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Trends in European Background Air Reflect Reductions in Primary Emissions of PCBs and PBDEs

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Data are presented for polychlorinated biphenyls (PCBs) and polybrominated diphenyls ethers (PBDEs) in passive air samplers (PAS) collected along a rural/remote latitudinal transect from southern UK to northern Norway during 2004–2008. This study is part of an ongoing campaign, using semipermeable membrane devices (SPMDs) as PAS over two year intervals since 1994. Absolute sequestered amounts of selected PCB congeners have decreased in a first order fashion between 1994–2008, with the average time of 8.4 ± 3.2 years for atmospheric concentrations to decline by 50%. PCBs have continued to fractionate with latitude during this period. PBDE concentrations declined by 50% between 2000 and 2008 every 2.2 ± 0.4 years. Results are discussed in terms of sources, long-range atmospheric transport, global fractionation, and clearance processes. It is concluded that the spatial and temporal trends in background European air mainly reflect the strength of primary diffusive emissions of these compounds and subsequently their ongoing declines. The direct evidence for this is similar rates of decline at all the sites; similar rates of decline for all congeners; no systematic change in the fractionation pattern since 1994. The latest results indicate a reduction in the rate of decline for PCBs (and hence in primary emissions).

Introduction

"Persistent organic pollutants" (POPs) is a generic term, encompassing several organic contaminant classes, including polynuclear aromatic hydrocarbons (PAHs), polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), polychlorinated biphenyls (PCBs), and other industrial and agricultural chemicals. Concerns about POPs center around their persistence, bioaccumulation, potential subchronic toxicity, and propensity to undergo long-range atmospheric transport (LRAT). National and international controls on the production, use and emission of POPs have been introduced, notably through the Stockholm Convention (SC) administered with the UN Environment Programme (UNEP) and the LRTAP Convention of the United Nations Economic Commission for Europe (UNECE). The role of the atmosphere is of key importance in supplying POPs to terrestrial and aquatic foodchains in remote areas, and in their recycling. This may follow emissions from point sources (e.g., PCDD/Fs from poorly operated incinerators), or from diffusive primary (e.g., PCBs from building sealants and electrical equipment etc.) and secondary (e.g., "old" pesticides reemitted from soils) sources. This has focused international regulation on reducing environmental emissions (*1, 2*), and risk assessment/modeling efforts on their ambient distribution (*3*).

Major drivers for the current monitoring and research of POPs are (a) Under the SC, signatory countries must conduct source inventories, identify ongoing sources, and provide environmental monitoring evidence that ambient levels of POPs are declining (*1, 2*). Passive air samplers (PAS) offer the opportunity to help address these issues and their deployment has therefore been specifically recommended as part of the global monitoring strategy for POPs (*4, 5*). (b) There is considerable interest in mapping the ambient distribution of POPs, to support national/international air monitoring networks, and to yield useful data for parametrization or evaluation of regional distribution models. Studies have been conducted to demonstrate the feasibility of such "national", "continental", or "global" measurement/modeling programmes using PAS deployed simultaneously across large areas (*6–8*). (c) PAS can also serve as tools in scientific investigations, for example by recording changes in atmospheric POP concentration and composition along environmental gradients (e.g., urban-rural; latitudinal; altitudinal; chiral signatures), to investigate source-sink relationships, and test the global redistribution hypothesis (*7–9*).

The principles behind PAS for POPs have been discussed in some detail elsewhere (e.g., refs *10–12*). Depending on the deployment conditions, the uptake rate may be affected by wind speed (i.e., air-side resistance can limit uptake rates). Samplers are therefore deployed in chambers to buffer the flow of air (to normalize uptake rates for PAS deployed in different locations and protect from compound photodegradation). It has been suggested that labeled (i.e., nonnative) depuration compounds (DCs) can be added to the PAS, so that loss (itself a function of wind speed) can be measured and used as a correction factor (*13–16*).

This study is an extension to the first project to deploy PAS as a tool to investigate atmospheric distribution and processing at the regional scale, which started in 1994 (*9, 17–19*). Semipermeable membrane devices (SPMDs) were used as the PAS. These are "high capacity samplers", so were selected to provide long-term, time integrated data on the distribution and composition of POPs with latitude at background sites in western Europe (see Figure 1). This paper presents the data from the 2004–2006 and 2006–2008 campaigns. PCBs have been monitored over time on the transect, so long-term changes and patterns are emerging. The longevity of the network makes it an extremely valuable way to monitor spatial and temporal trends of POPs, and to gain information on the regional/continental scale processes which influence them. Specifically, data derived from such long-term campaigns can be used to shed light on the processes controlling underlying trends, such as distinguish-

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FIGURE 1. Passive air sampling sites in UK and Norway.

ing between primary and secondary sources to atmosphere, which has important implications for further control strategies.

Materials and Methods

SPMDs. Standard U.S. Geological Survey (USGS) (80−90 cm × 2.5 cm, 75 um membrane thickness, 1 mL triolein) SPMDs were purchased from Environmental Sampling Technologies, St. Joseph, MO.

Sampling Sites and Deployment. Two SPMDs were deployed in Stevenson screen boxes at six sites in Norway and five sites in the UK (*9, 18, 19*). The sampling sites have been described previously and they are shown in Figure 1. Care was taken not to contaminate the SPMDs during deployment. They were transported in airtight containers to the sites and deployed in July/August 2004 and 2006 and collected 2 years later. The minimum and the maximum temperature for the deployment period was recorded by a thermometer in each Stevenson screen box (Supporting Information (SI) Table SI-1). ^{13}C-labeled PCBs (5000 pg each of PCBs 28, 52, 101, 138, 153, and 180) were used as DCs and spiked into the SPMDs.

Extraction and Cleanup. Care was taken to deploy, store and extract SPMDs in the same manner as reported for the previous studies (*9, 18, 19*). After collection SPMDs were stored in solvent-rinsed aluminum tins in the freezer (−18 °C) until extraction. The SPMDs were handled and extracted in a dedicated clean laboratory, which has filtered, charcoal-stripped air and positive pressure conditions. Each SPMD was shaken for 20 s with 100 mL of hexane to remove particles and yield what is referred to as the "exterior fraction". The "interior fraction" was extracted through dialysis in hexane of the SPMDs in the dark for 2 × 24 h. The exterior fraction was also analyzed for all the target analytes but concentrations were below the limit of detection (*9, 18, 19*).

Each sample extract was eluted on a mixed 3% water deactivated alumina and 6% water deactivated silica gel column. The extracts were concentrated using nitrogen evaporation and subsequently cleaned by gel permeation size exclusion chromatography. A mixed 3% water deactivated alumina and 6% water deactivated gel silica column was used as an extra cleaning step and to fractionate the sample. Fraction 1 (F1) contained PCBs and some chlorinated pesticides and Fraction 2 (F2) contained most of the PBDEs. Both fractions were reduced in volume to about 100 μL under N_2 gas and solvent exchanged to 25 μL of dodecane containing PCB 30, [$^{13}C_{12}$] PCB 141, and PBDE 69/180 as internal standard. All fractions (interior and exterior, F1 and F2) were analyzed using a gas chromatography−mass spectrometry (GC-MS) with an EI+ source operating in selected ion mode (SIM) for PCBs, PBDEs, and OC pesticides. Details of the instruments, temperature program and monitored ions are given elsewhere (*9, 20, 21*). The following compounds were monitored in the SPMDs: tri-PCBs 18, 22, 28, and 31; tetra-PCBs 44, 49, 53, 70, and 74; penta-PCBs 87, 90/101, 95, 99, 105, 110, 118, and 123; hexa-PCBs 138, 141, 149, 151, 153/132, and 158; hepta-PCBs 170, 174, 180, 183, and 187; octa-PCBs 194, 199, and 203; HCB; o,p′-DDT, o,p′-DDE, p,p′-DDT, and p,p′-DDE; PBDEs 28, 47, 49, 99, 100, 153, 154, 183.

QA/QC. Field blanks, laboratory blanks and solvent blanks were 50, 15, and 10%, respectively of the total of passive air samples analyzed. The results were blank corrected by subtracting the mean of the field blanks from the mass in the samples. The limit of detection (LOD) was calculated as 3 times the standard deviation of the mean blanks, and values below the limit of detection were not included in any further discussion. The laboratory and the solvent blanks were used as a method check. Surrogate standards were used to monitor the work quality. Recoveries ranged from 64−114% for PCBs (monitored with PCB 54/155) and 62−123% for PBDEs (monitored with PBDE 51/128/190).

Depuration Compounds. As noted earlier, the DCs can be used to estimate air volumes sampled by the PAS. This was done as described in Shoeib et al. (*11*) and Moeckel et al. (*22*), following the details given in SI 2.

Results and Discussion

Masses of Compounds Sampled by the SPMDs. SI Table SI-3 presents the mass of compound detected per SPMD for the deployment periods 2004−2006 and 2006−2008. Only PCB and PBDE congeners with the most complete data sets were included. Data for the previous sampling intervals is also given in the SI (Table SI-3).

Derived Air Volumes and Estimated Air Concentrations. Values for the estimated sampling rates, derived from the use of DCs are given in SI Table SI-2b. The estimated air concentrations derived from these sampling rates (in pg/m^3) are given in SI Table SI-2c. In summary, the spatial and

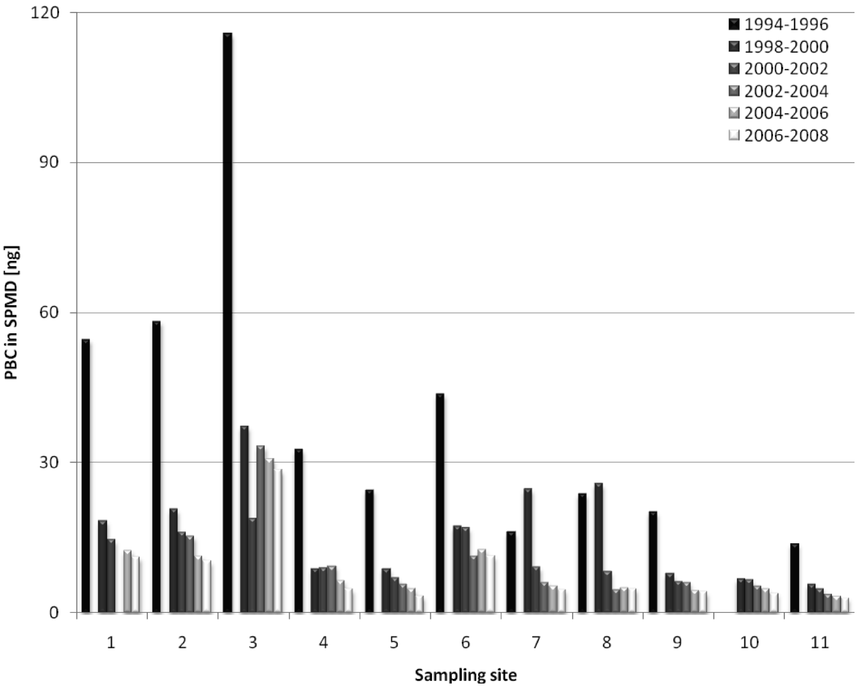

FIGURE 2. Time series for ∑PCB (52, 90/101, 118, 138, 153/132, 180) for all sampling sites.

temporal trends (i.e., the subject of this paper) expressed as masses per sample (pg/SPMD) and as estimated concentrations are similar, so it is appropriate to proceed to the following discussion based on mass per sample.

Spatial Trends for PCBs. The sum of PCBs sequestered in the SPMDs ranged from 6.7−67.3 ng for the deployment years 2004−2006 and 6.1−63.2 ng for 2006−2008. The lowest PCB concentration was observed at the most northerly site (Lakselv, Norway (site 11)) and the highest in Hazelrigg, UK (site 3). These results are consistent with those from the previous sampling campaigns (*9, 17−19*) (see Figure 2). The general spatial trend for all congeners is a decline in concentration with increasing latitude. However, there is a confounding factor, namely proximity to areas of population and likely emissions. The spatially resolved data for sequestered mass of PCB in SPMDs, estimated air concentrations and estimated area-specific emissions (1° latitude, 1° longitude grid, normalized to 1 km^2 for all sites) compiled by Breivik et al. 2007 (*23*) were compared, as explained in the SI Text SI-5. Emission estimates were themselves derived as a function of PCB budget per country and population density (Dr. Yi-Fan Li, Environment Canada).

The SPMD PCB data correlated well to the emission estimates for the individual sampling areas. The correlation is significant in all sampling campaigns (see SI Table SI-5 and Figure SI-5). We conclude from this analysis that diffusive primary emissions (for which population is a suitable proxy) influence the spatial distribution of air concentrations along this transect. Broadly, spatially remote, isolated locations have the lowest concentrations. The northern Norway sites are the most remote from areas of high population and past PCB usage. After splitting the data for the UK and Norway, correlation can still be observed for the UK sites, but not for the Norwegian sites. This might be explained by the higher primary source density in the UK as a controlling factor, whereas in Norway another contribution like LRAT of the pollutant might have a considerable impact (*18*).

Fractionation. A shift in the mixture of the PCB congeners was observed along the transect. Lighter congeners make up a greater proportion of the total PCB loading in the more remote (i.e., more northerly) sites (see Figure 3 and SI Figure SI-6). This has been observed previously along this transect (*9, 17−19*) and elsewhere (*24−26*). However, it is important to consider whether the fractionation pattern and strength has changed over time, because it would be expected to be different in a primary-source versus secondary-source-dominated world (*25*). Fractionation can occur along an urban-rural-remote gradient, purely driven by the relative atmospheric persistence/characteristic travel distances (LRAT potential) of the individual PCB congeners (*12, 27−29*). However, if all primary sources were removed, re-emission from environmental sources becomes a more complex function of environmental compartment properties and environmental conditions (*30*). SI Text SI-6 describes how the data from various campaigns was used to develop a comparison of the fractionation patterns over time.

Figure 3 and SI-6 indicate that there are no significant differences for the fractionation slopes (i.e., the slope derived from plotting the fraction of a single congener versus latitude) of different sampling years. The statistical information on significance for the *t* test is given in SI Table SI-6b.

Temporal Trends for PCBs. The samples analyzed integrate over two year periods, thereby reflecting the underlying net influence of sources and sinks. PCB concentrations for the periods 2004−2006 and 2006−2008 continue the general decline that has been observed since the start of this PAS campaign in 1994. Figure 2 shows the time series for all 11 sites for the six sampling campaigns from 1994−2008 for the sum of the PCB congeners 52, 90/101, 118, 138, 153/132, and 180 (see SI Figure SI-3a for single congeners).

The time trend data can be used to consider important questions, which give insights into the dominant controlling processes on ambient PCB concentrations:

1. Are the rates of decline different at different sites? If the answer is “no”, then this suggests that regional-scale primary emissions are ultimately controlling trends; if the answer is “yes”, then this suggests that secondary sources and local environmental conditions/processes are dominant (*25*).

2. Are there different rates of decline for different congeners? Any such differences may be informative, because they may be controlled by differences in the rates of release of congeners from primary sources (*31*) and/or rates of release

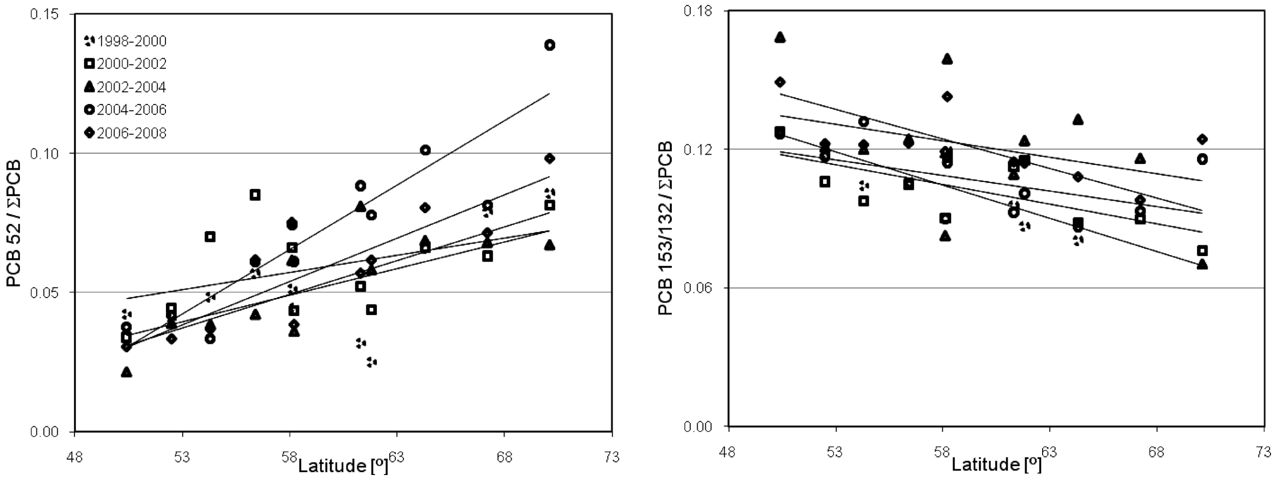

FIGURE 3. Fractionation for all campaigns since 1998 for the congeners PCB 52 (tetra-CB) and PCB 153/132 (hexa-CB).

from environmental reservoirs and degradation/removal processes (*21, 32*).

3. Do the rates of decline reflect the estimated trends in primary emissions? Emissions inventories have been developed for PCBs by various authors (*33, 34*). These are subject to large uncertainties, as discussed elsewhere (*23*), but a comparison of measured ambient trends and predicted emissions is potentially informative.

Derivation of the Time Trend Data. Initially analyses were performed to assess the best descriptor for the form of decline. Visual inspection as well as a comparison of different curve functions resulted in the conclusion that the most appropriate was an exponential function:

$$\mathrm{PCB}_i = \mathrm{PCB}_0{}^{*}e^{-\lambda t_i} \qquad (1)$$

The half-life of PCB concentration $t_{1/2}$ describes the time period it takes to reduce the initial PCB concentration to half its value and was calculated from λ.

$$t_{1/2} = \frac{\ln 2}{\lambda} \qquad (2)$$

Where PCB_i is the mass measured at the time t_i and PCB_0 is the hypothetical mass of PCB measured at t_0. (The end dates of PCB production have to be considered; t_i is restricted to the time period after main production ended in the direct area of influence of the sampling site). The decline constant λ was calculated using linear regression by plotting ln PCB_i against t_i. This definition of half-life should not be confused with half-lives which refer to degradation processes (e.g., the atmospheric reaction of PCB congeners with OH radicals). The average half-life for all congeners estimated in this campaign is 8.4 ± 3.2 years. In contrast, atmospheric half-lives due to reactions with OH-radicals range from days to about a year, depending on the congener (*35, 36*). The decline constant (λ) is therefore controlled by the reduced emissions of PCBs to the atmosphere.

The average half-lives for individual congeners (average across sites) were calculated for the period of 1998−2008 and are given in Table 1. The average was taken for all sites where rates of decline significantly differed from zero observed at the 95% confidence level. 47% of all decline curves could be considered significant with a confidence level of 95%, 67% with a confidence level of 90%. SI Figure SI-4a summarizes the congener data derived across all sites and SI Figure SI-4b illustrates data for PCB 52, 118, 149, and 187 at separate sites. SI Table SI-4 lists the individual half-lives for all congeners at all sites and the statistical parameters for the values.

TABLE 1. Average Time for the Mass of Compound Sampled to Decline by 50% Across All Sites (PCBs, 1998−2008; PBDEs, 2000−2008), Together with the Contribution of the Compound to the Latitudinal Fractionation Slope (All Data at Confidence Level 95%, Data * Confidence Level 90%)

congener		50%-decline period	slope [×1000% PCB per° latitude]
PCB	44	7.6 ± 2.3*	0.9 ± 0.2
	49	7.3 ± 2.4	1.5 ± 0.3
	52	7.4 ± 1.2	2.7 ± 0.4
	70	8.9 ± 4.3	0.5 ± 0.2
	74	7.6 ± 3.5	0.8 ± 0.3
	87	9.9 ± 4.4	−0.1 ± 0.3
	90/101	8.3 ± 3.4	1.1 ± 0.2
	95	7.8 ± 3.1	1.5 ± 0.4
	99	9.0 ± 1.3	0.5 ± 0.3
	105	8.5 ± 2.9	−0.2 ± 0.2
	110	9.0 ± 1.7	−0.5 ± 0.6
	118	8.4 ± 2.3	−0.7 ± 0.4
	138	8.1 ± 3.4	−1.7 ± 0.3
	141	6.6 ± 3.2	−0.2 ± 0.1
	149	7.4 ± 2.9	−0.8 ± 0.4
	153/132	8.7 ± 4.5	−1.8 ± 0.5
	158	9.0 ± 7.8*	−0.1 ± 0.1
	174	7.0 ± 4.9	−0.3 ± 0.1
	180	7.0 ± 5.9	−0.7 ± 0.2
	183	7.7 ± 4.5	−0.2 ± 0.1
	187	9.2 ± 6.4	−0.8 ± 0.2
PBDE	47	2.4 ± 0.2	
	49	1.4 ± 0.4	
	99	3.3 ± 0.3	
	100	4.0 ± 0.4	
	153	1.4 ± 0.3	
	154	3.3 ± 0.1	

At some of the Scandinavian sites of the *European Monitoring and Evaluation Programme (*EMEP) (*37*) PCB concentrations in the atmosphere have been monitored for more than a decade with high volume active air samplers. This data is available on the EMEP Web site. The average half-life of PCBs monitored at three Swedish sites (SE02 (1994−2002), SE12 (1995−2008), SE14 (2002−2008)), and two Norwegian sites (NO01 (2004−2009), NO42 (1998−2008)) was 8.2 ± 2.6 years, corresponding very well with the passive air sampling data discussed here. From another important active air monitoring network, the integrated atmospheric deposition network (IADN) for the Great Lakes area of North America, PCB half-lives for sites on Lake Superior, Lake Michigan and Lake Erie were reported by Buehler et al. (*38*)

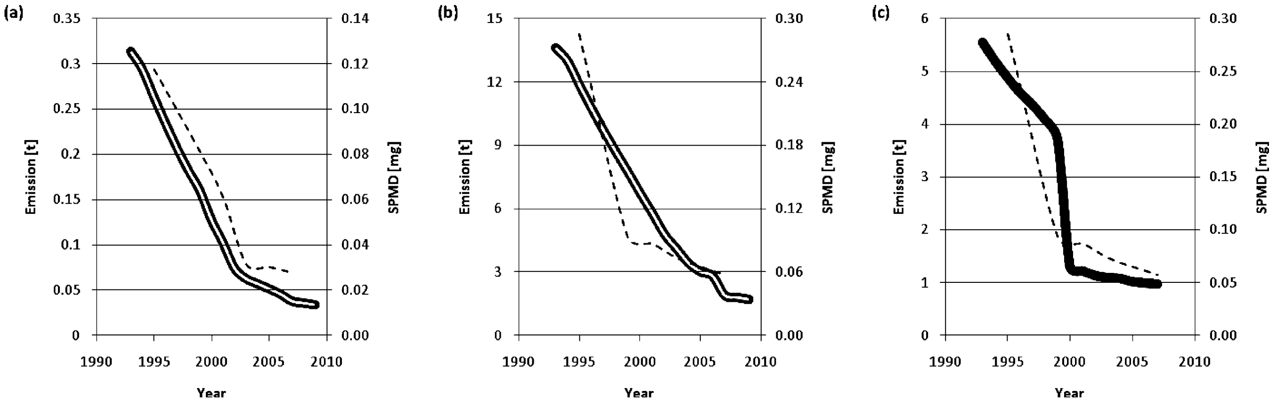

FIGURE 4. Comparison of temporal trends for $\sum$PCB (52, 90/101, 118, 138, 153/132, 180) for emission estimates from Breivik et al. (*23*) (=) and PCB masses monitored in all SPMDs in Norway (a) and the UK (b) (---); UK emission data from NAEI (*39*) for all PCB congeners (—) and PCB masses monitored in all SPMDs in the UK (c).

as 18.0 ± 7.1 years, 8.3 ± 1.5 years and 9.1 ± 1.4 years, respectively. As for the EMEP data the half-life values for Lake Michigan and Lake Erie are not significantly different from those derived in this study.

Summary of the Time Trend Data. In general there were no significant differences in trends *between sites* (SI Table SI-4). Similarly, the half-lives of the individual congeners cannot be considered significantly different (SI Figure SI-4a). These results are consistent with the hypothesis that primary emission sources are still the controlling influence of PCB concentrations and consequentially their decline.

Comparisons between the Field-Derived Measurements of Air Concentrations and Estimates of Atmospheric Emissions. Given that: (a) the results presented here support the hypothesis that primary sources are dominating underlying trends; (b) deriving accurate estimates of the amount and temporal trends of primary emissions is difficult for PCBs as the global mass production ceased decades ago; it is valuable to use this unique long-term field data set to cross-check or 'calibrate' the emissions estimates. Figure 4 therefore compares the estimated trends of PCB emissions to the measured trends in the SPMDs. The data for PCB emissions is taken from projected declines in PCB emissions (*23*) and the UK National Atmospheric Emissions Inventory (NAEI) (*39*). The temporal trends in the air data broadly follow the trends of the emission inventories.

The emission inventory compiled by Breivik et al. (*23*) estimates PCB emissions peaking in 1973 in the UK and Norway and a steady decline of ~13−15% per annum in PCB emission. The measurements clearly support the estimate of the slope of decline for much of the time series (see Figure 4).

PBDEs. SI Figure SI-3b shows the data for $\sum$PBDE for the four sampling campaigns spanning the years 2000−2008. The masses ranged between 130−3200 pg $\sum$PBDE per SPMD, considerably less than for the PCBs. Results were often close to detection limits. Not all the congeners monitored could be detected at all sites. The data (SI Table SI-3b) showed a general decline in PBDE levels over time, although with less consistency between sites than for PCBs. Indeed, a consistent decline was only observed at 4 of the 11 sites. This hindered the calculation of the rates of decline. Declines could only be calculated consistently for a selection of individual congeners (see Table 1), for which half-lives ranged from 1.4 to 4.0 years. The absolute decline of $\sum$PBDE levels found in SPMDs between 2000−2002 and 2006−2008 ranged from 35−57%. There was a correlation between levels and population density for the sampling period 2006−2008, but not for the other periods (unlike for PCBs).

Implications of the Time Trend Data. The declines in PCB levels through the 1990s (and indeed evidence of earlier declines through the 1980s) (*40*) presumably reflect the early voluntary and subsequent national bans on PCB production and use (*34*). The Stockholm Convention, which entered into force 2004, appears to have had no discernible effect yet in hastening the ambient decline of PCBs.

A recent study by Carlson et al. (*41*) reports on longer-term trends than possible here (1970−2003), in an investigation of PCBs in lake trout from the Great Lakes. With the longer time series and a much greater number of individual data points, they were able to discern a change in the *rates of decline*, before/after the 1980s. Half-lives generally increased in the fish in the latter part of the study, such that the overall data set was not best described as a simple exponential function. Such differences in rates of decline could not be unambiguously observed in our shorter and more limited data set.

The Carlson et al. (*41*) observations might be related to a change in source patterns over the last decades, i.e. decreasing decline of primary emissions especially with an increasing time interval to legislations for the regulation of productions, applications and disposal of PCBs. Their observations are particularly interesting in the context of the concept of the *temporal remote state* proposed by Stroebe et al. (*42*) and Scheringer et al. (*43*). It is hypothesized that persistent pollutants would approach this condition long after emissions stop. These authors argue that as primary sources reduce, ambient POPs will move to a state where the ambient rates of decline are essentially controlled by dissipation from the controlling environmental reservoir (e.g., soils) for the pollutant. The exchange between the "reservoir" compartment and other environmental compartments will regulate the overall distribution of the pollutant. The two main characteristics of pollutants in the temporal remote state are an equal decline rate in all compartments and a temporally constant distribution of the chemical between the compartments. The question arises as to whether PCBs are approaching the temporal remote state. This study indicates that primary sources are still controlling the trends in ambient levels, some 40 years after voluntary bans on PCBs were first introduced. The Carlson et al. (*41*) data set suggests the beginnings of a transition toward the temporal remote state. Our study and others on long-term ambient trends—now and into the future—should provide an important means of investigating these processes further.

Acknowledgments

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Supporting Information Available

Details about temperature conditions, depuration compounds and sampling rates, full data sets for the discussed compounds for mass per SPMD as well as air concentrations, emission data, information on half-live and fractionation data. This material is available free of charge via the Internet at http://pubs.acs.org.

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