**Comments Concerning the National Swedish Contaminant Monitoring Programme in Marine Biota, 2015**

Övervakning av metaller och organiska miljögifter i marin biota, 2015

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**Chemical analysis:**

**Organochlorines and perflourinated substances**
**Department of Environmental Science and Analytical Chemistry, Stockholm University**

**Trace metals**
**Department of Environmental Science and Analytical Chemistry, Stockholm University**

**PCDD/PCDF**
**Department of Chemistry, Umeå University**

**PAHs and Organotin compounds**
**IVL Swedish Environmental Research Institute**

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**Period in which underlying data were collected**
1968–2013

**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 concentrations 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 concentration 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 seen.

# Contents

# 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 the Swedish University of Agricultural Sciences, Department of Aquatic Resources (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 / Sammanfattning 2015

## 2.1 Summary in English

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 have 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 Fladen, perch muscle at Kvädöfjärden, and for herring at Ängskärsklubb in spring. Also, an increase in fat content was seen during the most recent ten years for herring at Ängskärsklubb in spring. There were also some sites where no log linear trends were seen.

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

Generally, higher mercury concentrations are found in the Bothnian Bay, but also from one station in the Northern parts of Baltic Proper, 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 concentrations 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. In most cases, the mercury concentrations are above the EQSbiota 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. The highest concentrations are seen in the southern part of the Baltic Sea. Elevated lead concentrations between 2003 and 2007 (e.g. Harufjärden) should be viewed with caution (see above regarding change in analysis methods). Lead concentrations are below the suggested target level at all stations.

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. Cadmium concentrations in herring and perch are all below the suggested target level of 160 µg/kg wet weight.

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 concentrations, 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 concentrations were 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 in TCDD-equivalents from the start in the late 1960s until about 1985 from where no change occurred for many years, however, during the most recent ten years a decrease in the concentration is seen. Concentrations of DDE and CB-118 are for some species and sites still above their respective target levels.

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 the Baltic Proper, while the investigated PBDEs show higher concentrations in the Bothnian Bay. 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 shows a decrease during the most recent ten years. For fish and blue mussels, BDE-47, -99, and -153 decreased at some sites and showed no trend at other sites. The concentration of HBCDD in fish and blue mussels showed inconsistent trends. The concentration of HBCDD is below the EQSbiota of 167 µg/kg wet weight for all fish species from all areas, while the concentration of BDE-47 alone is above the EQSbiota for sumPBDE of 0.0085 ng/g wet weight.

*PAHs*
Only blue mussels have been examined for spatial differences in PAH concentrations. Concentration of ∑PAH 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 ∑PAH, chrysene, fluoranthene and pyrene at Fjällbacka; for naphthalene at Kvädöfjärden; and for pyrene at Fladen.

All time series where concentrations of various PAHs were compared with the target value based on OSPAR Ecological Assessment Criteria, or EC Environmental Quality Standards were below the target value.

*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 overall increasing concentration 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. The longer herring time series from Harufjärden, Landsort, and Utlängan show increasing concentrations for PFOS and most carboxylates. For FOSA, on the other hand, decreasing concentrations are seen during the most recent ten years.

*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.

## 2.2    Sammanfattning på svenska

De miljögifter som undersökts i denna rapport kan delas in i fem miljögiftsgrupper - tungmetaller, klorerade föreningar, bromerade flamskyddsmedel, polyaromatiska kolväten och perfluorerade föreningar. Var och en av dessa föroreningar har undersökts från olika lokaler i upp till sex olika fiskarter, samt i blåmussla och sillgrisseägg. Undersökningarna har pågått under varierande antal år. Följande sammanfattning undersöker övergripande trender, geografiska och tidsmässiga, för de fem grupperna.

*Kondition och fetthalt*
Kondition och fetthalten i de olika arterna tenderade att följa samma mönster i samma lokaler, med några få undantag. De flesta fiskarter visade generellt en minskande trend i både kondition och fetthalt i de flesta undersökta lokalerna med undantag för en ökning i kondition i torsklever från Fladen, abborrmuskel från Kvädöfjärden och sill från Ängskärsklubb (vår). Dessutom ses en ökning av fetthalt de senaste tio åren för sill från Ängskärsklubb (vår). Det fanns också några platser där inga log-linjära trender observerades.

*Tungmetaller*
På grund av en förändring i metoderna för metallanalys (inte kvicksilver) år 2004 bör värden mellan 2003 och 2007 tolkas med försiktighet. Från och med 2009 analyseras metaller vid ACES, Stockholms universitet.

Generellt ses högre halter kvicksilver i Bottenviken, men också från en station i de norra delarna av Östersjön, jämfört med andra delar av den svenska kusten. Tidsserien visar varierande koncentrationer under studieperioden. De längre tidsserierna som finns för sillgrisseägg och vårfångad strömming från södra Bottenhavet och södra Östersjön visar signifikanta minskningar av kvicksilver. Å andra sidan, ökande koncentrationer ses i bl.a. torskmuskel, men halterna är relativt låga om man jämför med uppmätta halter i abborre

från insjöar och kustnära platser. I de flesta fall ligger kvicksilverkoncentrationerna över EQSbiota på 20 ng /g våtvikt.

Blyhalterna minskar generellt över tid (i tidsserier av tillräcklig längd), förmodligen på grund av avskaffandet av bly i bensin. De högsta halterna ses i södra delen av Östersjön. Förhöjda blyhalter mellan 2003 och 2007 (t.ex. Harufjärden) bör tolkas med försiktighet (se ovan om förändring i analysmetoder). Blyhalterna ligger under det föreslagna gränsvärdet vid alla lokaler.

Kadmiumhalterna visar varierande icke-linjära trender under övervakningsperioden. Det är värt att notera att trots att flera åtgärder har vidtagits för att minska utsläppen av kadmium, så är generellt de senaste årens koncentrationer i samma storleksordning som koncentrationerna som uppmättes för 30 år. Kadmiumhalterna i strömming och abborre ligger alla under det föreslagna gränsvärdet på 160 µg/kg våtvikt.

De rapporterade nickelkoncentrationerna visar inga konsekventa minskande trender. Vissa serier börjar med två förhöjda värden som utövar en stark hävstångseffekt på regressionslinjen och kan ge ett felaktigt intryck av minskande trender. Krom visar generellt minskande koncentrationer, detta kan möjligen förklaras av en förändring i analysmetoden. Koppar och zink visar inga konsekventa trender under övervakningsperioden. Det är generellt högre koncentrationer av arsenik och silver längs västkusten jämfört med andra delar av den svenska kusten, men för silver har några stationer i Bottenhavet och Bottenviken jämförbara koncentrationer med västkuststationerna.

### *Klorerade föreningar*
Generellt ses minskande koncentrationer för alla föreningar (DDTer, PCBer, HCHer och HCB) i alla undersökta arter, med några få undantag, till exempel ses ingen förändring i TCDD-ekvivalenter i strömmingsmuskel (utom vid Ängskärsklubb där mycket höga koncentrationer i början av provtagningsperioden sågs och även på västkuststationen Fladen). De längre tidsserierna i sillgrissla visar också en markant minskning av TCDD-ekvivalenter från slutet av 1960-talet fram till omkring 1985 och därefter sker ingen förändring under många år, men under de senaste tio åren ses en minskning av koncentrationen. Halterna av DDE och CB-118 är för vissa arter och lokaler fortfarande över, respektive gränsvärde.

De klorerade föreningarna visar generellt högre koncentrationer i Bottenhavet och / eller Östersjön jämfört med Bottenviken och den svenska västkusten.

### *Bromerade flamskyddsmedel*
Förhöjda nivåer av HBCDD ses på lokaler från Egentliga Östersjön, medan de undersökta PBDE'erna visar högre koncentrationer i Bottenviken. Dessutom ses lägre koncentrationer av alla undersökta PBDE'er och HBCDD på den svenska västkusten jämfört med ostkusten. Tidsmässigt har signifikanta ökningar av BDE-47, -99 och -100 setts i sillgrissleägg sedan slutet av 1960-talet fram till början av 1990-talet och därefter har koncentrationerna börjat minska. Även koncentrationen av HBCDD i sillgrissleägg minskar under de senaste tio åren. För fisk och blåmussla minskade BDE-47, -99 och -153 på vissa lokaler medan ingen trend ses på andra platser. Koncentrationen av HBCDD i fisk och blåmussla visar inga tydliga trender. Koncentrationen av HBCDD ligger under EQSbiota på 167 µg/kg våtvikt för alla fiskarter från alla lokaler medan koncentrationen av BDE-47 ligger över EQSbiota

på 0,0085 ng/g våtvikt som är satt för summan av PBDE.

*PAH*
Endast blåmussla har undersökts för koncentrationer av PAH'er. Koncentration av ΣPAH var högre vid Kvädöfjärden i Egentliga Östersjön jämfört med lokalerna vid västkusten, men enskilda PAH'er visade varierande spatiala mönster. Acenaftalen har med tiden sällan hittats över detektionsgränsen. Signifikanta minskande halter observerades för ΣPAH, krysen, fluoranten och pyren vid Fjällbacka; för naftalen vid Kvädöfjärden; och för pyren vid Fladen. Alla tidsserier där koncentrationerna av olika PAHer jämfördes med gränsvärden, antingen OSPAR EAC, eller EU Miljökvalitetsnormer låg under gränsvärdet.

*PFASs*
PFHxS och PFOS visar ett liknande spatialt mönster, men koncentrationen av PFOS var ungefär 25 gånger högre än PFHxS. Fördelningen av PFOS är ganska homogen längs den svenska kusten men med något högre koncentrationer i Egentliga Östersjön. Halten av PFOS i sillgrissleägg är cirka 100-200 gånger högre än i strömminglever. En övergripande ökande koncentration av PFOS i sillgrissleägg har observerats under hela tidsperioden, men under de senaste tio åren ses istället en minskning. De längre strömmingstidsserierna från Harufjärden, Landsort och Utlängan visar ökande koncentrationer av PFOS och de flesta karboxylsyror. För FOSA, å andra sidan, ses minskande koncentrationer under de senaste tio åren.

*Organiska tennföreningar*
Majoriteten av de analyserade tennorganiska föreningarna uppvisade koncentrationer under LOQ. Men TBT och DPhT visade koncentrationer över LOQ vid alla lokaler och den högsta rapporterade halten i fisk från Örefjärden i norra delen av Bottenhavet.

# 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 accessible from a database. These specimens are thus available for retrospective analyses or for control purposes.

## 3.3    Number of samples and sampling frequency

In general 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 (NMR, 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. 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 | 5389 | 49.0 |
| Cod | 1150 | 10.5 |
| Perch | 902 | 8.2 |
| Eelpout | 480 | 4.4 |
| Dab | 350 | 3.2 |
| Flounder | 340 | 3.1 |
| Guillemot | 634 | 5.8 |
| Common Tern | 4 | 0.0 |
| Eurasian Oystercatcher | 4 | 0.0 |
| Blue mussel | 1738 | 15.8 |
| Total | 10991 | 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: Rånefjärden, 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** <br> **(year)** | **body weight** <br> **(g)** | **Length** <br> **(cm)** | **liver weight** <br> **(g)** | **liver dry weight** <br> **(%)** |
|---|---|---|---|---|---|---|
| **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 organochlorines. 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., 1986). 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. Organo-chlorines 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, 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 polychlorinated compounds (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.
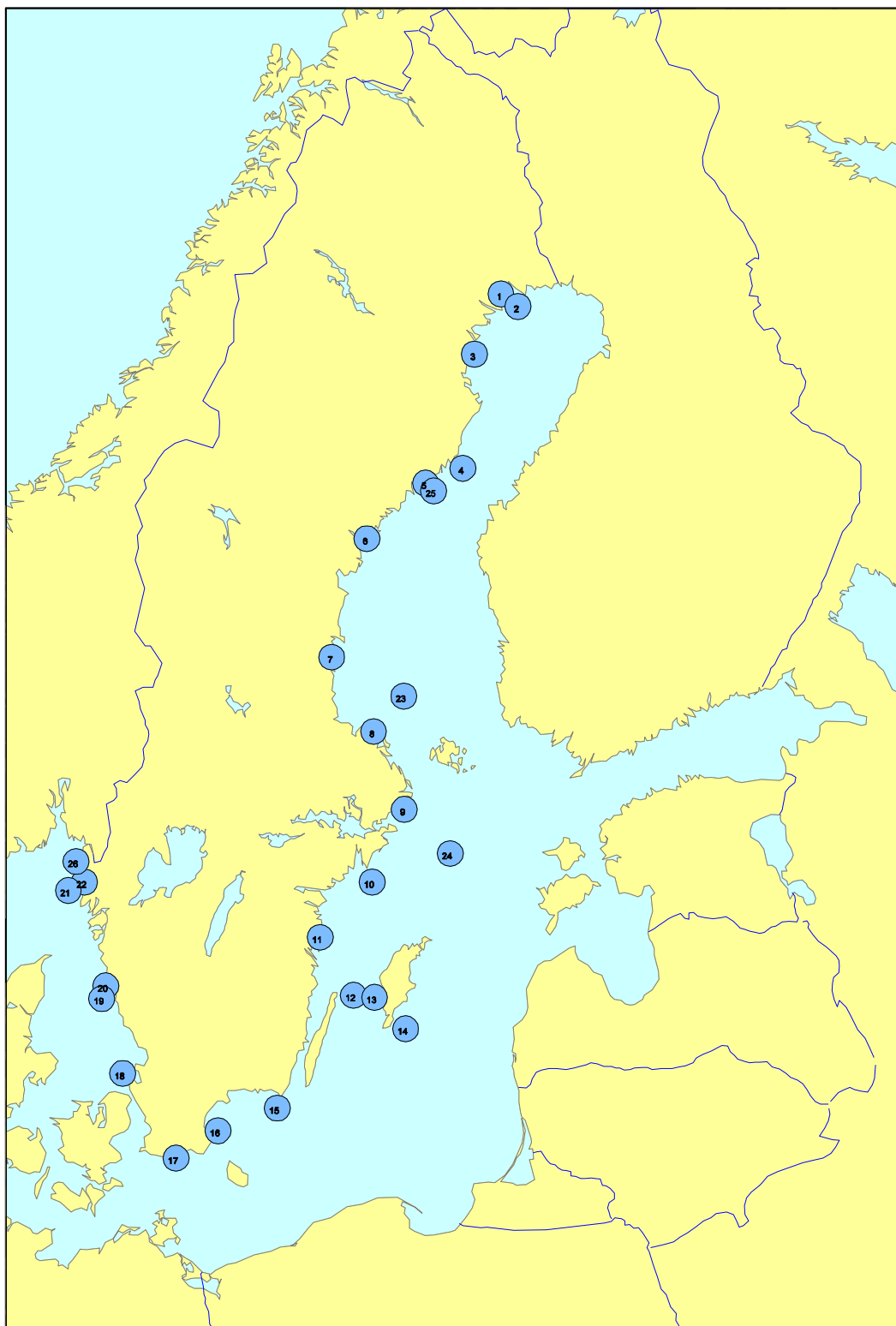
**Figure 5.1.** Sampling sites within the National Swedish Marine Monitoring Programme; 1) Rånefjärden, 2) Harufjärden, 3) Kinnbäcksfjärden, 4) Holmöarna, 5) Örefjärden, 6) Gaviksfjärden, 7) Långvindsfjärden, 8) Ängskärsklubb, 9) Lagnö, 10) Landsort, 11) Kvädöfjärden, 12) Byxelkrok, 13) St. Karlsö, 14) SE Gotland, 15) Utlängan, 16) V. Hanöbukten, 17) Abbekås, 18) Kullen, 19) Fladen, 20) Nidingen, 21) Väderöarna, 22) Fjällbacka, 23) Bothnian Sea offshore site, 24) Baltic Proper offshore site, 25) Bonden, 26) Tjärnö.

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## 5.1    Rånefjärden, 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 | 1989, -95 | 1991, -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 | 1984, -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

### 5.17.1 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

## 5.18 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.

## 5.19  Nidingen, Kattegat, Swedish west coast

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

## 5.20     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.

## 5.21  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.

## 5.22  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

## 5.23  Baltic Proper North, offshore site
Co-ordinates:  58° 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.

## 5.24  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.

## 5.25  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

Due to organizational reforms at Stockholm University the the Department of Applied Environmental Science (ITM) has been restructured and is since January 1$^{st}$ 2015 part of the Department of Environmental Science and Analytical Chemistry (ACES) at Stockholm University.

## 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 Environmental Science and Analytical Chemistry (ACES), 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. The laboratory participated in the periodic QUASIMEME intercalibration rounds.

Since 2007, Stockholm University 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.

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

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

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 Stockholm University. No comparison between the laboratories has been done for eelpout. No recalculation has been made for eelpout.

**Table 6.2**. Herring, cod and perch mean ratios of metal concentrations analysed by SLU versus Stockholm University (SU).

| mean fish ratios | n | Ratio SLU/SU |
|---|---|---|
| Mercury | 27 | 1.02 |
| Lead | 64 | 2.26 |
| Cadmium | 68 | 1.50 |
| Copper | 68 | 1.20 |
| Zinc | 68 | 1.21 |
| Nickel | 48 | 1.67 |
| Chromium | 41 | 1.71 |

## 6.2 Organochlorines and brominated flame retardants

The analyses of organochlorines and brominated flame retardants are carried out at the Department of Environmental Science and Analytical Chemistry (ACES) 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 and co-workers (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 CB-28, -52, -101, -118, -153, -138, -180, HCB, p,p'-DDE, p,p'-DDD, p,p'-DDT as well as 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 HBCDD 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 and Riego, 1990). Therefore CB-138 is reported as CB138+163. PBDE and HBCDD 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 HBCDD, 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 HBCDD 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 HBCDD 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 HBCDD follows a function where the relative standard deviations increase first at the very lowest concentration.

**Table 6.3**. Expanded uncertainty (%) at different concentrations

| | CB-28, -101, -118,-153, -138, -180, HCB | CB-52 | HCH α, β, γ | DDE & DDD | DDT | | PBDEs | HBCDD |
|---|---|---|---|---|---|---|---|---|
| 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, DDE and DDD and 4 ng/g fat weight for 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 and co-workers (Wiberg et al., 1998), the clean-up method by Danielsson and co-workers (Danielsson et al., 2005), and the instrumental analysis (GC-HRMS) by Liljelind and co-workers (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 2 h 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 Environmental Sciences and Analytical Chemistry (ACES), 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 et al., 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 D.R. and Hirsch R.M., 1992c, ICES, 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 '$\tau$', and the corresponding p-value. The Kendall's '$\tau$' 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 $\tau$-values of about 0.7 or above (Helsel D.R. and Hirsch R.M., 1992a). 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 J.C. 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 and co-workers (Nicholson et al., 1998).

### 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 and Fryer, 1992). 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(13)**= reports the concentration estimated from the smoother line for the last year together with a 95% confidence interval, e.g. y(13)=2.55(2.17,3.01) is the estimated concentration for the year 2013, where the residual variance around the smoother is used to calculate the confidence interval.

**tao=** reports Kendall's '$\tau$', 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', (Helsel D.R. and Hirsch R.M., 1992b). In these cases only the 'Theil'-slope and Kendall's '$\tau$' 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 Mercury 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 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mercury** | 1.0 | 1.0 | 1.0 | *1.0 | *1.0 | 1.0 | *1.0 | *1.0 | 1.0 | *1.0 | *1.0 | *1.0 | 0.97 | 1.0 | *0.99 | *1.0 | *1.0 | *1.0 | *1.0 |
| **Lead** | *1.0 | *1.0 | 0.76 | 1.0 | 1.0 | 0.99 | 1.0 | 1.0 | 0.97 | 0.99 | *1.0 | 1.0 | 0.11 | 0.97 | 1.0 | 0.96 | *1.0 | 1.0 | 0.74 |
| **Cadmium** | 1.0 | *1.0 | 0.96 | *1.0 | *1.0 | 1.0 | *1.0 | 1.0 | 1.0 | *1.0 | *1.0 | 1.0 | 0.57 | 0.95 | 1.0 | 1.0 | *1.0 | *1.0 | 0.34 |
| **Copper** | *1.0 | 1.0 | 1.0 | *1.0 | 1.0 | 1.0 | *1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 0.66 | *1.0 | 1.0 | *1.0 | 1.0 | 1.0 | *1.0 |
| **Zinc** | *1.0 | *1.0 | 1.0 | *1.0 | *1.0 | 1.0 | *1.0 | *1.0 | *1.0 | *1.0 | 1.0 | 1.0 | 0.96 | 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 | *0.21 | 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 | 0.36 | 0.99 | 1.0 | 1.0 | 1.0 | *1.0 | *1.0 |
| **α-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 | 0.32 | 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** | 0.97 | *1.0 | 0.19 | 1.0 | 1.0 | 0.45 | *1.0 | 0.99 | - | - | 1.0 | 0.91 | - | - | - | *0.88 | 0.96 | 1.0 | *1.0 |
| **HBCDD** | 0.84 | 1.0 | 0.24 | 1.0 | 0.90 | 0.55 | 0.94 | 0.83 | - | - | 1.0 | 0.25 | - | - | - | 0.31 | *0.42 | 0.49 | *1.0 |
| **PFOS** | *0.40 | 1.0 | - | 1.0 | 1.0 | - | 0.51 | 0.11 | - | - | - | - | - | - | - | - | - | - | *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. Since November 2014, hexabromocyclododecane (HBCDD) is also included in the Stockholm Convention. Six more substances have been nominated to be included on the list, and are currently under review by the Persistent Organic Pollutants Review Committee; decabromodiphenyl ether (commercial mixture, "c-decaBDE"), dicofol, short-chained chlorinated paraffins (SCCPs), chlorinated naphthalenes, hexachlorobutadiene and pentachlorophenol (SC, 2008).

## 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) (HELCOM).

## 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 (OSPAR).

## 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) (UNECE, 1979).

## 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 (OJEC No. L396 30.12.2006, 2006b).

### 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 (OJEC No. L 174 1.7.2011, 2011).

### 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 45 priority substances has been established (OJEC No. L226 24.8.2013, 2013). 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 (COM(2011) 876 31.1.2012, 2011, EC, 2011).

### 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" (OJEC No. L164 25.6.2008, 2008). The implementation for Swedish waters will be based on the regional international conventions of OSPAR and HELCOM.

## 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 (KEMI). 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.

# 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" (OJEC No. L164 25.6.2008, 2008). 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 No 1881/2006 (OJEC No. L364 20.12.2006, 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 (OJEC No. L226 24.8.2013, 2013). 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 Common Implementation Strategy for the Water Framework Directive (COM(2011) 876 31.1.2012, 2011, EC, 2011). Substance EQS Data Sheets (SDS) contains background information regarding the development of EQS, available at the CIRCABC webpage (CIRCABC). Here, data from ecotoxicological studies are compiled to Specific Quality Standards (QS), derived for water, sediment, biota (QSbiota), which is set to protect for secondary poisoning in predators, and human health (QShh). To date, EQSbiota 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 Commision, 2014). 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 chromium, copper, zinc, arsenic, silver, aluminium, tin and bismuth).

**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$_{biota, sec pois}$ |
| | Lead | 300 | 1500 ww | EC food regulation |
| | Mercury | 20 | | EQS |
| | Nickel | 12300* | | QS$_{biota, sec pois}$ |
| 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(ghi)perylene | | 110 | EAC |
| 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-118 | 24 lw | | EAC |
| | CB-138 | 316 lw | | EAC |
| | CB-153 | 1600 lw | | EAC |
| | CB-180 | 480 lw | | EAC |
| Other | ∑PBDEs (BDE-28, -47, -99, -100, -153, and -154) | 0.0085 | | EQS$_{biota}$ |
| | HBCDD | 167 | | EQS$_{biota}$ |
| | ∑PCDDs+PCDFs | 0.0035 | | EC food regulation |
| | ∑PCDDs+PCDFs+dl-PCBs | 0.0065 | | EQS$_{biota\,hh}$ /EC food regulation |
| | | 0.0012 | | QS$_{biota, sec pois}$ |
| | HCB | 10 | | EQS$_{biota}$ |
| | PFOS | 9.1 | | EQS$_{biota}$ |

*The target levels presented in the table for Cadmium and Nickel are based on QS$_{biota}$ secondary poisoning, however secondary poisoning  are not considered as the most sensitive protection objective for these substances and will thus not provide the highest protection level.

### 10.1 Metals

### 10.1.1 Cadmium

There is no $EQS_{biota}$ or EAC developed for cadmium. The $QS_{biota\ secondary\ poisoning}$ is set at 0.16 mg/kg prey tissue wet weight and evaluates whole fish concentrations in a freshwater system.  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 $EQS_{biota}$ or EAC developed for lead. The $QS_{biota}$ is set at 3600 µg/kg prey tissue wet weight and evaluates whole fish concentrations. The EC foodstuff regulation sets a maximum level for lead in muscle meat of fish at 300 µg/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: EC foodstuff regulation*

### 10.1.3 Mercury

The $EQS_{biota}$ for mercury is set at 20 µg/kg (methyl mercury) 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 $EQS_{biota}$ or EAC developed for nickel. The $QS_{biota\ secondary\ poisoning}$ is set at 12.3 mg/kg prey tissue wet weight. The $QS_{hh}$ is set at 40.8 mg/kg fishery product wet weight. There is no EC foodstuff regulation developed for nickel.

*Selected target level: no target suitable*

### 10.2 PAHs

There are EQSs set for Fluoroanthene (30 µg/kg ww) and Benzo(a)pyrene (5 µg/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 5.0 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 PCBs

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*

## 10.5 Brominated flame retardants

### 10.5.1 BDEs

The $EQS_{biota}$ for sumBDEs, based on protection of human health, is set to a concentration at 0.0085 µg/kg wet weight. The $QS_{biota\ secondary\ poisoning}$ are set at 44 µg/kg wet weight. There are no EAC or EC foodstuff regulation developed for BDEs.

*Selected target level: EQSbiota*

### 10.5.2 HBCDD

The $EQS_{biota}$ 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*

## 10.6 Other

### 10.6.1 Dioxins, furans and dioxin-like PCBs.

The $EQS_{biota}$ 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 secondary poisoning (0.0012 µgWHO05-TEQ /kg ww) The EC foodstuff regulation for only dioxins and furans is 0.0035 µgWHO05-TEQ /kg ww.

*Selected target level: EQSbiota*

### 10.6.2  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*

### 10.6.3  PFOS

The $EQS_{biota}$ for concentrations of PFOS is based on human health and set at 9.1 µg/kg wet weight while the $QS_{biota}$ for protection via secondary poisoning is set at 33 µg/kg ww. There are no EAC or EC foodstuff regulation developed for PFOS.

*Selected target level: EQSbiota*

# 11 Condition

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 and Lagler, 1961) is used:

$$K = 100 \; W / L3$$

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 (Fig. 11.1). 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 % average decrease annually, respectively) (Fig. 11.3, 11.4).

## Condition factor, herring
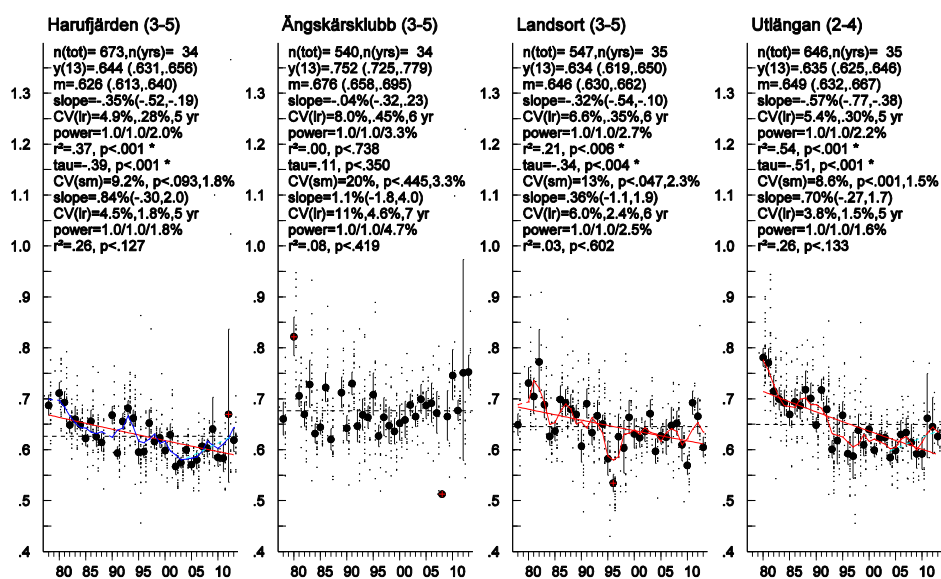


**Figure 11.1.** Condition factor for herring from Harufjärden, Ängskärsklubb, Landsort, and Utlängan (time series starting in 1978).

## Condition factor, herring
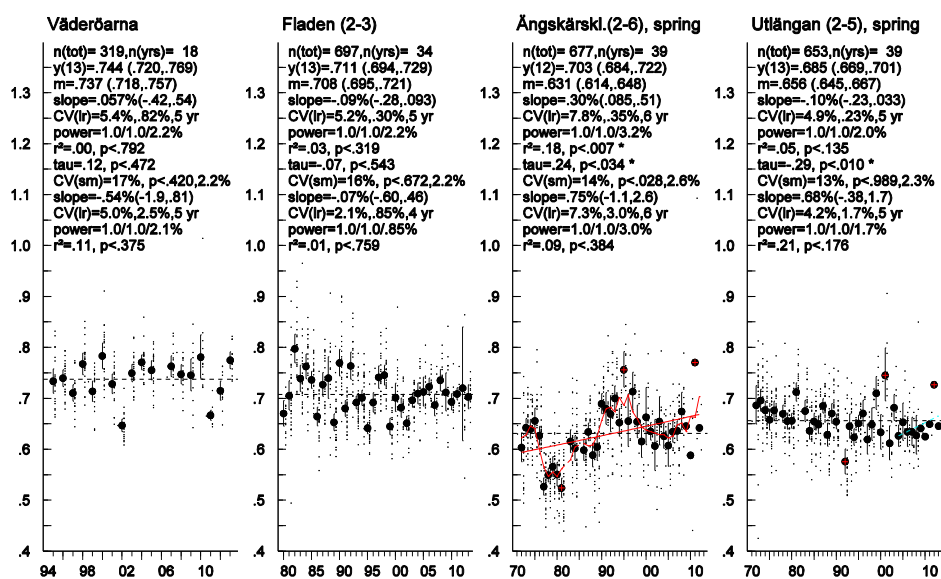


**Figure 11.2**. Condition factor for herring from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1994 respectively.

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## Condition factor, cod and perch

**Cod (2-4), SE Gotland**

n(tot)= 493,n(yrs)= 35
y(13)=.959 (.933,.984)
m=1.00 (.969,1.03)
slope=.10%(-.18,.39)
CV(lr)=8.5%,.46%,6 yr
power=1.0/1.0/3.5%
r²=.01, p<.483
tau=.069, p<.560
CV(sm)=2532%, p<.002,2.4%
slope=-1.3%(-2.9,.38)
CV(lr)=6.6%,2.7%,6 yr
power=1.0/1.0/2.7%
r²=.28, p<.112

**Cod (2-3), Fladen**

n(tot)= 518,n(yrs)= 37
y(13)=1.06 (1.04,1.08)
m=.993 (.969,1.02)
slope=.37%(.16,.58)
CV(lr)=6.3%,.34%,6 yr
power=1.0/1.0/2.6%
r²=.27, p<.001 *
tau=.28, p<.016 *
CV(sm)=674%, p<.008,1.9%
slope=.83%(.10,1.6)
CV(lr)=2.9%,1.2%,5 yr
power=1.0/1.0/1.2%
r²=.46, p<.029 *

**Perch, Holmöarna**

n(tot)= 362,n(yrs)= 28
y(13)=1.15 (1.13,1.18)
m=1.19 (1.16,1.21)
slope=-.26%(-.43,-.10)
CV(lr)=4.4%,.33%,5 yr
power=1.0/1.0/1.8%
r²=.29, p<.003 *
tau=-.36, p<.007 *
CV(sm)=25%, p<.374,1.7%
slope=-.54%(-1.5,.38)
CV(lr)=3.6%,1.7%,5 yr
power=1.0/1.0/1.5%
r²=.22, p<.205

**Perch, Kvädöfjärden (3-4)**

n(tot)= 366,n(yrs)= 33
y(13)=1.29 (1.27,1.31)
m=1.22 (1.20,1.23)
slope=.15%(.026,.27)
CV(lr)=3.5%,.21%,5 yr
power=1.0/1.0/1.4%
r²=.16, p<.019 *
tau=.32, p<.009 *
CV(sm)=17%, p<.343,1.4%
slope=.24%(-.71,1.2)
CV(lr)=3.8%,1.5%,5 yr
power=1.0/1.0/1.5%
r²=.03, p<.590

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**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).

## Condition factor, eelpout

**Holmöarna**

n(tot)= 109,n(yrs)= 12
y(07)=.306 (.297,.316)
m=.325 (.312,.338)
slope=-1.1%(-2.0,-.24)
CV(lr)=5.0%,1.5%,5 yr
power=1.0/1.0/2.0%
r²=.44, p<.018 *
tau=-.39, p<.075
CV(sm)=3.7%, p<.121,1.7%
slope=-.42%(-1.5,.65)
CV(lr)=4.2%,1.7%,5 yr
power=1.0/1.0/1.7%
r²=.09, p<.398

**Kvädöfjärden**

n(tot)= 123,n(yrs)= 18
y(13)=.405 (.392,.420)
m=.380 (.369,.392)
slope=.61%(.11,1.1)
CV(lr)=5.2%,.79%,5 yr
power=1.0/1.0/2.1%
r²=.30, p<.018 *
tau=.35, p<.045 *
CV(sm)=5.8%, p<.766,2.3%
slope=1.2%(.14,2.3)
CV(lr)=4.3%,1.7%,5 yr
power=1.0/1.0/1.8%
r²=.46, p<.031 *

**Fjällbacka**

n(tot)= 247,n(yrs)= 22
y(13)=.426 (.402,.452)
m=.432 (.413,.451)
slope=-.26%(-.90,.38)
CV(lr)=10%,1.1%,7 yr
power=1.0/1.0/4.2%
r²=.03, p<.409
tau=-.19, p<.225
CV(sm)=12%, p<.643,4.3%
slope=.30%(-1.7,2.3)
CV(lr)=7.8%,3.2%,6 yr
power=1.0/1.0/3.2%
r²=.01, p<.728

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**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 with slightly higher condition factors 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) | 673 | 34 | 78-13 | -0.35(-.52,-.19) | 0.0002 | --- | 5 | 2 | .644 (.631,.656) |
| Harufjärden (3-5) | | 10 | 04-13 | 0.84(-.30,2.0) | 0.1273 | | 5 | 1.8 | |
| Ängskärsklubb (3-5) | 540 | 34 | 78-13 | -0.04(-.32,.23) | 0.7375 | | 6 | 3.3 | .752 (.725,.779) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 1.1(-1.8,4.0) | 0.4189 | | 7 | 4.7 | |
| Landsort (3-5) | 547 | 35 | 78-13 | -0.32(-.54,-.10) | 0.0061 | -- | 6 | 2.7 | .634 (.619,.650) |
| Landsort (3-5) | | 10 | 04-13 | 0.36(-1.1,1.9) | 0.6023 | | 6 | 2.5 | |
| Utlängan (2-4) | 646 | 34 | 80-13 | -0.57(-.77,-.38) | 0 | --- | 5 | 2.2 | .635 (.625,.646) |
| Utlängan (2-4) | | 10 | 04-13 | 0.7(-.27,1.7) | 0.1329 | | 5 | 1.6 | |
| Ängskärsklubb spring (2-6) | 677 | 39 | 72-12 | 0.3(.085,.51) | 0.007 | ++ | 6 | 3.2 | .703 (.684,.722) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 0.75(-1.1,2.6) | 0.3837 | | 6 | 3 | |
| Utlängan spring (2-4) | 653 | 39 | 72-13 | -0.1(-.23,.033) | 0.135 | | 5 | 2 | .685 (.669,.701) |
| Utlängan spring (2-4) | | 10 | 04-13 | 0.68(-.38,1.7) | 0.1759 | | 5 | 1.7 | |
| Fladen (2-3) | 697 | 34 | 80-13 | -0.09(-.28,.093) | 0.3187 | | 5 | 2.2 | .711 (.694,.729) |
| Fladen (2-3) | | 10 | 04-13 | -0.07(-.60,.46) | 0.7594 | | 4 | 0.85 | |
| Väderöarna | 319 | 18 | 95-13 | 0.057(-.42,.54) | 0.7917 | | 5 | 2.2 | .744 (.720,.769) |
| Väderöarna | | 9 | 04-13 | -0.54(-1.9,.81) | 0.3752 | | 5 | 2.1 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 362 | 28 | 80-13 | -0.26(-.43,-.10) | 0.003 | -- | 5 | 1.8 | 1.15 (1.13,1.18) |
| Holmöarna | | 9 | 04-13 | -0.54(-1.5,.38) | 0.2047 | | 5 | 1.5 | |
| Kvädöfjärden | 366 | 33 | 80-13 | 0.15(.026,.27) | 0.0186 | + | 5 | 1.4 | 1.29 (1.27,1.31) |
| Kvädöfjärden | | 10 | 04-13 | 0.24(-.71,1.2) | 0.5901 | | 5 | 1.5 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 493 | 35 | 78-13 | 0.1(-.18,.39) | 0.4828 | | 6 | 3.5 | .959 (.933,.984) |
| SE Gotland (2-4) | | 10 | 04-13 | -1.3(-2.9,.38) | 0.1116 | | 6 | 2.7 | |
| Fladen (2-3) | 518 | 35 | 79-13 | 0.37(.16,.58) | 0.0014 | ++ | 6 | 2.6 | 1.06 (1.04,1.08) |
| Fladen (2-3) | | 10 | 04-13 | 0.83(.10,1.6) | 0.0292 | + | 5 | 1.2 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 109 | 12 | 95-07 | -1.1(-2.0,-.24) | 0.0176 | - | 5 | 2 | .306 (.297,.316) |
| Holmöarna | | 10 | 98-07 | -0.42(-1.5,.65) | 0.3977 | | 5 | 1.7 | |
| Kvädöfjärden | 123 | 18 | 95-13 | 0.61(.11,1.1) | 0.018 | + | 5 | 2.1 | .405 (.392,.420) |
| Kvädöfjärden | | 10 | 04-13 | 1.2(.14,2.3) | 0.0306 | + | 5 | 1.8 | |
| Fjällbacka | 247 | 22 | 88-13 | -0.26(-.90,.38) | 0.4094 | | 7 | 4.2 | .426 (.402,.452) |
| Fjällbacka | | 10 | 04-13 | 0.3(-1.7,2.3) | 0.7278 | | 6 | 3.2 | |

# 12 Fat content

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
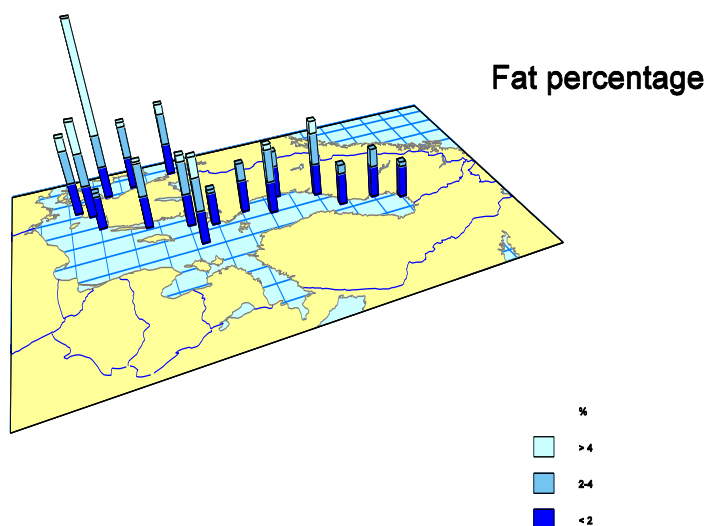


**Figure 12.1.** Spatial variation in fat percentage in herring muscle.

The fat content in autumn-caught herring is somewhat higher in the Southern Baltic proper and on the west coast (in general 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 Kullen with a fat content of approximately 11 %. The herring caught at Kullen are also larger i.e. longer than herring from other stations, which could be an explanation of the high fat content. The lowest fat content was found in herring from Lagnö (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 seven years with exception for last year. On the contrary, the fat content of Ängskärsklubb (spring) increased during the last ten years.

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). There is an indication of an increase in the fat content of cod liver from Fladen during the whole time series. 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 (monitoring ceased after 2007) 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).
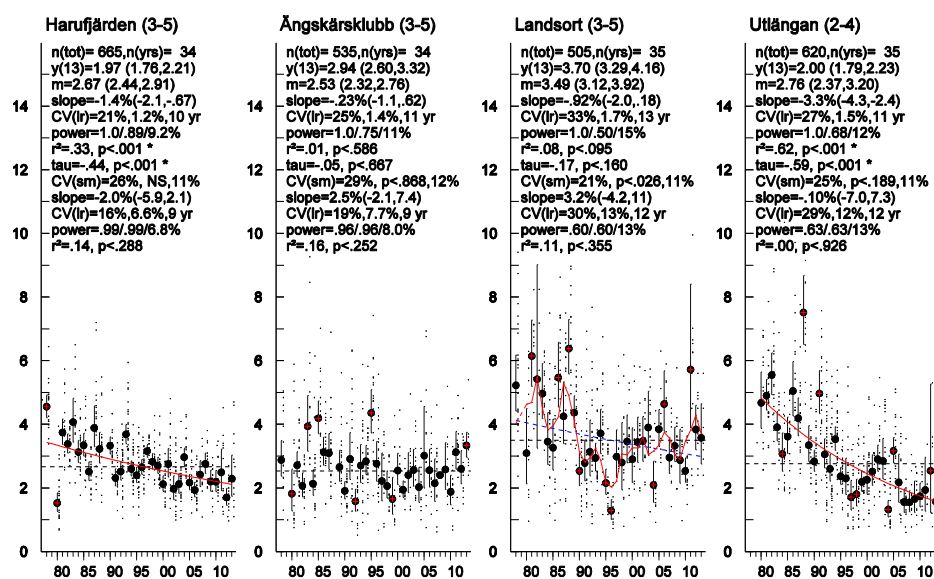
**Figure 12.2.** Fat percentage in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978 and 1980 respectively).
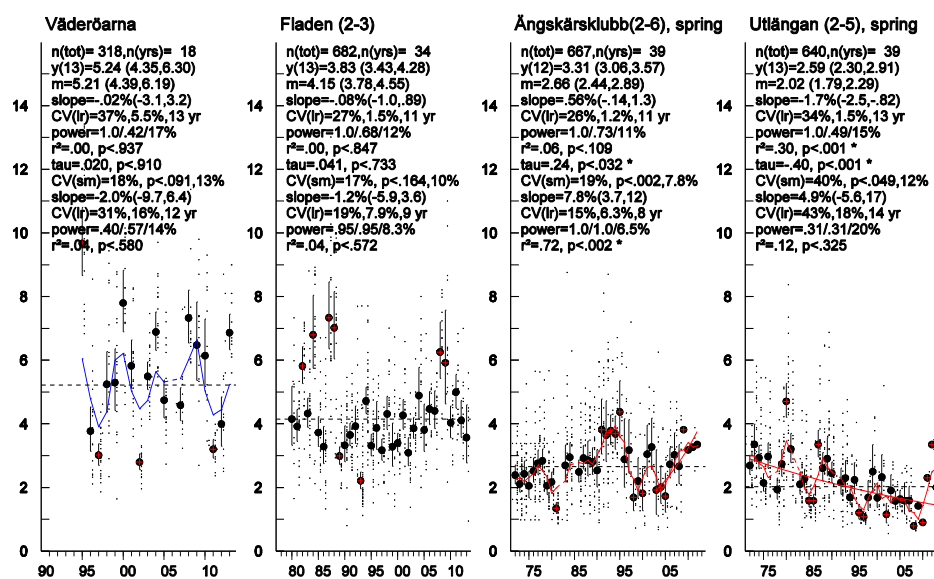


**Figure 12.3.** Fat percentage in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1995 respectively).
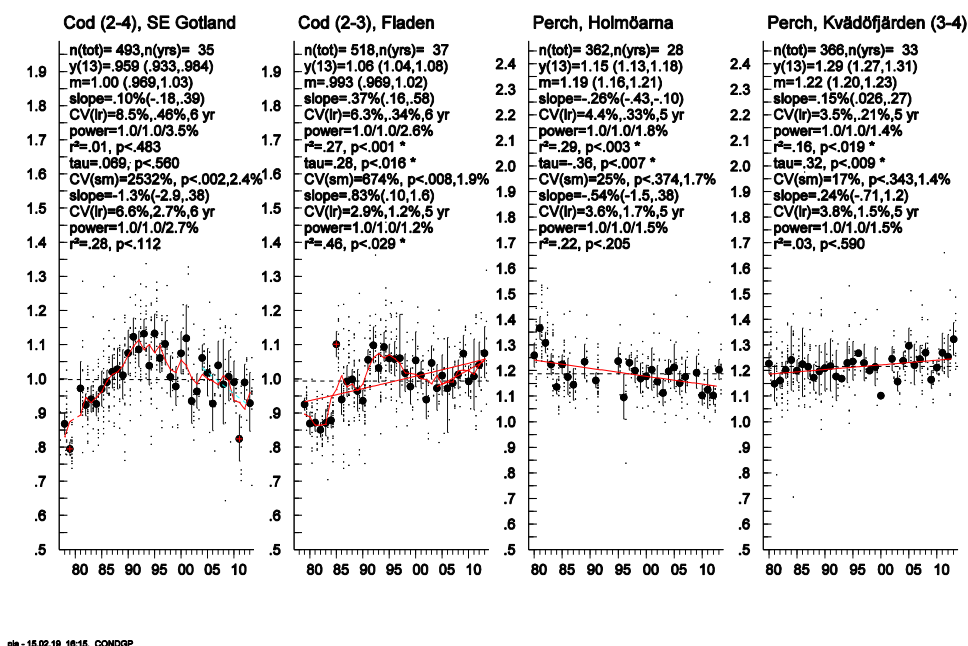
## Fat %, cod liver and perch muscle
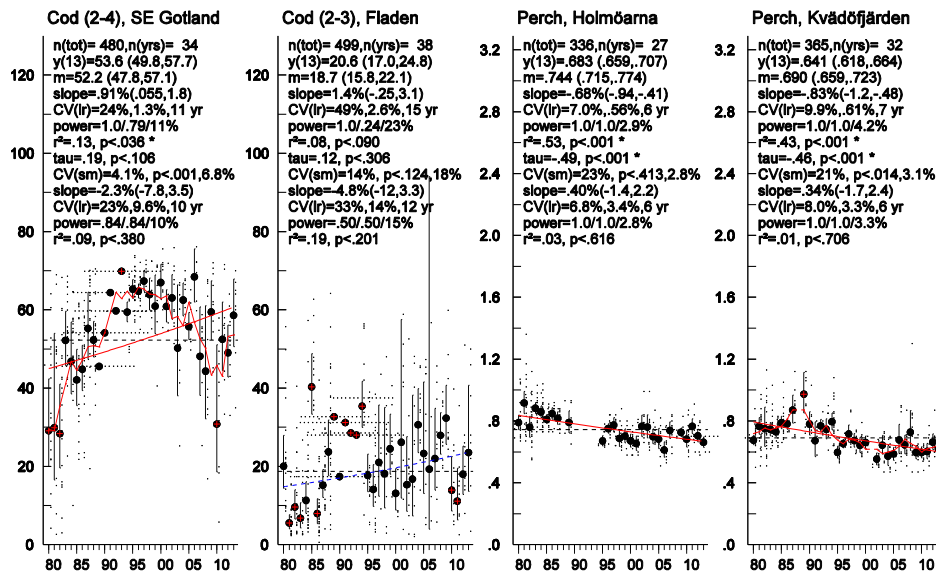


**Figure 12.4.** Fat percentage for cod liver from Southeast Gotland and Fladen (time series starting 1980), and perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1980)

## Fat %, blue mussel soft body
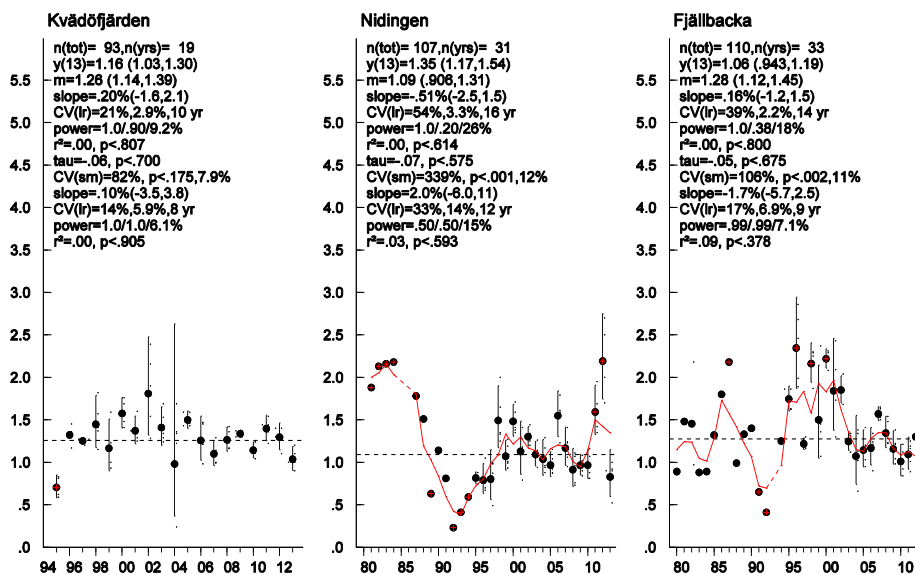


**Figure 12.5.** Fat percentage for blue mussel soft body from Nidingen, Väderöarna and Kvädöfjärden (time series starting in 1981, 1980, and 1995 respectively).

## Fat %, Eelpout

**Holmöarna**

n(tot)= 97,n(yrs)= 11
y(07)=.644 (.565,.734)
m=.722 (.608,.858)
slope=-4.6%(-7.8,-1.3)
CV(lr)=19%,6.6%,9 yr
power=.99/.95/8.2%
r²=.52, p<.012 *
tau=-.31, p<.186
CV(sm)=50%, p<.155,6.8%
slope=-3.6%(-8.5,1.7)
CV(lr)=20%,10%,10 yr
power=.77/.92/8.9%
r²=.27, p<.147

**Kvädöfjärden**

n(tot)= 123,n(yrs)= 18
y(13)=.624 (.574,.679)
m=.605 (.561,.653)
slope=.68%(-.76,2.2)
CV(lr)=15%,2.3%,8 yr
power=1.0/.99/6.6%
r²=.05, p<.335
tau=.15, p<.384
CV(sm)=27%, p<.141,5.6%
slope=2.4%(-.43,5.2)
CV(lr)=11%,4.5%,7 yr
power=1.0/1.0/4.6%
r²=.32, p<.085

**Fjällbacka**

n(tot)= 248,n(yrs)= 22
y(13)=.517 (.439,.610)
m=.652 (.565,.752)
slope=-2.7%(-4.3,-1.0)
CV(lr)=27%,2.9%,11 yr
power=1.0/.70/12%
r²=.37, p<.003 *
tau=-.49, p<.001 *
CV(sm)=69%, p<.936,13%
slope=-1.6%(-3.9,.70)
CV(lr)=9.2%,3.8%,7 yr
power=1.0/1.0/3.8%
r²=.25, p<.143



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

## Fat %, guillemot egg

**Stora Karlsö**

n(tot)= 453,n(yrs)= 43
y(13)=12.6 (12.2,13.0)
m=12.1 (11.7,12.5)
slope=-.01%(-.26,.23)
CV(lr)=10%,.40%,7 yr
power=1.0/1.0/4.3%
r²=.00, p<.874
tau=.034, p<.746
CV(sm)=3.3%, p<.015,3.4%
slope=.65%(-.31,1.6)
CV(lr)=3.8%,1.5%,5 yr
power=1.0/1.0/1.6%
r²=.23, p<.155
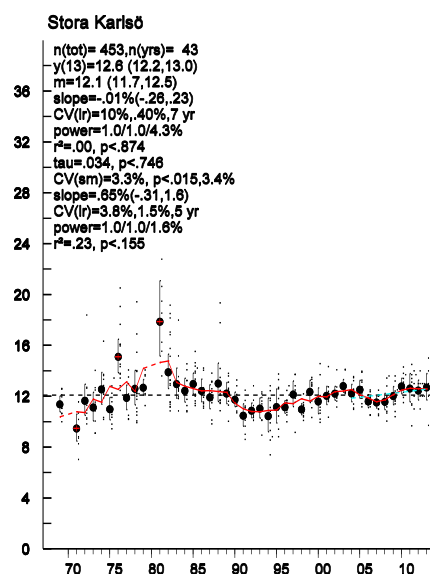


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**Figure 12.7.** Fat percentage in guillemot eggs from Stora Karlsö (time series starting in 1969).

## 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.

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**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) | 665 | 34 | 78-13 | -1.4(-2.1,-.67) | 0.0005 | --- | 10 | 9.2 | 1.97 (1.76,2.21) |
| Harufjärden (3-5) | 48 | 10 | 04-13 | -2(-5.9,2.1) | 0.2882 | | 9 | 6.8 | 2.89 (2.30,3.63) |
| Ängskärsklubb (3-5) | 535 | 34 | 78-13 | -0.23(-1.1,.62) | 0.5863 | | 11 | 11 | 2.94 (2.60,3.32) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 2.5(-2.1,7.4) | 0.2518 | | 9 | 8 | |
| Landsort (3-5) | 505 | 35 | 78-13 | -0.92(-2.0,.18) | 0.0954 | | 13 | 15 | 3.70 (3.29,4.16) |
| Landsort (3-5) | | 10 | 04-13 | 3.2(-4.2,11) | 0.3553 | | 12 | 13 | |
| Utlängan (2-4) | 620 | 34 | 80-13 | -3.3(-4.3,-2.4) | 0 | --- | 11 | 12 | 2.00 (1.79,2.23) |
| Utlängan (2-4) | | 10 | 04-13 | -0.1(-7.0,7.3) | 0.926 | | 12 | 13 | |
| Ängskärsklubb spring (2-6) | 667 | 39 | 72-12 | 0.56(-.14,1.3) | 0.1087 | | 11 | 11 | 3.31 (3.06,3.57) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 7.8(3.7,12) | 0.0022 | ++ | 8 | 6.5 | |
| Utlängan spring (2-4) | 640 | 39 | 72-13 | -1.7(-2.5,-.82) | 0.0004 | --- | 13 | 15 | 2.59 (2.30,2.91) |
| Utlängan spring (2-4) | | 10 | 04-13 | 4.9(-5.6,17) | 0.3246 | | 14 | 20 | |
| Fladen (2-3) | 682 | 34 | 80-13 | -0.08(-1.0,.89) | 0.8468 | | 11 | 12 | 3.83 (3.43,4.28) |
| Fladen (2-3) | | 10 | 04-13 | -1.2(-5.9,3.6) | 0.5715 | | 9 | 8.3 | |
| Väderöarna | 318 | 18 | 95-13 | -0.02(-3.1,3.2) | 0.9371 | | 13 | 17 | 5.24 (4.35,6.30) |
| Väderöarna | | 9 | 04-13 | -2(-9.7,6.4) | 0.5798 | | 12 | 14 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 336 | 27 | 80-13 | -0.68(-.94,-.41) | 0 | --- | 6 | 2.9 | .683 (.659,.707) |
| Holmöarna | | 9 | 04-13 | 0.4(-1.4,2.2) | 0.6165 | | 6 | 2.8 | |
| Kvädöfjärden | 365 | 32 | 80-13 | -0.83(-1.2,-.48) | 0.0001 | --- | 7 | 4.2 | .641 (.618,.664) |
| Kvädöfjärden | | 10 | 04-13 | 0.34(-1.7,2.4) | 0.7057 | | 6 | 3.3 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 480 | 34 | 80-13 | 0.91(.055,1.8) | 0.0357 | + | 11 | 11 | 53.6 (49.8,57.7) |
| SE Gotland (2-4) | | 10 | 04-13 | -2.3(-7.8,3.5) | 0.3804 | | 10 | 10 | |
| Fladen (2-3) | 499 | 34 | 80-13 | 1.4(-.25,3.1) | 0.09 | | 15 | 23 | 20.6 (17.0,24.8) |
| Fladen (2-3) | | 10 | 04-13 | -4.8(-12,3.3) | 0.2006 | | 12 | 15 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 97 | 11 | 95-07 | -4.6(-7.8,-1.3) | 0.0125 | - | 9 | 8.2 | .644 (.565,.734) |
| Holmöarna | | 9 | 98-07 | -3.6(-8.5,1.7) | 0.1465 | | 10 | 8.9 | |
| Kvädöfjärden | 123 | 18 | 95-13 | 0.68(-.76,2.2) | 0.3354 | | 8 | 6.6 | .624 (.574,.679) |
| Kvädöfjärden | | 10 | 04-13 | 2.4(-.43,5.2) | 0.085 | | 7 | 4.6 | |
| Fjällbacka | 248 | 22 | 88-13 | -2.7(-4.3,-1.0) | 0.0029 | -- | 11 | 12 | .517 (.439,.610) |
| Fjällbacka | | 10 | 04-13 | -1.6(-3.9,.70) | 0.1432 | | 7 | 3.8 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 107 | 31 | 81-13 | -0.51(-2.5,1.5) | 0.6135 | | 16 | 26 | 1.35 (1.17,1.54) |
| Nidingen | | 10 | 04-13 | 2(-6.0,11) | 0.5926 | | 12 | 15 | |
| Fjällbacka | 110 | 33 | 80-13 | 0.16(-1.2,1.5) | 0.8001 | | 14 | 18 | 1.06 (.943,1.19) |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Fjällbacka | | 10 | 04-13 | -1.7(-5.7,2.5) | 0.3777 | 9 | 7.1 | |
| Kvädöfjärden | 93 | 19 | 95-13 | 0.2(-1.6,2.1) | 0.807 | 10 | 9.2 | 1.16 (1.03,1.30) |
| Kvädöfjärden | | 10 | 04-13 | 0.1(-3.5,3.8) | 0.9049 | 8 | 6.1 | |

**Guillemot egg**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 453 | 43 | 69-13 | -0.01(-.26,.23) | 0.8737 | 7 | 4.3 | 12.6 (12.2,13.0) |
| Stora Karlsö | | 10 | 04-13 | 0.65(-.31,1.6) | 0.1547 | 5 | 1.6 | |

# 13  Mercury - Hg

## 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), $Hg_2^{2+}$ (mercurous), $Hg^{2+}$ (mercuric). Organic forms include $CH_3HgCH_3$ (dimethylmercury) and $CH_3Hg^+$ (monomethylmercury) (Suzuki T. 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 (Huber, 1997). Highly toxic and bioaccumulatory methylmercury compounds were previously used as fungicides and were produced as unwanted byproducts of the chemical industry (Clarkson, 1993).

Natural sources of mercury include volcanoes, forest fires, fossil fuels 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. Anthropogenic sources to soil and water include 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  I and Munthe J., 2001). However, mercury use has almost ceased in Sweden (AMAP and UNEP, 2008).

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 0.2 mg/kg to 0.5 mg/kg seen. 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 (EC, 2001).

### 13.1.2  Environmental Fate

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

### 13.1.3 Toxic Effects

Mercury is known to bioaccumulate (Clarkson, 1993). Methylmercury is the form of mercury 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 T. et al., 1991, Huber, 1997). High exposure can effect brain development, with young children and infants most at risk (Doetzel, 2007), as methylmercury disturbs cell division and therefore development (Huber, 1997) .

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 L. et al., 1974, Rustam and Hamdi, 1974, Clarkson, 1993, Huber, 1997). 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, 1997), the risk of which can be greater for *in utero* children in pregnant women (Koren and Bend, 2010). Exposure becomes problematic if contaminated fish (or other contaminated foodstuffs) are eaten often, and neurological effects in both adults and children *in utero* can be seen (Ratcliffe et al., 1996).

Wildlife in all environments is affected by mercury accumulation; however animals in aquatic systems appear to show more intense bioaccumulation/biomagnification effects than terrestrial species (Huber, 1997). Bioaccumulation usually occurs through diet (Huber, 1997). A biomagnification effect is seen in fish at higher trophic levels 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. The connection was made since birds of prey that predated on smaller birds that in turn had fed on methylmercury treated grains, suffered from severe population declines and a high mercury load (Clarkson, 1993). While methylmercury accumulates in fish muscle, the highest concentrations are generally seen in the blood, spleen, kidney and liver. In mammals and birds, the highest concentrations are typically seen in the feathers and fur. 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, 1997).

### 13.1.4 Conventions, aims and restrictions

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 (HELCOM, 1988).

The use of alkylmercury compounds for use in the agriculture as well as in the paper pulp industries has been banned in Sweden since 1966 (KEMI, 2010).

According to a governmental proposition (1993/94:163), the aim was that all mercury usage in Sweden should have ceased by 2000 (Prop. 1993/94:163, 1994).

### 13.1.5 Target Levels

The target level (TL) used for mercury in the time series for fish is 20 µg/kg wet weigh. The original target level is set for concentrations of mercury in whole-fish and the data presented in this report is measured in muscle. However, in a study on conversion factors between muscle and whole-fish (Faxneld et al., 2015) the existing target level was recalculated to the corresponding muscle value, and a value of 21 µg/kg wet weigh was derived. But, since this value is very close to the original target level, and probably within the margin of error, 20 µg/kg wet weigh is used. 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 (EC, 2001). 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 and Hennings, 2009).

## 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.

ITM – now called ACES –  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 Stockholm university. See chapter 6 section 6.1 for further details.

## 13.3  Results

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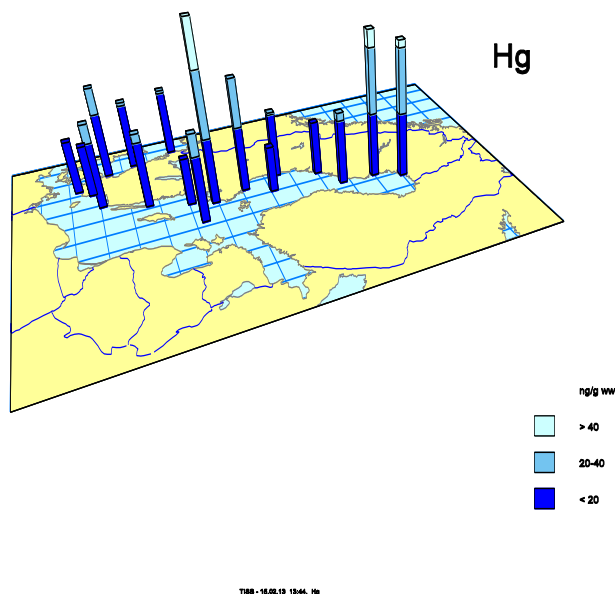
**Figure 13.1.** Spatial variation in mercury concentrations (ng/g wet weight) in herring muscle.

Herring muscle from Lagnö shows the highest mercury concentrations of all herring samples 2011–2013 and Landsort and Bothnian Sea offshore shows the lowest concentrations (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 (67 ng/g) showed higher concentrations than samples from Southeast of Gotland (30 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

In a majority of the samples there is a decrease of the mercury concentrations over either the whole time series or during the last ten years (Fig. 13.2 and 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 resumed in 1996. There was a significant decrease of 2.2 % for autumn-caught herring from Ängskärsklubb and 2.3% for spring-caught herring (Fig. 13.2 and 13.3). The time series from Fladen, Ängskärsklubb (autumn) Landsort show a significant average decrease of 7.4, 10 and 8.5% annually, respectively, during the last ten years (Fig. 13.2 and 13.3).
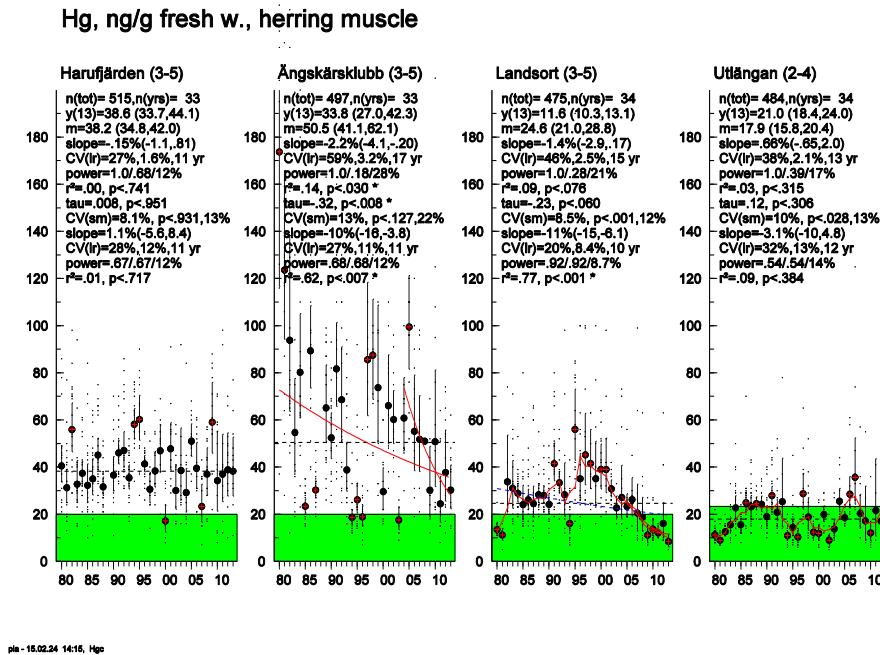


**Figure 13.2.** Mercury concentrations (ng/g fresh weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting 1980). The green line denotes the suggested target value for mercury in fish.

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.



**Hg, ng/g fresh w., herring muscle**

Väderöarna

n(tot)= 304,n(yrs)= 18
y(13)=21.2 (18.9,23.7)
m=23.8 (21.2,26.8)
slope=-.24%(-2.3,1.9)
CV(lr)=24%,3.7%,11 yr
power=1.0/.79/11%
r²=.00, p<.802
tau=-.03, p<.850
CV(sm)=5.8%, p<.035,7.6%
slope=-5.2%(-11,.39)
CV(lr)=21%,11%,10 yr
power=.73/.89/9.3%
r²=.41, p<.062

Fladen (2-3)

n(tot)= 573,n(yrs)= 34
y(13)=20.6 (18.5,22.8)
m=24.6 (22.4,27.2)
slope=.36%(-.63,1.4)
CV(lr)=29%,1.6%,12 yr
power=1.0/.64/13%
r²=.01, p<.471
tau=.073, p<.543
CV(sm)=7.2%, p<.029,9.7%
slope=-7.4%(-12,-2.4)
CV(lr)=21%,8.9%,10 yr
power=.89/.89/9.3%
r²=.58, p<.010 *

Ängskärsklubb, spring

n(tot)= 238,n(yrs)= 22
y(12)=28.3 (23.9,33.5)
m=31.1 (26.0,37.1)
slope=-2.3%(-3.2,-1.4)
CV(lr)=26%,3.0%,11 yr
power=1.0/.75/11%
r²=.61, p<.001 *
tau=-.41, p<.009 *
CV(sm)=8.5%, p<1.00,12%
slope=.63%(-6.0,7.7)
CV(lr)=27%,11%,11 yr
power=.69/.69/12%
r²=.00, p<.817

Utlängan, spring

n(tot)= 232,n(yrs)= 22
y(13)=16.3 (14.4,18.6)
m=20.2 (18.1,22.5)
slope=-.72%(-1.5,.065)
CV(lr)=23%,2.7%,10 yr
power=1.0/.84/10%
r²=.16, p<.067
tau=-.21, p<.184
CV(sm)=7.4%, p<.428,9.4%
slope=-2.0%(-7.6,4.0)
CV(lr)=24%,9.8%,10 yr
power=.82/.82/10%
r²=.07, p<.460

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**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 10–17
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, but a
decreasing trend the last ten years is indicated (Fig. 13.4).

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## Hg, ng/g fresh w., perch muscle

**Holmöarna**

n(tot)= 206,n(yrs)= 19
y(13)=58.5 (51.6,66.3)
m=61.0 (54.7,67.9)
slope=-.73%(-2.5,1.1)
CV(lr)=23%,3.2%,10 yr
power=1.0/.84/10%
r²=.04, p<.405
tau=-.08, p<.649
CV(sm)=5.0%, p<.198,8.7%
slope=-2.8%(-6.9,1.5)
CV(lr)=17%,8.4%,9 yr
power=.92/.99/7.1%
r²=.26, p<.162

**Kvädöfjärden**

n(tot)= 309,n(yrs)= 31
y(13)=57.4 (52.0,63.3)
m=38.4 (33.3,44.2)
slope=-.74%(-2.2,.73)
CV(lr)=40%,2.5%,14 yr
power=1.0/.36/18%
r²=.03, p<.310
tau=-.08, p<.507
CV(sm)=5.7%, p<.001,8.7%
slope=5.3%(.98,9.9)
CV(lr)=17%,6.9%,9 yr
power=.98/.98/7.2%
r²=.50, p<.021 *
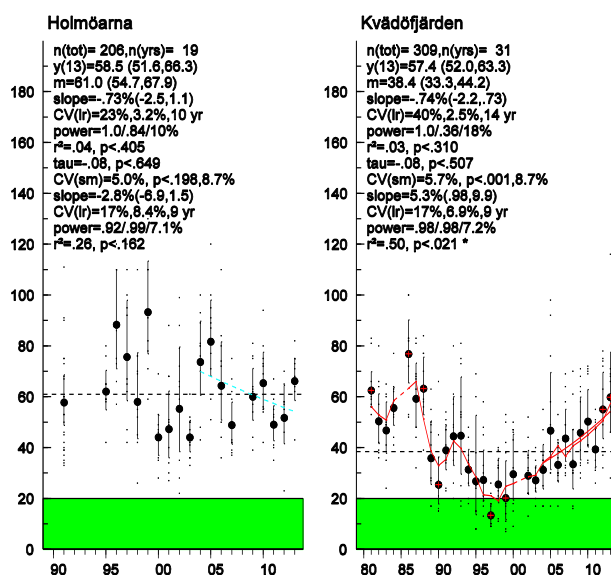


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**Figure 13.4.** Mercury concentrations (ng/g fresh weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1991 and 1981 respectively). The green area denotes the levels below the suggestedtarget value for mercury in fish.

Cod from both Fladen and Southeast of Gotland shows significant increasing trends of 1.2 and 2.2% respectively (Fig. 13.5).

## Hg, ng/g fresh w., cod muscle

**SE Gotland (2-4)**

n(tot)= 492,n(yrs)= 35
y(13)=30.1 (27.5,32.8)
m=27.4 (24.4,30.7)
slope=2.2%(1.3,3.1)
CV(lr)=25%,1.3%,11 yr
power=1.0/.75/11%
r²=.45, p<.001 *
tau=.49, p<.001 *
CV(sm)=6.0%, p<.017,8.4%
slope=-2.2%(-8.8,4.8)
CV(lr)=28%,12%,11 yr
power=.66/.66/12%
r²=.06, p<.478

**Fladen (2-4)**

n(tot)= 561,n(yrs)= 37
y(13)=67.1 (62.5,72.2)
m=48.2 (44.1,52.6)
slope=1.2%(.39,2.0)
CV(lr)=23%,1.2%,10 yr
power=1.0/.83/10%
r²=.22, p<.004 *
tau=.36, p<.002 *
CV(sm)=4.2%, p<.002,6.8%
slope=6.0%(.88,11)
CV(lr)=20%,8.1%,9 yr
power=.94/.94/8.5%
r²=.48, p<.026 *
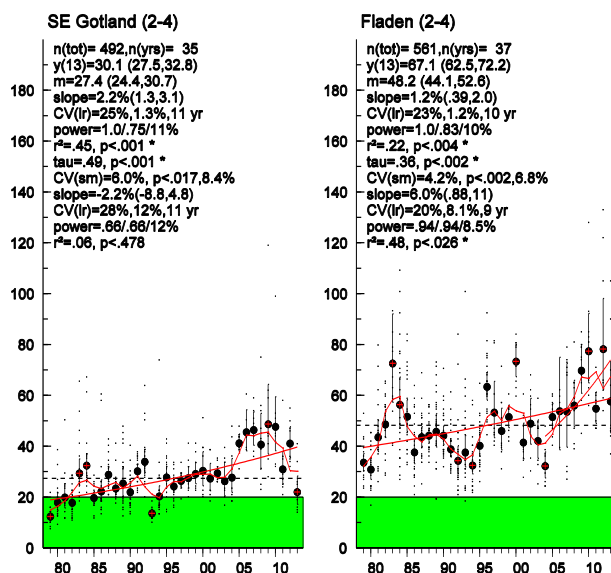


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**Figure 13.5.** Mercury concentrations (ng/g fresh weight) in cod muscle from Southeast Gotland and Fladen (time series starting in 1979).

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

## Hg, ng/g fresh w., eelpout muscle
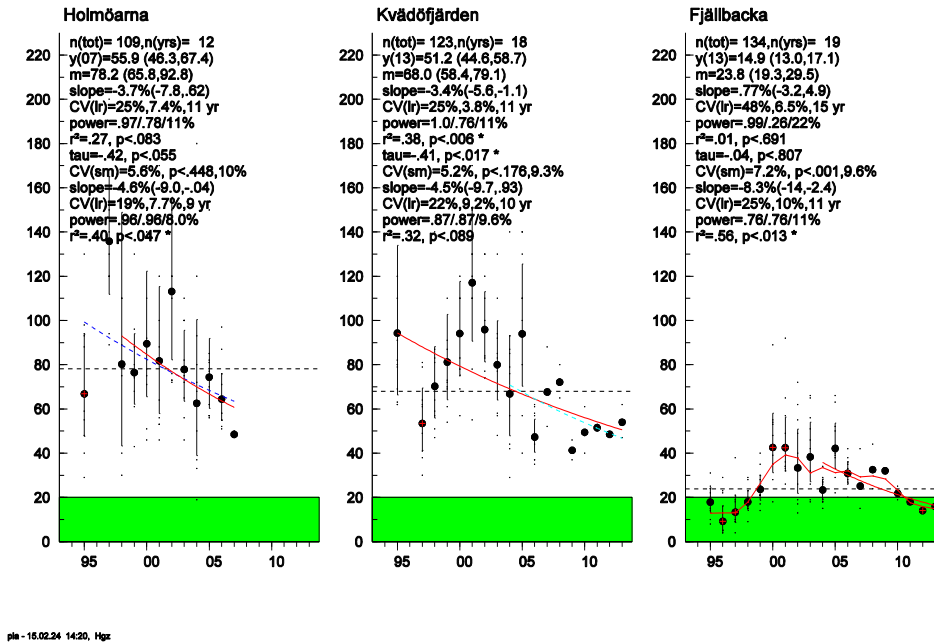


**Figure 13.6.** Mercury concentrations (ng/g fresh weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

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

## Hg, ng/g fresh w., blue mussel
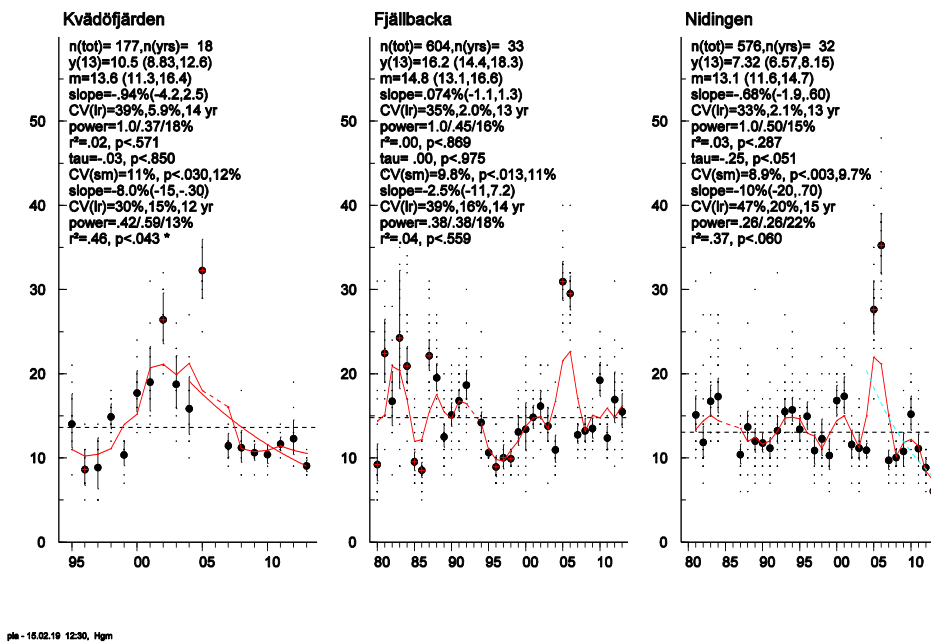


**Figure 13.7.** Mercury concentrations (ng/g fresh weight) in blue mussel soft body tissue from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1981, 1980 and 1995 respectively).

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.

Hg, ng/g fresh w., guillemot egg



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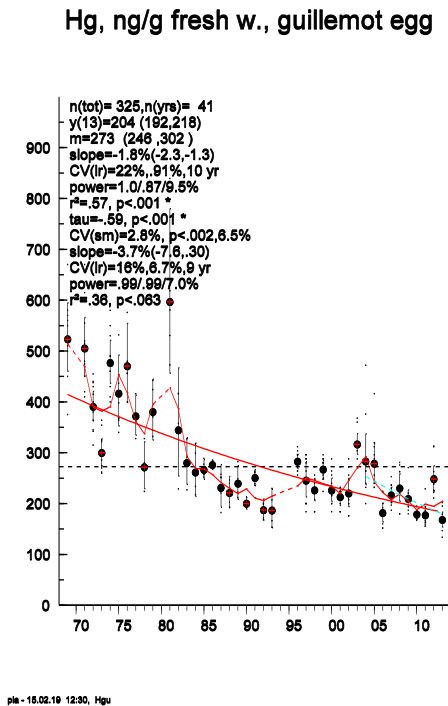
**Figure 13.8.** Mercury concentrations (ng/g fresh weight) in guillemot eggs (early laid) from St. Karlsö (time series starting in 1969).

### 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 (56) – Perch (59)
Kvädöfjärden: Perch (57) > Eelpout (51) > Blue mussel (11)
Fladen/Nidingen: Cod (67) > Herring (21) > Blue mussel (7)
Väderöarna/Fjällbacka: Herring (16) – Blue mussel (16) – Eelpout (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.

The differences in mercury concentrations were between spring- and autumn-caught herring from Utlängan was; autumn 21 ≥ spring 16, and at Ängskärsklubb; autumn 34 ≥ spring 28.

### 13.3.4 Comparison to threshold

The suggested target level for mercury based on ECs EQS of 20 ng/g wet weight was exceeded in 70% of the herring time series (Fig. 13.1). Furthermore, the concentration of

mercury was also exceeded in all perch and cod time series as well as in two out of three eelpout 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 and 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 but seems to decrease during the last decade. 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.

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 (NFA, 1993).

Perttilä and co-workers (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 µg/g 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 0.08–0.13µg/g (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) | 515 | 33 | 80-13 | -0.15(-1.1,.81) | 0.7414 | | 11 | 12 | 38.6 (33.7,44.1) |
| Harufjärden (3-5) | | 10 | 04-13 | 1.1(-5.6,8.4) | 0.7168 | | 11 | 12 | |
| Ängskärsklubb (3-5) | 497 | 33 | 80-13 | -2.2(-4.1,-.20) | 0.0304 | - | 17 | 28 | 33.8 (27.0,42.3) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -10(-16,-3.8) | 0.0067 | -- | 11 | 12 | |
| Landsort (3-5) | 475 | 34 | 80-13 | -1.4(-2.9,.17) | 0.0762 | | 15 | 21 | 11.6 (10.3,13.1) |
| Landsort (3-5) | | 10 | 04-13 | -11(-15,-6.1) | 0.001 | --- | 10 | 8.7 | |
| Utlängan (2-4) | 484 | 34 | 80-13 | 0.66(-.65,2.0) | 0.3149 | | 13 | 17 | 21.0 (18.4,24.0) |
| Utlängan (2-4) | | 10 | 04-13 | -3.1(-10,4.8) | 0.3841 | | 12 | 14 | |
| Ängskärsklubb spring (2-6) | 238 | 21 | 72-12 | -2.3(-3.2,-1.4) | 0.0000 | --- | 11 | 11 | 28.3 (23.9,33.5) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 0.63(-6.0,7.7) | 0.8172 | | 11 | 12 | |
| Utlängan spring (2-4) | 232 | 21 | 72-13 | -0.72(-1.5,.065) | 0.0672 | | 10 | 10 | 16.3 (14.4,18.6) |
| Utlängan spring (2-4) | | 10 | 04-13 | -2(-7.6,4.0) | 0.4603 | | 10 | 10 | |
| Fladen (2-3) | 573 | 34 | 80-13 | 0.36(-.63,1.4) | 0.4705 | | 12 | 13 | 20.6 (18.5,22.8) |
| Fladen (2-3) | | 10 | 04-13 | -7.4(-12,-2.4) | 0.0103 | - | 10 | 9.3 | |
| Väderöarna | 304 | 18 | 95-13 | -0.24(-2.3,1.9) | 0.8018 | | 11 | 11 | 21.2 (18.9,23.7) |
| Väderöarna | | 9 | 04-13 | -5.2(-11,.39) | 0.0618 | | 10 | 9.3 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 206 | 19 | 91-13 | -0.73(-2.5,1.1) | 0.405 | | 10 | 10 | 58.5 (51.6,66.3) |
| Holmöarna | | 9 | 04-13 | -2.8(-6.9,1.5) | 0.1618 | | 9 | 7.1 | |
| Kvädöfjärden | 309 | 31 | 81-13 | -0.74(-2.2,.73) | 0.3103 | | 14 | 18 | 57.4 (52.0,63.3) |
| Kvädöfjärden | | 10 | 04-13 | 5.3(.98,9.9) | 0.0214 | + | 9 | 7.2 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 492 | 35 | 79-13 | 2.2(1.3,3.1) | 0.0000 | | 11 | 11 | 30.1 (27.5,32.8) |
| SE Gotland (2-4) | | 10 | 04-13 | -2.2(-8.8,4.8) | 0.4778 | | 11 | 12 | |
| Fladen (2-3) | 561 | 35 | 79-13 | 1.2(.39,2.0) | 0.0044 | | 10 | 10 | 67.1 (62.5,72.2) |
| Fladen (2-3) | | 10 | 04-13 | 6(.88,11) | 0.0258 | + | 9 | 8.5 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 109 | 12 | 95-07 | -3.7(-7.8,.62) | 0.0826 | | 11 | 11 | 55.9 (46.3,67.4) |
| Holmöarna | | 10 | 98-07 | -4.6(-9.0,-.04) | 0.0469 | - | 9 | 8 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -3.4(-5.6,-1.1) | 0.0061 | -- | 11 | 11 | 51.2 (44.6,58.7) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | | 10 | 04-13 | -4.5(-9.7,.93) | 0.0889 | | 10 | 9.6 | |
| Fjällbacka | 134 | 19 | 95-13 | 0.77(-3.2,4.9) | 0.6911 | | 15 | 22 | 14.9 (13.0,17.1) |
| Fjällbacka | | 10 | 04-13 | -8.3(-14,-2.4) | 0.0126 | - | 11 | 11 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 576 | 31 | 81-13 | -0.68(-1.9,.60) | 0.2867 | | 13 | 15 | 7.32 (6.57,8.15) |
| Nidingen | | 10 | 04-13 | -10(-20,.70) | 0.0605 | | 15 | 22 | |
| Fjällbacka | 604 | 33 | 80-13 | 0.074(-1.1,1.3) | 0.8694 | | 13 | 16 | 16.2 (14.4,18.3) |
| Fjällbacka | | 10 | 04-13 | -2.5(-11,7.2) | 0.5585 | | 14 | 18 | |
| Kvädöfjärden | 177 | 18 | 95-13 | -0.94(-4.2,2.5) | 0.5709 | | 14 | 18 | 10.5 (8.83,12.6) |
| Kvädöfjärden | | 9 | 04-13 | -8(-15,-.30) | 0.0427 | - | 12 | 13 | |
| **Guillemot egg** | | | | | | | | | |
| Stora Karlsö | 325 | 41 | 69-13 | -1.8(-2.3,-1.3) | 0.0000 | --- | 10 | 9.5 | 204 (192,218) |
| Stora Karlsö | | 10 | 04-13 | -3.7(-7.6,.30) | 0.063 | | 9 | 7 | |

# 14 Lead - Pb

## 14.1 Introduction

### 14.1.1 Usage, Production and Sources

Lead occurs 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 elsewhere in Europe (Renberg et al., 2000). The main sources of lead pollution in Sweden come from ammunition, historic emissions from leaded petrol and associated contamination in road side soils (eventhough 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).

The primary use for lead is in car batteries. There are numerous other uses including, but not limited to, lead 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, 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 and Creger, 1994, Peryea and Kammereck, 1997).

### 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 water compared to lakes with a higher pH (Spry and 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 as well as causing brain and blood disorders. The toxic effects of lead involve several organ systems and biochemical activities. The risk is highest for children and the unborn, partly because of high permeability of lead across both the blood-brain barrier and the placenta (Klaassen C.D. and Rozman K., 1991). Some neurophysiological development affects 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 C.D. and Rozman K., 1991). Between 90% and 95% of the lead that is found in blood is distributed to the red blood cells, where haemoglobin synthesis can be inhibited, and subsequently symptoms such as anaemia can occur (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 and Trainer, 1966, Pattee et al., 1981), and there have been reports of fishing sinkers causing bird deaths (Locke et al., 1982). In Sweden, bird death from lead poisoning is more common in swans, geese and ducks, but has also been reported in woodpeckers. Lead levels were found to be highest in woodpecker liver and kidney(Mörner and 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) for lead used in the time series for perch and herring is 300 µg/kg wet weight fish muscle. Since lead data presented here are expressed as dry weight in liver, the original TL has been recalculated to represent the corresponding concentration in liver for comparison. Recalculation of the TL was based on a study that compares metal concentrations in liver, muscle and whole-fish in perch (Faxneld et al., 2015). However, concentrations in muscle were very low and no conversion to liver concentrations was established in the study. Instead whole body concentrations have been applied and used to recalculated the original TL to dry weight in liver for each time series to fit the presented data. After recalculating the existing target level of 300 µg/kg wet weight the new derived target level in liver is 0.085 µg/g wet weight. 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 (NFA, 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 lead, 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 Stockholm University. See chapter 6 section 6.1 for further details.

## 14.3 Results

### 14.3.1 Spatial variation
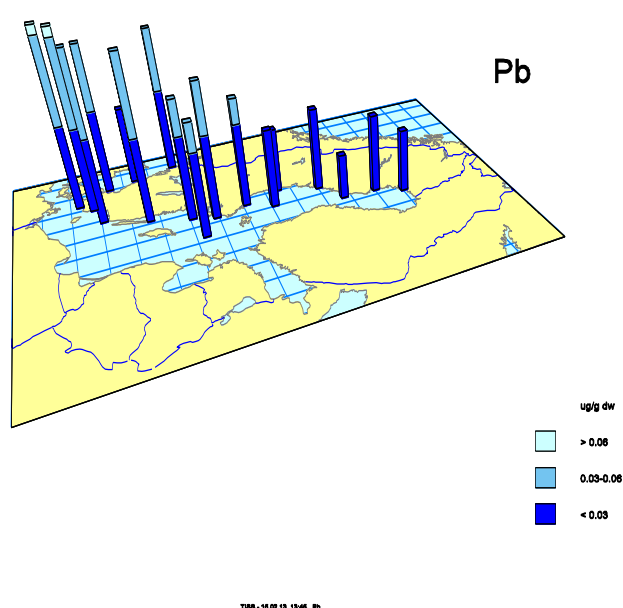


**Figure 14.1.** Spatial variation in lead concentrations (µg/g dry weight) in herring liver.

Abbekås and Västra Hanöbukten have the highest concentrations of lead in herring liver 2011—2013 and Holmöarna has the lowest concentration. (Fig 13.1).

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 Skei (Knutzen and Skei, 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 and 14.3).

# Pb, μg/g dry w., herring liver
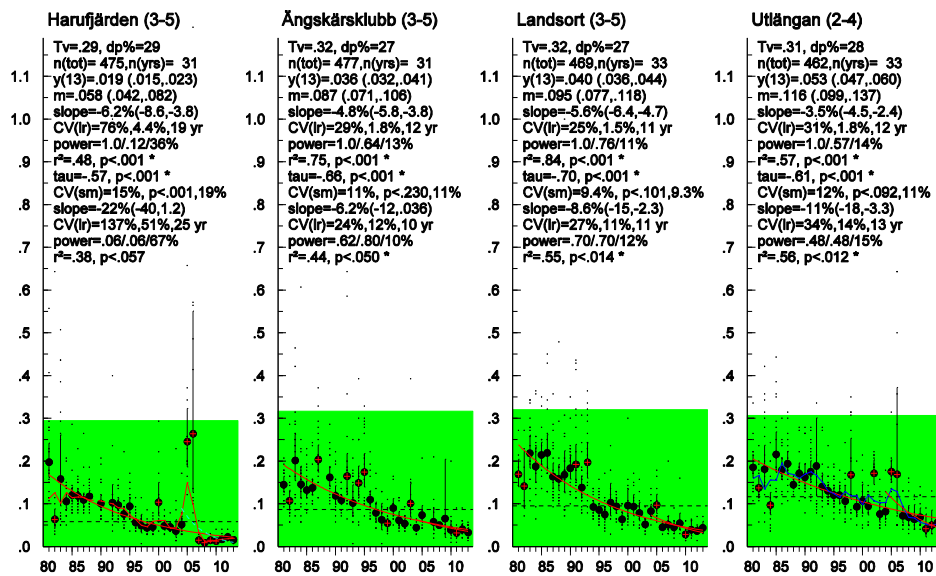


**Figure 14.2** (above) and **14.3** (below). Lead concentrations (μg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981)(above); and Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1997,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

# Pb, μg/g dry w., herring liver
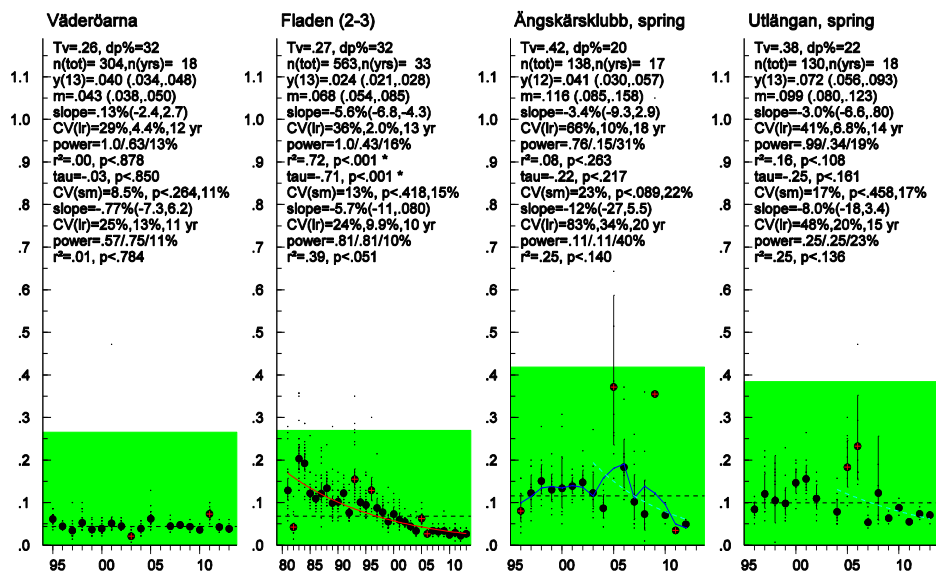


The number of years required to detect an annual change of 10% varied between 11–19 years for the herring time series, with a power to detect a 10% annual change ranging from 0.76 (shorter series) to 1.0 (longer series). An annual change greater than 10% would likely be detected.

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.
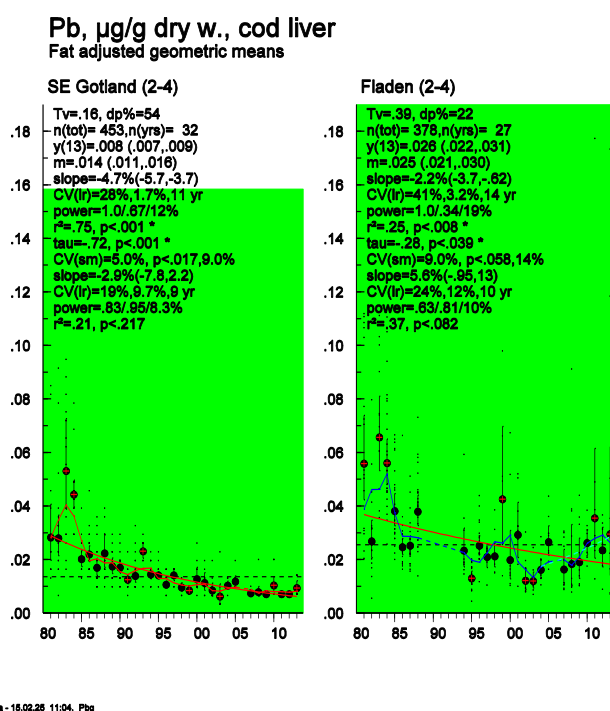


**Figure 14.4.** Lead concentrations (μg/g dry weight) in cod liver from Southeast Gotland and Fladen (time series starting in1981).

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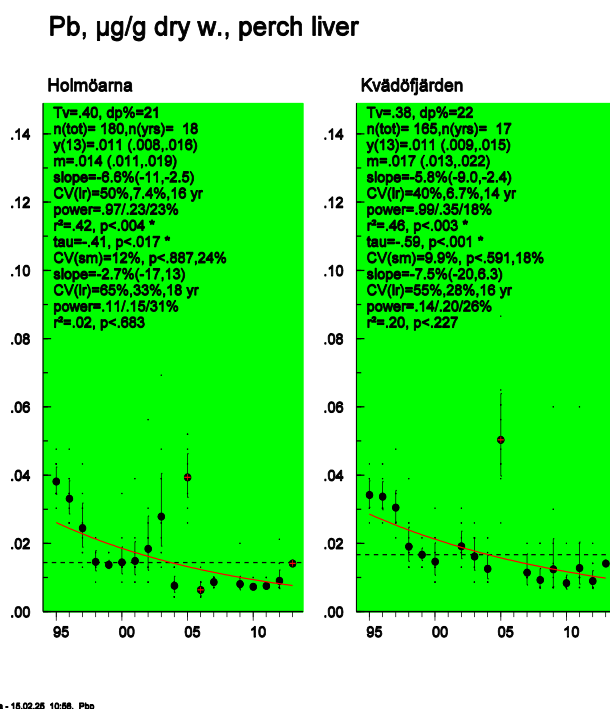


**Figure 14.5.** Lead concentrations (μg/g dry weight) in perch liver from Holmöarna and Kvädöfjären (time series starting in1995). The green area denotes the levels below the suggested target value for lead in fish.

The lead concentration in eelpout liver show significant decreasing trends at Kvädöfjärden and Fjällbacka and at Holmöarna a decreasing trend is indicated (Fig. 14.6).

**Pb, µg/g dry w., eelpout liver**
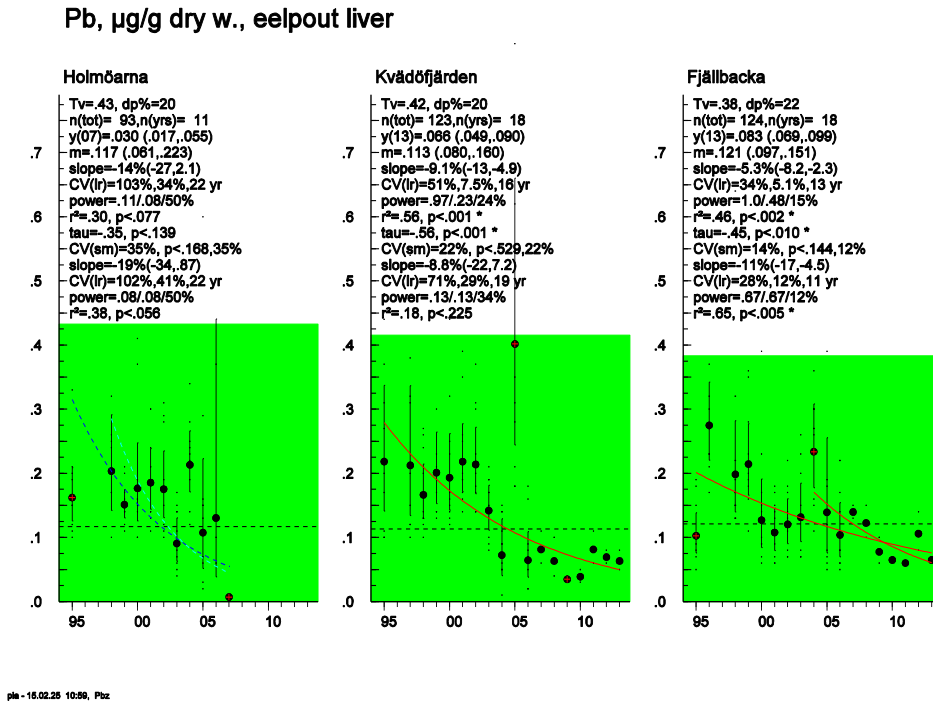


**Figure 14.6.** Lead concentrations (µg/g dry weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

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.

## Pb, µg/g wet w., blue mussel softbody

**Kvädöfjärden**

n(tot)= 188,n(yrs)= 19
y(13)=.198 (.150,.260)
m=.233 (.182,.300)
slope=-.10%(-4.7,4.7)
CV(lr)=57%,7.7%,17 yr
power=.96/.19/27%
r²=.00, p<.918
tau=-.15, p<.382
CV(sm)=31%, p<.097,20%
slope=-3.9%(-10,2.9)
CV(lr)=27%,11%,11 yr
power=.68/.68/12%
r²=.18, p<.215

**Fjällbacka**

n(tot)= 575,n(yrs)= 31
y(13)=.125 (.103,.152)
m=.222 (.187,.264)
slope=-1.5%(-3.1,.25)
CV(lr)=48%,2.9%,15 yr
power=1.0/.26/22%
r²=.09, p<.088
tau=-.30, p<.018 *
CV(sm)=28%, p<.172,18%
slope=-13%(-17,-8.3)
CV(lr)=20%,9.9%,9 yr
power=.81/.94/8.4%
r²=.85, p<.001 *

**Nidingen**

n(tot)= 568,n(yrs)= 31
y(13)=.049 (.040,.061)
m=.163 (.122,.217)
slope=-5.3%(-7.5,-3.2)
CV(lr)=62%,3.9%,17 yr
power=1.0/.16/29%
r²=.47, p<.001 *
tau=-.49, p<.001 *
CV(sm)=25%, p<.021,20%
slope=-9.5%(-20,2.9)
CV(lr)=50%,26%,16 yr
power=.17/.24/23%
r²=.32, p<.107

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**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 13% per year (Fig. 14.8).

## Pb, µg/g dry w., guillemot egg

**Stora Karlsö**

n(tot)= 180,n(yrs)= 18
y(13)=.007 (.005,.010)
m=.026 (.016,.043)
slope=-13%(-18,-6.8)
CV(lr)=76%,11%,19 yr
power=.74/.12/37%
r²=.55, p<.001 *
tau=-.59, p<.001 *
CV(sm)=16%, p<.113,26%
slope=-18%(-35,4.0)
CV(lr)=114%,44%,23 yr
power=.07/.07/56%
r²=.32, p<.089
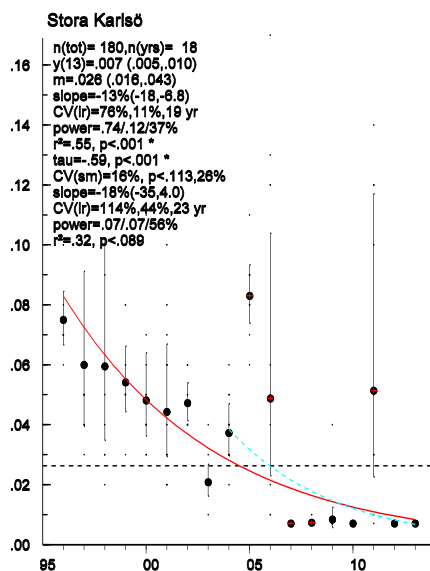
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**Figure 14.8**. Lead concentrations (µg/g dry weight) in guillemot eggs from Stora Karlsö (time series starting in 1996).

### 14.3.3 Species differences

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

Holmöarna: Eelpout (0.030) > Perch (0.011)
Kvädöfjärden: Blue mussel (20) > Eelpout (0.066) > Perch (0.011)
Fladen/Nidingen: Blue mussel (4.9) > Herring (0.029) > Cod (0.018)
Väderöarna/Fjällbacka: Blue mussel (13) > Eelpout (0.083) > Herring (0.040)

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.

The differences in lead concentrations were between spring- and autumn-caught hering from Utlängan was; autumn 0.053 < spring 0.072, and at Ängskärsklubb; autumn 0.036 ≤ spring 0.041.

### 14.3.4 Comparison to threshold

In all herring and perch time series, lead concentrations are below the suggested target level based on the food regulation limit of 300 μg/kg wet weight.The target level is supposed to be applied in edible parts witch in most cases refers to muscle tissue. In this case the whole body concentrations was compared with the target level instead (via recalculations to liver). Whole body concentrations have been shown to contain higher lead concentration than muscle tissue (Faxneld et al., 2015) and the use of whole body concentrations will result in a more restrictive approach.

### 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 (Jorhem and Sundström, 1993), compared with a previous study from 1973–1982 (Jorhem et al., 1984).

The mean values of the last years lead concentrations are all below the suggested target level based on EC food regulation, 300 ng/g wet weightThe recommended limit for children's food, as set by the Swedish National Food Administration, is 50 ng/g wet weight.

**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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 475 | 31 | 81-13 | -6.2(-8.6,-3.8) | 0.0000 | --- | 19 | 36 | .019 (.015,.023) |
| Harufjärden (3-5) | | 10 | 04-13 | -22(-40,1.2) | 0.0573 | | 25 | 67 | |
| Ängskärsklubb (3-5) | 477 | 31 | 81-13 | -4.8(-5.8,-3.8) | 0.0000 | --- | 12 | 13 | .036 (.032,.041) |
| Ängskärsklubb (3-5) | | 9 | 04-13 | -6.2(-12,.036) | 0.0497 | - | 10 | 10 | |
| Landsort (3-5) | 469 | 33 | 81-13 | -5.6(-6.4,-4.7) | 0.0000 | --- | 11 | 11 | .040 (.036,.044) |
| Landsort (3-5) | | 10 | 04-13 | -8.6(-15,-2.3) | 0.0138 | - | 11 | 12 | |
| Utlängan (2-4) | 462 | 33 | 81-13 | -3.5(-4.5,-2.4) | 0.0000 | --- | 12 | 14 | .053 (.047,.060) |
| Utlängan (2-4) | | 10 | 04-13 | -11(-18,-3.3) | 0.0121 | - | 13 | 15 | |
| Ängskärsklubb spring (2-6) | 138 | 17 | 96-12 | -3.4(-9.3,2.9) | 0.2625 | | 18 | 31 | .041 (.030,.057) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -12(-27,5.5) | 0.1402 | | 20 | 40 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | -3(-6.6,.80) | 0.1084 | | 14 | 19 | .072 (.056,.093) |
| Utlängan spring (2-4) | | 10 | 04-13 | -8(-18,3.4) | 0.1364 | | 15 | 23 | |
| Fladen (2-3) | 563 | 33 | 81-13 | -5.6(-6.8,-4.3) | 0.0000 | --- | 13 | 16 | .024 (.021,.028) |
| Fladen (2-3) | | 10 | 04-13 | -5.7(-11,.080) | 0.0509 | | 10 | 10 | |
| Väderöarna | 304 | 18 | 95-13 | 0.13(-2.4,2.7) | 0.8781 | | 12 | 13 | .040 (.034,.048) |
| Väderöarna | | 9 | 04-13 | -0.77(-7.3,6.2) | 0.7836 | | 11 | 11 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 180 | 18 | 95-13 | -6.6(-11,-2.5) | 0.0038 | -- | 16 | 23 | .011 (.008,.016) |
| Holmöarna | | 9 | 04-13 | -2.7(-17,13) | 0.6827 | | 18 | 31 | |
| Kvädöfjärden | 165 | 17 | 95-13 | -5.8(-9.0,-2.4) | 0.0027 | -- | 14 | 18 | .011 (.009,.015) |
| Kvädöfjärden | | 9 | 04-13 | -7.5(-20,6.3) | 0.2267 | | 16 | 26 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 453 | 32 | 81-13 | -4.7(-5.7,-3.7) | 0.0000 | --- | 11 | 12 | .008 (.007,.009) |
| SE Gotland (2-4) | | 9 | 04-13 | -2.9(-7.8,2.2) | 0.2165 | | 9 | 8.3 | |
| Fladen (2-3) | 378 | 27 | 81-13 | -2.2(-3.7,-.62) | 0.008 | -- | 14 | 19 | .026 (.022,.031) |
| Fladen (2-3) | | 9 | 04-13 | 5.6(-.95,13) | 0.0822 | | 10 | 10 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 93 | 11 | 95-07 | -14(-27,2.1) | 0.0768 | | 22 | 50 | .030 (.017,.055) |

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| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Holmöarna | | 10 | 98-07 | -19(-34,.87) | 0.0561 | | 22 | 50 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -9.1(-13,-4.9) | 0.0004 | --- | 16 | 24 | .066 (.049,.090) |
| Kvädöfjärden | | 10 | 04-13 | -8.8(-22,7.2) | 0.2252 | | 19 | 34 | |
| Fjällbacka | 124 | 18 | 95-13 | -5.3(-8.2,-2.3) | 0.0019 | -- | 13 | 15 | .083 (.069,.099) |
| Fjällbacka | | 10 | 04-13 | -11(-17,-4.5) | 0.0051 | -- | 11 | 12 | |

**Blue mussel**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Nidingen | 568 | 30 | 81-13 | -5.3(-7.5,-3.2) | 0.0000 | --- | 17 | 29 | .049 (.040,.061) |
| Nidingen | | 9 | 04-13 | -9.5(-20,2.9) | 0.1071 | | 16 | 23 | |
| Fjällbacka | 575 | 31 | 81-13 | -1.5(-3.1,.25) | 0.0884 | | 15 | 22 | .125 (.103,.152) |
| Fjällbacka | | 9 | 04-13 | -13(-17,-8.3) | 0.0005 | --- | 9 | 8.4 | |
| Kvädöfjärden | 188 | 19 | 95-13 | -0.1(-4.7,4.7) | 0.9183 | | 17 | 27 | .198 (.150,.260) |
| Kvädöfjärden | | 10 | 04-13 | -3.9(-10,2.9) | 0.2146 | | 11 | 12 | |

**Guillemot egg**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 180 | 18 | 96-13 | -13(-18,-6.8) | 0.0005 | --- | 19 | 37 | .007 (.005,.010) |
| Stora Karlsö | | 10 | 04-13 | -18(-35,4.0) | 0.0889 | | 23 | 56 | |

# 15  Cadmium – Cd

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 nickel-cadmium 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, 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 (HELCOM, 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 cadmiumsulfides 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 cadmium. 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 cadmiumchloride 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. 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. 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, 1991). 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 cadmium in the time series for perch and herring is 160 µg/kg wet weight in whole-fish. For further information on TL and selection of target level see chapter 10. Since cadmium data presented here are expressed as dry weight in liver, the original TL has been recalculated to represent the corresponding concentration in liver for comparison. The recalculation of the TL for whole-fish is based on a study that compared concentrations of cadmium in the liver and whole-fish of perch from the limnic environment (Faxneld et al., 2015). The new derived target level for liver was 6.65 µg/g wet weight. 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 Stockholm University. See chapter 6 section 6.1 for further details.

## 15.3  Results

### 15.3.1  Spatial variation
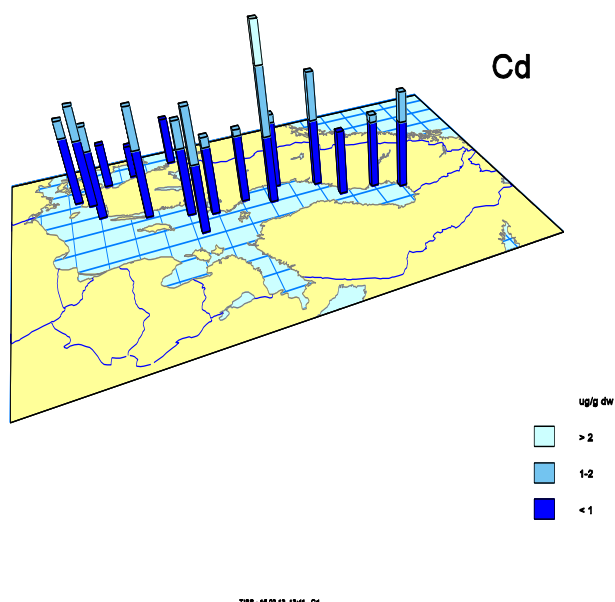


**Figure 15.1.** Spatial variation in cadmium concentrations (µg/g dry weight) in herring liver.

Generally, the Baltic Sea had higher concentrations  of cadmium in herring liver compared to the Swedish west coast. The highest level was observed at Bothnian Sea offshore followed byBaltic proper offshore, 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 1995–2013, 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 Skei (Knutzen and Skei, 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 1995–2013 and Fladen with an increasing trend the last ten years (Fig 15.3). The number of years required to detect an annual change of 10% varied between 10–16 years for the herring time series, with a power to detect a 10% annual change ranging from 0.96 to 1.0.

## Cd, µg/g dry w., herring liver

**Harufjärden (3-5)**

Tv=23, dp%=29
n(tot)= 495,n(yrs)= 32
y(13)=1.34 (1.12,1.61)
m=1.24 (1.09,1.42)
slope=.11%(-1.3,1.6)
CV(lr)=40%,2.4%,14 yr
power=1.0/.36/18%
r²=.00, p<.853
tau=.032, p<.795
CV(sm)=179%, p<.565,17%
slope=4.5%(-3.9,14)
CV(lr)=34%,14%,13 yr
power=.48/.48/15%
r²=.16, p<.257

**Ängskärsklubb (3-5)**

Tv=25, dp%=27
n(tot)= 488,n(yrs)= 32
y(13)=.554 (.463,.664)
m=1.27 (1.05,1.53)
slope=-.82%(-2.8,1.2)
CV(lr)=56%,3.2%,16 yr
power=1.0/.19/26%
r²=.02, p<.409
tau=-.06, p<.804
CV(sm)=165%, p<.007,17%
slope=-.17%(-16,19)
CV(lr)=77%,32%,19 yr
power=.12/.12/37%
r²=.00, p<.931

**Landsort (3-5)**

Tv=25, dp%=27
n(tot)= 469,n(yrs)= 33
y(13)=1.19 (1.09,1.30)
m=1.58 (1.40,1.74)
slope=-.36%(-1.5,.81)
CV(lr)=32%,1.8%,12 yr
power=1.0/.53/14%
r²=.01, p<.539
tau=-.08, p<.535
CV(sm)=43%, p<.001,8.0%
slope=.41%(-4.1,5.1)
CV(lr)=18%,7.5%,9 yr
power=.97/.97/7.8%
r²=.00, p<.820

**Utlängan (2-4)**

Tv=24, dp%=28
n(tot)= 462,n(yrs)= 33
y(13)=.926 (.845,1.02)
m=1.39 (1.24,1.57)
slope=.32%(-.94,1.6)
CV(lr)=35%,2.0%,13 yr
power=1.0/.46/16%
r²=.00, p<.615
tau=.030, p<.804
CV(sm)=61%, p<.001,8.5%
slope=-4.0%(-9.6,1.9)
CV(lr)=24%,9.9%,10 yr
power=.81/.81/10%
r²=.24, p<.150

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**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.

## Cd, µg/g dry w., herring liver

**Väderöarna**

Tv=21, dp%=32
n(tot)= 304,n(yrs)= 18
y(13)=.636 (.556,.727)
m=.378 (.316,.452)
slope=5.4%(3.6,7.3)
CV(lr)=20%,3.0%,10 yr
power=1.0/.93/8.6%
r²=.71, p<.001 *
tau=.63, p<.001 *
CV(sm)=22%, p<.827,9.1%
slope=8.6%(2.8,15)
CV(lr)=16%,10%,10 yr
power=.77/.91/8.9%
r²=.64, p<.010 *

**Fladen (2-3)**

Tv=21, dp%=32
n(tot)= 563,n(yrs)= 33
y(13)=.488 (.446,.534)
m=.438 (.402,.477)
slope=-.55%(-1.4,.34)
CV(lr)=24%,1.4%,11 yr
power=1.0/.79/11%
r²=.04, p<.217
tau=-.20, p<.101
CV(sm)=24%, p<.035,8.3%
slope=5.0%(2.0,8.2)
CV(lr)=12%,4.8%,7 yr
power=1.0/1.0/4.9%
r²=.65, p<.005 *

**Ängskärsklubb, spring**

Tv=33, dp%=20
n(tot)= 138,n(yrs)= 17
y(12)=1.61 (1.20,2.16)
m=3.04 (2.41,3.84)
slope=-2.1%(-6.7,2.7)
CV(lr)=48%,7.8%,15 yr
power=.96/.26/22%
r²=.05, p<.365
tau=-.10, p<.564
CV(sm)=41%, p<.481,20%
slope=.010%(-14,16)
CV(lr)=64%,27%,18 yr
power=.15/.15/30%
r²=.00, p<.948

**Utlängan, spring**

Tv=30, dp%=22
n(tot)= 130,n(yrs)= 18
y(13)=1.55 (1.31,1.83)
m=1.74 (1.51,2.00)
slope=-2.3%(-4.7,.047)
CV(lr)=25%,4.2%,11 yr
power=1.0/.76/11%
r²=.23, p<.052
tau=-.31, p<.084
CV(sm)=47%, p<.615,11%
slope=.18%(-7.0,7.9)
CV(lr)=30%,13%,12 yr
power=.59/.59/13%
r²=.00, p<.912

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**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 Southeast of Gotland but an increase in concentration is indicated for samples from Fladen during the last ten years of monitoring (Fig. 15.4).

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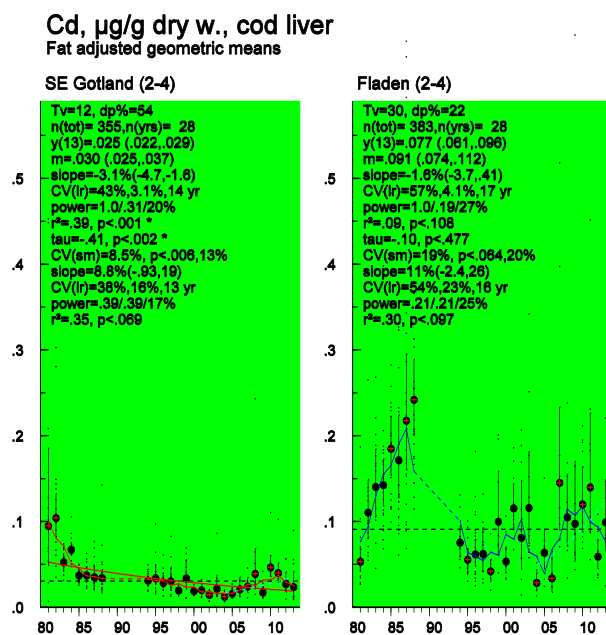
**Figure 15.4.** Cadmium concentrations (µg/g dry weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1980).

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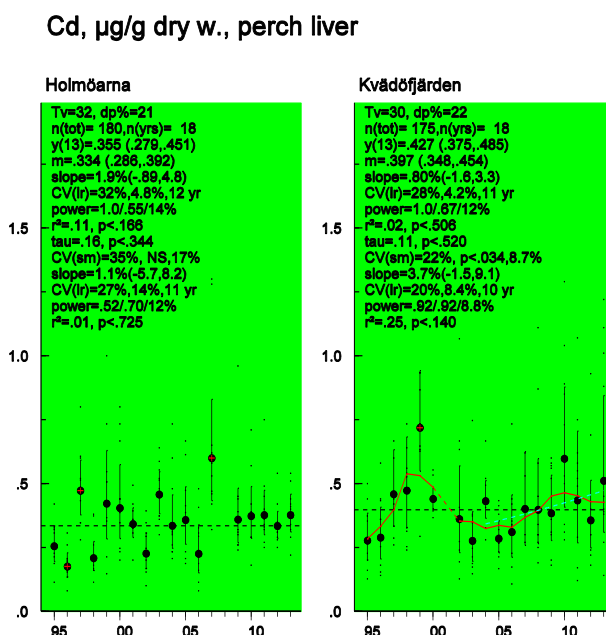


**Figure 15.5.** Cadmium concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995). The green area denotes the levels below the suggested target value for cadmium in fish.

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).

## Cd, µg/g dry w., eelpout liver
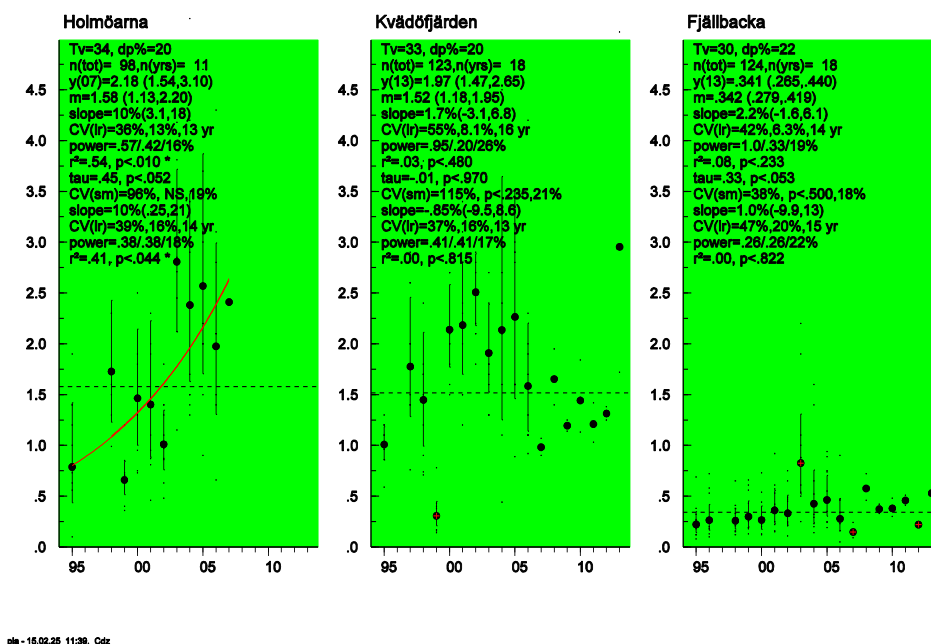


**Figure 15.6.** Cadmium concentrations (µg/g dry weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995).

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).

## Cd, µg/g wet w., blue mussel softbody
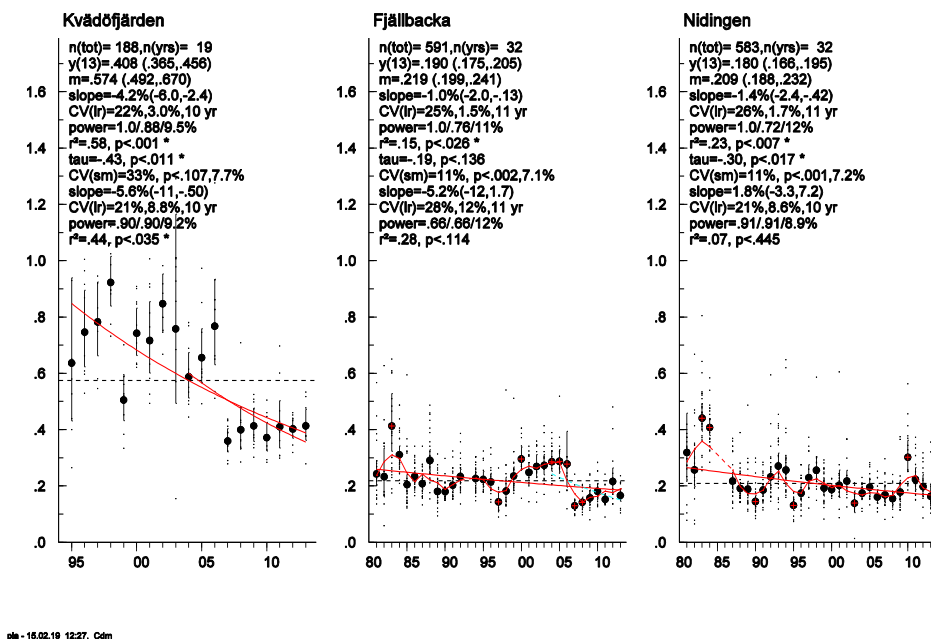


**Figure 15.7.** Cadmium concentrations (µg/g wet weight) in blue mussel soft body tissue from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1981, 1981 and 1995 respectively).

### 15.3.3 Species differences

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

Holmöarna: Eelpout (2.2) > Perch (0. 36)
Kvädöfjärden: Blue mussel (4.1) > Eelpout (2.0) > Perch (0.43)
Fladen/Nidingen: Blue mussel (1.8) > Herring (0.49) > Cod (0.077)
Väderöarna/Fjällbacka: Blue mussel (1.9) > Herring (0.64) > Eelpout (0.34)

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 (0.004 μg/g dry weight) when compared to herring liver. The concentrations in blue mussel are in general higher than in fish muscle.

The differences in cadmium concentrations were between spring- and autumn-caught hering from Utlängan was; autumn 0.053 < spring 0.072, and at Ängskärsklubb; autumn $0.036 \leq$ spring 0.041.

### 15.3.4 Comparison to threshold

In all herring and perch time series, cadmium concentrations are below the suggested target level based on the QSbiota of 0.16 μg/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.

## 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 A. et al., 2008). Cadmium concentrations of 0.8–4 ng/g dry weight (approximately 0.12–0.8 ng/g fresh weight) indicates that there is no immediate risk for top predators, since the suggested $QS_{biota\ sec.\ pois.}$ is set to 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.

**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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 495 | 32 | 81-13 | 0.11(-1.3,1.6) | 0.8529 | | 14 | 18 | 1.34 (1.12,1.61) |
| Harufjärden (3-5) | | 10 | 04-13 | 4.5(-3.9,14) | 0.2573 | | 13 | 15 | |
| Ängskärsklubb (3-5) | 488 | 32 | 81-13 | -0.82(-2.8,1.2) | 0.4087 | | 16 | 26 | .554 (.463,.664) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -0.17(-16,19) | 0.9313 | | 19 | 37 | |
| Landsort (3-5) | 469 | 33 | 81-13 | -0.36(-1.5,.81) | 0.5395 | | 12 | 14 | 1.19 (1.09,1.30) |
| Landsort (3-5) | | 10 | 04-13 | 0.41(-4.1,5.1) | 0.8204 | | 9 | 7.8 | |
| Utlängan (2-4) | 462 | 33 | 81-13 | 0.32(-.94,1.6) | 0.6153 | | 13 | 16 | .926 (.845,1.02) |
| Utlängan (2-4) | | 10 | 04-13 | -4(-9.6,1.9) | 0.1503 | | 10 | 10 | |
| Ängskärsklubb spring (2-6) | 138 | 17 | 96-12 | -2.1(-6.7,2.7) | 0.3646 | | 15 | 22 | 1.61 (1.20,2.16) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 0.01(-14,16) | 0.9476 | | 18 | 30 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | -2.3(-4.7,.047) | 0.0518 | | 11 | 11 | 1.55 (1.31,1.83) |
| Utlängan spring (2-4) | | 10 | 04-13 | 0.18(-7.0,7.9) | 0.9119 | | 12 | 13 | |
| Fladen (2-3) | 563 | 33 | 81-13 | -0.55(-1.4,.34) | 0.2167 | | 11 | 11 | .488 (.446,.534) |
| Fladen (2-3) | | 10 | 04-13 | 5(2.0,8.2) | 0.0048 | ++ | 7 | 4.9 | |
| Väderöarna | 304 | 18 | 95-13 | 5.4(3.6,7.3) | 0.0000 | | 10 | 8.6 | .636 (.556,.727) |
| Väderöarna | | 9 | 04-13 | 8.6(2.8,15) | 0.0096 | ++ | 10 | 8.9 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 180 | 18 | 95-13 | 1.9(-.89,4.8) | 0.1657 | | 12 | 14 | .355 (.279,.451) |
| Holmöarna | | 9 | 04-13 | 1.1(-5.7,8.2) | 0.7245 | | 11 | 12 | |
| Kvädöfjärden | 175 | 18 | 95-13 | 0.8(-1.6,3.3) | 0.506 | | 11 | 12 | .427 (.375,.485) |
| Kvädöfjärden | | 10 | 04-13 | 3.7(-1.5,9.1) | 0.1396 | | 10 | 8.8 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 355 | 28 | 81-13 | -3.1(-4.7,-1.6) | 0.0004 | --- | 14 | 20 | .025 (.022,.029) |
| SE Gotland (2-4) | | 10 | 04-13 | 8.8(-.93,19) | 0.0695 | | 13 | 17 | |
| Fladen (2-3) | 383 | 28 | 81-13 | -1.6(-3.7,.41) | 0.1083 | | 17 | 27 | .077 (.061,.096) |
| Fladen (2-3) | | 10 | 04-13 | 11(-2.4,26) | 0.0966 | | 16 | 25 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 98 | 11 | 95-07 | 10(3.1,18) | 0.0098 | ++ | 13 | 16 | 2.18 (1.54,3.10) |
| Holmöarna | | 10 | 98-07 | 10(.25,21) | 0.0441 | + | 14 | 18 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | 123 | 18 | 95-13 | 1.7(-3.1,6.8) | 0.4798 | | 16 | 26 | 1.97 (1.47,2.65) |
| Kvädöfjärden | | 10 | 04-13 | -0.85(-9.5,8.6) | 0.8151 | | 13 | 17 | |
| Fjällbacka | 124 | 18 | 95-13 | 2.2(-1.6,6.1) | 0.2333 | | 14 | 19 | .341 (.265,.440) |
| Fjällbacka | | 10 | 04-13 | 1(-9.9,13) | 0.8224 | | 15 | 22 | |

**Blue mussel**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Nidingen | 583 | 31 | 81-13 | -1.4(-2.4,-.42) | 0.0069 | -- | 11 | 12 | .180 (.166,.195) |
| Nidingen | | 10 | 04-13 | 1.8(-3.3,7.2) | 0.4449 | | 10 | 8.9 | |
| Fjällbacka | 591 | 32 | 81-13 | -1(-2.0,-.13) | 0.0261 | - | 11 | 11 | .190 (.175,.205) |
| Fjällbacka | | 10 | 04-13 | -5.2(-12,1.7) | 0.114 | | 11 | 12 | |
| Kvädöfjärden | 188 | 19 | 95-13 | -4.2(-6.0,-2.4) | 0.0002 | --- | 10 | 9.5 | .408 (.365,.456) |
| Kvädöfjärden | | 10 | 04-13 | -5.6(-11,-.50) | 0.0346 | - | 10 | 9.2 | |

**Guillemot egg**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 110 | 11 | 96-13 | -5.5(-11,.013) | 0.0488 | - | 15 | 23 | .004 (.002,.005) |
| Stora Karlsö | | 8 | 05-13 | -3.3(-20,16) | 0.6683 | | 17 | 27 | |

# 16  Nickel - Ni

Updated 15.02.23

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. $^{58}$Ni, $^{60}$Ni, $^{61}$Ni, $^{62}$Ni, and $^{64}$Ni. Seven radioactive isotopes of nickel are also known; however, only $^{63}$Ni 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 nickel 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 nickel 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 (WHO, 1991, Kasprzak et al., 2003). 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 (Denkhaus and Salnikow, 2002, Cempel and Nikel, 2006).

### 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 nickel presented in this report are analysed in liver and according to a study (Faxneld et al., 2015) where concentrations were compared between liver and whole-fish, no significant correlations were found. Thereby the available TL is not applicable on the results and thus not presented in the time-series for nickel.

## 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 Stockholm University. See chapter 6 section 6.1 for further details.

## 16.3 Results

### 16.3.1 Spatial variation
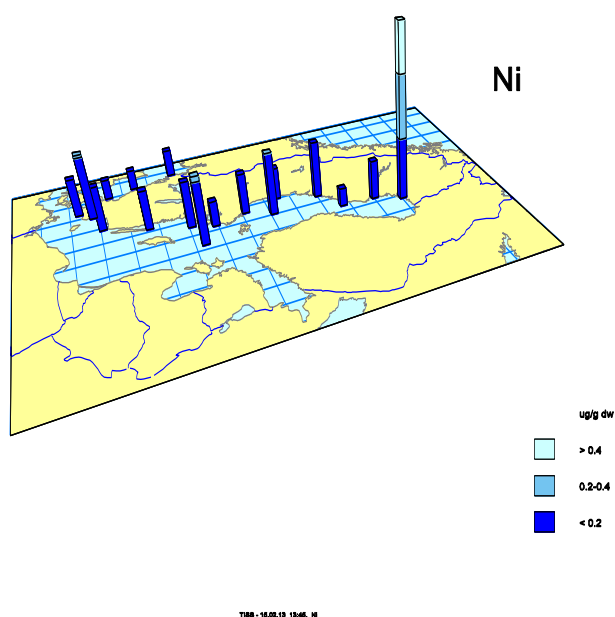


**Figure 16.1.** Spatial variation in nickel concentrations (µg/g dry weight) in herring liver.

Concentrations were generally lower on the Swedish West coast compared to 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 Skei (Knutzen and Skei, 1992) (table 16.1).

## 16.3.2  Temporal variation

The cod liver time series from Southeast of Gotland and Fladen (Fig. 16.4), show significant decreasing trends for the whole time period. Significant increasing trends for the last ten years were observed for herring at Harufjärden (Fig. 16.2).

### Ni, µg/g dry w., herring liver
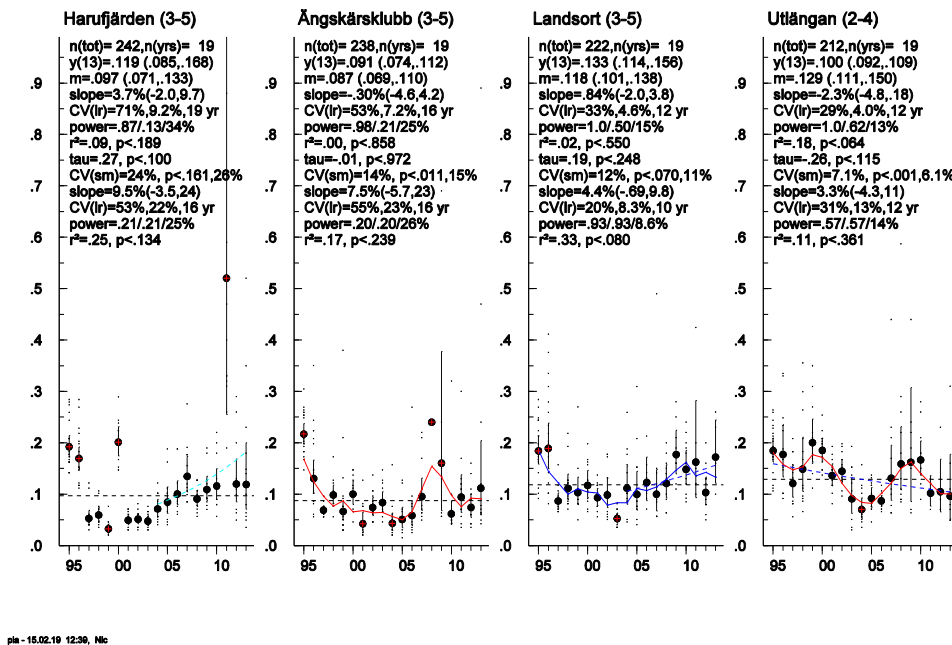


**Figure 16.2** (above) and **16.3** (below). Nickel concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1995) (above); and Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1996,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

### Ni, µg/g dry w., cod liver
Fat adjusted geometric means
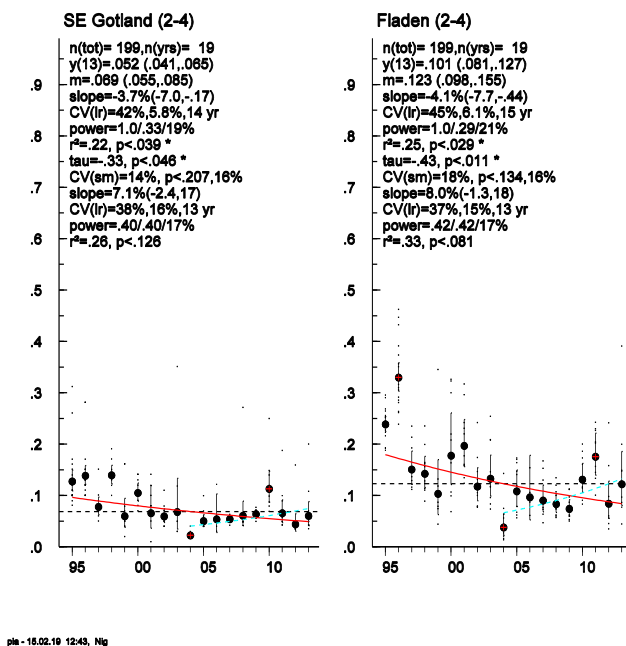


**Figure 16.4.** Nickel concentrations (µg/g dry weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1995).

## Ni, µg/g dry w., perch liver

### Holmöarna

n(tot)= 179,n(yrs)= 18
y(13)=.059 (.044,.078)
m=.082 (.060,.113)
slope=-4.6%(-9.6,.55)
CV(lr)=64%,9.3%,18 yr
power=.86/.15/31%
r²=.18, p<.073
tau=-.31, p<.075
CV(sm)=18%, p<.041,20%
slope=-1.9%(-14,12)
CV(lr)=55%,28%,16 yr
power=.14/.20/26%
r²=.01, p<.735

### Kvädöfjärden

n(tot)= 175,n(yrs)= 18
y(13)=.071 (.060,.085)
m=.085 (.065,.111)
slope=-4.2%(-8.3,.086)
CV(lr)=52%,7.7%,16 yr
power=.96/.22/24%
r²=.21, p<.052
tau=-.16, p<.344
CV(sm)=11%, p<.002,12%
slope=1.4%(-5.6,9.0)
CV(lr)=29%,12%,12 yr
power=.63/.63/13%
r²=.02, p<.665
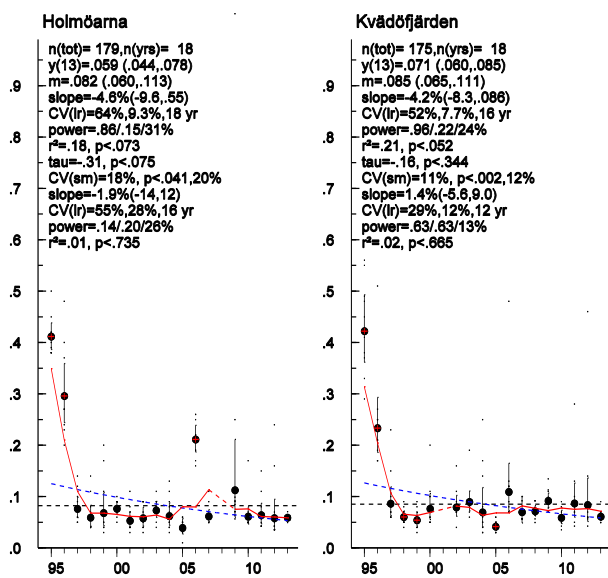
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**Figure 16.5.** Nickel concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

## Ni, µg/g dry w., eelpout liver

### Holmöarna

n(tot)= 98,n(yrs)= 11
y(07)=.177 (.135,.233)
m=.123 (.099,.154)
slope=2.8%(-3.6,9.7)
CV(lr)=34%,12%,13 yr
power=.64/.48/15%
r²=.09, p<.361
tau=.31, p<.186
CV(sm)=16%, p<.536,15%
slope=7.1%(-.16,15)
CV(lr)=28%,12%,11 yr
power=.65/.65/13%
r²=.39, p<.053

### Kvädöfjärden

n(tot)= 122,n(yrs)= 18
y(13)=.084 (.070,.102)
m=.112 (.094,.134)
slope=-3.8%(-6.5,-.93)
CV(lr)=31%,4.8%,12 yr
power=1.0/.55/14%
r²=.33, p<.012 *
tau=-.33, p<.053
CV(sm)=14%, p<.468,13%
slope=-3.7%(-9.3,2.3)
CV(lr)=24%,10%,11 yr
power=.80/.80/11%
r²=.20, p<.187

### Fjällbacka

n(tot)= 124,n(yrs)= 18
y(13)=.142 (.122,.165)
m=.148 (.124,.178)
slope=-1.8%(-5.1,1.5)
CV(lr)=37%,5.6%,13 yr
power=1.0/.41/17%
r²=.07, p<.258
tau=-.24, p<.171
CV(sm)=13%, p<.010,10%
slope=3.8%(-4.0,12)
CV(lr)=32%,13%,12 yr
power=.55/.55/14%
r²=.13, p<.308

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

## Ni, µg/g wet w., blue mussel softbody



**Kvädöfjärden**

n(tot)= 188,n(yrs)= 19
y(13)=.293 (.254,.337)
m=.319 (.286,.355)
slope=-1.7%(-3.5,.20)
CV(lr)=21%,3.0%,10 yr
power=1.0/.89/9.3%
r²=.17, p<.073
tau=-.32, p<.054
CV(sm)=21%, p<.879,9.9%
slope=-1.7%(-7.9,5.0)
CV(lr)=26%,11%,11 yr
power=.72/.72/12%
r²=.04, p<.576

**Fjällbacka**

n(tot)= 285,n(yrs)= 19
y(13)=.187 (.167,.210)
m=.226 (.196,.262)
slope=.85%(-1.8,3.6)
CV(lr)=31%,4.3%,12 yr
power=1.0/.55/14%
r²=.02, p<.522
tau=.041, p<.807
CV(sm)=13%, p<.004,8.0%
slope=-7.4%(-13,-1.7)
CV(lr)=24%,10%,11 yr
power=.79/.79/11%
r²=.52, p<.018 *

**Nidingen**

n(tot)= 294,n(yrs)= 19
y(13)=.225 (.196,.258)
m=.305 (.272,.343)
slope=-.08%(-2.3,2.1)
CV(lr)=25%,3.5%,11 yr
power=1.0/.76/11%
r²=.00, p<.896
tau=-.04, p<.807
CV(sm)=19%, p<.188,9.5%
slope=-.69%(-8.0,7.1)
CV(lr)=31%,13%,12 yr
power=.57/.57/14%
r²=.00, p<.819

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**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).

## Ni, µg/g dry w., guillemot egg



**Stora Karlsö**

n(tot)= 180,n(yrs)= 18
y(13)=.052 (.040,.067)
m=.061 (.047,.079)
slope=-2.9%(-7.7,2.1)
CV(lr)=56%,8.2%,16 yr
power=.94/.19/26%
r²=.09, p<.224
tau=-.32, p<.063
CV(sm)=15%, p<.045,18%
slope=9.0%(-1.7,21)
CV(lr)=42%,18%,14 yr
power=.32/.32/19%
r²=.32, p<.088
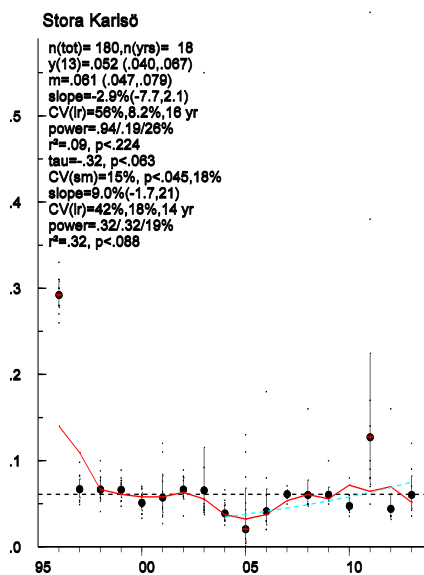
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**Figure 16.8.** Nickel concentrations (µg/g dry weight) in guillemot eggs Stora Karlsö (time series starting in 1996).

The number of years required in the herring series to detect an annual change of 10 % varies between 12–19 years. The power to detect an annual change of 10 % ranges from 0.85–1.0.

### 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 Skei (Knutzen and Skei, 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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 242 | 19 | 95-13 | 3.7(-2.0,9.7) | 0.1889 | | 19 | 34 | .119 (.085,.168) |
| Harufjärden (3-5) | | 10 | 04-13 | 9.5(-3.5,24) | 0.1344 | | 16 | 25 | |
| Ängskärsklubb (3-5) | 238 | 19 | 95-13 | -0.3(-4.6,4.2) | 0.858 | | 16 | 25 | .091 (.074,.112) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 7.5(-5.7,23) | 0.2389 | | 16 | 26 | |
| Landsort (3-5) | 222 | 19 | 95-13 | 0.84(-2.0,3.8) | 0.5495 | | 12 | 15 | .133 (.114,.156) |
| Landsort (3-5) | | 10 | 04-13 | 4.4(-.69,9.8) | 0.0799 | | 10 | 8.6 | |
| Utlängan (2-4) | 212 | 19 | 95-13 | -2.3(-4.8,.18) | 0.0644 | | 12 | 13 | .100 (.092,.109) |
| Utlängan (2-4) | | 10 | 04-13 | 3.3(-4.3,11) | 0.3607 | | 12 | 14 | |
| Ängskärsklubb spring (2-6) | 138 | 17 | 96-12 | 2.3(-1.5,6.2) | 0.2199 | | 13 | 17 | .150 (.124,.180) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 3.1(-6.4,14) | 0.4943 | | 14 | 18 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | 1.1(-1.0,3.3) | 0.2969 | | 10 | 9.7 | .156 (.141,.173) |
| Utlängan spring (2-4) | | 10 | 04-13 | 2.3(-2.2,7.1) | 0.2715 | | 9 | 7.7 | |
| Fladen (2-3) | 241 | 19 | 95-13 | -3.5(-7.5,.64) | 0.0882 | | 16 | 24 | .052 (.044,.061) |
| Fladen (2-3) | | 10 | 04-13 | 4.1(-4.7,14) | 0.3289 | | 13 | 16 | |
| Väderöarna | 304 | 18 | 95-13 | 1.4(-3.9,6.9) | 0.5977 | | 18 | 31 | .065 (.053,.080) |
| Väderöarna | | 9 | 04-13 | 21(6.1,38) | 0.011 | + | 16 | 24 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 179 | 18 | 95-13 | -4.6(-9.6,.55) | 0.0727 | | 18 | 31 | .059 (.044,.078) |
| Holmöarna | | 9 | 04-13 | -1.9(-14,12) | 0.7351 | | 16 | 26 | |
| Kvädöfjärden | 175 | 18 | 95-13 | -4.2(-8.3,.086) | 0.0518 | | 16 | 24 | .071 (.060,.085) |
| Kvädöfjärden | | 10 | 04-13 | 1.4(-5.6,9.0) | 0.6652 | | 12 | 13 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 199 | 19 | 95-13 | -3.7(-7.0,-.17) | 0.0393 | - | 14 | 19 | .052 (.041,.065) |
| SE Gotland (2-4) | | 10 | 04-13 | 7.1(-2.4,17) | 0.1258 | | 13 | 17 | |
| Fladen (2-3) | 199 | 19 | 95-13 | -4.1(-7.7,-.44) | 0.0293 | - | 15 | 21 | .101 (.081,.127) |
| Fladen (2-3) | | 10 | 04-13 | 8(-1.3,18) | 0.0813 | | 13 | 17 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 98 | 11 | 95-07 | 2.8(-3.6,9.7) | 0.3606 | | 13 | 15 | .177 (.135,.233) |
| Holmöarna | | 10 | 98-07 | 7.1(-.16,15) | 0.0526 | | 11 | 13 | |
| Kvädöfjärden | 122 | 18 | 95-13 | -3.8(-6.5,-.93) | 0.0125 | - | 12 | 14 | .084 (.070,.102) |
| Kvädöfjärden | | 10 | 04-13 | -3.7(-9.3,2.3) | 0.1869 | | 11 | 11 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Fjällbacka | 124 | 18 | 95-13 | -1.8(-5.1,1.5) | 0.2575 | | 13 | 17 | .142 (.122,.165) |
| Fjällbacka | | 10 | 04-13 | 3.8(-4.0,12) | 0.3077 | | 12 | 14 | |

**Blue mussel**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Nidingen | 294 | 19 | 95-13 | -0.08(-2.3,2.1) | 0.8957 | | 11 | 11 | .225 (.196,.258) |
| Nidingen | | 10 | 04-13 | -0.69(-8.0,7.1) | 0.8188 | | 12 | 14 | |
| Fjällbacka | 285 | 19 | 95-13 | 0.85(-1.8,3.6) | 0.5218 | | 12 | 14 | .187 (.167,.210) |
| Fjällbacka | | 10 | 04-13 | -7.4(-13,-1.7) | 0.0182 | - | 11 | 11 | |
| Kvädöfjärden | 188 | 19 | 95-13 | -1.7(-3.5,.20) | 0.0733 | | 10 | 9.3 | .293 (.254,.337) |
| Kvädöfjärden | | 10 | 04-13 | -1.7(-7.9,5.0) | 0.5763 | | 11 | 12 | |

**Guillemot egg**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 180 | 18 | 96-13 | -2.9(-7.7,2.1) | 0.2239 | | 16 | 26 | .052 (.040,.067) |
| Stora Karlsö | | 10 | 04-13 | 9(-1.7,21) | 0.088 | | 14 | 19 | |

# 17  Chromium - Cr

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

## 17.1  Introduction

The method for chromium analysis was changed in 2004. The new method gives lower concentrations in general. The level of quantification is also lower with the new method.

### 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 in the enivronment. Rocks or sediments present a wide range of chromium concentration whereas natural water contain quite small amounts (Richard and Bourg, 1991). Most chromium is produced from chromite ($FeCr_2O_4$). 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: $^{50}Cr$, $^{52}Cr$, $^{53}Cr$, $^{54}Cr$ and seven known radioactive isotopes (Eisler, 1986). Oxidation states of chromium can vary from chromium(0) to chromium(VI), in which chromium(III) and chromium(VI) are the most stable and important species for natural aquatic systems (Richard and Bourg, 1991). Aqueous chromium is present as the $Cr^{3+}$ cationunder reducing environments and pH lower than 3.6. In waters with a pH of 4–10, chromium exists as $CrOH^{2+}$, $Cr(OH)_2^+$ and $Cr(OH)_3$ with an increasing number of hydroxides counter ions with increasing pH. chromium(VI) is only present in oxidizing conditions and at pH over 10, as $Cr(OH)_4^-$ (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 rather than through weathering processes (Eisler, 1986). Chromium alloy, metal production, coal combustion, municipal incinerators, cement production, and cooling towers are responsible for major atmospheric emissions of chromium (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 activeties (i.e. electroplating, metal finishing industries and waste water treatment plants) and, of subordinate importance, by 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, chromium(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 chromium are also important factors. In general, chromium(III) is less toxic than chromium(VI) due to the latter's high oxidizing potential and its easier membrane permeability (Eisler, 1986, Richard and Bourg, 1991). For sensitive aquatic biota, $LC_{50}$ of chromium (III) were from 2000 to 3200 ppb while chromium (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 acids and nucleic acids (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 chromium.

## 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 Stockholm University. See chapter 6 section 6.1 for further details.

## 17.3 Results

### 17.3.1 Spatial variation

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, which also had the highest concentration in 2011–2013) (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 Skei (Knutzen and Skei, 1992).
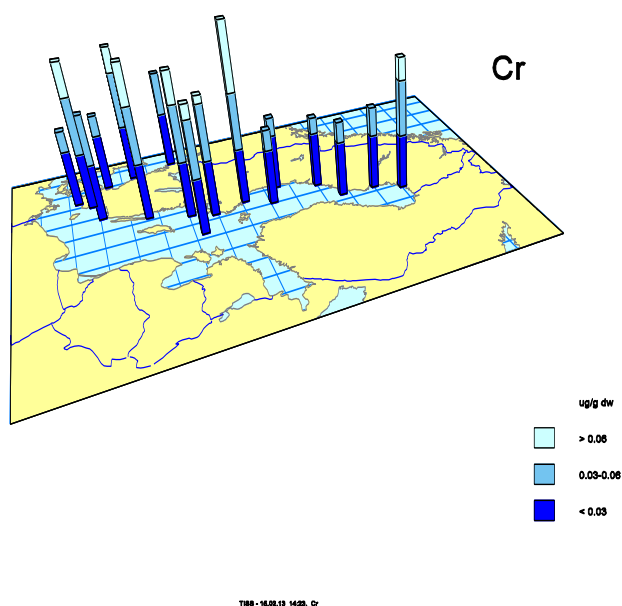
**Figure 17.1.** Spatial variation in chromium concentrations (µg/g dry weight) in herring liver.

## 17.3.2 Temporal variation

Chromium decreased significantly in all herring time series (Fig. 17.2 and 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 15–25 years for herring. The power to detect an annual change of 10 % ranges between 0.41–0.95.

## Cr, µg/g dry w., herring liver

**Harufjärden (3-5)**

n(tot)= 242,n(yrs)= 19
y(13)=.069 (.059,.081)
m=.072 (.050,.104)
slope=-8.6%(-13,-3.9)
CV(lr)=63%,8.3%,17 yr
power=.93/.16/30%
r²=.45, p<.002 *
tau=-.49, p<.004 *
CV(sm)=9.7%, p<.001,11%
slope=9.1%(-2.8,22)
CV(lr)=48%,20%,15 yr
power=.26/.26/22%
r²=.28, p<.117

**Ängskärsklubb (3-5)**

n(tot)= 238,n(yrs)= 19
y(13)=.100 (.077,.128)
m=.055 (.034,.090)
slope=-8.4%(-15,-.72)
CV(lr)=113%,13%,23 yr
power=.52/.07/55%
r²=.24, p<.033 *
tau=-.36, p<.033 *
CV(sm)=14%, p<.001,18%
slope=27%(12,43)
CV(lr)=50%,21%,16 yr
power=.23/.23/23%
r²=.72, p<.002 *

**Landsort (3-5)**

n(tot)= 222,n(yrs)= 19
y(13)=.059 (.040,.086)
m=.053 (.032,.089)
slope=-8.2%(-16,.038)
CV(lr)=126%,14%,24 yr
power=.46/.06/62%
r²=.21, p<.049 *
tau=-.37, p<.028 *
CV(sm)=21%, p<.005,29%
slope=18%(.27,39)
CV(lr)=72%,30%,19 yr
power=.13/.13/35%
r²=.41, p<.046 *

**Utlängan (2-4)**

n(tot)= 212,n(yrs)= 19
y(13)=.055 (.041,.075)
m=.056 (.034,.091)
slope=-10%(-17,-3.2)
CV(lr)=102%,12%,22 yr
power=.60/.08/50%
r²=.35, p<.007 *
tau=-.42, p<.013 *
CV(sm)=18%, p<.002,23%
slope=14%(.58,29)
CV(lr)=52%,22%,16 yr
power=.22/.22/24%
r²=.42, p<.041 *



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

## Cr, µg/g dry w., herring liver

**Väderöarna**

n(tot)= 304,n(yrs)= 18
y(13)=.049 (.040,.061)
m=.057 (.035,.094)
slope=-11%(-17,-4.9)
CV(lr)=85%,12%,20 yr
power=.65/.10/41%
r²=.47, p<.002 *
tau=-.58, p<.001 *
CV(sm)=12%, p<.001,15%
slope=15%(-2.3,34)
CV(lr)=64%,33%,18 yr
power=.11/.16/30%
r²=.37, p<.082

**Fladen (2-3)**

n(tot)= 241,n(yrs)= 19
y(13)=.063 (.047,.086)
m=.044 (.025,.079)
slope=-11%(-19,-2.8)
CV(lr)=136%,15%,25 yr
power=.41/.06/67%
r²=.31, p<.012 *
tau=-.43, p<.011 *
CV(sm)=16%, p<.001,22%
slope=24%(6.0,44)
CV(lr)=66%,27%,18 yr
power=.15/.15/32%
r²=.56, p<.013 *

**Ängskärsklubb, spring**

n(tot)= 138,n(yrs)= 17
y(12)=.046 (.039,.054)
m=.087 (.057,.133)
slope=-13%(-17,-8.3)
CV(lr)=49%,8.0%,15 yr
power=.95/.24/23%
r²=.70, p<.001 *
tau=-.72, p<.001 *
CV(sm)=11%, p<.002,11%
slope=-15%(-27,-.80)
CV(lr)=66%,27%,18 yr
power=.15/.15/31%
r²=.42, p<.040 *

**Utlängan, spring**

n(tot)= 130,n(yrs)= 18
y(13)=.055 (.042,.072)
m=.069 (.045,.106)
slope=-11%(-16,-5.9)
CV(lr)=62%,9.9%,17 yr
power=.81/.16/29%
r²=.57, p<.001 *
tau=-.63, p<.001 *
CV(sm)=15%, p<.024,18%
slope=-1.7%(-17,17)
CV(lr)=75%,31%,19 yr
power=.12/.12/36%
r²=.00, p<.809



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**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).

## Cr, ug/g dry w., perch liver

**Holmöarna**

n(tot)= 180,n(yrs)= 18
y(13)=.056 (.044,.072)
m=.069 (.044,.110)
slope=-10%(-16,-4.5)
CV(lr)=81%,11%,20 yr
power=.69/.11/39%
r²=.46, p<.002 *
tau=-.59, p<.001 *
CV(sm)=15%, p<.001,17%
slope=10%(-7.8,32)
CV(lr)=78%,40%,20 yr
power=.08/.11/38%
r²=.19, p<.237

**Kvädöfjärden**

n(tot)= 175,n(yrs)= 18
y(13)=.055 (.035,.086)
m=.077 (.047,.127)
slope=-11%(-17,-4.7)
CV(lr)=90%,12%,21 yr
power=.60/.09/44%
r²=.45, p<.002 *
tau=-.40, p<.021 *
CV(sm)=28%, p<.232,33%
slope=-3.9%(-21,17)
CV(lr)=53%,36%,21 yr
power=.09/.09/43%
r²=.02, p<.652
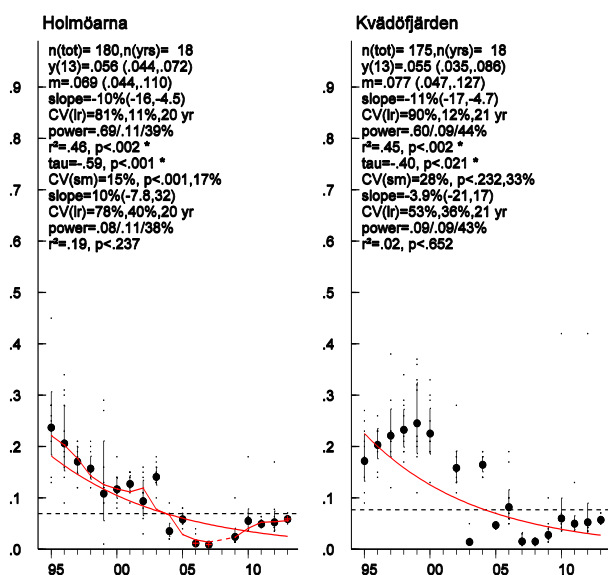


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**Fig. 17.4.** Chromium concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

## Cr, ug/g dry w., cod liver

**SE Gotland (2-4)**

n(tot)= 199,n(yrs)= 19
y(13)=.045 (.031,.064)
m=.049 (.031,.076)
slope=-8.2%(-14,-1.4)
CV(lr)=95%,12%,21 yr
power=.65/.08/46%
r²=.27, p<.020 *
tau=-.35, p<.039 *
CV(sm)=20%, p<.022,27%
slope=3.4%(-12,22)
CV(lr)=73%,30%,19 yr
power=.13/.13/35%
r²=.02, p<.659

**Fladen (2-4)**

n(tot)= 198,n(yrs)= 19
y(13)=.042 (.032,.054)
m=.065 (.039,.110)
slope=-13%(-19,-7.0)
CV(lr)=87%,11%,21 yr
power=.71/.09/42%
r²=.53, p<.001 *
tau=-.51, p<.002 *
CV(sm)=16%, p<.002,19%
slope=3.2%(-12,21)
CV(lr)=69%,29%,18 yr
power=.14/.14/33%
r²=.02, p<.660
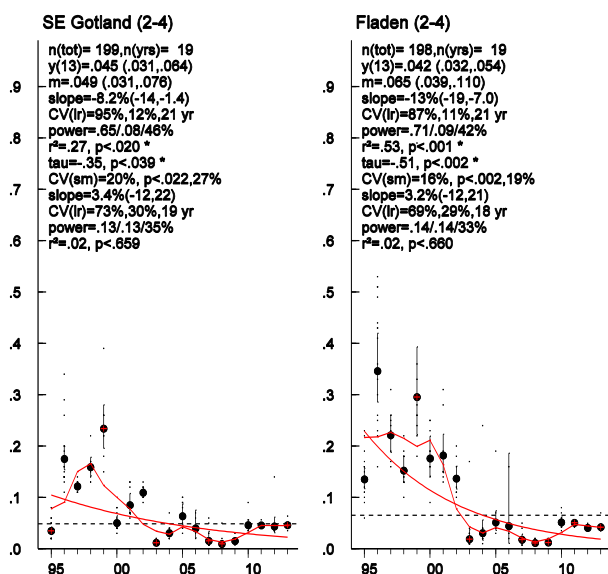


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**Fig. 17.5.** Chromium concentrations (µg/g dry weight) in cod liver from Southeast of Gotland and Fladen (time series starting in 1995).
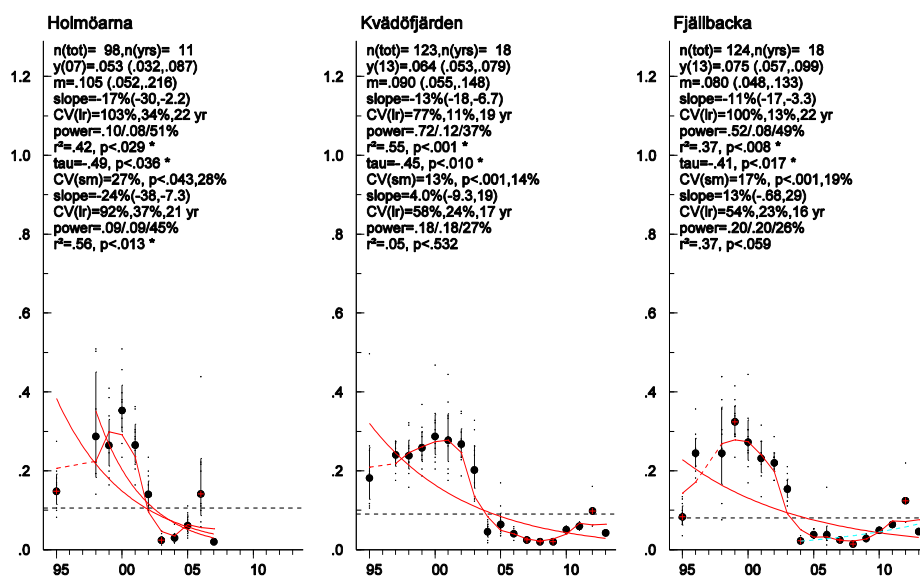
## Cr, µg/g dry w., eelpout liver



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

## Cr, µg/g dry w., eelpout liver
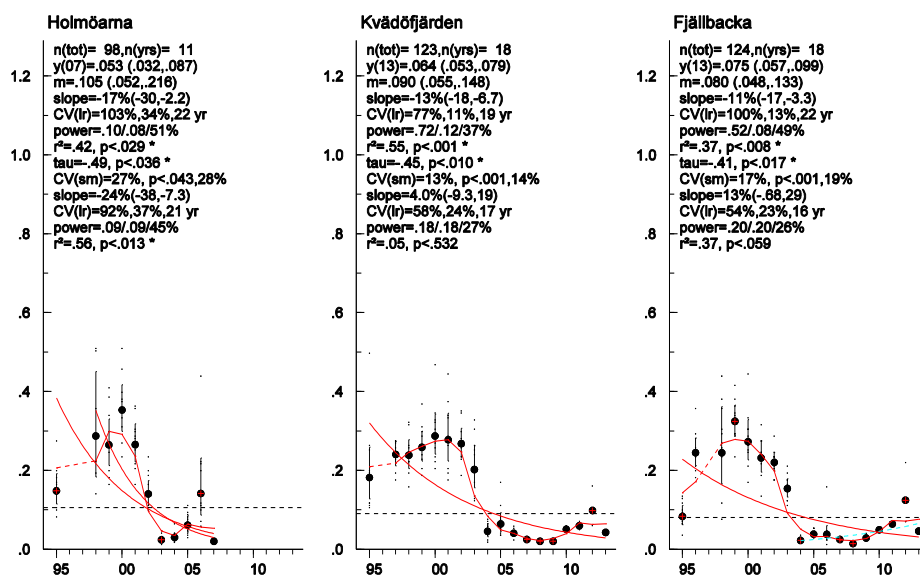


**Figure 17.7.** Chromium concentrations (µg/g wet weight) in blue mussel soft body from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1995).

Cr, µg/g dry w., guillemot egg

Stora Karlsö

n(tot)= 180,n(yrs)= 18
y(13)=.066 (.051,.086)
m=.028 (.018,.043)
slope=5.9%(-2.4,15)
CV(lr)=103%,14%,22 yr
power=.51/.08/50%
r²=.12, p<.152
tau=.37, p<.031 *
CV(sm)=12%, p<.001,19%
slope=35%(18,55)
CV(lr)=57%,24%,17 yr
power=.19/.19/27%
r²=.77, p<.001 *

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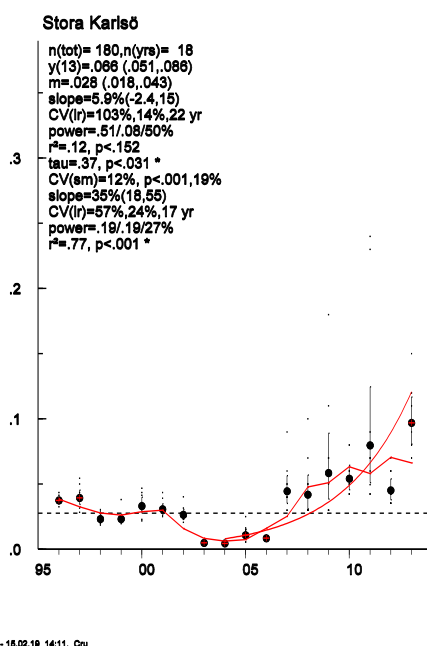
**Figure 17.8.** Chromium concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996)

## 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 fish since the start 1995. However for the blue mussels and the ten most recent years for guillemot eggs and herring from Ängskärsklubb, Landsort, Utlängan and Fladen the trends 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 chromium 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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 242 | 19 | 95-13 | -8.6(-13,-3.9) | 0.0017 | -- | 17 | 30 | .069 (.059,.081) |
| Harufjärden (3-5) | | 10 | 04-13 | 9.1(-2.8,22) | 0.1169 | | 15 | 22 | |
| Ängskärsklubb (3-5) | 238 | 19 | 95-13 | -8.4(-15,-.72) | 0.0328 | - | 23 | 55 | .100 (.077,.128) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 27(12,43) | 0.002 | ++ | 16 | 23 | |
| Landsort (3-5) | 222 | 19 | 95-13 | -8.2(-16,.038) | 0.0487 | - | 24 | 62 | .059 (.040,.086) |
| Landsort (3-5) | | 10 | 04-13 | 18(.27,39) | 0.0457 | + | 19 | 35 | |
| Utlängan (2-4) | 212 | 19 | 95-13 | -10(-17,-3.2) | 0.0074 | -- | 22 | 50 | .055 (.041,.075) |
| Utlängan (2-4) | | 10 | 04-13 | 14(.58,29) | 0.041 | + | 16 | 24 | |
| Ängskärsklubb spring (2- | 138 | 17 | 96-12 | -13(-17,-8.3) | 0.0000 | --- | 15 | 23 | .046 (.039,.054) |
| Ängskärsklubb spring (2- | | 10 | 03-12 | -15(-27,-.80) | 0.0401 | - | 18 | 31 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | -11(-16,-5.9) | 0.0005 | --- | 17 | 29 | .055 (.042,.072) |
| Utlängan spring (2-4) | | 10 | 04-13 | -1.7(-17,17) | 0.8093 | | 19 | 36 | |
| Fladen (2-3) | 241 | 19 | 95-13 | -11(-19,-2.8) | 0.0125 | - | 25 | 67 | .063 (.047,.086) |
| Fladen (2-3) | | 10 | 04-13 | 24(6.0,44) | 0.0127 | + | 18 | 32 | |
| Väderöarna | 304 | 18 | 95-13 | -11(-17,-4.9) | 0.0018 | -- | 20 | 41 | .049 (.040,.061) |
| Väderöarna | | 9 | 04-13 | 15(-2.3,34) | 0.0821 | | 18 | 30 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 180 | 18 | 95-13 | -10(-16,-4.5) | 0.0022 | -- | 20 | 39 | .056 (.044,.072) |
| Holmöarna | | 9 | 04-13 | 10(-7.8,32) | 0.2365 | | 20 | 38 | |
| Kvädöfjärden | 175 | 18 | 95-13 | -11(-17,-4.7) | 0.0025 | -- | 21 | 44 | .055 (.035,.086) |
| Kvädöfjärden | | 10 | 04-13 | -3.9(-21,17) | 0.652 | | 21 | 43 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 199 | 19 | 95-13 | -8.2(-14,-1.4) | 0.0203 | - | 21 | 46 | .045 (.031,.064) |
| SE Gotland (2-4) | | 10 | 04-13 | 3.4(-12,22) | 0.6586 | | 19 | 35 | |
| Fladen (2-3) | 198 | 19 | 95-13 | -13(-19,-7.0) | 0.0004 | --- | 21 | 42 | .042 (.032,.054) |
| Fladen (2-3) | | 10 | 04-13 | 3.2(-12,21) | 0.6602 | | 18 | 33 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 98 | 11 | 95-07 | -17(-30,-2.2) | 0.0295 | - | 22 | 51 | .053 (.032,.087) |
| Holmöarna | | 10 | 98-07 | -24(-38,-7.3) | 0.0127 | - | 21 | 45 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -13(-18,-6.7) | 0.0005 | --- | 19 | 37 | .064 (.053,.079) |
| Kvädöfjärden | | 10 | 04-13 | 4(-9.3,19) | 0.5316 | | 17 | 27 | |
| Fjällbacka | 124 | 18 | 95-13 | -11(-17,-3.3) | 0.0076 | -- | 22 | 49 | .075 (.057,.099) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Fjällbacka | | 10 | 04-13 | 13(-.68,29) | 0.0586 | | 16 | 26 | |

**Blue mussel**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Nidingen | 294 | 19 | 95-13 | -3.8(-9.2,1.9) | 0.1693 | | 19 | 35 | .069 (.054,.087) |
| Nidingen | | 10 | 04-13 | 6.1(-8.6,23) | 0.3903 | | 18 | 31 | |
| Fjällbacka | 285 | 19 | 95-13 | 8(4.2,12) | 0.0003 | +++ | 14 | 19 | .151 (.130,.175) |
| Fjällbacka | | 10 | 04-13 | 3.7(-7.3,16) | 0.4774 | | 15 | 21 | |
| Kvädöfjärden | 188 | 19 | 95-13 | 5(2.5,7.5) | 0.0006 | +++ | 11 | 12 | .227 (.210,.246) |
| Kvädöfjärden | | 10 | 04-13 | 7.4(2.1,13) | 0.0121 | + | 10 | 8.9 | |

**Guillemot egg**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 180 | 18 | 96-13 | 5.9(-2.4,15) | 0.1517 | | 22 | 50 | .066 (.051,.086) |
| Stora Karlsö | | 10 | 04-13 | 35(18,55) | 0.001 | +++ | 17 | 27 | |

# 18  Copper - Cu

Updated 15.02.23

## 18.1  Introduction

### 18.1.1  Usage, Production and Sources

Copper is a nutritionally essential metal, and its concentration is regulated by homeostatic mechanisms. Free copper is effectively controlled by metallothionein synthesis (Da Silva and 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 metallic form, copper is used in for example, plumbing, building wire, telecommunications, automotive electrical wiring and air conditioning systems (Dorsey et al., 2004). Copper compounds are used to create alloys such as brass and bronze. Other anthropogenic sources include road run off (Rice et al., 2002) and mining of copper ore. Copper compounds are commonly used in agriculture as fungicides, as well as in wood, leather and fabric preservatives, or for water treatment (Dorsey et al., 2004).

### 18.1.2  Conventions, Aims and Restrictions

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

### 18.1.3  Target Levels

No national target level for biota concerning copper is agreed upon.

Average copper concentration 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 Skei (Knutzen and Skei, 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 Stockholm University. See chapter 6 section 6.1 for further details.

## 18.3  Results

### 18.3.1  Spatial variation
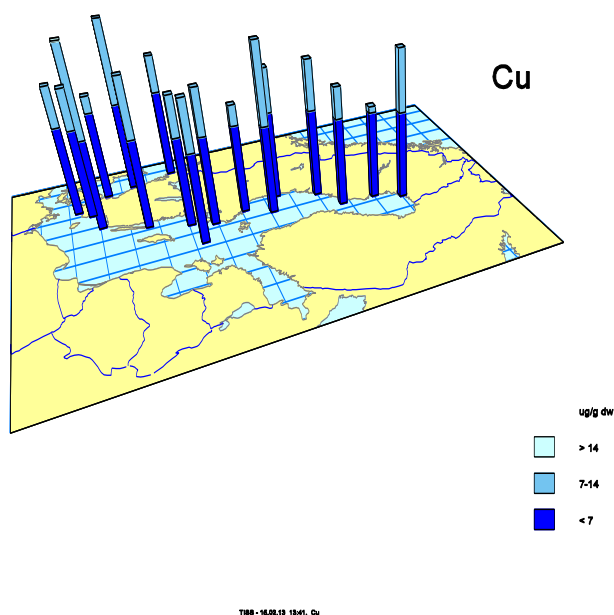
**Figure 18.1.** Spatial variation in copper concentrations (µg/g dry weight) in herring liver.

No general differences in mean copper concentrations were found in herring along the Swedish coast. The highest concentrations (around 14 ug/g dw) were found at the Bothnian sea offshore site, Utlängan, and Fladen (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 Skei (Knutzen and Skei, 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 and Landsort (Fig. 18.3). No other general trend was seen for copper concentration in fish. However, for blue mussels all stations showed significantly decreasing trends (Fig. 18.7). The number of years required to detect an annual change of 10% varied between 7–13 years for the herring time series at a power of 80%.

# Cu, µg/g dry w., herring liver
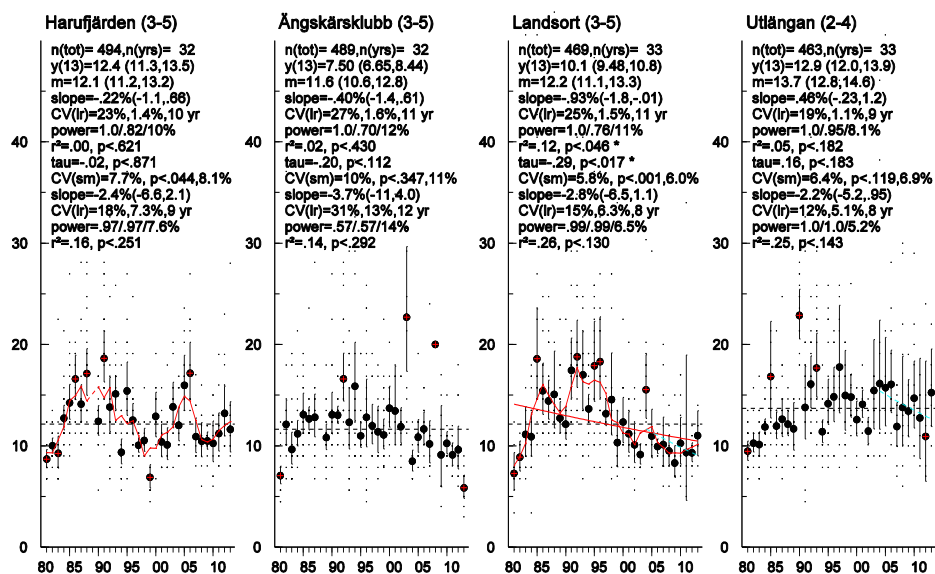


**Figure 18.2.** Copper concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981).

# Cu, µg/g dry w., herring liver
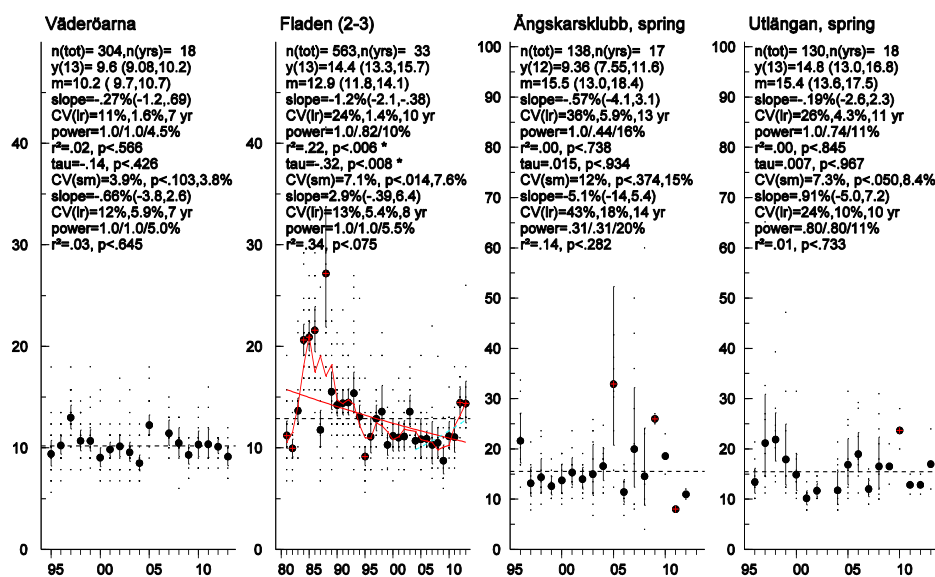


**Figure 18.3.** Copper concentrations (µg/g dry weight) in herring liver from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1996, 1996, 1981 and 1995 respectively).

## Cu, µg/g dry w., perch liver

**Holmöarna**

```
n(tot)= 180,n(yrs)= 18
y(13)=9.6 (8.19,11.1)
m=8.88 (7.89,10.0)
slope=1.5%(-.59,3.6)
CV(lr)=23%,3.5%,10 yr
power=1.0/.83/10%
r²=.12, p<.148
tau=.31, p<.075
CV(sm)=11%, p<.776,10%
slope=.27%(-2.9,3.6)
CV(lr)=12%,6.2%,8 yr
power=1.0/1.0/5.3%
r²=.00, p<.830
```

**Kvädöfjärden**

```
n(tot)= 175,n(yrs)= 18
y(13)=9.00 (8.04,10.1)
m=9.32 (8.45,10.3)
slope=.11%(-1.7,1.9)
CV(lr)=21%,3.1%,10 yr
power=1.0/.91/8.9%
r²=.00, p<.870
tau=.046, p<.791
CV(sm)=8.2%, p<.178,7.6%
slope=2.5%(-1.8,7.0)
CV(lr)=17%,7.1%,9 yr
power=.98/.98/7.3%
r²=.18, p<.219
```
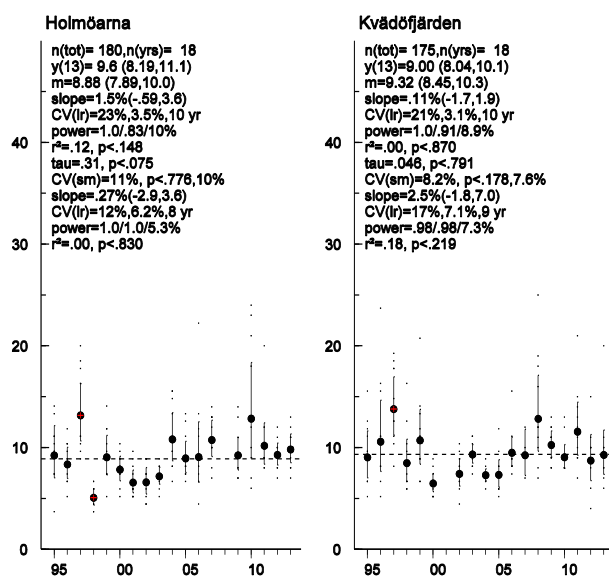


**Figure 18.4.** Copper concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

## Cu, ug/g dry w., cod liver

**SE Gotland (2-4)**

```
n(tot)= 458,n(yrs)= 33
y(13)=12.1 (10.5,14.0)
m=12.3 (11.1,13.7)
slope=-.19%(-1.3,.94)
CV(lr)=31%,1.8%,12 yr
power=1.0/.56/14%
r²=.00, p<.732
tau=-.04, p<.757
CV(sm)=13%, p<.725,14%
slope=2.2%(-6.6,12)
CV(lr)=36%,15%,13 yr
power=.43/.43/16%
r²=.03, p<.603
```

**Fladen (2-4)**

```
n(tot)= 523,n(yrs)= 35
y(13)=11.3 (9.14,13.9)
m=12.4 (10.5,14.6)
slope=-1.3%(-3.0,.34)
CV(lr)=48%,2.7%,15 yr
power=1.0/.26/22%
r²=.07, p<.110
tau=-.14, p<.252
CV(sm)=18%, p<.551,20%
slope=9.1%(.33,19)
CV(lr)=34%,14%,13 yr
power=.48/.48/15%
r²=.42, p<.042 *
```
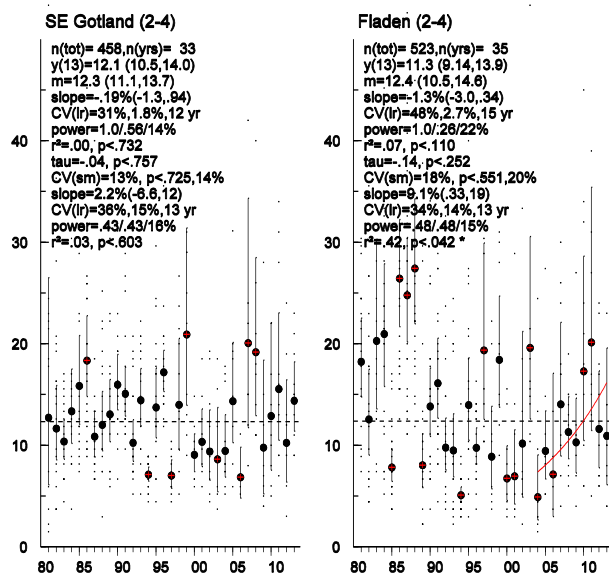


**Fig. 18.5.** Copper concentrations (µg/g dry weight) in cod liver from Southeast of Gotland and Fladen (time series starting in 1980).

## Cu, µg/g dry w., eelpout liver

**Holmöarna**

n(tot)= 98,n(yrs)= 11
y(07)=17.1 (13.7,21.5)
m=12.6 (10.1,15.6)
slope=2.6%(-3.7,9.3)
CV(lr)=33%,12%,12 yr
power=.66/.50/15%
r²=.08, p<.392
tau=.13, p<.586
CV(sm)=11%, p<.158,12%
slope=6.2%(-1.4,14)
CV(lr)=30%,12%,12 yr
power=.60/.60/13%
r²=.30, p<.096

**Kvädöfjärden**

n(tot)= 123,n(yrs)= 18
y(13)=28.1 (25.7,30.8)
m=22.6 (20.1,25.4)
slope=-1.1%(-3.3,1.1)
CV(lr)=24%,3.6%,10 yr
power=1.0/.81/10%
r²=.06, p<.310
tau=-.23, p<.185
CV(sm)=4.6%, p<.003,6.0%
slope=-1.6%(-9.0,6.4)
CV(lr)=32%,13%,12 yr
power=.54/.54/14%
r²=.02, p<.650

**Fjällbacka**

n(tot)= 124,n(yrs)= 18
y(13)=28.6 (22.4,36.4)
m=35.5 (29.6,42.7)
slope=1.4%(-2.1,5.0)
CV(lr)=38%,5.8%,14 yr
power=1.0/.38/18%
r²=.04, p<.413
tau=.12, p<.472
CV(sm)=11%, p<.049,17%
slope=-4.6%(-14,5.4)
CV(lr)=41%,17%,14 yr
power=.34/.34/19%
r²=.13, p<.308



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

## Cu, µg/g wet w., blue mussel softbody

**Kvädöfjärden**

n(tot)= 188,n(yrs)= 19
y(13)=1.01 (.946,1.08)
m=1.22 (1.11,1.34)
slope=-2.4%(-3.6,-1.1)
CV(lr)=14%,2.0%,8 yr
power=1.0/1.0/6.1%
r²=.49, p<.001 *
tau=-.50, p<.003 *
CV(sm)=58%, p<.047,4.7%
slope=-4.5%(-7.5,-1.4)
CV(lr)=13%,5.2%,8 yr
power=1.0/1.0/5.3%
r²=.58, p<.010 *

**Fjällbacka**

n(tot)= 591,n(yrs)= 32
y(13)=.617 (.534,.712)
m=1.02 (.873,1.19)
slope=-2.8%(-4.0,-1.6)
CV(lr)=34%,2.0%,13 yr
power=1.0/.49/15%
r²=.43, p<.001 *
tau=-.56, p<.001 *
CV(sm)=1722%, p<.257,13%
slope=-1.5%(-13,11)
CV(lr)=50%,21%,16 yr
power=.24/.24/23%
r²=.01, p<.765

**Nidingen**

n(tot)= 583,n(yrs)= 32
y(13)=.761 (.696,.833)
m=1.06 (.943,1.19)
slope=-2.6%(-3.3,-1.8)
CV(lr)=20%,1.3%,10 yr
power=1.0/.92/8.7%
r²=.61, p<.001 *
tau=-.65, p<.001 *
CV(sm)=331%, p<.290,8.0%
slope=-1.6%(-6.9,3.9)
CV(lr)=22%,9.1%,10 yr
power=.87/.87/9.5%
r²=.05, p<.516



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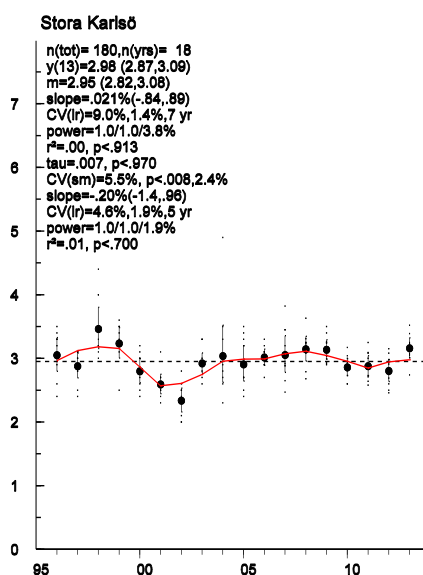
**Figure 18.8.** Copper concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996).

### 18.3.3 Species differences

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

Holmöarna: Eelpout (17.1) > Perch (9.6)
Kvädöfjärden: Eelpout (28.1) > Blue mussel (10.1) – Perch (9.00)
Fladen/Nidingen: Herring (14.4) ≥ Cod (11.3) >Blue mussel (7.61)
Väderöarna/Fjällbacka: Eelpout (28.6) > Herring (9.6) > Blue mussel (6.17)

The concentrations in blue mussels are in general lower than corresponding fish liver samples at all stations.

The differences in copper concentrations were between spring- and autumn-caught hering from Utlängan was; autumn 12.9 – spring 14.8, and at Ängskärsklubb; autumn 7.50 – spring 9.36.

### 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 (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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 494 | 32 | 81-13 | -0.22(-1.1,.66) | 0.6213 | | 10 | 10 | 12.4 (11.3,13.5) |
| Harufjärden (3-5) | | 10 | 04-13 | -2.4(-6.6,2.1) | 0.2513 | | 9 | 7.6 | |
| Ängskärsklubb (3-5) | 489 | 32 | 81-13 | -0.4(-1.4,.61) | 0.4297 | | 11 | 12 | 7.50 (6.65,8.44) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -3.7(-11,4.0) | 0.2923 | | 12 | 14 | |
| Landsort (3-5) | 469 | 33 | 81-13 | -0.93(-1.8,-.01) | 0.046 | - | 11 | 11 | 10.1 (9.48,10.8) |
| Landsort (3-5) | | 10 | 04-13 | -2.8(-6.5,1.1) | 0.13 | | 8 | 6.5 | |
| Utlängan (2-4) | 463 | 33 | 81-13 | 0.46(-.23,1.2) | 0.1816 | | 9 | 8.1 | 12.9 (12.0,13.9) |
| Utlängan (2-4) | | 10 | 04-13 | -2.2(-5.2,.95) | 0.1429 | | 8 | 5.2 | |
| Ängskärsklubb spring (2-6) | 138 | 17 | 96-12 | -0.57(-4.1,3.1) | 0.7376 | | 13 | 16 | 9.36 (7.55,11.6) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -5.1(-14,5.4) | 0.2819 | | 14 | 20 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | -0.19(-2.6,2.3) | 0.8449 | | 11 | 11 | 14.8 (13.0,16.8) |
| Utlängan spring (2-4) | | 10 | 04-13 | 0.91(-5.0,7.2) | 0.7329 | | 10 | 11 | |
| Fladen (2-3) | 563 | 33 | 81-13 | -1.2(-2.1,-.38) | 0.0063 | -- | 10 | 10 | 14.4 (13.3,15.7) |
| Fladen (2-3) | | 10 | 04-13 | 2.9(-.39,6.4) | 0.0747 | | 8 | 5.5 | |
| Väderöarna | 304 | 18 | 95-13 | -0.27(-1.2,.69) | 0.5662 | | 7 | 4.5 | 9.6 (9.08,10.2) |
| Väderöarna | | 9 | 04-13 | -0.66(-3.8,2.6) | 0.6448 | | 7 | 5 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 180 | 18 | 95-13 | 1.5(-.59,3.6) | 0.1478 | | 10 | 10 | 9.6 (8.19,11.1) |
| Holmöarna | | 9 | 04-13 | 0.27(-2.9,3.6) | 0.83 | | 8 | 5.3 | |
| Kvädöfjärden | 175 | 18 | 95-13 | 0.11(-1.7,1.9) | 0.8695 | | 10 | 8.9 | 9.00 (8.04,10.1) |
| Kvädöfjärden | | 10 | 04-13 | 2.5(-1.8,7.0) | 0.2194 | | 9 | 7.3 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 458 | 33 | 81-13 | -0.19(-1.3,.94) | 0.7317 | | 12 | 14 | 12.1 (10.5,14.0) |
| SE Gotland (2-4) | | 10 | 04-13 | 2.2(-6.6,12) | 0.6029 | | 13 | 16 | |
| Fladen (2-3) | 523 | 33 | 81-13 | -1.3(-3.0,.34) | 0.11 | | 15 | 22 | 11.3 (9.14,13.9) |
| Fladen (2-3) | | 10 | 04-13 | 9.1(.33,19) | 0.0421 | + | 13 | 15 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 98 | 11 | 95-07 | 2.6(-3.7,9.3) | 0.3915 | | 12 | 15 | 17.1 (13.7,21.5) |
| Holmöarna | | 10 | 98-07 | 6.2(-1.4,14) | 0.0958 | | 12 | 13 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -1.1(-3.3,1.1) | 0.3099 | | 10 | 10 | 28.1 (25.7,30.8) |
| Kvädöfjärden | | 10 | 04-13 | -1.6(-9.0,6.4) | 0.65 | | 12 | 14 | |
| Fjällbacka | 124 | 18 | 95-13 | 1.4(-2.1,5.0) | 0.4134 | | 14 | 18 | 28.6 (22.4,36.4) |
| Fjällbacka | | 10 | 04-13 | -4.6(-14,5.4) | 0.3079 | | 14 | 19 | |
| **Blue mussel** | | | | | | -- | | | |
| Nidingen | 583 | 31 | 81-13 | -2.6(-3.3,-1.8) | 0 | - | 10 | 8.7 | .761 (.696,.833) |
| Nidingen | | 10 | 04-13 | -1.6(-6.9,3.9) | 0.5156 | | 10 | 9.5 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Fjällbacka | 591 | 32 | 81-13 | -2.8(-4.0,-1.6) | 0.0001 | -- - | 13 | 15 | .617 (.534,.712) |
| Fjällbacka | | 10 | 04-13 | -1.5(-13,11) | 0.765 | | 16 | 23 | |
| Kvädöfjärden | 188 | 19 | 95-13 | -2.4(-3.6,-1.1) | 0.0009 | -- - | 8 | 6.1 | 1.01 (.946,1.08) |
| Kvädöfjärden | | 10 | 04-13 | -4.5(-7.5,-1.4) | 0.0103 | - | 8 | 5.3 | |

**Guillemot egg**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 180 | 18 | 96-13 | 0.021(-.84,.89) | 0.9125 | | 7 | 3.8 | 2.98 (2.87,3.09) |
| Stora Karlsö | | 10 | 04-13 | -0.2(-1.4,.96) | 0.6999 | | 5 | 1.9 | |

# 19 Zinc - Zn

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 (NIH, 2011). Zinc concentration is regulated by homeostatic mechanisms. Hence, zinc is not believed to *accumulate* with continued exposure, but changes found in biological tissues may still reflect changes in concentration of the ambient water. Zinc occurs naturally in the environment, but most zinc originates from human activities such as mining, steel production and coal burning. In its pure form, anthropogenic sources of zinc can include use in steel and iron galvanization to prevent rust and corrosion, ; production of brass and bronze and zinc is also used to make dry cell batteries . Zinc compounds are used in industry for things such as making white paints and ceramics, producing rubber, preserving wood and dyeing fabrics (ATSDR, 2005). 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 T.B. et al., 2004). Some sunscreens use zinc oxide nanoparticles (Osmond and Mccall, 2010), other zinc compounds can be found in, for example, deodorants, nappy rash creams and anti-dandruff shampoos (ATSDR, 2005).

### 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. Zinc dissolved in water can increase the acidity (ATSDR, 2005).

### 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 (HELCOM, 1988).

### 19.1.4 Target level

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

## 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) Stockholm University. See chapter 6 section 6.1 for further details.

## 19.3 Results

### 19.3.1 Spatial variation
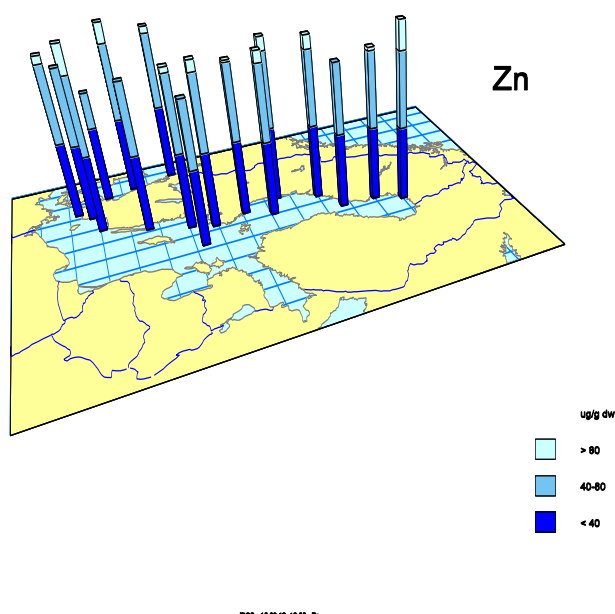


**Figure 19.1.** Spatial variation in zinc concentrations (µg/g dry weight) in herring liver.

In herring, the concentration of zink was rather homogenous among sampling sitesin the years 2011–2013 The highest concentration of zink was found at Harufjärden (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 Väderöarna, 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 Harusfjärden, Väderöarna 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.
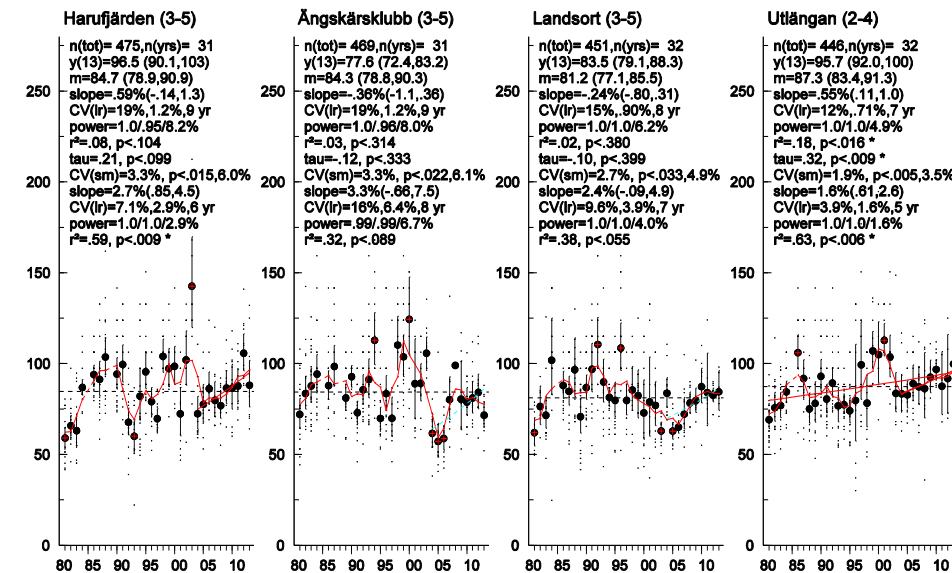


**Figure 19.2.** Zinc concentrations (µg/g dry weight) in herring liver from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1981).



**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).

## Zn, µg/g dry w., perch liver

**Holmöarna**

n(tot)= 180,n(yrs)= 18
y(13)=105 (100,110)
m=101 (96.0,107 )
slope=.42%(-.58,1.4)
CV(lr)=11%,1.7%,7 yr
power=1.0/1.0/4.7%
r²=.04, p<.392
tau=.22, p<.211
CV(sm)=1.7%, p<.013,3.1%
slope=.75%(.21,1.3)
CV(lr)=2.0%,1.0%,4 yr
power=1.0/1.0/.83%
r²=.61, p<.013 *

**Kvädöfjärden**

n(tot)= 175,n(yrs)= 18
y(13)=98.4 (93.7,103)
m=106 (96.7,116 )
slope=-.74%(-2.3,.88)
CV(lr)=18%,2.8%,9 yr
power=1.0/.97/7.8%
r²=.05, p<.348
tau=-.07, p<.677
CV(sm)=1.7%, p<.001,3.2%
slope=.62%(-.47,1.7)
CV(lr)=4.3%,1.7%,5 yr
power=1.0/1.0/1.8%
r²=.18, p<.225
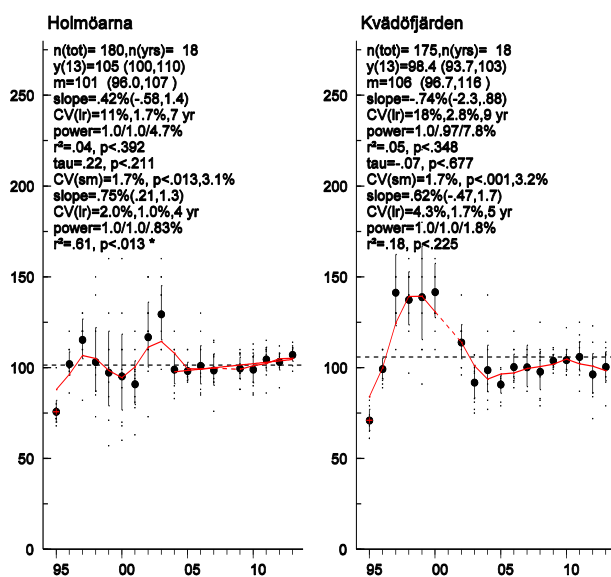
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**Fig. 19.4.** Zinc concentrations (µg/g dry weight) in perch liver from Holmöarna and Kvädöfjärden (time series starting in 1995).

## Zn, µg/g dry w., cod liver
Fat adjusted geometric means

**SE Gotland (2-4)**

n(tot)= 337,n(yrs)= 27
y(13)=34.0 (29.9,38.6)
m=34.2 (30.8,37.8)
slope=-.29%(-1.3,.77)
CV(lr)=27%,2.1%,11 yr
power=1.0/.71/12%
r²=.01, p<.579
tau=-.10, p<.466
CV(sm)=7.2%, p<.341,11%
slope=1.7%(-1.0,4.5)
CV(lr)=11%,4.4%,7 yr
power=1.0/1.0/4.5%
r²=.21, p<.186

**Fladen (2-4)**

n(tot)= 360,n(yrs)= 27
y(13)=68.0 (61.6,75.0)
m=69.6 (64.3,75.4)
slope=-.81%(-1.6,-.06)
CV(lr)=19%,1.5%,9 yr
power=1.0/.95/8.1%
r²=.17, p<.034 *
tau=-.24, p<.076
CV(sm)=4.6%, p<.670,8.2%
slope=3.9%(.64,7.3)
CV(lr)=13%,5.2%,8 yr
power=1.0/1.0/5.4%
r²=.49, p<.024 *
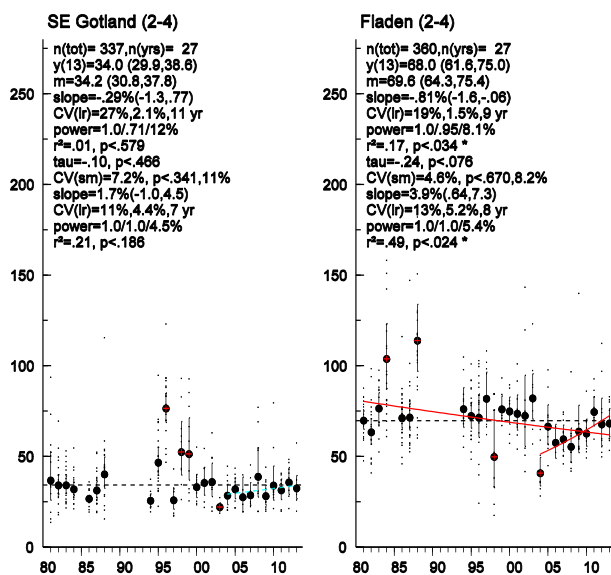
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**Figure 19.5.** Zinc concentrations (µg/g dry weight) in cod liver from Southeast Gotland and Fladen (time series starting in1981).

## Zn, µg/g dry w., eelpout liver

**Holmöarna**

n(tot)= 98,n(yrs)= 11
y(07)=167 (146,191)
m=132 (115 ,152 )
slope=.95%(-3.2,5.3)
CV(lr)=22%,7.6%,10 yr
power=.96/.88/9.5%
r²=.02, p<.627
tau=.13, p<.586
CV(sm)=3.5%, p<.078,7.1%
slope=.023%(-5.5,5.8)
CV(lr)=23%,9.4%,10 yr
power=.85/.85/9.8%
r²=.00, p<.941

**Kvädöfjärden**

n(tot)= 123,n(yrs)= 18
y(13)=158 (133,187)
m=147 (131 ,164 )
slope=-.51%(-2.7,1.7)
CV(lr)=24%,3.6%,10 yr
power=1.0/.82/10%
r²=.01, p<.636
tau=-.12, p<.494
CV(sm)=5.5%, NS,12%
slope=2.6%(.015,5.3)
CV(lr)=10%,4.1%,7 yr
power=1.0/1.0/4.2%
r²=.40, p<.048 *

**Fjällbacka**

n(tot)= 124,n(yrs)= 18
y(13)=183 (161,208)
m=183 (168 ,199 )
slope=.45%(-1.1,2.0)
CV(lr)=17%,2.6%,9 yr
power=1.0/.98/7.3%
r²=.02, p<.557
tau=.020, p<.910
CV(sm)=3.9%, NS,8.6%
slope=.30%(-2.2,2.9)
CV(lr)=10%,4.2%,7 yr
power=1.0/1.0/4.2%
r²=.00, p<.781



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

## Zn, µg/g wet w., blue mussel softbody

**Kvädöfjärden**

n(tot)= 188,n(yrs)= 19
y(13)=11.2 (10.4,12.1)
m=13.8 (12.1,15.6)
slope=-3.6%(-4.9,-2.2)
CV(lr)=16%,2.2%,9 yr
power=1.0/.99/6.9%
r²=.63, p<.001 *
tau=-.61, p<.001 *
CV(sm)=4.7%, p<.031,5.0%
slope=-2.4%(-4.4,-.40)
CV(lr)=8.0%,3.3%,6 yr
power=1.0/1.0/3.3%
r²=.49, p<.024 *

**Fjällbacka**

n(tot)= 566,n(yrs)= 31
y(13)=14.0 (12.4,15.8)
m=16.2 (14.6,18.0)
slope=-.71%(-1.8,.36)
CV(lr)=29%,1.8%,11 yr
power=1.0/.64/13%
r²=.06, p<.181
tau=-.30, p<.018 *
CV(sm)=9.3%, p<.194,11%
slope=-.33%(-3.0,2.4)
CV(lr)=11%,4.5%,7 yr
power=1.0/1.0/4.6%
r²=.00, p<.780

**Nidingen**

n(tot)= 583,n(yrs)= 32
y(13)=15.5 (14.3,16.9)
m=15.8 (14.6,17.1)
slope=-.91%(-1.7,-.11)
CV(lr)=21%,1.3%,10 yr
power=1.0/.91/9.0%
r²=.16, p<.026 *
tau=-.21, p<.099
CV(sm)=6.4%, p<.083,7.4%
slope=2.6%(-1.1,6.5)
CV(lr)=15%,6.0%,8 yr
power=1.0/1.0/6.2%
r²=.24, p<.145



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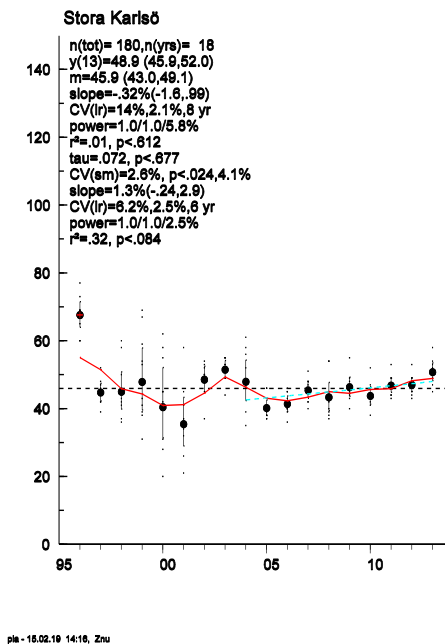
**Figure 19.8** Zinc concentrations (µg/g dry weight) in guillemot eggs from St. Karlsö (time series starting in 1996).

### 19.3.3  Species Differences

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

Holmöarna: Eelpout (167) > Perch (105)
Kvädöfjärden: Eelpout (158) > Perch (98.4) > Blue mussel (11.2)
Fladen/Nidingen: Herring (95.9) > Cod (62.1) > Blue mussel (15.5)
Väderöarna/Fjällbacka: Eelpout (183) > Herring (81.8) > Blue mussel (14.0)

The differences in zinc concentrations were between spring- and autumn-caught hering from Utlängan was; autumn 95.7 – spring 107, and at Ängskärsklubb; autumn 77.6 – spring 88.4.

### 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 (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 liver** | | | | | | | | | |
| Harufjärden (3-5) | 475 | 31 | 81-13 | 0.59(-.14,1.3) | 0.1045 | | 9 | 8.2 | 96.5 (90.1,103) |
| Harufjärden (3-5) | | 10 | 04-13 | 2.7(.85,4.5) | 0.0093 | ++ | 6 | 2.9 | |
| Ängskärsklubb (3-5) | 469 | 31 | 81-13 | -0.36(-1.1,.36) | 0.3145 | | 9 | 8 | 77.6 (72.4,83.2) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 3.3(-.66,7.5) | 0.0887 | | 8 | 6.7 | |
| Landsort (3-5) | 451 | 32 | 81-13 | -0.24(-.80,.31) | 0.3805 | | 8 | 6.2 | 83.5 (79.1,88.3) |
| Landsort (3-5) | | 10 | 04-13 | 2.4(-.09,4.9) | 0.0551 | | 7 | 4 | |
| Utlängan (2-4) | 446 | 32 | 81-13 | 0.55(.11,1.0) | 0.0158 | + | 7 | 4.9 | 95.7 (92.0,100) |
| Utlängan (2-4) | | 10 | 04-13 | 1.6(.61,2.6) | 0.006 | ++ | 5 | 1.6 | |
| Ängskärsklubb spring (2-6) | 138 | 17 | 96-12 | -2.2(-3.8,-.58) | 0.011 | - | 8 | 6.6 | 88.4 (79.5,98.2) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -1.5(-5.7,2.9) | 0.4496 | | 9 | 7.3 | |
| Utlängan spring (2-4) | 130 | 17 | 96-13 | -0.47(-1.9,.99) | 0.5077 | | 8 | 6.4 | 107 (98.0,117) |
| Utlängan spring (2-4) | | 10 | 04-13 | 0.004(-2.2,2.3) | 0.9445 | | 7 | 3.7 | |
| Fladen (2-3) | 538 | 32 | 81-13 | -0.04(-.66,.59) | 0.8747 | | 9 | 7 | 95.9 (91.9,100) |
| Fladen (2-3) | | 10 | 04-13 | 5.9(4.4,7.4) | 0.0000 | +++ | 6 | 2.3 | |
| Väderöarna | 304 | 18 | 95-13 | -1.5(-2.9,-.03) | 0.0443 | - | 9 | 7 | 81.8 (75.4,88.7) |
| Väderöarna | | 9 | 04-13 | 3.3(.92,5.7) | 0.013 | + | 6 | 3.5 | |
| **Perch liver** | | | | | | | | | |
| Holmöarna | 180 | 18 | 95-13 | 0.42(-.58,1.4) | 0.3923 | | 7 | 4.7 | 105 (100,110) |
| Holmöarna | | 9 | 04-13 | 0.75(.21,1.3) | 0.0129 | + | 4 | 0.83 | |
| Kvädöfjärden | 175 | 18 | 95-13 | -0.74(-2.3,.88) | 0.3482 | | 9 | 7.8 | 98.4 (93.7,103) |
| Kvädöfjärden | | 10 | 04-13 | 0.62(-.47,1.7) | 0.225 | | 5 | 1.8 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 337 | 27 | 81-13 | -0.29(-1.3,.77) | 0.5786 | | 11 | 12 | 34.0 (29.9,38.6) |
| SE Gotland (2-4) | | 10 | 04-13 | 1.7(-1.0,4.5) | 0.1857 | | 7 | 4.5 | |
| Fladen (2-3) | 360 | 27 | 81-13 | -0.81(-1.6,-.06) | 0.0337 | - | 9 | 8.1 | 68.0 (61.6,75.0) |
| Fladen (2-3) | | 10 | 04-13 | 3.9(.64,7.3) | 0.0239 | + | 8 | 5.4 | |
| **Eelpout liver** | | | | | | | | | |
| Holmöarna | 98 | 11 | 95-07 | 0.95(-3.2,5.3) | 0.627 | | 10 | 9.5 | 167 (146,191) |
| Holmöarna | | 10 | 98-07 | 0.023(-5.5,5.8) | 0.9405 | | 10 | 9.8 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -0.51(-2.7,1.7) | 0.6358 | | 10 | 10 | 158 (133,187) |
| Kvädöfjärden | | 10 | 04-13 | 2.6(.015,5.3) | 0.0475 | + | 7 | 4.2 | |
| Fjällbacka | 124 | 18 | 95-13 | 0.45(-1.1,2.0) | 0.5571 | | 9 | 7.3 | 183 (161,208) |
| Fjällbacka | | 10 | 04-13 | 0.3(-2.2,2.9) | 0.7815 | | 7 | 4.2 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 583 | 31 | 81-13 | -0.91(-1.7,-.11) | 0.0261 | - | 10 | 9 | 15.5 (14.3,16.9) |
| Nidingen | | 10 | 04-13 | 2.6(-1.1,6.5) | 0.1452 | | 8 | 6.2 | |
| Fjällbacka | 566 | 31 | 81-13 | -0.71(-1.8,.36) | 0.1811 | | 11 | 13 | 14.0 (12.4,15.8) |
| Fjällbacka | | 10 | 04-13 | -0.33(-3.0,2.4) | 0.78 | | 7 | 4.6 | |

| Kvädöfjärden | 188 | 19 | 95-13 | -3.6(-4.9,-2.2) | 0.0001 | --- | 9 | 6.9 | 11.2 (10.4,12.1) |
| Kvädöfjärden | | 10 | 04-13 | -2.4(-4.4,-.40) | 0.0239 | - | 6 | 3.3 | |

**Guillemot egg**

| Stora Karlsö | 180 | 18 | 96-13 | -0.32(-1.6,.99) | 0.6122 | | 8 | 5.8 | 48.9 (45.9,52.0) |
| Stora Karlsö | | 10 | 04-13 | 1.3(-.24,2.9) | 0.084 | | 6 | 2.5 | |

# 20  Arsenic - As

## 20.1  Introduction

### 20.1.1  Uses, Production and Sources

Arsenic is a natural component of the earth's crust, and is found in all environmental media (IPCS, 2001). Major anthropogenic sources of environmental arsenic contamination are via industrial smelters, coal power plants and production and use of arsenic pesticides and herbicides (Eisler, 1994).  An estimation of world arsenic production showed that copper chrome arsenate 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, 2011).

Elemental arsenic is produced by reduction of arsenic trioxide ($As_2O_3$) with charcoal. Arsenic trioxide is produced as a by-product of metal smelting operations, especially in copper smelting (IPCS, 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 (SGU, 2005, Eisler, 2007).
It is possible that dumped chemical munitions from the end of World War II contribute to increased arsenic levels in the Baltic Sea, Skagerakk and Kattegat environment (OSPAR Commision, 2005, Garnaga et al., 2006, HELCOM, 2010).

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 (IPCS, 2001). This form has a low toxicity and is quickly excreted via urine (SGU, 2005, Eisler, 2007).

### 20.1.2  Toxic Effects

Acute, subacute and chronic effects can involve a number of organ systems including the respiratory, gastrointestinal, cardiovascular, nervous, and haematopoietic systems. Furtermore, disturbance of the liver function has been observed in both humans and animals after chronic exposure. There is also evidence that arsenic affects the heart in humans (United Nations Environment Programme et al., 1981).

In general, inorganic arsenic is more toxic than organic arsenic to aquatic biota, with trivalent, arsenic(III), species being more toxic than pentavalent arsenic(V). 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 (OJEC No. L396 30.12.2006, 2006a) on the Registration, Evaluation and Authorisation of Chemicals (REACH).

The European Union has, in a directive from the European Commission concerning 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 placed on the EU market (OJEC No. L384 29.12.2006, 2006).

### 20.1.4 Target Levels

No national target level for biota is agreed upon for arsenic. Concentrations in water are usually < 10 µg/L (IPCS, 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 2011–2013 was observed at Fladen and Väderöarna (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. 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 and Francesconi, 2003).

# 21  Silver - Ag

## 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 are mainly smelting operations, the manufacture and disposal of certain photographic and electrical supplies, coal combustion and cloud seeding (IPCS, 2002).  Silver is used for jewellery, ornaments, tableware, utensils and currency (Eisler, 1996, IPCS, 2002, IVL, 2007).  Electronics, batteries and solders containing silver present as solid waste may either be deposited in landfills or burnt in waste incinerators. Dispersal of residues in the environment may occur via leaching or emissions to the air (IVL, 2007).

Medicinally, silver is used for its bactericidal properties. Soluble silver compounds are used as antiseptic and bacteriostatic agents, as disinfectants (IPCS, 2002); and as antiseptic and antiodour agents in products such as in 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 concentration in biota has been found to be higher near sewage outfalls, electroplating plants, mine waste and silver-iodide-seeded areas, than from more distant sites (Eisler, 1996).

### 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 $Ag^0$ and the monovalent cation $Ag^+$. Soluble silver salts are generally more toxic than insoluble salts. As ionic $Ag^+$, silver is one of the most toxic metals known to aquatic organisms in laboratory studies (Eisler, 1996, IVL, 2007) 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, IPCS, 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 and 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 (OJEC No. L123 24.4.98, 1998).

### 21.1.4  Target Levels

No national target level for biota concerning silver is agreed upon.

The tolerable daily intake of silver for humans has been set at 5 µg/kg body weight (IRIS, 1991). WHO recommendations for the protection of groundwater, reports a critical concentration of 50 µg/L (IPCS, 2002).

Silver is comparably rare in the earth's crust. The crustal abundance is estimated at 0.07 ppm (mg/kg), predominantly concentrated in basalt (Eisler, 1996). Average concentration of silver in natural waters is 0.2–0.3 µg/L (IPCS, 2002).

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, 2005). 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
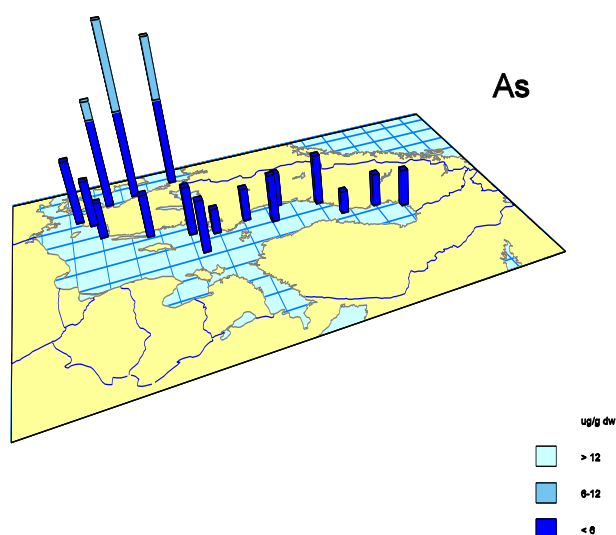
### 21.3.1  Spatial Variation
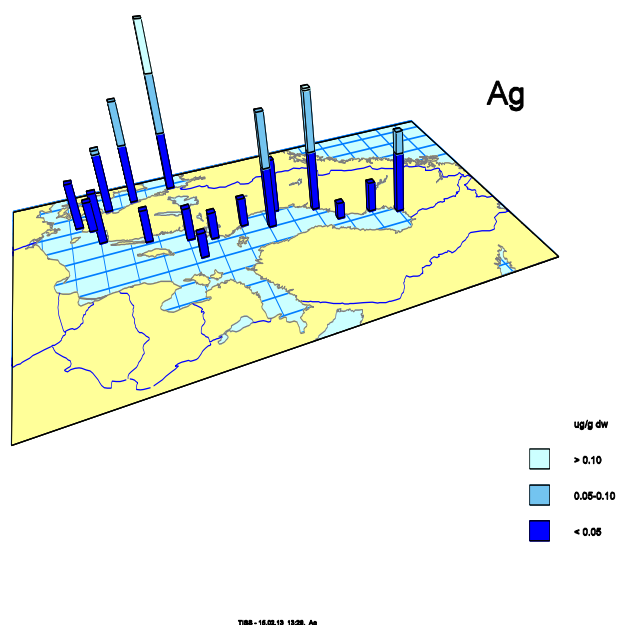


**Figure 21.1.** Spatial variation in silver concentrations (µg/g dry weight) in herring liver.

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.

# 22 PCBs, Polychlorinated biphenyles

Updated 15.02.23

## 22.1 Introduction

### 22.1.1 Usage, Production and Sources

Polychlorinated biphenyls (PCBs) consist of two linked phenyl rings substituted with one or more chlorine atoms. Out of a possible 209 congeners, depending on the number and position of the chlorine atoms, 20 have non-ortho chlorine substitutions and can thus attain a planar structure. Similar to the highly toxic polychlorinated dibenzo-*p*-dioxins and dibenzofurans (Mckinney et al., 1985) Serico et al. 1991), see chapter 26. PCBs are synthetic chemicals that have been used in a wide variety of manufacturing processes, especially as plasticizers, insulators and fire retardants. PCBs are widely distributed in the environment through inappropriate handling of waste material or e.g., leakage from large capacitors and hydraulic systems.

### 22.1.2 Toxicological Effects

PCBs can influence human health by affecting multiple organ systems (Carpenter, 1998, ATSDR, 2000, Carpenter, 2006) and their toxicological effects on e.g., reproduction in mink, is well documented (Aulerich and Ringer, 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 and 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 (HELCOM, 1988).

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

PCBs are 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, 2008).

In 1973, PCB use was banned in Sweden, except for within sealed systems. In 1978, all new use of PCBs was 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 the work by Roos and co-workers (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 ($\sum$PCB) presented in this report were estimated from the concentration of peak 10 (PCB10) in the chromatogram from packed column chromatography, using the ratio $R_1 = PCB10/\sum PCB$. 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 $R_2 = (CB\text{-}138 + CB\text{-}163)/PCB10$. 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:

$$\sum PCB = PCB10 \, / \, R_1$$

and after 1988:

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

**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
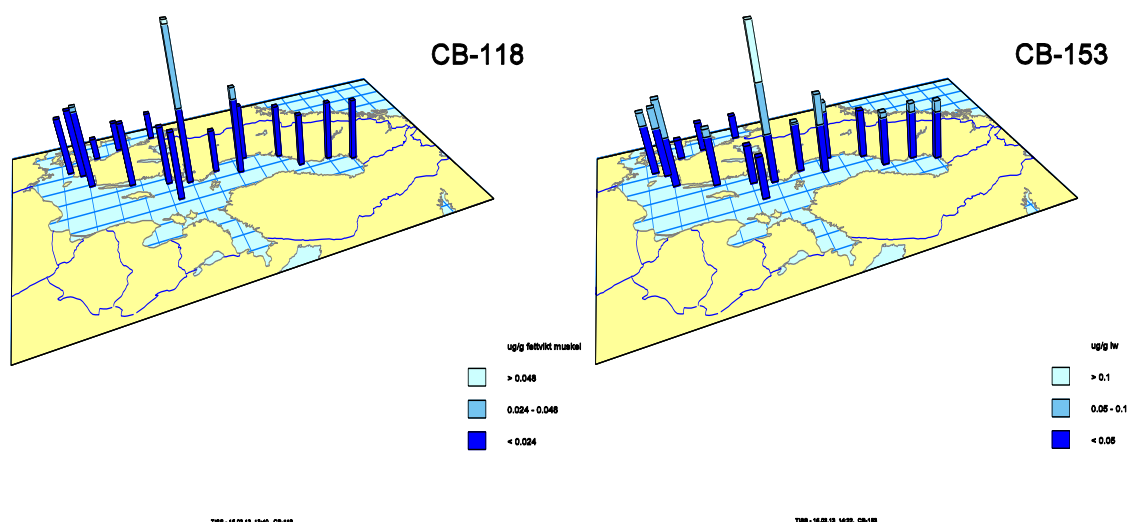


**Figure 22.1.** Spatial variation in concentrations (µg/g lipid weight) of CB-118 and -153 in herring muscle.

Herring muscle on the Swedish west coast has lower concentrations of CB-153 compared to the Baltic Sea (lipid weight) (Figure 22.1), Lagnö in the Baltic proper 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).

For CB-118, the pattern for herring muscle was similar was for CB-153 – lower concentrations on the Swedish west coast compared to the Baltic Sea, and Lagnö had the highest concentration (Fig. 22.1).

### 22.3.2 Temporal variation

∑PCB 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 ∑PCB (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 1978/80–2013 (Fig. 22.2 and 22.3). The average decrease varies between 5.1 and 6.9% per year. A similar significant decrease within the same range (5.0–8.3% per year) is also seen in the two time series of spring-caught herring between 1972–2013 (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**. ∑PCB concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978, 1978, 1978 and 1980 respectively).
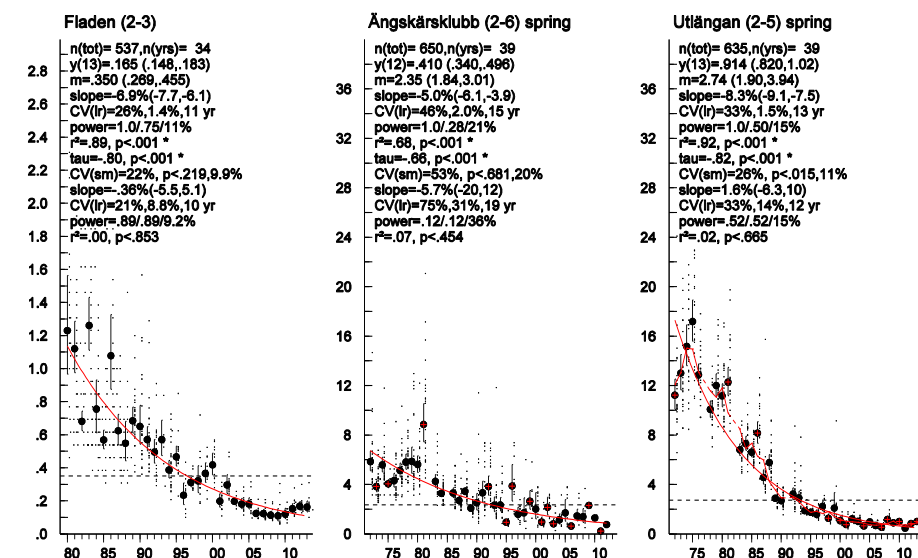


**Figure 22.3.** ∑PCB concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), and Fladen (time series starting in 1972, 1972 and 1980 respectively).

Significant decreasing trends for ∑PCB are observed in blue mussels from the Swedish west coast (Fig. 22.4) and guillemot eggs (1969–2013) (Fig. 22.5). The latter trend corresponds to a total decrease of almost 90% since the beginning of the 1970s.

sPCB, µg/g lipid w., blue mussel
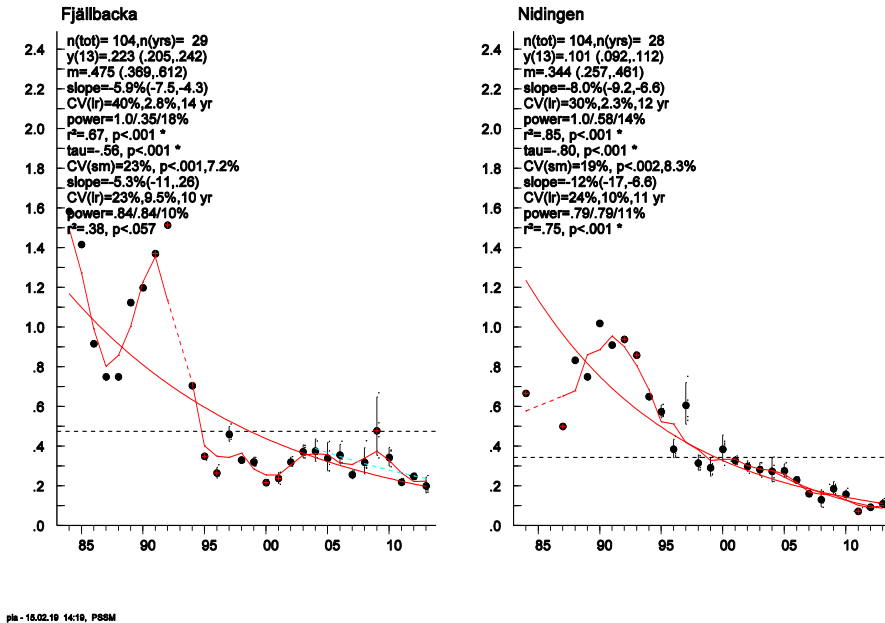


**Figure 22.4.** ∑PCB concentrations (µg/g lipid weight) in blue mussels from Nidingen and Fjällbacka (time series starting in 1984).

sPCB, µg/g lipid w., Guillemot eggs, St Karlsö
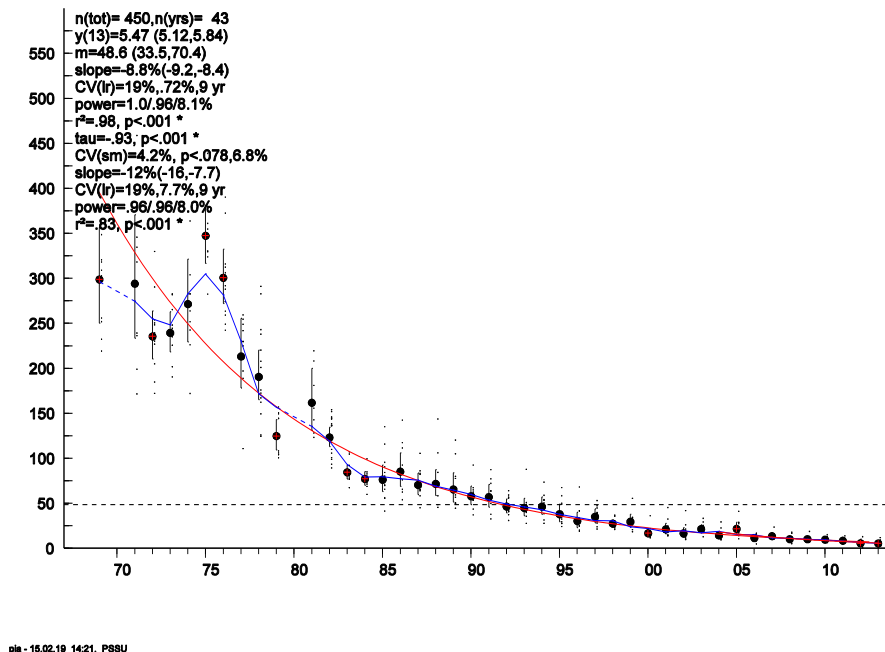


**Figure 22.5.** ∑PCB concentrations (µg/g lipid weight) in guillemot eggs from St. Karlsö (time series starting in 1969).

## CB-153, µg/g lipid w., herring muscle
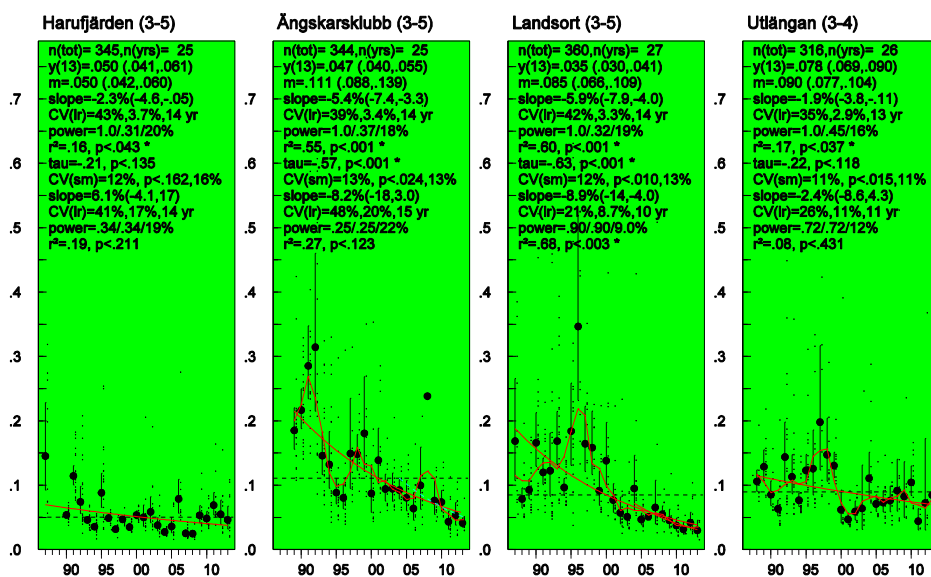


**Figure 22.6.** CB-153 concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for CB-153 in fish.

## CB-153, µg/g lipid w., herring muscle
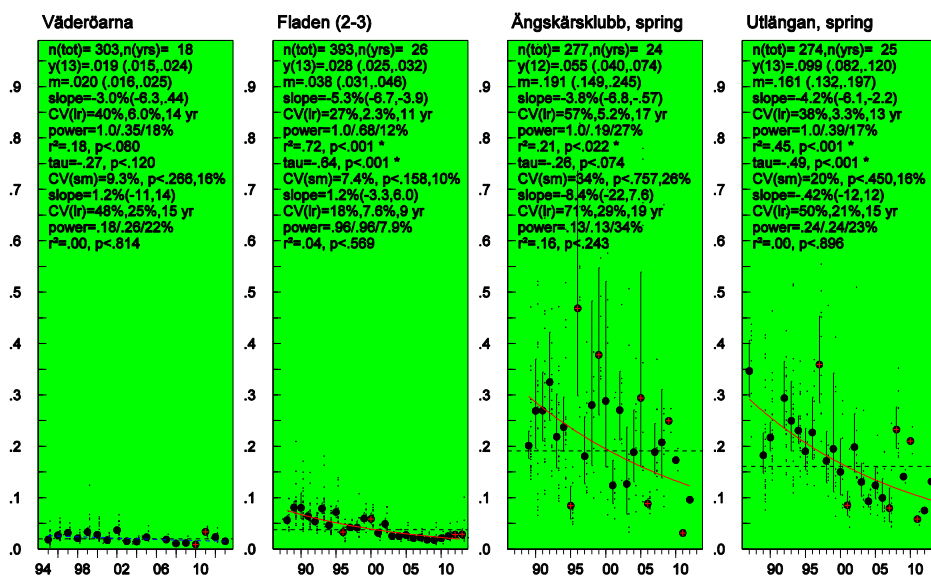


**Figure 22.7**. CB-153 concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for CB-153 in fish.

CB-153 shows a similar decreasing trend in herring muscle as ∑PCB at all sites, except for Väderöarna, where no trend is observed (Fig. 22.6 and 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 that year.

The cod time series from Southeast of Gotland in the Baltic Proper and Fladen on the west coast show significant decreasing trends for ∑PCB. On the contrary, an inreasing trend is observed for CB-153 in the cod time series from Fladen during the ten most recent years (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).
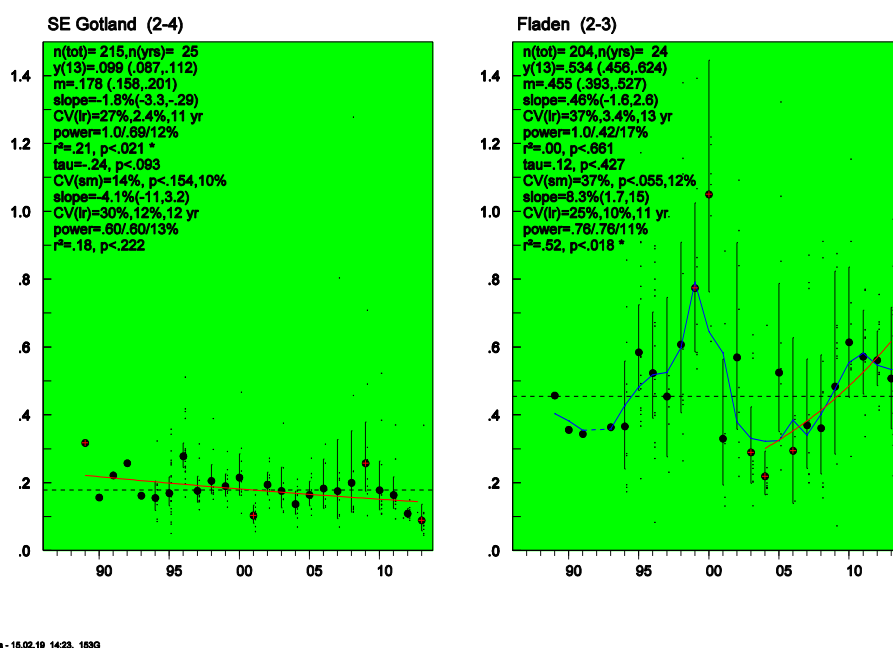


**Figure 22.8.** CB-153 concentrations (µg/g lipid weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1989. The green area denotes the levels below the suggested target value for CB-118 in fish.

## CB-153, µg/g lipid w., perch muscle
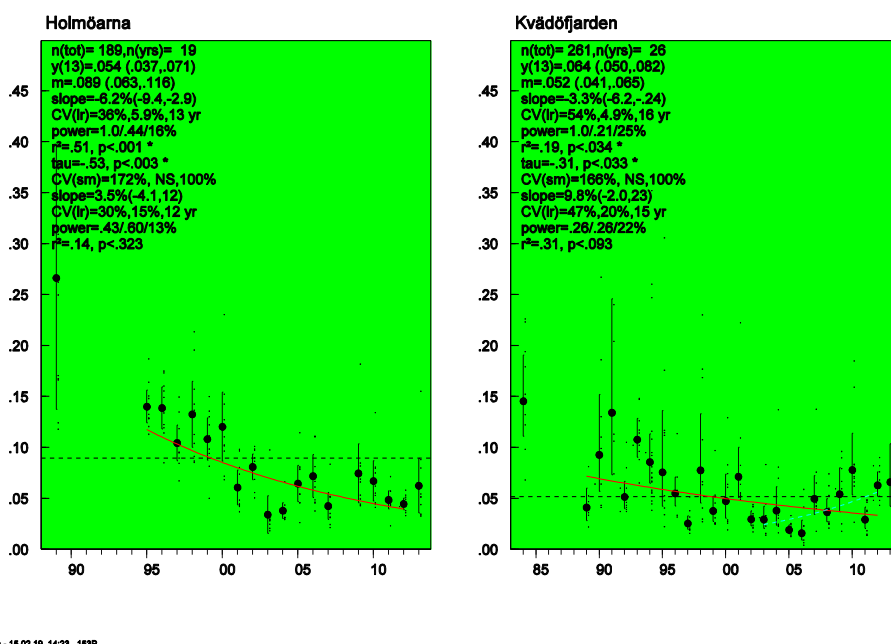


**Figure 22.9.** CB-153 concentrations (µg/g lipid weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 and 1984 respectively). The green area denotes the levels below the suggestedtarget value for CB-153 in fish.

## CB-153, µg/g lipid w. Eelpout muscle
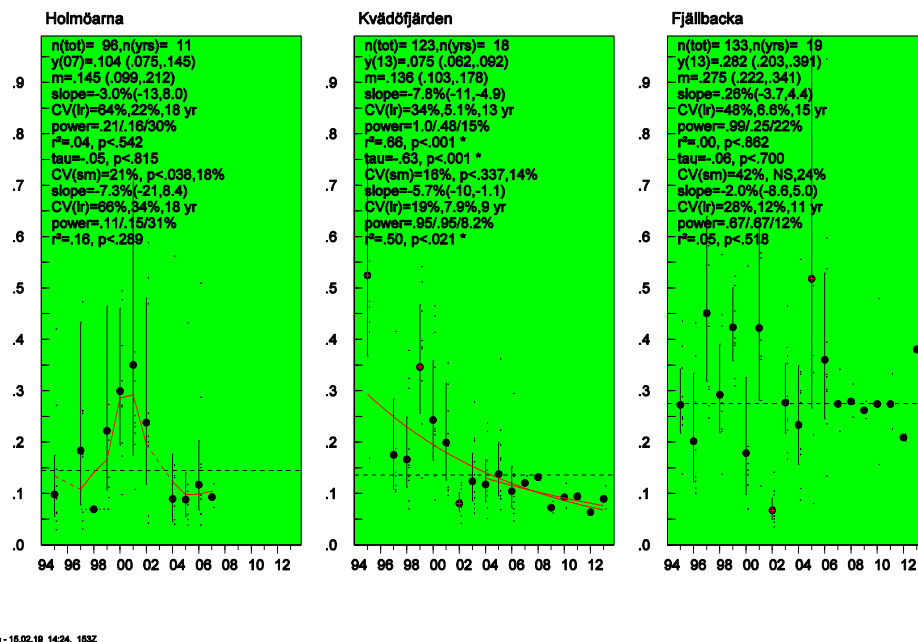


**Figure 22.10.** CB-153 concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for CB-153 in fish.

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

## CB-153, µg/g lipid w., blue mussel

**Kvädöfjärden**

```
n(tot)=  95,n(yrs)= 19
y(13)=.037 (.034,.041)
m=.055 (.048,.061)
slope=-3.1%(-4.6,-1.6)
CV(lr)=18%,2.4%,9 yr
power=1.0/.98/7.5%
r²=.52, p<.001 *
tau=-.51, p<.002 *
CV(sm)=5.9%, p<.388,7.1%
slope=-6.4%(-10,-2.6)
CV(lr)=16%,6.6%,8 yr
power=.99/.99/6.8%
r²=.65, p<.005 *
```

**Fjällbacka**

```
n(tot)= 100,n(yrs)=  25
y(13)=.033 (.029,.036)
m=.048 (.039,.059)
slope=-4.4%(-6.2,-2.5)
CV(lr)=36%,3.2%,13 yr
power=1.0/.43/16%
r²=.50, p<.001 *
tau=-.43, p<.002 *
CV(sm)=6.6%, p<.001,8.5%
slope=-2.7%(-7.3,2.2)
CV(lr)=19%,8.1%,9 yr
power=.94/.94/8.4%
r²=.17, p<.235
```

**Nidingen**

```
n(tot)= 102,n(yrs)=  26
y(13)=.015 (.013,.016)
m=.041 (.031,.054)
slope=-7.8%(-9.1,-6.6)
CV(lr)=26%,2.2%,11 yr
power=1.0/.72/12%
r²=.86, p<.001 *
tau=-.79, p<.001 *
CV(sm)=7.4%, p<.186,10%
slope=-10%(-17,-2.8)
CV(lr)=33%,14%,12 yr
power=.51/.51/15%
r²=.55, p<.014 *
```

**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).

## CB-153, µg/g lipid w., guillemot egg

**St Karlsö**

```
n(tot)= 258,n(yrs)=  26
y(13)=1.11 (1.00,1.24)
m=3.41 (2.64,4.40)
slope=-7.6%(-8.5,-6.8)
CV(lr)=18%,1.5%,9 yr
power=1.0/.98/7.5%
r²=.93, p<.001 *
tau=-.88, p<.001 *
CV(sm)=17%, p<1.00,8.5%
slope=-11%(-15,-6.7)
CV(lr)=19%,7.9%,9 yr
power=.95/.95/8.2%
r²=.80, p<.001 *
```
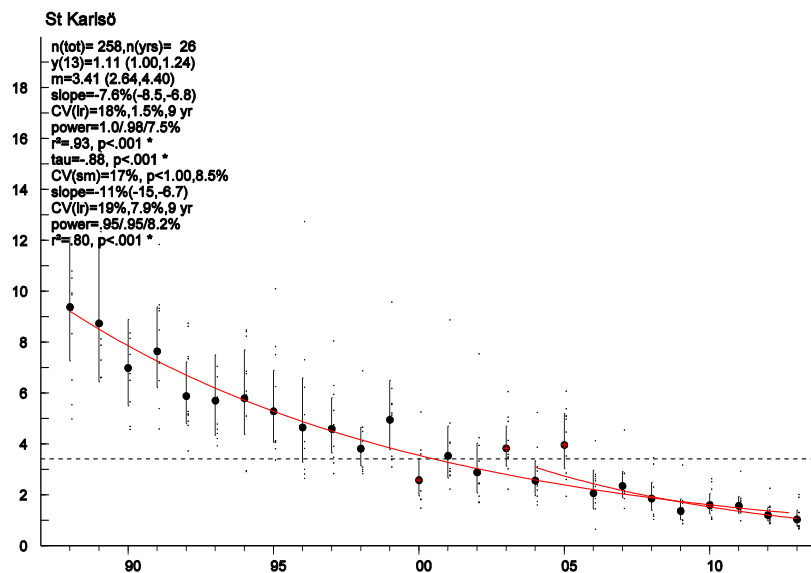
**Figure 22.12.** CB-153 concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1988).

The number of years required to detect an annual change of 10% for CB-153 varies between 10–17 years for the herring, perch, mussel, and cod time series.



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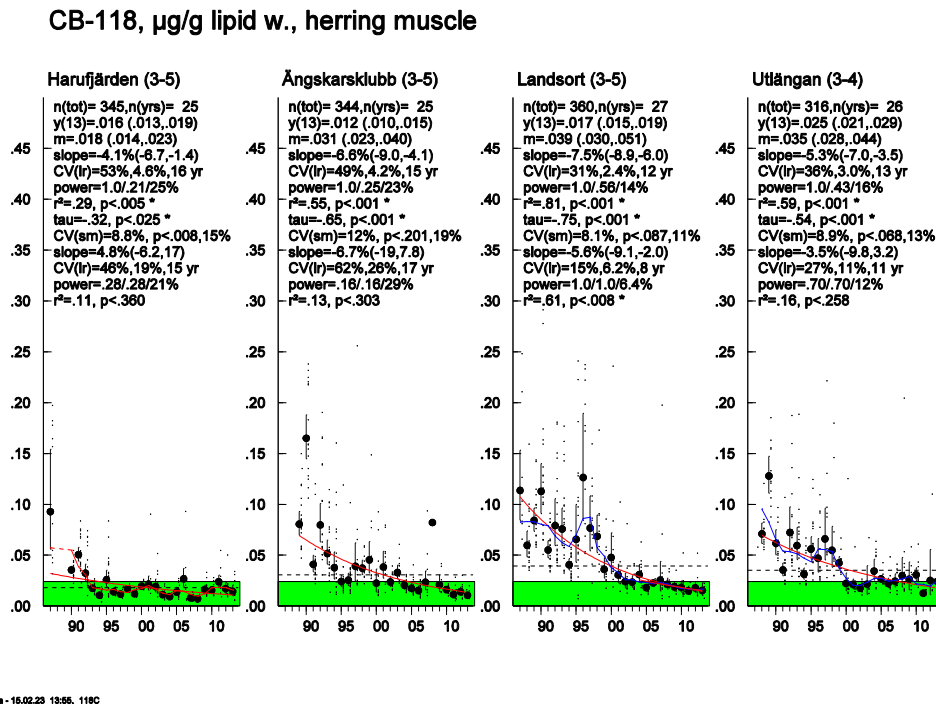
**Figure 22.13.** CB-118 concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for CB-118 in fish.



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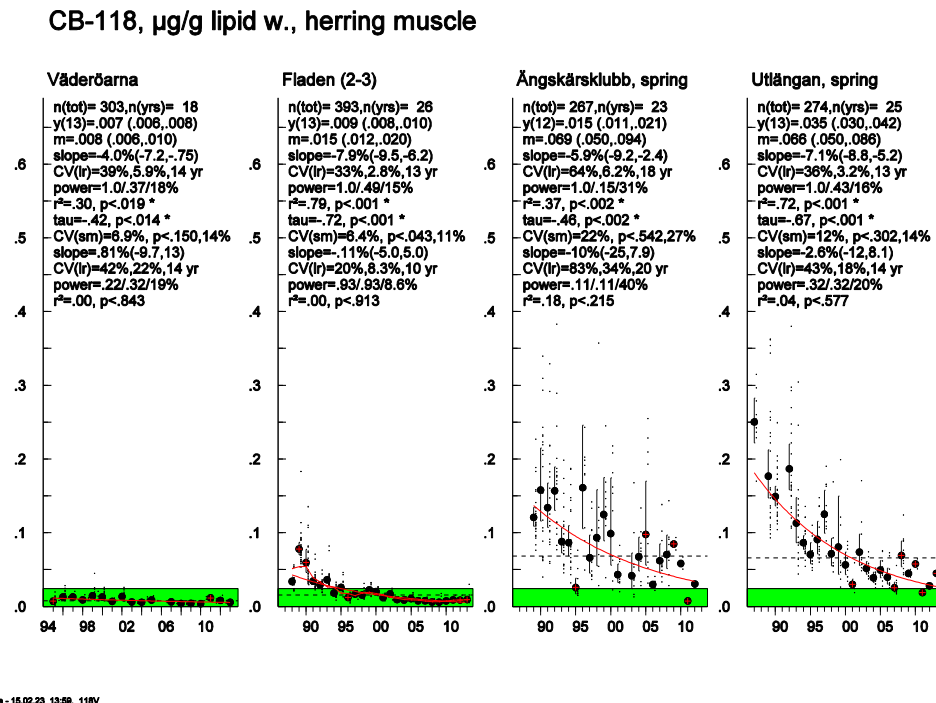
**Figure 22.14**. CB-118 concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1987, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for CB-118 in fish.

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All herring time series show decreasing trends of CB-118 with annual decreases between 4.0–7.9% per year (Fig. 22.13–14).

**CB-118, µg/g lipid w., cod liver**
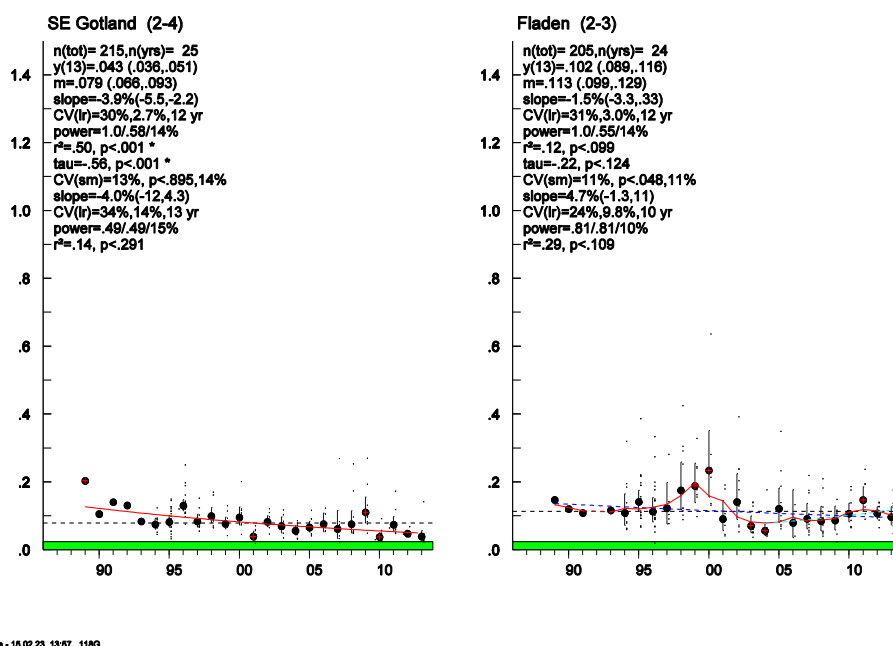


**Figure 22.15.** CB-118 concentrations (µg/g lipid weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1989. The green area denotes the levels below the suggested target value for CB-118 in fish.

**CB-118, µg/g lipid w., perch muscle**
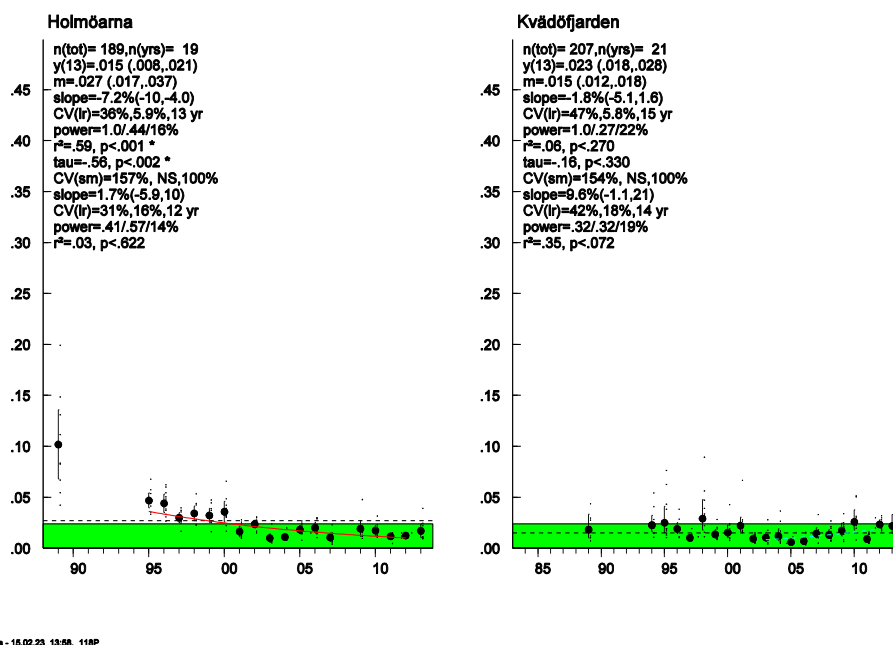


**Figure 22.16.** CB-118 concentrations (µg/g lipid weight) in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 and 1984 respectively). The green area denotes the levels below the suggestedtarget value for CB-118 in fish.

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Cod liver showed a decreasing trend for CB-118 at Southeast of Gotland (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).
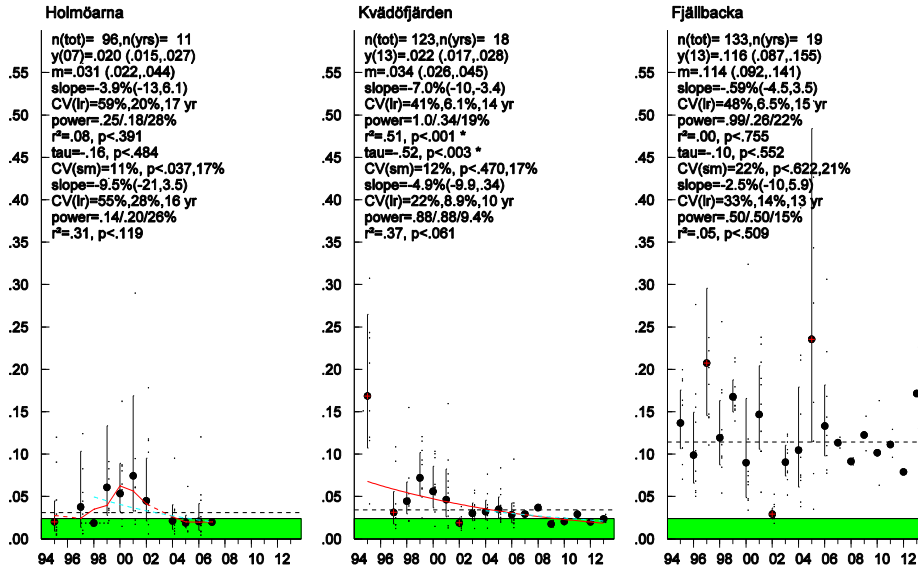


**Figure 22.17.** CB-118 concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for CB-118 in fish.
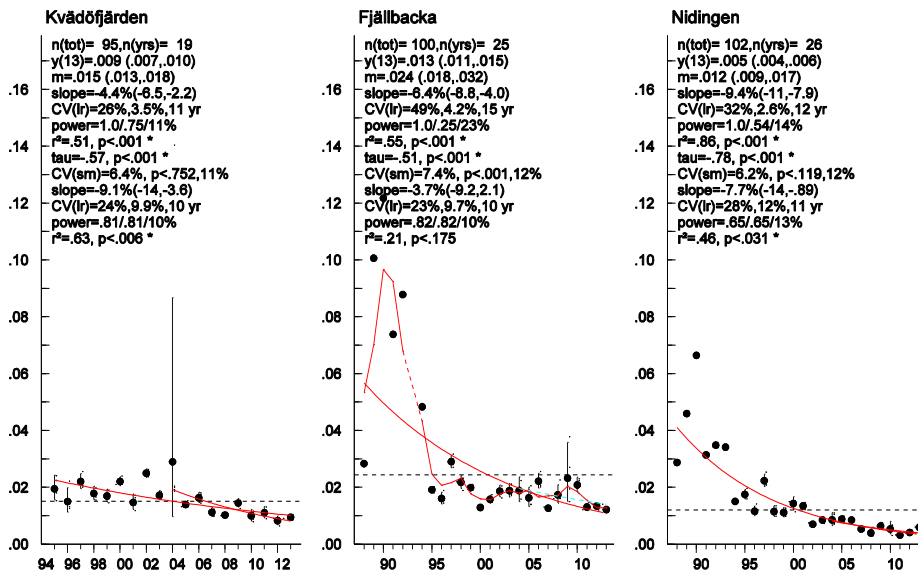


**Figure 22.18.** CB-118 concentrations (µg/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1988, 1988 and 1995 respectively).

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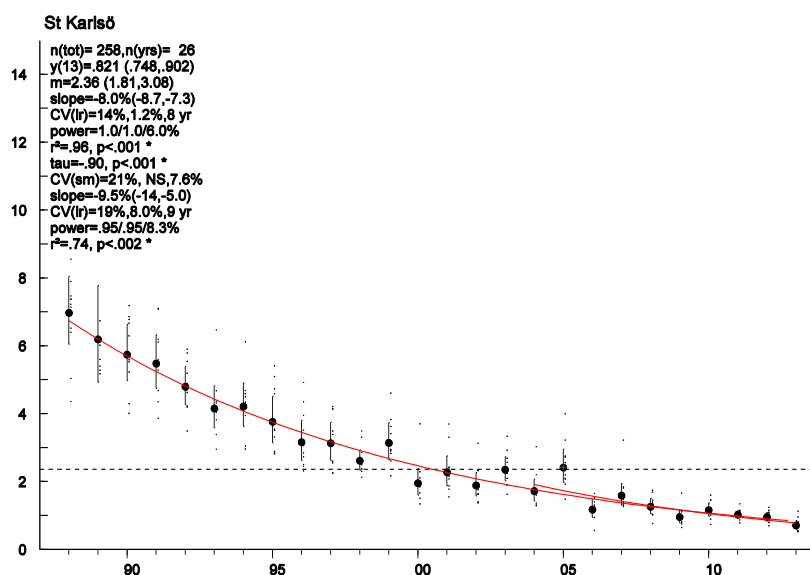
**Figure 22.19.** CB-118 concentrations (µg/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1988).

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 µg/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 µg/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 ∑**PCB** (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 ∑PCB 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) | 451 | 34 | 78-13 | -6.9(-8.1,-5.6) | 0.0000 | --- | 14 | 18 | .251 (.225,.279) |
| Harufjärden (3-5) | | 10 | 04-13 | 2.8(-5.3,12) | 0.4595 | | 12 | 15 | |
| Ängskärsklubb (3-5) | 400 | 34 | 78-13 | -6.7(-7.8,-5.6) | 0.0000 | --- | 13 | 16 | .260 (.228,.296) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -6.7(-18,5.8) | 0.2406 | | 16 | 25 | |
| Landsort (3-5) | 437 | 35 | 78-13 | -5.9(-6.7,-5.1) | 0.0000 | --- | 11 | 12 | .390 (.353,.430) |
| Landsort (3-5) | | 10 | 04-13 | -7(-11,-2.7) | 0.0061 | -- | 9 | 7.7 | |
| Utlängan (2-4) | 315 | 34 | 80-13 | -5.1(-5.9,-4.3) | 0.0000 | --- | 11 | 11 | .431 (.388,.477) |
| Utlängan (2-4) | | 10 | 04-13 | -5.4(-10,-.41) | 0.0365 | - | 10 | 8.8 | |
| Ängskärsklubb spring (2-6) | 650 | 39 | 72-12 | -5(-6.1,-3.9) | 0.0000 | --- | 15 | 21 | .410 (.340,.496) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -5.7(-20,12) | 0.4544 | | 19 | 36 | |
| Utlängan spring (2-4) | 635 | 39 | 72-13 | -8.3(-9.1,-7.5) | 0.0000 | --- | 13 | 15 | .914 (.820,1.02) |
| Utlängan spring (2-4) | | 10 | 04-13 | 1.6(-6.3,10) | 0.6652 | | 12 | 15 | |
| Fladen (2-3) | 537 | 34 | 80-13 | -6.9(-7.7,-6.1) | 0.0000 | --- | 11 | 11 | .165 (.148,.183) |
| Fladen (2-3) | | 10 | 04-13 | -0.36(-5.5,5.1) | 0.8532 | | 10 | 9.2 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 104 | 28 | 84-13 | -8(-9.2,-6.6) | 0.0000 | --- | 12 | 14 | .101 (.092,.112) |
| Nidingen | | 10 | 04-13 | -12(-17,-6.6) | 0.0013 | -- | 11 | 11 | |
| Fjällbacka | 104 | 29 | 84-13 | -5.9(-7.5,-4.3) | 0.0000 | --- | 14 | 18 | .223 (.205,.242) |
| Fjällbacka | | 10 | 04-13 | -5.3(-11,.26) | 0.0573 | | 10 | 10 | |
| **Guillemot egg** | | | | | | | | | |
| Stora Karlsö | 450 | 43 | 69-13 | -8.8(-9.2,-8.4) | 0.0000 | --- | 9 | 8.1 | 5.47 (5.12,5.84) |
| Stora Karlsö | | 10 | 04-13 | -12(-16,-7.7) | 0.0003 | --- | 9 | 8 | |

**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) | 345 | 25 | 87-13 | -2.3(-4.6,-.05) | 0.0433 | - | 14 | 20 | .050 (.041,.061) |
| Harufjärden (3-5) | | 10 | 04-13 | 6.1(-4.1,17) | 0.2111 | | 14 | 19 | |
| Ängskärsklubb (3-5) | 344 | 25 | 89-13 | -5.4(-7.4,-3.3) | 0.0000 | --- | 14 | 18 | .047 (.040,.055) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -8.2(-18,3.0) | 0.1233 | | 15 | 22 | |
| Landsort (3-5) | 360 | 27 | 87-13 | -5.9(-7.9,-4.0) | 0.0000 | --- | 14 | 19 | .035 (.030,.041) |
| Landsort (3-5) | | 10 | 04-13 | -8.9(-14,-4.0) | 0.0035 | -- | 10 | 9 | |
| Utlängan (2-4) | 316 | 26 | 88-13 | -1.9(-3.8,-.11) | 0.0366 | - | 13 | 16 | .078 (.069,.090) |
| Utlängan (2-4) | | 10 | 04-13 | -2.4(-8.6,4.3) | 0.4308 | | 11 | 12 | |
| Ängskärsklubb spring (2-6) | 277 | 24 | 89-12 | -3.8(-6.8,-.57) | 0.0223 | - | 17 | 27 | .055 (.040,.074) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -8.4(-22,7.6) | 0.2435 | | 19 | 34 | |
| Utlängan spring (2-4) | 274 | 25 | 87-13 | -4.2(-6.1,-2.2) | 0.0003 | --- | 13 | 17 | .099 (.082,.120) |
| Utlängan spring (2-4) | | 10 | 04-13 | -0.42(-12,12) | 0.896 | | 15 | 23 | |
| Fladen (2-3) | 393 | 26 | 88-13 | -5.3(-6.7,-3.9) | 0.0000 | --- | 11 | 12 | .028 (.025,.032) |
| Fladen (2-3) | | 10 | 04-13 | 1.2(-3.3,6.0) | 0.569 | | 9 | 7.9 | |
| Väderöarna | 303 | 18 | 95-13 | -3(-6.3,.44) | 0.0796 | | 14 | 18 | .019 (.015,.024) |
| Väderöarna | | 9 | 04-13 | 1.2(-11,14) | 0.8135 | | 15 | 22 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 189 | 19 | 95-13 | -6.2(-9.4,-2.9) | 0.0013 | -- | 13 | 16 | .054 (.037,.071) |
| Holmöarna | | 9 | 03-13 | 3.5(-4.1,12) | 0.3228 | | 12 | 13 | |
| Kvädöfjärden | 261 | 26 | 89-13 | -3.3(-6.2,-.24) | 0.034 | - | 16 | 25 | .064 (.050,.082) |
| Kvädöfjärden | | 10 | 03-13 | 9.8(-2.0,23) | 0.0927 | | 15 | 22 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 215 | 25 | 89-13 | -1.8(-3.3,-.29) | 0.021 | - | 11 | 12 | .099 (.087,.112) |
| SE Gotland (2-4) | | 10 | 04-13 | -4.1(-11,3.2) | 0.2221 | | 12 | 13 | |
| Fladen (2-3) | 204 | 24 | 89-13 | 0.46(-1.6,2.6) | 0.6612 | | 13 | 17 | .534 (.456,.624) |
| Fladen (2-3) | | 10 | 04-13 | 8.3(1.7,15) | 0.0184 | + | 11 | 11 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 96 | 11 | 95-07 | -3(-13,8.0) | 0.5416 | | 18 | 30 | .104 (.075,.145) |
| Holmöarna | | 9 | 98-07 | -7.3(-21,8.4) | 0.2893 | | 18 | 31 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -7.8(-11,-4.9) | 0.0001 | --- | 13 | 15 | .075 (.062,.092) |
| Kvädöfjärden | | 10 | 04-13 | -5.7(-10,-1.1) | 0.0208 | - | 9 | 8.2 | |
| Fjällbacka | 133 | 19 | 95-13 | 0.26(-3.7,4.4) | 0.8622 | | 15 | 22 | .282 (.203,.391) |
| Fjällbacka | | 10 | 04-13 | -2(-8.6,5.0) | 0.5179 | | 11 | 12 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 102 | 26 | 88-13 | -7.8(-9.1,-6.6) | 0.0000 | --- | 11 | 12 | .015 (.013,.016) |
| Nidingen | | 10 | 04-13 | -10(-17,-2.8) | 0.0142 | - | 12 | 15 | |
| Fjällbacka | 100 | 25 | 88-13 | -4.4(-6.2,-2.5) | 0.0001 | --- | 13 | 16 | .033 (.029,.036) |
| Fjällbacka | | 10 | 04-13 | -2.7(-7.3,2.2) | 0.2348 | | 9 | 8.4 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | 95 | 19 | 95-13 | -3.1(-4.6,-1.6) | 0.0005 | --- | 9 | 7.5 | .037 (.034,.041) |
| Kvädöfjärden | | 10 | 04-13 | -6.4(-10,-2.6) | 0.0052 | -- | 8 | 6.8 | |

**Guillemot egg**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 258 | 26 | 88-13 | -7.6(-8.5,-6.8) | 0.0000 | --- | 9 | 7.5 | 1.11 (1.00,1.24) |
| Stora Karlsö | | 10 | 04-13 | -11(-15,-6.7) | 0.0005 | --- | 9 | 8.2 | |

**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 (3-5) | 345 | 25 | 87-13 | -4.1(-6.7,-1.4) | 0.0052 | -- | 16 | 25 | .016 (.013,.019) |
| Harufjärden (3-5) | | 10 | 04-13 | 4.8(-6.2,17) | 0.3598 | | 15 | 21 | |
| Ängskärsklubb (3-5) | 344 | 25 | 89-13 | -6.6(-9.0,-4.1) | 0.0000 | --- | 15 | 23 | .012 (.010,.015) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -6.7(-19,7.8) | 0.3029 | | 17 | 29 | |
| Landsort (3-5) | 360 | 27 | 87-13 | -7.5(-8.9,-6.0) | 0.0000 | --- | 12 | 14 | .017 (.015,.019) |
| Landsort (3-5) | | 10 | 04-13 | -5.6(-9.1,-2.0) | 0.0076 | -- | 8 | 6.4 | |
| Utlängan (2-4) | 316 | 26 | 88-13 | -5.3(-7.0,-3.5) | 0.0000 | --- | 13 | 16 | .025 (.021,.029) |
| Utlängan (2-4) | | 10 | 04-13 | -3.5(-9.8,3.2) | 0.2579 | | 11 | 12 | |
| Ängskärsklubb spring (2-6) | 267 | 23 | 89-12 | -5.9(-9.2,-2.4) | 0.0022 | -- | 18 | 31 | .015 (.011,.021) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -10(-25,7.9) | 0.2147 | | 20 | 40 | |
| Utlängan spring (2-4) | 274 | 25 | 87-13 | -7.1(-8.8,-5.2) | 0.0000 | --- | 13 | 16 | .035 (.030,.042) |
| Utlängan spring (2-4) | | 10 | 04-13 | -2.6(-12,8.1) | 0.5771 | | 14 | 20 | |
| Fladen (2-3) | 393 | 26 | 88-13 | -7.9(-9.5,-6.2) | 0.0000 | --- | 13 | 15 | .009 (.008,.010) |
| Fladen (2-3) | | 10 | 04-13 | -0.11(-5.0,5.0) | 0.913 | | 10 | 8.6 | |
| Väderöarna | 303 | 18 | 95-13 | -4(-7.2,-.75) | 0.0189 | - | 14 | 18 | .007 (.006,.008) |
| Väderöarna | | 9 | 04-13 | 0.81(-9.7,13) | 0.8432 | | 14 | 19 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 189 | 19 | 95-13 | -7.2(-10,-4.0) | 0.0004 | --- | 13 | 16 | .015 (.008,.021) |
| Holmöarna | | 9 | 03-13 | 1.7(-5.9,10) | 0.6222 | | 12 | 14 | |
| Kvädöfjärden | 207 | 21 | 89-13 | -1.8(-5.1,1.6) | 0.2699 | | 15 | 22 | .023 (.018,.028) |
| Kvädöfjärden | | 10 | 03-13 | 9.6(-1.1,21) | 0.0717 | | 14 | 19 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 215 | 25 | 89-13 | -3.9(-5.5,-2.2) | 0.0001 | --- | 12 | 14 | .043 (.036,.051) |
| SE Gotland (2-4) | | 10 | 04-13 | -4(-12,4.3) | 0.2909 | | 13 | 15 | |
| Fladen (2-3) | 205 | 24 | 89-13 | -1.5(-3.3,.33) | 0.0989 | | 12 | 14 | .102 (.089,.116) |
| Fladen (2-3) | | 10 | 04-13 | 4.7(-1.3,11) | 0.1091 | | 10 | 10 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 96 | 11 | 95-07 | -3.9(-13,6.1) | 0.3913 | | 17 | 28 | .020 (.015,.027) |
| Holmöarna | | 9 | 98-07 | -9.5(-21,3.5) | 0.1195 | | 16 | 26 | |
| Kvädöfjärden | 123 | 18 | 95-13 | -7(-10,-3.4) | 0.0009 | --- | 14 | 19 | .022 (.017,.028) |
| Kvädöfjärden | | 10 | 04-13 | -4.9(-9.9,.34) | 0.061 | | 10 | 9.4 | |
| Fjällbacka | 133 | 19 | 95-13 | -0.59(-4.5,3.5) | 0.7547 | | 15 | 22 | .116 (.087,.155) |
| Fjällbacka | | 10 | 04-13 | -2.5(-10,5.9) | 0.5091 | | 13 | 15 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 102 | 26 | 88-13 | -9.4(-11,-7.9) | 0.0000 | --- | 12 | 14 | .005 (.004,.006) |
| Nidingen | | 10 | 04-13 | -7.7(-14,-.89) | 0.0308 | - | 11 | 13 | |
| Fjällbacka | 100 | 25 | 88-13 | -6.4(-8.8,-4.0) | 0.0000 | --- | 15 | 23 | .013 (.011,.015) |
| Fjällbacka | | 10 | 04-13 | -3.7(-9.2,2.1) | 0.1751 | | 10 | 10 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | 95 | 19 | 95-13 | -4.4(-6.5,-2.2) | 0.0006 | --- | 11 | 11 | .009 (.007,.010) |
| Kvädöfjärden | | 10 | 04-13 | -9.1(-14,-3.6) | 0.006 | -- | 10 | 10 | |

**Guillemot egg**

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 258 | 26 | 88-13 | -8(-8.7,-7.3) | 0.0000 | --- | 8 | 6 | .821 (.748,.902) |
| Stora Karlsö | | 10 | 04-13 | -9.5(-14,-5.0) | 0.0016 | -- | 9 | 8.3 | |

# 23 DDTs, Dichlorodiphenylethanes

<div align="right">Updated 5.02.23</div>

## 23.1 Introduction

Within this report the terms DDT, DDE and DDD are written with unspecified substitutionpattern but in fact refers to p,p'-DDT, p,p'-DDE and p,p'-DDD, respectively.

### 23.1.1 Usage

DDT is a persistent synthetic pesticide that primarily degrades to DDE and DDD. 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., 2001, Li and Macdonald, 2005). The presence of DDT and its metabolites in the Arctic area indicates long range transport (Welch et al., 1991).

### 23.1.2 Toxicological effects

DDT has severe health effects on wildlife. In fish-eating birds, reduced reproductive success is widely documented e.g., reduced productivity in top predator white-tailed sea eagles (Helander et al., 2008), the white-tailed sea eagle was almost extinct due to DDT pollution in the Baltic (Olsson and Reutergårdh, 1986). This is due to several factors such as failure to return to nesting sites, egg shell thinning, inability of eggs to hatch, reduced number of reproducing pairs and nestling brood size (Helander et al., 2008, Hamlin H.J. and Guillette Jr L.J., 2010). Also, embryo mortality, thyroid malfunction, and immunosupression have been documented (Hamlin H.J. and Guillette Jr L.J., 2010).

### 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 (HELCOM, 1988).

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 (Stockholm Convention). In Sweden, DDT was partially banned as a pesticide in 1970, and completely banned in 1975 due to its persistence and environmental impact. 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 (∑DDT), 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 ∑DDT 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 ∑DDT 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 | ∑DDT | 95% C.I. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Herring muscle** | | | | | | | | | | | | |
| Harufjärden | 6 | 1.1 | 0.99–1.2 | 6 | 0.96 | 0.89–1.0 | 4 | 1.5 | 1.1–2.0 | 4 | 1.1 | 0.98–1.2 |
| Ängskärsklubb | 16 | 1.1 | 1.0–1.2 | - | - | - | 15 | 0.63 | 0.55–0.70 | - | - | - |
| Spring | 24 | 1.0 | 1.0–1.1 | 1 | 0.62 | - | 21 | 0.77 | 0.68–0.85 | 1 | 0.75 | - |
| Landsort | 28 | 0.79 | 0.76–0.82 | 28 | 0.75 | 0.67–0.81 | 28 | 0.87 | 0.77–0.96 | 27 | 0.79 | 0.77–0.82 |
| Utlängan | 20 | 1.1 | 1.0–1.1 | 20 | 1.0 | 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 | 0.81 | 0.74–.88 | 10 | 1.1 | 1.0–1.1 | 10 | 1.0 | 0.98–1.1 |
| Fladen | 6 | 1.4 | 1.3–1.4 | 5 | 0.90 | 0.77–1.0 | 6 | 1.1 | 0.94–1.3 | 4 | 1.2 | 1.1–1.3 |
| **Cod liver** | | | | | | | | | | | | |
| SE Gotland | 6 | 1.0 | 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
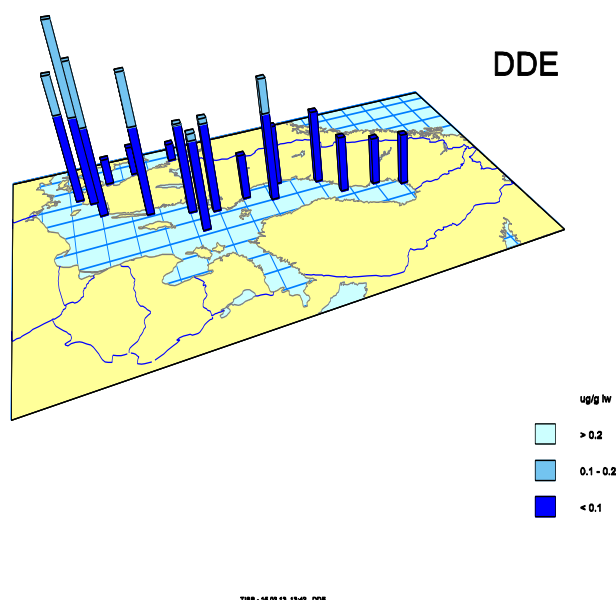


**Figure 23.1.** Spatial variation of DDE concentrations (µg/g lipid weight) in herring muscle.

The highest concentrations of DDE in herring (lipid weight) were detected at Utlängan and Hanöbukten (Figure 23.1) in the Southern Baltic Proper. While concentrations from the Swedish West coast were almost 10 times lower and in the Bothnian Bay 3 times lower.

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 and 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 1980–2013. This decrease varied between 3.9–9.0% per year (table 23.2). The time series for guillemot eggs (1969–2013) showed a significant decrease of 9.3% per year for DDE (Fig. 23.7).

## DDE, µg/g lipid w., herring muscle
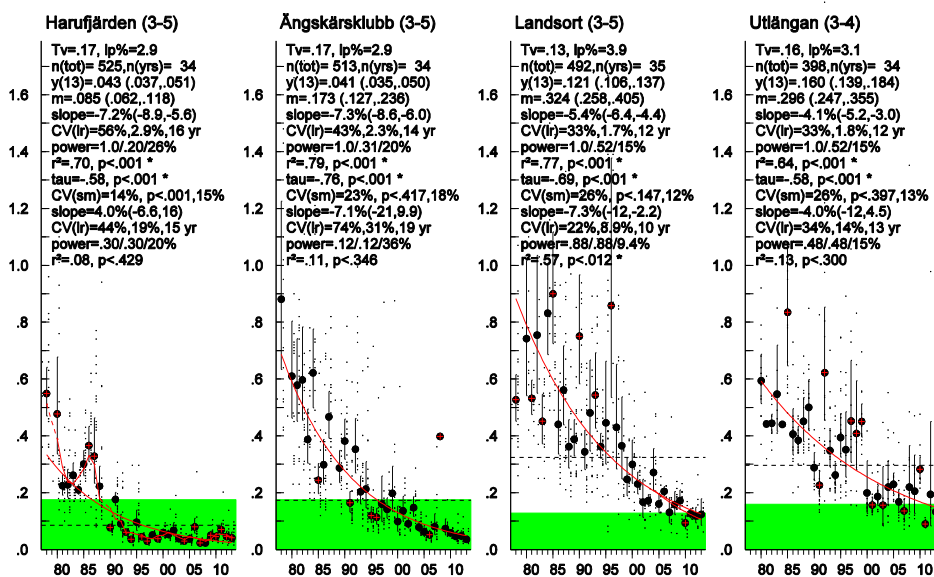


**Figure 23.2.** DDE concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1978, 1978, 1978 and 1980 respectively). The green area denotes the levels below the suggested target value for DDE in fish.

## DDE, µg/g lipid w., herring muscle
### Fat adjusted spring herring samples
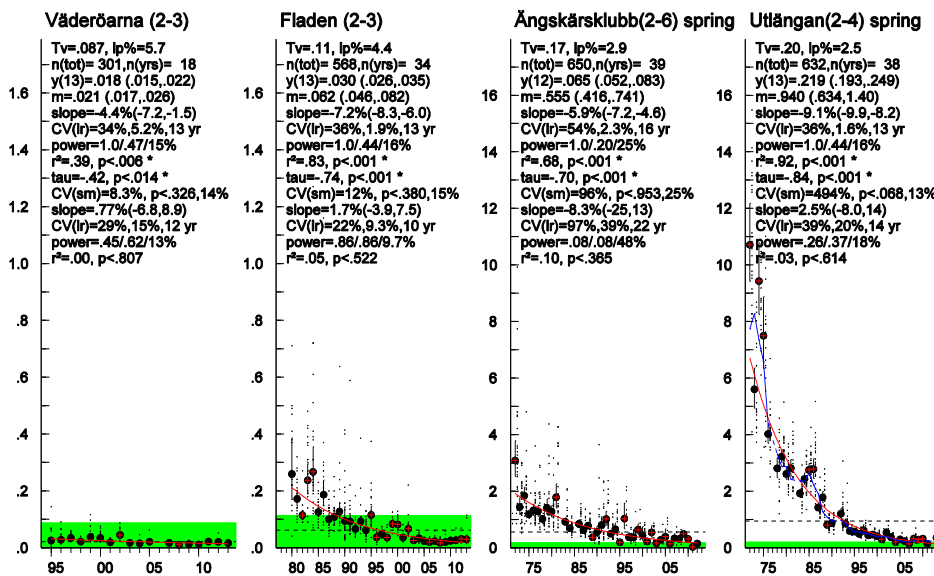


**Figure 23.3.** DDE concentrations (µg/g lipid weight) in herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1972, 1972, 1980 and 1995 respectively). The green area denotes the levels below the suggested target value for DDE in fish.

## DDE, µg/g lipid w., cod liver and perch muscle.
### Geometric means, fat adjusted for cod
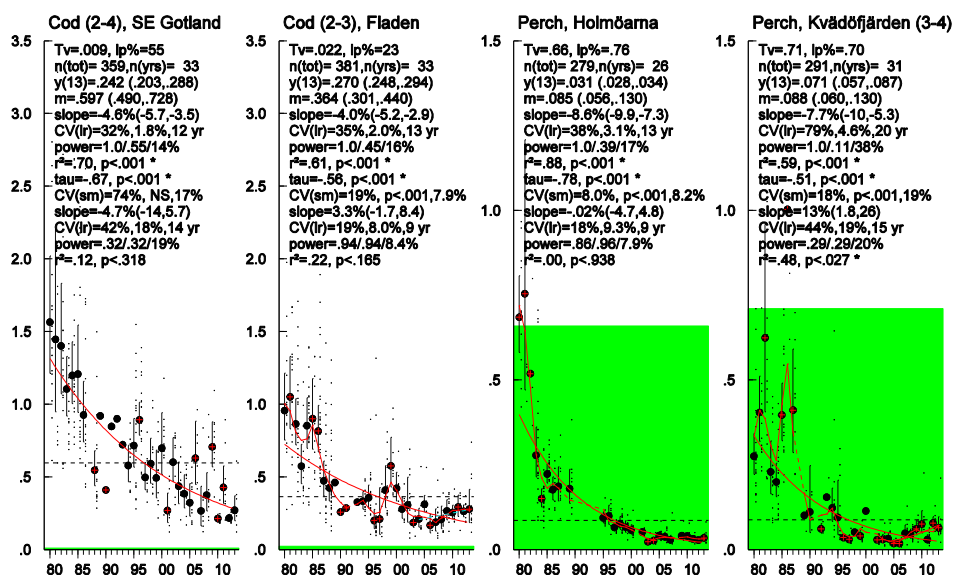


**Figure 23.4.** DDE concentrations (µg/g lipid weight) in cod liver from Southeast Gotland, Fladen; and perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1980). The green area denotes the levels below the suggested target value for DDE in fish.

## DDE, µg/g lipid w., Eelpout muscle
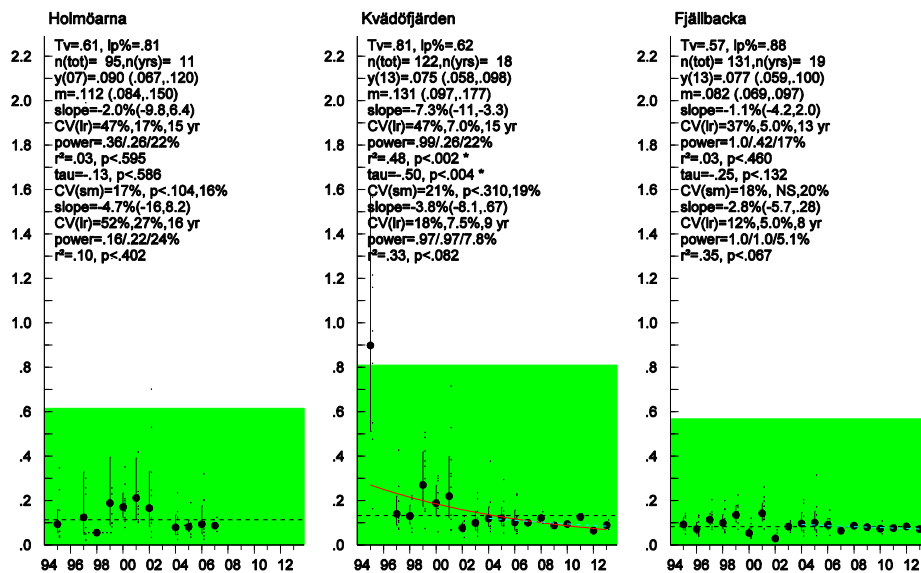


**Figure 23.5.** DDE concentrations (µg/g lipid weight) in eelpout muscle at Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for DDE in fish.

## DDE, µg/g lipid w., blue mussel

**Kvädöfjärden**

n(tot)= 95,n(yrs)= 19
y(13)=.036 (.032,.041)
m=.060 (.052,.070)
slope=-3.9%(-5.7,-2.1)
CV(lr)=22%,3.0%,10 yr
power=1.0/.88/9.4%
r²=.54, p<.001 *
tau=-.60, p<.001 *
CV(sm)=7.5%, p<.412,8.9%
slope=-8.5%(-13,-3.8)
CV(lr)=20%,8.3%,10 yr
power=.93/.93/8.7%
r²=.67, p<.004 *

**Fjällbacka**

n(tot)= 104,n(yrs)= 29
y(13)=.017 (.015,.020)
m=.031 (.024,.040)
slope=-6.3%(-7.8,-4.9)
CV(lr)=37%,2.6%,13 yr
power=1.0/.42/17%
r²=.73, p<.001 *
tau=-.67, p<.001 *
CV(sm)=8.1%, p<.023,12%
slope=-.94%(-5.1,3.4)
CV(lr)=17%,7.0%,9 yr
power=.98/.98/7.3%
r²=.03, p<.628

**Nidingen**

n(tot)= 101,n(yrs)= 29
y(13)=.027 (.022,.034)
m=.046 (.035,.061)
slope=-6.2%(-7.9,-4.5)
CV(lr)=45%,3.1%,15 yr
power=1.0/.29/21%
r²=.67, p<.001 *
tau=-.63, p<.001 *
CV(sm)=14%, p<.638,20%
slope=1.3%(-5.7,8.7)
CV(lr)=29%,12%,12 yr
power=.64/.64/13%
r²=.02, p<.694

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**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).

## DDE, µg/g lipid w., guillemot egg

**Stora Karlsö**

n(tot)= 450,n(yrs)= 43
y(13)=7.93 (7.46,8.44)
m=48.2 (32.3,71.8)
slope=-9.3%(-10,-8.6)
CV(lr)=30%,1.2%,12 yr
power=1.0/.58/14%
r²=.95, p<.001 *
tau=-.93, p<.001 *
CV(sm)=4.0%, p<.001,6.5%
slope=-8.5%(-13,-4.2)
CV(lr)=18%,7.5%,9 yr
power=.97/.97/7.8%
r²=.72, p<.002 *
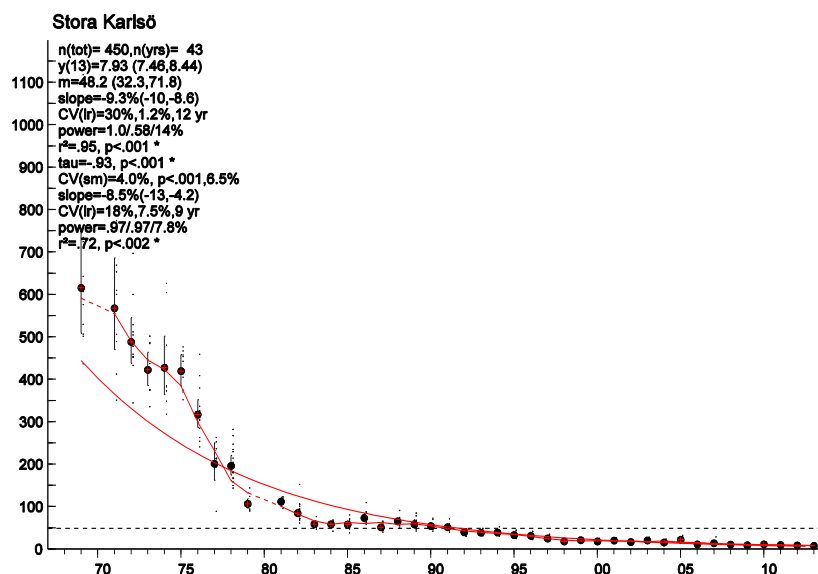
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**Figure 23.7.** DDE concentrations (µg/g lipid weight) in guillemot eggs at Stora Karlsö (time series starting in 1969).

The number of years required to detect an annual change of 10% for DDE in herring varied between 12–16 years.

In general, DDE varies somewhat less between years compared to DDT and DDD. The ratio of DDT/∑DDT has been shown to be significantly decreasing at all herring sites in previous years of monitoring. At present, the DDT and DDD concentrations are below the limit of quantification at a majority of sites and matrices. Hence, comparisons with DDT such as DDT/∑DDT-ratios are no longer performed.

### 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 µg/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 1980–2013. DDE concentration has decreased by 10% per year in guillemot eggs. DDT has been shown in previous years to 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 Southern 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) | 525 | 34 | 78-13 | -7.2(-8.9,-5.6) | 0.0000 | --- | 16 | 26 | .043 (.037,.051) |
| Harufjärden (3-5) | | 10 | 04-13 | 4(-6.6,16) | 0.4292 | | 15 | 20 | |
| Ängskärsklubb (3-5) | 513 | 34 | 78-13 | -7.3(-8.6,-6.0) | 0.0000 | --- | 14 | 20 | .041 (.035,.050) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -7.1(-21,9.9) | 0.3461 | | 19 | 36 | |
| Landsort (3-5) | 492 | 35 | 78-13 | -5.4(-6.4,-4.4) | 0.0000 | --- | 12 | 15 | .121 (.106,.137) |
| Landsort (3-5) | | 10 | 04-13 | -7.3(-12,-2.2) | 0.0116 | - | 10 | 9.4 | |
| Utlängan (2-4) | 398 | 34 | 80-13 | -4.1(-5.2,-3.0) | 0.0000 | --- | 12 | 15 | .160 (.139,.184) |
| Utlängan (2-4) | | 10 | 04-13 | -4(-12,4.5) | 0.2999 | | 13 | 15 | |
| Ängskärsklubb spring (2-6) | 650 | 39 | 72-12 | -5.9(-7.2,-4.6) | 0.0000 | --- | 16 | 25 | .065 (.052,.083) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -8.3(-25,13) | 0.3646 | | 22 | 48 | |
| Utlängan spring (2-4) | 632 | 38 | 72-13 | -9.1(-9.9,-8.2) | 0.0000 | --- | 13 | 16 | .219 (.193,.249) |
| Utlängan spring (2-4) | | 9 | 04-13 | 2.5(-8.0,14) | 0.6136 | | 14 | 18 | |
| Fladen (2-3) | 568 | 34 | 80-13 | -7.2(-8.3,-6.0) | 0.0000 | --- | 13 | 16 | .030 (.026,.035) |
| Fladen (2-3) | | 10 | 04-13 | 1.7(-3.9,7.5) | 0.5215 | | 10 | 9.7 | |
| Väderöarna | 301 | 18 | 95-13 | -4.4(-7.2,-1.5) | 0.0055 | -- | 13 | 15 | .018 (.015,.022) |
| Väderöarna | | 9 | 04-13 | 0.77(-6.8,8.9) | 0.8067 | | 12 | 13 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 279 | 26 | 80-13 | -8.6(-9.9,-7.3) | 0.0000 | --- | 13 | 17 | .031 (.028,.034) |
| Holmöarna | | 9 | 04-13 | -0.02(-4.7,4.8) | 0.9385 | | 9 | 7.9 | |
| Kvädöfjärden | 291 | 31 | 80-13 | -7.7(-10,-5.3) | 0.0000 | --- | 20 | 38 | .071 (.057,.087) |
| Kvädöfjärden | | 10 | 04-13 | 13(1.8,26) | 0.0267 | + | 15 | 20 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 359 | 33 | 80-13 | -4.6(-5.7,-3.5) | 0.0000 | --- | 12 | 14 | .242 (.203,.288) |
| SE Gotland (2-4) | | 10 | 04-13 | -4.7(-14,5.7) | 0.3176 | | 14 | 19 | |
| Fladen (2-3) | 381 | 33 | 80-13 | -4(-5.2,-2.9) | 0.0000 | --- | 13 | 16 | .270 (.248,.294) |
| Fladen (2-3) | | 10 | 04-13 | 3.3(-1.7,8.4) | 0.1653 | | 9 | 8.4 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 95 | 11 | 95-07 | -2(-9.8,6.4) | 0.5953 | | 15 | 22 | .090 (.067,.120) |
| Holmöarna | | 9 | 98-07 | -4.7(-16,8.2) | 0.4021 | | 16 | 24 | |
| Kvädöfjärden | 122 | 18 | 95-13 | -7.3(-11,-3.3) | 0.0016 | -- | 15 | 22 | .075 (.058,.098) |
| Kvädöfjärden | | 10 | 04-13 | -3.8(-8.1,.67) | 0.082 | | 9 | 7.8 | |
| Fjällbacka | 131 | 19 | 95-13 | -1.1(-4.2,2.0) | 0.4601 | | 13 | 17 | .077 (.059,.100) |
| Fjällbacka | | 10 | 04-13 | -2.8(-5.7,.28) | 0.0675 | | 8 | 5.1 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 101 | 29 | 82-13 | -6.2(-7.9,-4.5) | 0.0000 | --- | 15 | 21 | .027 (.022,.034) |
| Nidingen | | 10 | 04-13 | 1.3(-5.7,8.7) | 0.6944 | | 12 | 13 | |
| Fjällbacka | 104 | 29 | 84-13 | -6.3(-7.8,-4.9) | 0.0000 | --- | 13 | 17 | .017 (.015,.020) |
| Fjällbacka | | 10 | 04-13 | -0.94(-5.1,3.4) | 0.6284 | | 9 | 7.3 | |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | 95 | 19 | 95-13 | -3.9(-5.7,-2.1) | 0.0004 | --- | 10 | 9.4 | .036 (.032,.041) |
| Kvädöfjärden | | 10 | 04-13 | -8.5(-13,-3.8) | 0.0037 | -- | 10 | 8.7 | |

| **Guillemot egg** | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 450 | 43 | 69-13 | -9.3(-10,-8.6) | 0.0000 | --- | 12 | 14 | 7.93 (7.46,8.44) |
| Stora Karlsö | | 10 | 04-13 | -8.5(-13,-4.2) | 0.0021 | -- | 9 | 7.8 | |

**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

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 and Macdonald, 2005). Technical HCH contains various isomers: 60–75% α-HCH; 15% γ-HCH (lindane); 7–10% β-HCH; 7% δ-HCH; and 1–2% ε-HCH, and came into general use in 1950 (Gaul H., 1992). The γ-isomer is the most toxic isomer of the HCHs, being 500–1000 times as potent as the α-isomer (White-Stevens R., 1971). Lindane consists mainly of γ-HCH (Li and 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 (HELCOM, 1988). HCHs, α-HCH, β-HCH and γ-HCH,  is included as Persistent  Organic Pollutants (POPs) in The Stockholm Convention on POPs, an international agreement requiring measures for reducing or preventing release of dangerous substances into the environment (Stockholm Convention).

In Sweden, the use of lindane was severely restricted in 1970, and in 1978 prohibited for use in agriculture due to 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 and 1980. Since 1980, use of lindane in Europe has been allowed only as an insecticide. In a study investigating global HCH usage it found that both technical HCH and technical Lindane was used to a great extent in France and Italy as recently as 1990 (Li 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.

## 24.3 Results

### 24.3.1 Spatial Variation
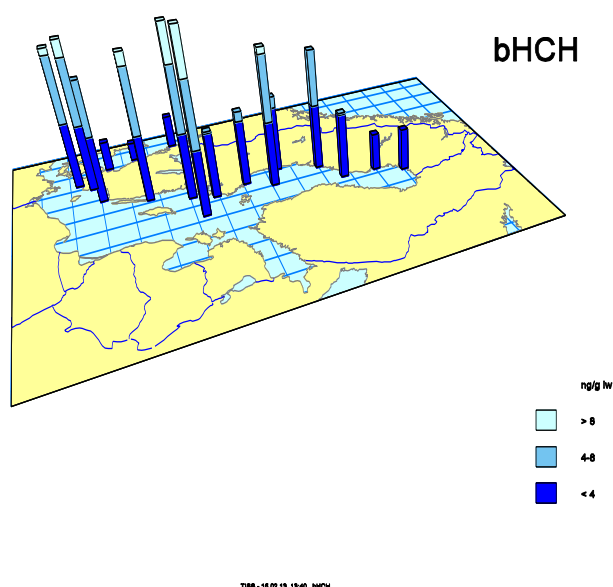


**Figure 24.1.** Spatial variation of β-HCH concentrations (ng/g lipid weight.) in herring muscle.

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

An annual decreasing trend of 11–15% was found for herring from all sites (Fig. 24.2, table 24.1). Concentrations in cod liver (Fig. 24.4) have significantly decreased in the time series from the Southeast of Gotland and Fladen. 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).

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 9–13 years (Fig. 24.2 and 24.3).



**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 α in fish. The bars represent years where all values were below LOQ.

## a-HCH, µg/g lipid w., herring muscle



**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 α-HCH in fish. The bars represent years where all values were below LOQ.

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



**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 α-HCH in fish. The bars represent years where all values were below LOQ.

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## a-HCH, µg/g lipid w., blue mussel

**Kvädöfjärden**

```
n(tot)= 95,n(yrs)= 19
y(13)=.003 (.003,.003)
m=.007 (.005,.011)
slope=-14%(-16,-12)
CV(lr)=28%,3.8%,11 yr
power=1.0/.67/12%
r²=.91, p<.001 *
tau=-.86, p<.001 *
CV(sm)=4.7%, p<.100,9.8%
slope=-13%(-21,-5.8)
CV(lr)=35%,14%,13 yr
power=.47/.47/16%
r²=.66, p<.004 *
```

**Fjällbacka**

```
n(tot)= 100,n(yrs)= 25
y(13)=.003 (.003,.003)
m=.005 (.004,.008)
slope=-9.9%(-12,-7.9)
CV(lr)=43%,3.7%,14 yr
power=1.0/.32/20%
r²=.80, p<.001 *
tau=-.70, p<.001 *
CV(sm)=4.5%, p<.001,10%
slope=.39%(-3.5,4.4)
CV(lr)=16%,6.4%,8 yr
power=.99/.99/6.6%
r²=.00, p<.807
```

**Nidingen**

```
n(tot)= 102,n(yrs)= 26
y(13)=.003 (.003,.004)
m=.006 (.004,.009)
slope=-10%(-12,-8.4)
CV(lr)=41%,3.4%,14 yr
power=1.0/.34/19%
r²=.82, p<.001 *
tau=-.63, p<.001 *
CV(sm)=4.1%, p<.001,8.8%
slope=.75%(-4.1,5.8)
CV(lr)=19%,8.1%,9 yr
power=.94/.94/8.4%
r²=.01, p<.729
```



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**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 in general follow similar patterns as α- and γ-HCH. 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 (not presented in the report), and in guillemot eggs from St Karlsö (Fig. 24.6).
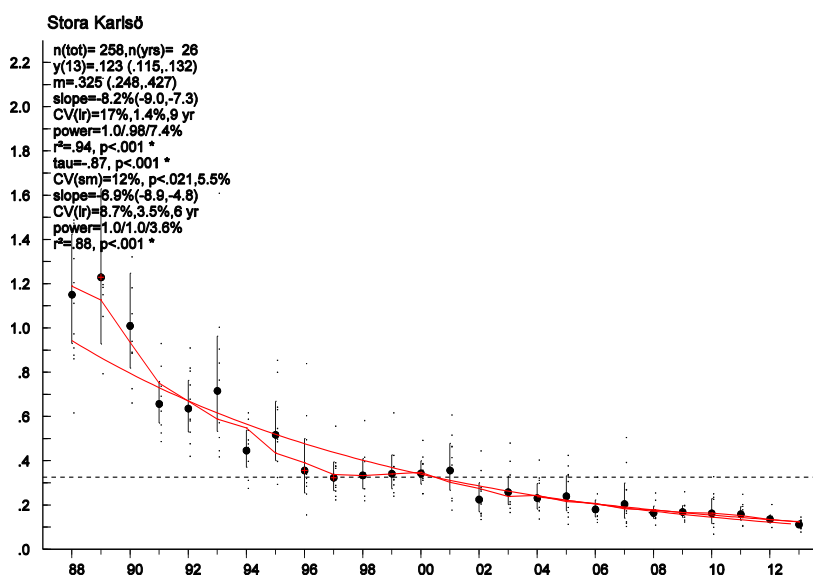
## b-HCH, µg/g lipid w., guillemot egg

**Stora Karlsö**

```
n(tot)= 258,n(yrs)= 26
y(13)=.123 (.115,.132)
m=.325 (.248,.427)
slope=-8.2%(-9.0,-7.3)
CV(lr)=17%,1.4%,9 yr
power=1.0/.98/7.4%
r²=.94, p<.001 *
tau=-.87, p<.001 *
CV(sm)=12%, p<.021,5.5%
slope=-6.9%(-8.9,-4.8)
CV(lr)=8.7%,3.5%,6 yr
power=1.0/1.0/3.6%
r²=.88, p<.001 *
```



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**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. 24.7–10). This annual decrease is in the magnitude of 9–14% for herring and blue mussels and 14–16% for cod (Fig. 24.7–10, table 24.2).

## Lindane, µg/g lipid w., herring muscle
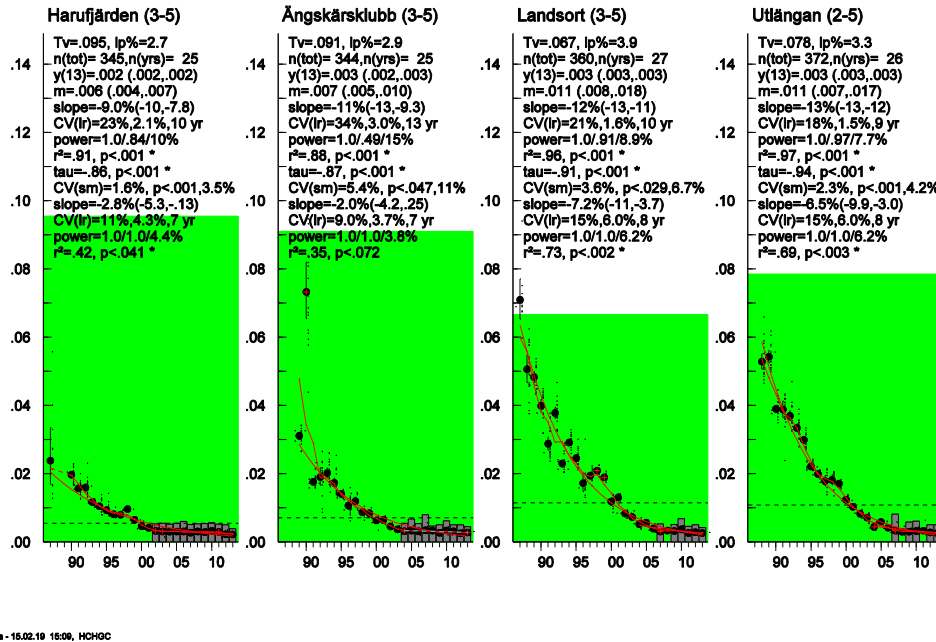


**Figure 24.7.** γ-HCH concentrations (µg/g lipid weight) herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series from 1987, 1989, 1987 and 1998 respectively). The green area denotes the levels below the suggested target value for lindane in fish. The bars represent years where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

## Lindane, µg/g lipid w., herring muscle
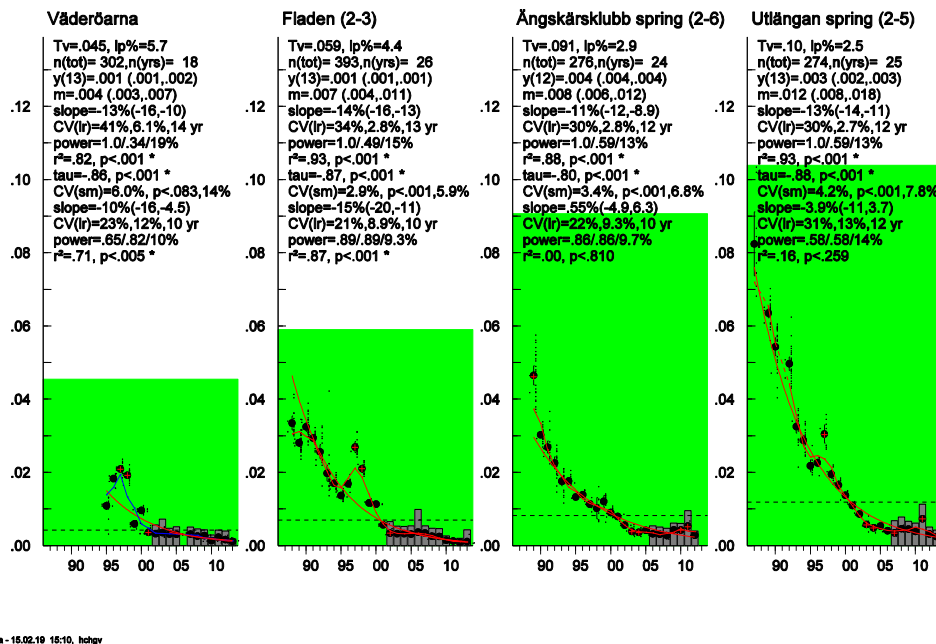


**Figure 24.8.** γ-HCH concentrations (µg/g lipid weight) herring muscle from Ängskärsklubb (spring), Utlängan (spring), Fladen and Väderöarna (time series starting in 1989, 1986, 1988 and 1995 respectively). The green area denotes the levels below the suggested target value for lindane in fish. The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

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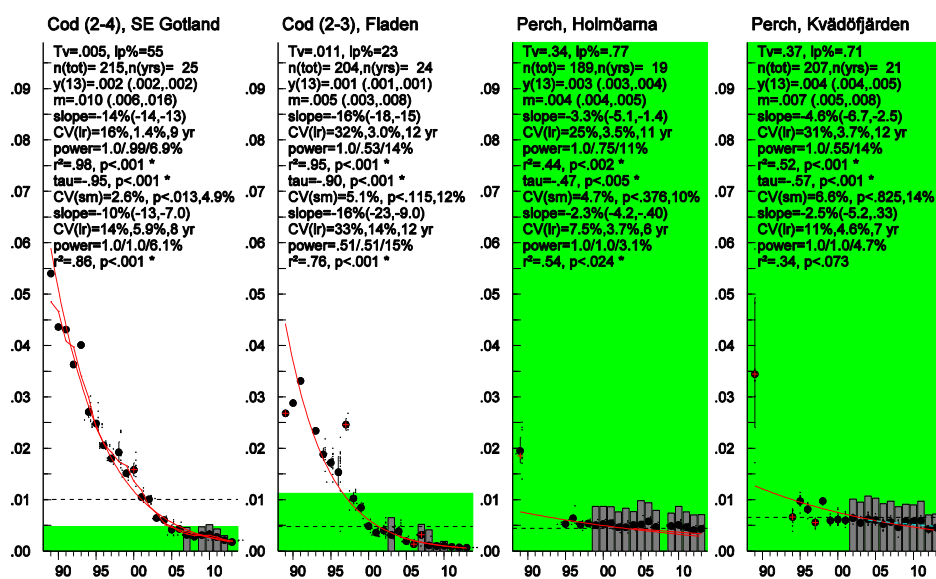


**Figure 24.9.** γ-HCH concentrations (µg/g lipid weight) in cod liver from Southeast Gotland and Fladen; and in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 (cod); and 1989 (perch). The green area denotes the levels below the suggested target value for lindane in fish.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

## Lindane, µg/g lipid w., blue mussel
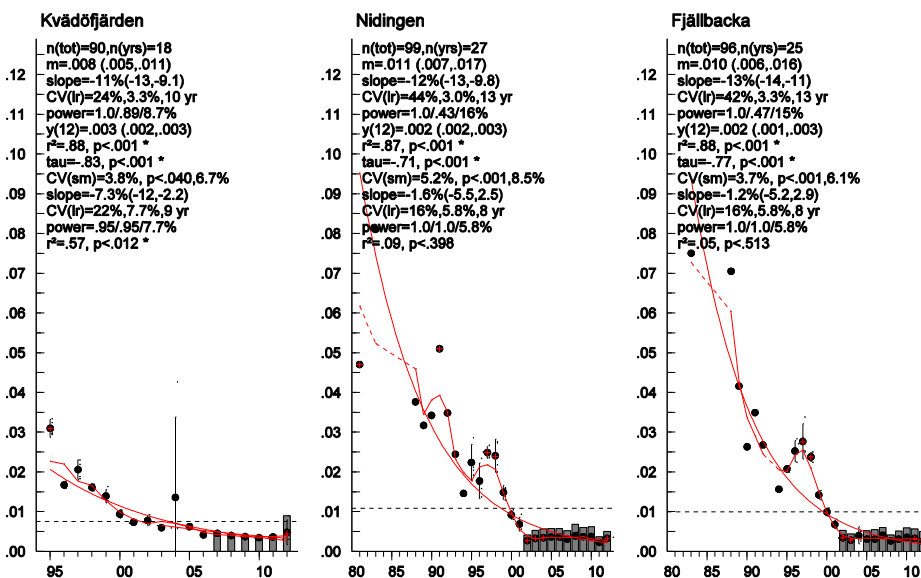


**Figure 24.10.** γ-HCH concentrations (µg/g lipid weight) in blue mussel from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1995; 1981, 1983 and 1983). The bars represent years where all values were below LOQ.

### 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% (40–90%) 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 α-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) in various matrices, but **ß-HCH** for guillemot eggs, assessed from the annual geometric mean. 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) | 342 | 25 | 87-13 | -13(-15,-12) | 0.0000 | --- | 11 | 11 | .002 (.002,.002) |
| Harufjärden (3-5) | | 10 | 04-13 | -3.4(-5.9,-.81) | 0.04 | - | 7 | 4.7 | |
| Ängskärsklubb (3-5) | 344 | 25 | 89-13 | -14(-16,-13) | 0.0000 | --- | 13 | 15 | .003 (.002,.003) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -1.1(-2.8,.55) | 0.244 | | 6 | 3 | |
| Landsort (3-5) | 360 | 27 | 87-13 | -15(-16,-14) | 0.0000 | --- | 10 | 9 | .003 (.003,.003) |
| Landsort (3-5) | | 10 | 04-13 | -7.6(-11,-4.4) | 0.0025 | -- | 8 | 6.1 | |
| Utlängan (2-4) | 316 | 26 | 88-13 | -15(-16,-14) | 0.0000 | --- | 9 | 8.6 | .003 (.003,.003) |
| Utlängan (2-4) | | 10 | 04-13 | -6.5(-9.7,-3.3) | 0.0066 | -- | 8 | 6.3 | |
| Ängskärsklubb spring (2-6) | 275 | 24 | 89-12 | -14(-16,-13) | 0.0000 | --- | 11 | 11 | .003 (.003,.004) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -4.5(-8.8,.092) | 0.1034 | | 9 | 8.6 | |
| Utlängan spring (2-4) | 264 | 24 | 87-13 | -14(-15,-13) | 0.0000 | --- | 11 | 12 | .003 (.003,.003) |
| Utlängan spring (2-4) | | 10 | 04-13 | -4.4(-8.6,-.01) | 0.0972 | | 9 | 8.2 | |
| Fladen (2-3) | 393 | 26 | 88-13 | -13(-14,-12) | 0.0000 | --- | 9 | 7.4 | .001 (.001,.001) |
| Fladen (2-3) | | 10 | 04-13 | -14(-17,-9.8) | 0.0003 | --- | 9 | 8.1 | |
| Väderöarna | 282 | 17 | 95-13 | -11(-12,-9.0) | 0.0000 | --- | 10 | 8.9 | .001 (.001,.001) |
| Väderöarna | | 9 | 04-13 | -8.4(-13,-3.9) | 0.01 | -- | 9 | 8.2 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 189 | 19 | 89-13 | -5(-7.3,-2.7) | 0.0004 | --- | 12 | 15 | .004 (.004,.005) |
| Holmöarna | | 9 | 04-13 | -0.22(-2.1,1.7) | 0.7773 | | 6 | 3 | |
| Kvädöfjärden | 261 | 26 | 84-13 | -9.2(-11,-7.1) | 0.0000 | --- | 15 | 22 | .004 (.004,.005) |
| Kvädöfjärden | | 10 | 04-13 | -0.04(-2.7,2.6) | 0.9223 | | 7 | 4.4 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 225 | 25 | 89-13 | -16(-17,-15) | 0.0000 | --- | 9 | 8.1 | .002 (.002,.002) |
| SE Gotland (2-4) | | 10 | 04-13 | -11(-14,-7.4) | 0.0001 | --- | 8 | 5.9 | |
| Fladen (2-3) | 218 | 25 | 89-13 | -14(-15,-13) | 0.0000 | --- | 10 | 8.6 | .001 (.001,.001) |
| Fladen (2-3) | | 10 | 04-13 | -14(-19,-7.9) | 0.0009 | --- | 11 | 11 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 102 | 26 | 88-13 | -10(-12,-8.4) | 0.0000 | --- | 14 | 19 | .003 (.003,.004) |
| Nidingen | | 10 | 04-13 | 0.75(-4.1,5.8) | 0.7292 | | 9 | 8.4 | |
| Fjällbacka | 100 | 25 | 88-13 | -9.9(-12,-7.9) | 0.0000 | --- | 14 | 20 | .003 (.003,.003) |
| Fjällbacka | | 10 | 04-13 | 0.39(-3.5,4.4) | 0.8069 | | 8 | 6.6 | |
| Kvädöfjärden | 95 | 19 | 95-13 | -14(-16,-12) | 0.0000 | --- | 11 | 12 | .003 (.003,.003) |
| Kvädöfjärden | | 10 | 04-13 | -13(-21,-5.8) | 0.0045 | -- | 13 | 16 | |
| **Guillemot egg** | | | | | | | | | |
| Stora Karlsö | 258 | 26 | 88-13 | -8.2(-9.0,-7.3) | 0.0000 | --- | 9 | 7.4 | .123 (.115,.132) |
| Stora Karlsö | | 10 | 04-13 | -6.9(-8.9,-4.8) | 0.0001 | --- | 6 | 3.6 | |

**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) | 345 | 25 | 87-13 | -9(-10,-7.8) | 0.0000 | --- | 10 | 10 | .002 (.002,.002) |
| Harufjärden (3-5) | | 10 | 04-13 | -2.8(-5.3,-.13) | 0.0409 | - | 7 | 4.4 | |
| Ängskärsklubb (3-5) | 344 | 25 | 89-13 | -11(-13,-9.3) | 0.0000 | --- | 13 | 15 | .003 (.002,.003) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -2(-4.2,.25) | 0.0717 | | 7 | 3.8 | |
| Landsort (3-5) | 360 | 27 | 87-13 | -12(-13,-11) | 0.0000 | --- | 10 | 8.9 | .003 (.003,.003) |
| Landsort (3-5) | | 10 | 04-13 | -7.2(-11,-3.7) | 0.0017 | -- | 8 | 6.2 | |
| Utlängan (2-4) | 372 | 26 | 88-13 | -13(-13,-12) | 0.0000 | --- | 9 | 7.7 | .003 (.003,.003) |
| Utlängan (2-4) | | 10 | 04-13 | -6.5(-9.9,-3.0) | 0.0029 | -- | 8 | 6.2 | |
| Ängskärsklubb spring (2-6) | 276 | 24 | 89-12 | -11(-12,-8.9) | 0.0000 | --- | 12 | 13 | .004 (.004,.004) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | 0.55(-4.9,6.3) | 0.8101 | | 10 | 9.7 | |
| Utlängan spring (2-4) | 274 | 25 | 87-13 | -13(-14,-11) | 0.0000 | --- | 12 | 13 | .003 (.002,.003) |
| Utlängan spring (2-4) | | 10 | 04-13 | -3.9(-11,3.7) | 0.2594 | | 12 | 14 | |
| Fladen (2-3) | 393 | 10 | 04-13 | -15(-20,-11) | 0.0001 | --- | 10 | 9.3 | .001 (.001,.001) |
| Väderöarna | 302 | 18 | 95-13 | -13(-16,-10) | 0.0000 | --- | 14 | 19 | .001 (.001,.002) |
| Väderöarna | | 9 | 04-13 | -10(-16,-4.5) | 0.0047 | -- | 10 | 10 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 189 | 19 | 89-13 | -3.3(-5.1,-1.4) | 0.0019 | -- | 11 | 11 | .003 (.003,.004) |
| Holmöarna | | 9 | 04-13 | -2.3(-4.2,-.40) | 0.0241 | - | 6 | 3.1 | |
| Kvädöfjärden | 207 | 21 | 89-13 | -4.6(-6.7,-2.5) | 0.0002 | --- | 12 | 14 | .004 (.004,.005) |
| Kvädöfjärden | | 10 | 04-13 | -2.5(-5.2,.33) | 0.0734 | | 7 | 4.7 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 215 | 25 | 89-13 | -14(-14,-13) | 0.0000 | --- | 9 | 6.9 | .002 (.002,.002) |
| SE Gotland (2-4) | | 10 | 04-13 | -10(-13,-7.0) | 0.0002 | --- | 8 | 6.1 | |
| Fladen (2-3) | 204 | 24 | 89-13 | -16(-18,-15) | 0.0000 | --- | 12 | 14 | .001 (.001,.001) |
| Fladen (2-3) | | 10 | 04-13 | -16(-23,-9.0) | 0.0012 | -- | 12 | 15 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 104 | 28 | 81-13 | -11(-13,-9.5) | 0.0000 | --- | 15 | 21 | .003 (.003,.004) |
| Nidingen | | 10 | 04-13 | -1.5(-5.5,2.6) | 0.4192 | | 9 | 7 | |
| Fjällbacka | 101 | 26 | 83-13 | -12(-14,-10) | 0.0000 | --- | 14 | 20 | .003 (.003,.003) |
| Fjällbacka | | 10 | 04-13 | -1.6(-5.4,2.3) | 0.3619 | | 8 | 6.5 | |
| Kvädöfjärden | 95 | 19 | 95-13 | -11(-13,-8.5) | 0.0000 | --- | 11 | 11 | .004 (.004,.005) |
| Kvädöfjärden | | 10 | 04-13 | -6.8(-12,-1.3) | 0.0208 | - | 10 | 9.8 | |

**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

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 (HELCOM, 1988). 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 (Stockholm Convention).

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

## 25.3  Results

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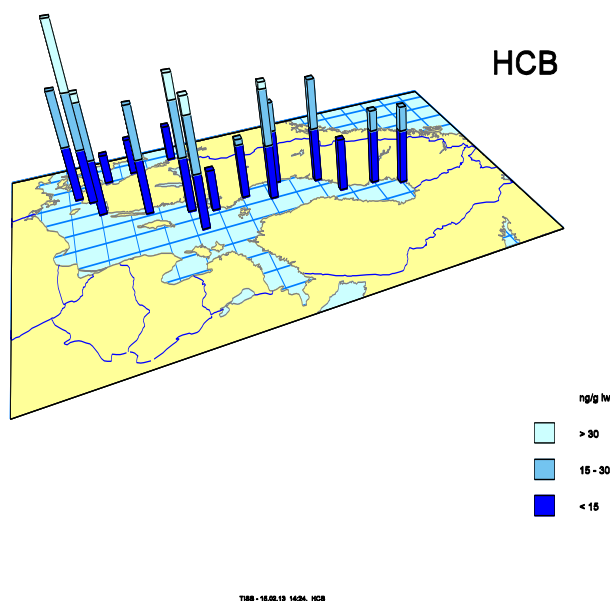
**Figure 25.1.** Spatial variation of HCB concentrations (ng/g lipid weight) in herring muscle.

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 Västra Hanöbukten 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 and Holmöarna (only eelpout), indicated that concentrations were around twice as high in the Baltic compared to the Kattegat and the Skagerrak (Fig. 25.5 and 25.6).

### 25.3.2 Temporal Variation

There were significant decreases in HCB concentrations in a majority of the herring and all of the cod sites, as well as in eelpout from Holmöarna (Fig. 25.2–5) 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 for the whole time series (Fig. 25. 6). The decrease is in the magnitude of 1.5–6.3% for herring, cod, perch and guillemot egg (Fig. 25.2–5 and 25.7, 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.

## HCB, µg/g lipid w., herring muscle
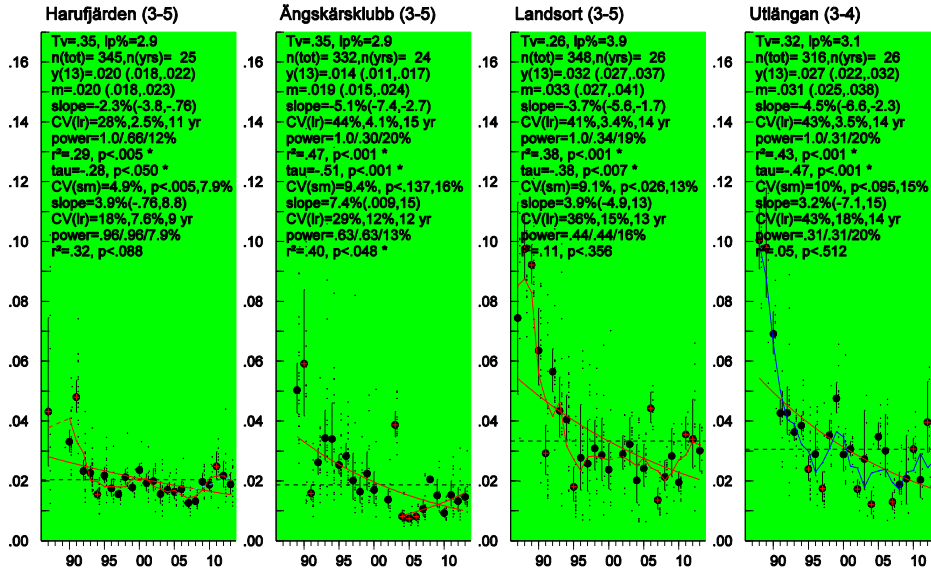


**Figure 25.2.** HCB concentrations (µg/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1987, 1989, 1987 and 1988 respectively). The green area denotes the levels below the suggested target value for HCB in fish.
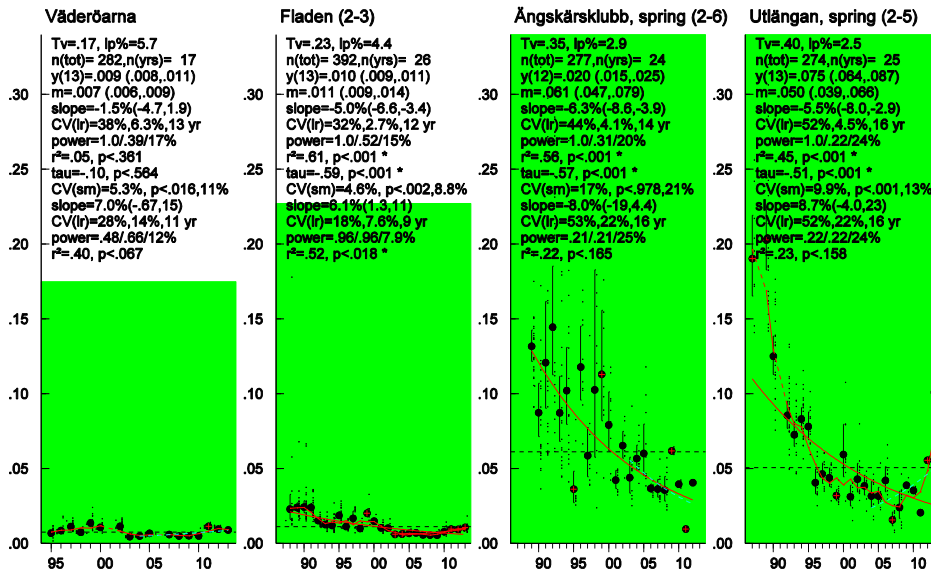
## HCB, µg/g lipid w., herring muscle



**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.

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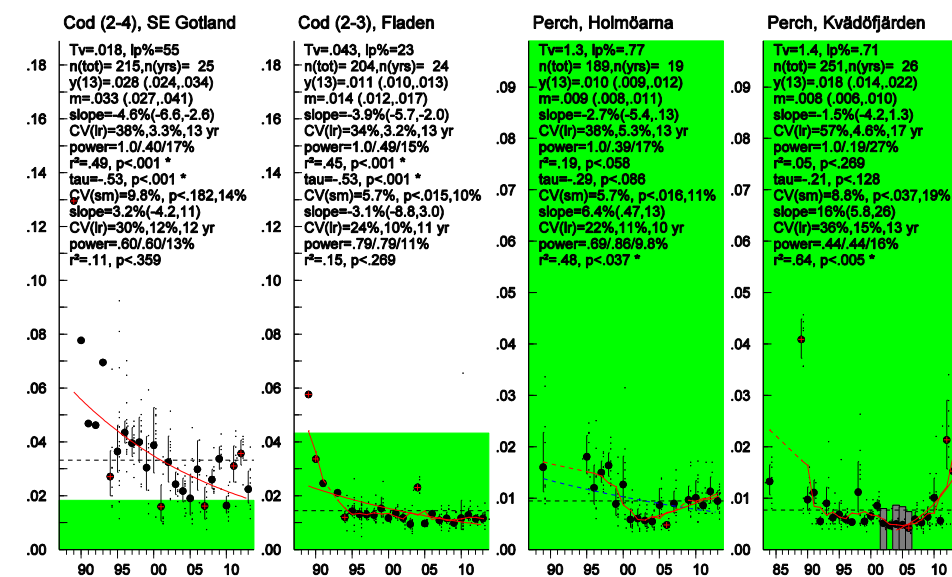


**Figure 25.4.** HCB concentrations (µg/g lipid weight) in cod liver from Southeast Gotland and Fladen, and in perch muscle from Holmöarna and Kvädöfjärden (time series starting in 1989 (cod); 1989 and 1984 perch). The green area denotes the levels below the suggested target value for HCB in fish. The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

## HCB, µg/g lipid w., eelpout muscle
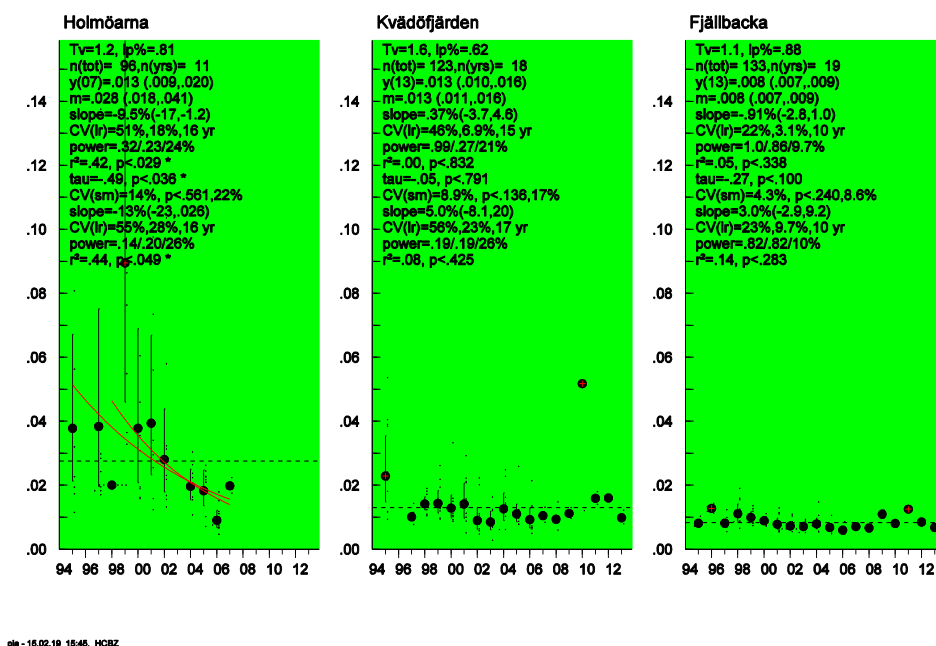


**Figure 25.5.** HCB concentrations (µg/g lipid weight) in eelpout muscle from Holmöarna, Kvädöfjärden and Fjällbacka (time series starting in 1995). The green area denotes the levels below the suggested target value for HCB in fish.

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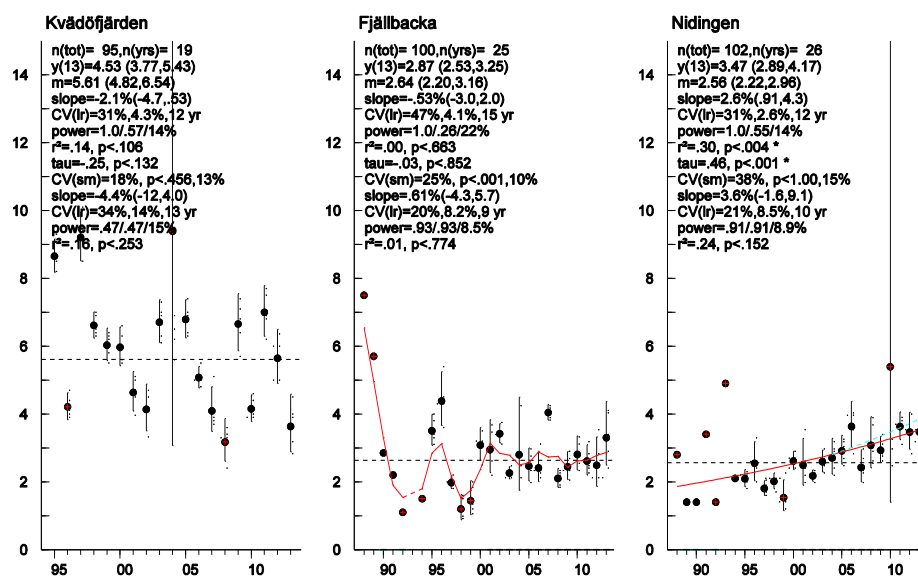
**Figure 25.6.** HCB concentrations (μg/g lipid weight) in blue mussel soft tissue from Kvädöfjärden, Nidingen and Fjällbacka (time series starting in 1988, 1988 and 1995 respectively).

The number of years required to detect an annual change of 10% varied between 12–15 years for the blue mussel series.
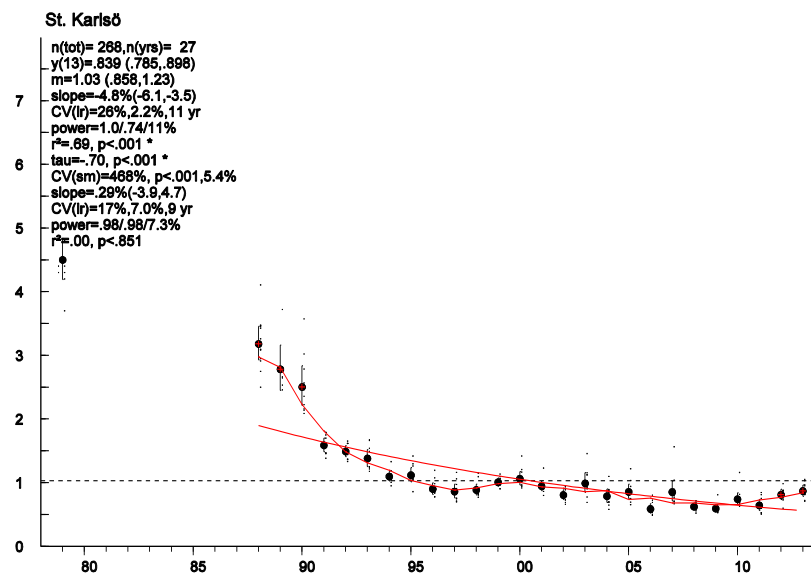


**Figure 25.7.** HCB concentrations (μg/g lipid weight) in guillemot eggs from Stora Karlsö (time series from 1979).

### 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 (13) > Perch (10)
Kvädöfjärden: Perch (18) > Eelpout (13) > Blue mussel (4.5)
Fladen/Nidingen: Cod (11) > Herring (10) > Blue mussel (3.5)
Väderöarna/Fjällbacka: Herring (9) – Eelpout (8) > Blue mussel (2.9)

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

Herring caught at Ängskärsklubb (autumn) 14 < 20 (spring) and Utlängan (autumn) 27 < 75 (spring).

### 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.

**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 (3-5) | 345 | 25 | 87-13 | -2.3(-3.8,-.76) | 0.0051 | -- | 11 | 12 | .020 (.018,.022) |
| Harufjärden (3-5) | | 10 | 04-13 | 3.9(-.76,8.8) | 0.0881 | | 9 | 7.9 | |
| Ängskärsklubb (3-5) | 332 | 24 | 89-13 | -5.1(-7.4,-2.7) | 0.0002 | --- | 15 | 20 | .014 (.011,.017) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 7.4(.009,15) | 0.0483 | + | 12 | 13 | |
| Landsort (3-5) | 348 | 26 | 87-13 | -3.7(-5.6,-1.7) | 0.0008 | --- | 14 | 19 | .032 (.027,.037) |
| Landsort (3-5) | | 10 | 04-13 | 3.9(-4.9,13) | 0.3556 | | 13 | 16 | |
| Utlängan (2-4) | 316 | 26 | 88-13 | -4.5(-6.6,-2.3) | 0.0003 | --- | 14 | 20 | .027 (.022,.032) |
| Utlängan (2-4) | | 10 | 04-13 | 3.2(-7.1,15) | 0.5119 | | 14 | 20 | |
| Ängskärsklubb spring (2-6) | 277 | 24 | 89-12 | -6.3(-8.6,-3.9) | 0.0000 | --- | 14 | 20 | .020 (.015,.025) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -8(-19,4.4) | 0.1648 | | 16 | 25 | |
| Utlängan spring (2-4) | 274 | 25 | 87-13 | -5.5(-8.0,-2.9) | 0.0003 | --- | 16 | 24 | .075 (.064,.087) |
| Utlängan spring (2-4) | | 10 | 04-13 | 8.7(-4.0,23) | 0.1576 | | 16 | 24 | |
| Fladen (2-3) | 392 | 26 | 88-13 | -5(-6.6,-3.4) | 0.0000 | --- | 12 | 15 | .010 (.009,.011) |
| Fladen (2-3) | | 10 | 04-13 | 6.1(1.3,11) | 0.0178 | + | 9 | 7.9 | |
| Väderöarna | 282 | 17 | 95-13 | -1.5(-4.7,1.9) | 0.3613 | | 13 | 17 | .009 (.008,.011) |
| Väderöarna | | 9 | 04-13 | 7(-.67,15) | 0.0667 | | 11 | 12 | |
| **Perch muscle** | | | | | | | | | |
| Holmöarna | 189 | 19 | 89-13 | -2.7(-5.4,.13) | 0.0578 | | 13 | 17 | .010 (.009,.012) |
| Holmöarna | | 9 | 04-13 | 6.4(.47,13) | 0.0369 | + | 10 | 9.8 | |
| Kvädöfjärden | 251 | 26 | 84-13 | -1.5(-4.2,1.3) | 0.2689 | --- | 17 | 27 | .018 (.014,.022) |
| Kvädöfjärden | | 10 | 04-13 | 16(5.8,26) | 0.0054 | ++ | 13 | 16 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 215 | 25 | 89-13 | -4.6(-6.6,-2.6) | 0.0001 | --- | 13 | 17 | .028 (.024,.034) |
| SE Gotland (2-4) | | 10 | 04-13 | 3.2(-4.2,11) | 0.3586 | | 12 | 13 | |
| Fladen (2-3) | 204 | 24 | 89-13 | -3.9(-5.7,-2.0) | 0.0004 | --- | 13 | 15 | .011 (.010,.013) |
| Fladen (2-3) | | 10 | 04-13 | -3.1(-8.8,3.0) | 0.2693 | | 11 | 11 | |
| **Eelpout** | | | | | | | | | |
| Holmöarna | 96 | 11 | 95-07 | -9.5(-17,-1.2) | 0.0295 | - | 16 | 24 | .013 (.009,.020) |
| Holmöarna | | 9 | 98-07 | -13(-23,.026) | 0.0491 | - | 16 | 26 | |
| Kvädöfjärden | 123 | 18 | 95-13 | 0.37(-3.7,4.6) | 0.8325 | | 15 | 21 | .013 (.010,.016) |
| Kvädöfjärden | | 10 | 04-13 | 5(-8.1,20) | 0.4253 | | 17 | 26 | |
| Fjällbacka | 133 | 19 | 95-13 | -0.91(-2.8,1.0) | 0.3377 | | 10 | 9.7 | .008 (.007,.009) |
| Fjällbacka | | 10 | 04-13 | 3(-2.9,9.2) | 0.2829 | | 10 | 10 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 102 | 26 | 88-13 | 2.6(.91,4.3) | 0.004 | ++ | 12 | 14 | 3.47 (2.89,4.17) |
| Nidingen | | 10 | 04-13 | 3.6(-1.6,9.1) | 0.1522 | | 10 | 8.9 | |
| Fjällbacka | 100 | 25 | 88-13 | -0.53(-3.0,2.0) | 0.6633 | | 15 | 22 | 2.87 (2.53,3.25) |
| Fjällbacka | | 10 | 04-13 | 0.61(-4.3,5.7) | 0.7744 | | 9 | 8.5 | |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Kvädöfjärden | 95 | 19 | 95-13 | -2.1(-4.7,.53) | 0.106 | | 12 | 14 | 4.53 (3.77,5.43) |
| Kvädöfjärden | | 10 | 04-13 | -4.4(-12,4.0) | 0.2529 | | 13 | 15 | |

**Guillemot egg**

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| Stora Karlsö | 268 | 10 | 04-13 | 0.29(-3.9,4.7) | 0.8515 | --- | 9 | 7.3 | .839 (.785,.898) |

# 26  PCDD/PCDFs – Polychlorinated dioxins/dibenzofurans

<div align="right">Updated 15.02.23</div>

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 the same toxic mode of action, 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 (OJEC No. L332 28.12.2000, 2000, OJEC No. L24 29.1.2008, 2008). The EU has also adopted a Community Strategy for dioxins, furans and PCBs (OJEC No. L332 17.11.2001, 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 priority hazardous substances of specific concern for the Baltic Sea (HELCOM, 2010), like OSPAR on the List of Chemicals for Priority Action (OSPAR Commision, 2013).

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 concentration in the muscle tissue of fish is 3.5 pg/g ww $WHO_{98}$-TEQ ($\Sigma$PCDD/Fs) or 6.5 pg/g ww $WHO_{98}$-TEQ ($\Sigma$PCDD/Fs + dl-PCBs) (OJEC No. L 320 3.12.2011, 2011). 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 (OJEC No. L321 6.12.2001, 2001, OJEC No. L37 7.2.2002, 2002, OJEC No. L364 20.12.2006, 2006, OSPAR Commision, 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 is 3.5 ng TEQ (2,3,7,8-tetrachlorodibenzo-*p*-dioxin equivalents) /kg wet weight, based on the $WHO_{05}$-TEF (toxic equivalent factors) values (Van den Berg et al., 2006). However, due to back-compatibility in the time series the same target value of 3.5 ng/kg TEQ was used but calculated using the $WHO_{98}$-TEF values (Van den Berg et al., 1998). The TEFs 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. In addition, a second target value based on the EC quality standard for biota derived in regards to secondary poisoning ($QS_{biota, sec pois}$), set at 1.2 ng/kg TEQ wet weight is also used in this report. However, since the $QS_{biota, sec pois}$ is based on the sum of PCDD/F and DL-PCBs and the times series only include PCDD/F concentrations, the target level was adjusted to correspond to PCDD/F part of Total TEQ target level (1.2 ng/kg wet weight). This was done by determining the ratio in TEQ concentrations between PCDD/F and Total TEQ (PCDD/F and DL-PCBs) of all herring samples during the last three years of monitoring (2011–2013). It was found that the contribution of PCDD/Fs to the Total TEQ of the samples was 53% on average. Hence the Target level for $QS_{biota, sec pois}$ (excluding DL-PCBs) was set to 50% of the original value, i.e. the used value is 0.6 ng/kg TEQ wet weight. See chapter for more information.

### 26.2  Methods

### 26.2.1  Analytical information

See for information on analysis methods for dioxins and dibenzofurans.

## 26.3  Results

### 26.3.1  Spatial Variation
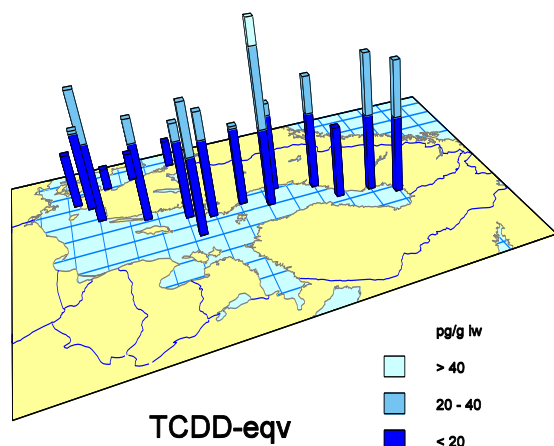
A)                                                        B)
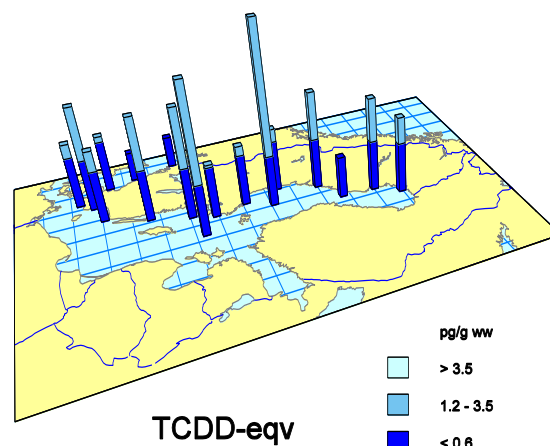


**Figure 26.1.** Spatial variation in concentration of WHO$_{05}$-TEQ (PCDD/PCDF) in herring muscle, in A) expressed as pg/g TEQ on lipid weight basis and B) expressed pg/g TEQ on wet weight basis In B) the quality standard in biota with regards to secondary poisoning is 0.6 pg/g wet weight and shown as the deep blue part of the bars.

TCDD-equivalents (pg/g lw) in herring muscle (Figure 26.1A) are generally higher  in the Baltic Sea compared to the Swedish West coast. The overall highest concentration from 2011-2013 was found at the Bothnian Sea offshore site. The same pattern is seen when TCDD-equivalents are expressed on wet weight basis. Note that all but one site (Holmöarna) from the Baltic exceed the quality standard for biota in regard to secondary poisoning.

### 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 1969-2013 (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.
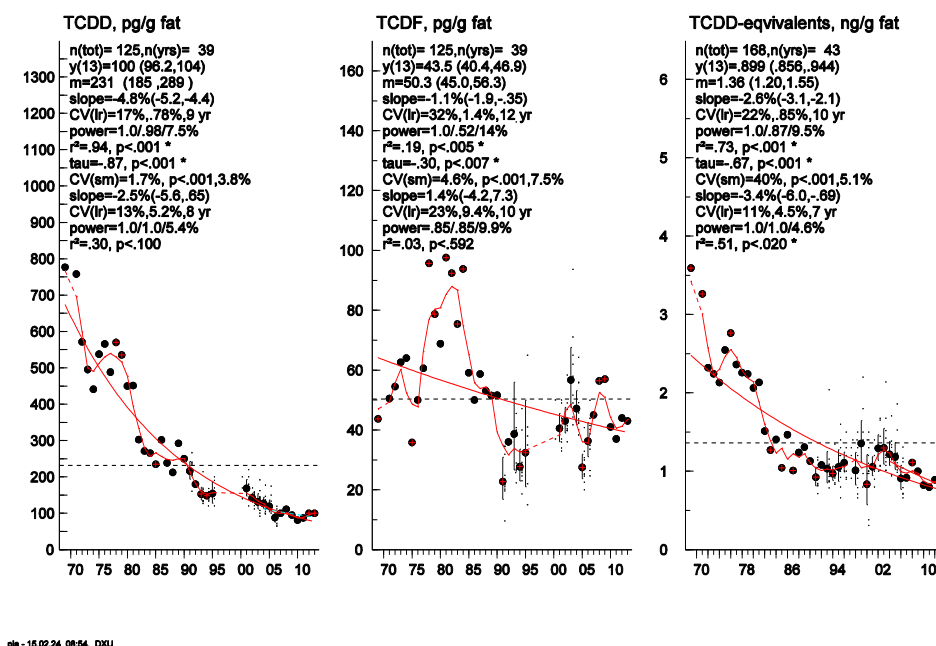
**Figure 26.2.** PCDD, PCDF (pg TCDD-eqv/g fat) and PCDD/F (ng TCDD-eqv/g fat) concentrations in guillemot eggs from Stora Karlsö (time series starting in 1969). The TCDD-EQV are calculated using the WHO$_{98}$-TEF.

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. Decreasing trends where observed in herring from Ängskärsklubb for all time series, at 6.5 and 10% per year for the dioxins (Fig. 26.5 and 26.9) and 3.6–4.9% per year or the furans (Fig. 26.7, 26.11 and 26.13). Both dioxins show decreasing trends in Utlängan and Fladen (26.5, 26.6, 26.9 and 26.10) whereas for the furans, a significant trend can only be observed at Fladen for 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF (Fig. 26.8 and 26.14). For the other investigated sample sites no log-linear trend can be observed.

The number of years required to detect an annual change of 10% varied between 9–19 years for the herring time series.

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



**Harufjärden**
n(tot)= 145,n(yrs)= 23
y(13)=.720 (.578,.897)
m=.775 (.657,.914)
slope=.60%(-1.9,3.2)
CV(lr)=40%,4.0%,14 yr
power=1.0/.35/18%
r²=.01, p<.632
tau=.051, p<.731
CV(sm)=157%, p<.601,18%
slope=.59%(-10,13)
CV(lr)=47%,20%,15 yr
power=.26/.26/22%
r²=.00, p<.874

**Ängskärsklubb**
n(tot)= 38,n(yrs)= 31
y(13)=.486 (.380,.621)
m=1.66 (1.23,2.26)
slope=-6.3%(-7.8,-4.7)
CV(lr)=50%,3.1%,16 yr
power=1.0/.24/23%
r²=.69, p<.001 *
tau=-.64, p<.001 *
CV(sm)=102%, p<.932,23%
slope=-5.1%(-20,13)
CV(lr)=28%,12%,17 yr
power=.12/.17/29%
r²=.07, p<.496

**Utlängan**
n(tot)= 184,n(yrs)= 23
y(13)=.620 (.535,.718)
m=.642 (.567,.727)
slope=-1.1%(-2.9,.78)
CV(lr)=29%,2.9%,12 yr
power=1.0/.63/13%
r²=.06, p<.241
tau=-.15, p<.328
CV(sm)=61%, p<.271,11%
slope=-1.4%(-7.9,5.7)
CV(lr)=28%,12%,11 yr
power=.67/.67/12%
r²=.02, p<.658

**Fladen**
n(tot)= 146,n(yrs)= 24
y(13)=.326 (.243,.436)
m=.327 (.263,.407)
slope=1.1%(-2.1,4.3)
CV(lr)=56%,5.1%,16 yr
power=1.0/.19/26%
r²=.02, p<.505
tau=.036, p<.804
CV(sm)=49%, p<.669,25%
slope=-1.6%(-5.3,2.2)
CV(lr)=19%,6.2%,8 yr
power=1.0/1.0/6.4%
r²=.11, p<.351

pia - 15.02.26 13:24, tcddecv

**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 target level for PCDD/Fs in fish (set for human consumption) and the blue area denotes the levels below QSbiota (secondary poisoning). The TCDD-EQV are calculated using the WHO98-TEF.

## TCDD-equivalents, pg/g fat, herring muscle



**Harufjärden**
Tv=120, lp%=2.9
Tv=21, lp%=2.9
n(tot)= 145,n(yrs)= 23
y(13)=30.3 (25.7,35.6)
m=29.6 (25.5,34.4)
slope=1.6%(-.57,3.8)
CV(lr)=34%,3.5%,13 yr
power=1.0/.47/15%
r²=.10, p<.139
tau=.23, p<.132
CV(sm)=8.7%, p<.133,13%
slope=-.67%(-10,9.7)
CV(lr)=41%,17%,14 yr
power=.35/.35/19%
r²=.00, p<.853

**Ängskärsklubb**
Tv=121, lp%=2.9
Tv=21, lp%=2.9
n(tot)= 38,n(yrs)= 31
y(13)=14.7 (12.0,17.9)
m=50.7 (37.9,68.0)
slope=-5.9%(-7.5,-4.4)
CV(lr)=49%,3.0%,15 yr
power=1.0/.24/23%
r²=.67, p<.001 *
tau=-.64, p<.001 *
CV(sm)=11%, p<.173,19%
slope=-5.5%(-21,13)
CV(lr)=65%,34%,18 yr
power=.11/.15/31%
r²=.07,p<.491

**Utlängan**
Tv=103, lp%=3.4
Tv=18, lp%=3.4
n(tot)= 190,n(yrs)= 24
y(13)=24.6 (21.0,28.9)
m=26.3 (23.7,29.3)
slope=-.72%(-2.2,.79)
CV(lr)=26%,2.5%,11 yr
power=1.0/.74/11%
r²=.04, p<.332
tau=-.04, p<.804
CV(sm)=9.1%, p<1.00,13%
slope=-1.5%(-6.5,3.7)
CV(lr)=21%,8.5%,10 yr
power=.91/.91/8.9%
r²=.05, p<.520

**Fladen**
Tv=79, lp%=4.4
Tv=14, lp%=4.4
n(tot)= 146,n(yrs)= 24
y(13)=7.50 (6.77,8.31)
m=7.93 (7.12,8.83)
slope=-1.6%(-3.0,-.14)
CV(lr)=24%,2.3%,10 yr
power=1.0/.81/10%
r²=.19, p<.031 *
tau=-.28, p<.059
CV(sm)=9.2%, p<.047,8.0%
slope=-1.6%(-6.2,3.2)
CV(lr)=19%,7.8%,9 yr
power=.95/.95/8.1%
r²=.07, p<.454

pia - 15.02.26 13:23, tcddec

**Figure 26.4. .** PCDD/F concentrations (pg TCDD-eqv/g lipid 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 target level for PCDD/Fs in fish (set for human consumption) and the blue area denotes the levels below QSbiota (secondary poisoning). The TCDD-EQV are calculated using the WHO98-TEF.

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## 2,3,7,8-TeCDD (pg/g lw), herring muscle

**Harufjärden**

n(tot)= 67,n(yrs)= 13
y(13)=1.59 (1.26,2.01)
m=1.98 (1.56,2.51)
slope=-3.5%(-7.8,.88)
CV(lr)=37%,9.8%,13 yr
power=.82/.40/17%
r²=.22, p<.102
tau=-.38, p<.067
CV(sm)=46%, p<.161,14%

**Ängskärsklubb**

n(tot)= 36,n(yrs)= 30
y(13)=1.13 (.902,1.43)
m=5.62 (3.53,8.95)
slope=-10%(-12,-8.3)
CV(lr)=57%,3.7%,17 yr
power=1.0/.19/27%
r²=.82, p<.001 *
tau=-.75, p<.001 *
CV(sm)=28%, p<.138,21%

**Landsort**

n(tot)= 15,n(yrs)= 9
y(13)=1.98 (1.35,2.89)
m=1.32 (.929,1.89)
slope=8.9%(-4.3,24)
CV(lr)=44%,23%,15 yr
power=.20/.29/20%
r²=.26, p<.161
tau=.50, p<.061
CV(sm)=151%, p<.399,19%

**Utlängan**

n(tot)= 68,n(yrs)= 14
y(13)=1.60 (1.31,1.96)
m=1.86 (1.55,2.24)
slope=-3.7%(-6.9,-.45)
CV(lr)=28%,6.4%,11 yr
power=1.0/.67/12%
r²=.34, p<.028 *
tau=-.43, p<.033 *
CV(sm)=46%, p<.609,12%



pla - 15.02.27 07:59, TCDD_c_a

**Figure 26.5. . 2,3,7,8-**TCDD concentrations (pg /g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (above) and from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) **Figure 26.6** (below).

## 2,3,7,8-TeCDD (pg/g lw), herring muscle

**Fladen**

n(tot)= 69,n(yrs)= 15
y(13)=.670 (.577,.778)
m=.836 (.653,1.07)
slope=-5.8%(-9.5,-2.1)
CV(lr)=33%,7.5%,12 yr
power=.97/.51/15%
r²=.48, p<.006 *
tau=-.56, p<.005 *
CV(sm)=119%, p<.015,8.9%

**Väderöarna**

n(tot)= 14,n(yrs)= 7
y(13)=.666 (.437,1.01)
m=.524 (.337,.814)
slope=12%(-9.8,39)
CV(lr)=47%,42%,15 yr
power=.08/.27/22%
r²=.27, p<.235
tau=.33, p<.293
CV(sm)=64%, p<.181,18%

**Ängskärskl. spr.**

n(tot)= 14,n(yrs)= 9
y(12)=1.76 (1.10,2.82)
m=4.19 (2.66,6.60)
slope=-5.6%(-16,6.4)
CV(lr)=63%,33%,18 yr
power=.11/.16/30%
r²=.16, p<.292
tau=-.17, p<.532
CV(sm)=37%, p<.211,24%

**Utlängan, spr.**

n(tot)= 12,n(yrs)= 6
y(13)=3.43 (2.22,5.29)
m=3.41 (2.26,5.13)
slope=-3.1%(-27,29)
CV(lr)=45%,60%,15 yr
power=.06/.28/21%
r²=.02, p<.765
tau=.067, p<.851
CV(sm)=32%, p<.109,17%



pla - 15.02.27 08:01, TCDD_c_b

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## 2,3,7,8-TeCDF (pg/g lw), herring muscle



**Harufjärden**

n(tot)= 69,n(yrs)= 14
y(13)=34.5 (28.3,42.1)
m=35.2 (30.1,41.2)
slope=-.02%(-3.5,3.5)
CV(lr)=29%,6.7%,12 yr
power=.99/.62/13%
r²=.00, p<.936
tau=.011, p<.956
CV(sm)=7.8%, p<.379,12%

**Ängskärsklubb**

n(tot)= 38,n(yrs)= 31
y(13)=19.0 (15.1,23.8)
m=42.3 (33.0,54.2)
slope=-4.8%(-6.3,-3.4)
CV(lr)=45%,2.8%,15 yr
power=1.0/.28/21%
r²=.61, p<.001 *
tau=-.64, p<.001 *
CV(sm)=13%, p<.961,22%

**Landsort**

n(tot)= 16,n(yrs)= 9
y(13)=28.7 (24.0,34.3)
m=27.1 (23.7,31.0)
slope=.38%(-5.1,6.2)
CV(lr)=19%,9.4%,9 yr
power=.85/.96/8.0%
r²=.00, p<.850
tau=-.06, p<.835
CV(sm)=6.1%, p<.716,8.4%

**Utlängan**

n(tot)= 70,n(yrs)= 14
y(13)=20.5 (15.8,26.6)
m=23.5 (19.9,27.7)
slope=-.23%(-3.8,3.5)
CV(lr)=30%,7.0%,12 yr
power=.99/.58/14%
r²=.00, p<.863
tau=-.05, p<.784
CV(sm)=12%, NS,16%

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**Figure 26.7.** . **2,3,7,8-**TCDF concentrations (pg /g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (above) and from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) **Figure 26.8** (below).

## 2,3,7,8-TeCDF (pg/g lw), herring muscle



**Fladen**

n(tot)= 69,n(yrs)= 15
y(13)=12.2 (10.6,14.0)
m=12.3 (10.8,13.9)
slope=-2.3%(-4.5,-.01)
CV(lr)=19%,4.4%,9 yr
power=1.0/.95/8.1%
r²=.28, p<.048 *
tau=-.30, p<.139
CV(sm)=7.8%, p<.585,8.2%

**Väderöarna**

n(tot)= 14,n(yrs)= 7
y(13)=11.9 (8.31,17.2)
m=9.39 (6.58,13.4)
slope=7.6%(-11,30)
CV(lr)=40%,35%,14 yr
power=.11/.36/18%
r²=.17, p<.363
tau=.24, p<.453
CV(sm)=16%, p<.182,15%

**Ängskärskl. spr.**

n(tot)= 14,n(yrs)= 9
y(12)=29.2 (20.8,41.2)
m=42.5 (31.2,57.7)
slope=.51%(-7.9,9.7)
CV(lr)=45%,23%,15 yr
power=.20/.29/21%
r²=.00, p<.864
tau=-.06, p<.835
CV(sm)=10%, p<.189,17%

**Utlängan, spr.**

n(tot)= 12,n(yrs)= 6
y(13)=50.9 (29.4,87.8)
m=39.4 (24.3,63.9)
slope=1.4%(-28,43)
CV(lr)=55%,75%,16 yr
power=.05/.20/26%
r²=.00, p<.880
tau=.33, p<.348
CV(sm)=13%, p<.160,22%

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## 1,2,3,7,8-PeCDD (pg/g lw), herring muscle

**Harufjärden**
n(tot)= 69,n(yrs)= 14
y(13)=4.91 (3.85,6.27)
m=6.33 (4.84,8.29)
slope=-3.3%(-8.5,2.3)
CV(lr)=48%,11%,15 yr
power=.72/.26/22%
r²=.12, p<.219
tau=-.32, p<.112
CV(sm)=19%, p<.047,15%

**Ängskärsklubb**
n(tot)= 38,n(yrs)= 31
y(13)=2.05 (1.67,2.51)
m=9.02 (6.59,12.3)
slope=-6.5%(-8.0,-4.9)
CV(lr)=51%,3.1%,16 yr
power=1.0/.23/24%
r²=.70, p<.001 *
tau=-.63, p<.001 *
CV(sm)=20%, p<.155,19%

**Landsort**
n(tot)= 16,n(yrs)= 9
y(13)=3.76 (2.88,4.90)
m=3.86 (3.30,4.52)
slope=.35%(-6.1,7.3)
CV(lr)=22%,11%,10 yr
power=.70/.87/9.6%
r²=.00, p<.872
tau=.056, p<.835
CV(sm)=22%, NS,13%

**Utlängan**
n(tot)= 70,n(yrs)= 14
y(13)=4.89 (4.25,5.62)
m=5.38 (4.65,6.24)
slope=-3.3%(-5.7,-.90)
CV(lr)=20%,4.7%,10 yr
power=1.0/.92/8.8%
r²=.42, p<.011 *
tau=-.47, p<.019 *
CV(sm)=12%, p<.388,8.3%



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**Figure 26.9.** 1,2,3,7,8-PeCDD concentrations (pg /g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (above) and from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) **Figure 26.10** (below).

## 1,2,3,7,8-PeCDD (pg/g lw), herring muscle

**Fladen**
n(tot)= 69,n(yrs)= 15
y(13)=1.80 (1.49,2.18)
m=1.82 (1.47,2.25)
slope=-4.1%(-7.8,-.29)
CV(lr)=33%,7.5%,12 yr
power=.97/.51/15%
r²=.31, p<.036 *
tau=-.47, p<.019 *
CV(sm)=44%, p<.101,11%

**Väderöarna**
n(tot)= 14,n(yrs)= 7
y(13)=1.18 (.774,1.81)
m=1.27 (.831,1.95)
slope=-6.0%(-26,19)
CV(lr)=51%,46%,16 yr
power=.07/.23/24%
r²=.08, p<.531
tau=-.33, p<.293
CV(sm)=173%, p<.121,18%

**Ängskärskl. spr.**
n(tot)= 14,n(yrs)= 9
y(12)=3.88 (2.39,6.31)
m=11.5 (6.57,20.0)
slope=-9.6%(-21,3.2)
CV(lr)=71%,37%,19 yr
power=.09/.13/34%
r²=.32, p<.113
tau=-.56, p<.037 *
CV(sm)=22%, p<.130,24%

**Utlängan, spr.**
n(tot)= 12,n(yrs)= 6
y(13)=9.44 (6.07,14.7)
m= 9.8 (6.77,14.1)
slope=-5.0%(-26,22)
CV(lr)=39%,50%,14 yr
power=.07/.38/18%
r²=.07, p<.601
tau=-.20, p<.573
CV(sm)=17%, NS,17%



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## 1,2,3,7,8-PeCDF (pg/g lw), herring muscle

**Harufjärden**

n(tot)= 69,n(yrs)= 14
y(13)=6.60 (5.48,7.94)
m=6.88 (5.69,8.32)
slope=1.1%(-3.0,5.4)
CV(lr)=35%,8.0%,13 yr
power=.95/.46/16%
r²=.02, p<.572
tau=.12, p<.547
CV(sm)=14%, p<.059,11%

**Ängskärsklubb**

n(tot)= 38,n(yrs)= 31
y(13)=2.86 (2.20,3.71)
m=8.08 (6.27,10.4)
slope=-3.6%(-5.5,-1.6)
CV(lr)=63%,3.8%,17 yr
power=1.0/.16/30%
r²=.32, p<.001 *
tau=-.43, p<.001 *
CV(sm)=27%, p<.324,25%

**Landsort**

n(tot)= 16,n(yrs)= 9
y(13)=6.74 (5.17,8.77)
m=5.56 (4.49,6.88)
slope=2.7%(-5.9,12)
CV(lr)=29%,15%,12 yr
power=.45/.62/13%
r²=.06, p<.499
tau=.17, p<.532
CV(sm)=17%, p<.504,13%

**Utlängan**

n(tot)= 70,n(yrs)= 14
y(13)=5.92 (4.92,7.11)
m=6.79 (5.82,7.91)
slope=-1.8%(-4.9,1.4)
CV(lr)=26%,6.1%,11 yr
power=1.0/.72/12%
r²=.12, p<.232
tau=-.16, p<.412
CV(sm)=14%, p<.444,11%

**Figure 26.11.** 1,2,3,7,8-PeCDF concentrations (pg /g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (above) and from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) **Figure 26.12** (below).

## 1,2,3,7,8-PeCDF (pg/g lw), herring muscle

**Fladen**

n(tot)= 69,n(yrs)= 15
y(13)=2.18 (1.93,2.46)
m=2.22 (1.95,2.53)
slope=-2.0%(-4.5,.64)
CV(lr)=22%,5.0%,10 yr
power=1.0/.88/9.4%
r²=.18, p<.122
tau=-.25, p<.208
CV(sm)=22%, p<.086,7.2%

**Väderöarna**

n(tot)= 14,n(yrs)= 7
y(13)=1.96 (1.35,2.85)
m=1.64 (1.13,2.37)
slope=4.4%(-15,28)
CV(lr)=44%,39%,15 yr
power=.09/.30/20%
r²=.05, p<.616
tau=-.05, p<.881
CV(sm)=74%, p<.120,16%

**Ängskärskl. spr.**

n(tot)= 14,n(yrs)= 9
y(12)=5.74 (3.59,9.17)
m=15.9 (9.43,26.7)
slope=-6.9%(-19,6.5)
CV(lr)=73%,37%,19 yr
power=.09/.13/35%
r²=.18, p<.249
tau=-.22, p<.404
CV(sm)=19%, p<.093,24%

**Utlängan, spr.**

n(tot)= 12,n(yrs)= 6
y(13)=15.4 (10.4,22.7)
m=15.4 (10.9,21.8)
slope=-5.5%(-25,19)
CV(lr)=36%,47%,13 yr
power=.07/.43/16%
r²=.10, p<.544
tau=-.20, p<.573
CV(sm)=13%, p<.241,15%

## 2,3,4,7,8-PeCDF (pg/g lw), herring muscle



**Harufjärden**
n(tot)= 69,n(yrs)= 14
y(13)=37.1 (30.6,45.1)
m=39.4 (32.0,48.6)
slope=.41%(-4.1,5.2)
CV(lr)=39%,8.9%,14 yr
power=.89/.37/18%
r²=.00, p<.828
tau=.077, p<.702
CV(sm)=7.5%, p<.034,12%

**Ängskärsklubb**
n(tot)= 38,n(yrs)= 31
y(13)=17.5 (14.2,21.4)
m=54.7 (41.7,71.8)
slope=-4.9%(-6.6,-3.1)
CV(lr)=56%,3.4%,16 yr
power=1.0/.19/26%
r²=.52, p<.001 *
tau=-.53, p<.001 *
CV(sm)=11%, p<.051,19%

**Landsort**
n(tot)= 16,n(yrs)= 9
y(13)=30.7 (26.0,36.2)
m=25.5 (21.3,30.6)
slope=2.8%(-4.3,10)
CV(lr)=24%,12%,10 yr
power=.63/.80/10%
r²=.11, p<.395
tau=.22, p<.404
CV(sm)=5.8%, p<.086,7.8%

**Utlängan**
n(tot)= 70,n(yrs)= 14
y(13)=29.2 (24.9,34.3)
m=31.7 (27.5,36.5)
slope=-2.4%(-5.0,.26)
CV(lr)=22%,5.2%,10 yr
power=1.0/.86/9.7%
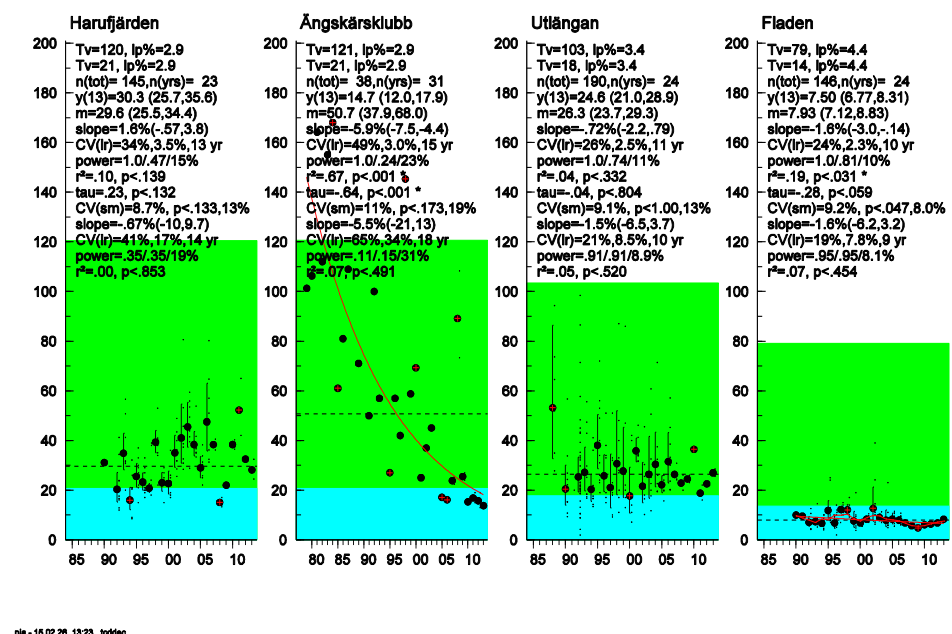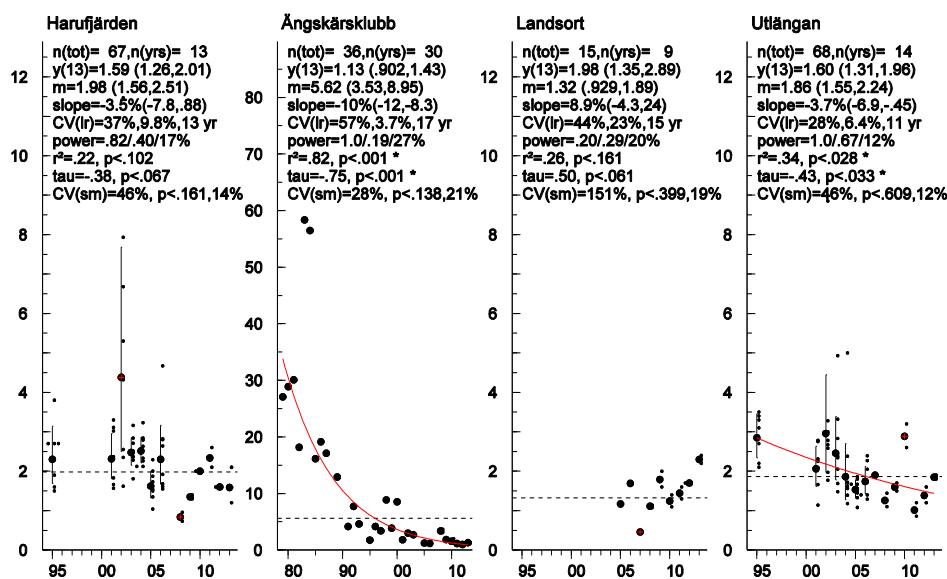r²=.24, p<.070
tau=-.27, p<.171
CV(sm)=6.5%, p<.516,9.5%

**Figure 26.13.** 2,3,4,7,8-PeCDF concentrations (pg /g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Utlängan and Fladen (above) and from Fladen, Väderöarna, Ängskärsklubb (spring) and Utlängan (spring) **Figure 26.14** (below).

## 2,3,4,7,8-PeCDF (pg/g lw), herring muscle



**Fladen**
n(tot)= 69,n(yrs)= 15
y(13)=6.20 (5.51,6.98)
m=6.23 (5.27,7.37)
slope=-3.1%(-6.1,-.01)
CV(lr)=26%,6.0%,11 yr
power=1.0/.73/11%
r²=.28, p<.047 *
tau=-.36, p<.071
CV(sm)=9.2%, p<.015,7.0%

**Väderöarna**
n(tot)= 14,n(yrs)= 7
y(13)=4.59 (3.31,6.38)
m=4.15 (3.00,5.75)
slope=3.3%(-14,24)
CV(lr)=39%,35%,14 yr
power=.11/.37/18%
r²=.04, p<.666
tau=-.05, p<.881
CV(sm)=23%, p<.112,14%

**Ängskärskl. spr.**
n(tot)= 14,n(yrs)= 9
y(12)=30.1 (19.1,47.5)
m=84.3 (50.1,142 )
slope=-8.5%(-19,3.8)
CV(lr)=68%,35%,18 yr
power=.10/.14/32%
r²=.28, p<.138
tau=-.33, p<.211
CV(sm)=12%, p<.117,23%

**Utlängan, spr.**
n(tot)= 12,n(yrs)= 6
y(13)=52.9 (36.4,76.8)
m=58.1 (42.2,80.0)
slope=-6.9%(-24,14)
CV(lr)=31%,40%,12 yr
power=.09/.55/14%
r²=.19, p<.387
tau=-.33, p<.348
CV(sm)=8.3%, NS,14%

### 26.3.3 Comparison to threshold

All herring stations show values below the suggested target level based on the EC food regulation of 3.5 pgWHO05-TEQ/g wet weight. However, when compared to the re-calculated QSbiota (secondary poisoning) target level of 0.6 pg WHO05-TEQ/g wet weight, only herring from the two West coast stations Fladen and Väderöarna, Lagnö in Northern Baltic Proper and Holmöarna in Southern Baltic Bay is below the target level. The concentrations in Harufjärden and Utlängan are, and have historically been, close to the target level but slightly above. Ängskärsklubb on the other hand have been well above the target level historically, but are in fact below the target level the last two years. Differences in congener pattern

The relative concentrations of the various congeners to the sum of PCDD/PCDF clearly vary over time in the long time series in autumn caught herring from Ängskärsklubb in the Southern Bothnian Sea. The relative concentrations of TCDD and HxCDD were considerably higher in the older samples from the period between 1979-1989, whereas during the recent period (2000-2013) the relative concentrations of TCDF and 1,2,3,7,8,9-HxCDF is higher.
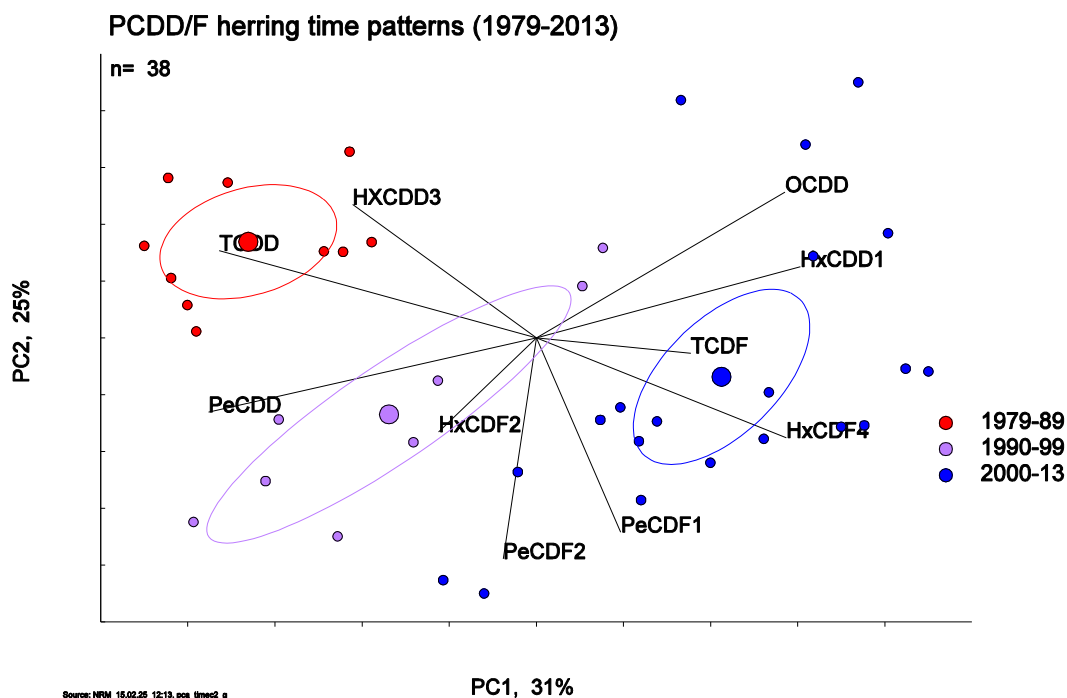


**Figure 26.15.** Principal component analysis, biplot and Hotellings 95% confidence ellipses for centers of gravity for each group. Changes over time in relative abundance of selected PCDD/F-congeners to the sum over time in autumn caught herring from Ängskärsklubb in the southern Bothnian Sea. Codes for the analytes are: TCDD = 2,3,7,8-TeCDD; TCDF = 2,3,7,8-TeCDF; PeCDD = 1,2,3,7,8-PeCDD; PeCDF1 = 1,2,3,7,8-PeCDF; PeCDF2 = 2,3,4,7,8-PeCDF; HxCDD1 = 1,2,3,4,7,8-HxCDD; HXCDD3 = 1,2,3,7,8,9-HxCDD; HxCDF2 = 1,2,3,6,7,8-HxCDF; HxCDF4 = 1,2,3,7,8,9-HxCDF.

### 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 when the ∑TEQ for PCDD/Fs are considered. However, the two dioxin congeners decrease at both Utlängan and Fladen. In addition, two furan congeners decrease at Fladen and there is an indication that the dioxins decrease faster in concentration than the furans at Ängskärsklubb. In guillemot eggs, significant decreasing trends were observed for TCDD, TCDF and PCDD/Fs during 1970–2013. For TCDFs, no trend can be observed between 1990–2013.

The spring caught herring has consequently higher concentrations than the autumn caught for all investigated congeners of PCDD/Fs at both Ängskärsklubb and Utlängan, 1.5–2 and 2–3 times higher concentrations at spring.

**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 | 145 | 23 | 90−13 | 1.6 | (-.57,3.8) | 0.1386 | | 13 | 15 | 30.3 (25.7,35.6) |
| Harufjärden | | 10 | 04−13 | -.67 | (-10,9.7) | 0.8530 | | 14 | 19 | |
| Ängskärsklubb | 38 | 31 | 79−13 | -5.9 | (-7.5,-4.4) | 0.0000 | --- | 15 | 23 | 14.7 (12.0,17.9) |
| Ängskärsklubb | | 9 | 05−13 | -5.5 | (-21,13) | 0.4906 | | 18 | 31 | |
| Utlängan | 190 | 24 | 88−13 | -.72 | (-2.2,.79) | 0.3320 | | 11 | 11 | 24.6 (21.0,28.9) |
| Utlängan | | 10 | 04−13 | -1.5 | (-6.5,3.7) | 0.5200 | | 10 | 8.9 | |
| Fladen | 146 | 24 | 90−13 | -1.6 | (-3.0,-.14) | 0.0310 | - | 10 | 10 | 7.50 (6.77,8.31) |
| Fladen | | 10 | 04−13 | -1.6 | (-6.2,3.2) | 0.4535 | | 9 | 8.1 | |
| **Guillemot egg** | | | | | | | | | | |
| Stora Karlsö | 168 | 43 | 69−13 | -2.6 | (-3.1,-2.1) | 0.0000 | --- | 10 | 9.5 | .899 (.856,.944) |
| Stora Karlsö | | 10 | 04−13 | -3.4 | (-6.0,-.69) | 0.0201 | - | 7 | 4.6 | |

**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 | 145 | 23 | 90±13 | .60 | (-1.9,3.2) | 0.6321 | | 14 | 18 | .720 (.578,.897) |
| Harufjärden | | 10 | 04±13 | .59 | (-10,13) | 0.8740 | | 15 | 22 | |
| Ängskärsklubb | 38 | 31 | 79±13 | -6.3 | (-7.8,-4.7) | 0.0000 | --- | 16 | 23 | .486 (.380,.621) |
| Ängskärsklubb | | 9 | 05±13 | -5.1 | (-20,13) | 0.4958 | | 17 | 29 | |
| Utlängan | 184 | 23 | 90±13 | -1.1 | (-2.9,.78) | 0.2414 | | 12 | 13 | .620 (.535,.718) |
| Utlängan | | 10 | 04±13 | -1.4 | (-7.9,5.7) | 0.6583 | | 11 | 12 | |
| Fladen | 146 | 24 | 90±13 | -1.1 | (-2.1,4.3) | 0.5045 | | 16 | 26 | .326 (.243,.436) |
| Fladen | | 10 | 04±13 | -1.6 | (-5.3,2.2) | 0.3513 | | 8 | 6.4 | |

# 27  Brominated flame retardants

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

Polybrominated diphenyl ethers (PBDEs) are produced as three different technical products; penta-, octa- and decabromo diphenyl ether (BDE). Each of these products includes a few major congeners. For pentaBDE these are BDE-47, -99, and -100. OctaBDE contains mainly BDE-183, while decaBDE includes almost exclusively BDE-209 (La Guardia et al., 2006). Hexabromocyclododecan (HBCDD) is produced as a mixture of three stereoisomers – α-, β- and γ-HBCDD (Covaci A. et al., 2006). Both PBDEs and HBCDD are used as additive flame retardants incorporated into materials such as plastics and textiles.

PBDEs leak into the environment during production, use, or disposal of such products. PBDEs are mainly spread via diffuse distribution in the atmosphere and in rivers. HBCDD is bioaccumulative, lipophilic and persistent, and accumulates in the food-web.

More comprenhensive information concerning PBDEs and HBCDD, e.g. sources and environmental fate, can be found in the extensive reports from the European Food Safety Authority (EFSA),on PBDEs (EFSA, 2012) and HBCDD (EFSA, 2011).

### 27.1.2  Toxicological effects

Several PBDE congeners and HBCDD have been shown to cause neurotoxic effects in rats and mice. In mammals, behaviour, learning (Eriksson et al., 2006a, Eriksson et al., 2006b) and affects on hormonal functions have been reported (Legler, 2008). Animals exposed to PBDEs and HBCDD during a sensitive stage of brain development have later shown reduced memory and learning disabilities (Viberg, 2004, Eriksson et al., 2006a, Eriksson et al., 2006b). In birds, several aspects regarding reduced reproductive success has been documented (Fernie et al., 2009). Chemical products and goods containing concentrations over a certain level of these BDEs are banned in the EU. Brominated flame retardants (BFR) are also considered to be endocrine disruptors, and in particular, effects on the thyroid hormone system are seen (Darnerud, 2008, UNEP and WHO, 2013).

### 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 (EC, 2008).

Since the autumn of 2014 HBCDD is included in The Stockholm Convention on POPs (Stockholm Convention).

### 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 is set to 0.0085 μg/kg. 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

Generally, for BDE-47, -99, -153 and HBCDD (Fig. 27.1) higher concentrations in herring muscle are seen in the Baltic Sea compared to the Swedish west coast. Hanöbukten and Baltic proper offshore had the highest concentrations of HBCDD, while for the other brominated substances, Kinnbäcksfjärden and Harufjärden in the Bothnian Bay show the highest concentrations. The concentration of BDE-47 is also elevated in the Bothnian Sea offshore site.

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. 27.1).

A)      B)

C)      D)
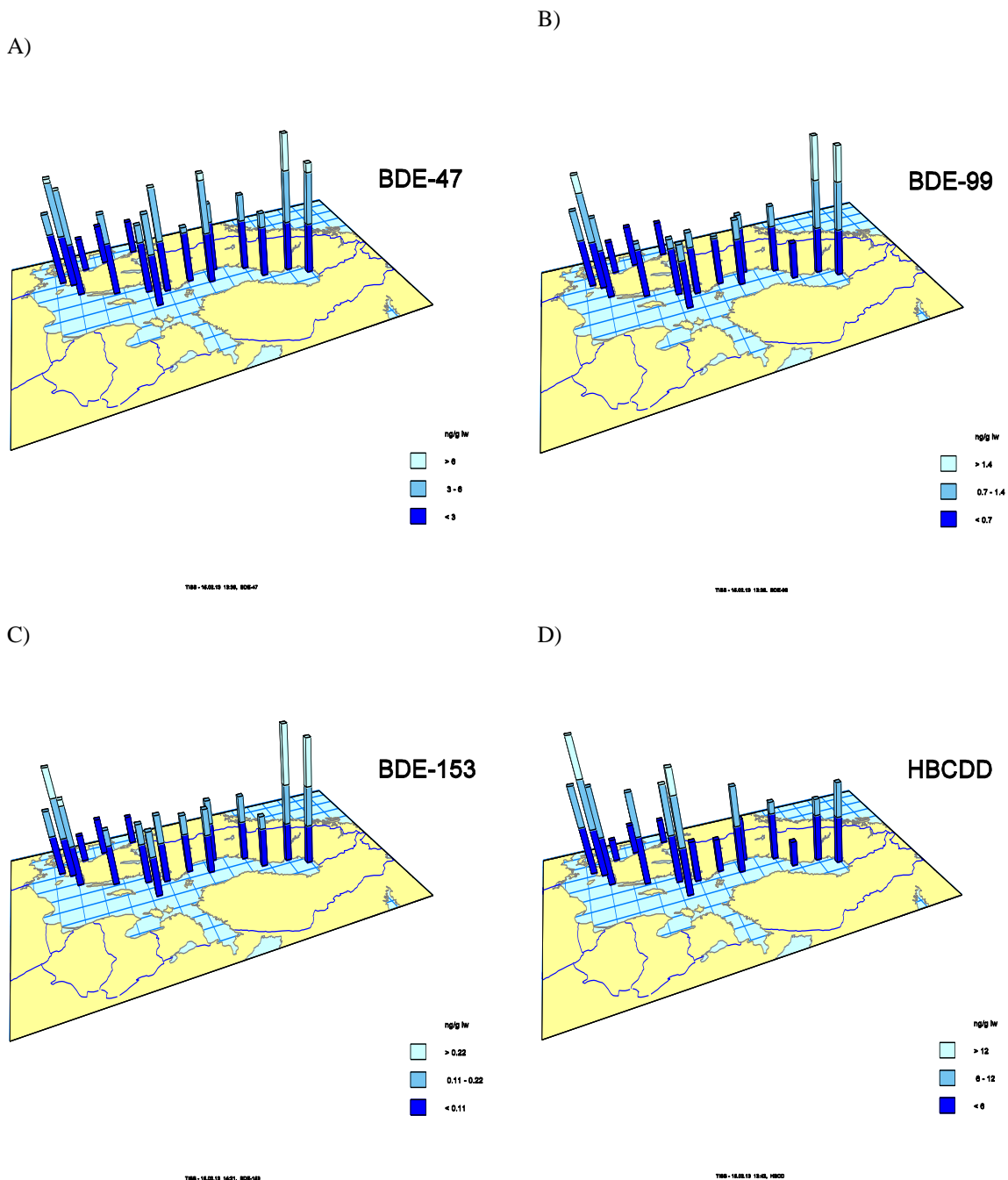
**Figure 27.1.** Spatial variation of BDE-47, -99 and -153 as well as HBCDD concentrations (ng/g lipid weight) in herring muscle.

## 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 since the peak in the early 1990s (Fig. 27.2).

Significant decreasing concentrations of BDE-47 are observed in herring from Ängskärsklubb (autumn), Landsort, Väderöarna, Fladen, and Utlängan (autumn) (Fig. 27.3 and 27.4). Decreasing concentrations are also observed in cod from Fladen and Southeast Gotland and in blue mussels from all sampling sites (Fig.27.5 and 27.6, Table 27.1).

The number of years required to detect an annual change of 10% in the concentration of BDE-47 is 11–18 years for herring, cod and blue mussel.
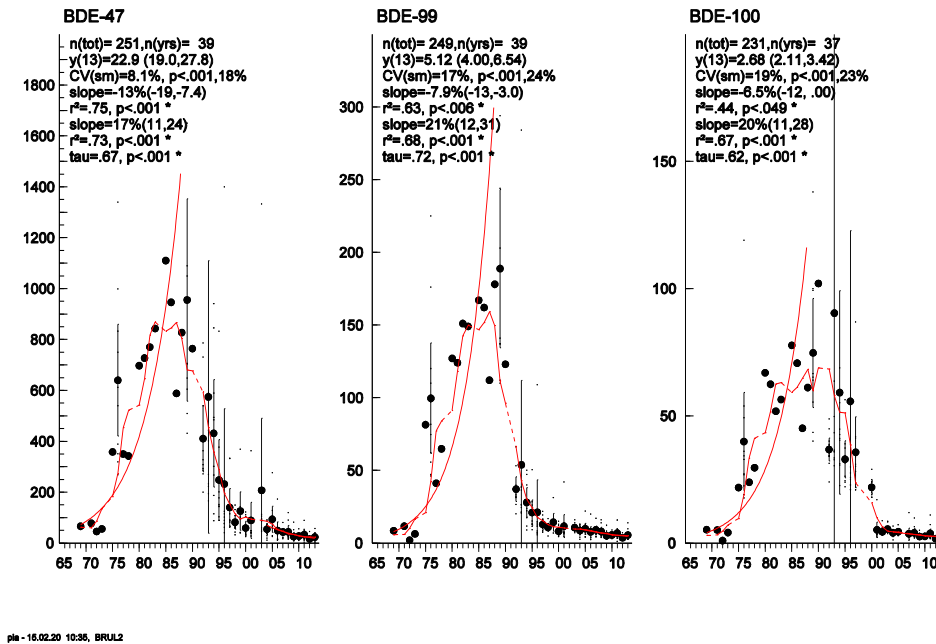


**Figure 27.2**. Temporal trends of BDE-47, -99, and 100 (ng/g lipid weight) in guillemot eggs (time series starting in 1968).



**Figure 27.3.** Temporal trends of BDE-47 (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).

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

**Väderöarna**

```
n(tot)= 224,n(yrs)= 14
y(13)=1.80 (1.51,2.14)
m=3.13 (2.21,4.42)
slope=-11%(-14,-7.7)
CV(lr)=28%,6.5%,11 yr
power=.99/.65/12%
r²=.80, p<.001 *
tau=-.76, p<.001 *
CV(sm)=22%, p<.190,10%
slope=-7.0%(-11,-2.4)
CV(lr)=18%,9.1%,9 yr
power=.87/.97/7.8%
r²=.64, p<.010 *
```

**Fladen**

```
n(tot)= 177,n(yrs)= 15
y(13)=2.40 (2.19,2.62)
m=2.98 (2.20,4.04)
slope=-9.9%(-13,-6.4)
CV(lr)=30%,6.2%,12 yr
power=1.0/.59/13%
r²=.73, p<.001 *
tau=-.62, p<.001 *
CV(sm)=12%, p<.001,5.4%
slope=-4.2%(-10,2.2)
CV(lr)=26%,11%,11 yr
power=.73/.73/11%
r²=.23, p<.161
```

**Ängskärsklubb spring**

```
n(tot)= 75,n(yrs)= 11
y(12)=4.07 (2.39,6.93)
m=11,7 (7.25,18.9)
slope=-11%(-22,1.6)
CV(lr)=69%,24%,18 yr
power=.19/.14/33%
r²=.31, p<.074
tau=-.38, p<.102
CV(sm)=27%, p<.630,31%
slope=-11%(-25,5.2)
CV(lr)=74%,31%,19 yr
power=.12/.12/36%
r²=.24, p<.144
```

**Utlängan, spring**

```
n(tot)= 68,n(yrs)= 11
y(13)=11.1 (7.97,15.4)
m=12.5 (9.42,16.5)
slope=-4.9%(-13,3.8)
CV(lr)=42%,15%,14 yr
power=.45/.33/19%
r²=.16, p<.225
tau=-.20, p<.392
CV(sm)=16%, p<.467,18%
slope=-3.8%(-14,7.0)
CV(lr)=44%,19%,15 yr
power=.30/.30/20%
r²=.08, p<.430
```



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**Figure 27.4.** 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).

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

**SE Gotland**

```
n(tot)= 161,n(yrs)= 29
y(13)=10.8 ( 9.6,12.1)
m=32.4 (23.8,44.3)
slope=-7.7%(-8.7,-6.7)
CV(lr)=27%,1.9%,11 yr
power=1.0/.69/12%
r²=.90, p<.001 *
tau=-.81, p<.001 *
CV(sm)=7.0%, p<.183,10%
slope=-6.8%(-11,-2.1)
CV(lr)=20%,8.2%,9 yr
power=.93/.93/8.6%
r²=.57, p<.011 *
```

**Fladen**

```
n(tot)= 146,n(yrs)= 15
y(13)=12.0 (9.40,15.2)
m=18.6 (13.0,26.8)
slope=-11%(-16,-6.1)
CV(lr)=43%,8.7%,14 yr
power=.91/.32/20%
r²=.63, p<.001 *
tau=-.71, p<.001 *
CV(sm)=12%, p<.131,15%
slope=-5.3%(-12,2.0)
CV(lr)=30%,13%,12 yr
power=.59/.59/13%
r²=.26, p<.127
```



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**Figure 27.5.** BDE-47 concentrations (ng/g lipid weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).

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## BDE-47, ng/g lipid w., blue mussel

**Kvädöfjärden**

n(tot)= 60,n(yrs)= 12
y(12)=1.52 (1.29,1.80)
m=2.07 (1.60,2.68)
slope=-7.4%(-12,-2.6)
CV(lr)=30%,9.0%,12 yr
power=.88/.59/13%
r²=.53, p<.007 *
tau=-.64, p<.004 *
CV(sm)=30%, p<.048,9.2%
slope=-8.5%(-15,-1.2)
CV(lr)=31%,13%,12 yr
power=.57/.57/14%
r²=.47, p<.027 *

**Fjällbacka**

n(tot)= 69,n(yrs)= 14
y(13)=1.86 (1.35,2.06)
m=2.33 (1.89,2.87)
slope=-6.5%(-9.7,-3.2)
CV(lr)=24%,5.6%,11 yr
power=1.0/.79/11%
r²=.60, p<.001 *
tau=-.54, p<.007 *
CV(sm)=35%, NS,13%
slope=-7.4%(-12,-2.4)
CV(lr)=21%,8.7%,10 yr
power=.90/.90/9.1%
r²=.59, p<.009 *

**Nidingen**

n(tot)= 64,n(yrs)= 13
y(12)=1.38 (1.17,1.62)
m=2.44 (1.70,3.48)
slope=-13%(-17,-8.3)
CV(lr)=30%,7.7%,12 yr
power=.96/.60/13%
r²=.78, p<.001 *
tau=-.72, p<.001 *
CV(sm)=25%, p<.055,9.4%
slope=-10%(-16,-3.8)
CV(lr)=27%,11%,11 yr
power=.68/.68/12%
r²=.62, p<.007 *



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**Figure 27.6.** 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 sample sites with the exception of Utlängan (spring) (Fig. 27.7 and 27.8). Cod showed a decrease in BDE-99 in Southeast Gotland and a significant decrease the last ten years of monitoring at Fladen (Fig. 27.9). Blue mussels from Kvädöfjärden and Nidingen show decreasing concentrations (Fig. 27.10).

## BDE-99, ng/g lipid w., herring muscle

**Harufjärden**

n(tot)= 179,n(yrs)= 15
y(13)=1.99 (1.69,2.34)
m=1.93 (1.58,2.36)
slope=-4.1%(-8.0,-.02)
CV(lr)=33%,6.7%,12 yr
power=.99/.51/15%
r²=.27, p<.047 *
tau=-.33, p<.083
CV(sm)=36%, p<.032,10%
slope=.95%(-6.1,8.5)
CV(lr)=29%,12%,12 yr
power=.62/.62/13%
r²=.01, p<.762

**Ängskärsklubb**

n(tot)= 180,n(yrs)= 25
y(13)=.645 (.534,.779)
m=1.54 (1.08,2.21)
slope=-7.0%(-9.0,-4.9)
CV(lr)=56%,4.8%,16 yr
power=1.0/.20/26%
r²=.66, p<.001 *
tau=-.63, p<.001 *
CV(sm)=83%, p<.005,16%
slope=1.4%(-4.6,7.7)
CV(lr)=24%,10%,11 yr
power=.79/.79/11%
r²=.03, p<.617

**Landsort**

n(tot)= 179,n(yrs)= 15
y(13)=.785 (.650,.949)
m=1.19 (.931,1.52)
slope=-8.0%(-11,-5.0)
CV(lr)=26%,5.2%,11 yr
power=1.0/.74/11%
r²=.70, p<.001 *
tau=-.66, p<.001 *
CV(sm)=159%, p<.835,12%
slope=-7.5%(-14,-.87)
CV(lr)=28%,12%,11 yr
power=.66/.66/12%
r²=.46, p<.031 *

**Utlängan**

n(tot)= 180,n(yrs)= 15
y(13)=.838 (.560,1.26)
m=1.64 (1.08,2.47)
slope=-12%(-17,-5.5)
CV(lr)=56%,11%,16 yr
power=.70/.20/26%
r²=.55, p<.002 *
tau=-.60, p<.002 *
CV(sm)=120%, p<.963,27%
slope=-5.0%(-18,9.8)
CV(lr)=62%,26%,17 yr
power=.16/.16/29%
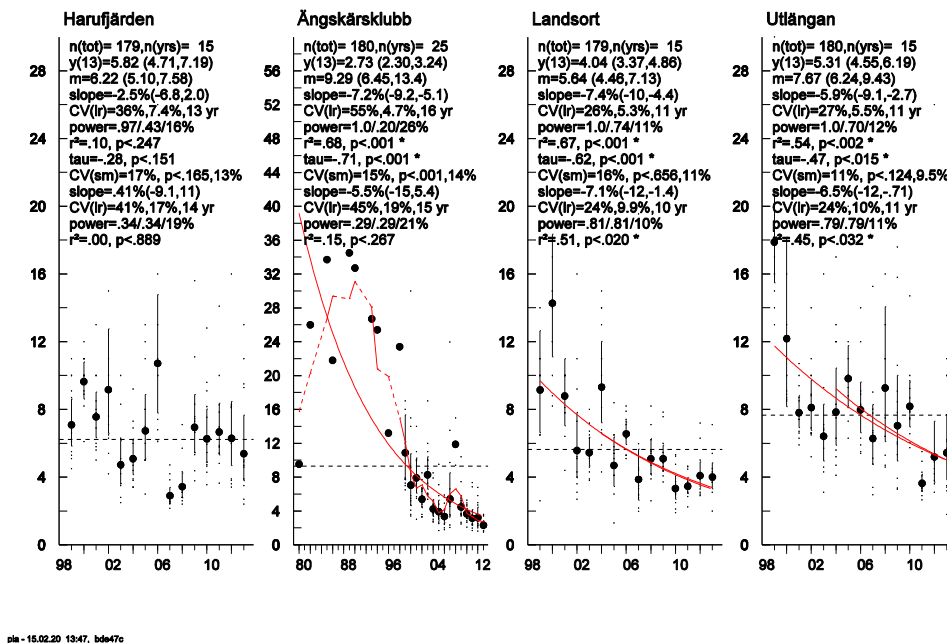r²=.07, p<.440



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**Figure 27.7.** BDE-99 concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).
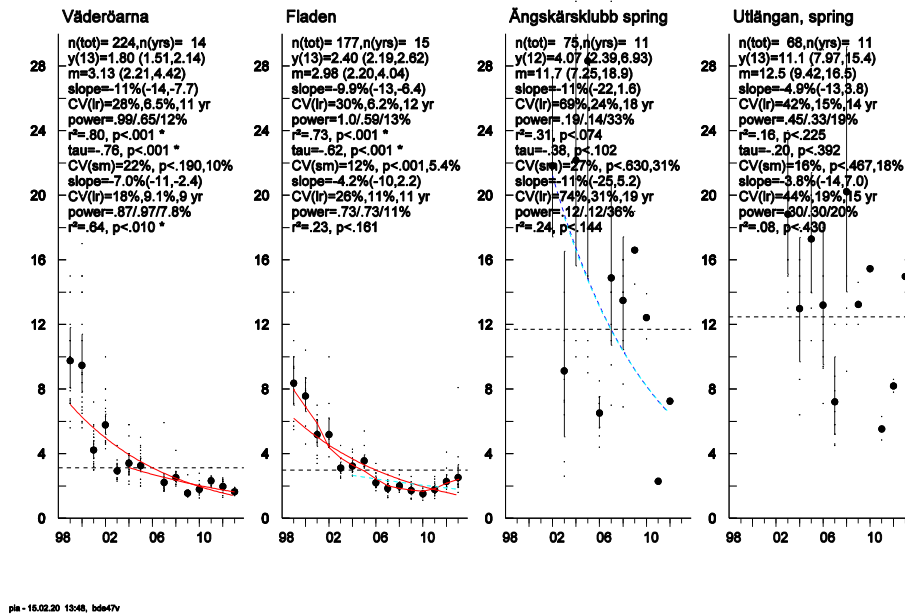
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## BDE-99, ng/g lipid w., herring muscle

**Väderöarna**

n(tot)= 224,n(yrs)= 14
y(13)=.513 (.439,.600)
m=.819 (.561,1.20)
slope=-12%(-15,-8.0)
CV(lr)=33%,7.5%,12 yr
power=.97/.51/15%
r²=.78, p<.001 *
tau=-.69, p<.001 *
CV(sm)=111%, p<.022,9.3%
slope=-4.3%(-8.4,-.08)
CV(lr)=16%,8.1%,9 yr
power=.94/.99/6.8%
r²=.45, p<.046 *

**Fladen**

n(tot)= 177,n(yrs)= 15
y(13)=.654 (.583,.733)
m=.797 (.571,1.11)
slope=-10%(-14,-6.3)
CV(lr)=37%,7.4%,13 yr
power=.97/.42/17%
r²=.68, p<.001 *
tau=-.62, p<.001 *
CV(sm)=74%, p<.001,7.0%
slope=-3.0%(-9.7,4.3)
CV(lr)=29%,12%,12 yr
power=.63/.63/13%
r²=.10, p<.369

**Ängskärsklubb spring**

n(tot)= 75,n(yrs)= 11
y(12)=.878 (.601,1.28)
m=1.85 (1.29,2.66)
slope=-10%(-18,-1.8)
CV(lr)=44%,15%,15 yr
power=.41/.30/20%
r²=.45, p<.024 *
tau=-.45, p<.052
CV(sm)=77%, p<.903,21%
slope=-9.8%(-19,1.1)
CV(lr)=47%,20%,15 yr
power=.27/.27/22%
r²=.35, p<.068

**Utlängan, spring**

n(tot)= 58,n(yrs)= 10
y(13)=3.34 (2.30,4.86)
m=2.65 (1.87,3.75)
slope=-3.7%(-14,7.8)
CV(lr)=53%,22%,16 yr
power=.21/.21/25%
r²=.06, p<.471
tau=-.16, p<.531
CV(sm)=45%, p<.177,19%
slope=.22%(-12,14)
CV(lr)=50%,26%,16 yr
power=.16/.23/23%
r²=.00, p<.921



**Figure 27.8.** BDE-99 concentrations (ng/g lipid weight) in herring muscle from Fladen, Väderöarna, Ängskärrsklubb and Utlängan (spring) (time series starting in 1999).

## BDE-99, ng/g lipid w., cod liver

**SE Gotland**

n(tot)= 161,n(yrs)= 29
y(13)=.305 (.226,.410)
m=1.59 (1.01,2.48)
slope=-10%(-12,-8.4)
CV(lr)=58%,3.9%,17 yr
power=1.0/.18/27%
r²=.80, p<.001 *
tau=-.75, p<.001 *
CV(sm)=133%, p<.987,28%
slope=-4.0%(-18,12)
CV(lr)=66%,27%,18 yr
power=.15/.15/31%
r²=.04, p<.557

**Fladen**

n(tot)= 143,n(yrs)= 15
y(13)=.369 (.240,.568)
m=.563 (.374,.847)
slope=-6.1%(-14,2.9)
CV(lr)=81%,15%,20 yr
power=.41/.11/39%
r²=.15, p<.156
tau=-.33, p<.083
CV(sm)=110%, p<.178,29%
slope=-18%(-27,-8.0)
CV(lr)=47%,20%,15 yr
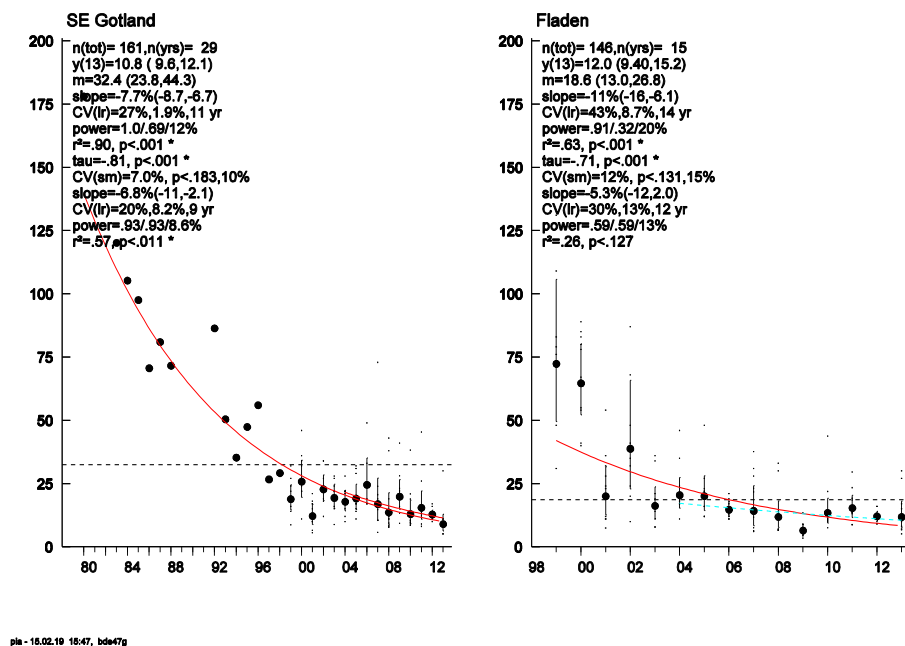power=.27/.27/22%
r²=.67, p<.004 *



**Figure 27.9.** BDE-99 concentrations (ng/g lipid weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).

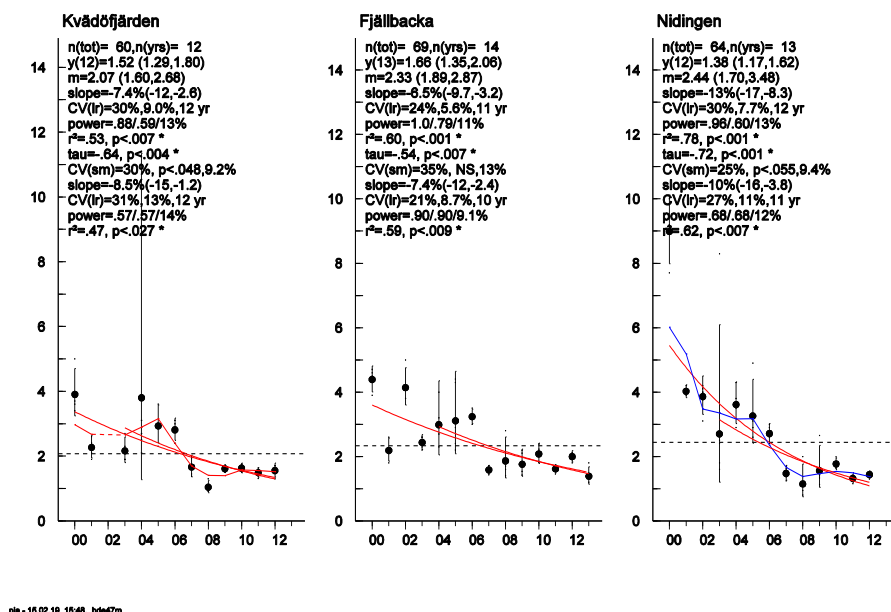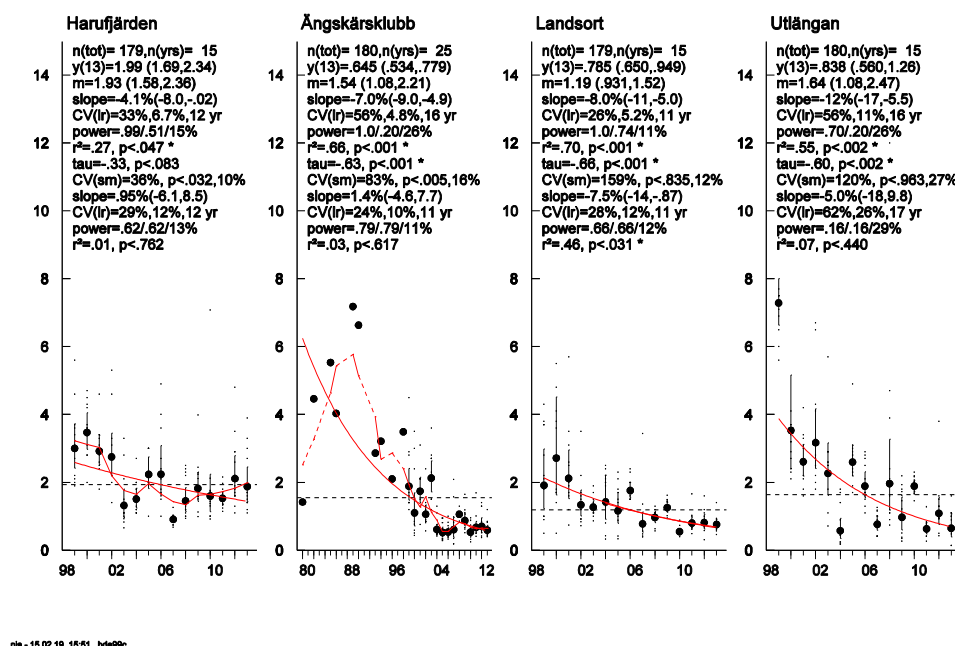## BDE-99, ng/g lipid w., blue mussel
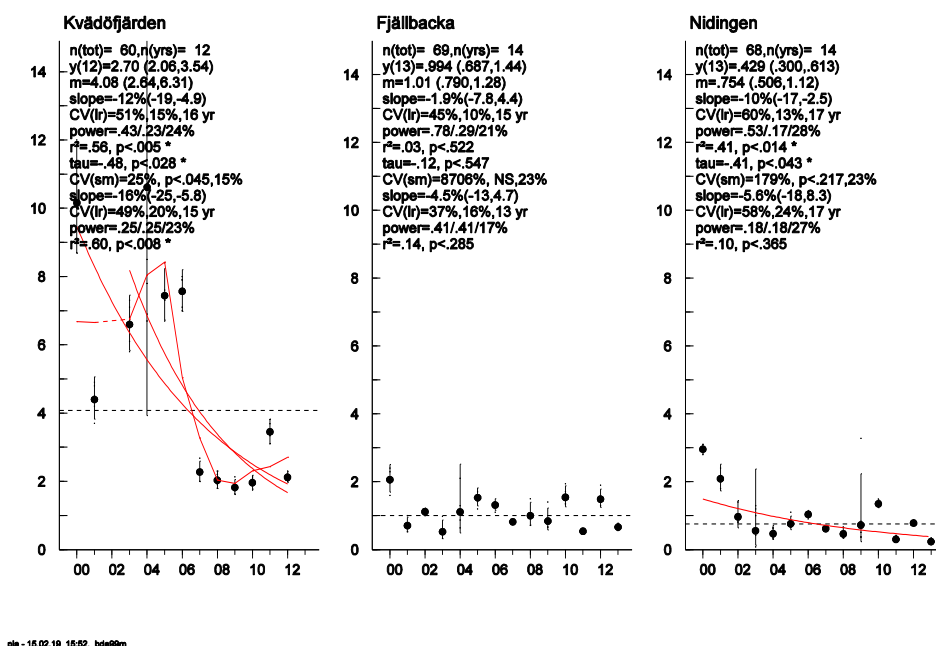


**Figure 27.10.** BDE-99 concentrations (ng/g lipid weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 2000).

Significant decreasing concentrations of BDE-153 are observed in herring from Utlängan, Fladen, Väderöarna and Ängskärsklubb (spring) (Fig. 27.12) and for cod from Southeast Gotland (Fig. 27.13).
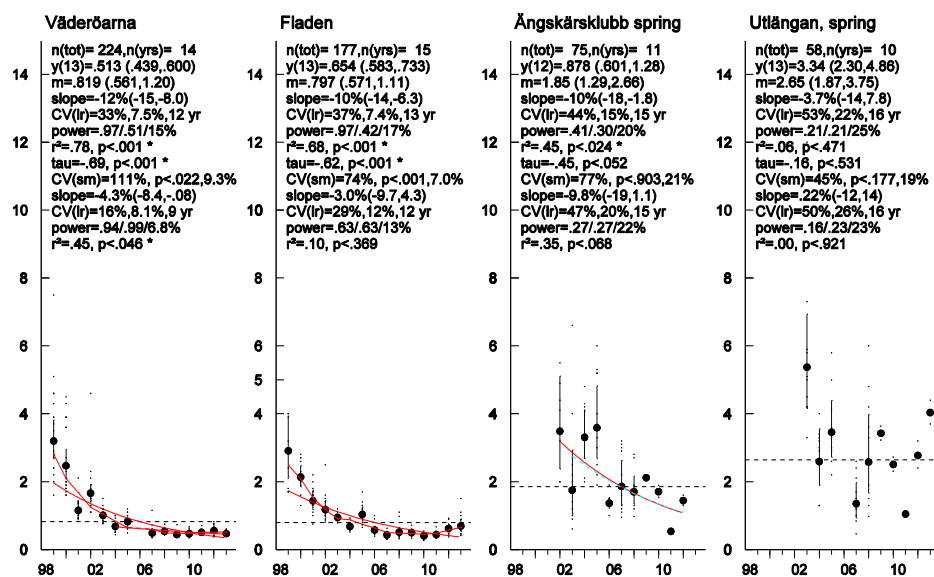
## BDE-153, ng/g lipid w., herring muscle
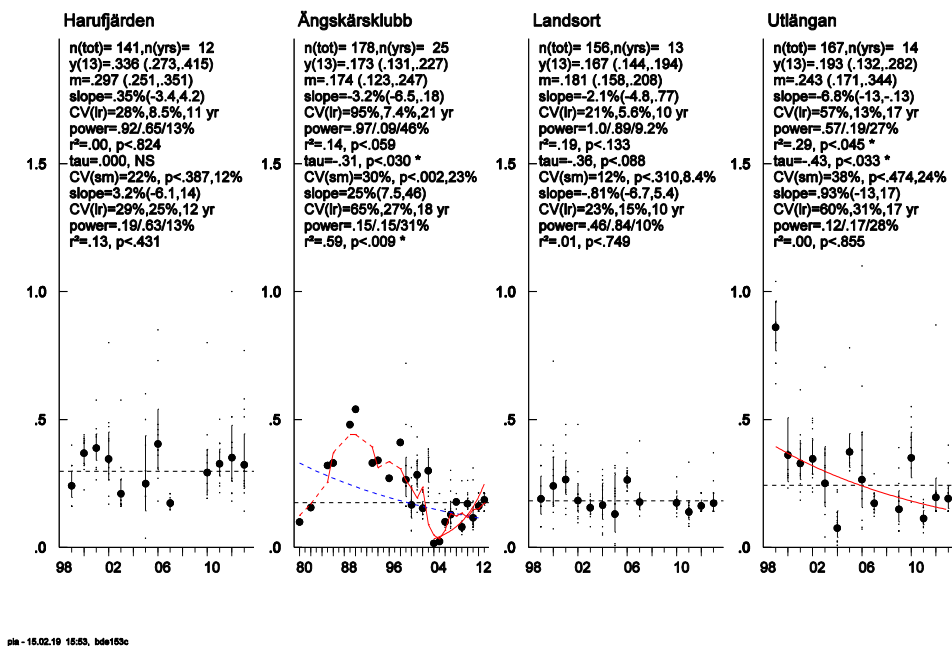


**Figure 27.11.** BDE-153 concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999).
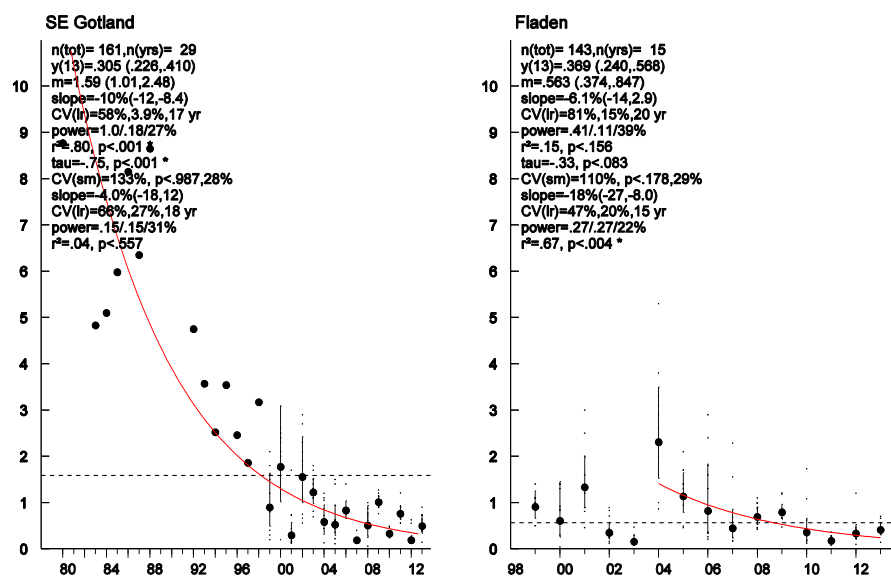
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BDE-153, ng/g lipid w., herring muscle

**Harufjärden**
n(tot)= 141,n(yrs)= 12
y(13)=.336 (.273,.415)
m=.297 (.251,.351)
slope=.35%(-3.4,4.2)
CV(lr)=28%,8.5%,11 yr
power=.92/.65/13%
r²=.00, p<.824
tau=.000, NS
CV(sm)=22%, p<.387,12%
slope=3.2%(-6.1,14)
CV(lr)=29%,25%,12 yr
power=.19/.63/13%
r²=.13, p<.431

**Ängskärsklubb**
n(tot)= 178,n(yrs)= 25
y(13)=.173 (.131,.227)
m=.174 (.123,.247)
slope=-3.2%(-6.5,.18)
CV(lr)=95%,7.4%,21 yr
power=.97/.09/46%
r²=.14, p<.059
tau=-.31, p<.030 *
CV(sm)=30%, p<.002,23%
slope=25%(7.5,46)
CV(lr)=65%,27%,18 yr
power=.15/.15/31%
r²=.59, p<.009 *

**Landsort**
n(tot)= 156,n(yrs)= 13
y(13)=.167 (.144,.194)
m=.181 (.158,.208)
slope=-2.1%(-4.8,.77)
CV(lr)=21%,5.6%,10 yr
power=1.0/.89/9.2%
r²=.19, p<.133
tau=-.36, p<.088
CV(sm)=12%, p<.310,8.4%
slope=-.81%(-6.7,5.4)
CV(lr)=23%,15%,10 yr
power=.46/.84/10%
r²=.01, p<.749

**Utlängan**
n(tot)= 167,n(yrs)= 14
y(13)=.193 (.132,.282)
m=.243 (.171,.344)
slope=-6.8%(-13,-.13)
CV(lr)=57%,13%,17 yr
power=.57/.19/27%
r²=.29, p<.045 *
tau=-.43, p<.033 *
CV(sm)=38%, p<.474,24%
slope=.93%(-13,17)
CV(lr)=60%,31%,17 yr
power=.12/.17/28%
r²=.00, p<.855

pia - 15.02.19 15:53, bde153c

**Figure 27.12.** 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).

BDE-153, ng/g lipid w., cod liver

**SE Gotland**
n(tot)= 160,n(yrs)= 29
y(13)=.166 (.141,.195)
m=.216 (.178,.260)
slope=-3.0%(-4.6,-1.4)
CV(lr)=43%,3.0%,14 yr
power=1.0/.32/20%
r²=.34, p<.001 *
tau=-.41, p<.002 *
CV(sm)=22%, p<.040,14%
slope=-.21%(-10,11)
CV(lr)=44%,18%,14 yr
power=.31/.31/20%
r²=.00, p<.917

**Fladen**
n(tot)= 140,n(yrs)= 15
y(13)=.202 (.140,.290)
m=.186 (.131,.266)
slope=-3.1%(-11,5.4)
CV(lr)=72%,14%,19 yr
power=.48/.13/35%
r²=.04, p<.433
tau=-.09, p<.656
CV(sm)=32%, p<.087,24%
slope=-9.6%(-23,6.1)
CV(lr)=70%,29%,19 yr
power=.13/.13/34%
r²=.21, p<.181

pia - 15.02.19 15:54, bde153g

**Figure 27.13.** BDE-153 concentrations (ng/g lipid weight) in cod liver from Southeast Gotland and Fladen (time series starting in 1980 and 1999 respectivley).
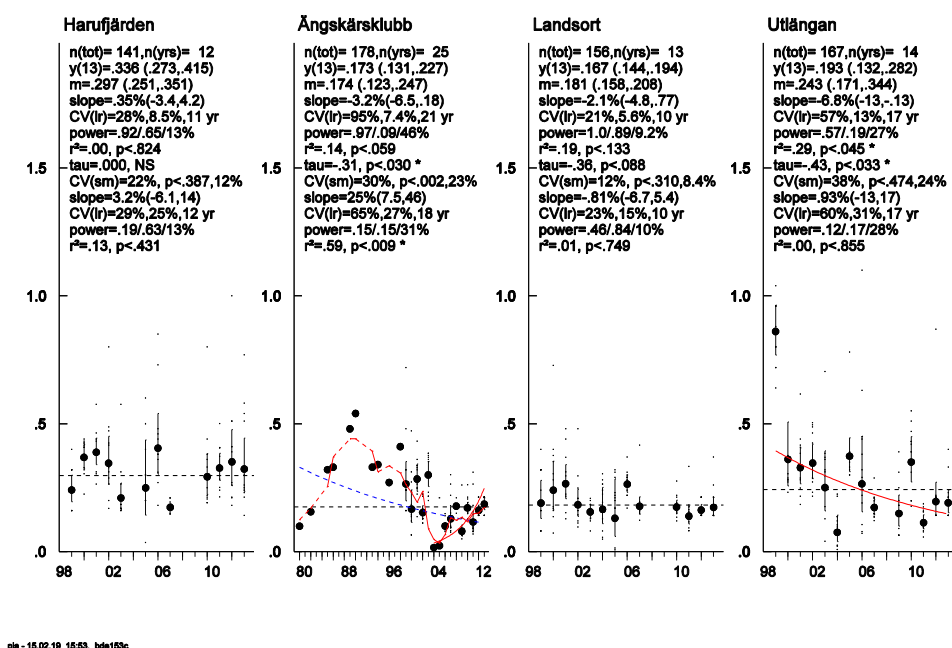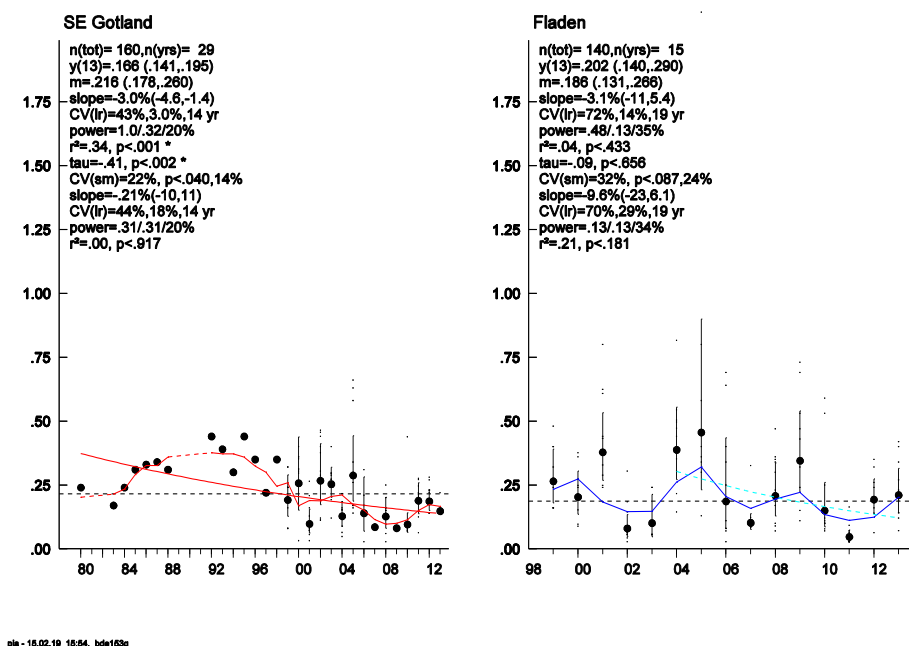
HBCDD in herring is decreasing at Utlängan (autumn), Väderöarna and Fladen (6.3, 8.9 and 8.8% per year, respectively) and in cod at Fladen (9.6% per year) (Fig. 27.14–27.16, table 27.4). At the same time, the concentration of HBCDD is increasing in herring from Ängskärsklubb (autumn)and cod at the Southeast of Gotland (4.1 and 6.3% per year) (Fig.

27.14 and 27.16, table 27.4). Concentrations of HBCDD are increasing in guillemot eggs by about 1.9% per year for the whole time period, however, during the last ten years a significant decrease of 9% per year is seen (Fig. 27.18, table 27.4).

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 11–19 years for herring and cod, and 14 years for guillemot egg.
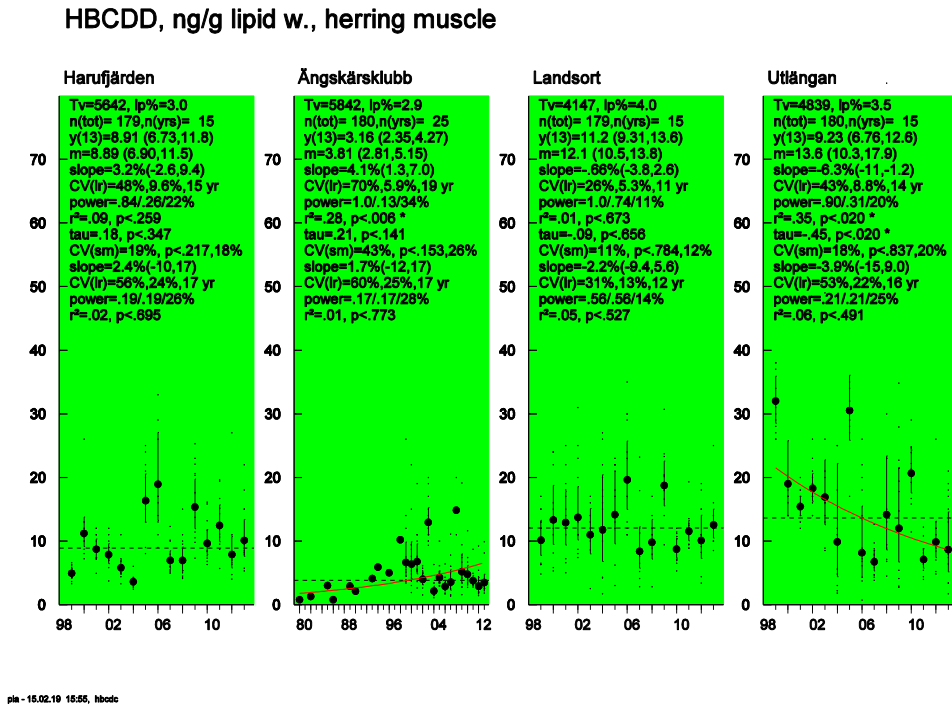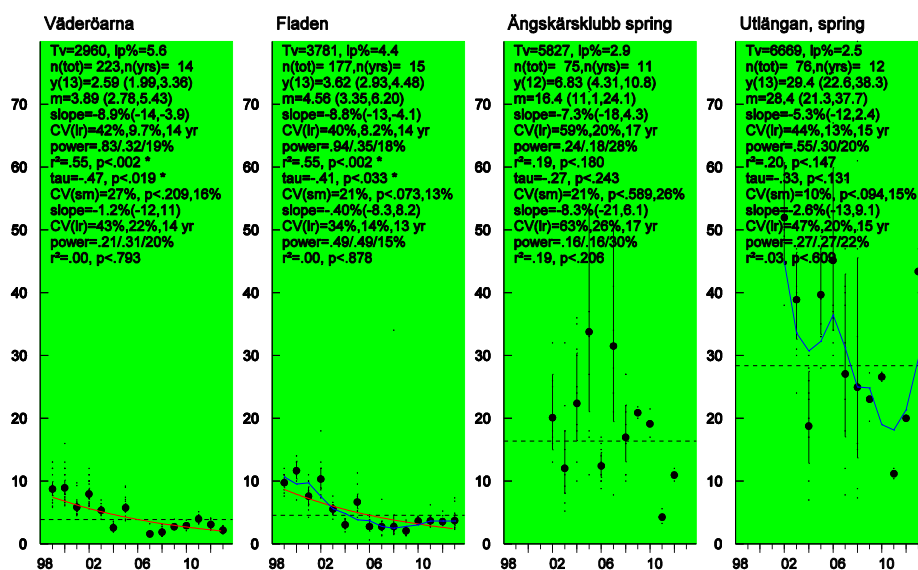


**Figure 27.14.** HBCDD concentrations (ng/g lipid weight) in herring muscle from Harufjärden, Ängskärsklubb, Landsort and Utlängan (time series starting in 1999). The green area denotes the levels below the suggested target value for HBCDD in fish.
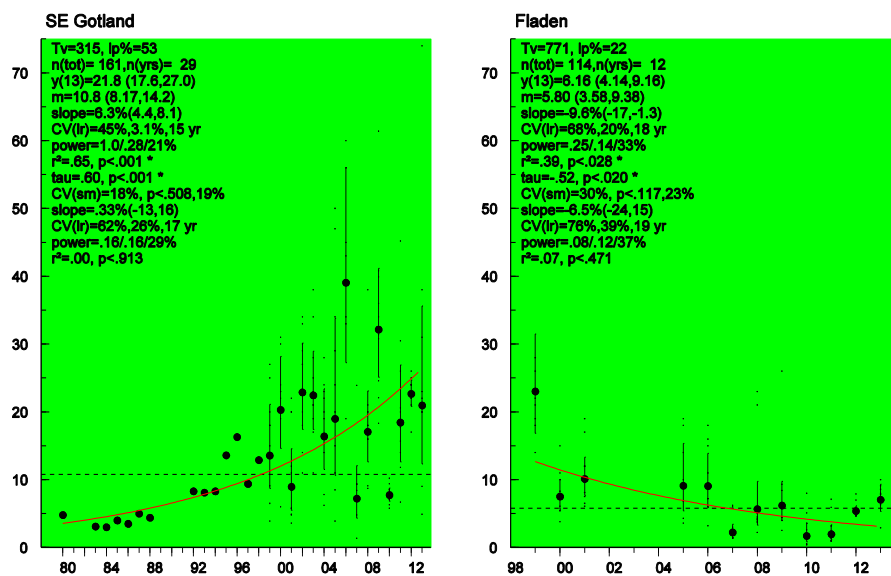
## HBCDD, ng/g lipid w., herring muscle



**Väderöarna**

Tv=2960, lp%=5.6
n(tot)= 223,n(yrs)= 14
y(13)=2.59 (1.99,3.36)
m=3.89 (2.78,5.43)
slope=-8.9%(-14,-3.9)
CV(lr)=42%,9.7%,14 yr
power=.83/.32/19%
r²=.55, p<.002 *
tau=-.47, p<.019 *
CV(sm)=27%, p<.209,16%
slope=-1.2%(-12,11)
CV(lr)=43%,22%,14 yr
power=.21/.31/20%
r²=.00, p<.793

**Fladen**

Tv=3781, lp%=4.4
n(tot)= 177,n(yrs)= 15
y(13)=3.62 (2.93,4.48)
m=4.56 (3.35,6.20)
slope=-8.8%(-13,-4.1)
CV(lr)=40%,8.2%,14 yr
power=.94/.35/18%
r²=.55, p<.002 *
tau=-.41, p<.033 *
CV(sm)=21%, p<.073,13%
slope=-.40%(-8.3,8.2)
CV(lr)=34%,14%,13 yr
power=.49/.49/15%
r²=.00, p<.878

**Ängskärsklubb spring**

Tv=5827, lp%=2.9
n(tot)= 75,n(yrs)= 11
y(12)=6.83 (4.31,10.8)
m=16.4 (11.1,24.1)
slope=-7.3%(-18,4.3)
CV(lr)=59%,20%,17 yr
power=.24/.18/28%
r²=.19, p<.180
tau=-.27, p<.243
CV(sm)=21%, p<.589,26%
slope=-8.3%(-21,6.1)
CV(lr)=63%,26%,17 yr
power=.16/.16/30%
r²=.19, p<.206

**Utlängan, spring**

Tv=6669, lp%=2.5
n(tot)= 76,n(yrs)= 12
y(13)=29.4 (22.6,38.3)
m=28.4 (21.3,37.7)
slope=-5.3%(-12,2.4)
CV(lr)=44%,13%,15 yr
power=.55/.30/20%
r²=.20, p<.147
tau=-.33, p<.131
CV(sm)=10%, p<.094,15%
slope=-2.6%(-13,9.1)
CV(lr)=47%,20%,15 yr
power=.27/.27/22%
r²=.03, p<.609

**Figure 27.15.** 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.

## HBCDD, ng/g lipid w., cod liver



**SE Gotland**

Tv=315, lp%=53
n(tot)= 161,n(yrs)= 29
y(13)=21.8 (17.6,27.0)
m=10.8 (8.17,14.2)
slope=6.3%(4.4,8.1)
CV(lr)=45%,3.1%,15 yr
power=1.0/.28/21%
r²=.65, p<.001 *
tau=.60, p<.001 *
CV(sm)=18%, p<.508,19%
slope=.33%(-13,16)
CV(lr)=62%,26%,17 yr
power=.16/.16/29%
r²=.00, p<.913

**Fladen**

Tv=771, lp%=22
n(tot)= 114,n(yrs)= 12
y(13)=6.16 (4.14,9.16)
m=5.80 (3.58,9.38)
slope=-9.6%(-17,-1.3)
CV(lr)=68%,20%,18 yr
power=.25/.14/33%
r²=.39, p<.028 *
tau=-.52, p<.020 *
CV(sm)=30%, p<.117,23%
slope=-6.5%(-24,15)
CV(lr)=76%,39%,19 yr
power=.08/.12/37%
r²=.07, p<.471

**Figure 27.16.** 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.
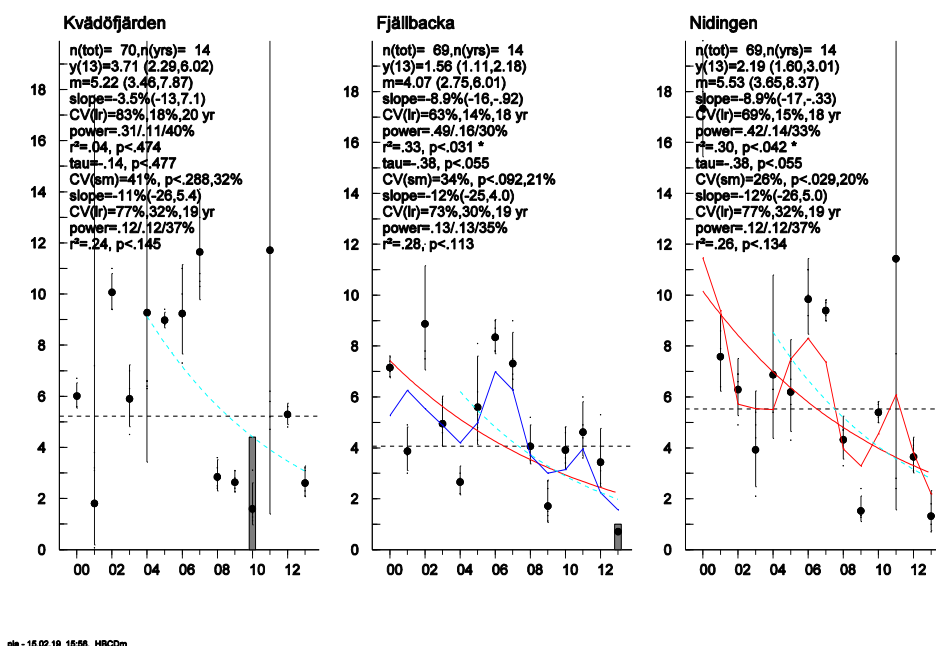
**Figure 27.17.** HBCDD concentrations (ng/g lipid weight) in blue mussel from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 2000).
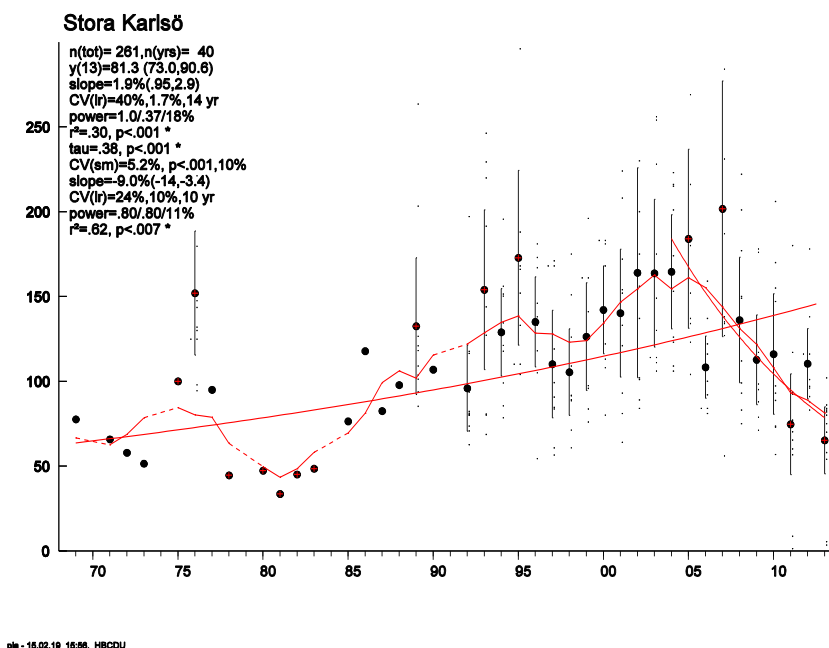


**Figure 27.18.** HBCDD concentrations (ng/g lipid weight) in guillemot eggs from Stora Karlsö (time series starting in 1969).

### 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 and from there onwards concentrations 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 (3-5) | 179 | 15 | 99-13 | -2.5(-6.8,2.0) | 0.2471 | | 13 | 16 | 5.82 (4.71,7.19) |
| Harufjärden (3-5) | | 10 | 04-13 | 0.41(-9.1,11) | 0.8891 | | 14 | 19 | |
| Ängskärsklubb (3-5) | 180 | 25 | 80-13 | -7.2(-9.2,-5.1) | 0.0000 | --- | 16 | 26 | 2.73 (2.30,3.24) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | -5.5(-15,5.4) | 0.2669 | | 15 | 21 | |
| Landsort (3-5) | 179 | 15 | 99-13 | -7.4(-10,-4.4) | 0.0002 | --- | 11 | 11 | 4.04 (3.37,4.86) |
| Landsort (3-5) | | 10 | 04-13 | -7.1(-12,-1.4) | 0.0202 | - | 10 | 10 | |
| Utlängan (2-4) | 180 | 15 | 99-13 | -5.9(-9.1,-2.7) | 0.002 | -- | 11 | 12 | 5.31 (4.55,6.19) |
| Utlängan (2-4) | | 10 | 04-13 | -6.5(-12,-.71) | 0.0318 | - | 11 | 11 | |
| Fladen (2-3) | 177 | 15 | 99-13 | -9.9(-13,-6.4) | 0.0001 | --- | 12 | 13 | 2.40 (2.19,2.62) |
| Fladen (2-3) | | 10 | 04-13 | -4.2(-10,2.2) | 0.1611 | | 11 | 11 | |
| Väderöarna | 224 | 14 | 99-13 | -11(-14,-7.7) | 0.0000 | --- | 11 | 12 | 1.80 (1.51,2.14) |
| Väderöarna | | 9 | 04-13 | -7(-11,-2.4) | 0.0096 | -- | 9 | 7.8 | |
| Ängskärsklubb spring (2-6) | 75 | 11 | 02-12 | -11(-22,1.6) | 0.0741 | | 18 | 33 | 4.07 (2.39,6.93) |
| Ängskärsklubb spring (2-6) | | 10 | 03-12 | -11(-25,5.2) | 0.1436 | | 19 | 36 | |
| Utlängan spring (2-4) | 68 | 11 | 03-13 | -4.9(-13,3.8) | 0.2253 | | 14 | 19 | 11.1 (7.97,15.4) |
| Utlängan spring (2-4) | | 10 | 04-13 | -3.8(-14,7.0) | 0.4295 | | 15 | 20 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 161 | 29 | 80-13 | -7.7(-8.7,-6.7) | 0.0000 | --- | 11 | 12 | 10.8 ( 9.6,12.1) |
| SE Gotland (2-4) | | 10 | 04-13 | -6.8(-11,-2.1) | 0.0113 | - | 9 | 8.6 | |
| Fladen (2-3) | 146 | 15 | 99-13 | -11(-16,-6.1) | 0.0004 | --- | 14 | 20 | 12.0 (9.40,15.2) |
| Fladen (2-3) | | 10 | 04-13 | -5.3(-12,2.0) | 0.1274 | | 12 | 13 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 64 | 13 | 00-12 | -13(-17,-8.3) | 0.0001 | --- | 12 | 13 | 1.38 (1.17,1.62) |
| Nidingen | | 10 | 03-12 | -10(-16,-3.8) | 0.0067 | -- | 11 | 12 | |
| Fjällbacka | 69 | 14 | 00-13 | -6.5(-9.7,-3.2) | 0.0013 | -- | 11 | 11 | 1.66 (1.35,2.06) |
| Fjällbacka | | 10 | 04-13 | -7.4(-12,-2.4) | 0.0095 | -- | 10 | 9.1 | |
| Kvädöfjärden | 60 | 12 | 00-12 | -7.4(-12,-2.6) | 0.0071 | -- | 12 | 13 | 1.52 (1.29,1.80) |
| Kvädöfjärden | | 10 | 03-12 | -8.5(-15,-1.2) | 0.0272 | - | 12 | 14 | |
| **Guillemot egg** | | | | | | | | | |
| Stora Karlsö | 251 | 39 | 69-13 | -5.3(-7.9,-2.7) | 0.0003 | --- | 26 | 74 | 22.9 (19.0,27.8) |
| Stora Karlsö | | 16 | 69-88 | 17(11,24) | 0.0000 | +++ | 18 | 31 | |

*gaps in the examined years

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**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 mussle** | | | | | | | | | | |
| Harufjärden | 141 | 12 | 99-13 | .35 | (-3.4,4.2) | 0.8239 | | 11 | 13 | .336 (.273,.415) |
| Harufjärden | | 7 | 05-13 | 3.2 | (-6.1,14) | 0.4312 | | 12 | 13 | |
| Ängskärsklubb | 178 | 25 | 80-13 | -3.2 | (-6.5,.18) | 0.0593 | | 21 | 46 | .173 (.131,.227) |
| Ängskärsklubb | | 10 | 04-13 | 25 | (7.5,46) | 0.0092 | ++ | 18 | 31 | |
| Landsort | 156 | 13 | 99-13 | -2.1 | (-4.8,.77) | 0.1334 | | 10 | 9.2 | .167 (.144,.194) |
| Landsort | | 8 | 04-13 | -.81 | (-6.7,5.4) | 0.7485 | | 10 | 10 | |
| Utlängan | 167 | 14 | 99-13 | -6.8 | (-13,-.13) | 0.0447 | - | 17 | 27 | .193 (.132,.282) |
| Utlängan | | 9 | 04-13 | .93 | (-13,17) | 0.8548 | | 17 | 28 | |
| Fladen | 164 | 14 | 99-13 | -8.2 | (-14,-2.2) | 0.0120 | - | 16 | 24 | .108 (.088,.133) |
| Fladen | | 9 | 04-13 | 2.2 | (-8.6,14) | 0.6564 | | 15 | 21 | |
| Väderöarna | 200 | 12 | 99-13 | -9.0 | (-13,-4.2) | 0.0022 | -- | 14 | 18 | .084 (.066,.107) |
| Väderöarna | | 7 | 04-13 | -.63 | (-8.8,8.3) | 0.8335 | | 12 | 13 | |
| Ängskärsklubb spring | 75 | 11 | 02-12 | -9.0 | (-15,-2.3) | 0.0145 | - | 13 | 15 | .169 (.128,.222) |
| Ängskärsklubb spring | | 10 | 03-12 | -9.3 | (-17,-.87) | 0.0341 | - | 13 | 16 | |
| Utlängan spring | 75 | 12 | 02-13 | -2.0 | (-9.5,6.1) | 0.5927 | | 15 | 21 | .668 (.508,.878) |
| Utlängan spring | | 10 | 04-13 | 3.5 | (-6.3,14) | 0.4533 | | 14 | 18 | |
| **Cod liver** | | | | | | | | | | |
| SE Gotland | 160 | 29 | 80-13 | -3.0 | (-4.6,-1.4) | 0.0009 | --- | 14 | 20 | .166 (.141,.195) |
| SE Gotland | | 10 | 04-13 | -.21 | (-10,11) | 0.9166 | | 14 | 20 | |
| Fladen | 140 | 15 | 99-13 | -3.1 | (-11,5.4) | 0.4329 | | 19 | 35 | .202 (.140,.290) |
| Fladen | | 10 | 04-13 | -9.6 | (-23,6.1) | 0.1814 | | 19 | 34 | |
| **Guillemot egg** | | | | | | | | | | |
| Stora Karlsö | 144 | 14 | 00-13 | -2.6 | (-7.3,2.4) | 0.2725 | | 13 | 16 | 1.36 (.933,1.99) |

**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 | LDT | Last year |
|---|---|---|---|---|---|---|---|---|---|---|
| **Herring mussle** | | | | | | | | | | |
| Harufjärden | 179 | 15 | 99−13 | -4.1 | (-8.0,-.02) | 0.0471 | - | 12 | 15 | 1.99 (1.69,2.34) |
| Harufjärden | | 10 | 04−13 | .95 | (-6.1,8.5) | 0.7625 | | 12 | 13 | |
| Ängskärsklubb | 180 | 25 | 80−13 | -7.0 | (-9.0,-4.9) | 0.0000 | --- | 16 | 26 | .645 (.534,.779) |
| Ängskärsklubb | | 10 | 04−13 | 1.4 | (-4.6,7.7) | 0.6169 | | 11 | 11 | |
| Landsort | 179 | 15 | 99−13 | -8.0 | (-11,-5.0) | 0.0001 | --- | 11 | 11 | .785 (.650,.949) |
| Landsort | | 10 | 04−13 | -7.5 | (-14,-.87) | 0.0309 | - | 11 | 12 | |
| Utlängan | 180 | 15 | 99−13 | -12 | (-17,-5.5) | 0.0017 | -- | 16 | 26 | .838 (.560,1.26) |
| Utlängan | | 10 | 04−13 | -5.0 | (-18,9.8) | 0.4398 | | 17 | 29 | |
| Fladen | 177 | 15 | 99−13 | -10 | (-14,-6.3) | 0.0002 | --- | 13 | 17 | .654 (.583,.733) |
| Fladen | | 10 | 04−13 | -3.0 | (-9.7,4.3) | 0.3690 | | 12 | 13 | |
| Väderöarna | 224 | 14 | 99−13 | -12 | (-15,-8.0) | 0.0000 | --- | 12 | 15 | .513 (.439,.600) |
| Väderöarna | | 9 | 04−13 | -4.3 | (-8.4,-.08) | 0.0456 | - | 9 | 6.8 | |
| Ängskärsklubb spring | 75 | 11 | 02−12 | -10 | (-18,-1.8) | 0.0236 | - | 15 | 20 | .878 (.601,1.28) |
| Ängskärsklubb spring | | 10 | 03−12 | -9.8 | (-19,1.1) | 0.0677 | | 15 | 22 | |
| Utlängan spring | 58 | 10 | 03−13 | -3.7 | (-14,7.8) | 0.4706 | | 16 | 25 | 3.34 (2.30,4.86) |
| Utlängan spring | | 9 | 04−13 | .22 | (-12,14) | 0.9209 | | 16 | 23 | |
| **Cod liver** | | | | | | | | | | |
| SE Gotland | 161 | 29 | 80−13 | -10 | (-12,-8.4) | 0.0000 | --- | 17 | 27 | .305 (.226,.410) |
| SE Gotland | | 10 | 04−13 | -4.0 | (-18,12) | 0.5570 | | 18 | 31 | |
| Fladen | 143 | 15 | 99−13 | -6.1 | (-14,2.9) | 0.1564 | | 20 | 39 | .369 (.240,.568) |
| Fladen | | 10 | 04−13 | -18 | (-27,-8.0) | 0.0040 | -- | 15 | 22 | |
| **Blue mussle** | | | | | | | | | | |
| Nidingen | 68 | 14 | 00−13 | -10 | (-17,-2.5) | 0.0139 | - | 17 | 28 | .429 (.300,.613) |
| Nidingen | | 10 | 04−13 | -5.6 | (-18,8.3) | 0.3654 | | 17 | 27 | |
| Fjällbacka | 69 | 14 | 00−13 | -1.9 | (-7.8,4.4) | 0.5220 | | 15 | 21 | .994 (.687,1.44) |
| Fjällbacka | | 10 | 04−13 | -4.5 | (-13,4.7) | 0.2853 | | 13 | 17 | |
| Kvädöfjärden | 60 | 12 | 00−12 | -12 | (-19,-4.9) | 0.0051 | -- | 16 | 24 | 2.70 (2.06,3.54) |
| Kvädöfjärden | | 10 | 03−12 | -16 | (-25,-5.8) | 0.0082 | -- | 15 | 23 | |

**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 | LDT | Last year |
|---|---|---|---|---|---|---|---|---|---|
| **Herring muscle** | | | | | | | | | |
| Harufjärden (3-5) | 179 | 15 | 99-13 | 3.2(-2.6,9.4) | 0.2594 | | 15 | 22 | 8.91 (6.73,11.8) |
| Harufjärden (3-5) | | 10 | 04-13 | 2.4(-10,17) | 0.6952 | | 17 | 26 | |
| Ängskärsklubb (3-5) | 180 | 25 | 80-13 | 4.1(1.3,7.0) | 0.0062 | ++ | 19 | 34 | 3.16 (2.35,4.27) |
| Ängskärsklubb (3-5) | | 10 | 04-13 | 1.7(-12,17) | 0.7731 | | 17 | 28 | |
| Landsort (3-5) | 179 | 15 | 99-13 | -0.66(-3.8,2.6) | 0.6728 | | 11 | 11 | 11.2 (9.31,13.6) |
| Landsort (3-5) | | 10 | 04-13 | -2.2(-9.4,5.6) | 0.5268 | | 12 | 14 | |
| Utlängan (2-4) | 180 | 15 | 99-13 | -6.3(-11,-1.2) | 0.0197 | - | 14 | 20 | 9.23 (6.76,12.6) |
| Utlängan (2-4) | | 10 | 04-13 | -3.9(-15,9.0) | 0.4915 | | 16 | 25 | |
| Fladen (2-3) | 177 | 15 | 99-13 | -8.8(-13,-4.1) | 0.0016 | -- | 14 | 18 | 3.62 (2.93,4.48) |
| Fladen (2-3) | | 10 | 04-13 | -0.4(-8.3,8.2) | 0.8779 | | 13 | 15 | |
| Väderöarna | 223 | 14 | 99-13 | -8.9(-14,-3.9) | 0.0025 | -- | 14 | 19 | 2.59 (1.99,3.36) |
| Väderöarna | | 9 | 04-13 | -1.2(-12,11) | 0.7932 | | 14 | 20 | |
| Ängskärsklubb spring (2-6) | 75 | 10 | 03-12 | -8.3(-21,6.1) | 0.2058 | | 17 | 30 | 6.83 (4.31,10.8) |
| Utlängan spring (2-4) | 76 | 12 | 02-13 | -5.3(-12,2.4) | 0.1472 | | 15 | 20 | 29.4 (22.6,38.3) |
| Utlängan spring (2-4) | | 10 | 04-13 | -2.6(-13,9.1) | 0.6095 | | 15 | 22 | |
| **Cod liver** | | | | | | | | | |
| SE Gotland (2-4) | 161 | 29 | 80-13 | 6.3(4.4,8.1) | 0.0000 | +++ | 15 | 21 | 21.8 (17.6,27.0) |
| SE Gotland (2-4) | | 10 | 04-13 | 0.33(-13,16) | 0.9128 | | 17 | 29 | |
| Fladen (2-3) | 114 | 12 | 99-13 | -9.6(-17,-1.3) | 0.028 | - | 18 | 33 | 6.16 (4.14,9.16) |
| Fladen (2-3) | | 9 | 05-13 | -6.5(-24,15) | 0.4715 | | 19 | 37 | |
| **Blue mussel** | | | | | | | | | |
| Nidingen | 69 | 14 | 00-13 | -8.9(-17,-.33) | 0.0417 | - | 18 | 33 | 2.19 (1.60,3.01) |
| Nidingen | | 10 | 04-13 | -12(-26,5.0) | 0.1335 | | 19 | 37 | |
| Fjällbacka | 69 | 14 | 00-13 | -8.9(-16,-.92) | 0.031 | - | 18 | 30 | 1.56 (1.11,2.18) |
| Fjällbacka | | 10 | 04-13 | -12(-25,4.0) | 0.1128 | | 19 | 35 | |
| Kvädöfjärden | 70 | 14 | 00-13 | -3.5(-13,7.1) | 0.4738 | | 20 | 40 | 3.71 (2.29,6.02) |
| Kvädöfjärden | | 10 | 04-13 | -11(-26,5.4) | 0.1448 | | 19 | 37 | |
| **Guillemot egg** | | | | | | | | | |
| Stora Karlsö | 261 | 40 | 69-13 | 1.9(.95,2.9) | 0.0003 | +++ | 14 | 18 | 81.3 (73.0,90.6) |
| Stora Karlsö | | 10 | 04-13 | -9(-14,-3.4) | 0.0067 | -- | 10 | 11 | |

# 28 PAHs, Polyaromatic Hydrocarbons

Updated 15.02.23

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 and 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 µg/kg dry weight. For further information on target levels and selection of target level see chapter 10.

Fluoranthene 110 µg/kg d.w.; Anthracene 290 µg/kg d.w.; Naphtalene 340 µg/kg d.w.; Phenantrene 1700 µg/kg d.w.; Pyrene 100 µg/kg d.w.; Benzo(a)antracene 80 µg/kg d.w.; benzo(a)pyrene 600 µg/kg d.w.; and Benzo(g,h,i)perylene 110 µg/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.
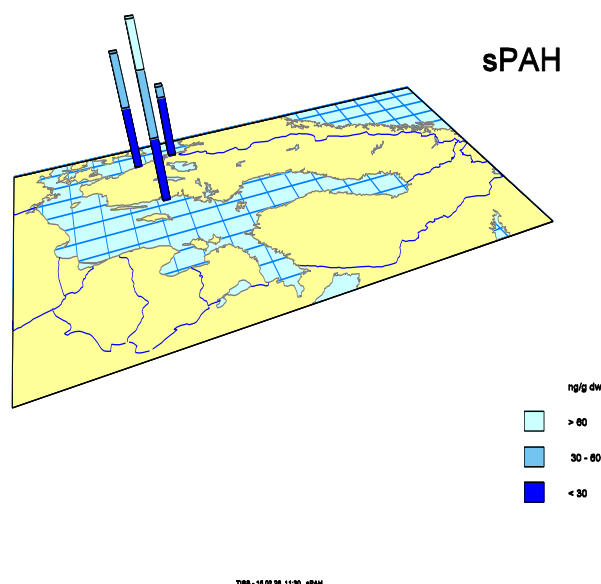
## 28.3 Results

### 28.3.1 Spatial Variation



**Figure 28.1.** Spatial variation in ∑PAH 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 (∑PAH) 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 ∑PAH (Fig. 28.2), chrysene (Fig. 28.9), fluoranthene (Fig. 28.12) and pyrene (Fig. 28.16) were found at Fjällbacka.Concentrations of pyrene and chrysene at Nidingen (Fig. 28.16) as well as naphtalene at Kvädöfjärden (Fig. 28.14).

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 15–26 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.
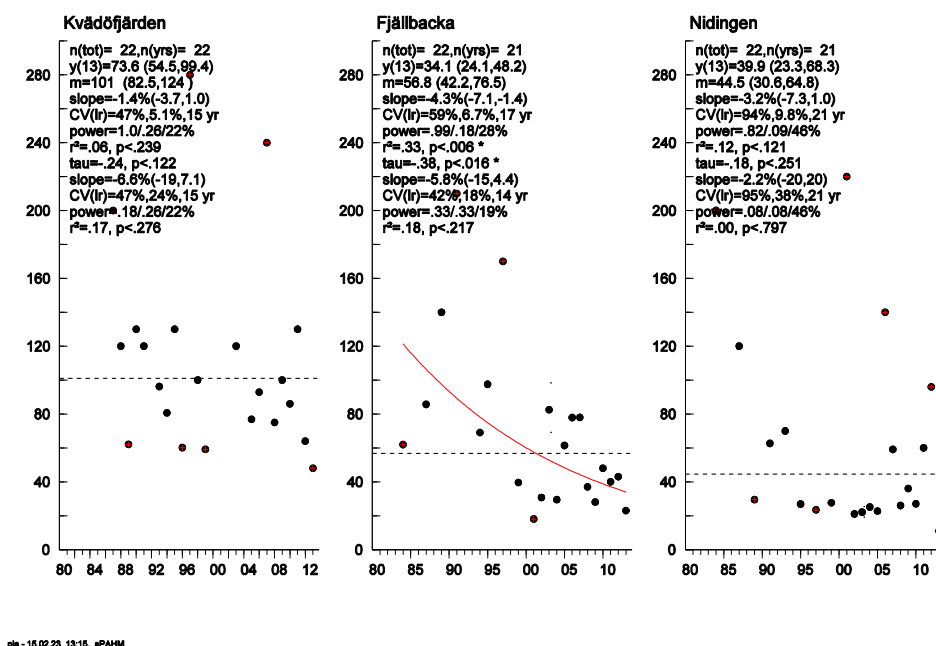
## sPAH, ng/g dry w., blue mussel



**Figure 28.2.** ∑PAH concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1986, 1983 and 1987 respectively).

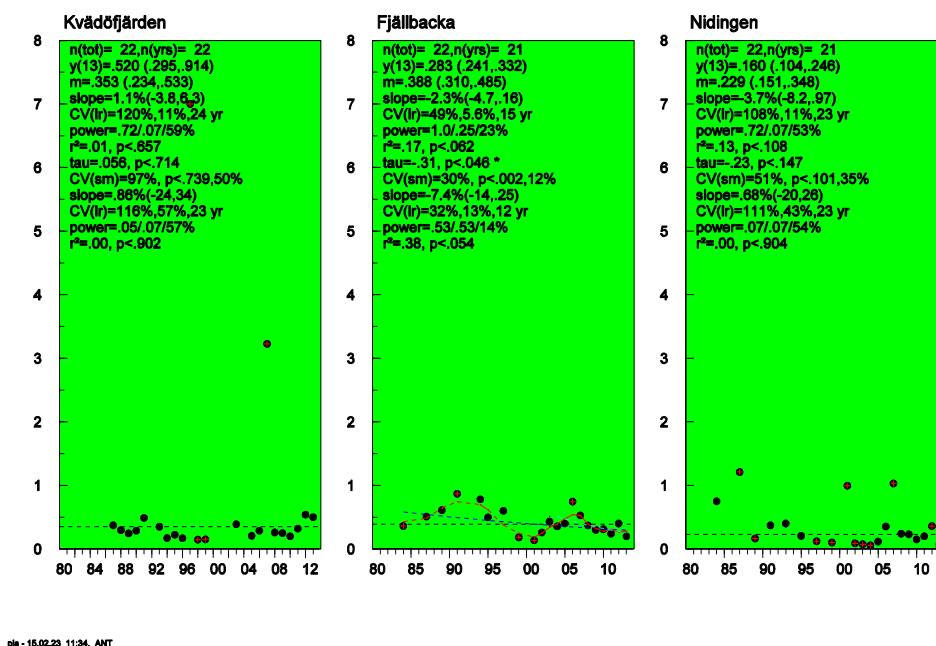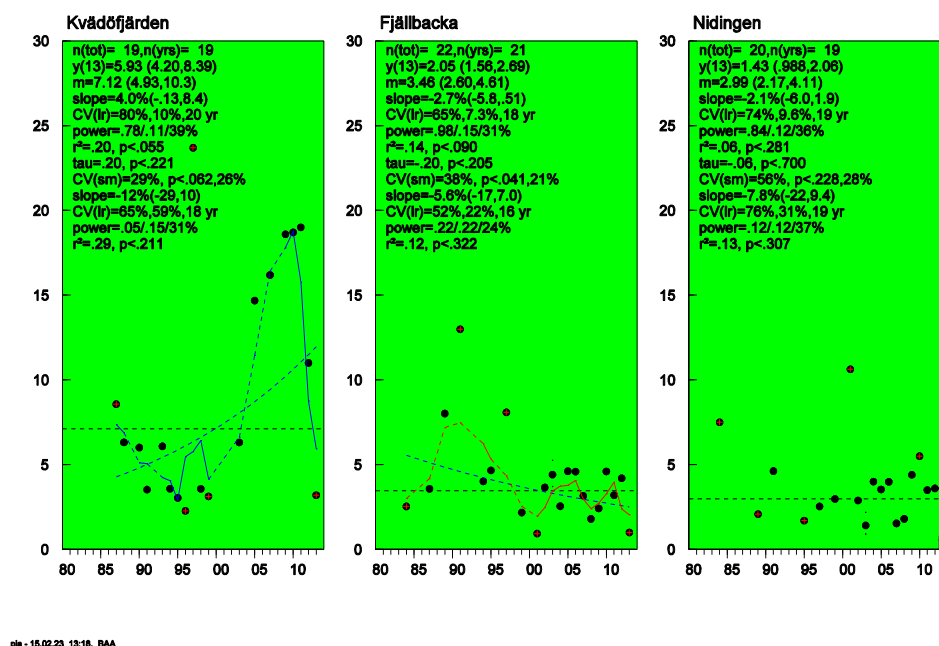## Anthracene, ng/g dry w., blue mussel



**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.

## Benzo(a)anthracene, ng/g dry w., blue mussel



**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.

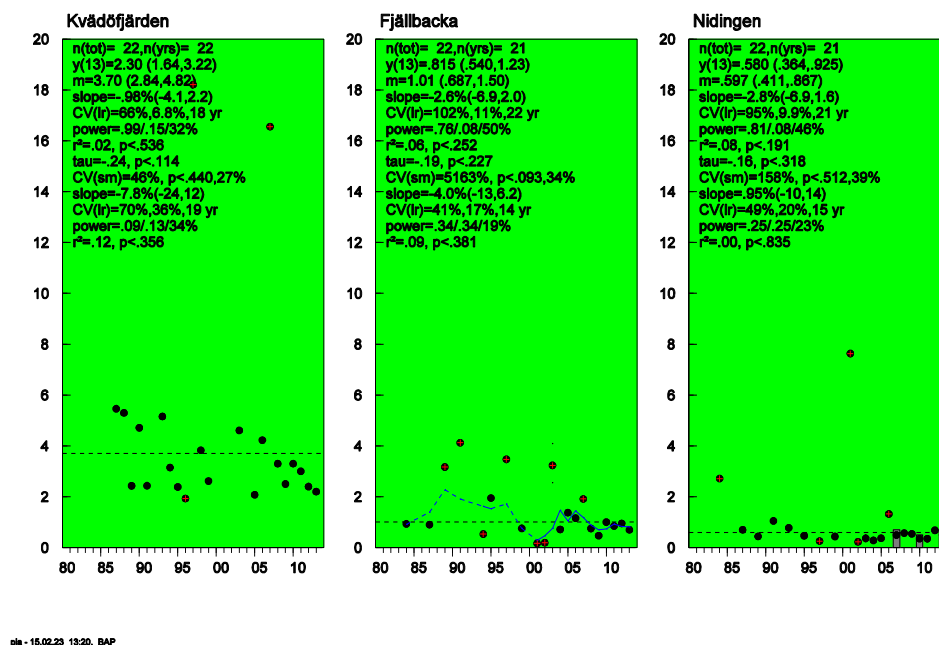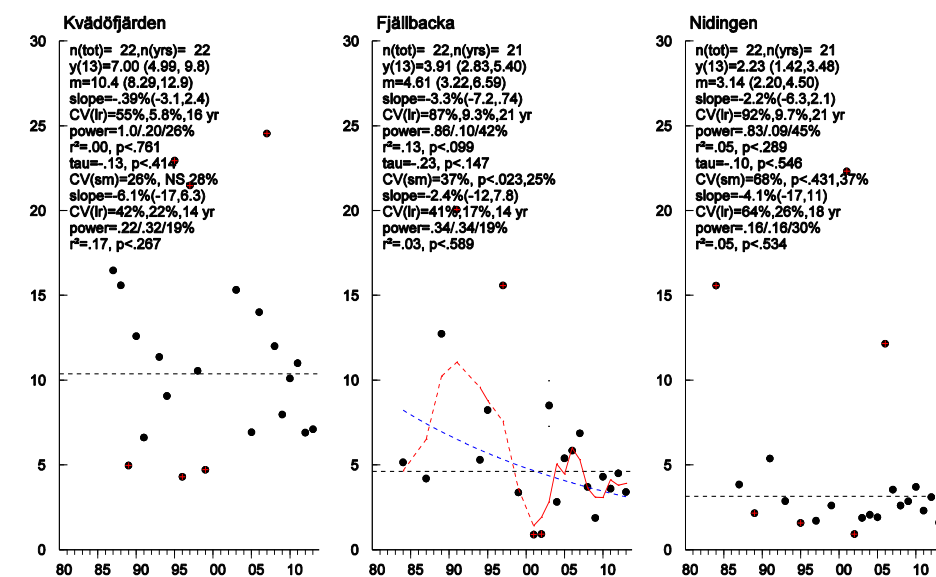## Benzo(a)pyrene, ng/g dry w., blue mussel



**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.
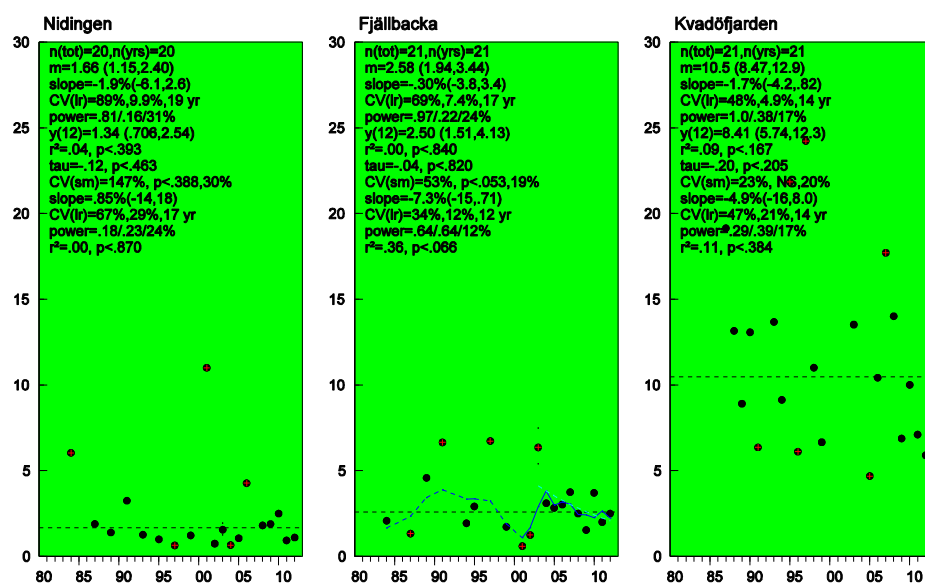
## Benzo(b)fluoranthene, ng/g dry w., blue mussel

**Kvädöfjärden**

```
n(tot)= 22,n(yrs)= 22
y(13)=7.00 (4.99, 9.8)
m=10.4 (8.29,12.9)
slope=-.39%(-3.1,2.4)
CV(lr)=55%,5.8%,16 yr
power=1.0/.20/26%
r²=.00, p<.761
tau=-.13, p<.414
CV(sm)=26%, NS,28%
slope=-6.1%(-17,6.3)
CV(lr)=42%,22%,14 yr
power=.22/.32/19%
r²=.17, p<.267
```

**Fjällbacka**

```
n(tot)= 22,n(yrs)= 21
y(13)=3.91 (2.83,5.40)
m=4.61 (3.22,6.59)
slope=-3.3%(-7.2,.74)
CV(lr)=87%,9.3%,21 yr
power=.86/.10/42%
r²=.13, p<.099
tau=-.23, p<.147
CV(sm)=37%, p<.023,25%
slope=-2.4%(-12,7.8)
CV(lr)=41%,17%,14 yr
power=.34/.34/19%
r²=.03, p<.589
```

**Nidingen**

```
n(tot)= 22,n(yrs)= 21
y(13)=2.23 (1.42,3.48)
m=3.14 (2.20,4.50)
slope=-2.2%(-6.3,2.1)
CV(lr)=92%,9.7%,21 yr
power=.83/.09/45%
r²=.05, p<.289
tau=-.10, p<.546
CV(sm)=68%, p<.431,37%
slope=-4.1%(-17,11)
CV(lr)=64%,26%,18 yr
power=.16/.16/30%
r²=.05, p<.534
```
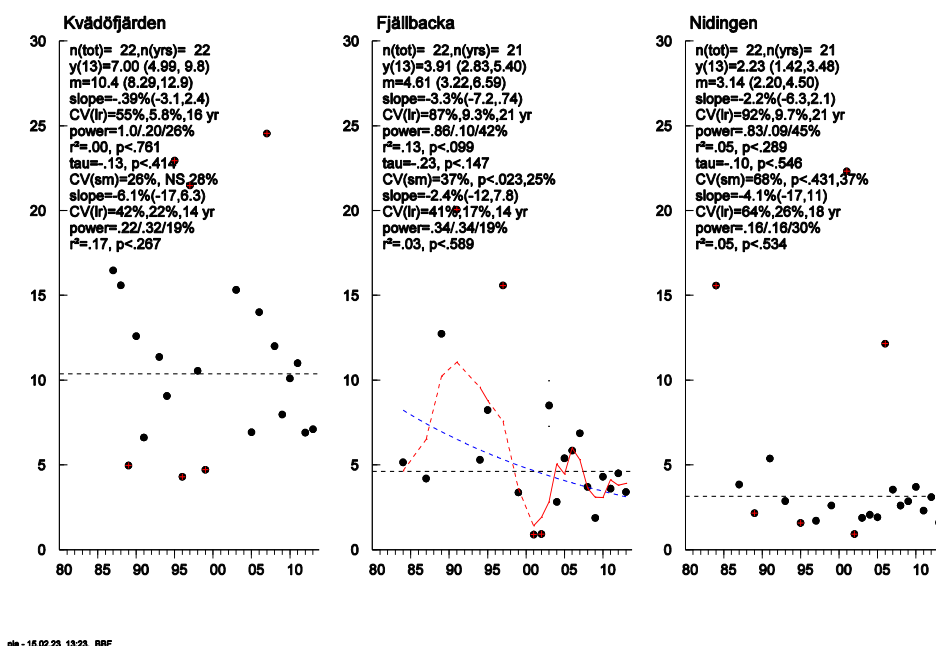
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**Figure 28.6.** Benzo(b)fluoranthene concentrations (ng/g dry weight) in blue mussels from Nidingen, Fjällbacka and Kvädöfjärden (time series starting in 1986, 1984 and 1986 respectively).

## Benzo(g,h,i)perylene, ng/g dry w., blue mussel

**Nidingen**

```
n(tot)=20,n(yrs)=20
m=1.66 (1.15,2.40)
slope=-1.9%(-6.1,2.6)
CV(lr)=89%,9.9%,19 yr
power=.81/.16/31%
y(12)=1.34 (.706,2.54)
r²=.04, p<.393
tau=-.12, p<.463
CV(sm)=147%, p<.388,30%
slope=.85%(-14,18)
CV(lr)=67%,29%,17 yr
power=.18/.23/24%
r²=.00, p<.870
```

**Fjällbacka**

```
n(tot)=21,n(yrs)=21
m=2.58 (1.94,3.44)
slope=-.30%(-3.8,3.4)
CV(lr)=69%,7.4%,17 yr
power=.97/.22/24%
y(12)=2.50 (1.51,4.13)
r²=.00, p<.840
tau=-.04, p<.820
CV(sm)=53%, p<.053,19%
slope=-7.3%(-15,.71)
CV(lr)=34%,12%,12 yr
power=.64/.64/12%
r²=.36, p<.066
```

**Kvadöfjarden**

```
n(tot)=21,n(yrs)=21
m=10.5 (8.47,12.9)
slope=-1.7%(-4.2,.82)
CV(lr)=48%,4.9%,14 yr
power=1.0/.38/17%
y(12)=8.41 (5.74,12,3)
r²=.09, p<.167
tau=-.20, p<.205
CV(sm)=23%, NS,20%
slope=-4.9%(-16,8.0)
CV(lr)=47%,21%,14 yr
power=.29/.39/17%
r²=.11, p<.384
```

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**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 reseptively). The green area denotes the levels below the suggested target value for benzo(g, h, i)perylene in blue mussels.

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## Benzo(b)fluoranthene, ng/g dry w., blue mussel



**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).

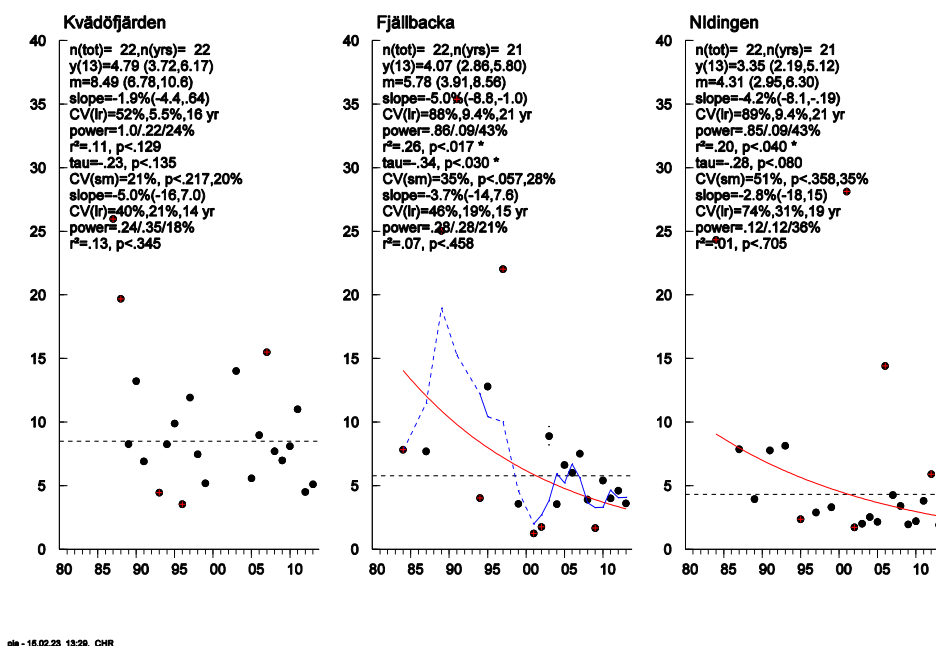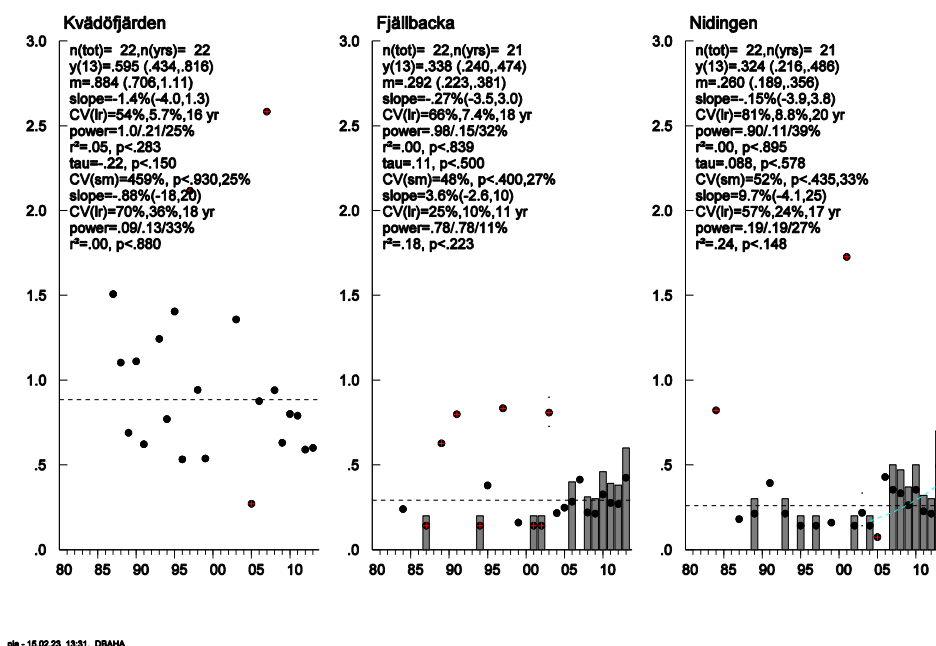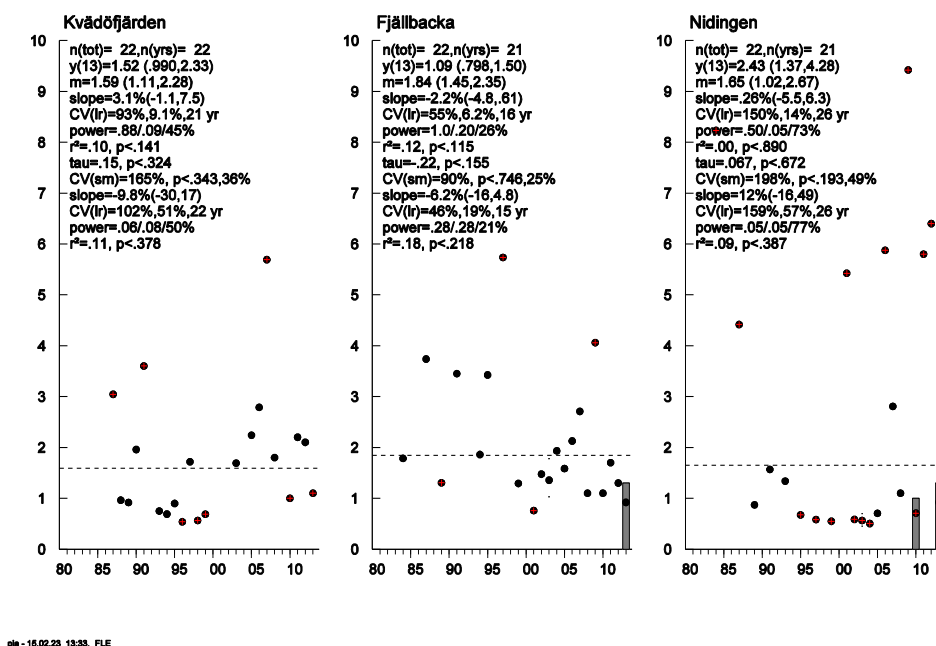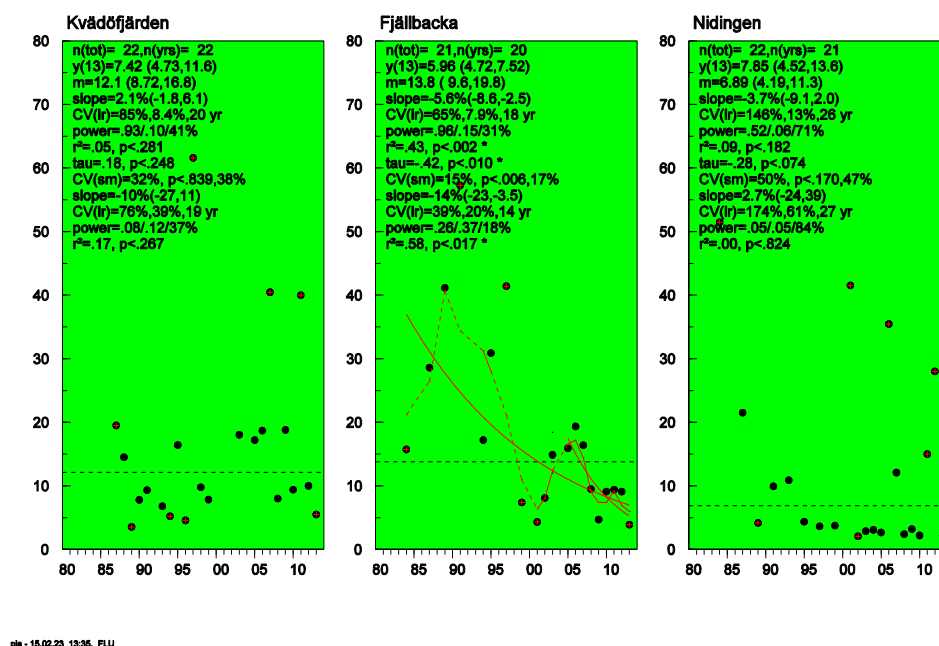## Chrysene, ng/g dry w., blue mussel



**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).

## Dibenzo(a,h)anthracene, ng/g dry w., blue mussel

### Kvädöfjärden

n(tot)= 22,n(yrs)= 22
y(13)=.595 (.434,.816)
m=.884 (.706,1.11)
slope=-1.4%(-4.0,1.3)
CV(lr)=54%,5.7%,16 yr
power=1.0/.21/25%
r²=.05, p<.283
tau=-.22, p<.150
CV(sm)=459%, p<.930,25%
slope=-.88%(-18,20)
CV(lr)=70%,36%,18 yr
power=.09/.13/33%
r²=.00, p<.880

### Fjällbacka

n(tot)= 22,n(yrs)= 21
y(13)=.338 (.240,.474)
m=.292 (.223,.381)
slope=-.27%(-3.5,3.0)
CV(lr)=66%,7.4%,18 yr
power=.98/.15/32%
r²=.00, p<.839
tau=.11, p<.500
CV(sm)=48%, p<.400,27%
slope=3.6%(-2.6,10)
CV(lr)=25%,10%,11 yr
power=.78/.78/11%
r²=.18, p<.223

### Nidingen

n(tot)= 22,n(yrs)= 21
y(13)=.324 (.216,.486)
m=.260 (.189,.356)
slope=-.15%(-3.9,3.8)
CV(lr)=81%,8.8%,20 yr
power=.90/.11/39%
r²=.00, p<.895
tau=.088, p<.578
CV(sm)=52%, p<.435,33%
slope=9.7%(-4.1,25)
CV(lr)=57%,24%,17 yr
power=.19/.19/27%
r²=.24, p<.148

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**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).

## Fluorene, ng/g dry w., blue mussel

### Kvädöfjärden

n(tot)= 22,n(yrs)= 22
y(13)=1.52 (.990,2.33)
m=1.59 (1.11,2.28)
slope=3.1%(-1.1,7.5)
CV(lr)=93%,9.1%,21 yr
power=.88/.09/45%
r²=.10, p<.141
tau=.15, p<.324
CV(sm)=165%, p<.343,36%
slope=-9.8%(-30,17)
CV(lr)=102%,51%,22 yr
power=.06/.08/50%
r²=.11, p<.378

### Fjällbacka

n(tot)= 22,n(yrs)= 21
y(13)=1.09 (.798,1.50)
m=1.84 (1.45,2.35)
slope=-2.2%(-4.8,.61)
CV(lr)=55%,6.2%,16 yr
power=1.0/.20/26%
r²=.12, p<.115
tau=-.22, p<.155
CV(sm)=90%, p<.746,25%
slope=-6.2%(-16,4.8)
CV(lr)=46%,19%,15 yr
power=.28/.28/21%
r²=.18, p<.218

### Nidingen

n(tot)= 22,n(yrs)= 21
y(13)=2.43 (1.37,4.28)
m=1.65 (1.02,2.67)
slope=.26%(-5.5,6.3)
CV(lr)=150%,14%,26 yr
power=.50/.05/73%
r²=.00, p<.890
tau=.067, p<.672
CV(sm)=198%, p<.193,49%
slope=12%(-16,49)
CV(lr)=159%,57%,26 yr
power=.05/.05/77%
r²=.09, p<.387

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**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).

## Fluoranthene, ng/g dry w., blue mussel



**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.
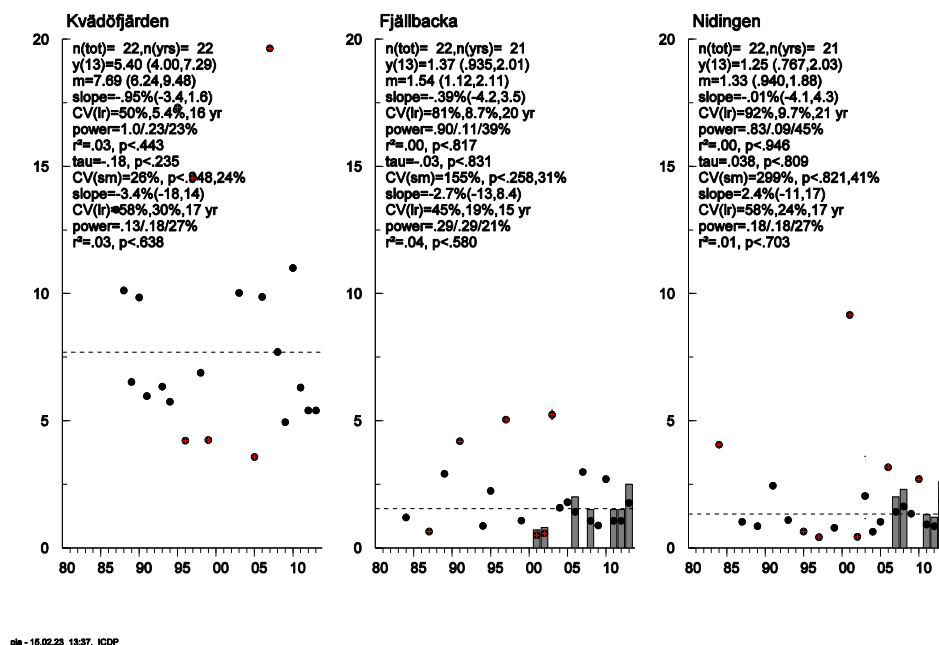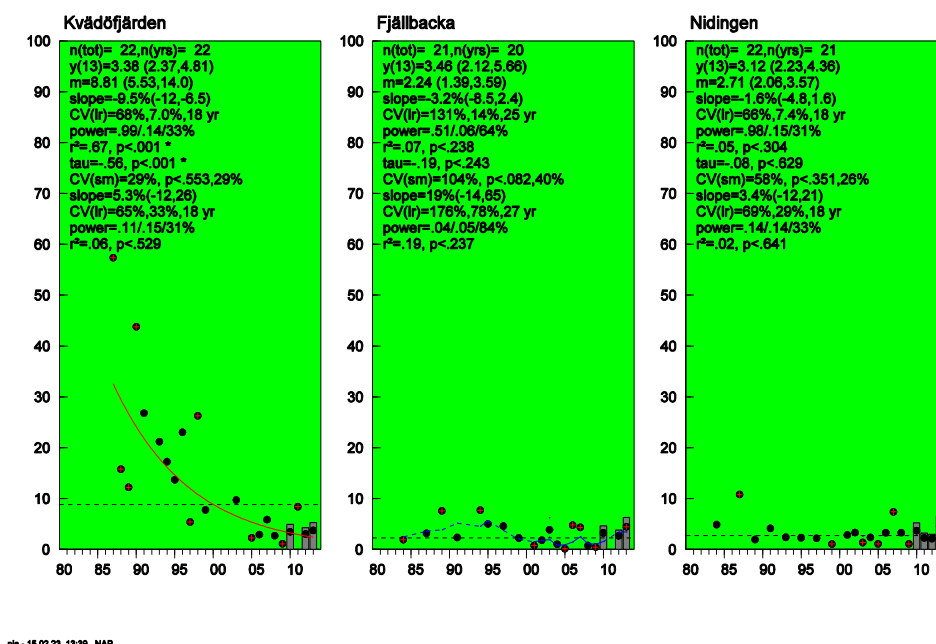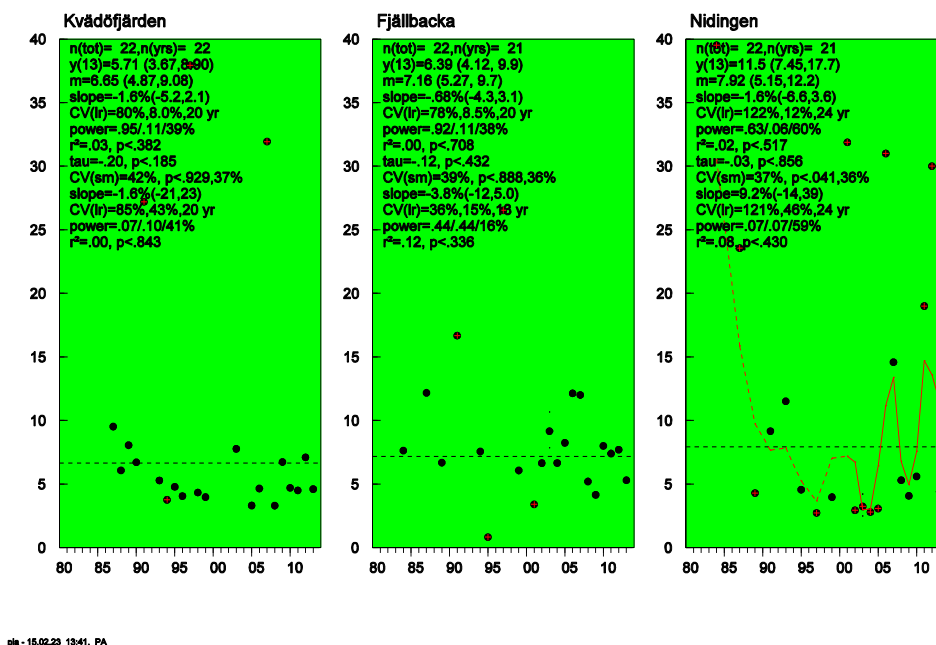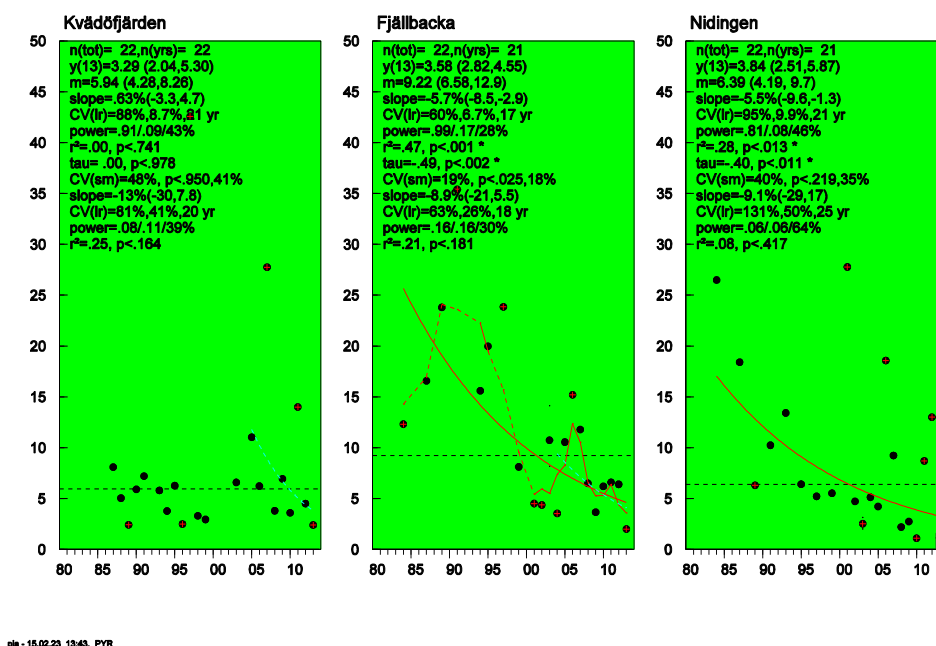
## Indeno(1,2,3-cd)pyrene, ng/g dry w., blue mussel



**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).

## Naphtalene, ng/g dry w., blue mussel



**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.

## Phenantrene, ng/g dry w., blue mussel



**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.

### Pyrene, ng/g dry w., blue mussel



**Kvädöfjärden**

```
n(tot)= 22,n(yrs)= 22
y(13)=3.29 (2.04,5.30)
m=5.94 (4.28,8.26)
slope=.63%(-3.3,4.7)
CV(lr)=88%,8.7%,ä1 yr
power=.91/.09/43%
r²=.00, p<.741
tau= .00, p<.978
CV(sm)=48%, p<.950,41%
slope=-13%(-30,7.8)
CV(lr)=81%,41%,20 yr
power=.08/.11/39%
r²=.25, p<.164
```

**Fjällbacka**

```
n(tot)= 22,n(yrs)= 21
y(13)=3.58 (2.82,4.55)
m=9.22 (6.58,12.9)
slope=-5.7%(-8.5,-2.9)
CV(lr)=60%,6.7%,17 yr
power=.99/.17/28%
r²=.47, p<.001 *
tau=-.49, p<.002 *
CV(sm)=19%, p<.025,18%
slope=-8.9%(-21,5.5)
CV(lr)=63%,26%,18 yr
power=.16/.16/30%
r²=.21, p<.181
```

**Nidingen**

```
n(tot)= 22,n(yrs)= 21
y(13)=3.84 (2.51,5.87)
m=6.39 (4.19, 9.7)
slope=-5.5%(-9.6,-1.3)
CV(lr)=95%,9.9%,21 yr
power=.81/.08/46%
r²=.28, p<.013 *
tau=-.40, p<.011 *
CV(sm)=40%, p<.219,35%
slope=-9.1%(-29,17)
CV(lr)=131%,50%,25 yr
power=.06/.06/64%
r²=.08, p<.417
```

pia - 15.02.23  13:43,  PYR

**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 ∑PAH 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 ∑PAH, chrysene, fluoranthene, pyrene at Fjällbacka, and naphthalene at Kvädöfjärden and pyrene at Nidingen.

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 28.1.** 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 | Ntot | Yrs | Year | Trend% 95% c.i. | P | YRQ | LDT | Last year |
|---|---|---|---|---|---|---|---|---|---|
| | **Blue mussel** | | | | | | | | |
| sPAH | Nidingen | 22 | 21 | 84-13 | -3.2(-7.3,1.0) | 0.1212 | 21 | 46 | 39.9 (23.3,68.3) |
| sPAH | Nidingen | | 10 | 04-13 | -2.2(-20,20) | 0.7968 | 21 | 46 | |
| sPAH | Fjällbacka | 22 | 21 | 84-13 | -4.3(-7.1,-1.4) | 0.006-- | 17 | 28 | 34.1 (24.1,48.2) |
| sPAH | Fjällbacka | | 10 | 04-13 | -5.8(-15,4.4) | 0.2168 | 14 | 19 | |
| sPAH | Kvädöfjärden | 22 | 22 | 87-13 | -1.4(-3.7,1.0) | 0.2395 | 15 | 22 | 73.6 (54.5,99.4) |
| sPAH | Kvädöfjärden | | 9 | 05-13 | -6.6(-19,7.1) | 0.2765 | 15 | 22 | |
| Anthracene | Nidingen | 22 | 21 | 84-13 | -3.7(-8.2,.97) | 0.1082 | 23 | 53 | .160 (.104,.246) |
| Anthracene | Nidingen | | 10 | 04-13 | 0.68(-20,26) | 0.9037 | 23 | 54 | |
| Anthracene | Fjällbacka | 22 | 21 | 84-13 | -2.3(-4.7,.16) | 0.0621 | 15 | 23 | .283 (.241,.332) |
| Anthracene | Fjällbacka | | 10 | 04-13 | -7.4(-14,.25) | 0.0544 | 12 | 14 | |
| Anthracene | Kvädöfjärden | 22 | 22 | 87-13 | 1.1(-3.8,6.3) | 0.6569 | 24 | 59 | .520 (.295,.914) |
| Anthracene | Kvädöfjärden | | 9 | 05-13 | 0.86(-24,34) | 0.9021 | 23 | 57 | |
| Benzo(a)anthracene | Nidingen | 20 | 19 | 84-13 | -2.1(-6.0,1.9) | 0.281 | 19 | 36 | 1.43 (.988,2.06) |
| Benzo(a)anthracene | Nidingen | | 10 | 04-13 | -7.8(-22,9.4) | 0.3074 | 19 | 37 | |
| Benzo(a)anthracene | Fjällbacka | 22 | 21 | 84-13 | -2.7(-5.8,.51) | 0.0899 | 18 | 31 | 2.05 (1.56,2.69) |
| Benzo(a)anthracene | Fjällbacka | | 10 | 04-13 | -5.6(-17,7.0) | 0.3221 | 16 | 24 | |
| Benzo(a)anthracene | Kvädöfjärden | 19 | 19 | 87-13 | 4(-.13,8.4) | 0.0546 | 20 | 39 | 5.93 (4.20,8.39) |
| Benzo(a)anthracene | Kvädöfjärden | | 7 | 05-13 | -12(-29,10) | 0.2108 | 18 | 31 | |
| Benzo(a)pyrene | Nidingen | 22 | 21 | 84-13 | -2.8(-6.9,1.6) | 0.1911 | 21 | 46 | .580 (.364,.925) |
| Benzo(a)pyrene | Nidingen | | 10 | 04-13 | 0.95(-10,14) | 0.835 | 15 | 23 | |
| Benzo(a)pyrene | Fjällbacka | 22 | 21 | 84-13 | -2.6(-6.9,2.0) | 0.2517 | 22 | 50 | .815 (.540,1.23) |
| Benzo(a)pyrene | Fjällbacka | | 10 | 04-13 | -4(-13,6.2) | 0.3807 | 14 | 19 | |
| Benzo(a)pyrene | Kvädöfjärden | 22 | 22 | 87-13 | -0.98(-4.1,2.2) | 0.5357 | 18 | 32 | 2.30 (1.64,3.22) |
| Benzo(a)pyrene | Kvädöfjärden | | 9 | 05-13 | -7.8(-24,12) | 0.356 | 19 | 34 | |
| Benzo(b)fluoranthene | Nidingen | 22 | 21 | 84-13 | -2.2(-6.3,2.1) | 0.2888 | 21 | 45 | 2.23 (1.42,3.48) |
| Benzo(b)fluoranthene | Nidingen | | 10 | 04-13 | -4.1(-17,11) | 0.5345 | 18 | 30 | |
| Benzo(b)fluoranthene | Fjällbacka | 22 | 21 | 84-13 | -3.3(-7.2,.74) | 0.0989 | 21 | 42 | 3.91 (2.83,5.40) |
| Benzo(b)fluoranthene | Fjällbacka | | 10 | 04-13 | -2.4(-12,7.8) | 0.5887 | 14 | 19 | |
| Benzo(b)fluoranthene | Kvädöfjärden | 22 | 22 | 87-13 | -0.39(-3.1,2.4) | 0.7611 | 16 | 26 | 7.00 (4.99, 9.8) |
| Benzo(b)fluoranthene | Kvädöfjärden | | 9 | 05-13 | -6.1(-17,6.3) | 0.2667 | 14 | 19 | |
| Benzo(g,h,i)perylene | Nidingen | 22 | 21 | 84-13 | -2.4(-6.3,1.6) | 0.2193 | 20 | 42 | 1.01 (.642,1.57) |
| Benzo(g,h,i)perylene | Nidingen | | 10 | 04-13 | -0.26(-15,17) | 0.9221 | 19 | 34 | |
| Benzo(g,h,i)perylene | Fjällbacka | 22 | 21 | 84-13 | -0.39(-3.7,3.0) | 0.793 | 18 | 32 | 2.35 (1.77,3.11) |
| Benzo(g,h,i)perylene | Fjällbacka | | 10 | 04-13 | -3.9(-10,2.8) | 0.2124 | 11 | 12 | |
| Benzo(g,h,i)perylene | Kvädöfjärden | 22 | 22 | 87-13 | -1.8(-4.1,.49) | 0.1103 | 15 | 21 | 6.52 (4.88,8.71) |
| Benzo(g,h,i)perylene | Kvädöfjärden | | 9 | 05-13 | -3.5(-16,10) | 0.557 | 15 | 22 | |
| Benzo(k)fluoranthene | Nidingen | 22 | 21 | 84-13 | -2.2(-6.3,2.1) | 0.2895 | 21 | 45 | .849 (.540,1.33) |
| Benzo(k)fluoranthene | Nidingen | | 10 | 04-13 | -3.8(-17,11) | 0.5629 | 17 | 29 | |

| Benzo(k)fluoranthene | Fjällbacka | 22 | 21 | 84-13 | -2.7(-6.8,1.5) | 0.1876 | 21 | 45 | 1.34 (.930,1.94) |
|---|---|---|---|---|---|---|---|---|---|
| Benzo(k)fluoranthene | Fjällbacka | | 10 | 04-13 | -2.7(-11,6.7) | 0.5142 | 13 | 17 | |
| Benzo(k)fluoranthene | Kvädöfjärden | 22 | 22 | 87-13 | -2(-4.5,.52) | 0.1081 | 16 | 24 | 2.80 (2.05,3.82) |
| Benzo(k)fluoranthene | Kvädöfjärden | | 9 | 05-13 | -6.6(-18,6.7) | 0.2641 | 15 | 21 | |
| Chrysene | Nidingen | 22 | 21 | 84-13 | -4.2(-8.1,-.19) | 0.0395- | 21 | 43 | 3.35 (2.19,5.12) |
| Chrysene | Nidingen | | 10 | 04-13 | -2.8(-18,15) | 0.7052 | 19 | 36 | |
| Chrysene | Fjällbacka | 22 | 21 | 84-13 | -5(-8.8,-1.0) | 0.0165- | 21 | 43 | 4.07 (2.86,5.80) |
| Chrysene | Fjällbacka | | 10 | 04-13 | -3.7(-14,7.6) | 0.4576 | 15 | 21 | |
| Chrysene | Kvädöfjärden | 22 | 22 | 87-13 | -1.9(-4.4,.64) | 0.1289 | 16 | 24 | 4.79 (3.72,6.17) |
| Chrysene | Kvädöfjärden | | 9 | 05-13 | -5(-16,7.0) | 0.3453 | 14 | 18 | |
| Dibenzo(a,h)anthracene | Nidingen | 22 | 21 | 84-13 | -0.15(-3.9,3.8) | 0.8952 | 20 | 39 | .324 (.216,.486) |
| Dibenzo(a,h)anthracene | Nidingen | | 10 | 04-13 | 9.7(-4.1,25) | 0.148 | 17 | 27 | |
| Dibenzo(a,h)anthracene | Fjällbacka | 22 | 21 | 84-13 | -0.27(-3.5,3.0) | 0.8385 | 18 | 32 | .338 (.240,.474) |
| Dibenzo(a,h)anthracene | Fjällbacka | | 10 | 04-13 | 3.6(-2.6,10) | 0.2229 | 11 | 11 | |
| Dibenzo(a,h)anthracene | Kvädöfjärden | 22 | 22 | 87-13 | -1.4(-4.0,1.3) | 0.2825 | 16 | 25 | .595 (.434,.816) |
| Dibenzo(a,h)anthracene | Kvädöfjärden | | 9 | 05-13 | -0.88(-18,20) | 0.8804 | 18 | 33 | |
| Fluorene | Nidingen | 22 | 21 | 84-13 | 0.26(-5.5,6.3) | 0.8897 | 26 | 73 | 2.43 (1.37,4.28) |
| Fluorene | Nidingen | | 10 | 04-13 | 12(-16,49) | 0.3871 | 26 | 77 | |
| Fluorene | Fjällbacka | 22 | 21 | 84-13 | -2.2(-4.8,.61) | 0.115 | 16 | 26 | 1.09 (.798,1.50) |
| Fluorene | Fjällbacka | | 10 | 04-13 | -6.2(-16,4.8) | 0.2184 | 15 | 21 | |
| Fluorene | Kvädöfjärden | 22 | 22 | 87-13 | 3.1(-1.1,7.5) | 0.141 | 21 | 45 | 1.52 (.990,2.33) |
| Fluorene | Kvädöfjärden | | 9 | 05-13 | -9.8(-30,17) | 0.3783 | 22 | 50 | |
| Fluoranthene | Nidingen | 22 | 21 | 84-13 | -3.7(-9.1,2.0) | 0.1824 | 26 | 71 | 7.85 (4.52,13.6) |
| Fluoranthene | Nidingen | | 10 | 04-13 | 2.7(-24,39) | 0.8243 | 27 | 84 | |
| Fluoranthene | Fjällbacka | 21 | 20 | 84-13 | -5.6(-8.6,-2.5) | 0.0016-- | 18 | 31 | 5.96 (4.72,7.52) |
| Fluoranthene | Fjällbacka | | 9 | 05-13 | -14(-23,-3.5) | 0.0173 - | 14 | 18 | |
| Fluoranthene | Kvädöfjärden | 22 | 22 | 87-13 | 2.1(-1.8,6.1) | 0.2808 | 20 | 41 | 7.42 (4.73,11.6) |
| Fluoranthene | Kvädöfjärden | | 9 | 05-13 | -10(-27,11) | 0.2672 | 19 | 37 | |
| Indeno(1,2,3-cd)pyrene | Nidingen | 22 | 21 | 84-13 | -0.01(-4.1,4.3) | 0.9462 | 21 | 45 | 1.25 (.767,2.03) |
| Indeno(1,2,3-cd)pyrene | Nidingen | | 10 | 04-13 | 2.4(-11,17) | 0.7026 | 17 | 27 | |
| Indeno(1,2,3-cd)pyrene | Fjällbacka | 22 | 21 | 84-13 | -0.39(-4.2,3.5) | 0.8166 | 20 | 39 | 1.37 (.935,2.01) |
| Indeno(1,2,3-cd)pyrene | Fjällbacka | | 10 | 04-13 | -2.7(-13,8.4) | 0.5796 | 15 | 21 | |
| Indeno(1,2,3-cd)pyrene | Kvädöfjärden | 22 | 22 | 87-13 | -0.95(-3.4,1.6) | 0.4431 | 16 | 23 | 5.40 (4.00,7.29) |
| Indeno(1,2,3-cd)pyrene | Kvädöfjärden | | 9 | 05-13 | -3.4(-18,14) | 0.6379 | 17 | 27 | |
| Naphtalene | Nidingen | 22 | 21 | 84-13 | -1.6(-4.8,1.6) | 0.304 | 18 | 31 | 3.12 (2.23,4.36) |
| Naphtalene | Nidingen | | 10 | 04-13 | 3.4(-12,21) | 0.6406 | 18 | 33 | |
| Naphtalene | Fjällbacka | 21 | 20 | 84-13 | -3.2(-8.5,2.4) | 0.2381 | 25 | 64 | 3.46 (2.12,5.66) |
| Naphtalene | Fjällbacka | | 9 | 04-13 | 19(-14,65) | 0.2372 | 27 | 84 | |
| Naphtalene | Kvädöfjärden | 22 | 22 | 87-13 | -9.5(-12,-6.5) | 0.0000--- | 18 | 33 | 3.38 (2.37,4.81) |
| Naphtalene | Kvädöfjärden | | 9 | 05-13 | 5.3(-12,26) | 0.529 | 18 | 31 | |
| Phenantrene | Nidingen | 22 | 21 | 84-13 | -1.6(-6.6,3.6) | 0.5169 | 24 | 60 | 11.5 (7.45,17.7) |
| Phenantrene | Nidingen | | 10 | 04-13 | 9.2(-14,39) | 0.43 | 24 | 59 | |
| Phenantrene | Fjällbacka | 22 | 21 | 84-13 | -0.68(-4.3,3.1) | 0.7084 | 20 | 38 | 6.39 (4.12, 9.9) |
| Phenantrene | Fjällbacka | | 10 | 04-13 | -3.8(-12,5.0) | 0.3359 | 13 | 16 | |
| Phenantrene | Kvädöfjärden | 22 | 22 | 87-13 | -1.6(-5.2,2.1) | 0.3815 | 20 | 39 | 5.71 (3.67,8.90) |
| Phenantrene | Kvädöfjärden | | 9 | 05-13 | -1.6(-21,23) | 0.8433 | 20 | 41 | |
| Pyrene | Nidingen | 22 | 21 | 84-13 | -5.5(-9.6,-1.3) | 0.0125 - | 21 | 46 | 3.84 (2.51,5.87) |
| Pyrene | Nidingen | | 10 | 04-13 | -9.1(-29,17) | 0.4174 | 25 | 64 | |

| Pyrene | Fjällbacka | 22 | 21 | 84-13 | -5.7(-8.5,-2.9) | 0.0006--- | 17 | 28 | 3.58 (2.82,4.55) |
|--------|------------|----|----|-------|-----------------|-----------|----|----|------------------|
| Pyrene | Fjällbacka |    | 10 | 04-13 | -8.9(-21,5.5)   | 0.1805    | 18 | 30 |                  |
| Pyrene | Kvädöfjärden | 22 | 22 | 87-13 | 0.63(-3.3,4.7) | 0.741    | 21 | 43 | 3.29 (2.04,5.30) |
| Pyrene | Kvädöfjärden |    | 9  | 05-13 | -13(-30,7.8)    | 0.1644    | 20 | 39 |                  |

# 29  PFASs, Perfluoroalkyl substances

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 the year 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). PFOA and PFNA  are intentionally produced and because of this 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 subsequent waterborne transport to remote locations. Hence, sewage treatment plant effluent from industry or larger cities could represent hot-spots. In contrast, longer-chain perfluoroalkyl carboxylic acids (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). The role of PFOS derivatives for the distribution and accumulation of PFOS in the environment is currently under investigation (Martin et al., 2010). FOSA is an intermediate product in the degradation of many PFOS precursors to PFOS, and is often analysed together with PFOS in environmental samples.

### 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 (Nordén et al., 2013). 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 B.J. et al., 2007, Fei et al., 2007), ponderal index, head circumference (Apelberg B.J. et al., 2007), and birth length (Fei et al., 2008b). 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., 2008a). 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 U. 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 , 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 (SC, 2008). Additionally, the use of PFOS and its derivatives is restricted in the European Union (OJEC No. L372 27.12.2006, 2006), 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 level used for PFOS in perch muscle is 9.1 µg/kg wet weight. For this report, we have used a conversion factor between liver and muscle, because PFOS is analysed in liver. This conversion factor is based on a study by Faxneld and co-workers (Faxneld et al., 2014), and the new derived target level for PFOS in herring and perch liver is 155 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

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.
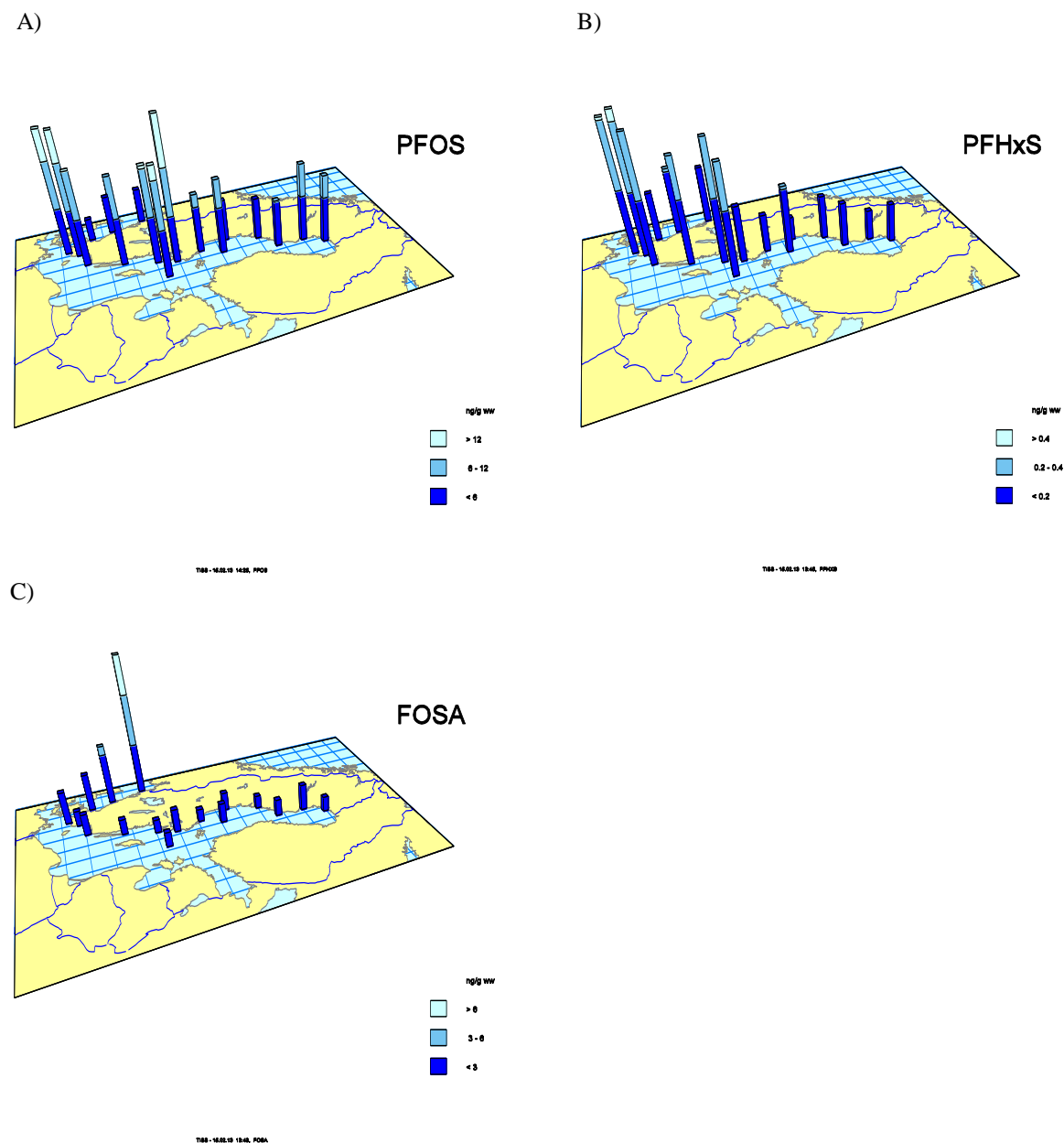
A)                                                                          B)



C)



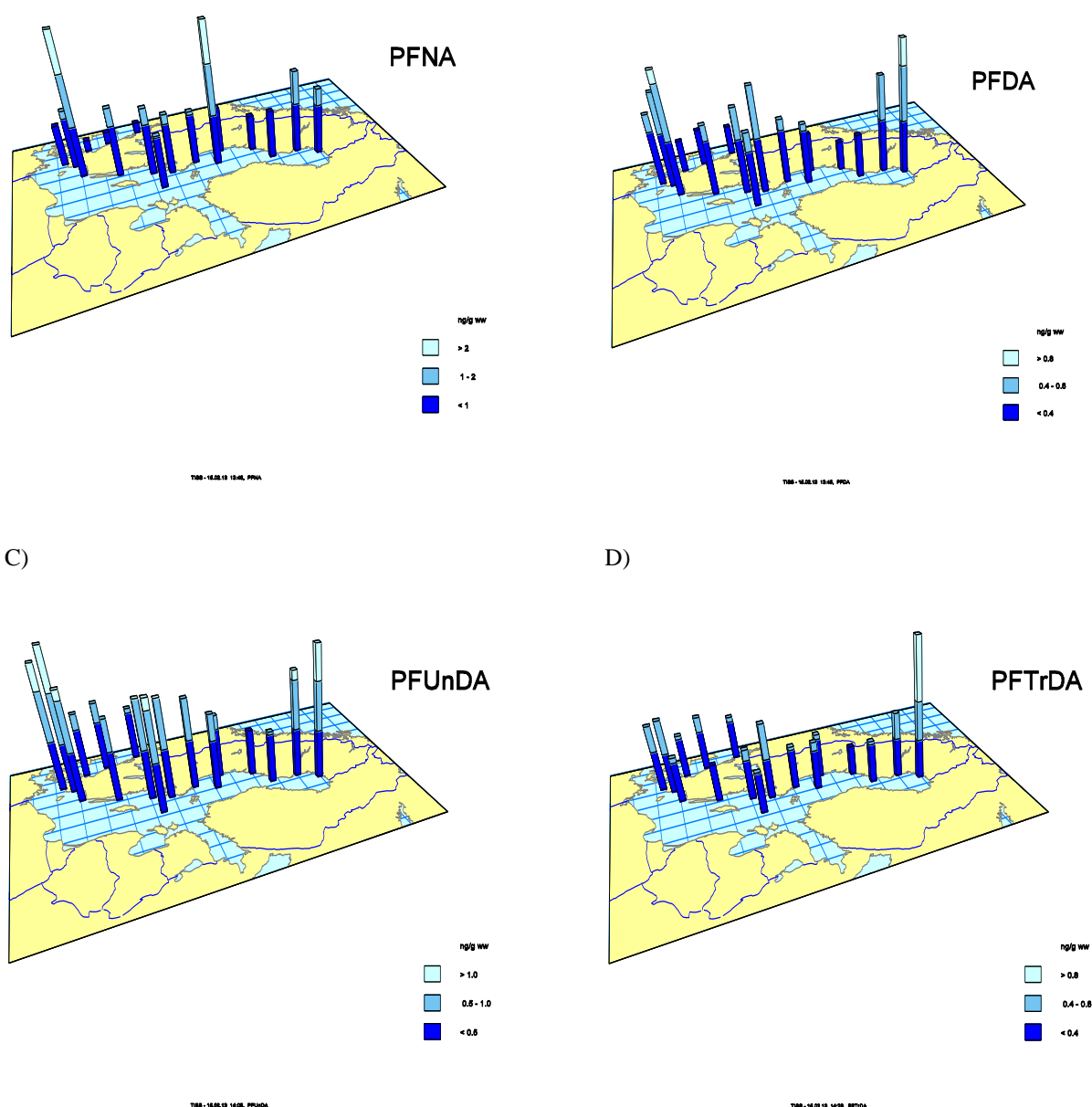**Figure 29.1** Spatial variations in concentrations of sulfonates and its precursors (ng/g wet weight) of A) PFHxS, B) PFOS and C) FOSA in herring liver.

A)                                                                          B)

**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 Västra Hanöbukten and Abbekås in the Southern Baltic Proper. Also, PFOS had higher concentrations in the Baltic Proper, where the highest concentration was found at Lagnö in the 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 and at Utlängan. 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 Southern Baltic proper (Fig. 29.2b) and for PFUnDA the highest concentration was seen in the Western Hanöbukten in the Southern Baltic proper, followed by Harufjärden (Fig. 29.2c). PFTrDA showed similar concentrations along the whole Swedish coast, except for Harufjärden in the Bothnian Bay, which had two to three times as high concentration compared to all the other sites.

## 29.3.2 Temporal Variation

### 29.3.2.1 Perfluorinated sulfonates and precursors

PFOS concentrations in herring liver show inconsistent trends at all the sites, increasing at three sites (Ängskärsklubb, Landsort and Utlängan), decreasing in one (Fladen) and no trend at two sites (Fig. 29.3–4). FOSA, on the other hand, which is a precursor to PFOS, shows a significant decreasing trend at Harufjärden, Ängskärsklubb and Fladen (Fig. 29.7–8, table 29.1). There are also significant decreasing concentrations for the last ten years of the monitoring of FOSA in herring from Utlängan and Landsort (Fig. 29.7–8). The concentration of PFHxS show increasing trends at Landsort and Utlängan over the examined time series (Fig. 29.5–6). The non-linear trends of PFOS and PFHxS at Harufjärden is very similar. PFBS and PFDS had only values under LOQ and are therefore not presented as time series (table 29.1).
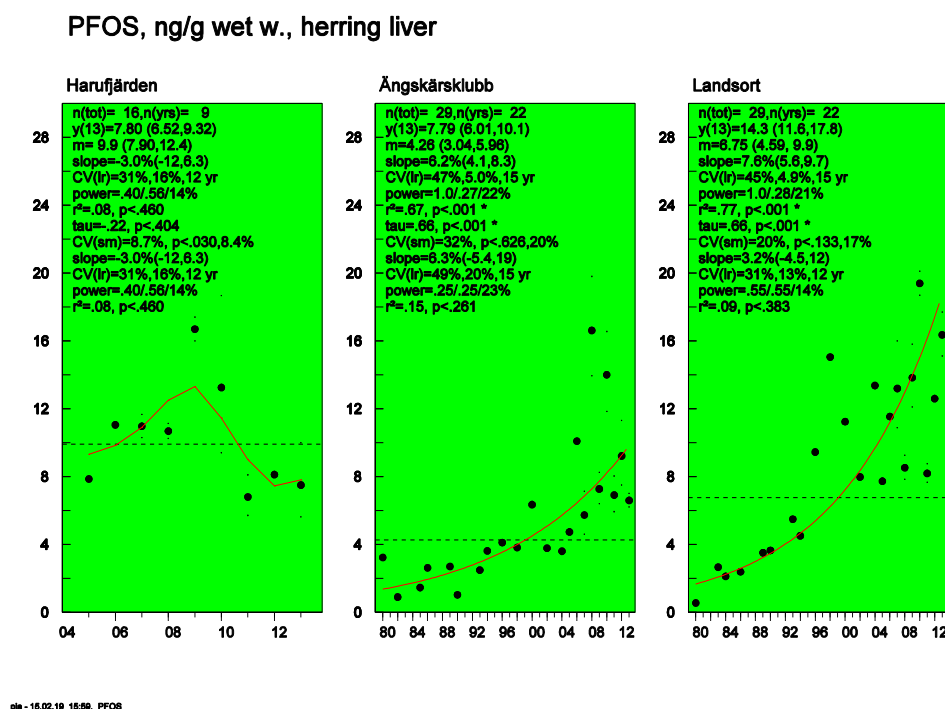


Figure 29.3. Temporal trend of PFOS in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The green area denotes the levels below the suggested target value for PFOS in fish.
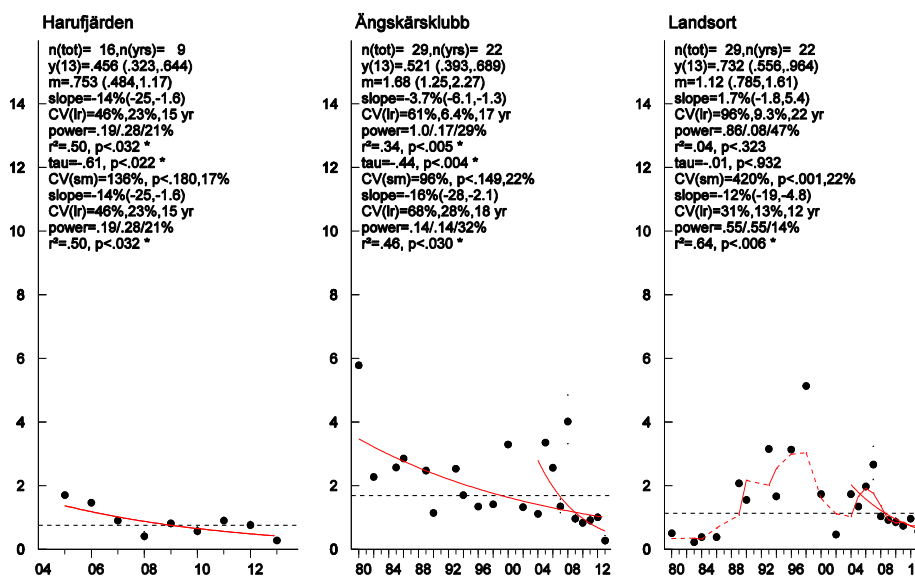
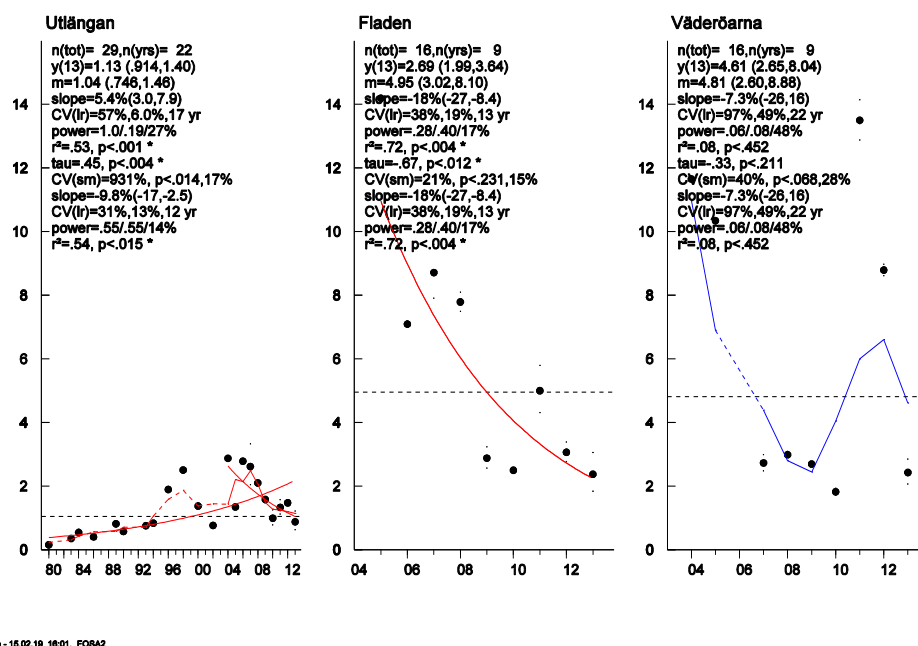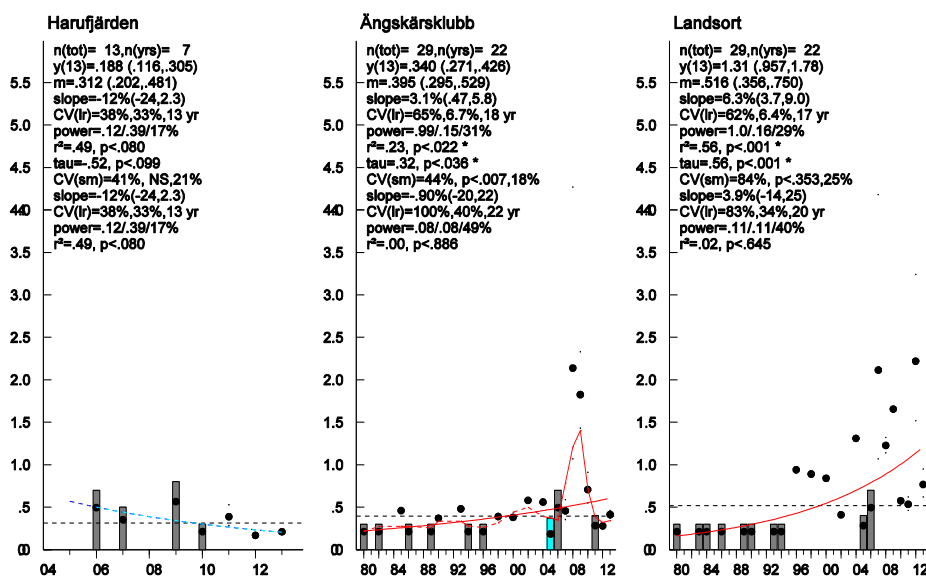## PFOS, ng/g wet w., herring liver
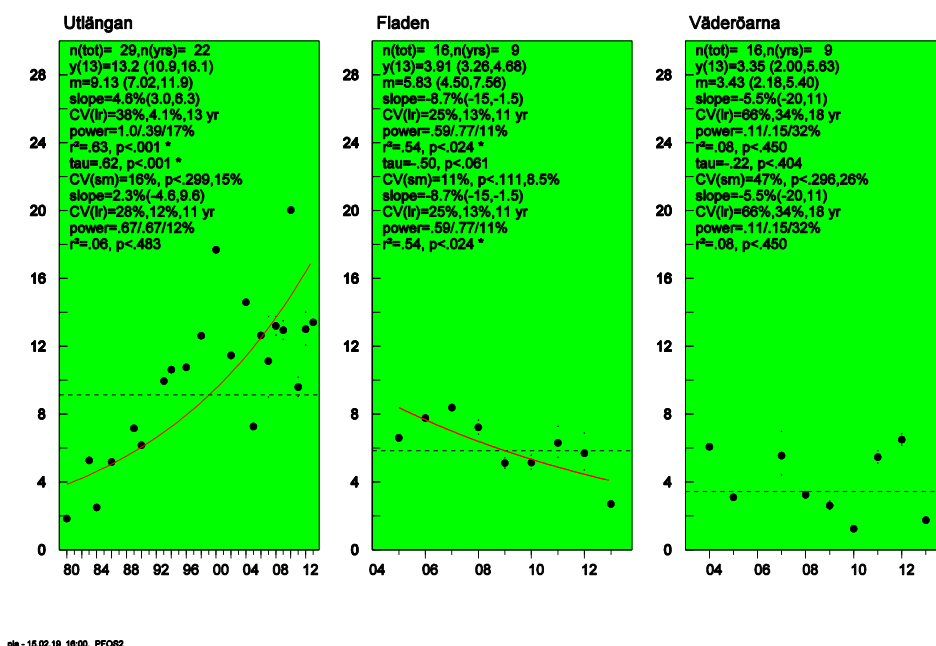


**Figure 29.4.** Temporal trend of PFOS in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005). The green area denotes the levels below the suggested target value for PFOS in fish.

## PFHxS, ng/g wet w., herring liver
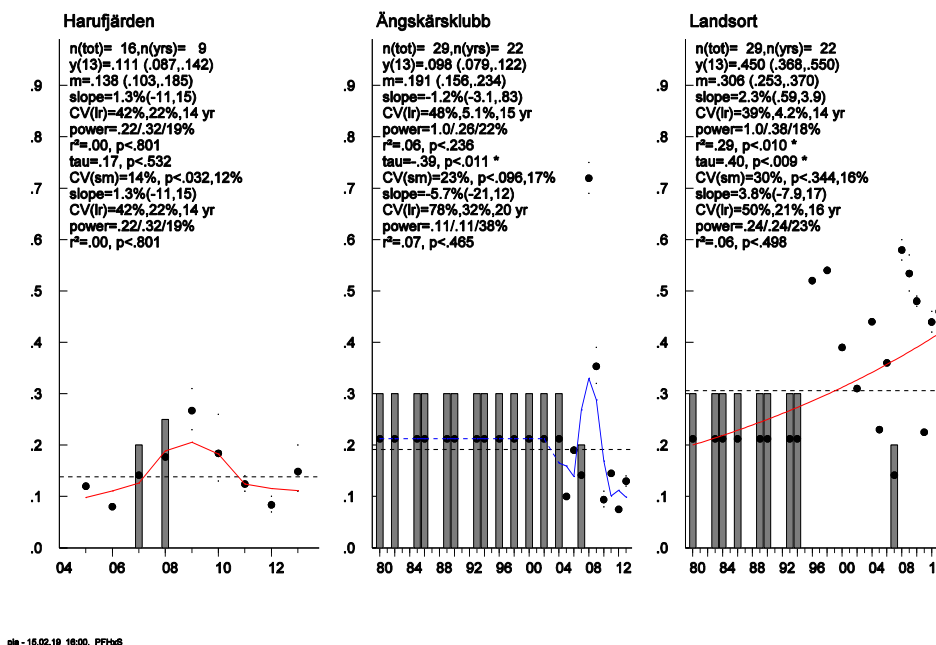


**Fig. 29.5.** Temporal trend of PFHxS in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bars represent years where all values were below LOQ.

## PFHxS, ng/g wet w., herring liver

**Utlängan**

n(tot)= 29,n(yrs)= 22
y(13)=.421 (.337,.527)
m=.321 (.263,.390)
slope=2.4%(.68,4.1)
CV(lr)=39%,4.3%,14 yr
power=1.0/.37/18%
r²=.30, p<.008 *
tau=.44, p<.004 *
CV(sm)=35%, p<.679,17%
slope=4.7%(-8.9,20)
CV(lr)=60%,25%,17 yr
power=.17/.17/28%
r²=.06, p<.472

**Fladen**

n(tot)= 16,n(yrs)= 9
y(13)=.182 (.146,.225)
m=.207 (.169,.253)
slope=1.4%(-6.9,10)
CV(lr)=28%,15%,11 yr
power=.47/.64/13%
r²=.02, p<.708
tau=.028, p<.916
CV(sm)=15%, p<.149,10%
slope=1.4%(-6.9,10)
CV(lr)=28%,15%,11 yr
power=.47/.64/13%
r²=.02, p<.708

**Väderöarna**

n(tot)= 16,n(yrs)= 9
y(13)=.139 (.097,.201)
m=.126 (.092,.173)
slope=3.6%(-7.8,16)
CV(lr)=45%,23%,15 yr
power=.20/.29/21%
r²=.06, p<.504
tau=.11, p<.677
CV(sm)=20%, p<.293,18%
slope=3.6%(-7.8,16)
CV(lr)=45%,23%,15 yr
power=.20/.29/21%
r²=.06, p<.504

**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.
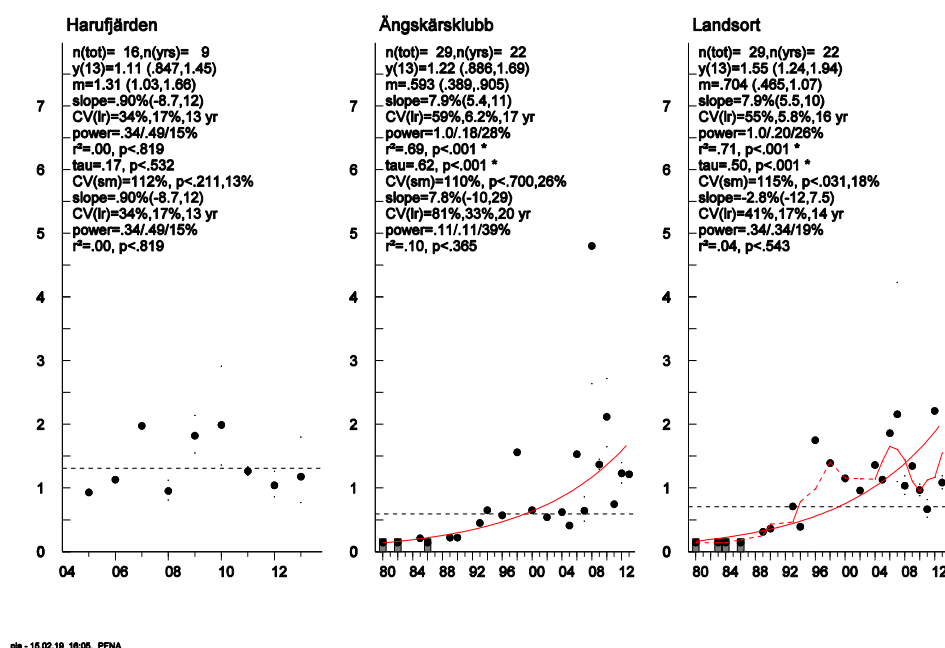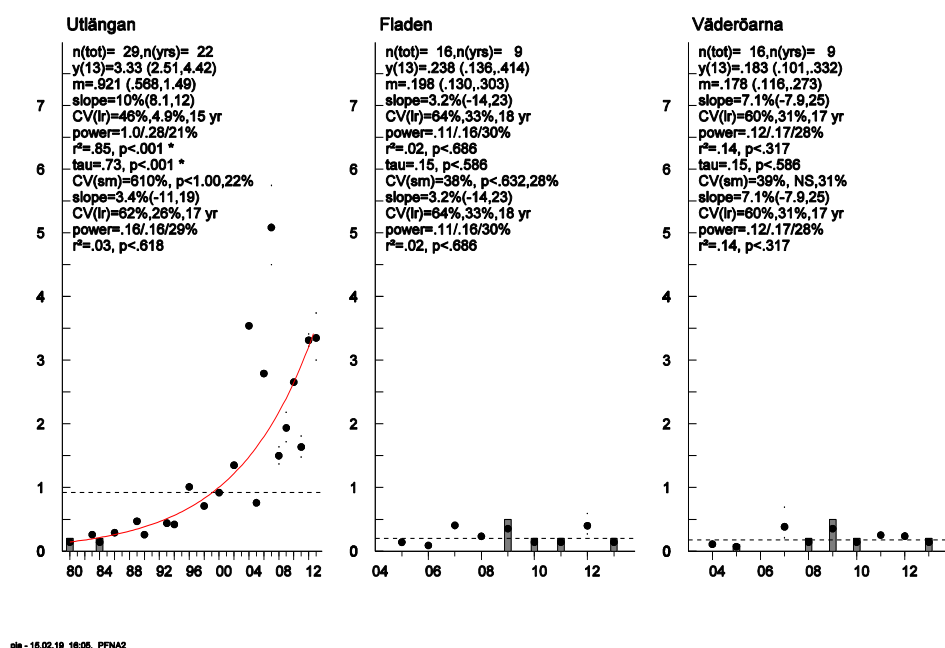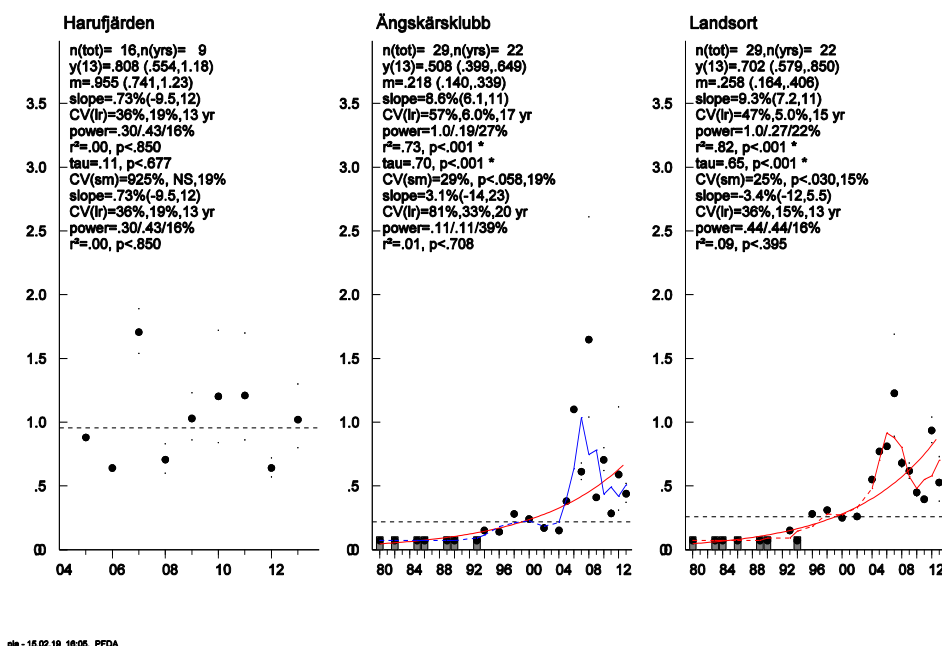
## FOSA, ng/g wet w., herring liver

**Harufjärden**

n(tot)= 16,n(yrs)= 9
y(13)=.456 (.323,.644)
m=.753 (.484,1.17)
slope=-14%(-25,-1.6)
CV(lr)=46%,23%,15 yr
power=.19/.28/21%
r²=.50, p<.032 *
tau=-.61, p<.022 *
CV(sm)=136%, p<.180,17%
slope=-14%(-25,-1.6)
CV(lr)=46%,23%,15 yr
power=.19/.28/21%
r²=.50, p<.032 *

**Ängskärsklubb**

n(tot)= 29,n(yrs)= 22
y(13)=.521 (.393,.689)
m=1.68 (1.25,2.27)
slope=-3.7%(-6.1,-1.3)
CV(lr)=61%,6.4%,17 yr
power=1.0/.17/29%
r²=.34, p<.005 *
tau=-.44, p<.004 *
CV(sm)=96%, p<.149,22%
slope=-16%(-28,-2.1)
CV(lr)=68%,28%,18 yr
power=.14/.14/32%
r²=.46, p<.030 *

**Landsort**

n(tot)= 29,n(yrs)= 22
y(13)=.732 (.556,.964)
m=1.12 (.785,1.61)
slope=1.7%(-1.8,5.4)
CV(lr)=96%,9.3%,22 yr
power=.86/.08/47%
r²=.04, p<.323
tau=-.01, p<.932
CV(sm)=420%, p<.001,22%
slope=-12%(-19,-4.8)
CV(lr)=31%,13%,12 yr
power=.55/.55/14%
r²=.64, p<.006 *

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**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.
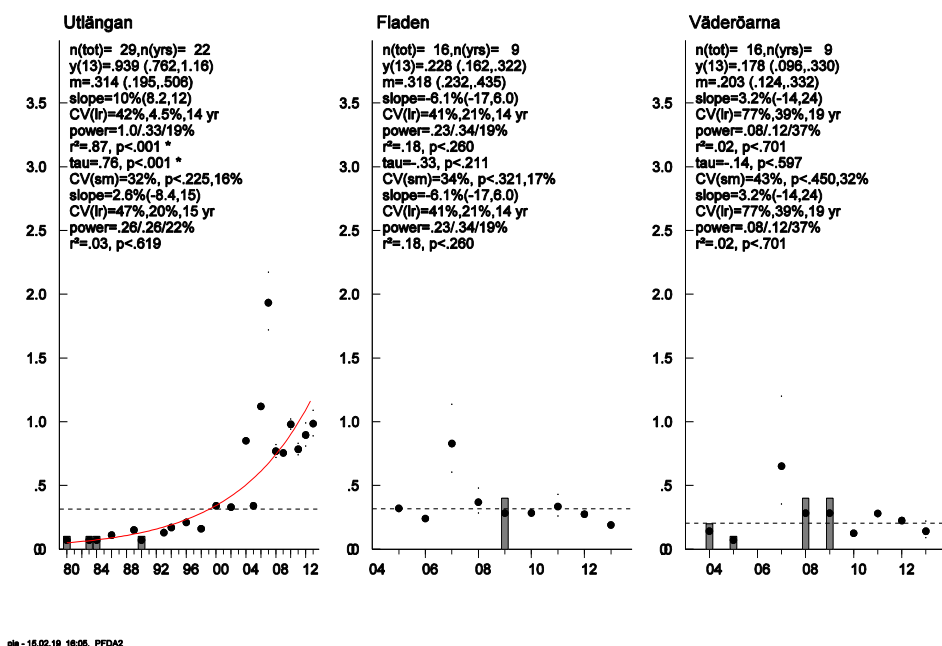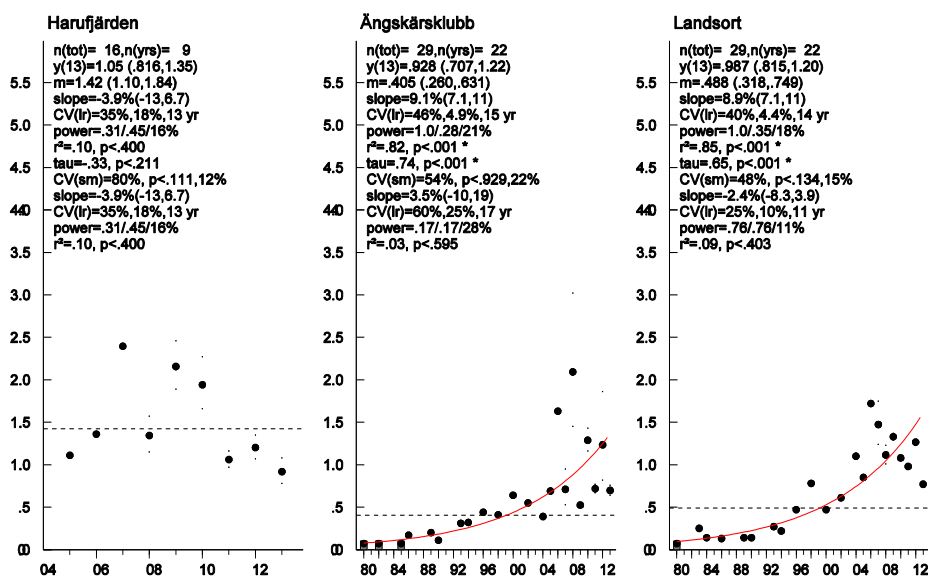
232

**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 Perfluorinated carboxylates

The time series of all investigated carboxylates show the same trend; increasing trends at Ängskärsklubb, Landsort and Utlängan and no trend in the Harufjärden, Fladen and Väderöarna time series. The increase per year in perfluorinated carboxylate concentrations are: PFOA 3.1–8.7%, PFNA 7.9–10%, PFDA 8.6–10, PFUnDA 7.8–9.1%, PFDoDA 6.2–7.0% and PFTrDA 8.7–9.7% (Fig. 29.15–20).

PFHpA, PFTeDA, and PFPeDA had only values under LOQ and are therefore not presented as time series (table 29.2).

## PFOA, ng/g wet w., herring liver

### Harufjärden

n(tot)= 13,n(yrs)= 7
y(13)=.188 (.116,.305)
m=.312 (.202,.481)
slope=-12%(-24,2.3)
CV(lr)=38%,33%,13 yr
power=.12/.39/17%
r²=.49, p<.080
tau=-.52, p<.099
CV(sm)=41%, NS,21%
slope=-12%(-24,2.3)
CV(lr)=38%,33%,13 yr
power=.12/.39/17%
r²=.49, p<.080

### Ängskärsklubb

n(tot)= 29,n(yrs)= 22
y(13)=.340 (.271,.426)
m=.395 (.295,.529)
slope=3.1%(.47,5.8)
CV(lr)=65%,6.7%,18 yr
power=.99/.15/31%
r²=.23, p<.022 *
tau=.32, p<.036 *
CV(sm)=44%, p<.007,18%
slope=-.90%(-20,22)
CV(lr)=100%,40%,22 yr
power=.08/.08/49%
r²=.00, p<.886

### Landsort

n(tot)= 29,n(yrs)= 22
y(13)=1.31 (.957,1.78)
m=.516 (.356,.750)
slope=6.3%(3.7,9.0)
CV(lr)=62%,6.4%,17 yr
power=1.0/.16/29%
r²=.56, p<.001 *
tau=.56, p<.001 *
CV(sm)=84%, p<.353,25%
slope=3.9%(-14,25)
CV(lr)=83%,34%,20 yr
power=.11/.11/40%
r²=.02, p<.645



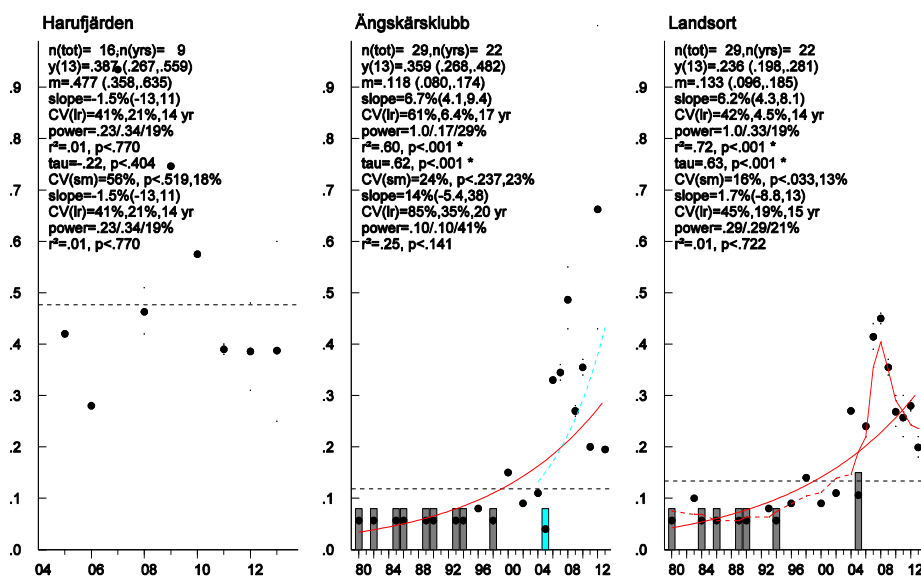**Figure 29.9.** Temporal trend of PFOA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005). The bars represent years where all values were below LOQ.

## PFOA, ng/g wet w., herring liver

### Utlängan

n(tot)= 29,n(yrs)= 22
y(13)=3.06 (2.15,4.36)
m=.691 (.439,1.09)
slope=8.7%(6.0,11)
CV(lr)=62%,6.4%,17 yr
power=1.0/.17/29%
r²=.71, p<.001 *
tau=.70, p<.001 *
CV(sm)=171%, p<.916,29%
slope=14%(-6.9,39)
CV(lr)=92%,37%,21 yr
power=.09/.09/45%
r²=.21, p<.176

### Fladen

n(tot)= 16,n(yrs)= 9
y(13)=.312 (.200,.485)
m=.402 (.275,.588)
slope=-4.8%(-18,11)
CV(lr)=54%,28%,16 yr
power=.14/.20/26%
r²=.07, p<.489
tau=-.06, p<.835
CV(sm)=54%, p<.318,22%
slope=-4.8%(-18,11)
CV(lr)=54%,28%,16 yr
power=.14/.20/26%
r²=.07, p<.489

### Väderöarna

n(tot)= 16,n(yrs)= 9
y(13)=.329 (.190,.569)
m=.355 (.240,.524)
slope=-4.7%(-17,9.7)
CV(lr)=55%,29%,16 yr
power=.14/.20/26%
r²=.08, p<.448
tau=-.20, p<.459
CV(sm)=59%, NS,28%
slope=-4.7%(-17,9.7)
CV(lr)=55%,29%,16 yr
power=.14/.20/26%
r²=.08, p<.448



**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.
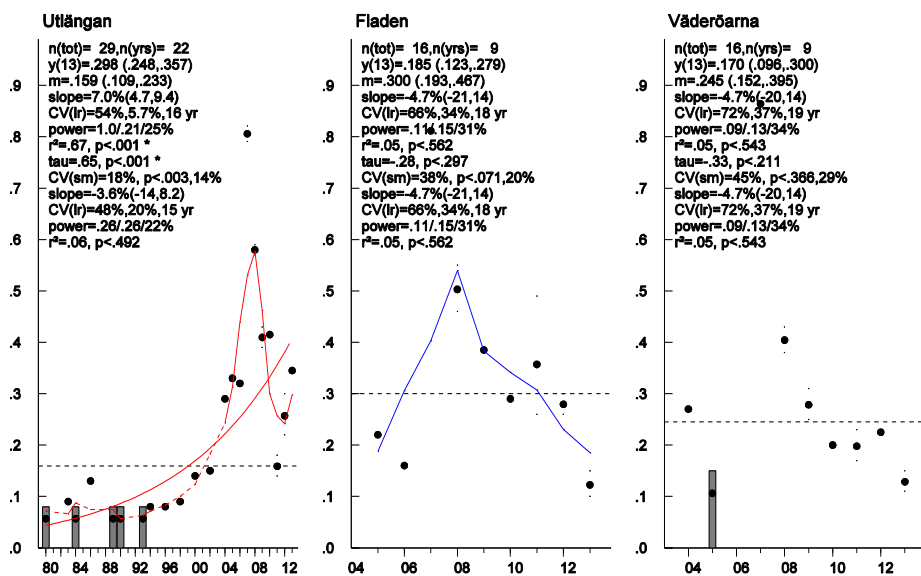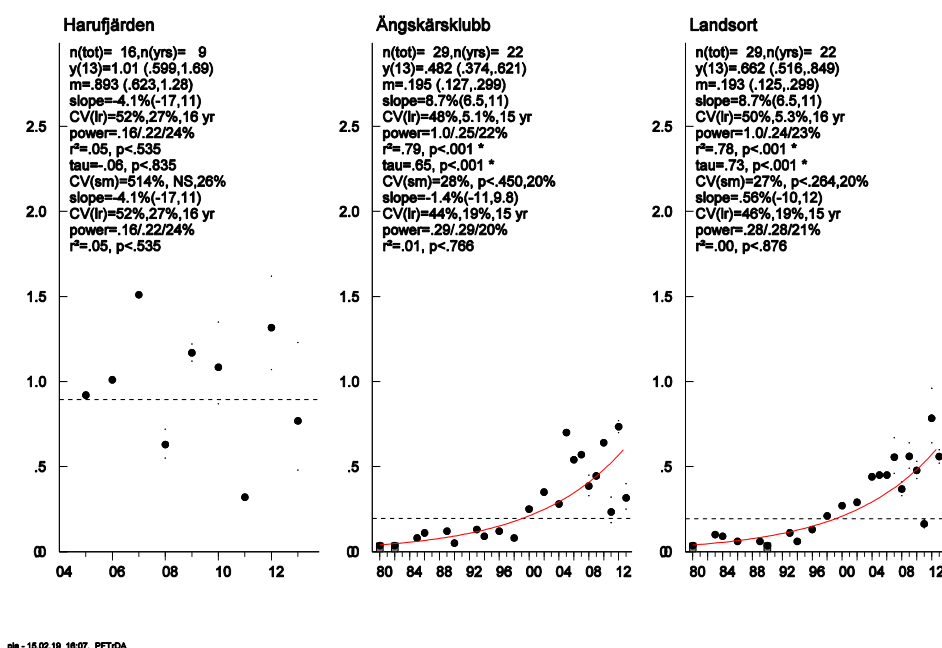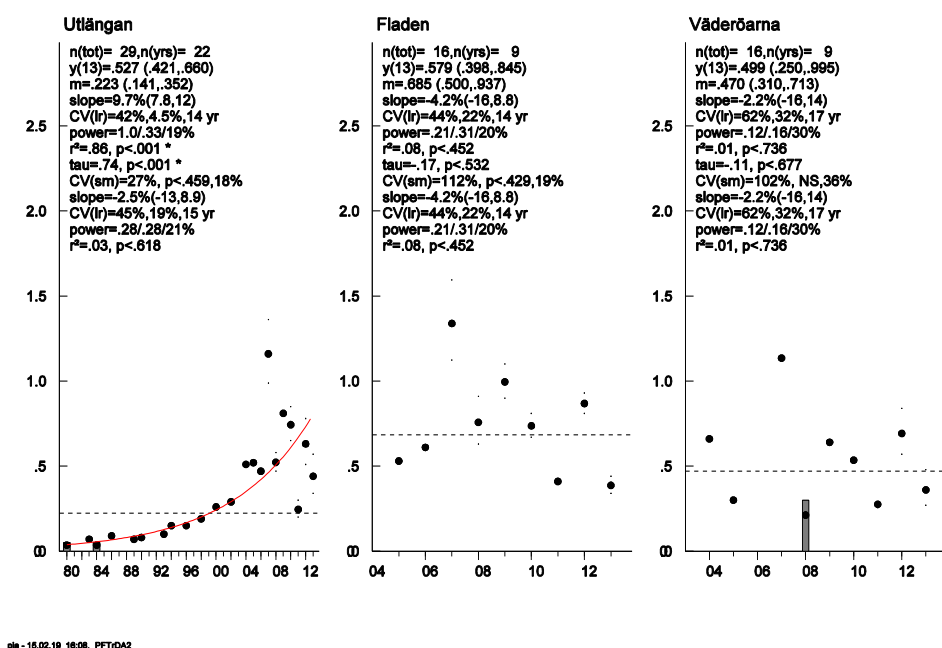
## PFNA, ng/g wet w., herring liver

**Harufjärden**

n(tot)= 16,n(yrs)= 9
y(13)=1.11 (.847,1.45)
m=1.31 (1.03,1.66)
slope=.90%(-8.7,12)
CV(lr)=34%,17%,13 yr
power=.34/.49/15%
r²=.00, p<.819
tau=.17, p<.532
CV(sm)=112%, p<.211,13%
slope=.90%(-8.7,12)
CV(lr)=34%,17%,13 yr
power=.34/.49/15%
r²=.00, p<.819

**Ängskärsklubb**

n(tot)= 29,n(yrs)= 22
y(13)=1.22 (.886,1.69)
m=.593 (.389,.905)
slope=7.9%(5.4,11)
CV(lr)=59%,6.2%,17 yr
power=1.0/.18/28%
r²=.69, p<.001 *
tau=.62, p<.001 *
CV(sm)=110%, p<.700,26%
slope=7.8%(-10,29)
CV(lr)=81%,33%,20 yr
power=.11/.11/39%
r²=.10, p<.365

**Landsort**

n(tot)= 29,n(yrs)= 22
y(13)=1.55 (1.24,1.94)
m=.704 (.465,1.07)
slope=7.9%(5.5,10)
CV(lr)=55%,5.8%,16 yr
power=1.0/.20/26%
r²=.71, p<.001 *
tau=.50, p<.001 *
CV(sm)=115%, p<.031,18%
slope=-2.8%(-12,7.5)
CV(lr)=41%,17%,14 yr
power=.34/.34/19%
r²=.04, p<.543

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**Fig. 29.11.** Temporal trend of PFNA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

## PFNA, ng/g wet w., herring liver

**Utlängan**

n(tot)= 29,n(yrs)= 22
y(13)=3.33 (2.51,4.42)
m=.921 (.568,1.49)
slope=10%(8.1,12)
CV(lr)=46%,4.9%,15 yr
power=1.0/.28/21%
r²=.85, p<.001 *
tau=.73, p<.001 *
CV(sm)=610%, p<1.00,22%
slope=3.4%(-11,19)
CV(lr)=62%,26%,17 yr
power=.16/.16/29%
r²=.03, p<.618

**Fladen**

n(tot)= 16,n(yrs)= 9
y(13)=.238 (.136,.414)
m=.198 (.130,.303)
slope=3.2%(-14,23)
CV(lr)=64%,33%,18 yr
power=.11/.16/30%
r²=.02, p<.686
tau=.15, p<.586
CV(sm)=38%, p<.632,28%
slope=3.2%(-14,23)
CV(lr)=64%,33%,18 yr
power=.11/.16/30%
r²=.02, p<.686

**Väderöarna**

n(tot)= 16,n(yrs)= 9
y(13)=.183 (.101,.332)
m=.178 (.116,.273)
slope=7.1%(-7.9,25)
CV(lr)=60%,31%,17 yr
power=.12/.17/28%
r²=.14, p<.317
tau=.15, p<.586
CV(sm)=39%, NS,31%
slope=7.1%(-7.9,25)
CV(lr)=60%,31%,17 yr
power=.12/.17/28%
r²=.14, p<.317

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**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.

## PFDA, ng/g wet w., herring liver



**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).

## PFDA, ng/g wet w., herring liver



**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.

PFUnDA, ng/g wet w., herring liver



**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).

PFUnDA, ng/g wet w., herring liver
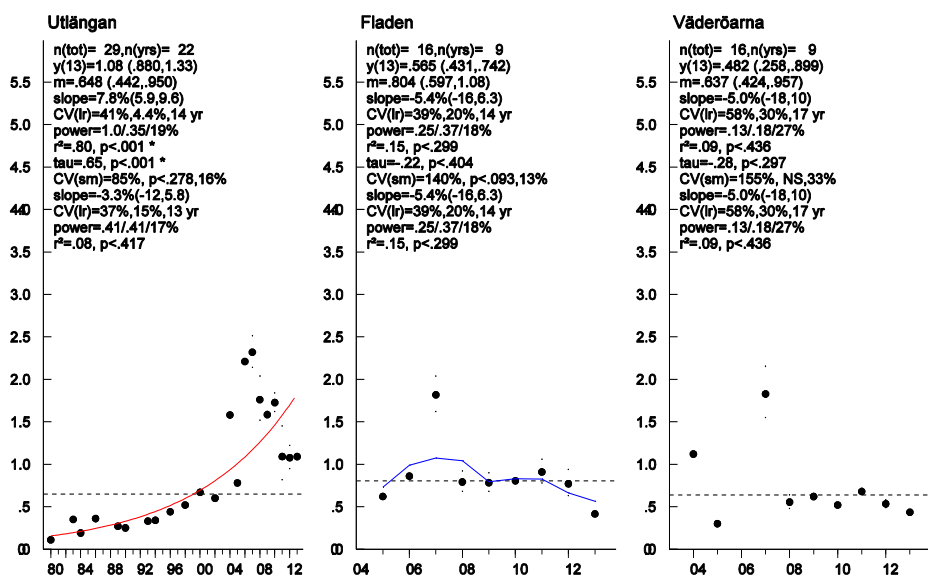


**Fig. 29.16.** Temporal trend of PFUnDA concentrations in herring liver (ng/g wet weight) from Utlängan, Fladen, and Väderöarna (time series starting in 2005).

# PFDoDA, ng/g wet w., herring liver



**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.

# PFDoDA, ng/g wet w., herring liver



**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.

## PFTrDA, ng/g wet w., herring liver



**Figure 29.19.** Temporal trend of PFTrDA in herring liver (ng/g wet weight) from Harufjärden, Ängskärsklubb, and Landsort (time series starting in 2005).

## PFTrDA, ng/g wet w., herring liver



**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 6% 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. PFNA, PFDA, PFUnDA, PFDoDA and PFTrDA all show significant increasing trends over the whole monitoring period of between 9.1–13 % per year (Fig. 29.21 and 29.22).
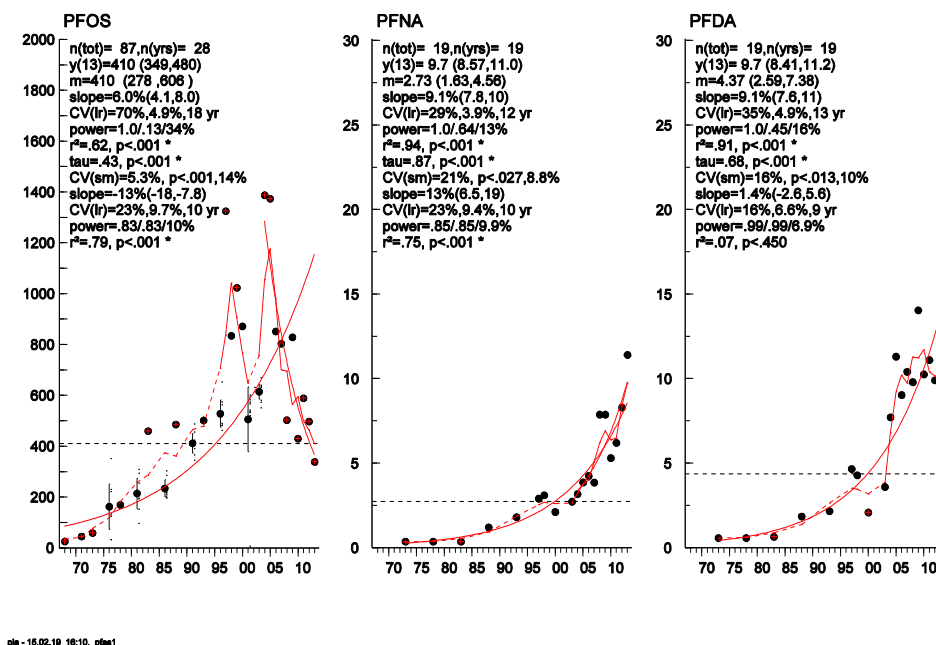


**Figure 29.21** Temporal trend of PFOS, PFTrDA and PFUnDA concentrations in guillemot eggs (ng/g wet weight) (time series starting in 1968 and 1973).
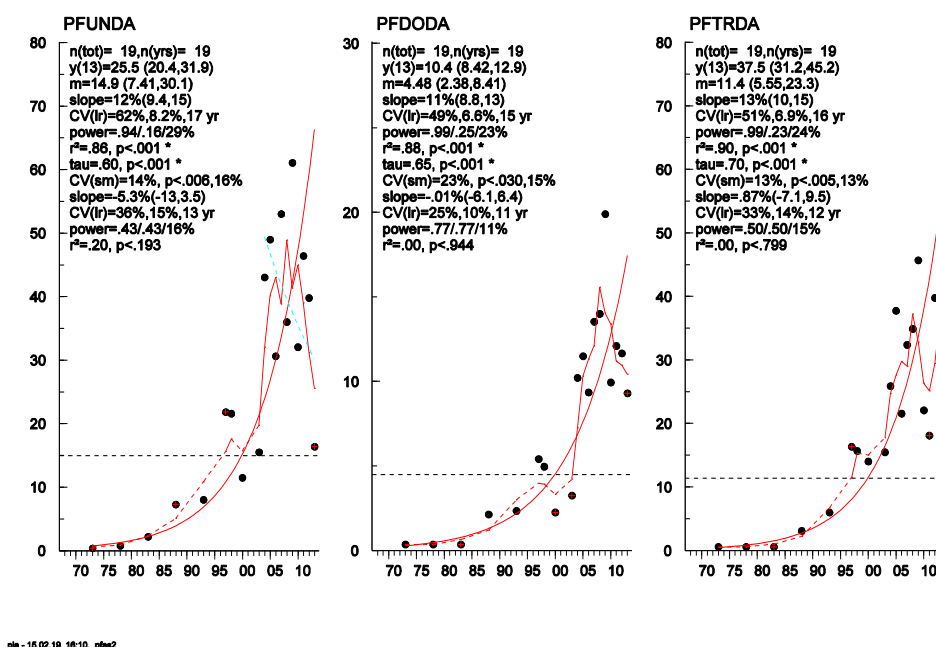


**Figure 29.22** Temporal trend of PFNA, PFDA and PFDoDA concentrations in guillemot eggs (ng/g wet weight) (time series starting in1973).

### 29.3.3  Comparison to threshold

In herring from all sites, the PFOS concentration is below the calculated liver value 155 ng/g ww corresponding to the target level of 9.1 ng/g wet weight based on $EQS_{biota,\,hh}$.

### 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 (Berger et al., 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 (Berger et al., 2007).

It is noteworthy that all perfluorocarboxylates show the same general trend irrespectively of sampling site and very similar average increase at 6.2-10% per year, the exception being PFOA 3.2–8.7% per year.

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 | | 87 | 28 | 68-13 | 6(4.1,8.0) | 0.0000 | +++ | 18 | 34 | 410 (349,480) |
| PFOS | | | 10 | 04-13 | -13(-18,-7.8) | 0.0006 | --- | 10 | 10 | |
| | **Herring liver** | | | | | | | | | |
| PFOS | Harufjärden | 16 | 9 | 05-13 | -3(-12,6.3) | 0.4599 | | 12 | 14 | 7.80 (6.52,9.32) |
| PFOS | Ängskärsklubb | 29 | 22 | 80-13 | 6.2(4.1,8.3) | 0.0000 | +++ | 15 | 22 | 7.79 (6.01,10.1) |
| PFOS | Ängskärsklubb | | 10 | 04-13 | 6.3(-5.4,19) | 0.2613 | | 15 | 23 | |
| PFOS | Landsort | 29 | 22 | 80-13 | 7.6(5.6,9.7) | 0.0000 | +++ | 15 | 21 | 14.3 (11.6,17.8) |
| PFOS | Landsort | | 10 | 04-13 | 3.2(-4.5,12) | 0.3826 | | 12 | 14 | |
| PFOS | Utlängan | 29 | 22 | 80-13 | 4.6(3.0,6.3) | 0.0000 | +++ | 13 | 17 | 13.2 (10.9,16.1) |
| PFOS | Utlängan | | 10 | 04-13 | 2.3(-4.6,9.6) | 0.4835 | | 11 | 12 | |
| PFOS | Fladen | 16 | 9 | 05-13 | -8.7(-15,-1.5) | 0.0239 | - | 11 | 11 | 3.91 (3.26,4.68) |
| PFOS | Väderöarna | 16 | 9 | 04-13 | -5.5(-20,11) | 0.4496 | | 18 | 32 | 3.35 (2.00,5.63) |
| PFBS | Harufjärden | 15 | 8 | 06-13 | -7.6(-29,21) | 0.5048 | | 20 | 39 | .071 (.041,.121) |
| PFBS | Ängskärsklubb | 28 | 21 | 80-13 | -2(-3.8,-.09) | 0.0395 | - | 15 | 21 | .071 (.057,.088) |
| PFBS | Ängskärsklubb | | 9 | 04-13 | -7.9(-24,11) | 0.3357 | | 19 | 35 | |
| PFBS | Landsort | 29 | 22 | 80-13 | -2.4(-4.7,-.04) | 0.0449 | - | 17 | 28 | .071 (.057,.088) |
| PFBS | Landsort | | 10 | 04-13 | -0.63(-19,22) | 0.9031 | | 22 | 48 | |
| PFBS | Utlängan | 29 | 22 | 80-13 | -2.4(-4.7,-.04) | 0.0449 | - | 17 | 28 | .071 (.057,.088) |
| PFBS | Utlängan | | 10 | 04-13 | -0.63(-19,22) | 0.9031 | | 22 | 48 | |
| PFBS | Fladen | 16 | 9 | 05-13 | 4(-20,35) | 0.7246 | | 22 | 50 | .071 (.047,.106) |
| PFBS | Väderöarna | 16 | 9 | 04-13 | 4.7(-17,31) | 0.6484 | | 22 | 49 | .071 (.040,.126) |
| PFDS | Harufjärden | 15 | 8 | 06-13 | -12(-27,4.3) | 0.1105 | | 15 | 23 | .088 (.055,.141) |
| PFDS | Ängskärsklubb | 29 | 22 | 80-13 | 8.1(4.5,12) | 0.0002 | +++ | 21 | 45 | .103 (.073,.144) |
| PFDS | Ängskärsklubb | | 10 | 04-13 | 14(-11,48) | 0.2596 | | 25 | 65 | |
| PFDS | Landsort | 29 | 22 | 80-13 | 2.7(.52,5.0) | 0.0172 | + | 16 | 25 | .163 (.125,.211) |
| PFDS | Landsort | | 10 | 04-13 | 7.8(-7.5,26) | 0.2937 | | 18 | 32 | |
| PFDS | Utlängan | 29 | 22 | 80-13 | 4.3(.59,8.2) | 0.0239 | + | 22 | 48 | .070 (.049,.099) |
| PFDS | Utlängan | | 10 | 04-13 | 8.3(-16,39) | 0.4891 | | 24 | 62 | |
| PFDS | Fladen | 16 | 9 | 05-13 | -1.4(-19,21) | 0.8496 | | 19 | 35 | .094 (.057,.157) |
| PFDS | Väderöarna | 16 | 9 | 04-13 | -6.1(-25,17) | 0.5232 | | 21 | 47 | .069 (.032,.150) |
| PFHXS | Harufjärden | 16 | 9 | 05-13 | 1.3(-11,15) | 0.8007 | | 14 | 19 | .111 (.087,.142) |
| PFHXS | Ängskärsklubb | 29 | 22 | 80-13 | -1.2(-3.1,.83) | 0.2357 | | 15 | 22 | .098 (.079,.122) |
| PFHXS | Ängskärsklubb | | 10 | 04-13 | -5.7(-21,12) | 0.4647 | | 20 | 38 | |
| PFHXS | Landsort | 29 | 22 | 80-13 | 2.3(.59,3.9) | 0.0097 | ++ | 14 | 18 | .450 (.368,.550) |
| PFHXS | Landsort | | 10 | 04-13 | 3.8(-7.9,17) | 0.4983 | | 16 | 23 | |
| PFHXS | Utlängan | 29 | 22 | 80-13 | 2.4(.68,4.1) | 0.0081 | ++ | 14 | 18 | .421 (.337,.527) |
| PFHXS | Utlängan | | 10 | 04-13 | 4.7(-8.9,20) | 0.4725 | | 17 | 28 | |
| PFHXS | Fladen | 16 | 9 | 05-13 | 1.4(-6.9,10) | 0.7082 | | 11 | 13 | .182 (.146,.225) |
| PFHXS | Väderöarna | 16 | 9 | 04-13 | 3.6(-7.8,16) | 0.5037 | | 15 | 21 | .139 (.097,.201) |

| FOSA | Harufjärden | 16 | 9 | 05-13 | -14(-25,-1.6) | 0.0319 | - | 15 | 21 | .456 (.323,.644) |
| FOSA | Ängskärsklubb | 29 | 22 | 80-13 | -3.7(-6.1,-1.3) | 0.0045 | -- | 17 | 29 | .521 (.393,.689) |
| FOSA | Ängskärsklubb | | 10 | 04-13 | -16(-28,-2.1) | 0.0298 | - | 18 | 32 | |
| FOSA | Landsort | 29 | 22 | 80-13 | 1.7(-1.8,5.4) | 0.3229 | | 22 | 47 | .732 (.556,.964) |
| FOSA | Landsort | | 10 | 04-13 | -12(-19,-4.8) | 0.0056 | -- | 12 | 14 | |
| FOSA | Utlängan | 29 | 22 | 80-13 | 5.4(3.0,7.9) | 0.0001 | +++ | 17 | 27 | 1.13 (.914,1.40) |
| FOSA | Utlängan | | 10 | 04-13 | -9.8(-17,-2.5) | 0.0155 | - | 12 | 14 | |
| FOSA | Fladen | 16 | 9 | 05-13 | -18(-27,-8.4) | 0.0041 | -- | 13 | 17 | 2.69 (1.99,3.64) |
| FOSA | Väderöarna | 16 | 9 | 04-13 | -7.3(-26,16) | 0.4518 | | 22 | 48 | 4.61 (2.65,8.04) |

**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 |
|---|---|---|---|---|---|---|---|---|---|---|
| | **Guillemot egg** | | | | | | | | | |
| PFNA | Stora Karlsö | 19 | 19 | 73-13 | 9.1(7.8,10) | 0.0000 | +++ | 12 | 13 | 9.7 (8.57,11.0) |
| PFNA | Stora Karlsö | | 10 | 04-13 | 13(6.5,19) | 0.0014 | ++ | 10 | 9.9 | |
| PFDA | Stora Karlsö | 19 | 19 | 73-13 | 9.1(7.6,11) | 0.0000 | +++ | 13 | 16 | 9.7 (8.41,11.2) |
| PFDA | Stora Karlsö | | 10 | 04-13 | 1.4(-2.6,5.6) | 0.4497 | | 9 | 6.9 | |
| PFUNDA | Stora Karlsö | 19 | 19 | 73-13 | 12(9.4,15) | 0.0000 | +++ | 17 | 29 | 25.5 (20.4,31.9) |
| PFUNDA | Stora Karlsö | | 10 | 04-13 | -5.3(-13,3.5) | 0.1933 | | 13 | 16 | |
| PFDODA | Stora Karlsö | 19 | 19 | 73-13 | 11(8.8,13) | 0.0000 | +++ | 15 | 23 | 10.4 (8.42,12.9) |
| PFDODA | Stora Karlsö | | 10 | 04-13 | -0.01(-6.1,6.4) | 0.9442 | | 11 | 11 | |
| PFTRDA | Stora Karlsö | 19 | 19 | 73-13 | 13(10,15) | 0.0000 | +++ | 16 | 24 | 37.5 (31.2,45.2) |
| PFTRDA | Stora Karlsö | | 10 | 04-13 | 0.87(-7.1,9.5) | 0.7988 | | 12 | 15 | |
| | **Herring liver** | | | | | | | | | |
| PFHPA | Harufjärden | 15 | 8 | 06-13 | -8.4(-19,3.8) | 0.1346 | | 13 | 15 | .212 (.175,.257) |
| PFHPA | Ängskärsklubb | 28 | 21 | 80-13 | 6(3.5,8.6) | 0.0001 | +++ | 17 | 27 | .212 (.178,.254) |
| PFHPA | Ängskärsklubb | | 9 | 04-13 | 3.9(-13,25) | 0.6365 | | 19 | 34 | |
| PFHPA | Landsort | 29 | 22 | 80-13 | 6.3(3.8,8.9) | 0.0000 | +++ | 17 | 28 | .212 (.188,.239) |
| PFHPA | Landsort | | 10 | 04-13 | -4.2(-15,8.2) | 0.4415 | | 16 | 24 | |
| PFHPA | Utlängan | 29 | 22 | 80-13 | 7.7(4.2,11) | 0.0002 | +++ | 21 | 43 | .212 (.158,.284) |
| PFHPA | Utlängan | | 10 | 04-13 | -9.8(-24,7.4) | 0.2069 | | 19 | 38 | |
| PFHPA | Fladen | 16 | 9 | 05-13 | -9.2(-20,2.4) | 0.0967 | | 14 | 19 | .212 (.168,.268) |
| PFHPA | Väderöarna | 16 | 9 | 04-13 | -9(-18,.78) | 0.0635 | | 14 | 18 | .212 (.169,.266) |
| PFOA | Harufjärden | 13 | 7 | 06-13 | -12(-24,2.3) | 0.0804 | | 13 | 17 | .188 (.116,.305) |
| PFOA | Ängskärsklubb | 29 | 22 | 80-13 | 3.1(.47,5.8) | 0.0221 | + | 18 | 31 | .340 (.271,.426) |
| PFOA | Ängskärsklubb | | 10 | 04-13 | -0.9(-20,22) | 0.8861 | | 22 | 49 | |
| PFOA | Landsort | 29 | 22 | 80-13 | 6.3(3.7,9.0) | 0.0001 | +++ | 17 | 29 | 1.31 (.957,1.78) |
| PFOA | Landsort | | 10 | 04-13 | 3.9(-14,25) | 0.6446 | | 20 | 40 | |
| PFOA | Utlängan | 29 | 22 | 80-13 | 8.7(6.0,11) | 0.0000 | +++ | 17 | 29 | 3.06 (2.15,4.36) |
| PFOA | Utlängan | | 10 | 04-13 | 14(-6.9,39) | 0.1758 | | 21 | 45 | |
| PFOA | Fladen | 16 | 9 | 05-13 | -4.8(-18,11) | 0.4886 | | 16 | 26 | .312 (.200,.485) |
| PFOA | Väderöarna | 16 | 9 | 04-13 | -4.7(-17,9.7) | 0.4483 | | 16 | 26 | .329 (.190,.569) |
| PFNA | Harufjärden | 16 | 9 | 05-13 | 0.9(-8.7,12) | 0.8186 | | 13 | 15 | 1.11 (.847,1.45) |
| PFNA | Ängskärsklubb | 29 | 22 | 80-13 | 7.9(5.4,11) | 0.0000 | +++ | 17 | 28 | 1.22 (.886,1.69) |
| PFNA | Ängskärsklubb | | 10 | 04-13 | 7.8(-10,29) | 0.365 | | 20 | 39 | |
| PFNA | Landsort | 29 | 22 | 80-13 | 7.9(5.5,10) | 0.0000 | +++ | 16 | 26 | 1.55 (1.24,1.94) |
| PFNA | Landsort | | 10 | 04-13 | -2.8(-12,7.5) | 0.5425 | | 14 | 19 | |
| PFNA | Utlängan | 29 | 22 | 80-13 | 10(8.1,12) | 0.0000 | +++ | 15 | 21 | 3.33 (2.51,4.42) |
| PFNA | Utlängan | | 10 | 04-13 | 3.4(-11,19) | 0.6175 | | 17 | 29 | |
| PFNA | Fladen | 16 | 9 | 05-13 | 3.2(-14,23) | 0.6864 | | 18 | 30 | .238 (.136,.414) |
| PFNA | Väderöarna | 16 | 9 | 04-13 | 7.1(-7.9,25) | 0.3174 | | 17 | 28 | .183 (.101,.332) |
| PFDA | Harufjärden | 16 | 9 | 05-13 | 0.73(-9.5,12) | 0.8504 | | 13 | 16 | .808 (.554,1.18) |

| PFDA | Ängskärsklubb | 29 | 22 | 80-13 | 8.6(6.1,11) | 0.0000 | +++ | 17 | 27 | .508 (.399,.649) |
|------|---------------|-----|-----|-------|-------------|--------|-----|-----|-----|------------------|
| PFDA | Ängskärsklubb | | 10 | 04-13 | 3.1(-14,23) | 0.7077 | | 20 | 39 | |
| PFDA | Landsort | 29 | 22 | 80-13 | 9.3(7.2,11) | 0.0000 | +++ | 15 | 22 | .702 (.579,.850) |
| PFDA | Landsort | | 10 | 04-13 | -3.4(-12,5.5) | 0.3951 | | 13 | 16 | |
| PFDA | Utlängan | 29 | 22 | 80-13 | 10(8.2,12) | 0.0000 | +++ | 14 | 19 | .939 (.762,1.16) |
| PFDA | Utlängan | | 10 | 04-13 | 2.6(-8.4,15) | 0.6188 | | 15 | 22 | |
| PFDA | Fladen | 16 | 9 | 05-13 | -6.1(-17,6.0) | 0.2596 | | 14 | 19 | .228 (.162,.322) |
| PFDA | Väderöarna | 16 | 9 | 04-13 | 3.2(-14,24) | 0.7009 | | 19 | 37 | .178 (.096,.330) |
| PFUNDA | Harufjärden | 16 | 9 | 05-13 | -3.9(-13,6.7) | 0.4 | | 13 | 16 | 1.05 (.816,1.35) |
| PFUNDA | Ängskärsklubb | 29 | 22 | 80-13 | 9.1(7.1,11) | 0.0000 | +++ | 15 | 21 | .928 (.707,1.22) |
| PFUNDA | Ängskärsklubb | | 10 | 04-13 | 3.5(-10,19) | 0.5947 | | 17 | 28 | |
| PFUNDA | Landsort | 29 | 22 | 80-13 | 8.9(7.1,11) | 0.0000 | +++ | 14 | 18 | .987 (.815,1.20) |
| PFUNDA | Landsort | | 10 | 04-13 | -2.4(-8.3,3.9) | 0.4028 | | 11 | 11 | |
| PFUNDA | Utlängan | 29 | 22 | 80-13 | 7.8(5.9,9.6) | 0.0000 | +++ | 14 | 19 | 1.08 (.880,1.33) |
| PFUNDA | Utlängan | | 10 | 04-13 | -3.3(-12,5.8) | 0.4166 | | 13 | 17 | |
| PFUNDA | Fladen | 16 | 9 | 05-13 | -5.4(-16,6.3) | 0.2988 | | 14 | 18 | .565 (.431,.742) |
| PFUNDA | Väderöarna | 16 | 9 | 04-13 | -5(-18,10) | 0.4357 | | 17 | 27 | .482 (.258,.899) |
| PFDODA | Harufjärden | 16 | 9 | 05-13 | -1.5(-13,11) | 0.7699 | | 14 | 19 | .387 (.267,.559) |
| PFDODA | Ängskärsklubb | 29 | 22 | 80-13 | 6.7(4.1,9.4) | 0.0000 | +++ | 17 | 29 | .359 (.268,.482) |
| PFDODA | Ängskärsklubb | | 10 | 04-13 | 14(-5.4,38) | 0.1413 | | 20 | 41 | |
| PFDODA | Landsort | 29 | 22 | 80-13 | 6.2(4.3,8.1) | 0.0000 | +++ | 14 | 19 | .236 (.198,.281) |
| PFDODA | Landsort | | 10 | 04-13 | 1.7(-8.8,13) | 0.7216 | | 15 | 21 | |
| PFDODA | Utlängan | 29 | 22 | 80-13 | 7(4.7,9.4) | 0.0000 | +++ | 16 | 25 | .298 (.248,.357) |
| PFDODA | Utlängan | | 10 | 04-13 | -3.6(-14,8.2) | 0.4915 | | 15 | 22 | |
| PFDODA | Fladen | 16 | 9 | 05-13 | -4.7(-21,14) | 0.5616 | | 18 | 31 | .185 (.123,.279) |
| PFDODA | Väderöarna | 16 | 9 | 04-13 | -4.7(-20,14) | 0.5427 | | 19 | 34 | .170 (.096,.300) |
| PFTRDA | Harufjärden | 16 | 9 | 05-13 | -4.1(-17,11) | 0.5349 | | 16 | 24 | 1.01 (.599,1.69) |
| PFTRDA | Ängskärsklubb | 29 | 22 | 80-13 | 8.7(6.5,11) | 0.0000 | +++ | 15 | 22 | .482 (.374,.621) |
| PFTRDA | Ängskärsklubb | | 10 | 04-13 | -1.4(-11,9.8) | 0.766 | | 15 | 20 | |
| PFTRDA | Landsort | 29 | 22 | 80-13 | 8.7(6.5,11) | 0.0000 | +++ | 16 | 23 | .662 (.516,.849) |
| PFTRDA | Landsort | | 10 | 04-13 | 0.56(-10,12) | 0.8755 | | 15 | 21 | |
| PFTRDA | Utlängan | 29 | 22 | 80-13 | 9.7(7.8,12) | 0.0000 | +++ | 14 | 19 | .527 (.421,.660) |
| PFTRDA | Utlängan | | 10 | 04-13 | -2.5(-13,8.9) | 0.6181 | | 15 | 21 | |
| PFTRDA | Fladen | 16 | 9 | 05-13 | -4.2(-16,8.8) | 0.4523 | | 14 | 20 | .579 (.398,.845) |
| PFTRDA | Väderöarna | 16 | 9 | 04-13 | -2.2(-16,14) | 0.7356 | | 17 | 30 | .499 (.250,.995) |
| PFTEDA | Harufjärden | 15 | 8 | 06-13 | -6.6(-30,25) | 0.5914 | | 21 | 44 | .129 (.084,.199) |
| PFTEDA | Ängskärsklubb | 29 | 22 | 80-13 | 5.6(2.2,9.2) | 0.0027 | ++ | 21 | 43 | .088 (.064,.122) |
| PFTEDA | Ängskärsklubb | | 10 | 04-13 | -2.1(-26,30) | 0.8394 | | 26 | 75 | |
| PFTEDA | Landsort | 29 | 22 | 80-13 | 4.8(1.2,8.6) | 0.0108 | + | 21 | 46 | .042 (.033,.053) |
| PFTEDA | Landsort | | 10 | 04-13 | -13(-33,12) | 0.2299 | | 25 | 64 | |
| PFTEDA | Utlängan | 29 | 22 | 80-13 | 5.8(2.0,9.8) | 0.0043 | ++ | 22 | 49 | .088 (.069,.112) |
| PFTEDA | Utlängan | | 10 | 04-13 | -13(-33,13) | 0.253 | | 25 | 65 | |
| PFTEDA | Fladen | 16 | 9 | 05-13 | -18(-38,8.7) | 0.1397 | | 23 | 56 | .075 (.041,.137) |
| PFTEDA | Väderöarna | 16 | 9 | 04-13 | -18(-39,11) | 0.1705 | | 26 | 75 | .056 (.034,.092) |
| PFPEDA | Harufjärden | 15 | 8 | 06-13 | -17(-42,19) | 0.2573 | | 24 | 60 | .078 (.042,.144) |
| PFPEDA | Ängskärsklubb | 29 | 22 | 80-13 | 9.6(5.0,14) | 0.0003 | +++ | 24 | 62 | .038 (.027,.055) |
| PFPEDA | Ängskärsklubb | | 10 | 04-13 | 6.5(-26,53) | 0.6968 | | 31 | 117 | |
| PFPEDA | Landsort | 29 | 22 | 80-13 | 10(5.2,15) | 0.0003 | +++ | 25 | 64 | .037 (.026,.052) |

| PFPEDA | Landsort | | 10 | 04-13 | -7.5(-34,30) | 0.6149 | | 29 | 104 | |
| PFPEDA | Utlängan | 29 | 22 | 80-13 | 12(7.2,16) | 0.0000 | +++ | 24 | 58 | .055 (.045,.068) |
| PFPEDA | Utlängan | | 10 | 04-13 | -9.8(-30,16) | 0.3798 | | 25 | 64 | |
| PFPEDA | Fladen | 16 | 9 | 05-13 | -17(-35,6.9) | 0.1235 | | 22 | 48 | .080 (.048,.132) |
| PFPEDA | Väderöarna | 16 | 9 | 04-13 | -18(-37,6.3) | 0.1096 | | 24 | 61 | .049 (.028,.089) |

# 30  OTCs – Organotin Compounds

<div align="right">Updated 14.02.28</div>

## 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 S., 2005).

### 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, SWE-EPA, 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 I. 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

A)                                                    B)
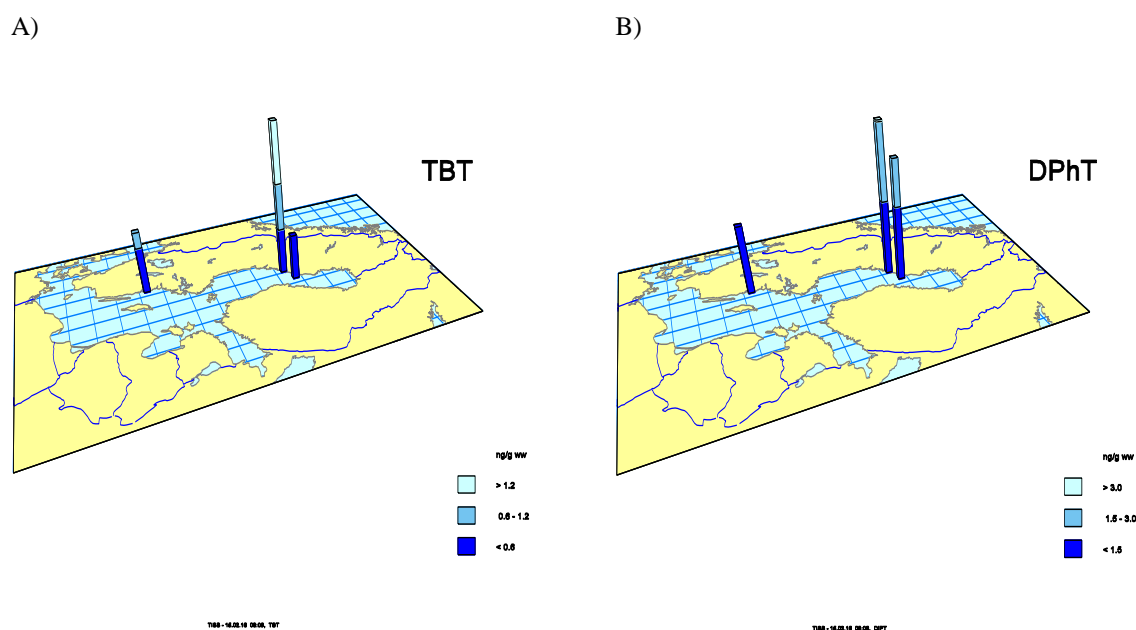


**Figure 30.1.** Spatial variation in TBT and DphT concentrations (ng/g wet weight) in perch liver.

Highest concentrations of both tributyltin (TBT) and diphenyltin (DPhT) were found in samples from Örefjärden with concentrations of 2.0 ng TBT/g wet weight and 3.0 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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