Environ. Sci. Technol. **1999**, *33,* 1509−1515

Back-Trajectory Analysis of Atmospheric Polychlorinated Biphenyl Concentrations over Lake Superior

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Vapor-phase concentrations of three polychlorinated biphenyl (PCB) congeners measured at a site on the Lake Superior shoreline are analyzed in conjunction with back-trajectories to assess the contribution of long-range transport to the measured concentrations. Most previous attempts to use back-trajectories to identify a potential signature of long-range transport of semivolatile organic compounds have been confounded by correlation between air mass source region and temperature, through temperature-dependent air/surface exchange processes in the sampling region. This effect is minimized in the present study through the use of a model of equilibrium air/surface exchange to remove temperature dependence from the data set prior to trajectory analysis. Back-trajectories corresponding to periods when observed concentrations were significantly greater than those expected based on the observed temperature dependence indicate rapid transport from urban and industrial regions well south of the sampling site; transport from south of 40° north latitude results in concentrations 1.6−1.9 times those observed during periods without such transport. The method presented here should be applicable to other semivolatile organic compounds for which long-range transport signals are obscured by highly temperature-dependent regional air/surface exchange processes.

Introduction

Polychlorinated biphenyls (PCBs) are ubiquitous environmental contaminants whose occurrence in the environment is of concern due to their toxicity and resistance to degradation. As a result of their persistent nature, PCBs may be transported to remote regions, as evidenced by the presence of these compounds in regions as remote as the Canadian and Scandinavian high Arctic and the Antarctic, Indian, and Pacific oceans (*1*−*3*). PCBs are associated with adverse and irreversible effects in many fish, birds, and mammals, and they are suspected of posing a threat to human health in the Great Lakes region (*4*−*6*). For these reasons, the impact of these compounds on human health and the ecosystem of the Great Lakes has been a topic of significant study.

Atmospheric PCBs enter the Great Lakes water column via vapor exchange across the air−water interface and through particulate deposition, with vapor exchange the most important contributor to the flux across the air/water interface (*7*). Long-range atmospheric transport is thought to be the major source of PCBs to the relatively pristine regions of the Great Lakes. However, day-to-day and seasonal variations in atmospheric concentration are driven by temperature-dependent exchange processes at the lake interface or within nearby regions. Many previous studies in the Lake Superior region have focused on the development of an understanding of such exchange processes (*e.g.*, *8*−*13*). Although PCB concentrations in the waters of Lake Superior are close to a state of long term (≥1 year) equilibrium with the atmosphere, they are in a constant state of short-term seasonal displacement (*14*). Since aqueous concentrations appear to adjust rapidly to conditions in the atmosphere, it is important to understand the processes that contribute to atmospheric concentrations of these compounds in the Lake Superior region.

In a previous study we analyzed the contribution of local temperature-controlled equilibrium exchange processes to PCB concentrations at a site near Eagle Harbor, MI, on the shore of Lake Superior (*13*). The results indicated that atmospheric concentrations at this site are dominated by equilibrium air/water exchange in a subset of the measurements—those obtained during periods of flow off of the lake during months when the over-lake atmosphere is thermally stable. However, it was found that the full set of measurements was poorly described by equilibrium exchange between the atmosphere and the lake or the surrounding surfaces. Other processes, such as long-range transport or vertical mixing, must therefore play a significant role in determining short-term variations in atmospheric concentration in the region.

Back-trajectories have been successfully used in a number of studies to identify potential source regions for compounds that do not undergo temperature-dependent air/surface exchange (*e.g.*, *15*−*17*). The role of long-range transport of PCBs to remote sites has also been investigated, using measurements at a remote continental site in southern Ontario (*18*) and observations at Bermuda (*19*). Hoff et al. (*18*) concluded that variations in atmospheric levels of PCBs were dominated by equilibrium air/surface exchange and that a signature of long-range transport could not be detected in the measurements. However, the observed lack of systematic variation of PCB concentrations with the origination region of back-trajectories may have been due to a strong correlation between atmospheric flow patterns and temperature at the Ontario site (*18*). Analysis of measurements from Bermuda was similarly confounded by correlation between atmospheric transport and local temperature through temperature-dependent local air/surface exchange processes. Higher PCB concentrations at the Bermuda site were associated with long-range transport from the remote eastern Atlantic and from Africa, while lower concentrations were associated with flow from the eastern United States (*19*). However, transport to Bermuda varies seasonally, and most of the samples with higher concentrations were obtained during the warmer summer months, while transport from industrial regions of North America is enhanced during winter. Thus, it is not clear whether the higher levels observed during summer were the result of transport from an unidentified source region or the result of shifting local air/surface exchange equilibria.

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10.1021/es9804621 CCC: $18.00

The goal of the present study is the identification of potential source regions for PCBs in the atmosphere over Lake Superior using back-trajectory analysis. To minimize the uncertainties resulting from temperature variations which confounded previous attempts to use back-trajectories with PCB measurements, we have attempted to remove the effects of local temperature-dependent exchange processes from the time series of atmospheric PCB measurements at the Eagle Harbor, Lake Superior, site before conducting a back-trajectory analysis. This is accomplished by applying the results of an equilibrium air/surface exchange model based on PCB measurements at the site (*13*). The difference between concentrations observed at the site and those predicted by the model (the model residual) is a better indication of transport effects than is the concentration itself, as the residual is uncorrelated to temperature and contains information on processes other than temperature that affect PCB levels at the site. In the present work, we use model residuals in conjunction with back-trajectories to identify the signature of long-range transport in measurements of vapor phase concentrations of PCB congeners at the Lake Superior shoreline during the period 1990−1992. To our knowledge, this is the first attempt to apply back-trajectory analyses to the deviation of atmospheric PCB concentrations from a temperature-dependent model of air/surface exchange; a similar analysis for other semivolatile organic compounds (SOCs) has been reported for polychlorinated bornanes and camphenes (*20*).

Methods

Concentration and Transport Data. A total of 95 vapor phase samples of PCBs were collected from November 1990 to August 1994 at the Eagle Harbor, MI, Integrated Atmospheric Deposition Network (IADN) site (88.15°W longitude, 47.46°N latitude). The site is located at the tip of the Keweenaw Peninsula, which extends into Lake Superior. The sampling protocol and analytical technique are described elsewhere (*13*, *21*). The analyses described here were conducted for five PCB congeners or congener pairs, which span homologue groups containing 3−7 chlorine atoms: PCB 28 + 31 (2,4,4′-trichlorobiphenyl plus 2,4′,5-trichlorobiphenyl), 52 (2,2′,5,5′-tetrachlorobiphenyl), 101 (2,2′,4,5,5′-pentachlorobiphenyl), 138 + 163 (2,2′,3,4,4′,5′-hexachlorobiphenyl plus 2,3,3′,4′,5,6-hexachlorobiphenyl), and 182 + 187 (2,2′,3,4,4′,5,6′-heptachlorobiphenyl plus 2,2′,3,4′,5,5′,6-heptachlorobiphenyl). For conciseness, we present only the results for congeners 28 + 31, 101, and 182 + 187. Results for the other congeners follow the trends reported here (*22*).

Over short transport periods, compounds with surface sources and sinks may be transported primarily within the atmospheric boundary layer or mixed-layer. To describe such transport, we have used mixed-layer back-trajectories calculated using the Air Resources Laboratories Atmospheric Transport and Dispersion Model (ARL-ATAD), developed by Heffter (*23*) and described recently by Kahl et al. (*24*). Airflow trajectories are available for only the first two years of the entire four-year sampling period, as the required meteorological data archive was discontinued. Three-day back-trajectories to Eagle Harbor were calculated four times per sampling day, with arrival times of 00, 06, 12, and 18 UTC. Each trajectory is composed of a series of 3-h segments determined from winds measured by the standard rawinsonde network. Winds were vertically averaged throughout the mixed layer, a layer which varies in height both diurnally and spatially and extends from the near-surface to the first significant upper-level temperature inversion. Three sampling days on which trajectories arrived from disparate directions were omitted from the data set. Synoptic patterns changed during these days, indicating a change of air mass during a single 24-h PCB sample. In total, 53 sampling days and 212 trajectories are used in this analysis, spanning the period from November 1990 through December 1992.

The median horizontal displacement error of three-day boundary layer back-trajectories is estimated to be approximately 350 km (*25*). However, groups of trajectories are used in the present analysis to identify potential PCB source regions much larger than 350 km in size. The results are thus not significantly degraded by expected uncertainties in the upwind location of individual back-trajectories.

Back-Trajectory Analysis Methods. The primary goal of this work is to determine whether long-range transport produces a significant and detectable enhancement in ambient vapor phase PCB concentrations over Lake Superior. This is accomplished by selecting and plotting back-trajectories during periods when concentrations were elevated at the measurement site. Transport during these periods is then compared to transport during periods when concentrations at the site were low.

In the following section, we first present results based on selection of trajectories corresponding to the highest 20% and lowest 20% of concentration measurements at the site. The results of this analysis may be confounded by correlation between local temperature and air mass origin, as discussed above, but are included for comparison with the residual-based method that follows.

The residual method is based upon a comparison between observed concentrations and those expected based on a model of equilibrium air/surface exchange at or near the site. The equilibrium exchange of a given SOC with a surface or aqueous reservoir is expected to lead to a linear dependence of log C upon reciprocal temperature, and thus equations of the form

$$\log C = a + b \cdot 1/T$$

have been used to investigate the temperature dependence of PCB concentrations (*13*, *18*, *19*, *26*). Use of this equation does not require prior knowledge of the governing equilibrium process, although different processes (e.g., air/water exchange governed by Henry's law or air/surface exchange governed by adsorption or absorption) would result in different values of a and b, due to differing enthalpies of reaction and differing concentrations in the non-gas phase.

A best estimate of the temperature dependence of atmospheric PCB concentrations at the Lake Superior site is provided by the results of a previous regression analysis of log C against reciprocal temperature, using the full suite of PCB measurements at the site over the period 1990−1994 (*13*). The best fit was obtained using air temperatures measured at the monitoring site (with missing data filled in with measurements from the nearby Houghton County airport), as described previously (*13*). Residuals with respect to this model, $[(\log C)_{\text{observed}} - (\log C)_{\text{predicted}}]$, where $(\log C)_{\text{predicted}} = a + b \cdot 1/T$, are uncorrelated to temperature but should retain information about potential long-range transport. In this analysis, periods of high and low concentration at the site, relative to temperature-dependent equilibrium, are determined based upon the model residual. In the following sections, periods when residuals exceed the mean residual value (equal to zero) by more than one standard deviation are termed "large positive residual" periods, while periods when residuals are greater than one standard deviation below the mean are termed "large negative residual" periods. A value of one standard deviation is used in these definitions as a compromise between the need to identify periods when concentrations were significantly higher than

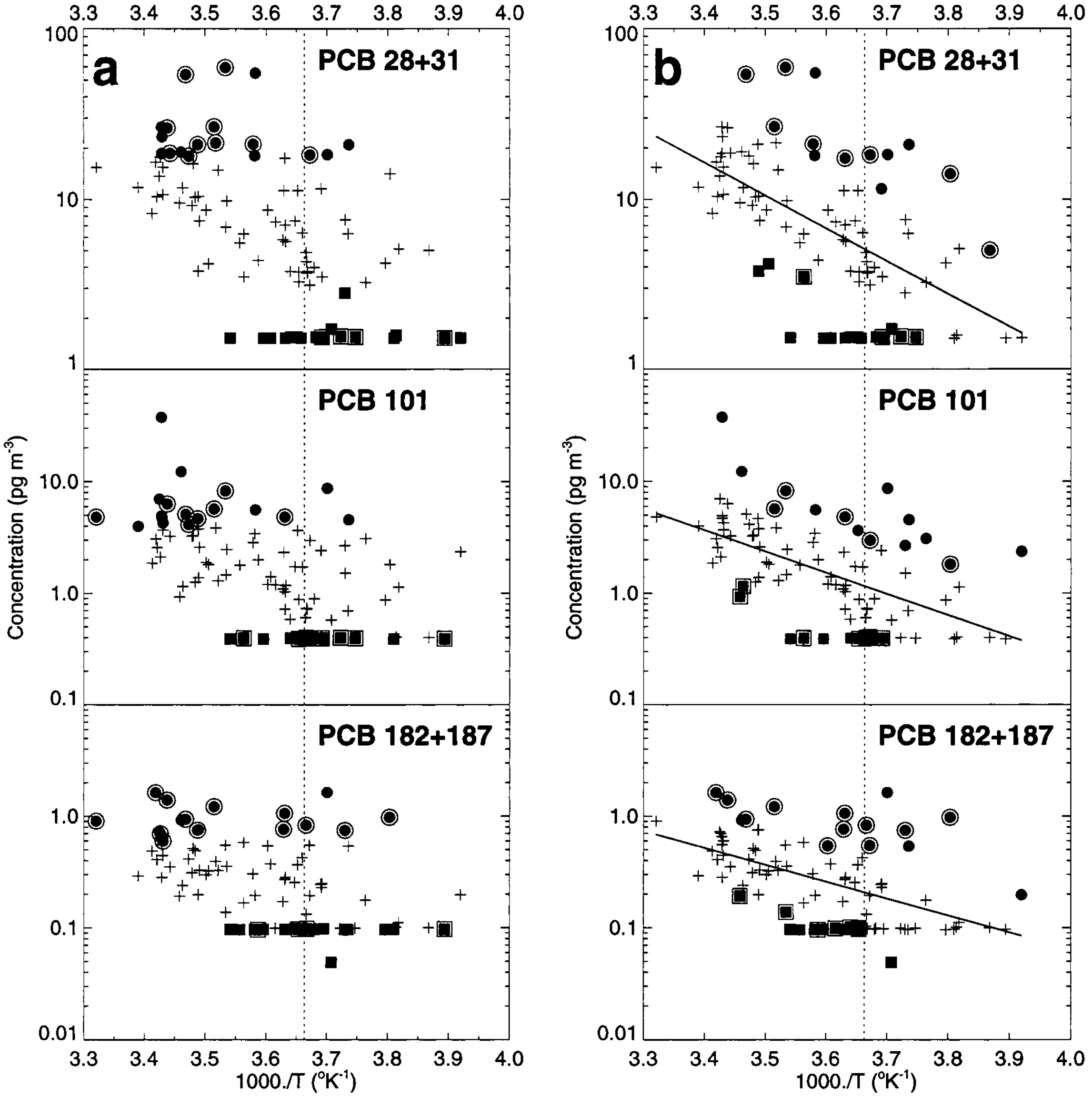

FIGURE 1. Observed concentration as a function of reciprocal temperature for PCB congeners 28 + 31, 101, and 182 + 187. (a) The highest and lowest 20% of the concentrations are identified by circles and squares, respectively. (b) The best-fit linear regression of log *C* versus reciprocal temperature (*13*) is shown; large-positive and large-negative residual samples with respect to the regression line are identified by circles and squares, respectively. Samples obtained between November 1990 and December 1992 and used in the trajectory analysis are indicated by double circles or squares. The vertical dotted line indicates 0 °C.

expected and the need for an adequate number of "large positive residual" periods.

Results

Figure 1 presents an Antoine plot of measurements obtained during the full four-year period and indicates the samples identified as high and low concentration (Figure 1a) and those with large positive and large negative residuals (Figure 1b). The primary difference between the two methods of identifying high-concentration periods lies in the colder temperature region on the right portion of the figures; few samples with high concentration were obtained when temperature was below approximately 0 °C, while high-residual samples are nearly uniformly distributed over the range of observed temperature.

Back-trajectories for sampling days corresponding to the high and low concentrations are shown in Figure 2. A clear difference is apparent: many of the back-trajectories during high-concentration periods indicate rapid transport from regions well to the south, while back-trajectories during low-concentration periods indicate local flow or flow from the north or northwest. However, the nonuniform distribution of temperature in the high- and low-concentration samples apparent in Figure 1a suggests that a portion of this difference may be a result of differences in local temperature-dependent air/surface equilibrium.

Figure 3 displays back-trajectories during periods corresponding to large positive and large negative residuals. Again, a clear difference is apparent between the flow patterns during positive residual and negative residual periods. Most back-trajectories during periods of large positive residuals indicate rapid flow passing over urban and industrialized regions of the midwest. In contrast, most back-trajectories during periods of negative residuals indicate slower flow and originate to the north or northwest of Lake Superior. Since the distribution of reciprocal temperature is relatively uniform among the periods included in Figure 3 (see Figure 1b), this difference is not attributable to temperature-dependent air/surface equilibrium exchange in the region of the sampling site.

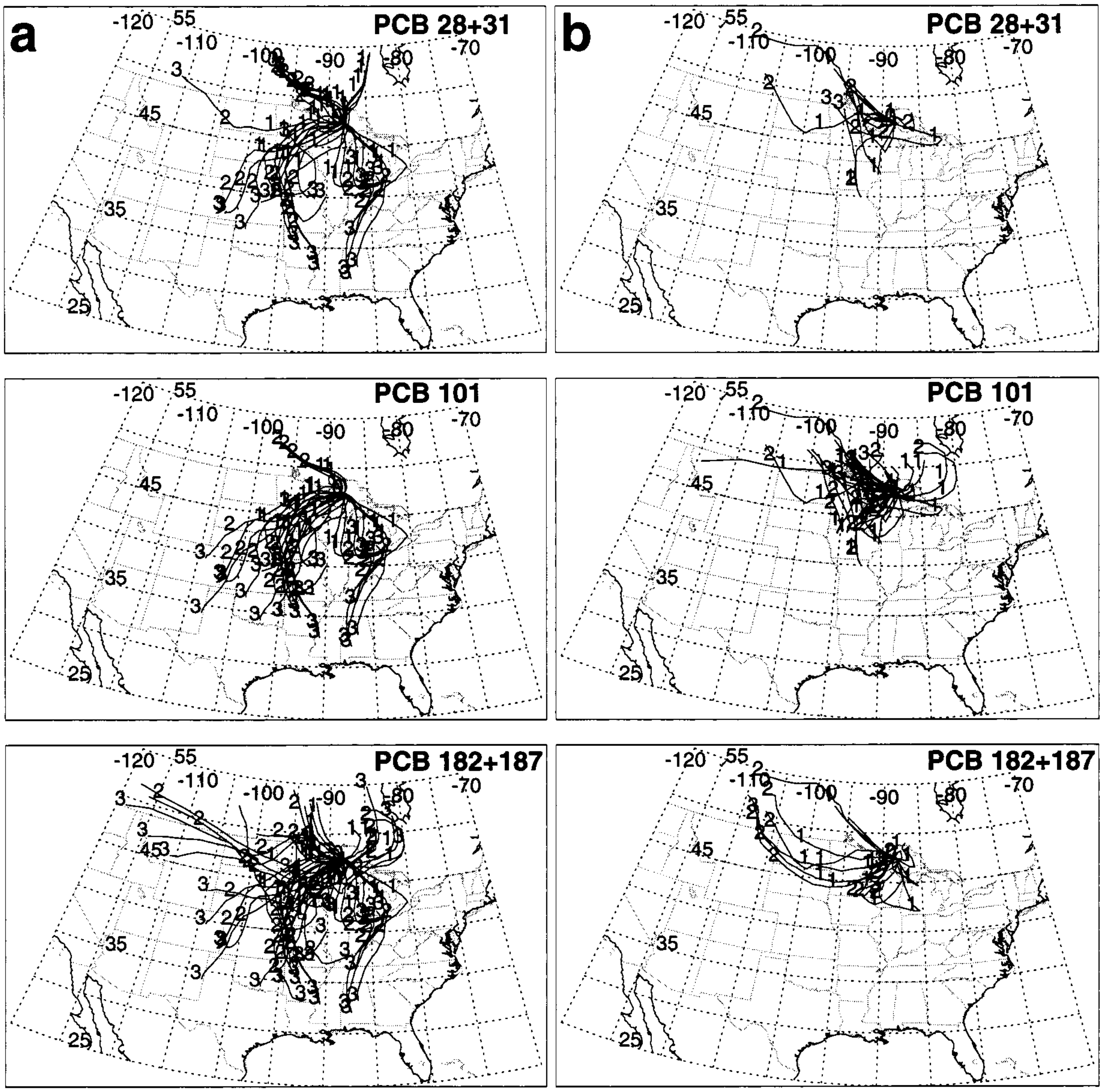

FIGURE 2. Back-trajectories for high and low concentration periods. (a) Trajectories during periods when concentration was in the top 20% of observations, corresponding to the samples identified with circles in Figure 1a. (b) Trajectories during periods when concentration was in the bottom 20% of observations, corresponding to the samples identified with squares in Figure 1a. The numerals printed along the trajectories indicate the number of days upwind from Eagle Harbor.

Discussion

These results indicate a strong association between elevated PCB concentrations at the Eagle Harbor site and transport from regions well to the south. We attribute this association to the following causes. First, significant latitudinal temperature gradients exist in the regions south of Lake Superior. As a result, equilibrium airborne PCB loadings in regions to the south are expected to be much higher than those at equilibrium with land or water at local temperature conditions. Rapid atmospheric transport from the south, if it occurs above the surface or occurs too rapidly for air/surface equilibrium to be maintained, would therefore carry elevated PCB levels to the Lake Superior region. This tendency of PCBs and other SOCs to migrate through the atmosphere from warmer to colder regions has been identified previously (*27*–*29*). Second, transport from regions with existing PCB sources, such as landfills or incinerators, could provide a source of PCBs to the air masses transported to the Lake Superior region. Finally, significant quantities of PCBs are still in use in closed systems, such as dielectric fluids in transformers and capacitors, in industrialized regions south of Lake Superior. Release of PCBs from leaks in these systems could also contribute to the elevated PCB levels observed in this study.

Back-trajectories during periods of large negative model residuals—that is, during periods when concentrations were lower than predicted by the equilibrium-based regression model—mainly originate in sparsely populated regions in the northern U.S. and Canada. Observations of concentrations lower than predicted by the model are attributed to two potential causes. First, many of the negative-residual samples were obtained during months when Lake Superior is largely frozen, and they may reflect a reduction in air/water exchange during those periods. Second, the regression line used in this study, which was based on the full set of measurements, does not adequately describe the temperature dependence of air/water equilibrium exchange. A sharper temperature dependence is obtained in regressions based upon only those samples obtained during periods when air/water equilibrium over the lake is expected (*13*). As a result,

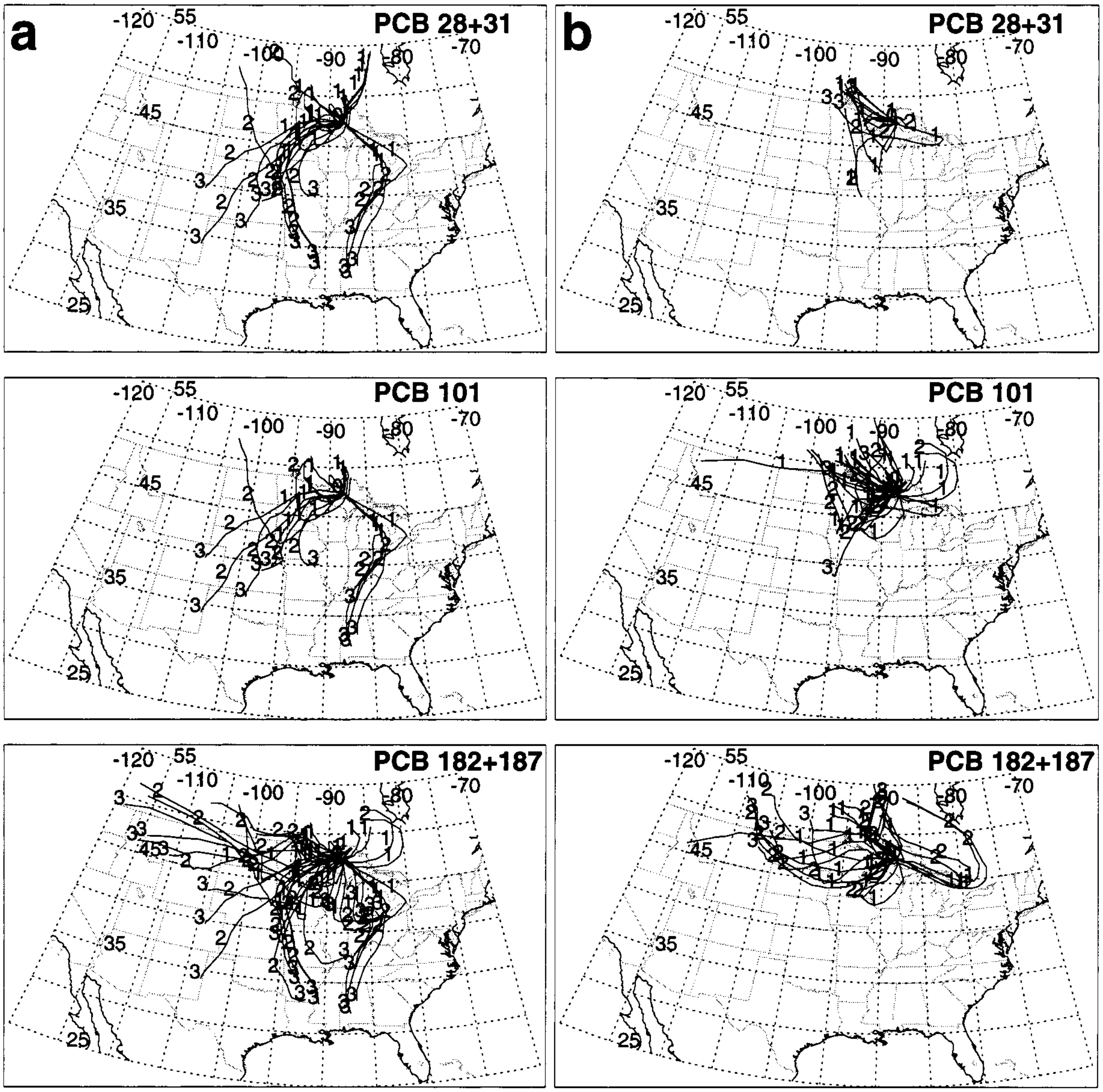

FIGURE 3. Back-trajectories for high and low residual periods. (a) Trajectories during periods when residuals were greater than one standard deviation above zero, corresponding to samples identified with circles in Figure 1b. (b) Trajectories during periods when residuals were greater than one standard deviation below zero, corresponding to samples identified with squares in Figure 1b. The numerals printed along the trajectories indicate the number of days upwind from Eagle Harbor.

PCB concentrations in many of the samples identified as negative residuals in the present work are actually close to expectations based upon over-lake equilibrium exchange. (In contrast, concentrations in most samples identified as positive residuals are significantly greater than those expected under conditions of over-water equilibrium exchange, and the patterns displayed in Figure 3a cannot be attributed to over-water equilibrium exchange.)

These results provide a qualitative indication that long-range transport from the south occurs during periods when atmospheric concentrations are elevated at Eagle Harbor. To provide a quantitative estimate of the impact that such flow has on PCB levels over Lake Superior, we consider the converse problem: to what degree are concentrations elevated at Eagle Harbor when long-range transport from the south occurs. This is accomplished by dividing the samples into two subsets: those obtained during periods of relatively rapid flow from the south and those obtained during other periods. Division of the trajectories into these two groups must be somewhat arbitrary, as the number of trajectories analyzed is insufficient to accurately identify the region(s) responsible for elevated model residuals during southerly flow periods. Therefore, we have arbitrarily selected a latitude cutoff of 40°N and define those periods when back-trajectories indicate flow from regions south of this latitude as “southerly flow” periods and those remaining periods as “northerly flow”. Trajectories on three sampling days indicated flow that shifted or varied between the northerly and southerly regions defined here; these trajectories were not included in either group. Back-trajectories corresponding to these two groups are shown in Figure 4.

Table 1 displays the mean residual [(log $C)_{\mathrm{observed}}$ − (log $C)_{\mathrm{predicted}}$] for the northerly flow and southerly flow subsets. For each PCB congener, the mean residual during periods of flow from the south is significantly larger at the 95% confidence level than the mean residual during periods of flow from the north. The difference between the mean residuals during southerly and northerly flow periods indicates that concentrations during periods of rapid, long-range southerly flow were 1.6−1.9 times higher than concentrations during periods of northerly flow.

In the present study, there is little difference between the atmospheric transport pathways corresponding to high-

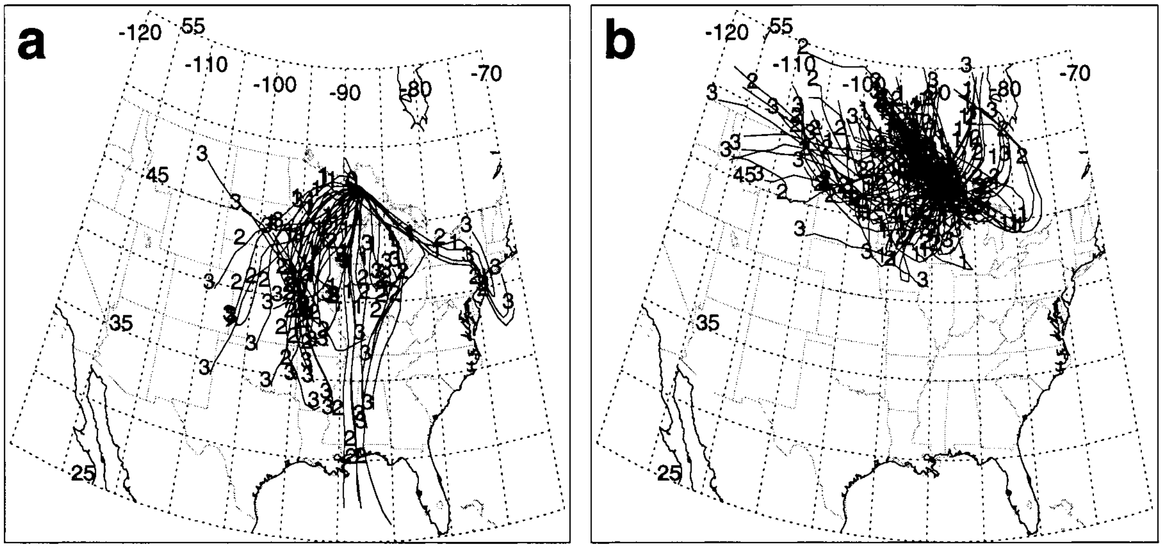

FIGURE 4. Back-trajectories for (a) southerly and (b) northerly flow periods. The numerals printed along the trajectories indicate the number of days upwind from Eagle Harbor.

TABLE 1. Mean Residuals During Periods of Northerly and Southerly Flow

congener(s)	back-trajectory group	N	mean residual[a]
28 + 31	southerly	11	0.24 ± 0.098
	northerly	39	0.039 ± 0.040
101	southerly	11	0.18 ± 0.082
	northerly	39	−0.11 ± 0.047
182 + 187	southerly	11	0.28 ± 0.080
	northerly	39	−0.0036 ± 0.050

[a] Mean ± one standard error of the mean.

concentration periods and those corresponding to high-residual periods. Nevertheless, we recommend the use of residuals from a model of equilibrium air/surface exchange, rather than concentrations, in back-trajectory analyses of PCBs and other semivolatile organic compounds for the following reason. When concentrations are used in such analyses, it is often not possible to unambiguously identify long-range transport as the cause of a finding of correlation between atmospheric transport patterns and elevated concentration. Air/surface equilibria are sensitive to temperature, and local temperature is affected by regional air transport patterns such that (in the northern midlatitudes) southerly flow often results in increased temperature. Thus, in the present study, temperature at the study site was skewed toward higher values during high-concentration periods, and, as a result, PCB concentrations during many of the high-concentration periods were not significantly higher than expected based on the temperature-dependent air/surface exchange model (Figure 1a). It is not possible to determine whether the increased concentrations during these periods were the result of long-range PCB transport or of changes in local air/surface equilibrium resulting from increased temperature (see also ref *18*). In contrast, this effect is minimized when model residuals are used, as demonstrated by the more uniform distribution of temperatures during high-residual periods (Figure 1b). This results in a greater level of certainty that long-range transport is responsible for the elevated concentrations observed during these periods.

Acknowledgments

This work was supported in part by the Michigan Department of Natural Resources, Michigan Great Lakes Protection Fund. Assistance was received from several people and is greatly appreciated. Dr. Clyde Sweet graciously allowed use of the PCB measurements, for which Ms. Karen S. Harlin and Ms. Ilora Basu (ISWS) conducted laboratory analyses. Dr. Theodore Bornhorst (MTU) provided guidance in statistical procedures.

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Received for review May 5, 1998. Revised manuscript received February 11, 1999. Accepted February 18, 1999.

ES9804621