Atmospheric Deposition of Toxic Pollutants to the Great Lakes As Measured by the Integrated Atmospheric Deposition Network

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To determine atmospheric deposition of anthropogenic contaminants to the Great Lakes, the United States and Canada established the Integrated Atmospheric Deposition Network (IADN), designed to collect regional data representative of the air over the lakes. In this paper, we present an update of atmospheric loadings to the Great Lakes for seven organochlorine pesticides, four polychlorinated biphenyl (PCB) congeners and total-PCBs, four polycyclic aromatic hydrocarbons (PAHs), and four trace metals. Calculations are based on gas, particle, and precipitation samples obtained in 1993 and 1994 at the five master IADN sampling stations. Air−water exchange is the dominant process for most organochlorines and lower molecular weight PAHs. Within the uncertainty in the data given here, current atmospheric loadings are indistinguishable from air−water equilibrium having been achieved over the lakes. In other words, the deposition of most organochlorine compounds *into* the Great Lakes is about balanced by the evaporation of these compounds *from* the lakes. Uncertainties in gas-transfer loadings are due to our inexact knowledge of physiochemical parameters, averaging of data over long time scales, and insufficient data for nonatmospheric sources.

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Introduction

Many ubiquitous and persistent anthropogenic pollutants are transferred through the atmosphere to regions far removed from their sources (*1−5*). Several scientists have found evidence that atmospheric transport and deposition of semivolatile organic compounds may be a major contributor to water pollution, and hence biota contamination, in the Great Lakes (*6−12*). Attempts have been made to quantify the relative importance of this atmospheric contribution (*10−12*), with estimates ranging as high as 90% for polychlorinated biphenyls (PCBs) to Lake Superior (*10*). These estimates, however, have been fraught with difficulties (*13*). Problems have included insufficient data, inadequate and nonstandardized analytical techniques, and inadequate knowledge of the physiochemical behavior of these compounds in the environment.

The United States and the Canadian governments recognized the need to better understand atmospheric deposition effects on the Great Lakes (*14, 15*), thus creating the Integrated Atmospheric Deposition Network (IADN). Sampling sites for this network were chosen to be representative of regional air near the lakes, with minimal impact from local sources. Gas, particle, and precipitation phases have been collected and analyzed. Data from all collaborators were carefully quality controlled, thus allowing results to be combined into one large database.

An important goal of this network is to estimate, on a biennial basis, the annual average, atmospheric deposition of selected toxic pollutants to the Great Lakes (*15*). The atmospheric concentrations of semivolatile organic compounds, however, have a seasonal component due to the effect of ambient temperature (*7, 16−19*). This temperature effect influences the direction of pollutant transfer across the air−water surface, with deposition occurring at some times of the year and volatilization at others (*12, 20−27*). Therefore, we have estimated loadings to the lakes on both a seasonal and annual time scale.

The first serious effort to ascertain loading estimates for each of the Great Lakes was undertaken by the International Joint Commission in 1987 (*10*). This report was published in 1988 and was based on data obtained between 1980 and 1986. Updated estimates of atmospheric loadings were presented in a 1992 report, frequently referred to as the Purple Document in the U.S. and (with greater chromatic accuracy) as the Mauve Bible in Canada (*11*). This report used data obtained between 1980 and 1990, emphasizing the later years but overlapping to some degree with the earlier report because of the paucity of available data. By 1992, five IADN master stations and 14 satellite stations were collecting samples, and recent estimates of atmospheric loadings, based on 1991−1992 IADN data (*12*), have been published.

In this paper, we provide an update of estimated atmospheric deposition to the Great Lakes using IADN data from samples collected in 1993 and 1994 from the master stations. Seasonal and annual average deposition rates are presented for both years for wet and dry deposition and for gas transfer at the air−water interface. Results for the calculated loadings for the combined 1993−1994 data are presented for all five lakes and compared to earlier estimates.

Experimental Section

Sampling Sites. The Integrated Atmospheric Deposition Network (IADN) includes five master sampling stations, located on remote shorelines of the Great Lakes in the United States and Canada; see Figure 1. The United States operates
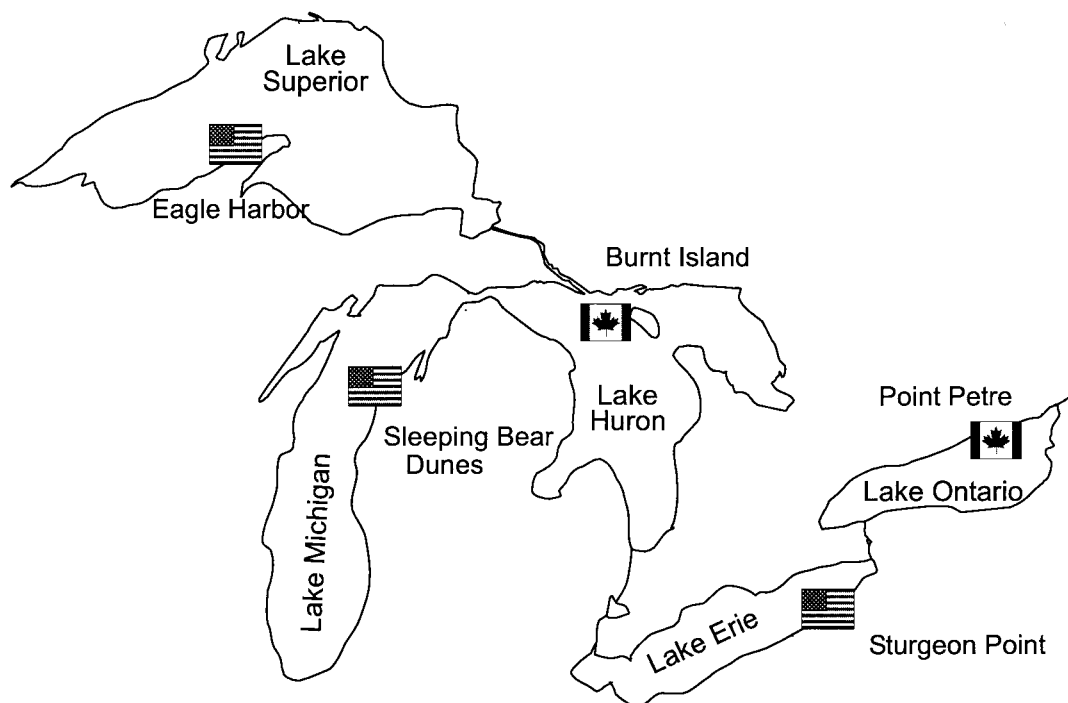
FIGURE 1. Map indicating the master sampling sites of the Integrated Atmospheric Deposition Network.

the stations at Eagle Harbor, MI, near Lake Superior (latitude 47°27′47″; longitude 88°08′59″); at Sleeping Bear Dunes, MI, near Lake Michigan (latitude 44°45′40″; longitude 86°03′31″); and at Sturgeon Point, NY, near Lake Erie (latitude 42°41′35″; longitude 79°03′18″). Canada operates the stations at Burnt Island, ON, near Lake Huron (latitude 45°48′30″; longitude 82°57′00″) and at Point Petre, ON, near Lake Ontario (latitude 43°50′34″; longitude 77°09′13″). All of these stations are equipped with apparatus for collecting meteorological data as well as wet and dry atmospheric samples. Sampling equipment is placed as close to the shoreline as logistically possible, always within 1 km.

Sampling Protocols. Details of the sampling and analytical procedures are available elsewhere (*28–30*). An important aspect of IADN is the standardization of procedures, which ensures data comparability. Nevertheless, there are a few differences in the procedures between the U.S. and Canadian teams. Polyurethane foam (PUF) is used for the collection of gas-phase organics at the two Canadian sites, and XAD-2 resin is used at the three U.S. sites (the U.S. sites used PUF prior to May 1992). At the U.S. sites, the high-volume air sampler flow rates are calibrated at 34 m^3/h, giving approximately 815 m^3/24 h collection period. At the Canadian sites, approximately 350 m^3 is collected/24 h sample. At the U.S. sites, air samples are collected every 12 days; at the Canadian sites, air samples were collected every 6 days until April 1994, when sampling was switched to every 12 days. All samplers employed a quartz fiber filter to collect particle-phase contaminants. Each site is equipped with a 10 m tower for the collection of meteorological data. Instruments include wind speed and direction sensors (Met-One or R. M. Young) installed at a height of 10 m and temperature, relative humidity, and solar radiance sensors (Campbell Scientific or Eppley) installed at 2 m. Meteorological data are recorded automatically every 6 s using a datalogger (Campbell Scientific) and output as mean hourly values. Average values are based on a meteorological year, where winter is December to February, spring is March to May, and so forth.

Quality Assurance. Extensive quality control (QC) sampling is used in this project, thus ensuring data comparability

even when there were slight differences in analytical procedures. Some sites have a second high-volume air sampler for the collection of either field blanks or duplicate samples; otherwise, field blanks are collected on the active sampler just prior to sampling. Laboratory blanks and spiked matrix samples are run routinely (*28–30*). Surrogate standards are added to all samples prior to extraction to monitor recovery. Despite these QA/QC procedures, there are a few inconsistencies in data handling, though these discrepancies are being eliminated as data are entered into a binational database, an ongoing process. For example, results reported from the U.S. sites have not been corrected for average field blanks, whereas data from the Canadian sites generally have been adjusted. This is, however, not a significant difference, because field blanks at the U.S. sites average well below 10% of the sample, a percent that is small compared to the analytical variability of generally better than 30–40% (*12*). The few differences that exist between the U.S. and Canadian data will not significantly affect the final calculations. All data were averaged on a seasonal and annual basis before being entered into the loadings calculation.

Results and Discussion

Loadings Calculations. The method of calculating atmospheric deposition for this project is defined in the Quality Assurance Project Plan [QAPP (*31*)], and it has been described in detail elsewhere (*12, 13, 32*). The QAPP states that determination of net atmospheric loadings (*L*) to the lakes is to be based upon five terms: atmospheric-tributary inputs, wet deposition, dry deposition, gas transfer, and bubble-spray production. It was recognized that fog contributes to lake loadings, but no quantitative model is available, so this factor has not been incorporated in the calculation. With one master station per lake, IADN does not acquire the data needed to determine actual tributary loads; therefore, this factor has been excluded from the current determinations. [It has been estimated that atmospheric-tributary inputs to the Great Lakes basin may increase wet and dry loads by 16–34% (*12*).] Calculating contaminant loss from the lakes due to bubble-spray production requires knowledge of the resuspension flux function. Unfortunately, no data exist for

this function, and it has been excluded from the current determinations. Thus, the equation for the net loadings (L) to the lake is

$$L = C_p R_p A \text{ (wet deposition)} + \\ C_a \phi_a \nu_d A \text{ (dry deposition)} + k_{ol}[(1 - \phi_a)C_a(RT/H) - \\ (1 - \phi_w)C_w]A \text{ (gas transfer)}$$

This is the same model used by Hoff et al. (12). Wet deposition is the product of the volume-weighted mean concentration in precipitation, C_p (kg/m³), the precipitation rate, R_p (m/year), and the area of the lake, A (m²). The surface areas of the lakes are Lake Superior = 82 100 km²; Michigan = 57 800 km²; Huron = 59 600 km²; Erie = 25 700 km²; and Ontario = 18 960 km² (31). Similarly, dry deposition is the product of the total concentration of the pollutant in the atmosphere, C_a (kg/m³), the fraction of the compound in the atmospheric particle phase, ϕ_a, the deposition velocity of the particles, ν_d (m/year), and the area of the lake. Because we collect the particle phase on a glass fiber filter, we are directly measuring the product of C_a and ϕ_a. Net gas transfer to the lake includes an absorption function and a volatilization function:

$$\text{absorption} = k_{ol}(1 - \phi_a)C_a(RT/H)A$$

$$\text{volatilization} = k_{ol}(1 - \phi_w)C_wA$$

where k_{ol} (m/year) is the overall air−water mass-transfer coefficient, R is the ideal gas constant (atm m³ K⁻¹ mol⁻¹), T (K) is the absolute temperature at the air−water interface, H (mol atm⁻¹ m⁻³) is the Henry's Law constant, and C_w (kg/m³) is the concentration of the compound in the lake water. For absorption, $(1 - \phi_a)C_a$ is the concentration of the compound in the atmospheric gas phase (kg/m³), which is measured directly. Given that ϕ_w is the fraction of the compound on the particle phase in the lake water, $(1 - \phi_w)$-C_w is the dissolved concentration of the compound (kg/m³). Contaminant concentrations in the water column are not measured by IADN. All water concentration data come from Hoff et al. (12) except for the polycyclic aromatic hydrocarbons (PAHs) which are from Bicksler and Eisenreich (34) and total-DDT (DDT + DDD + DDE) which are from Bicksler (35). When reporting flows for net gas transfer of a compound, a positive value indicates deposition to the lake and a negative value indicates volatilization from the lake.

The air concentrations used in the above equations are seasonal average concentrations. Seasonal loadings were calculated and summed to give the annual load as in Hoff et al. (12). All uncertainties presented in this paper were calculated in the same manner as Hoff et al. (12) in order to appropriately compare the 1993−1994 results to those of Hoff et al. (12). The uncertainties are, in general, propagations of individual errors of parameters in the loading calculation. The variance in concentration and physical chemical properties were pooled and the root square mean of the pooled variances were used for the averaged loading variances. Individual uncertainties in the physical chemical properties and water concentrations are the same as used in Hoff et al. (12); in a similar manner, the uncertainties in air concentrations were assigned the relative standard deviation of the seasonal averages. The relative standard deviations for the air concentrations ranged from 10−200%, but in general were approximately 70%.

Our resulting loading estimates are subject to two major sources of error (32). First, we are characterizing each lake by only one sampling site. Recent research has shown spatial differences in atmospheric concentrations of many semi-volatile organic compounds (36−39). The atmosphere sampled next to large urban areas, such as Chicago, has higher pollutant concentrations than the atmosphere sampled

several kilometers from shore (38, 39). Offenberg and Baker have estimated that the enriched urban precipitation of Chicago could increase wet deposition of PCBs to southern Lake Michigan by a factor of 2−5, from 50 to 250 kg in their work (38). Clearly, basing deposition calculations to Lake Michigan on the concentrations obtained at a remote northern site, such as Sleeping Bear Dunes, may underestimate the actual atmospheric contaminant load to the lake. Similarly, basing such calculations on concentrations obtained at an urban site such as Chicago would overestimate the load. The second source of error is linked to our observation (see below) that, for most semivolatile organic pollutants, loading rates are dominated by transfer across the air−water interface. A propagation of error analysis for previous loadings calculations has shown that the error in the net gas fluxes is 50−7400%, with the error increasing as the interfacial flux approaches zero (12, 32). Most of this error is caused by uncertainties in the physical properties such as H and k_{ol}. Improvements in our knowledge of these physical properties would increase precision of the estimated atmospheric loads to the lakes.

All dry deposition flows in this work were calculated using a deposition velocity of 0.2 cm s⁻¹. Actual deposition velocities are likely to vary, depending on particle size and micrometeorological conditions (40−44). Factors affecting partitioning between vapor and particles include the compound's vapor pressure, the ambient air temperature, and the concentration of particles in the atmosphere. None of these parameters are constant in the environment. By neglecting these parameters and by averaging data over broad time scales, uncertainties have been incorporated into the final results (32, 42, 43). By using the same parameters as used in previous studies (10−12), we are able to make direct comparisons between the results.

In incorporating seasonal average temperatures into the model, it was assumed that the air in contact with the water was at the same temperature as the water surface layer. In this paper, we have used the actual seasonal average air temperatures for the years 1993 and 1994 instead of the long-term average that was used in the 1991−1992 study (12). Actual water temperatures, however, will vary from year to year. There are also significant horizontal variations in lake surface temperatures, with regions near shore or in shallow bays as much as 10 °C higher than mid-lake locations (25). Honrath et al. have concluded that assuming water surface temperatures equal to air temperatures measured at near-shore sampling sites provides parameter estimates consistent with Henry's Law equilibrium (25).

1993−1994 Lake Loadings. Complete results for wet and dry deposition and net gas transfer for each season and annual averages for 1993 and 1994 are available in the Supporting Information. Where data were available, results were reported for both 1993 and 1994. Data unavailability was caused by several factors. In some cases, not all samples were collected, such as some of the precipitation samples for metals. For many of the semivolatile organic compounds, concentrations in the particle phase were less than 10% of the total air concentration; therefore, the particle phase was not always analyzed for these compounds. Metals were analyzed only on particulates; thus, there is no gas-transfer determination. [In any case, gas transfer is not expected to be a significant contribution to annual lake loadings of metals (10).] Where there are no gas-transfer flows available for organic compounds, this is generally due to a lack of water concentration data, making it impossible to calculate volatilization. Because this paper updates loading estimates made in previous years (10−12), the pollutant list has been kept consistent with earlier studies.

Because the full data set is so voluminous (see the Supporting Information), we have chosen to focus the

TABLE 1. Atmospheric Loadings (kg/yr) of Contaminants to the Great Lakes 1993−1994[a]

	Superior	Michigan	Huron	Erie	Ontario
net					
total-PCBs	−180 ± 600	−560 ± 720	−340 ± 490[b]	−340 ± 850	−370 ± 420[b]
total-HCHs	420 ± 870	270 ± 3300	−470 ± 650[b]	**600 ± 450**	0 ± 150[b]
total-DDT	**70 ± 35**	76 ± 90	−36 ± 37[b]	**110 ± 63**	−11 ± 30[b]
phenanthrene	5400 ± 5500	**7000 ± 4400**	640 ± 180[c]	**10 000 ± 6700**	−24 ± 560[c]
lead	**21 000 ± 20 000**[d]	**16 000 ± 13 000**[d]	**76 000 ± 23 000**	**13 000 ± 9700**[d]	**31 000 ± 6200**
dry					
total-PCBs	56 ± 56	32 ± 33	N/A[e]	22 ± 24	N/A
total-HCHs	**12 ± 8**	**7.4 ± 5.4**	N/A	**3.9 ± 2.9**	N/A
total-DDT	**4.8 ± 2.5**	**6.0 ± 4.5**	N/A	**2.9 ± 2.0**	N/A
phenanthrene	190 ± 170	120 ± 100	81 ± 69	130 ± 120	36 ± 41
lead	**21 000 ± 20 000**	**16 000 ± 13 000**	9500 ± 12 000	**13 000 ± 9700**	5900 ± 5800
wet					
total-PCBs	**110 ± 24**	**110 ± 24**	**140 ± 41**	**35 ± 7**	**62 ± 27**
total-HCHs	**69 ± 16**	**170 ± 31**	**420 ± 93**	**77 ± 15**	**77 ± 13**
total-DDT	**82 ± 21**	**86 ± 15**	**8.8 ± 1.7**	**68 ± 23**	**6.6 ± 2.8**
phenanthrene	**160 ± 22**	**220 ± 48**	**560 ± 170**	**360 ± 92**	**550 ± 74**
lead	N/A	N/A	**67 000 ± 20 000**	N/A	**25 000 ± 2100**
gas transfer					
total-PCBs	−350 ± 600	−700 ± 720	**−480 ± 490**	−390 ± 850	−440 ± 420
total-HCHs	340 ± 870	92 ± 3300	**−890 ± 640**	520 ± 450	−77 ± 150
total-DDT	−17 ± 28	−16 ± 89	**−45 ± 37**	39 ± 59	−18 ± 30
phenanthrene	5000 ± 5500	**6700 ± 4400**	N/A	**10 000 ± 6700**	N/A
lead	N/A	N/A	N/A	N/A	N/A

[a] Bold entries are significantly different from zero. Negative flows indicate net atmospheric loss from the lake. Uncertainties represent propagated error. [b] No dry deposition flows. [c] No gas transfer flows. [d] Dry deposition only [e] N/A indicates data not available.

following discussion on five representative substances: three organochlorine compounds, one polycyclic aromatic hydrocarbon, and one metal. Thus, the 1993−1994 loadings to each lake are summarized for total-PCBs, total-HCHs (α + γ), total-DDT (DDT + DDD + DDE), phenanthrene, and lead in Table 1. This table presents the net, dry, wet, and gas-transfer flows into or out of each of the five lakes. The net flow is the wet plus the dry minus the gas-transfer flows. Flows that are significantly different than zero are indicated in bold font.

The net flows of total-PCBs and total-HCHs were not significantly different from zero in any of the five lakes, suggesting that the concentrations of these compounds are indistinguishable from equilibrium between the surface water and the overlying atmosphere. In all cases, the net deposition of PCBs and HCHs was insignificant, because gas transfer out of the lakes counteracted the flow into the lakes from wet and dry deposition. Although wet deposition flows for both PCBs and HCHs indicated substantial deposition into all five of the lakes, gas transfer of these compounds had large uncertainties that contributed to the insignificance of the net flow. (Note that the lack of dry deposition flows for Lakes Huron and Ontario does not have much effect on the net deposition because dry deposition for these relatively volatile compounds is low.) Despite the large uncertainties, however, we conclude that the PCBs and HCHs were approximately at equilibrium between the surface water and atmosphere. If these compounds are in fact at equilibrium, then the atmospheric concentration of these contaminants could be monitored to track changes in the water concentrations as suggested by Mackay and Bentzen (45).

The net deposition of total-DDT was substantially into (positive flows) Lakes Superior and Erie in 1993−1994, due largely to significantly high wet deposition. Lake Michigan also had substantially high wet deposition, but large uncertainties in the gas transfer caused the overall deposition of total-DDT to Lake Michigan to be insignificant. On the other hand, Lakes Huron and Ontario had significantly lower wet deposition of total-DDT. As a result, Lake Huron showed a significant loss of total-DDT to the atmosphere, and the

net flow between Lake Ontario and the overlying atmosphere was not significantly different from equilibrium. (Because of the relatively high volatility of total-DDT, the lack of dry deposition flows for Lakes Huron and Ontario does not have much effect on the net deposition.)

Phenanthrene significantly deposited to Lakes Michigan and Erie, but Lake Superior was not significantly different from equilibrium. (Lakes Huron and Ontario are omitted from this discussion because of missing gas-transfer flows, which are expected to be significant.) Because of phenanthrene's relatively high affinity for atmospheric particles, this compound had significantly high flows into the lakes from both wet and dry deposition. Wet and dry deposition contributed approximately equally to the deposition of phenanthrene to Lakes Superior, Michigan, and Erie, but Lake Huron had significantly lower dry deposition compared to wet deposition.

For Lakes Huron and Ontario, the net loads of lead given in Table 1 are primarily the result of wet deposition. Unfortunately, wet deposition was not available for Lakes Superior, Michigan, or Erie, and of course, gas transfer of lead was assumed to be negligible for all of the lakes. Wet deposition to Lakes Huron and Ontario constituted 88 and 80% of the lead load to these two lakes. Assuming that wet deposition will also account for 80% of the net atmospheric load to Lakes Michigan, Superior, and Erie we can estimate the wet depositions to each lake as 130 000, 100 000, and 81 000 kg/year, respectively. The dry and wet deposition of lead to the Great Lakes is orders of magnitude larger than for the organochlorine compounds and phenanthrene because of lead's higher loads on atmospheric particles.

While the dry deposition of phenanthrene and lead are usually significantly different from zero, there are no differences among the five lakes despite the great differences among the surface areas of the lakes. This balance may be achieved because Lake Superior, while it has the largest surface area, has the least populated shoreline and the least amount of industry in its region. On the other hand, Lakes Erie and Ontario have the smallest surface areas, but they are surrounded by the most industry in the region.

TABLE 2. Temporal Comparison of Net Atmospheric Loadings[a]

year	Superior (kg/yr)	Michigan (kg/yr)	Huron (kg/yr)	Erie (kg/yr)	Ontario (kg/yr)
total-PCBs					
pre-1990	−1600	−4900	−2300	−1000	−622
1991−1992	**−1600 ± 1500**	−2600 ± 2600	180[b]	−380 ± 460	**−380 ± 330**
1993−1994	−180 ± 600	−560 ± 720	−340 ± 490[c]	−340 ± 850	−370 ± 420[c]
total-HCHs					
pre-1990	468	342	340	462	130
1991−1992	650 ± 1000	1200 ± 4200	310[b]	**290 ± 180**	79 ± 180
1993−1994	420 ± 870	270 ± 3300	−470 ± 650[c]	**600 ± 450**	0 ± 150[c]
total-DDT					
pre-1990	−650	−460	−470	−200	−150
1991−1992	**47 ± 45**[d]	**99 ± 140**[d]	37[b]	**81 ± 50**[d]	−140 ± 150[e]
1993−1994	**70 ± 35**	76 ± 90	−36 ± 37[c]	**110 ± 63**	−11 ± 30[c]
phenanthrene					
pre-1990	312	228	227	108	87
1991−1992	−3000 ± 4800[f]	**460 ± 170**[f]	N/A[g]	N/A[g]	610 ± 880
1993−1994	5400 ± 5500	**7000 ± 4400**	**640 ± 180**[f]	10 000 ± 6700	−24 ± 560
Pb					
pre-1990	62 000	130 000	9100	91 000	43 000
1991−1992	51 000 ± 70 000	**72 000 ± 37 000**	100 000[b]	**65 000 ± 60 000**	**46 000 ± 8100**
1993−1994	120 000[h]	150 000[h]	**76 000 ± 23 000**	94 000[h]	**31 000 ± 6200**

[a] Data for pre-1990 from Strachan and Eisenreich (*10*) and Eisenreich and Strachan (*11*), and 1991−1992 from Hoff et al. (*12*). Negative flows indicate net atmospheric loss from the lake. Bold entries are significantly different from zero. Uncertainties represent propagated error. [b] Wet deposition only. [c] No dry deposition flows. [d] No gas transfer flows for DDE or DDD. [e] No gas transfer flows for DDE. [f] No gas transfer flows. [g] N/A indicates data not available. [h] Estimated from a 5:1 ratio of wet:dry deposition; see text.

Temporal Trends. The data from this study are compared to the results obtained from the pre-1990 (*10, 11*) and 1991−1992 studies (*12*) in Table 2.

Total-PCBs seem to have had a steady decrease in their net loss to the atmosphere from Lakes Superior and Michigan, but the uncertainties make any definitive observation of trends impossible. The deposition of HCHs has remained relatively constant over the three studies, never showing any significant difference from equilibrium. Lindane (γ-HCH) is still used in the United States and Canada. Its use in the U.S. was cut in half from 1980 to 1990 (*46*), but Canada's use remained constant over the same time period (*46*). Despite the overall reduction in recent use of γ-HCH and the ban of other HCH isomers, the net flow of total-HCHs to the Great Lakes has not changed. The pre-1990 study suggested that there were net losses of total-DDT for all five lakes on the order of hundreds of kg/year. The 1991−1992 and 1993−1994 data indicate (but do not prove) a reversal from net volatilization to net deposition for most of the lakes. It appears that the net volatilization prior to 1990 was a response to historical contamination.

While the net deposition of phenanthrene seems to have increased since the pre-1990 study for most of the lakes, only deposition to Lake Michigan significantly increased from 1991−1992 to 1993−1994. Phenanthrene has continuing sources to the Great Lakes regional atmosphere; therefore, it is not surprising that the net flow between the atmosphere and surface water shows no trend over the time period covered by these three studies. None of the lakes exhibited any significant change in the net deposition of lead from 1991−1992 to 1993−1994. Leaded gasoline was phased out long before any of the studies represented by Table 2, so it is not surprising that the deposition of lead into the lakes has remained relatively unchanged since 1990. However, going back 15−20 years, we find that wet plus dry deposition of lead was estimated by Eisenreich (*47*) to be 640 000 kg/yr in 1975−1976 to Lake Michigan. The net deposition of lead to Lake Michigan from this study is about a factor of five lower. Presumably, this reduction in the atmospheric deposition of lead since the 1970s is due to the elimination of leaded gasoline.

Several researchers have noted that the lakes appear to be responding rapidly to the atmosphere (*25, 45*). On the basis of data from the 1991−1992 update (*12*), Mackay and Bentzen (*45*) estimated that most of the semivolatile contaminants in the lake water will approach equilibrium with the air in a few years. The results presented in this paper do not contradict this rapid response.

Because contamination from industrial sources has been largely controlled, the atmosphere is now the main source of toxic organic pollutants to the Great Lakes. Thus, the concentrations of these compounds in the water of the Great Lakes will soon depend on their concentrations in the air. As the air concentrations decrease, the water concentrations will continue to decrease. In fact, we are already seeing such a decrease for PCBs in both the air (*19*) and the water (*24, 48*), both with overall half-lives of about 5−9 years.

Acknowledgments

Supporting Information Available

Complete results for wet and dry deposition and net gas transfer for each season and annual averages for 1993 and 1994 (10 pages). Ordering information is given on any current masthead page.

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