Temporal Trends in a Long Term Study of Vapor Phase PCB Concentrations Over the Great Lakes

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1. Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants, having been found even in regions remote from anthropogenic activity. In the 1970s, for instance, PCBs were found in the relatively clean waters of Lake Superior, causing speculation about the source of these contaminants. Eisenreich *et al.*[1] attempted to quantify those sources and concluded that atmospheric deposition accounted for 85% of the total PCB inputs to the lake. Hites and coworkers[2] found PCBs in the air, water, and sediments of Siskiwit Lake, an isolated lake on Isle Royale, an island in Lake Superior. They also determined volatilization to be a significant output mechanism. The only reasonable explanation for the presence of these organic compounds in this insular water was atmospheric transport and deposition. The relative importance of this deposition to the overall contaminant loadings to the Great Lakes remained to be determined.

Several attempts have been made to estimate the relative importance of atmospheric deposition.[3,4] In each case it was noted that insufficient information existed to make this determination. Specifically, it was noted that there were insufficient data and that sampling and analytical methods needed to be standardized. In an attempt to rectify this situation, the United States and Canada established the Integrated Atmospheric Deposition Network (IADN), designed to collect regional data representative of the atmosphere over the lakes and to create a data base of semivolatile organic contaminant concentrations that could be used in research on atmospheric processes.

IADN consists of five master sampling stations, located primarily on remote shorelines of the Great Lakes in the U.S. and Canada, as shown in Figure 1. This paper will report on PCB data obtained from the three U.S. sites: 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 for investigations of temporal trends in atmospheric concentrations of PCBs and for comparisons between the three geographic locations.

2. Experimental Methods

Sampling. IADN vapor phase samples were collected for a period of 24 hours every 12 days. Total air flow through the high-volume sampler over the sampling period was approximately 800 m^3. A quartz fiber filter was installed for the collection of particulates, and vapor phase organics were collected on XAD-2 resin.

Analytical. Samples were Soxhlet extracted for 24 hours 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 the initial hexane fraction. Chromatographic separation was performed on a Hewlett-Packard 5890 gas chromatograph, using a 60 m x 0.25 mm (d_f = 0.15 μm) DB-5 column (J&W Scientific, Folsom, CA, USA). Approximately 100 individual PCB congeners were determined using an electron capture detector. Vapor phase concentrations were calculated for individual congeners, then converted to the natural logarithm of the partial pressure, thus adjusting for the molecular weight of the compound and for the actual average temperature over the sampling period. The partial pressures of the individual congeners were summed to give a value for total PCBs. A product-moment correlation analysis indicated that the majority of the individual congener values were strongly correlated with the total PCB value; therefore, total values were used for the investigation of trends and geographic comparisons.

3. Results

Generally, total PCB concentrations ranged from about 30 pg/m^3 to about 80 pg/m^3, though values in excess of 200 pg/m^3 were occasionally observed. High vapor phase concentrations did not correspond to high air temperatures as had been expected; the highest Eagle Harbor value occurred in the Spring, and the highest Sturgeon Point value occurred in the Winter. Previous studies had reported vapor phase concentrations followed temperature, with the highest values in the warmer summer months.[5,6] Concentrations were relatively consistent from year to year. Geographically, Eagle Harbor tended to have the most consistently low values. Sturgeon Point, within 20 kilometers of a major urban site (Buffalo, New York), exhibited the greatest range of concentrations. If concentration increased at one site, it generally increased at all the sites, though the amount of increase differed.

To further examine the temperature dependence of the system, Clausius-Clapeyron plots showing the relationship between vapor pressure and temperature were developed for each site, according to Equation 1. An example of this plot for data for Sleeping Bear Dunes is shown in Figure 2.

$$\ln(P) = \left(\frac{-\Delta H}{R}\right)\left(\frac{1}{T}\right) + \text{const} \qquad (1)$$

where P is the partial pressure in atmospheres; T is the temperature in K; ΔH is the heat of vaporization; and R is the gas constant.

This plot shows data from December 1991 to February 1995, but no differences were seen by plotting the data on a yearly basis. A linear regression applied to this data gives a linear correlation coefficient of 0.4487, which is significant at the 99% confidence level. The heat of vaporization, calcu

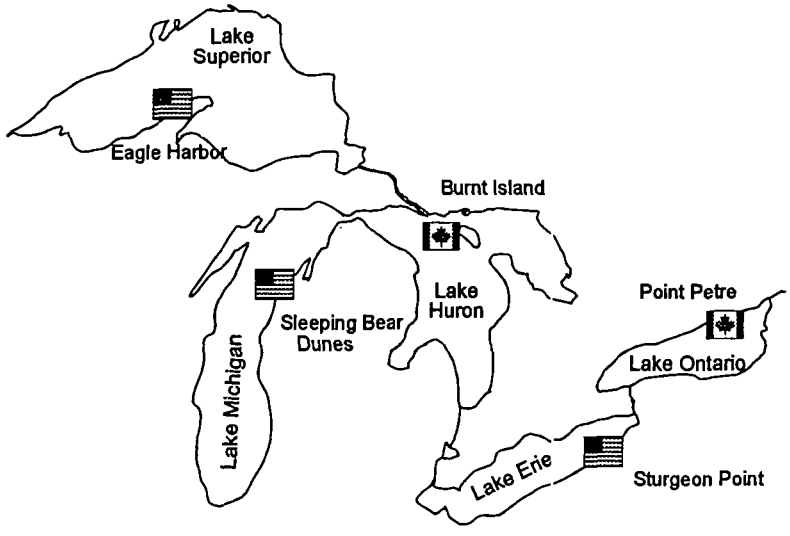

Figure 1. Map showing three U.S. and two Canadian sampling sites for IADN.

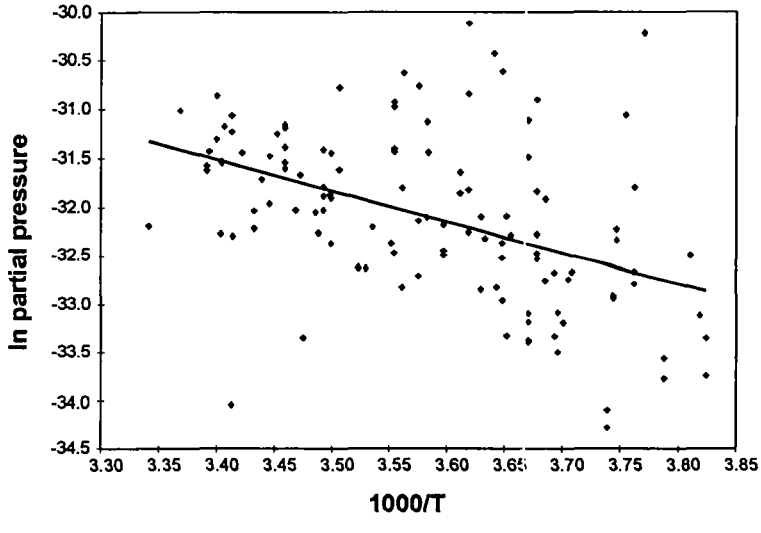

Figure 2. Clausius-Clapeyron plot for vapor phase PCB data from Sleeping Bear Dunes, 12/91 to 2/95.

lated from the slope of the regressed line, is about 26 kJ/mol. This is a factor of three lower than previously reported heats of vaporization for PCBs of approximately 74 kJ/mol[6] and 63 kJ/mol.[7]

4. Conclusions

No obvious decline is seen in atmospheric vapor phase concentrations of PCBs over time. While this study is long-term compared to other analytical studies, it is not yet long-term enough to account for normal climatic variability. Thus it is important to continue to monitor these sites. Temperature is a major factor controlling partial pressures of PCBs, but it is not sufficient to account for all of the variability. The heat of vaporization calculated from Clausius-Clapeyron plots in this study is significantly lower than that calculated from other studies, indicating a departure from thermodynamic control. It is believed that wind forces affecting air-water exchange play a significant role, and these investigations are continuing.

5. Acknowledgments

We warmly acknowledge the technical assistance of Ilora Basu. We also thank the Great Lakes National Program Office for funding of this project through U.S. EPA grant number GL995656.

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