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Sources of dioxins in Baltic Sea herring

A modelling study for identification of dioxin sources and quantification of their temporal and spatial impacts

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Summary

This study presents a step-by-step statistical analysis for tracing dioxins sources that have contributed to levels in Baltic herring during the last decades. The study is based on the concentrations of the 17 toxic (2,3,7,8-substituted) dioxin congeners in herring and sediment from the Baltic Sea, and it evaluates how the impacts of the sources may have changed during the studied periods, i.e. 1990–2009 in the Bothnian Bay, 1979–2009 in the Bothnian Sea and 1988–2009 in the Baltic Proper. The modelling technique used (PMF) extracted three dioxin patterns in herring that could be used to obtain source patterns after applying transformation factors. The transformed patterns were compared to real dioxin source patterns available through previous measurement and modelling studies. The identified sources included tetrachlorophenol (TCP), pentachlorophenol/atmospheric background (PCP/AB) and emissions from thermal activities.

The results indicate that the thermal source type has been the major contributor of dioxins to Baltic herring during the pre- and post-2000 periods (72% and 59%, respectively). Its impact appears, however, to have declined by 19% in the Bothnian Bay, by 67% in the Bothnian Sea, and by 48% in the Baltic Proper (TEQ-basis). On the other hand, the relative importance of TCP and PCP/AB appear to have increased over time, from 1.4% and 1.5% to 19% and 6.6% in the Bothnian Bay, from 3.3% and 7.2% to 12% and 10% in the Bothnian Sea, and from 8.9% and <1% to 33% and 13% in the Baltic Proper. Comparisons using absolute values (pg TEQ g^{-1} lipid weight) indicate an increase of the TCP source by five times in the Bothnian Bay from the pre-2000 to the post-2000 period, a slight increase in the Bothnian Sea, and more than a doubling of the levels in the Baltic Proper. The agreement between the trends in the three sub-basins is a good indication for an increased impact of the TCP source during recent years (post-2000). Corresponding analysis for the PCP/AB source type, indicate slightly decreased TEQ levels from the PCP/AB source type in the Bothnian Sea (by ~50%), more than twice as high in the Bothnian Bay, and more than triplicated in the Baltic Proper. While the declining trends of the thermal source type encourages continuing management efforts for air emissions, the apparent increase of TCP and PCP/AB call for more attention to such sources in the Baltic Sea. As the use of technical products containing TCP and PCP have been banned/restricted since the 1970s and 1980s, more focus on contaminated sites may be required in the mitigation actions of such sources.

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Summary

This report presents a modelling study aiming at identification and quantification of sources of dioxins that contaminate herring in the Baltic Sea. Positive Matrix Factorization, a multivariate data analysis technique, was used to extract model patterns of dioxins in Baltic herring sampled 1990–2009 in the Bothnian Bay, 1979–2009 in the Bothnian Sea and 1988–2009 in the Baltic Proper. The three extracted patterns were converted to sediment patterns using transformation factors (TFs) for comparison with previously established dioxin source patterns as they would appear in sediments and other abiotic matrices. The TFs were used to compensate for pattern changes due to bioavailability and transformation processes of the dioxins from the abiotic environment to fish. The main sources could then be suggested by matching the three transformed patterns to known dioxin source patterns. These matched sources include tetrachlorophenol (TCP), pentachlorophenol/atmospheric background (PCP/AB) and thermal sources.

The results indicate that emissions from thermal activities have been the major source of dioxins to Baltic herring during both pre- and post-2000 periods. Thermal sources contribute 59% of the total dioxin concentrations (17 ± 3.2 pg TEQ g^{-1} lipid weight (lw)) in the Bothnian Bay, 67% (18 ± 5.6 pg TEQ g^{-1} lw) in the Bothnian Sea and 51% (12 ± 3.1 pg TEQ g^{-1} lw) in the Baltic Proper during the post-2000 period. This is a decrease compared to the pre-2000 period with 19%, 67%, and 48% lower values in the Bothnian Bay, the Bothnian Sea and the Baltic Proper, respectively. The results also indicate that the relative impact of TCP and PCP/AB has increased during the post-2000 compared to the pre-2000 period and now constitute 19% and 6.6% of the total dioxin concentrations in the Bothnian Bay, 12% and 10% in the Bothnian Sea, and 33% and 13% in the Baltic Proper. Comparisons using absolute values (pg TEQ g-1 lipid weight) indicate an increase of the TCP source by five times in the Bothnian Bay from the pre-2000 to the post-2000 period, a slight increase in Bothnian Sea, and more than a doubling in the Baltic Proper. The agreement between the trends in the three sub-basins is a good indication for an increased impact of the TCP source during recent years (post-2000). Corresponding analysis for the PCP/AB source type indicate slightly decreased TEQ levels from the PCP/AB source type in the Bothnian Sea (by ~50%), more than twice as high in the Bothnian Bay, and more than triplicated in the Baltic Proper during the post-2000 compared to the pre-2000 period.

Measurements of dioxins in the atmosphere in Europe have shown steadily declining levels. The declining impact in herring of the thermal source type (the major contributor of atmospheric dioxins) can be explained by this observation. The contamination of Baltic herring with dioxins from TCP and PCP is understandable as technical products based on TCP and PCP have for example been extensively used as wood preservatives in the forestry industries in the countries surrounding the Baltic Sea. The production and use of TCP and PCP around the Baltic region has, however, been restricted and/or banned. It is therefore challenging to explain the increasing impact in absolute levels of the TCP and PCP/AB sources in the herring. It appears reasonable that it could be related to ecological changes, such as slower growth or changed feeding patterns, and not to increased source strengths in the environment per se.

The declining impact of the thermal source type in herring, sediment and air of the Baltic Sea illustrates the effectivity of previous mitigation actions and motivates a continued effort of managing emissions from thermal sources. On the other hand, the stable or even increasing impacts of TCP and PCP source types in Baltic herring highlights the importance of also recognizing dioxin contaminated sites in coastal environments when aiming at reducing levels in the ecosystem, including edible fish. Further studies should aim at a better understanding on the causes of impact from TCP and PCP sources, the apparent absolute increase of TCP and PCP sources in herring, and whether remediation of contaminated soil and sediment sites would be cost efficient methods for reducing dioxins in Baltic herring.

Abbreviations

AB	atmospheric background
BB	Bothnian Bay
BP	Baltic Proper
BS	Bothnian Sea
CDD/F	chlorinated dibenzo-*p*-dioxin/dibenzofuran
dw	dry weight
fg	femtogram
HRMS	high-resolution mass spectrometry
HxCDD	*hexa*-chlorodibenzo-*p*-dioxin
LOD	limit of detection
LOQ	limit of quantification
lw	lipid weight
n	number of data points
OCDD/OD	*octa*-chlorodibenzo-*p*-dioxin
OCDF/OF	*octa*-chlorodibenzofuran
PCDD	polychlorinated dibenzo-*p*-dioxin
PCDF	polychlorinated dibenzofuran
PCP	*penta*-chlorophenol
pg	picogram
PMF	positive matrix factorization
TCDD	*tetra*-chlorodibenzo-*p*-dioxin
TCP	*tetra*-chlorophenol
TEF	toxic equivalency factor
TEQ	toxic equivalent
TF	transformation factor
ww	wet weight

1 Background

1.1 Dioxins in the Baltic Sea ecosystem

As a result of industrialization and other human activities throughout the past century, large volumes of anthropogenic pollutants have ended up in the Baltic Sea [1]. One group of these pollutants are the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs), commonly referred to as dioxins. Due to natural formation processes, such as forest fires and volcanic eruptions, background levels of dioxins have existed for a long time [2-4]. However, the anthropogenic release of dioxins to the environment accelerated during the 20th century and peaked during the 1980s–1990s in the Baltic Sea, as reflected in levels in sediments [5]. This initiated several dioxin emission management efforts by Sweden and other Baltic and European countries [6, 7]. Consequently, the dioxins fluxes to the Baltic Sea have been declining as have the environmental levels in most parts of the ecosystem [5, 8-11]. For example, the dioxin levels in the Baltic Sea sediments in offshore and Swedish coastal areas had decreased to 860 and 1 800 pg g^{-1} dry weight (dw) in 2008/2009 from peak levels of 1 400 and 11 000 pg g^{-1} dw, respectively [5].

The situation in Baltic biota is, however, different. The total dioxin levels in Baltic herring (*Clupea harengus*) have not generally been declining (Figure 1), at least not to the same degree as the surrounding environment [12, 13]. Only in the long time series dating back to 1979 in the Bothnian Sea is a decline in levels apparent, while levels in other areas appear stable during the last decades. This causes health concerns, as levels of dioxins in fatty fish such as herring and other marine organisms in the Baltic Sea are too high for unrestricted consumption [8, 14, 15]. The sources of dioxins to the Baltic biota and the factors behind the lack of decline in dioxins levels in Baltic biota are not well understood [8]. It has been suggested that changing migration and feeding patterns, lipid content, and growth rates might have contributed to the elevated levels of dioxins in Baltic herring [8]. Another factor that needs elucidating is the sources of the dioxins to the biota and to what extent there is an ongoing impact from sources. In this report, dioxins in Baltic herring were examined to identify the sources and to establish their ongoing impact on the biota.

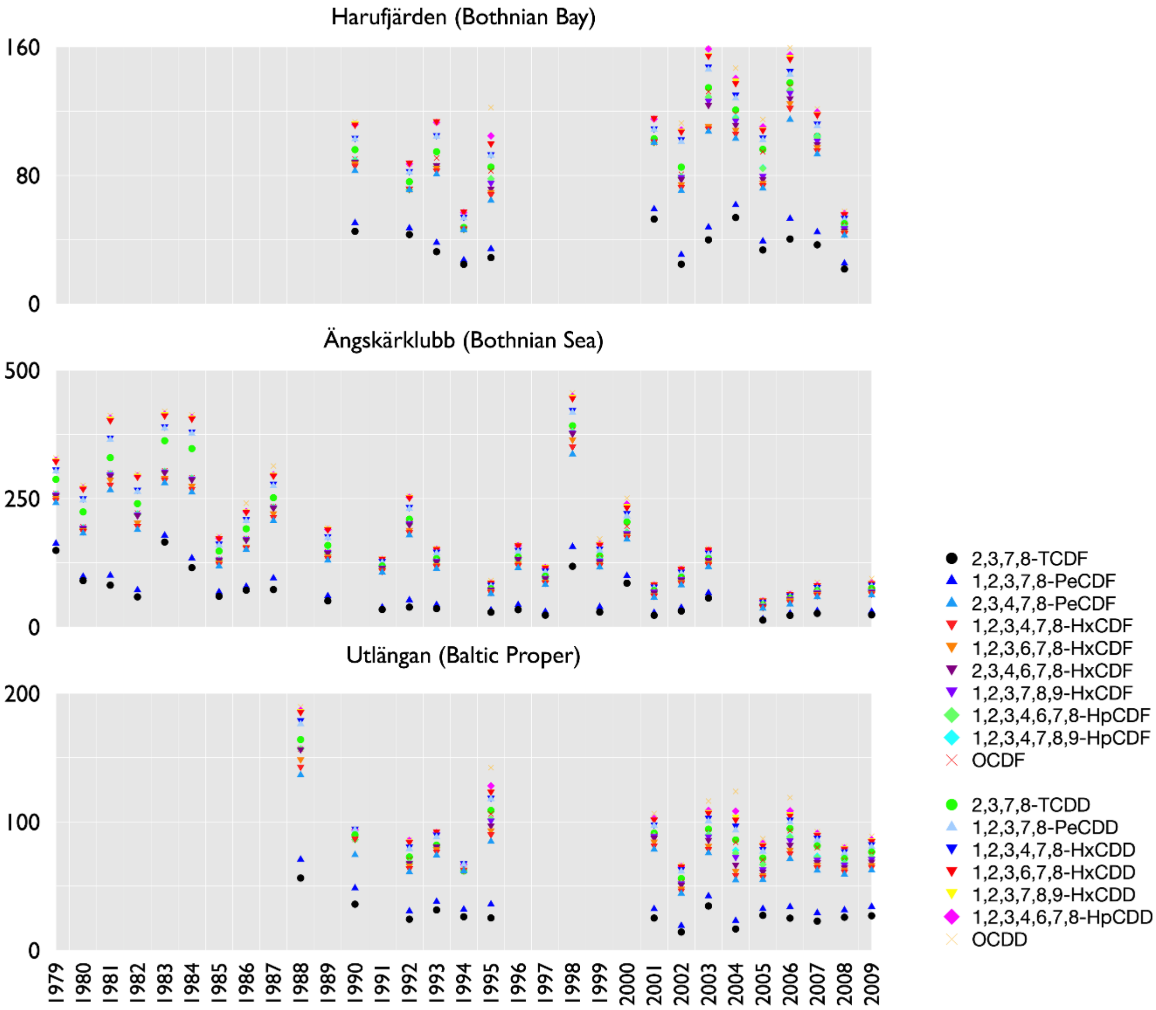

Figure 1. Concentrations of dioxins in Baltic Sea herring (monitoring data obtained from the Swedish Museum of Natural History) [8]. A blank bar indicates no available data for that specific year. Y-axis values are given in pg g^{-1} lw.

1.2 Dioxins and their toxicity

Because the number and placement of the chlorine atoms on the dibenzo-*p*-dioxin and dibenzofuran molecules can vary, the dioxin group consists of in total 210 congeners. They are known for their stability and toxicity, especially the 2,3,7,8-substituted CDD/F congeners (Figure 2). Due to their chemical structure, these dioxin congeners are usually poorly transformed and therefore bioaccumulated in higher organisms including humans and fish [16]. Dioxins are undesirable chemicals that can cause various health problems, both acute and chronic effects such as impairment of the immune, nervous, endocrine and reproductive systems [17-21].

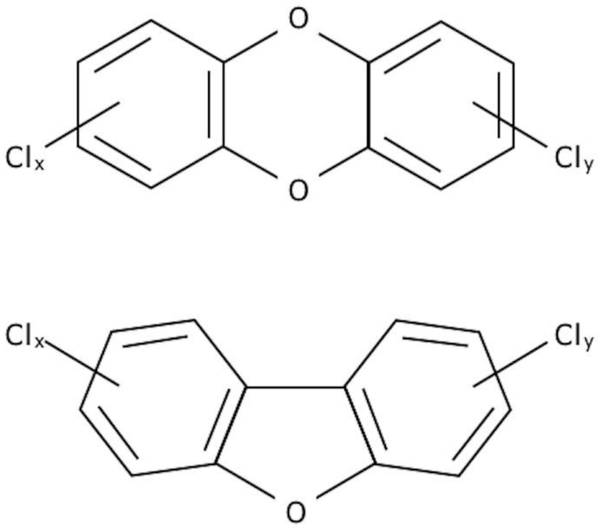

Figure 2. Structural formula of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), together commonly referred to as dioxins.

TCDD (short name for 2,3,7,8-*tetra*-chlorodibenzo-*p*-dioxin) is the most toxicologically potent dioxin congener [22]. Because the dioxins exert their toxicity through the same mechanism (binding to the AhR receptor), risk assessment schemes have been developed to relate the toxicities of the other 2,3,7,8-substituted dioxins to TCDD and thus provide a common measure of toxicity. The toxicities of the different congeners are represented with so called toxic equivalency factors (TEFs) as proposed by organizations such as WHO and US EPA (Table 1) [22-25]. The TEF of TCDD is 1.0 and the toxicities of the other congeners are expressed relative to TCDD with TEFs <1. Total toxic equivalents (TEQs) can therefore be calculated by multiplying the concentrations of the seventeen 2,3,7,8-substituted dioxins by their respective TEF values. WHO_{2005} is the latest and most used TEF scheme for reporting concentrations of dioxin congeners in different matrices as TEQs [25].

Table 1. Toxic equivalency factors (TEFs) proposed by various organizations.

Congener	USEPA 1987 [26]	Nordic 1988 [27]	NATO-I 1989 [28]	WHO 1998 [22]	WHO 2005 [25]
2,3,7,8-TCDF	0.1	0.1	0.1	0.1	0.1
1,2,3,7,8-PeCDF	0.1	0.01	0.05	0.05	0.03
2,3,4,7,8-PeCDF	0.1	0.5	0.5	0.5	0.3
1,2,3,4,7,8-HxCDF	0.01	0.1	0.1	0.1	0.1
1,2,3,6,7,8-HxCDF	0.01	0.1	0.1	0.1	0.1
2,3,4,6,7,8-HxCDF	0.01	0.1	0.1	0.1	0.1
1,2,3,7,8,9-HxCDF	0.01	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDF	0.001	0.01	0.01	0.01	0.01
1,2,3,4,7,8,9-HpCDF	0.001	0.01	0.01	0.01	0.01
OCDF	0	0.001	0.001	0.0001	0.0003
2,3,7,8-TCDD	1	1	1	1	1
1,2,3,7,8-PeCDD	0.5	0.5	0.5	1	1
1,2,3,4,7,8-HxCDD	0.04	0.1	0.1	0.1	0.1
1,2,3,6,7,8-HxCDD	0.04	0.1	0.1	0.1	0.1
1,2,3,7,8,9-HxCDD	0.04	0.1	0.1	0.1	0.1
1,2,3,4,6,7,8-HpCDD	0.001	0.01	0.01	0.01	0.01
OCDD	0	0.001	0.001	0.0001	0.0003

1.3 Sources of dioxins in the Baltic Sea

Dioxins are produced unintentionally in various thermal and chemical processes. Common anthropogenic sources include municipal solid waste incineration (MSWI), power generation using coal and wood as fuel, production of organochlorine pesticides, and production and bleaching of pulp and paper using elementary chlorine [6, 24, 29-31]. The sources have been relatively successfully managed during the past decades, and consequently the primary emissions have been declining since the 1970s [32-34]. For example, the production and use of pentachlorophenol (PCP), a wood preservative contaminated with dioxins, was restricted in several countries starting in the late 1970s [35, 36].

Both diffuse and local sources of dioxins have contributed to the dioxins in the Baltic Sea ecosystem. These sources have previously been identified and quantified by studying surface sediments and sediment cores and applying multivariate source tracing models [32]. Diffuse pollution can be caused by a variety of activities that have no specific point of emission, for example dioxins that have been transported and delivered to the Baltic Sea via air masses and atmospheric deposition. According to several studies, atmospheric sources have contributed to a substantial part of the dioxins in the Baltic Sea [5, 7, 10]. However, the Baltic Sea has also been impacted by direct emissions from local sources. These local sources are frequently connected to forestry related industries, such as the pulp and paper industry, in countries surrounding the Baltic Sea, although other industrial sectors have contributed as well. The current and historical sources [32] can be summarized as:

i. atmospheric emissions from various high temperature processes (e.g. waste incineration), also referred as thermal sources,
ii. background air, alternatively called atmospheric background,
iii. production and use of chlorine, e.g. bleaching of pulp using chlorine gas and chlor-alkali production,
iv. a *hexa*-CDD source that has been linked to e.g. kraft pulp production,
v. manufacture and use of tetrachlorophenol (TCP) products, and
vi. manufacture and use of pentachlorophenol (PCP) products.

This information is a good starting point for identifying sources that impact the biota in Baltic Sea, because the dioxins in Baltic fish most likely originate from some or all of these six source types. There are at least two major factors that play key roles in determining the relative importance of a source to aquatic organisms: *i)* the strength of a source, i.e. mass of dioxins delivered from the source, and *ii)* bioavailability of the delivered dioxins. The latter is important because dioxin congeners from a specific source can only be accumulated in biota if they are available for uptake. Dioxins are hydrophobic and prefer to attach to particles in aquatic systems. However, different dioxin congeners have different tendencies for this, with the lighter (less hydrophobic) congeners being more water soluble and therefore more bioavailable. Source specific bioavailability can thus be an important factor when tracking dioxin sources for biota. By this, and due to the difference in biotransformation between congeners and species, it also follows that the relative impact of a specific source can differ between environmental compartments, i.e. between sediment and fish. As dioxin levels in fish is a major concern in the Baltic Sea environment, source tracing for fish is highly motivated.

2 Tracing sources of dioxins in the environment

The process of back-tracing sources of pollutants for a specific environmental compartment is challenging. Multivariate data analysis techniques have been highly useful to overcome these challenges and to establish potential links between sources and exposed environmental compartment (e.g. soils and sediments). These methods commonly utilize the chemical patterns of the sources [32, 37, 38]. The chemical pattern of a source is the relative abundance of chemical species (e.g. dioxin congeners) and can be seen as the chemical fingerprint of a source. Fingerprinting approaches have been successful for tracing dioxin sources, because dioxin congeners are persistent and fingerprints are preserved in the environment. The chemical pattern of dioxins emitted from a source can be obtained by dividing the individual congener concentrations by the total concentration of all congeners, so that each congener will have a relative value between 0 and 1, the sum of all the scores becomes 1, and the dominant congeners have the highest values.

2.1 Tracing sources in abiotic systems using Positive Matrix Factorization

Positive Matrix Factorization (PMF) is a robust multivariate technique that has been applied for the purpose of pollution source tracing [32, 38]. PMF decomposes an environmental data matrix (for example, a data matrix of concentrations of dioxin congeners for a number of analysed environmental samples) into the fundamental source patterns that make up the environmental pattern (Figure 3). The relative contribution of each source is calculated in subsequent steps of the PMF modelling. Detailed explanations and applications of PMF in Baltic Sea sediment studies have been presented by Assefa et al. [32] and Sundqvist et al. [38].

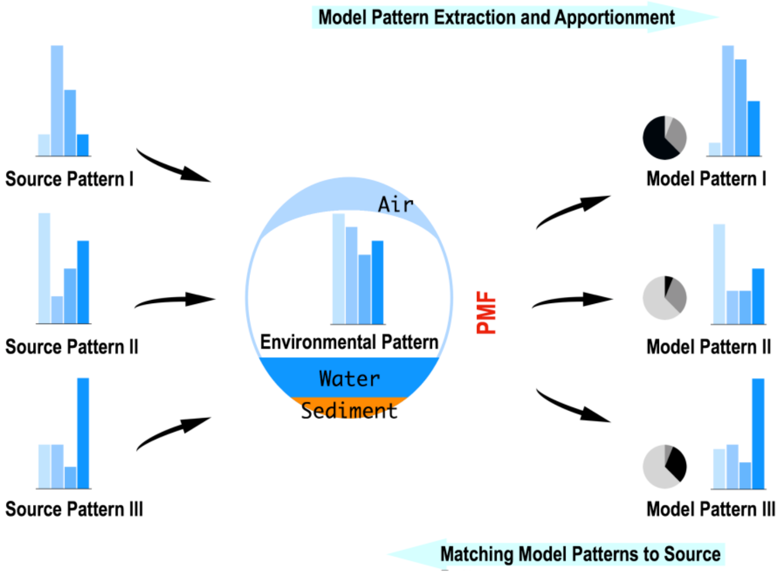

Figure 3. Conceptual illustration of the source tracing process for abiotic environments (sediment, air and water) using PMF.

2.2 Tracing sources in fish

A typical PMF based source tracing process starts by decomposing the environmental data matrix back to the basic patterns that formed the matrix. These decomposed patterns are then compared to real source fingerprints to identify the source they are representing. This is usually a correct approach as long as the receptor (the polluted environment of interest) is abiotic. It is, however, not informative to directly compare decomposed patterns detected in biota (or water) to real source fingerprints. This is mainly due to the fact that dioxin congeners have different physico-chemical properties (e.g. water solubility) and environmental stability (e.g. biotransformation rates) [39]. This result in completely different dioxin patterns in biota as compared to those in adjacent abiotic environments such as sediment.

To overcome this challenge, we implemented an additional step in the process by including transformation factors (TFs) to account for the complex processes of environmental fate and transformation. A conceptual illustration of our source tracing process is shown in Figure 4. First, source patterns are extracted by PMF. Then, these modelled source patterns are transformed to source patterns as they would appear in sediments, using so called fish-to-sediment TFs. By using this approach, it is not necessary to have detailed understanding and do step-wise simulations of pattern changes occurring from the dioxin source to the receptor (fish). In the third (final) step, the transformed sediment patterns are compared to real source patterns. For this, we use established dioxin source patterns as demonstrated in previous Baltic Sea studies [32, 38].

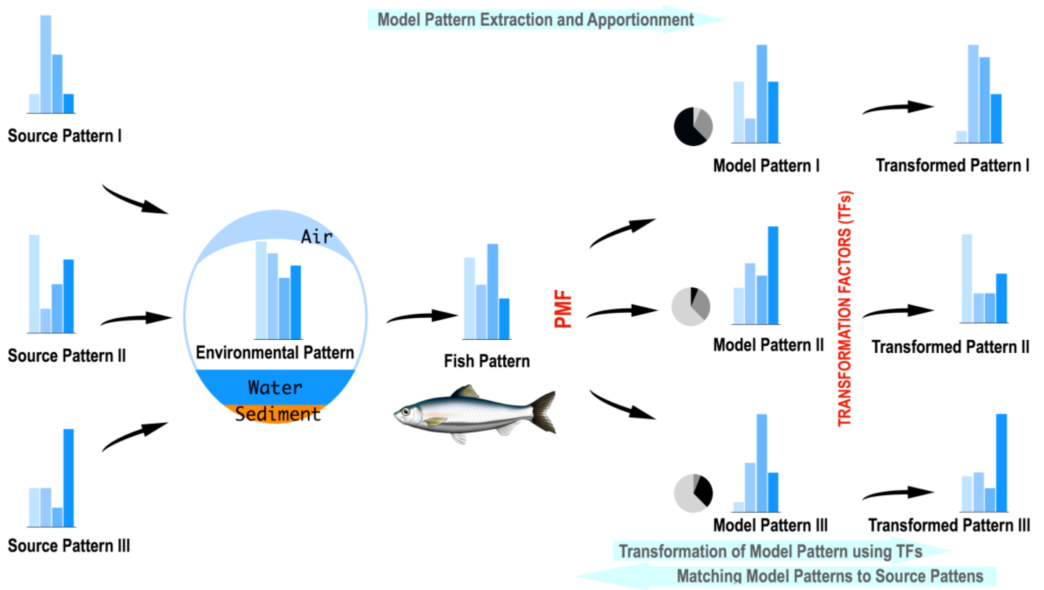

Figure 4. Conceptual illustration of the source tracing process for fish using PMF.

3 Data collection

3.1 Herring data

Two independent sets of herring data were used in the current study, one for the PMF modeling and one for calculating Transformation Factors (TFs). The first dataset contained lipid weight (lw) based concentrations of 2,3,7,8-CDD/Fs in herring and was obtained from the Swedish Museum of Natural History (also published in Miller et al. [15] and Miller et al. [12]). This dataset was used in the PMF process for extracting chemical patterns of sources. It contains dioxin concentrations for pooled samples of adult Baltic herring, defined here as 3–9 years old specimens. Each data point represents an annual geometric mean obtained from 10–12 archived adult herring specimens collected from three sub-basins of the Baltic

Sea: the Bothnian Bay (BB; Harufjärden), the Bothnian Sea (BS; Ängskärsklubb), and the Baltic Proper (BP; Utlängan) (Figure 5). The Swedish Museum of Natural History has been coordinating the collection of these herring samples for decades as a part of the National Swedish Monitoring Program [12].

Figure 5. Herring sampling locations in the Baltic Sea.

The time series from the BS covers the longest time period (1979–2009), while the series in the BB (1990–2009) and the BP (1988–2009) are approximately one decade shorter. This means that in total 14 values (geometric means) were available for the BB, 26 values for the BS and 15 values for the BP. This dioxin data was normalized prior to PMF by dividing the concentrations of each dioxin congener by the sum of all congeners (annual average) so that each congener got a value between 0 and 1 (representing a fraction) and the sum of all fractions (per sampling site) was 1. The PMF modelling was then performed using EPA PMF version 5.0.13 software [40]. PMF also requires a data matrix that represents the spread of the data points in the normalized concentration data matrix. This uncertainty data matrix was prepared by using 35% for each data point, which is a conservative approach that does not underestimate variation.

The second herring dataset was obtained from Bignert et al. [41]. It comprised geometric mean-based concentrations of the 2,3,7,8-CDD/Fs in pooled adult (5–10 years old) herring samples collected from BB (*n*=137), BS (*n*=310) and BP (*n*=183), respectively. This dataset was used for calculating fish-to-sediment TFs (more explanation follows below).

3.2 Sediment data

In addition to the herring data, corresponding sediment data is also required for calculating fish-to-sediment TFs. The corresponding sediment data contained dry weight (dw) based concentrations of the 17 dioxin congeners (2,3,7,8-CDD/Fs) in surface sediments, originally published by Sundqvist et al. [37]. The concentrations were obtained from 34 surface sediment samples collected from both coastal areas with minimum human impact and offshore areas in the Baltic Sea. These sediment data were also divided per sub-basin (BB *n*=4; BS *n*=19, and BP *n*=11) and average concentrations were calculated (one average per sub-basin). Both coastal and offshore sediment data were included in the average sediment dioxin concentrations to obtain a value that represents the entire sub-basin.

4 Identification of dioxin sources

4.1 Extraction of model PCDD/Fs patterns

After applying the PMF, three herring PCDD/F patterns were extracted (Figure 6). The first model pattern showed substantial fractions of all congeners, but with relatively high fractions of 2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF (30%, 10% and 26%, respectively). The second model pattern had substantial fractions of all congeners except 2,3,7,8-TCDF and 1,2,3,7,8-PeCDF, and with the highest fractions of 2,3,4,7,8-PeCDF and OCDD (33% and 17%, respectively). The last pattern was clearly dominated by three congeners (2,3,7,8-TCDF, 1,2,3,7,8-PeCDF and 2,3,4,7,8-PeCDF), with a cumulative contribution of 78% of the sum, but had less of highly chlorinated congeners than the first model pattern.

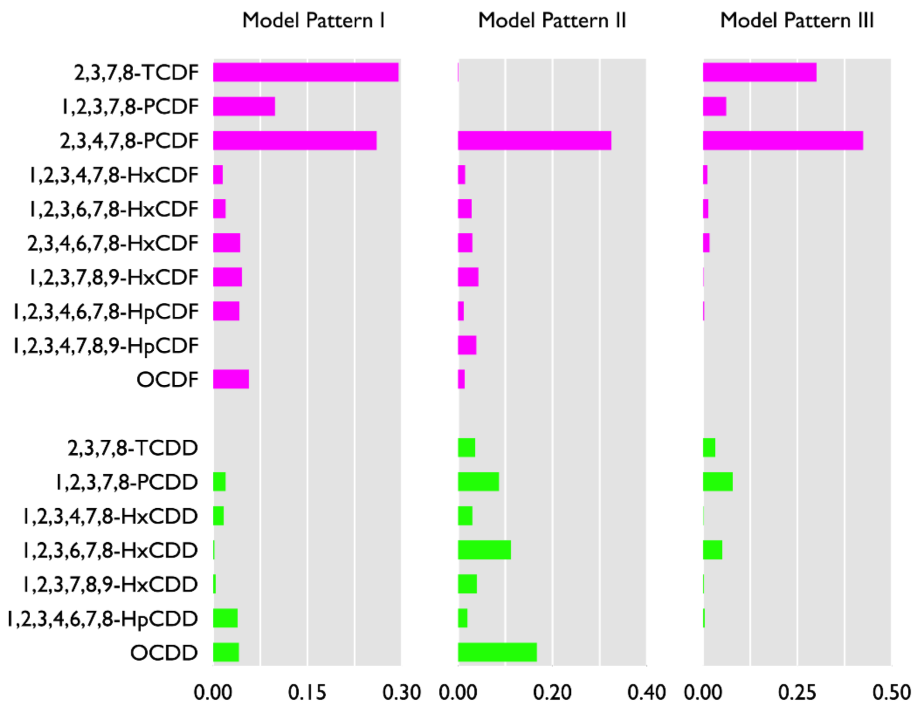

Figure 6. Extracted source patterns in Baltic herring obtained by applying PMF.

4.2 Transformation of patterns using transformation factors

The next step in the source tracing process was to transform the herring patterns using TFs. Separate sets of TFs were calculated for the three sub-basins to minimize the potential effects of differences in ecosystem characteristics (e.g. fish growth rate). The TFs were calculated as the ratios of concentration of dioxin congener in herring (ww basis) to those in sediment (dw basis) (Table 2). The congeners 2,3,4,7,8-PeCDF and 1,2,3,7,8-PeCDD showed the highest values with ratios up to 2.3 and 1.1, respectively. The TF of 1,2,3,4,7,8-CDD could not be estimated because of missing data and was given a nominal value of 0.

To obtain transformed dioxin patterns, the individual congeners in the extracted modelled (PMF) fish patterns were divided by their respective TFs.

Table 2. Calculated fish-to-sediment transformation factors (TFs) for the three studied sub-basins in the Baltic Sea.

	Bothnian Bay		**Bothnian Sea**		**Baltic Proper**		**Transformation factor**		
	HER	**SED**	**HER**	**SED**	**HER**	**SED**	**BB**	**BS**	**BP**
2,3,7,8-TCDF	2.0	3.8	2.1	7.8	1.2	15	0.52	0.27	0.082
1,2,3,7,8-PCDF	0.81	1.7	1.1	3.6	0.70	7.3	0.48	0.31	0.10
2,3,4,7,8-PCDF	6.0	2.6	7.4	4.6	3.8	9.3	2.3	1.6	0.41
1,2,3,4,7,8-HxCDF	0.17	4.1	0.26	6.6	0.19	17	0.040	0.039	0.011
1,2,3,6,7,8-HxCDF	0.26	1.8	0.42	3.0	0.26	7.9	0.15	0.14	0.032
2,3,4,6,7,8-HxCDF	0.27	2.2	0.42	3.5	0.27	8.3	0.12	0.12	0.033
1,2,3,7,8,9-HxCDF	0.063	0.75	0.061	1.2	0.061	2.3	0.083	0.052	0.026
1,2,3,4,6,7,8-HpCDF	0.065	32	0.092	33	0.065	66	0.0020	0.0028	0.00099
1,2,3,4,7,8,9-HpCDF	0.034	1.3	0.0084	1.9	0.023	4.3	0.026	0.0045	0.0053
OCDF	0.056	29	0.047	53	0.052	77	0.0019	0.00090	0.00067
2,3,7,8-TCDD	0.19	1.7	0.28	2.0	0.13	3.3	0.11	0.14	0.038
1,2,3,7,8-PCDD	0.81	0.72	1.0	1.2	0.60	2.2	1.1	0.81	0.27
1,2,3,4,7,8-HxCDD	<LOQ	NA	<LOQ	NA	<LOQ	NA	NE	NE	NE
1,2,3,6,7,8-HxCDD	0.72	3.3	0.88	4.5	0.38	8.0	0.22	0.20	0.047
1,2,3,7,8,9-HxCDD	0.077	3.3	0.088	3.4	0.054	6.5	0.023	0.026	0.0083
1,2,3,4,6,7,8-HpCDD	0.063	8.7	0.069	17	0.064	46	0.0072	0.0040	0.0014
OCDD	0.43	29	0.45	64	0.45	186	0.015	0.0070	0.0024

HER: herring; SED: sediment; NA: not available, chromatographic peak was quantified with that of 1,2,3,6,7,8-HxCDD; LOQ: limit of quantification; NE: not estimated, a TF value of 0 was used in the calculations

4.3 Transformed patterns and identification of dioxin sources

The transformed patterns (Figure 7), corresponding to modeled source patterns as they would appear in sediments, were compared with patterns of real sources to identify sources that impact the Baltic herring.

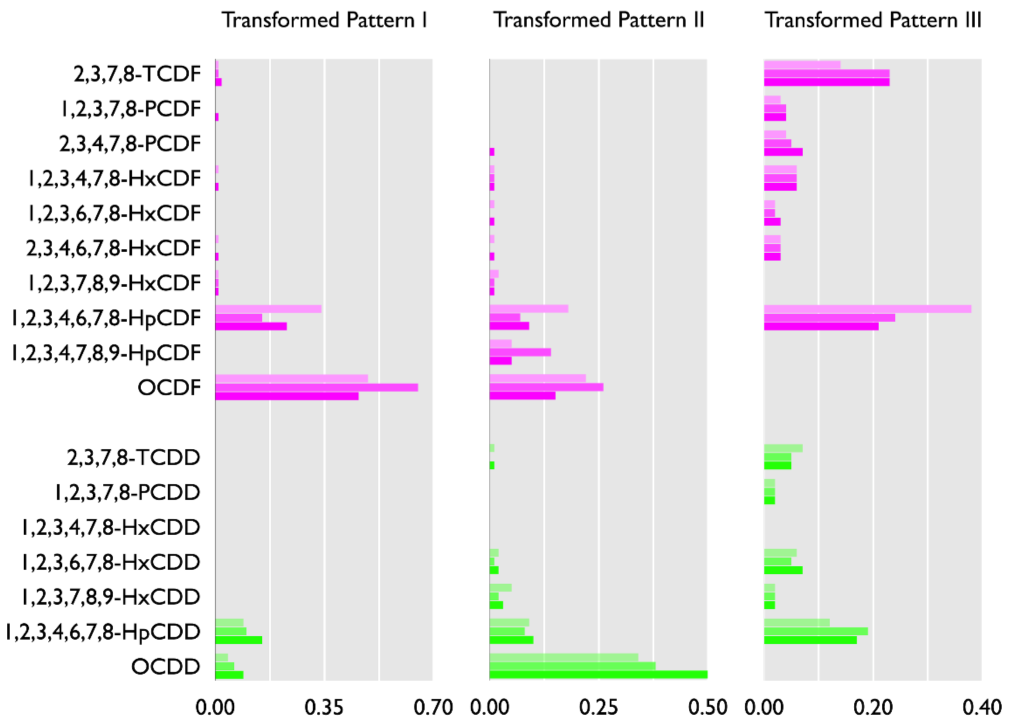

Figure 7. Transformed fish patterns. The three different bars for each congener represent the three investigated sub-basins (as TFs were calculated separately).

Transformed Pattern I: This pattern was completely dominated by 1,2,3,4,6,7,8-*hepta*-CDF and *octa*-CDF (Figure 7). According to Assefa et al. [32] and other studies [42, 43], these congeners are two of the three marker congeners for dioxin contamination from the use of TCP technical products as wood preservatives. The third marker congener is a non-2,3,7,8-CDF (1,2,3,4,6,8,9-HpCDF) and cannot appear in this pattern since the current study only consider the 2,3,7,8-substituted congeners.

Transformed Pattern II: Contamination from pentachlorophenol (PCP) are frequently identified by *hepta*- and *octa*-CDD/F marker congeners [4, 36, 37, 44-46], i.e. highly chlorinated PCDDs (unlike the TCP pattern where PCDFs dominate). The transformed pattern II was dominated by 1,2,3,4,6,7,8-HpCDF, 1,2,3,4,7,8,9-HpCDF, OCDF, 1,2,3,4,6,7,8-HpCDD and OCDD (Figure 7). This pattern has also been found at or near contaminated sites where technical products of PCP have been used as wood preservative

[37, 44]. However, similar dioxin patterns have been reported for atmospheric background (AB), which usually is highly dominated by *hepta*-CDD and OCDD. This makes it challenging to distinguish between PCP and AB. In previous sediment studies, this pattern has been identified as either PCP or AB source (Figure 8), and here we identified the transformed pattern II as a combination of the two, PCP and/or AB.

Transformed Pattern III: Unlike the other two patterns, this transformed pattern displayed considerable fractions of most congeners without clear marker congeners. The identification of a source type associated with this pattern was not as straightforward as for Transformed Pattern I and II. One useful characteristic of this pattern is, however, that it has a generally high fraction of furans (PCDFs). Thermal source patterns share this characteristic (Figure 8). The main difference between the two patterns is that OCDF is missing in the Transformed Pattern III. Despite this discrepancy, the Transformed Pattern III is more similar to the thermal pattern than to any of the other known real source patterns. The thermal source type has been shown to be the highest contributor of dioxins in the Baltic Sea sediments [32], and it is therefore expected to have an impact also in biota. We therefore propose that the Transformed Pattern III represents the thermal source type.

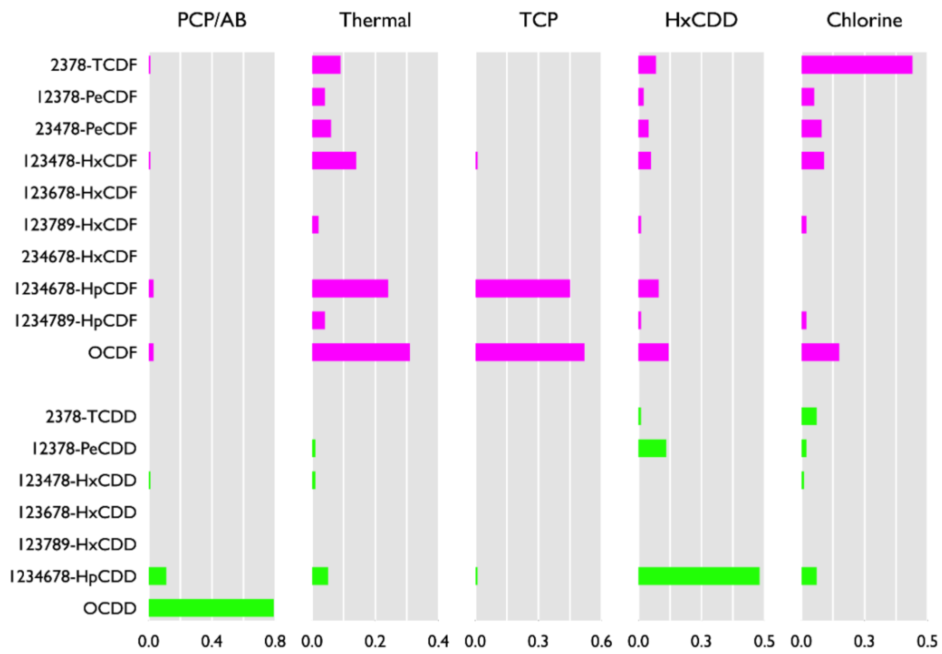

Figure 8. Modeled patterns of dioxin sources in Baltic sediments [32].

5 Quantification of dioxin source contributions in Baltic herring

In addition to identification of source profiles, the PMF also performs source apportionments, i.e. the model calculates the quantitative impact of the identified dioxin sources (TCP, PCP/AB and Thermal) to each data point. The PMF also calculates the residual, i.e. the fraction of the variation in the data that cannot be explained by the three identified sources.

The impact of the identified dioxin sources in Baltic herring was calculated using absolute concentrations (pg g^{-1} lw) and relative proportions of the total concentrations (%). This was done using both absolute 2,3,7,8-PCDD/F concentrations and TEQ-based concentrations. The calculations were done for the three studied sub-basins (BB, BS and BP) as well as per sub-basin. All data are given in Appendix A - D. The contributions of the dioxin sources based on both TEQ and absolute concentrations (Appendix E) appear very similar. As the EU-guidelines for food consumption are based on TEQ-concentrations, we focus on the TEQ-based data in the report, while the source apportioning figures calculated on absolute concentrations (pg g^{-1} lw) are given in Appendix F.

To evaluate time trends, the samples were divided into a pre-2000 and a post-2000 period. By using year 2000 as a cut-off point, the number of samples in the two-time periods became relatively well balanced for the Bothnian Bay (BB) and the Baltic Proper (BP). Because of the longer time series in the Bothnian Sea (BS), the pre-2000 period includes a higher number than the post-2000. More specifically, the years and number of samples covered were for *Pre-2000:* BB: 1990 -1995 (n = 5), BS: 1979-1999 (n=18) and BP: 1988-1995 (n=6), and for *Post-2000:* BB: 2001-2009 (n=9), BS: 2000-2009 (n=8), and BP: 2001-2009 (n=9). Uncertainties of averages were estimated for a 90% confidence level.

5.1 Quantification of sources in absolute concentrations

5.1.1 Contributions of the thermal source type

The PMF modelling results indicate that the thermal source type has contributed on average 21 (± 6.2) pg TEQ g^{-1} lw during the pre-2000 period in the BB (Figure 9), which is the highest contribution of all the sources. This value decreased to 17 (± 3.2) pg TEQ g^{-1} lw during the post-2000 period. Similarly, the contribution decreased from 54 (± 12) to 18 (± 5.6) pg TEQ g^{-1} lw in the BS and from 23 (± 9.5) to 12 (± 3.1) pg TEQ g^{-1} lw in the BP. These are reductions by 19% (BB), 67% (BS) and 48% (BP). This is a good indication that the impact of thermal related sources on herring has declined in the Baltic Sea over time. A similar study of dioxin sources using Baltic Sea sediment cores from Swedish coastal and off-shore sediments also found that the impact of thermal sources has been declining over the last decades throughout the Baltic Sea [32].

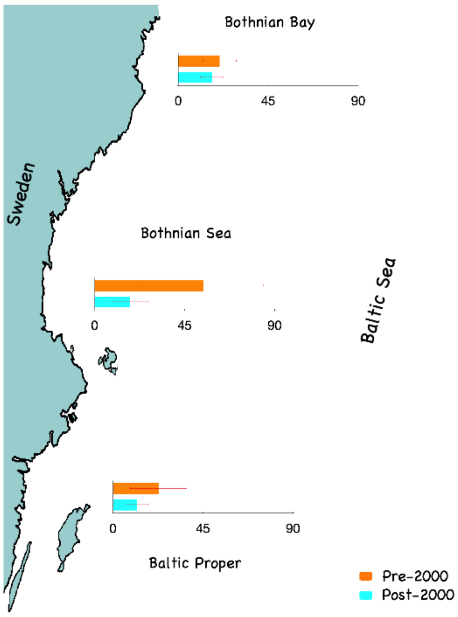

Figure 9. Average contributions (pg TEQ g^{-1} lw) of thermal sources.

5.1.2 Contributions of the TCP source type

As can be seen in Figure 10, the impact of TCP sources appears to have increased over time in the BB and the BP and has been relatively stable in the BS. The TCP source contributed on average <1 pg TEQ g^{-1} lw (pre-2000) and 5.5 (± 1.6) pg TEQ g^{-1} lw (post-2000) in the BB. The corresponding values for the BS were 2.5 (± 0.54) pg TEQ g^{-1} lw and 3.1 (± 1.3) pg TEQ g^{-1} lw, and for the BP, 2.6 (± 2.4) pg TEQ g^{-1} lw and 7.8 (± 2.1) pg TEQ g^{-1} lw. These values indicate an increase in the TEQ concentration by five times in the BB from the pre-2000 to the post-2000 period, a slight increase in the BS, and more than a doubling in the

BP. The agreement between the trends in the three sub-basins is a good indication for an increased impact of the TCP source during recent years (post-2000). The increasing trends on an absolute basis are unexpected as the use of TCP based products has been restricted and banned since the 1970s and 1980s in the countries around the Baltic Sea [47, 48] and will be discussed more in chapter 5.3

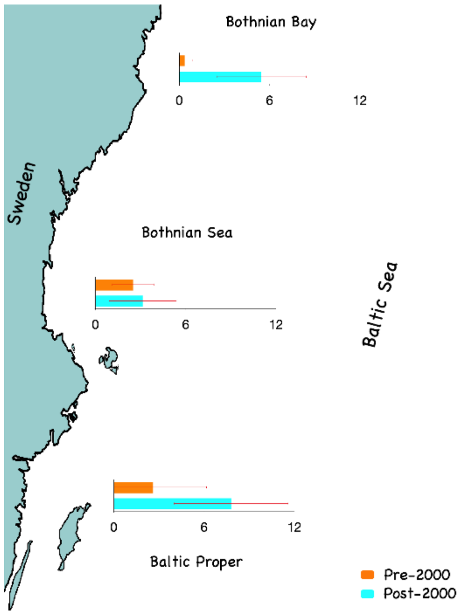

Figure 10. Average contributions (pg TEQ g^{-1} lw) of the TCP source type.

5.1.3 Contributions of the PCP/AB source type

The impact of the PCP/AB source also showed increasing tendencies in the BB and the BP. For pre-2000 data, the average contributions of the PCP/AB source were <1 pg TEQ g^{-1} lw, 5.5 (± 0.95) pg TEQ g^{-1} lw and <1 pg TEQ g^{-1} lw in the BB, BS and BP, respectively (Figure 11). The corresponding average concentrations for the post-2000 period were 1.9 (± 1.2) pg TEQ g^{-1} lw, 2.7 (± 1.5) pg TEQ g^{-1} lw and 3.1 (± 2.7) pg TEQ g^{-1} lw, respectively. This suggests that the TEQ-levels of PCP/AB decreased slightly in the BS (by ~50%), increased by more than double in the BB and by more than three times in the BP. It is, however, important to note that the data from the BB and BP show high variability, which causes high uncertainty, and their proportional increases should therefore be interpreted with care – the pre-2000 absolute concentrations were very low.

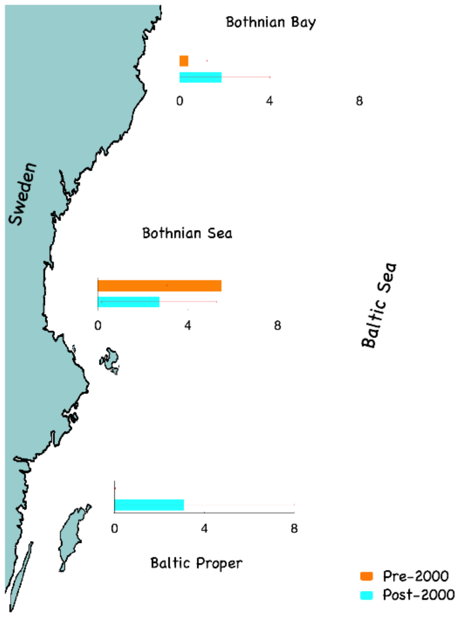

Figure 11. Average contributions (pg TEQ g^{-1} lw) of PCP/AB sources. The absolute concentration contribution in the Baltic Proper pre-2000 was low (0.014 pg TEQ g^{-1} lw) and is not visible in the figure.

5.1.4 Time trends on yearly basis

In Figure 12, the temporal trends of the three source types (TCP, PCP/AB and thermal) as contributions in absolute concentrations to levels in herring are shown on an annual basis. The temporal trend lines tend to have poor R^2 values (<0.5) as a result of the large variabilities in the temporal data of the PCDD/F concentrations. Due to these large variabilities, inconsistent statistical significances between basins and generally low R^2 values, we opted for not discussing the time trends on an annual basis and instead focus on the pre-2000 and post-2000 comparisons.

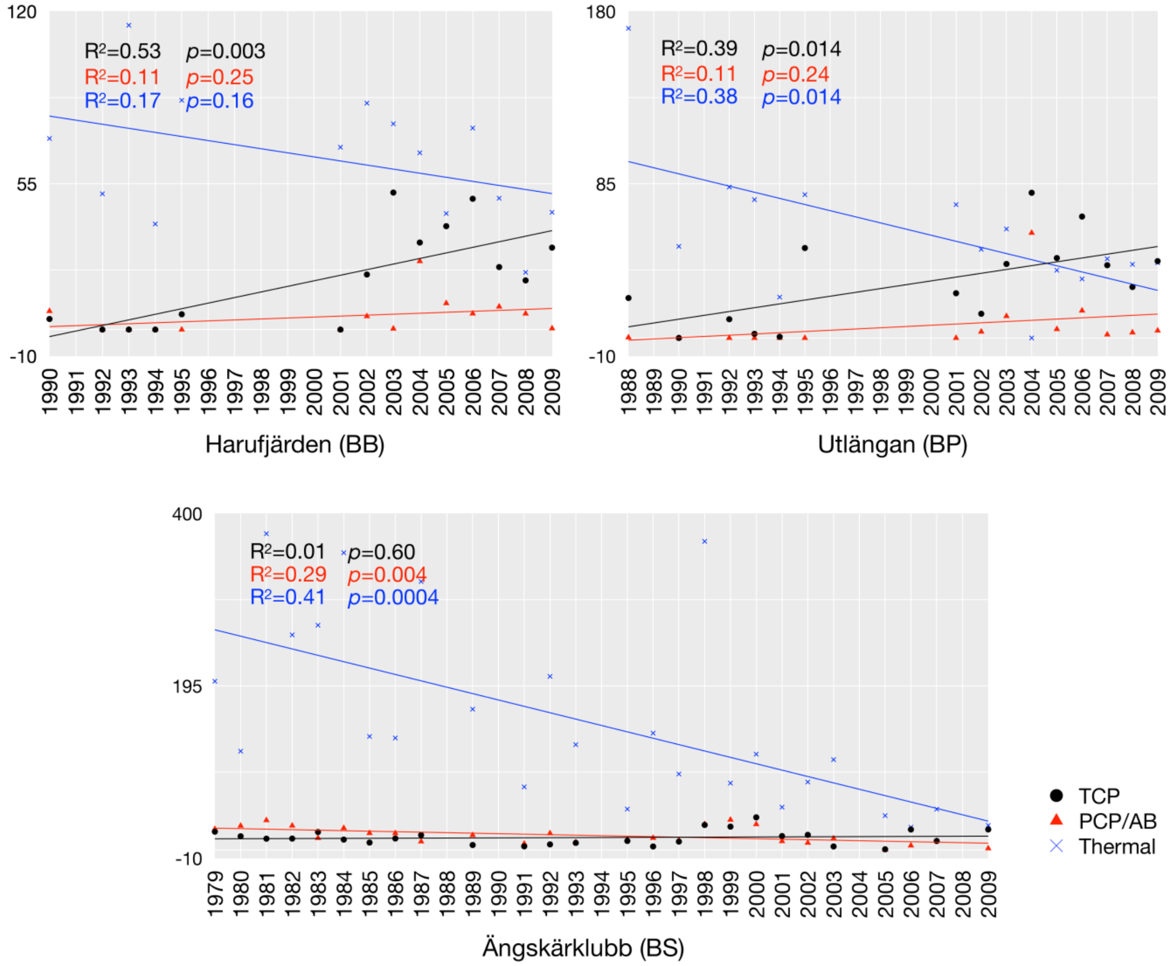

Figure 12. Temporal trends of TCP, PCP/AB and the thermal sources in Baltic herring per sub-basin expressed in pg TEQ g^{-1} lw.

5.2 Relative contributions of sources

5.2.1 Pre-2000

Averaging all pre-2000 TEQ-data for the three sub-basins, the relative contribution (proportion) of the thermal source type was high (72%), while the contributions of PCP/AB and TCP were considerably lower (6.0% and 3.7%, respectively). The average residuals (variation in data not explained by the three source types) varied between 10% and 18% with a decreasing trend from north to south.

The relative contributions per sub-basin are illustrated in Figure 13. In the BB, the thermal source contributed 80% whereas PCP/AB and TCP respectively contributed 1.5% and 1.4% during this early period. In the BS, the PCP/AB and TCP sources had on average a slightly higher contribution than in the BB (7.2% and 3.3%, respectively) and the thermal source contributed 71%. In the BP, the relative relations among the sources were similar to the other sub-basins with the thermal source type being the largest contributor (78%) and PCP/AB and TCP contributing at significantly lower proportions (<1% and 8.9%, respectively).

5.2.2 Post-2000

Going from the pre-to the post-2000 period, there were clear shifts in the relative contributions of the dioxin sources (Figure 13). The overall average contribution of the thermal source type to the three basins during the post-2000 period decreased to 59% while those of TCP and PCP/AB increased to 21% and 9.8%. Despite the reduction, the contribution from the thermal source type was still dominant in all sub-basins, with an average contribution of 59% in the BB, 67% in the BS and 51% in the BP. The average relative contribution from TCP increased in all sub-basins and reached 19%, 12%, and 33%, respectively, and similarly, the contribution of the PCP/AB source types increased to 6.6% for the BB, 10% for the BS, and 13% for the BP. The time trends were consistent for all sub-basins and clearly suggest that the relative impact of thermal sources have declined in the Baltic Sea area, while those of TCP and PCP/AB have increased in importance.

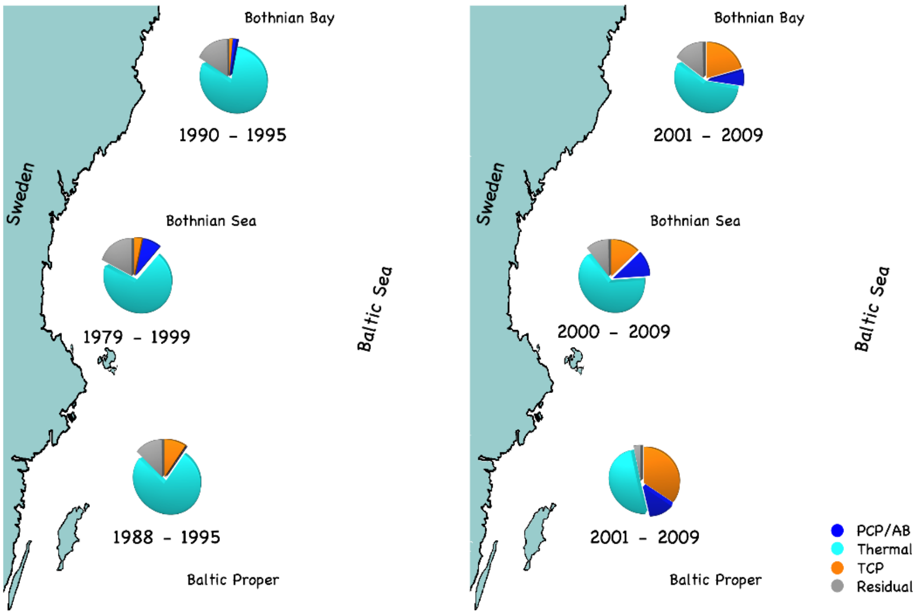

Figure 13. Percentage contributions of dioxin sources in Baltic herring calculated on a TEQ per lw basis. The relative contribution of the thermal source type has decreased, while the contribution of the TCP source type has increased substantially, and the PCP/AB source type has increased but less than the TCP.

5.3 Discussion on time trends

The increasing impact of the TCP source in absolute concentrations is puzzling, as the production and use of TCP has been banned. One possible explanation is an increased impact from contaminated soils and sediment leaching out dioxins that eventually reach Baltic Sea biota, although what the factors behind the increased remobilization would be are not clear. Another possible explanation could be changes in ecological factors – if the growth rate for herring has declined over time, a herring of the same size would be older in 2009 than at the start of the monitoring time series. As older fish tend to have higher dioxin levels because they have had more time to accumulate the pollutants, this could cause an increase in the absolute concentrations of a dioxin source although the source strength per se has not increased. Fish length is the criterion used for sampling in the Swedish monitoring program, and changes in length-at-age could therefore counteract declining source strengths. This possible explanation and the reason for the similarity in trends between the BB and the

BP, but not the BS, need to be further investigated, as these possible ecological changes are not verified.

The PCP/AB source type is a combination of the PCP source type (which would be expected to have similar trends as the TCP source) and the AB source type (which is an atmospheric source type and thus would be similar to the thermal source type, if any). Changes in the AB source type would presumably occur more slowly over time than changes in the thermal source type, which is more directly affected by decreases in direct emissions from various thermal processes. It was not possible to, in this study, determine to what extent the PCP/AB reflects PCP and AB, respectively, but what can be seen in Figure 12 is that the time trend appears to display minor changes over time, thus being less extreme than both the thermal source type (decreasing in all basins) or the TCP source type (increasing in two basins).

6 Concluding remarks

Three dioxin source types of importance to levels in fish were identified using the PMF modelling technique: tetrachlorophenol (TCP), pentachlorophenol/atmospheric background (PCP/AB) and a thermal source type. In sediment, an impact from two other sources has also been discerned, namely the Chlorine and the Hexa-CDD source types [32]. These two sources tend to have an overall low contribution to sediment levels in comparison to the other sources (Thermal, TCP and PCP/AB), and that may be one reason for not detecting them as important sources for herring. Another reason is probably the limited number of congeners that can be used in fish modelling. The non-2,3,7,8-substituted congeners are readily biotransformed and normally not detected or detected at low levels in fish. In previous sediment modelling studies [32, 38], more dioxin congeners (> 50 of the 210 possible) were included, which increases the possibility for detecting a larger variety of sources. For example, the "HxCDD-source" has several non-2,3,7,8-substituted congeners as markers in its pattern (along with some 2,3,7,8-substituted congeners; Figure 8). Without the information from the non-2,3,7,8-congeners, the detection of the HxCDD source is much more challenging.

The thermal source type contributed most of the dioxins to the herring during the studied periods (72% during pre-2000 and 59% during post-2000 periods, as an average for all three studied basins). Its impact has, however, decreased over time, which demonstrates that the measures to decrease emissions from thermal sources have had an effect also on levels in herring. These results agree with the general knowledge that atmospheric sources (of which the thermal source is the main contributor) are the major sources of dioxins to the Baltic Sea overall, and that their impacts have been decreasing steadily.

The decrease of the relative importance of the thermal source has led to an increased impact of the TCP and PCP/AB sources on dioxin levels in fish. As an average for the three studied basins, the TCP source contributed 3.7% during pre-2000 and 21% during post-2000 periods, while the PCP/AB source type contributed 4.7% during pre-2000 and 9.8% during post-2000 periods. This indicates that the historical releases of TCP and PCP may have been influencing the dioxin contents in Baltic fish more strongly than previously thought, and that the influence is increasing over time.

The modelled decreasing relative importance of thermal sources over time is not contradictory to measurement observations. Levels of dioxins in European air have been declining faster than those in Baltic sediments, with half-lives of 3-18 years in urban to semirural air, in comparison to half-lives of 29 years in offshore sediments of the Baltic Sea (Table 2 in [5]). This means that for the water and biota compartments, the dispersal of dioxins from the sediments are becoming increasingly important over time, and the sediment thus functions as a secondary source of pollutants. Baltic Sea sediments have large contributions from TCP and PCP sources along with the thermal source types, and it can be concluded from this study that TCP and PCP sources are likely gaining in impact for the Baltic Sea ecosystem.

In addition to an increased relative contribution of the TCP and PCP/AB source types to dioxin levels in fish, an increase also in absolute concentrations could be observed in this study, which is puzzling. This increase was more pronounced for TCP than for PCP/AB and occurred primarily in the Bothnian Bay and the Baltic Proper. A possible explanation to this is increased remobilization of dioxins originating from these sources (i.e. increased source strength), although factors behind this are not apparent. It could also be due to ecological changes, such as a decline in the growth rate of fish leading to a higher age (and more time to accumulate dioxins) in herring samples from the later years of the monitoring data compared to the earlier years. Additional studies are thus required to further evaluate the outcome of this study.

To conclude, the declining impact of the thermal source type in Baltic herring, as well as in sediment and air, is a good indicator that previous actions have been effective in reducing dioxin levels in Baltic Sea ecosystems. Still, the continued major impact of thermal sources motivates continuous efforts of managing emissions from thermal sources. The increasing/stable impacts of TCP and PCP source types in Baltic herring highlights the importance of also recognizing dioxin contaminated sites in coastal areas and marine environments when aiming at reducing levels in the ecosystem, including edible fish. Future studies are needed for a better understanding on the causes of impact from TCP and PCP sources, the apparent absolute increase of TCP and PCP sources in herring, and whether remediation of contaminated soil and sediment sites would be cost efficient methods for reduction of dioxins in Baltic herring.

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Appendix A

Absolute and TEQ based contributions of identified dioxin sources in herring from Harufjärden (BB) using 2,3,7,8-CDD/F concentrations

Year	Absolute concentration (pg g^{-1} lw)				TEQ (pg TEQ g^{-1} lw)			
	TCP	PCP/AB	Thermal	Residual	TCP	PCP/AB	Thermal	Residual
1990	4.0	7.0	72	30	0.74	1.9	20	5.0
1992	0.0	0.0	51	36	0.0	0.0	14	8.6
1993	0.0	0.0	115	0.0	0.0	0.0	32	0.0
1994	0.0	0.0	40	17	0.0	0.0	11	4.6
1995	5.8	0.0	86	30	1.1	0.0	24	3.4
2001	0.0	0.0	69	46	0.0	0.0	19	7.2
2002	21	5.0	85	1.4	3.8	1.4	24	8.0
2003	52	0.36	78	29	9.5	0.10	22	12
2004	33	26	67	22	6.1	7.0	19	0.0
2005	39	9.9	44	22	7.2	2.7	12	2.1
2006	49	6.0	76	28	9.1	1.6	21	2.8
2007	24	8.7	50	40	4.3	2.4	14	7.6
2008	19	6.0	22	12	3.4	1.6	6.1	1.1
2009	31	0.45	44	6.3	5.7	0.12	13	0.0
Z (α = 0.10)	1.645	1.645	1.645	1.645	1.645	1.645	1.645	1.645
1990–1995								
n	5	5	5	5	5	5	5	5
SD	2.7	3.1	30	14	0.51	0.85	8.4	3.1
AV	2.0	1.4	73	23	0.36	0.38	21	4.3
UNC (90%)	2.0	2.3	22	11	0.37	0.62	6.2	2.3
Perc. (%)	2.0	1.4	74	23	1.4	1.5	80	17
2001–2009								
n	9	9	9	9	9	9	9	9
SD	16	8.0	21	15	3.0	2.2	5.9	4.2
AV	30	6.9	59	23	5.5	1.9	17	4.5
UNC (90%)	8.9	4.4	11	8.1	1.6	1.2	3.2	2.3
Perc. (%)	25	5.8	50	19	19	6.6	59	16
1990–2009								
n	14	14	14	14	14	14	14	14
SD	19	7	24	14	3.5	1.9	6.8	3.7
AV	20	4.9	64	23	3.6	1.3	18	4.4
UNC (90%)	8.2	3.1	11	6.2	1.5	0.84	3.0	1.6
Perc. (%)	18	4.4	57	20	13	4.9	66	16

n: number of data points; SD: Standard deviation; AV: Average; UNC: Uncertainty; Perc.: Percent

Appendix B

Absolute and TEQ based contributions of identified dioxin sources in herring from Ängskärsklubb (BS) using 2,3,7,8-CDD/F concentrations

	Absolute concentration (pg g^{-1} lw)				TEQ (pg TEQ g^{-1} lw)			
Year	TCP	PCP/AB	Thermal	Residual	TCP	PCP/AB	Thermal	Residual
1979	22	25	200	82	4.0	6.7	57	20
1980	16	29	117	114	3.0	7.8	33	47
1981	13	35	376	0.0	2.4	9.6	106	15
1982	13	29	256	0.20	2.5	7.8	72	7.8
1983	21	14	267	117	3.9	3.8	76	53
1984	12	26	353	22	2.2	7.0	100	35
1985	8.6	20	135	13	1.6	5.4	38	7.3
1986	14	20	133	75	2.5	5.4	38	24
1987	18	10	319	0.0	3.2	2.7	90	0.0
1989	5.7	18	167	2.6	1.1	4.8	47	4.5
1991	4.1	7.4	75	46	0.76	2.0	21	13
1992	6.5	20	206	23	1.2	5.3	58	11
1993	8.3	9.1	125	11	1.5	2.5	35	3.7
1995	11	12	48	19	1.9	3.4	14	2.3
1996	4.0	14	139	3.9	0.73	3.8	39	0.0
1997	10	11	90	5.8	1.8	3.1	26	2.1
1998	30	31	367	29	5.5	8.3	104	0.0
1999	28	36	79	29	5.1	9.7	22	7.8
2000	39	30	114	68	7.1	8.3	32	11
2001	16	10	51	6.6	3.0	2.8	14	0.20
2002	18	8.4	81	8.5	3.3	2.3	23	1.0
2003	4.0	14	107	28	0.74	3.7	30	0.085
2005	0.65	0.10	41	12	0.12	0.026	12	2.4
2006	24	5.1	27	10	4.5	1.4	7.6	0.25
2007	11	11	48	17	1.9	2.9	14	0.69
2009	24	1.8	29	39	4.5	0.48	8.2	8.0
Z (α = 0.10)	1.645	1.645	1.645	1.645	1.645	1.645	1.645	1.645
1979–1999								
n	18	18	18	18	18	18	18	18
SD	7.5	9.0	107	38	1.4	2.4	30	16
AV	14	20	192	33	2.5	5.5	54	14
UNC (90%)	2.9	3.5	41	15	0.54	0.95	12	6.3
Perc. (%)	5.2	7.8	74	13	3.3	7.2	71	18
2000–2009								
n	8	8	8	8	8	8	8	8
SD	12	9.4	34	21	2.3	2.6	10	4.1
AV	17	10	62	24	3.1	2.7	18	2.9
UNC (90%)	7.1	5.5	20	12	1.3	1.5	5.6	2.4
Perc. (%)	15	8.9	55	21	12	10	67	11
1979–2009								

n	26	26	26	26	26	26	26	26
SD	9.1	10	109	34	1.7	2.8	31	14
AV	15	17	152	30	2.7	4.7	43	11
UNC (90%)	2.9	3.3	35	11	0.54	0.89	9.9	4.7
Perc. (%)	6.8	8.0	71	14	4.4	7.6	70	18

n: number of data points; SD: Standard deviation; AV: Average; UNC: Uncertainty; Perc.: Percent

Appendix C

Absolute and TEQ based contributions of identified dioxin sources in herring from Utlängan (BP) using 2,3,7,8-CDD/F concentrations

	Absolute concentration (pg g^{-1} lw)				TEQ (pg TEQ g^{-1} lw)			
Year	TCP	PCP/AB	Thermal	Residual	TCP	PCP/AB	Thermal	Residual
1988	22	0.30	171	0.0	4.1	0.082	48	0.0
1990	0.0	0.0	50	43	0.0	0.0	14	6.2
1992	10	0.0	83	0.0	1.9	0.0	24	0.0
1993	2.3	0.0	76	13	0.42	0.0	22	1.4
1994	0.66	0.0	23	44	0.12	0.0	6.4	10
1995	50	0.0	79	14	9.1	0.0	22	5.4
2001	25	0.0	73	8.2	4.5	0.0	21	2.3
2002	13	3.5	49	0.69	2.5	0.94	14	2.1
2003	41	12	60	3.2	7.5	3.3	17	0.0
2004	80	58	0.0	0.0	15	16	0.0	0.0
2005	44	4.9	37	0.61	8.1	1.3	11	0.0
2006	67	15	33	4.5	12	4.1	9.2	0.57
2007	40	1.9	44	7.0	7.4	0.51	12	1.0
2008	28	3.0	41	8.9	5.2	0.82	11	0.82
2009	42	4.1	41	1.1	7.8	1.1	12	0.0
Z (α = 0.10)	1.645	1.645	1.645	1.645	1.645	1.645	1.645	1.645
1990–1995								
n	6	6	6	6	6	6	6	6
SD	19	0.12	50	20	3.6	0.034	14	4.1
AV	14	0.051	80	19	2.6	0.014	23	3.9
UNC (90%)	13	0.083	33	13	2.4	0.023	9.5	2.8
Perc. (%)	12	0.045	71	17	8.9	0.047	78	13
2001–2009								
n	9	9	9	9	9	9	9	9
SD	21	18	20	3.5	3.8	4.9	5.7	0.90
AV	42	11	42	3.8	7.8	3.1	12	0.75
UNC (90%)	11	9.9	11	1.9	2.1	2.7	3.1	0.49
Perc. (%)	42	11	42	3.8	33	13	51	3.2
1990–2009								
n	15	15	15	15	15	15	15	15
SD	24	15	39	14	4.4	4.0	11	3.0
AV	31	7	57	10	5.7	1.9	16	2.0
UNC (90%)	10	6.3	16	6.1	1.9	1.7	4.6	1.3
Perc. (%)	30	6.5	55	9.4	22	7.2	63	7.7

n: number of data points; SD: Standard deviation; AV: Average; UNC: Uncertainty; Perc.: Percent

Appendix D

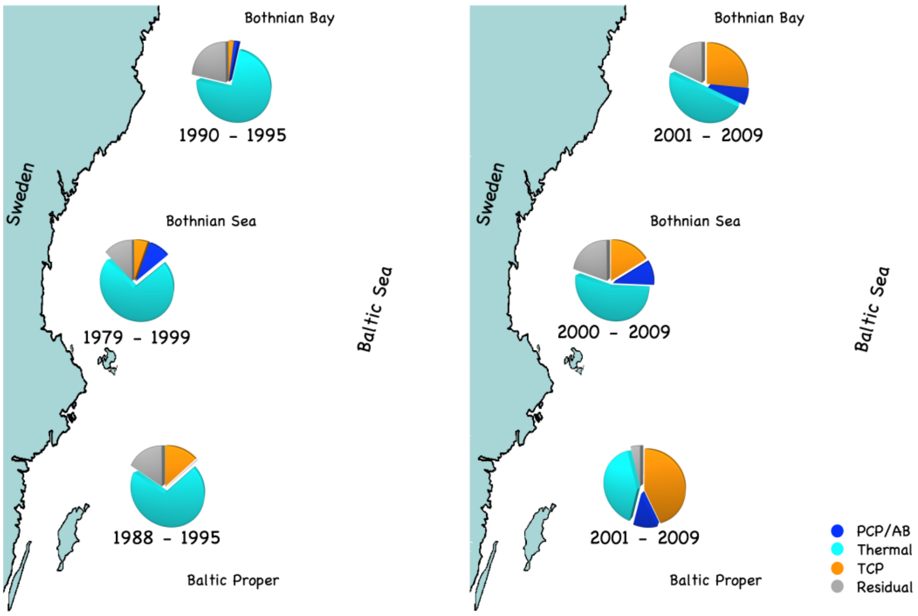
Overall (BB, BS and BP) absolute and TEQ based contributions of identified dioxin sources in Baltic herring using 2,3,7,8-CDD/F concentrations

	Absolute concentration (pg g^{-1} lw)				TEQ (pg TEQ g^{-1} lw)			
Year	TCP	PCP/AB	Thermal	Residual	TCP	PCP/AB	Thermal	Residual
1979– 1999								
n	29	29	29	29	29	29	29	29
SD	11	12	104	32	2.0	3.3	29	14
AV	12	13	148	28	2.1	3.5	42	10
UNC (90%)	3.4	3.7	32	9.8	0.62	1.0	9.0	4.2
Perc. (%)	5.8	6.4	74	14	3.7	4.7	72	18
2000–2009								
n	26	26	26	26	26	26	26	26
SD	19	12	26	17	3.5	3.4	7.4	3.6
AV	30	9.4	54	17	5.6	2.6	15	2.7
UNC (90%)	6.2	4.0	8.4	5.5	1.1	1.1	2.4	1.2
Perc. (%)	27	8.5	49	15	21	9.8	59	10
1979–2009								
n	55	55	55	55	55	55	55	55
SD	18	12	90	27	3.3	3.3	26	11
AV	20	11	104	23	3.8	3.0	29	6.7
UNC (90%)	4.0	2.7	20	5.9	0.73	0.74	5.7	2.4
Perc. (%)	13	7.1	66	14	8.8	7.1	68	16

n: number of data points; SD: Standard deviation; AV: Average; UNC: Uncertainty; Perc.: Percent

Appendix E

Percentage contributions of dioxin sources in Baltic herring calculated on absolute concentration per lipid weight basis (pg g^{-1} lw).



Appendix F

Average contributions (pg g^{-1} lw) of dioxin sources in Baltic herring.