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Temporal Trends of PCDD/Fs in Baltic Sea Sediment Cores Covering the 20th Century

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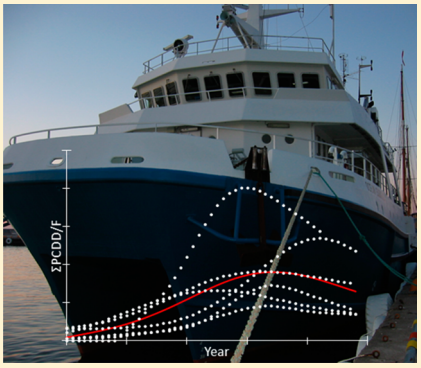
Supporting Information

ABSTRACT: The pollution trend of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the Baltic Sea region was studied based on depth profiles of PCDD/Fs in sediment cores collected from six offshore areas, eight coastal sites impacted by industrial/urban emissions, and one coastal reference site. A general trend was observed for the offshore and coastal reference sites with substantial increase in PCDD/F concentrations in the mid−late 1970s and peak levels during 1985−2002. The overall peak year for PCDD/Fs in Baltic Sea offshore areas was estimated (using spline-fit modeling) to 1994 ± 5 years, and a half-life in sediments was estimated at 29 ± 11 years. For the industrial/urban impacted coastal sites, the temporal trend was more variable with peak years occurring 1−2 decades earlier compared to offshore areas. The substantial reductions from peak levels (38 ± 11% and 81 ± 12% in offshore and coastal areas, respectively) reflect domestic and international actions taken for reduction of the release of PCDD/Fs to the environment. The modeled overall half-life and reductions of PCDD/Fs in offshore Baltic Sea sediment correspond well to both PCDD/F trends in European lakes without any known direct PCDD/F sources (half-lives 30 and 32 years), and previously modeled reduction in atmospheric deposition of PCDD/Fs to the Baltic Sea since 1990. These observations support previous findings of a common diffuse source, such as long-range air transport of atmospheric emissions, as the prime source of PCDD/Fs to the Baltic Sea region. The half-life of PCDD/Fs in Baltic Sea offshore sediments was estimated to be approximately 2 and 4−6 times longer than in semirural and urban European air, respectively. This study highlights the need for further international actions to reduce the levels of PCDD/Fs in Baltic Sea air specifically and in European air in general.



INTRODUCTION

The semienclosed Baltic Sea, being surrounded by industrialized countries, is vulnerable to pollution with combustion-related chemicals and byproducts of industrial processes. One such group of pollutants is the polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/Fs). Starting in the 1960s, a number of actions were taken which significantly reduced primary emissions of PCDD/Fs and other chlorinated industrial compounds to the environment.[1,2] However, PCDD/Fs still remain of high concern in the Baltic Sea region. High levels of PCDD/Fs are observed in fatty fish and other seafood from the Baltic Sea, occasionally exceeding the maximum limit for food and feed assigned by the European Commission.[3−6] In addition to the Baltic Sea region, the concern about PCDD/Fs extends to other European countries. The Scientific Committee on Food of the European Commission emphasizes that the tolerable weekly intake (TWI = 14 pg WHO TEQ kg^{-1} bw day^{-1}) is exceeded by a large portion of the European population.[7] Several studies have shown that atmospheric deposition is the most important source of PCDD/Fs to the Baltic Sea as a whole,[4,8−10] although specific sources may play a more important role locally. Recent sediment layers in the Baltic Sea exhibit elevated levels of PCDD/Fs in primarily coastal areas as a consequence of industrial activity.[10−13] Sundqvist et al.[12] compiled recent data for Baltic Sea surface sediment and found high variability with hot-spot concentrations up to 210 000 pg g^{-1} dry weight (dw) for the sum of *tetra*- to *octa*-CDD/Fs. The lowest values were found in off-shore and reference areas (43−530 pg g^{-1} dw) in the northern sub-basins (Bothnian Bay and Bothnian Sea; see Figure 1), while concentrations in offshore areas in the

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Figure 1. Offshore stations (O1−O6: yellow dots) and coastal stations (C1−C9: red dots) in the Baltic Sea where sediment cores were taken.

southern part (Baltic Proper; see Figure 1) were generally higher (290−2200 pg g^{-1} dw). Background levels of PCDD/Fs are difficult to determine. However, an average concentration of 110 pg g^{-1} dw (sum of *tetra*- to *octa*-CDD/Fs), from Baltic Sea preindustrial sediment samples (1878−1925)[14] can be considered as a possible background level for the Baltic Sea. Apart from evidence for the existence of PCDD/Fs during the preindustrial period, their natural sources have not been properly investigated. Some researchers speculate that combustion activities, mainly domestic use of firewood, coal, and peat, along with forest fires, had acted as preindustrial/natural sources of PCDD/Fs.[14,15]

The current knowledge of PCDD/F time trends in Baltic Sea sediment is limited. Two decades ago, PCDD/F levels for one dated sediment core (1882−1985) from an offshore area in the central sub-basin of the Baltic Proper were reported.[14] A peak level was found for sediment layers dated late 1970s, and thereafter a gradual decrease in PCDD/F concentrations was observed. Subsurface peaks of PCDD/Fs and declining trends have also been observed in sediment cores from the Gulf of Finland (see Figure 1).[10,16] This area is, however, heavily impacted by a previous production of chlorophenol in the Kymijoki River area connecting to the Gulf. The ban of chlorophenol use in 1978[17] followed by the goal set in the fifth EU Action Programme to reduce industrial atmospheric emissions of PCDD/Fs by 90% before 2005,[1] the Stockholm Convention on Persistent Organic Pollutants in 2001,[18] and other actions can be seen as a chain of events that resulted in the reduction of PCDD/Fs in the environment. It is also important to mention the efforts of HELCOM (Helsinki Commission) with regards to monitoring the pollution situation of Baltic Sea and its role in preventing emissions of hazardous substances (including PCDD/Fs) to the Baltic Sea.

The high PCDD/F levels in fatty Baltic Sea fish in combination with exceedance of the TWI by the European population calls for a better understanding of the general PCDD/F pollution trend in the Baltic Sea region as well as on a European scale. The current study is an extensive investigation of PCDD/F contamination time trends in Baltic Sea sediment. We sampled and dated sediment cores from offshore areas of the Baltic Sea and compared their depth profiles to those of coastal areas. Further, we used literature data for European lake sediment, air, and plants from both remote and urban areas for comparison and to gain insight on temporal and spatial trends of PCDD/F levels over a broad scale. The overall objective of this study was to contribute to an improved understanding of the PCDD/F contamination history in the Baltic Sea specifically and in Europe in general. Such new knowledge is important for future science-based actions to further reduce PCDD/F levels in the environment.

MATERIALS AND METHODS

Sampling, Dating, and PCDD/F Analysis of the Sediments. Sediment cores were collected from accumulation bottoms at fifteen stations in the Baltic Sea. Six cores were sampled at stations in offshore regions (>20 km from the shore; Figure 1: O1−O6). These stations are part of the National Swedish Status and Trends Monitoring Programme (NSSTMP) for offshore sediments.[19] Nine cores were sampled near the Swedish coast (Figure 1: C1−C9) in the Gulf of Bothnia (Bothnian Bay and Bothnian Sea). This coastal zone has a long record of industrial activities related to the wood and paper production industry, and previous research has identified industry-related sources of PCDD/F contamination in surface sediments in this region.[8] Based on their proximity to industrial activities, the coastal sites were selected and classified as industrialized areas (Figure 1: C1, C3−C9) or as a reference site (Figure 1: C2). The sampling of coastal sediment cores was conducted from a research vessel (R/V *Sunbeam*) during May and June 2010, whereas the offshore sampling was conducted from a survey vessel (S/V *Ocean Surveyor*) by the Geological Survey of Sweden (SGU) in 2008 (O1−O4 and O6) and 2010 (O5). More information about the samples is given in Table S1 of the Supporting Information (SI).

The sediment cores were sampled using a Gemini Corer (a twin-barrel corer). The physical qualities of the sediment were examined visually and using an X-ray technique as described in the SI. Only undisturbed sediment cores were retained for analysis. The cores were sliced into disks with vertical depth of 2 or 3 cm and were stored at −18 °C until analysis. In total, 8−11 selected slices per core were dated and analyzed for PCDD/Fs (Table S1, SI), adding up to 81 coastal and 60 offshore sediment disks. Samples were prepared for PCDD/F analysis using a protocol which involved spiking with ^{13}C-labeled recovery standards (1,2,3,4-TCDD, 1,2,3,4,6-PeCDF, and 1,2,3,4,6,9-HxCDF), Soxhlet extraction followed by copper treatment, then cleanup using multilayer silica and activated carbon columns as described in Sundqvist et al.[12] All *tetra*- through *octa*-CDD/F congeners were quantified by GC-HRMS using a 60-m DB-5 column.[12] Loss on ignition (LOI) was estimated by heating the samples at 550 °C for 24 h. The fraction of total organic carbon (TOC) was calculated from LOI using a conversion factor specific for Baltic surface sediment (TOC = 0.35 × LOI).[20] The average TOC was 4.0 ± 2.0% (Table S2, SI). No TOC time trends within the cores could be discerned.

Dating of the sediment disks was performed by different methods (Table S1, SI), but mainly by estimating the sediment accumulation rates using the ^{137}Cs method, which was additionally supported by studying the lamination of the cores. The ^{137}Cs method makes use of the fallout of the ^{137}Cs resulting from the Chernobyl accident in 1986[21] (see SI and Figure S1 for details). For stations C1−C3, where the ^{137}Cs

Table 1. Peak years, Peak and Surface Concentrations (pg g^{-1} dw of Sum *tetra*−*octa*-CDD/Fs), and Percentage Reduction from Peak to Surface Concentration in Baltic Sea Coastal and Offshore Sediment Cores

site	characterization of site	period	peak year[a]	peak concentration (pg g^{-1} dw)[b]	reduction from peak[c] (%)	half-life[d] (years)
O1	offshore	1943−2007	1994	1100	52	13
O2	offshore	1941−2008	1985	860	47	22
O3	offshore	1956−2008	1994	590	27	32
O4	offshore	1971−2002	1986	2700	36	26
O5	offshore	1941−2010	2003	1900	39	NA[e]
O6	offshore	1921−2007	1985	1200	24	50
mean ± SD[f]			1991 ± 7	1400 ± 780	38 ± 11	29 ± 14
mean ± SD[g]			1991 ± 5	850 ± 260	42 ± 13	22 ± 10
			Coastal Sites			
C1	industrial	1971−2010	1984	3900	94	6
C2	reference	1902−2010	1986	630	31	41
C3	industrial	1866−2010	1966	5000	77	20
C4	industrial	1969−2008	1982	1400	57	23
C5	industrial	1961−2009	1977	1700	75	17
C6	industrial	1960−2009	1971	1700	89	11
C7	industrial	1925−2009	1968	14000	88	15
C8	industrial	1970−2010	1971	47000	84	15
C9	industrial	1973−2009	1979	17000	86	12
mean ± SD[h]			1975 ± 7	11000 ± 16000	81 ± 12	15 ± 5

[a]Estimated age of a sediment disk that exhibited maximum concentration of PCDD/Fs. [b]Concentration of PCDD/Fs (sum *tetra*−*octa*-CDD/Fs) associated to peak year. [c]Percentage by which the concentration of PCDD/Fs in most recent sediment disk was reduced in relation to peak concentration. [d]Half-life after peak concentration, calculated using measured data and by assuming first-order kinetics. [e]NA = not available due to insufficient data points. [f]For stations O1−O6. [g]For stations O1−O3 (Gulf of Bothnia). [h]For station C1, C3−C9 (Industrialized).

Chernobyl peak could not be identified clearly, dating was performed using the ^{210}Pb method[22] in combination with the ^{137}Cs method (Flett Research Ltd., Canada) and applying the Constant Rate of Supply model (CRS)[23] (Figure S2, SI). The CRS model assumes a constant net rate of supply of unsupported ^{210}Pb, but the rate of sediment accumulation can be variable (see SI for details). The ^{210}Pb measurements showed that the accumulation rates were fairly uniform throughout the cores. Estimated ages by the ^{210}Pb and ^{137}Cs methods were in good agreement for those sediment disks where both methods could be applied (see Figure S3). In the following, the mean age of the top 1 cm and bottom 1 cm of a sediment disk is used to express the year of sedimentation.

Characterization of Time Trends. We used four parameters to describe time trends of PCDD/Fs in the sediment cores: (i) peak year, (ii) peak concentration, (iii) reduction from peak year to current levels (%), and (iv) rate of decline from peak year to current levels (half-life in sediment, $t_{1/2}$). For the individual cores, these parameters were determined by rough methods, e.g. for (i) and (ii), data for the disk that contained the highest PCDD/F level was used. The half-lives in sediment (time for 50% decrease, $t_{1/2}$) were calculated assuming first-order kinetics as applied by Katsoyiannis et al.[24] and Meijer et al.[25] using eqs 1 and 2:

$$C = C_0 e^{-kt} \quad (1)$$

and

$$t_{1/2} = \ln 2/k \quad (2)$$

where C and C_0 are the concentrations of PCDD/Fs in the surface disk and the peak level disk (pg g^{-1} dw), respectively; k is the rate constant (yr^{-1}), and t is time in years (yr). Half-life ($t_{1/2}$) was calculated for cores that had PCDD/F data for a minimum of 3 disks after the peak year (all stations except O5).

As only selected disks (n = 8−11) for each core were analyzed for PCDD/Fs, some uncertainty will be associated with the trend analysis. Still, from these data it could be concluded that the offshore cores exhibited closely resembling characteristics, which justified an estimation of an overall common trend. For this purpose, spline smoothing,[26] a method to fit a smooth curve to a set of observations, was employed (JMP software, version 10, SAS Institute Inc., Cary, NC). This method was selected because other polynomial fittings (such as quadratic and cubic polynomial) could not properly capture the true shape of the trends before and after peak years. We defined that a good fit of the line should have an $r^2 > 0.8$ and the line should pass through the uncertainty range of the measured data points (±29%, see below) for the chemical analysis. Fitted concentrations for each year and each core (O1−O6) from 1960 to the most recent year were obtained, resulting in 286 data points in total. These data points were then used to generate an overall Baltic Sea spline smoothing line.

Quality Control. For identification of PCDD/Fs in the sediment samples, chromatographic peaks with a signal-to-noise ratio (S/N) >3 was required. Limit of quantification (LOQ) was estimated from the average blank concentration (solvent blanks including empty thimbles) plus five times the standard deviation of blank replicates. For congeners with concentrations below LOQ, half of the LOQ-value was used in the data evaluation. Blanks were generally below 10% of the sample concentrations, and therefore no blank correction was done. The average recovery ± SD (standard deviation) of the ^{13}C-labeled recovery standards used for quantification was 84 ± 21%. The analytical uncertainty for the PCDD/F analyses was 29% (estimated from five replicates using the highest relative standard deviation as worst case (OCDD, RSD = 12.4%); 1/4 of this RSD was added to cover for other analytical uncertainties and a factor of 2 was used as safety factor). The reported levels are the sums of all *tetra*−*octa*-CDD/F congeners

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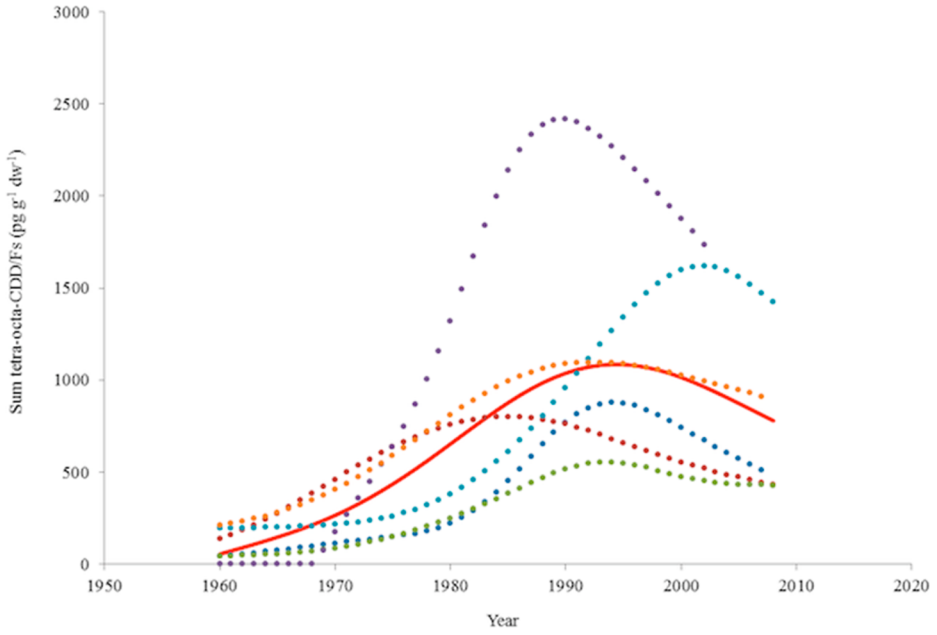

Figure 2. General and individual spline fit curves for the temporal trends of PCDD/Fs in Baltic Sea sediment. Dotted lines: blue, Station O1; red, Station O2; green, Station O3; purple, Station O4; light blue, Station O5; orange, Station O6; red line, Model.

unless otherwise stated. The estimated uncertainties of the Cs-137 and the Pb-210 methods were ±8% and ±11%, respectively.

RESULTS AND DISCUSSION

Reduction from Peak Level. In all of the sediment cores, a distinct increase of PCDD/F levels was seen starting in the mid−late 1970s for offshore areas and in the 1940s−1960s for coastal stations (Figure S4, SI). The increase was followed by a peak level (at a peak year) and subsequent reduction in recent layers (Table 1 and SI Figure S4). In the offshore areas (O1−O6), peak concentrations (590−2700 pg g^{-1} dw) occurred between 1985 and 2003 (average 1991 ± 7 years). The mean reduction from peak to surface layer levels was 38 ± 11%, and the half-life of the PCDD/Fs in the sediment was estimated at 29 ± 14 years. Interestingly, the coastal reference site (C2) exhibited a peak level (630 pg g^{-1} dw), peak year (1986), decline to surface level (31%), and half-life (41 years) similar to the those of the offshore stations. The coastal stations that were impacted by industrial and urban emissions (C1 and C3−C9) had more variable peak levels (1400−47 000 pg g^{-1} dw) which occurred approximately 1−2 decades earlier (1966−1984) than in the offshore and reference areas. The coastal stations also had significantly steeper declines from peak year to current levels (81 ± 12%, p = 0.00001) and shorter half-lives (15 ± 5 years, p = 0.03). Considering only the stations within the Gulf of Bothnia subbasin, the average peak year for the industrialized coastal sites (C1 and C3−C9, 1975 ± 7) occurred 16 years earlier than for those offshore (O1−O3, 1991 ± 5).

Our data thus confirm that national and international actions taken for reduction of the release of PCDD/Fs to the environment[2,27] have been effective in reducing Baltic Sea PCDD/F pollution over time. The later peak levels observed offshore could be a time-lag effect in the slow postdepositional lateral transport of sediment from coastal to offshore areas. Although this explanation may be partly correct, the similar trends for the coastal reference site (C2) and the offshore stations (O1−O6) suggest that a common diffuse source, such as long-range air transport of atmospheric emissions, has had a major impact on the general trends of PCDD/F levels in offshore areas. There are many reports of long-range air transport of PCDD/Fs in general,[28,29] its importance as the most significant input pathway of PCDD/Fs to the Baltic Sea,[8−10] as well as source regions of the air emissions.[30,31] The decrease in PCDD/F levels from the 1990s until current time in Baltic Sea offshore areas observed in this study (38 ± 11%) agrees with a modeled 52% reduction in atmospheric deposition of PCDD/Fs to the Baltic Sea from 1990 to 2010.[32] The peak years for PCDD/Fs in the Baltic Sea offshore areas do not necessarily reflect the peak year of atmospheric PCDD/F emissions, but rather a delayed lag time for the Baltic Sea system to respond to declines in atmospheric pollution. The overall importance of air emissions as the most important current source of PCDD/Fs to the Baltic Sea is supported by the significantly higher surface sediment levels found in the southern parts of the Baltic Sea (1300 ± 420 pg g^{-1} dw for stations O4−O6) compared to the northern stations (470 ± 50 pg g^{-1} dw for stations O1−O3; p = 0.03; Figure S4, SI). Similar data were also reported by Sundqvist et al.[20] Hence, the shorter distance to the hot spot areas for European PCDD/F air emissions[30,31] is reflected in the higher PCDD/F levels of the southern-most stations of the Baltic Sea.

Evaluation of the Temporal Trends of PCDD/Fs in Baltic Offshore Sediments. The overall importance of atmospheric deposition for PCDD/Fs levels and trends justifies an estimate of a regional time trend of PCDD/Fs in Baltic Sea sediments. This was done by using the offshore data on PCDD/F levels and spline smoothing. The r^2 values of the six spline curves were between 0.88 and 0.99 (Table S3, SI), and all the spline curves fitted well through the uncertainty ranges of the data points with few exceptions (all occurring before the peak year (Figure S5, SI)). The half-lives obtained from the spline smoothing were similar to those obtained from the original data, deviating from 0 up to 3 years only (Table S3, SI). The spline smoothing was also used to estimate the half-life for station O5 (32 years), for which too few data points were

Table 2. Environmental Half-Lives of PCDD/Fs in European Sediment, Air, and Plants Based on This Study and Literature Data[a]

country	location (characterization)	media	matrix	peak year[b]	half-life (years)[c]	time period used	reference
Sweden	Baltic Sea (offshore)	sediment	sediment	1994	29 (n = 15)[d,e]	1994−2008	this study
Germany	Lake Stechlin (background)	sediment	sediment	1959	30 (n = 4)[e]	1959−1991	Schramm et al.[33]
Germany	Großer Arbersee (remote)	sediment	sediment	1979	32 (n = 3)[e]	1977−1993	Bruckmeler et al.[34]
Switzerland	Lake Greifen (urban)	sediment	sediment	1959	9 (n = 7)[f]	1959−1998	Zennegg et al.[35]
England	Rothamsted (semirural)	air	herbage	n/k (before 1960)	18 (n = 45)[g]	1960−2004	Hassanin et al.[39]
Germany	Warndt (urban)	air	spruce needles (*P. abies*)	n/k (before 1985)	8 (n = 4)[f]	1985−2004	Rappolder et al.[40]
Germany	Duebener Heide Mitte (urban)	air	Scots pine needles (*P. sylvestris*)	n/k (before 1991)	8 (n = 3)[f]	1991−2004	Rappolder et al.[40]
England	London (urban)	air	air	n/k (before 1991)	3.2−5.9 (n = 66)[h]	1991−2008	Katsoyiannis et al.[24]
England	Manchester (urban)	air	air	n/k (before 1991)	4.1−5.9 (n = 65)[h]	1991−2008	Katsoyiannis et al.[24]
England	Middlesbrough (urban)	air	air	n/k (before 1991)	3.9−11.1 (n = 59)[h]	1991−2008	Katsoyiannis et al.[24]

[a] n = number of data points used. n/k = peak year is denoted as not known, but is likely to be before the start of the monitoring. [b] Year corresponding to maximum PCDD/F concentration, unless otherwise stated. If a range of years is given for the sediment disk, the average year is given. [c] Half-lives were calculated applying first order kinetics (as in this study), unless otherwise stated. All data used are given in SI Table S4. [d] Spline fitting data. [e] Sum of *tetra-* to *octa*-CDD/Fs (pg g^{-1} dw). [f] Sum of 2,3,7,8-PCDD/Fs (pg g^{-1} dw). [g] Sum of *mono* to *octa*-CDD/Fs (pg g^{-1} dw). [h] Half-life given herein.

available for the first-order kinetics approach. The smoothed time trend lines for the six offshore stations allowed for the development of an overall Baltic Sea time trend model as described in the Materials and Methods section (Figure 2). As seen from Figure 2, the peak years of the individual trend lines were similar (1993−1995), with exception of station O2 and O5 (peak years of 1985 and 2002, respectively), indicating that these two stations were influenced by local sources. The overall peak year and half-life obtained for the model are 1994 ± 5 years and 29 ± 11 years, respectively. We argue that these half-lives are more accurate than the calculated half-lives from nonsmoothed data (1991 ± 5 and 29 ± 14 years) based on a small number of disks for each core. To gather information about specific sources that contributed to the trends in the Baltic Sea sediment cores, a detailed examination of congener patterns is required, e.g. as was done for Baltic surface sediments in a previous PCDD/F source apportionment study.[8] Preliminary congener pattern analyses of the sediment cores suggest that atmospheric emissions have been the most dominant external PCDD/F sources for the Baltic Sea as a whole during the 20th century,[4] but that the contamination in coastal areas and in off-shore areas of the northern sub-basins is more complex and variable. A detailed analysis will be presented in a subsequent paper.

Comparison of PCDD/F Time Trends in Sediment, Air, and Plants. The overall temporal trends of PCDD/Fs in Baltic Sea sediment were compared to time trends of PCDD/Fs in other environmental media (lake sediment, air, and plants) by applying the first-order kinetics approach (see Materials and Methods) to data found in literature (Table S4, SI). A detailed description of the literature data used for half-life estimations is presented in Table 2 and SI Table S4. PCDD/F sediment core data covering the last century were published for three European lakes: Lake Stechlin, Germany,[33] Lake Arber (Großer Arbersee), Germany,[34] and Lake Greifen, Switzerland.[35] Lake Stechlin is located in northeastern Germany (Brandenburg province) and can be classified as a background lake that has low impact from point sources because of the absence of industrial activities in its catchment area.[33] Lake Arber is located in southeast Germany (in the Bavarian Forest). Mining and iron smelting activities exist in the region which act as important point sources of atmospheric emissions; however, there are no direct discharges into the lake.[34] Lake Greifen, located near the city of Zürich (11 km) in Switzerland, is highly impacted by urban and industrial activities. As for the Baltic Sea, the three lake cores showed a significant increase in PCDD/Fs levels during the last century, followed by peak levels (during early 1960s or late 1970s; Table 2) and thereafter a decline to current levels. In the background lake (Lake Stechlin) and remote lake (Lake Arber), the half-lives in sediments were calculated to 30 and 32 years respectively (Table 2). These half-lives agree well with the average Baltic Sea half-life of 29 ± 11 years found in this study. Hence, the similarity in PCDD/F half-lives in sediment in the Baltic Sea and the two background and remote lakes support the hypothesis of a general trend for nonindustrialized/non-urbanized (remote) areas in a larger region including the Baltic Sea and supposedly also central Europe driven by a decline in PCDD/F air pollution. The half-life at the more locally impacted Lake Greifen was much shorter (9 years; Table 2), which is similar to the half-lives observed for the coastal Baltic sites in this study. These short half-lives demonstrate that a fast and significant reduction in PCDD/F levels in sediment is achieved when emissions from adjacent point sources are reduced.

Trends in air pollution can be monitored by time series of air or terrestrial plants such as herbage[36] and tree needles.[37,38] Data for archived herbage from the UK (Rothamsted) covering the years 1903 to 2004,[39] and tree needles from two German sites covering the years 1985 to 2004 (Warndt) and 1991 and 2004 (Duebener Heide Mitte)[40] were compiled and used for used for time trend studies of PCDD/Fs in air. Rothamsted is situated 42 km north of London in a semirural location, but with no known major PCDD/F sources in the nearby area. The

sites Warndt and Duebener Heide Mitte, on the other hand, are urban areas located in western and eastern Germany, respectively. It was not possible to identify the peak years for these time series samples, as the peak year appeared earlier than the start of monitoring studies.[24,39,40] The data compiled in Table 2 suggest, however, that the peak year in air had occurred before the peak year of the Baltic Sea off-shore sediments (1994). At one site, (Rothamsted, U.K), herbage date indicate that the peak year in air has occurred as early as before 1960 (Table 2). However, considering the actions to reduce PCDD/Fs, which mainly started in the 1960s, it is likely that the overall European peak year of PCDD/Fs in air occurred after 1960.[1,2]

The calculated atmospheric half-lives (Table 2) show a fairly rapid decline of PCDD/Fs in urbanized and semirural areas during the last decades ($t_{1/2}$ of 3−18 years), i.e. in the same range as for urban lake and Baltic Sea sediment near point sources (Lake Greifen; Baltic Sea sites C1, and C3−C9). Sediment in offshore and remote accumulation bottom areas reflect direct inputs of pollutants (primary sources) combined with recycling of pollutants (secondary sources) previously deposited from air, transported from land to lakes and sea via soil erosion, and subsequently to sediment accumulation bottoms. There is also a continuous resuspension of sediment particles caused by water turbulence, bioturbation, and land rising, etc. It can therefore be expected that offshore sediments respond more slowly to emission reductions in primary inputs to air than the air compartment itself. Our study implies that the half-lives of PCDD/Fs in Baltic Sea offshore sediment and remote lake sediment (range: 29−32 years, Table 2) are approximately 2 times and 4−6 times longer than the half-lives of PCDD/Fs in semirural and urban European air, respectively (including all urban air and plant data in SI Table S4 and using an average of 5 years for the European air studies[24] gives a range of 5−8 years).

Although declining levels in air concentrations of PCDD/Fs are followed by declining levels in Baltic Sea and European lake sediments there are worrying observations for European air. Shatalov et al.[31] concluded from empiric modeling that European emission estimates are underestimated, and that there is a poor quantitative understanding of PCDD/Fs emissions contributing to the Baltic region. Thus there is an urgent need of developing and applying methods capable of identifying the relative importances of sources. These conclusions in combination with evidence for atmospheric deposition being the primary external PCDD/F source for the Baltic Sea presented in this study and in several other independent studies[8−10] urge for further scientific and societal efforts in finding ways for pollution control of PCDD/Fs in European air.

■ ASSOCIATED CONTENT

Supporting Information

Figures of time trends of all fifteen individual cores, spline smoothing lines, Cs-137 and Pb-210 activity plots, and age of sediment disks vs sediment depth from the Pb-210 method (CRS model) and the Cs-137 model. Tables of sediment core characteristics, half-lives in sediments, and literature data used for calculating half-lives. This information is available free of charge via the Internet at http://pubs.acs.org/.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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