

The **Great Lakes'** Integrated **ATMOSPHERIC** **DEPOSITION** Network

The United States and Canada continue an effective partnership that measures nonpoint source pollution.

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The Great Lakes basin is home to 18% of the world's freshwater supply and more than 10% and 25% of the people in the United States and Canada, respectively (1). Economic activity in the region accounts for approximately 18% of the combined U.S. and Canadian gross domestic product, according to the U. S. Department of Commerce's Bureau of Economic Analysis (www.bea.doc.gov) and Statistics Canada (www.statcan.ca). These facts alone make the environmental health of the Great Lakes important. Indeed, the Great Lakes were the focus of early, classic water pollution studies. For example, phosphate, which contributed to the eutrophication of Lake Erie, was studied extensively in the 1970s (1–3).

Studies and attention from the United States and Canada helped correct many of these problems during the 1980s. Soon, the presence of toxic substances in Great Lakes fish became the focus of environmental agencies in both countries. Eventually, this binational cooperation led to the creation of the Integrated Atmospheric Deposition Network (IADN) to monitor trends of nonpoint source pollution in the Great Lakes basin. This article presents some of IADN's cur-

rent research results. The Web site (www.smc-msc.ec.gc.ca/iadn/index.html) provides more details, in French and English, about IADN projects for the interested reader. The actual data are available through the IADN data request form also found on the site.

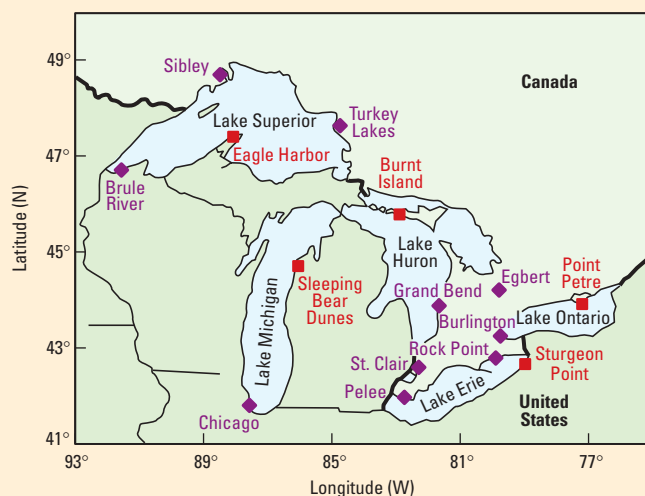
A joint venture

In the late 1980s, as point sources were brought under control, suspicions grew that toxic substances were entering the Great Lakes by atmospheric deposition. This meant that airborne pollutants from outside the Great Lakes basin were an additional source of contaminants to the lakes (4). Indeed, following a 1986 workshop sponsored by the International Joint Commission, an independent adviser on boundary water issues to the United States and Canada, participants produced a document confirming that atmospheric deposition was a major source of contamination to the Great Lakes (5). This report led to Annex 15 of the 1987 revisions to the Great Lakes Water Quality Agreement of 1978, which called for the creation of a network to measure the atmospheric concentrations of toxic substances near the Great Lakes (www.ijc.org/agree/quality.html). As a result, IADN was created in 1990.

FIGURE 1

Integrated Atmospheric Deposition Network sites

Master stations (red squares) are the main sites in the network and the first to be established for each lake. Satellite stations (purple diamonds) have been added to augment the master stations.



IADN, which is a joint venture of Environment Canada, the Ontario Ministry of the Environment, and the U.S. EPA's Great Lakes National Program Office, consists of a master monitoring station located on each of the five Great Lakes and several satellite stations (see Figure 1). IADN collects gas and particle-phase air samples for 24 hours every 12 days at all master and some satellite sites using high-volume air samplers. Precipitation samples are taken during every rain or snow event and composited every 28 days in the United States and every 14 days in Canada using samplers that open only during a rain or snow event. Meteorological data such as air temperature and wind speed and direction are also collected at most sites and averaged on an hourly basis.

IADN sites now measure 13 polycyclic aromatic hydrocarbons (PAHs), 18 organochlorine pesticides (including those banned and in use), and 56 polychlorinated biphenyl (PCB) congeners or congener groups. Gas chromatography coupled with mass spectrometry, gas chromatography with electron capture detection, and liquid chromatography with fluorescent detection are used for chemical analysis. IADN also features extensive quality assurance/quality control procedures,

including laboratory and field blanks and duplicates, matrix spike experiments, and round-robin studies (6–8). References (9) and (10) and the IADN Web site provide more information on the sampling and analytical procedures.

Over its 12-year lifetime, IADN studies have determined that the Great Lakes have, indeed, been threatened by the deposition of many airborne toxic pollutants. However, these same long-term measurements indicate the threat has diminished for many of these substances as policies and regulations restricting their use have taken effect. EPA recently announced the 2002 Great Lakes Strategy, which has the goal of protecting and restoring the lakes. More specifically, the strategy includes plans to integrate IADN with regional, national, and international monitoring efforts to help pursue its goal of restoring the “chemical integrity” of the Great Lakes basin.

Temporal trends

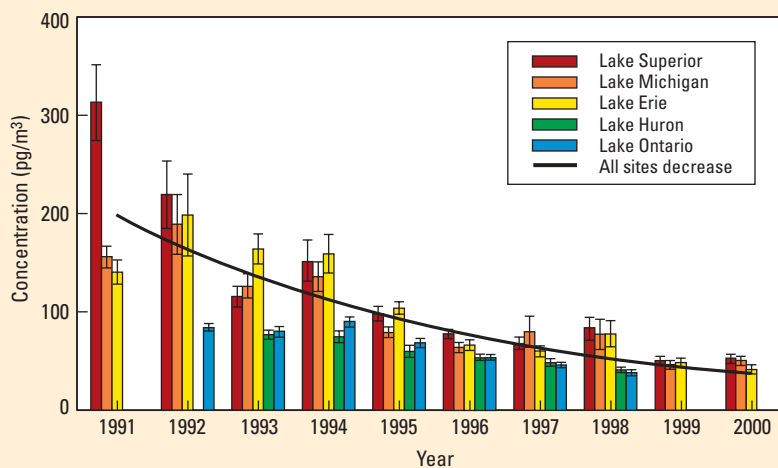
One of the goals of IADN is to determine whether the concentrations of toxic organic compounds in air and precipitation near the Great Lakes are changing as a function of time. Understanding these temporal trends is important both scientifically and politically. Analysis of trends can help researchers determine whether and how fast the atmospheric concentrations are decreasing and provide clues about the sources of a chemical. These trends can also help policy makers determine if bans or restrictions on using a given chemical are working and how long it will take before these chemicals are eliminated from the environment.

Most of the chemicals measured by IADN have either been banned or heavily restricted. One such chemical is α -hexachlorocyclohexane (α -HCH), the isomer that comprises about 60% by weight of technical HCH, which was a mixture of five HCH isomers

FIGURE 2

Annual average atmospheric gas-phase α -HCH concentrations at IADN master stations

The fitted exponential curve has a correlation coefficient (r^2) of 0.950 for the average of all sites and is statistically significant with 99% confidence. Concentrations are in picograms per cubic meter. Error bars represent the standard error of each average. (Data for 1999 and 2000 for Lakes Huron and Ontario are not yet available.)



used as a broad-spectrum insecticide starting in 1942. Technical HCH has since been banned, restricted, or deregistered in 70 countries. U.S. and Canadian product registrations were cancelled in 1978. Thus, examining the temporal trend of α -HCH at each of the Great Lakes helps us determine whether this ban on technical HCH has been effective.

Figure 2 shows the gas-phase, annual average concentrations of α -HCH in picograms per cubic meter (pg/m^3) from each IADN master station beginning in 1991. Clearly, there has been a dramatic decline in α -HCH concentrations in the air near each lake in the past 10 years. If the total loss rate of a given compound from the atmosphere is proportional to the amount of that compound in the atmosphere at any moment, then the concentrations should follow a first-order rate law such as Equation 1,

$$C_t = C_0 e^{-kt} \quad (1)$$

in which C_t is the atmospheric concentration at time t and k is a first-order rate constant. We fitted the average annual concentration of all sites for each year in Figure 2 to this equation and obtained a rate constant of 0.19 per year for the basin. The curve in Figure 2 is a plot of Equation 1 where $k = 0.19$. By dividing the rate constant into the natural logarithm of 2, we obtain an overall environmental half-life of approximately four years for α -HCH in the air near the Great Lakes. In other words, we expect that the atmospheric concentrations of α -HCH near the Great Lakes will decrease by a factor of 2 every four years.

Assuming first-order kinetics and minimal future inputs, we can use this temporal information to estimate a virtual elimination date for α -HCH, that is, when we will no longer be able to detect this compound in the atmosphere (11). Using the data in Figure 2 and a minimally detectable concentration of $0.1 \text{ pg}/\text{m}^3$, one can calculate the year to be ~ 2040 . Thus, α -HCH will be with us even after most of us retire.

Other banned pesticides and PCBs follow similarly declining concentration patterns, but the virtual elimination dates differ for each substance (11–19). On average, the virtual elimination date is 2034, with a standard deviation of 20 years. In contrast, PAHs are still being released into the atmosphere, mainly as the byproducts of fossil fuel combustion. As a result, PAHs do not show declining concentration trends and generally have maintained their levels in the Great Lakes atmosphere over time.

Spatial trends

Another goal of IADN is to determine the spatial trends of atmospheric pollutants in the Great Lakes basin. This analysis can help determine where problems remain for certain substances and how the physical differences in the lakes and areas surrounding each lake affect atmospheric pollution levels. PCBs provide a good example of this approach. Using a logarithmic scale, Figure 3 shows the annual average concentrations of gas-phase total PCBs (the sum of the individual congeners measured by IADN) in picograms per cubic meter from each of IADN's master stations, as well as from the two satellite stations at Brule River on Lake Superior and Chicago on Lake Michigan. Figure 3 shows that total PCB concentrations at the Chicago station have been about an order of magnitude higher than at all other sites.

PCBs were used in a wide array of industrial applications from 1930 until they were banned in the United States in 1976. Because their use was concentrated in urban areas, we expected Chicago's PCB levels to be higher than those at IADN's other sites, which are remote from major population centers. Not all of these remote sites, however, are immune to urban influences. For example, Figure 3 indicates that Sturgeon Point, the IADN master station on Lake Erie, consistently has the second highest total PCB annual average, whereas the PCB concentrations for the other sites tend to be similar to one another. Although considered a remote sampling site, Sturgeon Point is located approximately 20 kilometers (km) southwest of Buffalo, N.Y., a relatively large urban center. Even at this distance, there is an "urban effect" on the PCB concentrations at Sturgeon Point.

FIGURE 3

Annual average atmospheric gas-phase total PCB concentrations for IADN master stations and two U.S. satellite sites

Polychlorinated biphenyl (PCB) concentrations are in picograms per cubic meter and error bars represent the standard error for each average. (Data for 1999 and 2000 are not yet available for Lakes Huron and Ontario.)

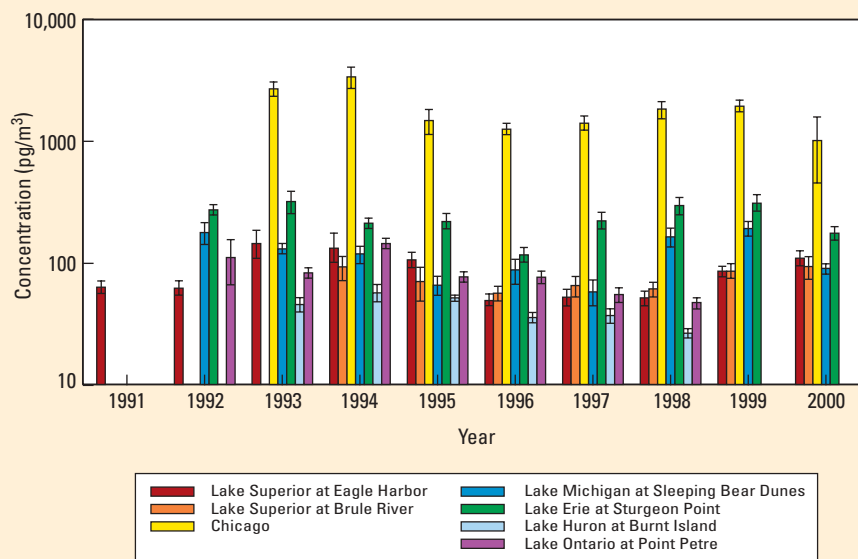
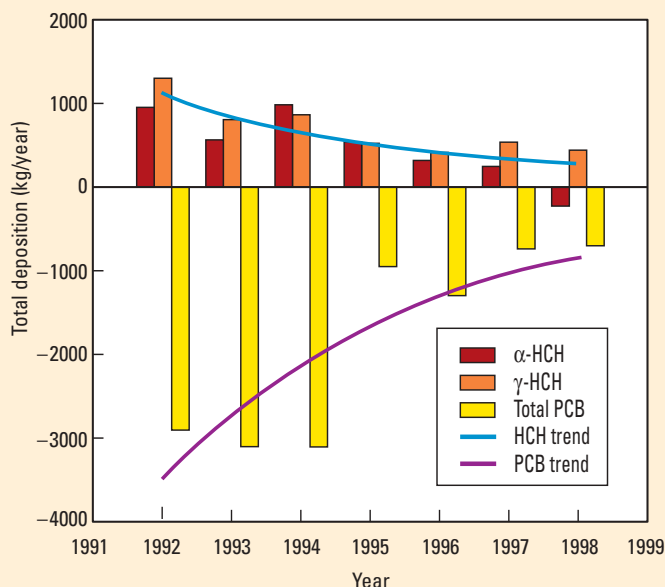


FIGURE 4

Annual loadings for α -HCH, γ -HCH (lindane), and total PCBs into or out of the five Great Lakes collectively

Total deposition is the sum of wet and dry deposition and gas absorption minus volatilization. Negative total deposition indicates that, overall, the lakes are volatilizing the compound into the atmosphere. The two curves indicate general trends in the hexachlorocyclohexane (HCH) (average of α and γ isomers) and polychlorinated biphenyl (PCB) loadings. The fitted exponential curves have correlation coefficients (r^2) of 0.833 and 0.744 for the HCH and PCB loadings, respectively; both are statistically significant with 99% confidence.



Our studies of particle-phase PAH concentrations at Sturgeon Point have also shown that levels were higher than at the other master stations (16). In fact, detailed analyses indicated that the PAH concentrations were especially elevated at Sturgeon Point when the winds blew from Buffalo (17). We can infer from these findings that Buffalo is a source of PCBs and PAHs at the Sturgeon Point location.

But Sturgeon Point is not the only site influenced by a city. Brule River, Wis., a satellite station on Lake Superior, is located 40 km southeast of Duluth, Minn. Even this small city caused elevated PAH particle-phase concentrations at Brule River compared to the other Lake Superior site at Eagle Harbor, Mich. (18). These results show that PAHs and PCBs are largely urban pollutants that can travel tens of kilometers through the atmosphere.

It is important to note, however, that increased urban concentrations are not found for all pollutants. For example, pesticide concentrations tend to be similar at remote and urban sites, presumably because the use of such chemicals is mainly agricultural. Nonetheless, the relative lack of urban sites in IADN represents a gap in our spatial understanding of air toxics around the basin and deserves attention if IADN's role in the 2002 Great Lakes Strategy is to be as beneficial as possible.

Loadings

IADN also determines loadings of these toxic compounds to the Great Lakes on a biennial basis to fulfill another network goal. In this context, "loadings" means an estimate of the amount of a toxic substance being deposited to the waters of the Great Lakes from the atmosphere minus the amount of that substance being volatilized or released from the water to the atmosphere. To make these estimates, IADN calculates wet and dry deposition, gas absorption, and volatilization of the various substances using yearly IADN atmospheric concentration data and using water concentration data for the Great Lakes measured by other researchers. Loadings estimates have been published for data from 1991 to 1996 (18–21), and the most recent estimates have just been completed (22).

The most current loadings report lists estimated loadings for pesticides, PCBs, PAHs, and some metals over the entire Great Lakes basin from 1992 to 1998, in addition to estimates for each individual lake (22). This systemwide estimate was obtained by summing the total deposition for each substance across all five lakes (when available) for each year. Figure 4 shows these total regional loadings for α -HCH, γ -HCH (lindane), and total PCBs.

Although α -HCH is banned worldwide, γ -HCH is currently used, particularly in Canada, although with restrictions (23). Figure 4 shows that the total deposition of α - and γ -HCH into the Great Lakes has generally decreased since 1992. On the other hand, regionwide loading estimates for in-use chemicals, such as PAHs and metals, show no real declining trends. These chemicals continue to have many anthropogenic sources, allowing them to directly enter the atmosphere, which, in turn, transports them to and deposits them in the Great Lakes region.

PCB loadings to the Great Lakes as a function of time are also shown in Figure 4. In this case, we find that the waters of the Great Lakes have been volatilizing PCBs into the atmosphere for at least seven years, which accounts for negative loadings, and the rate of volatilization has generally decreased with time. Clearly, when PCBs were used in the 1960s, there were substantial inputs into the lakes. Now that PCBs have been banned and the atmospheric concentrations have decreased, the air-water equilibrium has shifted, so the water is releasing its stores of PCBs back into the atmosphere (12).

As indicated by the two curves in Figure 4, the deposition of HCHs into the Great Lakes and the evaporation of PCBs from the Great Lakes seem to be approaching zero. Because these compounds are relatively volatile and have little or no dry or wet depo-

sition into the lakes (22), we know that the total deposition shown in Figure 4 is driven almost entirely by air–water exchange. This observation suggests that air–water partitioning—at least for these compounds—is approaching equilibrium. Combined with other IADN studies, these findings suggest that the restrictions on the use of PCBs and other chlorinated pesticides have helped to reduce their levels in the Great Lakes atmosphere and water, providing a healthier ecosystem for all inhabitants of the basin.

As shown in Figure 3, urban areas in the Great Lakes basin have significantly higher PCB concentrations than remote sites. To account for higher pollutant concentrations, the recent loadings reports explored the impact of the Chicago urban area on lakewide loadings in nearby Lake Michigan (21, 22). A subarea of the lake affected by urban atmospheric concentrations when the wind was blowing from Chicago was assigned for wet and dry deposition (1.7% of the total lake area) and for gas exchange (3.5% of the total lake area), and the loading estimates were recalculated to include this information. The results indicated that Chicago had little effect on the loadings of pesticides to Lake Michigan, increased the loadings of PAHs to the lake by 20–200%, and significantly decreased the volatilization of PCBs from the lake. The loadings estimates themselves are the culmination of the IADN data and present much-needed insights on the contribution of the atmosphere to the pollution in the Great Lakes (19–22). But as the Chicago impact estimates point out, more work is still needed to fully understand these processes.

Pinpointing the pollution

IADN data have become an important tool for those doing research on the Great Lakes because IADN possesses the best, continuous, long-term data set for studying the behavior of pollutants in the Great Lakes' atmosphere. Over the past four years alone, dozens of researchers or research groups, ranging from universities to government agencies, have requested IADN data for models, to compare to their findings, or to augment their data. Despite the usefulness of the current data, IADN must continue to grow and change to keep pace with emerging concerns in the region. In the future, we hope to pinpoint possible sources of pollution to the Great Lakes using IADN meteorological and concentration data (24); to incorporate polychlorinated dioxins, polybrominated diphenyl ethers (flame retardants), mercury, and toxaphene into the list of analytes (25); and to establish new urban study sites.

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