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The Impact of an Urban-Industrial Region on the Magnitude and Variability of Persistent Organic Pollutant Deposition to Lake Michigan

A predictive model for gas-phase PCBs and trans-nonachlor over Lake Michigan has been constructed and the resulting data examined for trends. In this paper, we describe the model results to show how the magnitude and variability of a plume of contaminants from the Chicago area contributes to a highly variable region of net contaminant deposition over the entire lake. For the whole lake, gross annual deposition of PCBs is ~ 3200 kg, although the net annual gas exchange is not significantly different from zero. The data-driven model illustrates that on a daily basis, the net exchange of persistent organic pollutants (POPs) can change from net deposition to net volatilization depending on the area of plume impact. These findings suggest that i) control of urban areas can accelerate the rate of volatilization from lakes; and ii) release of POPs from urban areas is largely a result of volatilization processes.

INTRODUCTION

The United States Environmental Protection Agency (US EPA) initiated the Lake Michigan Mass Balance (LMMB) Study in order to investigate the cycling of potentially toxic, bioaccumulating and persistent compounds in the lake. The LMMB study included a large field study conducted over 18 months in 1994 and 1995 and is expected to continue with modeling efforts beyond 2003. Both the field sampling and modeling efforts focus on 4 potentially toxic compound groups; polychlorinated biphenyl congeners (PCBs), trans-nonachlor, atrazine, and mercury. The central goal of the LMMB study is to model the behavior of these chemicals in Lake Michigan. This requires an estimate of the compound loads to and losses from the system and an understanding of the controlling factors. In this paper, we discuss the atmospheric component of the study on gas-phase concentration and deposition of the persistent organic pollutants (POPs) studied, polychlorinated biphenyls (PCBs) and trans-nonachlor. Although these compounds have been banned from use in many countries, including the United States, they continue to be found in the surface waters of the globe in sufficiently high concentrations as to cause health concern for humans who consume fish (1, 2). In the Great Lakes, consumption advisories still prevent full commercial development of fisheries due to the contamination of fish by PCBs and other contaminants.

The heavy use of PCBs in the North American Great Lakes region resulted in contamination of the waters through spills, release to direct discharge, inadequate storage and wastewater treatment. Over the last three decades, direct sources of PCBs to the Great Lakes have been significantly reduced and/or removed and water concentrations have become nearly uniform over the lake and show decreasing concentrations (3). There has been no effort to control atmospheric sources of these compounds, however. POPs desorb from surfaces and volatilize as a function of temperature, which causes them to exhibit a seasonal atmospheric trend evident from the data produced by the LMMB and by other studies (4–6). Over time, atmospheric sources, which may be the result of local or long-range transport, as gases and as particles (7), may have become a more important component of the overall lake contaminant cycles.

Trans-nonachlor provides an interesting comparison to PCBs. Its physical-chemical properties of water solubility and vapor pressure are very similar to PCBs (8, 9), but its sources are quite different. Unlike PCBs, its principle use was agricultural, not industrial, as it was a principal component of the technical mixture of chlordane, an insecticide banned in 1988 (10). Although the insecticide was not intentionally discharged to the lake, its widespread use for commercial, residential, and agricultural purposes may have resulted in it entering the lake through non-point sources, including atmospheric deposition.

The current atmospheric sources of PCBs and trans-nonachlor are not well understood. The LMMB dataset and modeling effort provide a unique opportunity to investigate the nature and origin of current sources. We have developed an atmospheric model for predicting the concentrations of these compounds over Lake Michigan. The model is data-dependent and uses a statistical interpolation technique for temporal and spatial analysis. The model development is described in detail in Green et al. (11) and the central strategies are reviewed here. In this paper, the results from the model are described to illustrate the dynamic nature of these effects and Chicago’s contribution to the annual deposition load of these POPs to Lake Michigan. The findings of this work are indicative of the dynamics of the release and deposition of toxics from urban areas to waterbodies and suggest strategies for the control and reduction of atmospheric sources of POPs to waterbodies.

MATERIALS AND METHODS

The Lake Michigan Mass Balance (LMMB) study included the collection of over 400 atmospheric samples at 8 sampling stations on the shore of the lake and 20 sites over the lake that were sampled aboard the US EPA research vessel Lake Guardian. The air samples collected at the shoreline sites around Lake Michigan, including Beaver Island, were collected at 12-day intervals for the duration of the 18-month study. The air samples collected aboard the Lake Guardian were collected by the US EPA during 7 cruises in May, August, and October of 1994 and January, August and September of 1995. During winter of 1994–1995 there was negligible ice cover. This made the January cruise possible, but may also result in a prediction for winter dynamics that is atypical of the lake, which usually experiences significant ice cover in the northern region and southern coastal regions. Details of the collection sites, analytical methods and resulting concentrations have been described elsewhere (11–14). Wet deposition of atrazine, PCBs, and trans-nonachlor has been described elsewhere and is not discussed here (15).

Atmospheric Modeling

We estimated the concentration of 30 gas-phase PCB congeners, \( \Sigma PCB \) (sum of 98 individually measured congeners or coeluting congeners)
congener groups), and trans-nonachlor for every day of the 18-month field season and for the air over each of ~2300 cells of lake surface area. The grid size of each 25 km² cell matches the scale required by the hydrodynamic model used in the LMMB (16). As discussed below, one of the greatest benefits of using this fine grid scale is the resulting use of the model for predicting the spatial impact of the Chicago source. The modeling effort required a 2-fold approach to estimating the concentration of gas-phase chemicals over the lake. The first step was to predict the daily variation in gas-phase concentrations at each site. The second step was to interpolate the discrete site predictions over the entire surface area of Lake Michigan.

To predict the temporal variability of the gas-phase pollutants on a daily basis, 2 parameters were considered: wind direction and temperature. We hypothesized that the direction of the wind would affect the concentration of pollutants measured at each site, especially those sites that were located on the shore of the lake. For the shoreline sites, there were 2 different wind domains: i) when the air traveled over the land before reaching the air sampler; and ii) when the air traveled over the water before reaching the air sampler. This was a difficult problem because each sample consisted of more than 24 hours of collection, during which the wind direction (and temperature) would change. There was no way to directly sort each sample with respect to the wind domain (water-based or land-based). Instead, an indirect, stochastic fractionation method was used to predict the effect of wind direction on concentrations.

To fractionate each sample into land-based domain and water-based domain components, temperature and wind direction data collected at each of the shoreline locations were applied. These local meteorological data were collected and integrated on an hourly basis. The wind direction data and the corresponding air temperature data were parsed into 2 sets: i) over-land wind directions; and ii) over-water wind directions. To estimate the fractional contributions of the 2 domains to the total measured concentration, a stochastic approach where the partial pressure of the land-based domain is represented by a random variable and the resulting water-based partial pressure is calculated to maintain a perfect fractionation for each site. Several thousand trials are performed and the best-fit parameter values obtained are refined with a more robust nonlinear fitting routine. The result was a best-fit equation of the temporal variation in gas-phase concentrations at each site. This equation (illustrated in Fig. 1) was a function of the following measured parameters: the number of hours that the land domain was sampled; the number of hours that the water domain was sampled; air temperature for air flow over the land, T; air temperature for air flow over the water, T; and 4 fitting coefficients, B, A, B, and A. This fitting routine was completed for each sample. Once the fitting coefficients were determined, the concentration, C, of the compound was predicted at each of the sites for any day during the analysis period. All that was required was the wind direction and temperature measurements at each site.

The B term fitting coefficients are a measure of the effect of temperature on measured concentrations of gas-phase pollutants. The fact that there is a log-linear relationship between partial pressure of the compound (or concentration) and inverse temperature confirms that the predominant source of these gas-phase pollutants is the volatilization from surfaces (17). If the gas-phase PCBs were truly at equilibrium with the land or water surfaces prior to sampling, the terms B and B could be approximated by the enthalpies of exchange, DH (kJ mol⁻¹). Although each site has different B terms, the ΣPCBs the average of the B values provides an average DH value of 92 kJ mol⁻¹ and the average of the B values provide an average DH of 40.3 kJ mol⁻¹. These values are similar to the laboratory-measured gas-solid and gas-water DH values calculated for vapor pressure (18) and Henry’s Law (19, 20), respectively.

Figure 2 illustrates the prediction of gas-phase ΔPCB concentrations at the Chicago site. This prediction indicates a great deal of day-to-day variation in the gas-phase concentrations at this site. For example, our model predicts that Chicago air concen-

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**Figure 1. Illustration of the stochastic fractionation technique for calibrating the model for predicting the temporal variation in the gas-phase compound concentration at each of the shoreline sites.**
trations in the summer can change from < 1 ng m⁻³ on one day to > 12 ng m⁻³ on the next day. This predicted variability is primarily a result of changing wind directions and has been confirmed in other studies that have conducted daily sampling near Chicago (21). Chicago is clearly a major source of volatilized PCBs. This is clear from the strong dependence on wind direction and the good fit with temperature as a predictor. Other sites around the lake also exhibit significant variability in the day-to-day predicted concentrations, although the magnitude of the differences is less. Predicted variability is much less at the over-water sites than at any of the shoreline sites. This is because there is only one wind domain (over-water) at the over-water sites and the day-to-day air temperature variability is smaller.

Once the daily concentrations were predicted at each of the 8 shoreline sites and 12 over-water sites, these concentrations were interpolated in space, to predict concentrations at all ~ 2300 cells over the lake, on a daily basis. Green Bay, in northeast Lake Michigan, was not included in the model because the atmospheric concentrations were not measured during the 1994–1995 field effort and previous measurement indicate that interpolation in this region would underestimate actual concentrations (22). For the rest of the lake, an inverse distance weighting approach was used to estimate the concentrations of gas-phase compounds over the water, between the sampling locations. This approach estimates the concentrations as a function of all of the concentrations at the sampling locations, relative to the distance the predicted site is from each sampling location. A second order weighting power was used, determined by comparing the prediction of the gas concentrations to independent measurements and by minimizing the global and local errors resulting from this interpolation (11).

RESULTS

One of the benefits of this approach is that our predictions are primarily dependent on the most important dataset—the chemical concentrations that were measured over and around the lake. This approach takes advantage of the unique chemical dataset available from the LMMB field study. This dataset was collected over an unusually long time period and included an unusually large number of samples. The second set of major factors affecting the outcome are the wind direction at the sampling locations, and the air temperature at each of the 2300 cells of lake surface area. In this way, the 2 major, and well known, meteorological factors influencing gas-phase organic chemicals are considered. One of the more important disadvantages to this approach is its conservative outcome. Because air mass trajectories are not used, and we do not consider unsampled sites, we cannot find unknown sources and we cannot implicate regions as potential sources. Because of the long history of PCB use, it is likely that there are a number of important 'hot spots' for these chemicals in the region. For example, we have previously suggested that the Milwaukee area is a likely source of volatilizing PCBs (11).

Trans-nonachlor is an insecticide that was used on agricultural fields and in urban areas. Although not as strong as observed for PCBs, the concentrations of trans-nonachlor at the Chicago site are higher, on average, than at any of the other sites around the lake. Overall, the concentrations of trans-nonachlor are significantly higher in the southern part of the lake than in the northern part, perhaps reflecting the historical use in the central Midwestern states of Indiana, Illinois and southern Michigan. The over-water concentrations of trans-nonachlor were lower than measured at the shoreline locations, suggesting a re-equilibration of the gas-phase pesticide with water surfaces. This variation is evident in Figure 3, which describes the modeling result for gas-phase concentrations of trans-nonachlor in May 1995.

The modeled gas-phase trans-nonachlor over Lake Michigan exhibits 2 different phenomena. i) The early springtime concentrations of the pesticide in the southern part of the lake are not well explained by temperature (13). It appears that other factors, such as spring tillage, may cause a release of gas-phase chloranes into the Lake Michigan atmosphere. It is unlikely that the signal is a result of new application of the pesticides. We suspect the signal is a result of continuous volatilization of this highly persistent compound from disturbed soil. This effect has not been previously reported for this banned chemical. ii) Figure 3 illustrates an unusual pattern in the air concentrations over

Figure 3. Predicted average monthly gas-phase concentrations of trans-nonachlor in May 1994. The black regions correspond to concentrations greater than 16 pg m⁻³. The white regions correspond to concentrations less than 1 pg m⁻³. Labelled points are locations of sampling sites.
the lake. Gas-phase concentrations of the pesticide are much higher near the shore, and presumably over the terrestrial inland areas, than the gas-phase concentrations over the water. This pattern suggests a re-equilibration of trans-nonachlor with the water surface. This would occur if the concentration of trans-nonachlor was lower in the water, relative to the air/water equilibrium ratio, than the concentration of trans-nonachlor in the terrestrial soils and vegetation. Because the true air/water and air/soil equilibrium ratios are not well understood, it is difficult to confirm this hypothesis. Nevertheless, this model result does suggest a pattern of release of trans-nonachlor from the terrestrial surfaces south of Lake Michigan and deposition of trans-nonachlor into the southern coastal waters of the lake.

**Atmospheric Deposition**

Deposition of gas-phase organic chemicals is a major contributor to these potentially toxic compounds to surface waters. For PCBs and trans-nonachlor, up to 90% of the total atmospheric concentration is associated with the free vapor phase, and is not associated with atmospheric particles. This proportion in the gas phase increases over the lake, as coarse particles are removed by deposition close to the shoreline. Previous studies have shown that deposition of PCBs by dry particles and by precipitation to Lake Michigan is significantly less than by gas exchange for compounds with strong gas-phase sources to the air (13).

Net gas-exchange of PCBs and trans-nonachlor was calculated as the product of the relevant concentration gradient multiplied by a mass transfer coefficient (23, 24): Flux (ng m⁻² d⁻¹) = kₐ(Cₑ – Cₑ/[H⁺]), where kₐ is the overall mass transfer coefficient, Cₑ is the dissolved-phase water concentration, Cₑ is the gas-phase concentration, and H⁺ is the dimensionless Henry’s law constant. This algorithm has been used to estimate gas exchange of sulfurhexafluoride (25, 26), ammonia (27), PCBs (21, 28, 29), and other organic compounds (30, 31). This study is unique in the level of resolution for the gas-phase concentrations over time and space. As described above, gas-phase concentrations were determined for 25 km² cells for every day over 18 months. Dissolved water concentrations were estimated from measurements reported by the US EPA for the same time period. The dissolved water concentrations were estimated as an average for the whole lake, with outliers removed, and interpolated only with respect to time. The Henry’s Law constant (H⁺ is dimensionless, ng L⁻¹ in the gas phase divided by ng L⁻¹ in the dissolved phase) was corrected for the surface water temperature at each cell and estimated as a weighted average of the PCB congeners (19, 32). The overall mass transfer coefficient, kₐ, was determined as a function of local wind speed at 10 m, and the diffusivity of the compound in air and water. The exact formulation of kₐ was estimated using the results of gas tracer experiments (33) in open waters and is described in detail elsewhere (11, 21). Wind speeds and surface water temperatures are specific for the date and cell as described by Schwab et al. (16, 34).

With the addition of wind speed and surface water temperature to the prediction of net gas exchange flux, there are now 5 meteorological parameters that determine the magnitude of the potential gas deposition (or volatilization) of atmospheric PCBs and trans-nonachlor to Lake Michigan. Two of these parameters, air temperature (when the wind is from the land) and wind direction, are only used in the initial calibration of the air concentrations at the shoreline. Air temperature over the water is used to predict the gas-phase chemical concentrations at the over-water stations. The remaining 2 parameters, wind speed and surface water temperature, are only used to estimate the gas exchange fluxes: i.e. to predict the magnitude of the mass transfer coefficient and to correct Henry’s Law constant for the interfacial temperature.

**DISCUSSION**

**Effect of Chicago is a Function of Season and Source**

The resulting air/water exchange fluxes for PCBs and trans-nonachlor exhibit intense variability over space and time. This variability includes changes in the net direction of flux between net deposition and net volatilization. For PCBs, both air temperature and wind direction are strong contributors to this variability. At low temperature and northern wind regimes, PCBs exhibit volatilization fluxes over most of the lake. This is primarily a result of low air concentrations predicted (and measured) during cooler weather and to negligible transport of air from the Chicago area over the lake. When the winds are from

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Figure 4. Net gas exchange of PCBs to Lake Michigan on 4 consecutive days, starting with October 3, 1994 on the left. The darkest shade represents net deposition (most evident on October 6) while the white represents zero net exchange and the light shade represents net volatilization fluxes. The arrows indicate the average wind direction on that date. The average daily temperatures for October 3 to 6 were: 14.1°C; 13.6°C; 13.2°C; and 17.0°C, respectively.
the northeast and therefore the Chicago site is predicted by the water-based domain, the influence of Chicago on the lake is very small. Figure 4 illustrates this result for 4 consecutive days. On 3 October 1994, the measured winds were primarily northeasterly and the temperature was cool. On the following day, the winds shifted and were primarily southeasterly. On this second day, the model predicts a small region of PCB deposition fluxes just north of the Chicago area. But as the air temperature is still quite cool, the predicted gas-phase concentrations over the lake and resulting deposition fluxes are not large. On October 5th and 6th, the winds are predominantly southerly and the air toxics plume out of Chicago is observed to cause a larger region of deposition to the lake. On October 6th, the gas deposition zone covers almost the entire lake. This is a result of the increase in air temperature on that day that causes high predicted concentrations in Chicago and elsewhere. Combined with southerly winds, this study confirms that the Chicago area is a major source of PCBs to Lake Michigan. It is interesting to notice that although most of the southern basin of the lake experiences net gas deposition of PCBs, there are large regions along the southern coasts that still exhibit volatilization fluxes. This is primarily a result of gas-phase concentration variability across the lake, although water temperatures, and the prevailing wind directions at each of the sampling sites also contribute to this complex pattern of air/water exchange.

Chicago’s Contribution of Air Toxics to Lake Michigan

Atmospheric inputs are a major pathway for POPs emitted from the Chicago region and deposited in the lake. Most the city is outside the Lake Michigan watershed (the Chicago River runs west, away from the lake) and the major wastewater effluents do not discharge to the lake. However, the contribution of other Chicago-area sources of POPs to Lake Michigan is not well understood, so the relative impact of the atmospheric source can not be calculated. We can, however, calculate the impact of the Chicago region relative to other regions assessed by this study.

In Green et al. (11), we showed that the annually averaged area of impact is about 40 km around the Chicago site. On a daily basis, the area of impact can vary enormously. The area of impact is primarily a function of wind direction and air temperature. This large daily variability was also noted by consecutive daily and diurnal measurements by Simcik et al. (35) over the lake near Chicago. Due to these large daily variations in air concentrations and depositional fluxes, contribution should be integrated over larger time periods and over larger areas. In fact, because the concentrations over the lake tend to decrease exponentially with distance from Chicago, the best approach should be a consideration of the impact of Chicago on deposition load, rather than an area of impact.

The contribution of Chicago to the total gas-phase loading of PCBs and trans-nonachlor to Lake Michigan has been calculated using the total gross gas deposition, rather than as a net gas exchange. This method removes the effect of water concentrations, which exhibit some seasonal and spatial variability (36). Gross deposition fluxes are equal to \( k_{i0}(C_l/H) \). For consistency with previous reports, the gross depositional loads are assigned a negative value. By examining the gross deposition rather than net gas exchange, the effect of each individual site is clear. Figure 5 (bars) shows the predicted monthly loading to the entire lake for 2 examples: PCB #31+28 and trans-nonachlor. For both PCBs and trans-nonachlor, the gross deposition shows a highly seasonal variability, with the greatest deposition occurring during the summertime, when air concentrations are high.

The percent contribution of the Chicago site to the whole lake monthly gas-phase loads (solid lines in Fig. 5) ranges from \(< 5\%\) to \(20\%\), depending on the congener and the month. For the whole lake, gross annual deposition of \(\Sigma PCB\) (sum of the modeling results for all 98 congener groups) is \(\sim 3200\) kg. Although beyond the scope of this paper, we have found that the net annual PCB exchange includes zero when propagated error is considered. However, on any one day or location, net exchange is often not zero (Fig. 4). On an annual basis, Chicago is the largest single source of all 20 sites considered. Annually, Chicago contributed 10% or about 300 kg, apparently not from a volatilization source, of the total deposition load of gas-phase \(\Sigma PCB\). The percentage contribution shows no obvious trends with respect to water temperature, air temperature, or congener physical-chemical properties.

The percentage contribution of Chicago to the whole lake loading of trans-nonachlor is smallest in the warmest weather. No similar trend is apparent for PCBs. The difference is likely due to wider distribution of the source(s) of trans-nonachlor than is the case for PCBs. This is consistent with a large area source of trans-nonachlor such as agricultural lands. However, because the trans-nonachlor signal is highly seasonal and temperature dependent, it appears that the source is volatilization from historically treated fields, not a new application or current use.

Implications for Control and Reduction of POPs Release

Both groups of compounds, PCBs and trans-nonachlor, exhibit higher concentrations (measured and modelled) when the air is warm. This is a likely effect of volatilization from contaminated land surfaces. Current sources of gas-phase PCBs around Lake Michigan are clearly due to volatilization from surfaces, and not dominated by combustion processes, point source release, or vehicular exhaust.

The LMBM atmospheric modeling shows that Chicago is a source of gas-phase PCBs. The Chicago region contributes 2 to 20% of the total deposition of PCB to the lake, depending on the congener and time of year. For an annual year the total gas-phase deposition of \(\Sigma PCB\) is \(\sim 3200\) kg and the Chicago contribution is \(\sim 330\) kg. The Chicago source behaves like a non-point release by volatilization from contaminated sites open to
the atmosphere and subject to the same temperature fluctuations as the air temperature. Strategies to reduce the deposition of PCBs to Lake Michigan should include covering land surfaces contaminated with PCBs, removing structures contaminated on their surfaces with PCBs, and conducting remediation activities in cool weather.

In the case of trans-nonachlor, there appears to be a strong source region south of the lake. It is difficult to determine if the region south of the lake is a source of trans-nonachlor because it is warmer or because there is a reservoir of the chemical available there. The Chicago source of trans-nonachlor is most important in the winter. During the summertime, the source of trans-nonachlor is more diffuse. Sources of trans-nonachlor are associated with high temperatures and southern winds. Although this model cannot identify the range of transport, the trans-nonachlor signal is not consistent with current use of the pesticide or of seasonal application. Reduction of volatilization sources of this pesticide, and probably many POPs can be achieved by covering known sources, preventing new uses, and by conducting remediation activities in cool weather.

References and Notes


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