The Impact of Chicago on Lake Michigan: Results of the Lake Michigan Mass Balance Study

A white paper prepared for the workshop on "Using Models to Develop Air Toxics Reduction Strategies: Lake Michigan as a Test Case."

Keri C. Hornbuckle[1] and Mark L. Green[2]

[1] Department of Civil and Environmental Engineering, University of Iowa, Iowa City, IA 52242 , email: keri-hornbuckle@uiowa.edu; [2] Department of Civil, Structural and Environmental Engineering, State University of New York at Buffalo, NY 14260.

Abstract: As part of the U.S. EPA's Lake Michigan Mass Balance Study, a predictive model for gas-phase persistent organic compounds over Lake Michigan has been constructed. Using air temperature, wind direction and atmospheric PCB concentration collected around and over the lake, the model predicts the concentration of PCB congeners (~100) and *trans*-nonachlor over the lake and gas exchange fluxes. The model shows that gas-phase PCB and *trans*-nonachlor concentrations over Lake Michigan vary considerably as a function of temperature, wind direction, and distance from the urban-industrial region of southwest Lake Michigan. The combined effects of southerly winds and high temperatures cause a large 'plume' of gas-phase PCBs from Chicago. The Chicago urban air toxics plume can impact the whole lake when warm southerly winds are strong. In this paper, we examine the magnitude of the Chicago plume on gas deposition of these potentially toxic compounds to the lake.

Findings-PCBs

1. The LMMB 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 depositon of ΣPCBs is ~3200 kg and the Chicago contribution is ~330 kg.
2. 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.

Recommendations – PCBs

1. Reduce the deposition of PCBs to Lake Michigan by:
a. Covering land surfaces contaminated with PCBs
b. Removing structures contaminated with PCBs
c. Conduct remediation activities in cool weather

Findings – trans-nonachlor

1. The Chicago source of *trans*-nonachlor is most important in the winter. During the summertime, the source of *trans*-nonchlor is more diffuse.
2. The *trans*-nonachlor signal is not consistent with current use of the pesticide or of seasonal application.
3. Sources of *trans*-nonachlor are associated with high temperatures and southern winds. This model cannot identify the range of transport.

Recommendations – trans-nonachlor

1.Reduce the deposition of *trans*-nonachlor to Lake Michigan:
a. Prevent new application of *trans*-nonachlor inside and outside the Great Lakes basin
b. Conduct remediation activities in cool weather.

INTRODUCTION

The United States Environmental Protection Agency (U.S.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 study included a large field study conducted over eighteen months in 1994 and 1995 and is expected to continue with modeling efforts through 2002. Both the field sampling and modeling efforts focus on four potentially toxic compound groups; polychlorinated biphenyl congeners (PCBs), *trans*-nonachlor, atrazine, and mercury. The central goal of the 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 two of the compound groups, polychlorinated biphenyls (PCBs) and *trans*-nonachlor, a chlorinated pesticide. Although these compounds have been banned from use in 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. In the Great Lakes, consumption advisories still prevent full commercial development of fisheries due to the contamination of fish by PCBs and other contaminants. PCBs and *trans*-nonachlor are semi-volatile, meaning that they have a significant gas-phase component that contributes to global dispersion. These compounds desorb from surfaces and volatilize as a thermodyamically predictable function of temperature, which causes them to exhibit a seasonal atmospheric trend evident from the data produced by the LMMB and by other studies (*1-3*)

PCB mixtures were widely used as additives to oils used in lubrication and insulation from 1929 through the early 1970s. PCBs improved the viscosity and performance in oils under extreme thermal or chemical applications. They were used in energy generation, pulp and paper processing, hydraulic equipment, light ballasts, and transformers. 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, sources of PCBs to the Great Lakes have been significantly reduced and/or removed. Over that time, atmospheric sources, which may be the result of local or long range transport, as gases and as particles (*4*), 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 (*5-7*), 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 (*8*). 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* (2000) and the central strategies are reviewed here. In this paper, we use the results from the model to illustrate the dynamic nature of these effects. Furthermore, we examine the resulting predicted deposition fluxes to and from the lake and Chicago's contribution to the annual load.

ATMOSPHERIC CONCENTRATIONS

The Lake Michigan Mass Balance (LMMB) study included the collection of over 400 atmospheric samples at eight sampling stations on the shore of the lake and twenty sites over the lake that were sampled aboard the U.S. EPA research vessel Lake Guardian. The air samples collected at the shoreline sites around Lake Michigan, including Beaver Island, were collected at twelve-day intervals for the duration of the eighteen month study. The air samples collected aboard the Lake Guardian were collected during seven cruises in May, August, and October of 1994 and January, August and September of 1995. Locations of the shoreline and overwater sites are illustrated in Fig. 1. Details of the methods used in collection have been described elsewhere (*9*). Concentrations of gas and particulate-phase PCBs and *trans*-nonachlor measured at the shoreline sites are illustrated in Fig. 2 and have been described in detail elsewhere (*10-12*). Wet deposition of atrazine, PCBs, and trans-nonachlor has been described elsewhere and is not discussed here (*7*).

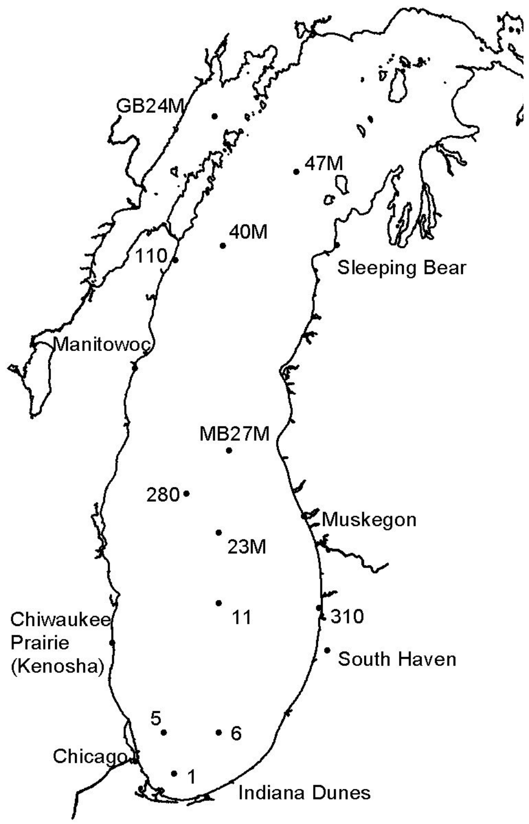


Fig. 1. Air sampling locations over and around Lake Michigan.

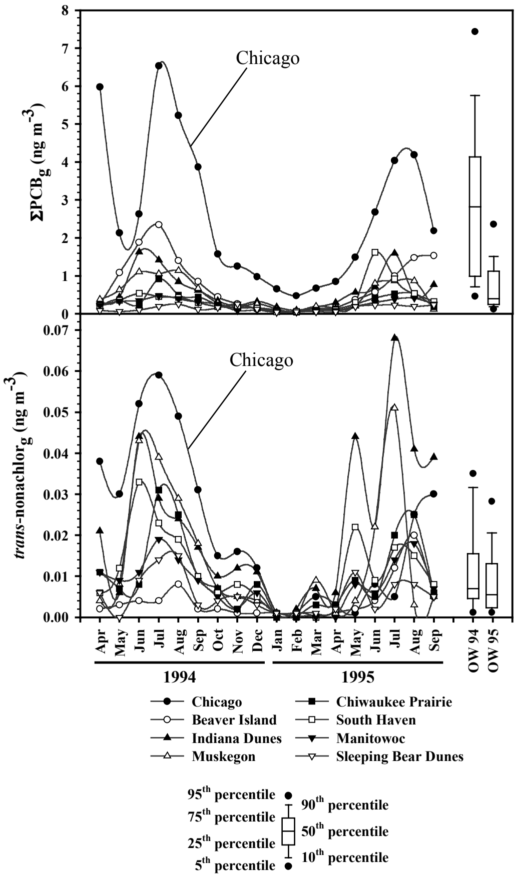


Fig. 2. Gas-phase concentrations of ΣPCBs and *trans*-nonachlor at the LMMB shore-line locations (point connected by a spline curve) and over water (box plots on the right) (adapted from ref 12).

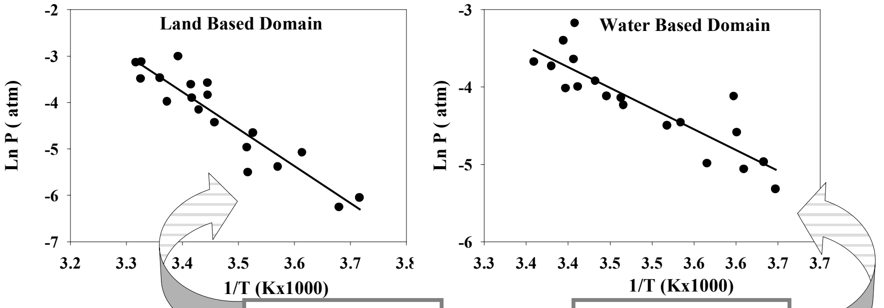
Atmospheric Modeling

The goal of the LMMB atmospheric model was to estimate the concentration of thirty gas-phase PCB congeners, ΣPCB (sum of ~100 individually measured congeners or coeluting congener groups), and *trans*-nonachlor for every day of the eighteen month field season and for the air over each of ~2300 cells of lake surface area. The grid size of each 25 km^2 cell matches the scale required by the hydrodynamic model used in the LMMB (*13*). As discussed below, one of the greatest benefits of using this fine of a grid scale is the resulting use of the model for predicting the spatial impact of the Chicago source. In addition, previous mass balance efforts (*14*) have indicated that the variability of atmospheric deposition over space and time is one of the major contributors to uncertainty in the final estimation of chemical loadings to the lake. We therefore constructed the model with the specific goal of reducing spatial and temporal uncertainty.

The modeling effort required a two-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, we considered two parameters: 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, we recognized that there were two different wind domains: when the air traveled over the land before reaching the air sampler and when the air travel over the water before reaching the air sampler. This was a difficult problem because each sample consisted of more than twenty-four 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, we used an indirect, stochastic fractionation method to predict the effect of wind direction on concentrations.

To fractionate each sample into land-based domain and water-based domain components, we used the temperature and wind direction data that was collected at each of the shoreline locations. This local meteorological data was collected and integrated on an hourly basis. The wind direction data and the corresponding air temperature data was parsed into two sets: over-land wind directions and over-water wind directions. To estimate the fractional contributions of the two 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. 3) 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^L; air temperature for air flow over the water, T^W; and four fitting coefficients, B^L, A^L, B^W, and A^W. This fitting routine was completed for each sample.



$$C_{total} = \frac{MW}{RN}\left\{\sum_{i=1}^{N^L}\frac{\exp\boxed{\left(-\frac{B^L}{T_i^L}+A^L\right)}}{T_i^L}+\sum_{i=1}^{N^W}\frac{\exp\boxed{\left(-\frac{B^W}{T_i^W}+A^W\right)}}{T_i^W}\right\}$$

Fig. 3. 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.

Fig. 3 illustrates the approach for determining the fitting coefficients. The B terms represents a fitted slope of the partial pressure (gas concentration) versus inverse temperature while the A terms represent an intercept. Two slopes are determined for the land-based domain and water-based domains, respectively. Once the fitting coefficients were determined, we could predict the concentration, C_{total}, of the compound 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 (*15*). If the gas-phase PCBs were truly at equilibrium with the land or water surfaces prior to sampling, the terms B^L and B^W could be approximated by the enthalpies of exchange, ΔH (kJ/mol).

Although each site has different B terms, for ΣPCBs the average of the B^L values provides an average ΔH value of 92 kJ/mol and the average of the B^W values provide an average ΔH of 40.3 kJ/mol. These values are similar to the laboratory-measured gas-solid and gas-water ΔH values calculated for vapor pressure (*16*) and Henry's Law (*17*), respectively.

Figure 4 illustrates the prediction of gas-phase ΣPCB concentrations at the Chicago site. This prediction indicates a great deal of day-to-day variation in the gas-phase concentrations at this site. This kind of variability is normal and was predicted at all the shoreline sites. This is a result in the strong variability in air temperature and wind direction. For example, our model predicts that Chicago air concentrations 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 (*18*). Chicago is clearly a major source of volatilized PCBs. We can see this 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.

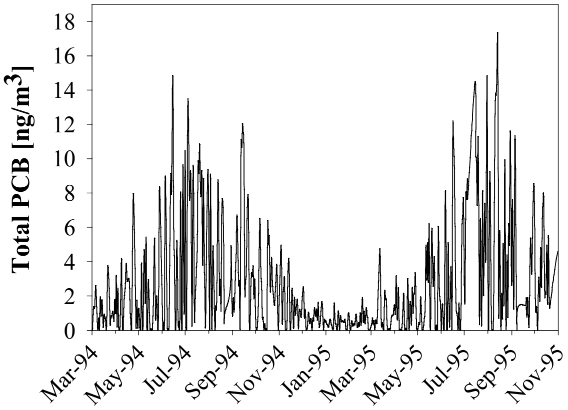


Fig. 4. Predicted daily concentrations of gas-phase ΣPCB at the Chicago site.

Once we predicted the daily concentrations at each of the eight shoreline sites and twelve over-water sites, we interpolated these concentrations in space, to predict concentrations at all ~2300 cells over the lake, on a daily basis. 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. That is, the further from a sampling site, the less influence it would have on the prediction. We used a second order weighting power, determined by comparing the prediction of the gas concentrations to independent measurements and by minimizing the global and local errors resulting from this interpolation (*10*). One of the benefits of this approach is that our predictions are primarily dependent on the more 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. Never have so many air samples been collected over such a large area over such a long time period. 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 two major, and well known, meteorological factors influencing gas-phases 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 in the Lake Michigan region, it is likely that there are a number of important 'hot spots' for these chemicals in the region. Future modification of the model is possible if such locations are identified and short sampling studies are completed. For example, we have previously suggested that the Milwaukee area is a likely source of volatilizing PCBs (*10*). To include Milwaukee as a source to the air over the lake in our model, a study of the effect of temperature on PCB concentrations at this site is necessary. A two-week study in two or three seasons could be sufficient to support addition of this potential source.

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 south 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 Fig. 5, which describes the modeling result for gas-phase concentrations of *trans*-nonachlor in May 1995. This figure is interesting in that it exhibits two different phenomena.

First, the early springtime concentrations of the pesticide in the southern part of the lake are not well explained by temperature. It appears that other factors, such as spring tillage, may cause a release of gas-phase chlordane*s* into the Lake Michigan atmosphere. It is unlikely that the May 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. Second, fig. 5 illustrates an unusual pattern in the air concentrations over 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 (or fugacity) of *trans*-nonachlor was lower in the water, relative to the air/water equilibrium ratio, than the concentration (or fugacity) 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.

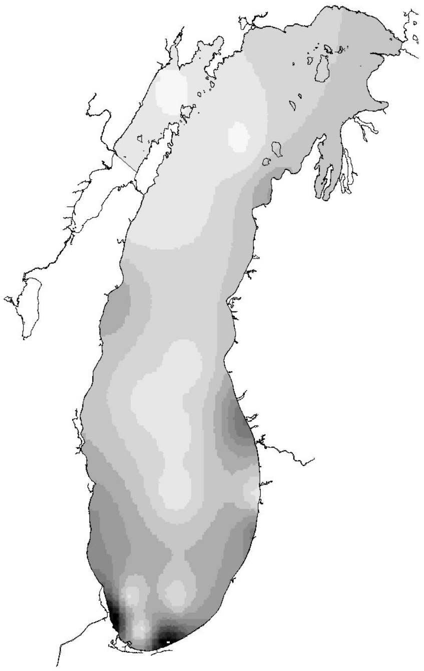


Fig. 5. Predicted average monthly gas-phase concentrations of *trans*-nonachlor in May 1994. The black regions correspond to concentrations greater than 16 pg m^{-3}. The white regions correspond to concentrations less than 1 pg m^{-3}.

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 ratio in the gas phase increases over the lake, as course 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 (*7, 12*).

We estimated net gas-exchange of PCBs and *trans*-nonachlor as a function of gas-phase concentrations, dissolved water concentrations, the physical-chemical properties of the compounds, wind speed, and surface water temperatures (*19, 20*). The overall net flux (ng m^{-2} d^{-1}) is described in equation (1).

$$F = k_{ol} (C_w - C_g/H') \tag{1}$$

Gas phase concentrations at each cell were determined using the method outlined above. Dissolved water concentrations were estimated from measurements reported by the U.S. EPA. The dissolved water concentrations were estimated as an average for the whole lake, with outliers removed, and interpolated only with respect to time. The most important physical-chemical parameter is Henry's Law constant (H' is dimensionless, ng/L in the gas phase divided by ng/L in the dissolved phase) which defines the ratio of air to water concentrations at equilibrium. H' is a strong function of temperature: warmer temperatures increase the H' value and cooler temperatures lower the H' value. The overall mass transfer coefficient, k_{ol}, 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 k_{ol} was estimated using the results of gas tracer experiments in open waters and is described in detail elsewhere (*20, 21*). We used the wind speeds and surface water temperatures over the water as estimated by Schwab *et al.* (*13, 22, 23*) on a daily basis for the individual cells. An example of the surface water and wind speed data is illustrated in fig. 6.

With the addition of wind speed and surface water temperature to the prediction of net gas exchange flux, there are now five 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 two 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.

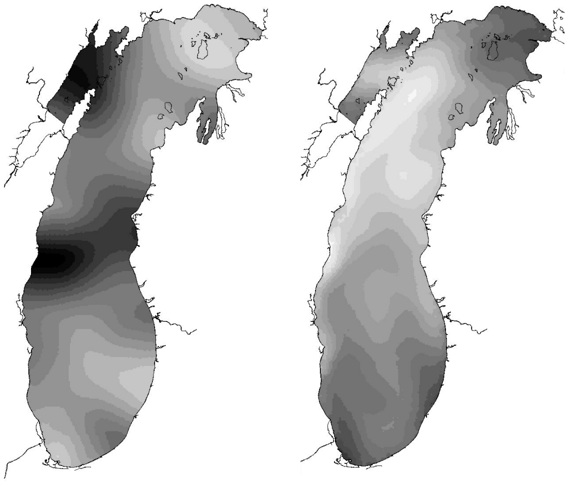


Fig. 6. The spatial variation in wind speed (left plot) and surface water temperature (right plot) in Lake Michigan. The illustrated wind speeds are the average for May 1994 and range from 4.6 to 7.2 m s^{-1} (white to black). The illustrated water temperatures are the average for September 1994 and range from 15.8 to 20.3 °C (white to black).

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 the northeast and therefore the Chicago site is predicted by the water based domain, the influence of Chicago on the lake is very small. Fig 7 illustrates this result for October 3, 1994. On that day, the measured winds were primarily northeasterly and the temperature was cool. On the following day, the winds shifted and were primarily southeasterly. On this 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, we predict 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 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.

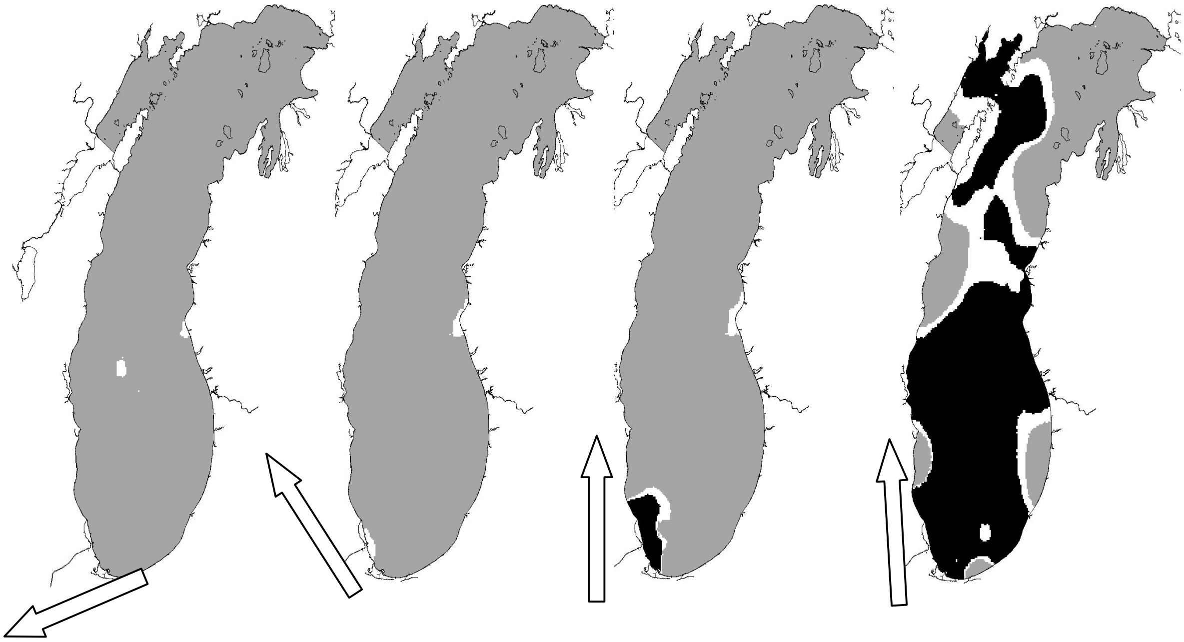


Fig. 7. Net gas exchange of ΣPCBs to Lake Michigan on four consecutive days, starting with October 3, 1994 on the left. The darkest shade represents net deposition (most evident on October 6) while the white represents zero net exchange and the light shade represents net volatilization fluxes. The arrows 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 17.9°C, respectively.

CHICAGO'S CONTRIBUTION OF AIR TOXICS TO LAKE MICHIGAN

In the previous section, we have discussed the Chicago contribution in terms of area of impact. In Green *et al.*(*10*), we showed that the annually averaged area of impact is about 40 km around the Chicago site. In the section above, we show that 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.* (*24*) over the lake near Chicago. Due to these large daily variations in air concentrations and depositional fluxes, we should probably consider the contribution 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.

We have calculated the contribution of Chicago to the total gas-phase loading of PCBs and *trans*-nonachlor to Lake Michigan. We have calculated this 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 (*25*). Gross deposition fluxes are equal to $k_{ol}(Cg/H')$. The resulting monthly deposition to the whole lake is plotted in Figure 8 for two example compounds. For consistency with equation 1, the gross depositional loads are assigned a negative value. By examining the gross deposition rather than net gas exchange, we can better consider the effect of each individual site. The Chicago site is a major source for both PCBs and *trans*-nonachlor, and this is reflected in figure 2 and in our modeling results. Figure 8 shows the predicted monthly loading to the entire lake for two compounds: 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 ranges from <5% to 20%, depending on the congener and the month. For the whole lake, gross annual deposition of SPCB (sum of the modeling results for all 98 congener groups) is ~3200 kg. On an annual basis, Chicago is the largest single source of all twenty sites considered. Annually, Chicago contributed 10% of the total deposition load of gas phase ΣPCBs. The percentage contribution shows no obvious trends with respect to water temperature, air temperature, or congener physical-chemical properties. Figure 8 (top) illustrates the percentage contribution for one PCB congener group. With respect to season, it appears that all the sites behave similarly, except that the amplitude of the response is much larger for Chicago than elsewhere.

The percentage contribution of Chicago to the whole lake loading of *trans*-nonachlor is smallest in the warmest weather. In the summer, the other sites have a higher contribution than does the Chicago site. We presume that this is due to more diverse sources 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.

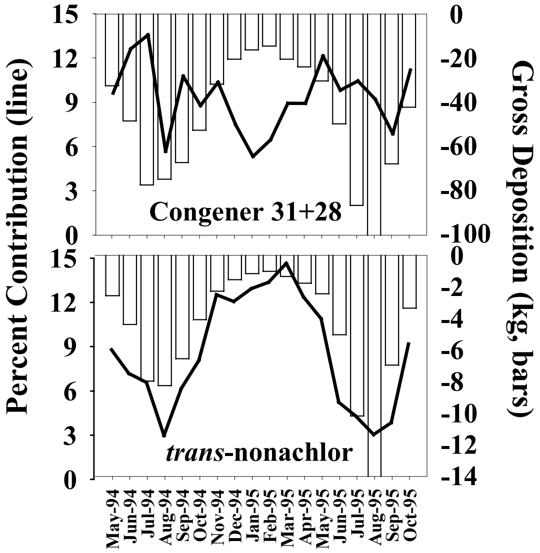


Fig. 8. Monthly whole-lake gross deposition (bars) of PCB 31+28 (top plot) and *trans*-nonachlor (bottom plot). The percentage contribution of the whole lake load from the Chicago site is described by the solid line for each month of the LMMB field season.

CONCLUSIONS

We have constructed a data-driven model to describe and predict gas-phase concentrations of PCBs and *trans*-nonachlor over Lake Michigan. The model estimates gas-phase concentration on a 5 x 5 km scale over the lake, on a daily basis. The predicted gas-phase concentrations over Lake Michigan are a strong function of air temperature and wind direction. For PCBs, the influence of the Chicago area dominates the potential deposition fluxes of PCBs to the lake. When the winds are from the southwest, deposition of PCBs greatly increases. Both groups of compounds, PCBs and *trans*-nonachlor, exhibit higher concentrations 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. In the case of *trans*-nonachlor, there appears to be a strong source region south of the lake. It is difficult to determine the 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. Warmer temperatures in the southern region of the lake are clearly correlated to higher gas-phase concentrations for both groups of chemicals. Deposition patterns across the lake are highly complex. The magnitude and direction is a function of five major meteorological factors: wind direction, wind speed, air temperature over land surfaces, air temperatures over water surfaces, and water temperatures. One of the benefits of this model is the ability to identify the day-to-day variations in deposition and to better determine the net deposition to the whole lake the effects of climate variability.

FINDINGS-PCBS

1. The LMMB 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 depositon of ΣPCBs is ~3200 kg and the Chicago contribution is ~330 kg.
2. 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.

RECOMMENDATIONS – PCBS

1. Reduce the deposition of PCBs to Lake Michigan by:
    a. Covering land surfaces contaminated with PCBs
    b. Removing structures contaminated with PCBs
    c. Conduct remediation activities in cool weather

FINDINGS – TRANS-NONACHLOR

1. The Chicago source of *trans*-nonachlor is most important in the winter. During the summertime, the source of *trans*-nonchlor is more diffuse.
2. The *trans*-nonachlor signal is not consistent with current use of the pesticide or of seasonal application.
3. Sources of *trans*-nonachlor are associated with high temperatures and southern winds. This model cannot identify the range of transport.

RECOMMENDATIONS – *TRANS*-NONACHLOR

1. Reduce the deposition of *trans*-nonachlor to Lake Michigan by:
    a. Preventing new application of *trans*-nonachlor inside and outside the Great Lakes basin
    b. Conducting remediation activities in cool weather

ACKNOWLEDGEMENTS

Funding for this work has been provided by the Great Lakes National Program Office (GLNPO) of the United States Environmental Protection Agency (U.S. EPA), Angela Bandemehr and Glenn Warren, Project Directors. The chemical data used in this modeling work was collected and analyzed by the Illinois State Water Survey (all sites - Clyde Sweet, project director) and by Indiana University (Sleeping Bear Dunes site - Ron Hites, project director). The atmospheric data has been released by the EPA after quality control review.

REFERENCES

1. R. M. Hoff, D. C. G. Muir, and N. P. Grift, *Environ. Sci. Technol.* **26**, 266 (1992).
2. B. R. Hillery, I. Basu, C. W. Sweet, and R. A. Hites, *Environ. Sci. Technol.* **31**, 1811 (1997).
3. D. R. Cortes, I. Basu, C. W. Sweet, K. A. Brice, R. M. Hoff, and R. A. Hites, *Environ. Sci. Technol.* **32**, 1920 (1998).
4. T. M. Holsen, *Environ. Sci. Technol.* **25**, 1075 (1991).
5. D. Mackay, W. Y. Shiu, and K. C. Ma, "Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals,". Lewis Publishing Co., Chelsea, MI, 1992.
6. H. Iwata, S. Tanabe, and K. Ueda, *Environ. Sci. Technol.* **29**, 792 (1995).
7. S. M. Miller M.S. Thesis, State University of New York at Buffalo, 1999.
8. P. J. Horvatin *Lake Michigan mass balance budget / mass balance work plan*. U.S. Environmental Protection Agency / Great Lakes National Program Office October 14, 1993.
9. USEPA *Lake Michigan Mass Balance Study (LMMB) Methods Compendium, Volume 1: Sample Collection Techniques*. EPA-905/R-97-012a. U.S. EPA, Great Lakes National Program Office, Chicago, Illinois.
10. M. L. Green, J. V. Depinto, C. Sweet, and K. C. Hornbuckle, *Environ. Sci. Technol.* **34**, 1833 (2000).
11. S. M. Miller, C. W. Sweet, J. V. Depinto, and K. C. Hornbuckle, *Environ. Sci. Technol.* **34**, 55 (2000).
12. S. M. Miller, M. L. Green, J. V. DePinto, and K. C. Hornbuckle, *Environ. Sci. Technol.* (in press).
13. D. J. Schwab and D. Beletsky *Lake Michigan Mass Balance Study: Hydrodynamic Modeling Project*. ERL GLERL-108. NOAA Great Lakes Environmental Research Laboratory, Ann Arbor, Michigan 1998 53 pp.
14. R. F. Pearson, K. C. Hornbuckle, S. J. Eisenreich, and D. L. Swackhamer, *Environ. Sci. Technol.* **30**, 1429 (1996).
15. F. Wania, J. E. Haugen, Y. D. Lei, and D. Mackay, *Environ. Sci. Technol.* **32**, 1013 (1998).
16. R. L. Falconer and T. F. Bidleman, *Atmos. Environ.* **28**, 547 (1994).
17. T. E. M. ten Hulscher, L. E. van der Velde, and W. A. Bruggeman, *Environ. Toxicol. Chem.* **11**, 1595 (1992).
18. H. Zhang, S. J. Eisenreich, T. R. Franz, J. E. Baker, and J. H. Offenberg, *Environ. Sci. Technol.* **33**, 2129 (1999).
19. D. R. Achman, K. C. Hornbuckle, and S. J. Eisenreich, *Environ. Sci. Technol.* **27**, 75 (1993).
20. M. L. Green Ph.D. Dissertation, State University of New York at Buffalo, 2000.
21. H. X. Zhang, S. J. Eisenreich, T. R. Franz, J. E. Baker, and J. H. Offenberg, *Environ. Sci. Technol.* **33**, 2129 (1999).
22. D. Beletsky and D. J. Schwab 4th International Conference on Estuarine and Coastal Modeling, 1997; p 511.
23. D. J. Schwab, G. A. Leshkevich, and G. C. Muhr, *J. Great Lakes Res.* **18**, 521 (1992).
24. M. F. Simcik, H. X. Zhang, S. J. Eisenreich, and T. P. Franz, *Environ. Sci. Technol.* **31**, 2141 (1997).
25. J. H. Offenberg and J. E. Baker, *J. Great Lakes Res.* **26**, 196 (2000).