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Temperature Dependence and Temporal Trends of Polychlorinated Biphenyl Congeners in the Great Lakes Atmosphere

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As part of the Integrated Atmospheric Deposition Network (IADN), we have measured gas-phase polychlorinated biphenyl (PCB) concentrations in the atmosphere around the Great Lakes since November of 1990. In this paper, we use these data to explore the temperature and time dependencies of gas-phase PCB concentrations near Lakes Superior, Michigan, and Erie and in Chicago. Concentrations of individual PCB congeners were well correlated to temperature for the three remote sites using the Clausius−Clapeyron equation, but the calculated heats of surface−air exchange did not correlate (on a congener basis) with laboratory-measured heats of vaporization. On the other hand, the heats of surface−air exchange for PCB congeners measured in Chicago are well correlated with laboratory-measured heats of vaporization. We conclude that the gas-phase PCB concentrations measured at Chicago are controlled by short-range transport, but at the three remote sites, these concentrations are controlled by long-range transport. Gas-phase PCBs also exhibited decreasing concentrations over the period 1991−1997 near Lakes Michigan and Erie and in Chicago. Significant half-lives ranged from 0.5 to 7.5 years for individual congeners and 2.8 to 3.3 years for total PCBs. Gas-phase PCBs near Lake Superior showed no general trend in gas-phase concentration over this same time period.

Introduction

In an attempt to better understand the spatial and temporal behavior of PCBs in the Great Lakes atmosphere, the United States and Canadian governments created the Integrated Atmospheric Deposition Network (IADN). The IADN established one “master” air sampling site on each of the five Great Lakes in rural areas removed from urban influences. Several “satellite” sites were also established, some near or in urban areas. This paper will present PCB results from the three remote sites near Lakes Superior, Michigan, and Erie and from the one site in Chicago from their dates of inception to August of 1997.

Hillery et al. (*1*) previously reported PCB results from the U.S. IADN sites up to 1995. These authors concluded that the atmospheric abundance of the sum of PCB congeners (ΣPCB) was well correlated with temperature using the Clausius−Clapeyron equation

$$\ln P = (-\Delta H_v/RT) + \text{const} \qquad (1)$$

where P is the gas-phase PCB partial pressure (atm), ΔH_v is the enthalpy of vaporization (kJ/mol), R is the gas constant, and T is the average atmospheric temperature (K) during the sampling period. Strictly speaking, ΔH_v is the heat of phase change for the pure compound from the liquid phase to the gas phase. However, in the real world, this term is actually the energy necessary to cause the phase transition from the surface of soil, vegetation, or water to the atmosphere, and as such, it may be more appropriate to define this term as ΔH_{sa}, the enthalpy of surface−air exchange. In fact, previous studies (*1, 2*) indicate that ΔH_{sa} is often much less than ΔH_v.

Wania et al. (*3*) have suggested that the slopes of Clausius−Clapeyron plots, and hence these ΔH_{sa} values, can be interpreted in terms of the relative importance of short- vs long-range transport. Their hypothesis is that lower ΔH_{sa} values indicate that long-range transport controls atmospheric concentrations and that higher ΔH_{sa} values indicate that volatilization from local sources dominates atmospheric concentrations. We propose an alternative hypothesis. Since different compounds volatilize from many different surfaces, both aquatic and terrestrial, the energy associated with this volatilization will likely vary. Therefore, we suggest that it is not the overall magnitude of ΔH_{sa} that matters, rather it is the dependence of ΔH_{sa} on physical−chemical properties that really is important. For example, Wania et al. (*3*) observed a dependence of the Clausius−Clapeyron slope on the number of chlorines in PCBs for three rural studies. A more robust approach would be to regress ΔH_{sa} against the enthalpy of vaporization, ΔH_v, for each PCB congener. We hypothesize that field data will exhibit two complementary features: (a) the ΔH_{sa} of individual PCB congeners would be a linear function of ΔH_v if the PCB source was near to the sampling site (short-range transport); (b) if the PCB source was remote from the sampling site (long-range transport), this functional relationship would break down, and the ΔH_{sa} values would approach a constant. This idea is analogous to the equilibrium partitioning of PCBs between gas- and particle-phases in an aerosol (*4*).

This paper extends the work of Hillery et al. (*1*) by two years, with the addition of 1996 and 1997 PCB data. We have also separated the PCBs into individual congeners and further investigated the meteorological processes governing their gas-phase concentrations. Of the meteorological factors, we particularly considered wind direction. Hillery et al. (*1*) concluded that there was only a weak and inconsistent relationship between atmospheric PCB concentrations and wind direction at the IADN sites, but their correlations lacked power because they fitted a continuous, circular function to a wind direction distribution that should really have had just two discreet values: (a) wind directions coming to the sampling site from the lake and (b) wind directions coming to this site from the land. This bifurcation is a result of the observation (*2*) that the gas-phase concentrations of PCBs near a lake can be influenced by two different exchange mechanisms: water−air processes and terrestrial−air processes. Thus, we have segregated our samples into over-land, over-water, and ambiguous air samples. Ambiguous air samples are those that have an approximately equal

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frequency of over-land and over-water wind directions during the 24 h sampling period.

Experimental Methods

The Lake Superior site is located at Eagle Harbor on the Keweenaw Peninsula about 50 m from the shore; sampling began there in November 1990. The Lake Michigan site is located at Sleeping Bear Dunes on the northwest coast of Michigan's lower peninsula about 3 km from the shore. The Sturgeon Point site is located about 50 m from the shore of Lake Erie and about 30 km southwest of Buffalo, NY. Sampling at these two sites began in November 1991. An urban sampling site is located near Lake Michigan at the Illinois Institute of Technology on the south side of Chicago; it is about 1.6 km from the shore of Lake Michigan. Sampling began there in March 1993.

Details of the sampling and analytical procedures are described elsewhere (*1*). In general, air samples were taken every 12 days for 24 h 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. Subsequently, Amberlite XAD-2 resin has been used as the adsorbent. Air flow rates through the samplers were 34 m^3/h and checked quarterly. Variability in air flow rates was consistently less than 10%.

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

Each site was also equipped with a 10 m tower to collect meteorological data. Temperature, wind speed, wind direction (all at 10 m), relative humidity, and solar radiation (at 2 m) were collected every 6 s and reported as hourly means.

Results and Discussion

Because of the great number of samples associated with each site, it was 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 originating from both over the lake and land. Those samples with ambiguous wind directions (originating over both the lake and land) were not included in this study. Using these segregated data, the natural logarithms of the partial pressures of individual PCB congeners and of ΣPCB were regressed using a multiple linear regression model including temperature, time, and wind speed

$$\ln P = a_0 + a_1(1/T) + a_2(\text{day}) + a_3(\text{WS}) \qquad (2)$$

where "day" is the number of days since January 1, 1990, and "WS" is the average wind speed (in m/s) during the 24 h sampling period. The multiple linear regression was run for each congener and ΣPCB at each of the four sites for both the over-water and over-land wind sectors using SAS on a personal computer. The model was run in the backward elimination mode in order to remove any insignificant parameters. Only parameters that were significant at the 0.10 significance level were retained.

Wind speed was usually not a significant parameter (see a_3 in eq 2) in controlling gas-phase PCB congener concentrations at either the Lakes Superior or Michigan remote sites. A few of the gas-phase PCB congener concentrations were dependent on wind speed at the Lake Erie site, and most of the congener concentrations were dependent on wind speed at the Chicago site. Those congeners that exhibited significant dependencies on wind speed were negatively correlated. A negative correlation is consistent with higher concentrations resulting from lower atmospheric boundary layers, which are often associated with low wind speeds. The Chicago site is in an urban area, and the Lake Erie site is close to an urban area. One would expect atmospheric mixing to have a greater effect on concentrations when the sampling site is closer to the source. Another effect of wind speed could be simple dilution of PCBs from a local source. As the wind moves faster, the PCBs from that source would be diluted more and more with clean air, and the atmospheric PCB concentration would go down.

The other fitted parameters in eq 2 were almost always significant. As a convenience and to simplify comparing these parameters to the literature, we have converted a_1 [called *m* by Wania et al. (*3*)] to ΔH_{sa} by multiplying it by $-R$, and we have converted a_2 to a half-life ($t_{1/2}$) by dividing it into $-\ln 2$ and changing the units from days to years. Results for all congeners at all sites are available in the Supporting Information.

Temperature Trends. The concentrations of most PCB congeners exhibited significant ($p < 0.10$) temperature dependencies at all sites. The resulting ΔH_{sa} values at the four sampling sites are plotted vs the laboratory-measured heats of vaporization (ΔH_v from refs *2* and *5*) in Figure 1 on a congener-by-congener basis. There is an obvious lack of correlation at the three remote sites for both the over-water and over-land samples (see Figure 1a−f). Furthermore, the average ΔH_{sa} value for these six cases is 38 ± 2 kJ/mol, which is one-half to one-third of the laboratory ΔH_v values for these PCB congeners. In this case, the uncertainty in ΔH_{sa} is the standard error of the regression parameter, which is much greater than the propagated uncertainty in the atmospheric concentrations.

In contrast to the remote sites, the site at Chicago was chosen to specifically measure the urban influence on atmospheric PCB gas-phase concentrations near Lake Michigan. The greater Chicago urban area represents a significant source of atmospheric contaminants to the lake's coastal atmosphere. In fact, Simcik et al. (*6*) concluded that the urban area increased coastal atmospheric gas-phase PCB concentrations by a factor of 4 over continental background levels. In this case, the ΔH_{sa} values correlate strongly ($p < 0.01$) with laboratory-based ΔH_v values (see Figure 1g,h) for both over-land and over-water air masses. However, even in this case, the ΔH_{sa} values continue to be less than the laboratory-measured H_v values. The ΔH_{sa} values for the Chicago over-water air masses were about 1.5 times higher (on average) than those for the over-land air masses; compare parts g and h of Figure. This observation is just the opposite of that of Honrath et al. (*2*), who studied PCBs at our Lake Superior site. The difference between these observations suggests that the source of gas-phase PCBs at our Chicago site, on those days when the wind is from the lake, is not the water but the land between the lake and the sampling site (a distance of about 1.6 km). This suggestion is supported by the observations of Simcik et al. (*6*), who measured PCB concentrations of about 200 ± 70 pg/m^3 20 km off-shore of Chicago under similar wind conditions but simultaneously measured elevated PCB concentrations of about 1500 ± 600 pg/m^3 in Chicago. Another possible explanation is that over-water winds cause vertical air circulation and bring PCBs from sources further inland to our site. Either explanation involves local sources impacting the concentrations measured at our site in Chicago.

Wania et al. (*3*) observed seemingly contradictory evidence. They reported a significant dependence of the Clausius−Clapeyron slope on the number of chlorines for three rural/remote studies, but no relationship for urban

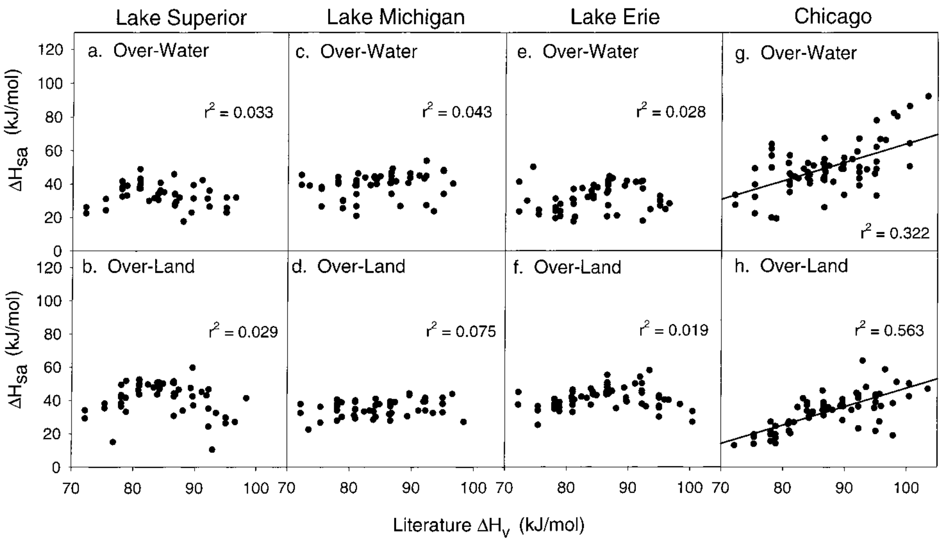

FIGURE 1. ΔH_{sa} values for PCB congeners calculated from eq 2 vs laboratory-measured heats of vaporization (*2, 5*) for (a) Lake Superior over-water, (b) Lake Superior over-land, (c) Lake Michigan over-water, (d) Lake Michigan over-land, (e) Lake Erie over-water, (f) Lake Erie over-land, (g) Chicago over-water, and (h) Chicago over-land samples.

studies. There is, however, no direct link between the remoteness of a site and the importance of short-range or long-range transport to that site. For instance, the study by Hornbuckle and Eisenreich (*7*) was designed to measure equilibrium exchange between the local terrestrial surface with little lateral transport of the air mass. We, therefore, conclude that our results do not necessarily contradict the observations of Wania et al. (*3*).

In absolute terms, the ΣPCB concentrations in Chicago's air averaged 1600 pg/m^3, which is approximately 20 times higher than concentrations measured near northern Lake Michigan. With these high concentrations resulting from local sources and with low concentrations from long-range transport, it is not surprising that the ΔH_{sa} values at Chicago correlate with and are closer to the measured heats of vaporization. This differential observation (compare Figure 1a,f versus Figure 1g,h) is a strong indicator that PCBs at Chicago come from short-range transport but that PCBs measured at the remote IADN sites come primarily from long-range transport.

There also appears to be a difference at each of the three remote sites between the over-water and over-land samples. The over-water and the over-land ΔH_{sa} values were compared on a congener-by-congener basis for each of these three sites, and a sign test was performed on these paired values. This test indicated that the Lake Superior site (50 paired congener values) and the Lake Erie site (52 paired congener values) had significantly higher ΔH_{sa} values for the over-land samples than for the over-water samples ($p < 0.0001$). This behavior has been previously predicted from differences in heats of solubility and heats of vaporization, both of which affect air–water exchange (*2*). Conversely, the situation was just the opposite for the values at the Lake Michigan site, which had higher ΔH_{sa} values for the over-water samples. When comparing the same congeners between these three sites, it is apparent that the Lake Michigan over-water ΔH_{sa} values were higher than those from Lakes Superior and Erie, rather than the over-land values being unusually low. This could be a result of either higher dissolved-phase PCB concentrations in the lake (*2*) or a larger PCB contribution from local sources (*3, 8*). While Lake Michigan did exhibit relatively high dissolved-phase ΣPCB concentrations, as measured by Eisenreich and Bicksler in 1992 (*9*), the concentrations are not necessarily significantly higher than those for the other lakes. Many investigators have concluded that Lake Michigan is continually volatilizing PCBs (*10–13*), and the relatively higher over-water ΔH_{sa} values at this location may reflect contributions to the gas phase from this volatilization.

Temporal Trends. As determined from the coefficient a_2 in eq 2, we find that most of the gas-phase atmospheric PCB congener concentrations measured near Lakes Michigan and Erie and Chicago showed significant decreases over time. Significant half-lives for all individual congeners near Lake Michigan ranged from 0.5 to 5.9 years and averaged 2.1 ± 0.1 years. Significant half-lives for all individual congeners near Lake Erie ranged from 0.7 to 7.5 years and averaged 2.6 ± 0.1 years. Significant half-lives for all individual PCB congeners at Chicago ranged from 0.6 to 5.6 years and averaged 2.7 ± 1.3 years. There were no significant differences in half-lives between over-water and over-land samples taken near Lakes Michigan and Erie or at Chicago, suggesting that, regardless of the exchange process involved, PCB congeners are being lost at the same rate. There was also no correlation between observed half-lives with any physical or chemical parameter of the individual PCB congeners, parameters that include number of chlorines and vapor pressure.

Anderson and Hites (*14*) concluded that the major environmental loss of PCBs is from OH radical reactions and reported atmospheric lifetimes on the order of tens of days for many PCB congeners. However, the data here and from other environmental compartments (*1*) indicate that PCB lifetimes are actually much longer. Of course, the Anderson and Hites lifetimes were calculated assuming that there is no continuing source of PCBs to the atmosphere. Volatilization from terrestrial and aquatic surfaces does, in fact, represent a large continuous source of PCBs to the atmosphere. Mackay et al. (*15*) have shown that the overall environmental residence time of a given compound is much longer than its residence time in any given compartment because of extensive intercompartmental transfer.

Most of the PCB congener concentrations measured near Lake Superior had no significant dependence as a function of time. Of those that did show a significant change over time, many actually increased in gas-phase concentration during the time period of IADN sampling. The Lake Superior site at Eagle Harbor is the northernmost of the IADN sites, and as such it experiences the coldest temperatures. The lack of a significant decrease in most of the PCB congeners may be a result of global distillation transporting PCBs from more temperate regions of the country and thus bolstering the gas-phase concentrations in the colder regions.

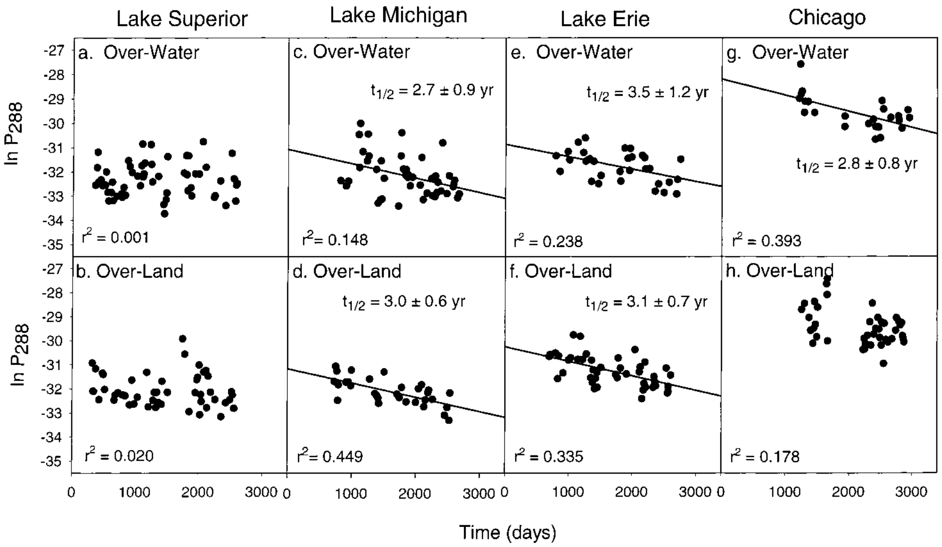

FIGURE 2. Natural logarithm of the partial pressure of ΣPCBs at a reference temperature of 288 K vs time for (a) Lake Superior over-water, (b) Lake Superior over-land, (c) Lake Michigan over-water, (d) Lake Michigan over-land, (e) Lake Erie over-water, (f) Lake Erie over-land, (g) Chicago over-water, and (h) Chicago over-land samples.

Using the temperature parameter from eq 2 for ΣPCBs, it is possible to normalize the partial pressures to a reference temperature of 288 K using the same equation as Cortes et al. (*16*):

$$P_{288} = P \exp\left[\frac{-\Delta H_{\mathrm{sa}}}{R}\left(\frac{1}{288} - \frac{1}{T}\right)\right] \qquad (3)$$

In Figure 2, we have plotted the natural logarithm of the ΣPCB partial pressure adjusted to 288 K vs time. This gives us a closer look at the temporal trend at each site when the wind is bringing air to our samplers from either the lake or from land.

The gas-phase ΣPCB partial pressures near Lake Superior, like the individual congeners, show no significant decreasing trend in concentration from November 1990 to August 1997 for either the over-water or over-land samples (see Figure 2a,b). The data from the Lake Michigan site offer a clear justification for the segregation of the samples into over-land and over-water air sectors (see Figure 2c,d). The over-land samples are controlled primarily by temperature and time (r^2 = 0.449), but the over-water samples exhibit much greater unexplained variability (r^2 = 0.148). Some periodic behavior still seems to be present in the temperature-corrected gas-phase ΣPCB partial pressures near Lake Michigan for the over-water samples. The period is approximately 2 years; the cause of these oscillations is not yet clear. The half-life calculated for ΣPCB partial pressures near Lake Michigan is 2.8 ± 0.7 years. These values are approximately half the value of 6 ± 2 years observed by Hillery et al. (*1*) using only 1992−1995 data.

The Lake Erie ΣPCB partial pressures are well described by temperature and time for both the over-water and over-land samples as observed by the significant correlation coefficients in Figures 2e and 2f. These temporal dependencies near Lake Erie are the same for over-water and over-land samples and translate into a half-life of 3.3 ± 1 years. This value is on the order of half the value of 7 ± 3 years observed by Hillery et al. (*1*) using only 1992−1995 data. The addition of two years of data has reduced both the atmospheric half-life of ΣPCBs and the uncertainty of this half-life. It appears that both the over-water and over-land samples also exhibit some residual periodicity with a period of about 2 years similar to that observed for the Lake Michigan over-water samples.

Gas-phase ΣPCB partial pressures at Chicago exhibited a significant half-life of 2.8 ± 0.8 years for the over-water samples, but no significant decrease was observed for the over-land samples (see Figure 2g,h). The over-water half-life is similar to those observed at the remote sites, again suggesting that PCBs are being lost at the same relative rate all around the Great Lakes. The lack of a significant decrease for the over-land samples may result from the relative paucity of data.

The addition of two years of data to the Hillery et al. (*1*) study has shown that the PCB gas-phase concentrations continue to decrease near Lakes Michigan and Erie but not near Lake Superior. Environmental half-lives for gas-phase ΣPCBs and the uncertainties in these values have also decreased. Individual congeners exhibited half-lives that ranged over an order of magnitude, but most were close to the corresponding values for ΣPCBs.

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Supporting Information Available

ΔH_{sa}, $t_{1/2}$, and a_3 values for all congeners at all sites. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hillery, B. R.; Basu, I.; Sweet, C. W.; Hites, R. A. *Environ. Sci. Technol.* **1997**, *31*, 1811−1816.

(2) Honrath, R. E.; Sweet, C. W.; Plouff, C. J. *Environ. Sci. Technol.* **1997**, *31*, 842−852.

(3) Wania, F.; Haugen, J.-E.; Lei, Y. D.; Mackay, D. *Environ. Sci. Technol.* **1998**, *32*, 1013−1021.

(4) Simcik, M. F.; Franz, T. P.; Zhang, H.; Eisenreich, S. J. *Environ. Sci. Technol.* **1998**, *32*, 251−257.

(5) Falconer, R. L.; Bidleman, T. F. *Atmos. Environ.* **1994**, *28*, 547−554.

(6) Simcik, M. F.; Zhang, H.; Eisenreich, S. J.; Franz, T. P. *Environ. Sci. Technol.* **1997**, *31*, 2141−2147.

(7) Hornbuckle, K. C.; Eisenreich, S. J. *Atmos. Environ.* **1996**, *30*, 3935−3945.

(8) Hoff, R. M.; Brice, K. A.; Halsall, C. J. *Environ. Sci. Technol.* **1998**, *32*, 1793−1798.

(9) Eisenreich, S. J.; Bicksler, J. L. *Hydrophobic Organic Chemicals in the Springtime Waters of the Great Lakes-1992*; Great Lakes National Program Office, U.S. Environmental Protection Agency: Washington, DC, 1996.

(10) Hornbuckle, K. C.; Sweet, C. W.; Pearson, R. F.; Swackhamer, D. L.; Eisenreich, S. J. *Environ. Sci. Technol.* **1995**, *29*, 869−877.

(11) Pearson, R. F.; Hornbuckle, K. C.; Eisenreich, S. J.; Swackhamer, D. L. *Environ. Sci. Technol.* **1996**, *30*, 1429−1436.

(12) Hoff, R. M.; Strachan, W. M. J.; Sweet, C. W.; Chan, C. H.; Shackleton, M.; Bidleman, T. F.; Brice, K. A.; Burniston, D. A.; Cussion, S.; Gatz, D. F.; Harlin, K.; Schroeder, W. H. *Atmos. Environ.* **1996**, *30*, 3505−3527.

(13) Hillery, B. R.; Simcik, M. F.; Basu, I.; Hoff, R. M.; Strachan, W. M. J.; Burniston, D.; Chan, C. H.; Brice, K. A.; Sweet, C. W.; Hites, R. A. *Environ. Sci. Technol.* **1998**, *32*, 2216−2221.

(14) Anderson, P. N.; Hites, R. A. *Environ. Sci. Technol.* **1996**, *30*, 1756−1763.

(15) Mackay, D.; Shiu, W. Y.; Ma, K. C. *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*; Lewis Publishers: Chelsea, MI, 1992.

(16) Cortes, D. R.; Basu, I.; Sweet, C. W.; Brice, K. A.; Hoff, R. M.; Hites, R. A. *Environ. Sci. Technol.* **1998**, *32*, 1920−1927.

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