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

Results and policy brief from the research project BalticPOPs
Managing the dioxin problem in the Baltic region with focus on sources to air and fish

Karin Wiberg,
Department of Aquatic Sciences and Assessment, Swedish University of Agricultural Sciences (SLU)

Anteneh T. Assefa, Kristina L. Sundqvist,
Department of Chemistry, Umeå University

Ian T. Cousins, Jana Johansson, Michael S. McLachlan, Anna Sobek, Gerard Cornelissen,
Department of Applied Environmental Science (ITM), Stockholm University

Aroha Miller, Jenny Hedman, Anders Bignert,
Swedish Museum of Natural History

Heikki Peltonen,
Finnish Environment Institute (SYKE)

Mikko Kiljunen,
Department of Biological and Environmental Science, University of Jyväskylä

Victor Shatalov,
Meteorological Synthesizing Centre-East (MSC-East), EMEP

Ingemar Cato,
Geological Survey of Sweden and Department of Earth Sciences, University of Gothenburg

SWEDISH ENVIRONMENTAL PROTECTION AGENCY
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.

This publication gives a summary of the results of the project and suggests policy measures. A full report of the research results is published separately (Wiberg K. et al. (2013). Managing the dioxin problem in the Baltic region with focus on sources to air and fish, Swedish Environmental Protection Agency Report 6566, ISBN 978-91-620-6566-9).

The research project was 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.

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

The Swedish Environmental Protection Agency, May 2013
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Main conclusions</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>Introduction</td>
<td>7</td>
</tr>
<tr>
<td>3</td>
<td>Temporal and spatial trends of dioxins and dl-PCBs in herring from the Bothnian Sea</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>Temporal and spatial trends of dioxins and PCBs in sediment cores and source tracing</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>Sorption of dioxins and PCBs to aerosols in Baltic air</td>
<td>15</td>
</tr>
<tr>
<td>6</td>
<td>Tracing the origin of dioxins in Baltic air</td>
<td>16</td>
</tr>
<tr>
<td>7</td>
<td>Recommended action for regulatory authorities and further research</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>References</td>
<td>23</td>
</tr>
</tbody>
</table>
1 Main conclusions

- Research undertaken in the BalticPOPs project confirms the conclusion of previous work that the atmosphere is the major external source of polychlorinated dibenzo-\(p\)-dioxin (PCDD) and polychlorinated dibenzofuran (PCDF; collectively termed “dioxins” or PCDD/Fs) pollution in the Baltic Sea. 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 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 spatial differences in dioxin concentrations in herring between the coast and open sea within the Bothnian Sea (observed in this study).

- Emissions of dioxins have declined in recent decades as a result of regulation. This has resulted in declines in concentrations in Baltic sediments but only in some of the herring populations studied in the Baltic in recent years. Temporal changes in herring ecology (e.g., slower growth rates of herring/decreased lipid content in some herring populations caused by for instance changes in feeding ecology) may halt downward temporal trends of concentrations of dioxins and dioxin-like polychlorinated biphenyls (dl-PCBs) in some herring populations.

- It is uncertain if the slow downward time trend of dioxins in herring will continue because it is difficult to predict future time trends of emissions or future changes in herring ecology. It is probable, however, that the best way to decrease dioxin concentrations in herring is to reduce the atmospheric deposition of dioxins to the Baltic Sea. More action is needed to reduce emissions to air in Europe and thus atmospheric deposition to the Baltic Sea. If action is not taken, levels of dioxins in herring will remain close to and occasionally above EU threshold values.

- Clean-up of dioxin-contaminated sediments in coastal regions of the Baltic will have important local benefits such as lowering contamination levels in species which reside mainly in contaminated regions. These local 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 to coastal regions to spawn during a few weeks in the spring/summer.

- Dioxin emissions are still poorly quantified. Atmospheric modelling demonstrated that current European emission inventories underestimate dioxin emis-
sions by at least a factor of 2-10 for selected PCDD/F congeners. The uncer-
tainty in source inventories means that it is not currently possible to use these
emission estimates in models to determine which source categories are the
dominating sources of dioxin in atmospheric deposition to the Baltic.

- Although it is not possible to accurately pinpoint source categories using
  models due to poor emission inventories from some regions, it is probable,
  based on monitoring and modelling, that Eastern Europe makes the largest
  contribution to dioxins in atmospheric deposition in most Baltic Sea basins.

- PCDFs dominate the current total concentrations of PCDD/Fs in winter air,
  the season with the highest atmospheric levels of PCDD/Fs. Higher winter
  concentrations indicate that non-industrial combustion sources are dominant,
  presuming that industrial production is not seasonal.

- An attempt was made to identify important source types for dioxins by using
  metals as source markers for co-emission with dioxins. However, it was not
  possible to from this work draw firm conclusions about the dominant source
types contributing to dioxin levels in atmospheric deposition.
2 Introduction

The BalticPOPs project was commissioned by the Swedish Environmental Protection Agency (Swedish EPA) to investigate i) spatial and temporal trends of persistent organic pollutants (POPs) in Baltic biota (especially fatty fish such as herring), and ii) to trace the sources of these pollutants in the atmosphere. BalticPOPs was focused on PCDD/Fs, which are of particular concern in the Baltic region.

Dioxins are widely encountered toxic organic substances, which are resistant to degradation and tend to accumulate in wildlife as well as humans. Even very low dioxin concentrations can cause negative effects on the environment and on human health. Human health effects include impairment of the immune system, the nervous system, the hormonal system and reproductive functions. Dioxins are also carcinogenic. The toxic equivalence (TEQ) levels of dioxins in Baltic fatty fish still occasionally exceed the European Union (EU) limits for food and feed. For this reason, restrictions on the sale of herring to other EU countries and restrictions on sale within domestic markets apply for some regions within the Baltic Sea for both Sweden and Finland (SFS 2011:1494; LIVSFS 2011:19). The persistence of dioxins combined with their semi-volatility mean that they are transported over long distances in the atmosphere. Previous research pointed towards the dominance of the atmosphere as an important external dioxin source to the Baltic Sea (Armitage et al. 2009, Sundqvist 2009, Sundqvist et al. 2010, Verta et al. 2007, Wiberg et al. 2009), and dioxins in the atmosphere above the Baltic Sea have been shown to originate from continental Europe (Sellström et al. 2009, Wiberg et al. 2009).

The BalticPOPs project builds on the results of previous research in Wiberg et al. (2009). An important aim is to use the findings of this research to develop recommendations for the Swedish EPA on emission reduction strategies for dioxins, which should lead to reductions in dioxin levels in Baltic fatty fish such as herring. A multidisciplinary approach was implemented in BalticPOPs, and the project consortium therefore included experts from many different research fields. The main findings of the research are summarised in the following sections. Additional details of the research conducted are included in the full BalticPOPs report (Wiberg et al., 2013).
3 Temporal and spatial trends of dioxins and dl-PCBs in herring from the Bothnian Sea

Recent reports investigating temporal trends of dioxins in Baltic herring (*Clupea harengus*) have shown that dioxin levels have not been declining as would be expected from the observed environmental dioxin decreases in recent years (Bignert *et al.* 2011). In BalticPOPs, we further examined long-term trends in dioxins and dl-PCBs in Baltic herring, and investigated various factors that could explain the observed time trends. Long-term interannual *temporal trends* for PCDD/Fs and dl-PCBs in Baltic herring were monitored for different time periods at three coastal sites in the Baltic Sea: Harufjärden (1990-2009), Ångskärsklubb (1979-2009), Utlängan (1988-2009); and one in the Kattegat Sea: Fladen (1990-2009). The main findings were as follows:

- At Ångskärsklubb and Fladen, all six dominant PCDD/F and dl-PCB congeners showed statistically significant decreases in concentrations on a lipid weight (l.w.) basis (Figure 1). Significant decreases were also observed for TEQ$_{PCDD}$, TEQ$_{PCDF}$ and TEQ$_{dl-PCB}$. These trends were also observed on a wet weight (w.w.) basis at Ångskärsklubb. However, no significant decreasing trends were observed at Fladen on a w.w. basis.
- At Harufjärden, significant decreases were only observed for 2,3,7,8-TCDD (l.w. basis) and TEQ$_{PCDD}$ (l.w. and w.w. basis). No significant trends were observed for all other dominant congeners and TEQ values (TEQ$_{PCDD}$, TEQ$_{PCB}$ and TEQ$_{PCDD/F+dl-PCB}$) on a l.w. or w.w. basis.
- At Utlängan, the two dominant PCDD congeners (2,3,7,8-TCDD and 1,2,3,7,8-PeCDD) showed significant decreases in concentrations over time. Significant decreases in concentrations on a l.w. basis were observed for TEQ$_{PCDD}$, TEQ$_{PCB}$ and TEQ$_{PCDD/F+dl-PCB}$, but not TEQ$_{PCDF}$. On a wet weight basis, all TEQ values showed significant decreases at this site.
- At all sites, TEQ$_{PCDD}$ showed a significant decrease (l.w.), whereas TEQ$_{PCDF}$ only displayed significant decreases at Ångskärsklubb and Fladen, which suggests a temporal shift in the composition of PCDD/F sources.
- The strong statistical decreases in dioxins, dl-PCBs and TEQ values (l.w.) in herring at Ångskärsklubb and Fladen demonstrate that reductions in emissions in recent decades (see sections 4 and 6) have potentially been a key factor driving these significant declines, although other factors are probably also involved.
The lack of a statistically significant decrease at some sites could be attributed to several factors:

- A lack of 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 that have not declined, but this is not a convincing explanation given the lack of clear spatial variation in dioxin contamination between different herring populations (see below), and the substantial decrease of dioxin and PCB concentrations in a number of coastal sediment cores observed within another recent Swedish EPA research project (Sobek et al., 2012, Assefa et al., 2012).

- A shorter and less data rich time series which reduces statistical power. In other words, there may be a time trend, but it is not possible to see a statistically significant trend due to lack of data.

- The observed slower growth rates of herring in the Bothnian Sea and Baltic Proper. Bioenergetics modelling conducted in BalticPOPs demonstrated that slower growth rates strongly affect downward temporal trends of dioxin concentrations in herring, potentially counteracting emission reduction measures.

- There are indications from stable isotope analysis (SIA) that a shift in herring diet in the Bothnian Sea may have occurred over the last few years.

The regression equation is given by

\[ y = 3E+54e^{-0.061x} \]

with \( r^2 = 0.6912, p < 0.01 \)
decades, with herring in the Bothnian Sea gradually shifting their feeding almost a single trophic level upwards. However, the SIA lacks baseline data and is therefore not considered conclusive. This shift occurred at roughly the same time as the collapse of the cod fishery, the release in predation from cod, and increased inter-specific competition for food resources with sprat. A change in diet can be connected to slower growth rates and increased inter-specific competition for food resources. The bioenergetics modelling confirms that slower growth rates could counteract emission reductions by increasing bioaccumulation.

**Seasonal variations** in dioxin concentrations could be important in regards to timing of herring sampling for dioxin monitoring used for setting environmental target levels and safe food consumption guidelines. In the BalticPOPs project, we investigated whether annual variations in dioxin concentrations in Baltic herring are i) due to seasonal shifts in dioxin concentrations, and ii) if so, are they related to biological parameters. The findings were as follows:

- Seasonal variations in the dioxin concentration on a l.w. basis could be observed in Baltic herring (Figure 2). As the lipid content increases, the dioxin concentration decreases. The decrease is probably not caused by elimination of dioxins, but rather by a dilution of dioxin concentrations on a l.w. basis when the lipid content of the herring increases. The lipid content of herring changes over the year due to spring/summer spawning and seasonal dietary changes (Figure 2). On a wet weight basis, seasonal changes in dioxins were not as apparent.

![Figure 2. TEQPCDD/F (pg g⁻¹ l.w.) and lipid content (%) for the southern Bothnian Sea site with over the 12 months data was collected. Numbers on the x axis correspond to month (1 = January, 2 = February, etc.).](image_url)
Spatial variations in dioxin concentrations in Baltic herring have been observed (Bignert et al. 2011, Bignert et al. 2007, Karl and Ruoff 2007). Concentrations from herring in the Bothnian Sea and Bothnian Bay are often elevated (Bignert et al. 2011, Isosaari et al. 2006), and it has been noted that herring from the Swedish west coast are less contaminated compared to herring from within the Baltic Sea area (Karl and Ruoff 2007). However, although inter-basin variation has been studied previously, little was known about intra-basin variation of dioxin concentrations in biota prior to BalticPOPs. We therefore examined the spatial variation of dioxin concentrations in herring, mysids, zooplankton, sediment and water, and also conducted stable isotope analyses on herring, mysids and zooplankton, from four coastal sites within the Bothnian Sea. In addition, we examined dioxin concentrations of herring caught from four offshore sites. This was done to investigate whether herring diet, biological variables or sediment/water concentrations can explain spatial variations in dioxin concentrations in herring. The findings were as follows:

- Congener patterns did not differ between herring caught from coastal and offshore sites (Figure 3). Among the TEQ values, only $\text{TEQ}_{\text{PCDD/F}}$ (w.w. basis) differed between coastal and offshore herring, being higher in coastal herring. No other TEQ values showed any difference on either l.w. or w.w. basis. This general lack of spatial variation in herring concentrations is attributable 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 primarily be impacted by dioxins delivered to the water column via atmospheric deposition.

- Stable isotope analysis of herring was used to examine the origin of herring diet from the four coastal locations sampled in the Bothnian Sea. Herring diet at two of the four sites consisted primarily of coastally sourced food, while herring from the other two sites consisted mainly of offshore food sources). A significant difference was seen for $\text{TEQ}_{\text{dl-PCB}}$ on a l.w. basis and for all TEQ values on a w.w. basis, with herring from the two sites with more coastally sourced food in the diet generally having significantly higher values compared to herring from the other two sites.
Figure 3. PCDD concentrations (pg g⁻¹ l.w.) and congener composition for a) coastal and b) offshore herring (see Wiberg et al. (2013) for information on sampling locations).
4 Temporal and spatial trends of dioxins and PCBs in sediment cores and source tracing

Sediment time trends can be used as an indicator of dioxin trends in the overlying water, although it should be noted that a time lag effect may occur due to particle transport from erosion areas to accumulation bottoms. In the BalticPOPs project, the aim was to determine how dioxin sources have changed over time and if emission reductions of these known sources are reflected in declines in the sediment cores. Cores were sampled at five offshore sites of the Baltic Sea in order to probe geographical and temporal variations. In addition, seven coastal sediment cores were provided from a project managed by the Administrative County Board of Gävleborg, and data from two coastal cores were provided by the Administrative County Board of Uppsala. Dioxin levels were determined in all cores, while for the offshore cores PCB and hexachlorobenzene (HCB) levels were also measured. The findings were as follows:

- A clear decreasing time trend for both PCBs and dioxins was demonstrated in sediment cores in all areas of the Baltic Sea (example in Figure 4). For the dioxins, which were determined in both coastal and offshore cores, the decline was slower in offshore areas. The decline in PCB and dioxin concentrations is consistent with reported emission reductions in recent decades. In contrast, increasing time trends for the concentration of HCB could be seen for all sampling sites, except for the Baltic Proper.
- The source tracing for dioxins showed that for the Baltic Sea as a whole, air emissions are, and have been, the most important external sources.
- Direct emissions were also important additional contributors to dioxin levels in sediment cores, particularly at coastal sites but also in offshore areas. Although little influence of the chlorine bleaching and its related industry was seen in the sediments at the offshore sites, impact from typical land-based sources, such as chlorophenol use and kraft pulp emissions, was of importance particularly in the northern sub-basins.
- The pollution composition of sediments is showing only slow fingerprint changes with time (Figure 4), indicating a slow system recovery from past pollution.
- Previous modelling (Armitage et al. 2009, Wiberg et al. 2009) predicted a decline of a factor of 3 in surface sediment levels of dioxins between 1986 and 2006 (on a total TEQ basis), whereas sediment core data from BalticPOPs 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 most plausible explanation for the discrepancy between model-estimated declines in sediments and the sediment core time trends is the
oversimplification of sedimentation/resuspension/burial dynamics in the model.

Figure 4. Concentrations of TEQ$_{PCDD/F}$ (pg g$^{-1}$ d.w.) in sediment cores from an offshore site in the Bothnian Sea (left) and the relative contribution to TEQ from different PCDD/F congeners (right; each coloured bar represents an individual congener, see Wiberg et al. (2013) information on individual congeners).
5 Sorption of dioxins and PCBs to aerosols in Baltic air

Atmospheric deposition of particles is believed to be the major input pathway for dioxins to the Baltic Sea. The strength of sorption to aerosols of these compounds and thus their availability for uptake by biota after they are deposited to the water is unknown. In BalticPOPs, we investigated the “availability” of dioxins and PCBs sorbed to aerosols by determining aerosol-water distribution ratios for aerosols collected in Stockholm, close to the Baltic Sea. It is commonly thought that only the freely dissolved concentration is available for biological uptake, while sorbed chemicals are unavailable. Aerosol-water distribution ratios measured in BalticPOPs were compared to sediment-pore water distribution ratios previously measured 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). The findings were as follows:

- 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.
6 Tracing the origin of dioxins in Baltic air

Although atmospheric deposition is believed to be the main input pathway for dioxins to the Baltic Sea, the geographical origins of the dioxins in Baltic air are not well known. In BalticPOPs, several approaches were taken in an attempt to trace the origin of the dioxins in Baltic air.

In a previous study (Sellström et al. 2009), monitoring of dioxins in Baltic air (Aspvreten) revealed that winter air originating from central and eastern directions contains the highest levels of dioxins. In this work, we attempted to use metal concentrations in air as a guide to which source types are important for dioxin air emissions. The air monitoring study of Sellström et al. (2009) was repeated, but extended to also include metals, HCB and PCBs. The aim was to investigate trends for dioxins, PCBs and HCB, and to identify important source types for dioxins by using metals as source markers for co-emission with dioxins. The findings of this work were as follows:

- For the summer season, there were no significant differences in TEQ levels among air from different compass sectors sampled at Aspvreten. 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 5), in line with the earlier study by Sellström et al. (2009). PCBs showed an opposing pattern to PCDD/Fs 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 high PCDD/F levels during the winter season indicate a dominance of non-industrial combustion sources, presuming that there is no seasonal trend in industrial production.

- 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 patterns in flue gases from municipal solid waste incinerators (MSWI) and coal-fired power plants, rather than with emission patterns from electric furnaces, aluminium smelters, and unleaded gas-fuelled and diesel-fuelled vehicles (Lee et al. 2004, Lin et al. 2007).
• Although there are several indications that combustion is responsible for the high PCDD/F levels in Aspvreten winter air, our PCDD/F and metal data could not be used to pinpoint one combustion source category as more important than others.

• Emission databases for the European region suggest that industrial emissions of dioxins peaked in the 1980s, and active abatement policies have now reduced emissions from industry by up to 90% (BiPRO 2009). On the other hand, the reduction of dioxin emissions from domestic sources in Europe has been much lower. 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 in Europe have been estimated to be heating and cooking with solid fuels and burning of waste (BiPRO 2009). The dioxin emissions reported to the European Monitoring and Evaluation Programme (EMEP 2012) indicate, however, large regional variations in the source sectors contributing to national emissions of dioxins. It is uncertain how much of the variability is true variability in emissions and how much is due to the different methods used to estimate emissions at a national level.

• The winter season increase and mostly non-quantifiable concentrations of PCCD/Fs during the summer season together indicate that primary emission sources of PCDD/Fs rather than temperature-driven re-volatilization from soils (“secondary sources”) control dioxin levels in air. The POPCYCLING-Baltic model simulations also indicate that re-volatilization from soils is a relatively minor source of dioxins to air (contributing less than 10% to the estimated TEQ emissions in Sweden).

Figure 5. 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.
In BalticPOPs, we also attempted to trace the origin of dioxins in Baltic air and deposition using a spatially and temporally resolved atmospheric model. We further investigated whether current emission estimates can explain Baltic air levels and deposition fluxes of four selected 2,3,7,8-substituted PCDD/F congeners, using an atmospheric modelling approach. The EMEP database of emissions for dioxins was used to provide inputs to the selected model (MSCE-POP model), and model-predicted levels were compared with measurements of dioxins in air and deposition at three monitoring stations in Sweden. If model predictions and measurements were in good agreement, we could be confident in the model’s ability to determine the approximate source regions contributing to dioxins in Baltic air, deposition and thus Baltic Sea levels.

A secondary objective of this work 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. Additional model simulations were undertaken in which emissions were enlarged in some selected areas to try to optimize agreement between model predictions and measurements. A more complete description of the work is available in a separate publication (Shatalov et al., 2012). The findings of this work were as follows:

- Using the default emissions from the EMEP database, the model underestimated air concentrations with a factor of 5 - 30, with the level of agreement depending on congener, monitoring station, and the compass sector from which the contaminated air mass had arrived. This indicates the approximate magnitude of error in the European emission estimates, which is valuable information.
- The emission adjustment demonstrated that adjusting congener composition and doubling emissions in two source regions improved the agreement between model predictions and measurements for air masses originating from almost all compass sectors. However, the agreement was still relatively poor when air masses originated from the south-southeast and south-southwest. Increasing the emissions with a factor of 10 in several source regions did not further improve the agreement between model predictions and measurements.
- This work demonstrates that there is currently a poor quantitative understanding of dioxin emissions contributing to the pollution in the Baltic region. Furthermore, there is a lack of dioxin monitoring data, particularly for the congener composition of PCDD/Fs in atmosphere and precipitation. Both these factors hamper accurate tracing of emissions using modelling tools.
- 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. However, the use of the modelling tool for dioxins is limited by the poor quality of emission databases.
The atmospheric transport model estimated that the dioxins in Baltic air mainly originate from continental Europe, with the eastern parts of Europe making a strong contribution, which is consistent with air mass back trajectories calculated from air monitoring data (Figure 6). It can also be noted that the contributions from different source regions differ between Baltic sub-basins (Figure 6).

Figure 6. Model-estimated contributions of various source groups to the deposition of 2,3,4,7,8-PeCDF to the Baltic Proper and Gulf of Finland, calculated using the default emissions from the EMEP emission database. (DK – Denmark, EE – Estonia, FI – Finland, 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, Rest – all other sources).
7  Recommended action for regulatory authorities and further research

To reduce the atmospheric deposition of dioxins, and thus levels in herring, it will be necessary to introduce a pan-European reduction in dioxin emissions by wide-scale introduction of best available techniques for pollution control. There is some indication from this work that emission reductions targeted at the eastern parts of Europe would make a particularly large contribution to reducing atmospheric deposition of dioxins to the Baltic Sea.

Although it is challenging to pinpoint the most important source categories contributing to the dioxin pollution in the Baltic Sea, there is evidence that non-industrial combustion sources are important relative to the industrial sources. An earlier study suggested that heating, cooking and waste disposal are becoming relatively more important dioxin sources in Europe as a whole (BiPRO 2009). This study stated, 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 backyard) 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 fuels (e.g., biofuels) or 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 fuel/technologies.
- Increasing shipping activities are expected to contribute significantly to air and sea pollution in the Baltic Sea region (Cooper 2004). These emissions are not well-quantified for PCDD/Fs, and thus their importance cannot be properly compared to other emission sources. We made rough estimates of dioxin emissions from ships in the BalticPOPs modelling work which could have potentially affected the conclusions. It is recommended therefore that i) emissions of POPs from ships are quantified through monitoring activities and ii) if possible, shipping emissions 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, 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. 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 dioxin 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 to inform about the potential adverse effects of dioxins on human health and the environment is vital for public acceptance and application of measures that reduce dioxin emissions.

- Any monitoring program 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 different sampling methods for atmospheric deposition of dioxins used in Sweden do not provide comparable measurements for particle-sorbed pollutants.

- 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 e.g., Peltonen et al. (2007), could be by fishery management with the aim to improve the growth rate of herring. The idea is to reduce the number of herring individuals so that feeding conditions for the remaining individuals 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.
8 References


Cooper D. 2004. HCB, PCB, PCDD and PCDF emissions from ships. IVL (Swedish Environmental Research Institute), Report B1620.


Gasic B, MacLeod M, Klanova J, Scheringer M, Ilic P, et al. 2010. Quantification of sources of PCBs to the atmosphere in urban areas: A comparison...
of cities in North America, Western Europe and former Yugoslavia. *Environmental Pollution* 158:3230-3235.


**Hopke P.** Personal communication. Department of Chemical and Biomolecular Engineering and Center for Air Resources Engineering and Science, Clarkson University.


**Josefsson S, Bergknut M, Wiberg K.** Manuscript in preparation. Influence of landscape type, stream order and hydrological conditions on terrestrial export of POPs.


**Livsmedelsverket 2011.** Livsmedelsverkets föreskrifter om utförsel och export av vissa vildfångade fiskarter från Östersjöområdet. LIVSFS 2011:19.


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

Results and policy brief from the research project BalticPOPs

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.

KARIN WIBERG, ANTENEH T. ASSEFA, KRISTINA L. SUNDOQVIST, IAN T. COUSINS, JANA JOHANSSON, MICHAEL S. MCLACHLAN, ANNA SOBEK, GERARD CORNELISSEN, AROHA MILLER, JENNY HEDMAN, ANDERS BIGNERT, HEIKKI PELTONEN, MIKKO KILJUJEN, VICTOR SHATALOV OCH INGMAR CATO