Managing the dioxin problem in the Baltic region with focus on sources to air and fish

Final report from the research project BalticPOPs

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Preface

During the years 2009-2012, the Swedish Environmental Protection Agency has funded the research project *BalticPOPs – Managing the dioxin problem in the Baltic Sea*.

Baltic herring and other oil-rich fish contain levels of dioxins that exceed the limit set by the EU for sale of fish for consumption. The aim of this project was to increase our knowledge about the causes and the emission sources of the high levels of dioxins in oil-rich fish in the Baltic Sea. The knowledge is needed to establish a basis that would enable us to implement the most efficient measures for reducing emissions of dioxins from both Swedish and foreign sources.

The research project has been led by Professor Karin Wiberg at the Swedish University of Agricultural Sciences. Researchers from eight universities and research organizations in Sweden, Finland and Russia have participated.

The views expressed in this report are those of the authors and do not necessarily represent the views of the Swedish EPA. A summary of the results and policy briefs are available in separate publications both in English (ISBN 978-91-620-8652-7) and in Swedish (ISBN 978-91-620-8651-0).

The project has been funded by the Swedish EPA´s Environmental Research Grant.

The Swedish Environmental Protection Agency, May 2013

Förord

Naturvårdsverket har under åren 2009-2012 finansierat forskningsprogrammet
BalticPOPs – Hur ska dioxinproblemet i Östersjön hanteras?

Halterna av dioxiner i strömming och annan fet fisk i Östersjön är så höga att de ofta överskrider EU:s gränsvärde för försäljning av konsumtionsfisk. Syftet med satsningen på forskningsprogrammet var att ta fram mer kunskap om orsakerna och källorna till de höga dioxinhalterna i fet fisk i Östersjön. Kunskapen behövs för att kunna verka för att de mest effektiva åtgärderna vidtas för att minska utsläppen och tillförsel av dioxiner från såväl svenska som utländska källor.

Programmet har letts av Professor Karin Wiberg, Sveriges lantbruksuniversitet. Forskare från åtta lärosäten och forskningsorganisationer i Sverige, Finland och Ryssland har deltagit.

Författarna svarar för innehållet i rapporten. En sammanfattning av resultaten och förslag till åtgärder finns i separata publikationer både på svenska (ISBN 978-91-620-8651-0) och på engelska (ISBN 978-91-620-8652-7).

Forskningsprogrammet har finansierats med medel från Naturvårdsverkets miljöforskningsanslag.

Naturvårdsverket, maj 2013

Contents

1 Sammanfattning

BalticPOPs är ett forskningsprogram som genomförts på uppdrag av Naturvårdsverket med syfte att i) undersöka tidstrender och geografiska trender av persistenta organiska miljöföreningar (POPs) i biota i Östersjön (framför allt i fet fisk såsom strömming) samt ii) spåra källorna till luftförorening av POPs. BalticPOPs har framför allt fokuserat på dioxiner, eftersom dioxinförorening är särskilt problematiskt i Östersjöregionen. BalticPOPs bygger vidare på forskningsresultat publicerade av Wiberg *et al.* (2009). Ett viktigt syfte är att använda de nya forskningsresultaten för att diskutera strategier att minska utsläpp, något som bör leda till minskade dioxinhalter i fet Östersjöfisk. BalticPOPs har varit tvärvetenskapligt med experter från ett flertal olika forskningsområden. Projektets huvudsakliga slutsatser summeras nedan:

i) Varför är halterna av dioxiner i fet fisk från Östersjön så höga? De huvudsakliga anledningarna till att strömming i Östersjön är mer förorenad än fisk från omgivande hav anses vara att uppehållstiden för vatten i Östersjön är lång och att tillväxthastigheten för strömming i vissa bassänger är låg. Det är möjligt att de höga dioxinhalterna i strömming från vissa populationer kan bero på påverkan från kustnära källor, men eftersom strömming är en migrerande fisk (som endast tillbringar en begränsad tid vid kusten under lek) och det inte finns tydliga skillnader i dioxinförorening mellan strömming provtagen i kustområden respektive på öppet vatten, framstår detta som en osannolik förklaring.

ii) Vilka är de huvudsakliga källorna till dioxiner i Östersjöströmming? De forskningsresultat som tagits fram inom BalticPOPs bekräftar slutsatsen från en tidigare studie (Wiberg *et al.* 2009)nämligen att atmosfärisk deposition är den huvudsakliga källan till förorening av dioxiner i Östersjön. Detta kan styrkas bland annat med hjälp av:

- spridningsmodeller (Armitage *et al.* 2009, Wiberg *et al.* 2009);
- källspårning med hjälp av receptormodellering och sedimentdata (Sundqvist *et al.* 2010, Assefa *et al.,* 2011 samt denna studie);
- mätningar av dioxinkoncentrationer i Umeälven (Josefsson *et al.*, manuskript) och i luft i Östersjöområdet (Sellström *et al.* 2009), vilka indikerade att bidrag från floder är låga i förhållande till bidrag från atmosfärisk deposition;
- att bidrag av utsläpp från industri och avloppsvatten är relativt låga i förhållande till bidrag från atmosfärisk deposition (Andersson *et al.* 2012, Fridmanis *et al.* 2012, Laht och Volkov 2012);
- att föroreningsnivåer i strömmingspopulationer inte skiljer sig åt mellan fisk provtagna i kustnära områden och fisk från utsjöområden (denna studie).

iii) Vilka är de huvudsakliga källorna till förorening av luft i Östersjöregionen? Det är svårt att exakt fastställa vilka typer av källor som dominerar, men mätning och modellering som genomförts inom BalticPOPs indikerar att icke-industriell förbränning är viktigare än industriella utsläpp. Enligt europeiska emissionsdatabaser utgör hushållens utsläpp mer än en tredjedel av de totala europeiska utsläppen av dioxiner idag. I vissa regioner kan de bidra med så mycket som 70 % av de totala utsläppen. De huvudsakliga källorna till utsläpp av dioxiner från europeiska hushåll har uppskattats vara uppvärmning och matlagning med fast bränsle samt avfallsförbränning.

iv) Är dessa utsläpp (*ii* och *iii*) resultat av primära eller sekundära utsläpp? Att halterna av dioxiner är högre på vintern och mestadels ej kvantifierbara under sommaren tyder på att direkta källor snarare än temperaturstyrd avdunstning från jord (ibland kallade sekundära utsläpp) styr halterna av dioxiner i luft. Simuleringar med modellen POPCYCLING-Baltic visar också att avdunstning från jord är en relativt obetydlig källa av dioxiner till luft.

v) Sker dessa utsläpp (*ii* och *iii*) huvudsakligen i Sverige eller internationellt? Det är inte möjligt att identifiera specifika regioner vars dioxinutsläpp är avgörande för föroreningen av luft i Europa. Man har dock, med hjälp av mätningar och modeller, kunnat sluta sig till att de dioxiner som uppmätts i Östersjöområdets luft huvudsakligen har sitt ursprung på den europeiska kontinenten, och att bidraget från Östeuropa är stort. Svenska källor står endast för ett mindre bidrag till halterna av dioxiner i Östersjöområdets luft.

vi) Hur har situationen förändrats över tid? De senaste decennierna har emissioner av dioxiner minskat som följd av införandet av nya regelverk. Forskning som genomförts inom BalticPOPs har visat att detta resulterat i långsiktiga nedgångar av dioxinhalter i Östersjösediment, men bara i vissa av de strömmingspopulationer i Östersjöns som studerats under senare år. Möjligen har långsammare tillväxthastigheter och förändringar i diet hämmat nedåtgående tidstrender av dioxiner och dioxinlika PCB:er i strömming och på så vis motverkat effekten av sänkta utsläpp.

vii) Hur lång tid kommer det att ta innan halterna av dioxiner i strömming sjunker till nivåer som säkert ligger under EU:s riktlinjer, förutsatt att utsläppen till Östersjön minskar? I och med att halterna av dioxiner i Östersjöströmming överstiger EU:s riktlinjer och att den europeiska befolkningens allmänna exponering för dioxiner är hög, behövs fler åtgärder för att begränsa utsläppen till luft i Europa. Det är dock oklart huruvida halterna av dioxiner i strömming kommer att fortsätta att sjunka, i och med att framtida utsläpp av dioxiner och framtida förändringar i strömmingens ekologi är svåra att förutspå.

viii) Finns kostnadseffektiva åtgärder som inom kort tid skulle kunna minska halterna av dioxiner i Östersjöströmming till nivåer under EU:s riktlinjer? De forskningsresultat som tagits fram i det här projektet visar att en minskning av den atmosfäriska depositionen av dioxiner till Östersjön skulle vara det mest effektiva sättet att sänka halterna av dioxiner i strömming, även om halterna skulle gå ner långsamt. Införandet av nya regelverk har gjort att industrins utsläpp av dioxiner minskat med upp till 90 %, medan utsläppen av dioxiner från hushåll inte minskat särskilt mycket. Således utgör hushållens utsläpp nu huvuddelen av de totala utsläppen av dioxiner i vissa regioner. På grund av ekologiska faktorer (såsom tillväxthastighet) och svårigheten att reglera diffusa utsläpp, finns inga garantier för att en snabb nedgång av dioxinnivåerna i Östersjöströmming kan åstadkommas genom ny lagstiftning. Ytterligare ett sätt att minska halterna av dioxiner i strömming kunde vara att styra fiskeriet i Östersjön så att strömmingens tillväxthastighet ökar. Detta rör komplexa ekologiska samband, och en sådan åtgärds biologiska konsekvenser och eventuella framgång har inte undersökts inom BalticPOPs. Det skulle därför behöva undersökas vidare i samarbete med forskare inom fiskekologi.

ix) Sanering av förorenade sediment i Östersjöns kustområden skulle kunna ha betydande positiv lokal påverkan, och kunna förbättra vattenkvaliteten samt minska dioxinnivåerna i de arter som lever i dessa förorenade områden. Det skulle dock troligtvis inte ha någon inverkan på halterna av dioxiner i migrerande fisk (såsom strömming), vilken tillbringar huvudelen av sin tid på öppet vatten och endast tar sig till kustregioner för att leka under några få veckor sommartid.

2 Summary

The BalticPOPs project was commissioned by the Swedish Environmental Protection Agency (Swedish EPA) to i) investigate spatial and temporal trends of persistent organic pollutants (POPs) in Baltic biota (especially fatty fish such as herring), and to ii) trace the sources of these pollutants to the atmosphere. BalticPOPs was focused on polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs; collectively termed PCDD/F or "dioxins" in this report), which are of particular concern in the Baltic region. BalticPOPs builds on the results of previous research in Wiberg *et al*. (2009). An important aim was to use the findings of this research to develop recommendations for the Swedish EPA on emission reduction strategies for dioxins, in order to achieve reductions in dioxin levels in Baltic fatty fish such as herring. A multidisciplinary approach was implemented, and the project consortium therefore included experts from many different research fields. The main questions posed in the project proposal and the answers provided from the research undertaken in the project are listed below:

i) Why are dioxin levels in fatty fish from the Baltic Sea so high? The slow growth of herring in some Baltic sub-basins combined with the long residence time of Baltic Sea water are considered the main reasons why Baltic herring have higher dioxin concentrations than in surrounding seas. It is possible that some herring populations could have been impacted by coastal sources resulting in high concentrations, but the migratory nature of herring (they spend limited time at the coast during spawning) and the lack of clear spatial variation in dioxin contamination between different herring populations in the Bothnian Sea makes this seem an unlikely explanation.

ii) What are the main sources of the dioxins in Baltic herring? Research undertaken in the BalticPOPs project confirms the conclusion of previous work (Wiberg *et al.* 2009) that the atmosphere is, and will continue to be, the major external source of dioxin pollution to the Baltic Sea, and thus dioxin contamination in herring populations. Key evidence for the dominance of atmospheric sources includes:

- Environmental fate modelling (Armitage *et al*. 2009, Wiberg *et al*. 2009);
- Sediment source tracing modelling (Sundqvist *et al*. 2010, Assefa and this study);
- Measurements of dioxins in the Umeå River (Josefsson *et al*., manuscript in preparation) and in air in the Baltic region (Sellström *et al*. 2009), indicating relatively low contribution of riverine inputs in comparison to atmospheric deposition;
- The relatively low contribution of inputs from wastewater/industrial discharges (Andersson *et al*. 2012, Fridmanis *et al*. 2012, Laht and Volkov 2012);
- The general lack of observed spatial differences in dioxin concentrations in herring between the coast and open sea within the Bothnian Sea (this study).

iii) What are the main sources of dioxins and other POPs to Baltic air? Air monitoring combined with receptor modelling was not able to pinpoint the sources responsible for dioxins and other POPs in Baltic air, but indicated a dominance of diffuse combustion sources. Emission databases for the European region suggest that domestic combustion sources now account for more than one third of total dioxin emissions and this fraction can be as high as 70% in some regions. The main domestic sources of dioxins have been estimated to be heating and cooking with solid fuels and burning of waste. The project did not address question *iii* for other POPs due to limited resources.

iv) Are these sources (*ii* and *iii*) the result of on-going primary emissions or of recirculation from environmental reservoirs? Seasonal air concentrations of dioxins with peaks during winter months indicate that primary emission sources of dioxins rather than temperature-driven re-volatilisation from soils (sometimes called secondary emissions) control dioxin levels in air. The POPCYCLING-Baltic model simulations also indicate that re-volatilisation from soils is a relatively minor source of dioxins to air.

v) Are these sources (*ii* and *iii*) mainly national or international? It is not possible to accurately pinpoint the geographical regions which are the dominant sources of dioxin emissions to air in Europe, but it is known, based on monitoring and modelling, that continental Europe and especially Eastern Europe make the largest contribution to atmospheric deposition in most Baltic basins. Swedish sources make only a minor contribution to levels of dioxins in Baltic air.

vi) How has the pollution situation changed over time? Emissions of dioxins have declined in recent decades as a result of active abatement policies, and research undertaken in BalticPOPs has shown that this has resulted in long-term declines in concentrations in Baltic sediment and in some herring populations. Bioenergetics modelling undertaken in BalticPOPs has shown that slower growth rates of herring and changes in feeding ecology may be slowing downward temporal trends of dioxin concentrations in herring and potentially counteracting emission reduction measures.

vii) Assuming dioxin inputs to the Baltic Sea are reduced – how long will it take until the concentrations in herring decrease to levels safely below threshold values? More action is needed to reduce the emissions of dioxins to air and thus atmospheric deposition to the Baltic Sea, because levels of dioxins in herring remain above EU threshold values and the general intake of dioxins of the European population is high. It is uncertain if the downward time trend in herring will continue because we do not know the future time trends of emissions/atmospheric deposition as well as future changes in herring feeding ecology and growth rates.

viii) Are there cost-effective measures that can reduce dioxin levels in Baltic herring below the regulatory thresholds within a relatively short time period? Based on the findings of this project, the main way to decrease concentrations in herring is to reduce atmospheric deposition of dioxins to the Baltic Sea, even if the time response in herring may be slow. Although active abatement policies have reduced dioxin emissions from industry by up to 90%, reduction of dioxin emissions from domestic sources has been much lower, and consequently domestic combustion sources now dominate total estimated emissions in some regions. Policy actions have to provide a means of reducing these diffuse domestic combustion sources of dioxins to the atmosphere. It cannot be guaranteed that policy actions to reduce emissions will result in rapid reduction of dioxin levels in herring to below EU threshold values. Although reductions in dioxin emissions will ultimately reduce levels of dioxins in Baltic seawater, observed changes in herring ecology (e.g., slowing growth rates and/or feeding ecology) in some herring populations could cause dioxin levels in herring to respond more slowly than seawater to emission reductions. An additional way to decrease herring dioxin concentrations, suggested by Peltonen *et al*. (2007), is to reduce the number of herring individuals through fishing so that feeding conditions for the remaining herring are improved. This is a complex ecological issue, and the biological implications and potential success of such a management alternative were not addressed in BalticPOPs. Hence, if considered, this alternative would need to be further investigated in collaboration with fish ecology researchers.

ix) Clean-up of dioxin-contaminated sediments in coastal regions of the Baltic will have important local benefits such as improvement of water quality and lowering of contamination levels in species which reside mainly in the contaminated regions. These clean-up actions are not likely to have much impact on the levels of dioxins in migratory fish (e.g., herring), which spend most of their time in the open sea and only move into coastal regions to spawn during a few weeks in the spring/summer.

3 Abbreviations

BC	black carbon
CB	chlorobiphenyl. The PCBs are referred to with their IUPAC numbers, i.e. CB 28, CB 52 etc.
dl-PCBs	dioxin-like PCBs (the PCBs with no chlorines (non-*ortho*) or one chlorine (mono-*ortho*) in the *ortho* position, i.e., CBs 77, 81, 126, 169 and 105, 114, 118, 123, 156, 157, 167, 189)
d.w.	dry weight
EMEP	European Monitoring and Evaluation Program (Co-operative programme for monitoring and evaluation of the long-range transmission of air pollutants in Europe)
EPA	Environmental Protection Agency
fg	femtogram (1 fg = 0.001 pg)
HCB	hexachlorobenzene
HpCDD	heptachlorinated dibenzo-*p*-dioxin
HpCDF	heptachlorinated dibenzofuran
HRGC/HRMS	high resolution gas chromatography/high resolution mass spectrometry
HxCDD	hexachlorinated dibenzo-*p*-dioxin
HxCDF	hexachlorinated dibenzofuran
I-TEF	toxic equivalency factors according to NATO/CCMS 1988
I-TEQ	toxic equivalents according to I-TEFs
$K_{aer\text{-}water}$	aerosol-water distribution ratio
$K_{sed\text{-}water}$	sediment-water distribution ratio
$K_{aer\text{-}water,\ OC}$	aerosol-water distribution ratio on an OC basis
$K_{sed\text{-}water,\ OC}$	sediment-water distribution ratio on an OC basis
K_{ow}	octanol-water partition coefficient
LOD	limit of detection
LOI	loss on ignition
LOQ	limit of quantification
l.w.	lipid weight
mg	milligram (1 mg = 0.001 g)
MSWI	municipal solid waste incineration
ng	nanogram (1 ng = 0.001 µg)
OC	organic carbon
OCDD	octachlorinated dibenzo-*p*-dioxin
OCDF	octachlorinated dibenzofuran
OM	organic matter
PAH(s)	polycyclic aromatic hydrocarbon(s)
PCA	principal component analysis
PCB(s)	polychlorinated biphenyl(s)
PCDD(s)	polychlorinated dibenzo-*p*-dioxin(s)
PCDD/F(s)	polychlorinated dibenzo-*p*-dioxin(s) and polychlorinated dibenzofuran(s); commonly known as dioxins
PCDF(s)	polychlorinated dibenzofurans(s)
PCP	pentachlorophenol
PeCDD	pentachlorinated dibenzo-*p*-dioxin
PeCDF	pentachlorinated dibenzofuran
pg	picogram (1 pg = 0.001 ng)
PMF	positive matrix factorization
POM	polyoxymethylene (material used for passive sampling)
POP(s)	persistent organic pollutant(s)
PUF	polyurethane foam

PVC	polyvinyl chloride
SIA	stable isotope analysis
SPM	settling (or suspended) particulate matter
TCDD	tetrachlorinated dibenzo-*p*-dioxin
TCDF	tetrachlorinated dibenzofuran
TEF	toxic equivalency factor; factor indicating the estimated toxic potency of an individual DD, DF or dioxin-like compound as compared to 2,3,7,8-TCDD. Note that many different sets of TEFs have been proposed since the 1980s.
TEQ	toxic equivalent; concept developed to express the overall toxicity of a mixture of dioxins and dioxin-like compounds as a single value. The TEQ value is obtained by adding the product of the concentration or amount and the TEF for each toxic compound.
TOC	total organic carbon
WHO	World Health Organization
WHO-TEF	toxic equivalency factor according to WHO; two sets issued, in 1998 and 2005
WHO-TEQ	toxic equivalents according to one of the WHO-TEF sets
w.w.	wet weight
µg	microgram (1 µg = 0.001 mg)
ΣPCB_7	sum of the PCB congeners 28, 52, 101, 118, 138, 153 and 180
2,3,7,8-chlorinated dioxins	the 17 congeners with chlorines at position 2,3,7 and 8 (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 1,2,3,4,7,8-HxCDD, 1,2,3,6,7,8-HxCDD, 1,2,3,7,8,9-HxCDD, 1,2,3,4,6,7,8-HpCDD, OCDD, 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF, 2,3,4,7,8- PeCDF, 1,2,3,4,7,8-HxCDF, 1,2,3,6,7,8-HxCDF, 1,2,3,7,8,9-HxCDF, 2,3,4,6,7,8-HxCDF, 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF)

4 Introduction

4.1 Background

The Swedish Environmental Protection Agency (Swedish EPA) commissioned a consortium of researchers to *i*) investigate spatial and temporal trends of persistent organic pollutants (POPs) in Baltic biota and *ii*) trace the sources of these pollutants to the atmosphere. Although the original idea was to investigate a wide range of POPs, it was realised that to successfully reach the aim of the project it would only be possible to focus on a limited subset of POPs. This Swedish EPA project (BalticPOPs) therefore focuses mainly on the polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs; collectively termed PCDD/F or "dioxins"), which are of particular concern in the Baltic region. Additional pollutants are included in some of the project's components, but the main focus throughout is on dioxins.

The BalticPOPs project was undertaken between December 2009 and August 2012 by a research consortium consisting of: Karin Wiberg (project coordinator; Swedish University of Agricultural Sciences and previously Umeå University); Kristina L. Sundqvist and Anteneh T. Assefa (Umeå University); Ian T. Cousins, Jana Johansson, Gerard Cornelissen, Michael S. McLachlan, Ulla Sellström, and Anna Sobek (Stockholm University); Aroha Miller, Jenny Hedman and Anders Bignert (Swedish Museum of Natural History); Heikki Peltonen (Finnish Environment Institute, SYKE); Mikko Kiljunen (University of Jyväskylä, Finland); Victor Shatalov (Meteorological Synthesizing Centre-East (MSC-East), EMEP, Moscow, Russia); and Ingemar Cato (Geological Survey of Sweden and University of Gothenburg). Eva-Maria Diehl (Umeå University) was the project's communication officer.

The BalticPOPs project follows on from a recent Swedish EPA project (Report 5912), which evaluated the mass flows of dioxins, polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB) to the Baltic Sea as a whole (Wiberg *et al.* 2009). The conclusion of this previous work was that atmospheric deposition is the primary external source of these POPs, and that a reduction of atmospheric levels would expedite the decline of POP levels in the water. The current project builds on the results of this previous study, but the scope is directed towards understanding POP levels in Baltic biota and the atmospheric sources of these contaminants. As mentioned previously, there is a strong focus on dioxins in this project. The aim of the BalticPOPs project was to answer the following questions:

i) Why are dioxin levels in fatty fish from the Baltic Sea so high?
ii) What are the main sources of the dioxins in Baltic herring?
iii) What are the main sources of dioxins and other POPs in Baltic air?
iv) Are these sources (*ii* and *iii*) the result of on-going primary emissions or of recirculation of chemical stored in environmental reservoirs?
v) Are these sources (*ii* and *iii*) mainly national or international?
vi) How has the pollution situation changed over time?
vii) Assuming dioxin inputs to the Baltic Sea are reduced – how long will it take until the concentrations in herring decrease?
viii) Are there cost-effective measures that can reduce dioxin levels in Baltic herring below the regulatory thresholds within a relatively short time period?

These questions are answered in turn in Chapter 12.

It is worth providing some background information to explain why the above listed research questions were considered to be important. Previous research had shown that Baltic Sea fish were considerably more contaminated with dioxins compared to nearby seas, and the reasons for this were not fully elucidated (Wiberg *et al.* 2009). The toxic equivalent (TEQ) levels of dioxins in Baltic fatty fish still exceeded the European Union (EU) limits for food and feed, restricting the fish to domestic markets only. It was known that levels of dioxins in herring have generally declined since the 1980s, but levels appeared to have stopped declining and have remained above EU threshold values in the last decade (Wiberg *et al.* 2009). Prior to the BalticPOPs project, little was known about the spatial variation of dioxins in herring within and between Baltic basins, the short-term seasonal variation in dioxin levels in herring and the temporal trends of dioxins in herring in the last decade. These different pieces of data are vital for properly interpreting the spatial and temporal trends of dioxins in herring and reliably determining whether the pollution situation is improving, or if it is static or even worsening.

Previous research pointed towards the dominant importance of the atmosphere as a dioxin source to the Baltic Sea (Armitage *et al.* 2009, Sundqvist 2009, Sundqvist *et al.* 2010, Verta *et al.* 2007, Wiberg *et al.* 2009). The contribution of coastal sources to the total dioxin inventories in the Baltic Sea was estimated to be small compared to atmospheric deposition (Wiberg *et al.* 2009). It was hypothesised that highly contaminated sediments mainly occurred in coastal regions near industrialised/urbanised areas (Sundqvist *et al.* 2009a, Sundqvist *et al.* 2009b, Verta *et al.* 2007) and that the pollution problem is largely a local one. Coastal sources were therefore expected to have important local impacts on Baltic biota that remain in close proximity to a contaminated area during their lifetime.

EMEP modelling performed prior to the BalticPOPs project suggested a decrease of ~60% in atmospheric deposition to the Baltic Sea from 1990 to 2006 (Gusev 2008). Previous modelling work also predicted that the declines in atmospheric deposition would lead to declines in levels of dioxins in the abiotic environment and a similar downward trend in fatty fish such as herring (Armitage *et al.* 2009, Wiberg *et al.* 2009). Little was known, however, about the temporal trends of dioxins in the different abiotic components of the Baltic Sea sub-basins and it was previously noted (Armitage *et al.* 2009, Wiberg *et al.* 2009) that the rates of declines in the abiotic environment are critical in determining the rates of decline in biota. A further complication is that although there may have been long-term declines in abiotic concentrations, including dissolved water concentrations in Baltic sub-basins, the levels in biota may not have followed this trend due to changes in ecological factors (e.g., the observed declining growth rates of herring; Peltonen *et al.* 2007).

Before the BalticPOPs project started, there was good understanding of the bioaccumulation of dioxins. For example, Peltonen *et al.* (2007) predicted the dioxin concentrations in herring of various ages from the Bothnian Sea using a bioenergetics accumulation model and obtained very good agreement with measured data on a TEQ-basis. There was thus no need to further improve understanding of these processes. Instead, there was a need for studying how current sources, such as contaminated sediment hotspots and atmospheric emissions, affect levels in fish, and if emission reductions have led to reductions in fish levels. Given that levels of dioxins in fatty fish still exceeded EU threshold values, it was also important to determine the best management strategy to ensure future reductions in fish levels.

As already mentioned, previous work demonstrated that atmospheric deposition is the dominant source of dioxins to the Baltic Sea. We knew little, however, about the origin of the dioxins in atmospheric deposition. In our previous work (Sellström *et al.* 2009, Wiberg *et al.* 2009), we aimed to identify the compass sectors from which the dioxins in ambient air over the Baltic Sea originated, using air mass back trajectory analysis on measurements undertaken in this region during the winter half of the year (November 2006 to April 2007). Air masses originating from the European continent and the former Soviet Union (the south-southwest, south-southeast and east compass sectors) were shown to represent

65% of the PCDD contamination and 75% of the PCDF contamination over the Baltic Sea (TEQ-basis; Sellström *et al.* 2009). Although this earlier work was useful in identifying the main geographical regions in Europe contributing to dioxins in atmospheric deposition over the Baltic Sea, we did not know if current source emission estimates of dioxins in the European region could account for dioxin levels in the air and deposition. If the main source areas and source types could be reliably identified, then it would facilitate effective management to reduce levels of dioxins in Baltic atmospheric deposition and thus in Baltic fatty fish.

4.2 Organization of the BalticPOPs project

The Baltic Sea pollution problem is linked to a multitude of current and historical activities, and the processes governing POP fate and bioaccumulation are complex. To manage the POP pollution problem, including the dioxin problem which is the focus of this project, a better understanding of the complex interactions of the different processes is required. We therefore implemented a multidisciplinary approach, with experts from many research fields. The work was organised into three work packages (WPs):

- WP1 - Why are dioxin levels of fatty fish from the Baltic Sea so high?
- WP2 - Inventory of atmospheric emission sources for dioxins and other POPs.
- WP3 - Synthesis of the results of WP1 and WP2, including other knowledge.

These three work packages are briefly summarised below:

WP1: WHY ARE DIOXIN LEVELS OF FATTY FISH FROM THE BALTIC SEA SO HIGH?

Prior to of the BalticPOPs project, we knew the following:

- The dioxin levels in Baltic fatty fish were high in relation to levels in nearby seas. Levels of dioxins in herring had remained above the EU threshold values for food and feed despite long-term declines in atmospheric deposition.
- A spatial and seasonal variation of dioxin levels in Baltic herring had been observed, but more data were required for a clearer picture of spatiotemporal trends.
- The relationships between dioxin levels in Baltic herring and corresponding levels in water could be described using our existing understanding of bioaccumulation and bioenergetics.

The following research questions were unresolved prior to the BalticPOPs project:

- Is it possible to describe and interpret the between-basin and within-basin dioxin levels of Baltic biota?
- Is it possible to describe the seasonal variability in dioxin levels in herring?
- How bioavailable are dioxins that reach the sea attached to atmospheric particles?
- How has the dioxin contamination in the abiotic Baltic media changed over the last 20 years and how does this relate to the time trends of dioxin levels in emissions, atmospheric levels and herring?

These questions were addressed in four interrelated project tasks (1A-1D):

- Task 1A: Understanding the spatial variation of dioxin levels in the Baltic herring
- Task 1B: Understanding the seasonal variation and time trends of dioxin levels in Baltic herring
- Task 1C: Are dioxins that reach the Baltic Sea via the atmosphere bioavailable?
- Task 1D: How has the pollution situation in the Baltic region changed over time?

The results of these research tasks are reported in chapters 5, 6, 7, 8 and 9.

WP2: INVENTORY OF ATMOSPHERIC EMISSION SOURCES FOR DIOXINS AND OTHER POPs

Prior to the BalticPOPs project, we knew the following:

- Atmospheric deposition was estimated to be the most important external source of dioxins and some other POPs to the Baltic Sea.

The following research questions were unresolved prior to the BalticPOPs project:

- What are the main emission sources contributing to the atmospheric deposition of dioxins and other POPs to the Baltic Sea?
- Do existing dioxin and other POP emission inventories account for all major sources to atmospheric deposition to the Baltic Sea?
- What fraction of the atmospheric deposition of dioxins and other POPs to the Baltic Sea originates from emissions in Sweden?
- How important is volatilization of dioxins from soil as a (secondary) source of dioxins to atmospheric deposition to the Baltic Sea?

These questions were addressed in two interrelated project tasks (2A and 2B):

- Task 2A: Atmospheric emission and deposition of dioxins
- Task 2B: Tracing atmospheric sources for dioxins and other POPs

The results of these research tasks are reported in chapters 10 and 11.

WP3: SYNTHESIS

In WP3, previous and new knowledge gained from WP1 and WP2 was combined and evaluated in a system synthesis. The aim of the work was to employ the multimedia fate and transport model POPCYCLING-Baltic as a knowledge synthesizing tool, building on the work and experience gained in a recent Swedish EPA project (Report 5912; Wiberg *et al.* 2009). In this previous study, POPCYCLING-Baltic was used to calculate mass balances for dioxins and other selected POPs in sub-basins of the Baltic Sea. A bioaccumulation model was used to predict the concentrations in herring from the output from POPCYCLING-Baltic. Some potential limitations in the models were identified and addressed in the research undertaken in WP1 and WP2. The various research tasks that were addressed as part of the project synthesis in WP3 were as follows:

- A literature search for new research results of relevance was conducted. This information was incorporated in the results and discussion of many of the chapters.
- POPCYCLING-Baltic was used to determine if volatilization/resuspension is an important source of dioxins to atmospheric deposition to the Baltic Sea.
- The information from the review of sediment burial rates in Task 1D was used to check the parameterization of the POPCYCLING-Baltic model.
- The predicted concentrations in surface sediment over time were compared with the sediment core data from Task 1D.
- It was determined if riverine inputs and land-based industrial inputs of dioxins to the Baltic Sea were underestimated in previous modelling work.
- Recommendations were developed for emission reduction strategies.

- A proposed monitoring strategy that can be applied to follow up different emission reduction strategies was developed.
- Recommendations were developed, based on the experience in the Baltic Sea, on how environmental contamination with dioxins and other POPs could be evaluated in an international context.

The results of these synthesis tasks are reported mainly in Chapter 12.

5 Long-term temporal trends in dioxins and dioxin-like PCBs in herring within the Baltic Sea

5.1 Introduction

Levels of dioxins in fatty fish from the Gulf of Bothnia, the two northernmost sub-basins of the Baltic Sea, still occasionally exceed threshold values for human consumption within EU countries. Before the mid-80s, a clear decrease in dioxins was observed both in guillemot eggs and in herring from Ängskärsklubb in the southern Bothnian Sea. Long-term national monitoring of dioxins within the national monitoring programmes has shown that the decrease of dioxin concentrations in Baltic herring has slowed over the last 20 years, and in guillemot eggs over the last 25 years, in contrast to other organic contaminants that show continuous decreases, e.g., PCBs (Bignert *et al.* 2011). In the present report, some years of dioxin analyses performed using a simplified method have been excluded and the time-series are not altogether comparable with the time-series reports from the national monitoring.

During the last three decades, substantial decreases in herring weight-at-age have occurred in the Baltic Sea (Cardinale and Arrhenius 2000, ICES 2011, Persson 2010, Vuorinen *et al.* 2004). A number of hypotheses have been given to explain this decreasing herring weight-at-age. In particular the crash in cod stocks caused a decrease in predation pressure on herring and sprat (Cardinale and Arrhenius 2000, Casini *et al.* 2010, Flinkman *et al.* 1998, Mollmann *et al.* 2004, Peltonen *et al.* 2007), resulting in a population explosion of sprat in particular and increased competition for food between and within sprat and herring stocks (Flinkman *et al.* 1998). This phenomenon has also been attributed to lower salinity due to greater fresh water input in this area affecting for instance zooplankton composition and abundance (Flinkman *et al.* 1998), and thus herring diet. Periods of high growth are hypothesized to cause a corresponding decrease in dioxin concentrations (w.w.) in fish, and vice versa. This kind of phenomenon is known as growth dilution (Berntssen *et al.* 2005).

Here, we examine if the observed temporal trends in dioxin concentrations in herring can be attributed to *i*) fish biological traits, such as length, weight, age, and lipid content; *ii*) a reduced growth rate of herring, which could have masked the impacts of dioxin mitigation measures; and/or *iii*) shifts in herring diet.

5.2 Methods

5.2.1 Sampling sites and matrices

Baltic herring (*Clupea harengus*) have been collected in a national monitoring program for more than 20 years at four sites along the Swedish coast – Harufjärden in the Bothnian Bay, Ängskärsklubb in the Bothnian Sea, Utlängan in the southern Baltic Proper, and Fladen in the Kattegat (Table 1, Figure 1). All sites are reference sites, with no known local source points; however, several important paper/pulp mills are located along the coast close to Gävle, near Ängskärsklubb. Near Harufjärden, there is considerable fresh water input from streams and rivers. All data presented here originate from samples collected in autumn (September-December), unless otherwise stated. The number of herrings sampled has varied over the years. In some years, 7-15 individuals were pooled at each site, while in other years 8-10 individual fish were analysed from each site. Geometric means have been calculated to give a single concentration for each congener in each year for each site.

Biological measurements were taken from all fish used for analysis – age (determined via scale reading), weight, total fish length, and reproductive phase. Fishing date was recorded each year, and lipid content was determined. To minimise between-year variation in dioxin concentrations due to differences in gender and age of the sampled herring, and as sexual maturation occurs anywhere between 2 and 4 years of age depending on site, female herring of 2-5 years of age were selected for analysis as often as possible. At Ängskärsklubb, mean herring age from pooled samples were within this age range in 12 of the 26 years sampled; mean herring age exceeded 5 years in the other years. Poor age determination of herring from this site, in particular in earlier years of sampling, may be partly responsible for the overall higher herring age at Ängskärsklubb. At both Harufjärden and Fladen, herring age was always within the 2-5 year range, while at Utlängan, herring age was within the 2-5 year range in 18 of 20 years sampled.

To minimise the between-year and spatial variation in concentrations of lipid-soluble contaminants due to differences in the amount of subcutaneous fat, pure muscle tissue without subcutaneous fat was analysed. Dorso-lateral herring muscle tissue of approximately 10 g per specimen or pool was removed under strict laboratory protocols, and sent for analysis. Generally, if the skin is included the lipid content increases by a factor of 1.64 compared to pure muscle (Bignert *et al.* 2005). However, this ratio is not fixed and can vary over time. Within the current research, temporal changes in this fat ratio have not been analysed.

Table 1. Sites, season and years when sampling occurred. For site location, see Figure 1.

Site, location	**Season**	**Years sampled (Missing years)**
Harufjärden, Bothnian Bay	Autumn	1990, (1991), 1992-1995, (1996-2000), 2001-2009
Ängskärsklubb, Bothnian Sea	Autumn	1979-1987, (1988),1989, (1990), 1991-1993, (1994), 1995-2003, (2004), 2005-2007, (2008), 2009
Utlängan, southern Baltic Proper	Autumn	1988, (1989), 1990, (1991), 1992-1995, (1996-2000), 2001-2009
Fladen, Kattegat	Autumn	1990, (1991), 1992-1995, (1996-2000), 2001-2009

5.2.2 Dioxin and dl-PCB analytical methods

The analyses of dioxins and dl-PCBs were carried out at the Department of Chemistry, Umeå University. The extraction method is described by Wiberg *et al.* (1998), the clean-up method by Danielsson *et al.* (2005), and the instrumental analysis (high resolution gas chromatography/high resolution mass spectrometry; HRGC/HRMS) by Liljelind *et al.* (2003). The laboratory is accredited for these analyses, participates in the annual FOOD intercalibration rounds, and includes laboratory reference material (salmon tissue) with each set of samples.

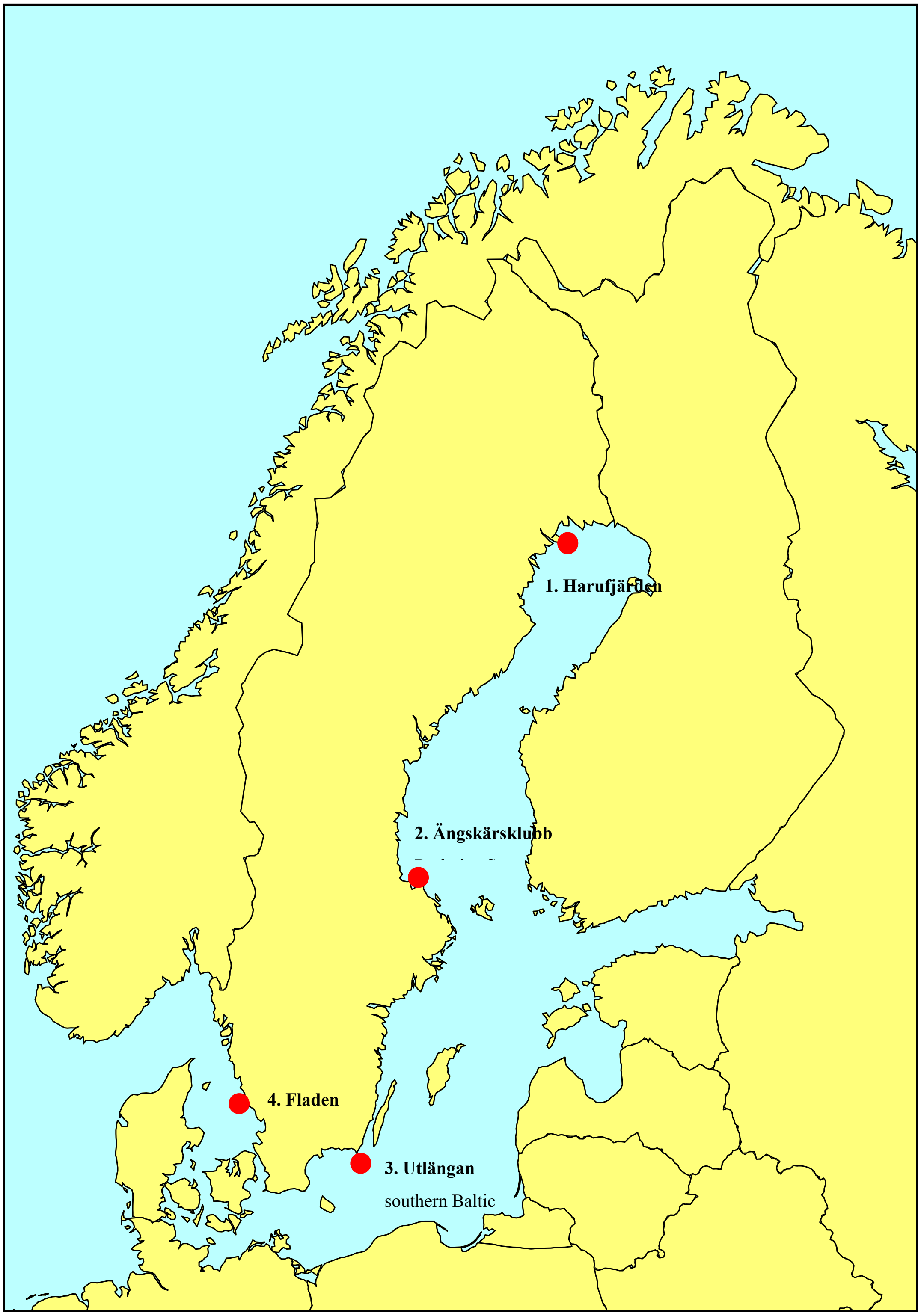


Figure 1. Map of Scandinavia showing the Baltic Sea and surrounding countries. Red dots indicate the location of the four sites of the national monitoring sampling: From top of map – 1. Harufjärden (Bothnian Bay), 2. Ängskärsklubb (Bothnian Sea), 3. Utlängan (southern Baltic Proper), and 4. Fladen (Kattegat).

5.2.3 Calculation of TEQs

TEQs were calculated using the individual congener concentrations and the WHO 2005 TEFs published by the World Health Organisation (Van den Berg *et al.* 2006). Unless otherwise stated, TEQ values referred to are the sum of the TEQ concentrations for each year i.e., the TEQ values for each individual congener summed.

5.2.4 Statistical treatment of biological variables and contaminant data

Data quality control was conducted for all sites. Any values below the limit of quantification (LOQ) were replaced with LOQ divided by the square root of two. Herring from Ängskärsklubb were generally older than at the other three sites. However, age-adjusted log-linear regression values showed a poorer relationship compared to unadjusted log-linear regression values for all of the examined data. Therefore, age-adjusted data were not used in the following analyses. Correlation coefficients between $\text{TEQ}_{\text{PCDD/F + dl-PCB}}$ values and biological variables were calculated and p values reported if <0.05.

Time trends in TEQ values on a lipid weight (l.w.) and wet weight (w.w.) basis for each site are shown using scatterplots, with log-linear regression indicating relationships between concentration and time. To assess whether the temporal trends for TEQ or dominant congener (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, CB105, CB 118, absolute basis, l.w. only) concentrations were statistically significant at $p<0.05$, Mann-Kendall trend tests were used (Statistica v10). This is a non-parametric alternative of the Pearson’s correlation coefficient. It is robust against outliers and does not rely on assumptions of the distributions of x and y. Mann-Kendall trend tests were conducted for each site for the entire time series.

5.2.5 Stable isotope analysis to investigate potential shifts in herring diet

Muscle samples, i.e., no skin or subcutaneous fat included, were taken from the same individuals/ pooled herring samples that were analysed each year for dioxins. Stable isotope analysis (SIA) was performed at the University of Jyväskylä, Finland, using a Carlo Erba Flash EA1112 elemental analyser connected to a mass spectrometer (CF-IRMS), via methods outlined in Kiljunen *et al.* (2006). All samples were freeze-dried to a constant weight and ground to a fine powder before analysis. The international standards of Vienna Pee Dee belemnite (for carbon) and atmospheric N_2 (for nitrogen) were used as reference materials, and dried pike muscle was used as an internal working standard. Results are expressed using the δ notation as parts per thousand (‰) difference from the international standards. Lipid normalisation was carried out for the $\delta^{13}C$ values using calculations presented in Kiljunen *et al.* (2006), as lipids are known to be ^{13}C depleted relative to other major tissues (Bodin *et al.* 2007, Ehrich *et al.* 2011). No baseline data were available for comparison. Baseline data refers to stable isotope ratios for the basal resources within a food web e.g., planktonic or benthic primary consumers, which can vary over time (Solomon *et al.* 2008) and thus affect the stable isotope ratios of organisms feeding at higher trophic levels within the same food web. These results should therefore be interpreted with caution.

5.2.6 Modelling to investigate the impacts of decreased herring growth rates

Modelling of the feeding rates and the associated bioaccumulation of persistent pollutants was applied to explore the hypothesis that the reduced growth rate of herring (e.g., ICES, 2011) has masked the impacts of dioxin mitigation measures. The bioenergetics bioaccumulation model is a modified version (Peltonen *et al.* 2007) of the Hanson *et al.* (1997) model, which has previously been evaluated for Baltic Sea herring (Kiljunen *et al.* 2007, Peltonen *et al.* 2007). The mode parameter set for the Baltic herring was from Rudstam (1988) using modifications described by Peltonen *et al.* (2007). Data on dynamic shifts in weight-at-age of the Baltic Proper and the Bothnian Sea herring were from the material which national fisheries agencies collect from the commercial herring catches and the Baltic Sea

Fishery Assessment Working Group annually compiles (ICES 2011). The data on temperature regime was from the oceanographic database of the ICES.

5.3 Results and discussion

The temporal data series begin in different years for the different sites. At Ängskärsklubb, retrospective analyses were carried out on freeze-stored fish from 1979 and onwards; at Fladen and Harufjärden, data collection began in 1990; and at Utlängan, in 1988 (Table 1). All temporal series for all sites are presented until 2009. Gaps are present between 1996 and 2000 for Fladen, Harufjärden and Utlängan due to the fact that a simplified, non-congener specific analytical method was used during these years. All results are presented on a l.w. basis, unless otherwise stated.

5.3.1 Biological variables

Herring age ranged from 2 to 3 years at Fladen, 3 to 4 years at Harufjärden, 3 to 7 years at Utlängan, and 3 to 9 years at Ängskärsklubb. Herring age increased significantly over time at Harufjärden (*n*=20, *d.f.*=18, *p*<0.05) and decreased significantly over time at Fladen (*n*=20, *d.f.*=18, *p*<0.05). Fish length across all four sites ranged from 14.2 to 22.9 cm and fish weight across all four sites ranged from 20.8 to 91.9 g. Herring from Fladen were the largest, and herring from Harufjärden the smallest. Lipid content decreased significantly over time at both Harufjärden and Utlängan (*n*=20, *d.f.*=18, *p*<0.05; *n*=21, *d.f.*=19, *p*<0.05, respectively), whereas at Fladen a significant increase was seen over time (*n*=20, *d.f.*=18, *p*<0.05).

To explore the relationship between each biological variable and the $TEQ_{PCDD/F + dl\text{-}PCB}$ values at each site, log-linear regression analyses were conducted (Table 2). For the whole time series, the strongest overall relationship was seen between lipid content and $TEQ_{PCDD/F + dl\text{-}PCB}$ value at Fladen. This was a significant negative relationship. At the other three sites, age showed the strongest relationship (all positive, although only significant at Harufjärden and Ängskärsklubb). However, most of the relationships between any one biological variable and $TEQ_{PCDD/F + dl\text{-}PCB}$ values were non-significant (Table 2).

5.3.2 Congener patterns

The congener patterns for PCDDs, PCDFs and dl-PCBs are similar between each site. The two most dominant PCDD congeners are 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD for the majority of the time series, both on a TEQ and an absolute concentration basis. For the PCDFs, 2,3,7,8-TCDF and 2,3,4,7,8-PeCDF are the dominant congeners for all sites on an absolute concentration basis, whereas on a TEQ basis, 2,3,4,7,8-PeCDF is dominant. For the dl-PCBs, CB105 and CB118 are the dominant congeners at all sites on an absolute concentration basis. However, CB126 is the dominant congener on a TEQ basis

Table 2. Regression (log-linear) value (r^2) for each biological variable and for fishing date, with the summed TEQ$_{PCDD/F+dl\text{-}PCB}$ concentration for each site. Significant correlations are indicated by * ($p<0.05$).

	***n* (years)**	**Fat %**	**Weight**	**Length**	**Fishing date**	**Reproductive phase[1]**	**Age**
Harufjärden	18	0.05	0.09	0.36*	0.09	0.02	0.55*
Ängskärsklubb	26	0.01	0.06	0.05	0.05	0.10	0.20* 0.53*,[2]
Utlängan	18	0.25*	0.17*	0.27*	0.03	0.04	0.29
Fladen	18	0.47*	0.12	0.10	0.05	0.03	0.03

[1] Herring reproductive phase is equivalent to no detectable development (1), developing reproductive follicle (2), mature reproductive follicle (3), post-spawning reproductive follicle (4), and resorbing reproductive follicle (5) (Elston *et al.* 1997). Herring reproductive phase varied between sites.

[2] Log-linear regression for the first 10 years (1979 - 1988) of age data at Ängskärsklubb.

Over time, a general decrease is seen for TEQ$_{PCDD}$, TEQ$_{PCDF}$ and TEQ$_{dl\text{-}PCB}$. This trend is seen most clearly at Ängskärsklubb, most likely because this station has been monitored longer (since the late 1970s). In almost every year at every site, PCDDs contributed the least to total TEQ. In some years and sites TEQ$_{PCDD}$ contribute less than 20% to total TEQ. TEQ$_{PCDF}$ make up the greatest relative contribution of dioxins at Ängskärsklubb since 1996, while pre-1996, TEQ$_{dl\text{-}PCB}$ dominated. At Harufjärden, TEQ$_{PCDF}$ and TEQ$_{dl\text{-}PCB}$ alternate in dominating contribution from 2001 onwards. TEQ$_{dl\text{-}PCB}$ contributed the most in every year at Utlängan and Fladen, often between 40 and 60% of total toxicity. Over time, congener patterns in herring were similar at each site, indicating similar exposure sources.

Certain congeners dominating over others can be due to a number of reasons, and may include source strength, differences in mobility and elimination rates for different congeners (Aberg *et al.* 2010, Assefa *et al.* 2011, Muir and Yarechewski 1988), distance from source points (Parmanne *et al.* 2006), differences in exposure and/or bioaccumulation of different congeners, related to differences in herring diet between areas (Kiviranta *et al.* 2003).

5.3.3 Temporal trends in total TEQ and in dominant congener concentrations

Below, graphs showing temporal trends in TEQ values are presented on a l.w. basis. For comparison, graphs for TEQ$_{PCDD/F}$ values are also presented on a w.w. basis for each site. Temporal trends of dominant congeners are not presented in figures.

At Harufjärden, only 2,3,7,8-TCDD and TEQ$_{PCDD}$ showed a significant decreasing trend over time (Figure 2a, l.w.). The other dominant congeners (absolute concentration) and TEQ concentrations did not show any significant trends (Figure 2b-e, l.w.). Similarly, on a wet weight basis TEQ$_{PCDD}$ was the only TEQ value to show any significant trend, while TEQ$_{PCDD/F}$ did not show any significant trend (Figure 2f). Over time, herring age increased significantly and lipid content decreased significantly at this site. These are two biological parameters that would have a strong influence on dioxin concentrations in herring.

At Ängskärsklubb, all six dominant congeners (2,3,7,8-TCDD, 1,2,3,7,8-PeCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, CB105, CB118; absolute concentration, l.w.) showed significant decreases when the whole time series was examined. A significant decrease over the whole time series was also observed for all TEQ values, both on a l.w. and w.w. basis (Figure 3a-f). None of the biological parameters measured from herring at this site showed any change over time. Dioxin concentrations are slightly elevated at this site compared to the other sites, which is probably connected to the higher herring age observed at this site, among other factors.

At Utlängan, only two dominant congeners showed significant decreases over time - 2,3,7,8-TCDD and 1,2,3,7,8-PeCDD. However, TEQ_{PCDD}, $TEQ_{dl\text{-}PCB}$ and $TEQ_{PCDD/F+dl\text{-}PCB}$ all showed significant decreases over time (4a, c, e; l.w.) while TEQ_{PCDF}, and the $TEQ_{PCDD/F}$ on a l.w. or w.w. basis did not (Figure 4b, d, f). A particularly high concentration was measured in 1988 for PCDDs and PCDFs (Figure 4a, b, d, f); however, examination of the data with this value removed did not change the outcome of the regression. CB105 was close to a significant decrease (p=0.051). The significant decrease seen for $TEQ_{dl\text{-}PCB}$ was largely caused by significant decreases in the non-dominant congeners.

At Fladen, as at Ängskärsklubb, all dominant congeners showed significant decreases in concentration (l.w.) over the whole time series. This was also the case for TEQ_{PCDD}, TEQ_{PCDF}, $TEQ_{PCDD/F}$ and $TEQ_{dl\text{-}PCB}$ (Figure 5a-d), whereas $TEQ_{PCDD/F\ +\ dl\text{-}PCB}$ (Figure 5e) did not show a significant decreasing trend. This lack of significant trend is most likely because dl-PCBs were not analysed in 1990 at this site, and therefore, the summed TEQ value for this year is low. By contrast, no TEQ values showed any significant changes over time on a wet weight basis ($TEQ_{PCDD/F}$, Figure 5f). Since dioxins partition to lipids in fish and the lipid content of herring at Fladen increased significantly over time, it is not surprising that the dioxin concentrations on a w.w. basis did not decrease over time at this site.

Overall, PCDDs showed significant decreases at all sites (both l.w. and w.w., except for w.w. in Fladen). PCDFs and dl-PCBs showed significant decreases at Ängskärsklubb, Utlängan and Fladen. However, some of these decreases were only seen on a l.w. or on a w.w. basis, not both. Consistency in the decreases is generally lacking, with some TEQ values decreasing at all sites (TEQ_{PCDD}) and others decreasing at only some sites, and varying depending on whether they are on l.w. or w.w. basis. Dioxin concentrations are not showing such large decreases in recent years as they were at the beginning of the monitoring period. Changes in biological parameters, such as age, lipid content, and slower growth rate (see section 5.3.5), are playing a role in the lack of decreases, and where decreases have slowed in recent years.

Absolute concentrations (l.w.) of PCDD/Fs, dl-PCBs, and all TEQ concentrations at Ängskärsklubb were considerably higher than at the other three sites, especially in the earlier years of monitoring. In more recent years, e.g., 2005 and later, dioxin concentrations at Ängskärsklubb have become more in line with concentrations observed in herring at Harufjärden and Utlängan, although continue to be higher than concentrations observed in herring from Fladen. A number of reasons, for instance higher average herring age and emissions from local industry, probably contributed to the high dioxin concentrations seen in herring at Ängskärsklubb in the early years of monitoring, while emission reductions undoubtedly contributed to the observed concentration decreases. Several important paper/pulp mills are located along the coast in this area (close to Gävle). Therefore, the higher dioxin concentrations in herring observed at Ängskärsklubb may be partially explained by local environmental impacts caused by industrial usage and discharge at the coast near Ängskärsklubb (Gävle) compared to the other three sites. However, the higher age of herring from this site, in particular in the earlier years of monitoring (Bignert et al. 2011; this report), may also be a reason. Increasing lipid content in herring in the last 6 – 7 years at Fladen, younger age of herring, and overall efforts to reduce dioxin emissions seem to be the most likely explanations for the decreases seen here on a l.w. basis. The lack of decreases seen on a w.w. basis is probably due to changes in lipid content over time.

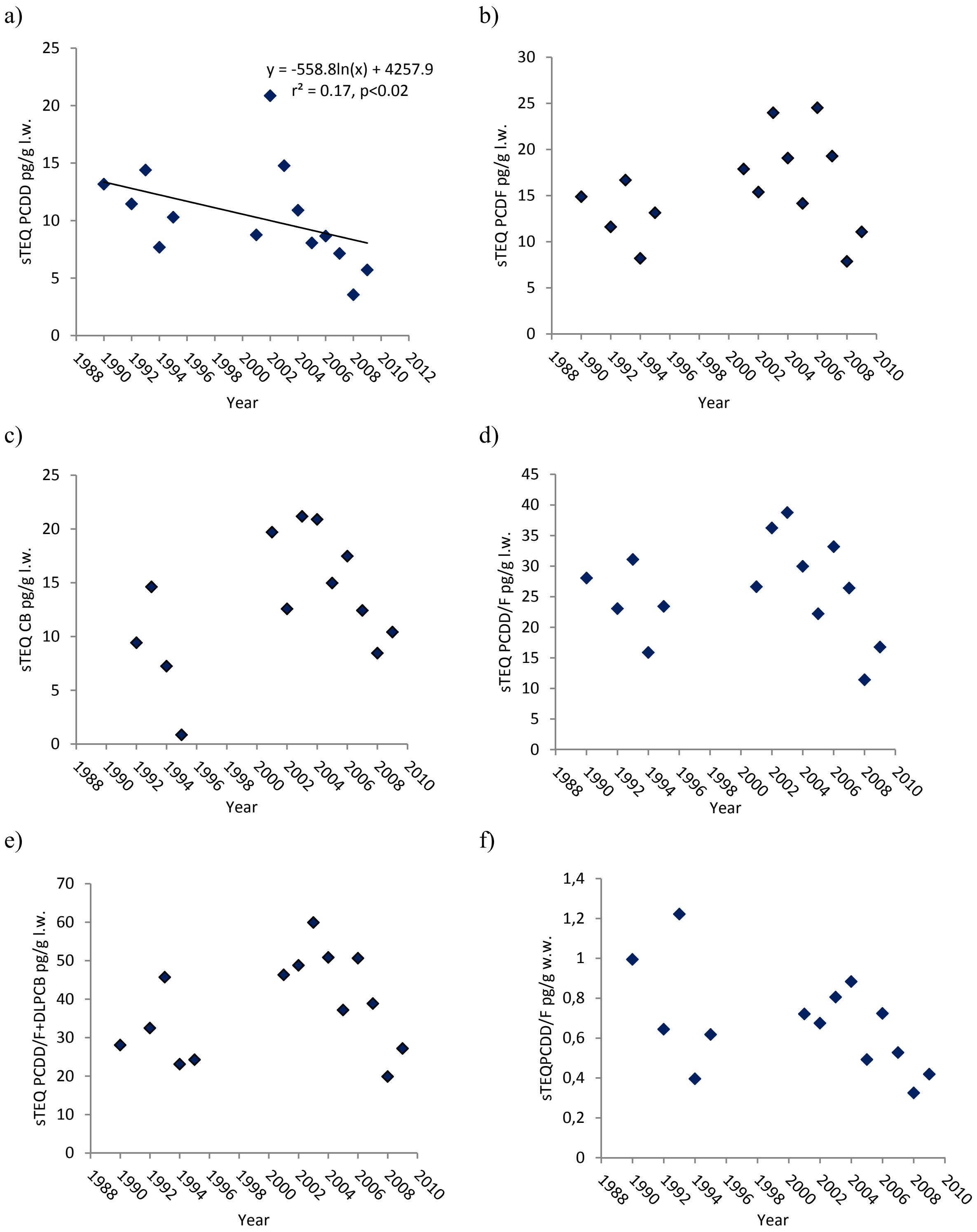


Figure 2. TEQ concentrations on a l.w. basis for (a) PCDDs, (b) PCDFs, (c) dl-PCBs, (d) PCDD/Fs, (e) PCDD/Fs + dl-PCBs, and on a w.w. basis for (f) PCDD/Fs for the whole time series at Harufjärden. Log-linear regression equation, r^2 value and p values are shown only where there is a significant change (p<0.05) over time.

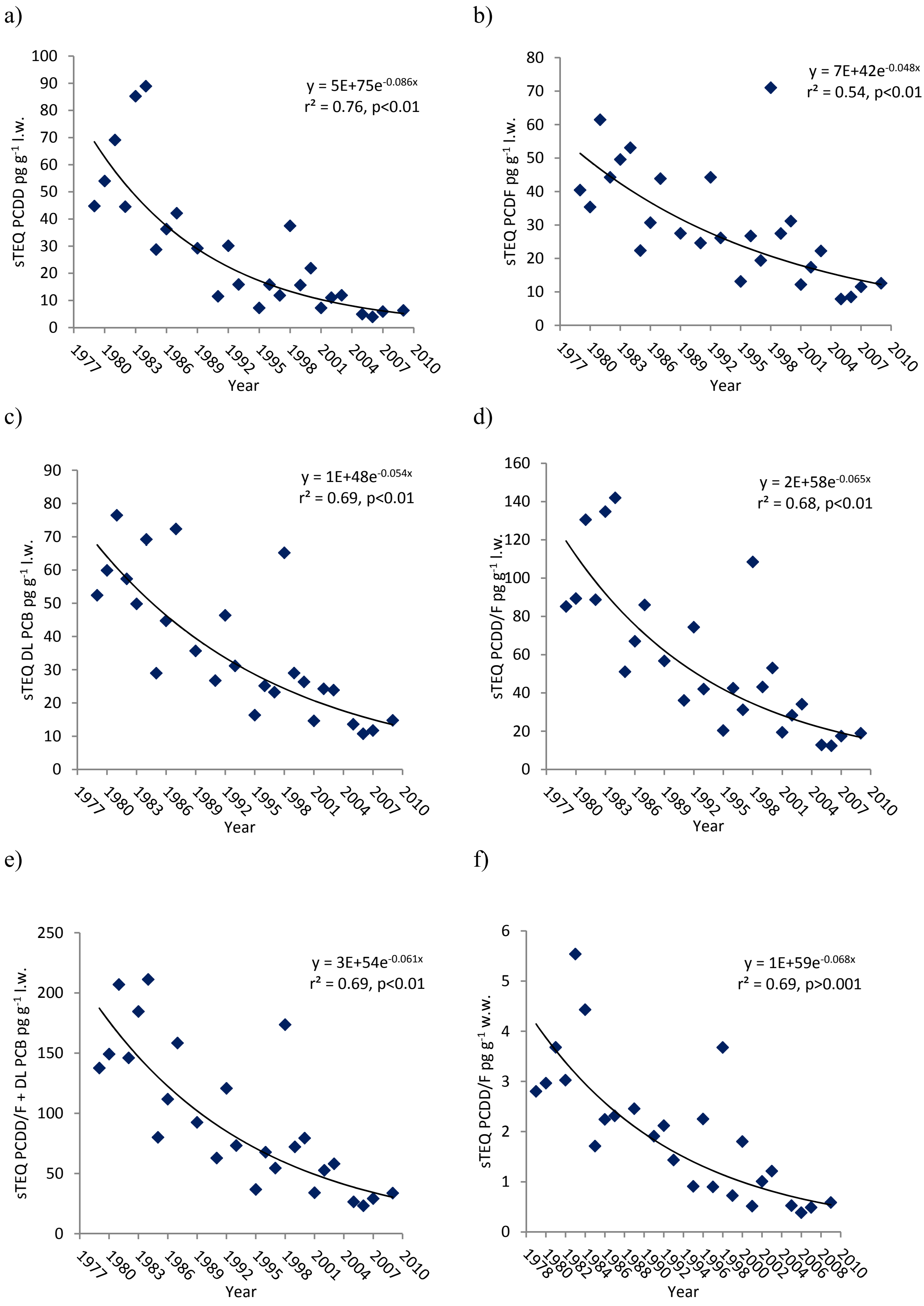


Figure 3. TEQ concentrations on a l.w. basis for (a) PCDDs, (b) PCDFs, (c) dl-PCBs, (d) PCDD/Fs, (e) PCDD/Fs + dl-PCBs, and on a w.w. basis for (f) PCDD/Fs for the whole time series at Ängskärsklubb. Log-linear regression equation, r^2 and p values are shown only when there is a significant change ($p<0.05$) over time.

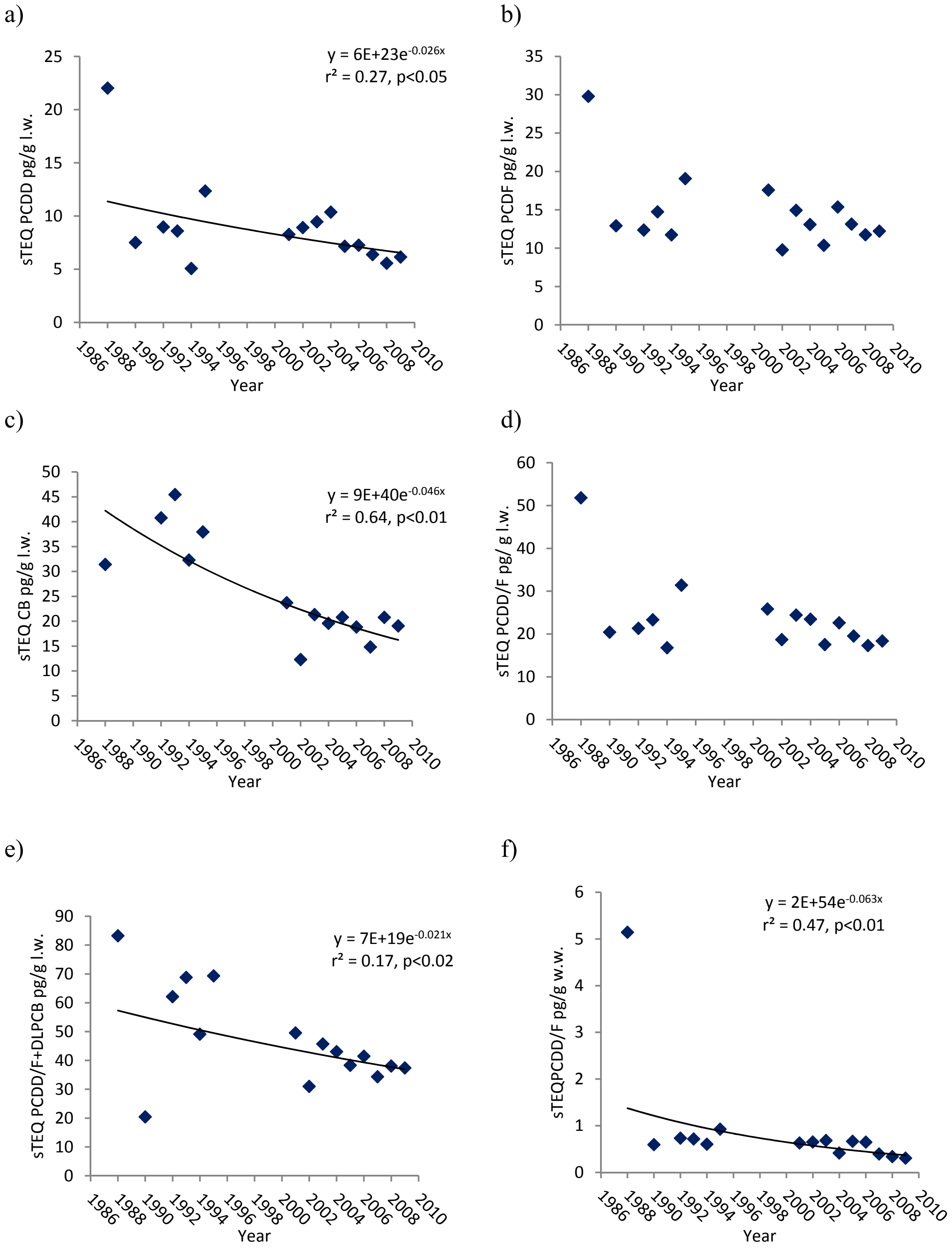


Figure 4. TEQ concentrations on a l.w. basis for (a) PCDDs, (b) PCDFs, (c) dl-PCBs, (d) PCDD/Fs, (e) PCDD/Fs + dl-PCBs, and on a w.w. basis for (f) PCDD/Fs for the whole time series at Utlängan. Log-linear regression equation, r^2 and p value are shown only where there is a significant change over time.

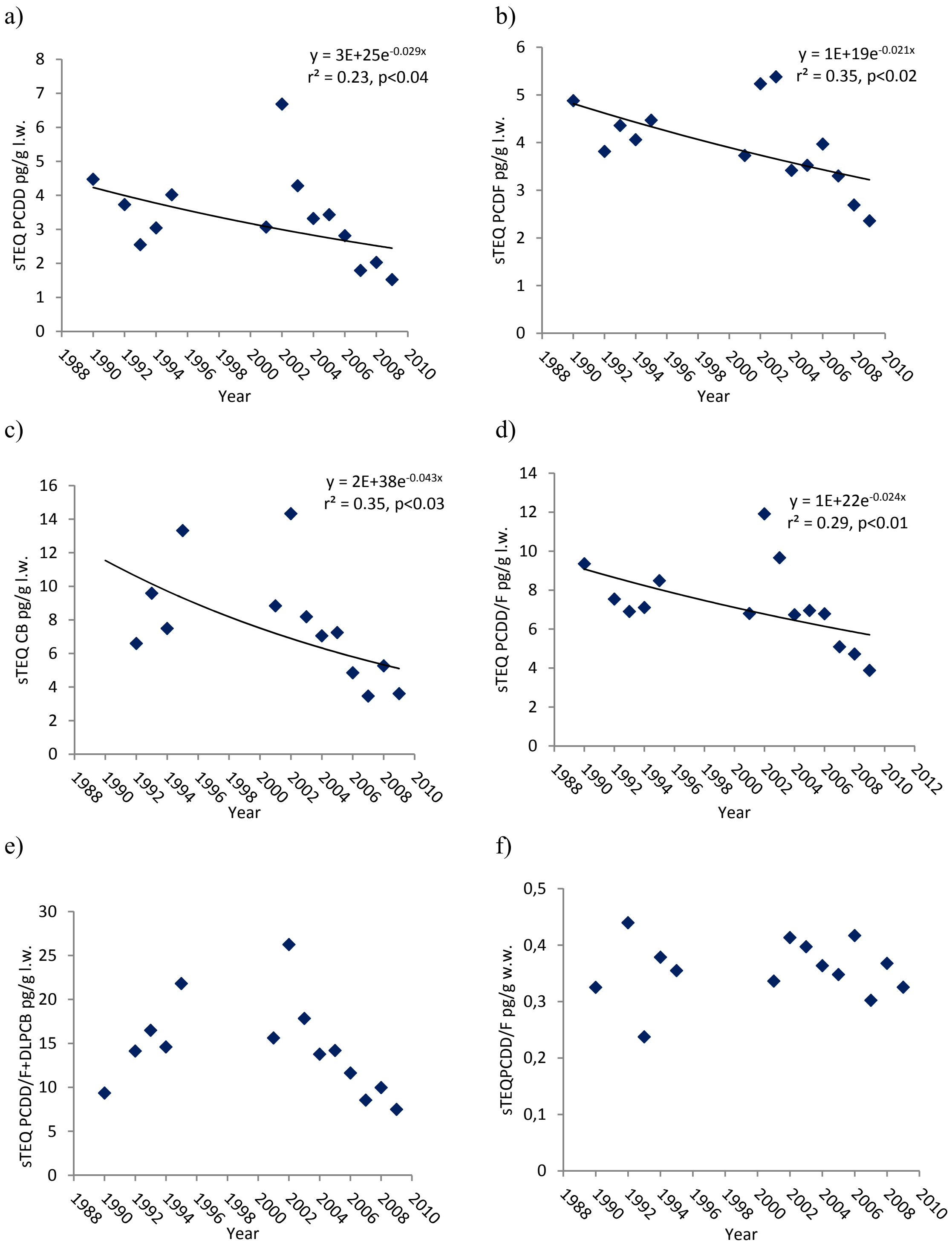


Figure 5. TEQ concentrations on a l.w. basis for (a) PCDDs, (b) PCDFs, (c) dl-PCB, (d) PCDD/Fs, (e) PCDD/Fs + dl-PCBs, and on a w.w. basis for (f) PCDD/Fs for the whole time series at Fladen. Log-linear regression equation, r^2 and *p* values are shown only where there is a significant change over time.

Decreases in PCDDs, but not PCDFs, at Harufjärden and Utlängan (l.w. basis only) or dl-PCBs at Harufjärden, may be related to source strength, reduced exposure, changes in diet over time that would impact on lipid content, increasing herring age over time at Harufjärden, and varying environmental factors over time e.g., salinity and net water turnover time. Elimination rates are not examined here, but as dioxins are very stable chemicals (OSPAR 2007) with slow rates of degradation (HELCOM 2004), this is unlikely to be a primary mechanism driving concentration decreases.

5.3.4 Potential shifts in herring diet at Ängskärsklubb

Stable isotope analysis is used to examine diet: where the energy is sourced from, in this context, marine, brackish, freshwater, or terrestrial; and at what level in the trophic web an organism is feeding. Stable isotope data was analysed to investigate if there has been a shift in the Baltic Sea herring diet that could possibly explain the observed temporal decline in dioxin levels. Stable isotope data for both spring- and autumn-caught herring from Ängskärsklubb were examined. Stable isotope data from spring-caught herring were available for 1991-2004, while data from autumn-caught herring were available for 1979-2007. Ängskärsklubb temporal data analysed for dioxins and dl-PCBs presented above are from autumn-caught herring.

The δ^{13}C values for both spring and autumn data indicate that all energy sources are Baltic, meaning that they are neither fully marine nor of a fully fresh-water origin. The δ^{15}N for the spring-caught herring increased by approximately 1.5‰ over the examined period, whereas an increase of almost 3‰ was observed for the autumn-caught herring. Fractionation of 3.2‰ is generally accepted as a change in trophic feeding level (Michener and Schell 1994). Therefore, autumn-caught herring appear to have shifted upward by close to one trophic level over time, a change that was observed from the mid-late 1980s, continuing until the most recent data reported. However, these results must be interpreted with caution, and cannot be considered definitive until baseline data on the isotopic composition of zooplankton over time are made available.

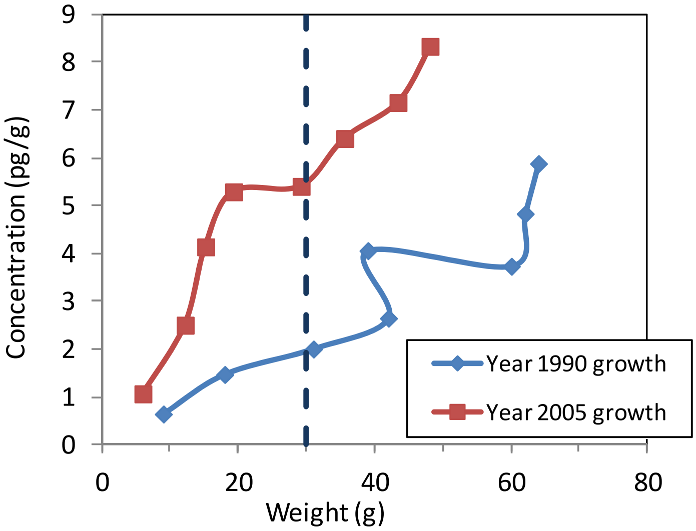
An upward shift in diet means that the dominant food source for the autumn-caught herring sampled at Ängskärsklubb has changed, from being e.g., predominantly zooplankton to e.g., predominantly mysids. As stomach content analysis was not carried out on these particular herring, it cannot be said that this is the exact shift that has occurred, but it is possible based on literature published on herring diet (Arrhenius and Hansson 1993, Casini *et al.* 2004, Flinkman *et al.* 1992, Mollmann *et al.* 2004, Parmanne *et al.* 2006). There are various hypotheses to explain such a shift in diet, however, reasons driving a shift in herring diet will not be discussed in detail here as they are outside the scope of this research. However, increased inter-specific competition with sprat for food resources following release from predator (cod) pressure when the cod fishery collapsed is one likely driver of a change in herring diet.

At higher levels in the trophic food web, dioxin concentrations become higher because of bioaccumulation and biomagnification, and since many dioxins are very persistent chemicals (HELCOM 2004, OSPAR 2007). Therefore, an upward shift in trophic feeding level of the herring would result in a greater dioxin concentration caused by biomagnification. As dioxin emissions have decreased over time, an increase in trophic level in herring diet might rather be observed as a stabilisation of dioxin concentrations. Results here showed that this upward shift in trophic level occurred over a number of years, but the largest change occurred between the late 1980s, and the late 1990s/early 2000s. Such a shift occurring over this period could explain the smaller reductions in dioxin concentrations in herring observed from Ängskärsklubb over the same period (Bignert *et al.* 2011) as compared to earlier in the monitoring data. The shift also coincides with the timing of the crash in cod stocks in the Baltic Sea (Flinkman *et al.* 1998, Mollmann *et al.* 2004).

5.3.5 Impact of decreased growth rates on concentrations

To investigate the impact of growth rate on dioxin concentrations, bioenergetics modelling was conducted using Baltic herring growth rate data (5.2.6). The results of the modelling (where all factors except growth rates were constant) indicated that herring growth rate has a major influence on herring dioxin concentrations both in the Bothnian Sea and in the Baltic Proper. In the Bothnian Sea, the dioxin concentrations on a w.w. basis were about 60% higher in 2005 than they would have been in case the growth rate had not decreased but stayed at the higher level seen in 1990. This percentage was derived using a covariance analysis (Figure 6). In the Baltic Proper, the modelling indicated that the concentrations were about 130% higher in 2005 compared to what they would have been if growth rate had remained stable since 1990. Thus, these results clearly suggest that decreased herring growth rate strongly counteracted the decreasing dioxin concentrations in the environment and contributed to the observed slow decline in herring dioxin concentrations. To better understand the bioaccumulation processes in the different basins of the Baltic Sea, factors affecting the bioenergetics of herring should be further investigated. For instance, shifts in diet over time are likely to influence concentration especially in large herring. A large fraction of large food items and a smaller fraction of zooplankton can contribute to elevated concentrations in herring. Even shifts in species composition in zooplankton can influence dioxin concentrations in herring over time. Shifts in food web structure and available food items can be caused by for instance climate and other environmental changes, but also by fishery.

Although differences in dioxin concentrations between basins were not a focus of the bioenergetics modelling, there are some factors highlighted within the current project that stand out as potentially having an influence on this issue. Different basins in the Baltic are subject to differences in salinity and temperature. Shifts in these factors may increase energetic costs in maintenance metabolism, thereby reducing energy that can be spent on growth. In turn, this would contribute to lower growth rates, and a lack of decreases in dioxin concentrations. Bioenergetics modelling carried out within this project indicated that a slower growth rate in the north of the Baltic Sea was likely a major factor impacting dioxin concentrations in herring over time, but it could also cause spatial differences. Another factor that may cause spatial differences in dioxin levels is the diet of the herring; for instance, the zooplankton composition and the trophic level can differ between basins. The diet is linked to the lipid content. As has been observed in the current study, lipid content in herring varies between basins, with lower lipid content seen further north. As already discussed, lipid content is a factor that influences dioxin concentrations. Therefore, differences in physical conditions between basins, coupled with herring biology, are likely to contribute to the variation in dioxin concentrations observed between basins of the Baltic Sea.



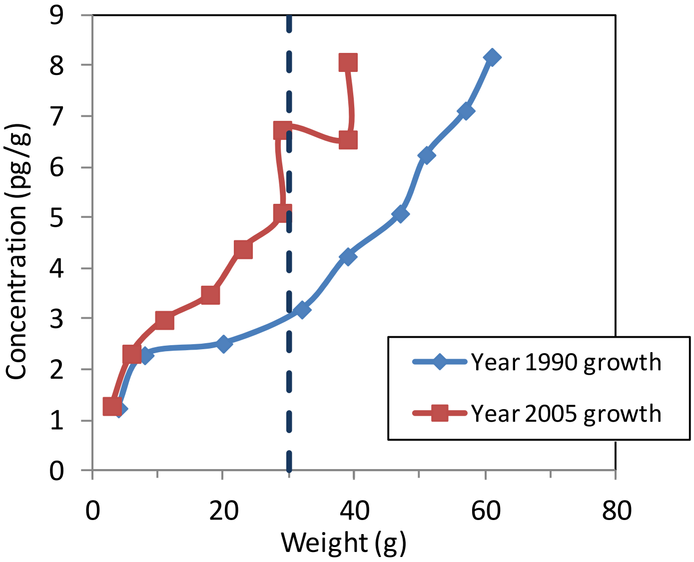


Figure 6. Model-based estimates of the impact of decreased growth rate between 1990 and 2005 on PCDD/F concentrations (sum of the 2,3,7,8-TCDD, 1,2,3,7,8-PeCDD and 2,3,4,7,8-PeCDF concentrations in w.w.) in herring in the Baltic Proper (upper graph) and Bothnian Sea (lower graph). The concentrations were estimated with the growth rates of 1990 and 2005. All other factors were held constant. The intersections of the dashed line with the curves indicate the difference in concentrations of a 30 g fish in case the growth rate had in 2005 been as high as in 1990. The points along the curves represent fish of ages 1 to 9 years.

5.4 Conclusions

- At Harufjärden, significant decreases were only observed for 2,3,7,8-TCDD (l.w.) and TEQ_{PCDD} (l.w. and w.w.), whereas no significant trends were observed for any other dominant congener (l.w.) or TEQ values (l.w. or w.w.). Over time, herring from Harufjärden showed a significant increase in age and a significant decrease in lipid content, but no change in length or weight. These biological changes indicate that a slower growth rate and decreased lipid content are masking other decreases in dioxins. The lack of significant decreases in PCDFs and dl-PCBs at this site are supported by the findings of the growth rate modelling. However, it is uncertain why PCDDs decrease significantly, while PCDFs and dl-PCBs do not, and may be related to changes in dioxin input from different sources.

- At Ängskärsklubb, all six dominant PCDD/F and dl-PCB congeners (l.w.) and TEQ values (l.w. and w.w.) showed significant decreases over time. These decreases can be related to the relatively long time series at this site, and probably to reduced emissions over time. No biological parameters showed any change over time in herring from this site. However, herring age at this site continues to be slightly higher than herring from other sites, which may explain the slightly elevated dioxin concentrations here.
- At Utlängan only two dominant congeners showed significant decreases over time (l.w.), but significant decreases were observed for TEQ_{PCDD}, $TEQ_{dl\text{-}PCB}$ and $TEQ_{PCDD/F+dl\text{-}PCB}$ values on a l.w. basis, and for all TEQ values on a w.w. basis. A significant decrease in lipid content over time was observed here, which is most likely due to changes in diet. On a l.w. basis, leaner fish would indicate dioxin concentrations are higher than they would be otherwise. Therefore, even though significant decreases are seen at this site, changes in herring ecology could drive further decreases in concentrations.
- At Fladen, all six dominant PCDD/F and dl-PCB congeners and all TEQ values except $TEQ_{PCDD/F\ +\ dl\text{-}PCB}$ showed statistically significant decreases in concentrations on a l.w. basis; however, no significant trends were seen in TEQ values on a w.w. basis. The significant decrease in age and increase in lipid content observed in herring from this site would explain the significant decreases seen on a l.w. basis, and the changing lipid content over time would increase variation and result in a lack of significant decreases.
- PCDDs decreased significantly at Harufjärden, Ängskärsklubb and Utlängan on both a lipid and wet weight basis, but only on a lipid weight basis at Fladen. Some decreases in PCDFs were also seen, but not at all sites. Biological parameters are exerting a strong influence on observed concentrations, and, in the Bothnian Bay in particular, a decrease in lipid content and an increase in age are masking dioxin changes.
- Bioenergetics modelling indicates that decreased herring growth rate counteracted the decreasing dioxin concentrations in the environment, and contributed to the observed slower decline in dioxin levels in herring. Slower growth rates of herring in the Baltic Sea were shown to strongly affect downward temporal trends of dioxin concentrations in herring, and could potentially counteract emission reduction measures.
- Stable isotope analysis was used to investigate if there has been a temporal shift in herring diet at Ängskärsklubb over the last few decades, which could potentially impact on temporal trends of POP concentrations in herring. SIA data indicates that the Bothnian Sea herring have gradually shifted up one trophic level from where they fed in the past. However, a lack of baseline SIA data means these results are not yet verified and should be interpreted with caution. The bioenergetics modelling confirms that shifts in diet could counteract emission reductions.
- Although it is positive that PCDD concentrations have declined over the long-term in herring, there are some causes for concern, namely: *i*) the slower growth rates and dietary shifts causing herring to feed at higher trophic levels can counteract emission reductions and potentially cause concentrations to stabilise at concentrations above the EU thresholds, and *ii*) PCDF and dl-PCB concentrations in herring, while decreasing at some sites, do not appear to be declining as markedly as PCDDs at other sites.

6 Seasonal variation in dioxins in herring from the Bothnian Sea

6.1 Introduction

Previous research has shown evidence for seasonal variation in dioxin concentrations in Baltic herring (Bignert *et al.* 2009a, Bignert *et al.* 2009b) and other POPs in fish species at other locations (e.g., Larsson *et al.* 1993, Stapleton *et al.* 2002). Seasonal variation in dioxin concentrations could be important in regards to the timing of herring sampling for monitoring of dioxins used for setting environmental target levels and safe food consumption levels. A number of biological and ecological parameters can influence dioxin concentration in herring e.g., lipid content of sampled individuals, diet/trophic feeding level, spawning, fishing date, age and habitat (Larsson *et al.* 1993), and thus should be considered when investigating dioxin concentrations in herring.

Here, we investigate whether annual variations in dioxin concentrations in Baltic herring (*Clupea harengus*) are *i*) due to seasonal changes in dioxin concentrations, and *ii*) if so, are they related to biological parameters.

6.2 Methods

Herring was caught between November 2005 and October 2006 at two sites, one in the northern and one in the southern Bothnian Sea (11 months sampled in southern Bothnian Sea, 9 months sampled in the northern Bothnian Sea; Bignert *et al.* 2009b; Figure 7). Herring size was representative of that usually taken for human consumption – approximately 20 cm length, corresponding to an age of between 5 and 10 years. A total of 15 individual herring were collected at each site on each sampling occasion. Biological measurements were taken, but age and sex were not determined. Muscle tissue from each individual fish was sampled by removing skin and subcutaneous fat and sampling the dorso-lateral muscle. Muscle was then pooled for each group of 15 individuals. Pooled muscle samples were sent to the Department of Chemistry, Umeå University, for analysis of PCDD/Fs (see section 5.2.2).

Results for seasonal data are presented in pg g^{-1} l.w., and also on a w.w. basis where specified. TEQ concentrations were calculated using WHO 2005 TEF values, and congeners were summed for each site and month within the PCDD and PCDF group to give total TEQ_{PCDD}, TEQ_{PCDF}, and $TEQ_{PCDD/F}$ concentrations. Simple regression analysis and correlation coefficients were run on lipid content and $TEQ_{PCDD/F}$. Principal component analyses (PCA) were used to investigate patterns in PCDDs, PCDFs and PCDD/Fs at each site over the sampled time period using PIA Plot and Image Analysis (Bignert *et al.* 2007).

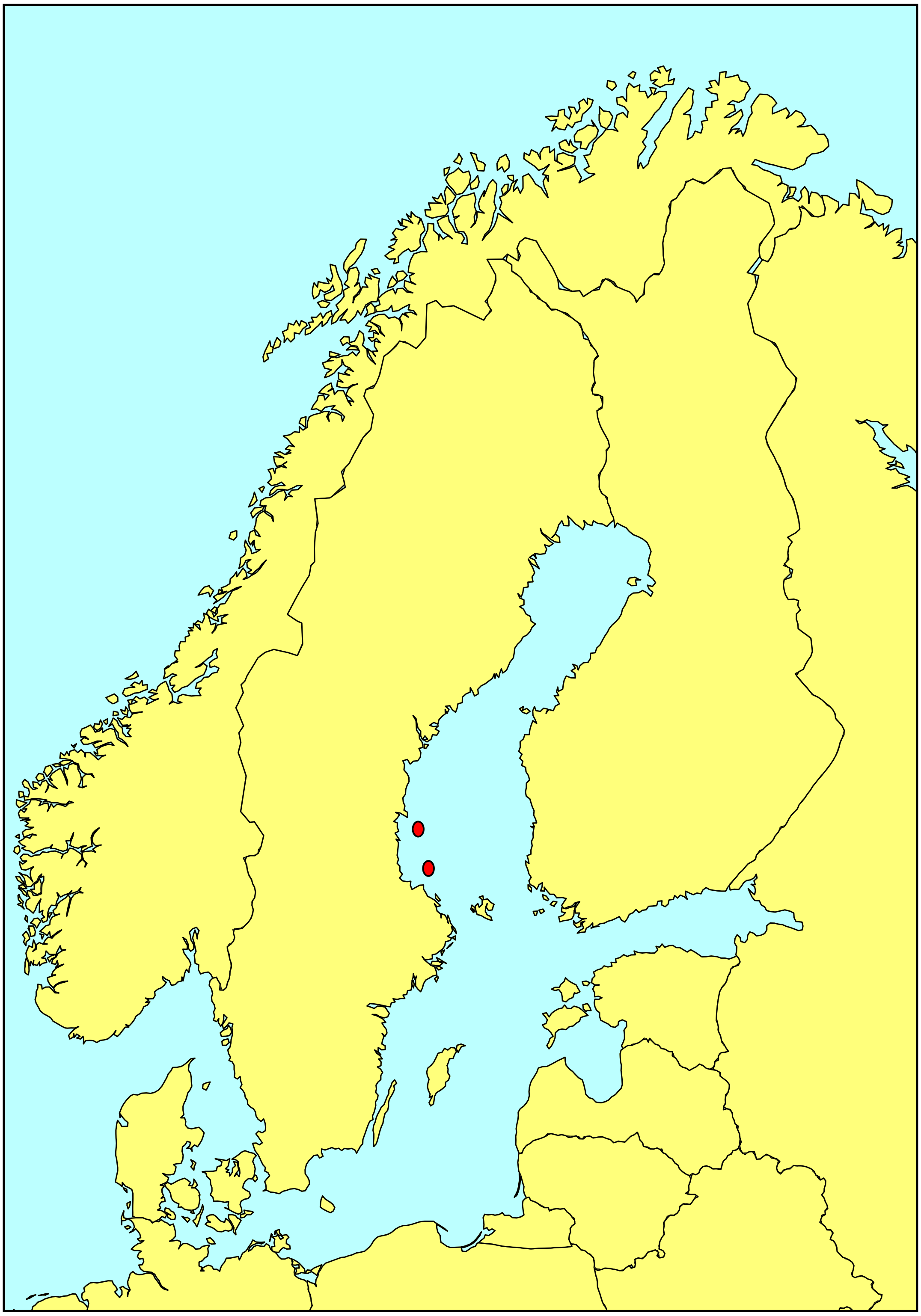


Figure 7. Map of Scandinavia showing the Baltic Sea and surrounding countries. Red dots indicate the general location of the two sites where sampling occurred.

6.3 Results

The fish size did not vary much between the two investigated sites. Total fish length, i.e., length including the tail, ranged from 19.1 to 20.7 cm at the southern Bothnian Sea site, and from 18.7 to 20.9 cm at the northern site. Weight ranged from 42.5 to 51.3 g (southern site) and from 40.6 to 52.3 g (northern site) corresponding to an age of between 5 and 10 years. Weight, total length and body length (i.e., length not including the tail) did not show any obvious pattern with $\text{TEQ}_{\text{PCDD/F}}$ concentrations on either a l.w. or w.w. basis (Figures 8 and 9; only l.w. presented). For lipid content, a pattern of increased $\text{TEQ}_{\text{PCDD/F}}$ concentrations when lipid concentration decreased, and vice versa, could be discerned (Figure 10).

The highest $\text{TEQ}_{\text{PCDD/F}}$ concentrations on a l.w. basis were observed in January for the southern Bothnian Sea and in May for the northern Bothnian Sea, while on a w.w. basis, the highest concentrations were observed in January for both sites. An increase in lipid corresponds to a decrease in $\text{TEQ}_{\text{PCDD/F}}$ (l.w.) concentration, and vice versa (Figure 10, top). This trend is also seen on a w.w. basis, although not as pronounced (Figure 10, bottom). Lipid content showed a significant negative correlation with $\text{TEQ}_{\text{PCDD/F}}$ concentrations for both sites on a l.w. basis ($n = 11$, $d.f. = 9$, $p<0.01$, $r^2 = 0.79$ (southern); $n = 9$, $d.f. = 7$, $p<0.01$, $r^2 = 0.90$ (northern)). On a w.w. basis, only the southern site showed a significant negative correlation between lipid content and $\text{TEQ}_{\text{PCDD/F}}$ ($n = 11$, $d.f. = 9$, $p<0.05$; $r^2 = 0.39$). The northern site showed a non-significant negative relationship ($r^2 = 0.39$).

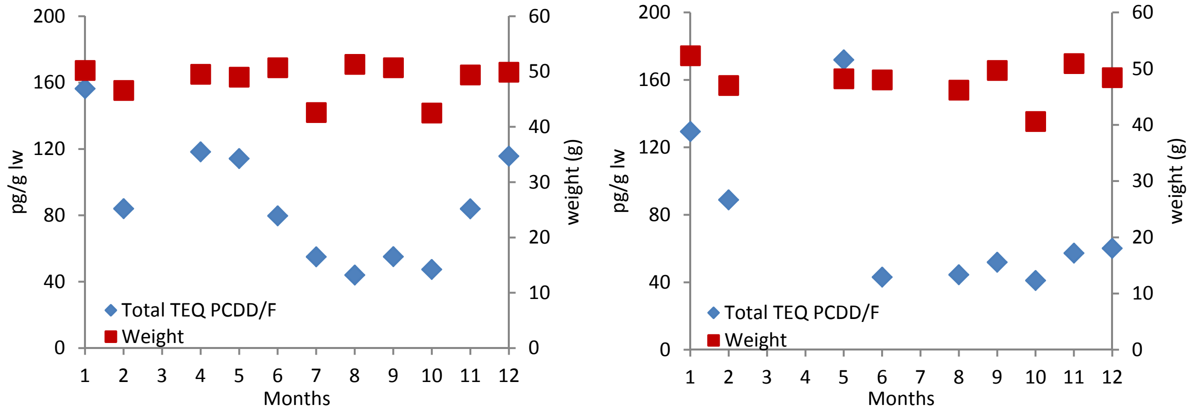


Figure 8. $\text{TEQ}_{\text{PCDD/F}}$ (l.w. basis) and herring weight for the southern (left) and northern (right) Bothnian Sea sites over the 12 months data were collected. Numbers on the x axis correspond to month (1 = January, 2 = February, etc.).

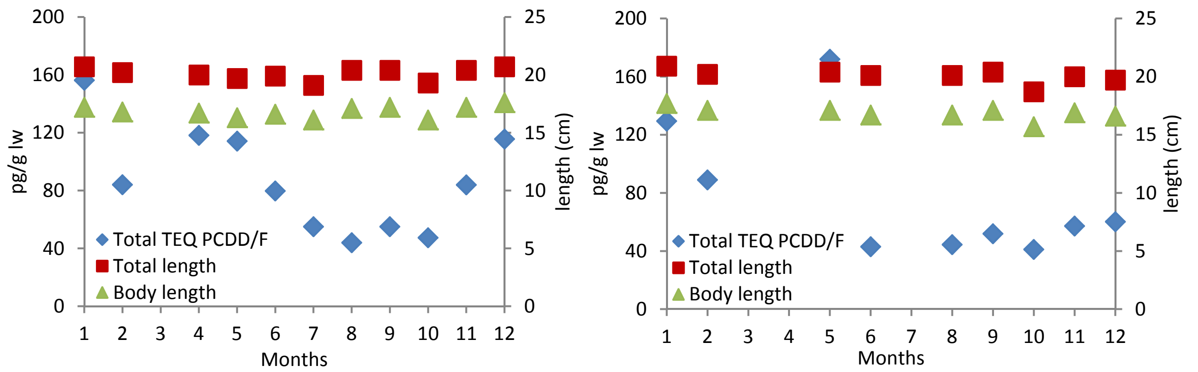


Figure 9. $\text{TEQ}_{\text{PCDD/F}}$ (l.w. basis), body length and total length for the southern (left) and northern (right) Bothnian Sea sites over the 12 months data were collected. Numbers on the x axis correspond to month (1 = January, 2 = February, etc.).

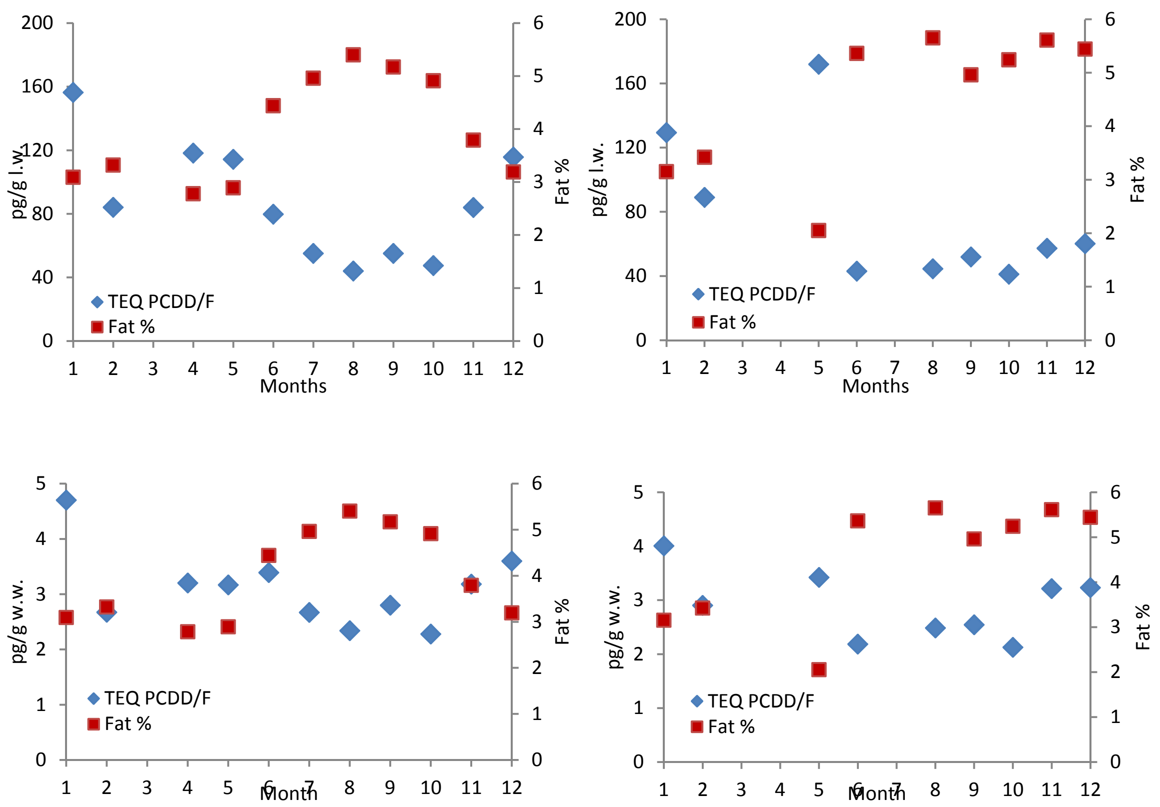
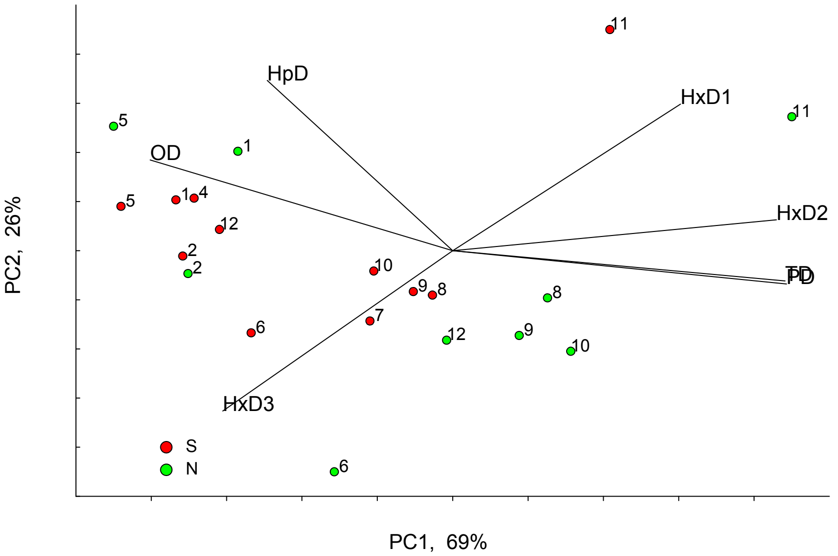


Figure 10. $TEQ_{PCDD/F}$ on a lipid weight (top) and wet weight basis (bottom), and lipid content (fat %) for the southern (left) and northern (right) Bothnian Sea sites for the 12 months of sampling. Numbers on the x axis correspond to month (1 = January, 2 = February, etc.).

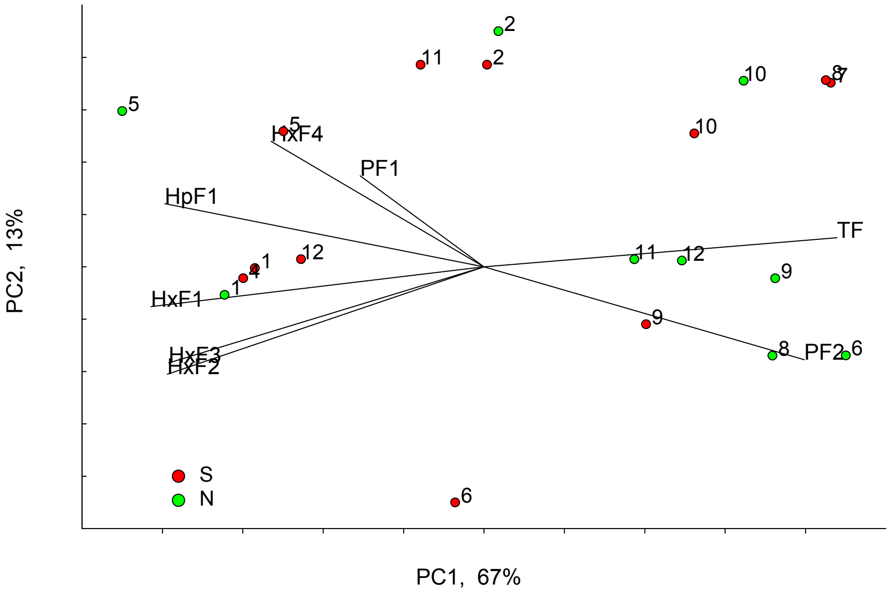
The PCA examining TEQ_{PCDD} congener concentrations shows that samples from the southern Bothnian Sea site have formed two groups – June to September and December to April (Figure 11). The June to September group is near the centre of the PCA and therefore no congener is exerting a particularly strong influence. The group formed by the December to April samples form a group close to OCDD. This indicates a change in dominant congeners between summer and winter/spring. A similar pattern can be seen for the northern Bothnian Sea site, although the groups are not as tightly clustered as for the southern site. November samples from both sites sit near 1,2,3,4,7,8-HxCDD, separate from all other samples.

When examining TEQ_{PCDF} congener concentrations (l.w.) over the sampled months using PCA, no seasonal pattern is apparent for either site (Figure 12).



Source: NRM 13.01.28 16:55, PCDD_3

Figure 11. Principal component analysis (PCA) showing TEQ$_{PCDD}$ congener loadings (l.w.) over the sampled months for both sites. S = southern Bothnian Sea, N = northern Bothnian Sea. Numbers indicate months, e.g., 1 = January. Congener names are abbreviated: TD = 2,3,7,8-TCDD, PD = 1,2,3,7,8-PeCDD, HxD1 = 1,2,3,4,7,8-HxCDD1, HxD2 = 1,2,3,6,7,8-HxCDD2, HxD3 = 1,2,3,7,8,9-HxCDD3, HpD = 1,2,3,4,6,7,8-HpCDD,OD = OCDD.



Source: NRM 13.01.28 16:55, PCDF_3

Figure 12. Principal component analysis (PCA) showing TEQ$_{PCDF}$ congener loadings (l.w.) over the sampled months for both sites. S = southern Bothnian Sea, N = northern Bothnian Sea. Numbers indicate months, e.g., 1 = January. Congener names are abbreviated: TF = 2,3,7,8-TCDF, PF1 = 1,2,3,7,8-PeCDF1, PF2 = 2,3,4,7,8-PeCDF2, HxF1 = 1,2,3,4,7,8-HxCDF1, HxF2 = 1,2,3,6,7,8-HxCDF2, HxF3 = 1,2,3,7,8,9-HxCDF3, HxF4 = 2,3,4,6,7,8-HxCDF4, HpF1 = 1,2,3,4,6,7,8-HpCDF1.

6.4 Discussion

Seasonal changes in dioxin concentrations in Baltic herring were observed on a lipid weight basis. On a wet weight basis, seasonal changes in dioxins were not as apparent. There are a number of chemical, biological and ecological factors that could contribute to seasonal variation, but as lipid content was the biological parameter most strongly aligned with dioxin concentrations, it seems likely that factors affecting lipid content e.g., spawning and seasonal changes in diet, are the drivers of the observed dioxin changes.

A strong negative correlation exists between organochlorine concentration expressed on a lipid weight basis and fat content in spring-caught herring (Bignert *et al.* 1993). A low fat content due to e.g., scarcity of food can cause elevated concentrations of organochlorines on a l.w. basis, and vice versa (Bignert *et al.* 2011). A likely explanation for this phenomenon is that as lipids are consumed, dioxins are redistributed to other tissues in the body rather than being excreted from the body, which affects the lipid-normalised concentrations.

Lipid content is closely related to spawning. Significant depletion of lipids due to spawning has been observed in Pacific herring (*Clupea harengus pallasi*; Huynh *et al.* 2007). Changes seen in dioxin concentration here are possibly influenced by spawning activity and related lipid depletion, followed by lipid restoration after spawning, causing fat dilution of dioxins. High concentrations of dioxins and corresponding lower lipid content in the first few months of the year for both sites indicate the sampled herring could be spring spawners. Egg production has been reported as acting as a vector of depuration in female fish (Larsson *et al.* 1993, Miller 1993, Stapleton *et al.* 2002), which could also explain some of the observed dioxin fluctuations, although sex was not determined for these fish.

It seems very likely that diet plays a large role in influencing seasonal lipid content and therefore dioxin concentration. Seasonal fluctuations in prey source availability, shifts in dominant food source, inter- and intra-specific competition, and/or environmental conditions can all influence dioxin concentrations. Different dominant food items have been identified from Baltic herring diet during different seasons (Popiel 1951, Parmanne et al. 2004, both in Parmanne et al. 2006; Arrhenius and Hansson 1993; Mollmann *et al.* 2004), leading to changes in bioaccumulation rate depending upon trophic level, dioxin concentration, and lipid content in the dominant prey source at the time.

Herring diet from the Baltic Sea is usually dominated by zooplankton and mysids (Arrhenius and Hansson 1993, Mollmann et al. 2004). Consumption of zooplankton varies with season and peaks between July and October (Arrhenius and Hansson 1993). The highest feeding activity for herring has been reported as occurring in spring and summer, which is the main reproductive period for calanoid copepods, one of the dominant zooplankton sources for herring (Mollmann *et al.* 2004). Thus, large amounts of food from a low trophic level would be available at this time. This relates well to results reported here, with lower dioxin concentration and higher lipid content seen in this same period.

In late autumn and winter, herring food consumption decreases and a shift in diet to prey with higher energy values e.g., mysids, occurs (Arrhenius and Hansson 1993). As mysids are higher trophic level organisms than zooplankton, they bioaccumulate more dioxins (Strandberg *et al.* 1998) leading to greater dioxin bioaccumulation in herring as well. OCDD was a dominant congener in mysids and zooplankton sampled within the Bothnian Bay (see chapter 7), and here, appeared to have a stronger influence on herring during the winter months. A change in diet, along with the potentially slower metabolism/excretion of heavier PCDD/F congeners during winter when fat content in herring was lower, is one explanation for the observed grouping of herring in the PCA.

6.5 Conclusions

- Seasonal variations in concentrations of dioxins in Baltic herring were observed on a lipid weight basis but to a lesser extent on a wet weight basis. These variations in concentrations are negatively correlated with seasonal cycles in lipid content due to spring/summer spawning and seasonal dietary changes. The seasonal dioxin changes are most likely due to the re-distribution of dioxins to other tissues when lipid content decreases, and a dilution when lipid content increases.
- The highest $TEQ_{PCDD/F}$ concentrations (w.w. basis) were observed in January for both the southern and northern Bothnian Sea sites. On a l.w. basis, the highest $TEQ_{PCDD/F}$ concentrations were observed in January for the southern and in May for the northern Bothnian Sea site.

7 Spatial variation in dioxins and dioxin-like PCBs in herring from the Bothnian Sea

7.1 Introduction

Spatial variations in dioxin concentrations in Baltic herring has previously been observed, for instance along the coast of the Bothnian Sea and between sub-basins (Bignert *et al.* 2011, Bignert *et al.* 2007, Karl and Ruoff 2007). Concentrations in herring from the Bothnian Sea and Bothnian Bay are often elevated (Bignert *et al.* 2011, Isosaari *et al.* 2006). Reasons for the spatial differences in dioxin concentrations in herring from within the Bothnian Sea are not clear. Various hypotheses exist, such as differences in exposure from local sources, contaminated sediments acting as secondary dioxin sources, ecological factors, fish growth rate, metabolism or prey availability (Arrhenius and Hansson 1993, Peltonen *et al.* 2007). As herring is a key-stone species within the Baltic ecosystem, and are popular for human consumption within the Baltic countries, improving knowledge about causes of spatial differences in dioxins is important from both an ecological and a human health perspective.

Here, we examine spatial variation of dioxin concentrations in herring, mysids, zooplankton, sediment and water data, as well as stable isotope analysis from herring, mysids and zooplankton, from four sites within the Bothnian Sea, to investigate whether herring diet, biological variables or sediment/water concentrations can explain the observed spatial variations in dioxin concentrations in herring.

7.2 Methods

7.2.1 Sampling sites and matrices

Five sites were sampled along the coast of the Bothnian Sea in September 2009 – Köpmanholmen, Lörudden, Hornslandet, Norrsundet and Skutskär (Figure 13); however, at Köpmanholmen only zooplankton was sampled. Based on previous observations (Bignert *et al.* 2007), Hornslandet can be used as a reference area, and concentrations of dioxins and dl-PCBs in herring from this site were expected to be more similar to herring caught offshore, while the other coastal sites are considered contaminated areas. From each site, Baltic herring (*Clupea harengus*), mysids and zooplankton were sampled. Herring were collected by trawling and kept frozen (-20 °C) until further analysis. For comparison, herring were also sampled from four offshore sites by the Swedish Board of Fisheries (Figure 13). It must be noted that two of these sites, Utsjö 3 and 4, are located within the Baltic Proper, and it is known that dioxin levels in herring from this region differ from herring in the Bothnian Sea region. Therefore, herring from these two sites are not directly comparable with the rest of the data.

From each coastal site, 36 individual herring were sampled, except at Hornslandet where only 18 individuals were sampled, and Köpmanholmen where no herring was collected. From each offshore site, 24 individual herring were sampled. These were divided into three even pools for sampling (*n* = 12x3 at Skutskär, Norrsundet and Lörudden, *n* = 6x3 for Hornslandet, *n* = 8x3 for all offshore sites).

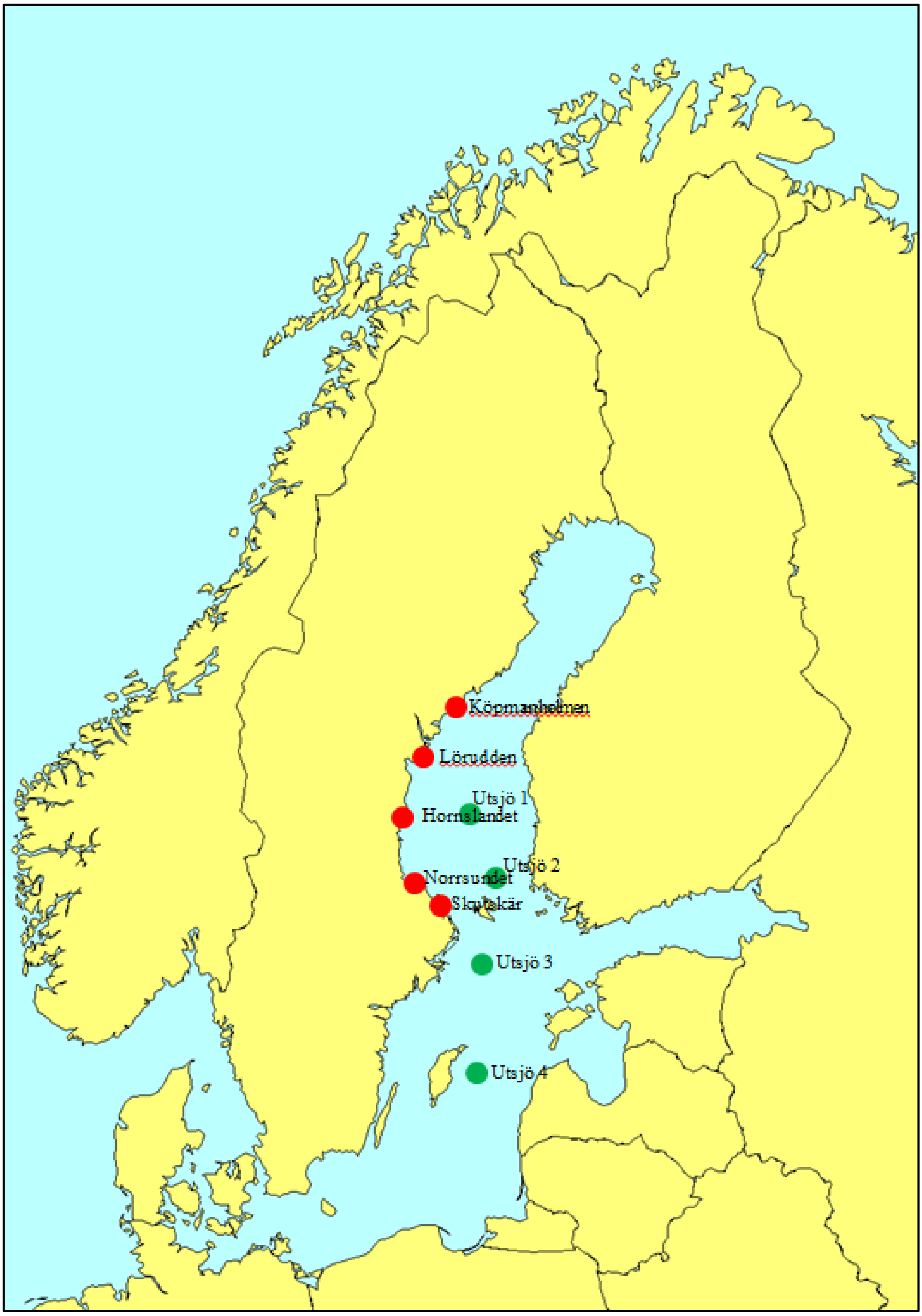


Figure 13. Map of Scandinavia showing the Baltic Sea and surrounding countries. The sampled coastal sites within the Bothnian Sea are indicated by red dots, offshore sites by green dots.

Herring biological measurements were taken for each individual (sex, age, weight, body length, total length, liver weight, gonad weight, stomach weight). Scales were used for age determination.

Mysids from coastal sites were collected using a 90 µm plankton net at depths generally >40 m. Two species (*Mysis relicta* and *M. mixta*) were identified and frozen separately. Zooplankton from coastal sites were sampled using a 90 µm plankton net dragged behind a boat at a depth of 1-5 m, concentrated, and stored frozen in glass jars. A sub-sample of zooplankton from each coastal site was fixed in 95% ethanol to determine the relative taxonomic composition. Mysids and zooplankton were collected from offshore areas by dragging a plankton net (mesh size 200 mm) from the bottom to the surface. These offshore sampled areas differed to the offshore sites as they were collected within another project, but were still within the Bothnian Sea.

For dioxin analysis, three pooled samples of 30 g w.w. of herring fillet (muscle including subcutaneous fat and skin) were sampled for each site. Muscle only (skin and subcutaneous fat removed) were simultaneously sampled from the same individuals from two coastal (Lörudden, Skutskär) and two offshore (2, 4) sites. There was only enough biomass of *M. relicta* and *M. mixta* for dioxin analysis from Lörudden and Skutskär. Bulk zooplankton samples from all coastal (excluding Köpmanholmen) and offshore sites were analysed for dioxins.

For stable isotope analysis, dorso-lateral herring muscle tissue of approximately 0.5 g w.w. from each individual was sampled from coastal samples only. Five individual *M. relicta* and 3 *M. mixta* from each coastal and offshore site were analysed for stable isotopes. Bulk zooplankton samples from all coastal and offshore sites were analysed for stable isotopes.

7.2.2 Dioxin analytical methods

The analyses of dioxins and dl-PCBs from herring fillet, muscle, mysids and zooplankton were carried out at Eurofins Ökometri laboratory in Bayreuth, using dioxin analysis standard method EPA 1613 B with HRGC/HRMS. Fat extraction was done via column extraction using hexane:dichloromethane 1:1 in accordance with the German extraction method ASU L00.00-12; ASU L00.00-38.

7.2.3 Stomach content analysis

Herring stomachs from each coastal site were removed and preserved in glass jars with 95% ethanol. Following laboratory protocols, each stomach was cut open, and contents were removed and examined under a binocular microscope. Contents were divided into groups (e.g., zooplankton, mysids, and fish) and the number in each group was recorded.

7.2.4 Stable isotope analysis

Stable isotope analysis (SIA) was conducted for muscle samples at the University of Jyväskylä, Finland, using a Carlo Erba Flash EA1112 elemental analyser connected to a mass spectrometer (CF-IRMS), via methods outlined in Kiljunen *et al.* (2006). All samples were freeze-dried to a constant weight and ground to fine powder before analysis. The international standards of Vienna Pee Dee belemnite (for carbon) and atmospheric N_2 (for nitrogen) were used as reference materials and dried pike muscle as an internal working standard. Results are expressed using the standard δ notation as parts per thousand (‰) difference from the international standards.

Lipid normalisation was carried out for the $\delta^{13}C$ values for herring, mysids and zooplankton, using calculations presented in Kiljunen *et al.* (2006), as lipids are known to be ^{13}C depleted relative to other major tissues (Bodin *et al.* 2007, Ehrich *et al.* 2011) i.e., fatty tissues can have lower $\delta^{13}C$ values than lean tissues (Ehrich *et al.* 2011).

7.2.5 Statistical treatment of the data

Data quality control was conducted for all sites. Any values below limit of quantification (LOQ) were replaced with the LOQ divided by the square root of two. Herring biological variables were compared between coastal and offshore sites using Student's *t*-tests (Excel 2010); differences between coastal sites, and between offshore sites, were examined using one-way analysis of variance (ANOVA) and Tukey's post-hoc tests (Statistica v10). As there were significant differences ($p<0.05$) seen in herring biological variables between coastal and offshore sites, with coastal herring being older, dioxin data were age-adjusted. Age was chosen as both length and weight are closely related to age, and because dioxin levels are known to be related to age, with older fish having higher concentrations compared to younger fish (Isosaari *et al.* 2006, Karl and Ruoff 2007, Pandelova *et al.* 2008). As there was some spread in the age data, the median age of the offshore fish was chosen as the age to correct coastal fish age to. Dioxin data from coastal-caught herring were age adjusted using the following equation:

$$\text{Congener}_{\text{adjusted}} = \text{Congener}_{\text{observed}} + \beta^* (\text{Age}_{\text{median}} - \text{Age}_{\text{observed}})$$

where β is the beta value from the regression equations (herring age vs. the absolute concentration (l.w.) for the dominant congeners for PCDDs, PCDFs and dl-PCBs), and $\text{Age}_{\text{median}}$ was 5, based on herring age from the offshore sites. Muscle samples were only taken at four of the eight sites where herring was caught, resulting in half as many muscle samples compared to fillet. This led to a poor fit when age and TEQ values were regressed together, and therefore age-adjustment of herring muscle data was poor compared to the adjustment for herring fillet. It is indicated throughout the results section where adjusted and/or unadjusted data have been used.

Student's *t*-tests were used to examine differences in absolute concentration of the dominant congeners (1,2,3,6,7,8-HxCDD, OCDD, 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, CB105, CB 118) between coastal and offshore herring, and one-way ANOVAs with Tukey's post hoc tests (Statistica v10) were used to examine differences in absolute concentration of the dominant congeners between coastal sites, and between offshore sites, using age-adjusted fillet data. Pearson's correlation coefficients were used to attempt to establish a link between dioxin concentrations in sediment and herring fillet. A conversion factor between congener concentration in herring fillet and muscle was calculated. Principal component analysis (PCA) with Hotelling's tests were used to examine any patterns in congener groups between coastal and offshore herring, and between coastal sites, using normalised data (each congener divided by the sum of all congeners for each of PCDD, PCDF and dl-PCBs, with values below LOQ removed; Bignert 2010). Graphs of zooplankton composition from each coastal site, and herring stomach content were compiled. Stable isotope data were used to determine dietary proportion of herring at the four coastal sites where herring was sampled. Bi-plots and correlation coefficients were calculated and graphed using SIAR (2011), an R statistical package developed specifically for stable isotope data analysis.

7.3 Results

As only zooplankton was caught at Köpmanholmen, this site was removed from all but the zooplankton graphs in the following analyses. All results are presented in pg g^{-1} l.w. unless otherwise specified. Skutskär, Lörudden, Utsjö 2 and Utsjö 4 had both fillet and muscle sampled from herring. At all other sites, only fillet samples were taken from herring. Mysids were only caught from Skutskär and Lörudden.

7.3.1 Biological variables of herring at coastal and offshore sites

Age, weight, total length, lipid content (fat %), as well as liver, gonad and stomach weight were measured in all herring sampled. Here we focus on age, weight, total length and lipid content (fillet only, as muscle samples were only taken at half of the sites). The oldest herring were caught from Skutskär, and the youngest from Utsjö 1. The largest herring (weight and length) were from Lörudden, and smallest herring were from Utsjö 1.

Significant differences in age, weight and length ($p<0.01$) were seen between coastal and offshore caught herring with coastal herring being older and larger (Table 3). One-way ANOVAs with Tukey's HSD post-hoc tests showed significant differences in herring weight ($f = 52.6$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 123$, $p<0.01$), length ($f = 63.2$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 121$, $p<0.01$) and age ($f = 32.4$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 123$, $p<0.01$) between the four coastal sites. In all cases, herring from Skutskär and Lörudden were similar, as were herring from Norrsundet and Hornslandet; herring from Skutskär and Lörudden were significantly larger/older than herring from Norrsundet and Hornslandet. For the offshore sites, significant differences were seen for weight ($f = 116.4$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 96$, $p<0.01$), length ($f = 192.2$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 95$, $p<0.01$) and age ($f = 18.9$, $d.f._{\text{between}} = 3$, $d.f._{\text{within}} = 95$, $p<0.01$).

Table 3. Student's *t*-test results for age, weight, total length and lipid content for coastal versus offshore herring. Arithmetic means, degrees of freedom (*d.f.*) and *p* values are shown.

	Coastal sites	**Offshore sites**	***d.f.***	***p***
Age (years)	6.2	5.3	127	<0.01
Weight (g)	38.6	27.2	225	<0.01
Total length (cm)	18.0	16.3	197	<0.01
Lipid content (fat % w.w.)	7.0	5.5	16	<0.05

7.3.2 Congener patterns and concentrations

HERRING

Congener pattern did not vary much between coastal and offshore caught herring. PCDDs, PCDFs and dl-PCBs (l.w.) show very similar congener patterns and concentrations between coastal and offshore sites (Figures 14-16). The dominant PCDF and dl-PCB congeners are the same as those seen in the temporal dioxin data; however, dominant PCDD congeners seen here (OCDD and 1,2,3,6,7,8-HxCDD) differ to those in the temporal data (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD; section 5.3.2).

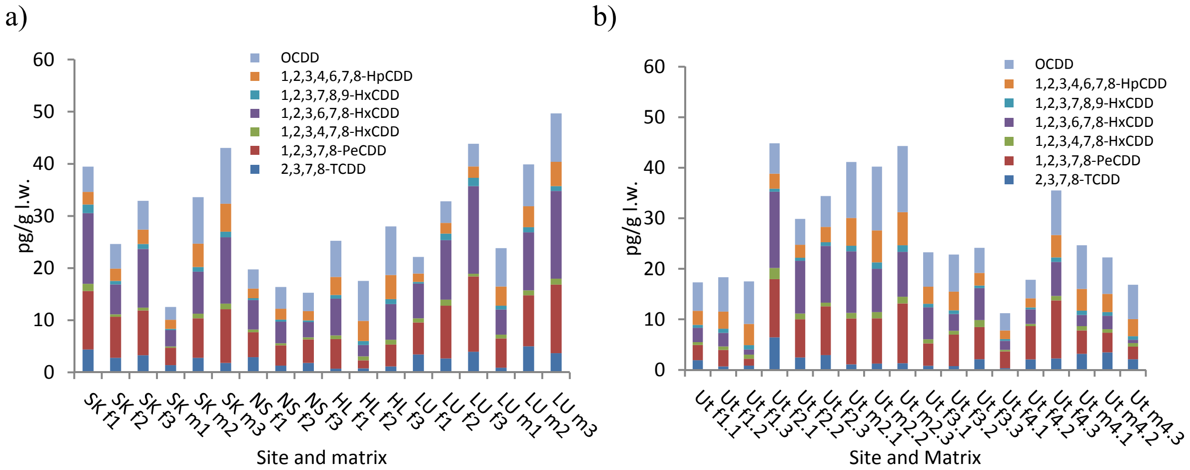


Figure 14. PCDD concentrations (l.w.) and congener patterns for a) coastal and b) offshore herring. SK = Skutskär, NS = Norrsundet, HL = Hornslandet, LU = Lörudden, Ut 1 = Utsjö 1, Ut 2 = Utsjö 2, Ut 3 = Utsjö 3, Ut 4 = Utsjö 4; f = fillet, m = muscle; 1,2 or 3 refers to which pooled sample is represented; e.g., Ut f1.1 refers to herring fillet sampled at Utsjö 1, pooled group 1. Unadjusted data is used.

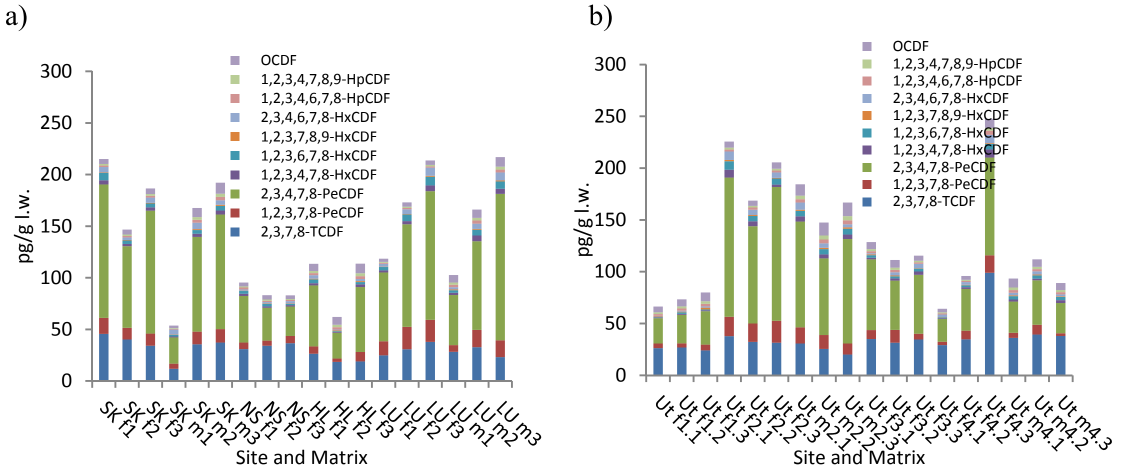


Figure 15. PCDF concentrations (l.w.) and congener patterns for a) coastal and b) offshore herring. SK = Skutskär, NS = Norrsundet, HL = Hornslandet, LU = Lörudden, Ut 1 = Utsjö 1, Ut 2 = Utsjö 2, Ut 3 = Utsjö 3, Ut 4 = Utsjö 4; f = fillet, m = muscle; 1, 2 or 3 refers to which pooled sample is represented; e.g., Ut f1.1 refers to herring fillet sampled at Utsjö 1, pooled group 1. Unadjusted data is used.

In both coastal and offshore herring, TEQ$_{\text{PCDD}}$ contributed the least to total TEQ (Figure 17, 18). This result is in agreement with results seen from the temporal data (5.3.3).

When the TEQ$_{\text{PCDD}}$, TEQ$_{\text{PCDF}}$, TEQ$_{\text{dl-PCB}}$, TEQ$_{\text{PCDD/F}}$ and TEQ$_{\text{PCDD/F + dl-PCB}}$ (l.w.) values were compared between coastal and offshore herring using Student's *t*-tests, no significant differences were found when unadjusted fillet or muscle data was used. When age-adjusted data was used, TEQ$_{\text{PCDD}}$ and TEQ$_{\text{PCDF}}$ concentrations showed significant differences for muscle samples only (TEQ$_{\text{PCDD}}$: *d.f.* = 4, $p<0.01$, arithmetic mean 19.0 and 6.6 for coastal and offshore, respectively; TEQ$_{\text{PCDF}}$: *d.f.* = 4, $p<0.02$, arithmetic mean 32.6 and 13.0 for coastal and offshore, respectively). Fillet samples continued to show no significant differences in concentrations between coastal and offshore herring. It must be kept in mind that muscle samples had a very low number of observations ($n = 6$) and therefore confidence in muscle *t*-test results is poor.

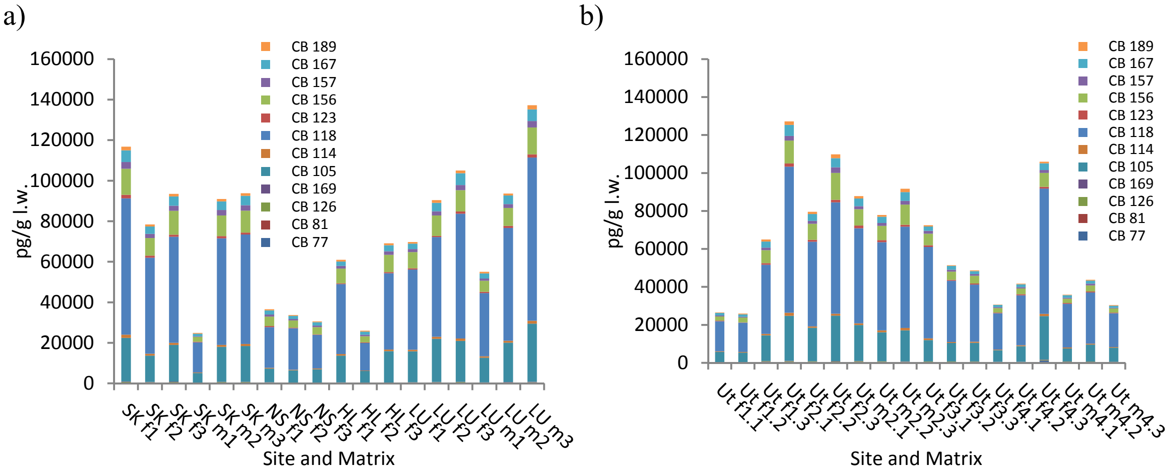


Figure 16. dl-PCB concentrations (l.w.) and congener patterns for a) coastal and b) offshore herring. SK = Skutskär, NS = Norrsundet, HL = Hornslandet, LU = Lörudden, Ut 1 = Utsjö 1, Ut 2 = Utsjö 2, Ut 3 = Utsjö 3, Ut 4 = Utsjö 4; f = fillet, m = muscle; 1,2 or 3 refers to which pooled sample is represented; e.g., Ut f1.1 refers to herring fillet sampled at Utsjö 1, pooled group 1. Unadjusted data is used.

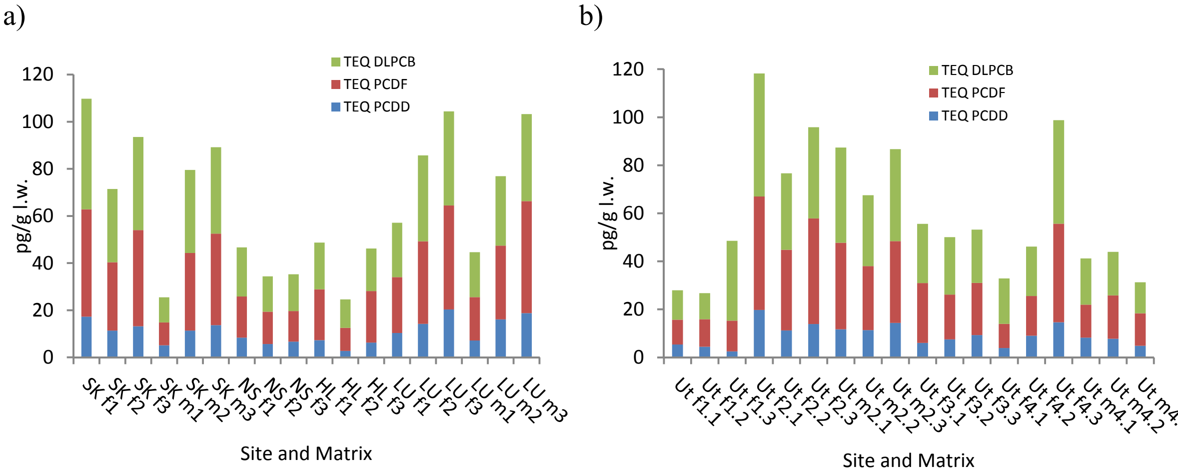


Figure 17. TEQ concentrations (l.w.) for PCDD, PCDF and dl-PCBs for a) coastal and b) offshore herring. SK = Skutskär, NS = Norrsundet, HL = Hornslandet, LU = Lörudden, Ut 1 = Utsjö 1, Ut 2 = Utsjö 2, Ut 3 = Utsjö 3, Ut 4 = Utsjö 4; f = fillet, m = muscle; 1,2 or 3 refers to which pooled sample is represented; e.g., Ut f1.1 refers to herring fillet sampled at Utsjö 1, pooled group 1. Unadjusted data is used.

Student's *t*-tests were repeated using both unadjusted and age-adjusted fillet data on a wet weight basis, but not muscle data, because of the low number of muscle observations. No significant differences were seen between any TEQ values from coastal or offshore herring for the unadjusted data. However, when the age-adjusted data was examined, a significant difference between coastal and offshore sites was seen, but only for $TEQ_{PCDD/F}$ values (*d.f.* = 14, $p<0.04$, arithmetic mean 2.7 and 1.7 for coastal and offshore, respectively).

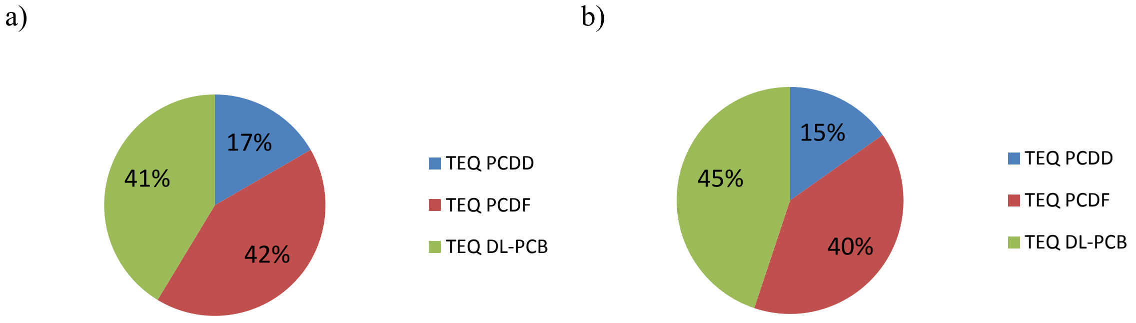


Figure 18. Relative proportion to total TEQ contributed by TEQ_{PCDD}, TEQ_{PCDF} and $\text{TEQ}_{\text{dl-PCB}}$ (unadjusted data) for a) coastal and b) offshore herring.

When the four coastal sites were compared for differences in TEQ_{PCDD}, TEQ_{PCDF}, $\text{TEQ}_{\text{PCDD/F}}$ and $\text{TEQ}_{\text{dl-PCB}}$ concentrations (l.w.), and dominant congeners (l.w.) using one-way ANOVAs (age-adjusted fillet data), a significant difference was only seen for $\text{TEQ}_{\text{dl-PCB}}$ ($f = 9.05$, *d.f.* = 3, $p<0.01$). Skutskär and Lörudden had significantly higher values compared to Hornslandet and Norrsundet. However, as Hornslandet is a reference site, it is expected that herring from this site would have lower concentrations than herring from the other three sites. When the offshore sites were examined in the same way, no significant differences in dominant congener concentrations or TEQ concentrations were seen.

By contrast, when one-way ANOVAs were carried out using age-adjusted w.w. data, significant differences were seen between all sites for TEQ_{PCDD}, TEQ_{PCDF}, $\text{TEQ}_{\text{PCDD/F}}$ and $\text{TEQ}_{\text{dl-PCB}}$ ($f = 7.24$, *d.f.* = 3, $p<0.02$; $f = 4.45$, *d.f.* = 3, $p<0.05$; $f = 16.99$, *d.f.* = 3, $p<0.01$; $f = 4.41$, *d.f.* = 3, $p<0.05$ respectively). Tukey's post hoc tests showed that Hornslandet had significantly lower values compared to Lörudden for all TEQ values. Norrsundet did not differ from any of the other three sites, except in the case of $\text{TEQ}_{\text{PCDD/F}}$, when Norrsundet had a significantly lower value compared to Lörudden. Skutskär had significantly lower TEQ_{PCDD} value compared to Lörudden, and significantly higher $\text{TEQ}_{\text{PCDD/F}}$ value compared to Hornslandet. For the offshore sites, no significant differences were seen.

MYSIDS AND ZOOPLANKTON

OCDD was highly dominant in both mysids and zooplankton from all sites (Figure 19a). 2,3,7,8-TCDF was dominant in mysids from Skutskär, while OCDF dominated in zooplankton from Skutskär and Norrsundet, and mysids from Lörudden (Figure 19b). For PCDFs and dl-PCBs, but not for PCDDs, mysids tended to have higher concentrations than zooplankton.

The relative proportion that TEQ_{PCDD}, TEQ_{PCDF} and $\text{TEQ}_{\text{dl-PCB}}$ contributed to total TEQ in mysids (Figure 20a) and zooplankton (Figure 20b) is similar to that seen in herring. The main difference is that $\text{TEQ}_{\text{dl-PCB}}$ contributes far more to total TEQ in zooplankton than it contributes in herring (coastal or offshore) and mysids.

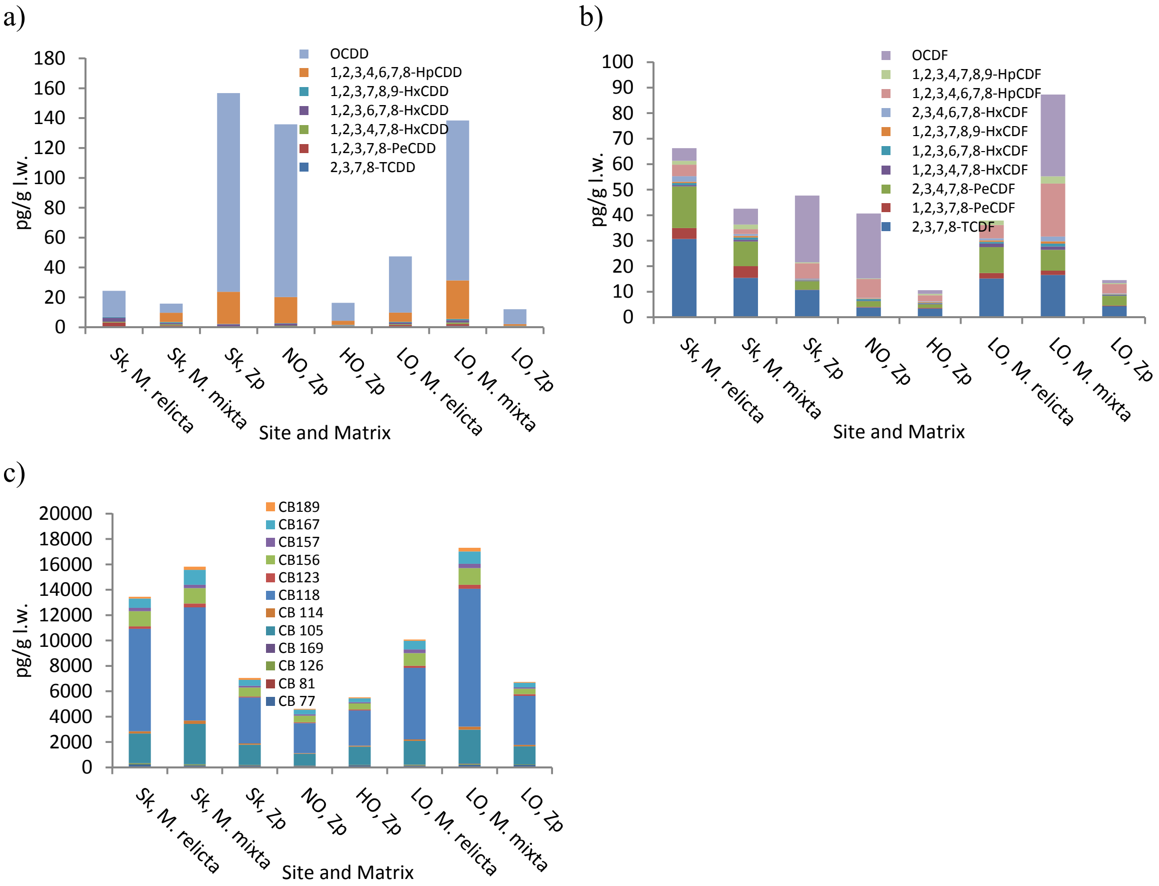


Figure 19 a) PCDD, b) PCDF and c) dl-PCBs (l.w.) in mysids and zooplankton. Sk = Skutskär, NO = Norrsundet, HO = Hornslandet, LO = Lörudden, Zp = zooplankton.

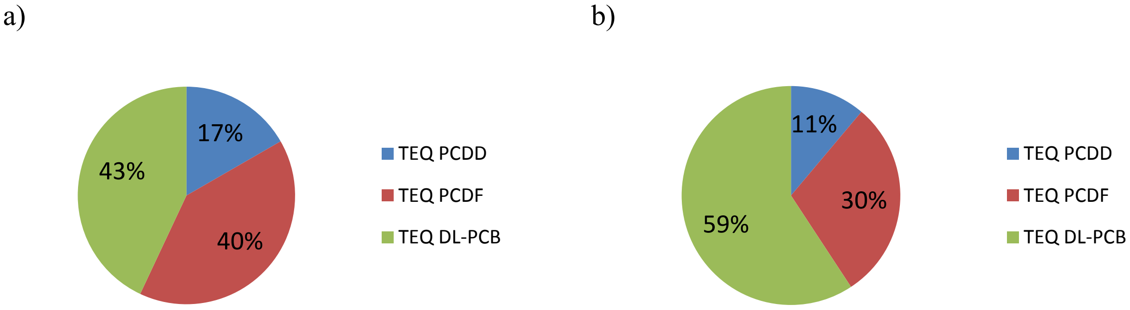


Figure 20. Relative proportion to total TEQ contributed by TEQ_{PCDD}, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$ (l.w., unadjusted data) for a) mysids and b) zooplankton, coastal sites.

SEDIMENT AND WATER

Sediment data are from Sundqvist et al. (2009a), and the chosen sites were in close proximity to where coastal herring were sampled (Figure 21). Sediment congener patterns were dominated by OCDD (Figure 22a), OCDF (Figure 22b), and CB118 and CB105 (Figure 22c). The water pattern was different from the sediment pattern for the PCDFs (Figure 22b), but not for the PCDDs (Figure 22a). This similarity between the sediment and water pattern (truly dissolved concentrations) for PCDDs is, however, not in accordance to other studies (Josefsson and Wiberg, unpublished data). The relative proportion of the TEQ concentrations from each group for sediment shows that dl-PCBs contribute the least, and PCDDs contribute the most to total TEQ (Figure 23a-d). Although dl-PCBs are shown as contributing 0% at Norrsundet (Figure 23b), in fact, this is 0.5%. Of the four sites, PCDDs contribute the least to total TEQ at Lörudden (50%; Figure 23d).

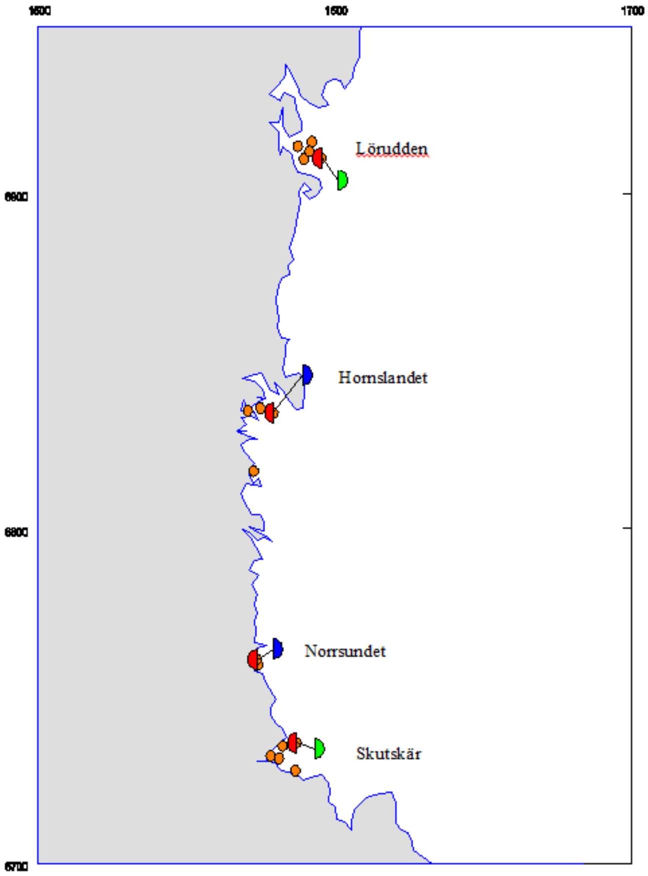


Figure 21. Green and blue half circles represent herring, red half circles represent the closest sediment site to the coastal sampling sites, and small orange dots indicate the cluster of closest sediment sites.

COMPARISON BETWEEN COMPARTMENTS

Pearson's correlation coefficients were used to try to establish a statistical link between dioxin concentrations in the sediment and in herring. The $TEQ_{PCDD/F}$ values for the sediment sites closest to the coastal sampling sites for herring were examined; however, no significant correlations between sediment TEQ and herring TEQ were found, probably due to the low number of sites (*n*=4; Figure 21).

Overall, congeners in herring did not differ much in concentration or pattern between coastal or offshore sites. Mysids and zooplankton had patterns similar to each other. Sediment patterns were more similar to the zooplankton pattern, which may indicate some suspended particulate matter was sampled with the zooplankton, while the water pattern was different again, in line with previous investigations (Wiberg *et al.* 2009). Contributions to total TEQ of the three groups of dioxins varied – in all biota, PCDDs contributed the least, while PCDF and dl-PCBs contributed the most; in sediment, PCDDs contributed the most and dl-PCBs contributed the least.

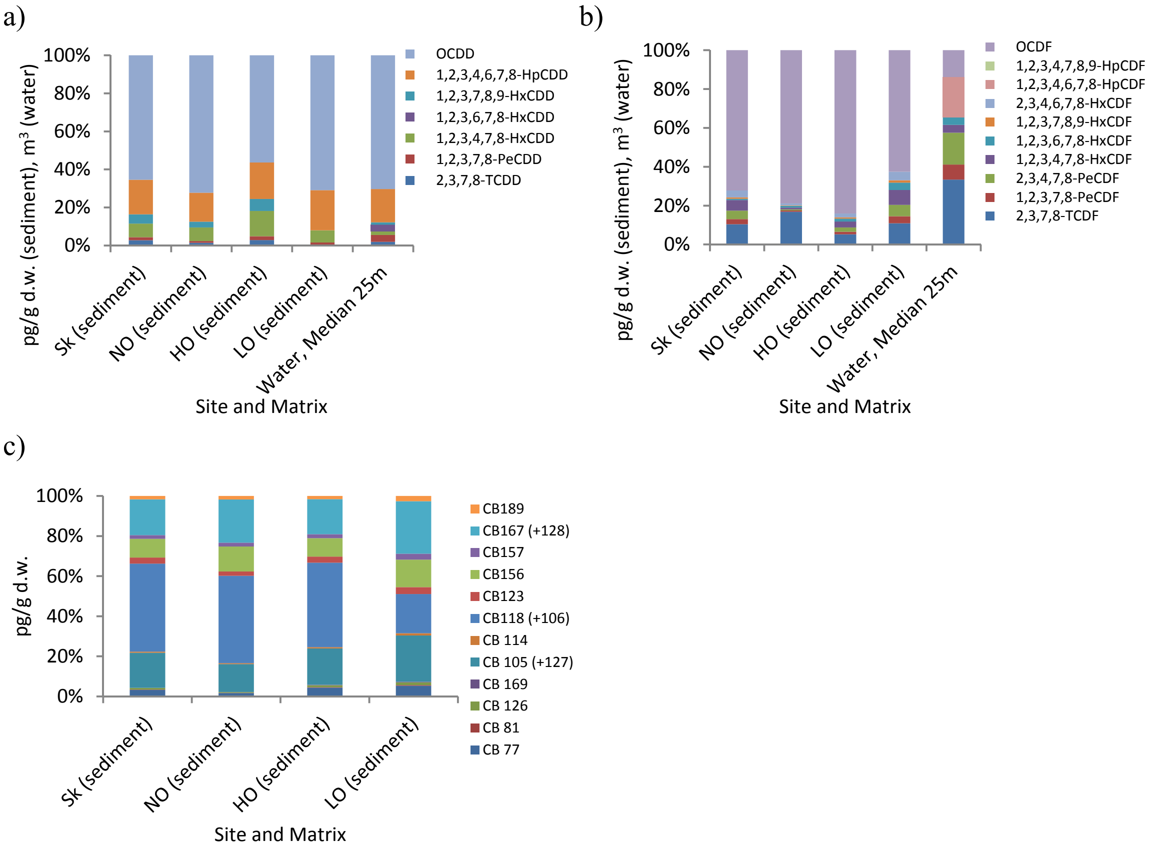


Figure 22. Congener patterns as a fraction of each congener in relation to the total concentration for sediment and water for a) PCDD, and b) PCDF; and for sediment only for c) dl-PCBs. Sk = Skutskär, NO = Norrsundet, HO = Hornslandet, LO = Lörudden. Coeluted dl-PCB congeners are indicated in the figure legends. Water data is from Cornelissen *et al.* (2008), and is based on the median congener concentration of the truly dissolved fraction from six sites sampled within the Bothnian Sea and Baltic Proper. dl-PCB data was not available for water within this data set.

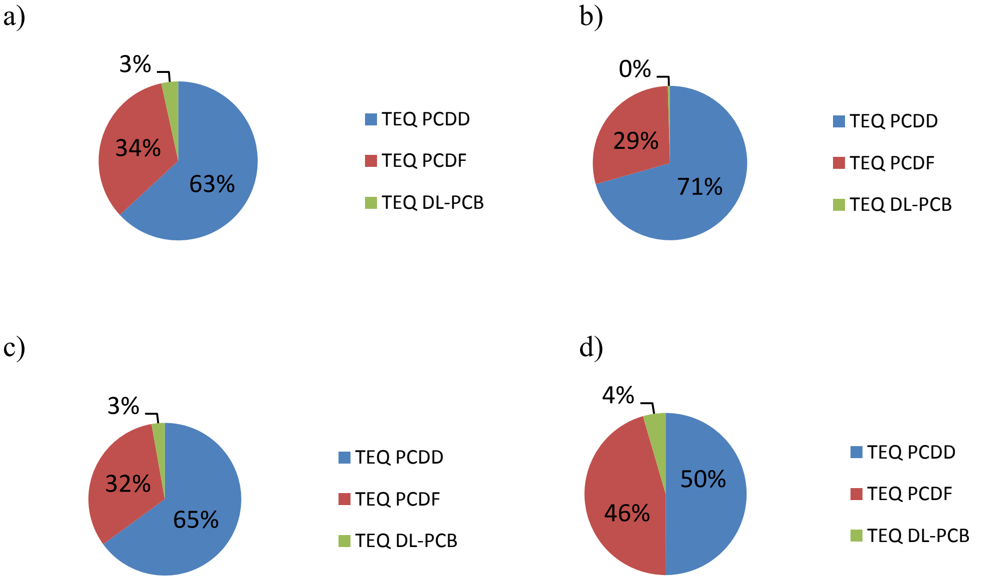


Figure 23. Relative proportion to total TEQ contributed by TEQ_{PCDD}, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$ for sediment from a) Korsnäs (near Skutskär), b) Norrsundet, c) Hornslandet and d) Lörudden.

7.3.3 Congener influence on offshore and coastal herring

Principal component analysis (PCA) was carried out to investigate what, if any, congener exerts the greatest influence on herring contamination load between coastal and offshore sites. As muscle samples were taken from only half of the sites, muscle was removed from the analyses, making a total of three pooled herring fillet samples at each site. As no significant differences were found in TEQ concentrations between coastal and offshore herring for fillet samples for either adjusted or unadjusted data, the PCAs are presented using unadjusted data.

For PCDDs and PCDFs, there is no clear pattern discernible in the data (Figure 24a, b), although for PCDFs, coastal herring appear to group more closely towards 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF (Figure 24b). For dl-PCBs, coastal and offshore herring form two groups (Figure 24c), which are significantly different (Hotelling's *t*-squared test, *f* = 5.8, *d.f.* = 12, *p*<0.02); however, there is still some scatter and overlap. Overall, there does not seem to be much difference in congeners influencing concentrations in herring caught from coastal and offshore sites.

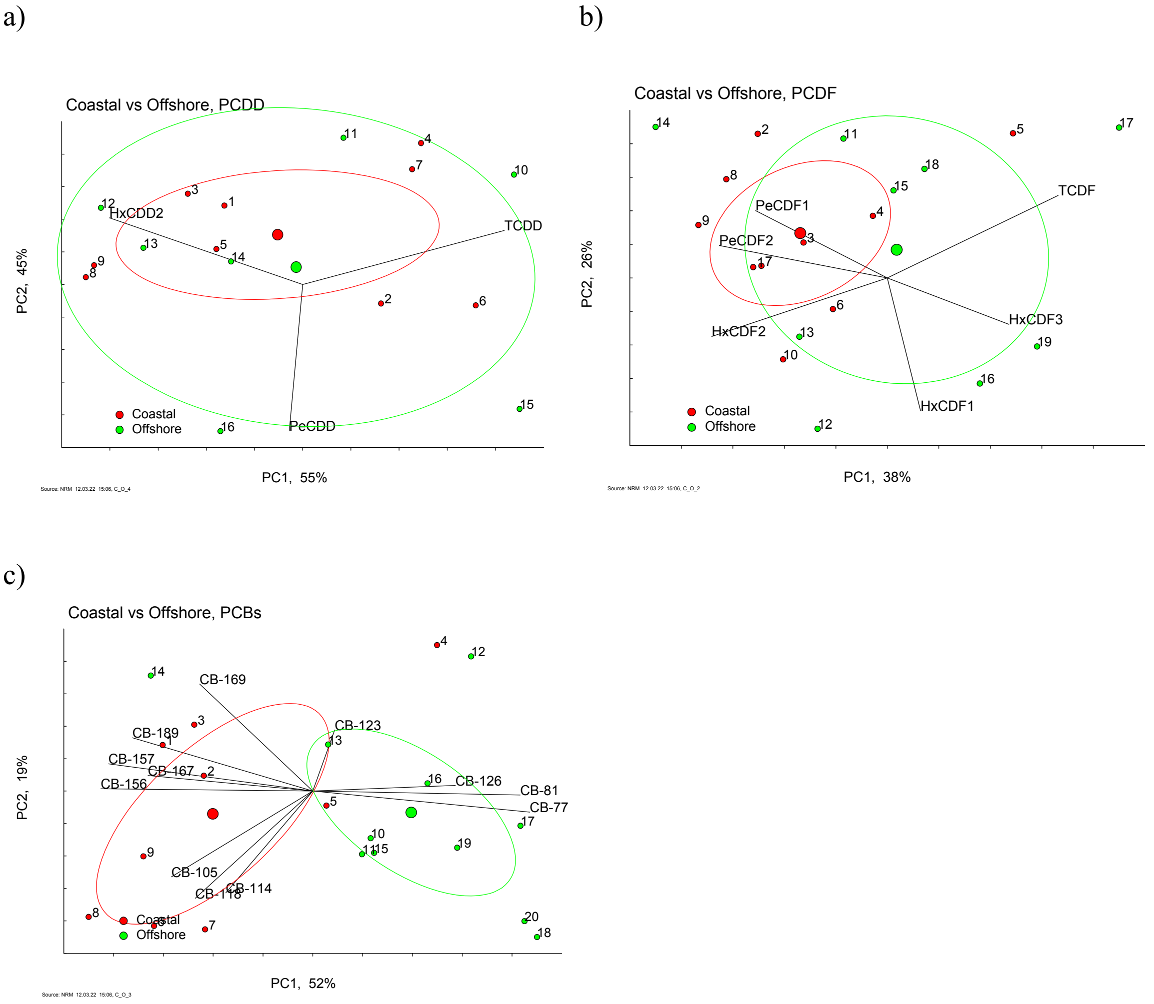


Figure 24. Principal component analysis for a) PCDDs, b) PCDFs and c) dl-PCBs in herring for coastal (red dots) and offshore (green dots) sites. The large red and green ovals are the Hotelling's 95% confidence ellipses. Numbers are equivalent to sites, where 1,2,3 = Skutskär; 4,5,6 = Norrsundet; 7,8,9 = Hornslandet; 10,11,12 = Lörudden; 13,14,15 = Utsjö 1; 16,17,18 = Utsjö 2; 19,20,21 = Utsjö 3; 22,23,24 = Utsjö 4.

7.3.4 Zooplankton composition

At Skutskär and Norrsundet, copepods were the dominant zooplankton, comprising 67 and 50% of total zooplankton composition, respectively. At Hornslandet, Lörudden and Köpmanholmen, *Bosmina* species were the dominant zooplankton, comprising 63, 50 and 60% respectively, of total zooplankton, with copepods being the secondary dominant group. Skutskär and Norrsundet are situated in the southern Bothnian Sea, while Köpmanholmen, Lörudden and Hornslandet are located in the central to northern Bothnian Sea (see Figure 13). Zooplankton community structure is largely regulated by the environment e.g., hydrography and stratification within the Baltic Sea (Flinkman *et al.* 1998 and references therein). Therefore, distances and different environmental conditions between sites could explain the observed differences in zooplankton composition.

7.3.5 Herring stomach content

The stomach contents of herring from the four coastal sites varied somewhat between sites. Zooplankton dominated at Norrsundet, both zooplankton and mysids occurred in most stomachs from Lörudden, while mysids and other food items e.g., chironomid pupae, fish, and *Gammarus*, dominated at Hornslandet and Skutskär. Skutskär had the highest percentage of empty stomachs (25%).

7.3.6 Stable isotope analysis

From the SIA analysis conducted, it was estimated that herring from Skutskär and Lörudden have a higher proportion of coastal mysids in their diet compared to offshore mysids and zooplankton (Figure 25). The diet of herring from Norrsundet is dominated by offshore mysids, with coastal mysids and zooplankton making up a smaller proportion of the diet. Herring diet at Hornslandet is dominated firstly by offshore mysids, and then by coastal mysids and zooplankton. While zooplankton plays a small role in the diet of herring at any site, offshore zooplankton features more prominently than coastal zooplankton in herring diet from Norrsundet and Hornslandet. In the previous section on stomach content analyses, mysids were only found from herring at Skutskär and Lörudden. However, unlike SIA, stomach content analysis only gives a snapshot overview of diet.

The proportion of coastal-sourced food resources in the herring diet is greater at Skutskär and Lörudden than at Norrsundet and Hornslandet (Figure 25). When herring biological parameters were measured and compared between these four sites (section 7.3.1), herring from Norrsundet and Hornslandet were similar to each other and differed significantly in weight, length and age to herring from Skutskär and Lörudden. These biological differences may be a reflection of herring diet.

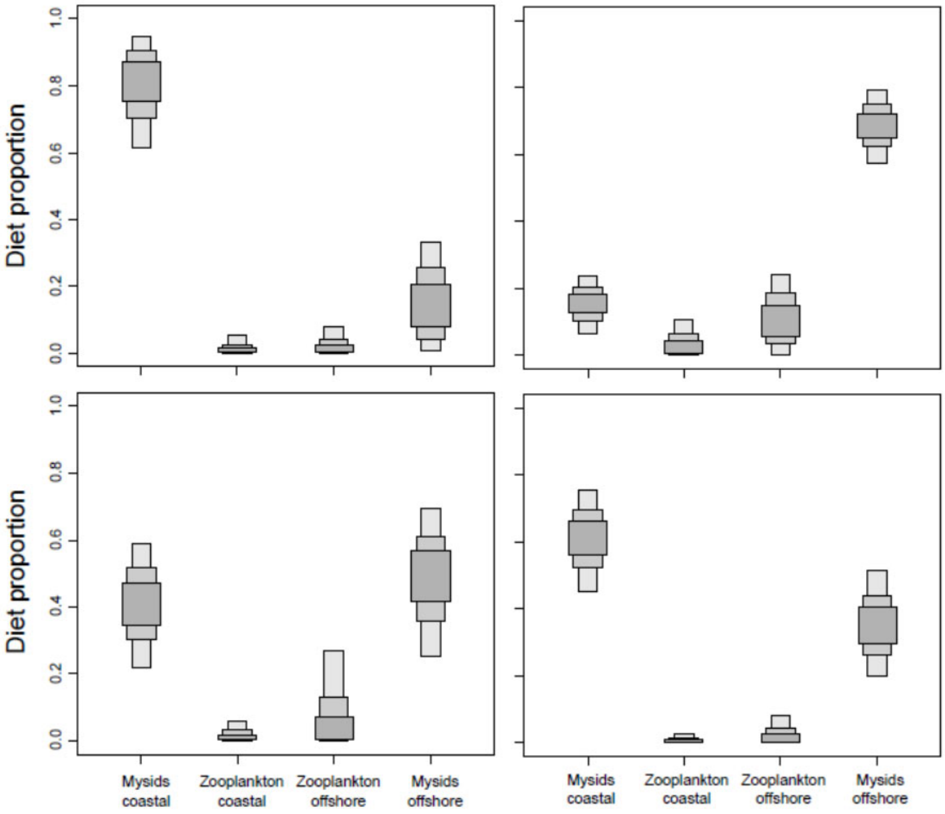


Figure 25. Proportion of coastal and offshore prey items in coastal herring diet estimated with the SIAR model for Skutskär (top left), Norrsundet (top right), Hornslandet (bottom left), and Lörudden (bottom right). The light grey boxes represent 95%, medium grey represents 75% and darker grey represents the 25% credibility interval.

7.4 Discussion

Investigation of herring from coastal and offshore sites from the Bothnian Sea revealed little variation in congener patterns, absolute congener and TEQ concentrations (l.w. basis). However, on a wet weight basis and using age-adjusted data, a difference between coastal and offshore herring was seen, but only for $TEQ_{PCDD/F}$ (higher in coastal than in offshore herring). This difference was not seen when unadjusted data was used. The relative contributions of TEQ_{PCDD}, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$ to total TEQ did not differ between coastal and offshore caught herring. Some populations of herring are known to feed offshore, and migrate to coastal areas for spawning (Lundin 2011). This phenomenon may have influenced results seen here. The overall lack of differences may also be because a limited geographical range was examined here.

By contrast, comparisons between the different coastal sites showed significant differences in $TEQ_{dl\text{-}PCB}$ (l.w. basis). $TEQ_{dl\text{-}PCB}$ values in herring from Skutskär and Lörudden were significantly higher than in herring from Hornslandet and Norrsundet. The pattern of these differences, with two sites grouping together, is the same as seen for the biological differences. On a w.w. basis and using age-adjusted data, all TEQ values differed significantly between coastal sites. In general, Hornslandet had lower TEQ values compared to the other sites, while Lörudden had higher values. Age-adjusting the data removes age, and consequently size, as potential confounding factors. Therefore, there are perceptible differences between herring sampled at different sites within the one basin on a wet weight basis. Depending on how far these fish travel/migrate, variable local sources of dioxin, or variation in herring diet and consequently lipid content, may be responsible for the observed differences.

SIA results support the observed differences between coastal sites seen on a w.w. basis. Herring caught at Skutskär and Lörudden had a higher proportion of coastal mysids present in their diet, whereas Hornslandet and Norrsundet had a greater proportion of offshore mysids in their diet. It appears that differences in diet (predominantly coastal verse offshore) explain much of the variation seen between the four sites.

Congener patterns and congener absolute concentrations (l.w. basis) in mysids and zooplankton differed somewhat from herring. Different dominant congeners as well as lower concentrations for both PCDDs and PCDFs, but not for dl-PCBs, were observed. Reasons for differences in dominant congeners between herring and mysids/zooplankton are likely related to differences in biotransformation ability and differential accumulation efficiencies between species (Armitage *et al.* 2009, HELCOM 2004), or suspended particulate matter sampled with the zooplankton.

No significant correlation could be established between PCDD/F and dl-PCB concentrations in sediment and herring, indicating a lack of influence of local environmental contamination on these herring; however, this lack of significant result could be due to a low number of samples, so a link between local sources from sediment to herring contaminant loads cannot be ruled out. Bignert *et al.* (2007) were also unable to establish a link between PCDD/F patterns in sediment and herring from the southern Bothnian Sea. It is unsurprising that sediment patterns differ to herring, as dioxins have low water solubility and therefore settle in the sediments close to the source point. Sediments in these areas would therefore receive the full spectrum of locally produced pollutants, whereas herring only receive what they accumulate through diet and/or diffusion across the gills (Wiberg *et al.* 2009). Only one data set for water was available, which did not include dl-PCBs. It is difficult to make any inference about similarities or otherwise with the biota or sediment patterns. For this reason, water was not included on any PCA.

Contribution of TEQ_{PCDD}, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$ to total TEQ differed considerably between sediment and biota. In herring, mysids, and zooplankton, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$ contributed the most, and TEQ_{PCDD} the least, with this trend being even more pronounced in zooplankton. However, in sediment, $TEQ_{dl\text{-}PCB}$ contributed negligible amounts, while TEQ_{PCDD} contributed the most to total TEQ, the complete opposite to biota. Results from biota are similar to Isosaari *et al.* (2006), where the contribution of dl-PCBs to the WHO-TEQ was equal to or greater than the contribution of PCDD/Fs. As mentioned above, dioxins have low water solubility and tend to sorb to sediments in the vicinity of the local source. Over time, small amounts of dioxins are released from sediment and suspended particulate matter to become biologically available for uptake in the food web. Biota are then exposed to these small amounts, but at the same time, biological organisms are often able to biotransform the accumulated pollutants creating species-specific congener patterns. Thus the differing water solubility of the congeners and biotransformation explains the difference in contribution to total TEQ seen between biota and sediment.

Differences in dioxin concentrations previously observed in herring between Baltic Sea basins (Bignert *et al.* 2011, Bignert *et al.* 2007, Karl and Ruoff 2007) may be caused in part by variations in herring diet between basins. Herring diet from the Baltic Sea is usually dominated by zooplankton and mysids, however, different dominant food items have been identified from Baltic herring diet during different seasons (Popiel 1951, Parmanne *et al.* 2004, both in Parmanne *et al.* 2006; Arrhenius and Hansson 1993, Mollman *et al.* 2004). In the Bothnian Sea, a large proportion of mysids are often seen in herring diet (Parmanne *et al.* 2006), whereas in the Baltic Sea Proper, herring feed predominantly on zooplankton (Arrhenius and Hansson 1993). Feeding at different trophic levels can influence bioaccumulation of dioxins (Kiviranta *et al.* 2003), and may contribute to differences between basins in dioxin concentrations in herring.

Generally, coastal and offshore herring did not differ from each other in congener pattern or concentrations levels, indicating that the sampled herring may not be strictly coastal/offshore populations. Coastally caught herring differed between sites for all TEQ values on a w.w. basis, but only in $TEQ_{dl\text{-}PCB}$ value on a l.w. basis. Mysids and zooplankton congener patterns show a slight shift away from the herring pattern, while sediment is even further removed, although showing similarities to mysids and zooplankton. SIA results indicate that herring diet from Hornslandet and Norrsundet includes a greater proportion of offshore food resources while coastal dietary resources predominate in herring from Skutskär and Lörudden. These differences likely explain the differences observed in TEQ values between sites on a w.w. basis. Coastal caught herring appear little influenced by dioxins in coastal sediments, as seen from the lack of significant correlation between sediment and herring dioxin concentrations, although the low number of sites included here may have influenced the outcome.

7.5 Conclusions

- The spatial variation of dioxin concentrations was examined within the Bothnian Sea by comparing concentrations in herring at coastal and offshore sites. Congener pattern and absolute concentrations did not differ between coastal and offshore sites (l.w.), but on a w.w. basis $TEQ_{PCDD/F}$ displayed higher values in coastal herring than in offshore herring. The overall lack of differences can be attributed to the migratory nature of herring populations within the Bothnian Sea, feeding mainly offshore and migrating to coastal areas for spawning for only a few weeks in the spring/summer (Lundin, 2011).
- Stable isotope analysis of herring was used to examine the origin of herring diet from the four coastal locations sampled in the Bothnian Sea. A higher proportion of coastally sourced food was apparent in herring from two of the four sites, while herring diet from the other two sites was comprised mainly of offshore food sources. These results supported the differences seen on a wet weight basis between the four coastal sites, indicating that variations in diet were overall a large contributor to dioxin levels in herring in this basin.

8 Pollution time trends in sediments

8.1 Introduction

Changes in the pollution concentration in the water column are closely linked to changes in surface sediment concentrations. Sediment time trends can thus be used as an indicator when estimating the rate at which pollutants are entering the water body. However, due to the time lag effect caused by particle transport from erosion areas to accumulation bottoms, the pollution records in sediments show a stretched and delayed time trend compared to actual emissions. The hypotheses for the current study was that the pollution sources have changed over time, and that emission reductions of these known sources are reflected as declines in the sediments over time.

In order to probe geographical and temporal variations, sediment cores were sampled at five offshore sites of the Baltic Sea (Figure 26). In addition, seven coastal sediment cores were provided from a project managed by the County Board of Gävleborg (financed by Swedish EPA through Havsmiljöanslaget), and data from two coastal cores were provided by the County Board of Uppsala.

Figure 26. Selected offshore sampling sites within the BalticPOPs project (marked in black) and coastal stations from the county board projects (marked in red). At the Lövsta Bay, two cores were sampled.

The chemical characterization was combined with a multivariate source tracing technique known as Positive Matrix Factorization. This method uses statistics to explore the contamination composition of the samples in order to identify sources and apportion their contributions.

8.2 Method

8.2.1 Sampling of offshore sediment cores

The five offshore sampling stations were selected to represent a north-to-south gradient in the Baltic Sea (Figure 26). Sampling was conducted by the Geological Survey of Sweden (SGU) within the framework of the Swedish Status and Trend Monitoring Program (SSTMP). Table 4 shows details of the sampling locations.

Table 4. The sampling sites for the offshore cores.

Station	SGU site	Sample ID SGU	X (RT90)	Y (RT 90)	Sampling date	Water depth (m)	Sed. rate (mm yr^{-1})
N Bothnian Bay	SE-17	08_0170	7253357	1854916	2008	88	0.32
N Bothnian Sea	SE-2	08_0156	6956506	1663306	2008	200	0.91
S Bothnian Sea	SE-3	08_0149	6796985	1625135	2008	79	0.76
Baltic Proper	SE-7	05k-0001	6326299	1714352	2003	177	0.62
Arkona basin	SE-12	08_0039	6098014	1381802	2008	47	0.47

In addition, three sediment layers from very old cores (>1000 years) sampled in the northern Bothnian Sea and in the Arkona Basin (Table 5) were analysed. The cores were sub-sampled in the oldest part of the postglacial strata at depths varying from 300 to 550 cm. These fine-grained sediment layers were deposited during the recession of the Weichselian land ice (last ice age), thus they were formed well before the industrial era. More details can be found in Cato *et al.* (2012).

Table 5. Sampling data for very old sediment layers (>1000 years).

Station	Sample ID SGU	Subsample core length (cm)	Type of sediment	Latitude N WGS84 (m)	Latitude E WGS84 (m)	Water depth (m)	LOI[1] (%)
N Bothnian Sea	11-0258	520-530	Postglacial gyttja clay	631558.1	184331.6	16	2.6
N Bothnian Sea	11-0419	540-550	Postglacial clay gyttja	622817.8	172023.2	18	2.1
Arkona Basin	01d_0014	300-305	Postglacial clay	551347.5	134004.0	42	6.2

[1] LOI: Loss on ignition

To ensure undisturbed sediment, accumulation bottoms were located using hydro-acoustic methods (side-scan sonar and sub-bottom profiler) and inspected with a video camera prior to sampling. All sampling was performed using a Gemini corer (a twin-barrel Niemistö Corer). The physical quality of the sediment cores was additionally examined using X-ray technique by a digital sediment scanner (Cato *et al.* 2000) on board the vessel. The samples were visually inspected prior to subsampling for any signs of sediment disturbance. The subsamples were kept frozen (-18°C) in glass jars until analysis.

8.2.2 Dating of offshore sediment cores

The sedimentation rates were calculated based on ^{137}Cs-dating by the Swedish Radiation Safety Authority (SSM). The sedimentation rate at each sampling site was determined by first measuring the activity of the isotope ^{137}Cs in each 1-cm thick subsample cut out from the sediment core, and then identifying the activity peak caused by the Chernobyl accident in April 1986. The average sedimentation rate was then calculated from the quota sediment depth/sampling year. Based on ^{137}Cs-dating, sedimentation rates were determined to be between 0.32 and 0.91 mm yr^{-1} at the different stations (Table 4). Reported years are based on Ge-Li-detector dating performed in 2003 (the previous sampling round at the same sampling sites as in 2008).

8.2.3 Quantification

All tetra-octa-CDD/Fs, tri-deca CBs and HCB were determined in the five sediment cores using methods described by Sundqvist *et al.* (2009a). Unlike the previous chapters in this report, where only the seventeen 2,3,7,8-substituted PCDD/Fs were analysed, all congeners were determined here to enable the multivariate source tracing. Analyses were performed at the Department of Chemistry, Umeå University. TEQs were calculated using the WHO 2005 TEFs. The concentration of ΣPCB_7 refers to the sum level of the PCB congeners 28, 52, 101, 118, 138, 153 and 180.

In the Arkona Basin core, the layer corresponding to 1961-1965 showed disproportionately high concentrations as compared to adjacent levels. The same trend was noted for all the analysed compound groups (Figure 28, 31 and 37). Although natural causes cannot be ruled out, contamination or mislabelling during sampling, handling or analysis appears more likely. This layer was disregarded in the discussions.

8.2.4 Pollution fingerprints and source tracing

The composition of pollutants (such as the relative abundance of congeners) in emissions from anthropogenic and natural processes is often relatively constant over time. Such stable and source-specific compositions, fingerprints, can be used to investigate from which type of emission sources pollutants origin. Sometimes, a simple fingerprint consisting of the ratio of two substances can be used, but usually a much more detailed fingerprint is required to distinguish between different emission types. When dealing with complex source fingerprints, sophisticated statistical methods are required due to the large amount of data. This report uses two kinds of multivariate techniques to explore the data, the non-quantitative method Principal Component Analysis (PCA) and the quantitative method Positive Matrix Factorization (PMF).

In multivariate source tracking, the following general assumptions are made:

- the pollution composition of the emissions are constant over the study period,
- the studied compounds do not react with each other (i.e., they can be added linearly) and,
- the pollution composition is not affected during transport from the source to the environmental sample (receptor).

The chemical fingerprints in this report are not individual in the sense that specific industries can be identified. Instead, the fingerprint can be used to identify a type of industrial activity or natural process. In some instances, industrial processes with large similarities cannot be separated and thus only a source category can be identified instead of a specific activity or process.

Fingerprints or chemical composition of environmental samples are expressed in the form of congener patterns, where the concentration of the individual congener is normalised to the total PCDD/F concentration of the sample. Through this normalization procedure, focus is put purely on the chemical pattern, while disregarding the contamination level. Fingerprints and composition can also be expressed in other ways, which may have advantages in certain situations.

Two multivariate techniques were used for source tracing - PCA and PMF. PCA is a well-known multivariate statistical projection method, where the composition of different samples can be related to each other. PMF is a multivariate statistical method that can be used to identify and quantify the contribution of various sources of pollution, a so-called receptor model. By assuming that there is no degradation or selective retention in soils or other matrixes on the way from sources to environmental samples (receptors), PMF can estimate how much each different source type contributes to each environmental sample (Figure 27). For dioxin source tracing, uncertainty in this assumption can be handled by comparing model patterns with processed source samples (e.g., soils that have been sampled near the recipient, atmospheric deposition instead of air samples; Sundqvist *et al.*, 2009b, Sundqvist *et al.* 2010), hence reducing the (time) distance between source and receptor. A disadvantage of PMF method is the need for a large number of environmental samples that are affected by the same type of sources. While a PCA extracts the new principal components one by one, each time describing as much as possible of the remaining variation in the samples, PMF calculates all model fingerprints and their contributions at the same time through iteration.

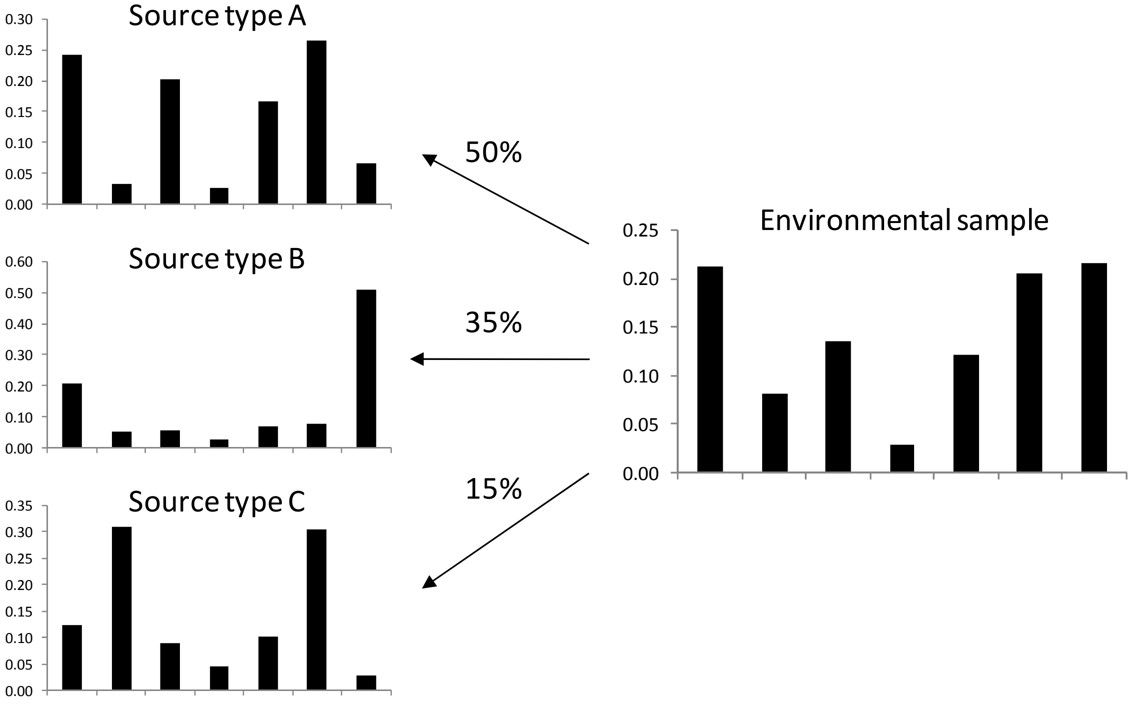


Figure 27. Receptor modelling can extract source fingerprints from a large database of environmental samples by assuming that no degradation or other pattern-changing process occurs between release and receptor. At the same time, the PMF model estimates how big the contribution must be from each source type in order to be able to explain the concentrations of individual congeners found in each receptor sample. From Sundqvist (2009).

PMF cannot determine the number of source types that contribute to the samples. Therefore, many simulations must be performed (with different numbers of source types), and then evaluated to determine which model provides the most reliable results. After each simulation, the model results are compared with the available knowledge on the actual pollution patterns in emissions. PMF is not the only multivariate receptor modelling method, but it has an advantage over many others because the model can take into account the uncertainty in the measurement data (i.e., the measured concentrations in environmental samples). In that way, higher uncertainty can be given to values close to the chemical detection or quantification limit, as these values are significantly more uncertain than values well above the limit.

8.3 Results and discussion

8.3.1 Concentration time trends in offshore areas

DIOXINS

The total tetra-octa-CDD/F concentrations in the surface sediments were fairly similar at the three northernmost stations, ranging from 430 to 530 pg g^{-1} d.w. (Figure 28). By far the highest surface concentration was noted in the Baltic Proper, 1 700 pg g^{-1} d.w. The surface sediments of the Arkona station showed an intermediate concentration of 910 pg g^{-1} d.w. Based on the calculated sedimentation rates, the peak concentrations were found in material deposited in the late 1980s and early 1990s in all cores.

Previously published time trend studies in the Baltic Sea are scarce, but Kjeller and Rappe (1995) reported total concentrations of tetra-octa-CDD/Fs in a core sample from the Baltic Proper (station P18, between the island of Gotland and the Swedish mainland) corresponding to the time period 1878-1988. The highest concentration was noted in the 1978 layer (1800 pg g^{-1} d.w.); however, the concentration in the surface sediments remained high (1 500 pg g^{-1} d.w.). Despite the somewhat earlier peak concentration noted by Kjeller and Rappe, the shape of the time trend noted in the core from 1988 corresponds well with those reported here (Figure 29). All of the investigated cores show a rather steep increase during a period of approximately 20 years prior to the peak concentrations. However, the decreasing trends are more varied with a sharper initial trend in the northern sites.

Koistinen *et al.* (1997) showed decreasing concentrations of 2,3,7,8-substituted PCDD/Fs in the Gulf of Finland, an area polluted by chlorophenol and PVC production, as well as in the Gotland deep in the Baltic Proper based on analysis of the top 3 cm of the sediments sampled in 1993.

Furthermore, previous measurements in the Bothnian Sea have indicated decreasing time trend based on 2,3,7,8-PCDD/F congeners (station SR5, in the southern Bothnian Sea; Verta *et al.* 2007). A core sampled in 2002-2003 showed a maximum concentration at approximately 8 to 16 cm depth depending on the congener, which is roughly in line with the present study.

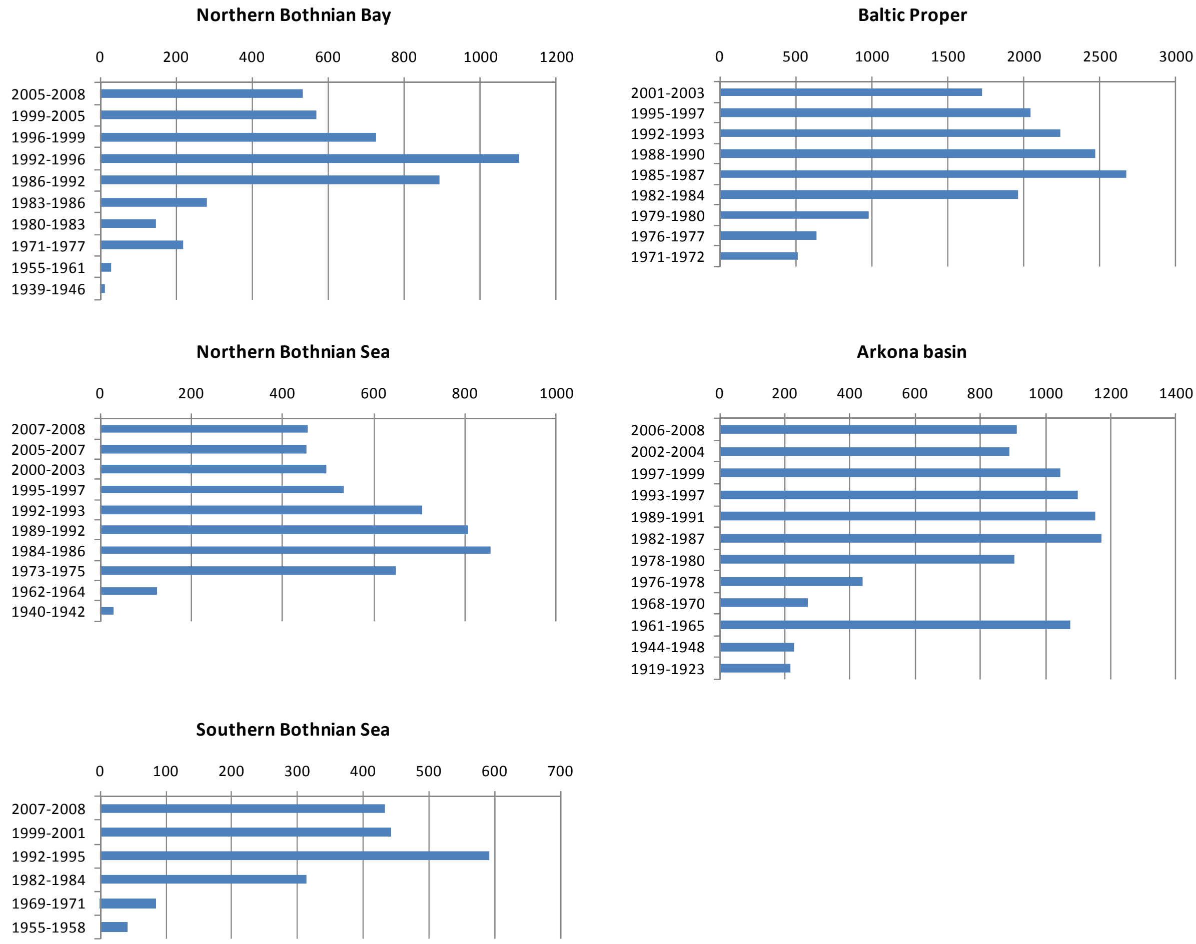


Figure 28. Total concentrations of tetra-octa-CDD/Fs (pg g^{-1} d.w.) in sediment cores from offshore areas.

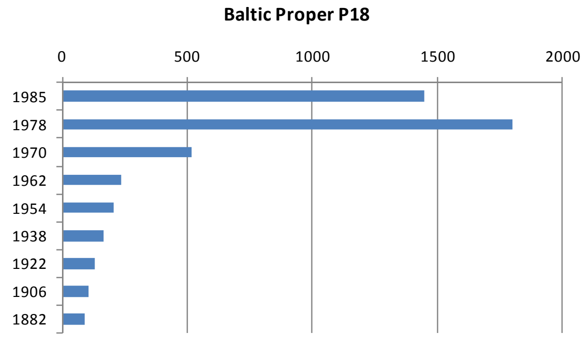


Figure 29. Total concentrations of tetra-octa-CDD/Fs (pg g^{-1} d.w.) in sediment core P18 (Kjeller *et al*. 1995).

On a TEQ-basis, the highest $TEQ_{PCDD/F}$ (50 pg g^{-1} d.w.) was found in the Baltic Proper sediment core, where the surface concentration was also high (29 pg g^{-1} d.w., Figure 30). In the three northern most stations, the TEQ in surface sediments were <10 pg g^{-1} d.w. This is below the recommended exposure limit set by the Netherlands (13 pg I-TEQ g^{-1} d.w.), but much higher than the Canadian interim sediment quality guideline (0.85 pg WHO-TEQ g^{-1} d.w.). The PCDD/F contribution to the total TEQ of the sediments is dominating over the contribution from the PCB congeners, contributing in general more than 93% in the north, and down to 88% in the south.

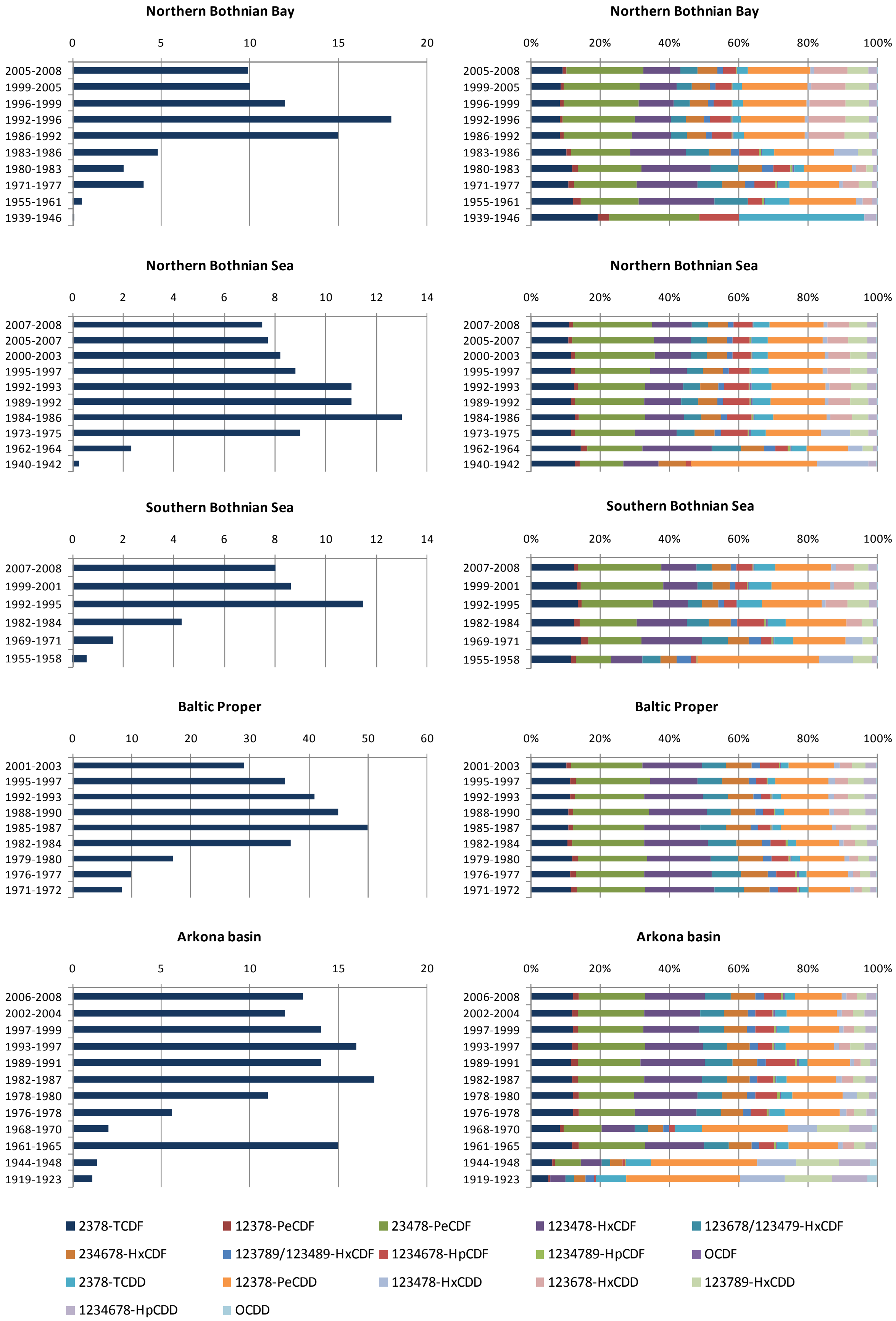


Figure 30. Concentrations of TEQ $_{PCDD/F}$ (pg g^{-1} d.w.) in sediment cores from offshore areas and the relative contribution to TEQ from different PCDD/F congeners.

The time trends of $TEQ_{PCDD/F}$ followed those of the total tetra-octa-CDD/F concentrations. The relative contributions from individual congeners were fairly constant over time, except in the oldest layers. This may in part be due to the low concentrations in the deepest layers, with several congeners below the LOQ. Generally, 2,3,4,7,8-PeCDF contributed the most to the $TEQ_{PCDD/F}$, but 2,3,7,8-TCDF, 1,2,3,4,7,8-HxCDF and 1,2,3,7,8-PeCDD were also important, and in some cases contributed equally, or even higher than 2,3,4,7,8-PeCDF.

PCBs

The total tri-deca-CB concentrations in surface sediments showed similar spatial and temporal trends as PCDD/Fs. The peak concentrations at the three northern stations ranged from 5 800 to 7 100 pg g^{-1} d.w. (Figure 31), while the peak concentration in the Baltic Proper sediment core was more than 10 times higher (94 000 pg g^{-1} d.w.). Again, the Arkona Basin site showed an intermediate concentration compared to the other sites, with a peak of 18 000 pg g^{-1} d.w., and a surface concentration of 14 000 pg g^{-1} d.w.

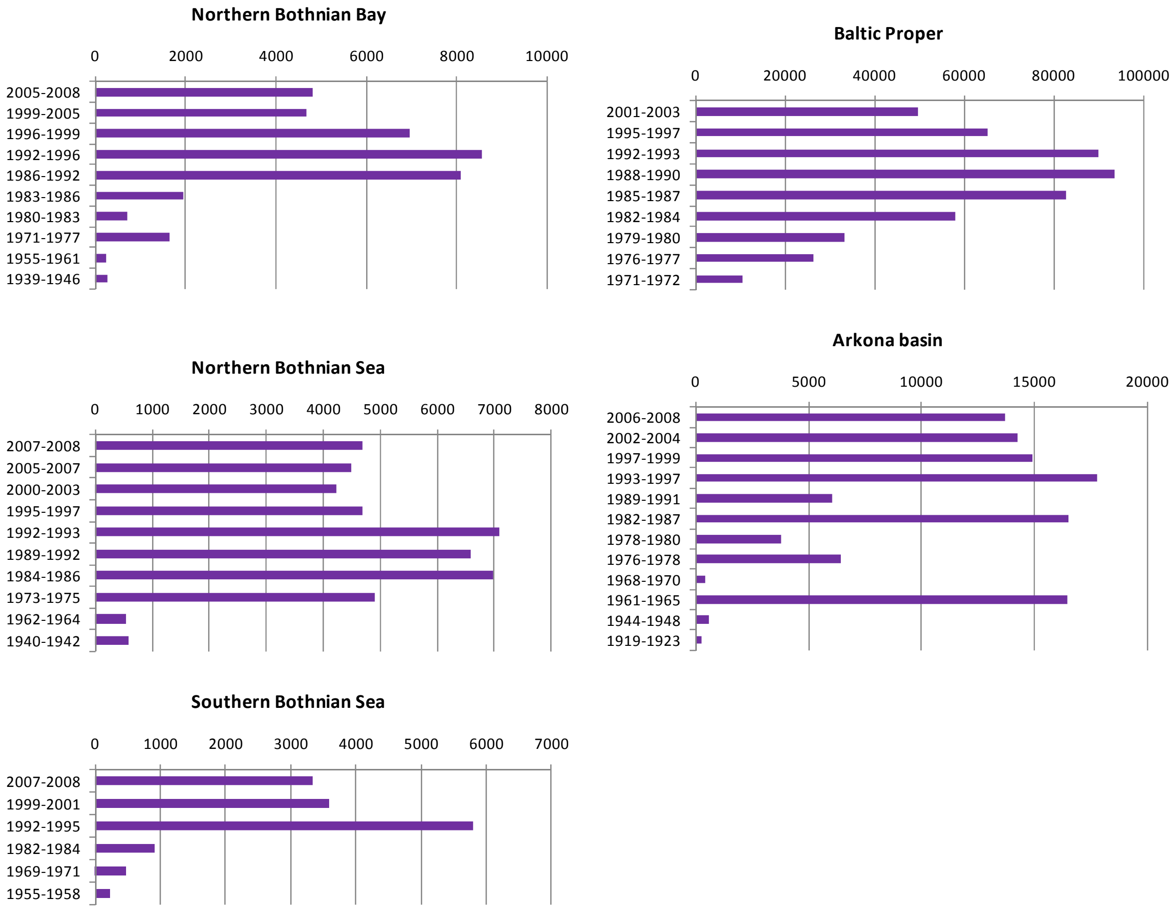


Figure 31. Concentrations of tri-deca-CBs (pg g^{-1} d.w.) in sediment cores from offshore areas.

In most cores, the homologue composition was fairly constant down to layers corresponding to the early 1970s, but deeper layer showed a clearly increased proportion of the tri- and tetra-chlorinated homologues (Figure 32). Looking at the homologue concentrations, tri- and tetra-CBs are actually much more constant over the studied time period than the higher chlorinated homologues. The highest relative increases over time were noted for penta- to octa-CBs (up to over 10 000 times). One reason for the time trend seen in the composition may be changes in emissions, but differences in environmental behaviour because of differences in physical-chemical properties, environmental persistence, and formation through degradation of other congeners may also be influential.

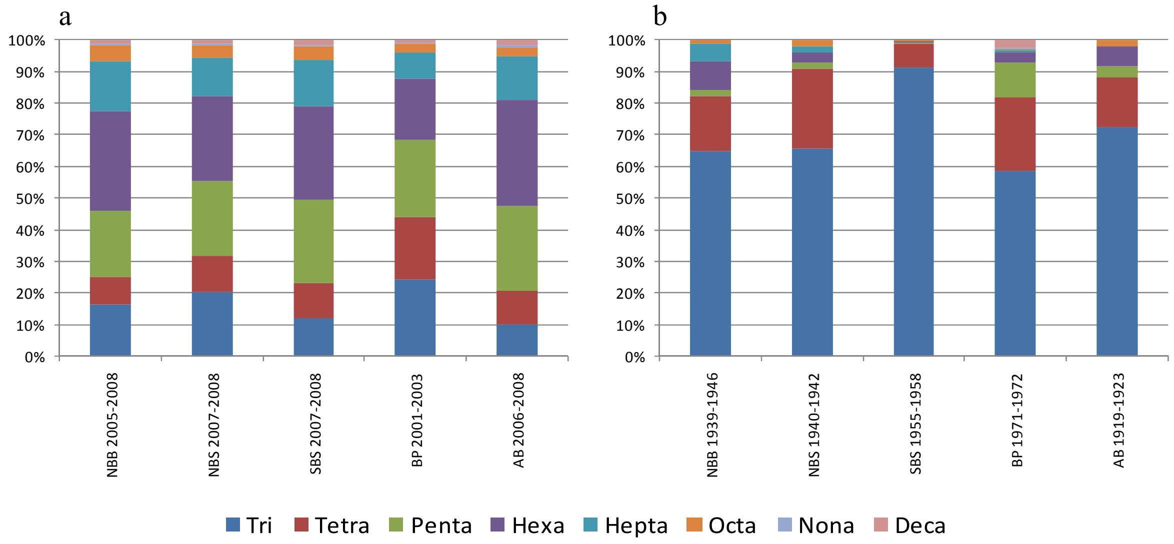


Figure 32. Contributions of PCB homologue groups in sediment cores from offshore areas (NBB=northern Bothnian Bay, NBS=northern Bothnian Sea, SBS=northern Bothnian Sea, BP=Baltic Proper and AB=Arkona Basin) for a) the surface layer and b) the deepest layer.

The ΣPCB_7 shows the same time trends as the total tri-deca-PCB concentrations. The composition within each core was relatively stable, although there was a tendency for a higher proportion of low-chlorinated congeners in the deeper layers, as noted for the homologues (Figures 32, 33).

ΣPCB_7 in a core sample from the Baltic Proper (station P18, between Gotland and the Swedish mainland) corresponding to a time period between 1880 and 1988 shows concentrations ranging between 180 and 11 000 pg g^{-1} d.w. (Figure 34; Kjeller and Rappe 1995). The highest concentration was noted in the 1978 layer, similar to PCDD/F. The concentration in the surface layer was drastically lower (2 600 pg g^{-1} d.w.) than the concentration measured in the corresponding layer in the Baltic Proper in the current study. Thus, the older study suggests a lower peak concentration with a much sharper decrease in overlying sediments. The discrepancy noted between the concentrations in the two studies may be caused by the distance between the sampling locations.

The time trends of $TEQ_{dl\text{-}PCB}$ were similar to total tri-deca-CB and ΣPCB_7 (Figure 35). Again, the Baltic Proper core showed the highest surface concentration (2.9 pg TEQ_{PCB} g^{-1} d.w.) and overall maximum concentration (6.1 pg TEQ_{PCB} g^{-1} d.w.). The main contributors to TEQ_{PCB} were PCB 126 and 169, while PCB 118 (+106) shows the highest concentrations among the PCB congeners (Figure 36).

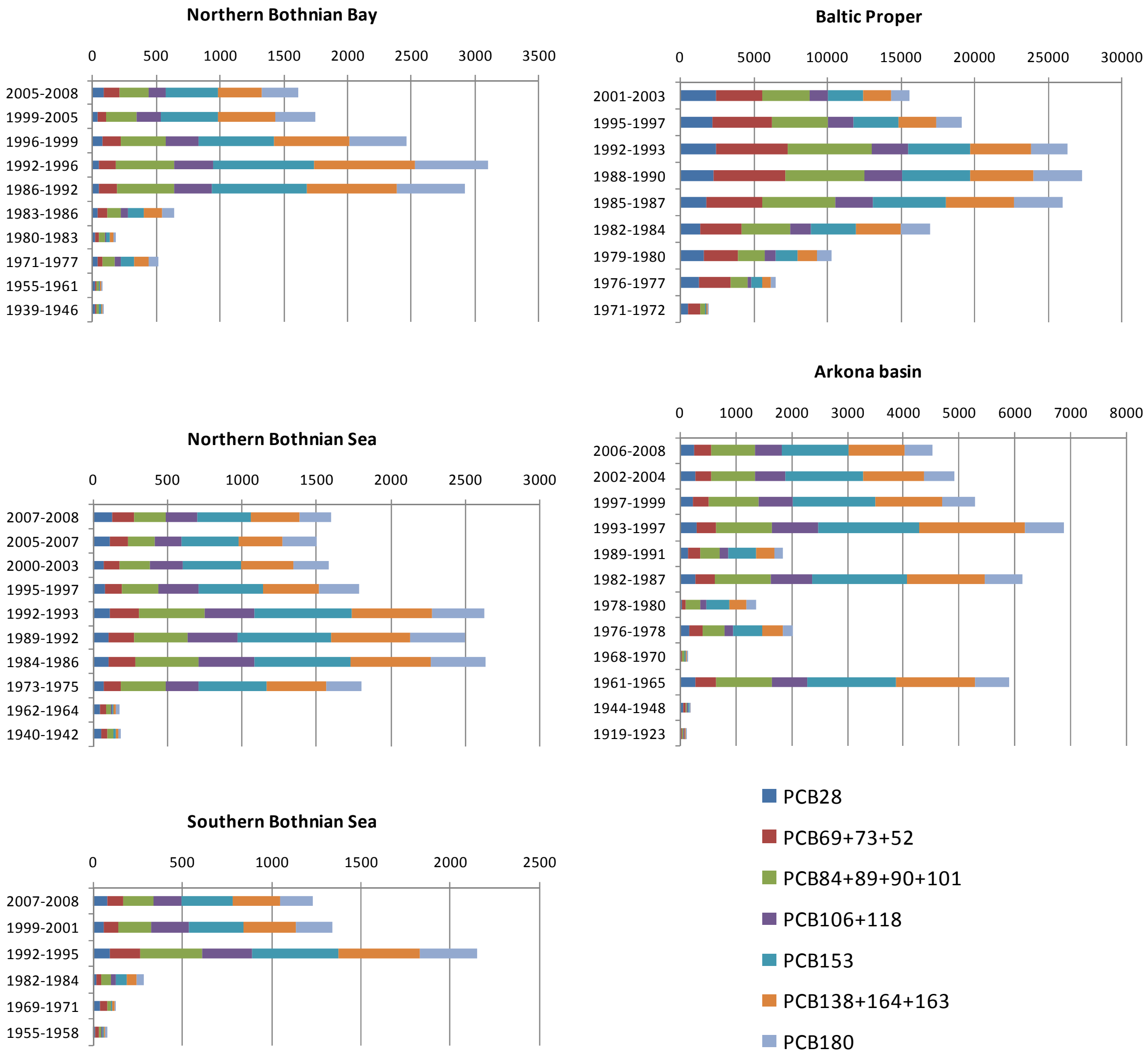


Figure 33. Concentrations of ΣPCB_7 (pg g^{-1} d.w.), in sediment cores from offshore areas.

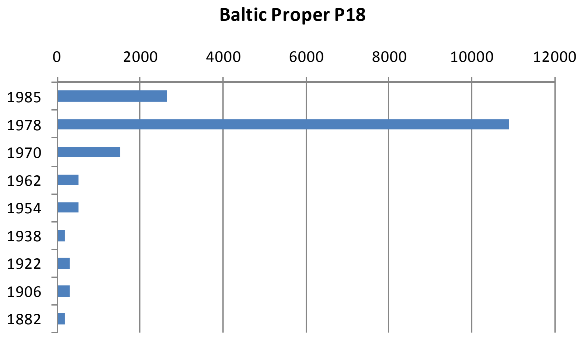


Figure 34. Concentrations of ΣPCB_7 (pg g^{-1} d.w.) in sediment core P18 (Kjeller *et al*. 1995).

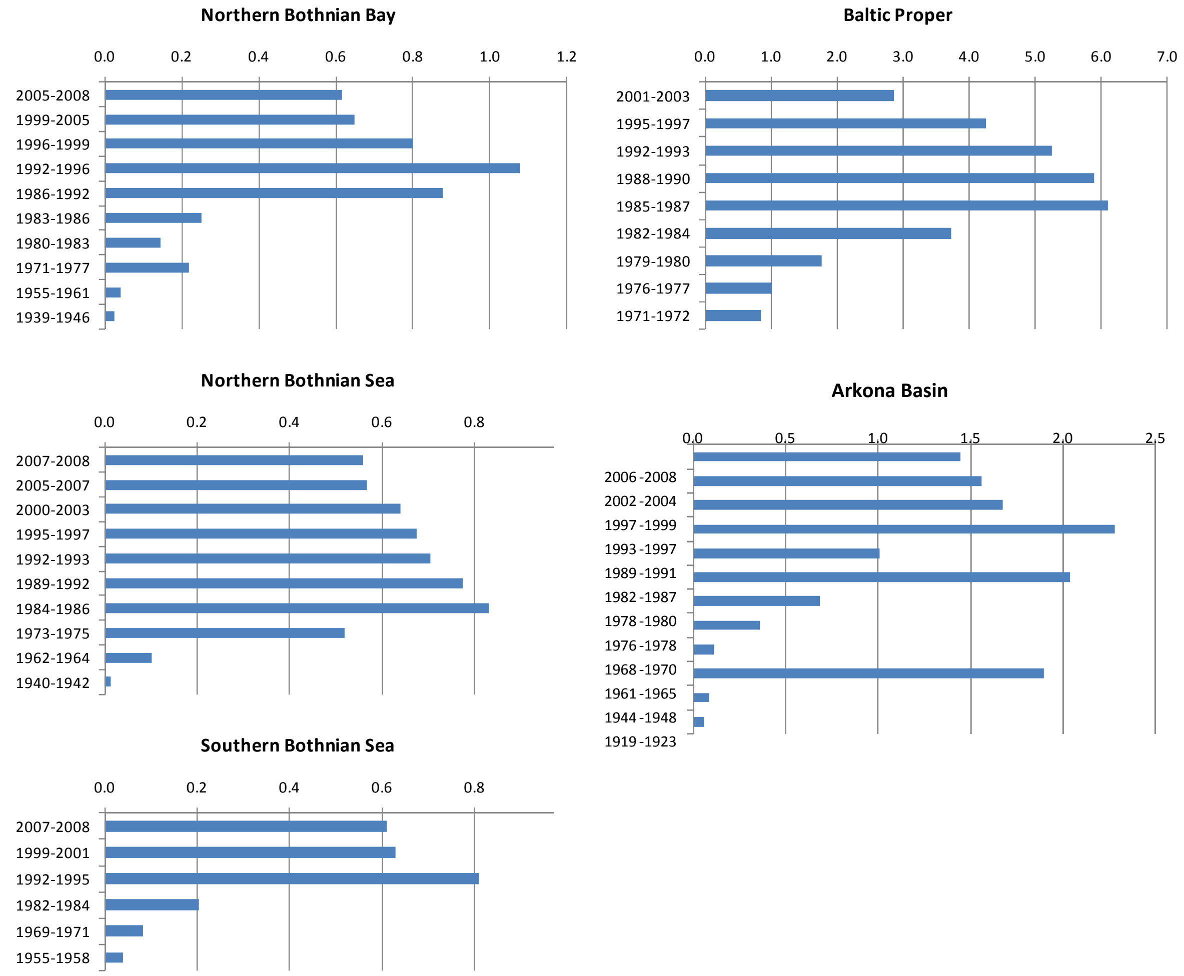


Figure 35. Concentrations of TEQ$_{\text{dl-PCB}}$ (pg g^{-1} d.w.) in sediment cores from offshore areas.

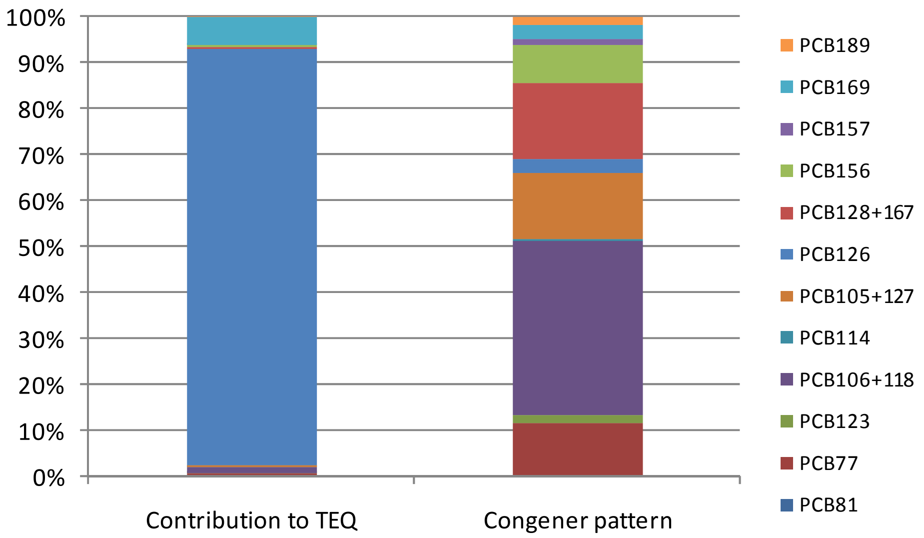


Figure 36. Average congener contributions to TEQ$_{\text{dl-PCB}}$ concentration and congener pattern in sediment cores from offshore areas.

HEXACHLOROBENZENE

The time trends of HCB were clearly different from the time trends of dioxins and PCB. After a decrease, starting in the early to mid-1990s, increasing levels from around 2000 were seen, and the peak level was detected at the surface layer (Figure 37). The Baltic Proper core was an exception, with lowest concentrations observed in the surface layer. The peak concentration was generally between 400 and 500 pg g^{-1} d.w., but for the Baltic Proper, a concentration of 1 400 pg g^{-1} d.w. was noted. HCB was banned in Sweden in 1980, thus emissions are expected to have decreased since then. The increasing trend opposes the general decreasing trends seen in many other sediment core studies around the world (Barber *et al.* 2005), and trends in Baltic biota (Bignert *et al.* 2010). These observations may not be alarming, but continuous monitoring within the framework of the Swedish Status and Trend Monitoring Program is advisable.

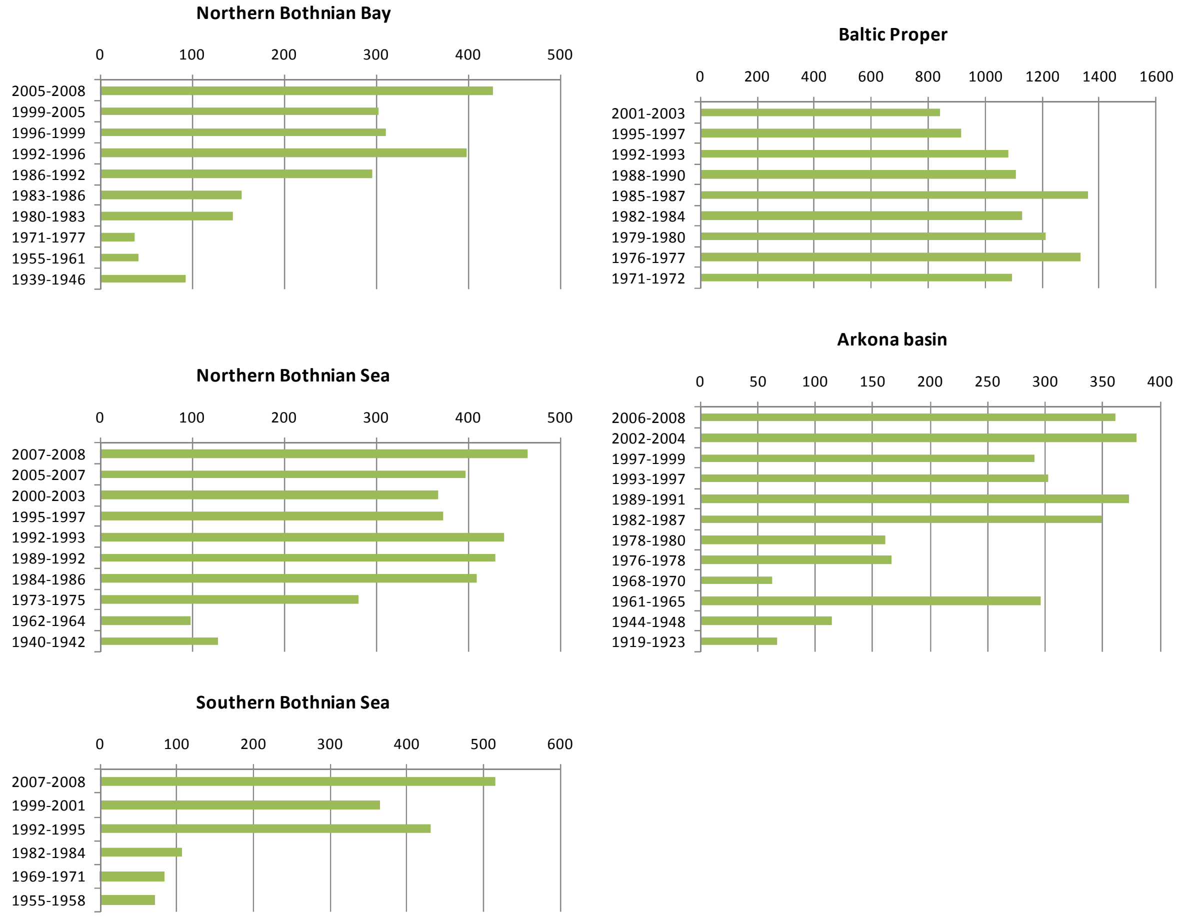


Figure 37. Concentrations of HCB (pg g^{-1} d.w.) in sediment cores from offshore areas.

8.3.2 Dioxin time trends in coastal areas

Results obtained from two studies run by Swedish County Boards present information on dioxin concentration time trends in coastal areas. The coastal sampling locations were not chosen to represent the most contaminated spots, but rather to reflect different industrial activity or locations where the contamination source is unknown. In total, nine coastal sediment cores were investigated; three from the Bothnian Bay and six from the Bothnian Sea. This study is published separately, but is presented here in short for comparison to the offshore data (Assefa *et al.* 2012, Sobek *et al.* 2012).

The time trends in coastal areas varied more than in offshore areas, and the decrease from peak concentrations were generally more dramatic (Figure 38). The largest decrease in coastal areas was noticed for Seskarö Bay, where the surface concentration has decreased to 6% of the peak concentration. Most of the investigated coastal locations showed maximum concentrations in layers corresponding to an earlier time period than for the offshore cores.

8.3.3 PCDD/F source tracing for sediment cores of the Baltic Sea

The sediment core data were first explored using PCA to get an initial view of the compositional variation and major source types. PCA can also be used as an indicator as to the maximum number of sources that contributes to the samples. The PCA results are not presented or discussed here, because the receptor modelling using PMF gave results in line with the PCA, and additionally gives the quantitative source contributions.

PMF modelling was carried out for scenarios with three to eight source types. Samples and congeners with many values below detection limits were removed because they mainly add uncertainty in the model, or add little or no relevant information from a tracking standpoint. In order to achieve reliable results, it is important to include many samples with high pattern variation. Therefore, PCDD/F data from a previous study was included in the modelling (Sundqvist *et al.* 2010). The final data matrix contained 56 chromatographic peaks (each corresponding to one or more congeners) and 269 samples. Using the diagnostic tools available, it was concluded that six source types could explain the composition of PCDD/F in the studied samples in a satisfactory manner. Three of the estimated model patterns could be linked to diffuse atmospheric sources, including combustion and other high-temperature sources, while the other three could be related to sources of point source character. The model patterns were very similar to those obtained in Sundqvist *et al.* (2010), and the source identification process is described in detail in that publication. Below is a short description on how the source identification was carried out in this study.

IDENTIFICATION OF MAJOR SOURCE TYPES

The three model patterns associated with diffuse atmospheric sources are presented in Figure 39. The first pattern is essentially identical to that seen in the background atmospheric deposition at a research station in Vindeln in northern Sweden (Figure 40a), whereas the other two have characteristics similar to patterns from combustion (Figure 40b). Incineration and other high temperature processes are difficult to characterise and differentiate from each other because the emission pattern depends on combustion conditions and the fuel composition. These emission patterns can therefore vary over time, and the pollution pattern in Figure 40b should only be seen as an example and not necessarily as a typical combustion source pattern. Despite the known variability, certain characteristic congeners were noted, and the composition within each homologue tended to be relatively stable, although the congener pattern varied.

It is important to note that the model pattern referred to as Atmospheric background also shows large similarities with the pollution patterns in wood preservatives of PCP type. An assessment must be made in each sample based on what is known about the sampling area, as well as the other pollutants present in the sample. PCP has, in contrast to the atmospheric background, been shown to contain three highly chlorinated PCDFs. These congeners can be used as additional markers to identify chlorophenol use.

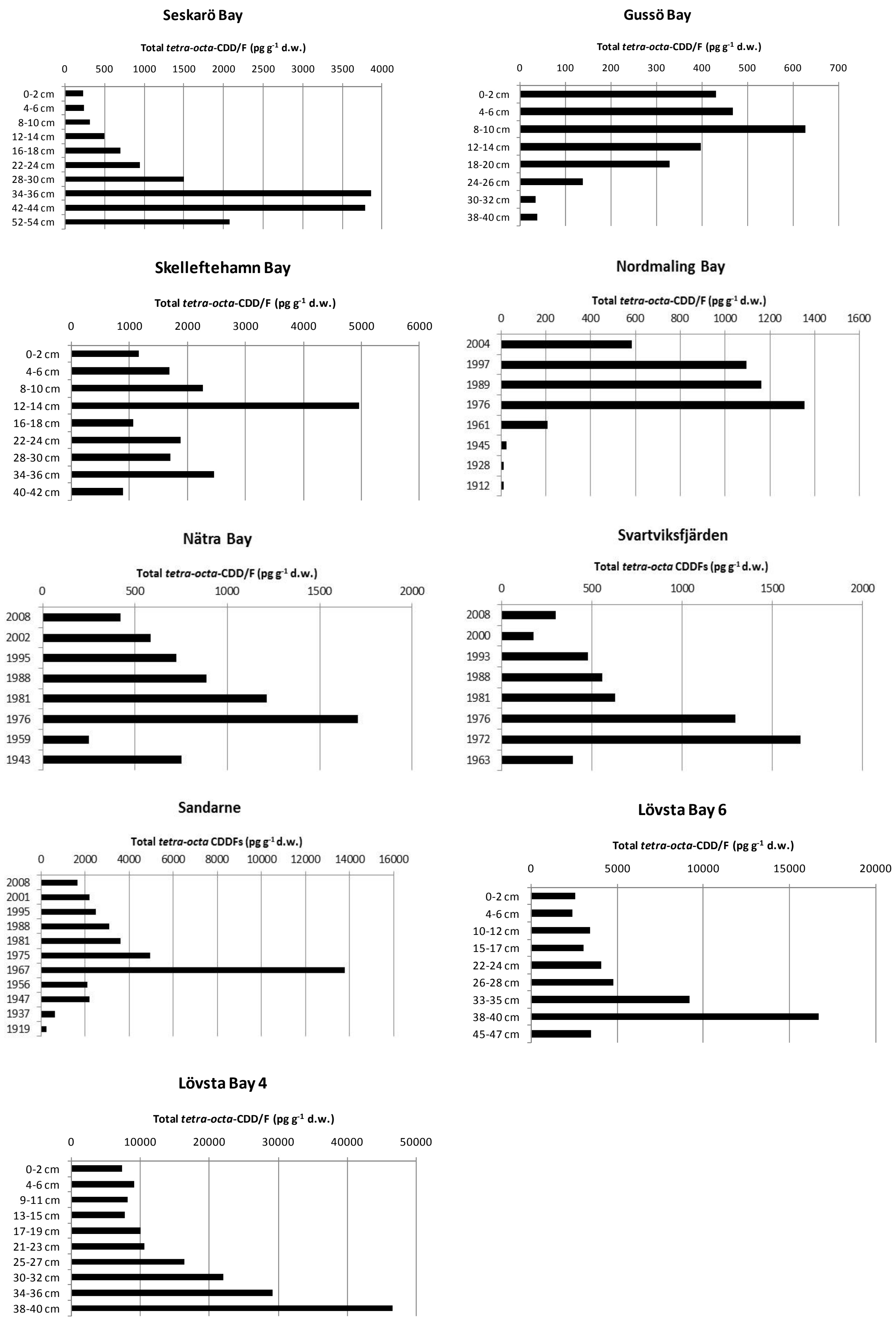


Figure 38. Total concentrations of tetra-octa-CDD/Fs (pg g^{-1} d.w.) in sediment cores from coastal areas. For dated cores, the given year is an average for the time span that the sediment layer represents.

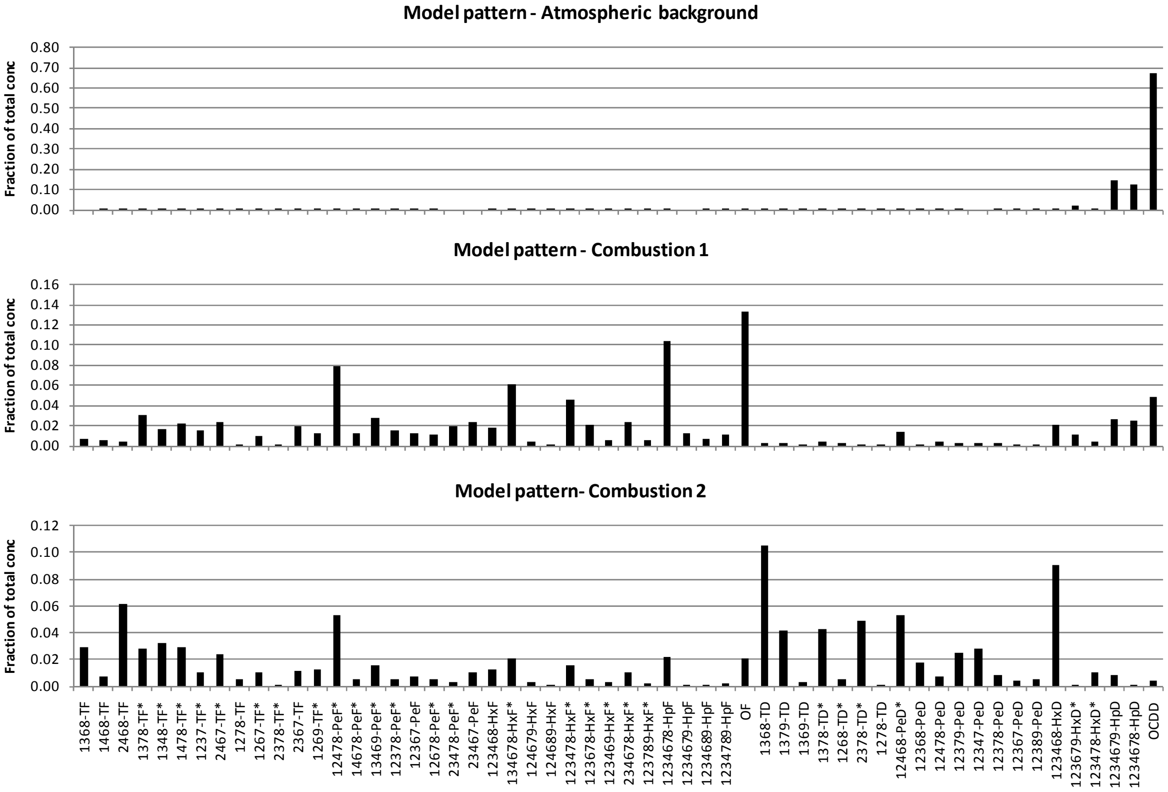


Figure 39. PMF model patterns related to atmospheric sources, including combustion and other high temperature processes.

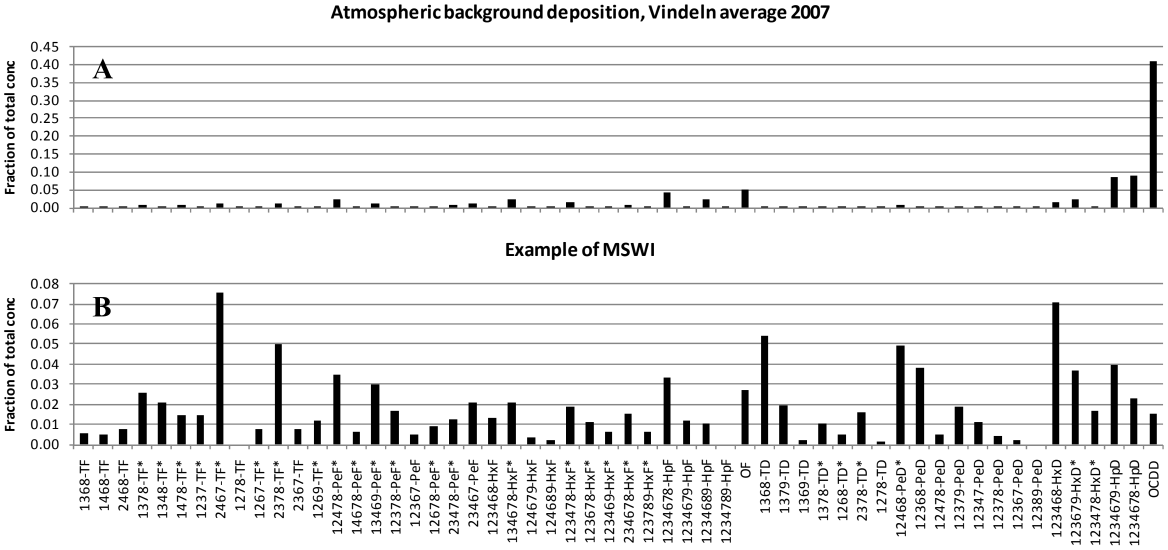


Figure 40. a) Atmospheric deposition pattern from a background station at Vindeln in northern Sweden, and b) an example of emission patterns from waste combustion. Note that combustion patterns vary with fuel composition and combustion conditions.

Among the three model patterns that are connected to the direct point sources, one pattern was virtually identical to the pollution patterns that have been measured at some sawmills areas where chlorophenols have been used in wood treatment (Figure 41). This pattern was dominated by three highly chlorinated PCDF, which also dominate in chlorophenol formulations where tetrachlorophenol constitutes a significant component (as opposed to pure PCP products; Sundqvist *et al.* 2010). As mentioned above, the model pattern known as Atmospheric background may also reflect chlorophenol preparations. Two different model patterns could thus potentially represent the use of chlorophenol. The relative abundance of its two model patterns were used as an indicator to determine whether Atmospheric background in the individual samples should be interpreted as background pollution or as PCP use.

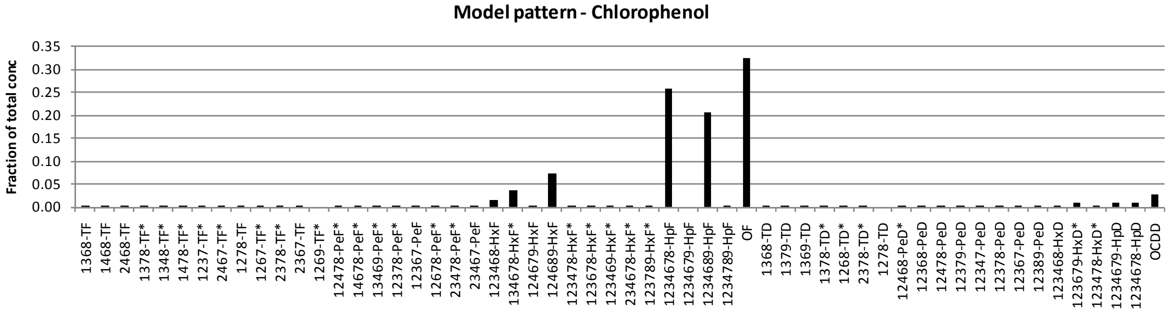


Figure 41. PMF model pattern identified as related to tetrachlorophenol.

The second model pattern that was assumed to represent point sources was totally dominated by two HxCDD congeners (1,2,3,6,7,9/1,2,3,6,8,9-HxCDD; Figure 42). These congeners were identified in several different products in the early 1990s: pulp, paper, ink, pine resin and tall oil fatty acid (Bichlmaier *et al.* 1992, Kitunen and Salkinoja-Salonen 1990, Rappe *et al.* 1990a, Rappe *et al.* 1990b, Santl *et al.* 1994a, Santl *et al.* 1994b, Sundqvist *et al.* 2010). Experiments reported by Luthe *et al.* (1993) showed that these congeners were formed during the kraft pulp process when specific chemical precursors were available. The precursors were identified as hepta-phenoxyphenols, which have been found in large quantities in certain chlorophenol preparations (Luthe *et al.* 1993, Persson *et al.* 2007). This pollution pattern may thus be indirectly linked to the use of chlorophenol. The reasons for why this pattern was also seen in, for example pine resin and tall oil, is likely due to the fact that these products are produced via distillation of residues from the kraft pulp process.

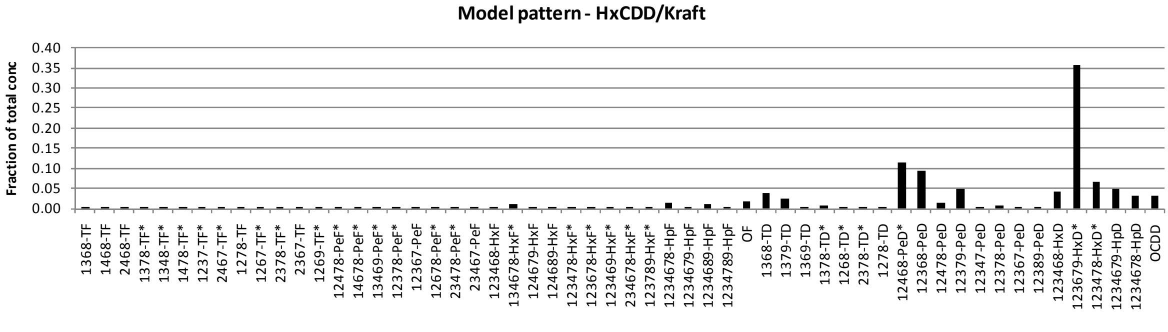


Figure 42. PMF model pattern identified as being related to kraft pulp production and related industries.

The last model pattern shows a clear dominance of 2,3,7,8-TCDF (Figure 43). The pattern also includes 1278-TCDF and 2,3,7,8-TCDD, indicating that this pattern may reflect emissions from chlorine bleaching of pulp and the production of chlorine gas using graphite electrodes in the mercury method. The use of graphite electrodes continued until the mid-1970s in Sweden, when titanium electrodes were introduced as a replacement. Measurements showed that although the changed electrodes greatly reduced the emissions of PCDD/Fs, emissions still occurred when titanium electrodes were used.

Graphite electrodes were also used in chlorate production and are expected to have resulted in similar contamination at those facilities.

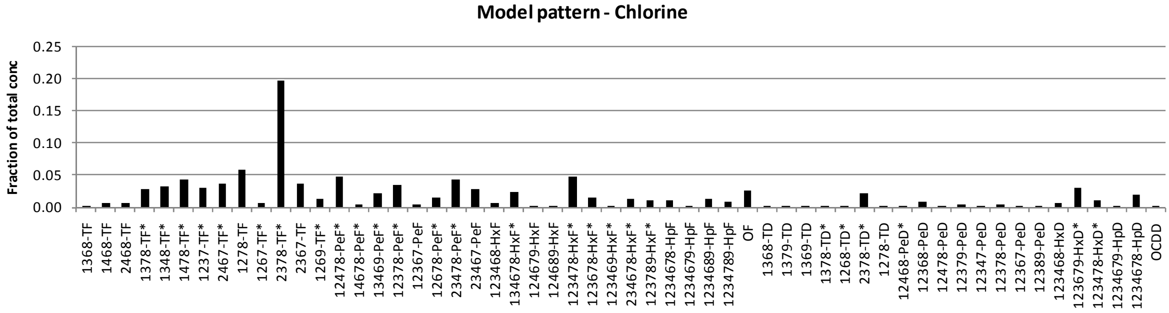


Figure 43. PMF model pattern identified as chlorine-related. The pattern is assumed to reflect the chlorine bleaching of pulp and the production of chloralkali by graphite electrodes in the mercury method.

SOURCE APPORTIONMENT

For source apportionment, relative contributions from the modelled source types are calculated. They were assigned in accordance to the reasoning in the previous section, but it is important to keep in mind that these are our best estimates and that they represent source types. In the following, the contribution from the source types are given only as capitalised key-words, i.e., Chlorine, HxCDD, etc.

SOURCE CONTRIBUTIONS FOR COASTAL STATIONS

As noted above, the time trends in coastal areas varied more than in offshore areas. Receptor modelling also revealed that source apportionment showed large variation at coastal stations. In most cases, the candidate sources could be linked to industrial activity that had taken place at or near the sampling area. Source apportionment for these stations is given in a report to be published by the County Board of Gävleborg (Sobek *et al.* 2012).

SOURCE CONTRIBUTIONS FOR OFFSHORE STATIONS

Compared to the costal stations, the offshore stations showed less variation in the source contributions, which was expected due to the larger distance from point sources. However, in the two northern most stations, a high proportion was estimated to originate from HxCDD/Kraft and Chlorophenol, respectively. In several cores, there appears to be a minor influence from the Chlorine pattern. However, the large fraction of low-chlorinated PCDFs in this source candidate pattern may, in particular, cause contributions from combustion processes to be interpreted as Chlorine. This makes it challenging to draw conclusions regarding the possible influence of the chlorine bleach/chloralkali production in offshore areas.

In the northern Bothnian Bay sediment core, HxCDD/Kraft pulp appeared to be an important contributor (Figure 44). In addition, Chlorophenol also contributed to the PCDD/F pollution. The increase in contributions from the Kraft pulp pattern happened in the late-1980s to early-1990s, and a slow decrease can be seen from the mid- to late-1990s.

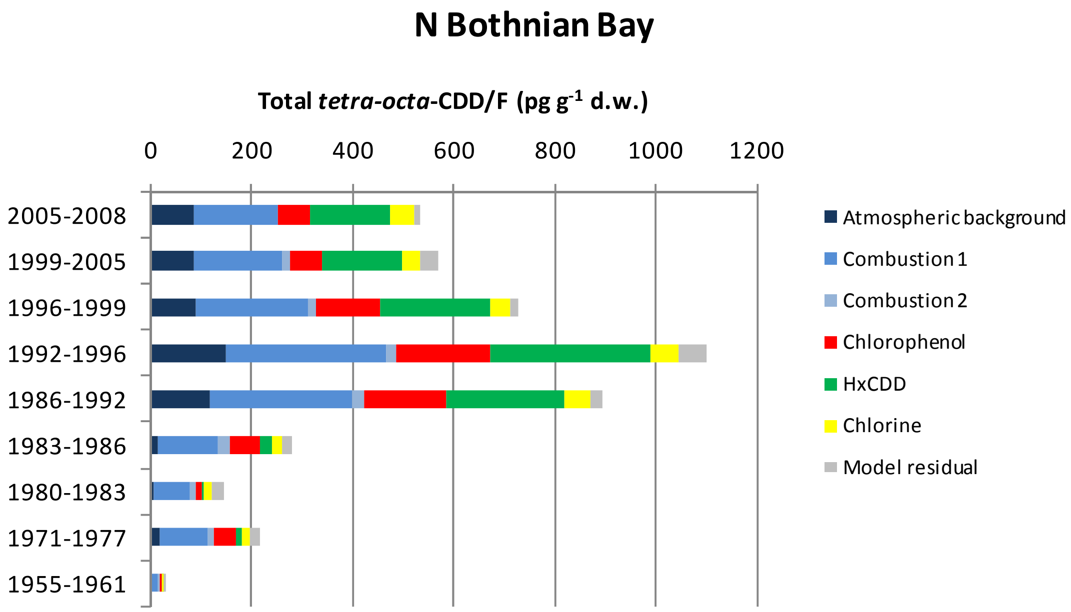


Figure 44. PCDD/F source contributions in the offshore sediment core of the northern Bothnian Bay according to the PMF model.

In the northern Bothnian Sea sediment core, a clear influence from chlorophenol use was identified starting during late 1960s or early 1970s (Figure 45). It is even clearer in the offshore areas than in the coastal areas that chlorophenol use has had a large influence even after the ban in 1978. In fact, the time trend in the offshore areas suggests a significant time lag for point source emissions directly to the water. However, for chlorophenol use, emissions to the water may be direct (primary) by dumping of leftover chemicals and surface water runoff from areas with drying lumber, but emissions may also be stretched over a longer period of time with leakage from contaminated soils (secondary sources).

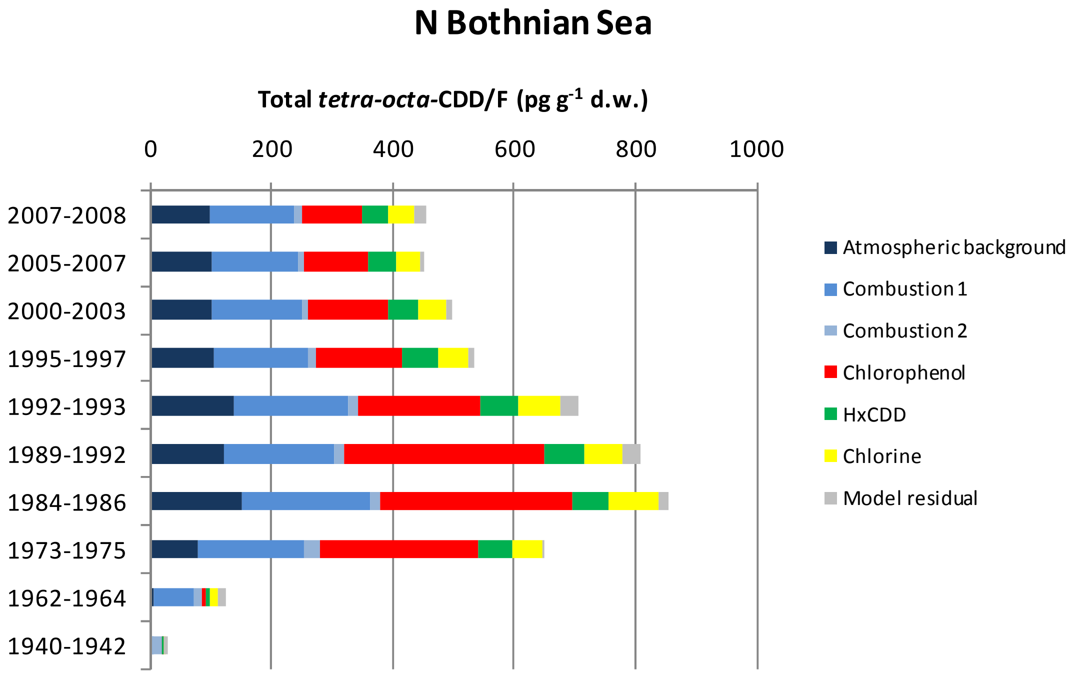


Figure 45. PCDD/F source contributions in the offshore sediment core of the northern Bothnian Sea according to the PMF model.

The relative proportion of Combustion 1 compared to the other atmospheric patterns is lower in the northern Bothnian Sea sediment core than in the northern Bothnian Bay, but it increases again in offshore areas further south.

In the sediment core from the southern Bothnian Sea, only a few of the deeper layers were available for analysis, which limits the retrospective information gained. The large time gaps make it impossible to evaluate the shape of the peak and compare it to other areas. However, the source contributions indicate an increased importance of Chlorophenol between the early 1970s and early 1980s (Figure 46).

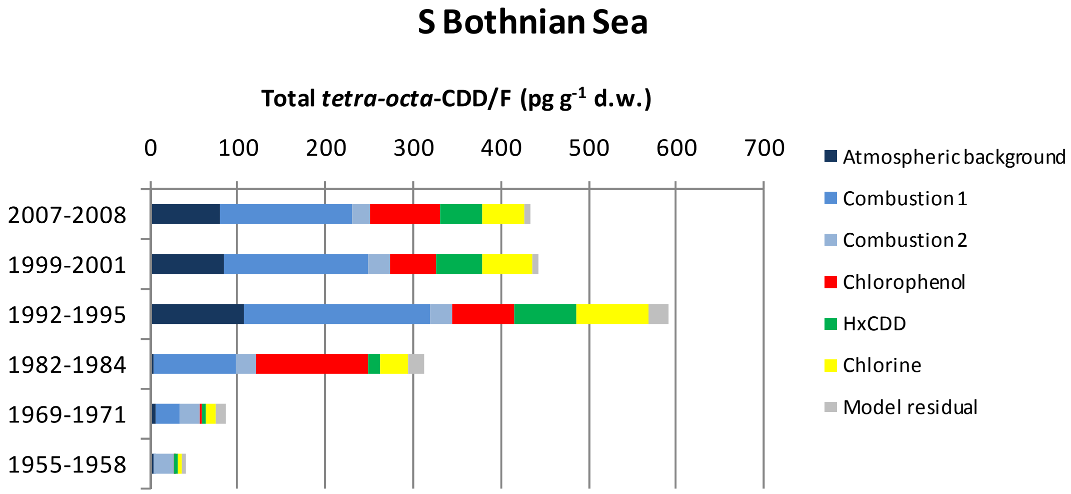


Figure 46. PCDD/F source contributions in the offshore sediment core of the southern Bothnian Sea according to the PMF model.

In the Baltic Proper (Figure 47) and the Arkona Basin (Figure 48), atmospheric sources were indicated as more important than in more northern cores. Measurements of PCDD/F in air have shown that when the sampled air masses have travelled over the European continent, the levels were higher than when air arrived at the Baltic Sea from the north or west (Sellström *et al.* 2009). Air measurements by Sellström *et al.* (2009) did not show a consistent pollutant pattern in air masses from high concentration regions, but the sediment cores indicate that Combustion 1 was more important in the southern Baltic Sea than further north. This could possibly be the result of combustion-related sources on the European continent contributing to the Baltic Sea.

The three northernmost offshore cores (N Bothnian Bay, N Bothnian Sea and S Bothnian Sea; Figure 44-46) show relatively constant proportions between the Chlorophenol pattern and Atmospheric background, except during the Chlorophenol peak in the northern Bothnian Sea. The Arkona Basin sediment core did show a bit more variation over time in contributions from Atmospheric background and Chlorophenol (even when excluding the layer corresponding to 1961-1965, Figure 46). This variation may be the result of a poor fit between the model and the measurement. However, a detailed study of the congener patterns throughout the core suggests that there are in fact clear variations in the composition between layers.

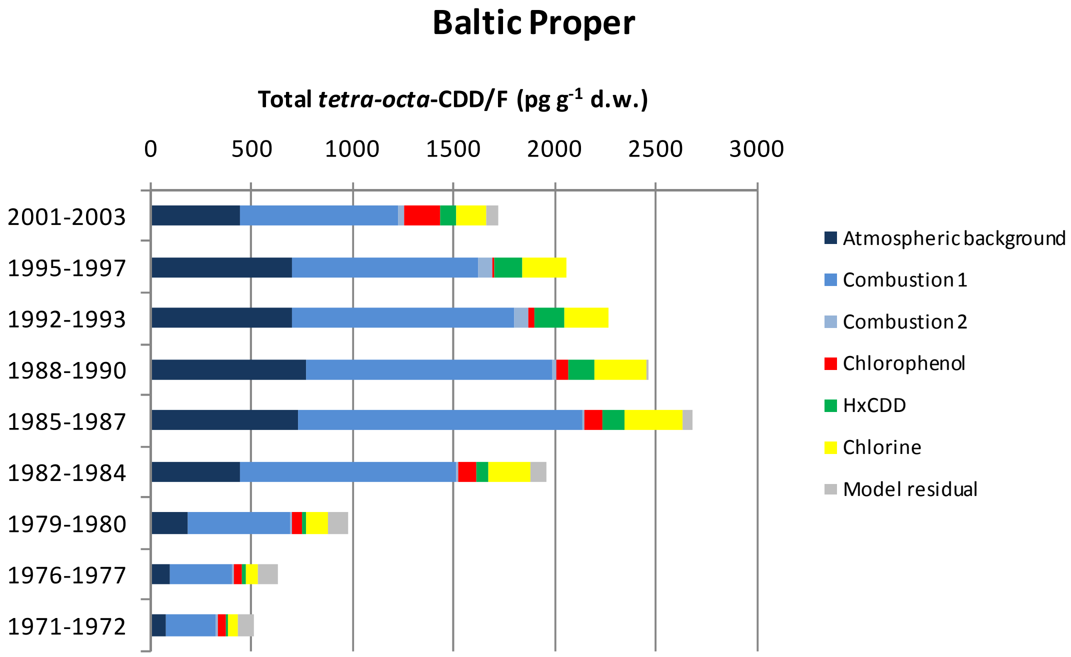


Figure 47. PCDD/F source contributions in the offshore sediment core of the Baltic Proper according to the PMF model.

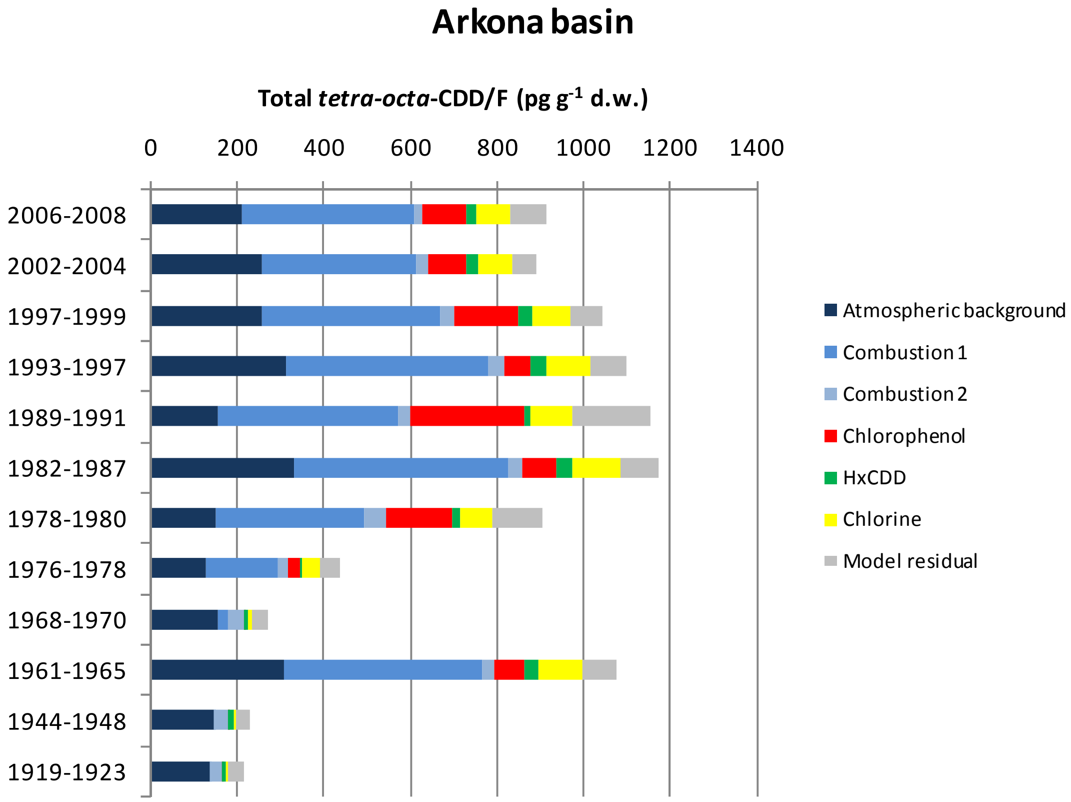


Figure 48. PCDD/F source contributions in the offshore sediment core of the Arkona Basin according to the PMF model.

8.3.4 Dioxins in preindustrial sediment layers

The analyses of the very old (>1000 years) fine-grained sediment layers showed very low concentrations of PCDD/Fs with TEQs ranging from 0.2 to 1.5 pg g^{-1} d.w. (non-detect congeners included with concentration set to half of the LOQ). These levels are comparable to those found in layers pre-1925 (the oldest layer from Arkona Sea, Nordmaling and Sandarne), which ranged from 0.5 to 5.5 pg TEQ g^{-1} d.w. These values should be compared to current levels of top layers in offshore areas of the Baltic Sea, which ranged from 8 to 29 pg TEQ g^{-1} d.w. (mean 14 pg TEQ g^{-1} d.w.) in the current study, implying that Baltic offshore areas are still elevated compared to natural background levels.

8.4 Conclusions

- Clear decreasing time trends for both PCBs and PCDD/F was demonstrated in sediment cores in all investigated areas of the Baltic Sea. For dioxins, which were measured both in coastal and offshore areas, the decline was slower in offshore areas. The levels of PCDD/Fs in coastal sediments declined by a factor of approximately 2 between the mid-1980s and today, whereas the offshore sediments mostly declined by less than a factor of 2 between the mid-1980s and today. The consistent decreasing time trend throughout the Baltic shows that emission reduction measures for these pollutants have been effective. By contrast, increasing concentration time trends for HCB were shown for all sampling sites, except for the Baltic Proper.
- Peak concentrations of PCDD/Fs generally appeared earlier in coastal areas than in offshore areas, particularly if only the typical point source areas in the coastal category were included (mid-1960s to late-1970s versus mid-1980s to late-1990s). These findings indicate that terrestrial sources will eventually affect the open sea after some time lag, and that the declining levels in the Baltic Sea can be attributed to reductions in air emissions as well as in direct emissions.
- Source tracing for PCDD/Fs showed that for the Baltic Sea as a whole, air emissions are and have been the most important external sources. This is particularly true for offshore areas in the south.
- Direct emissions were shown to be an important contributor to PCDD/F levels in sediment cores. Although little influence of the chlorine bleaching and its related industry was seen in the sediments, impact from typical land-based sources, such as chlorophenol use and kraft pulp emissions, were shown to be of importance in the northern sub-basins, both in coastal and offshore areas.
- Analysis of preindustrial sediment layers showed TEQ-levels of approx. 1 pg TEQ g^{-1} d.w., significantly lower than levels in offshore top sediments of today (8-29 pg TEQ g^{-1} d.w.). The input of dioxins to the sea has changed over time with both changing concentrations and clear congener pattern changes following the increase of pollution. It should, however, be noted that the pollution composition is showing slow fingerprint changes. Thus, although the concentrations have decreased as a result of measures taken, the pollution patterns of the sediment in these remote areas are still affected by previous emissions. These observations suggest a slow system recovery, which may be one reason for the lack of decline or slow decline in Baltic herring dioxin concentrations.
- The previously predicted sediment time trends from the model in Wiberg *et al.* (2009) are likely slightly too fast. The model predicted a decline of a factor of 3 between 1986 and 2006, whereas data in this chapter indicates a decline of a factor of 2 or less depending on location. The most plausible explanation for the discrepancy between model estimated declines in sediments and the sediment time trends data from this chapter is the oversimplification of sediment dynamics in the model.

9 Aerosol-water distribution of dioxins and PCBs in the Baltic Sea region

9.1 Introduction

Several studies have indicated that atmospheric deposition is the major input pathway for dioxins to the Baltic Sea (Armitage *et al.* 2009, Sundqvist *et al.* 2010, Verta *et al.* 2007). For dioxins, deposition with aerosols is the dominating pathway from the atmosphere to water whereas gaseous air-water exchange seems to be more important for PCBs, as suggested by a previous study in the Atlantic Ocean (Jurado *et al.* 2004). Hence, knowledge about the availability of these compounds after they are deposited to the water will have implications for future actions to be taken to reduce levels of dioxins in fish of the Baltic Sea. To investigate the availability of dioxins and PCBs sorbed to aerosols, aerosol-water distribution ratios were determined for aerosols collected in Stockholm, close to the Baltic Sea. These were compared to previously reported sediment-pore water distribution ratios in Baltic Sea surface sediments (Cornelissen *et al.* 2008). A more complete description of the work is available in a separate publication (Sobek *et al.*, 2013).

9.2 Methods

A high-volume air sampler was deployed at 10 m height at Stockholm University, around 1 km from the shore of the Baltic Sea (59°37'N, 18°06'E). Aerosols were sampled on GFF filters once a month from February through November 2010. In total, 261 000 m^3 of air and 5.0 g of aerosol were sampled. The average aerosol content of the air was 18 ± 11 $\mu g\ m^{-3}$. The filters were carefully cut into eight pieces to allow parallel exhaustive extraction (Soxhlet) and passive sampler extraction (POM) from the same filter. In addition to the individual samples, triplicates of an integrated nine-month sample (a pool of all the individual monthly samples) were also extracted. Extraction of total PCDD/F and PCB content in the aerosol particulate matter was carried out using Soxhlet-Dean-Stark by refluxing with toluene.

In order to assess the available fraction of dioxins and PCB in the aerosols, filter samples were shaken with distilled water, polyoxymethylene (POM-17), NaN_3 and NaCl (concentrations similar to Baltic Sea water, 6 g L^{-1}) continuously for 180 days. The seventeen 2,3,7,8-substituted PCDD/F congeners, the dl-PCBs (non-*ortho* and mono-*ortho* PCBs), and the indicator PCBs (28, 52, 101, 118, 138, 153 and 180) were analysed. The sum of the latter are referred to as ΣPCB_7. TEQs for PCDD/Fs and PCBs were calculated using the WHO 2005 TEFs. Field, laboratory and POM blanks were analysed for PCDD/Fs and PCBs in parallel with the samples. The total organic carbon (TOC) and black carbon (BC) content of the aerosol samples were determined following procedures outlined by Gustafsson *et al.* (2001).

To assess the availability of dioxins and PCBs sorbed to aerosols once they have entered the water column, aerosol OC-water distribution ratios ($K_{aer\text{-}water,OC}$) were calculated from total concentrations on aerosols and the freely dissolved aqueous concentrations determined in the POM experiments. The equilibrium aerosol-water distribution ratios, normalised to the mass fraction of organic carbon (f_{OC}), is defined as:

$$K_{aer\text{-}water,OC}\ (L_{water}/kg_{TOC}) = C_{aerosol} / (C_{water} \times f_{OC})$$

where the contaminant in the aerosols, $C_{aerosol}$, and water, C_w, are at equilibrium.

To assess the relative sorption strength and thus the availability of the dioxins and PCBs entering the Baltic Sea via aerosols, measured $K_{aer\text{-}water,OC}$ was compared to sediment OC-water distribution ratios ($K_{sed\text{-}water,OC}$) reported in a previous Baltic Sea study (Cornelissen *et al.* 2008). The $K_{sed\text{-}water,OC}$ were determined in the same way as $K_{aer\text{-}water}$ using extraction with POM.

9.3 Dioxin and PCB concentrations in aerosols

Dioxin and PCB aerosol contents ranged from 65 to 1300 pg g^{-1} d.w. TEQ and from 5 to 44 pg g^{-1} d.w. TEQ (values <LOQ excluded), respectively, with the highest concentrations observed in the winter months (Table 6). Aerosol concentrations of ΣPCB_7 ranged between 22 and 100 ng g^{-1} d.w. Concentrations normalised to air volume (0.3 to 1.4 fg TEQ m^{-3}) agreed well with concentrations previously reported for air samples collected in Sweden (Sellström *et al.* 2009).

The nine-month average aerosol dioxin concentrations (d.w. basis) were a factor 11 higher than the concentrations reported for the Baltic Sea sediment top layer in a previous study (Cornelissen *et al.* 2008), whereas the PCB concentrations in aerosols were a factor 7 higher than in the sediment top layer (Table 6). The relatively high concentrations in aerosols compared to sediment suggest that aerosols form an important pathway of dioxins and PCBs into the Baltic Sea.

The difference in sediment and aerosol concentrations was smaller on an OC-normalised basis compared to total concentrations (Table 6). Thus, dioxins and PCBs associated with OC apparently become diluted during settlement in the water column, not only by co-sedimentation of autochthonous OC, but also by terrestrial particulate matter.

9.4 Aerosol TOC and BC content

Aerosol TOC content varied from 6 to 21%, without any clear seasonal trend. BC content varied from 0.3 - 1.4%, with the highest BC content in February and March (no data available for December and January). The fraction of BC in TOC (BC/TOC) varied between 1 and 10 % with a nine-month average of 4.6%. Baltic Sea offshore sediments have reported BC/TOC ratios of 3.1 - 4.9% (Cornelissen *et al.* 2008) and 4.6 - 47% (Sanchez-Garcia *et al.* 2010).

Table 6. Concentrations of $TEQ_{PCDD/F}$ and ΣPCB_7 in aerosols and in the freely dissolved water phase of the sorption experiments. Data for offshore Baltic Sea sediment are from Cornelissen *et al.* (2008).

	$TEQ_{PCDD/F}$			**ΣPCB_7**		
	pg g^{-1} aerosol	**pg g^{-1} aerosol OC**	**pg m^{-3} water**	**ng g^{-1} aerosol**	**ng g^{-1} aerosol OC**	**pg m^{-3} water**
Feb-March	290	2300	<LOQ	100	810	<LOQ
April	180	2100	<LOQ	37	430	<LOQ
April-May	95	790	<LOQ	22	180	<LOQ
May-June	240	2100	<LOQ	39	330	<LOQ
July-Aug	65	460	<LOQ	41	290	<LOQ
Sept-Oct	430	2400	<LOQ	55	310	<LOQ
Nov	1300	6500	<LOQ	88	420	<LOQ
Aerosols nine month average (*n*=3)	200 ± 11	1500 ± 90	9 ± 2	36 ± 8	260 ± 60	9 ± 1
Sediment Baltic Sea (*n*=6)	16 ± 13	380 ± 170	4 ± 2	5 ± 5	100 ± 80	2 ± 2

9.5 Comparison of aerosol-water and sediment-water distribution ratios

$K_{aer\text{-}water,OC}$ is presented on a nine-month-average basis (Table 7), because the measured freely dissolved water concentrations in the POM experiments were below LOQ for many of the PCDD/Fs and PCBs in the monthly collected samples (Table 6). $K_{aer\text{-}water,OC}$ generally increased with chlorination and ranged from 7.9 for 2,3,7,8-TCDD to 10.2 for 1,2,3,4,6,7,8-HpCDF.

Nine-month-averaged $K_{aer\text{-}water,OC}$ were consistently lower than $K_{sed\text{-}water,\ OC}$ by a factor of 3 - 35 (median 5) for PCDD/Fs, and a factor of 2 - 60 (median 8) for PCBs. Several factors could cause the observed stronger sorption in sediment compared to aerosols ($K_{sed\text{-}water,OC} > K_{aer\text{-}water,OC}$). These include *i*) a greater contribution of strongly sorbing components (like BC) in the sediments; *ii*) a change in sediment OC that causes stronger sorption such as increased aromaticity through weathering since sorption generally increases with weathering (Hawthorne *et al.* 2011), and *iii*) differences in the experimental set-ups for deriving the two sets of partition coefficients. The lower organic carbon-water partition coefficients of aerosols ($K_{aer\text{-}water,OC}$) compared to sediment ($K_{sed\text{-}water,OC}$) cannot be explained by only BC content, since BC:OC ratios in the aerosols (average 3.4%) were comparable to those in the Baltic Sea sediments (3 - 5%; Cornelissen *et al.* 2008). Instead, these results indicate that a difference in the characteristics of the organic and/or BC in sediment and in aerosols cause the lower availability and strong sorption of dioxins and PCBs in sediment. Deposition of aerosol-OC contributes only 0.02% of the total flux of OC to the Baltic Sea (Kulinski and Pempkowiak 2011). Hence, the organic matter of the Baltic Sea sediments has a completely different origin, and therefore different characteristics compared to the organic matter of the aerosols.

Table 7. Aerosol-water distribution ratios measured in this study and sediment-water distribution ratios reported by Cornelissen *et al.* (2008), both on an OC basis.

Compound	**Log $K_{sed\text{-}water,OC}$ (L kg_{TOC}^{-1})**	**Log $K_{aer\text{-}water,OC}$ (L kg_{TOC}^{-1})**
2378 TCDD	8.9 ± 0.13	7.9 ± 0.12
12378 PeCDD	9.1 ± 0.07	8.2 ± 0.14
123478 HxCDD	10.0 ± 0.13	9.1 ± 0.00
123678 HxCDD	10.1 ± 0.12	9.5 ± 0.03
123789 HxCDD	10.1 ± 0.16	9.1 ± 0.46
1234678 HpCDD	10.8 ± 0.18	10.4 ± 0.11
OCDD	11.6 ± 0.25	<LOQ
2378 TCDF	8.3 ± 0.15	7.7 ± 0.08
12378 PeCDF	9.0 ± 0.18	8.0 ± 0.09
23478 PeCDF	9.0 ± 0.10	8.0 ± 0.04
123478 HxCDF	9.8 ± 0.12	9.2 ± 0.01
123678 HxCDF	9.9 ± 0.13	9.2 ± 0.07
234678 HxCDF	9.5 ± 0.12	9.0 ± 0.04
123789 HxCDF	9.8 ± 0.17	<LOQ
1234678 HpCDF	10.6 ± 0.24	10.2 ± 0.08
1234789 HpCDF	10.4 ± 0.17	<LOQ
OCDF	11.4 ± 0.21	<LOQ

9.6 Conclusions

- The measured aerosol-water distribution ratios indicate that dioxins and PCBs that enter the Baltic Sea via aerosols are less strongly bound and therefore presumably more bioavailable than dioxins and PCBs sorbed to organic matter in Baltic Sea surface sediments (Cornelissen *et al.* 2008).
- Sorption of dioxins and PCBs to the organic matter fraction of aerosols is, however, about a factor 5 stronger than predicted from the equilibrium partitioning model (Seth *et al.* 1999), which is an empirical model that can be used to predict the distribution of pollutants between organic carbon and water. This large sorption capacity may indicate that soot (black) carbon present in the aerosols, and in sediments, enhances sorption of dioxins and PCBs to the aerosols.
- Since atmospheric deposition is a significant pathway of especially PCDD/Fs to the Baltic Sea, these findings have implications for the bioaccumulation and potential ecotoxicity of these toxic chemicals.

10 Tracing the origin of dioxins in Baltic air using an atmospheric modelling approach

10.1 Introduction

Here we aim to trace the origin of dioxins in Baltic air using a spatially and temporally resolved atmospheric model. The primary objective is to investigate whether the levels of measured concentrations in air and deposition flux samples at three monitoring stations in Sweden and Finland can be reproduced using state-of-the-knowledge emission estimates. In a similar study (Zhang *et al.* 2009), total atmospheric concentrations of PCDD/Fs over the North American continent were reproduced using a modified version of the CMAQ model. The factor of agreement ranged from 1 to about 12. Over- and underestimations were attributed to uncertainty in the official emission estimates used as model input. If the model predictions and measurements are in good agreement, the model can be used to determine the approximate source regions contributing to dioxins in Baltic air and deposition, and thus Baltic Sea levels. A secondary objective was to identify deficiencies in the emission database by determining the degree of disagreement between model predictions and measurements when emissions originated from different source regions. Adjusted emission scenarios were constructed and new model simulations undertaken to try to optimise agreement between model predictions and measurements. A more complete description of the work is available in a separate publication (Shatalov *et al.*, 2012).

10.2 Methods

10.2.1 Selected congeners

In previous air and deposition flux monitoring campaigns conducted by scientists from Stockholm and Umeå Universities, the 17 most toxic 2,3,7,8-substituted PCDD/Fs were measured. We selected a subset of four congeners for model evaluation. One of the most important criteria for selecting these four congeners was a low inter-correlation between the concentrations of each congener in the monitoring data set. A low correlation is an indication that the congeners originate from distinct source types. Air data from the monitoring site at Svartberget and Aspvreten (Bergknut *et al.* 2011, Sellström *et al.* 2009) were statistically analysed, and the congeners 2,3,4,7,8-PeCDF, OCDF, 1,2,3,7,8,9-HxCDD and OCDD were proposed. In addition to relatively low inter-correlation, these four congeners also had a high detection frequency and represent a range of chlorination level, i.e. a range of physical-chemical properties and partitioning behaviour. The selected congeners are representative of the full range of physical-chemical properties for the 2,3,7,8-substituted PCDD/F congeners. For example, the range of the log octanol-water partition coefficient (log K_{ow}) is 6.2-8.2 for all of the 2,3,7,8-substituted PCDD/F congeners and 6.8-8.2 for the four congeners selected here (Aberg et al. 2008).

10.2.2 The MSCE-POP model

The model selected for this study was the MSCE-POP model (Gusev *et al.* 2005a, Malanichev *et al.* 2004), which is a three-dimensional Eulerian multi-compartment model operating with a spatial resolution of 50 × 50 km^2. It includes environmental compartments to represent the troposphere, surface soils, seawater and vegetation as well as basic processes describing emissions, long-range atmospheric transport, deposition flux, degradation and gaseous exchange between the atmosphere and the underlying surfaces. Meteorological data reported for the timespan of interest is used as model input. The horizontal dimensions of the model domain are confined by the EMEP grid and described by Ilyin and Travnikov (2005). Figure 49 provides a map of the EMEP domain, which includes the entire European continent and some surrounding areas. A full description of the MSCE-POP model is given in EMEP/MSC-E Technical Report 5/2005 (Gusev *et al.* 2005a).

The model outputs used for this study are total (sums of gaseous and particulate) air concentrations in fg I-TEQ m^{-3}, deposition rates (monthly sums of dry particulate deposition and wet deposition fluxes in pg I-TEQ m^{-2} month) and contributions of “source regions” (explained further in 10.2.4) to annual concentrations and deposition rates. The TEQs were calculated using the international toxicity equivalency factors I-TEFs adopted by NATO/CCMS (1988). In order to evaluate the contribution of an emission source region to concentrations and deposition fluxes in each model grid cell, the model calculates the transport of a pollutant from each emission source region separately.

10.2.3 Model parameterisation

The physical-chemical property data are compiled in Annex A of EMEP/MSC-E Technical Report 5/2005 (Gusev *et al.* 2005a). The MSCE-POP model uses chemical-specific dry deposition velocities over land, sea and forest as well as chemical-specific washout ratios for particle-bound scavenging by precipitation (also described in Annex A in Gusev *et al.* 2005a).

The MSCE-POP model requires environmental input data on soil and vegetation properties, water currents, meteorology etc. The environmental data sets were the default values used in the MSCE-POP model. The model uses real meteorological data for parameterising atmospheric transport. The details of the environmental inputs and meteorological parameterisation are described in EMEP/MSC-E Technical Report 5/2005 (Gusev *et al.* 2005a).

To account for long-term accumulation in the environmental media and for dioxins advecting into the EMEP region from background air, a hemispheric model (Gusev *et al.* 2005b) was run for the period 1970-2007. Levels of dioxins advecting into the EMEP region were estimated using all emission sources for the Northern Hemisphere except for those within the EMEP grid as model input. The dioxin emissions in the Asian part of Russia were estimated using numbers for the European part of the country and data on population density. The dioxin emissions of Tajikistan, Turkmenistan and Uzbekistan were taken from the unofficial inventory of dioxin emissions in the Central Asian countries made in the framework of the global International POPs Elimination Project (IPEP) (Hodjamberdiev 2006). The latest available information on dioxin emission in the USA was taken from the dioxin inventories prepared by UNEP for 1995 (UNEP 1999). The spatial distribution of dioxin emissions in the Central Asian countries and the Asian part of Russia was constructed on the basis of population density data (Li 1996).

10.2.4 Emission data used for model simulations

The official emission data reported by EMEP countries as I-TEQs to the United Nations Economic Commission for Europe (UNECE) were used as model input in the base emission scenario. The emission data were divided into different “source regions”. All source regions comprised a country/region or a group of countries. National emissions considered likely to affect dioxin deposition fluxes over the Baltic Sea (Belarus, Denmark, Estonia, Finland, France, Germany, Latvia, Lithuania, Norway, Poland, and Sweden) were assigned to individual source regions. The Russian Federation was treated as two source regions - the north-western part (Russian north-west) and the remaining part. The final three source regions were the Black Triangle region (the area where the borders of Poland, Germany and the Czech Republic intersect), the rest of the European countries together, and shipping emissions in the Baltic Sea region. The last two “source regions” are the only ones that are not concentrated in a single geographical area.

Some countries reported a spatial distribution of dioxin emissions, whereas others did not. In cases where spatial emissions were not reported, estimates of spatial emission distribution were made following guidelines made by the Netherlands Organization for Applied Scientific Research (TNO; Denier van der Gon *et al.* 2005). In order to obtain data for specific PCDD/F congeners, estimates of congener profiles in European emissions produced in the POPCYCLING-Baltic project (Pacyna *et al.* 2003) were applied. Expert estimates made by TNO (Denier van der Gon *et al.* 2005) were applied if there were no officially reported data for a specific region and year. In addition, emission data for the north-western part of the Russian Federation were updated using official information on benzo[*a*]pyrene (B[*a*]P) emissions in this region and regression relationships between B[*a*]P and dioxin emissions obtained using data from the Russian Federation (national totals) and from the Ukraine ($r^2 \geq 0.65$). Shipping emissions (including their spatial distribution) were produced using available data on NO_x emissions (Bartnicki *et al.* 2009) and data from the EMEP/EEA emission inventory guidebook (EMEP/EEA 2009). Seasonal variations of dioxin emissions were constructed based on the available measurements (Umlauf *et al.* 2010, Vikelsøe *et al.* 2005) and variations of other pollutants, particularly B[*a*]P (Ilyin *et al.* 2010), which are emitted by a similar group of emission sources.

From examination of the reported EMEP emissions, it is evident that data for some regions and sectors are missing (Table 8). It is clear, for example, that the contributions of the transport sector to the emissions of dioxins in Latvia and Poland are not taken into account. In Poland, waste incineration is a significant source of dioxins whereas in other countries the contribution of this sector is minimal or absent. The range of contributions from industrial processes is rather large and for the Russian Federation no official information on emission sectors is available. The major uncertainties in emission estimation are due to infrequent testing and an inherently high variability in emissions (Cohen *et al.* 2002). The variability at a single plant can vary by an order of magnitude between different sampling periods (Parma *et al.* 1995). Because many of the sources are not well characterised there is great uncertainty associated with the congener composition of the emissions.

10.2.5 Monitoring data for comparison with model predictions

Air concentrations (annual averages, monthly averages, daily averages, here recalculated in fg I-TEQ m^{-3}) have been measured at two well established atmospheric monitoring stations: Aspvreten (58°80′N, 17°40′E) and Pallas (68°00′N, 24°14′E) (Sellström *et al.* 2009). Aspvreten monitoring station is situated in a rural area south of Stockholm. This site provides information on air masses impacting the southern and central parts of the Baltic Sea. Pallas monitoring station is situated in a remote area in the Finnish Arctic. Results from this site represent air masses impacting the northern part of the Baltic Sea. Deposition data were obtained from a study conducted at Svartberget (64°14′N, 19°46′E) field station (Bergknut *et al.* 2011), which is situated in a rural boreal area approximately 70 km from Umeå in northern Sweden.

Table 8. PCDD/F emissions in 2006 as reported to UNECE (EMEP 2012). The emissions of the main emission sectors in the countries surrounding or located close to the Baltic Sea are given in g I-TEQ. Their percentage contributions to total emissions for each country are given in brackets (percentages do not always add up to 100% because they have been rounded to the nearest whole number). DK – Denmark, EE – Estonia, FI – Finland, DE – Germany, LV – Latvia, LT - Lithuania, NO – Norway, PL – Poland, SE – Sweden, RF – the Russian Federation.

	DK	EE	FI	DE	LV	LT	NO	PL	SE	RF
Combustion in power plants and industry	2.3 (8)	1.26 (47)	5.1 (36)	6.0 (8)	12.6 (42)	1.5 (13)	3.1 (13)	44.9 (10)	27.2 (72)	–
Transport	0.28 (1)	0.05 (2)	2.7 (19)	3.0 (4)	0	0.2 (2)	3.3 (14)	0	0.8 (2)	–
Commercial, residential and other stationary combustion	19 (67)	1.34 (50)	1.1 (8)	21.2 (28)	14.1 (47)	9.5 (85)	9.2 (39)	202 (45)	3.0 (8)	–
Industrial processes	7.1 (25)	0	5.0 (35)	43.1 (57)	0.6 (2)	0	4.0 (17)	13.5 (3)	6.0 (16)	–
Agriculture	0	0	0	0	2.4 (8)	0	1.7 (7)	0	0	–
Waste incineration	0	0.05 (2)	0.1 (1)	0	0	0	2.1 (9)	184 (41)	1.1 (3)	–

10.2.6 Generating adjusted emission scenarios

Using the base scenario, we could determine the degree of disagreement between model predictions and measurements when the air arrived to the monitoring sites from different compass sectors. In constructing the adjusted emission scenarios, we attempted to identify deficiencies in the emission database by determining the degree of disagreement when emissions originated from different source groups. Two new emission scenarios were constructed using upward adjustment of total I-TEQ emissions in selected source regions suspected of having underestimated reported emissions as well as adjustment of congener composition in all source regions. An attempt to identify source regions likely to give rise to underestimation of emissions and thus modelled levels in the Baltic region was undertaken by making statistical correlations (K_{corr}) between the contributions of the considered source region to the average air concentrations at the Aspvreten monitoring station, and the "calculation deficiency". The calculation deficiencies are a measure of the model error. These are calculated by subtracting the modelled concentration from the measured concentration (fg I-TEQ m^{-3}). A correlation coefficient (K_{corr}) close to one implies a strong correlation i.e., that upward adjustment of the source region's emissions has a significant impact on calculation deficiency. Thus, in order to improve agreement between modelled and measured values, the emissions of source regions that display high correlation coefficients (K_{corr}), combined with large contributions to overall concentrations at the monitoring stations (Fract, %), can be increased in the construction of adjusted emission scenarios.

This statistical correlation approach failed to unequivocally identify deficits in the emission database, reflecting the complexity of dioxin emissions. Poland was somewhat of an exception, because it was identified as the only region with high correlation coefficients (K_{corr}) as well as large contributions (Fract, %) to the monitoring stations. In other words, Poland is the only region with both large contribution and at the same time a strong candidate for having large underestimations. This finding is consistent with Sellström *et al.* (2009) who show that air masses originating from the European continent and the former Soviet Union contributed 65% of PCDD contamination and 75% of PCDF contamination over the Baltic Sea.

Further regions were also identified as contributing to the "calculation deficiencies" in the first scenario from consideration of K_{corr} and Fract, namely; the Black Triangle, Germany, and France. These source regions were chosen based on the fact that they have correlations (K_{corr}) >0.2 for two of the selected congeners. These regions do not necessarily have high contributions (Fract, %) for those congeners showing relatively high correlations, but do have relatively high contributions (around 3%) for at least one congener.

In spite of the difficulty in identifying specific source regions where emissions were underestimated, we proceeded to make some adjustments for a second and third emission scenario based on the above analysis combined with expert judgment (note the first emission scenario uses the reported EMEP emissions in their unadjusted form). The two adjusted emission scenarios were constructed by multiplication of the emission data reported by the EMEP countries with two types of coefficients: the congener-specific coefficients represent emission inventory errors related to emission congener composition; and the source region-specific coefficients represent emission inventory errors related to emission totals reported for the different source regions. Coefficients for the two scenarios are displayed in Table 9.

Congener-specific coefficients for the two scenarios were chosen after comparison of the congener composition of reported emissions with the congener profiles of air concentrations measured at Aspvreten. In addition, congener patterns obtained from measurements at three sites near the Great Lakes (Venier *et al.* 2009) were also considered. Given the similar congener patterns observed in air monitoring stations for PCDD/Fs, we believe that the congener pattern measured in background air in the Baltic should roughly correspond to the congener pattern in source regions in Europe. The fraction of 2,3,4,7,8-PeCDF in the emission inventory used for calculations, corresponds approximately to its fraction in air concentrations. The fractions of the remaining congeners are lower in the emission estimates used as input in the first emission scenario than in the measured air concentrations. The fractions of these congeners in the emission estimates were therefore adjusted upwards for the second and third emission scenarios to match the fractions observed in air concentrations (Table 9).

The source-specific coefficients are increased in the second scenario relative to the first (default) scenario to simulate increased emissions, but only for Poland and the Russian north-west by a factor of two (Table 9). An increase of a factor of two in emission estimates seems arbitrary, but was selected by systematically varying the emissions upwards in these two source regions by different factors until the best fit with measured data was achieved. As mentioned, Poland was identified from the statistical correlation to be a region which may under-report emissions; however, the Russian north-west was not identified from the statistical correlation approach, which failed to provide strong evidence of underprediction for all other source regions. We motivate our decision to increase the emissions in the Russian north-west in the second emission scenario based on evidence from Sellström *et al.* (2009) that this region strongly contributes to PCDD/F air pollution over the Baltic and knowledge that emissions in this region are poorly reported (see Table 8 and associated discussion).

In the third scenario, emissions for Poland, France, Germany and the Black Triangle were increased by a factor of 10 relative to the first scenario. The adjustment factors (Table 9) in some regions may be artificially high. Under-reporting of emissions by a factor of 10 in France and Germany is unlikely. However, as a good fit was found for all compass sectors in the second scenario, except for south-

southeast (SSE) and south-southwest (SSW), the main purpose of the third scenario was to attempt to reduce the deficiencies for these two remaining compass sectors.

Table 9. Coefficients for adjustments of emission input data for the second and the third emission scenarios. PL – Poland, DE - Germany, FR – France, BT –Black Triangle region, RW – Russian West.

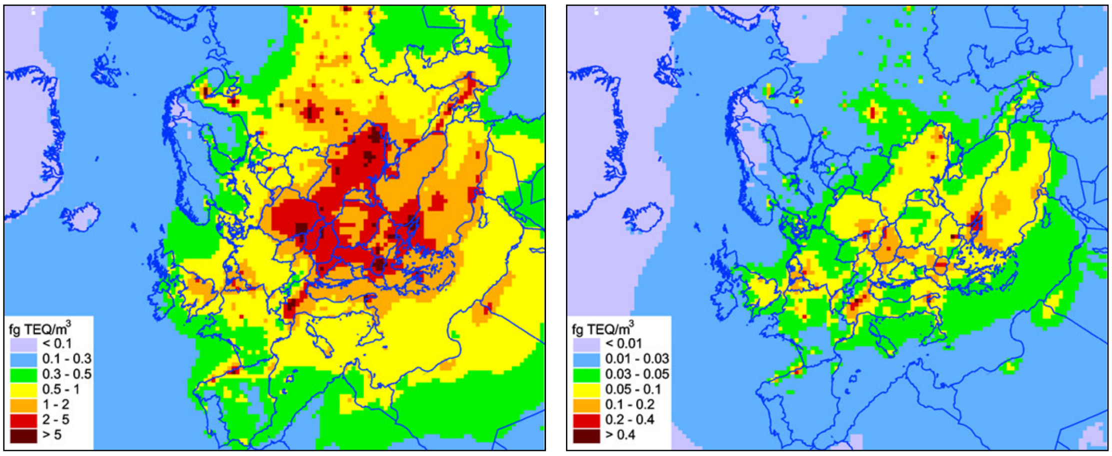
Scenario	**Congener**	**Congener-specific coef-ficient**	**Source-specific coefficients***				
			PL	**DE**	**FR**	**BT**	**RW**
Second	2,3,4,7,8-PeCDF	1.5	2	1	1	1	2
	1,2,3,7,8,9-HxCDD	3					
	OCDD	6					
	OCDF	5					
Third	2,3,4,7,8-PeCDF	1.5	10	10	10	10	2
	1,2,3,7,8,9-HxCDD	3					
	OCDD	5					
	OCDF	5					

* The remaining source groups’ coefficients are equal to 1.

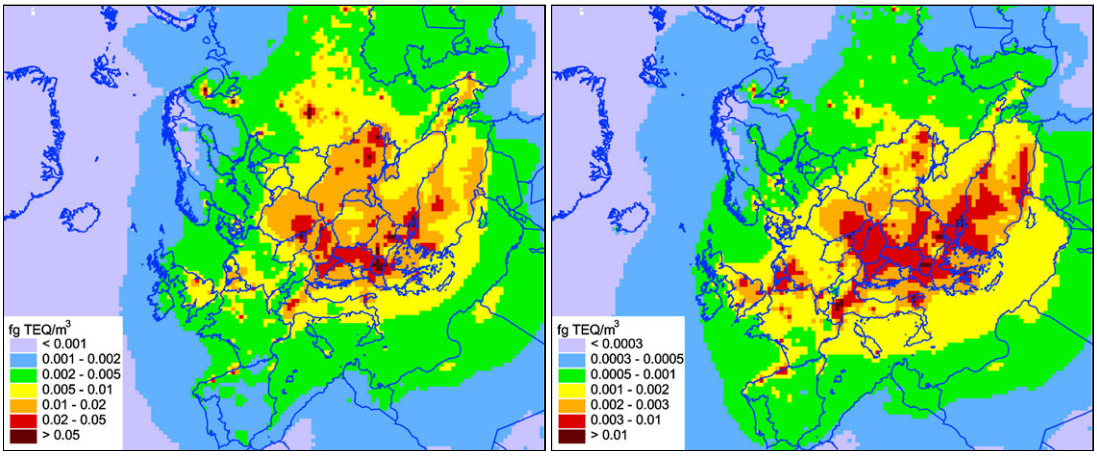
10.3 Results and discussion

10.3.1 First emission scenario

According to the model results, the central, eastern and southern parts of Europe have the highest air dioxin pollution levels. Figure 49 displays spatial distributions of air concentrations of the four selected congeners. The spatial distribution in air concentrations is similar to the spatial emission distribution (not shown). The levels of dioxins in the western part of Europe are considerably lower, and northern Europe is relatively uncontaminated. Annual averages of modelled air concentrations over the Baltic area are 0.2 - 2 fg I-TEQ m^{-3} for 2,3,4,7,8-PeCDF; 0.01 - 0.1 fg I-TEQ m^{-3} for 1,2,3,7,8,9-HxCDD; 0.001 - 0.01 fg I-TEQ m^{-3} for OCDD; and 0.0005 - 0.005 fg I-TEQ m^{-3} for OCDF.



2,3,4,7,8-PeCDF 1,2,3,7,8,9-HxCDD

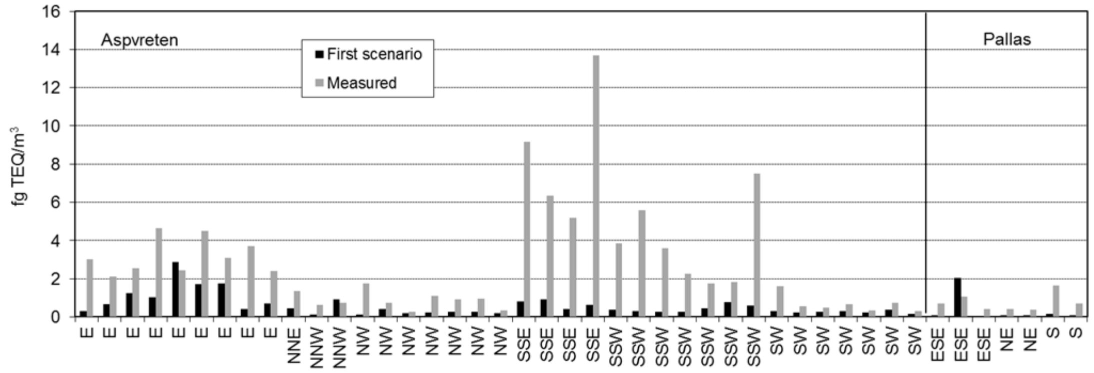


OCDD OCDF

Figure 49. Spatial distributions of annual averages of air concentrations (fg I-TEQ m^{-3}) for the four selected congeners for 2006, for the first scenario.

For the first (default) emission scenario, which uses the official emission data reported by EMEP countries, the comparison of modelling results and field data shows significant underestimation of calculated air concentrations by about a factor of 5 for 2,3,4,7,8-PeCDF (Figure 50), a factor of 10 for 1,2,3,7,8,9-HxCDD, a factor of 20-30 for OCDD, and a factor of 15-20 for OCDF. The agreement between calculations and measurements strongly depends on the compass sectors from which air masses have arrived. The agreement is particularly poor for the south-southeast (SSE) and south-southwest (SSW) compass sectors.

a)



b)

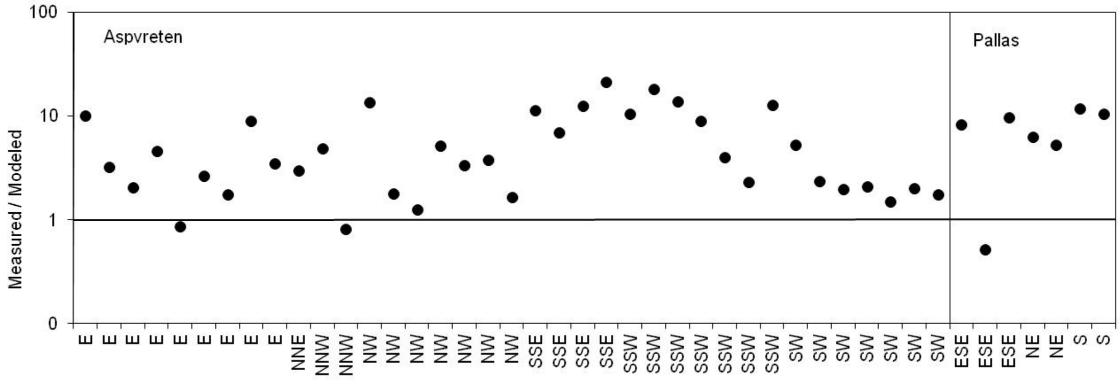
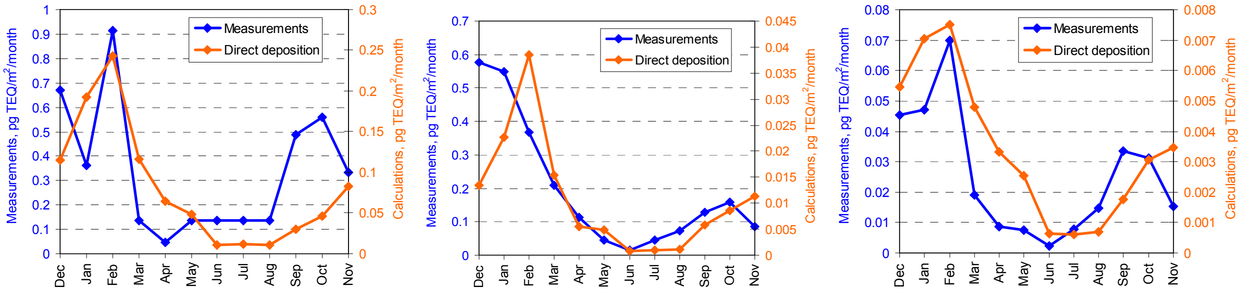


Figure 50. a) Comparison of values of 2,3,4,7,8-PeCDF calculated using the first emission scenario and air concentrations measured at Aspvreten and Pallas for 2006 and 2007 in fg I-TEQ m^{-3} and b) unit less measured-to-modelled concentration ratios. In both figures the x-axis displays the compass sector from which air masses originated on each sampling event. The compass sectors are defined according to Sellström *et al.* (2009). The vertical line marks the division of values based on measurements conducted in Aspvreten and Pallas. The bold horizontal line in (b) intersecting the x-axis at 1.0 indicates perfect agreement between measured and modelled air concentrations.

The comparison of the first scenario model estimates to the monthly sums of dry particulate deposition and wet deposition fluxes reported from the Svartberget site showed that while the measured levels were underestimated to an extent that was similar to the air concentrations, the model captures the observed seasonal variations of deposition fluxes (Figure 51).



a b c

Figure 51. Comparison of modelled values of total deposition flux with measurements made at Svartberget between December 2006 and November 2007 for the first scenario: a) 1,2,3,7,8,9-HxCDD, b) OCDD, and c) OCDF. Please observe that the scales for model predictions and measurements differ.

According to a sensitivity study performed on the MSCE-POP model using CB-153, the uncertainty in physical-chemical input parameters can give rise to a 20% uncertainty in model output (Shatalov *et al.* 2005). In a model intercomparison study, air concentrations produced using the MSCE-POP model agreed to a precision of 50% with concentrations produced using other models (Shatalov *et al.* 2005). For CB153 the log K_{ow} is 6.9 (Schenker *et al.* 2005) and the atmospheric degradation rate is 3 * 10^{-7} s^{-1} (global and seasonal average extrapolated from Anderson and Hites 1996). The ranges of these properties used as model input in the present study are 6.8-8.2 and 2.7 * 10^{-9} - 6 * 10^{-7} s^{-1}, respectively. Evidently, the atmospheric fates of dioxins and PCB-153 are not governed by the exact same properties and a model comparison will give different results depending on the chemical and the scenario studied. Hence, the analogy is not ideal. However, it indicates that model error is small and cannot solely account for the discrepancies between measurements and model predictions. The probable cause of the discrepancy is therefore underestimation of the emissions used as model input (Baker and Hites 2000, Cohen *et al.* 2002, Harrad and Jones 1992, Wintermeyer and Rotard 1994), as is indicated in 10.2.4. However, there is a risk that adjusting emissions up in the following emission scenarios might compensate for model errors that are not related to errors in emission estimation.

Estimates of the various regions' contributions to annual deposition fluxes to individual Baltic Sea sub-basins are displayed in Figure 52. Estimates displayed were produced using the first emission scenario. The results indicate that many different countries – not just the adjacent countries – are contributing to dioxin pollution in the Baltic Sea.

10.3.2 Adjusted emission scenarios

The second emission scenario improves the agreement between modelled results and field data for almost all measurements, except for those corresponding to dates when air masses came from SSE and SSW. For 2,3,4,7,8-PeCDF, about 60% of the modelled concentrations agree with measurements within a factor of three. 100% of the modelled concentrations agree with measurements within a factor of ten. Similar results are obtained for 1,2,3,7,8,9-HxCDD and OCDF. However, the second emission scenario leads to underestimation of OCDD for the southwest (SW) and northwest (NW) compass sectors and to overestimation for the east (E) compass sector.

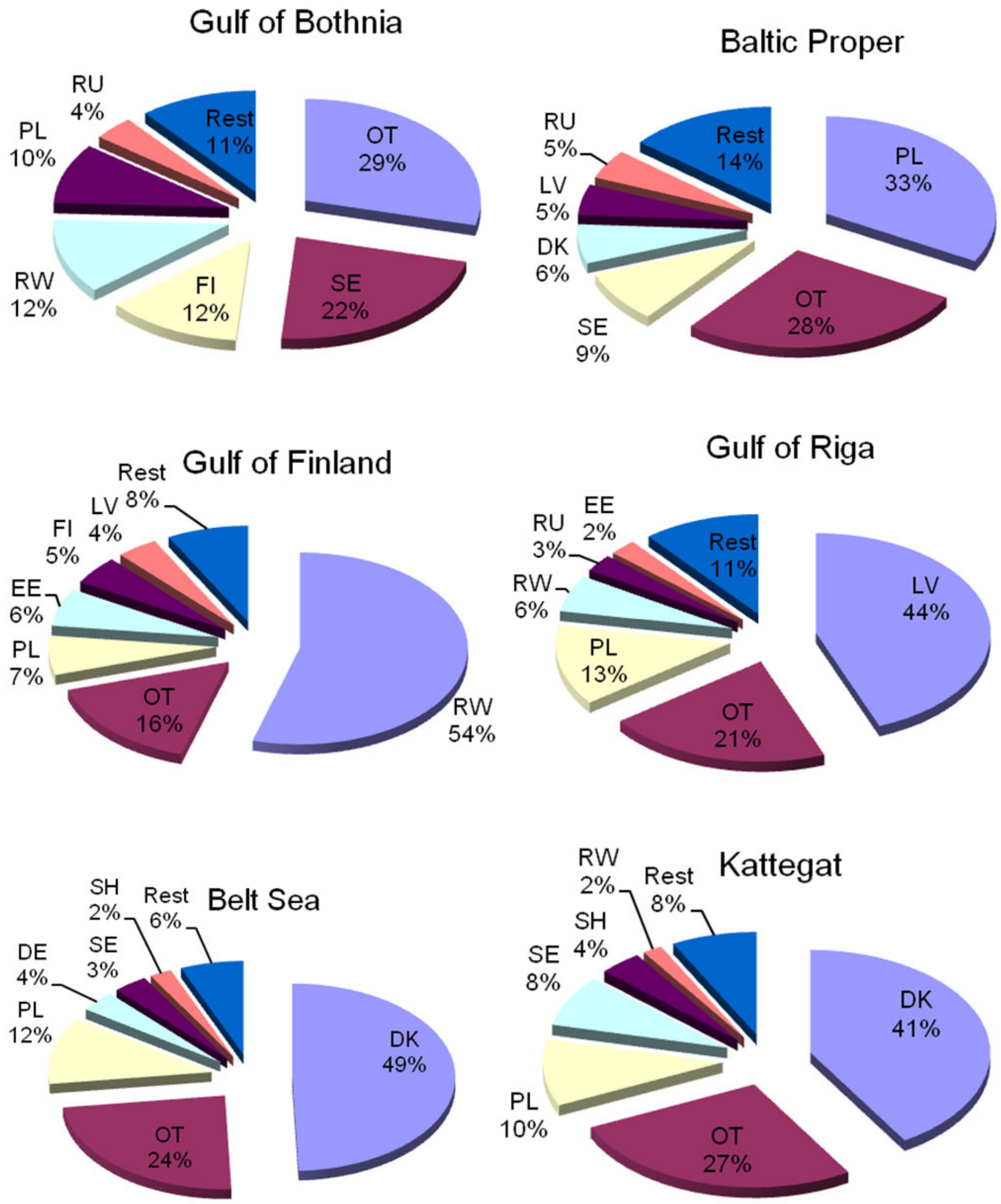


Figure 52. Contributions of various source groups to the deposition flux of 2,3,4,7,8-PeCDF to the sub-basins of the Baltic Sea calculated using the first scenario. DK – Denmark, EE – Estonia, FI – Finland, DE – Germany, LV – Latvia, PL – Poland, SE – Sweden, RU – the Eastern part of the Russian Federation, RW –- the north-western part of the Russian Federation, OT – the rest of the European countries altogether, SH – emissions from shipping within the Baltic Sea, Rest – all other sources.

The application of the third emission scenario leads to an improvement by a factor of 0.5 - 4.5 in the agreement between measured and modelled air concentrations corresponding to days when air masses came from the SSE and the SSW. However, the disagreement between measurements and calculations for air coming from other compass sectors is larger than in the second scenario, and can reach as high as 10 times or more. Thus, adjusting emissions up in regions other than the ones included in the second scenario made the agreement between model predictions and measurements better in the SSE and SSW, but worse in other compass sectors.

It should be noted that the adjustments are only two examples of many possible upward adjustments that could be made to the emission inventory, resulting in an improved comparison between model predictions and measurements. Even if an improved model comparison with measurements is observed as a result of the upward adjustments, this does not necessarily imply that emissions in these source regions are underreported. In future work, it will be important to improve the emission adjustment procedure. This can only be achieved using a combination of improved emission inventories and more high quality monitoring data from different sites around the Baltic region. We believe that given enough quality input data, the approach presented here can be used to identify contributors to emission inventory uncertainty and to Baltic Sea air pollution with high accuracy.

The statistical correlation, carried out in order to investigate how the contributions of various source regions to Baltic air levels correlated to calculation deficiencies, demonstrated that different source regions are important for different congeners (e.g., Finland for HxCDD, and shipping for PeCDF), but no source region is consistently important for all four congeners. This may be indicative of different source sectors being important in different regions, but also that different countries are focusing their monitoring on different source sectors. A more sophisticated emission adjustment procedure would adjust emissions from different regions on a congener-specific basis for a wider range of congeners.

10.4 Conclusions

- The modelling work undertaken in Chapter 10 demonstrates that there is currently a poor quantitative understanding of dioxin emissions contributing to the Baltic region. Besides, there is a lack of dioxin monitoring data particularly reporting congener composition of PCDD/Fs in the atmosphere and precipitation. Both these factors hamper accurate tracing of emissions using modelling tools.
- Current emission databases for dioxins are not accurate and cannot be used confidently to estimate either total TEQ emissions in a region or the dominant emission sectors.
- The modelling tool and emission adjustment approach presented here can potentially be used to identify the source regions for which the emission estimates are most in error. The use of the modelling tool for dioxins is limited though by the poor quality of emission databases.
- The emission adjustment demonstrated that by adjusting congener composition and by elevating emissions by a factor of two in two source regions, the agreement between modelled and measured values improved for air masses originating from almost all compass sectors. However, increasing the emissions with a factor of 10 in several source regions did not improve the agreement between model predictions and measurements. This indicates the approximate magnitude of error in the European emission estimates, which is valuable information.

11 Sources and source regions for atmospheric emissions of dioxins and other POPs affecting the Baltic Sea environment

11.1 Introduction

In a previous study, monitoring of PCDD/Fs in Baltic air revealed that winter air originating from central and eastern directions contained the highest levels of PCDD/Fs (Sellström *et al.* 2009). Here, we hypothesised that the metal concentrations in air could give guidance as to which source types are important for PCDD/F air emissions. We repeated the study by Sellström *et al.* (2009), but extended the sampling to also include metals, HCB and PCB. The aim was to investigate trends for PCDD/Fs, PCBs and HCB, and to identify important source types for PCDD/Fs by using metals as source markers for co-emission with PCDD/Fs.

11.2 Methodology

Air samples were collected at Aspvreten monitoring station, a rural site near the shore of the Baltic Proper (see also 10.2.5). Sampling was conducted during the summer season 2010 (August-September) and winter season 2010/11 (November-February). Because air mass origin was of interest for this project, high volume (HiVol) samplers were run continuously on a 24-h basis with only a few breaks for technical maintenance. The total number of samples was 45 for the summer and 58 for the winter season. The samplers were equipped with glass fibre filters to collect POPs associated with atmospheric particles, and PUFs to collect POPs in gaseous phase following the methodology described in Sellström *et al.* (2009). In parallel, air sampling for metal analysis was conducted using a Derenda PNS 16T sampler (Comde-Derenda GmbH, Germany). This sampling device is a reference device according to the European Guidelines CEN 12341 (PM10) and CEN 14907 (PM2.5).

Air mass back trajectory analyses were conducted for all collected samples by using the NOAA HYSPLIT model (http://www.arl.noaa.gov/ready.html), including three different heights (20, 100 and 500 m). At the 20 m height, 48 h was used with measurements every 4th hour, and for 100 m and 500 m heights 96 h with measurements every 6th hour. The criterion for a stable air mass back trajectory was that the three heights should agree. Samples that had stable air mass back trajectories were selected and analysed for 2,3,7,8-PCDD/Fs, ΣPCB_7, and HCB by Ökometric GmbH (Bayreuth, Germany) and metals (As, Cd, Co, Cr, Cu, Fe, Hg, K, Mn, Ni, Pb, Sb, Se, Tl, V, Zn) by ALS Scandinavia AB (Luleå, Sweden). The samples were divided into seven compass sectors depending on air mass origin: SW (southwest), SSW (south-southwest), SSE (south-southeast), E (east), NNE (north-northeast), NNW (north-northwest), and NW (northwest). In total, 18 summer samples and 19 winter samples were analysed: 6 (3+3) SW, 4 SSW (4+0), 3 SSE (0+3), 11 E (5+6), 7 NNE (3+4), 4 NNW (1+3), and 2 (2+0) NW.

Plots of concentrations for compass sectors and correlation matrix studies were made on the data, together with the metals, in order to *i*) identify possible sources of the air emissions by using metals as markers, and *ii*) observe the pollutant contributions of the compass sectors

Samples and variables for which more than 40% of the data were missing or below LOQ were eliminated from data analysis. As most of the PCDD/F data for the summer samplings were <LOQ (>80%), the data analysis and interpretation were done for the winter samples only. In all data analysis, remaining <LOQs were replaced by half of the LOQ. The following abbreviations are used: PCDD/Fs represents the sum of the seventeen 2,3,7,8-PCDD/F congeners; PCDDs is the sum of the seven 2,3,7,8-PCDDs; PCDFs is the sum of the ten 2,3,7,8-PCDFs; ΣPCB_7 is the sum of CBs 28, 52, 101, 118, 138, 153, 180, HxCDD-1 represents 1,2,3,4,7,8-HxCDD; HxCDD-2 is 1,2,3,6,7,8-HxCDD; HxCDD-3 is 1,2,3,7,8,9-HxCDD; PeCDF-1 is 1,2,3,7,8-PeCDF; PeCDF-2 is 2,3,4,7,8-PeCDF; HxCDF-1 is 1,2,3,4,7,8-HxCDF; HxCDF-2 is 1,2,3,6,7,8-HxCDF; HxCDF-4 is 2,3,4,6,7,8-HxCDF; HpCDF-1 is 1,2,3,4,6,7,8-HpCDF; HpCDF-2 is 1,2,3,4,7,8,9-HpCDF. TEQs were calculated using the WHO 2005 TEFs (Van den Berg *et al.* 2006).

11.3 Results and discussion

11.3.1 Levels of PCDD/Fs

The levels of PCDD/Fs during the summer season were generally below LOQ, with an average of approx. 1 fg TEQ m^{-3} (values below the LOQ replaced with LOQ/2 and included in the average). There were no significant differences in TEQ levels among compass sectors for the summer season, as seen in Figure 53a and based on significance tests. It was also observed that PCDDs contributed more to the total TEQ than PCDFs. During the winter season, there was a significant increase in TEQ levels in air arriving from all directions. The increase was particularly pronounced for air arriving from the southern and eastern compass sectors (Figure 53b), in line with Sellström *et al.* (2009). The average concentration during winter was 6.0 ± 4.7 fg TEQ m^{-3}. This average concentration is similar to the average found previously by Sellström *et al.* (2009) (~10 fg TEQ m^{-3}). Similarly to the previous study, PCDFs contributed more than PCDDs to the total TEQ in air from the SSE, E and NNE compass sectors. Because the air that had travelled from the SSE and E compass sectors showed the highest TEQ levels, special focus should be given to these regions in order to identify important PCDD/F air emission sources.

11.3.2 Levels of PCBs and HCB

In contrast to the PCDD/F air concentrations, PCBs in Baltic air were significantly higher during summer than winter (average ± stdv 19 ± 7 pg m^{-3} vs. 5.8 ± 2.5 pg m^{-3}; Figure 54). This indicates that emissions from secondary sources, such as volatilisation from buildings and waste sites during the warm summer season, are of significant importance for these contaminants. It also demonstrates that PCBs and PCDD/Fs have distinctly different sources. As for the PCDD/Fs, there were significant differences between compass sectors during the high level season (in this case the summer season) with higher levels from highly populated sectors (SW: 18 ± 1.1, SSW: 26 ± 1.7, E: 21 ± 1.7, NNE: 13 ± 1.1, NW: 11± 0.83), but not during the winter season. In contrast, there were no significant differences observed in the HCB levels among compass sectors for both seasons. However, similar to the PCDD/Fs, the winter air levels of HCB were significantly higher (79 ± 22 pg m^{-3}) than the summer levels (43 ± 14 pg m^{-3}), although the difference between summer and winter was not at all as marked as for the PCDD/Fs. The reason for the higher HCB winter levels is not known but could be due to breakthrough through the sampling media, which has been shown to occur particularly during the warmer summer months (Halsall *et al.* 1998).

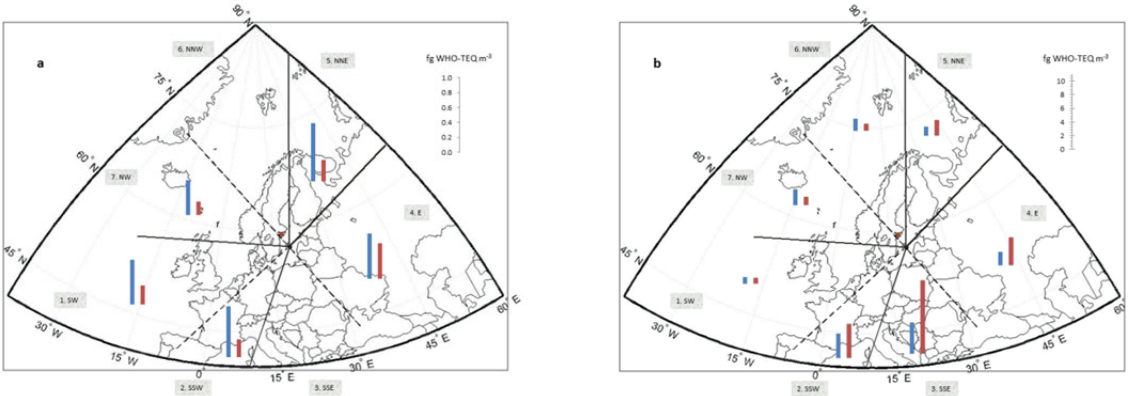


Figure 53. Average concentration of PCDDs (blue bars) and PCDFs (red bars) in Aspvreten air (fg TEQ m^{-3}) during a) summer 2010 (current study), and b) winter season 2006/2007 (Sellström *et al.* 2009) and 2010/11 (current study), divided into seven compass sectors based on air mass origin.

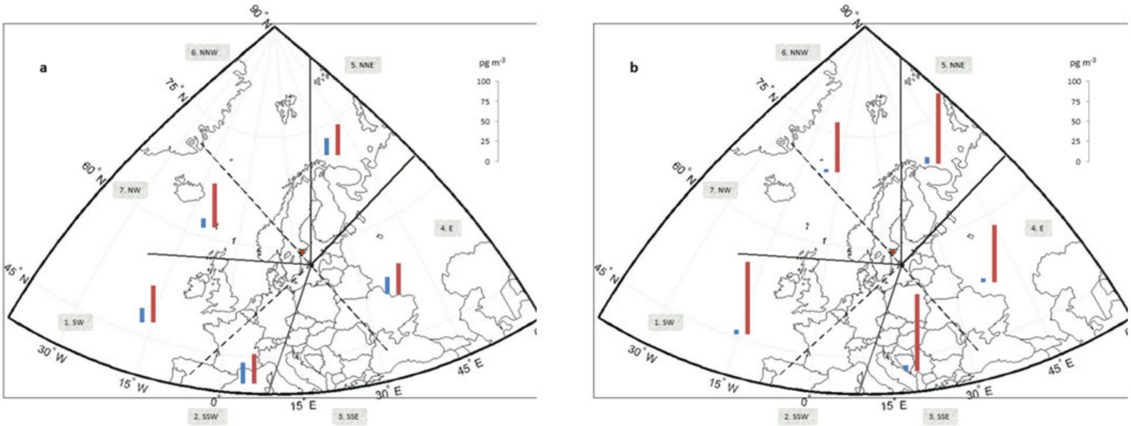


Figure 54. ΣPCB_7 (blue bars) and HCB (red bars) in Aspvreten air during a) summer season 2010, and b) winter season 2010/2011.

11.3.3 PCDD/F and metal level correlation studies and possible sources

Because we hypothesised that the metal concentrations in air could indicate which source types are important for PCDD/F air emissions, we searched for metals that showed similar air concentration trends as the PCDD/Fs. A correlation matrix study analysis was conducted for all compounds and elements except TCDD, PeCDD, HxCDF-2, As, Hg, Se and Tl, which were excluded because of a high fraction of missing data (>70% below LOQ). Because of a low number of samples per sector, the air mass directions were divided into four compass sectors in this data evaluation stage: a) SW-SSW (southwest and south-southwest directions), b) SSE-E, c) NNE, and d) NNW-NW. We knew from previous work (Sellström *et al.* 2009), and the work reported here that the winter air from SSE-E (compass sector b) is clearly the most important for air mass transport of PCDD/Fs to Baltic air.

The total sum of PCDD/Fs (labelled 'Total') was highly correlated to PCDFs (r>0.86). PCDFs are also the most important contributors to TEQ during the winter season, the season with the highest air levels. The furans (PCDFs) should therefore receive special attention in the source tracing.

For the SSE-E sector, K, Se, Pb, Sb, Cd, Zn, and V were enhanced compared to the other sectors (Figure 55). Thus, our data indicates that activities related to these metals may be related to emissions of PCDD/Fs from SSE-E regions in winter.

Enhanced concentrations in the same sector are not evidence for a similar origin; however, a strong correlation between PCDFs and metals should strengthen a co-emission relation. Among the six candidate metals, V showed a very weak correlation with PCDFs (*r* from 0.25 to 0.40) in the SSE-E region (Figure 56). The other five metals (Cd, K, Pb, Sb and Zn) correlated well with PCDFs and can be considered as key elements. These correlations were not specific for SSE-E, although the correlations were slightly stronger for this sector (Table 10, Figure 56). In the search for literature dealing with metals as markers for specific activities, it was concluded that it was a challenging task to find up-to-date studies. A discussion on the metals as indicators for source types follows later in this chapter.

It is also worth to noting that higher winter levels may be related to variation in atmospheric mixing height, i.e., a non-emission related factor may affect the concentration of pollutants in air. In general, lower mixing heights in winter have been observed, potentially resulting in higher pollution concentrations, as the volume of air in which the pollutant is diluted is lower. The decrease in mixing height during winter has been reported to vary from 15% (Robinson 1966) up to 66% (Seinfeld 1986) of the mixing height during the summer season. The increases in the PCDD/F concentrations at Aspvreten were significantly larger, particularly in air from the SSE-E sector (Table 11). Since Aspvreten is a rural field station (see section 10.2.5), this indicates that the increased PCDD/F winter concentrations observed at Aspvreten is due to inputs from emissions that were transported long-range and not primarily to seasonal mixing height variation.

The marked winter season increase of PCDD/Fs thus indicates that non-industrial related winter activities, such as combustion for heating, are accountable. To elaborate further, a comparison was made for the average summer and winter congener pattern of the E and SSE sectors (Figure 57), and the patterns of municipal solid waste incinerators (MSWI; Lee *et al.* 2004, Lin *et al.* 2010) and stack flue gas of coal-fired power plants (Lin *et al.* 2007; Figure 58). As can be seen, there is a good match between the Aspvreten air and the two combustion sources. A similar match could not be found for other source types such as electric furnaces, aluminium smelters, unleaded gas-fuelled vehicles and diesel-fuelled vehicles (Lee *et al.* 2004). Emission from domestic burning may also be one of the important sources, but no good reference could be obtained for comparison of congener profiles.

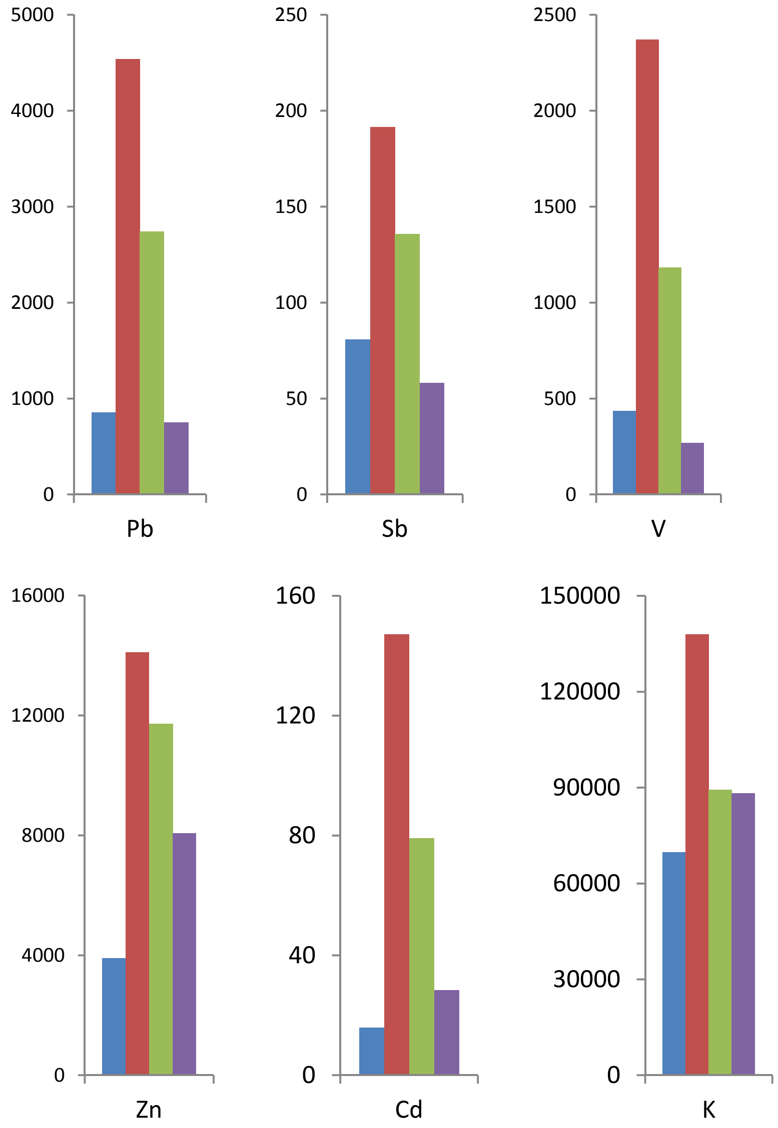
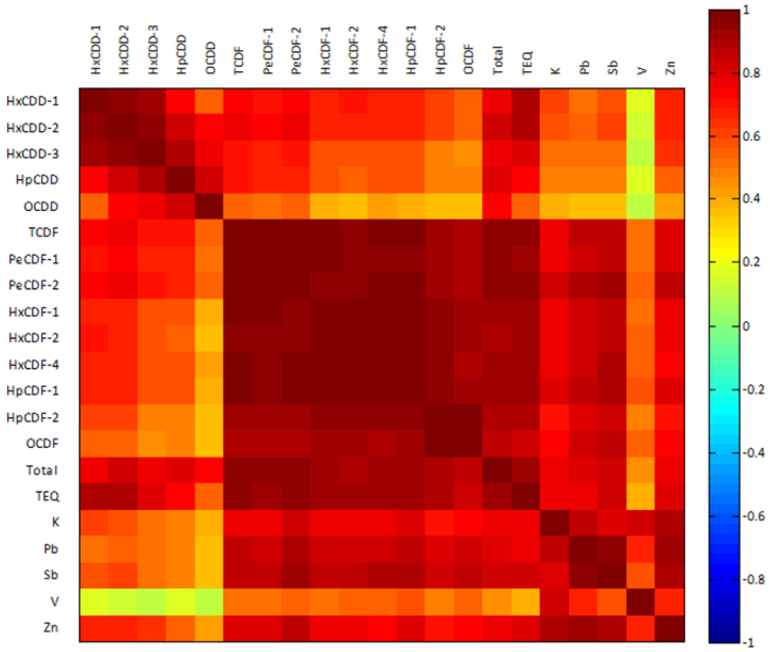


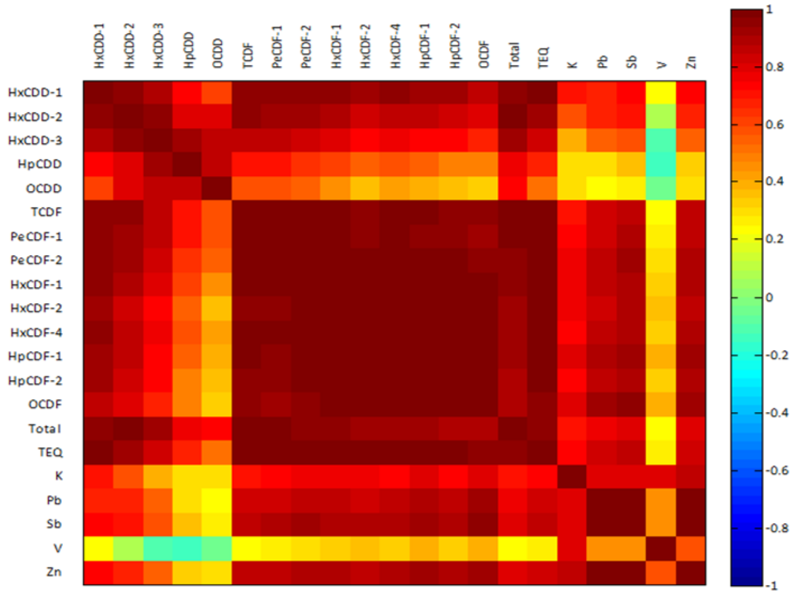
Figure 55. Metal concentrations (pg m^{-3}) in Aspvreten air in winter 2010/11 🟦 SW-SSW 🟥 SSE-E 🟩 NNE 🟪 NNW-NW

Table 10. Correlation coefficients (*r*) for PCDFs and selected metals in Baltic air during winter 2010/2011. The range refers to correlation with various PCDF congeners.

	Pb	Sb	Zn	Cd	K
Winter overall	0.78-0.90	0.84-0.91	0.69-0.85	0.78-0.90	0.69-0.82
SSE-E	0.83-0.94	0.87-0.96	0.85-0.93	0.83-0.95	0.71-0.79
Non-SSE-E	0.63-0.95	0.54-0.92	0.57-0.95	0.55-0.90	0.52-0.91


HxCDD-1
HxCDD-2
HxCDD-3
HpCDD
OCDD
TCDF
PeCDF-1
PeCDF-2
HxCDF-1
HxCDF-2
HxCDF-4
HpCDF-1
HpCDF-2
OCDF
Total
TEQ
K
Pb
Sb
V
Zn
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1

a


HxCDD-1
HxCDD-2
HxCDD-3
HpCDD
OCDD
TCDF
PeCDF-1
PeCDF-2
HxCDF-1
HxCDF-2
HxCDF-4
HpCDF-1
HpCDF-2
OCDF
Total
TEQ
K
Pb
Sb
V
Zn
1
0.8
0.6
0.4
0.2
0
-0.2
-0.4
-0.6
-0.8
-1

b

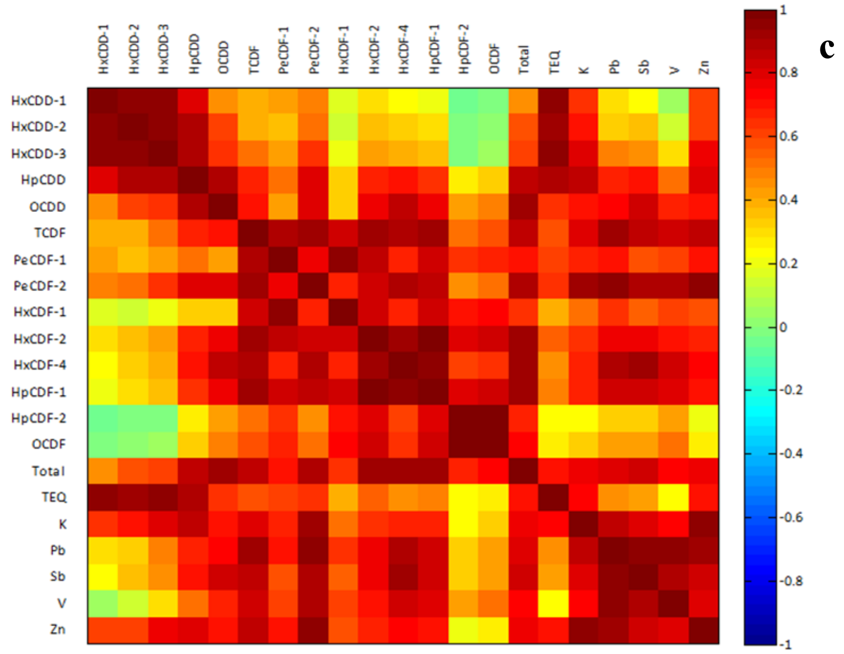


Figure 56. Correlation matrices of winter season data for a) all air measurements at Aspvreten b) SSE-E compass sector only, and c) all except the SSE-E region.

Table 11. Average ratio of PCDD/Fs concentrations in winter as compared to summer (C_{winter}/C_{summer}) at Aspvreten for the SSE-E sector and remaining sectors (SW-SSW, NNE and NNW-NW).

PCDFs		
TCDF	6.1	5.1
PeCDF-1	12	7.1
PeCDF-2	16	9.0
HxCDF-1	12	8.6
HxCDF-2	13	9.6
HxCDF-4	12	7.4
HpCDF-1	7.2	6.4
HpCDF-2	4.2	1.9
OCDF	5.9	3.2
PCDDs		
HxCDD-1	4.8	3.9
HxCDD-2	8.4	4.2
HxCDD-3	9.9	4.8
HpCDD	2.9	1.1
OCDD	3.2	1.2

Cd, Pb, Zn and Sb showed strong correlations among each other ($r>0.93$, $p<0.01$), indicating a common emission source. The relative abundance of these key elements in the Aspvreten air and the combustion sources could be a good indicator of whether a source-receptor relationship exists. In Table 12, available data for coal-fired power stations has been compiled. These ratios agree well with what was observed in Aspvreten air. Corresponding ratios for MSWI and biomass burning could not be found in the literature.

According to Pacyna (1986), emissions from wood combustion are dominated mainly by Zn, Pb and Cu. Potassium (K) is also associated with biomass burning (Hopke P, pers. communication), indicating that combustion of biofuel may play a role. However, biofuel is no longer a primary source of heat and energy in developed countries. It is still possible that domestic biofuel heating including fractions of waste is common in Europe. This kind of combustion generating diffuse pollution is poorly characterised in terms of emission factors for PCDD/Fs and trace elements. Open burning of agricultural wastes could also result in PCDF and K emissions because of the use of K in fertilizers. In summary, although this study could not provide clear evidence for dominating sources types, there are indices that point towards a dominance of combustion sources, such as MSWI, coal combustion, and domestic combustion for heating.

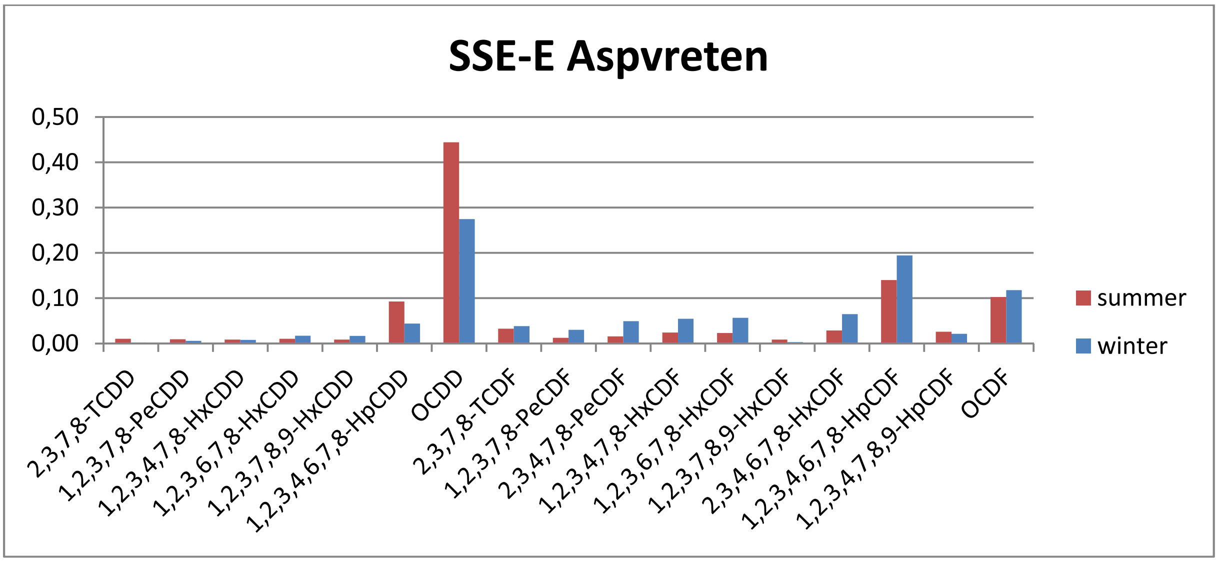


Figure 57. The 2,3,7,8-PCDD/F congener pattern in Aspvreten air during summer (this study) and winter (this study and Sellström *et al.* 2009).

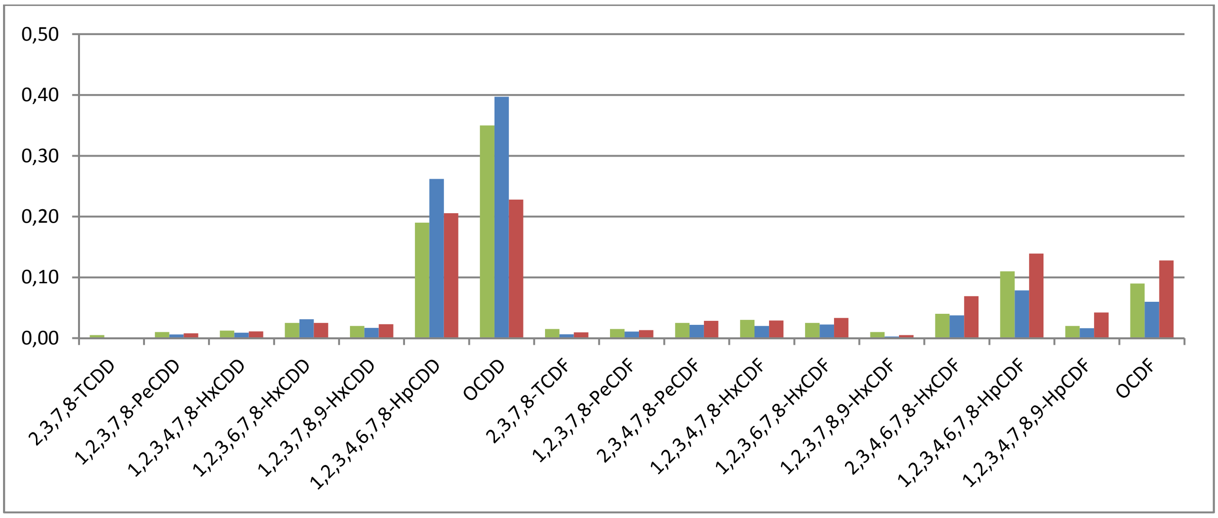


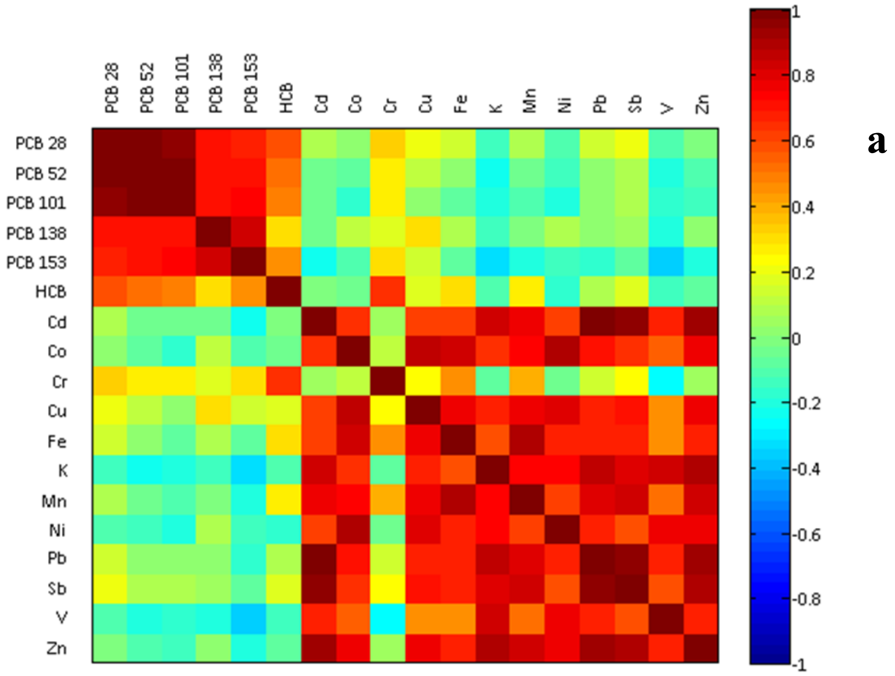
Figure 58. The PCDD/F congener pattern in flue gases from MSWI (green: Lee *et al.* 2004; blue: Lin *et al.* 2007), and coal-fired power plant (red: Lin *et al.* 2007).

Table 12. Ratios between metals in fly ashes and flue gases from coal-fired power stations and in Aspvreten air.

	Coal-fired power stations		**Aspvreten air**	
	López-Antón et al. (2011)	Meij and Winkel (2007)	SSE	E
Zn/Pb	1.6 (plant A) 1.0 (plant B)	3.0	2.9	3.3
Pb/Sb	30 (plant A) 37 (plant B)	N/A	21	29

N/A – not available

No correlation between the air concentrations of ΣPCB_7 and metals during the winter season could be observed (Figure 59a). However, relatively strong correlations could be seen for summer (Figure 59b), e.g., between Cu and ΣPCB_7 (r=0.49-0.67). HCB generally showed no or negative correlations with metals in summer and winter, with correlation coefficients *(r)* varying from -0.07 to -0.68 for summer, and from -0.16 to 0.60 for winter samples. These observations together with the seasonal and compass sector studies, support previous studies which suggest that elevation of PCBs in air is closely linked to urbanised and industrialised areas where it was previously used (Harner *et al.* 2004), while HCB is more globally distributed and not highly associated to areas with high anthropogenic activities (Barber *et al.* 2005).



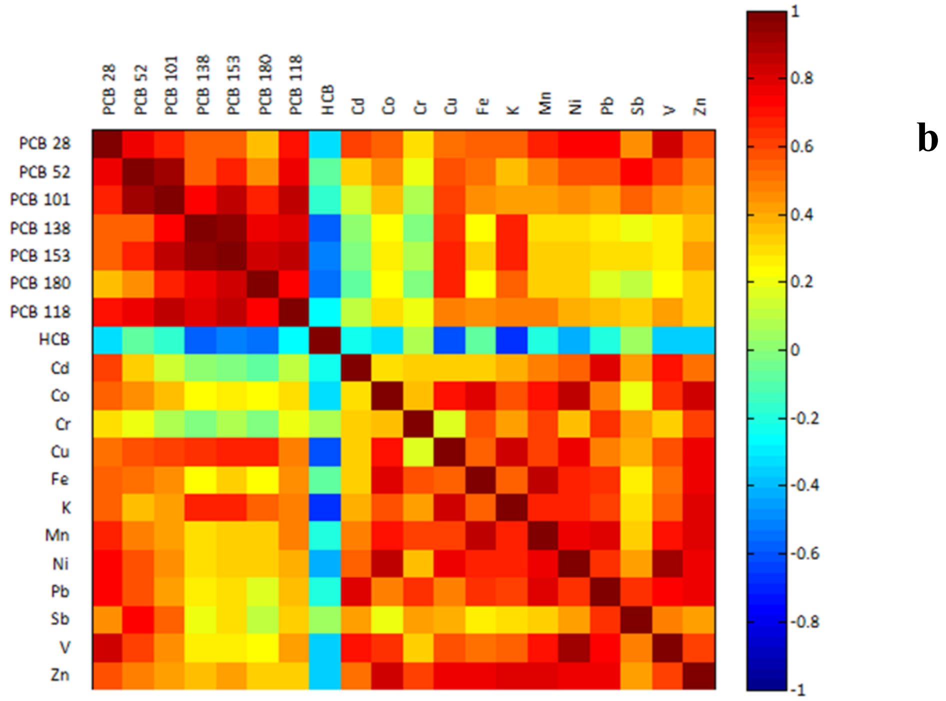


Figure 59. Correlation matrix for Aspvreten air concentrations (all compass sectors) of ΣPCB_7, HCB and metals during a) winter season and b) summer season.

11.4 Conclusions

- For the summer season, there were no significant differences in levels of $TEQ_{PCDD/F}$ in air sampled at Aspvreten among compass sectors, and it was also observed that PCDDs contributed more to the total TEQ than PCDFs. During the winter season, PCDFs dominated and there was a significant increase in TEQ levels in air arriving from all directions. The increase was particularly pronounced for air arriving from the southern and eastern compass sectors (Figure 53), in line with the earlier study by Sellström *et al.* (2009). PCBs showed an opposing pattern to PCDD/Fs with higher concentrations during summer, but as for the PCDD/Fs, there were significant differences between compass sectors during the high level season (in this case the summer season). HCB showed the same seasonal pattern as PCDD/Fs, but no differences related to compass sectors.
- The high PCDD/F levels during the winter season indicate a dominance of non-industry related combustion sources, presuming that there is no seasonal trend in industrial production.
- The PCDFs are the main contributors to the total (and TEQ) concentration of PCDD/Fs in the Aspvreten winter air.
- It was hypothesised that metal concentrations in air could be used as indicators of which source types are important for PCDD/F air emissions. Correlations were observed between PCDF concentrations and Cd, K, Pb, Sb and Zn concentrations in air sampled during the winter months. K, Pb, Sb and Zn are associated with combustion of wood (Pacyna 1986, Hopke, personal communication) and other biofuels, and the Aspvreten air showed similar ratios of Zn/Pb and Pb/Sb as flue gases from coal-fired power stations.
- The general PCDD/F congener pattern of Aspvreten air matched well with municipal solid waste incinerators (MSWI) and coal-fired power plants combustion patterns, in contrast to emission patterns from electric furnaces, aluminium smelters, unleaded gas-fuelled vehicles and diesel-fuelled vehicle (Lee *et al.* 2004, Lin *et al.* 2007).

- In summary, there are several indications that combustion is responsible for the high PCDD/F levels in Aspvreten winter air. However, our PCDD/F and metal data could not be used to pin-point one combustion source category as more important than others.

12 Synthesis

12.1 Introduction

In this chapter the new knowledge gained from the preceding chapters is integrated and evaluated in a system synthesis. In a preceding study undertaken for the Swedish EPA (Wiberg *et al.* 2009), the POPCYCLING-Baltic model (Wania *et al.* 2000) was used as a tool to aid the synthesis work by calculating mass balances for dioxins and other selected POPs in the whole Baltic Sea as well as in the separate basins. Some potential limitations in the inputs and parameterisation of the POPCYCLING-Baltic model were identified (Wiberg *et al.* 2009) and were addressed in research undertaken in WP1, WP2 and WP3 in the present study. One of the main aims of WP3 was to identify, based on this new research, if the POPCYCLING-Baltic model required to be re-parameterised. Potentially, new simulations with a re-parameterised POPCYCLING-Baltic model could lead to different conclusions than those reached in Wiberg *et al.* (2009). In this chapter we systematically address the various issues of concern with the previous parameterisation and model runs of the POPCYCLING-Baltic model in Wiberg *et al.* (2009), namely:

- Were temporal trends of dioxins in air and thus atmospheric deposition between 1986 and 2006 correctly defined in the previous modelling work?
- Was the parameterisation of sedimentation, resuspension and burial rates in the POPCYCLING-Baltic model correct in the previous modelling work?
- Is soil volatilisation/resuspension of dioxins an important source of dioxins to atmospheric deposition to the Baltic Sea?
- Were riverine inputs and land-based industrial inputs of dioxins to the Baltic Sea underestimated in previous modelling work?

We consider these issues in turn below in sections 12.2.1-12.2.4. The chapter then continues by identifying the main conclusions reached in the BalticPOPs project (section 12.3) and finally recommends actions by authorities as well as further research areas (section 12.4).

12.2 Re-evaluation of POPCYCLING-Baltic modelling

12.2.1 Were temporal trends in air and thus atmospheric deposition between 1986 and 2006 correctly defined in previous modelling work?

In Wiberg *et al.* (2009), the POPCYCLING-BALTIC model used air concentrations of dioxins as the model input, rather than using primary emissions of dioxins. The contemporary air and deposition measurements made in the Wiberg *et al.* (2009) and in this project (see Chapter 11) are of high quality, so current estimates of atmospheric deposition to the Baltic Sea are judged reliable. For the retrospective simulations, however, the atmospheric concentrations were assumed to have decreased in a linear manner between 1986 and 2006 by a factor of 4. This assumption was based on estimates of the time trends of dioxin emissions during this period (Quaß *et al.* 2004) and on time trends of dioxin concentrations in tree foliage from Germany (Rappolder *et al.* 2007). What was lacking at the time of writing the previous report (Wiberg *et al.* 2009) were any time trend data for the Baltic region, although it should be noted that most of the dioxins in the air over the Baltic originate from the European continent and thus using time trends in German tree foliage can be considered a reasonable approach.

The model simulations undertaken in Wiberg *et al.* (2009) suggested that the concentrations in Baltic sediments decreased approximately by a factor of 3 between 1986 and 2006, whereas air concentrations were assumed to have decreased by approximately a factor of 4 in the same period. It is expected that sediments respond relatively slower than air to changes in emissions given the higher storage capacity of sediments and the slower loss rates in sediment compared to air. However, it is important to evaluate if the model is predicting the time response of sediments correctly because this will have large implications for the time response of other compartments, notably the water compartments where the fatty fish (e.g., herring) reside.

Measurements of PCDD/Fs in surface sediments collected between 1986 and 1988 (Kjeller and Rappe 1995, Rappe *et al.* 1989) indicated that concentrations at that time were similar to the concentrations today (Sundqvist *et al.* 2009a), but as noted in Wiberg *et al.* (2009) these limited and fragmented data did not provide a reliable temporal trend in Baltic sediments. In Chapter 8 of this report temporal trend data for Baltic sediments are presented for several separate locations and these data can be used to re-evaluate the assumed time trends in the modelling in Wiberg *et al.* (2009). To recap, the time trends in Chapter 8 varied depending on where the sediment cores were collected with slower declines observed in offshore areas. The levels of PCDD/Fs in coastal sediments declined by a factor of approximately 2 between the mid-1980s and the current day. The offshore sediments mostly declined by less than a factor of 2 between the mid-1980s and the current day. The previous POPCYCLING-Baltic model simulations undertaken in Wiberg *et al.* (2009) appear to overestimate the time response of dioxins in sediments to reductions in atmospheric deposition (the model predicted a decline of a factor of 3 between 1986 and 2006, whereas data in Chapter 8 indicates a decline of a factor of 2 or less depending on location). There are a few possible explanations for the discrepancy between model-estimated declines in sediments and the sediment time trends data from Chapter 8: *i*) the temporal trends in air and atmospheric deposition were wrongly defined in the model simulations (i.e., a decline of a factor of 4 between 1986 and 2006 was too extreme); *ii*) the actual recovery time of the Baltic sediments following reduction of dioxin inputs may be different from the model estimated recovery time; and *iii*) other on-going (e.g., coastal, riverine and industrial) sources of dioxins have contributed to a slower decline. We address each of these hypotheses in turn below:

- ***i) The temporal trends in air and atmospheric deposition were wrongly defined in the model simulations.*** In addition to time trends in emissions (Quaß *et al.* 2004) and tree foliage from Germany (Rappolder *et al.* 2007) cited in Wiberg *et al.* (2009), we have identified further studies which report relevant time trends in the region, namely: time trends in UK air (Katsoyiannis *et al.* 2010), UK herbage (Hassanin *et al.* 2006) and also in European emissions (Gusev *et al.* 2011). These additional time trend studies agree reasonably well with assumptions used in modelling in that they suggest a fall in air concentrations of about a factor of 3-4 from the mid-1980s until the current day. The number of studies reporting temporal trend data in European PCCD/F emissions to air, Baltic air concentrations and Baltic atmospheric deposition are scarce, but without stronger empirical evidence we do not have a justification to refine the temporal trends in the air data used in the previous modelling work. Indeed, the few existing data agree reasonably well with the assumed air time trends.

- ***ii) The actual recovery time of the Baltic sediments following reduction of dioxin inputs may be different from the model estimated recovery time.*** Wiberg *et al.* (2009) recommended that an improved understanding of surface sediment accumulation and mixing is needed to produce more reliable estimates of the response time of the Baltic Sea to changes in dioxin inputs. We undertook a re-evaluation of the parameterisation of sedimentation rates in the POPCYCLING-Baltic model (see section 12.2.2) and came to the conclusion that newer estimations of sedimentation were in fact comparable to the estimates used to parameterise the POPCYCLING-Baltic model. We therefore do not have any empirical basis for performing a re-parameterisation of the sedimentation, resuspension and burial rates in the POPCYCLING-Baltic model. As discussed in more detail in section 12.2.2, we believe that a potentially bigger problem than the parameterisation of the model, is the simple one-dimensional and steady-state description of sediment dynamics used in the POPCYCLING-Baltic model. Rather than a simple re-parameterisation of the existing simplified model an improved model framework is probably required to accurately describe the time response of sediments to changes in atmospheric deposition.

iii) ***Other on-going (e.g., coastal, riverine and industrial) sources of dioxins have contributed to a slower decline.*** In Chapter 8, the source tracing for the offshore sites, where sediment levels declined less dramatically between the mid-1980s and the present day, concluded that atmospheric sources were the dominant source contributing to sediment levels of dioxins, although coastal-based industrial sources did make an important, but still minor, contribution. Sediments nearer the coast were impacted to a higher extent by coastal-based sources, and dioxin levels in the coastal sediments demonstrated a more rapid decline than in offshore sediments between the mid-1980s and current day. Furthermore, peak concentrations of dioxins generally appeared earlier in coastal areas than in offshore areas (mid-1960s to late-1970s versus mid-1980s to late-1990s). These findings indicate that terrestrial sources will eventually affect the open sea after some time lag, which is evidence that sediment contamination is moving horizontally from coastal areas to open sea areas. Horizontal movement of contamination through sediment transport is not described by the POPCYCLING-Baltic model.

The observation that dioxins are decreasing in sediments in all areas of the Baltic Sea shows that emission reduction measures in the last decades for these pollutants have been effective in reducing sources and thus levels in Baltic environmental media. The POPCYCLING-Baltic model, however, is estimating a more rapid decline in sediment concentrations than has actually occurred. The most plausible explanation appears to be the simplification of sediment dynamics in the POPCYCLING-Baltic model. Since the sediment response time is incorrectly estimated in the POPCYCLING-Baltic model, it can be expected that model predicted declines in other media (notably dissolved water concentrations) will also be estimated to be more rapid than they are in reality. This model error is one contributing factor to over-prediction of declines in dioxin concentrations in Baltic herring (Wiberg *et al.* 2009).

12.2.2 Was the parameterisation of sedimentation, resuspension and burial rates in the POPCYCLING-Baltic model correct in the previous modelling work?

As pointed out in Wiberg *et al.* (2009), the POPCYCLING-Baltic model predicted rate of decrease of dioxins in surface water in the Baltic Sea is linked to the model assumptions regarding the surface area and mixing depth of the surface sediments as well as the sediment burial rates. The rate of decrease of surface water concentrations of dioxins was suspected to be overestimated in the POPCYCLING-Baltic model due to its oversimplified model structure (Wiberg *et al.* 2009). This suspicion was supported by the model overestimation of declines in Baltic sediment cores (see above). It was recommended that an improved understanding of surface sediment accumulation and mixing is required to produce more reliable estimates of the response time of the Baltic Sea to changes in dioxin inputs.

In this project we undertook a re-evaluation of the parameterisation of sedimentation rates in the POPCYCLING-Baltic model. New data on sediment accumulation rates in the Baltic Sea has been made available since Report 5912 (Wiberg *et al.* 2009) was published. To investigate whether the parameterisation of the POPCYCLING-Baltic in the previous study was reasonable, the model input was compared to new sedimentation data collected by the Geological Survey of Sweden (SGU). The sediment accumulation rates were measured using dating with Cs-137 according to a method described by Cato and Apler (2011). The Cs-137 isotope is produced anthropogenically in nuclear fission processes. It does not occur naturally in the environment, but can only have reached Baltic Sea sediments with fallout from the Chernobyl catastrophe in 1986. Thus, the isotope can be used as a marker of time. In the Cato and Apler method, the volume of sediment that has deposited since the Cs-137 isotope first occurs in a sediment core is simply divided with the number of years that has passed since the Chernobyl catastrophe to obtain the sediment accumulation rate.

Traditionally, the accumulation rates have been determined by dividing the number of laminae (thin layers) visible in the radiography image of the sediment core by the length of the studied segment. Each laminae is assumed to represent one year. These methods are only suitable for use on sediments whose laminae can be clearly distinguished. They are therefore not successful on bioturbated sediment bottoms and bottoms where bubbles of methane gas are released in the degradation of organic material.

Cato and Apler (2011) found that the agreement between their method and the traditional one is very good. They reported an r^2 of 0,88 for a regression between accumulation rates measured using the two methods.

For the evaluation of the POPCYCLING-Baltic parameterisation, basin-specific accumulation rates in tonnes/year were calculated using data on accumulation bottom surface areas provided by SGU (Cato 2012). These surface areas were assumed to be equal to the bottom areas covered by postglacial clay. In reality, the accumulation bottom areas are likely 15-20% smaller.

A comparison of the sediment accumulation rates is displayed in Table 13. The SGU data exceeds the data used in the previous study by a factor of 2.2 for the Baltic Proper, while for the Bothnian Sea and the Bothnian Bay the SGU data is a factor of 2.5 lower than in the previous study. Considering that the two independent estimates employed different methods for determining sedimentation rates, the agreement is good. We see no need to re-parameterise the POPCYCLING-Baltic model because it is uncertain which estimate of the percentage of accumulation bottoms is most correct and as both estimates of percentages covered by accumulation bottoms are similar a reparameterisation would have little influence on model outputs.

Table 13. Comparison of the sediment accumulation rates (tonnes/year) in three Baltic Sea basins (coastal areas not included) obtained from SGU and used as model input by Wiberg *et al.* (2009).

	Baltic Proper	**Bothnian Sea**	**Bothnian Bay**
SGU data	81 700 000	13 500 000	2 710 000
Previous study	37 200 000[1]	37 900 000[2]	6 720 000[2]

1. Compiled from analyses of dated cores in Jonsson *et al.* (1990) and Perttilä *et al.* (2003).
2. Compiled from analyses in (Algesten *et al.* 2005, Borg and Jonsson 1996, Jonsson unpublished data, Jonsson *et al.* 1990), and assuming the same deposition rate and TOC content in the Archipelago Sea as in 17 bays from Stockholm archipelago (Jonsson *et al.* 2003).

12.2.3 Is soil volatilisation of dioxins an important source of dioxins to atmospheric deposition to the Baltic Sea?

Soils are the most important reservoirs for dioxins in the terrestrial environment (Cousins *et al.* 1999, Duarte-Davidson *et al.* 1996). This is due to the fact that they have high organic carbon content and that they constitute large surfaces for atmospheric deposition. A report from the European Monitoring and Evaluation Programme (EMEP) stated that about 47% of the dioxins emitted within the EMEP region are deposited to soil and vegetation in this area (EMEP 2004). During plant decay, soils receive additional input of dioxins.

Dioxins are mainly removed from soils by volatilisation (Cousins *et al.* 1999). This is a very slow process in comparison to atmospheric deposition. Thus, as primary emissions are on-going the input to soil will be much faster than the removal, leading to disequilibrium between soil and air. It has been hypothesised that when primary emissions are reduced the large amounts of dioxins that have been accumulated in soil will gradually be released to the environment and soil will become an important secondary source of dioxins to the air (Duarte-Davidson *et al.* 1996). Previous studies have shown that for other semi-volatile organic compounds, such as PCBs and lighter PAHs, soil can be a significant source to the atmosphere (Cousins and Jones 1998, Shatalov *et al.* 2001).

Soil was not taken into account as a source of dioxins when Wiberg *et al.* (2009) investigated temporal trends of dioxin concentrations in the marine Baltic Sea environment. Here we investigate whether the soil in the Baltic Sea region is or will in the future become a source of dioxins to the atmosphere using the same approach and input parameters as Wiberg *et al.* (2009), but focusing on air-soil fluxes.

The version of the POPCYCLING-Baltic model used in Wiberg *et al.* (2009) was re-coded so that it would give simulated data on the exchange of POPs between air and soil. Figure 60 displays the modelled net flux of the seventeen 2,3,7,8-substituted dioxins between soil and air in the Baltic Proper catchment area. All of the congeners have negative net fluxes (i.e. fluxes from air to soil) that are decreasing over time. The decreasing negative fluxes can be attributed to the fact that the input to soil from atmospheric deposition has decreased due to decreasing air concentrations (set in the model input). For most congeners the fluxes are approaching zero towards the end of the model simulation period. In the future it may be possible to observe a positive net flux from soil to air due to gaseous diffusion (volatilisation) of dioxins, but volatilisation will only dominate soil-air exchange if ambient air concentrations are reduced to such an extent that the atmospheric deposition is substantially diminished.

Figures 61 and 62 display modelled gaseous fluxes of the seventeen 2,3,7,8-substituted dioxins between soil and air in the Baltic Proper catchment area between 1986 and 2006. The tetra- and penta-congeners generally have positive fluxes that increase over the studied period. The fluxes are increasing because the concentration disequilibrium between air and soil is becoming larger over time. For the heavier congeners the net gaseous fluxes are close to zero or slightly negative. The slow transport across the soil/air interface means that the soil-air flux of the heavy congeners will be low even if there is a strong driving force for transport (i.e. a high soil-to-air concentration gradient). There are very few studies on the volatilization of dioxins in soils, probably because it is not practically possible to measure the extremely low dioxin volatilization fluxes. The only evidence of the slow transport across the air-soil interface of 2,3,7,8-substituted dioxins can be found in Jones and Duarte-Davidson (1997). In this study approximately 200 m^3 of clean air was pumped through soil columns containing soils that were highly contaminated with dioxins. Exhaust air from the soil columns was sampled using polyurethane foam plugs and all 2,3,7,8-substituted dioxins analysed on the PUF-plugs were below detection limits.

In summary, we are approaching a point in time when the primary emissions of dioxins have been reduced so that soils in the Baltic Sea catchment area will start acting as secondary sources of dioxins to the atmosphere. However, gaseous fluxes may still be relatively low compared to other sources of dioxins because the resistance to transport across the soil-air boundary layer is very high. From Figures 61 and 62 it can be observed that the total gaseous flux of dioxins from the soil in the Baltic Proper catchment area in the POPCYCLING-Baltic model is 56 µg WHO-TEQ/h at the end of the model simulation period in 2005. Assuming that the gaseous flux of dioxins does not vary much between Swedish regions, the total gaseous flux from soil to air in Sweden in 2005 is estimated to be 3.43 g WHO-TEQ. This model estimate compares to the reported emissions of dioxins to air in Sweden of 43 g I-TEQ in 2010 (EMEP 2012). Although soil volatilisation fluxes of dioxins are estimated to be less than 10% of current estimated primary emissions in Sweden, it should be noted that if primary emissions are cut significantly then volatilisation from soils could become an important (secondary) source of dioxins to Baltic air.

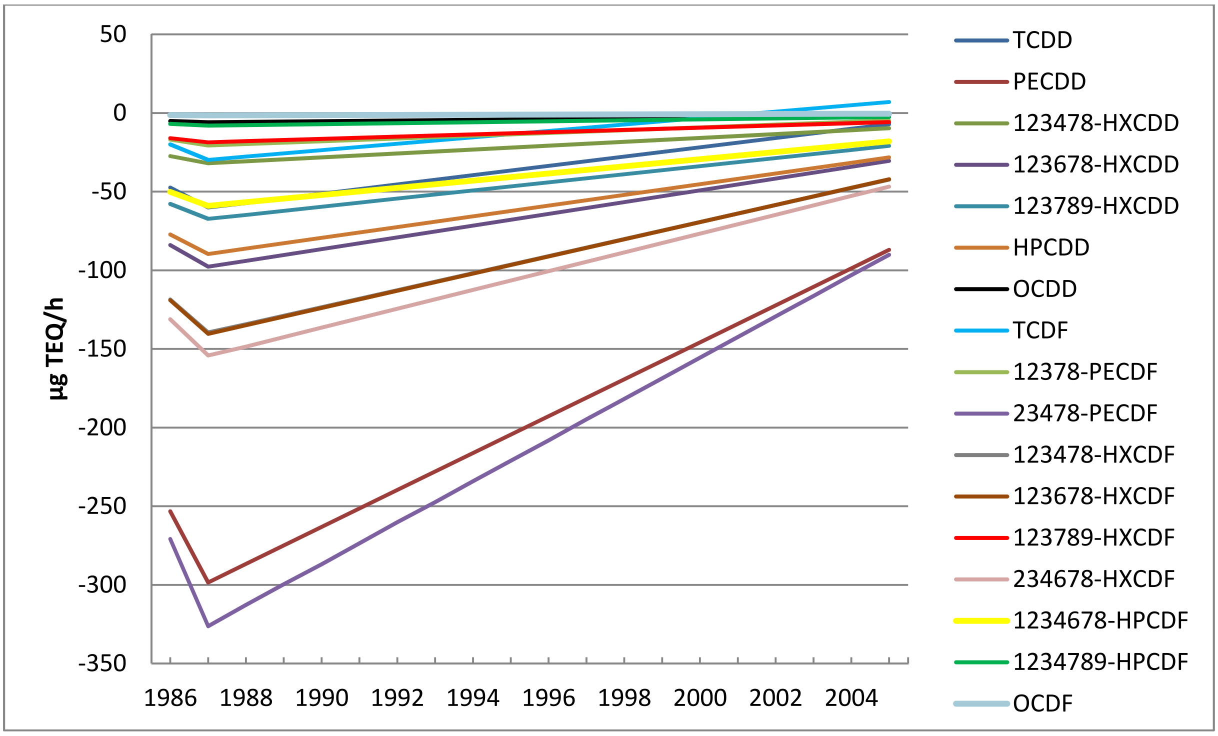


Figure 60. Modelled net fluxes (µg WHO-TEQ h^{-1}) of the seventeen 2,3,7,8-substituted dioxins between soil and air in the Baltic Proper catchment area 1986-2006. Positive values correspond to fluxes from soil to air.

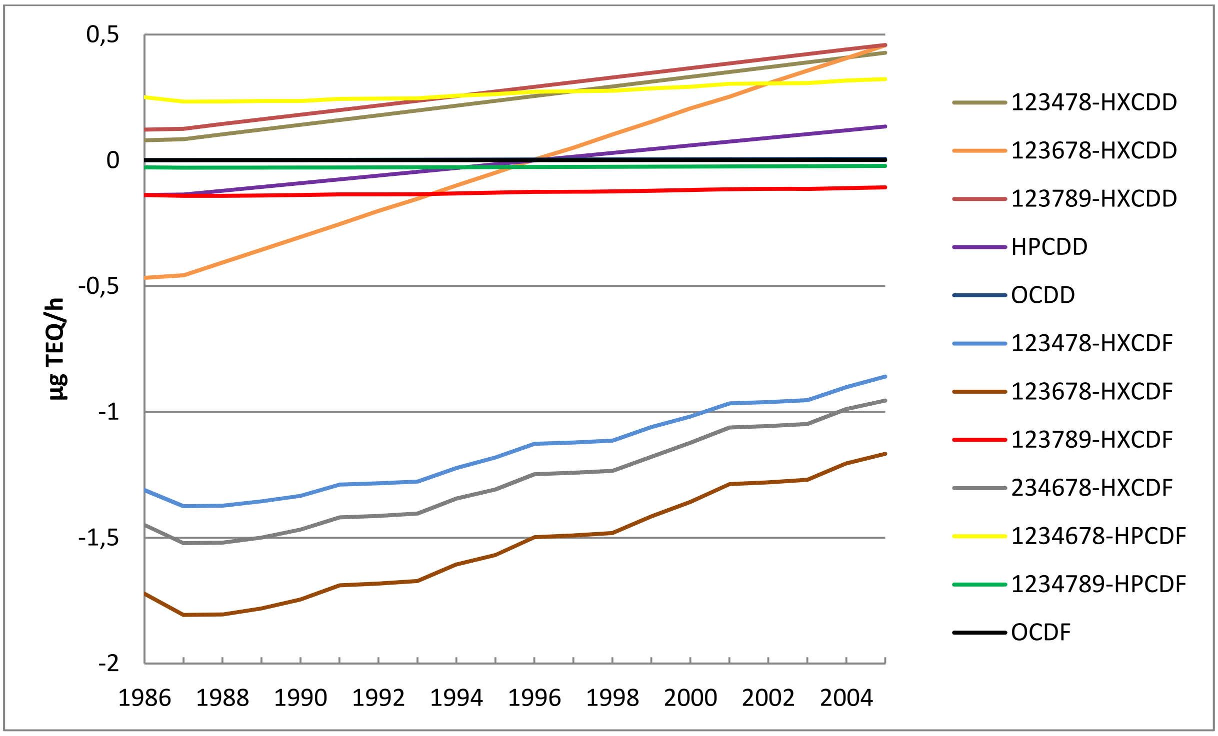


Figure 61. Modelled gaseous fluxes (µg WHO-TEQ h^{-1}) of the hexa- to octa-chlorinated PCDD/Fs between soil and air in the Baltic Proper catchment area 1986-2006. Positive values correspond to fluxes from soil to air.

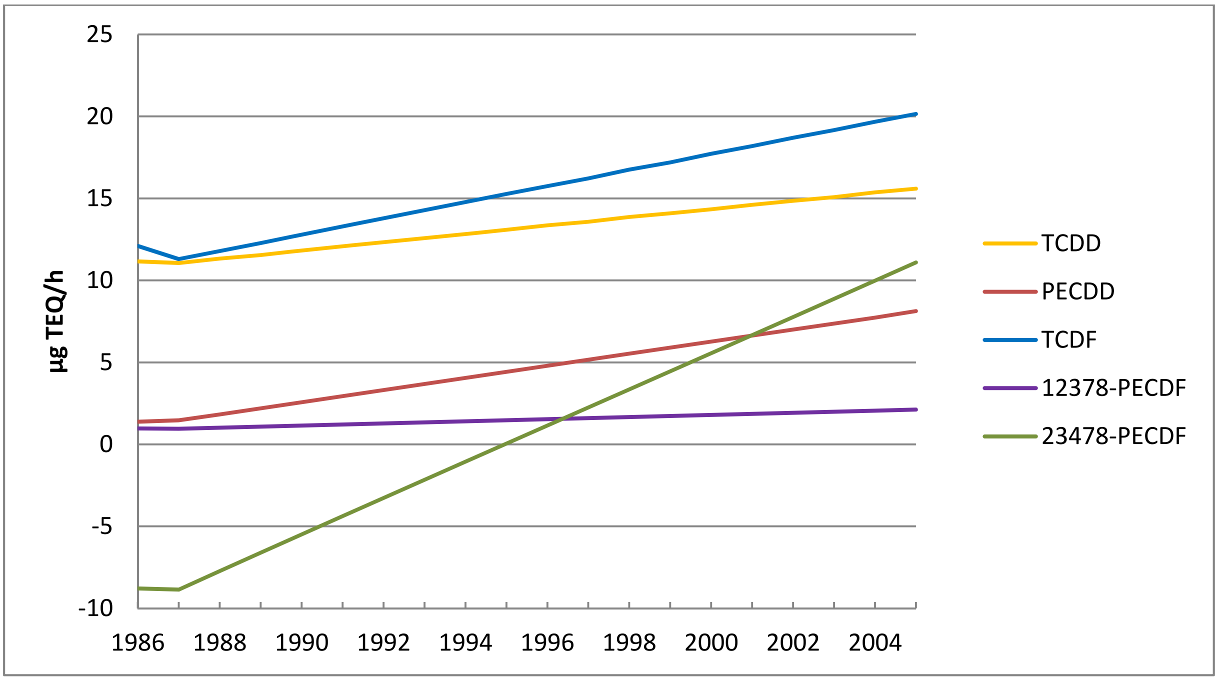


Figure 62. Modelled gaseous fluxes (µg WHO-TEQ h^{-1}) of the tetra- and penta-chlorinated PCDD/Fs between soil and air in the Baltic Proper catchment area 1986-2006. Positive values correspond to fluxes from soil to air.

12.2.4 Were riverine inputs and land-based industrial inputs of dioxins to the Baltic Sea underestimated in previous modelling work?

In the previous study of Wiberg *et al.* (2009), a major conclusion was that the atmosphere is the major source of dioxins to the Bothnian Sea and Baltic Proper (and the Baltic Sea as a whole). Riverine inputs and direct land-based industrial effluent inputs to the Baltic Sea were considered to be relatively minor sources in comparison to atmospheric deposition. The modelling results were convincing in providing a mass balance between atmospheric inputs and inventories of dioxins. Estimates of inputs from other known sources were small compared to atmospheric deposition. There was, however, a paucity of data on riverine and industrial inputs to totally exclude the possibility that they could make an important contribution, so newly available data have been used to make a re-evaluation of the previous report's conclusions.

Within the scope of the COHIBA project, the inputs of dioxins and dl-PCBs to the Baltic Sea were quantified using substance flow analysis and chemical fate modelling. Data on riverine input of dioxins to the Baltic Sea are not available, but for some countries COHIBA reports estimates of direct emissions to inland surface waters. In Sweden 1.0-20 g I-TEQ PCDD/Fs and dl-PCBs are emitted to surface waters each year (Andersson *et al.* 2012). For Estonia and Latvia the corresponding estimates takes only one source sector into account. The Latvian industry releases 0.0053 g I-TEQ/year PCDD/Fs and dl-PCBs to surface waters (Fridmanis *et al.* 2012). In Estonia 0.03 g I-TEQ/year is released from waste water treatment plants (Laht and Volkov 2012). Although these estimates do not make out a sufficient foundation for a Baltic Sea mass balance, they indicate that the riverine input of dioxins originating from direct sources is very low in relation to the input from atmospheric deposition (133 g WHO-TEQ/year to the Bothnian Sea and the Baltic Proper, according to Wiberg *et al.* (2009).

Newly available average PCDD/F water concentrations measured at six occasions between November 2007 and May 2009 in the Umeå river (Josefsson *et al.,* manuscript in preparation) were also used to make a rough estimate of the total riverine input to the Bothnian Sea for comparison with our previous model estimates (Wiberg *et al*. 2009). It is assumed that the water concentration in the Umeå River is a good approximation for the average riverine water concentrations in the Bothnian Sea basin. According to our calculations, which estimate the entire riverine discharge to the Bothnian Sea and assume that it has the same concentration as the Umeå River, the yearly riverine input to the basin is 0.88 g WHO-TEQ. According to the modelling study by Wiberg *et al.* (2009), the input from direct atmospheric deposition to this basin is 27.3 g WHO-TEQ yr^{-1}. The riverine input is 11.1 g WHO- TEQ yr^{-1}.This estimate of the riverine input does not include direct emissions, but only indirect transfer via the atmosphere.

12.2.5 Concluding remarks concerning the lack of necessity for new POPCYCLING-Baltic model simulations

The plan in the project proposal was to undertake reruns of a re-parameterised POPCYCLING-Baltic model if necessary. We did undertake some additional model runs using the version of the POPCYCLING-Baltic model form the previous work (Wiberg *et al.* 2009) to assess if volatilisation/resuspension could significantly contribute to atmospheric deposition of dioxins to the Baltic Sea (see section 12.2.3), but we did not alter the parameterisation of the model in these simulations. After careful consideration (see above discussion), we did not believe that there was any justification for a re-parameterisation of the POPCYCLING-Baltic model based on the new knowledge generated within and outside this project in the last 3 years.

In our opinion, the main conclusions from the previous modelling undertaken by Wiberg *et al.* (2009) are correct. ***The atmosphere is the dominant external source of dioxins to the Baltic Sea and therefore reducing atmospheric deposition will lead to a reduction in Baltic water concentrations.*** There is evidence from Chapter 8, however, that the model slightly overestimated the decline in concentrations in the Baltic Sea sediments. Although this is suspected to be due to an oversimplification of the sediment dynamics, as discussed above, it would be a major modelling effort to correctly describe the sediment dynamics in the model. Furthermore there is no evidence that the parameterisation is incorrect based on the latest information. The parameterisation of sedimentation rates in the POPCYCLING-Baltic model agrees fairly well with new sedimentation data collected by the Geological Survey of Sweden (see 12.2.2) so a simple re-parameterisation based on these new data would not markedly change the modelling results.

We predict, according to the modelling in (Wiberg *et al.* 2009) that further future reductions in atmospheric deposition will result in declines in water and fatty fish concentrations, but the exact magnitude of this decline in concentrations is likely to be slightly slower than predicted in the previous POPCYCLING-Baltic model simulations.

12.3 Main conclusions

At the end of each of the chapters 5-11 there are overall conclusions related to that specific chapter. We will not repeat all of those conclusions here but instead try to draw some overall conclusions from the BalticPOPs project. We will also specifically address the main questions that we aimed to address in this project and that are listed in the introduction in 4.1.

12.3.1 Temporal and spatial trends in herring

- Temporal trends for PCDD/Fs and dl-PCBs in Baltic herring were monitored at three coastal sites in the Baltic Sea for different time periods: Ängskärsklubb (1979-2009), Harufjärden (1990-2009), and Utlängan (1988-2009), and one site in the Kattegat Sea; Fladen (1990-2009). The conclusions were as follows:
  - At Ängskärsklubb and Fladen, all six dominant PCDD/F and dl-PCB congeners showed statistically significant decreases in concentrations. Significant decreases were also observed for TEQ_{PCDD}, TEQ_{PCDF} and $TEQ_{dl\text{-}PCB}$.
  - At Harufjärden significant decreases were only observed for 2378-TCDD and TEQ_{PCDD}, whereas no significant trends were observed for all other dominant congeners and TEQ values.
  - At Utlängan only two dominant congeners showed significant decreases over time, but significant decreases were observed for TEQ values.
  - At all sites, PCDDs showed a significant decrease, whereas PCDFs and dl-PCBs only displayed significant decreases in herring sampled at Ängskärsklubb and Fladen. This could suggest a temporal shift in the composition of PCCD/F sources.
- The strong statistical decreases in PCDD/Fs, dl-PCBs and TEQ values at Ängskärsklubb and Fladen demonstrate that reductions in emissions in recent decades have resulted in significant declines in PCDD/F and dl-PCB concentrations in Baltic herring in some locations of the Bothnian Sea.
- The lack of a statistically significant decrease at some sites could be attributed to several factors:
  - A lack of a reduction in pollutant emissions over time. However, evidence suggests that there has been a long-term decrease in dioxin and PCB emissions as well as levels in the Baltic environment. It is possible that some herring populations could be impacted by coastal sources which have not declined, but this is not a convincing explanation given the lack of clear spatial variation in dioxin contamination between different herring populations in the same Baltic sub-basin (see below).
  - A shorter time series which reduces statistical power. On other words, there may be a time trend, but it is not possible to observe it due to lack of data.

  - The slower observed growth rates of herring in the Bothnian Sea and Baltic Proper. Bioenergetics modelling demonstrated that slower growth rates strongly affect downward temporal trends of dioxin concentrations in herring and potentially counteract emission reduction measures.
  - A temporal shift in the Baltic herring diet in herring over the last few decades, which is interrelated to the slower growth rates. Stable isotope analysis indicates that the Baltic herring in the Bothnian Sea has gradually shifted to feeding at one trophic level higher than in the past. The bioenergetics modelling confirms that these shifts in diet could also counteract emission reductions by increasing bioaccumulation through the food web.
  - With the slow improvement of cod populations currently observed in the Baltic Sea, we can only speculate that processes that occurred when the cod population collapsed, for instance decreased predation of herring and sprat causing increased inter- and intra-specific competition for resources, will slowly reverse themselves in time. Such a reverse in ecological interactions could contribute to decreasing dioxin levels in herring, however, at the present time, not enough is known to give a conclusive answer.
- Seasonal variations in dioxin concentrations on a l.w. basis in Baltic herring, caused by seasonal changes in herring feeding ecology, were observed with a factor of approximately 3 times higher concentrations observed in winter months compared to summer months. The strong seasonal variation in herring concentrations has important implications for monitoring of POPs in herring populations.
- Spatial variation of dioxin concentrations was examined within the Bothnian Sea. Herring did not differ in congener pattern or absolute concentrations (l.w.) between coastal and offshore sampling sites, but $TEQ_{PCDD/F}$ (w.w.) did differ, with values in coastal herring being higher than offshore herring. The lack of clear spatial variation in herring concentrations is attributed to the migratory nature of herring populations within the Bothnian Sea. Herring only move into potentially contaminated coastal areas for spawning during a few weeks in the spring/summer each year. Because herring are pelagic offshore fish, they will be primarily impacted by dioxins delivered to the water column via atmospheric deposition.
- Stable isotope analysis of herring stomach contents was used to examine the origin of the diet of herring sampled at 4 coastal locations in the Bothnian Sea. A higher proportion of the diet at two of the four sites was comprised of coastal-sourced food indicating that the herring populations had been feeding close to the coast prior to sampling. A high proportion of coastal sourced food in the diet did not, however, result in herring sampled near the coast to have higher dioxin concentrations than herring sampled from the open sea.

12.3.2 Temporal and spatial trends in sediment cores and source tracing

- A clear decreasing time trend for both PCBs and PCDD/Fs was demonstrated in sediment cores in all areas of the Baltic Sea, although a slower decline is seen in offshore areas (Assefa *et al.* 2012). The decline in PCB and PCDD/F concentrations is consistent with reported reductions in emission in recent decades. For HCB, on the other hand, increasing concentration time trends were shown for all sampling sites, except for the Baltic Proper.
- The source tracing for PCDD/Fs showed that for the Baltic Sea as a whole, air emissions are, and have been, the most important external sources (Assefa *et al.* 2011).
- Direct emissions were also shown to be an important additional contributor to PCDD/F levels in sediment cores. Although little influence of the chlorine bleaching and its related industry was seen in the sediments, impact from typical land-based sources, such as chlorophenol use and kraft pulp emissions, were shown to be of importance in the northern sub-basins.

- The pollution composition of sediments is only showing slow fingerprint changes with time, indicating a slow system recovery from past pollution.
- The POPCYCLING-Baltic model predicted a decline in sediment levels of PCDD/F of a factor of 3 between 1986 and 2006 (on total TEQ basis), whereas sediment core data indicated a decline of a factor of 2 or less depending on location. The model therefore predicts that the abiotic environment in the Baltic will respond faster to emission reductions than is observed in reality. The plausible explanation for the discrepancy between model estimated declines in sediments and the sediment core time trends is the oversimplification of sedimentation/re-suspension/burial dynamics in the model.

12.3.3 Strong sorption and the effect on availability of dioxins

- Native dioxins and PCBs that enter Baltic Sea via aerosols are more strongly bound to aerosol organic carbon than would be predicted using models which estimate particulate organic carbon-water partitioning (e.g., Seth *et al.* 1999). Nevertheless, the measured aerosol-water partition coefficients indicate that the dioxins are less strongly bound than the same pollutants sorbed to organic matter in top layer sediments (Sobek *et al.* 2013) from a previous study (Cornelissen *et al.* 2008).
- Since atmospheric deposition is a significant pathway of especially PCDD/Fs to the Baltic Sea, the strong sorption of these pollutants to aerosols has implications for their availability and potential ecotoxicity.

12.3.4 Tracing the origin of dioxins in Baltic air

- Air masses from the SSE-E compass sector sampled at the Aspvreten monitoring station in Sweden during the winter season showed the highest concentrations of PCDD/Fs. PCBs showed an opposite pattern with higher concentrations during summer, and no distinction between compass sectors, while HCB showed the same seasonal pattern as PCDD/Fs, but similar to the PCBs, with no differences related to compass sectors.
- The PCDFs correlated highly with the total sum of PCDD/Fs (r>0.86). The PCDFs are also the most important contributors to the TEQ during the winter season, the season with highest air levels. This compound group should therefore receive special attention in the source tracing.
- It was hypothesised that metal concentrations in air could be used as indicators of source types also important for PCDD/F air emissions. Correlations were observed between PCDF concentrations and Cd, K, Pb, Sb and Zn concentrations in air sampled during the winter months. The metals K, Pb, Sb and Zn are associated with combustion of wood and other biofuels.
- The general PCDD/F congener pattern of Aspvreten air matched well with municipal solid waste incinerator (MSWI) and coal-fired power plant combustion patterns, in contrast to emission patterns from electric furnaces, aluminium smelters, unleaded gas-fuelled vehicles and diesel-fuelled vehicle (Lee *et al.* 2004, Lin *et al.* 2007).
- The higher PCDD/F concentrations during winter season and the mostly non-quantifiable concentrations during summer season indicate that primary emission sources of PCDD/Fs rather than temperature-driven re-volatilisation from soils (secondary emissions) control dioxin levels in air. The POPCYCLING-Baltic model simulations (see 12.2.3) also indicate that re-volatilisation from soils is a relatively minor source of PCDD/Fs to air (contributing with less than 10% of the estimated TEQ emissions in Sweden).
- Emission databases for the European region suggest that industrial emissions of dioxins peaked in the 1980s and that active abatement policies have now reduced emissions from industry by up to 90%. On the other hand, reduction of dioxin emissions from domestic sources has been much

lower and consequently domestic sources now account for more than one third of total dioxin emissions, a fraction that can be as high as 70% in some regions. The main domestic sources of dioxins have been estimated to be heating and cooking with solid fuels and burning of waste.

- An evaluation of current emission databases for dioxins concluded that they cannot currently provide reliable spatially-resolved emissions or be used to reliably estimate total TEQ emissions in a region. As atmospheric transport modelling tools rely very much on good quality spatially-resolved emission estimates, it is therefore not possible to accurately trace the origin of dioxins in Baltic air using these tools.
- The atmospheric transport model estimated that the origin of PCDD/Fs in Baltic air is mainly from continental Europe, with Eastern Europe making a strong contribution, which is consistent with air-mass back trajectories calculated from air monitoring data.
- An emission adjustment procedure was attempted with an atmospheric transport model to identify the source regions for which the emission estimates are most in error (Shatalov *et al.* 2012). The utility of the emission adjustment procedure was limited, however, by the lack of emission reports for several European regions and the lack of knowledge concerning the congener composition of the emissions. Total TEQ emissions were largely underestimated (by a factor of 2-10 in some regions), and the congener composition in emission databases did not match the congener pattern in air samples.

12.3.5 Suggested answers to the main questions posed in the project

In the proposal and introduction we set out to answer the following questions. Brief answers based on the research undertaken are given after each question.

i) Why are dioxin levels in fatty fish from the Baltic Sea so high? The slow growth of herring in some Baltic sub-basins combined with the long residence time of Baltic Sea water are considered the main reasons why Baltic herring have higher dioxin concentrations than in surrounding seas. It is possible that some herring populations could have been impacted by coastal sources resulting in high concentrations, but the migratory nature of herring (they spend limited time at the coast during spawning) and the lack of spatial variation in dioxin contamination between different herring populations in the Bothnian Sea makes this seem an unlikely explanation.

ii) What are the main sources of the dioxins in Baltic herring? Research undertaken in the BalticPOPs project confirms the conclusion of previous work (Wiberg *et al.* 2009) that the atmosphere is, and will continue to be, the major external source of dioxin pollution in the Baltic Sea and thus dioxin contamination in herring populations. Key evidence for the dominance of atmospheric sources includes:

  - Environmental fate modelling (Armitage *et al.* 2009, Wiberg *et al.* 2009);
  - Sediment source tracing modelling (Sundqvist *et al.* 2010, Assefa *et al.* 2011, and this study);
  - Measurements of dioxins in the Umeå River (Josefsson *et al.*, manuscript in preparation) and in air in the Baltic region (Sellström *et al.* 2009), indicating relatively low contribution of riverine inputs in comparison to atmospheric deposition;
  - The relatively low contribution of inputs from wastewater/industrial discharges (Andersson *et al.* 2012, Fridmanis *et al.* 2012, Laht and Volkov 2012);
  - The general lack of observed spatial differences in dioxin concentrations in herring between the coast and open sea within the Bothnian Sea (this study).

iii) What are the main sources of dioxins and other POPs in Baltic air? Air monitoring combined with receptor modelling was not able to pinpoint the sources responsible for dioxins and other POPs in Baltic air, but indicated a dominance of diffuse combustion sources. Emission databases for the European region suggest that domestic combustion sources now account for more than one third of total dioxin emissions and this fraction can be as high as 70% in some regions. The main domestic sources of dioxins have been estimated to be heating and cooking with solid fuels and burning of waste. The project did not address question *iii*) for other POPs due to limited resources.

iv) Are these sources (*ii* and *iii*) the result of on-going primary emissions or of recirculation of chemical stored in environmental reservoirs? Seasonal air concentrations of dioxins with peaks during winter months indicate that primary emission sources of dioxins rather than temperature-driven re-volatilisation from soils (secondary emissions) control dioxin levels in air. The POPCYCLING-Baltic model simulations also indicate that re-volatilisation from soils is a relatively minor source of dioxins to air.

v) Are these sources (*ii* and *iii*) mainly national or international? It is not possible to accurately pinpoint the geographical regions which are most likely to be responsible for dioxin emissions to air in Europe, but it is known, based on monitoring and modelling, that continental Europe and especially Eastern Europe makes the largest contribution to atmospheric deposition in most Baltic basins. Swedish sources make only a minor contribution to levels of dioxins in Baltic air.

vi) How has the pollution situation changed over time? Emissions of dioxins have declined in recent decades as a result of active abatement policies, and research undertaken in BalticPOPs has shown that this has resulted in long-term declines in concentrations in Baltic sediment and in some herring populations. Bioenergetics modelling undertaken in BalticPOPs has shown that slower growth rates of herring and changes in feeding ecology may be slowing downward temporal trends of dioxin concentrations in herring and potentially counteracting emission reduction measures.

vii) Assuming dioxin inputs to the Baltic Sea are reduced – how long will it take until the concentrations in herring decrease to levels safely below EU threshold values? More action is needed to reduce the emissions of dioxins to air and thus atmospheric deposition to the Baltic Sea, because levels of dioxins in herring remain above EU threshold values. It is uncertain if the observed long-term downward decreasing time trend in herring will continue because we are unable to predict the future of the key factors affecting these future trends. We are not able to predict if emissions will continue to decrease or will level off in the future. Furthermore, we are not able to predict how herring ecology (growth rates and feeding behaviour) will change in the future. Slowing growth rates and changing feeding ecology have previously been identified in this report as factors which can affect the levels and trends of dioxins in herring populations.

viii) Are there cost-effective measures that can reduce dioxin levels in Baltic herring below the regulatory thresholds within a relatively short time period? Based on the findings of this project, the main way to decrease herring concentrations is to reduce atmospheric deposition of dioxins to the Baltic Sea, even if the response in herring may be slow. Although active abatement policies have reduced dioxin emissions from industry by up to 90%, reduction of dioxin emissions from domestic sources has been much lower and consequently domestic combustion sources now dominate total estimated emissions in some regions. Policy actions have to address reducing these diffuse domestic combustion sources of dioxins to the atmosphere. It cannot be guaranteed that policy actions to reduce emissions will result in rapid reduction of dioxin levels in herring below EU threshold values. Although reductions in dioxin emissions will ultimately reduce levels of dioxins in Baltic seawater, observed changes in herring ecology (e.g., slowing growth rates and/or feeding ecology) in some herring populations could cause dioxin levels in herring to respond more slowly than seawater to emission reductions.

ix) Clean-up of dioxin-contaminated sediments in coastal regions of the Baltic will have important local benefits such as improvement of water quality and lowering of contamination levels in species which reside mainly in the contaminated regions. These clean-up actions are not likely to have much impact on the levels of PCDD/Fs in migratory fish (e.g., herring) which spend most of their time in the open sea and only move into coastal regions to spawn during a few weeks in the spring/summer.

12.4 Recommended action by regulatory authorities and further research

- To reduce atmospheric deposition and thus levels in herring, it would be necessary to introduce a pan-European reduction in dioxin emissions by wide-scale introduction of best available techniques for pollution control. European industry has already been effective in reducing point source dioxin emissions. There is, however, an indication from this study that reductions of dioxin emissions in Eastern Europe may have been less effective and that further work may be required in this area.
- Although it is challenging to pinpoint the most important dioxin source categories contributing to the dioxin pollution in the Baltic Sea, there is evidence that non-industrial combustion sources are important relative to the legacy industrial sources. An earlier study (BiPRO 2009) suggested that heating, cooking and waste disposal are becoming relatively more important dioxin sources in Europe as a whole. The previous study states that, in order to further reduce dioxin emissions from combustion sources, action is needed which include:
    - continued efforts to reduce illegal waste burning (domestic and back-yard) with the aid of education campaigns to inform on the ban as well as strengthened control
    - a ban on domestic heating using solid fuels
    - improvements in industrial and household energy efficiency to reduce emissions from power generation
    - improvements of insulation and temperature regulation in households
    - replacement of old heating appliances with new equipment that is more efficient and/or use greener technologies (e.g., solar and geothermal); and
    - promotion of centralised district heating schemes which are especially effective in urban areas and can also utilise green technologies.
- Increasing shipping activities are expected to contribute significantly to air and sea pollution in the Baltic Sea region (Cooper 2004). These emissions are currently not well-quantified for dioxins, and thus their importance cannot be properly compared to other emission sources. In the BalticPOPs modelling work we made rough estimates of dioxin emissions from ships which could have potentially affected the conclusions. It is recommended that *i*) emissions of POPs from ships

are quantified through monitoring activities and *ii*) if possible, shipping emission are reduced by fitting ships with pollution control equipment.

- A general reduction in combustion sources would, as well as reducing dioxin emissions, have the co-benefit of reducing emissions of other pollutants such as PAHs, black carbon, metals and even carbon dioxide, the most well-known greenhouse gas. Other policies such as those related to climate change and clean air thus contribute to the reduction of dioxin emissions. A key consideration for regulators is if they can fully rely on existing legislation to take care of the dioxin problem in the Baltic Sea. A more responsible course of action, in our opinion, is to continue to support research that aims to pinpoint the specific sources of dioxins to air. Such research would support the introduction of more targeted and effective policy for reduction of dioxin emissions.
- Any additional emission reduction strategy should be closely monitored to determine its effectiveness. We recommend, for example, extending and improving monitoring programmes that provide data on long-term temporal trends in PCDD/F levels in air, atmospheric deposition and biota. It would also be advisable to co-monitor other pollutants which could be markers of dioxin sources (e.g., metals and black carbon).
- Education campaigns on the potential adverse effects of dioxins on human health and the environment is vital for public acceptance of measures that reduce dioxin emissions. These education campaigns could also emphasise the co-benefits of reducing diffuse combustion sources (as mentioned above).
- Any monitoring programme should implement state-of-the-art methods for the sampling and analysis of POPs, and the same methods should be used at each monitoring station to ensure consistency. There is evidence to suggest that the two existing methods currently used in Sweden for sampling atmospheric deposition do not provide comparable measurements for particle-sorbed pollutants. The PUF plugs used as adsorbents in the standard deposition POP sampler in Sweden are not efficient for collecting very hydrophobic (particle-sorbed) pollutants such as dioxins. Two other samplers have been tested based on other POP adsorbent principles (Bergknut *et al.* 2011). Both types sampled dioxins with significantly higher efficiency than the standard sampler (Wiberg *et al.* unpublished), although they also showed some discrepancies between each other (Bergknut *et al.* 2011).
- Pinpointing the important contributing dioxin point sources in the European region is a challenging exercise. It has been demonstrated here that existing emission databases are deficient. It is therefore recommended to support efforts to improve international reporting of emissions for POPs. Information exchange, coordination and harmonisation of emission data in estimating national dioxin emissions are necessary to obtain more reliable and comparable inventories.
- A promising approach to identifying important contributing emission sources is to use cost-effective spatial air-monitoring strategies such as long-term spatial passive air sampling campaigns to simultaneously monitor POPs together with other useful markers of different types of combustion sources. There have been large advances in the passive air sampling technology in recent years, as well as in the establishment of large spatial monitoring programmes in Europe and globally.
- We recommend the following research, using various monitoring and modelling approaches for understanding source and fate of dioxins:
    - An approach for estimating emissions of POPs from large urban areas has recently been developed (e.g., Gasic *et al.* 2010, Gasic *et al.* 2009, Moeckel *et al.* 2010). The approach uses a combination of atmospheric modelling and urban air monitoring to back-calculate emissions for urban areas.

  - Current modelling tools (e.g., the POPCYCLING-Baltic model) for estimating the fate of POPs in the Baltic region are over-simplified in their description of, for example, atmospheric transport and sediment dynamics. New, more advanced, modelling tools with improved descriptions of the physical environment are required to support decision making processes.
  - The atmospheric modelling tool used in this project (MSCE-POP model) is useful for identifying sources of dioxins and other POPs in air. However, improved pollutant emission and monitoring data are needed for further model evaluation. Multiple measurement sites with a more homogenous distribution than were available in the current study (only Scandinavian sites: Aspvreten, Pallas and Vindeln) within the region are desired for a better evaluation of model results. The aforementioned passive sampling networks would provide a cost-effective approach for model evaluation in the future.
- An additional way to decrease herring dioxin concentrations, suggested by Peltonen *et al.* (2007), is to reduce the number of herring individuals through fishing so that feeding conditions for the remaining herring are improved. This is a complex ecological issue, and the biological implications and potential success of such a management alternative was not addressed in BalticPOPs. Hence, if considered, it would need to be further investigated in collaboration with fish ecology researchers.

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Final report from the research project BalticPOPs

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Baltic herring and other oil-rich fish contain levels of dioxins that exceed the limit set by the EU for sale of fish for consumption. The levels vary along the Baltic Sea coast. What are the causes of high levels of dioxins in oil-rich fish in the Baltic Sea? What are the emission sources of dioxins and other organic environmental toxins that reach the Baltic Sea? These two questions have been examined by the BalticPOPs research project, financed by the Swedish Environmental Protection Agency.

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