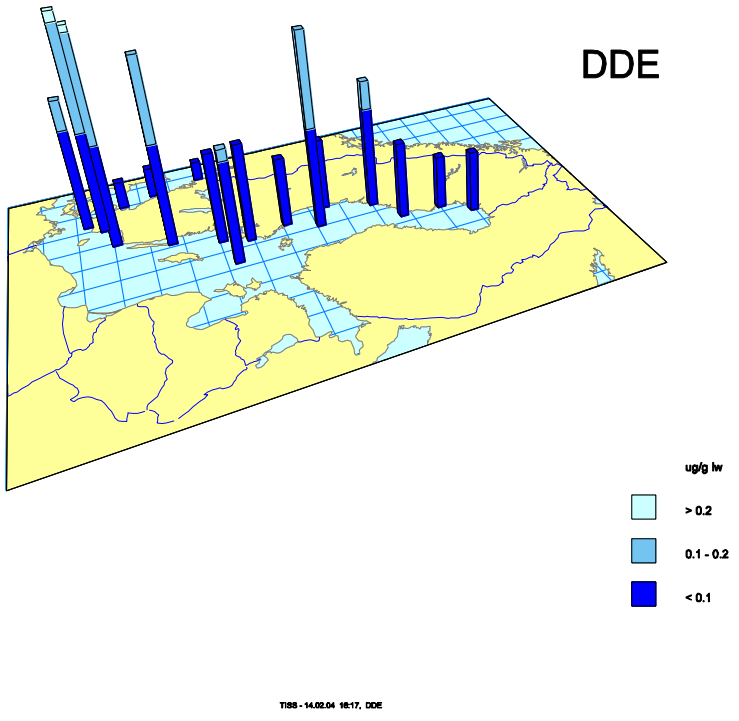


Figure 23.1. Spatial variation of DDE concentrations (µg/g lipid weight) in herring muscle.

The highest concentrations of DDE in herring (lipid weight) were detected at Utlängan and Hanöbukten (Figure 23.1) in the south Baltic Proper, and was significantly higher than concentrations detected in the Bothnian Bay and at locations on the Swedish west coast.

DDE concentrations in cod from the Baltic Proper (southeast of Gotland) were about twice as high compared to cod from Fladen on the Swedish west coast (table 23.2, Fig. 23.4).

DDE concentration in blue mussels from Kvädöfjärden were almost three times as high compared to blue mussels from the Swedish west coast (Nidingen and Fjällbacka) (Fig. 23. 6).

23.3.2 Temporal variation

DDE concentrations in herring muscle (Fig. 23.2, 23.3), cod liver and perch muscle (Fig. 23.4), in eelpout from Kvädöfjärden (Fig. 23.5) and in blue mussels (Fig. 23.6) decreased significantly between 1980 - 2012. This decrease varied between 4 - 10% per year (table 23.2). The time series for guillemot eggs (1969 - 2012) showed a significant decrease of -9% per year for DDE (Fig. 23.7). The ratio of DDT/sDDT is significantly decreasing at all herring sites, except for Väderöarna where there are not enough data points (due to levels under quantification) to detect a change.

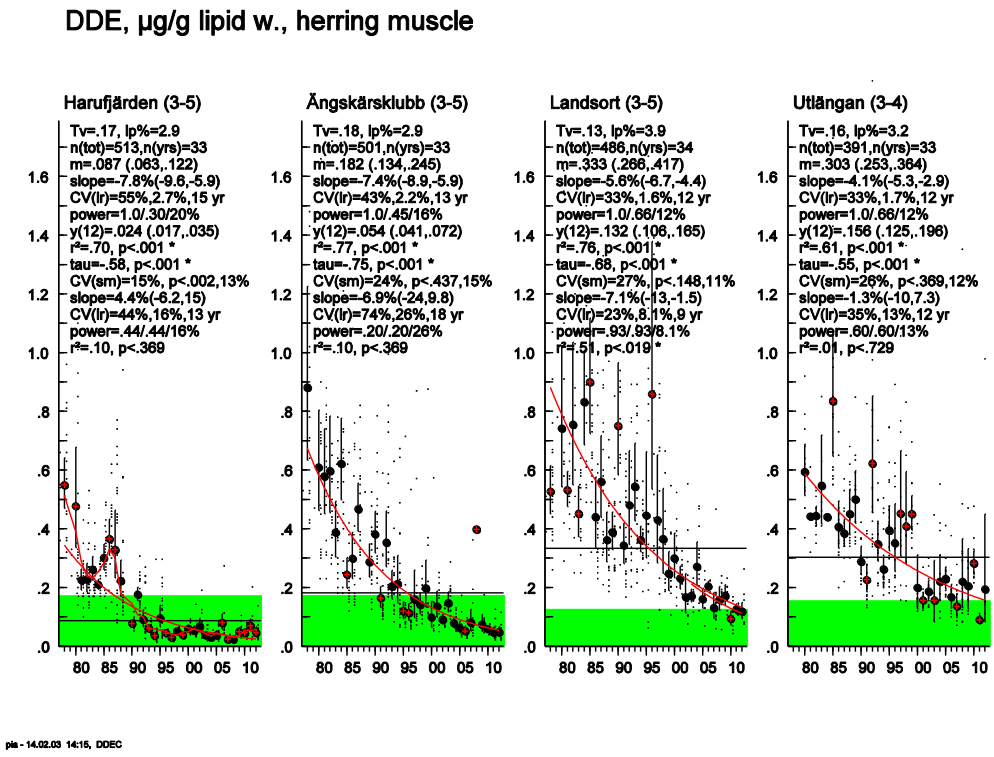


Figure 23.2. DDE concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978, 1978, 1978 and 1980 respectively). The green area denotes the levels below the suggested target value for DDE in fish.

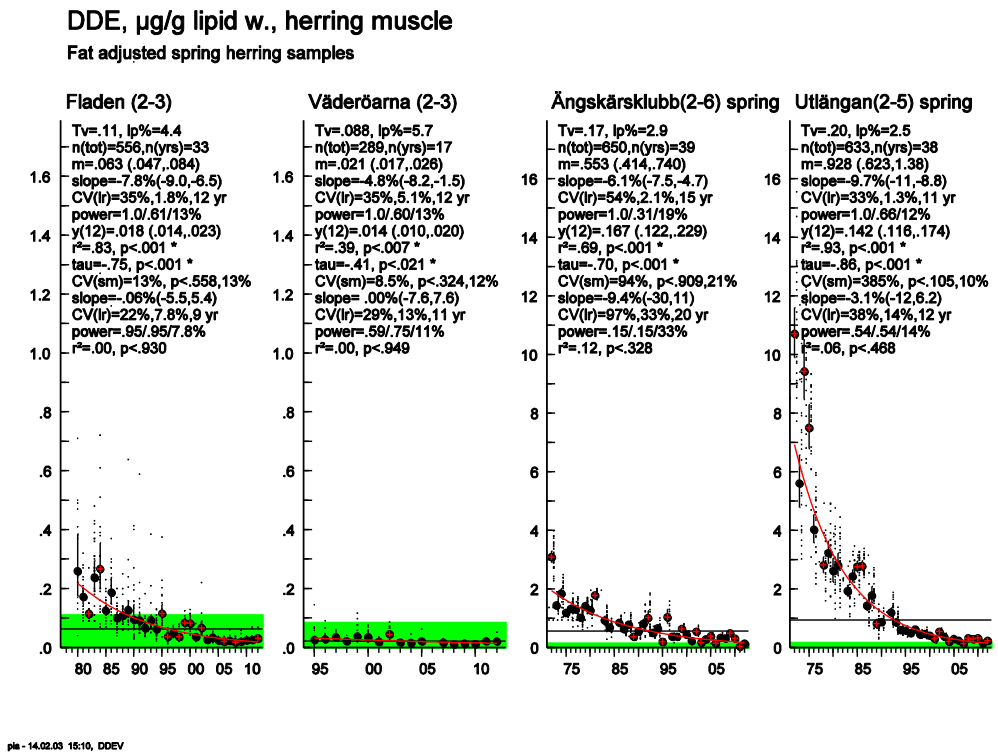


Figure 23.3. DDE concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1995 respectively). The green area denotes the levels below the suggested target value for DDE in fish.

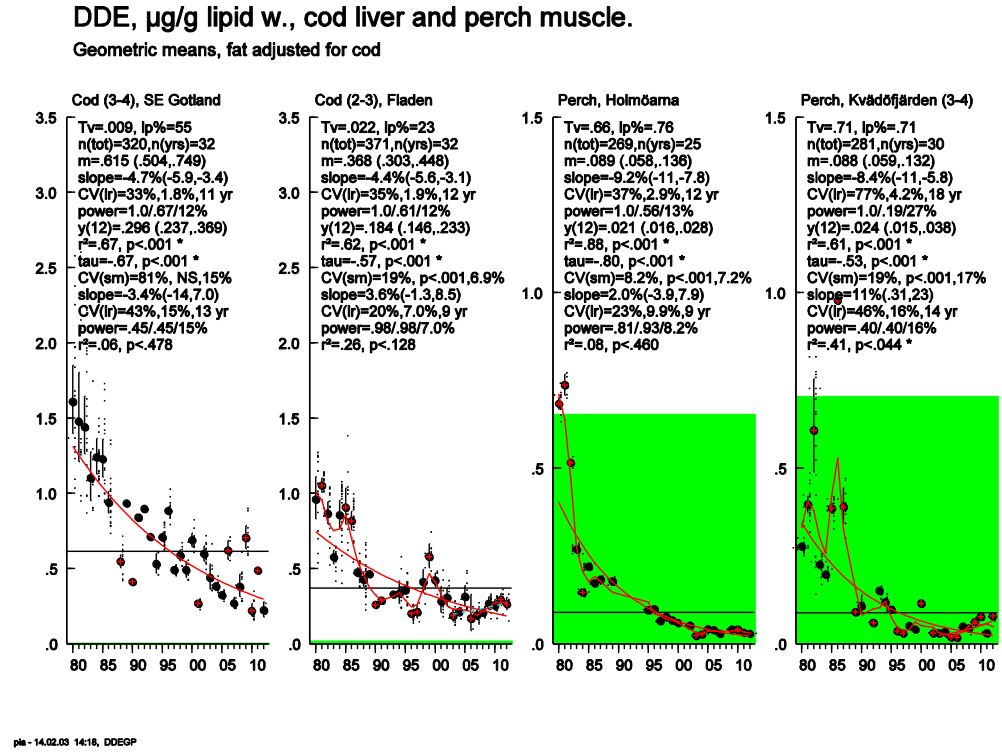


Figure 23.4. DDE concentrations (µg/g lipid weight) in cod liver from southeast Gotland, Fladen; and perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1980). The green area denotes the levels below the suggested target value for DDE in fish.

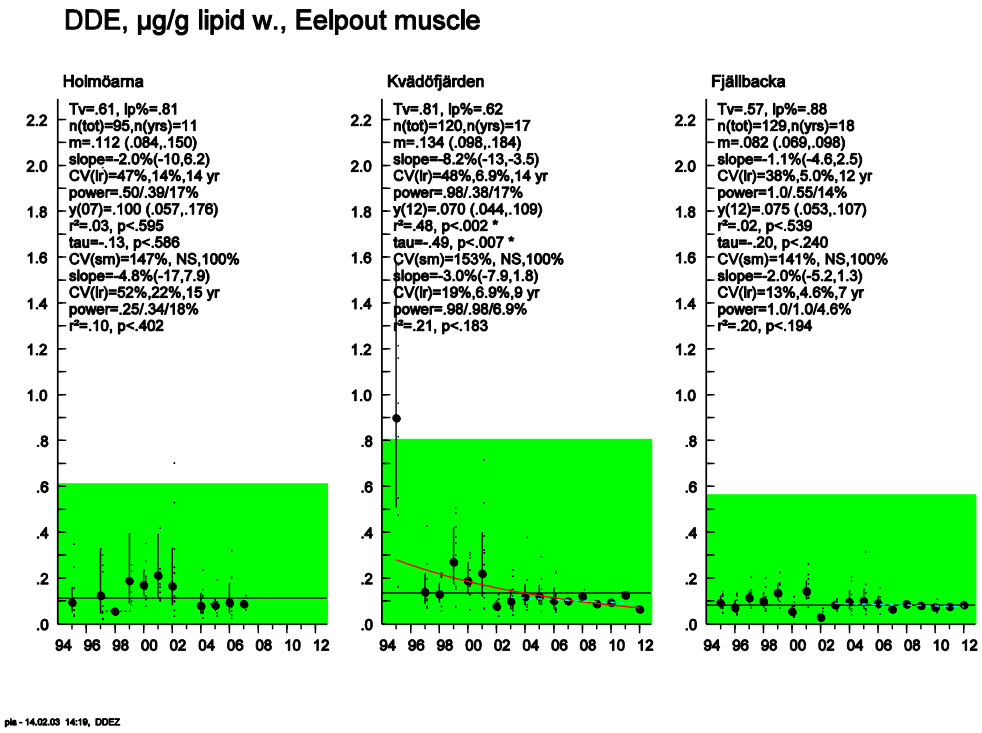


Figure 23.5. DDE concentrations (µg/g lipid weight) in eelpout muscle at Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for DDE in fish.

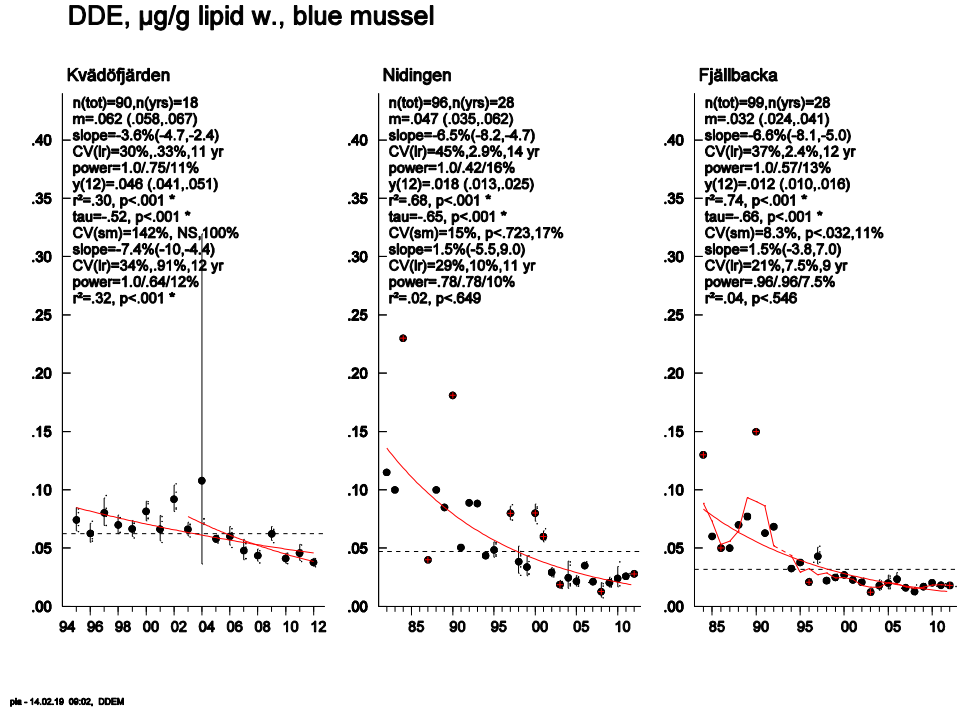


Figure 23.6. DDE concentration (µg/g lipid weight) in blue mussel at Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1982, 1984 and 1995 respectively).

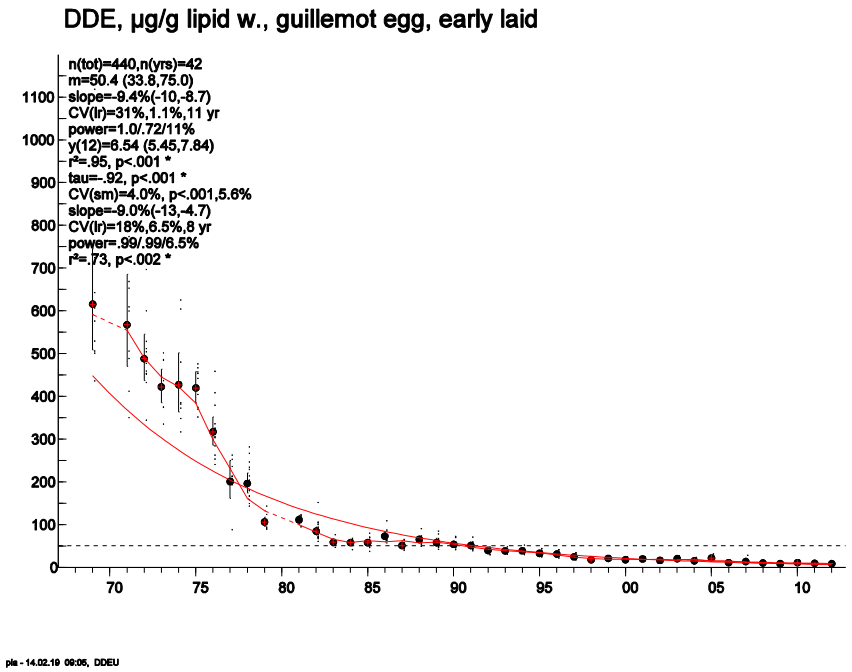


Figure 23.7. DDE concentrations (µg/g lipid weight) in guillemot eggs at Stora Karlsö (time series starting in 1969).

The discharge of fresh DDT during 1983 - 84 (Bignert et al. 1990) is clearly noticeable in the time series from Landsort and Utlängan in the Baltic proper, and Fladen on the Swedish west coast.

The number of years required to detect an annual change of 10% for DDE in herring varied between 11 - 15 years. In general, DDE varies somewhat less between years compared to DDT and DDD.

23.3.3 Comparison to threshold

In all herring (except at Landsort which is very close to the target level), perch and eelpout time series, the DDE concentration is below the suggested target level based on OSPAR EAC (Environmental Assessment Criteria) of 0.0005 ug/g wet weight. Cod from both Fladen and southeast of Gotland is on the other hand above the suggested target level.

23.4 Conclusion

The concentration of DDEs in herring and cod are higher from sites in the Baltic Proper compared to sites on the west coast of Sweden.

The concentration of DDE in herring, perch, cod and blue mussels has decreased at a rate of between 3 - 10% per year from all investigated sites between the years 1980 - 2012. DDE concentration has decreased by 10% per year in guillemot eggs. DDT has generally decreased faster than the sum of DDTs.

DDE concentrations for cod from both the Baltic and the Swedish west coast and for herring from the Baltic Proper and spring caught herring from the south Bothnian Sea are above the suggested target level.

Table 23.2. Trend (in %) for **DDE** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's DDE concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	513	33	78-12	-7.8(-9.6,-5.9)	.0000 ---	15	21.9	.024 (.017,.035)
Harufjärden(3-5)		10	03-12	4.4(-6.2,15)	0.3686	13	17	
Ängskärsklubb(3-5)	501	33	78-12	-7.4(-8.9,-5.9)	.0000 ---	13	16.8	.054 (.041,.072)
Ängskärsklubb(3-5)		10	03-12	-6.9(-24,9.8)	0.369	18	29.4	
Landsort(3-5)	486	34	78-12	-5.6(-6.7,-4.4)	.0000 ---	12	12.6	.132 (.106,.165)
Landsort(3-5)		10	03-12	-7.1(-13,-1.5)	-0.0194	9	8.39	
Utlängan(3-4)	391	33	80-12	-4.1(-5.3,-2.9)	.0000 ---	12	12.6	.156 (.125,.196)
Utlängan(3-4)		10	03-12	-1.3(-10,7.3)	0.7289	12	13.5	
Ängskärsklubb spring(2-6)	650	39	72-12	-6.1(-7.5,-4.7)	.0000 ---	15	21.3	.169 (.123,.232)
Ängskärsklubb spring(2-6)		10	03-12	-8.7(-29,12)	0.3646	20	39	
Utlängan spring(2-4)	633	38	72-12	-9.7(-11,-8.8)	.0000 ---	12	12.9	.144 (.118,.177)
Utlängan spring(2-4)		10	03-12	-2.2(-12,7.3)	0.6129	13	15	
Fladen(2-3)	556	33	80-12	-7.8(-9.0,-6.5)	.0000 ---	12	13.4	.018 (.014,.023)
Fladen(2-3)		10	03-12	-.06(-5.5,5.4)	0.9302	9	8.1	
Väderöarna	289	17	95-12	-4.8(-8.2,-1.5)	.0074 --	12	13.5	.014 (.010,.020)
Väderöarna		9	03-12	.00(-7.6,7.6)	0.9492	11	11.2	
Cod liver								
SE Gotland(3-4)	320	32	80-12	-4.7(-5.9,-3.4)	.0000 ---	11	12.5	.296 (.237,.369)
SE Gotland(3-4)		10	03-12	-3.4(-14,7.0)	0.4783	13	16.6	
Fladen(2-3)	371	32	80-12	-4.4(-5.6,-3.1)	.0000 ---	12	13.3	.184 (.146,.233)
Fladen(2-3)		10	03-12	3.6(-1.3,8.5)	0.1281	9	7.23	
Perch muscle								
Holmöarna	269	25	80-12	-9.2(-11,-7.8)	.0000 ---	12	14.3	.021 (.016,.028)
Holmöarna		9	03-12	2.0(-3.9,7.9)	0.4605	9	8.53	
Kvädöfjärden	281	30	80-12	-8.4(-11,-5.8)	.0000 ---	18	30.7	.024 (.015,.038)
Kvädöfjärden		10	03-12	11(.31,23)	.0439 +	14	17.9	
Eelpout muscle								
Holmöarna	95	9	98-07	-4.8(-17,7.9)	0.4021	15	20.2	.112 (.084,.150) m
Kvädöfjärden	120	17	95-12	-8.2(-13,-3.5)	.0022 --	14	18.8	.070 (.044,.109)
Kvädöfjärden		10	03-12	-3.0(-7.9,1.8)	0.1833	9	7.12	
Fjällbacka	129	18	95-12	-1.1(-4.6,2.5)	0.5385	12	14.5	.082 (.069,.098) m
Fjällbacka		10	03-12	-2.0(-5.2,1.3)	0.1937	7	4.67	
Blue mussel								
Nidingen	96	28	82-12	-6.7(-8.6,-4.8)	.0000 ---	14	17.4	.018 (.013,.025)

Nidingen		10	03-12	1.5(-5.7,8.6)	0.6491	11	10.9	
Fjällbacka	99	28	84-12	-6.8(-8.4,-5.2)	.0000 ---	12	14.2	.012 (.010,.016)
Fjällbacka		10	03-12	1.5(-3.8,6.8)	0.5461	9	7.82	
Kvädöfjärden	90	18	95-12	-3.6(-5.7,-1.6)	.0019 --	9	8.05	.046(.037,.056)
Kvädöfjärden		10	03-12	-7.7(-13,-2.4)	.0101 -	9	7.89	
Guillemot egg								
Stora Karlsö	440	42	69-12	-9.8(-11,-9.1)	.0000 ---	11	11.6	6.54 (5.45,7.84)
Stora Karlsö		10	03-12	-9.4(-14,-4.8)	.0016 --	8	6.75	

Table 23.3. The estimated proportion of DDT, DDE, DDD (%) 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						
Nidingen			81-95	17	63	20
Fjällbacka			80-95	18	65	17

24 HCHs, Hexachlorocyclohexanes

Updated 14.02.28

The isomers α-HCH, β -HCH and γ-HCH i.e. lindane, have been analysed in muscle tissue for various fish species (liver tissue for cod), blue mussel soft body and guillemot eggs since 1988 (Table 24.1). Samples from 1987 at Harufjärden and Landsort have been retrospectively analysed. The concentrations of β -HCH are in many cases close to the quantification limit, which implies analytical problems.

24.1 Introduction

24.1.1 Uses, Production and Sources

HCHs have been used as insecticides and for controlling agricultural pests and parasites of farm animals (Walker et al. 2001, Li & Macdonald 2005). 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 HCHs, being 500 - 1000 times as potent as the α-isomer (White-Stevens 1971). Lindane consists mainly of γ-HCH (Li & Macdonald 2005).

24.1.2 Conventions, Aims and Restrictions

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

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

HCHs are three of the initial 12 Persistent Organic Pollutants (POPs) included in The Stockholm Convention on POPs, an international agreement requiring measures for reducing or preventing release of dangerous substances into the environment. The Stockholm Convention was adopted in 2001 and entered into force in 2004.

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

The use of technical HCH stopped in 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 as recently as 1990 (Yi-Fan et al. 1996).

24.1.3 Target Levels

The target level (TL) used for α-HCH and lindane in the time series for fish is 2.6 µg/kg wet weight. The original TL is set for the sum of HCH but is used separately for α-HCH and lindane in the time-series to avoid loss of information, since many of the values the last 10 years is below LOQ. For further information on TLs and selection of target level see chapter 10. The original TL has been recalculated for each time series based on the lipid

percentage. The recalculated target level (Tv) together with the lipid percentage (lp) is shown above the statistical information in each time series.

24.2 Methods

24.2.1 Analytical Information

See chapter 6, section 6.2 for further information on analysis methods for HCHs.
The quantification 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.

24.3 Results

24.3.1 Spatial Variation

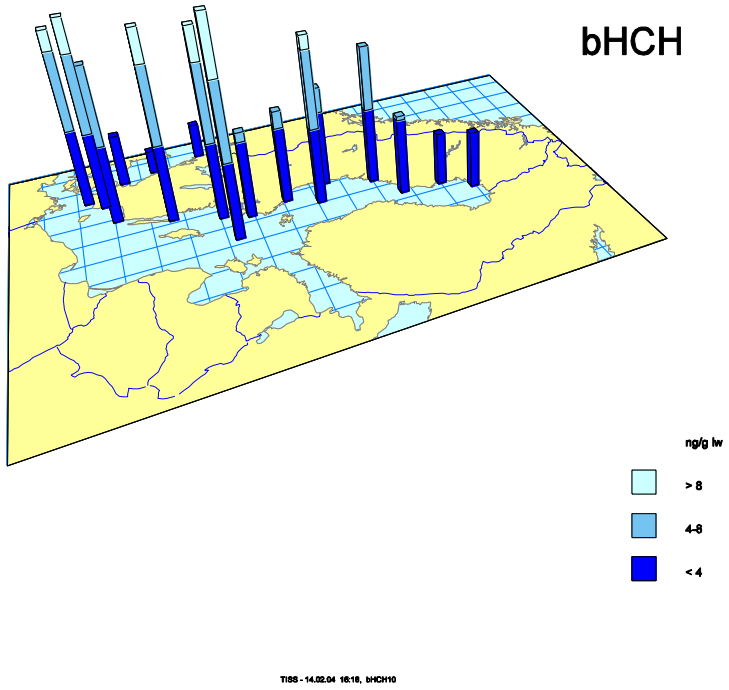


Figure 24.1. Spatial variation of β-HCH concentrations (ng/g lipid weight.) in herring muscle.

Figure 24.1 shows higher concentrations of β-HCH in herring from the Baltic Proper than in herring from the Bothnian Sea and the Swedish west coast.

Neither for α-HCH nor for lindane are there any spatial differences between the Baltic proper and the Swedish west coast for herring, cod, perch, or blue mussels.

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

24.3.2 Temporal Variation

The variation for α-HCH concentrations in herring muscle was generally low and the number of years required to detect an annual change of 10 % varied between 8 – 11 years (Fig. 24.2, 24.3).

An annual decreasing trend of 15 - 17% was found for herring from all sites (table 24.1). Concentrations in cod liver (Fig. 24.4) have significantly decreased in the time series from southeast of Gotland and Fladen (in the Kattegat on the Swedish west coast). Concentrations of α-HCH have also decreased significantly in perch (Fig. 24.4) from Kvädöfjärden and Holmöarna, guillemot eggs from St Karlsö, and in blue mussels (Fig. 24.5) from all sites sampled (in the Baltic and at the Swedish west coast).

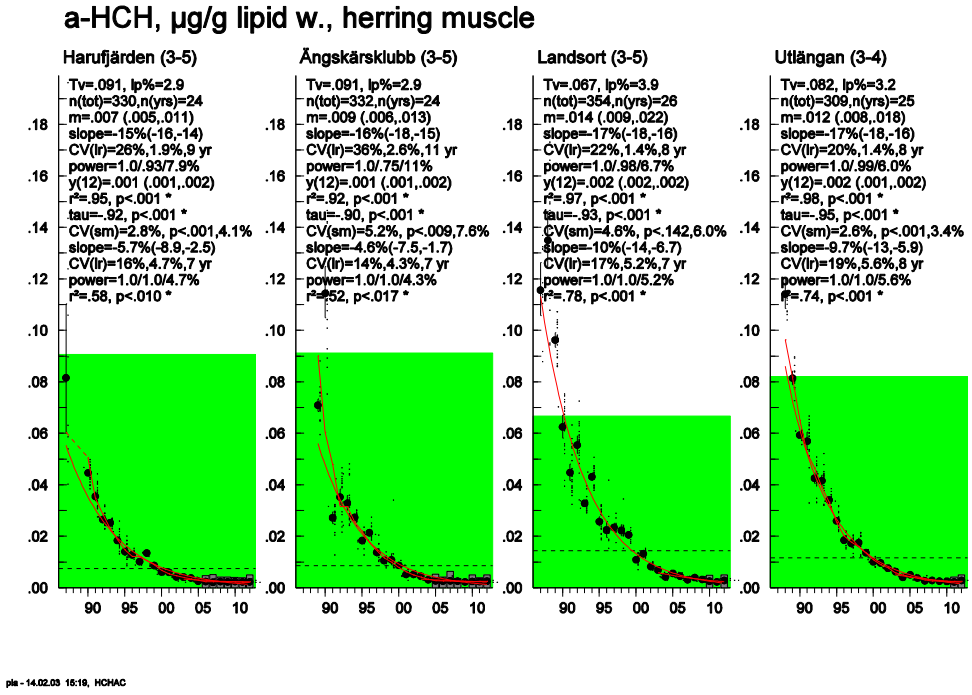


Figure 24.2. α-HCH concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for a-HCH in fish. The bars represent years where all values were below LOQ.

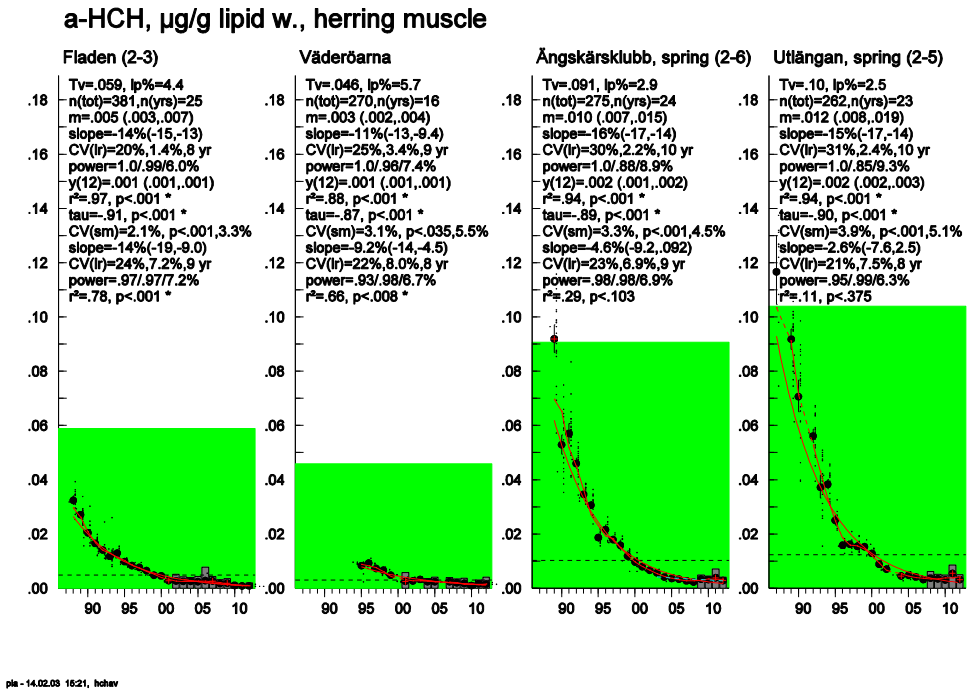


Figure 24.3. α-HCH concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for a-HCH in fish. The bars represent years where all values were below LOQ.

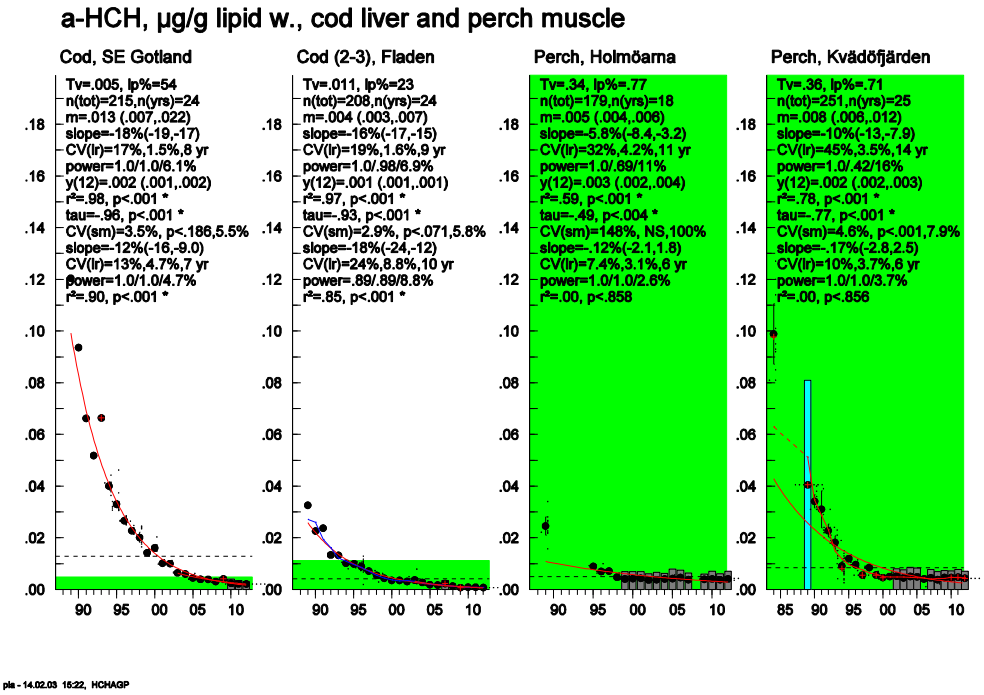


Figure 24.4. α-HCH concentrations (µg/g lipid weight) in cod liver from southeast Gotland and Fladen; and in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 (cod); 1989 and 1984 (perch). The green area denotes the levels below the suggested target value for a-HCH in fish. The bars represent years where all values were below LOQ.

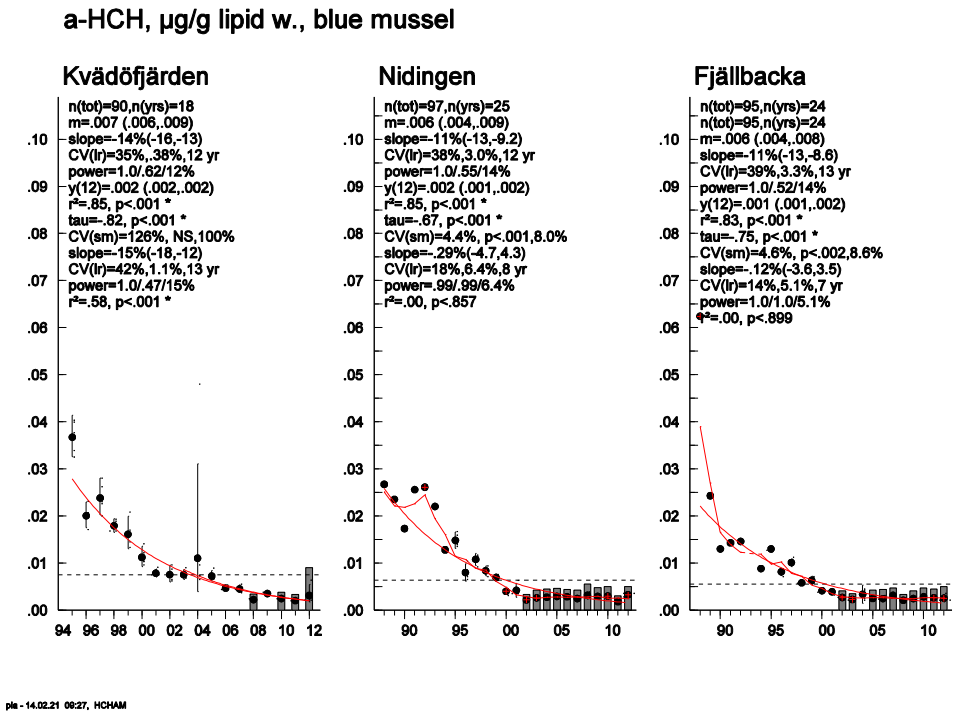


Figure 24.5. α-HCH concentrations (µg/g lipid weight) in blue mussel from Nidingen,Fjällbacka and Kvädöfjärden (time series starting in 1995, 1988 and 1988 respectively). The bars represent years where all values were below LOQ.

Concentrations of β-HCH are generally decreasing, and are now approaching the quantification limit, making it less suitable 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 in herring from Ängskärsklubb, Landsort and Utlängan, in cod from southeast of Gotland, and in guillemot eggs from St Karlsö (Fig. 24.6).

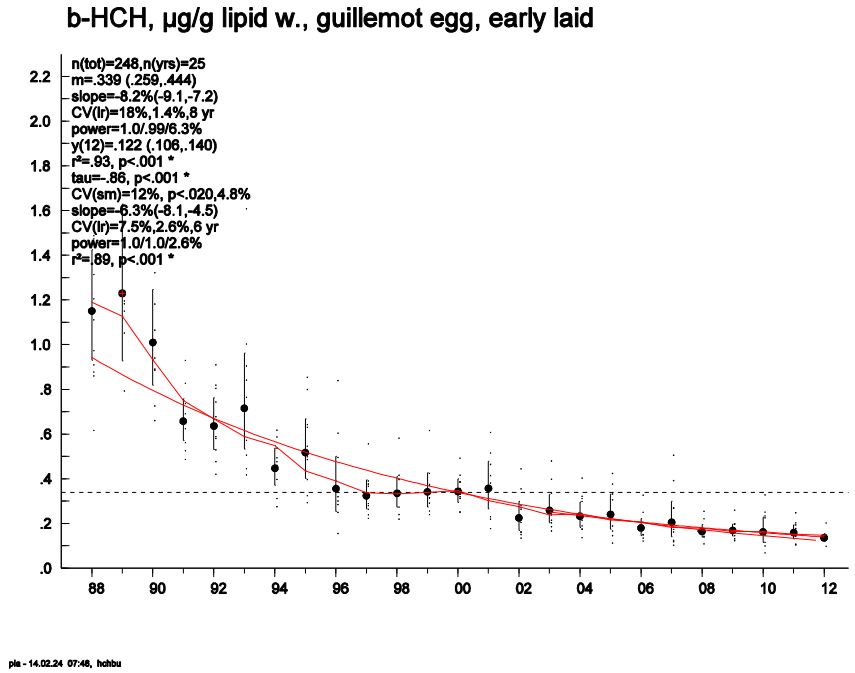


Figure 24.6. β-HCH concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1988).

The concentrations of lindane (γ-HCH) have decreased significantly in all analysed matrices at all sampling sites (Fig. 24.7, 24.8, 24.9, 24.10). This annual decrease is in the magnitude of 10 - 15% for herring and blue mussels and –11-13% for cod and perch (table 24.2).

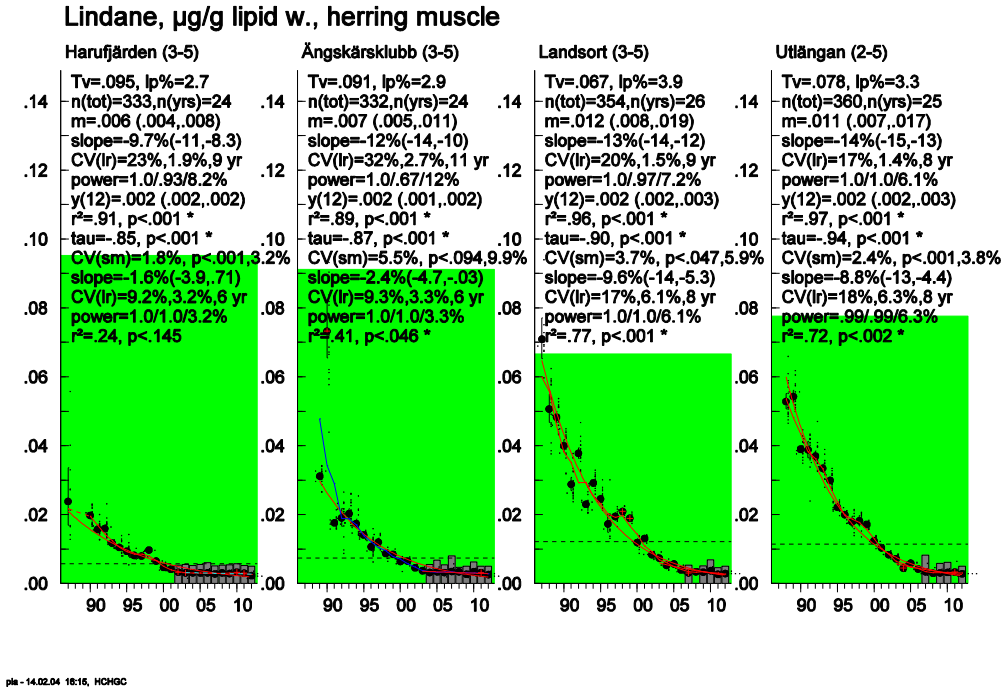


Figure 24.7. γ-HCH concentrations (µg/g lipid weight) herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series from 1987, 1989, 1987 and 1998 respectively). The green area denotes the levels below the suggested target value for lindane in fish. The bars represent years where all values were below LOQ.

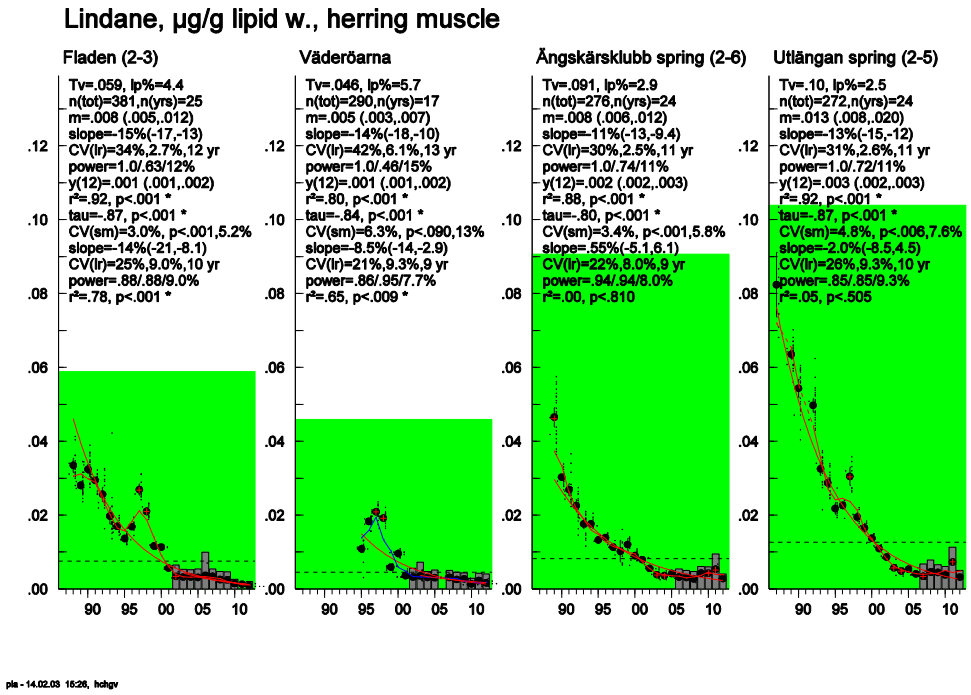


Figure 24.8. γ-HCH concentrations (µg/g lipid weight) herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1986, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for lindane in fish. The bars represent years where all values were below LOQ.

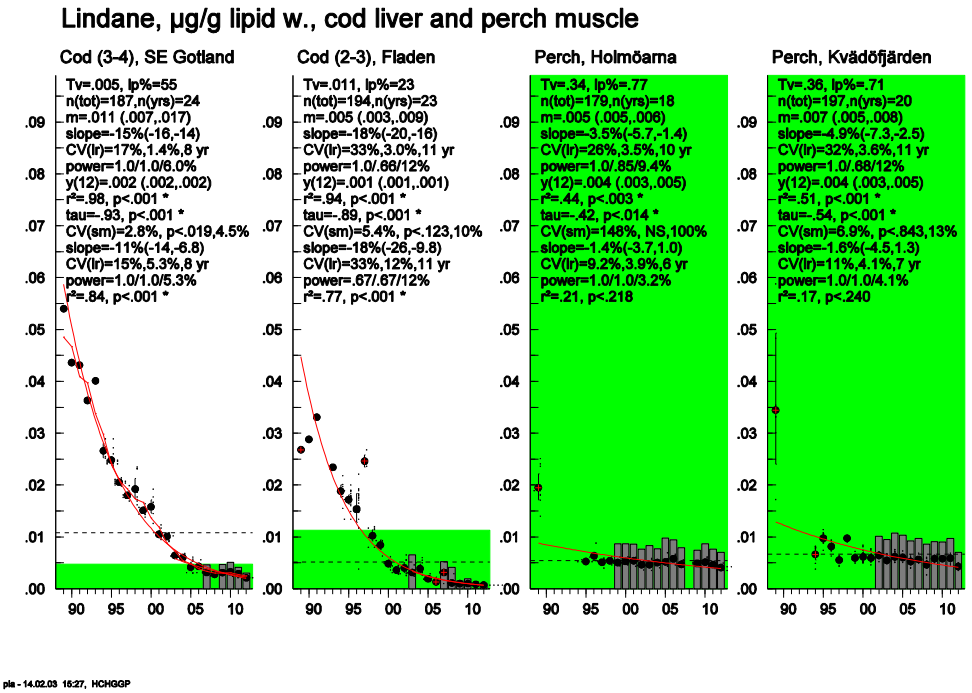


Figure 24.9. γ-HCH concentrations (µg/g lipid weight) in cod liver from southeast Gotland and Fladen; and in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 (cod); and 1989 (perch). The green area denotes the levels below the suggested target value for lindane in fish. The bars represent years where all values were below LOQ.

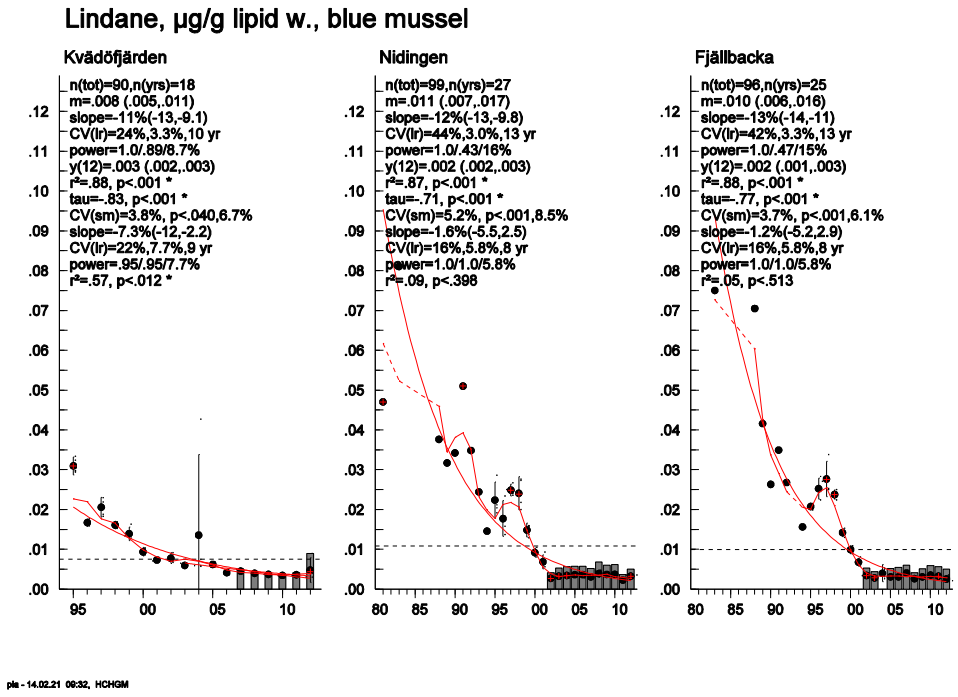


Figure 24.10. γ-HCH concentrations (µg/g lipid weight) in blue mussel from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1995; 1981, 1983 and 1983). The bars represent years where all values were below LOQ.

24.3.3 Comparison to threshold

When assessing the α-HCH and lindane individually, all herring, cod (but cod from SE Gotland is very close to the target level), and perch time series are below the suggested target level of 2.6 µg/kg wet weight, based on IVLs (The Swedish Environmental Research Institute) conversion of the EQS for surface water to biota.

24.4 Conclusion

Higher concentrations of β-HCH in herring from the Baltic Proper than in herring from the Bothnian Sea and the Swedish west coast are observed.

In general, the concentrations of HCHs seem to have decreased at a rate of about 9% or more per year in various species from the Baltic as well as the Swedish west coast, since the end of the 1980s. From 10 time series on herring, cod and guillemot eggs for 1987 - 95, a median decrease of 65% (38 - 88%) could be estimated. In general, α-HCH is decreasing faster than lindane.

Unlike PCBs, DDTs and HCB, HCHs showed no significant seasonal difference in concentrations between herring caught in spring and autumn.

In all areas, the measured sum of the a-HCH, β-HCH and Lindane concentrations in herring, perch and cod liver from Fladen, at least during the last 5 years, are below the suggested target level. The concentration in cod liver from southeast of Gotland is above the suggested target level.

Table 24.1. Trend (in %) for **α-HCH** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's α-HCH concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	330	24	87-12	-15(-16,-14)	.0000 ---	9	8.25	.001 (.001,.002)
Harufjärden(3-5)		10	03-12	-5.7(-8.9,-2.5)	0.0105	7	4.84	
Ängskärsklubb(3-5)	332	24	89-12	-16(-18,-15)	.0000 ---	11	11.3	.001 (.001,.002)
Ängskärsklubb(3-5)		10	03-12	-4.6(-7.5,-1.7)	0.0175	7	4.35	
Landsort(3-5)	354	26	87-12	-17(-18,-16)	.0000 ---	8	6.91	.002 (.002,.002)
Landsort(3-5)		10	03-12	-10(-14,-6.7)	.0008 ---	7	5.34	
Utlängan(3-4)	309	25	88-12	-17(-18,-16)	.0000 ---	8	6.13	.002 (.001,.002)
Utlängan(3-4)		10	03-12	-9.7(-13,-5.9)	.0015 --	8	5.73	
Ängskärsklubb spring	275	24	89-12	-16(-17,-14)	.0000 ---	10	9.3	.002 (.001,.002)
Ängskärsklubb spring		10	03-12	-4.6(-9.2,.092)	0.1034	9	7.17	
Utlängan spring	262	23	87-12	-15(-17,-14)	.0000 ---	10	9.7	.002 (.002,.003)
Utlängan spring		9	04-12	-2.6(-7.6,2.5)	0.3747	8	6.49	
Fladen(2-3)	381	25	88-12	-14(-15,-13)	.0000 ---	8	6.13	.001 (.001,.001)
Fladen(2-3)		10	03-12	-14(-19,-9.0)	.0008 ---	9	7.45	
Väderöarna	270	16	95-12	-11(-13,-9.4)	.0000 ---	9	7.67	.001 (.001,.001)
Väderöarna		9	03-12	-9.2(-14,-4.5)	.0075 --	8	6.94	
Cod liver								
SE Gotland	215	24	89-12	-18(-19,-17)	.0000 ---	8	6.27	.002 (.001,.002)
SE Gotland		10	03-12	-12(-16,-9.0)	.0000 ---	7	4.79	
Fladen	208	24	89-12	-16(-17,-15)	.0000 ---	9	7.11	.001 (.001,.001)
Fladen		10	03-12	-18(-24,-12)	.0002 ---	10	9.17	
Perch muscle								
Holmöarna	179	18	89-12	-5.8(-8.4,-3.2)	.0002 ---	11	12	.003 (.002,.004)
Holmöarna		9	03-12	-.12(-2.1,1.8)	0.8582	6	2.65	
Kvädöfjärden	251	25	84-12	-10(-13,-7.9)	.0000 ---	14	17.6	.002 (.002,.003)
Kvädöfjärden		10	03-12	-.17(-2.8,2.5)	0.8564	6	3.76	
Blue mussel								
Nidingen	97	25	88-12	-12(-14,-9.6)	.0000 ---	12	14.6	.002 (.001,.002)
Nidingen		10	03-12	-.29(-4.8,4.2)	0.8566	8	6.57	
Fjällbacka	95	24	88-12	-11(-13,-9.0)	.0000 ---	13	15.1	.001 (.001,.002)
Fjällbacka		10	03-12	-.12(-3.7,3.5)	0.8994	7	5.18	
Kvädöfjärden	90	18	95-12	-16(-18,-13)	.0000 ---	10	9.9	.002(.002,.003)
Kvädöfjärden		10	03-12	-16(-24,-8.4)	.0014 --	11	11.9	
Guillemot egg								
Stora Karlsö	168	18	88-08	-14(-16,-12)	.0000 ---	10	9.6	.002 (.001,.002)

Table 24.2. Trend (in %) for **γ-HCH** (μg/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's γ-HCH concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden(3-5)	333	24	87-12	-9.7(-11,-8.3)	.0000 ---	9	8.55	.002 (.002,.002)
Harufjärden(3-5)		10	03-12	-1.6(-3.9,.71)	0.1451	6	3.29	
Ängskärsklubb(3-5)	332	24	89-12	-12(-14,-10)	.0000 ---	11	12.3	.002 (.001,.002)
Ängskärsklubb(3-5)		10	03-12	-2.4(-4.7,-.03)	-0.0463	6	3.33	
Landsort(3-5)	354	26	87-12	-13(-14,-12)	.0000 ---	9	7.51	.002 (.002,.003)
Landsort(3-5)		10	03-12	-9.6(-14,-5.3)	.0009 ---	8	6.24	
Utlängan(3-4)	360	25	88-12	-14(-15,-13)	.0000 ---	8	6.33	.002 (.002,.003)
Utlängan(3-4)		10	03-12	-8.8(-13,-4.4)	.0019 --	8	6.48	
Ängskärsklubb spring	276	24	89-12	-11(-13,-9.4)	.0000 ---	11	11.4	.002 (.002,.003)
Ängskärsklubb spring		10	03-12	.55(-5.1,6.1)	0.8101	9	8.32	
Utlängan spring	272	24	87-12	-13(-15,-12)	.0000 ---	11	11.7	.003 (.002,.003)
Utlängan spring		10	03-12	-2.0(-8.5,4.5)	0.5051	10	9.8	
Fladen (2-3)	381	25	88-12	-15(-17,-13)	.0000 ---	12	13.1	.001(.001,.002)
Fladen (2-3)		10	03 - 12	-10(-21,-8.1)	.0008 ---	10	9.37	.002 (.001,.002)
Väderöarna	290	17	95-12	-14(-18,-10)	.0000 ---	13	16.4	.001 (.001,.002)
Väderöarna		9	03-12	-8.5(-14,-2.9)	.0090 --	9	7.97	
Cod liver								
SE Gotland	187	24	89-12	-15(-16,-14)	.0000 ---	8	6.17	.002 (.002,.002)
SE Gotland		10	03-12	-11(-14,-6.8)	.0002 ---	8	5.45	
Fladen	194	23	89-12	-18(-20,-16)	.0000 ---	11	12.5	.001 (.001,.001)
Fladen		10	03-12	-18(-26,-9.8)	.0010 --	11	12.4	
Perch muscle								
Holmöarna	179	18	89-12	-3.5(-5.7,-1.4)	.0028 --	10	9.8	.004 (.003,.005)
Holmöarna		9	03-12	-1.4(-3.7,1.0)	0.2181	6	3.29	
Kvädöfjärden	197	20	89-12	-4.9(-7.3,-2.5)	.0004 ---	11	12.2	.004 (.003,.005)
Kvädöfjärden		10	03-12	-1.6(-4.5,1.3)	0.2399	7	4.15	
Eelpout muscle								
Holmöarna	95	11	95-07	-9.1(-13,-5.4)	.0004 ---	9	7.4	.005 (.004,.006)
Holmöarna		9	98-07	-8.0(-13,-2.5)	0.0104	9	7.83	
Kvädöfjärden	120	17	95-12	-8.0(-11,-5.5)	.0000 ---	10	9.49	.004 (.003,.005)
Fjällbacka		10	03-12	4.4(-3.1,12)	0.2097	11	11.4	
Fjällbacka	123	18	95-12	-5.7(-9.6,-1.8)	.0067 --	13	16.3	.004 (.003,.007)
Blue mussel								
Nidingen	99	27	81-12	-12(-14,-10)	.0000 ---	13	17.1	.002 (.002,.003)

Nidingen		10	03-12	-1.6(-5.7,2.5)	0.3978	8	5.95	
Fjällbacka	96	25	83-12	-14(-16,-11)	.0000 ---	13	16.1	.002 (.001,.003)
Fjällbacka		10	03-12	-1.2(-5.3,2.8)	0.5128	8	5.92	
Kvädöfjärden	90	18	95-12	-12(-14,-9.5)	.0000 ---	10	9.12	.003 (.002,.003)
Kvädöfjärden		10	03-12	-7.6(-13,-2.2)	0.0118	9	8.05	

Table 24.3. The estimated proportion of α-, β-, γ- HCH (%) in various matrices and sites.

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

25 HCB, Hexachlorobenzene

Updated 14.02.28

Since 1988, HCB has been analysed in various species (Table 25.1). At Harufjärden and Landsort, samples from 1987 have been retrospectively analysed.

25.1 Introduction

25.1.1 Uses, Production and Sources

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

25.1.2 Conventions, Aims and Restrictions

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

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

HCB is one of the initial 12 Persistent Organic Pollutants (POPs) included in The Stockholm Convention on POPs, an international agreement requiring measures for reducing or preventing release of dangerous substances to the environment. The Stockholm Convention was adopted in 2001 and entered into force in 2004.

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

The use of the highly persistent HCB as a fungicide is banned in the Baltic countries.

25.1.3 Target Levels

The target level (TL) used for HCB in the time series for fish is 10 µg/kg wet weight. For further information on TL and selection of target level see chapter 10. The original TL has been recalculated for each time series based on the lipid percentage. The recalculated target level (Tv) together with the lipid percentage (lp) is shown above the statistical information in each time series.

25.2 Methods

25.2.1 Analytical Information

See chapter 6, section 6.2 for further information on analysis methods for HCBs.
The quantification limit is estimated to approximately 1 ng/g fat weight.

25.3 Results

25.3.1 Spatial variation

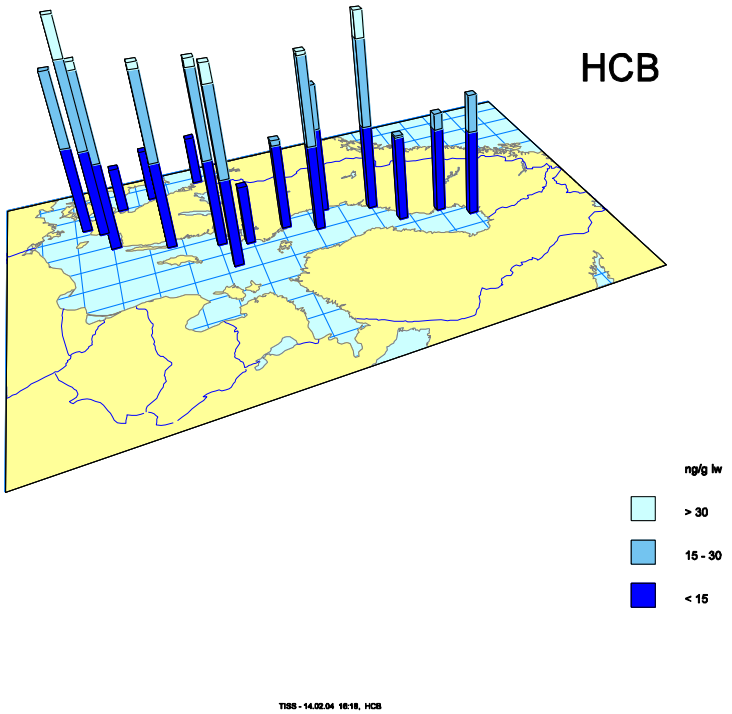


Figure 25.1. Spatial variation of HCB concentrations (ng/g lipid weight) in herring muscle.

Generally, herring muscle from almost all sites in the Baltic Proper and the Bothnian Sea had higher HCB concentrations compared to the Swedish west coast and the Bothnian Bay. The highest concentration was found at Utlängan in the southern Baltic Proper(Fig. 25.1).

However, since the concentrations had decreased considerably in samples from the Baltic Proper, and the variance from the Bothnian Bay and the Baltic Sea were large, no significant differences could be seen in the estimated concentrations for 2012 in the time series in the autumn-caught herring from the various sites in the Baltic (Fig. 25.2). The estimated concentrations from 2011 were more than three times as high in herring from most of the sites in the Baltic compared to herring from the Swedish west coast (Fig. 25.2, 25.3).

Cod from southeast of Gotland had twice as high HCB concentration compared to cod from Fladen (Fig. 25.4).

The results from eelpout and blue mussel samples from Kvädöfjärden that were analysed for HCB for the first time in 1995, *indicated that concentrations were at least twice as high in the Baltic compared to the Kattegat and the Skagerrak*. This difference was significant for blue mussels and for eelpout when comparing Holmöarna and Väderöarna/Fjällbacka (Fig. 25.5-6).

25.3.2 Temporal Variation

There were significant decreases in HCB concentrations in all analysed fish species (Fig. 25.2, 25.3, 25.4, 25.5) and in guillemot eggs (Fig. 25.7). However, for perch increases in concentrations are seen during the most recent ten years from Holmöarna and Kvädöfjärden (Fig. 25.4). For blue mussels an increase in concentration is seen at Nidingen (Fig. 25. 6).

The decrease is in the magnitude of 2 - 7% for herring, cod, perch and guillemot egg(table 25.1).

The number of years required to detect an annual change of 10% is about 12 - 13 years for cod and perch, and varies between 10 - 14 years for the herring time series.

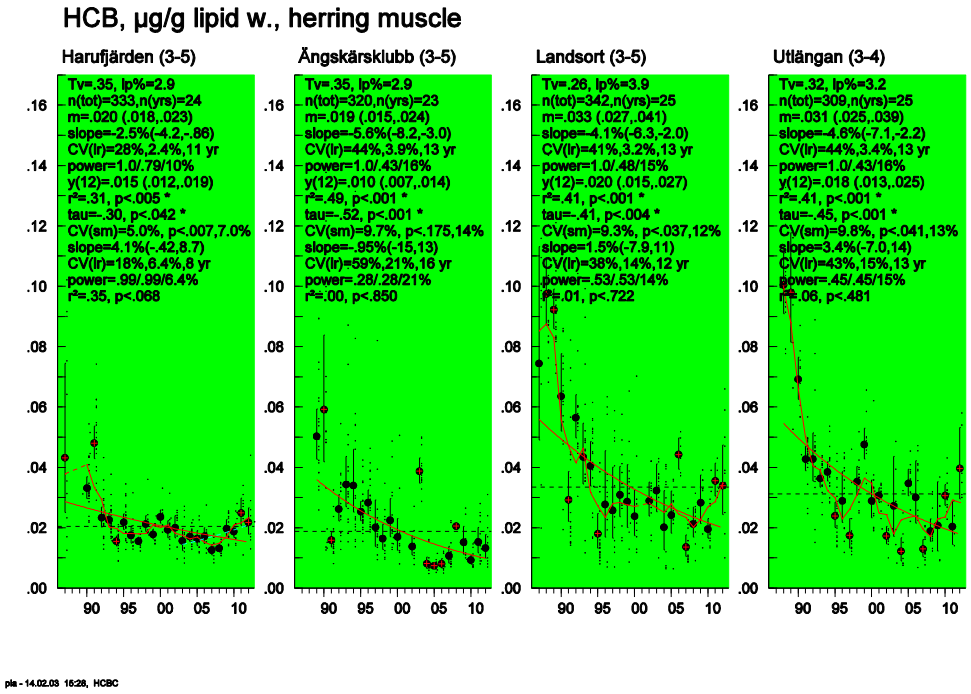


Figure 25.2. HCB concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for HCB in fish.

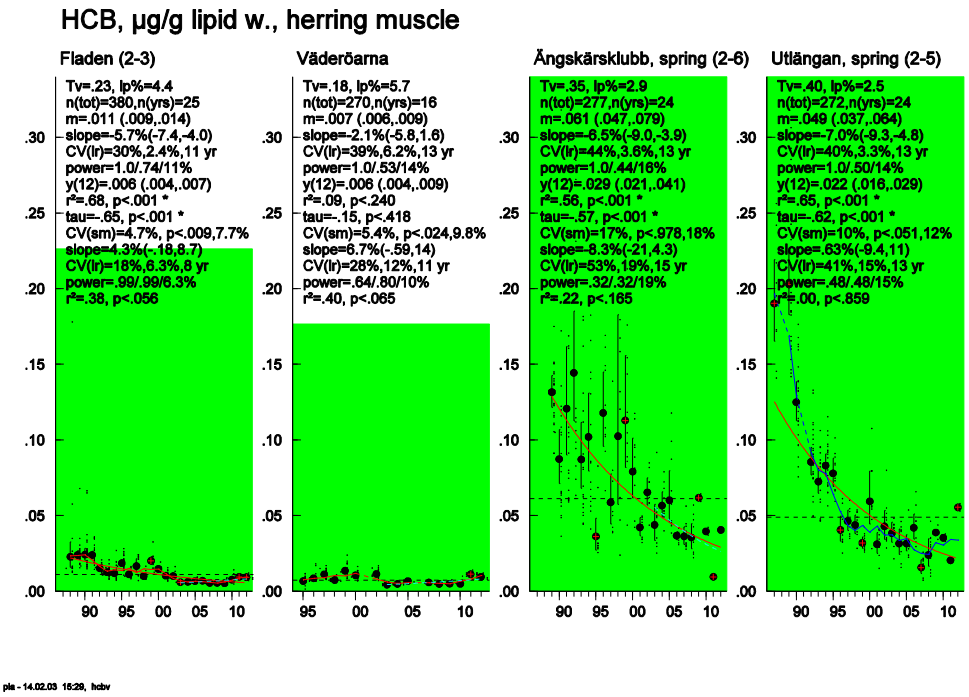


Figure 25.3. HCB concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for HCB in fish.

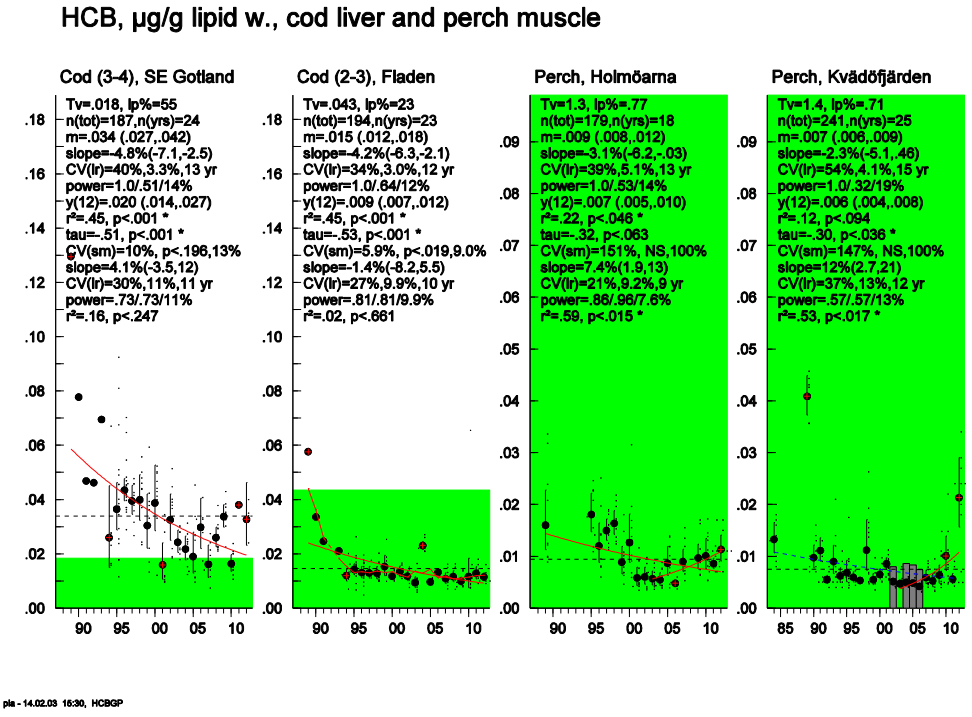


Figure 25.4. HCB concentrations (µg/g lipid weight) in cod liver from southeast Gotland and Fladen, and in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 (cod); 1989 and 1984 perch). The green area denotes the levels below the suggested target value for HCB in fish. The bars represent years where all values were below LOQ.

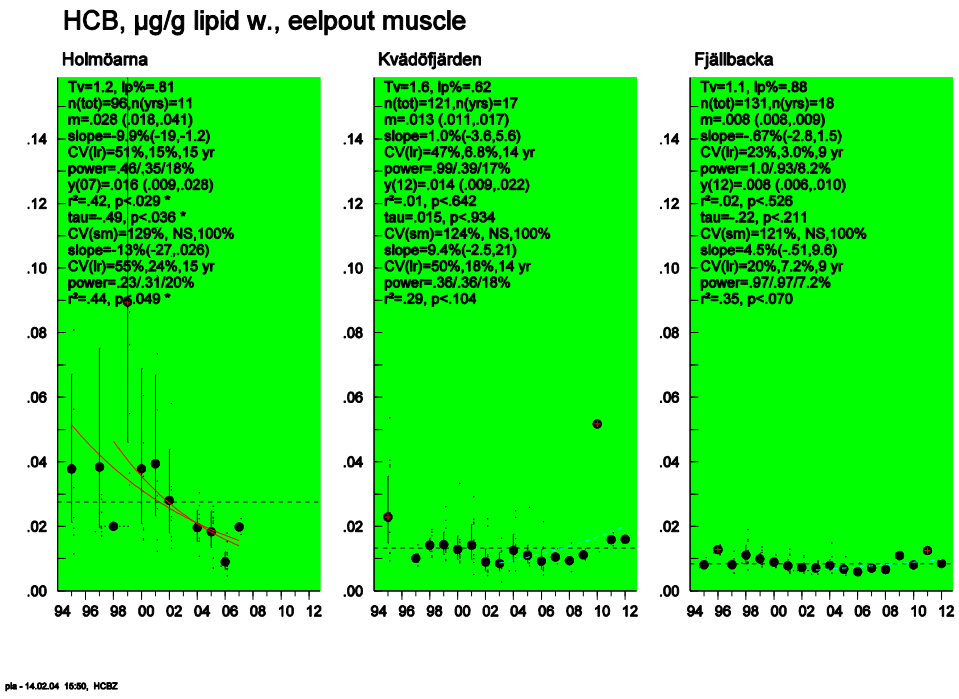


Figure 25.5. HCB concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for HCB in fish.

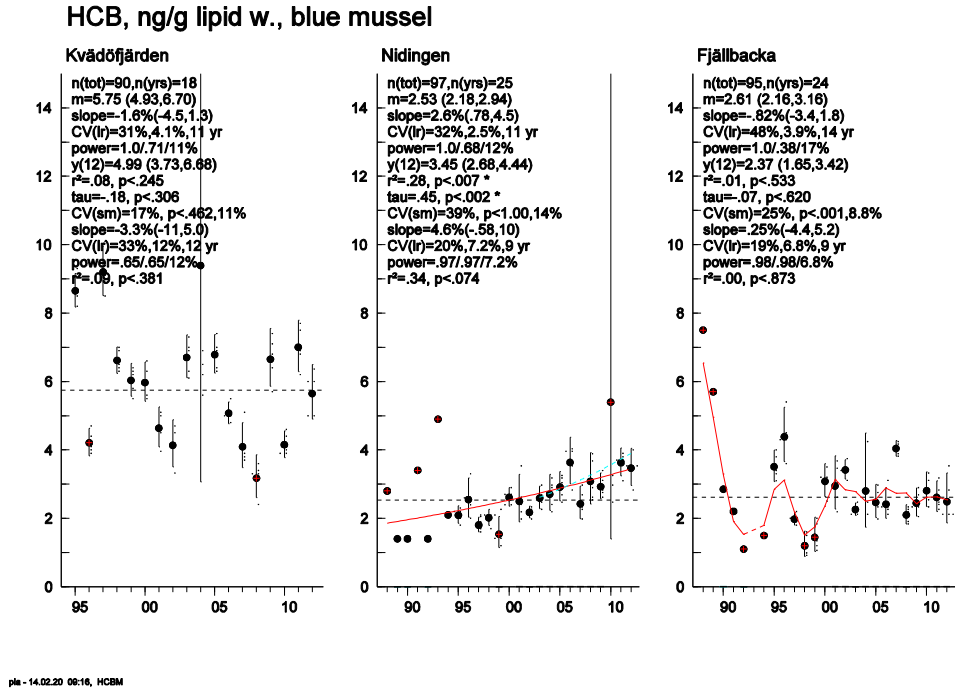


Figure 25.6. HCB concentrations (µg/g lipid weight) in blue mussel soft tissue from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1988, 1988 and 1995 respectively).

In blue mussels from the Swedish west coast, the concentrations were very low (Fig. 25.6).

The number of years required to detect an annual change of 10% varied between 11-14 years for the blue mussel series.

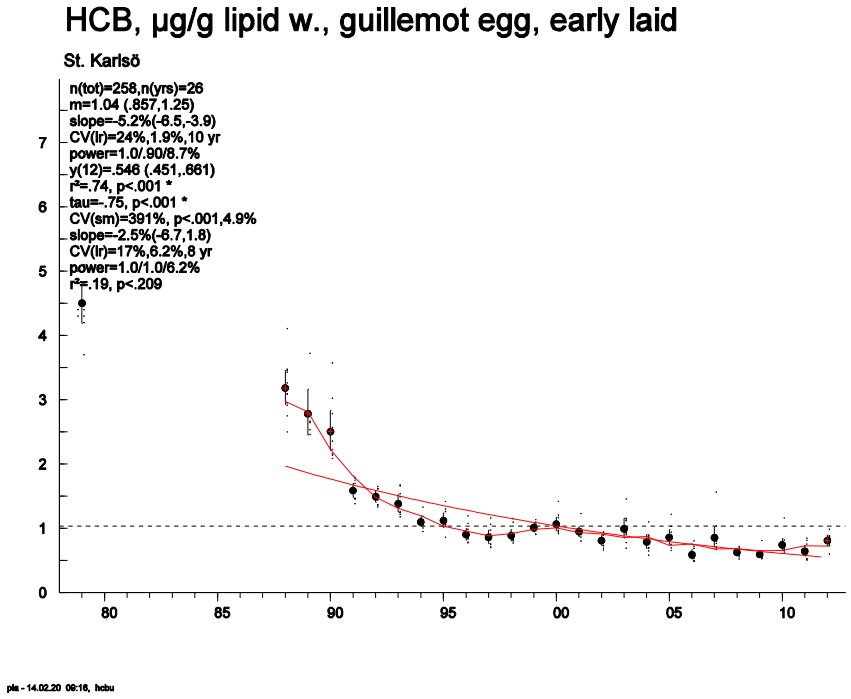


Figure 25.7. HCB concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series from 1979).

25.3.3 Species Differences

At some of the sampling sites, specimens of different species were collected within the same area. HCB was analysed in fish muscle tissue, except for cod where the liver was used, whereas whole soft body was analysed in blue mussels. The mean concentrations (last year) (ng/g lipid weight) found are listed in decreasing order below.

Holmöarna: Eelpout (16) > Perch (7)
Kvädöfjärden: Eelpout (13) > Perch (6) - Blue mussel (6)
Fladen/Nidingen: Cod (9) > Herring (6) >Blue mussel (3)
Väderöarna/Fjällbacka: Eelpout (8) > Herring (7) > Blue mussel (3)

The lowest concentrations were found in blue mussels, and the highest were found in guillemot eggs.

Herring caught in the spring at Ängskärsklubb showed two times higher HCB concentrations on a lipid-weight basis compared to samples collected in autumn.

25.3.4 Comparison to threshold

In all areas and species, except cod from southeast of Gotland, HCB concentration is below the target level based on the EQS_{biota} 10 µg/kg wet weight.

25.4 Conclusion

Concentrations of HCBs are higher at sites from the Baltic Proper for herring, eelpout, cod and blue mussels, compared to the Swedish west coast, although a considerable decrease in HCBs in herring muscle from the Baltic Proper has been observed.

All time series, where concentrations were compared with the target value, were below the suggested level, except for cod from southeast of Gotland.

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

Table 25.1. Trend (in %) for **HCB** (μg/g lipid weight, blue mussels ng/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's HCB concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	333	24	87-12	-2.5(-4.2,-.86)	.0046 --	11	10.6	.015 (.012,.019)
Harufjärden		10	03-12	4.1(-.42,8.7)	0.0679	8	6.64	
Ängskärsklubb(3-5)	320	23	89-12	-5.6(-8.2,-3.0)	.0002 ---	13	17.2	.010 (.007,.014)
Ängskärsklubb(3-5)		10	03-12	-.95(-15,13)	0.8501	16	23.1	
Landsort(3-5)	342	25	87-12	-4.1(-6.3,-2.0)	.0006 ---	13	15.9	.020 (.015,.027)
Landsort(3-5)		10	03-12	1.5(-7.9,11)	0.7225	12	14.8	
Utlängan(3-4)	309	25	88-12	-4.6(-7.1,-2.2)	.0007 ---	13	17.1	.018 (.013,.025)
Utlängan(3-4)		10	03-12	3.4(-7.0,14)	0.4805	13	16.6	
Ängskärsklubb spring	277	24	89-12	-6.5(-9.0,-3.9)	.0000 ---	13	16.9	.029 (.021,.041)
Ängskärsklubb spring		10	03-12	-8.3(-21,4.3)	0.1648	15	20.9	
Utlängan spring	272	24	87-12	-7.0(-9.3,-4.8)	.0000 ---	13	15.5	.022 (.016,.029)
Utlängan spring		10	03-12	.63(-9.4,11)	0.8592	13	15.9	
Fladen(2-3)	380	25	88-12	-5.7(-7.4,-4.0)	.0000 ---	11	11.4	.006 (.004,.007)
Fladen(2-3)		10	03-12	4.3(-.18,8.7)	0.0563	8	6.49	
Väderöarna	270	16	95-12	-2.1(-5.8,1.6)	0.2402	13	14.8	.007 (.006,.009) m
Väderöarna		9	03-12	6.7(-.59,14)	0.0647	11	10.6	
Cod Liver								
SE Gotland(3-4)	187	24	89-12	-4.8(-7.1,-2.5)	.0004 ---	13	15.2	.020 (.014,.027)
SE Gotland(3-4)		10	03-12	4.1(-3.5,12)	0.2474	11	11.5	
Fladen(2-3)	194	23	89-12	-4.2(-6.3,-2.1)	.0005 ---	12	12.9	.009 (.007,.012)
Fladen(2-3)		10	03-12	-1.4(-8.2,5.5)	0.6613	10	10.4	
Perch muscle								
Holmöarna	179	18	89-12	-3.1(-6.2,-.03)	0.0457	13	14.9	.007 (.005,.010)
Holmöarna		9	03-12	7.4(1.9,13)	.0152 +	9	7.92	
Kvädöfjärden	241	25	84-12	-2.3(-5.1,.46)	0.0936	15	21.2	.006 (.004,.008)
Kvädöfjärden		10	03-12	12(2.7,21)	.0170 +	12	14.1	
Eelpout muscle								
Holmöarna	96	11	95-07	-9.9(-19,-1.2)	0.0295	15	19.9	.016 (.009,.028)
Holmöarna		9	98-07	-13(-27,.026)	0.0491	15	21.6	
Kvädöfjärden	121	17	95-12	1.0(-3.6,5.6)	0.6424	14	18.3	.013 (.011,.017) m
Kvädöfjärden		10	03-12	9.4(-2.5,21)	0.1041	14	19.4	
Fjällbacka	131	18	95-12	-.67(-2.8,1.5)	0.5263	9	8.49	.008 (.008,.009) m
Fjällbacka		10	03-12	4.5(-.51,9.6)	0.0701	9	7.41	
Blue mussel								
Nidingen	97	25	88-12	2.6(.78,4.4)	.0068 ++	11	12.2	3.45 (2.68,4.44)
Nidingen		10	03-12	4.5(-.59,9.5)	0.0738	9	7.42	
Fjällbacka	95	24	88-12	-.83(-3.5,1.8)	0.5326	14	18.6	2.61 (2.16,3.16) m
Fjällbacka		10	03-12	.25(-4.5,5.0)	0.8734	9	7.05	
Kvädöfjärden	90	18	95-12	-1.7(-4.6,1.3)	0.2453	11	11.8	5.75 (4.93,6.70) m
Kvädöfjärden		10	03-12	-3.3(-12,4.9)	0.3813	12	12.7	

Guillemot egg								
Stora Karlsö	258	10	03-12	-2.6(-6.9,1.8)	0.2087	8	6.34	.546 (.451,.661)

26 PCDD/PCDFs – Polychlorinated dioxins/dibenzofurans

Updated 14.02.28

Dioxins in guillemot eggs from St. Karlsö have been retrospectively analysed in a time serie dating back to 1969. Herring muscle tissue has been analysed since 1989.

26.1 Introduction

26.1.1 Uses, Production and Sources

"Dioxins" refer to polychlorinated dibenzo-*p*-dioxin (PCDD) and dibenzofuran (PCDF) compounds. Seventeen (10 furans, 7 dioxins) of the 210 possible congeners, substituted in the positions 2,3,7,8, are considered to be of toxicological importance. Some polychlorinated biphenyls (PCBs) are called dioxin-like PCBs (dl-PCBs) because they have a structure similar to that of dioxins and have dioxin-like effects, however, they are not included in this chapter. PCDD/Fs are characterized by low water solubility and low vapor pressure. In the environment, they can undergo photolysis, however, they are generally very resistant to chemical and biological degradation. Due to their persistent and hydrophobic properties, PCDD/Fs accumulate in sediments and organisms in the aquatic environment.

PCDD/Fs are not produced intentionally. They are formed as by-products in several industrial processes and from most combustion processes, such as municipal waste incineration and small-scale burning under poorly controlled conditions. They are also minor impurities in several chlorinated chemical products (e.g. PCBs, chlorophenols, hexachlorophene etc.). Formerly, pulp bleaching using chlorine gas was an important source of PCDD/Fs.

26.1.2 Toxicological Effects

PCDD/Fs can cause a variety of biological and toxicological effects in animals and humans. The most relevant toxic effects are developmental toxicity, carcinogenity and immunotoxicity. Most toxic effects are explained by the binding of PCDD/Fs to the aryl hydrocarbon (Ah) receptor. The sensitivity of various species to the toxic effects of PCDD/Fs varies significantly. 2,3,7,8-TCDD is the most toxic and well-studied congener and is used as a reference for all other related chemicals.

Each of the 17 relevant congeners is assigned a toxic equivalency factor (TEF), where 2,3,7,8-TCDD equals 1 (Van den Berg et al. 1998; Van den Berg et al. 2006). Dioxin concentrations are here reported as TCDD-equivalents (TEQ), which is the sum of the individual congener concentrations multiplied with its specific TEF.

26.1.3 Conventions, aims and restrictions

Dioxins are included in several international agreements, of which the Stockholm Convention and the Convention on Long Range Transboundary Air are among the most important for the control and reduction of sources to the environment. Several EU legislations regulate dioxins, e.g. the plan for integrated pollution prevention and control (IPPC) and directives on waste incineration (EC 2000, 2008). The EU has also adopted a Community Strategy for dioxins, furans and PCBs (EC 2001). PCDD/Fs are currently not included in the Water Framework Directive but are on the list of substances to be revised for adoption in the near future. HELCOM has listed PCDD/Fs and dl-PCBs as prioritized hazardous substances of specific concern for the Baltic Sea (HELCOM 2010), like OSPAR on the List of Chemicals for Priority Action (OSPAR 2010b).

WHO and FAO have jointly established a maximum tolerable human intake level of dioxins via food, and within the EU there are maximum allowable levels of dioxins in food and feed stuff (EC 2006). The European limit for dioxin levels in the muscle tissue of fish is 4 pg/g ww WHO_{98}-TEQ (ΣPCDD/Fs) or 8 pg/g ww WHO_{98}-TEQ (ΣPCDD/Fs + dl-PCBs)[*]. PCDD/F levels in fat fish, mainly herring and salmon, from the Baltic Sea often exceed this limit. Sweden and Finland have since 2002 been authorised a derogation from this directive, allowing to sell on the domestic market or to non-member states (EC 2375/2001, EC 201/2002, EC 199/2006, EC 1881/2006).

However, the TEQ levels in herring from the reference sites in this investigation do not exceed the prescribed maximum

26.1.4 Target Levels

The target level used for the sum of PCDD/F in WHO_{98}-TEQ in the time series for fish is 3.5 ng/kg wet weight (WHO_{05}-TEQ). The TEFs (Toxic equivalent factors) from 2005 do not differ to a high extent for the PCDDs and PCDFs compared to the TEFs from 1998 so, the WHO_{98}-TEQs in the time series are therefore compared directly with the target level in WHO_{05} TEQ since older data on WHO_{05} TEQs is not available. The original target level has been recalculated for each time series based on the lipid percentage. The recalculated target level (Tv) together with the lipid percentage (lp) is shown above the statistical information in each time series. See chapter see chapter 10 for more information.

26.2 Methods

26.2.1 Analytical information

See chapter 6, section 6.3 for information on analysis methods for dioxins and dibenzofurans.

26.3 Results

26.3.1 Spatial Variation

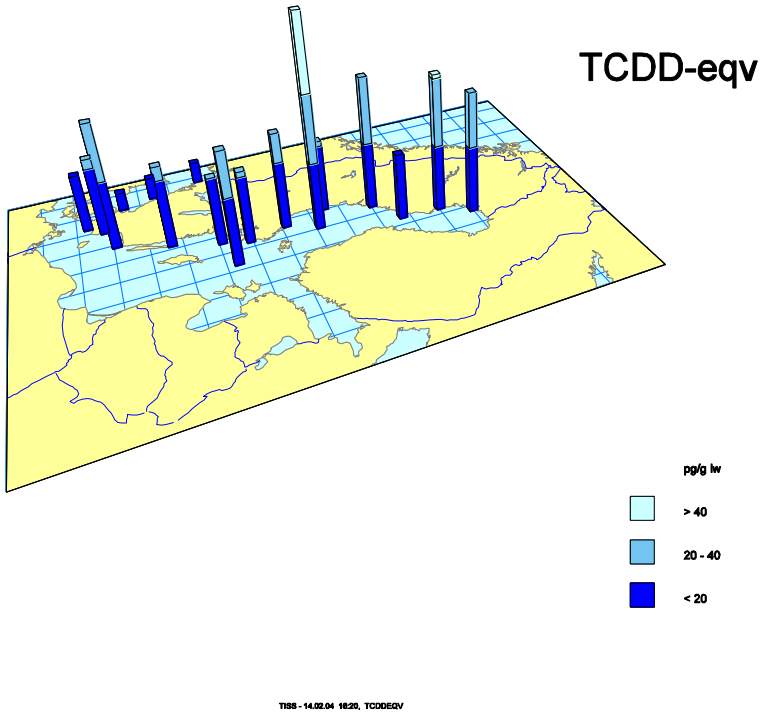


Figure 26.1. Spatial variation in concentration (pg/g lipid weight) of WHO_{05}-TEQ (PCDD/PCDF) in herring muscle.

TCDD-equivalents (pg/g lw) in herring muscle (Figure 26.1) from 2010-2012 are higher at the Bothnian Sea offshore site compared to locations in the Bothnian Bay, the Baltic Proper and on the Swedish west coast.

26.3.2 Temporal Variation

In guillemot eggs, significant decreasing trends were observed for TCDD, TCDF and total PCDD/Fs (TCDD-equivalents) during the period 1969-2012 (Fig. 26.2, table 26.1). However, contrary to the TCDDs, the TCDFs show no decreasing trend since 1990, which may explain the levelling off of the trend for total PCDD/Fs during the last 20 years (Fig. 26.2).

The number of years required to detect an annual change of 10% varied between 8 - 11 years in the time series of guillemot.

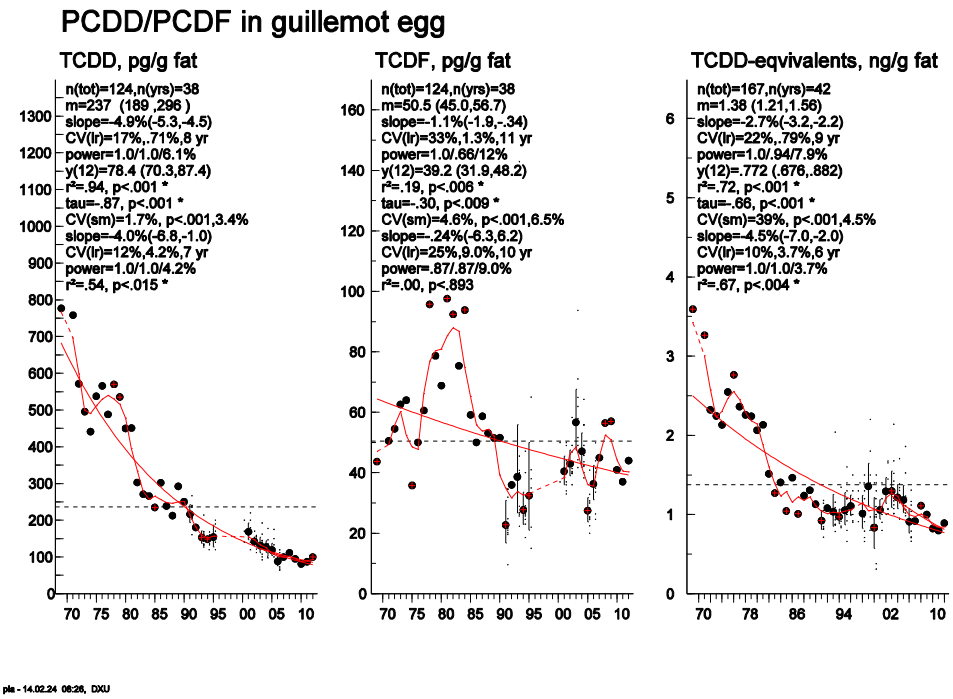


Figure 26.2. PCDD, PCDF (pg TCDD-eqv/g fat) and PCDD/F (ng TCDD-eqv/g fat) concentrations in guillemot eggs from Stora Karlsö (time series starting in 1969). The TCDD-EQV are calculated using the WHO_{98} TEF.

There were no significant changes in the PCDD/F concentrations over time in herring muscle at Harufjärden and Utlängan, either on a wet weight or a lipid weight basis (Fig 26.3 and 26.4). At Ängskärsklubb, however, which had very high levels at the start of the sampling period, a significant decreasing trend is seen (Fig. 26.3 and 26.4) and a significant decreasing trend was also seen at Fladen (lipid weight basis) (Fig. 26.4). Between 2000-2007, an increasing trend was observed at Harufjärden (Fig. 26.4), but the very low level of TCDD-equivalents in herring from 2008/2009 eliminated that trend, however, the concentrations from 2010 and 2011 are again higher (Fig. 26.4). The low levels of TCDD-equivalents cannot be explained by fat content, weight or length (these parameters were normal) so further investigations are needed.

The number of years required to detect an annual change of 10% varied between 10 - 16 years for these time series.

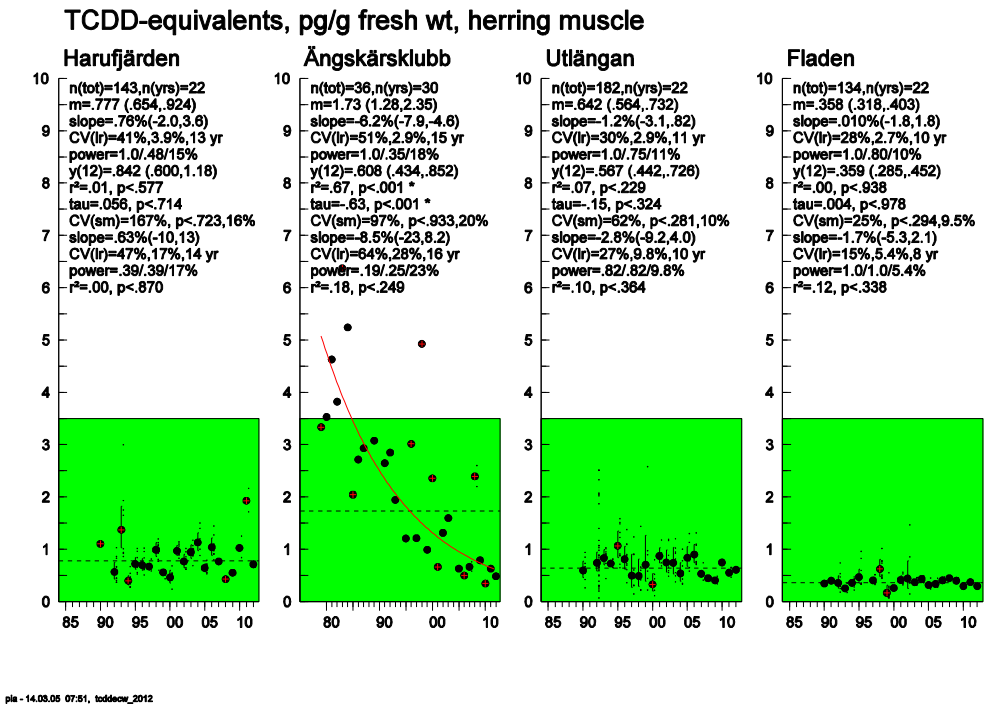


Figure 26.3. PCDD/F concentrations (pg TCDD-eqv/g fresh weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (time series starting in 1990, 1979, 1988 and 1990 respectively). The green area denotes the levels below the suggested target value for PCDD/Fs in fish (secondary poisoning). The TCDD-EQV are calculated using the WHO_{98} TEF.

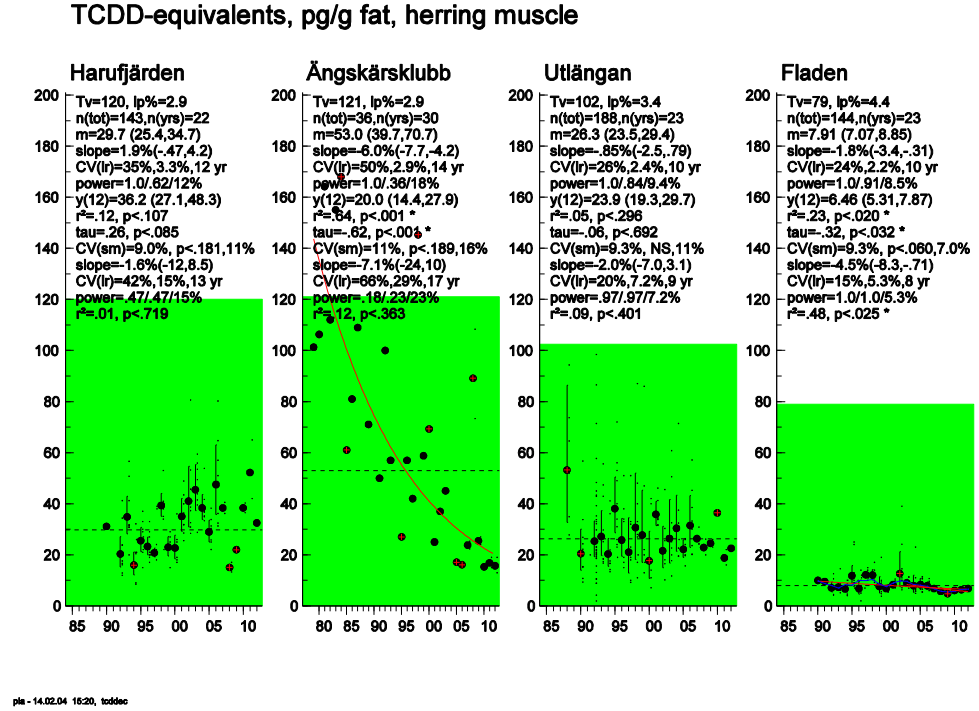


Figure 26.4. PCDD/F concentrations (pg TCDD-eqv /g fat weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (time series starting in 1990, 1979, 1988 and 1990 respectively). The green area denotes the suggested target value for PCDD/Fs in fish (secondary poisoning). The TCDD-EQV are calculated using the WHO_{98} TEF.

26.3.3 Comparison to threshold

All herring time series are below the suggested target level based on the EC EQS (Environmental Quality Standard) of 3.5 pgWHO_{05}-TEQ/g wet weight.

26.4 Conclusion

PCDD/F concentrations are higher in herring muscle from the Bothnian Sea compared to the Baltic Proper, Bothnian Bay, and the Swedish west coast.

In herring a significant decreasing trend for concentrations of PCDD/Fs is seen for Ängskärsklubb and Fladen over the whole time period (lipid weight), but no trend is observed at Harufjärden and Utlängan. In guillemot eggs, significant decreasing trends were observed for TCDD, TCDF and PCDD/Fs during 1970-2012. For TCDFs, no trend can be observed between 1990-2012.

In all areas, the PCDD/F concentrations are below the suggested target level.

Table 26.1. Trend (in %) of **PCDD/F** concentrations in herring (pg TCDD-eqv/g **lipid weight**) and guillemot eggs (ng TCDD-eqv/g lipid weight) assessed from the annual geometric mean in various matrices. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	143	22	90-12	1.9(-.47,4.2)	0.1073	12	13.3	29.7 (25.4,34.7) m
Harufjärden		10	03-12	-1.6(-12,8.5)	0.7187	13	16.1	
Ängskärsklubb	36	30	79-12	-6.0(-7.7,-4.2)	.0000 ---	14	19.5	20.0 (14.4,27.9)
Ängskärsklubb		9	03-12	-7.1(-24,10)	0.363	17	26.4	
Utlängan	188	23	88-12	-.85(-2.5,.79)	0.2961	10	9.9	26.3 (23.5,29.4) m
Utlängan		10	03-12	-2.0(-7.0,3.1)	0.4009	9	7.43	
Fladen	144	23	90-12	-1.8(-3.4,-.31)	0.0199	10	8.86	6.46 (5.31,7.87)
Fladen		10	03-12	-4.5(-8.3,-.71)	0.0247	8	5.45	
Guillemot egg								
St.Karlsö	622	45	68-12	-.60(-1.1,-.13)	0.0141	9	7.76	.007 (.007,.008)
St.Karlsö		10	03-12	6.2(-3.4,16)	0.1729	13	15.1	

Table 26.2. Trend (in %) of **PCDD/F** concentrations in herring (pg TCDD-eqv/g **fresh weight**) assessed from the annual geometric mean in herring muscle. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	143	22	90-12	.76(-2.0,3.5)	0.5774	13	14.8	.777 (.654,.924) m
Harufjärden		10	03-12	.62(-11,12)	0.87	14	16.9	
Ängskärsklubb	36	30	79-12	-6.4(-8.2,-4.7)	.0000 ---	15	18.1	.608 (.434,.852)
Ängskärsklubb		9	03-12	-8.9(-26,7.8)	0.2493	16	22.7	
Utlängan	182	22	90-12	-1.2(-3.2,.82)	0.2286	11	10.6	.642 (.564,.732) m
Utlängan		10	03-12	-2.9(-9.7,4.0)	0.3637	10	9.8	
Fladen	144	23	90-12	1.1(-2.4,4.6)	0.5279	16	20.5	.326 (.259,.409) m
Fladen		10	03-12	-1.7(-5.5,2.1)	0.3379	8	5.35	

27 Brominated flame retardants

Updated 14.02.28

Polybrominated flame retardants in guillemot eggs from St. Karlsö have been retrospectively analysed in a time serie dating back to 1968. Herring muscle tissue has also been analysed during recent years. Polybrominated diphenyl ethers (PBDEs) and hexabromocyclododecane (HBCDD) were included in these trend studies.

27.1 Introduction

27.1.1 Uses, Production and Sources

PBDEs are produced as three different technical products; penta-, octa and deca BDE. Each of these products includes a few major congeners. For pentaBDE these are BDE-47, -99, and-100. OcatBDE contains mainly BDE-183, while decaBDE includes almost exclusively BDE-209 (LaGuardia et al. 2006). HBCDD is produced as a mixture of three stereoisomers α-, β- and γ-HBCDD (Covaci et al. 2006). Both PBDE and HBCDD are used as additive flame retardants incorporated into materials such as plastics and textiles in products that need to be prevented from catching fire.

Leakage of these substances to the environment occurs from production and use of products, and long-range transport via air borne particles. The PBDE congeners that are most commonly found in fish are BDE-47, -99 and -100, while PBDE congeners with a higher degree of bromination are more common in the terrestrial environment.

27.1.2 Toxic effects

The low brominated PBDEs (i.e. tetra-, penta-, and hexa BDE) shows a high affinity for lipids and can thus accumulate in animals and humans. Several PBDE congeners and HBCDD have been shown to cause neurotoxic effects in rats and mice. Animals exposed to PBDEs and HBCDD during a sensitive stage of brain development have later shown reduced memory and learning abilities (Viberg 2004; Eriksson et al. 2006). Brominated flame retardants (BFR) are also considered to be endocrine disruptors, and in particular, effects on the thyroid hormone system are seen (Darnerud 2008).

27.1.3 Conventions, aims and restrictions

The PBDEs, tetrabromodiphenyl ether, pentabromodiphenyl ether, hexabromodiphenyl ether and heptabromodiphenyl ether are among the nine new Persistent Organic Pollutants (POPs) included in The Stockholm Convention on POPs. Within the EU, the penta- and octaBDE products were banned for use in 2004. A Swedish ban of decaBDE was established in 2007, but this ban was withdrawn when decaBDE was included in the RoHS directive in 2008. PBDEs are also on the list of prioritized substances within the Water Framework Directive.

HBCDD is under review by the **Persistent Organic Pollutants Review Committee** (POPRC) as a proposed substance to be listed under the Stockholm Convention (Arnot et al. 2009).

27.1.4 Target Levels

The target level (TL) used for HBCDD in the time series for fish is 167 µg/kg wet weight. The target level used for the sum of BDE-28, 47, 99, 100, 153 and 154 (0.0085 µg/kg) for fish is not evaluated in time series since BDE-28 is not included in the analysis for BDEs. For further information on TL and selection of target level see chapter 10. The original TL has been recalculated for each time series based on the lipid percentage. The recalculated target level (Tv) together with the lipid percentage (lp) is shown above the statistical information in each time series.

27.2 Methods

27.2.1 Analytical information

See chapter 6, section 6.2 for further information regarding analytical methods for BFRs.

27.3 Results

27.3.1 Spatial variation

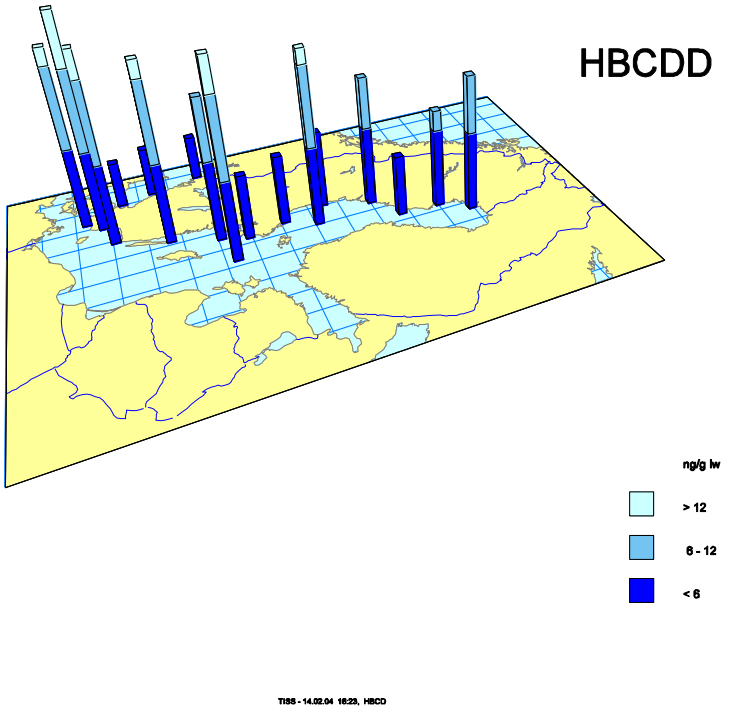


Figure 27.1. Spatial variation of HBCDD concentrations (ng/g lipid weight) in herring muscle.

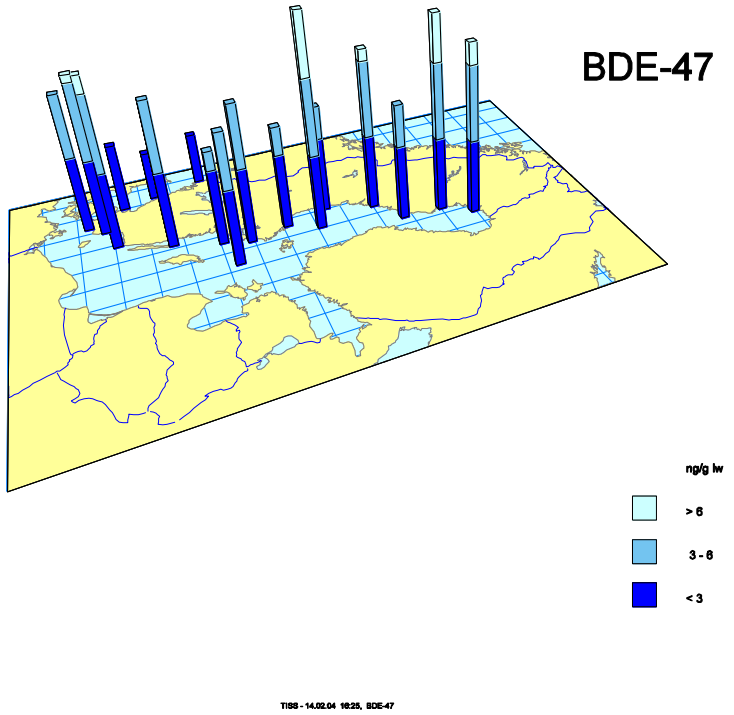


Figure 27.2. Spatial variation of BDE-47 concentrations (ng/g lipid weight) in herring muscle.

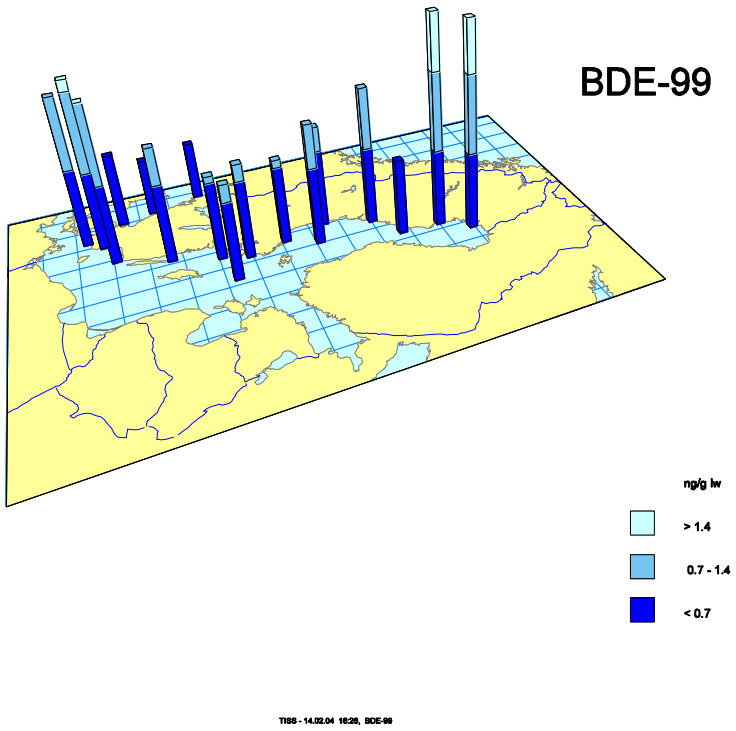


Figure 27.3. Spatial variation of BDE-99 concentrations (ng/g lipid weight) in herring muscle.

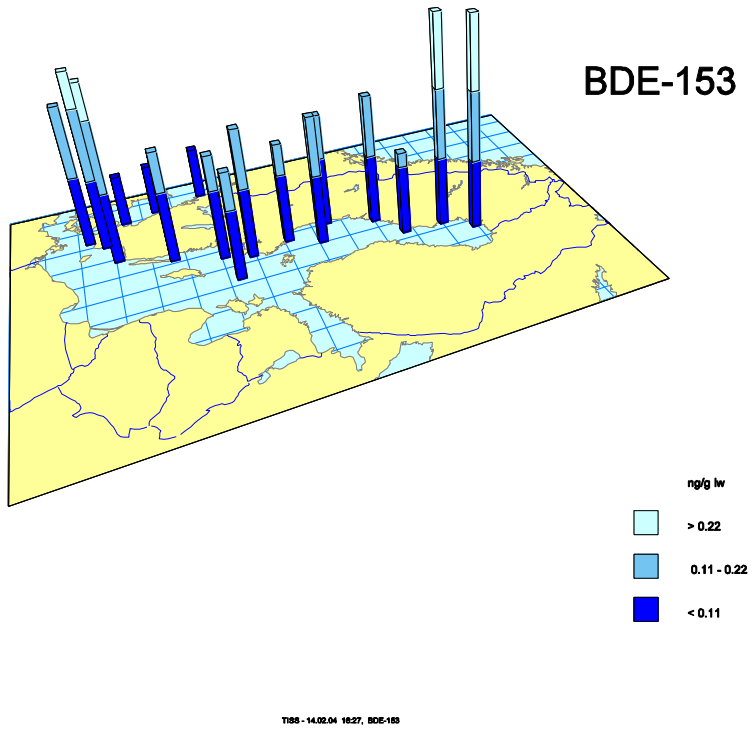


Figure 27.4. Spatial variation of BDE-153 concentrations (ng/g lipid weight) in herring muscle.

Generally, for HBCDD (Fig. 27.1), BDE-47 (Fig. 27.2), BDE-99 (Fig. 27.3), and BDE-153 (Fig. 27.4) higher concentrations in herring muscle are seen in the Baltic Sea compared to the Swedish west coast. Hanöbukten in the south Baltic Proper and Gaviksfjärden and Harufjärden in the Bothnian Bay show the highest concentrations for all of these compounds. The concentration of BDE-47 is also elevated in the Bothnian Sea offshore site (Fig. 27.2), while for BDE-99 and BDE-153 higher concentrations are seen in the Gulf of Bothnia (Fig. 27.3-4).

There are large differences in HBCDD concentration in cod liver between the Baltic and the Swedish west coast, where cod from the southeast of Gotland has eight times higher concentration compared to cod from Fladen on the Swedish west coast (Fig. 27.19).

27.3.2 Temporal Variation

Significant increasing concentrations of BDE-47, BDE-100 and BDE-99 in guillemot eggs from the late 1960s until the early 1990s, are followed by decreasing values during the more recent period (Fig. 27.5).

Significant decreasing concentrations of BDE-47 are observed in herring from Ängskärsklubb (autumn), Landsort, Väderöarna, Fladen, and Utlängan (autumn). Decreasing concentrations are also observed in cod from Fladen and southeast Gotland and in blue mussels from all sampling sites (Fig.27.6-9, Table 27.1).

The number of years required to detect an annual change of 10% in the concentration of BDE-47 is 8-17 years for herring, cod and blue mussel.

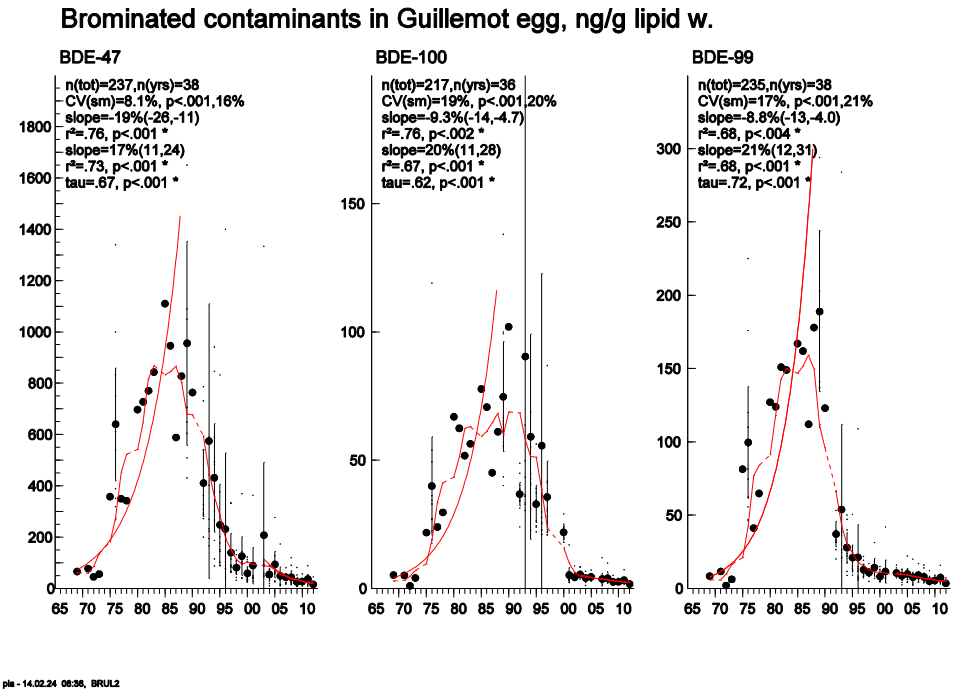


Figure 27.5. Temporal trends of BDE-47, -99, and 100 (ng/g lipid weight) in guillemot eggs (time series starting in 1968).

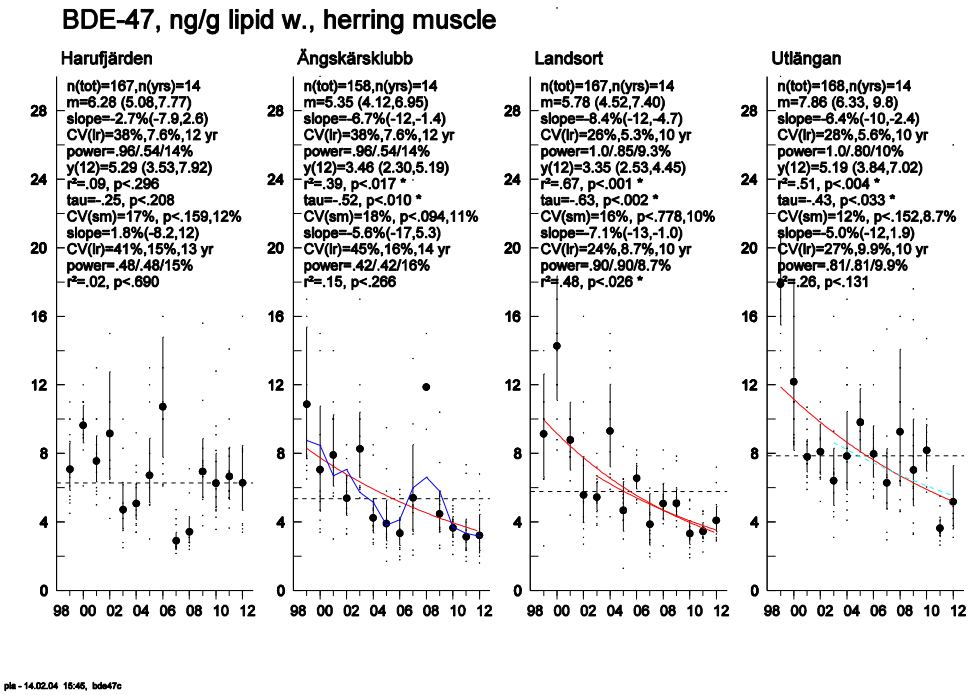


Figure 27.6. Temporal trends of BDE-47 (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).

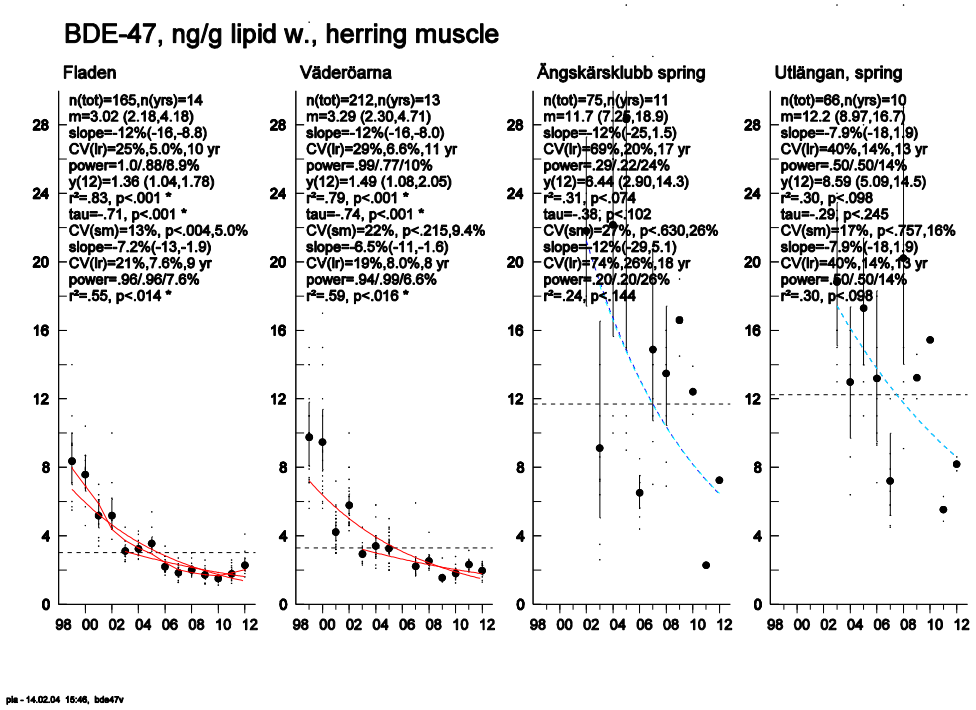


Figure 27.7. Temporal trends of BDE-47 (ng/g lipid weight) in herring muscle from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) (time series starting in 1999).

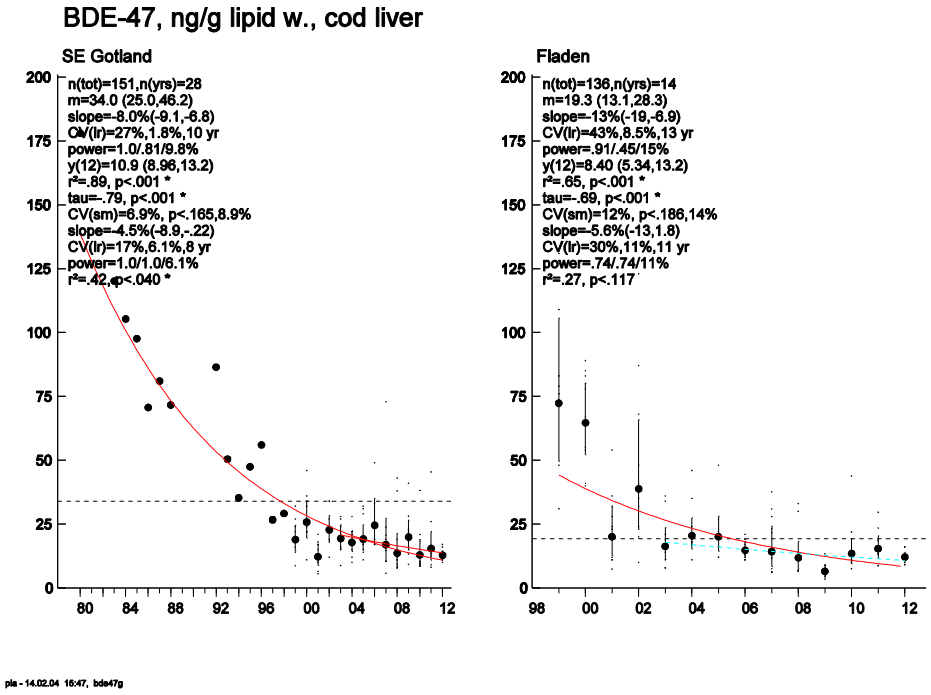


Figure 27.8. BDE-47 concentrations (ng/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).

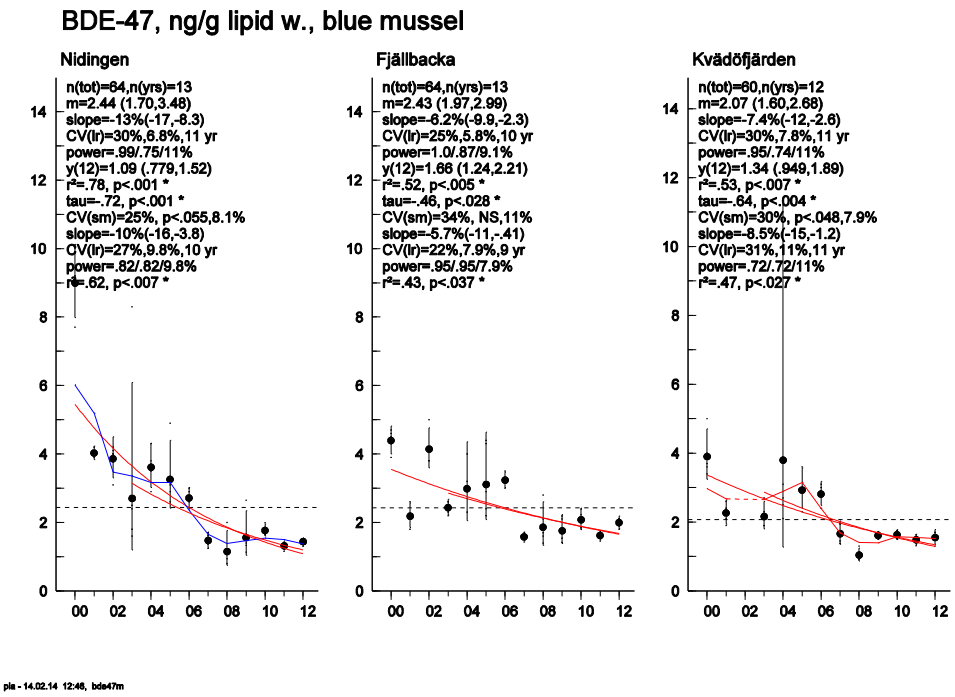


Figure 27.9. BDE-47 concentrations (ng/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 2000).

Significant decreasing concentrations of BDE-99 are observed in herring from Harufjärden, Ängskärsklubb (autumn), Landsort, Utlängan (autumn), Fladen Väderöarna, and Änskärsklubb (spring) (Fig. 27.10, 27.11). Cod showed a decrease in BDE-99 in southeast Gotland (Fig. 27.12). Blue mussels from Kvädöfjärden show decreasing concentrations (27.13).

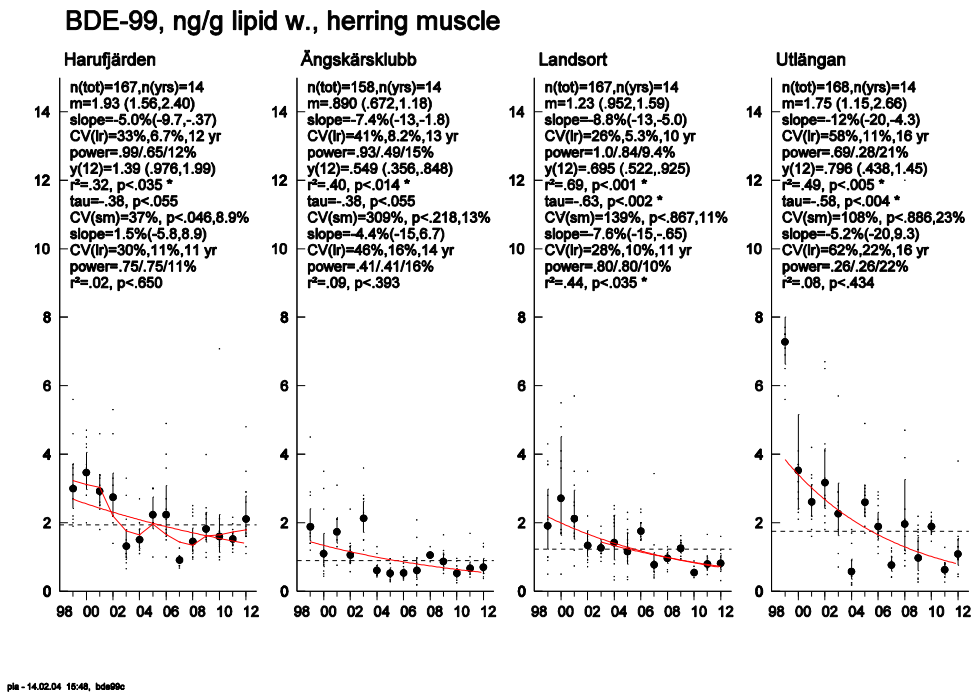


Figure 27.10. BDE-99 concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).

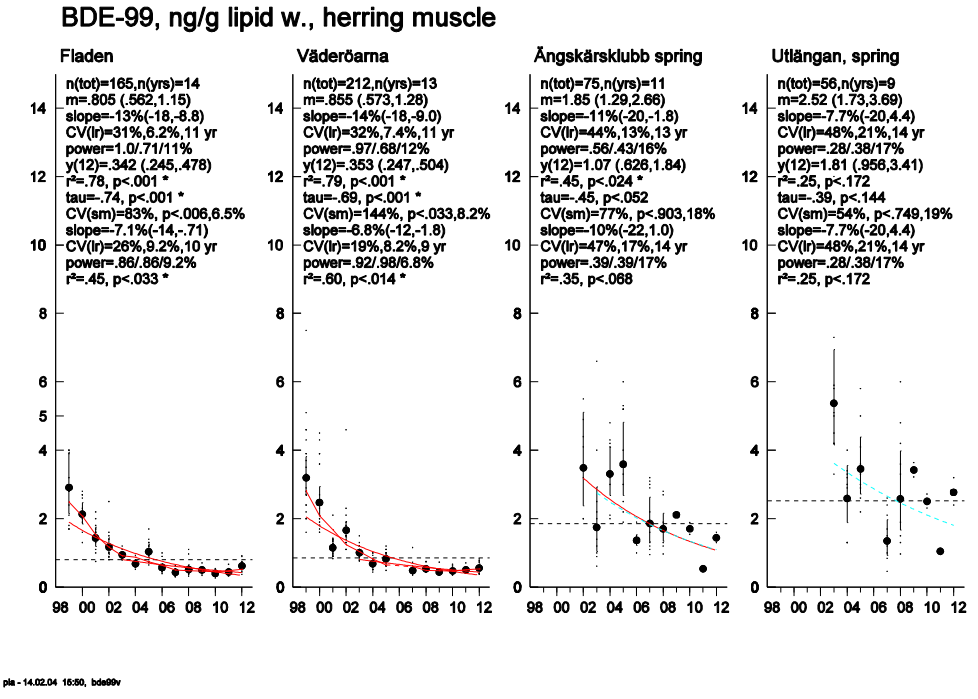


Figure 27.11. BDE-99 concentrations (ng/g lipid weight) in herring muscle from Fladen, Väderöarna, Ängskärrsklubb and Utlängan (spring) (time series starting in 1999).

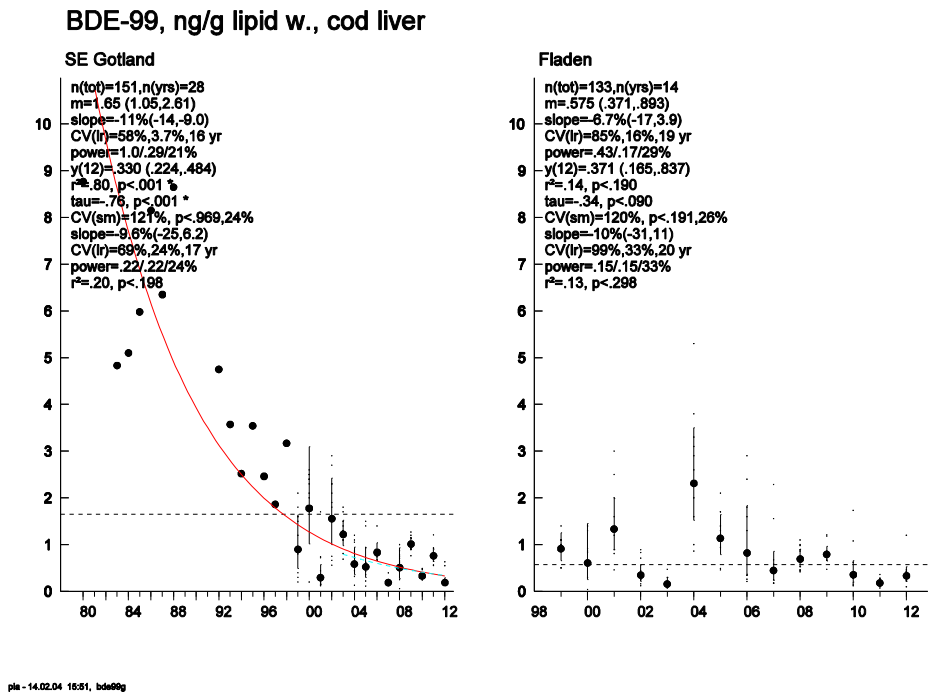


Figure 27.12. BDE-99 concentrations (ng/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).

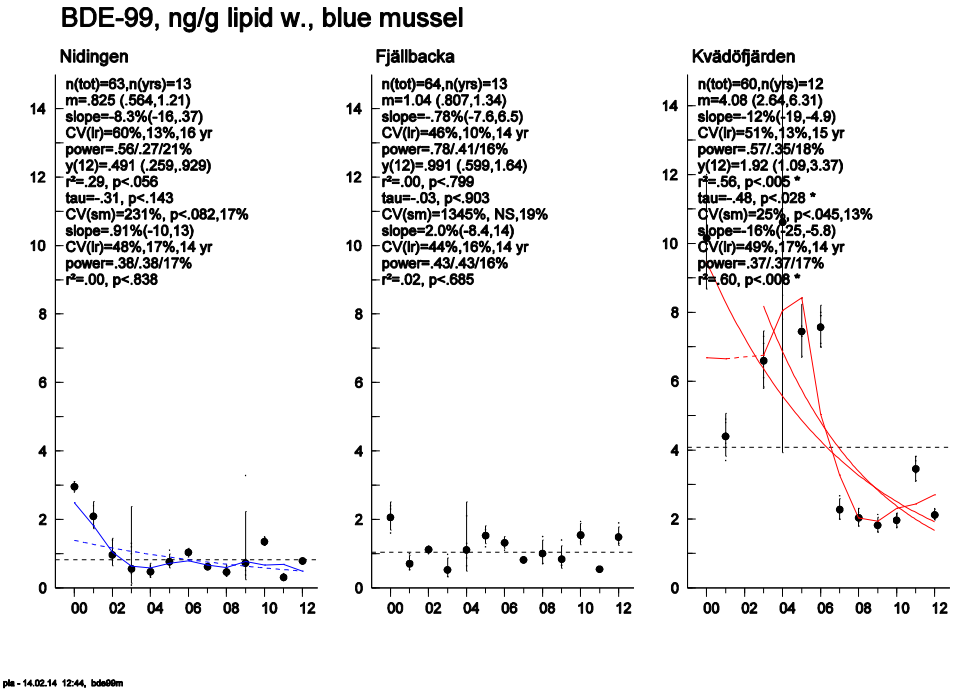


Figure 27.13. BDE-99 concentrations (ng/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 2000).

Significant decreasing concentrations of BDE-153 are observed in herring from Utlängan, Fladen, Väderöarna and Ängskärsklubb (spring) (Fig. 27.15) and for cod from southeast Gotland (Fig. 27.16).

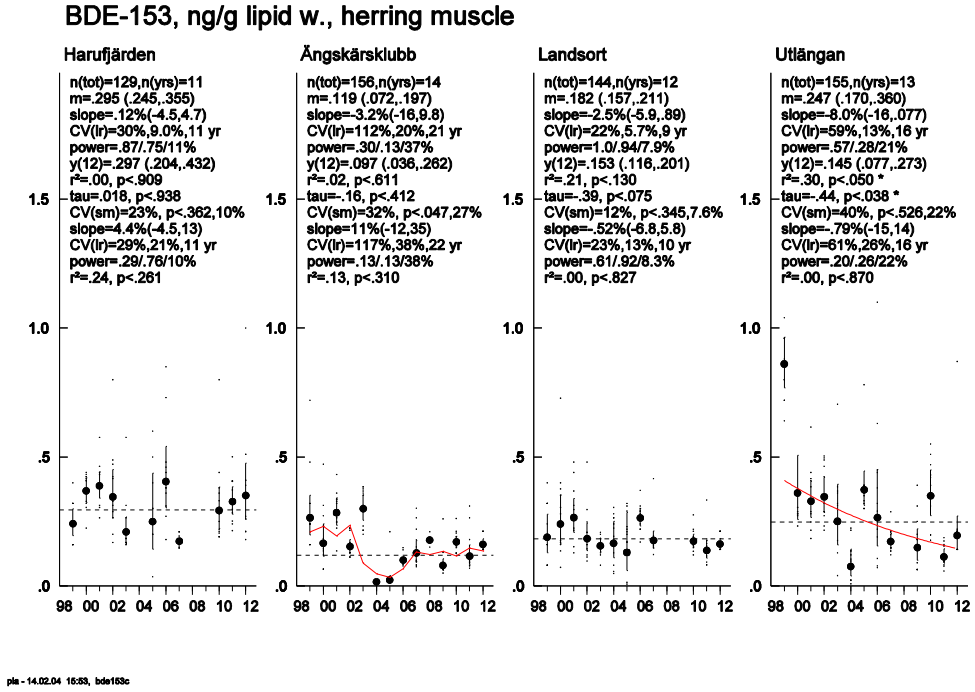


Figure 27.14. BDE-153 concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).

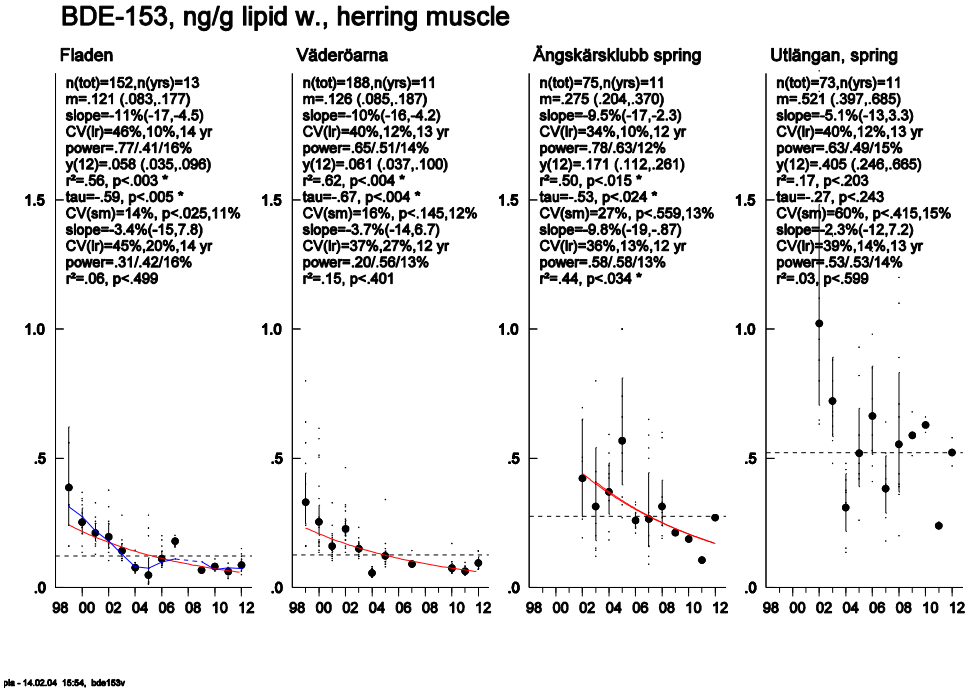


Figure 27.15. BDE-153 concentrations (ng/g lipid weight) in herring muscle from Fladen, Väderöarna, Ängskärrsklubb and Utlängan (spring) (time series starting in 1999, 1999, 2003 and 2002 respectively).

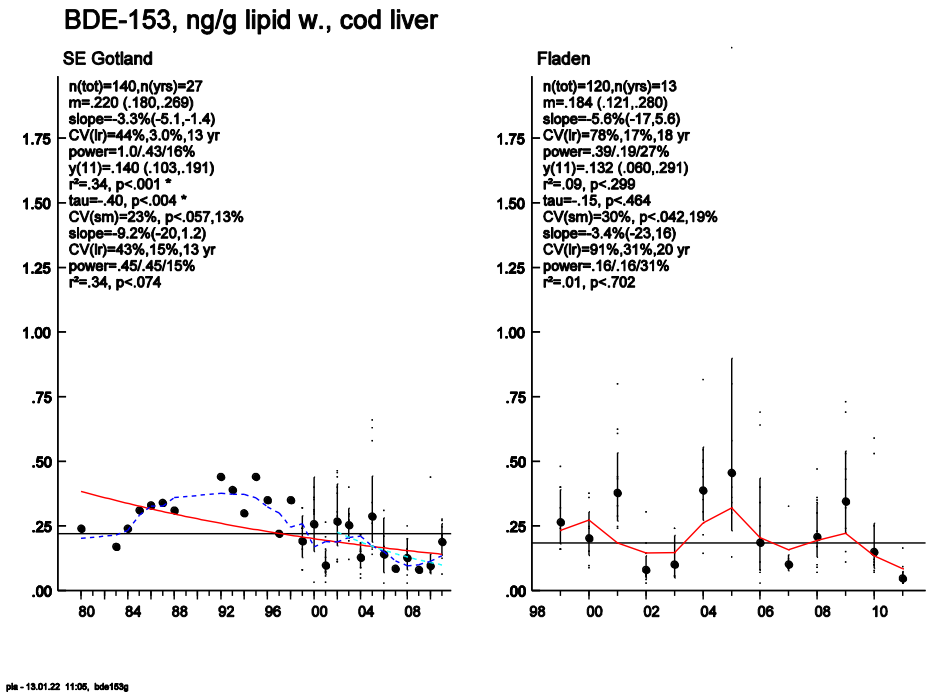


Figure 27.16. BDE-153 concentrations (ng/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).

HBCDD in herring is decreasing at Utlängan (autumn) (6.3% per year, table 27.4), Väderöarna (9.5% per year, table 27.4), Fladen (11% per year, table 27.4), and Utlängan (spring) (9.4% per year, table 27.4) (Fig. 27.18) and in cod at Fladen (14% per year, table 27.4) (Fig. 27.19). At the same time, concentration of HBCDD is increasing in cod in southeast Gotland (6.1% per year, table 27.4) (Fig. 27.19). Concentrations of HBCDD are increasing in guillemot eggs by about 2.5% per year for the whole time period, however, during the last ten years a significant decrease is seen (table 27.4, Fig. 27.21).

Two extreme values were reported at Nidingen and one at Kvädöfjärden 2011, these values must be further investigated).

The number of years required to detect an annual change of 10% in the concentrations of HBCDD is 10 - 16 years for herring and cod, and 12 years for guillemot egg.

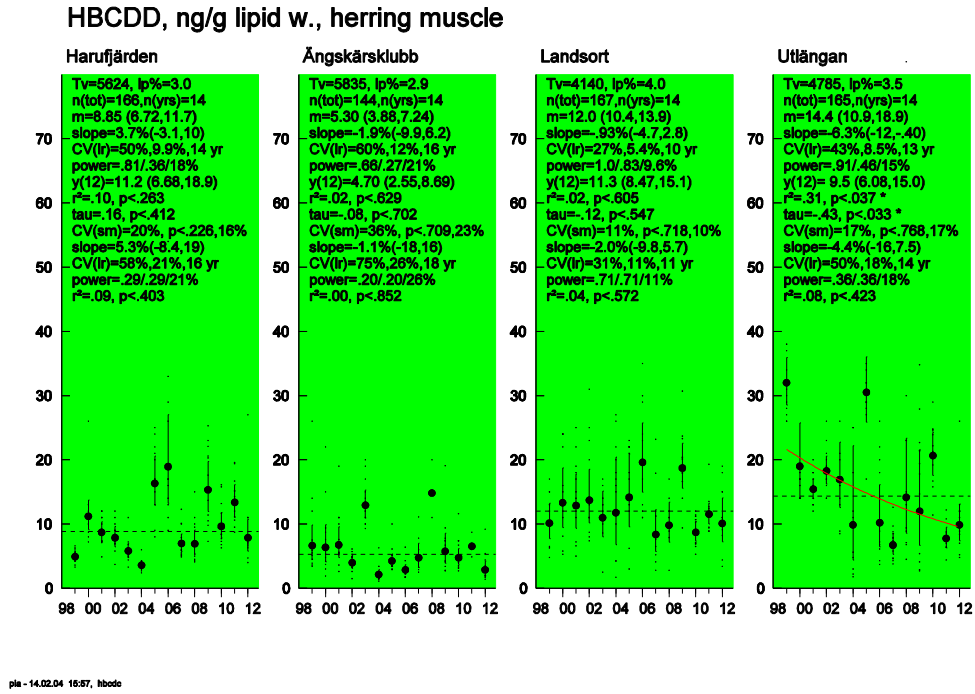


Figure 27.17. HBCDD concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999). The green area denotes the levels below the suggested target value for HBCDD in fish.

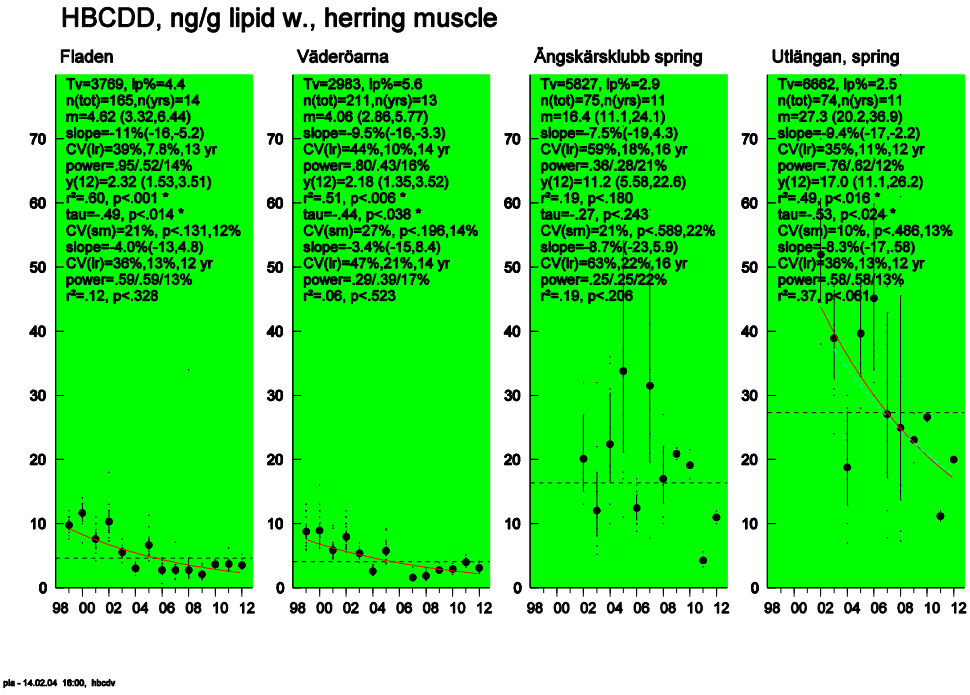


Figure 27.18. HBCDD concentrations (ng/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen, and Väderöarna (time series starting in 2002, 2002, 1999 and 1999 respectively). The green area denotes the levels below the suggested target value for HBCDD in fish.

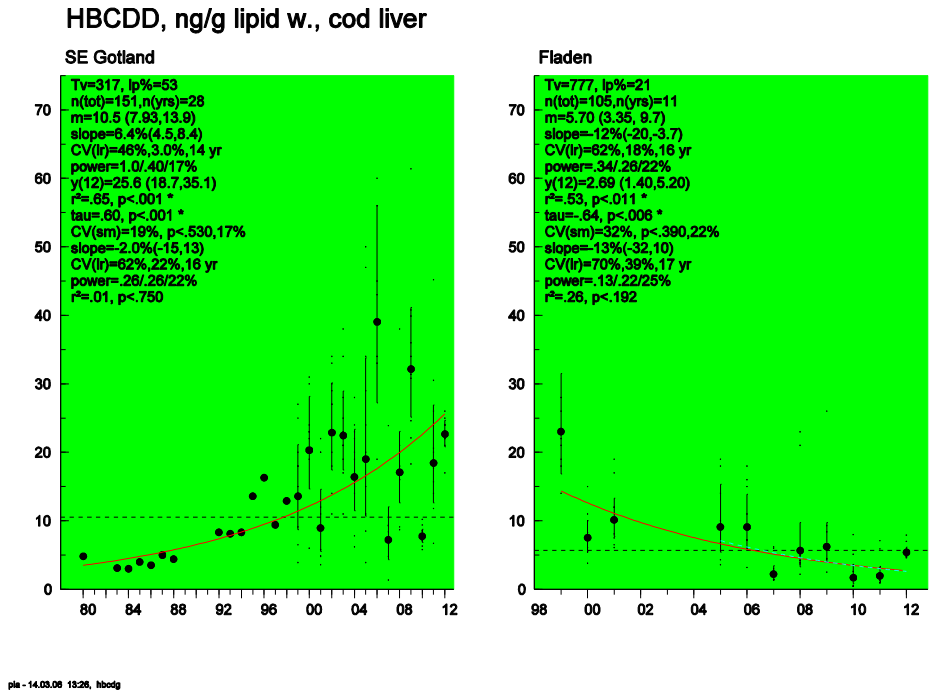


Figure 27.19. HBCDD concentrations (ng/g lipid weight) in cod liver from southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley). The green area denotes the levels below the suggested target value for HBCDD in fish.

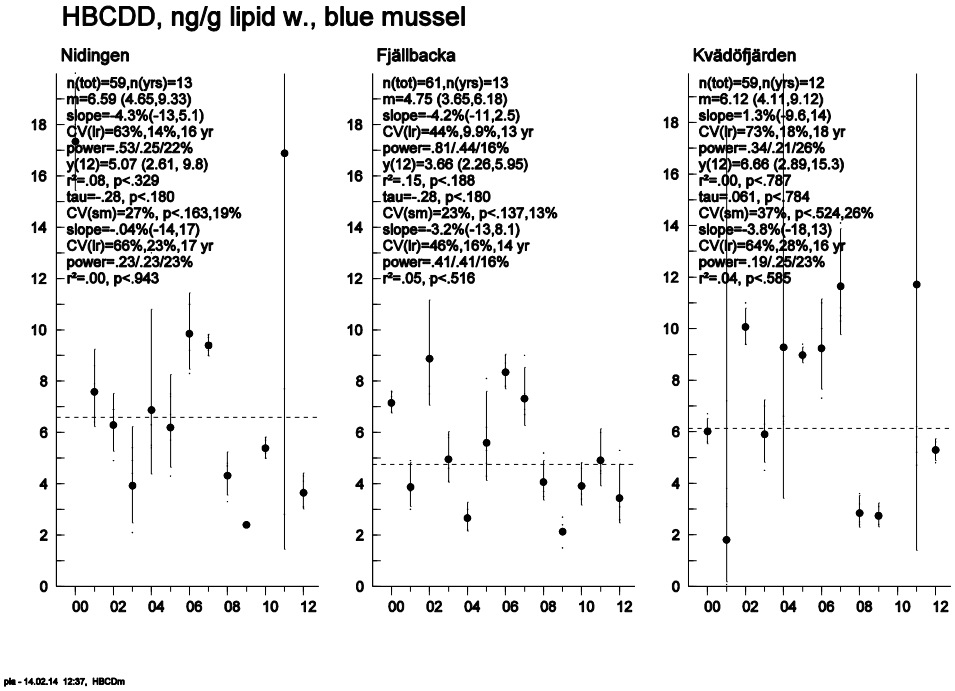


Figure 27.20. HBCDD concentrations (ng/g lipid weight) in blue mussel from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 2000).

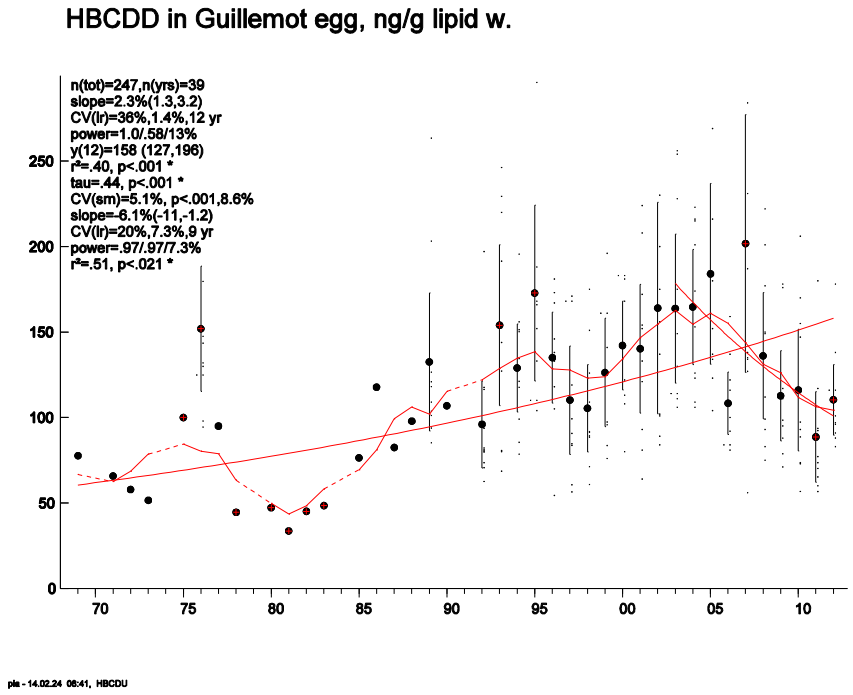


Figure 27.21. HBCDD concentrations (ng/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1969).

27.3.3 Comparison to threshold

In all fish species from all areas HBCDD concentration is below the suggested target level of 167 µg/kg wet weight based on the EQS_{biota}.

In all areas, the BDE-47 concentration alone is above the target level for the sum of BDE-28, 47, 99, 100, 153 and 154 of 0.0085 ng/g wet weight based on the EQS_{biota}.

27.4 Conclusions

HBCDD, BDE-47, 99, and 153 in herring muscle shows generally higher concentrations in the Baltic Sea compared to the Swedish west coast. Also, cod shows the same pattern. A significant increase in BDE-47, 99 and 100 has been seen in guillemot eggs since the late 1960s until the early 1990s, where concentrations then began to show a decrease. BDE-47 and 99 are showing decreases at most herring, cod, and blue mussel sites. For BDE-153, a decrease is seen for some of the sites for herring and cod. At four out of eight herring sites, HBCDD is decreasing and the same trend is seen for cod at Fladen, while cod from southeast of Gotland shows an increase in HBCDD concentration. Overall, the concentration of HBCDD in in guillemot eggs has increased since the start in 1969, however, for the last ten years a significant decrease in is observed. In all areas, HBCDD concentrations are below the suggested target level but for PBDEs concentrations of PBDEs exceeds the target level at all stations.

Table 27.1. Trend (in %) for **BDE-47** (ng/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's BDE-47 concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	167	14	99-12	-2.7(-7.9,2.6)	0.296	12	14.6	6.28 (5.08,7.77) m
Harufjärden		10	03-12	1.8(-8.2,12)	0.6898	13	15.8	
Ängskärsklubb	147	13	99-11	-6.5(-13,-.20)	0.0426	13	15.4	3.78 (2.43,5.88)
Ängskärsklubb		10	02-11	-3.9(-15,6.9)	0.431	14	17.4	
Landsort	155	13	99-11	-9.1(-13,-4.9)	.0006 ---	10	9.9	3.43 (2.55,4.62)
Landsort		10	02-11	-6.7(-13,-.46)	0.0371	10	9.35	
Utlängan	156	13	99-11	-6.4(-11,-1.7)	0.0115	11	11	5.54 (3.98,7.69)
Utlängan		10	02-11	-3.9(-11,2.9)	0.2213	10	10.3	
Cod Liver								
SE Gotland	151	28	80-12	-8.0(-9.1,-6.8)	.0000 ---	10	9.8	10.9 (8.96,13.2)
SE Gotland		10	03-12	-4.5(-8.9,-.22)	0.0404	8	6.12	
Fladen	136	14	99-12	-13(-19,-6.9)	.0006 ---	13	15.4	8.40 (5.34,13.2)
Fladen		10	03-12	-5.6(-13,1.8)	0.1174	11	10.8	
Blue Mussel								
Nidingen	64	13	00-12	-13(-18,-8.7)	.0001 ---	11	11.2	1.09 (.779,1.52)
Nidingen		10	03-12	-11(-18,-3.9)	.0067 --	10	10.3	
Fjällbacka	64	13	00-12	-6.4(-10,-2.3)	.0053 --	10	9.47	1.66 (1.24,2.21)
Fjällbacka		10	03-12	-5.9(-11,-.41)	0.0372	9	8.18	
Kvädöfjärden	60	12	00-12	-7.7(-13,-2.6)	.0071 --	11	11.4	1.34 (.949,1.89)
Kvädöfjärden		10	03-12	-8.9(-16,-1.2)	0.0272	11	11.7	
Guillemot egg								
Stora Karlsö	239	38	69-12	-5.2(-8.1,-2.3)	.0009 ---	24	59.9	63.1 (31.7,126)

* gaps in the examined years

Table 27.2. Trend (in %) for **BDE-153** (ng/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's BDE-153 concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Herring muscle								
Harufjärden	129	11	99-12	.12(-4.5,4.7)	0.9088	11	10.7	.295 (.245,.355) m
Harufjärden		7	03-12	4.4(-4.5,13)	0.2614	11	10.5	
Ängskärsklubb	156	14	99-12	-3.2(-16,9.8)	0.6114	21	36.8	.119 (.072,.197) m
Ängskärsklubb		10	03-12	11(-12,35)	0.3102	22	38.1	
Landsort	144	12	99-12	-2.5(-5.9,.89)	0.1295	9	7.87	.182 (.157,.211) m
Landsort		8	03-12	-.52(-6.8,5.8)	0.8271	10	8.34	
Utlängan	155	13	99-12	-8.0(-16,.077)	0.05	16	20.9	.145 (.077,.273)
Utlängan		9	03-12	-.79(-15,14)	0.87	16	21.7	
Fladen	152	13	99-12	-11(-17,-4.5)	.0033 --	14	16.4	.058 (.035,.096)
Fladen		9	03-12	-3.4(-15,7.8)	0.4987	14	16.1	
Väderöarna	188	11	99-12	-10(-16,-4.2)	.0041 --	13	14.3	.061 (.037,.100)
Väderöarna		7	03-12	-3.7(-14,6.7)	0.4012	12	13.3	
Ängskärsklubb spring	75	11	02-12	-9.5(-17,-2.3)	0.0145	12	12.2	.171 (.112,.261)
Ängskärsklubb spring		10	03-12	-9.8(-19,-.87)	0.0341	12	13	
Utlängan spring	73	11	02-12	-5.1(-13,3.3)	0.2034	13	14.5	.521 (.397,.685) m
Utlängan spring		10	03-12	-2.3(-12,7.2)	0.5989	13	13.8	
Cod Liver								
SE Gotland	150	28	80-12	-3.1(-4.8,-1.3)	0.0015 --	13	16.9	.141(.105,.190)
SE Gotland		10	03-12	-4.1(-.15,7.2)	.4309	14	18.3	
Fladen	130	14	99-12	-4.3(-14,5.3)	.3507	18	29.9	.185(.126,.271) m
Fladen		10	03-12	-7.2(-25,11)	.3815	18	32.0	
Guillemot egg								
Stora Karlsö	132	13	00-12	-2.9(-8.8,2.9)	0.2915	12	14.2	

Table 27.3. Trend (in %) for **BDE-99** (ng/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's BDE-99 concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LTD	Last Year
Herring Muscle								
Harufjärden	167	14	99-12	-5.0(-9.7,-.37)	-0.0353	12	11.9	1.39 (.976,1.99)
Harufjärden		10	03-12	1.5(-5.8,8.9)	0.6502	11	10.6	
Ängskärsklubb	158	14	99-12	-7.4(-13,-1.8)	-0.014	13	14.6	.549 (.356,.848)
Ängskärsklubb		10	03-12	-4.4(-15,6.7)	0.3926	14	16.5	
Landsort	167	14	99-12	-8.8(-13,-5.0)	.0003 ---	10	9.43	.695 (.522,.925)
Landsort		10	03-12	-7.6(-15,-.65)	-0.0348	11	10.1	
Utlängan	168	10	03-12	-5.2(-20,9.3)	0.4335	16	22	.796 (.438,1.45)
Fladen	165	14	99-12	-13(-18,-8.8)	.0000 ---	11	11.1	.342 (.245,.478)
Fladen		10	03-12	-7.1(-14,-.71)	-0.0327	10	9.23	
Väderöarna	212	13	99-12	-14(-18,-9.0)	.0001 ---	11	11.6	.353 (.247,.504)
Väderöarna		9	03-12	-6.8(-12,-1.8)	-0.0143	9	6.81	
Ängskärsklubb spring	75	11	02-12	-11(-20,-1.8)	-0.0236	13	15.9	1.07 (.626,1.84)
Ängskärsklubb spring		10	03-12	-10(-22,1.0)	0.0677	14	16.8	
Utlängan spring	56	9	03-12	-7.7(-20,4.4)	0.1725	14	17.3	2.52 (1.73,3.69) m
Utlängan spring		9	03-12	-7.7(-20,4.4)	0.1725	14	17.3	
Cod Liver								
SE Gotland	151	28	80-12	-11(-14,-9.0)	.0000 ---	16	20.5	.330 (.224,.484)
SE Gotland		10	03-12	-9.6(-25,6.2)	0.198	17	24.1	
Fladen	133	14	99-12	-6.7(-17,3.9)	0.1901	19	29.2	.575 (.371,.893) m
Fladen		10	03-12	-10(-31,11)	0.2976	20	33.3	
Blue mussel								
Nidingen	63	13	00-12	-8.7(-18,.37)	0.0565	16	23.7	.491 (.259,.929)
Nidingen		10	03-12	.90(-11,12)	0.8377	14	18.7	
Fjällbacka	64	13	00-12	-.78(-7.9,6.3)	0.7989	14	17.8	1.04 (.807,1.34) m
Fjällbacka		10	03-12	2.0(-8.8,13)	0.6852	14	17.2	
Kvädöfjärden	60	12	00-12	-13(-22,-5.0)	.0051 --	15	19.9	1.92 (1.09,3.37)
Kvädöfjärden		10	03-12	-18(-29,-6.0)	.0082 --	14	19	
Guillemot egg								
Stora Karlsö	237	38	69-12	-4.9(-8.0,-1.7)	.0033 --	26	68.7	9.29 (4.37,19.8)

Table 27.4. Trend (in %) for **HBCDD** (ng/g lipid weight) assessed from the annual geometric mean in various matrice. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's HBCDD concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LTD	Last Year
Herring Muscle								
Harufjärden	166	14	99-12	3.7(-3.1,10)	0.2627	14	17.8	8.85 (6.72,11.7) m
Harufjärden		10	03-12	5.3(-8.4,19)	0.4031	16	20.6	
Ängskärsklubb	144	14	99-12	-1.9(-9.9,6.2)	0.6285	16	21.4	5.30 (3.88,7.24) m
Ängskärsklubb		10	03-12	-1.1(-18,16)	0.8522	18	26.1	
Landsort	167	14	99-12	-.93(-4.7,2.8)	0.6053	10	9.6	12.0 (10.4,13.9) m
Landsort		10	03-12	-2.0(-9.8,5.7)	0.5721	11	11.2	
Utlängan	165	14	99-12	-6.3(-12,-.40)	0.0368	13	15.3	9.5 (6.08,15.0)
Utlängan		10	03-12	-4.4(-16,7.5)	0.4228	14	17.8	
Fladen	165	14	99-12	-11(-16,-5.2)	.0012 --	13	14	2.32 (1.53,3.51)
Fladen		10	03-12	-4.0(-13,4.8)	0.3279	12	12.8	
Väderöarna	211	13	99-12	-9.5(-16,-3.3)	.0060 --	14	15.9	2.18 (1.35,3.52)
Väderöarna		9	03-12	-3.4(-15,8.4)	0.5232	14	16.9	
Ängskärsklubb spring	75	10	03-12	-8.7(-23,5.9)	0.2058	16	22.2	16.4 (11.1,24.1) m
Utlängan spring	74	11	02-12	-9.4(-17,-2.2)	0.0161	12	12.5	17.0 (11.1,26.2)
Utlängan spring		10	03-12	-8.3(-17,.58)	0.0614	12	13	
Cod Liver								
SE Gotland	151	28	80-12	6.2(4.4,8.1)	.0000 +++	14	18.0	25.6 (18.7,35.1)
SE Gotland		10	03-12	-2.0(-16,12)	0.7500	16	24.4	
Fladen	105	11	99-12	-13(-22,-3.8)	0.0106-	16	24.6	2.69(1.40,5.20)
Fladen		8	05-12	-14(-38,9.6)	0.1925	17	28.1	
Blue Mussel								
Nidingen	59	13	00-12	-4.4(-14,5.0)	0.3291	16	24.9	6.59 (4.65,9.33) m
Nidingen		10	03-12	-.04(-15,15)	0.9426	17	26.4	
Fjällbacka	61	13	00-12	-4.3(-11,2.5)	0.1884	13	17	4.75 (3.65,6.18) m
Fjällbacka		10	03-12	-3.3(-14,7.8)	0.5162	14	17.8	
Kvädöfjärden	59	12	00-12	1.3(-10,13)	0.7869	18	29.2	6.12 (4.11,9.12) m
Kvädöfjärden		9	03-12	-3.9(-20,12)	0.5854	16	25.4	
Guillemot egg								
Stora Karlsö	249	39	69-12	2.2(1.2,3.1)	.0000 ++	12	14.3	156 (125,194)
Stora Karlsö		10	03-12	-7.1(-13,-1.3)	0.0216	9	8.57	

28 PAHs, Polyaromatic Hydrocarbons

Updated 14.02.28

Polyaromatic hydrocarbons were retrospectively analysed in blue mussels from Kvädöfjärden in the Baltic, and Fladen and Fjällbacka on the Swedish west coast, in time series from 1987 - 2003, 1985 - 2003 and 1984 - 2003, respectively. Since 2003, PAHs have been analysed on a yearly basis from these three blue mussel sites. Other species are not analysed, as the extent to which PAHs metabolise in other species is not known.

28.1 Introduction

28.1.1 Uses, Production and Sources

PAHs are produced both naturally in nature (e.g. can be found in the smoke from forest fires or in oil deposits deep within the earth) but also by human activities, such as incomplete combustion of organic materials (Nisbet & Lagoy 1992). They are thus generated after burning of oil, petrol, or coal and when people smoke cigarettes. Most input to the environment comes from human activities, such as wastes from industrialized and urbanized areas or petroleum production and transportation (Soclo et al. 2000).

PAH sources are either pyrolytic or petrogenic. They can be evaluated by molecule indexes and are based on concentration relationships between individual PAHs (Pikkarainen 2004). PAHs occur in nature as complex mixtures of many components with varying toxic potencies, and many are considered carcinogens (Petry et al. 1996).

28.1.2 Target Levels

The target levels used for PAHs in blue mussels are listed below in ug/kg dry weight. For further information on target levels and selection of target level see chapter 10.

Fluoranthene 110 ug/kg d.w.; Anthracene 290 ug/kg d.w.; Naphtalene 340 ug/kg d.w.; Phenantrene 1700 ug/kg d.w.; Pyrene 100 ug/kg d.w.; Benzo(a)antracene 80 ug/kg d.w.; benzo(a)pyrene 600 ug/kg d.w.; and Benzo(g,h,i)perylene 110 ug/kg d.w..

28.2 Methods

28.2.1 Analytical Information

The PAHs analysed are: naphthalene, acenaphtene, fluorene, phenantrene, antracene, fluoranthene, pyrene, benzo(a)antracene, chrysene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, dibenzo(a,h)antracene, benzo(g,h,i)perylene and indeno(1,2,3-cd)pyrene. Metabolic capacity of the species sampled has to be considered.

See chapter 6, section 6.4 for further information regarding analytical methods for PAHs.

28.3 Results

28.3.1 Spatial Variation

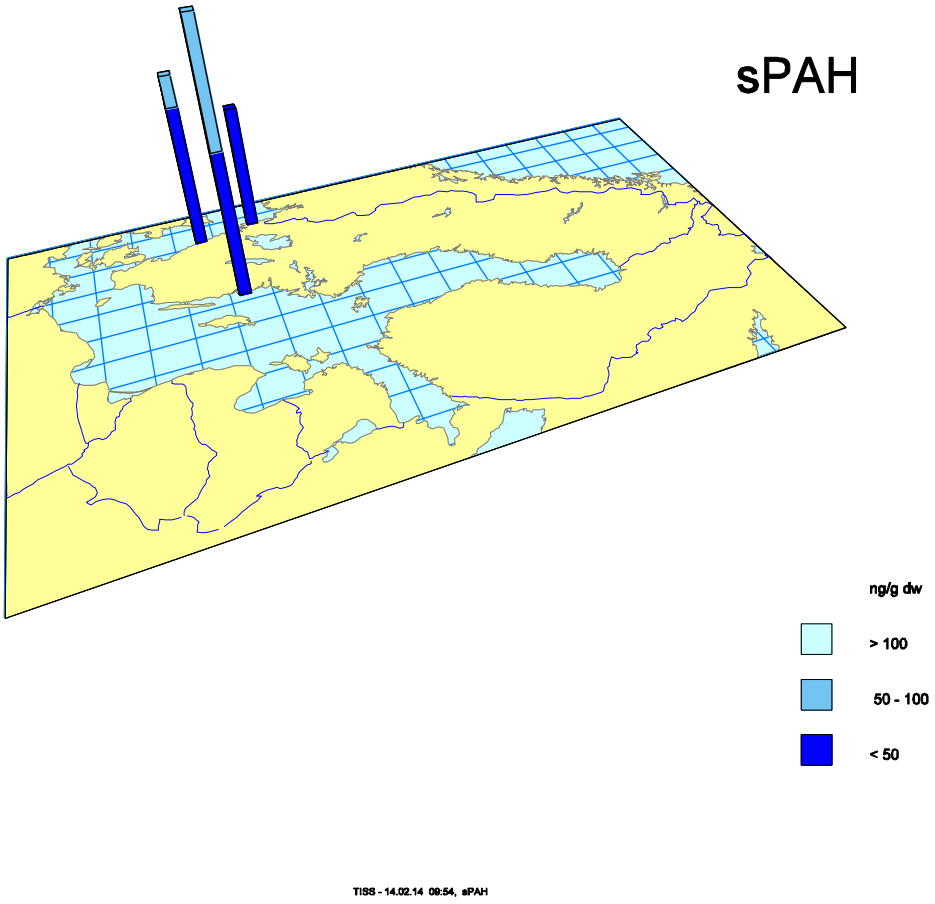


Figure 28.1. Spatial variation in sPAH concentrations (ng/g dry weight) in blue mussel soft body.

Blue mussel soft body from Kvädöfjärden in the Baltic Proper represent the highest sum of PAHs (sPAH) concentrations of the blue mussel samples (Fig. 28.1). Retrospective studies showed that the PAHs were not all systematically higher at Kvädöfjärden, for example flouranthene and pyrene showed higher concentrations at Fjällbacka.

28.3.2 Temporal Variation

All PAHs analysed (except acenaphthene, which was rarely found above the quantification limit) are presented as time series below (Fig. 28.2 – 28.16). Decreasing trends of sPAH (Fig. 28.2), chrysene (Fig. 28.9), fluoranthene (Fig. 28.12) and pyrene (Fig. 28.16) were found at Fjällbacka.Concentrations of pyrene at Nidingen (Fig. 28.16) and naphtalene at Kvädöfjärden (Fig. 28.14) also showed decreasing trends. Increasing trends were observed for benzo(a)anthracene at Kvädöfjärden (Fig. 28.4).

The number of years required to detect an annual change of 10% in concentration varied a lot depending on the type of PAH and sampling site. Generally the statistical power to detect trends is low compared to other contaminants, and is between 14 - 24 years. Some PAHs (eg. anthracene and fluoranthene (Fig. 28.3, 28.12) show extremely high concentrations in certain years compared to the average concentrations. These results could possibly be outliers. The power and number of years required to detect a trend would improve if these outliers were excluded.

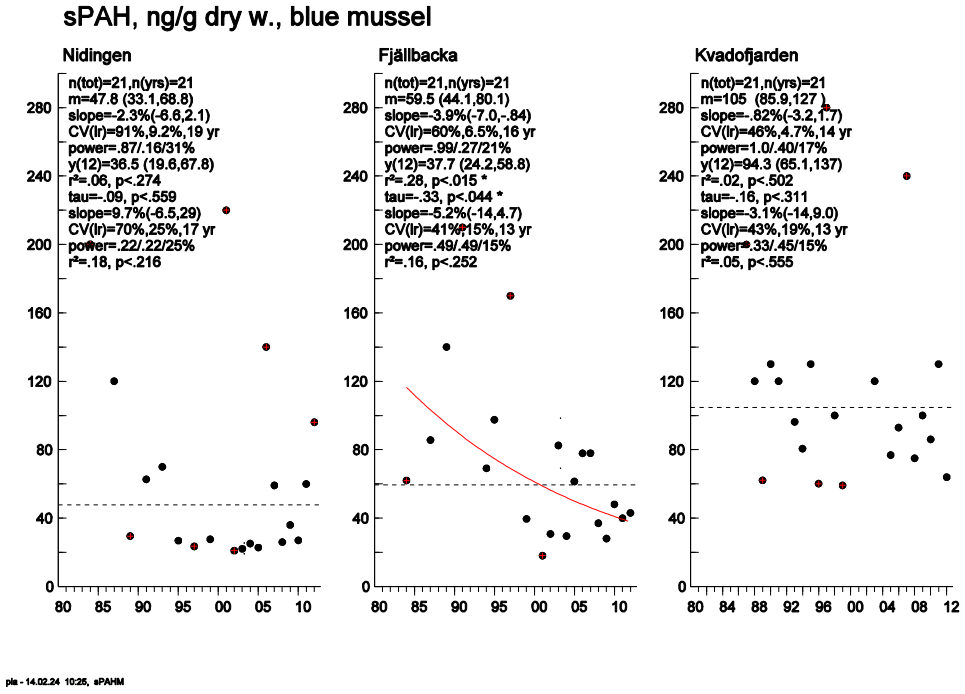


Figure 28.2. sPAH concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1986, 1983 and 1987 respectively).

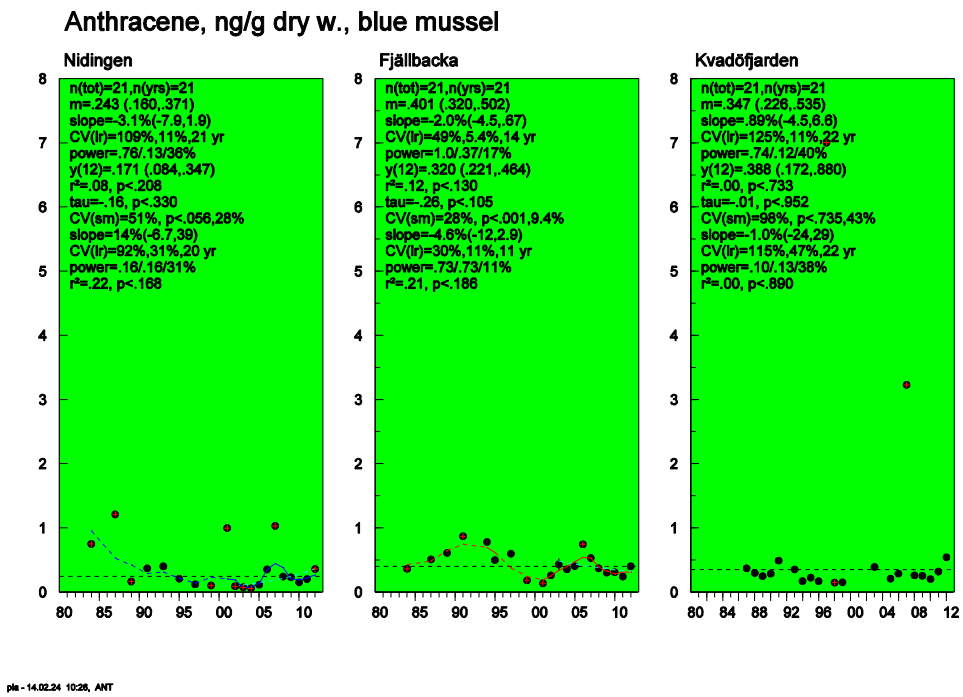


Figure 28.3. Anthracene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1986, 1984 and 1987 respectively). The green area denotes the levels below the suggested target value for anthracene in blue mussels.

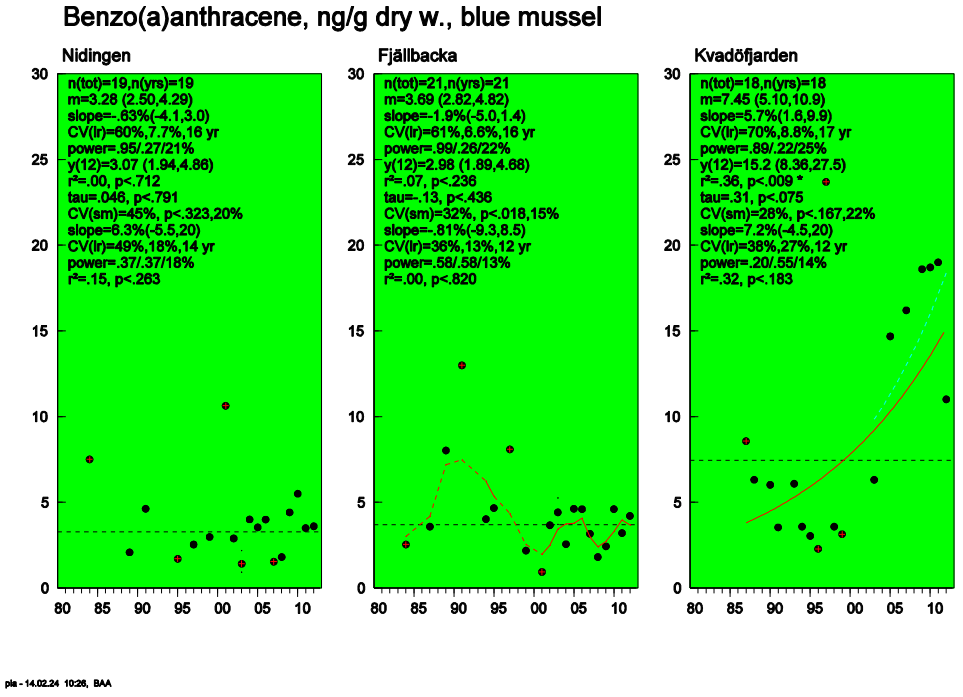


Figure 28.4. Benzo(a)anthracene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1989, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for benzo(a)anthracene in blue mussels.

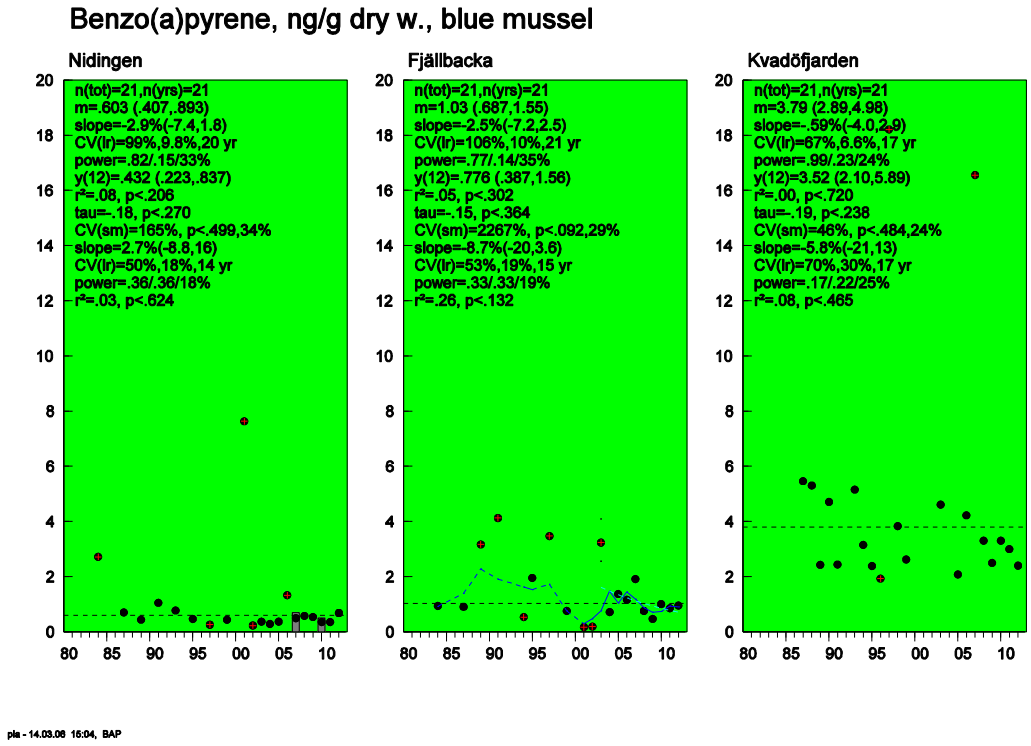


Figure 28.5. Benzo(a)pyrene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for benzo(a)pyrene in blue mussels.

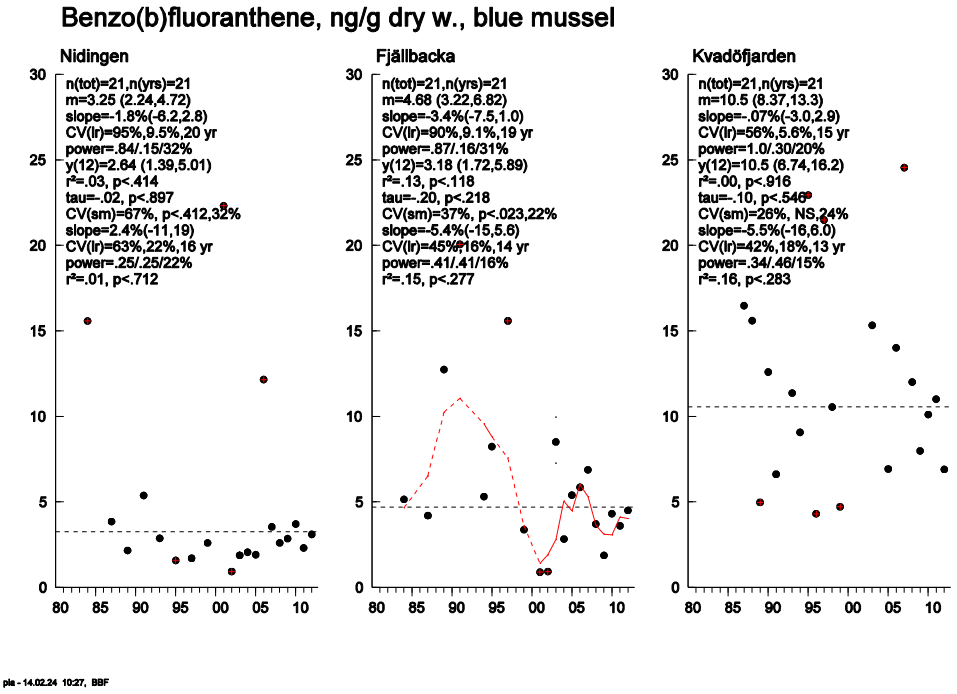


Figure 28.6. Benzo(b)fluoranthene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1986, 1984 and 1986 respectively).

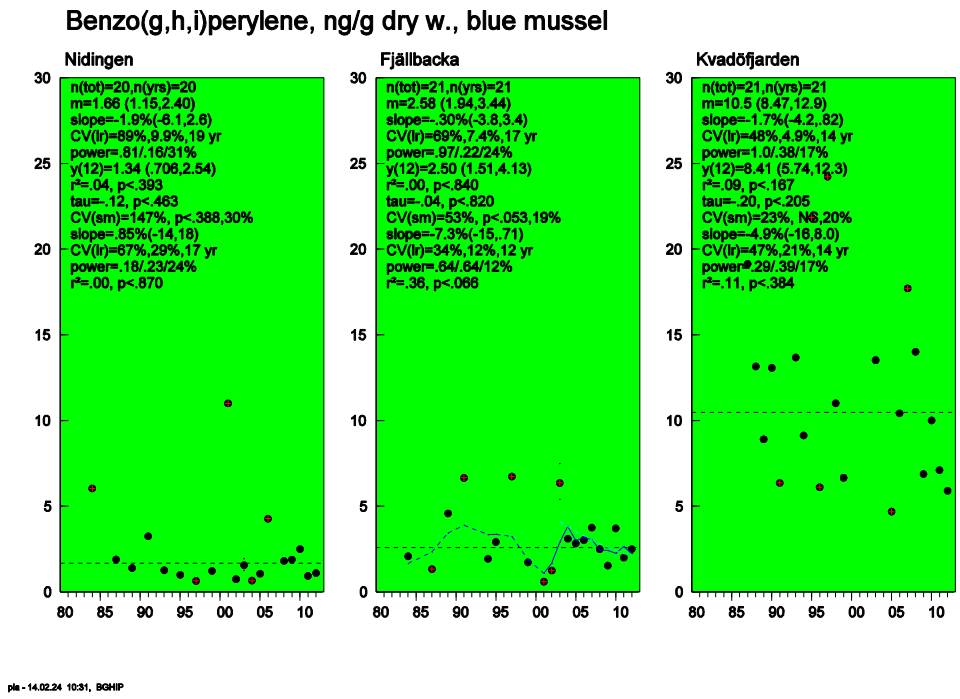


Figure 28.7. Benzo(g, h, i)perylene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 resepctively). The green area denotes the levels below the suggested target value for benzo(g, h, i)perylene in blue mussels.

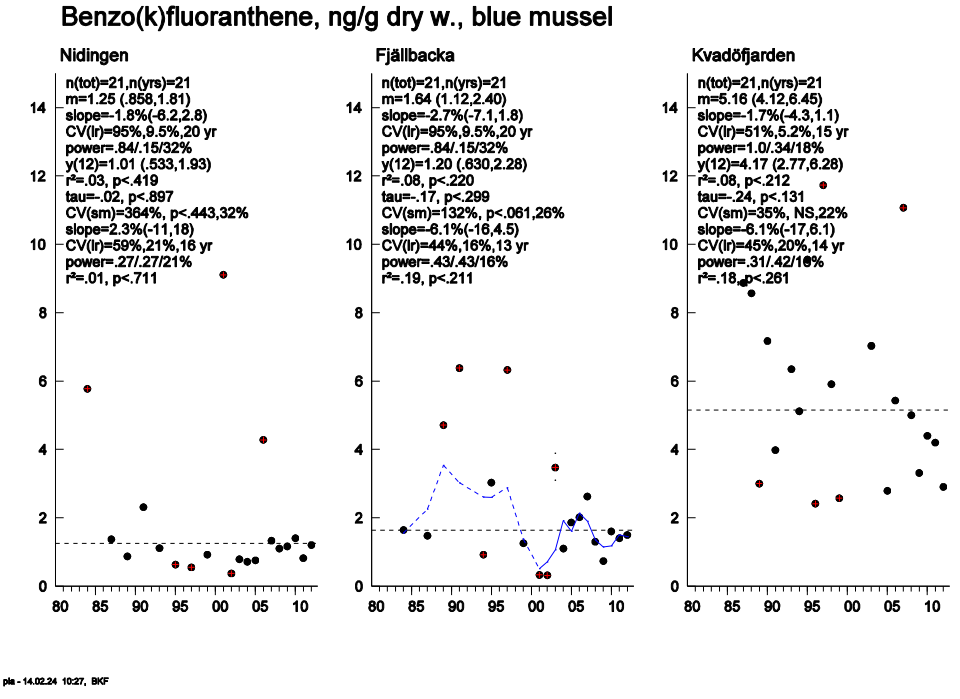


Figure 28.8. Benzo(k)fluoranthene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively).

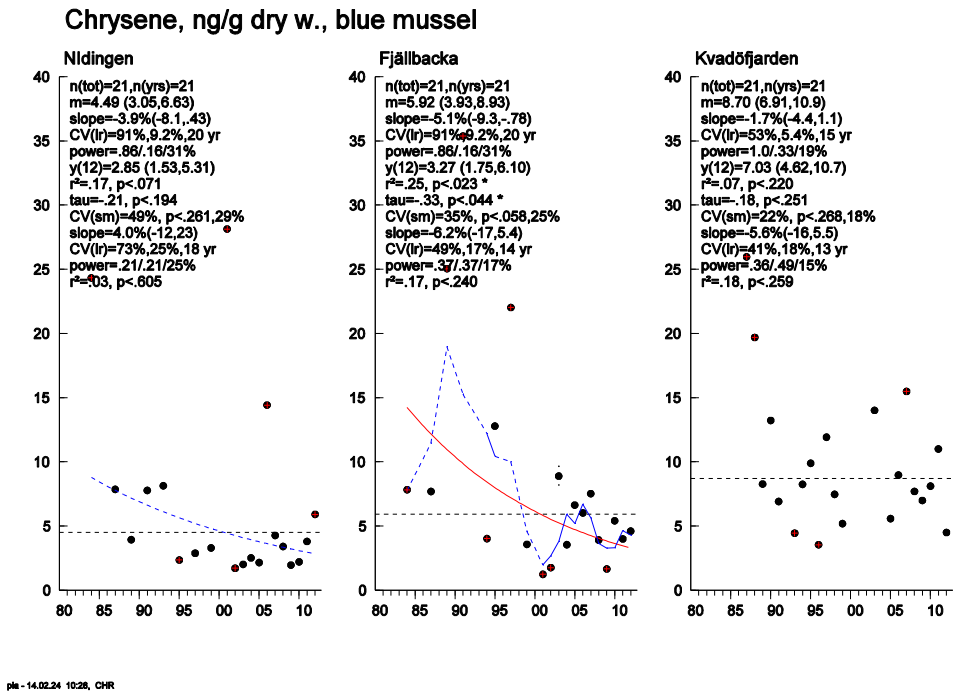


Figure 28.9. Chrysene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively).

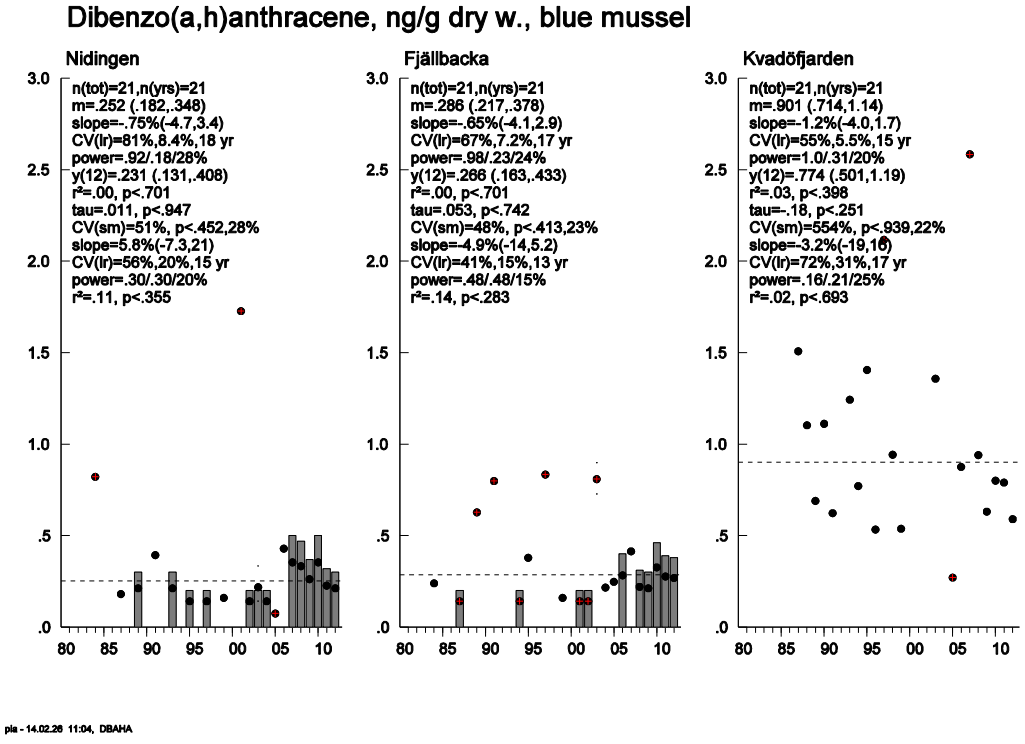


Figure 28.10. Dibenzo(a, h)anthracene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively).

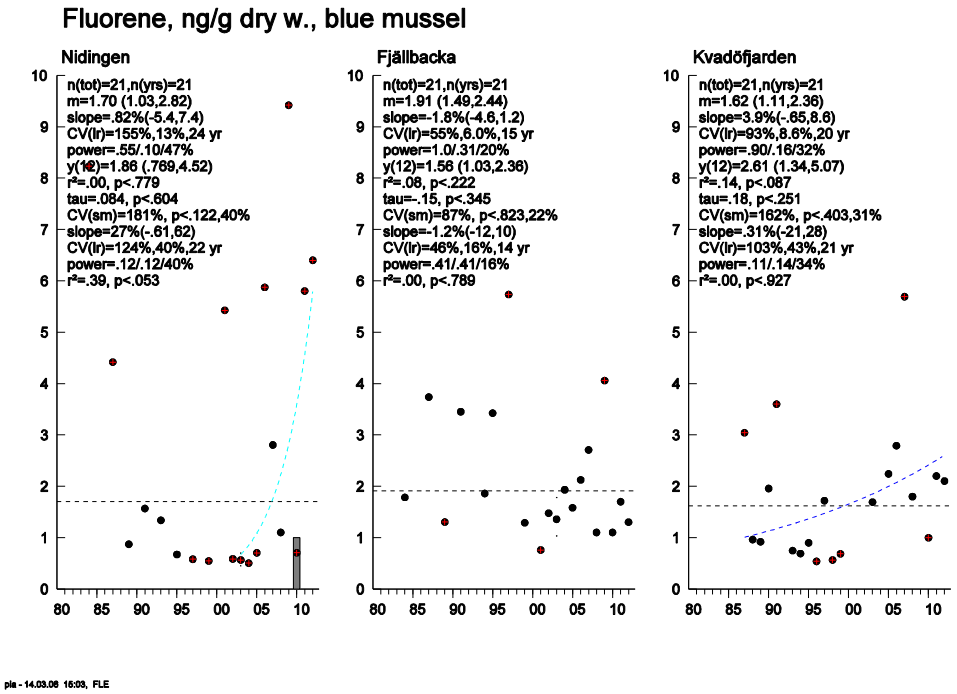


Figure 28.11. Fluorene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively).

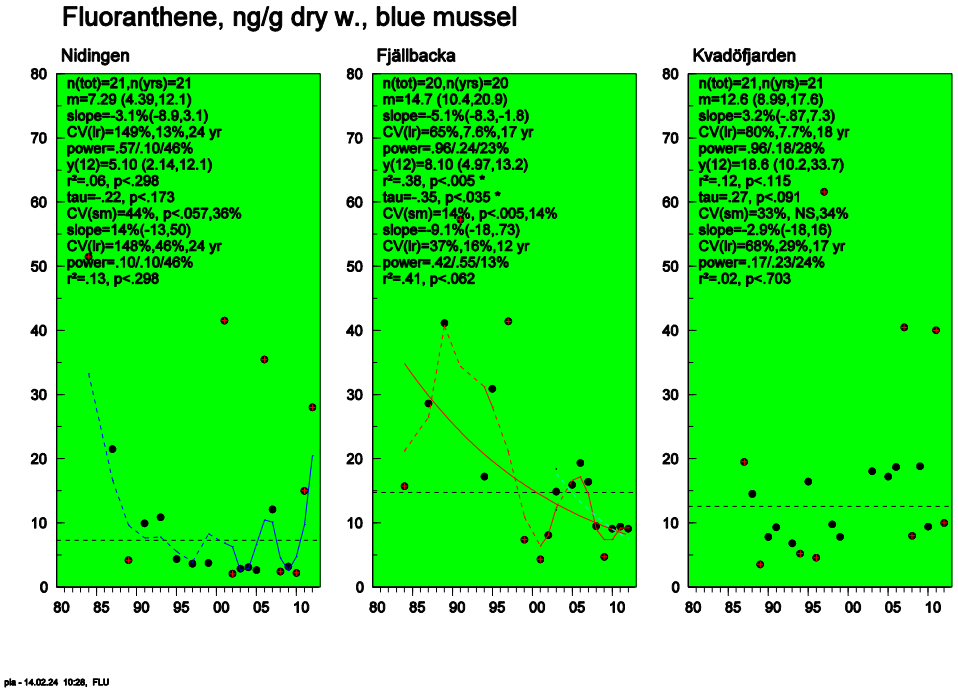


Figure 28.12. Fluoranthene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for fluoranthene in blue mussels.

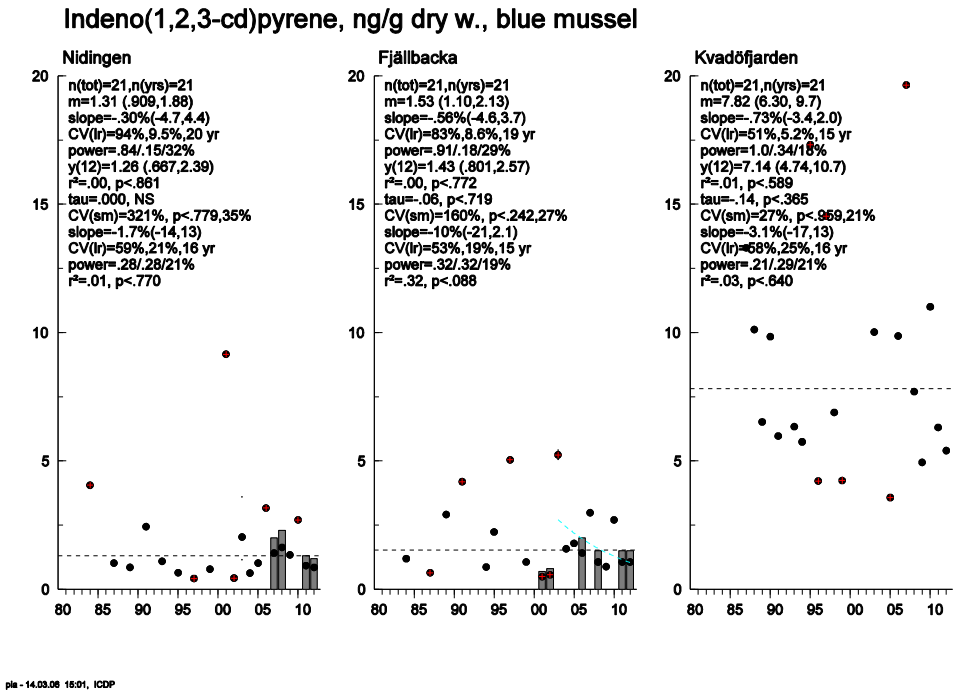


Figure 28.13. Indeno(1, 2, 3-cd)pyrene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively).

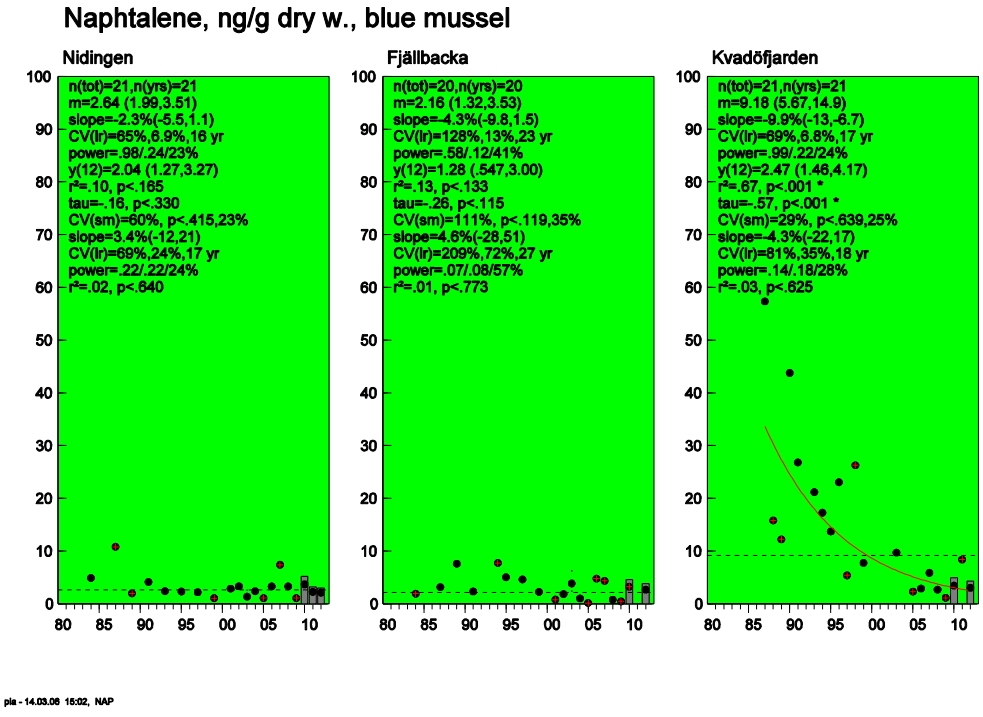


Figure 28.14. Naphthalene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for naphthalene in blue mussels.

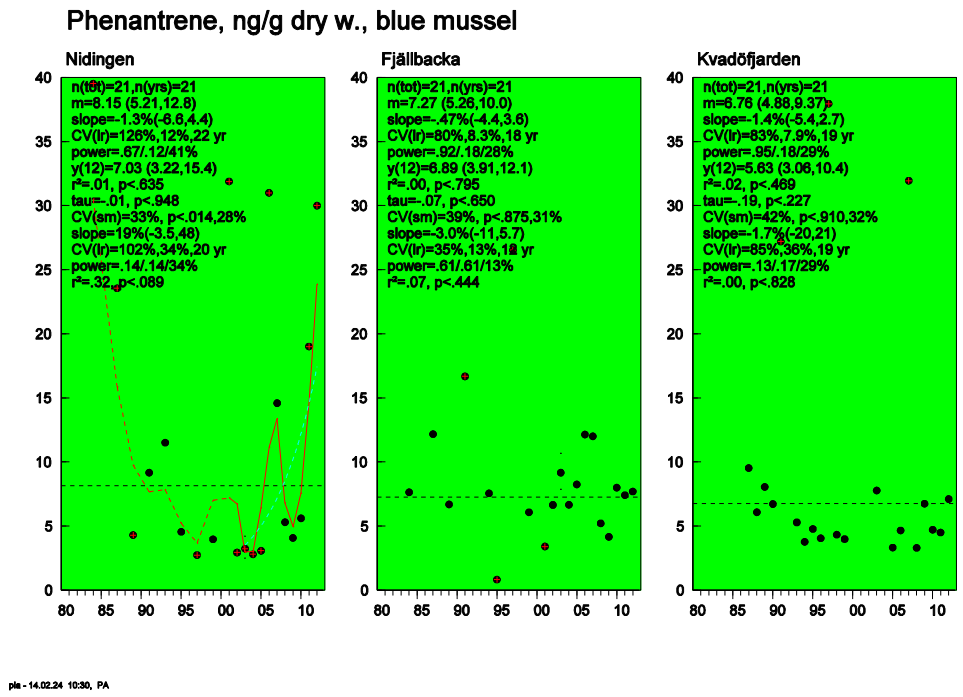


Figure 28.15. Phenanthrene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for phenanthrene in blue mussels.

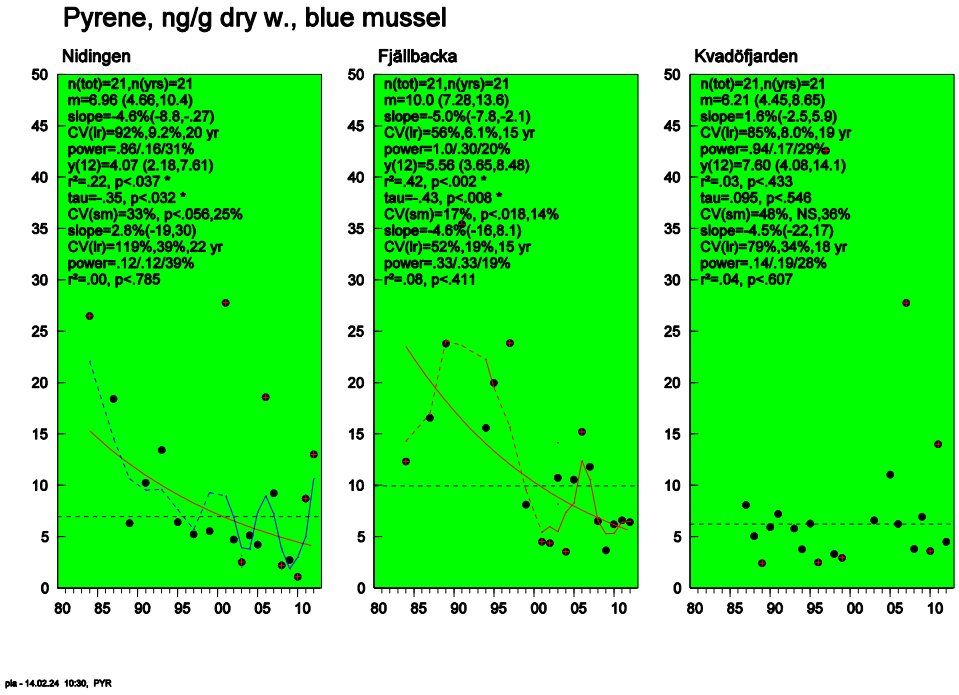


Figure 28.16. Pyrene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1987, 1984 and 1986 respectively). The green area denotes the levels below the suggested target value for pyrene in blue mussels.

28.4 Conclusion

Only blue mussels have been examined for spatial differences in PAH concentrations; concentration of sPAH was found to be higher from Kvädöfjärden in the Baltic Proper compared to the west coast. However, not all PAHs were systematically higher at Kvädöfjärden, for example flouranthene and pyrene showed higher concentrations at Fjällbacka.

Over time, acenaphtene was rarely found above the quantification limit.

The variation in the time series for PAHs is most often large with many extreme values, so one should interpret the trends with caution. Significant decreasing trends were observed for sPAH, chrysene, fluoranthene, pyrene at Fjällbacka, and naphthalene at Kvädöfjärden and pyrene at Nidingen. Significant increasing trends were seen for benzo(a)anthracene and at Kvädöfjärden.

All time series where concentrations of various PAHs were compared with the target value based on OSPAR EAC (Ecological Assessment Criteria), were below the target value.

Concentrations of fluoranthene and benzo(a)pyrene in blue mussels from the three stations are all below the existing EQSs (fluoranthene, 30 ng/g ww and benzo(a)pyrene, 5 ng/g ww).

Table 27.7. Trend (in %) for **PAHs** (ng/g lipid weight) assessed from the annual geometric mean in various matrices. The age interval for fish is written between brackets after the name of the site. The total number of samples and the number of years for the various time-series are shown in columns two to four. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ p<0.05, --/++ p<0.01, ---/+++ p<0.001. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's PAHs concentration values are estimated from the trend (%) if p<0.05, or from the mean (m) if no trend is present.

Compound	Matrix Blue mussel	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
Anthracene	Nidingen	21	20	84-12	-3.1(-8.2,1.9)	0.2081	21	43.5	.243 (.160,.371) m
Anthracene	Nidingen		10	03-12	13(-6.9,33)	0.1677	20	37	
Anthracene	Fjällbacka	21	20	84-12	-2.0(-4.6,.67)	0.1301	14	19.1	.401 (.320,.502) m
Anthracene	Fjällbacka		10	03-12	-4.7(-12,2.8)	0.1857	11	11.5	
Anthracene	Kvädöfjärden	21	21	87-12	.89(-4.6,6.4)	0.7332	22	49.4	.347 (.226,.535) m
Anthracene	Kvädöfjärden		9	03-12	-1.0(-27,25)	0.89	22	45.7	
Anthracene	Fladen	21	20	84-12	-3.1(-8.2,1.9)	0.2081	21	43.5	.243 (.160,.371) m
Anthracene	Fladen		10	03-12	13(-6.9,33)	0.1677	20	37	
Anthracene	Väderöarna	21	20	84-12	-2.0(-4.6,.67)	0.1301	14	19.1	.401 (.320,.502) m
Anthracene	Väderöarna		10	03-12	-4.7(-12,2.8)	0.1857	11	11.5	
Benzo(a)anthracene	Fladen	19	18	84-12	-.63(-4.2,3.0)	0.7119	16	23.9	3.28 (2.50,4.29) m
Benzo(a)anthracene	Fladen		10	03-12	6.1(-5.6,18)	0.2633	14	19.2	
Benzo(a)anthracene	Väderöarna	21	20	84-12	-1.9(-5.1,1.4)	0.2363	16	24.3	3.69 (2.82,4.82) m
Benzo(a)anthracene	Väderöarna		10	03-12	-.81(-9.8,8.1)	0.8205	12	14	
Benzo(a)anthracene	Kvädöfjärden	18	18	87-12	5.5(1.6,9.5)	.0086 ++	17	27.8	15.2 (8.36,27.5)
Benzo(a)anthracene	Kvädöfjärden		7	03-12	6.9(-4.7,19)	0.1829	12	14.5	
Benzo(a)pyrene	Fladen	21	20	84-12	-2.9(-7.6,1.8)	0.2061	20	39.5	.603 (.407,.893) m
Benzo(a)pyrene	Fladen		10	03-12	2.7(-9.2,15)	0.6238	14	19.4	
Benzo(a)pyrene	Väderöarna	21	20	84-12	-2.5(-7.5,2.5)	0.3015	21	42.4	1.03 (.687,1.55) m
Benzo(a)pyrene	Väderöarna		10	03-12	-9.1(-22,3.5)	0.1323	15	20.8	
Benzo(a)pyrene	Kvädöfjärden	21	21	87-12	-.59(-4.0,2.9)	0.7203	17	26.8	3.79 (2.89,4.98) m
Benzo(a)pyrene	Kvädöfjärden		9	03-12	-6.0(-24,12)	0.4649	17	28	
Benzo(b)fluoranthene	Fladen	21	20	84-12	-1.8(-6.4,2.7)	0.414	20	37.9	3.25 (2.24,4.72) m
Benzo(b)fluoranthene	Fladen		10	03-12	2.4(-12,17)	0.7123	16	24.8	
Benzo(b)fluoranthene	Väderöarna	21	20	84-12	-3.4(-7.8,1.0)	0.1178	19	36	4.68 (3.22,6.82) m
Benzo(b)fluoranthene	Väderöarna		10	03-12	-5.6(-17,5.4)	0.2769	14	17.7	
Benzo(b)fluoranthene	Kvädöfjärden	21	21	87-12	-.07(-3.0,2.9)	0.9155	15	22	10.5 (8.37,13.3) m
Benzo(b)fluoranthene	Kvädöfjärden		9	03-12	-5.7(-17,5.8)	0.283	13	16.3	
Benzo(g,h,i)perylene	Fladen	20	19	84-12	-1.9(-6.3,2.6)	0.3928	19	35.7	1.66 (1.15,2.40) m
Benzo(g,h,i)perylene	Fladen		9	03-12	.85(-15,17)	0.8701	17	26.5	
Benzo(g,h,i)perylene	Väderöarna	21	20	84-12	-.30(-3.9,3.3)	0.8405	17	27.7	2.58 (1.94,3.44) m
Benzo(g,h,i)perylene	Väderöarna		10	03-12	-7.6(-16,.71)	0.0659	12	12.9	
Benzo(g,h,i)perylene	Kvädöfjärden	21	21	87-12	-1.7(-4.3,.81)	0.1668	14	18.6	10.5 (8.47,12.9) m
Benzo(g,h,i)perylene	Kvädöfjärden		9	03-12	-5.0(-18,7.7)	0.3842	14	18.4	
Benzo(k)fluoranthene	Fladen	21	20	84-12	-1.8(-6.4,2.8)	0.4188	20	38	1.25 (.858,1.81) m
Benzo(k)fluoranthene	Fladen		10	03-12	2.3(-12,16)	0.7112	16	23.5	

Benzo(k)fluoranthene	Väderöarna	21	20	84-12	-2.8(-7.4,1.8)	0.2195	20	38	1.64 (1.12,2.40) m
Benzo(k)fluoranthene	Väderöarna		10	03-12	-6.3(-17,4.4)	0.2112	13	17.1	
Benzo(k)fluoranthene	Kvädöfjärden	21	21	87-12	-1.7(-4.4,1.1)	0.2119	15	20.2	5.16 (4.12,6.45) m
Benzo(k)fluoranthene	Kvädöfjärden		9	03-12	-6.3(-19,5.9)	0.2613	14	17.5	
Chrysene	Fladen	21	20	84-12	-4.0(-8.5,.43)	0.0708	20	36.6	2.85 (1.53,5.31)
Chrysene	Fladen		10	03-12	3.9(-13,20)	0.6045	18	29	
Chrysene	Väderöarna	21	20	84-12	-5.3(-9.7,-.79)	0.0227	20	36.5	3.27 (1.75,6.10)
Chrysene	Väderöarna		10	03-12	-6.4(-18,5.3)	0.2405	14	19.1	
Chrysene	Kvädöfjärden	21	21	87-12	-1.7(-4.5,1.1)	0.2203	15	20.8	8.70 (6.91,10.9) m
Chrysene	Kvädöfjärden		9	03-12	-5.8(-17,5.4)	0.2588	13	15.8	
Dibenz(a,h)anthracene	Fladen	20	19	84-12	-4.3(-9.5,.97)	0.1005	21	43.4	.205 (.131,.321) m
Dibenz(a,h)anthracene	Fladen		9	03-12	-15(-40,8.8)	0.1737	21	43.9	
Dibenz(a,h)anthracene	Väderöarna	21	20	84-12	-3.6(-7.7,.49)	0.0775	18	32.5	.157 (.089,.278)
Dibenz(a,h)anthracene	Väderöarna		10	03-12	-21(-32,-10)	.0022 --	14	17.6	
Dibenz(a,h)anthracene	Kvädöfjärden	21	21	87-12	-1.2(-4.1,1.7)	0.3976	15	21.7	.901 (.714,1.14) m
Dibenz(a,h)anthracene	Kvädöfjärden		9	03-12	-3.2(-22,15)	0.6928	17	28.8	
Fluorene	Fladen	20	19	84-12	1.6(-5.0,8.2)	0.629	24	60.4	1.78 (1.05,3.01) m
Fluorene	Fladen		9	03-12	30(8.7,51)	.0126 +	20	36.7	
Fluorene	Väderöarna	21	20	84-12	-1.8(-4.7,1.2)	0.222	15	21.7	1.91 (1.49,2.44) m
Fluorene	Väderöarna		10	03-12	-1.3(-12,9.8)	0.7886	14	17.9	
Fluorene	Kvädöfjärden	21	21	87-12	3.8(-.65,8.2)	0.0866	20	37.2	2.61 (1.34,5.07)
Fluorene	Kvädöfjärden		9	03-12	.31(-24,25)	0.9265	21	41.1	
Fluorene	Fladen	21	20	84-12	-3.2(-9.3,3.0)	0.2983	24	58.1	7.29 (4.39,12.1) m
Fluorene	Fladen		10	03-12	13(-14,41)	0.2985	24	57.8	
Fluorene	Väderöarna	20	19	84-12	-5.2(-8.6,-1.8)	.0051 --	17	25.8	8.10 (4.97,13.2)
Fluorene	Väderöarna		9	03-12	-9.6(-20,.73)	0.0624	12	14.4	
Fluorene	Kvädöfjärden	21	21	87-12	3.1(-.88,7.1)	0.1154	18	32.2	12.6 (8.99,17.6) m
Fluorene	Kvädöfjärden		9	03-12	-2.9(-20,15)	0.7032	17	27	
Indenol(1,2,3-cd)pyrene	Fladen	17	16	84-10	.36(-5.8,6.6)	0.8693	21	43.8	1.35 (.852,2.13) m
Indenol(1,2,3-cd)pyrene	Fladen		8	01-10	-.04(-30,30)	0.9457	24	55.5	
Indenol(1,2,3-cd)pyrene	Väderöarna	17	16	84-10	.63(-5.0,6.2)	0.7986	20	38.1	1.64 (1.09,2.49) m
Indenol(1,2,3-cd)pyrene	Väderöarna		8	01-10	9.3(-14,33)	0.3763	20	40.4	
Indenol(1,2,3-cd)pyrene	Kvädöfjärden	21	21	87-12	-.73(-3.5,2.0)	0.5893	15	20.2	7.82 (6.30, 9.7) m
Indenol(1,2,3-cd)pyrene	Kvädöfjärden		9	03-12	-3.2(-18,12)	0.6405	16	22.8	
Naphthalene	Fladen	18	17	84-09	-3.1(-7.4,1.2)	0.1416	17	27.6	2.65 (1.90,3.71) m
Naphthalene	Fladen		9	01-09	-.33(-21,20)	0.9216	18	30.3	
Naphthalene	Väderöarna	18	17	84-09	-6.4(-13,.42)	0.0615	23	51	1.09 (.461,2.57)
Naphthalene	Väderöarna		9	01-09	-5.0(-43,33)	0.7572	26	72.4	
Naphthalene	Kvädöfjärden	19	19	87-11	-11(-15,-6.7)	.0001 ---	18	29.2	2.55 (1.37,4.76)
Naphthalene	Kvädöfjärden		7	03-11	-5.0(-38,28)	0.7124	20	40.6	
Phenanthrene	Fladen	21	20	84-12	-1.3(-6.9,4.3)	0.6352	22	50	8.15 (5.21,12.8) m
Phenanthrene	Fladen		10	03-12	18(-3.6,39)	0.0888	20	40.6	
Phenanthrene	Väderöarna	21	20	84-12	-.48(-4.5,3.6)	0.7949	18	32.2	7.27 (5.26,10.0) m
Phenanthrene	Väderöarna		10	03-12	-3.0(-12,5.6)	0.4439	12	13.4	

Phenanthrene	Kvädöfjärden	21	21	87-12	-1.5(-5.5,2.6)	0.4692	19	33.2	6.76 (4.88,9.37) m
Phenanthrene	Kvädöfjärden		9	03-12	-1.8(-23,19)	0.8278	19	34	
Pyrene	Fladen	21	20	84-12	-4.7(-9.2,-.27)	0.0372	20	36.7	4.07 (2.18,7.61)
Pyrene	Fladen		10	03-12	2.7(-21,27)	0.7851	22	47.3	
Pyrene	Väderöarna	21	20	84-12	-5.2(-8.2,-2.1)	.0022 --	15	22.3	5.56 (3.65,8.48)
Pyrene	Väderöarna		10	03-12	-4.7(-17,7.7)	0.4107	15	20.6	
Pyrene	Kvädöfjärden	21	21	87-12	1.6(-2.5,5.8)	0.4334	19	34	6.21 (4.45,8.65) m
Pyrene	Kvädöfjärden		9	03-12	-4.6(-25,15)	0.6067	18	31.8	

29 PFASs, Perfluoroalkyl substances

Updated 14.02.28

PFOS was retrospectively analysed in guillemot eggs from St. Karlsö in a time series starting from 1968. Additionally, a selection of perfluoroalkyl substances (see 29.2.1) were analysed in herring liver tissue over the last seven years.

29.1 Introduction

29.1.1 Uses, Production and Sources

Perfluoroalkyl substances (PFASs) are anthropogenic surfactants with exceptional stability and surface tension lowering potential. PFASs have been used industrially (e.g., production of fluoropolymers) and commercially (water and stain proofing agents and fire-fighting foams) since the beginning of the 1950s. It was not until recently (2000) that the main producer, 3M, started to phase out production of the main compounds of concern, perfluorooctane sulfonate (PFOS) and PFOS derivatives, perfluorooctanoate (PFOA) as well as perfluorohexane sulfonate (PFHxS) (Buck et al. 2011).

Environmental PFAS contamination has multiple emission sources. These include primary emissions of PFASs to air and water from industrial production and application, as well as secondary emissions from consumer products or sewage treatment plant effluents. For the persistent perfluoroalkyl acids (PFAAs) a further distinction can be made between direct sources from manufacturing and use of PFAAs and indirect sources from degradation of semi-volatile precursor compounds (Buck et al. 2011). Perfluoroalkyl carboxylates (PFCAs) as PFOA (perfluorooctanoate) and PFNA (perfluorononanoate) are intentionally produced and therefore a large portion of the PFOA and PFNA found in the environment probably originates from direct sources (mainly the production process of fluoropolymers, Prevedouros et al. 2006), and waterborne transport to remote locations. Therefore, sewage treatment plant effluent from industry or larger cities could represent hot-spots. In contrast, longer-chain PFCAs such as PFUnDA (perfluoroundecanoate) and PFTrDA (perfluorotridecanoate) are unintentionally produced substances, and their presence in the environment is probably due to both direct sources (impurities in PFOA and PFNA productions) and indirect sources (atmospheric transport and degradation of precursors). Also the role of PFOS derivatives for the distribution and accumulation of PFOS in the environment is currently under investigation (Martin et al. 2010). Perfluorooctane sulfonamide (FOSA) is an intermediate product in the degradation of many PFOS precursors to PFOS, and is often analysed together with PFOS in the environment.

29.1.2 Toxicological Effects

Exponentially increasing concentrations of PFOS in wildlife were reported during the 1990s (Holmström et al. 2005). In biota, PFASs tend to accumulate in protein rich tissues such as blood, liver and eggs. Toxic effects in laboratory experiments with mostly rodents include weight loss, liver enlargement, immunotoxicity and a number of developmental effects such as postnatal mortality. The common carp (*Cyprinus carpio*) exposed in lab to different PFOS concentrations experienced decreases in glycogen, and declines in condition factor and hepatosomatic index with increases in PFOS concentrations (Hagenaars et al. 2008). Due to large inter-species variations and even gender differences in toxicological effects, it is difficult to extrapolate observed effects to potential effects in humans. However, epidemiological studies on humans have increased in recent years. For instance, concentrations of PFOA in maternal blood and PFOA and PFOS in cord blood during pregnancy have been found to be negatively associated with birth weight (Apelberg et al. 2007; Fei et al. 2007), ponderal index, head circumference (Apelberg et al. 2007), and birth length (Fei et al. 2008a). In contrast, no associations between concentrations of PFOA and PFOS in maternal plasma during pregnancy and developmental milestones in early childhood have been found (Fei et al. 2008b). Current human exposure to PFASs is believed to be primarily the result of dietary intake (Vestergren and Cousins 2009). Intake of contaminated fish from the Baltic Sea is one source of human exposure to PFASs (Berger et al. 2009).

29.1.3 Conventions, aims and restrictions

Perfluorooctane sulfonic acid, its salts, and perfluorooctane sulfonyl fluoride are among the nine new Persistent Organic Pollutants (POPs) included in Annex B of The Stockholm Convention on POPs (UNEP 2009), an international agreement requiring measures for reducing or preventing release of dangerous substances to the environment. The Stockholm Convention was adopted in 2001 and entered into force in 2004. The nine new POPs were adopted in 2009 and the amendments entered into force in 2010. Additionally, the use of PFOS and its derivatives is restricted in the European Union by the Marketing and Use Directive 2006/122/EC, but large scale production continues in other parts of the world.

Due to their concentrations and/or temporal trends, PFOS, PFOA and PFNA are currently the PFASs of most concern for the Baltic Sea environment (HELCOM 2010). Based on their documented relevance for the marine environment long-chain PFCAs and FOSA are additionally included in this report.

29.1.4 Target Levels

The target levels used for PFOS in herring liver is 9.1 µg/kg wet weight. For further information on target levels and selection of target level see chapter 10.

29.2 Methods

29.2.1 Analytical Information

The PFASs analysed included: perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDA), perfluoroundecanoate (PFUnDA), perfluorododecanoate (PFDoDA), perfluorotridecanoate (PFTrDA), perfluorotetradecanoate (PFTeDA), perfluoropentadecanoate (PFPeDA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perflourooctane sulfonate (PFOS), perfluorodecane sulfonate (PFDS) and perfluorooctane sulfonamide (FOSA). However, since some PFAS only had values below LOQ, these time series are not presented in the chapter.

See chapter 6, section 6.5 for further details regarding analytical methods for PFASs.

29.3 Results

29.3.1 Spatial Variation

So far analysis of herring liver from only eight years (2005 - 2012) (pooled samples, 12 fish in each) from the old sampling sites, and five years from the new sampling sites (four years at the offshore sites) are available. Therefore, the results should be treated with caution. However, it has been shown that the concentration variation of PFASs between individuals is relatively small compared to classical POPs (Verreault et al. 2007). The spatial variations of seven PFASs (figure 29.1: PFHxS, PFOS and FOSA; and figure 29.2: PFNA, PFDA, PFUnDA and PFTrDA) are presented below. The selection of substances was based on number of results above LOQ.

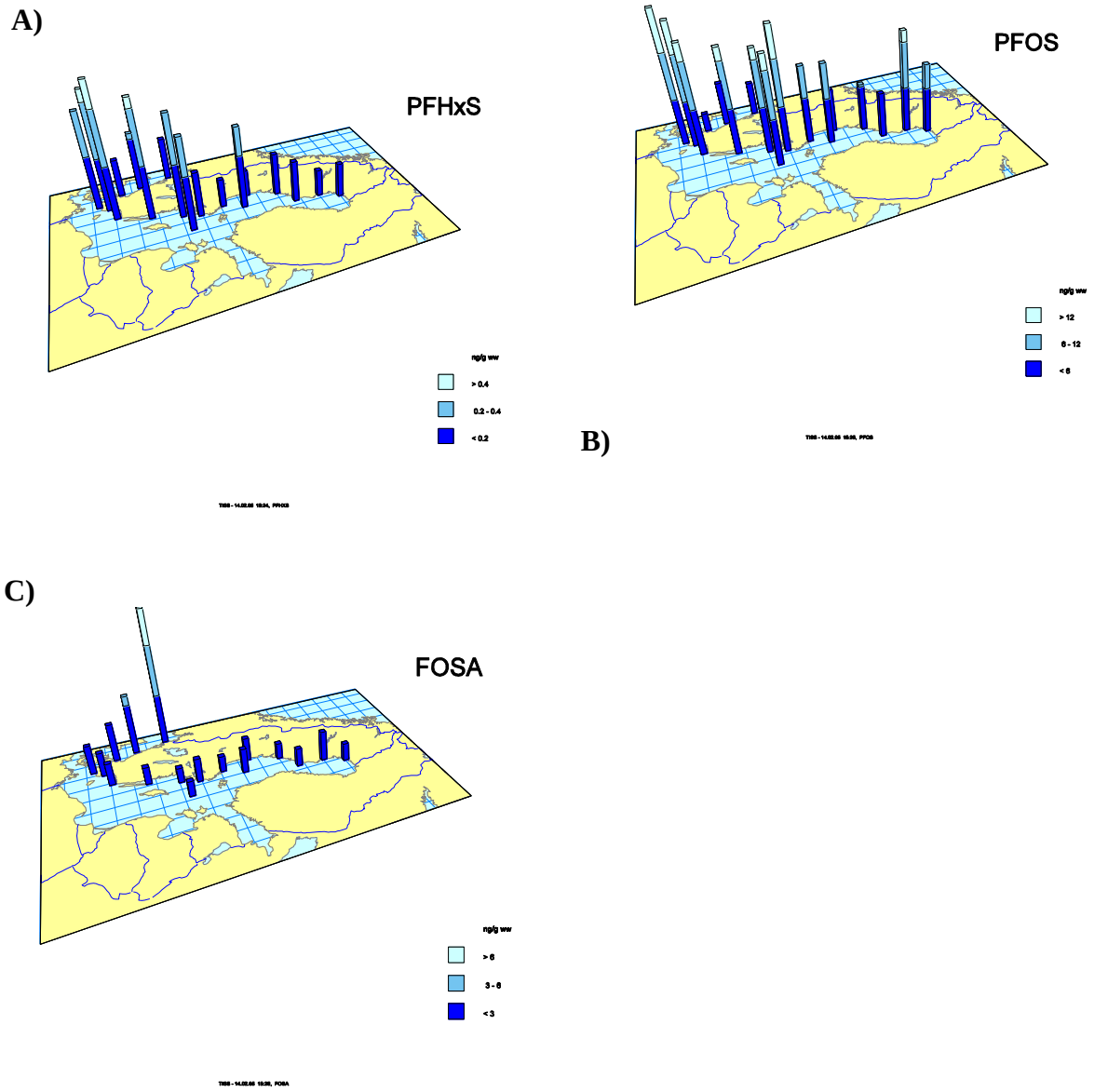


Figure 29.1 Spatial variations in concentrations of sulfonates and its precursors (ng/g wet weight) of **A)** PFHxS, **B)** PFOS and **C)** FOSA in herring liver.

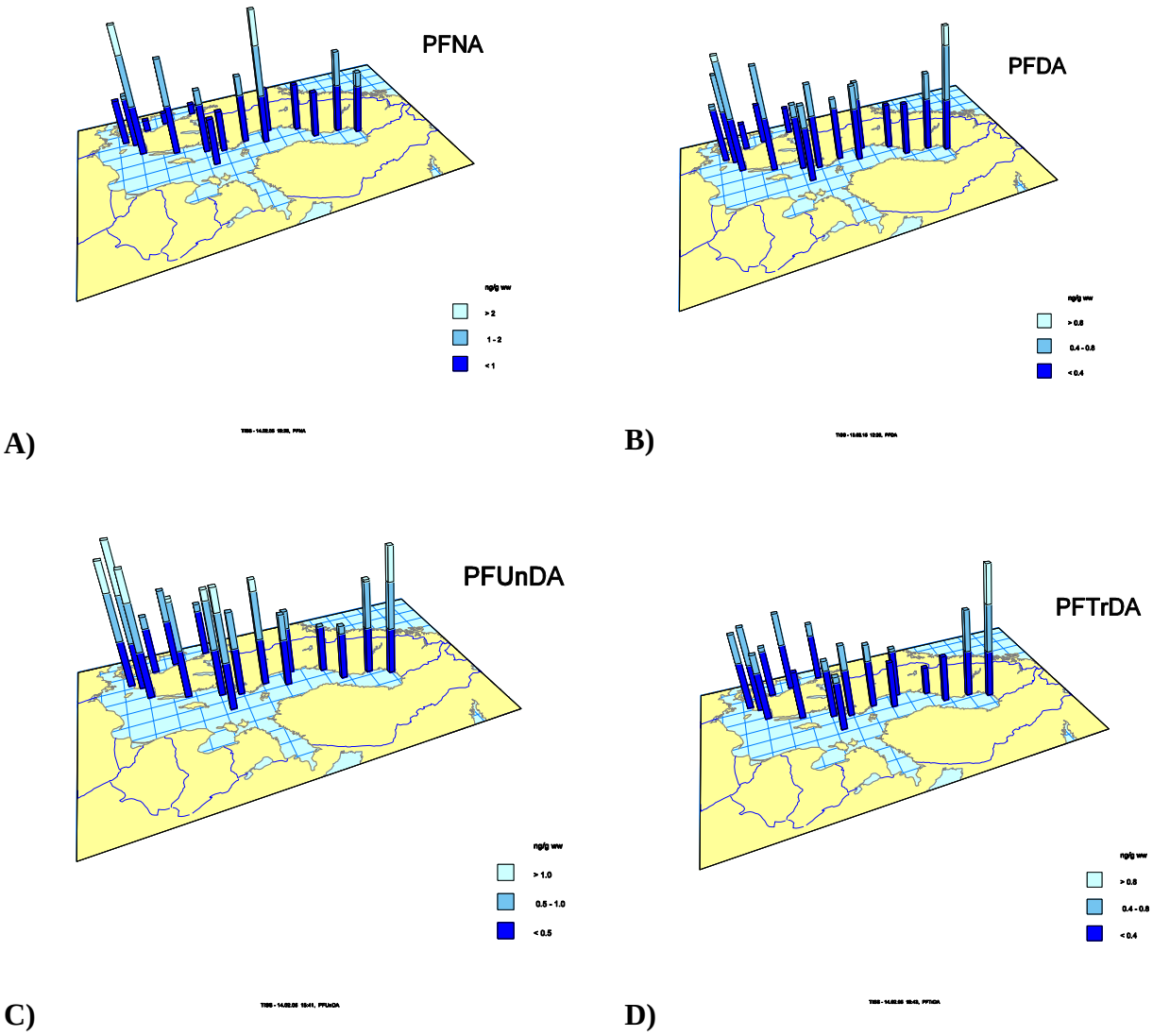


Figure 29.2 Spatial variations in concentrations of carboxylates (ng/g wet weight) of **A)** PFNA, **B)** PFDA, **C)** PFUnDA and **D)** PFTrDA in herring liver.

There were higher concentrations of PFHxS in the Baltic Proper compared to the Bothnian Bay and the Swedish west coast (Fig. 29.1a). The highest concentration of PFHxS was at Ängskärsklubb in the southern Baltic Proper. Also, PFOS had higher concentrations in the Baltic Proper, where the highest concentration was found at Abbekås in the southern Baltic Proper (Fig. 29.1b). FOSA on the other hand showed the highest concentrations on the Swedish west coast, where Väderöarna in Skagerrak had the highest concentration (Fig. 29.1c). PFNA showed higher concentrations at several sites in the Baltic compared to the west coast (Fig. 29.2a). The highest concentration of PFNA was found at the Bothnian Sea offshore site. PFDA and PFUnDA showed quite consistent concentrations along the whole coast of the Baltic, but lower concentrations at the Swedish west coast. The concentration of PFDA was highest in Harufjärden in the Bothnian Bay, followed by Utlängan in the south Baltic proper (Fig. 29.2b) and for PFUnDA the highest concentration was seen in Hanu Bay in the south Baltic proper, followed by Abbekås, Utlängan and Harufjärden (Fig. 29.2c). PFTrDA showed similar concentrations along the whole Swedish coast, with the highest concentration found at Harufjärden.

29.3.2 Temporal Variation

29.3.2.1 Sulfonates and its precursors

PFOS concentrations in herring liver show inconsistent trends at all the sites (Fig. 29.3-4). FOSA, on the other hand, which is a precursor to PFOS, shows a significant decreasing trend at Ängskärsklubb and Fladen (Fig. 29.7-8, table 29.1). There are also indications of decreasing trends in FOSA concentrations at Harufjärden and Landsort (Fig. 29.7-8). The concentration of PFHxS show inconsistent trend over the examined time serie (Fig. 29.5-6). However, at Fladen an increasing trend is indicated for the concentration of PFHxS (Fig. 29.6). PFBS and PFDS had only values under LOQ and are therefore not presented in time series (table 29.1).

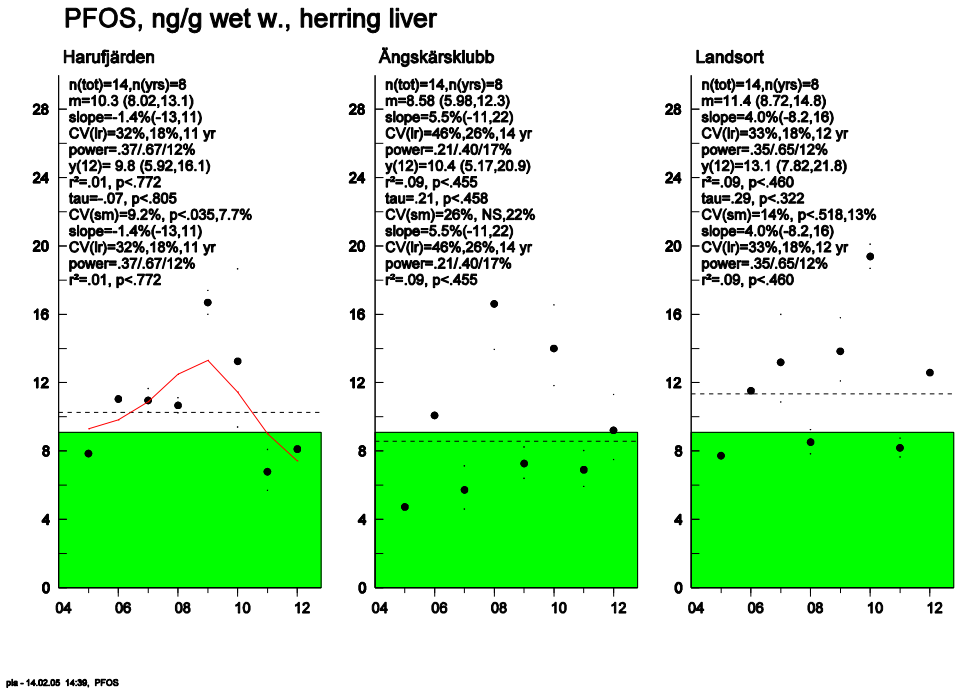


Figure 29.3. Temporal trend of PFOS in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The green area denotes the levels below the suggested target value for PFOS in fish.

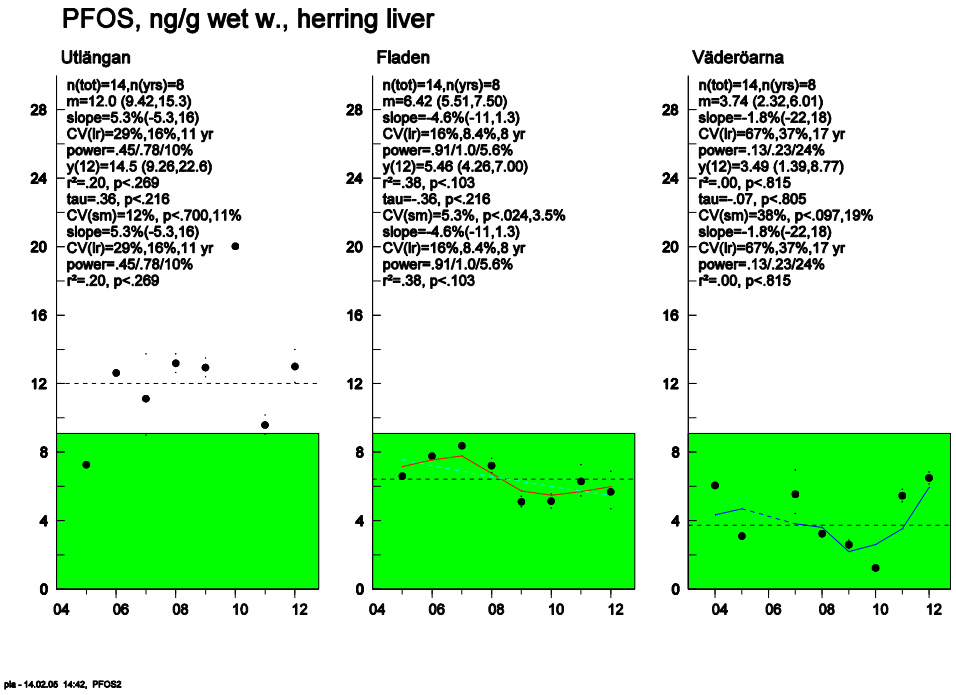


Figure 29.4. Temporal trend of PFOS in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The green area denotes the levels below the suggested target value for PFOS in fish.

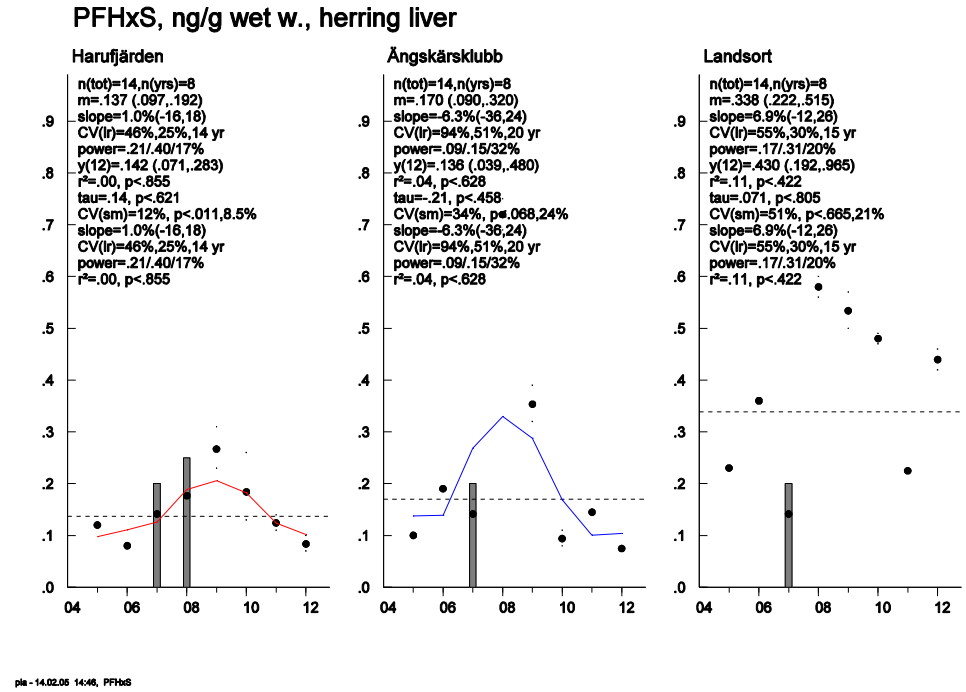


Fig. 29.5. Temporal trend of PFHxS in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bars represent years where all values were below LOQ.

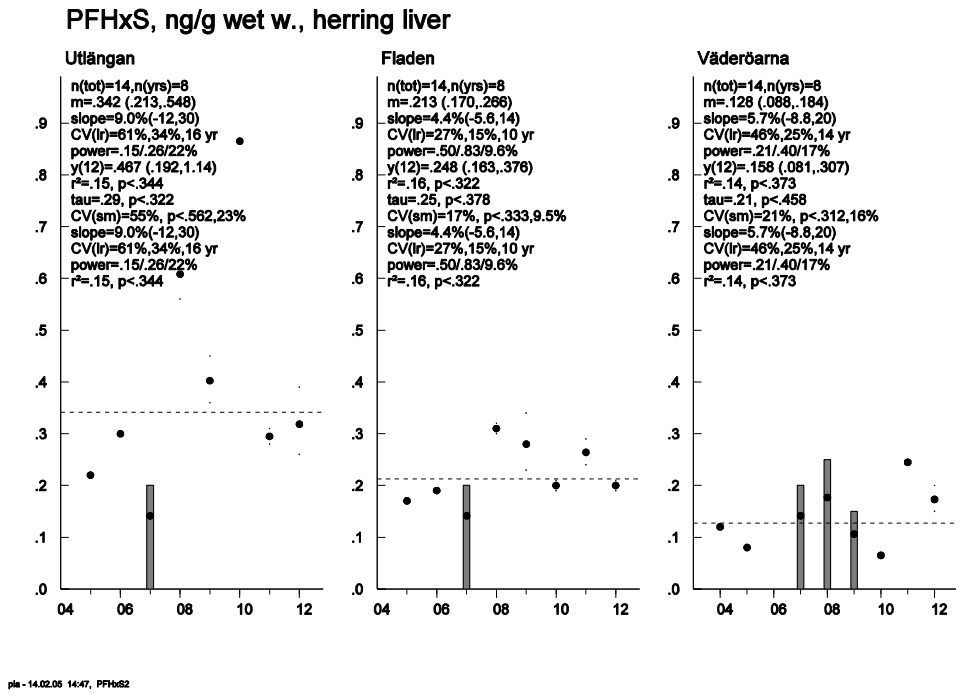


Fig. 29.6. Temporal trend of PFHxS in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

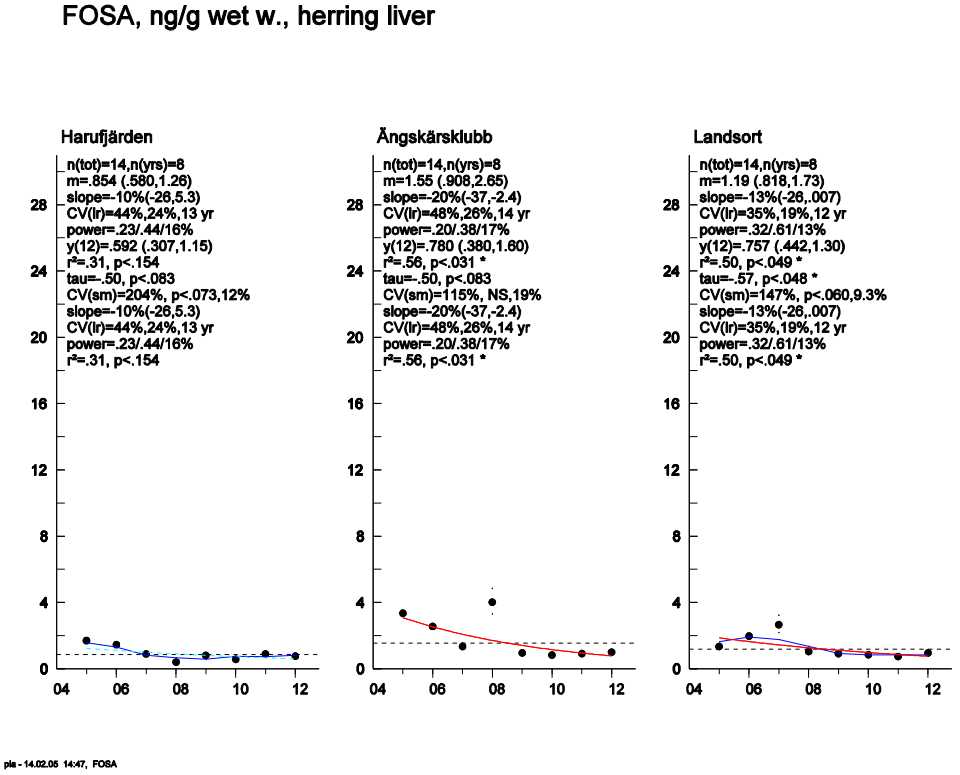


Figure 29.7. Temporal trend of FOSA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bars represent years where all values were below LOQ.

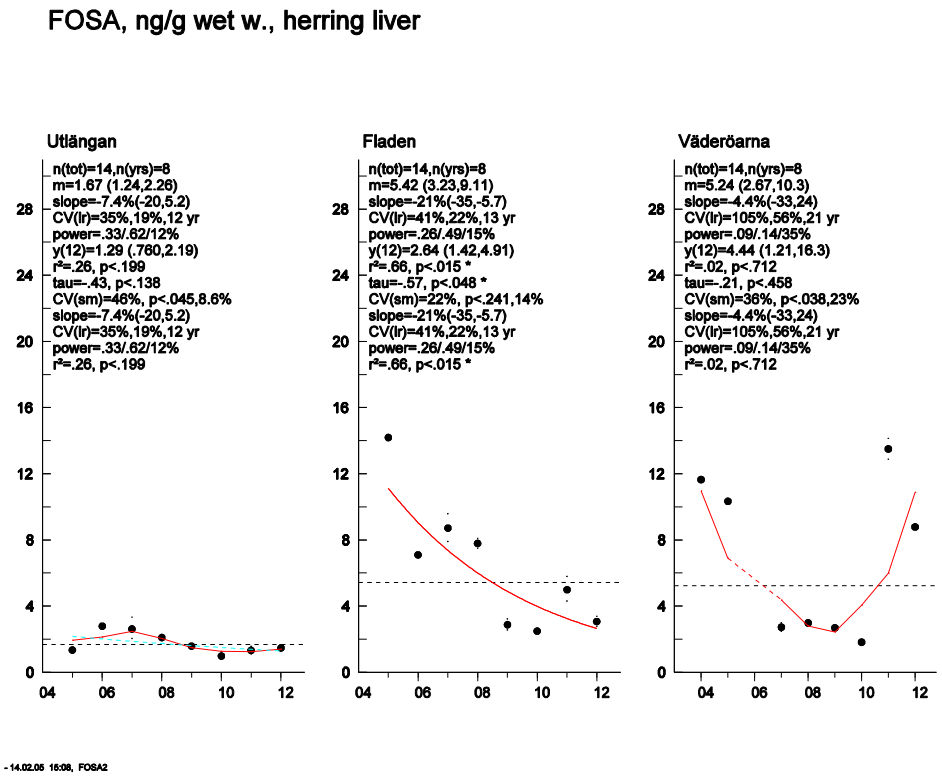


Figure 29.8. Temporal trend of FOSA in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

29.3.2.2 Carboxylates

PFUnDA show inconsistent trends over the examined time series (Fig. 29. 15-16). For PFOA, an increasing trend is indicated at Utlängan (Fig. 29.9-10). A decreasing trend is indicated for PFNA and PFDA shows a significant decreasing trend at Landsort (29.11-14, table 29.2). Also, at Ängskärsklubb a decreasing trend is indicated for PFTrDA (Fig. 29.19-20). PFHpA, PFTeDA, and PFPeDA had only values under LOQ and are therefore not presented in time series (table 29.2).

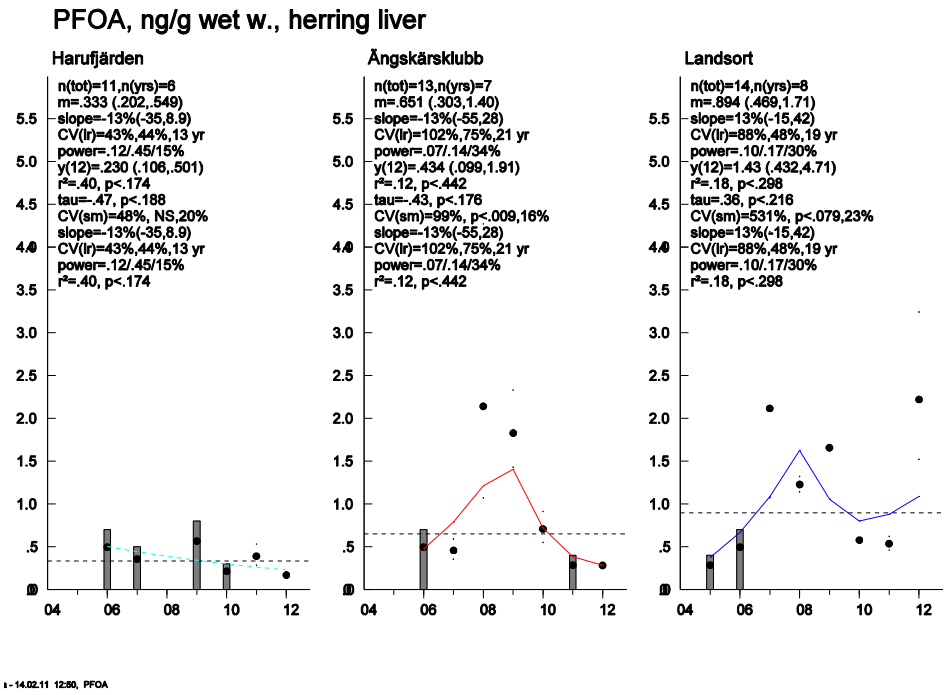


Figure 29.9. Temporal trend of PFOA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bars represent years where all values were below LOQ.

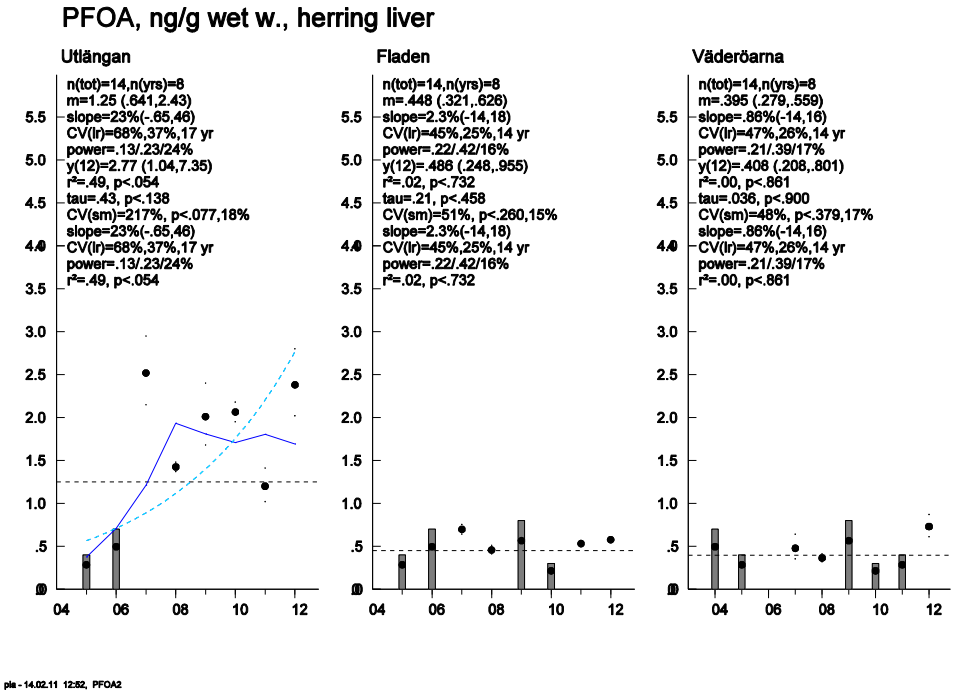


Figure 29.10. Temporal trend of PFOA in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

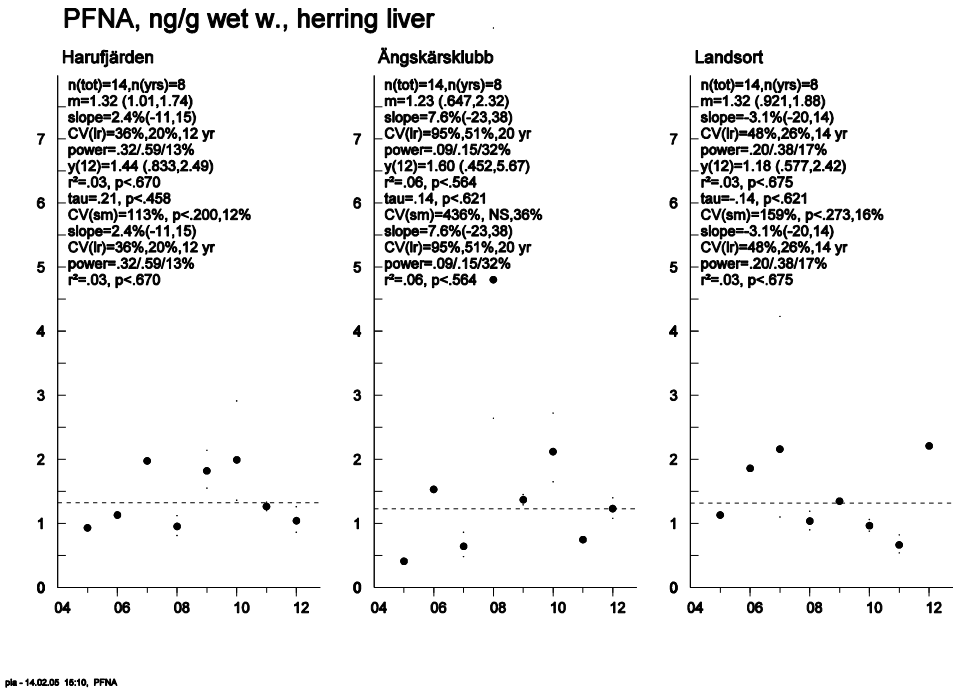


Fig. 29.11. Temporal trend of PFNA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

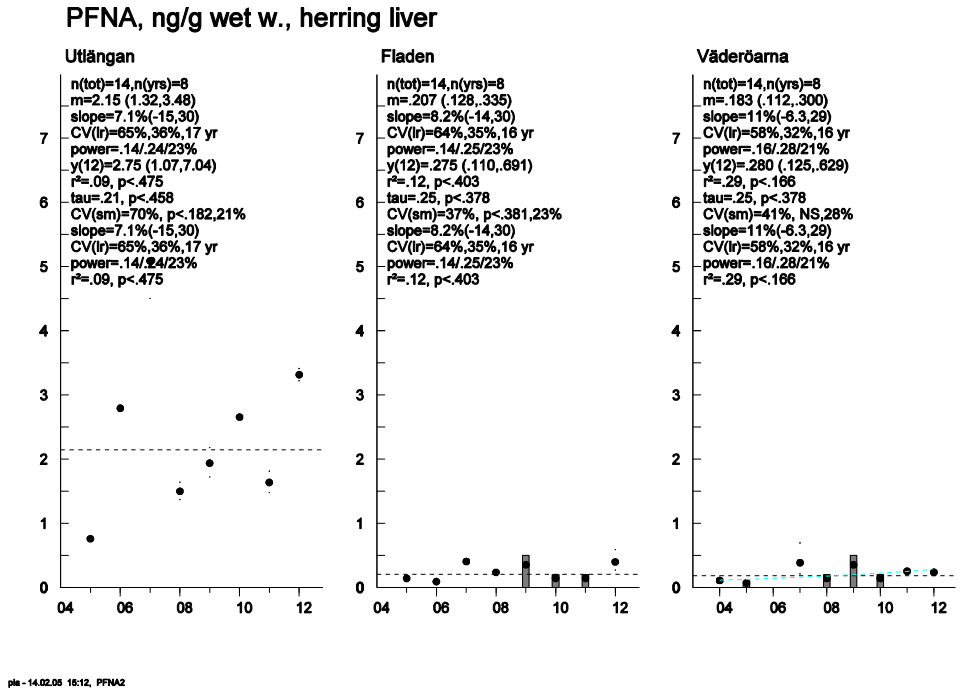


Fig. 29.12. Temporal trend of PFNA in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

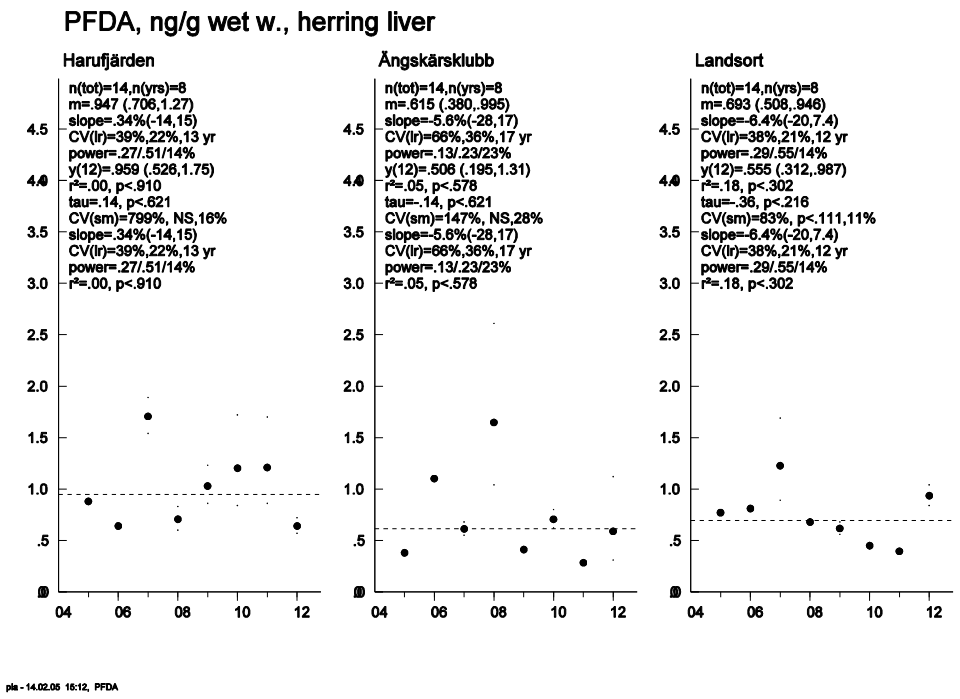


Figure 29.13. Temporal trend of PFDA concentrations in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

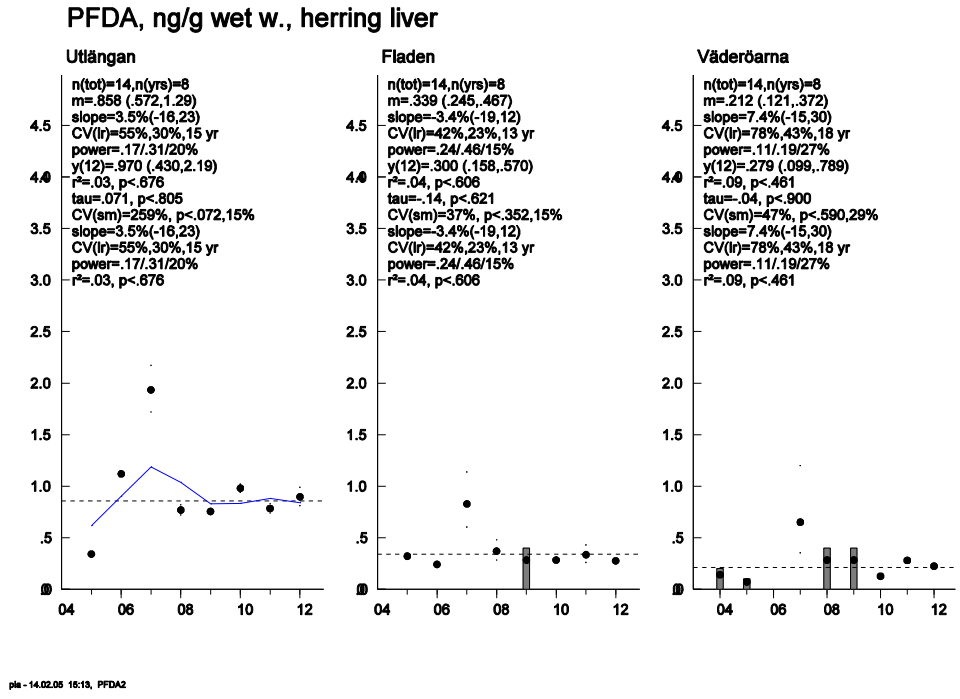


Figure 29.14. Temporal trend of PFDA concentrations in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

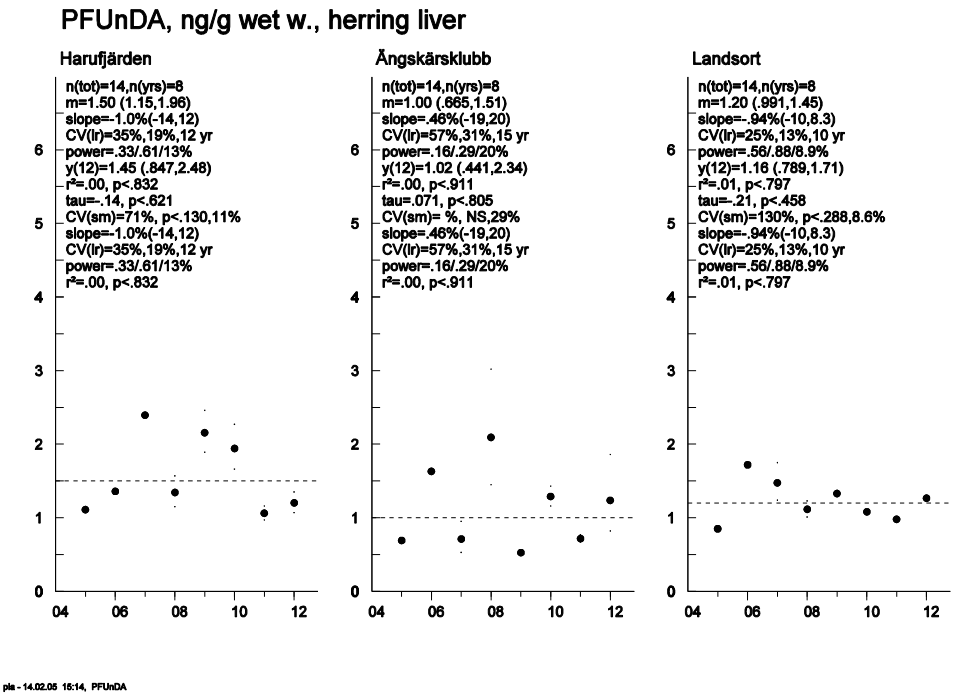


Fig. 29.15. Temporal trend of PFUnDA concentrations in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

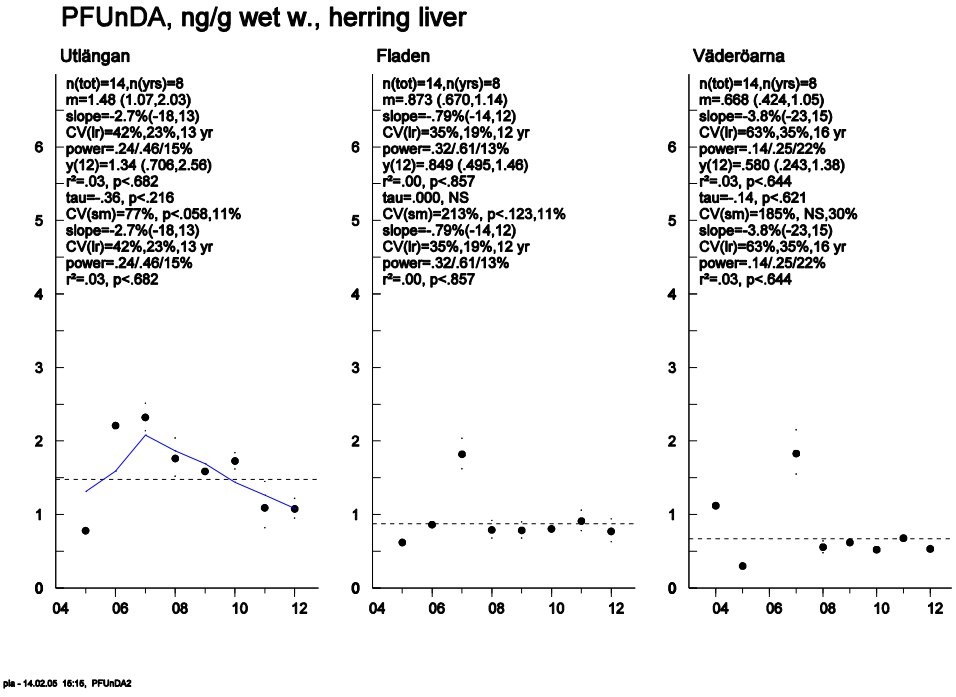


Fig. 29.16. Temporal trend of PFUnDA concentrations in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005).

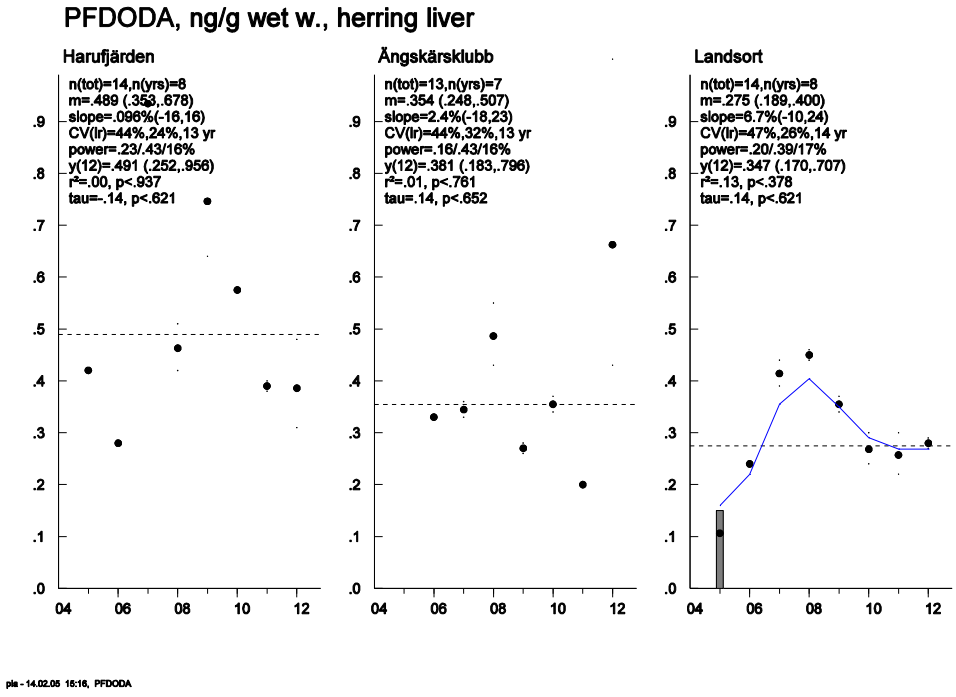


Fig. 29.17. Temporal trend of PFDoDA concentrations in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bar represent years where all values are below LOQ.

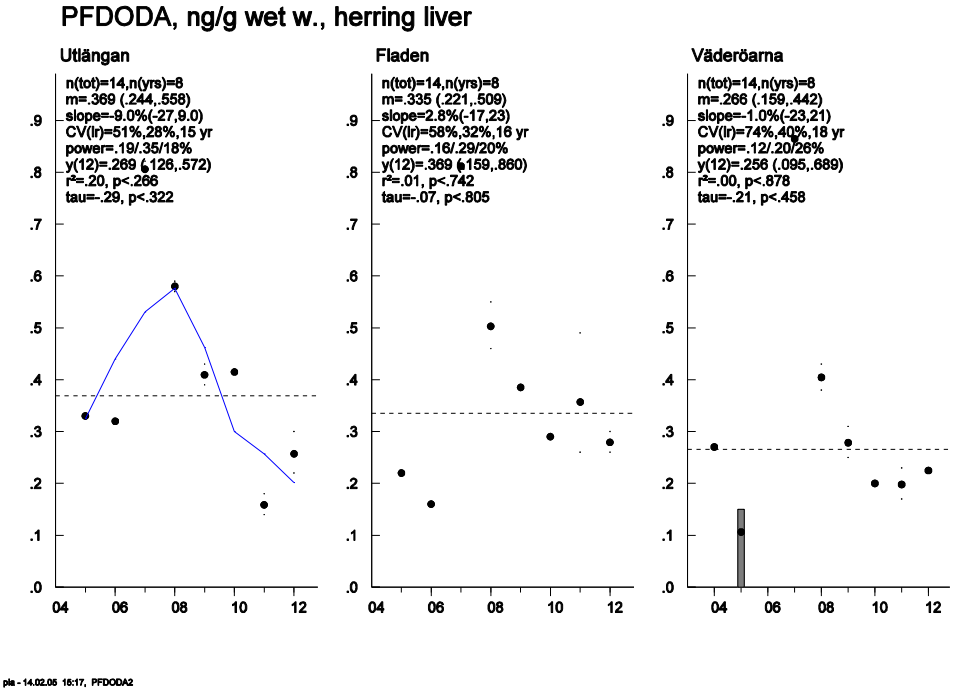


Fig. 29.18. Temporal trend of PFDoDA concentrations in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bar represent years where all values are below LOQ.

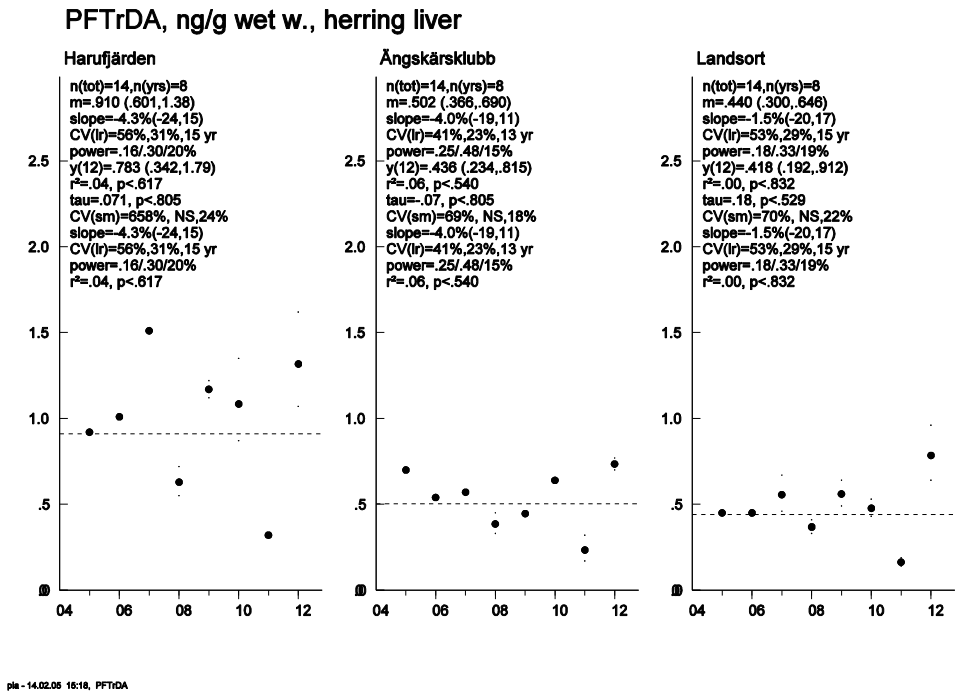


Figure 29.19. Temporal trend of PFTrDA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

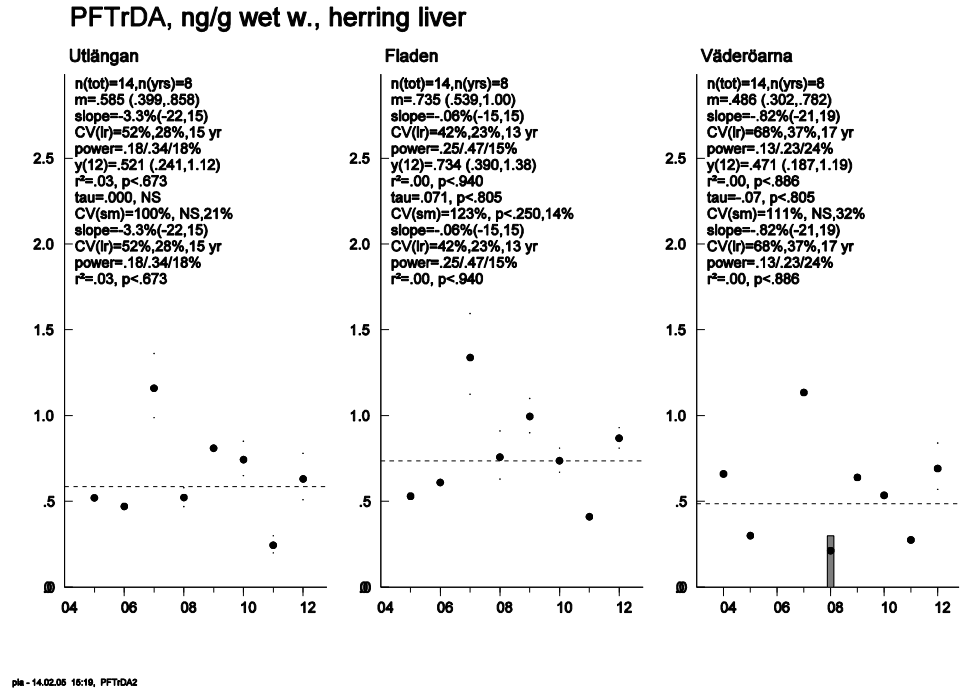


Figure 29.20. Temporal trend of PFTrDA in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The bars represent years where all values were below LOQ.

Over the whole time period, from 1968, a significant increasing trend of approximately 7% per year was observed for PFOS in guillemot eggs (Fig. 29.21, table 29.1), which is equivalent to 25 - 30 times higher concentrations in the early 2000s compared to the late 1960s**.** However, during the last ten years a significant decreasing trend is observed for the concentration of PFOS. PFTrDA, PFUnDA, PFNA, PFDA and PFDoDA (Fig. 29.21-22) all show significant increasing trends over the whole monitoring period of between 9-12 % per year. During the ten most recent years, no trend is seen for PFTrDA and PFUnDA, an increase is indicated for PFDA and PFDoDA and a significant increase is seen for PFNA.

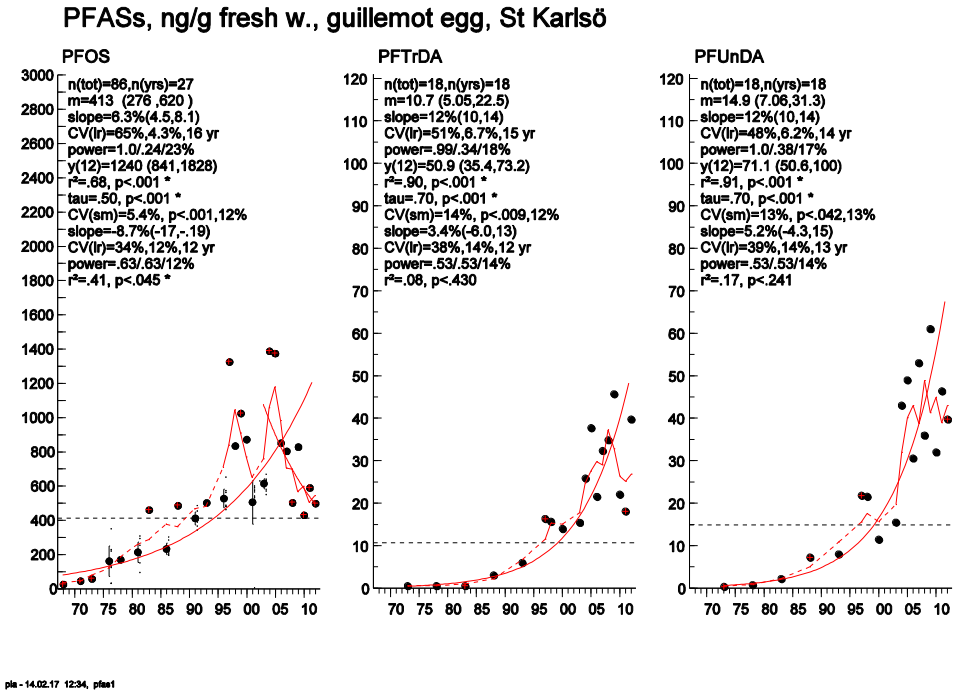


Figure 29.21 Temporal trend of PFOS, PFTrDA and PFUnDA concentrations in guillemot eggs (ng/g wet weight) (time series starting in 1968 and 1973).

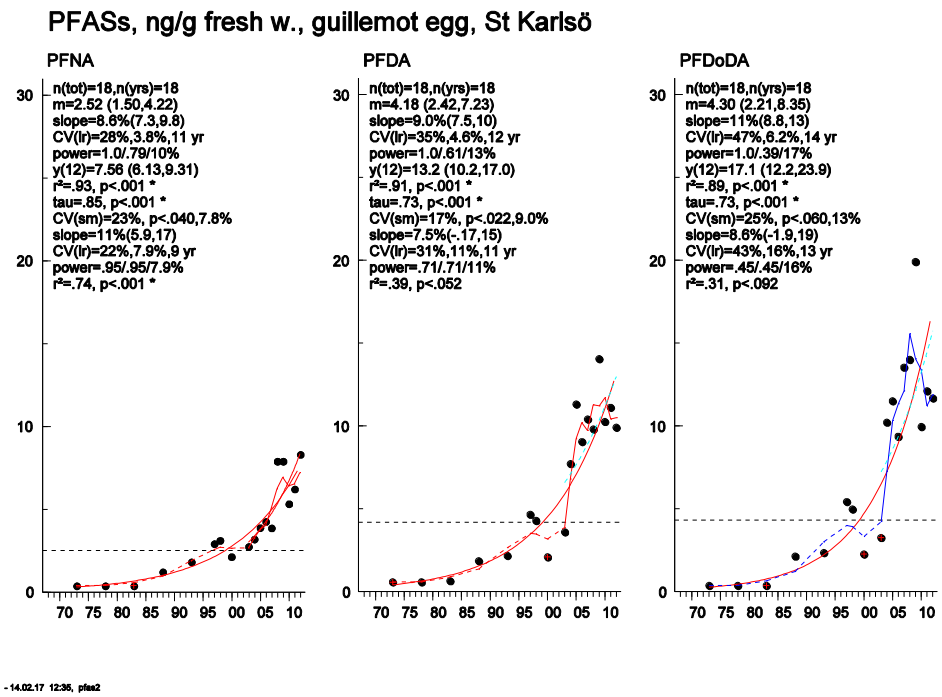


Figure 29.22 Figure 29.21 Temporal trend of PFNA, PFDA and PFDoDA concentrations in guillemot eggs (ng/g wet weight) (time series starting in1973).

29.3.3 Comparison to threshold

In herring from all sites, except Utlängan, PFOS concentration is below, but close to, the suggested target level of 9.1 ng/g wet weight based on EQS for human health. The analyses are done in liver so the results have to be interpreted carefully. ConclusionPFOS concentrations in herring at Utlängan were above the target level of 9.1 ng/g wet weight based on food uptake by humans via fish products. Also, the concentration of PFOS at Landsort was very close to the target level.

29.4 Conclusion

PFHxS and PFOS show a similar spatial pattern, except that PFOS also showed elevated levels in the northern Bothnian Bay, while PFHxS did not, and PFOS concentrations were approximately 25 times higher than PFHxS levels. This was expected, since PFHxS production volumes were much lower than for PFOS, and the PFHxS found in the environment probably originates to a large extent from PFHxS as by-product of technical PFOS.Furthermore, the distribution of PFOS is quite homogenous along the Swedish east coast (with the exception of Lagnö), which is a result of the extraordinary persistency of the compound and the long history of use (5-6 decades). Elevated levels may be expected at sites with a higher population density and associated current emissions from consumer products still leaking PFOS or its precursors. FOSA, however, is not persistent, but a precursor compound to PFOS. The relatively high concentrations at the Swedish west coast in the beginning of our time series reflected a current source probably located around the North Sea. However, levels of FOSA generally seem to have gone down recently. But,

FOSA concentration is still much higher on the Swedish west coast compared to the Baltic.The relatively short environmental half-life of FOSA did not allow it to diffuse into the Baltic, due to the low water exchange between the two seas. Degradation of FOSA to PFOS might also contribute to higher PFOS concentrations. Taking into account that liver generally contains about five times higher concentrations than fish muscle, PFOS levels in herring liver are comparable with levels found in other fish species from the Baltic (Swedish Environmental Protection Agency 2007). PFOS concentrations in guillemot eggs from 2005, however, are about 200 times higher than in herring liver (herring and sprat being the main prey of guillemot), showing the high retention of this compound in guillemot and the transport potential to the forming egg (Holmström and Berger 2008). PFCAs in the environment can have two sources - direct sources from manufacturing and use of PFCAs, and indirect sources from degradation of semi-volatile precursor compounds (Prevedouros et al. 2006). PFOA and PFNA are intentionally produced and therefore a large portion of these compounds found in the environment probably originates from direct sources (mainly the production process of fluoropolymers), and waterborne transport to remote locations (Prevedouros et al. 2006). This may partly explain the spatial variations of PFNA in this study, as sewage treatment plant effluent from industry or larger cities could represent hot-spots. In contrast, PFUnDA and PFTrDA are unintentionally produced substances, and their presence in the environment is probably due to both direct sources (impurities in PFOA and PFNA productions) and indirect sources (atmospheric transport and degradation of precursors). The fact that the odd-chain PFUnDA and PFTrDA are more highly concentrated than PFDA and PFDoDA, and the homogenous spatial distribution of these compounds, supports the theory that indirect sources are important for these long-chain PFCAs. Also, levels and compound patterns of PFCAs are in good agreement with concentrations in other Baltic fish (Swedish Environmental Protection Agency 2007).

A consistently increasing trend in PFOS in guillemot eggs has been observed throughout the whole examined time period, however, during the most recent ten years indications of a decreasing trend is seen. Due to relatively high inter-annual variations in recent years, the future temporal trend for PFOS concentrations in the Baltic marine environment cannot be predicted. Further monitoring will reveal if the phase out by 3M will make a difference for the PFOS concentrations in biota.

Table 29.1. Trend (in %) for several **sulfonates and its precursors** (ng/g wet weight) assessed from the annual geometric mean in various matrices. The total number of samples and the number of years for the various time-series are shown in columns three to five. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Compound	Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
	Guillemot egg								
PFOS	Stora Karlsö	86	27	68-12	6.3(4.5,8.1)	.0000 +++	16	22.8	1240 (841,1828)
PFOS	Stora Karlsö		10	03-12	-8.7(-17,-.19)	0.0447	12	12.3	
	Herring muscle								
PFOS	Harufjärden	14	8	05-12	-1.4(-13,11)	0.7719	11	11.7	10.3 (8.02,13.1) m
PFOS	Ängskärsklubb	14	8	05-12	5.5(-11,22)	0.4548	14	16.7	8.58 (5.98,12.3) m
PFOS	Landsort	14	8	05-12	4.0(-8.2,16)	0.46	12	12	11.4 (8.72,14.8) m
PFOS	Utlängan	14	8	05-12	5.3(-5.3,16)	0.2691	11	10.3	12.0 (9.42,15.3) m
PFOS	Fladen	14	8	05-12	-4.6(-11,1.3)	0.1028	8	5.63	6.42 (5.51,7.50) m
PFOS	Väderöarna	14	8	04-12	-1.8(-22,18)	0.8149	17	23.7	3.74 (2.32,6.01) m
PFHxS	Harufjärden	14	8	05-12	1.0(-16,18)	0.855	14	16.5	.137 (.097,.192) m
PFHxS	Ängskärsklubb	14	8	05-12	-6.3(-36,24)	0.6282	20	32.1	.170 (.090,.320) m
PFHxS	Landsort	14	8	05-12	6.9(-12,26)	0.4217	15	19.5	.338 (.222,.515) m
PFHxS	Utlängan	14	8	05-12	9.0(-12,30)	0.3443	16	21.7	.342 (.213,.548) m
PFHxS	Fladen	14	8	05-12	4.4(-5.6,14)	0.3221	10	9.6	.213 (.170,.266) m
PFHxS	Väderöarna	14	8	04-12	5.7(-8.8,20)	0.3727	14	16.6	.128 (.088,.184) m
FOSA	Harufjärden	14	8	05-12	-10(-26,5.3)	0.1537	13	15.6	.854 (.580,1.26) m
FOSA	Ängskärsklubb	14	8	05-12	-20(-37,-2.4)	0.0311	14	17.2	.780 (.380,1.60)
FOSA	Landsort	14	8	05-12	-13(-26,.007)	0.0491	12	12.6	.757 (.442,1.30)
FOSA	Utlängan	14	8	05-12	-7.4(-20,5.2)	0.1988	12	12.4	1.67 (1.24,2.26) m
FOSA	Fladen	14	8	05-12	-21(-35,-5.7)	0.0147	13	14.6	2.64 (1.42,4.91)
FOSA	Väderöarna	14	8	04-12	-4.4(-33,24)	0.7124	21	35.1	5.24 (2.67,10.3) m

Table 29.2. Trend (in %) for several **carboxylates** (ng/g wet weight) assessed from the annual geometric mean in various matrices. The total number of samples and the number of years for the various time-series are shown in columns three to five. Numbers in brackets are 95% confidence intervals (CI). P shows the p-value and – after the p-value means that the trend is negative and + means that the trend is positive; -/+ $p<0.05$, --/++ $p<0.01$, ---/+++ $p<0.001$. YRQ: years required to detect an annual change of 10% with a power of 80%. LDT: lowest detectable trend within a 10 year period with a power of 80%. Last year's concentration values are estimated from the trend (%) if $p<0.05$, or from the mean (m) if no trend is present.

Compound	Matrix	Ntot	Yrs	Year	Trend% 95% c.i.	P	YRQ	LDT	Last year
	Herring muscle								
PFOA	Harufjärden	11	6	06-12	-13(-35,8.9)	0.1738	13	15.4	.333 (.202,.549) m
PFOA	Ängskärsklubb	13	7	06-12	-13(-55,28)	0.4416	21	34.3	.651 (.303,1.40) m
PFOA	Landsort	14	8	05-12	13(-15,42)	0.2979	19	30.2	.894 (.469,1.71) m
PFOA	Utlängan	14	8	05-12	23(-.65,46)	0.0538	17	24.1	2.77 (1.04,7.35)

PFOA	Fladen	14	8	05-12	2.3(-14,18)	0.7316	14	16.1	.448 (.321,.626) m
PFOA	Väderöarna	14	8	04-12	.86(-14,16)	0.8613	14	16.9	.395 (.279,.559) m
PFNA	Harufjärden	14	8	05-12	2.4(-11,15)	0.6701	12	12.8	1.32 (1.01,1.74) m
PFNA	Ängskärsklubb	14	8	05-12	7.6(-23,38)	0.5642	20	32.2	1.23 (.647,2.32) m
PFNA	Landsort	14	8	05-12	-3.1(-20,14)	0.6751	14	17.1	1.32 (.921,1.88) m
PFNA	Utlängan	14	8	05-12	7.1(-15,30)	0.4747	17	23	2.15 (1.32,3.48) m
PFNA	Fladen	14	8	05-12	8.2(-14,30)	0.4026	16	22.5	.207 (.128,.335) m
PFNA	Väderöarna	14	8	04-12	11(-6.3,29)	0.1658	16	20.6	.183 (.112,.300) m
PFDA	Harufjärden	14	8	05-12	.34(-14,15)	0.9102	13	14.2	.947 (.706,1.27) m
PFDA	Ängskärsklubb	14	8	05-12	-5.6(-28,17)	0.5775	17	23.4	.615 (.380,.995) m
PFDA	Landsort	14	8	05-12	-6.4(-20,7.4)	0.3023	12	13.6	.693 (.508,.946) m
PFDA	Utlängan	14	8	05-12	3.5(-16,23)	0.6759	15	19.7	.858 (.572,1.29) m
PFDA	Fladen	14	8	05-12	-3.4(-19,12)	0.606	13	15.2	.339 (.245,.467) m
PFDA	Väderöarna	14	8	04-12	7.4(-15,30)	0.4613	18	27.2	.212 (.121,.372) m
PFUnDA	Harufjärden	14	8	05-12	-1.0(-14,12)	0.8323	12	12.6	1.50 (1.15,1.96) m
PFUnDA	Ängskärsklubb	14	8	05-12	.46(-19,20)	0.9113	15	20.2	1.00 (.665,1.51) m
PFUnDA	Landsort	14	8	05-12	-.94(-10,8.3)	0.797	10	8.88	1.20 (.991,1.45) m
PFUnDA	Utlängan	14	8	05-12	-2.7(-18,13)	0.6824	13	15.3	1.48 (1.07,2.03) m
PFUnDA	Fladen	14	8	05-12	-.79(-14,12)	0.8567	12	12.6	.873 (.670,1.14) m
PFUnDA	Väderöarna	14	8	04-12	-3.8(-23,15)	0.6445	16	22.3	.668 (.424,1.05) m
PFTrDA	Harufjärden	14	8	05-12	-4.3(-24,15)	0.6172	15	20	.910 (.601,1.38) m
PFTrDA	Ängskärsklubb	14	8	05-12	-4.0(-19,11)	0.5402	13	14.8	.502 (.366,.690) m
PFTrDA	Landsort	14	8	05-12	-1.5(-20,17)	0.8323	15	18.8	.440 (.300,.646) m
PFTrDA	Utlängan	14	8	05-12	-3.3(-22,15)	0.6731	15	18.5	.585 (.399,.858) m
PFTrDA	Fladen	14	8	05-12	-.06(-15,15)	0.9398	13	15	.735 (.539,1.00) m
PFTrDA	Väderöarna	14	8	04-12	-.82(-21,19)	0.8865	17	23.9	.486 (.302,.782) m
PFDoDA	Harufjärden	14	8	05-12	.096(-16,16)	0.9366	13	17.2	.489 (.353,.678) m
PFDoDA	Ängskärsklubb	13	7	06-12	2.4(-18,23)	0.7611	13	17.1	.354 (.248,.507) m
PFDoDA	Landsort	14	8	05-12	6.7(-10,24)	0.3785	14	18.5	.275 (.189,.400) m
PFDoDA	Utlängan	14	8	05-12	-9.0(-27,9.0)	0.2659	15	19.9	.369 (.244,.558) m
PFDoDA	Fladen	14	8	05-12	2.8(-17,23)	0.7424	16	22.7	.335 (.221,.509) m
PFDoDA	Väderöarna	14	8	04-12	-1.0(-23,21)	0.8776	18	29.4	.266 (.159,.442) m
	Guillemot egg								
PFTRDA	Stora Karlsö	18	18	73-12	12(10,14)	.0000 +++	15	18.3	50.9 (35.4,73.2)
PFTRDA	Stora Karlsö		10	03-12	3.4(-6.0,13)	0.4304	12	13.8	
PFUNDA	Stora Karlsö	18	18	73-12	12(10,14)	.0000 +++	14	17.1	71.1 (50.6,100)
PFUNDA	Stora Karlsö		10	03-12	5.2(-4.3,15)	0.241	13	13.9	
PFNA	Stora Karlsö	18	18	73-12	8.6(7.3,9.8)	.0000 +++	11	10.2	7.56 (6.13,9.31)
PFNA	Stora Karlsö		10	03-12	11(5.9,17)	.0015 ++	9	7.86	
PFDA	Stora Karlsö	18	18	73-12	9.0(7.5,10)	.0000 +++	12	12.5	13.2 (10.2,17.0)
PFDA	Stora Karlsö		10	03-12	7.5(-.17,15)	0.0524	11	11.2	
PFDODA	Stora Karlsö	18	18	73-12	11(8.8,13)	.0000 +++	14	16.9	17.1 (12.2,23.9)
PFDODA	Stora Karlsö		10	03-12	8.6(-1.9,19)	0.0919	13	15.5	

30 OTCs – Organotin Compounds

Updated 14.02.28

30.1 Introduction

The two most common OTC's are Tributyltin (TBT) and Triphenyltin (TPhT). They are organometallic chemicals with the presence of one or more carbon-tin bonds (C-Sn) (Murata et al., 2008). In water TBT decomposes into less toxic DBT (Dibutyltin) and MBT (Monobutyltin) species, however, in sediment this decomposition takes place far more slowly, which creates an ecotoxicological risk long after it has been released. Recently, DBT and MBT have been found to leach into the environment from PVC (Tesfalidet, 2004).

30.1.1 Uses, Production and Sources

The main usage of both TBT and TPhT was as antifouling agents in paints for preventing the attachment of barnacles and slime on boats. The paint was primarily used on ship hulls, docks, buoys, and fishnets, and from where it could slowly leach into the waters. TBT and TPhT has also been used as wood preservative in industry and agriculture and as a stabilizer in PVC plastics manufacturing (Encinar et al., 2001; Naturvårdsverket, 2008; Sternberg et al., 2010).

30.1.2 Toxic Effects

TBT belongs to one of the most toxic substances that is released into the environment, and it is said to be almost as toxic as dioxins and furans (Cato et al., 2007). It is toxic already at very low doses. TBT bioaccumulates in gastropods and the highest concentrations have been measured in the digestive/reproductive complex where levels up to 100 000 higher than what has been measured in the aquatic environment have been found (Sternberg et al., 2010). TBT is an endocrine disruptor and it has been found to induce imposex (females with male sexual characteristics) in gastropods (Smith, 1981). Imposex gastropods are globally distributed and at least 195 species of prosobranch gastropods are known to be affected (reviewed in Sternberg et al., 2010). Imposex appears to be irreversible and thus this can have long-term impacts on the organism fitness.

30.1.3 Conventions, Aims and Restrictions

Since 1989 the usage of TBT on small boats (less than 25 m) has been banned in Sweden and since 1993 all usage of TBT has been prohibited. In EU a ban on small boats came in 1999. In 1998 the Marine Environmental Protection Committee (MEPC) of the

International Maritime Organization (IMO) voted to impose a worldwide prohibition on the application and presence of TBT and other organotin compounds within 5 years (2003, painting with TBT-based paint on boats) and 10 years (2008, total ban on the presence of TBT and other OTC's). The total international ban on TBT and other OTC's entered into force in September 2008.

30.1.4 Target Levels

No national target level for biota is agreed upon for OTCs.

30.2 Methods

30.2.1 Analytical Information

The OTC's analysed are: Monobutyltin (MBT), Dibutyltin (DBT), Tributyltin (TBT), Monophenyltin (MPhT), Diphenyltin (DPhT), Triphenyltin (TPhT), Monooctyltin (MOT) and Dioctyltin (DOT). OTC's have only been analysed for a few years within the national Swedish monitoring programme (2009 and onwards) and only in perch from three sampling sites. See chapter 6 for further details.

30.3 Results

The concentrations of MBT, DBT, MPhT, TPhT, MOT and DOT are below LOQ for almost all of the samples and are therefore not presented in the spatial maps.

30.3.1 Spatial Variation

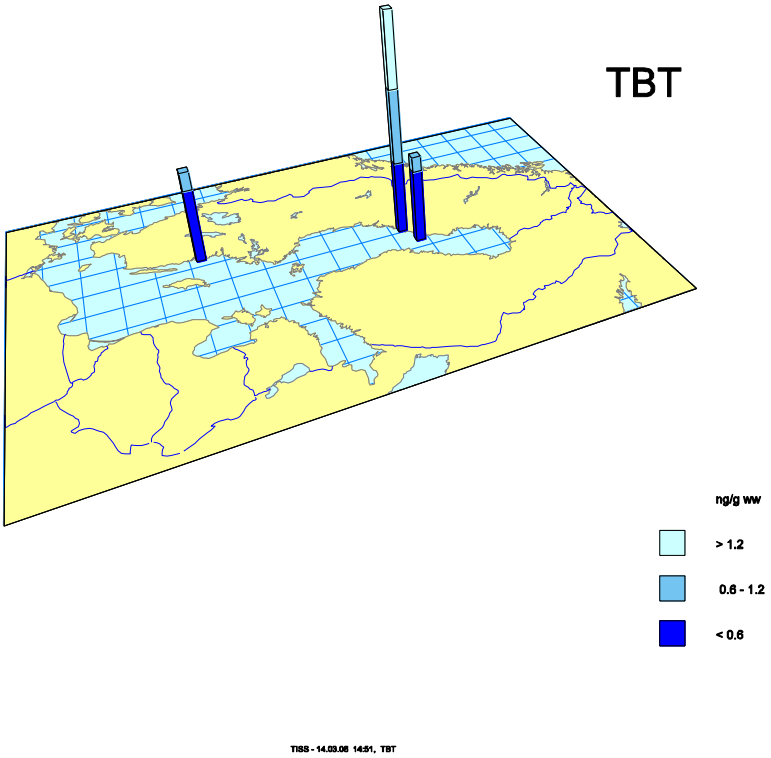


Figure 30.1. Spatial variation in TBT concentrations (ng/g wet weight) in perch liver.

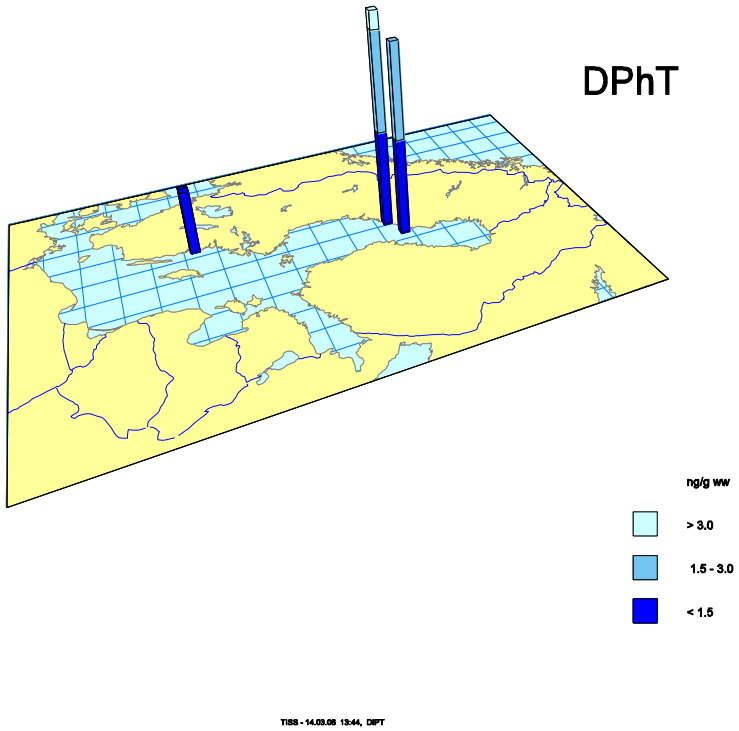


Figure 30.2. Spatial variation in DPhT concentrations (ng/g wet weight) in perch liver.

Highest concentrations of both tributyltin (TBT) and diphenyltin (DPhT) were found in samples from Örefjärden with concentrations of 1.8 ng TBT/g wet weight and 3.3 ng DPhT/g wet weight. Concentrations of TBT were at similar levels in perch from Holmöarna in the northern part of Bothnian Sea and from Kvädöfjärden in Baltic proper. Concentrations of DPhT were higher at both stations in the northern part of the Bothnian Sea compared to Kvädöfjärden.

30.4 Conclusion

The majority of the analysed organotin compounds showed concentrations below LOQ (with LOQ varying between 0.5 and 1 ng/g wet weight for the analysed compounds). However TBT and DPhT showed concentrations above LOQ at all stations with highest reported concentrations in fish from Örefjärden in the northern part of Bothnian Sea.

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