

Temporal and Spatial Trends of Gas Phase Polychlorinated Biphenyls in the Great Lakes Atmosphere

Matt F. Simcik, Ilora Basu, Clyde W. Sweet*, and Ronald A. Hites

School of Public and Environmental Affairs and Department of Chemistry, Indiana University, Bloomington, Indiana 47405 USA. *Illinois State Water Survey, Champaign, Illinois 61820 USA

Introduction

The input of polychlorinated biphenyls (PCBs) to the Great Lakes has been suggested to be primarily through atmospheric deposition (1). In an attempt to better understand the spatial, and temporal behavior of PCBs in the Great Lakes atmosphere and how they affect atmospheric deposition, the United States and Canadian governments together created the Integrated Atmospheric Deposition Network (IADN). The IADN established one master air sampling station on each of the five Great Lakes in a rural area removed from urban influence. Several satellite stations were also established, some near urban areas. This paper will present results from the three American master stations for Lakes Superior, Michigan, and Erie from date of inception to August, 1997. The Lake Superior master station is located at Eagle Harbor on the Keweenaw Peninsula and sampling began in November 1990. The Lake Michigan master station is located at Sleeping Bear Dunes on the Northwest coast of Michigan, and Sturgeon Point is the master station on Lake Erie located Southwest of Buffalo, New York. Sampling at the Sleeping Bear Dunes and Sturgeon Point sites began in November 1991. All sampling equipment is located within 1 km of the shoreline.

Hillery et al. (2) previously reported results from the U.S. sites for the first 5 years of the IADN study. These authors concluded that the sum of PCB congeners (Σ PCB) concentration was well correlated with temperature using the Clausius-Clapeyron equation:

$$\ln P = a_0 + a_1 \left(\frac{1}{T} \right) \quad (1)$$

where P is atmospheric partial pressure of PCBs (in atm) and T is the atmospheric temperature (in K). These authors also concluded that there was a correlation at some of the sites between PCB concentrations and wind speed, wind direction, and/or time. The significant correlation with time for Sleeping Bear Dunes and Sturgeon Point led to atmospheric half-lives of approximately 6 years for Σ PCB at these two sites. This paper extends the work of Hillery et al. (2) by

two years, and takes a more in depth look at individual congeners and processes governing their gas phase concentrations.

Because of the great number of samples associated with each site, it is possible to segregate the samples into three types of air masses: those originating over the lake surface, those originating over the land surface, and those with air masses varying over both lake and land. This type of data segregation reduces the need to model the PCB concentrations using wind direction. Thus, the natural logarithms of the partial pressures of individual PCB congeners and Σ PCB were regressed using a multiple linear regression as a function of temperature, time, and wind speed:

$$\ln P = a_0 + a_1 \left(\frac{1}{T} \right) + a_2 (\text{time}) + a_3 (\text{WS}) \quad (2)$$

where *time* is in days and WS is wind speed in m/s. The multiple regression model was run by backward elimination on SAS for over-water and over-land samples at each site. An enthalpy of vaporization and a half-life were calculated from the temperature and time parameters in equation (2) for each wind sector and site.

Materials and Methods

Details of the sampling and analytical procedures are described elsewhere (2). In general, air samples were taken every 12 days for 24 hours at each site using a high-volume air sampler equipped with a quartz fiber filter and adsorbent to collect the particle and gas phase PCBs, respectively. Prior to May 4, 1992, the adsorbent was polyurethane foam plugs (PUF). Subsequently, Amberlite XAD-2 resin has been used as the adsorbent. Air flow rates through the samplers were 34 m³/hr, and this rate was checked periodically.

The adsorbents were extracted for 24 hours in Soxhlet apparatuses using 50% acetone in hexane. The extracts were concentrated, and the solvent exchanged to hexane using rotary evaporation. Interfering compounds were removed by eluting the extracts on a silica gel column with hexane. The eluents were further concentrated under a gentle stream of pre-purified nitrogen. The PCBs were separated on a Hewlett Packard 5890 gas chromatograph and quantified using an electron capture detector.

Each site was also equipped with a 10-m tower to collect meteorological data. Temperature, relative humidity, wind speed, wind direction, and solar radiation were collected every 6 seconds and reported as hourly means.

Results and Discussion

Significant dependence of the natural logarithm of the partial pressure on wind speed was only found for a few individual congeners. PCBs at all sites exhibited a strong dependence on temperature. For most congeners, temperature had the strongest influence on the variability in gas phase concentration. From the temperature parameters of equation (2) enthalpies of vaporization were calculated. Over-land samples at all sites produced enthalpies of vaporization within a range of 13 to 65 kJ/mol. These values are about one third those predicted by Falconer and

Bidleman (3) (64-106 kJ/mol) in the laboratory using gas chromatographic retention, but our values were similar to values observed by Honrath et al. (4) near Lake Superior (20-40 kJ/mol). There was no difference in over-land enthalpies for specific congeners among the sites. This suggests that the same process is occurring for the over-land samples at all three sites, but it is not well predicted using laboratory based enthalpies. There was, however, some difference between the over-land and over-water enthalpies at each site.

Honrath et al. (4) estimated enthalpies of vaporization from Henry's Law to give a range in values of 60 to 70 kJ/mol. For each congener, the enthalpy estimated from Henry's Law was lower than that from the Falconer and Bidleman (3) data. Honrath et al. (4) observed enthalpies similar to estimates from Henry's Law for over-water samples when the air above Lake Superior was stable, but found lower values during unstable periods. Over-water enthalpies from our study ranged from 18 to 70 kJ/mol for the three sites, but showed differences among sites and from over-land samples. While the calculated enthalpies are not statistically different for each congener between over-land and over-water samples for each site, there are consistent differences in the values calculated. There seems to be no difference in enthalpies for over-water samples between Lakes Superior and Erie, but they have consistently lower enthalpies of vaporization for over-water samples vs. over-land samples. This agrees with the estimates and measurements of Honrath et al. (4). Lake Michigan enthalpies exhibited the opposite behavior: over-water enthalpies were consistently higher than over-land enthalpies and consistently higher than the over-water enthalpies from Lakes Superior and Erie. Differences among observed and predicted enthalpies may be a result of instability in the atmosphere above the lake surface as seen in Honrath et al. (4), or there may be other confounding factors.

Similar to the findings of Hillery et al. (2) the Σ PCB at Lake Superior exhibited a strong relationship with temperature, and no trend over time was found. While 54 of the 91 individual congeners exhibited significant dependencies on temperature, only 16 congeners showed a significant relationship for both temperature and time, and 6 of those had positive time parameters indicating that the concentration actually increased over the time sampled. Lake Superior is the northernmost of the Great Lakes, and as such it has the coldest climate. Global fractionation may be augmenting the regional gas phase concentration around Lake Superior, or the PCBs in this region may be at equilibrium between the many environmental compartments. It is also possible that Lake Superior's low water and air temperatures slow down loss processes so much that we are not yet able to detect any trends in the gas phase PCB concentrations.

The natural logarithms of partial pressures for the majority of PCB congeners for the Lake Michigan and Lake Erie sites exhibited significant dependencies on both temperature and time for over water and over land samples. The half-lives of individual congeners ranged from 1 to 6 years, while the Σ PCB half-lives for Lake Erie were 3.5 ± 1.2 years and 3.1 ± 0.7 years over-water and over-land, respectively. Lake Michigan over-land samples exhibited a similar Σ PCB half-life of 2.5 ± 0.6 years. While not significantly different from the findings of Hillery et al. (2) the half-lives all seem to be shorter with the addition of recent data. Over-water samples from Lake Michigan exhibited a much different behavior.

Figure 1 shows the partial pressures, corrected to a common temperature of 288 K using the modeled temperature parameters, plotted against time for the over-water and over-land samples,

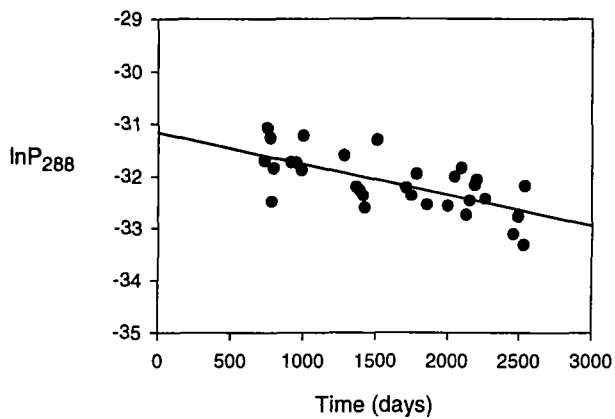
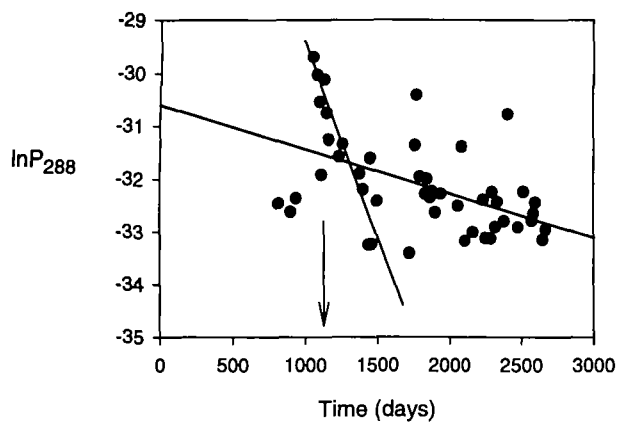


Figure 1. Natural logarithm of temperature adjusted (to 288 K) atmospheric partial pressures of total-PCBs at Sleeping Bear Dunes (near Lake Michigan) versus Julian day (since 1/1/90). **Top:** only over-water air-masses. **Bottom:** only over-land air masses.

respectively. The over-land samples (see the bottom plot) show a steady decline over time with relatively little scatter. The over-water samples (see the top plot) are "spiky" with a definite "event" beginning in November 1992; see arrow. This event has its own separate half-life for Σ PCBs of 130 days. Because this event is only seen in the samples with the air masses coming off of the lake, it appears that Lake Michigan has had a massive and sudden efflux of PCBs causing a peak in gas phase concentration. There are many scenarios that could cause Lake Michigan to "erupt". All scenarios involve an increased dissolved phase concentration of PCBs. This increase may occur slowly as a result of an usual ice-free winter or rapidly as a result of massive upwelling of sediments. Causes for this event are still under investigation.

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