A Quantitative Investigation of Temporal Effects on Atmospheric PCB Concentrations Near the Great Lakes

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Abstract

Atmospheric concentrations of gas-phase polychlorinated biphenyls (PCBs) were measured at three sites near the Great Lakes as part of the Integrated Atmospheric Deposition Network. Multiple regression analysis was used to relate atmospheric PCB concentrations to meteorological conditions and time. As expected, atmospheric temperature had a very significant effect on gas-phase PCB concentrations. Atmospheric levels of PCBs have remained unchanged as a function of time near Lake Superior but have declined slightly over time near Lakes Michigan and Erie. The rate constants at the latter two sites indicate an environmental half-life in the atmosphere of approximately 6 years, which agrees well with PCB half-lives in other environmental compartments

Introduction

Though production of PCBs in the United States stopped in 1977, they have lingered as ubiquitous environmental contaminants due to their chemical stability. Considerable effort has been put into determining their fate and clearance time. Concentrations have been decreasing in soils, sediment and peat cores, vegetation, and water.[1-4] Studies in biota have shown concentrations to be decreasing with a half-life of approximately 6-15 years, though occasionally no change was seen.[5-12] Atmospheric PCB concentrations, however, seem to have remained constant over this time,[13-16] which is anomalous given that the atmosphere is the transport medium to the other environmental compartments.

Atmospheric concentrations of PCBs on a relatively long-term basis have been studied by several groups.[13-16] Unfortunately, seasonal variability has obscured the long-term trends, if any. In addition, differences in the frequency and duration of previous studies have complicated attempts to understand temporal trends. This paper will report on gas-phase PCB data obtained from three U. S. sites of the Integrated Atmospheric Deposition Network: Eagle Harbor on Lake Superior, Sleeping Bear Dunes on Lake Michigan, and Sturgeon Point on Lake Erie. As much as five years worth of data now exist for some of these sites, allowing us to investigate temporal trends in atmospheric PCB concentrations.

Experimental Methods

Sampling protocol. Air samples were collected using high-volume samplers fitted with automatic filter covers to prevent passive loading. Samples were collected every 12 days for a period of 24 hours, starting in November 1990 at Eagle Harbor and in November 1991 at Sleeping Bear Dunes and Sturgeon Point. Total air flow through the high-volume sampler was approximately 800 m^3. A quartz fiber filter was installed for the collection of particulates, and gas-phase organics were collected on XAD-2 resin. Each site was equipped with a 10 m tower for the collection of meteorological data. Data were recorded automatically every six seconds using a data-logger and output as mean hourly values.

Analytical. PCBs and other compounds were removed from the adsorbent material by 24 hour Soxhlet extraction using a 1:1 mixture of acetone and hexane. Silica gel was used to fractionate the concentrated Soxhlet extract, with the PCB fraction eluting in hexane. Chromatographic separation was performed on a Hewlett Packard 5890 gas chromatograph (GC), using a 60 m × 0.25 mm i.d. (d_f = 0.10 μm) DB-5 column (J&W Scientific). The GC was equipped with an electron capture detector and an autosampler (Hewlett Packard 7673A). Injection of 1 μL was performed in the splitless mode. The carrier gas was hydrogen, and the detector make up gas was nitrogen. The temperature program was 100 °C for 1 min, 1 °C/min to 240 °C, 10 °C/min to 280 °C with a 20 min hold. The injector temperature was 250 °C, and the detector temperature was 350 °C.

Data manipulation. Approximately 100 individual PCB congeners were quantified using internal standards (PCB 30 or PCB 204) which had been added just prior to chromatographic analysis. Each congener concentration was converted to a partial pressure using the ideal gas law, thus adjusting for the molecular weight of the compound and for the average atmospheric temperature during the sampling period. The partial pressures of the individual congeners were then summed to give a value for total PCBs. A product-moment correlation analysis indicated that the individual congener partial pressures were strongly correlated with the total PCB value; therefore, total partial pressures have been used for the investigation of trends.

Results and Discussion

One of the objectives of the Integrated Atmospheric Deposition Network is to identify temporal trends in concentrations of persistent substances such as PCBs, and to determine if atmospheric levels have been declining since PCBs were banned. The atmosphere, however, is a dynamic system, subject to both cyclical and non-cyclical fluctuations. There are major fluctuations in temperature, for instance, and this is responsible for seasonal trends. Thus, any attempt to determine temporal trends must consider atmospheric temperature. Starting with the relationship between the natural logarithm of the partial pressure and the inverse temperature, we added meteorological conditions (wind speed and direction) and time as parameters, giving equation 1.

$$\ln(P) = a_0 + a_1\left(\frac{1}{T}\right) + a_2\ln WS + a_3\sin WD + a_4\cos WD + a_5 time \qquad (1)$$

Notice that a_5 is a first-order rate constant. The results for equation 1 are shown in Table 1. Not surprisingly, temperature is the predominant parameter, but the coefficients for the time term (a_5)

Table 1. Regression Parameters and Standard Errors for Equation 1.[a]

	Eagle Harbor	Sleeping Bear Dunes	Sturgeon Point
	$\ln P = a_0 + a_1 (1/T) + a_2 \ln WS + a_3 \sin WD + a_4 \cos WD + a_5\ time$		
a_0	**-17 ± 11%**	**-16 ± 11%**	**-15 ± 9%**
a_1	**-4221 ± 13%**	**-4426 ± 11%**	**-4450 ± 8%**
a_2	-0.01 ± 100%	-0.18 ± 89%	**-0.32 ± 35%**
a_3	-0.09 ± 90%	**-0.20 ± 39%**	**0.16 ± 40%**
a_4	-0.17 ± 65%	-0.05 ± 158%	-0.08 ± 102%
a_5	0.00009 ± 130%	**-0.00037 ± 33%**	**-0.00031 ± 34%**
-r	0.625	0.686	0.773

a. Coefficients with a standard deviation less than 50% are shown in bold-face.

Table 2. The Half-lives of PCBs in Various Environmental Compartments.

Compartment	Half-life (years)	Reference
Air, Lake Superior	no change (in 10 years)	Baker & Eisenreich (*13*)
Air, Bermuda	no change (in 23 years)	Panshin & Hites (*14*)
Air, Bloomington	no change (in 7 years)	Panshin & Hites (*15*)
Water, Lake Superior	2.5-6.3	Jeremiason *et al.* (*3*)
Water, Lake Michigan	9	Pearson *et al.* (*4*)
Moss, Norway	6-14	Lead *et al.* (*2*)
Soil, U.K.	3-17	Alcock *et al.* (*1*)
Bloaters, Lake Michigan	8	Hesselberg *et al.* (*6*)
Trout, Lake Michigan	4	Devault *et al.* (*5*)
Trout, Lake Ontario	10	Borgmann & Whittle (*7*)
Fish, Lake Michigan	7	Stow (*8*)
Gull eggs, Lake Ontario	6	Irwin & Lageroos (*9*)
Gull eggs, Lake Ontario	≥ 21	Smith (*10*)
Arctic ringed seals	6	Addison *et al.* (*11*)
Arctic polar bears	15	Norstrom *et al.* (*12*)

are interesting. For Eagle Harbor, this term has a standard error of about ±130%; however, note that the standard error for this term at Sleeping Bear Dunes is ±33%, and at Sturgeon Point it is ±34%. At both Sleeping Bear Dunes and Sturgeon Point, the time coefficients are about the same and negative, indicating a decline in partial pressures over time.

Based on an average rate constant of 0.00034 day^{-1}, the environmental half-life of PCBs in the atmosphere near Lake Michigan and Lake Erie is about 6 years. This differs considerably from previously reported atmospheric PCB data; see Table 2. Panshin and Hites[15] sampled air in Bloomington, IN in 1993 and compared the results to the 1986-87 study of Hermanson and Hites.[16] They found no evidence that atmospheric concentrations were changing. Panshin and Hites[14] also sampled air coming in off the ocean to Bermuda. These results were compared to 20 years of literature data, and again no decline in atmospheric PCB concentrations could be detected. These later experiments focused on background atmospheric PCB levels, and these authors avoided any local influence by sampling only when the wind was blowing over the open ocean. Thus, the situation in Bermuda may be similar to the situation at Eagle Harbor, where there is no statistical indication that atmospheric PCB levels are changing. This result is similar to that of Baker and Eisenreich,[13] who reported that atmospheric PCB concentrations over Lake Superior remained relatively constant during a 10 year period.

The half-life of about 6 years for atmospheric PCBs at Sleeping Bear Dunes and Sturgeon Point compares favorably with trends observed in other environmental compartments; see Table 2 for selected examples. PCBs have been declining in water with half-lives of 3-9 years.[3,4] A half-life of 6-14 years can be estimated for PCB concentrations in moss,[2] and 3-17 years for soil.[1] The average half-life of PCBs in fish is about 7 years,[5-8] but in gull eggs, it seems to vary from about 6 to over 25 years.[9,10] For both fish and gull eggs, determining temporal trends in PCBs is complicated by internal lake processes such as changes in prey dynamics.[10] The half-life of PCBs in Arctic ringed seals[11] is about 6 years, and in polar bears[12] it is about 15 years. This latter value may be higher due to the paucity of data available for analysis of temporal trends, or it may be attributable to the higher trophic level of polar bears.

In contrast to these clear changes in the water and biota PCB concentrations, the lack of any observable change (until now) in the atmospheric PCB concentrations was peculiar. It seems likely that long-term changes have been hidden by large seasonal (temperature) effects. In addition, most long-term comparisons were based on data obtained by different researchers, using different analytical methods and different time periods, making direct comparisons nebulous. This problem was one of the reasons for the creation of the Integrated Atmospheric Deposition Network. The atmosphere is a dynamic system, and it is impossible to account for its normal variations without long-term study. While this study is long compared to other such studies, it is not yet long enough to sufficiently account for normal climatic variability. Thus, it is important to continue to make measurements of PCBs (and other compounds) at these sites.

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