COOPERATING TO IMPLEMENT THE GREAT LAKES WATER QUALITY AGREEMENT

MIS EN OEUVRE DE L'ACCORD SUR LA QUALITÉ DE L'EAU DES GRANDS LACS

Technical Summary of Progress of the

Integrated Atmospheric Deposition Network (IADN) 1997-2002

United States - Canada IADN Scientific Steering Committee

October 2002

ABSTRACT

This report is a technical summary of the progress made by the Integrated Atmospheric Deposition Network (IADN) during the last five years. IADN is a joint Canadian-United States monitoring and research program called for in the Great Lakes Water Quality Agreement. IADN measures the concentrations of polychlorinated biphenyls, several organochlorine pesticides, several polycyclic aromatic hydrocarbons, and trace metals in the atmosphere (both gas- and particle-phases) every 12 days at five Master Stations and at several Satellite Stations located on the shores of all of the Great Lakes. The concentrations of these compounds in precipitation are also measured in monthly composite samples. IADN has been in operation continuously since 1990 and has generated a unique time-series of measurements.

This report presents:

- the history and mandates of IADN
- a brief status report on the Network 's operation (including QA status)
- IADN's scientific results on temporal and spatial trends and on loadings
- other associated research efforts
- future plans

The results show that the lakes are sensitive to atmospheric deposition of toxic chemicals but that concentrations and loadings of these compounds are generally decreasing. In addition, IADN data indicate that the atmosphere and the water are approaching equilibrium; thus future improvements in toxic chemical levels in the water will be directly related to future diminutions of these compounds in the atmosphere. IADN results have also demonstrated the susceptibility of the Great Lakes to long-range transport of toxic chemicals.

This report, particularly the suggestions for the future, will be reviewed in late 2002 by a peer review panel. This review will provide the basis for the Third Implementation Plan (IP3) for IADN, which is expected to cover the period 2003-2008.

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1. History and Mandates

1. 1. History of the Integrated Atmospheric Deposition Network (IADN)

The Great Lakes Water Quality Agreement calls for the U.S. and Canada "to virtually eliminate the input of persistent toxic substances in order to protect human health and to ensure the continued health and productivity of living aquatic resources." During the 1970s and 1980s several bioaccumulative toxic substances were banned or restricted in Canada and the United States, and in the years following, numerous point sources of toxic pollutants into the Great Lakes were eliminated. However, monitoring revealed that even after initial sharp declines in concentrations, the system continued to be contaminated at levels above standards in fish, a primary route of exposure to humans. It was surmised that atmospheric deposition had an important role in the continued contamination of the Great Lakes.

In fact, atmospheric deposition of persistent toxic chemicals to the Great Lakes had been first observed in rainfall by Sanderson and Frank (1977), followed rapidly by Murphy and Rzeszutko (1978), Swain (1978), and Strachan and Huneault (1979). The initial focus was on PCBs, and the observed concentrations, coupled with annual rainfall deposition, suggested that the atmospheric inputs were several tonnes of PCBs per lake. An International Joint Commission (IJC) mass balance workshop in 1986 concluded that the atmosphere was indeed a major source of the contaminants of concern, particularly for the upper Great Lakes (Strachan and Eisenreich, 1988). This workshop provided scientific support for the inclusion of a separate Annex (#15) in the "Protocol" revision to the 1978 Great Lakes Water Quality Agreement (GLWQA; 1987 Revision).

At the same time as these Protocol revisions were being developed, the IJC Water Quality Board's Surveillance Work Group created a Task Force to prepare a plan for accomplishing the surveillance aspects of what was then in the draft Protocol. The "Plan" (IJC, 1988), outlined the need for 17 investigations on measurement and process-related subjects. This Task Force Report formed the basis for the subsequent development of IADN. The management of the process, however, was transferred to Environment Canada and U.S. EPA ("the Parties") in the Protocol, and thereafter, the IJC played a smaller role in determining the atmospheric input of persistent toxic substances to the Great Lakes.

In 1989, the Canada-Ontario Agreement created an Air Toxics Committee under Canadian Atmospheric Environment Service (AES) leadership, and this group developed plans to implement Annex 15 and the Task Force recommendations on the Canadian side. The Canadian effort identified which chemicals should be monitored, what the criteria for an IADN site should be, what equipment would be needed, and what QA/QC program was needed. Liaison with the EPA's Great Lakes National Program Office was initiated, and a meeting was held in Detroit on December 4-5, 1989 to agree on details for a program for IADN and potentially for Annex 15. The outcome of that meeting was the formation of three working groups that further defined the IADN network activities. In 1990, the process was formalized with a signed 6-year Implementation Plan (Egar and Adamkus, 1990).

The first IADN station to be initiated was at Point Petre, on the north shore of Lake Ontario in November 1988. A station at Green Bay (Lake Michigan) was opened in 1989, but this location was moved to Eagle Harbor on the Keeweenaw Peninsula (on Lake Superior) in 1990. The official designation for the commencement of IADN was January 1990. Stations at Sturgeon Point (on Lake Erie), Burnt Island (on Lake Huron) and Sleeping Bear Dunes (on Lake Michigan) followed in 1991-92.

The first Implementation Plan (IP1) for the IADN was promulgated in June, 1990. Its stated objective was the acquisition of "… *sufficient, quality assured data to estimate with a specified degree of confidence the loading to the Great Lakes Basin of selected toxic substances*". Elsewhere in IP1, it is clear that the purpose of this objective was to determine the relative importance of the atmospheric pathway. While IADN is intended to estimate the relative loadings of the identified chemicals, IP1 also acknowledged the report of the IJC's Atmospheric Deposition Task Force outlining many critical research issues and the fact that these needed resolution "… *in order to understand and quantify the importance of the atmospheric pathway for toxic substances*.". In IP1, however, research, other than equipment needs and method development, was not addressed.

The goals for IADN, taken from the directions in IP1, were to:

- identify which chemicals were to be investigated and to monitor atmospheric deposition,
- define the number and the local criteria for locating the sampling sites,
- describe the sampling and analytical methodology, and
- develop a quality assurance/control plan to ensure data comparability.

IP1 also identified the chemicals to be investigated. These were PCBs, α- and γ-HCH, lead, and polycyclic aromatic hydrocarbons (PAHs, with benzo[*a*]pyrene as a target chemical). A second set of chemicals was established that listed chemicals to be added to the monitoring program as methods were confirmed, and a third set of chemicals for which methods were to be developed. IP1 also called for the establishment of one "Master" station and up to four "Satellite" stations per lake plus "upwind and downwind" sites (totaling of a maximum of 22 Satellite stations). The Satellite stations were originally identified in the IJC's Plan to provide a broader geographic coverage than that provided by single sites on each lake. IP1 predicted the installation of 11 Satellite stations in the second two years of the program and 11 more during the third two-year period. However, during IP1, a decision was made not to proceed with the installation of new IADN Satellite stations, but instead to adopt sites already operating in several existing networks, since these other networks were either linked by cooperative sampling at the Point Petre Master Station or were part of the Lake Michigan Mass Balance Project (and, hence, using IADN protocols). In addition to the number of stations, IP1 directed that the stations were to be as close to the lakes as possible, and proximity to urban centers was generally to be avoided. Further local site criteria were identified later in 1990.

In the case of the sampling and analytical methodology, the directions (and IADN goals) were most specific for the list of equipment to be employed at each Master Station, although it was left open whether these could be changed.

IP1 directed, in some detail, that IADN would prepare and individual agencies would adhere to a vigorous quality assurance program. Each participating agency has developed and exchanged documentation on sampling and analytical protocols. The first IADN Quality Assurance Program Plan (QAPP) was signed in 1994. Everything prescribed for this was designed to ensure data comparability among the various agencies that would participate in the two countries. The IP1 further recommended the establishment of a QA program and a common data base. The QA/QC program during 1992-1994 consisted of site audits at the Canadian Master Stations, and nine inter-laboratory round robin studies. These studies focused on both precipitation and air analyses; covered both organics (organochlorines, PCBs and PAHs) and metals; and addressed a range of concentrations. The round-robin results showed that inter-laboratory differences were greater for the organic than for the inorganic analyses, but the studies were not designed to determine the specific causes of the variability. Based on an analysis by Hoff (1994), it was concluded that, for almost all species measured by IADN, laboratory analytical errors were a small portion of the total loading error budget. More recent QA/QC activities are discussed in Section 2.4.

In summary, the establishment of the IADN network to conduct regular measurements of a limited number of pollutants in air and precipitation for atmospheric deposition was the major achievement of IP1. There were, however, several key areas of IP1 which were not fulfilled; these were carried over into the next implementation plan, IP2.

1. 2. The Present Goals of IADN's Second Implementation Plan (1998)

Prior to developing the Second Implementation Plan (IP2), the progress of the IADN program was described in a technical summary similar to this one. This summary and a series of presentations were the subject of a Peer Review meeting held in San Francisco in 1997. The Peer Review Committee was made up of five eminent scientists of international stature. The 1997 technical summary and the comments of this Peer Review committee were used to generate IP2. The new Implementation Plan was designed to restate the goals of IADN, briefly outline the future plans for IADN for the period 1998-2004, and provide a timeline from which annual work plans could be developed.

The IP2 clearly articulates the goals of IADN, which are to:

- determine, with a specified degree of confidence, the atmospheric loadings and trends (both spatial and temporal) of priority toxic chemicals to the Great Lakes and its basin on, at least, a biennial basis;
- acquire quality-assured air and precipitation concentration measurements, with attention to continuity and consistency of those measurements, so that trend data are not biased by changes in network operations or personnel; and
- help determine the sources of continuing inputs of those chemicals.

In response to recommendations from the IADN Peer Review, IP2 allows for some revision to IADN operations during the six-year period, but each change is to be documented in the IADN Quality Assurance Program Plan (QAPP).

The importance of maintaining the location and operation of the Master Stations, as well as the longer-term Satellite Stations, is recognized as being crucial for developing time series information. However, during IP2, rationalization of the placement and number of Satellite Stations was addressed, based on spatial trend information derived to date. Chan et al. (*in press*) have conducted an analysis of spatial trends in precipitation, while Buehler et al. (2001a) have looked at spatial trends in air. Discussions regarding Satellite Stations have been occurring in the context of this information, as well as in consideration of additional IADN commitments. There was a commitment in IP2 to develop one or more paired urban/rural or urban/remote stations to assess the impact of large urban areas on the lakes. This is currently being implemented through a pair of stations at Sleeping Bear Dunes and Chicago on Lake Michigan. The US EPA is also in the process of locating a station in Cleveland, Ohio. Furthermore, during IP2, the feasibility of maintaining a routine monitoring site over the waters of one of the Great Lakes was to be determined. The use of a large buoy in Lake Ontario as a routine over-water site is currently being explored.

IP2 called for a review of the chemical list that was established in IP1. It was expected that new chemicals would be added, while others would be deleted, the latter based on an analysis of their frequency of detection. The new chemical list, as well as protocols for the addition and deletion of chemicals, is presented in Section 2.1.

The IADN Peer Review panel recognized the importance and validity of data obtained from IADN. In order to ensure its continued legitimacy, commitments had been made in IP2 to expand and enhance the IADN QA/QC program. A jointly-funded QA/QC Officer has been contracted to oversee maintenance of the sampling and analytical protocol documentation, implement laboratory inter-comparison studies, conduct site audits, screen the data, and provide annual QA/QC reports to the Steering Committee (see Section 2.4.). In addition, multi-agency sampling at the Point Petre Master Station has been re-established, to link the measurements made by the various agencies contributing to IADN.

Finally, in IP2 the IADN Steering Committee agreed to continue its excellent record of joint biennial reporting of the data (Hoff et al., 1996; Hillery et al., 1998; Galarneau et al., 2000; Buehler et al., 2001b). The data analytical tools that have been used to generate these reports have been incorporated into the QAPP and built in to the data reporting system (Research Data Management Quality Assurance System, RDMQ). Reporting and outreach is also conducted through presentations to the public, government officials, and the research community, as well as through the media. A new IADN website was also created during IP2.

1. 3. IADN Mandates and Driving Forces

1. 3. 1. Annex 15 GLWQA

Annex 15 of the Great Lakes Water Quality Agreement (the 1987 Protocol) is reproduced in its entirety in Appendix 8. 1. The Parties (Canada and the United States) are committed to carrying out the requirements of the GLWQA and its Annexes. Items 3 and 4 of Annex 15 clearly provide a direct mandate for the existing IADN program. Items 2(b) and 5 are not directly related to the work activities of IADN.

By definition, IADN is a crucial part of Annex 15, but it is not Annex 15. That being the case, the research components of Annex 15 [items 2(a) and 2(c)] are addressed on an *ad hoc* basis, by the research community on either side of the border. IADN will continue to support such efforts by allowing sampling at its sites and by providing sampling and analytical protocols. Some of the additional studies being done in support of Annex 15 will be discussed in Section 5.

1. 3. 2. The Great Lakes Binational Toxics Strategy (BTS)

In keeping with the objective of the GLWQA to restore and protect the Great Lakes, the BTS was signed in 1997 by Environment Canada and U.S. EPA (the "Parties") to set forth a collaborative process by which the Parties, in consultation with other federal, provincial and state agencies, as well as Tribes and First Nations, would work cooperatively with their public and private partners towards the goal of virtual elimination of persistent toxic substances resulting from human activities. The BTS, in recognition of the fact that the continuing presence of these persistent toxic substances is partially the result of atmospheric deposition, commits Canada and the U.S. to assess atmospheric inputs of BTS Level I and II substances to the Great Lakes. Specifically, Environment Canada and U.S. EPA will:

- *"…maintain atmospheric deposition monitoring stations to detect deposition and transport of Strategy substances."*
- *"…continue research on the atmospheric science of toxic pollutants to refine and improve existing source, receptor and deposition models, fundamental to impact assessment. They will also improve integration of existing air toxic monitoring networks and data management systems to track deposition of contaminants within the Great Lakes*."

1. 3. 3. Clean Air Act Amendments of 1990

The United States Congress passed the Amendments to the U.S. Clean Air Act (CAA) of 1990. Section 112(m) directs EPA, in cooperation with the National Oceanic and Atmospheric Administration (NOAA), to identify and assess the extent of atmospheric

deposition of toxic pollutants to the Great Waters[*]. As part of the assessment, EPA undertakes the following activities:

- research for developing and improving monitoring methods and for determining the relative contribution of atmospheric pollutants to total pollutants in the Great Waters, and investigation of sources and deposition rates of air pollutants,
- evaluation of adverse human health and environmental effects,
- monitoring of atmospheric deposition, including the establishment of monitoring networks in the Great Lakes and other locations,
- determination of whether regulatory programs under Section 112 are "*adequate to prevent serious adverse effects to public health and serious or widespread environmental effects"* associated with atmospheric deposition to the Great Waters. Based on this determination, EPA is directed to take additional measures that are necessary and appropriate to prevent such adverse effects to human health and the environment, to identify of exceedences of water quality standards, to sample fish and wildlife for atmospherically-deposited pollutants, and to characterize the sources of such pollutants.

It is clear that many of the above activities are very similar to those of the Annex 15 and IADN requirements. Scientific results from IADN activities can also serve to provide some of the input required by the CAAA (112) at least for the Great Lakes Region.

1. 3. 4. U.S. Great Lakes Strategy

Great Lakes Strategy 2002 was created by the U.S. Policy Committee – a forum of senior-level representatives from the Federal, State, and Tribal agencies responsible for environmental and natural resources management of the Great Lakes – to help coordinate and streamline efforts of the many governmental partners involved with protecting the Great Lakes. The Strategy was developed cooperatively by U.S. EPA and other partners in consultation with the Great Lakes public. It focuses on basin-wide environmental issues, such as atmospheric deposition and establishes common goals for the partners. The Strategy sets forth specific objectives and actions that will reduce contaminants, restore habitat, and protect the resources of the basin. Some of the objectives and actions are simply supportive of current activities, while others are "stretch goals" that encourage new efforts.

Goals put forth in the Strategy that relate to atmospheric deposition and IADN include:

- Integrate IADN with new regional, national, and international monitoring efforts and report on the deposition of persistent bioaccumulative toxic compounds.
- Add mercury deposition monitoring to at least one U.S. IADN station and evaluate the feasibility and cost of adding additional chemicals of concern to the network, as appropriate.

[*] "Great Waters" includes the Great Lakes, Chesapeake Bay, Lake Champlain, and various coastal estuaries as designated by the US EPA and NOAA.

- Evaluate the expansion of the IADN network to include new urban sites in order to determine urban sources and evaluate current and future regulations.
- Support the expansion of state and tribal monitoring efforts related to air toxic deposition, particularly for persistent bioaccumulative toxic compounds, which support legislation and policy efforts.
- Study the relationship between the Great Lakes Regional Air Toxics Emissions Inventory and atmospheric deposition monitoring data. Work to better understand source/receptor relationships.

1. 3. 5. Canada-Ontario Agreement Respecting the Great Lakes Basin Ecosystem

Since 1971, Canada-Ontario Agreements Respecting the Great Lakes Basin Ecosystem (COA) have been in effect to assist Canada in meeting its obligations under the Canada-U.S. Great Lakes Water Quality Agreement. The latest COA, comprised of 4 Annexes, came into effect March 22, 2002. Specifically, the Harmful Pollutants Annex commits Canada to:

> "*Maintain the Great Lakes Integrated Atmospheric Deposition Monitoring Network (IADN) stations, expand to monitor mercury, dioxins and furans, and review monitoring coverage to ensure a comprehensive substance list and sufficient spatial coverage."*

Additionally, in the Lakewide Management Annex, Canada is committed to:

> "*Monitor precipitation for contaminants and conventional pollutants at selected locations*."

1. 3. 6. State of the Lakes Ecosystem Conference (SOLEC)

The Governments of Canada and the United States (the Parties to the GLWQA) established SOLEC in 1992 to provide independent reporting on the state of health of the Great Lakes basin ecosystem. In order to report on the state of the Lakes, and stresses to the lakes, SOLEC has adopted a series of indicators, which objectively represent the condition of the Great Lakes basin ecosystem, the stresses on the ecosystem, and the human responses to these stresses. These indicators are intended to provide a predictable set of signs of the health of the system, and the progress being made to remedy existing problems.

One of the SOLEC indicators (#117) is "*Atmospheric Deposition of Toxic Chemicals*", specifically:

> "*This indicator will estimate the annual average loadings of priority toxic chemicals from the atmosphere to the Great Lakes, and it will be used to infer potential impacts of toxic chemicals from atmospheric deposition on the Great Lakes aquatic ecosystem, as well as to infer the progress of various Great Lakes programs toward virtual elimination of toxics from the Great Lakes*."

Information from the IADN program was used to develop the indicator report for the 2000 and 2002 SOLEC meetings, and it is expected that future SOLEC meetings will rely on the IADN program for continued contributions.

In addition to the above mandates, atmospheric deposition of toxic chemicals has been identified as an indicator for both the Lake Superior Binational Program, and the Lake Huron Initiative. U.S. EPA-GLNPO also reports atmospheric concentrations of persistent toxic substances to fulfill Government Performance and Results Act requirements.

2. Current Status of the Network

2. 1. Chemicals

As previously stated, IP2 called for a review of the chemical list. In addition, procedures for the addition and deletion of chemicals from the monitoring list were to be developed.

After considerable discussion by the Steering Committee, the concept of a hierarchy of chemicals has been discarded. Initially a tiered list of chemicals was used to separate chemicals with well-established methods from those for which method development was needed. However, at present the number and variety of chemicals analyzed by the network is limited more by resources rather than lack of established methods. Instead, two IADN lists have been compiled. The first is a list of chemicals measured in all phases at all Master Stations. It was agreed that IADN would strive to determine loadings estimates for these, assuming necessary supplementary information (such as Henry's Law constants and open lake concentration data) were available. The second list is a compilation of chemicals monitored in any phase by at least one agency. The purpose of this list is to advise interested parties that there is some information available for these chemicals, albeit on a limited basis. These two lists are given in Table 1. Although the tier concept has been dropped, the network has still succeeded in making measurements for most of the chemicals in Tier 1 from IP2.

Table 1. IADN Chemical List, Revised May 2000

Chemicals measured at all Master Stations in air and precipitation

PCBs (see Table 2)

Organochlorine pesticides:
Aldrin
trans-Chlordane (γ)
cis-Chlordane (α)
p,p'-DDT
p,p'-DDD
p,p'-DDE
o,p'-DDT
Dieldrin
α-Endosulfan (I)
β-Endosulfan (II)
Endrin
Heptachlor epoxide
Hexachlorobenzene (HCB)
α-HCH
β-HCH
γ-HCH (lindane)
Methoxychlor
trans-Nonachlor

Polycyclic aromatic compounds:
Anthracene
Benz[*a*]anthracene
Benzo[*b*]fluoranthene
Benzo[*k*]fluoranthene
Benzo[*ghi*]perylene
Benzo[*a*]pyrene
Chrysene + Triphenylene
Dibenz[*a,h*]anthracene
Fluoranthene
Indeno[*1,2,3,cd*]pyrene
Phenanthrene
Pyrene

Additional chemicals for which data are available.
Monitoring done by at least one agency

o,p'-DDD (MSC, IU/EPA)
o,p'-DDE (MSC)
Endosulfan sulphate (MSC, IU/EPA)
Heptachlor (MSC, EHD)
Mirex (MSC, EHD)
Octachlorostyrene (IU/EPA)
Oxychlordane (MSC, IU/EPA)
Di- thru pentachlorobenzenes (EHD)
Photomirex (MSC)
Acenaphthene (MSC, EHD)
Acenaphthylene (MSC, EHD)
Anthanthrene (MSC)
Benzo[*ghi*]fluoranthene (MSC)
Benzo[*e*]pyrene (MSC, IU/EPA)
2-Chloronaphthalene (EHD)
Coronene (MSC, IU/EPA)
Dibenz[*a,c*]anthracene (MSC)
Fluorene (MSC, IU/EPA)
Indene (EHD)
1-Methylnaphthalene (EHD)
2-Methylnaphthalene (EHD)
Retene (MSC, IU/EPA)
1,2,3,4-Tetrahydronaphthalene (EHD)

Trace elements:
Arsenic (MSC)
Cadmium (MSC, EHD)
Lead (MSC, EHD)
Selenium (MSC)
Mercury (MSC, EHD)

Chemicals for which loadings estimates are available
(Based on loadings report published in May 2000)

trans-Chlordane	IADN-suite PCBs
cis-Chlordane	PCB congeners 18, 44, 52, 101
p,p'-DDD	Benzo[*b*]fluoranthene
p,p'-DDE	Benzo[*k*]fluoranthene
p,p'-DDT	Benzo[*a*]pyrene
Dieldrin	Indeno[*1,2,3,cd*]pyrene
α-Endosulfan	Phenanthrene
Endosulfan sulphate	Pyrene
Hexachlorobenzene (HCB)	Arsenic
α-HCH	Cadmium
γ-HCH	Lead
trans-Nonachlor	Selenium

- Participating agencies are the Meteorological Service of Canada (MSC), part of Environment Canada and formerly Atmospheric Environment Service (AES); Ecosystem Health Division of Environment Canada (EHD); and the U.S. Environmental Protection Agency in cooperation with Indiana University (IU/EPA).

A further refinement of the chemical list was the adoption of a standardized suite of PCB congeners (herein known as the "IADN PCB Suite"; see Table 2) for the purposes of estimating total PCBs in air and precipitation. This shortened list of PCB congeners was a recommendation of the last peer review in 1997. The selection of congeners was based on an analysis of the 1995 and 1996 air and precipitation results from the five Master stations, against the following criteria:

- the congener was common to all agencies reporting PCB congener results at the time (Meteorological Service of Canada, Indiana University, and National Water Research Institute); and
- it contributed >1% to the total PCB mass for at least one site; or
- it was one of the toxicologically important congeners (77, 105, 118, 126, 128, 138, 156, 169 and 170); or
- it had been previously identified in a similar effort by Hoff (internal IADN report) to have contributed significantly to the PCB congener mass in 1997 air samples collected at Eagle Harbor.

All participating agencies are striving to measure these congeners, at a minimum. IADN quality assurance efforts, including laboratory round-robins and RDMQ, and the most recent as well as future IADN loadings estimates (including trend reporting) are based on the IADN PCB Suite.

Table 2. IADN PCB Suite congeners.

4+10	28	70+76	100	156+171+202
5+8	31	74	101	169
6	33+53	77+110	105+132+153	170+190
7+9	37+42	83	114+131	172
12+13	41+64+71	85	118	174
15+17	44	87+81	119	180
16+32	45	89	123+149	194+205
18	47+48	91	126	199
19	49	95+66	128+167	201
22	52	97	135+144	206
26	56+60+84+92	99	138+163	207

To investigate the relevancy of IADN's list of analytes, a comparison was made with the target lists of chemicals for various related programs/agreements such as Annex 1 of the GLWQA, Great Waters Pollutants of Concern, and Lakewide Management Plan critical pollutants. IADN addresses most of these target chemicals.

In response to recommendations from the IADN Peer Review, a procedure has been devised for nomination and possible addition of new chemicals to the IADN chemical list. The approach that has been adopted is to request interested stakeholders to prepare a chemical dossier, providing the rationale for their nominated chemical. A call letter is sent out to potentially interested stakeholders (e.g., LaMP Co-Chairs; BTS Co-Chairs; SOLEC Co-Chairs). Stakeholders interested in nominating substances receive an information sheet giving the background on IADN, including a current list of chemicals measured and methods used; and a form requesting information on the nominated chemical and reasons for possible inclusion in IADN's monitoring program (i.e., adverse effects, known elevated concentrations, etc.). The nomination packet is available online. Nominations are reviewed by the Steering Committee biennially, and the resulting chemical lists included in IADN's biennial report. Thus far, this exercise in consultation has not been successful, because no nominations have been received. Throughout the duration of the IADN program, however, new chemicals have been added; this has largely been achieved by adding chemicals that can easily be accommodated within existing analytical methodologies. In some cases (e.g., mercury at Canadian sites and polybrominated diphenyl ethers at some U.S. sites), chemicals have been added through the infusion of supplementary funding.

In developing a protocol for the deletion of chemicals from IADN's monitoring list, consideration was given to the fact that different chemicals might be frequently detected only during selected seasons, in specific lake basins, or preferentially in one phase versus another. Hence, the IADN Steering Committee examined the detectability of chemicals in each media, season and lake. It was determined that all of the chemicals being monitored are detected in at least 25% of the samples for one season, lake, and media. It was agreed

that a chemical would remain on the IADN list as long as it continued to meet this criteria (i.e., if it was detected in at least 25% of the samples for one season, lake, and media). Hence, as chemicals reach their limit of detectability, consideration will be given to dropping that chemical, perhaps in favor of adding new substances to the list.

2. 2. IADN Sites

As discussed in Section 1. above, IADN operates five Master stations, one on each of the Great Lakes, and several Satellite stations. These locations are given in Figure 1. The locations of the Satellite sites have changed slightly over time. The Ontario Ministry of the Environment dropped out of the program in 1999, with the subsequent loss of their stations from IADN. In addition, we have recently determined that the concentrations of most PCBs and chlorinated pesticides are about the same at the Eagle Harbor and Brule River sites (Buehler et al., 2001a); therefore, in August 2002, we have closed the Brule River site and started to move the equipment to the urban center of Cleveland, Ohio. This will allow further investigations of the impact of urban areas on lake-wide deposition as recommended by the previous peer-review.

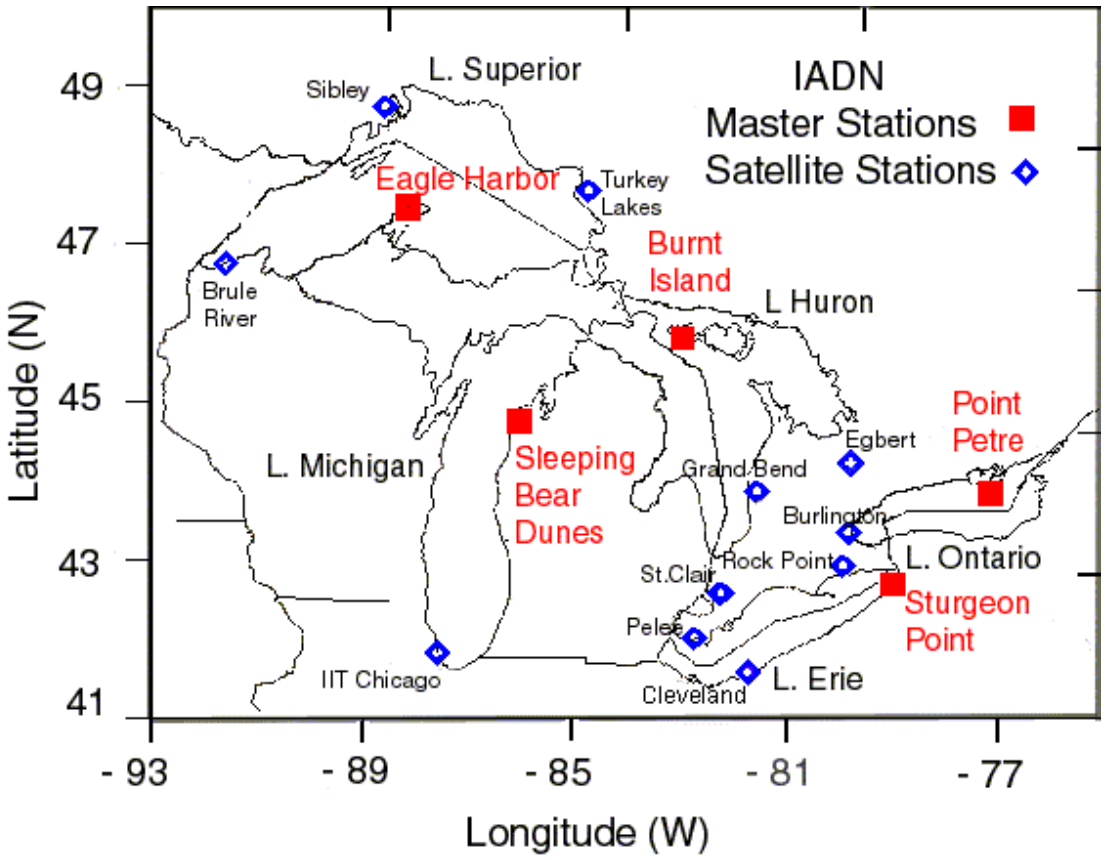

Figure 1. Map of IADN sites. Master stations are the main sites in the network. Satellite stations have been added or adopted throughout the project to augment the master stations.

2. 3. Sampling and Analytical Methods

The following sections refer to the current status of IADN, but it should be pointed out that the Ontario Ministry of the Environment and the National Water Research Institute were participants in this project during the period from 1990 to 1999. Because their methods were reported in the 1998 Technical Summary, we have omitted their protocols and procedures from the following sections.

2. 3. 1. Sampling Protocols

2. 3. 1. 1. Precipitation

The details of all sampling protocols are given in the Sampling Procedures Manuals for each agency. These details will be reviewed briefly here and shown in Table 3. All stations (including all Satellite facilities except Egbert) have samplers to measure wet deposition of gaseous organics. The precipitation sampler used for the organics measurements is uniform across the network, a MIC-B collector with a stainless steel funnel.

Indiana University uses XAD-2 resin column cartridges for accumulating the organics. EHD uses a dichloromethane solvent extraction system in which the rainwater is stabilized with 250 mL of dichloromethane then liquid/liquid extracted using fresh dichloromethane. Indiana University samples precipitation on a 28-day cumulative basis. EHD takes 14-day cumulative samples; however, as of 2000, the 14-day samples are composited to 28-day samples prior to analysis. The start and finish dates for the 28-day period are aligned between the two agencies. For trace metals, EHD uses a MIC-B precipitation sampler. The precipitation samples are collected in pre-cleaned polyethylene buckets. Indiana University does not measure trace metals.

2. 3. 1. 2. Air

Organics air sampling uses modified high volume samplers with filter and absorbent combinations. Indiana University uses a HiVol sampler with an XAD absorbent cartridge. This allows for a > 800 m^3 sample volume. MSC uses polyurethane foam as the absorbent for organics. In this case, sample volumes are kept below 400 m^3 to avoid breakthrough of lighter organics during warm summer months. All agencies have now adopted a sampling frequency of a 24-hour sample every 12 days. Due to the low analyte masses on the filters, agency protocols have changed over the course of IADN. Early results showed that little organochlorine mass was found on the filter. For example, at the Point Petre station in 1992, the particulate/gaseous mass ratio was 2.3% for total PCBs and < 1% for the HCHs, *p,p'*-DDE, and HCB. The general absence of most organochlorine pesticides and PCBs on the filters led Environment Canada to terminate the measurements of these compounds on filters in 1993. Indiana University stopped PCB analysis on filters in 1995; however, IU continues to analyze the pesticides on the filters because of their higher concentrations in the urban samples.

Table 3. Summary of current sampling and analysis methods

Media/ Parameter	Agency	Sampling Method	Sampling Frequency	Analytical Method	Reporting Units	Status
air organics (PCBs, pesticides, PAHs)	MSC	HiVol: GFF + PUF	24 hr every 12 days	Soxhlet/GC-ECD (PCBs, Pesticides); HPLC fluo-rescence (PAHs)	pg/m^3	continuing
	IU	HiVol: QFF + XAD-2	24 hr every 12 days	Soxhlet/GC-ECD (PCBs, Pesticides); GC/MS (PAH)	pg/m^3	continuing
air metals	MSC	PM-10/15 HiVol	24 hr every 12 days	ICP-MS or INAA	ng/m^3	continuing
	IU/EPA	PM-10 Dichot	96 hr every 28 days	XRF	ng/m^3	stopped analysis in 1997 & sam-pling 2000
precipitation or-ganics (PCBs, pes-ticides, PAH)	EHD	MIC-B/DCM	14 days	GC-ECD or GC-MS	pg/L	continuing
	IU	MIC-B/XAD-2	28 days	GC-ECD, GC/MS	ng/L	continuing
precipitation met-als	EHD	MIC-B	monthly	ICP	µg/ L	continuing

Media/ Parameter	Agency	Sampling Method	Sampling Frequency	Analytical Method	Reporting Units	Status
Related air measurements						
total suspended particles	MSC	HiVol/GFF	24 hr every 6 days	gravimetric	µg/m³	stopped in 1998
	IU	HiVol/QFF	24 hr every 12 d	gravimetric	µg/m³	continuing
PM-10	MSC	TEOM	continuous	mass concentration & total	µg/m³ µg	June 1997 – March 2000
Meteorology						
Temperature	MSC, IU	thermistor	hourly average	direct reading	°C	continuing
relative humidity	MSC, IU	hygristor	hourly average	direct reading	percent	continuing
barometric pressure	MSC, IU		hourly average	direct reading	kPa	continuing
wind speed	MSC, IU	anemometer	hourly average	direct reading	m/s	continuing
vector wind speed	MSC	anemometer	hourly average	calculated by data logger	degrees	continuing
wind direction	MSC, IU	Vane	hourly average	direct reading	degrees	continuing
standard deviation of wind direction	MSC	anemometer	hourly average	calculated by data logger	degrees	continuing
precipitation amount	MSC	type B rain gauge	24 hrs	direct reading	mm	continuing
	IU, MSC	Belfort gauge	continuous	direct reading	mm	MSC 2000

Media/ Parameter	Agency	Sampling Method	Sampling Frequency	Analytical Method	Reporting Units	Status
solar irradiation	MSC	pyranometer	hourly average	direct reading	W/m^2	continuing
	IU	pyranometer	hourly average	direct reading	Langleys	continuing

NOTES:

a. Sampling and analysis methods used by different groups may appear similar, but are different in operational and other details.
b. Sampling frequency is sometimes given as sample duration/sampling interval.

KEY TO ABBREVIATIONS

DCM	dichloromethane solvent
Dichot	dichotomous sampler
ECD	electron capture detector
GC	gas chromatography
GFF	glass fiber filter
HiVol	high volume sampler
ICP	inductively coupled plasma spectrometry
INAA	instrumental neutron activation analysis
IU	Indiana University
MIC-B	MIC type B precipitation sampler
MS	mass spectrometry
PM-xx	particulate matter less than xx µm in diameter
PUF	polyurethane foam plug
QFF	quartz fiber filter
XAD	XAD resin
XRF	x-ray fluorescence

The two agencies involved in measuring trace metals in air used different sampling equipment and sampling frequencies, as shown in Table 3. MSC uses a HiVol sampler, and IU used a Dichotomous sampler. The EPA discontinued the metal analysis in air in 1994, although sample collection was continued until 2000.

2. 3. 1. 3. Estimating Variability

The Point Petre and Eagle Harbor Master Stations both featured triplicate sampling for air and precipitation organics from late 1988 until 1990. This triplication study (Hoff and Brice, 1993) showed that the coefficient of variation between the three MSC collocated air samplers was 31% for PCB 16+32, 13% for α-HCH, 15% for γ-HCH, 12% for *trans*-chlordane, 22% for benzo[*k*]fluoranthene, and 14% for benzo[*a*]pyrene. These results were consistent at all sampling sites, where replication studies were also occurring. Because of this reproducibility in measurements and due to resource pressures, it was decided that continuous triplicate sampling was no longer necessary at the Point Petre Master Station for all measurements; however, some duplicate sampling continues at this site and also at Sleeping Bear Dunes on Lake Michigan, Eagle Harbor on Lake Superior, and Sturgeon point on Lake Erie. During 1994, EHD installed three organic precipitation samplers at the IADN Satellite station in Burlington to determine the total (field and laboratory) variability in deposition estimates at a given site. Deposition estimates from the three samplers showed variability of <10% for the organochlorine pesticides and 24% for total PCBs. Statistical analysis of the data showed that, at the 95% level, there were no significant differences in results from the three samplers. At the U.S. sites, a protocol of rotating replication between air samplers is used where one duplicate sample per month is obtained from one of the three sites.

2. 3. 2. Analytical Protocols

Laboratory analysis protocols generally call for solvent extraction of the organic sampling media with addition of surrogate recovery standards. Extracts are then concentrated followed by column chromatographic cleanup, fractionation, nitrogen blow-down to small volume (about 1 mL) and injection (typically 1 μL) into GC-ECD or GC-MS instruments. Details of these analyses can be found in the Laboratory Protocol Manuals or the agency-specific Quality Assurance Project Plans (QAPPs). Variations in columns and GC temperature programming lead to different chromatography between agencies. Thus, the PCB congeners reported by various laboratories may not identically match (some laboratories resolve certain congeners, other laboratories do not). As stated in Section 2.2. in 2001 a list of PCB congeners was adopted by IADN (see Table 2).

Metals analysis is conducted using instrumental neutron activation analysis (dropped in October 1998) and inductively coupled plasma emission analysis in Canada for particulates and precipitation. Mercury in air has been measured at the Canadian Master Stations since 1997 and in precipitation since 2000 as part of the Canadian Atmospheric Mercury Network (CAMNet).

Total suspended particulate (TSP) and a total organic carbon (TOC) analyses have not been as useful as originally intended. The main use of these two parameters was to have been the apportionment of material between the gaseous and particulate phases (Pankow, 1987). TSP is a surrogate for particulate surface area in these calculations, and it was hoped that TOC would provide a better scaling parameter than TSP. In practice, however, the TOC/TSP ratio has been remarkably well defined, averaging 0.11 ± 0.09 at the three Canadian sites. With such a low variability for this parameter, TSP/TOC analysis was discontinued. A second factor in this decision was the availability of new continuous monitors (TEOMs, R&P Inc., Rochester, NY), which have become available to give real-time measurements of PM-2.5 and PM-10. These devices are now acceptable as EPA methods for particulate mass. The use of these continuous monitors will be preferable to the gravimetric filter analysis used previously; however, because of resource limitations, IADN has not added these newer instruments to the U.S. measurement arsenal, whereas the Canadian sites used these instruments for a short time (from June 1997 to March 2000) and then discontinued these measurements.

2. 3. 3. Method Development

Over the course of IP1 and IP2, considerable method development has been carried out in order to add new chemicals to the analyte list:

- HPLC and fluorescence detection have been applied for the determination of polycyclic aromatic hydrocarbons (PAHs) in background ambient air (Alexandrou and Brice, 1997).
- Methods to reliably analyze coplanar PCBs using multidimensional GC (Brice et al., 1996a) and toxaphene (Brice et al., 1996b; Shoeib et al., 1999) have been developed.
- Field methods to include gaseous and particulate mercury in the network have been developed (Lu and Schroeder, 1999) and are now being employed at the two Canadian Master stations.
- The use of enantiomeric ratios of certain pesticides has given potentially important results as a tracer of organochlorine sources (Ridal et al., 1997; Ulrich and Hites, 1998).

Analytical methods were developed for other toxic compounds at the Indiana University laboratory using archived IADN sample extracts. These other compounds include chlorothalonil, dacthal (James and Hites, 1999), toxaphene (Glassmeyer et al., 1999), and polybrominated diphenyl ethers (Strandberg et al., 2001). These can be useful preliminary studies for the future expansion of IADN.

2. 4. Quality Assurance / Quality Control Status

IP2 described QA/QC as the hallmark of the IADN program and discussed how the QA/QC program was to be continued and augmented for the future of the program. A Quality Assurance Officer has been part of the program throughout its history as recommended by IP1. Quality Assurance workshops were held both in 2000 and 2001.

A regular set of laboratory and field or handling blanks are taken and recorded for comparison to the IADN field samples. Regular use of field blanks is an essential component of the program as the field data often challenge detection limits of the analytical equipment. Data for the program is not blank corrected, rather the blank data is used to evaluate loadings estimates for the lakes. In addition, a suite of chemical surrogates and internal standards are used extensively in most analyses.

The IADN Quality Assurance Project Plan (QAPP), originally produced in 1994, was updated and signed by the Canadian and U.S. Program Directors in 2001. In July 2000, each of the participating laboratories was contacted to request both paper and electronic copies of their laboratory and analytical Standard Operating Procedures (SOPs) related to the IADN program. All available SOPs were collated, placed in a binder and sent to the Database Manager (DBM). The available electronic SOP files were also archived by the DBM. In addition, a number of the analytical SOPs were updated during the process and the Meteorological Service of Canada (MSC) sampling SOP was rewritten.

2. 4. 1. Audits

Both field and laboratory Technical Systems Audits were carried out during the reporting period. Field site audits of the five Master Sampling Stations and three Satellite Stations done during 1999-2000 described differences between the procedures used by the different agencies and provided detailed observations and recommended corrective actions. All corrective actions have been implemented.

Laboratory audits were carried out during 2000 at Indiana University (IU), Meteorological Service of Canada (MSC), Ecosystem Health Division (EHD), National Laboratory for Environmental Testing (NLET) and Philip Analytical Services Corp. (PASC). The laboratories provided their analytical method SOPs. The QA Officer examined how those SOPs were being implemented by visiting the individual laboratories. A comparison of the different analytical approaches used by each laboratory was made and findings for each laboratory were presented.

The approach to sampling and analysis of IADN parameters is quite different in each of the laboratories. The analytical methods used in each laboratory are logical and capable of producing defensible data. For the most part, the SOPs are adequate and are implemented as written. However, it was recommended that a few of the SOPs be updated, and this is being addressed. A few cases were noted where the laboratory practice as observed varied from a current SOP. These noted variances were all relatively minor, and are being addressed.

Although no major errors are evident in the laboratory operations, some risks to continuing data quality were identified. The different sampling and analysis methods used in the program have the potential to cause between laboratory bias in the data. Some of the laboratories did not use independent control standards to confirm continuing suitability and stability of their regular calibration standards. Calibration of temperatures, volumetric devices and balances was not done regularly in all cases.

As a result of the audit program the implementation of independent check standards and the use of a Common Reference Standard as a quality check have been adopted for analysis of PCB, PAH and pesticides.

2. 4. 2. Round Robin Experiments

The need for a Common Reference Standard was identified as a result of the IADN round robins held in 1992 and 1993 and implemented for the IADN suite of PCBs, Pesticides and PAHs in the program in 2001. Although these standards do not replace the existing calibration standards used in participating laboratories, they were used as round robin standards and are used as independent check standards to verify continuing calibrations.

Split sample round robin programs were conducted in 1998 and again in 2001. The 1998 study carried out by Indiana University involved exchange of standard solutions, sample extracts and paired samples taken from replicate samplers. Results showed better agreement on standards than on samples. Contamination of a sampler, due to storage in a contaminated environment, was discovered. Low recovery of some pesticides was traced to the inclusion of material used to wipe the sampler in the Soxhlet extractor. Extraction efficiency for HCHs in the precipitation samples was improved at Indiana University by omitting the sampler wipes from the extraction.

The 2001 Round Robin used split samples and sample extracts for PCB, pesticides and PAHs in precipitation, air and particulate filters. The Common Reference Standard was also analyzed as an unknown as part of the Round Robin. With the exception of a few compounds, the round robin demonstrated reasonable agreement for trace organic data. Precipitation data is less precise than PUF data that is, in turn, less precise than glass-fiber filter (GFF) data.

In general, the 2001 Round Robin study showed that, for PAHs, IU reports data about 30% higher than MSC for PUF samples but there was no such bias for GFF or melted snow. For PCBs, NLET reports data about 40% higher than IU in melted snow. IU reported data about 30% higher than MSC on PUF. For pesticides, IU reports data about 30% higher than MSC in PUF but comparable to NLET on the melted snow.

It is important to note that round robin results can only be applied to one point in time and should be applied with caution to the 10-year dataset of the IADN program.

2. 4. 3. QA Results Overview

A collocated sampler program has been operating at the Point Petre Master Station since 2000 as recommended by the last peer-review panel in 1997. Air, airborne particulates and precipitation are sampled monthly and analyzed for IADN organics using the different sampling and analytical techniques used by the different agencies. Data are being used to establish variability due to the different techniques employed.

Data from the Common Reference Standard, the 2001 Round Robin and the Point Petre collocated samplers can be used to evaluate the various components of the sampling and analysis process and results obtained using the different sampling media. Figure 2 presents data for γ-HCH (lindane) from these three QA activities. Overall, these data are representative of the approximately 300 chemicals and media combinations currently being monitored under IADN.

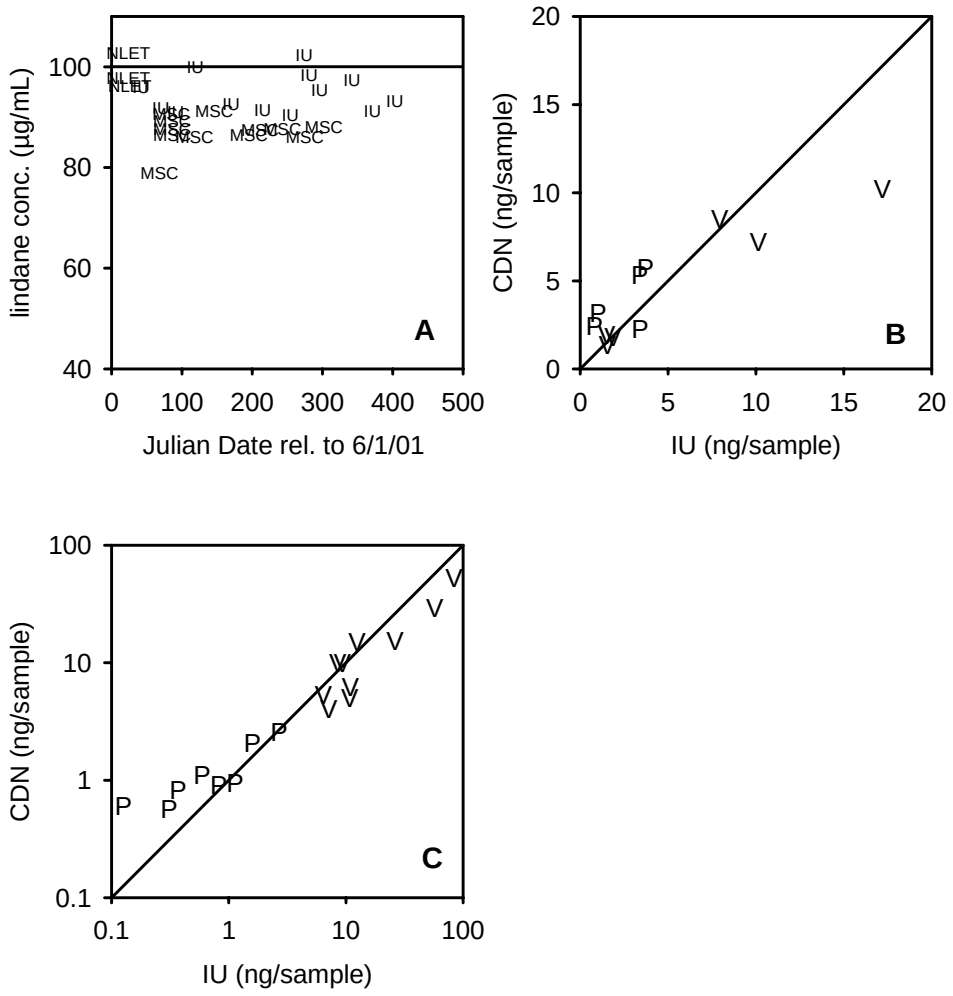

Figure 2. Lindane QA results. (**A**) Lindane concentrations in the common reference standard as a function of date; the reference value was 100 µg/mL. (**B**) Lindane concentrations in the round robin experiments; the 1:1 line represents perfect agreement between the Canadian (CDN) and Indiana University (IU) laboratories. *P* indicates precipitation samples, and *V* indicates vapor samples. (**C**) Lindane concentrations in collocated samplers at Point Petre; the 1:1 line represents perfect agreement between the CDN and IU laboratories. Note the logarithmic scale.

In analyzing the Common Reference Standard, the various laboratories reported lindane concentrations that were comparable, at 90% of the reference value. The round robin experiment, however, showed that NLET generally reported lindane concentrations that were 50% higher than IU for the precipitation samples, while IU reported data 50% higher than MSC for vapor. Results from the Point Petre collocation study showed that IU systematically reported higher vapor data than MSC by about 30%, while agreement was good between IU and NLET for precipitation samples.

The QA program works to identify chemicals exhibiting low data quality. Concentrations of chemicals are very low in most IADN samples and are often close to laboratory detection limits (which vary with the chemical), but reasonable agreement is often obtained when the chemical is present at above 1 ng per sample or 1 pg/m^3.

QA results to date show that differences between the organizations are caused partly by different standards, partly by processing of the samples in the different laboratories, and partly by differences in the sampling protocols. The Common Reference Standard is being used in the participating laboratories to identify incorrect standards and as a spiking solution. The IADN Quality Assurance Working Group will continue to obtain QA information and to adjust procedures to ensure adequate data.

2. 5. Data Management & Generation of Loadings Estimates

As called for in IP2, a centralized database was established in 1995. Data and loading workshops were held in 1999, 2001, and another is scheduled for January 2003 to develop loadings for 1995-96, 1997-98 and 1999-2000, respectively.

All chemical data for IADN are subjected to a quality assurance process using the Research Data Management and Quality Control (RDMQ™) System. RDMQ provides a unified set of quality assured data including flags for each data point that can be used to evaluate the usability of the data. The use of the flagging system is essential as a number of the IADN trace organics are subject to interference and chromatographic coelution. Statistical summaries of annual concentrations are generated by the program and used as input into the loading calculation. For all loadings reports to date, values that are reported as “below detection limit”, have been substituted with 2/3 of the value of the level of detection during the concentration calculation program. During the loading workshop of 2001, the Steering Committee made the decision to discontinue de-censoring data using 2/3 of the level of detection value. For the 1999-2000 loadings report, the below detection value will be substituted with zero. The loading workshop in 2003 will investigate the effect of this change in procedure by recalculating past loading estimates. The revised estimates will be reported in the next loading report, due to be released in mid-2003.

The goal in IP2 was to report loadings every two years; that is, the 1999-2000 loadings report would be complete by 2003. Thus, the turn-around time for the loadings calculations is now three years. This is an improvement from the early years, but increased

funding may be required to improve the turn-around time beyond the present level, especially in Canada.

3. Temporal and Spatial Trends

3. 1. Air

3. 1. 1. Pesticides

The determination of trends in the air concentration of gas-phase organic compounds is complicated by a highly variable seasonal component to the concentrations (Hillery et al., 1997; Burgoyne et al., 1993; Hoff et al., 1992; Hermanson and Hites, 1989). Fluctuations in ambient temperature are largely responsible for seasonal trends in the gas-phase concentrations. The relationship between temperatures and gas-phase partial pressures of semi-volatile organic compounds can be described by the Clausius-Clapeyron equation:

$$\ln P = -\frac{\Delta H}{R}\left(\frac{1}{T}\right) + const \qquad (1)$$

where P is the partial pressure of the compound (in atm), ΔH is a characteristic phase-transition energy of the compound (in kJ/mol), R is the gas constant, and T is the temperature (in K).

If the introduction of a pesticide into the environment ceases, the decrease in atmospheric concentration can be modeled by a first-order decay. Therefore, the gas-phase partial pressure can be expressed as a function of both temperature and time as

$$\ln P = a_0 + a_1\left(\frac{1}{T}\right) + a_2 time \qquad (2)$$

where *time* is the date on which the sample was taken (in relative Julian days) and the a values are fitted constants. The parameters a_1 and a_2, which can be estimated using multiple linear regression, represent $-\Delta H/R$ from equation 1 and $-k$ (a first-order elimination rate constant), respectively. Atmospheric half-lives can then be determined by dividing a_2 into the natural logarithm of 2.

Using equation 2, we were able to estimate the half-lives for 10 pesticides at each IADN master station on each of the Great Lakes. The results are shown in Table 4. Data for Burnt Island and Point Petre were available through 1998 while data for Sturgeon Point, Sleeping Bear Dunes, and Eagle Harbor were available through 2000.

Table 4. Atmospheric half-lives ($t_{1/2}$) and relative standard errors (RSE) of gas-phase pesticides at IADN stations as determined from equation 2.[a]

	Eagle Harbor		*Sleeping Bear Dunes*		*Sturgeon Point*		*Burnt Island*		*Point Petre*	
	$t_{1/2}$ (yr)	RSE (%)	$t_{1/2}$ (yr)	RSE (%)	$t_{1/2}$ (yr)	RSE (%)	$t_{1/2}$ (yr)	RSE (%)	$t_{1/2}$ (yr)	RSE (%)
α-HCH	3.8	4	3.9	6	3.2	5	4.9	8	4.8	6
γ-HCH	6.4	12	4.6	13	4.6	11	8.4	25	6.8	17
Dieldrin	3.9	12	4.5	17	4.3	13	8.7	36	8.3	24
DDT	5.7	20	5.4	22	4.5	16	2.9	14	5.4	20
DDD	*NS*[b]	*NS*[b]	*NS*[b]	*NS*[b]	10.4	52	4.6	22	5.0	17
DDE	5.3	11	5.7	12	5.9	12	4.5	17	6.3	17
α-chlordane	5.1	15	5.8	18	5.4	13	6.8	28	6.0	18
γ-chlordane	17.3	42	16.8	42	8.6	16	9.0	30	7.5	19
***t*-nonachlor**	17.9	42	*NS*[b]	*NS*[b]	8.2	18	5.5	20	5.3	14
HCB	36.7	33	22.1	22	19.2	16	*na*[c]	*na*[c]	*na*[c]	*na*[c]

[a] Half-lives calculated from parameters significant at the 90% confidence level or greater.
[b] Data not significant at the 90% confidence level.
[c] HCB data at Burnt Island and Point Petre are considered unreliable and therefore not included.

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p, *p′*-DDT and its metabolites are decreasing at similar rates at all sites with two exceptions. *p*, *p′*-DDT at Burnt Island has a half-life of about 3 years, nearly half of those at the other sites. The half-life of *p*, *p′*-DDD at Sturgeon Point is approximately 10 years, almost double that at Burnt Island and Point Petre. α-HCH is decreasing with a half-life of 3-5 years, while γ-HCH is taking longer to decline, with half-lives ranging from 5 to 8 years. γ-HCH is still in use in Canada, so it is not surprising that it has longer half-lives. Dieldrin exhibits longer half-lives at Lakes Huron and Ontario, with half-lives of 8-9 years at these sites, while the three other lakes indicate a half-life of around 4 years. Half-lives for the chlordane compounds range from 5 years for α-chlordane to 18 years for *t*-nonachlor. HCB has the longest half-lives at all sites; although no longer used as a pesticide, HCB is still released as a byproduct of many industrial processes.

The results of this study are relevant to the Great Lakes Binational Toxic Strategy, which was signed by the United States and Canada in April 1997. The purpose of this strategy is to facilitate virtual elimination of persistent toxic substances in the Great Lakes Basin. Because most of these pesticides are no longer in widespread use and the atmosphere is

considered to be the primary contributor of current contamination to the Great Lakes, the estimation of regional atmospheric virtual elimination dates is relevant to the strategy.

Assuming first-order kinetics and minimal future inputs, we can use the temporal information gained from equation 2 to estimate a virtual elimination date (Cortes et al., 1998) for the pesticides in Table 4. This date is the time when we will no longer be able to detect these compounds in the atmosphere. These estimates are represented in Figure 3. Annex I of the Great Lakes Water Quality Agreement defines "absent" as the detection limit using best available technology; thus, we used a minimally detectable concentration of 0.1 pg/m^3 to determine the elimination dates shown in Figure 3. New technology and improved methodology will almost certainly cause lower detection limits as environmental concentrations decrease, so these are minimum elimination dates.

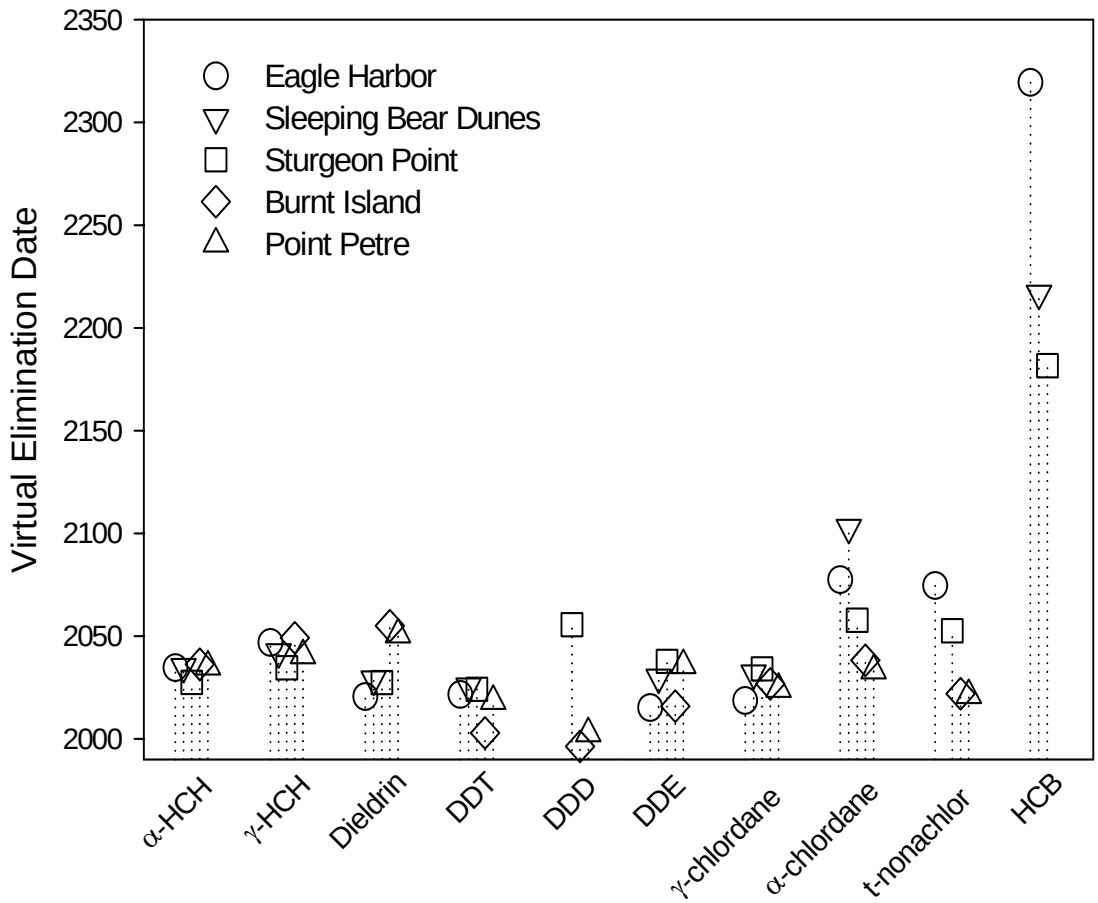


Figure 3. Estimated virtual elimination dates. No virtual elimination dates were calculated where rate constants were not significant.

In general, DDT and its metabolites will be the first to disappear at each site. This is primarily due to current, low atmospheric concentrations. This is logical since DDT was the first pesticide to be banned and probably has the fewest current sources in the environment. In fact, DDD should have been virtually eliminated at Burnt Island in 1996. Inspection of DDD annual averages at this site indicate that in 1996 the average was indeed below 0.1 pg/m^3. Virtual elimination dates average around 2035 for α-HCH at all sites, with the date at Sturgeon Point being slightly lower. Estimates for the virtual elimination of γ-HCH are 5-10 years later. HCB will remain in the atmosphere the longest of the pesticides at all sites until sometime in the 23rd century. Virtual elimination dates for dieldrin and the chlordane compounds vary among the sites with dieldrin taking longer to be removed from the Canadian sites and chlordane compounds having longer elimination dates at the U.S. sites. Overall, it appears that the virtual elimination date for most pesticides will occur by the middle of this century.

3. 1. 2. PCBs

An analysis similar to that done on the pesticides above was performed on PCBs in the gas-phase at IADN master stations in order to obtain half-lives for total PCBs (ΣPCB, which is simply the sum of all individual PCB congeners). This analysis was done on almost 10 years of data from Sleeping Bear Dunes (1992-2000) and Eagle Harbor (1991-2000). Hillery et al. (1997) and Simcik et al. (1999) looked at IADN gas-phase ΣPCB trends through 1995 and 1997, respectively. As a continuation of these studies, we will look at IADN ΣPCB data through 2000.

Lake Michigan (Sleeping Bear Dunes) gas-phase ΣPCB for all time periods show statistically significant declines over time, but these trends vary greatly depending on the years included in the analysis. For data through 1995, ΣPCB has a half-life of 3 years. When two more years of data are added, the half-life increases to 5 years. When ΣPCB data through 2000 are added, the half-life quadruples to 20 years. The increase in half-life from 1995 to 1997 is most likely due to some high ΣPCB concentrations at the end of 1997, and the unusually high half-life for data through 2000 is likely due to the apparent increase in ΣPCB concentrations in 1998 and 1999.

ΣPCB concentrations at Lake Superior (Eagle Harbor) also had varying half-lives over time. ΣPCB through 1995 had no statistically significant declining trend. With the addition of data through 1997, a half-life of 9 years was observed, almost twice as long as the same period at the northern Lake Michigan site. Analysis on all IADN ΣPCB data through 2000 at Lake Superior gave a half-life of 19 years, similar to that found at Lake Michigan for the same period. An apparent increase in ΣPCB concentrations was also observed at this site, with levels beginning to rise in late 1999 and maximizing in 2000.

Since production and use of PCBs have been banned for almost 25 years, there should be no new anthropogenic sources of these compounds. With no new sources, one would expect ΣPCB concentrations to continue to decline as their supply in terrestrial and aquatic surfaces diminishes. Thus, the apparent increase in ΣPCB atmospheric concentrations

near the Great Lakes in 1998-99 is anomalous. Previous analyses relied solely on IADN data to infer long-term trends in atmospheric concentrations of ΣPCB. Given the abnormal behavior of recent trends from this study, we felt it necessary to examine the IADN data from a different perspective in order to gain a better understanding of how ΣPCB are behaving in the Great Lakes atmosphere. To this end, we analyzed the data presented above in a broader, historical context by incorporating ΣPCB data that had been collected previously by other researchers (Eisenreich et al., 1981; Doskey and Andren, 1981; Eisenreich et al., 1983, 1987; Manchester-Neesvig and Andren, 1989; Baker et al., 1990; Hornbuckle et al., 1993, 1994; Achman et al., 1993; Cotham and Bidleman, 1995; Pirrone et al., 1995; Monosmith and Hermanson, 1996). A paper on the approach has recently been accepted for publication in *Environmental Science and Technology*.

Eight years of gas-phase ΣPCB data from 1978-1990 were added to Lake Superior atmospheric data collected by IADN, while 7 years of data from 1977-1991 were found to supplement the Lake Michigan IADN data. As noted in equation 1, temperature has a large effect on the atmospheric partial pressures of PCBs. We can remove this temperature effect by adjusting the partial pressures to a reference temperature of 288 K by using the following equation:

$$P_{288} = P \exp\left[\frac{-\Delta H}{R}\left(\frac{1}{288} - \frac{1}{T}\right)\right] \tag{3}$$

where P_{288} is the compound's partial pressure at the reference temperature of 288 K and $-\Delta H/R$ is taken from equation 1. This approach provides results similar to and not significantly different from the multiple linear regression technique given in equation 2. We plotted all these data as annual average, temperature-corrected, partial pressures (P_{288}) versus time. The plots for ΣPCB for Lakes Michigan and Superior are shown in Figure 4. With ΣPCB data as far back as 1977, we are able to track its trend from the time it was banned until present.

The data for both lakes (see Figure 4) follow exponential curves showing first order rate loss processes for ΣPCB. Both lakes show large declines in ΣPCB concentrations from the late 1970's to the mid-1990s, when concentrations start to become relatively steady. Though the IADN data themselves do show some fluctuations, the overall exponential curve indicates that, since the production of PCBs was banned in 1977, levels in the basin have decreased by a factor of 7 to 10, with annual concentrations dropping from around 1000 pg/m^3 to approximately 100 pg/m^3.

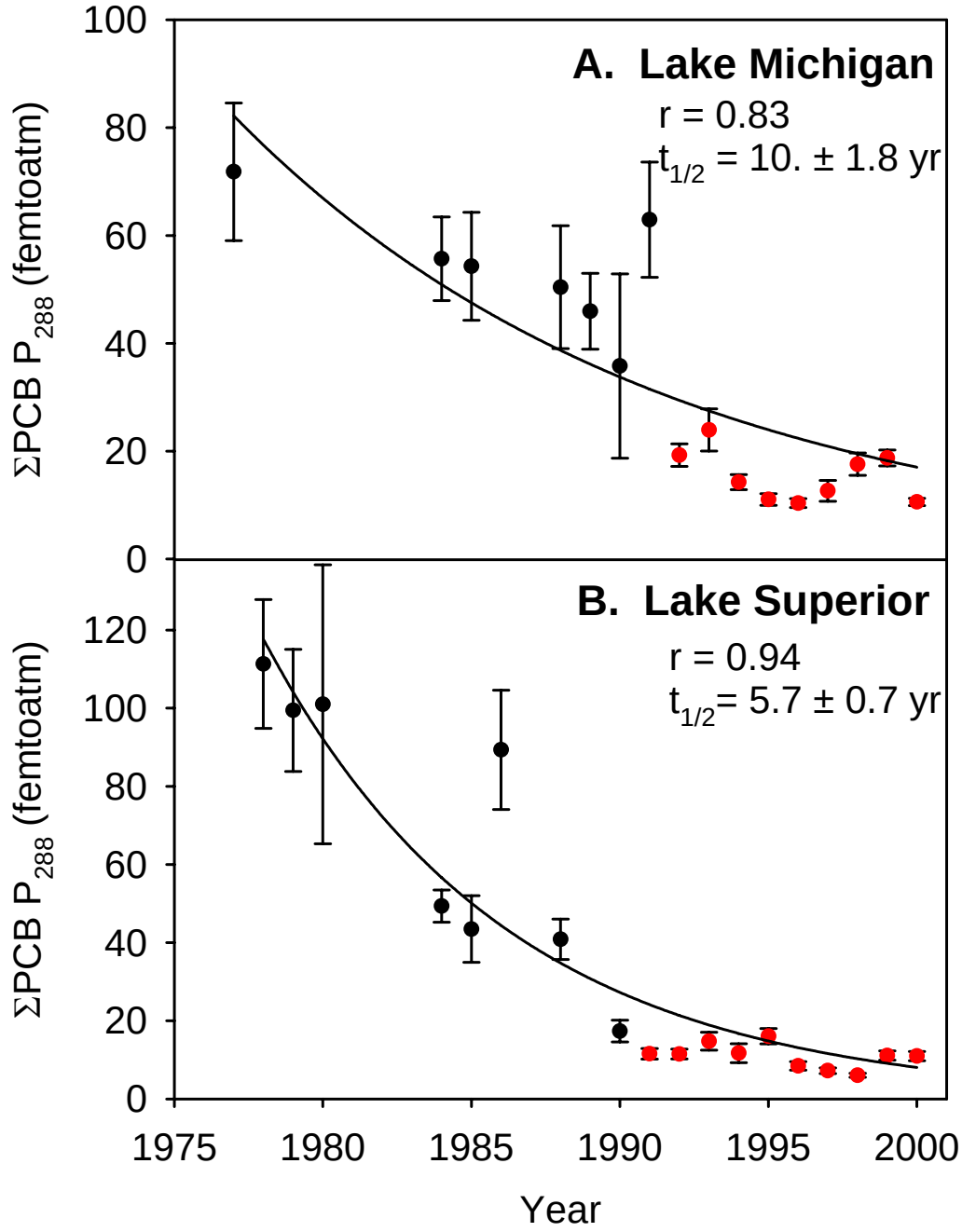


Figure 4. Annual average temperature-corrected partial pressures (P_{288}) of gas-phase ΣPCB in femtoatmospheres (10^{-15} atm) as a function of time for Lakes Michigan (**A**) and Superior (**B**). Averages in red indicate IADN data. All other points are historical data. Error bars represent the standard error for each annual average. Correlation coefficients (*r*) and half-lives ($t_{1/2}$) (with asymptotic errors) are given for each exponential curve and are significant at the 95% confidence level or greater.

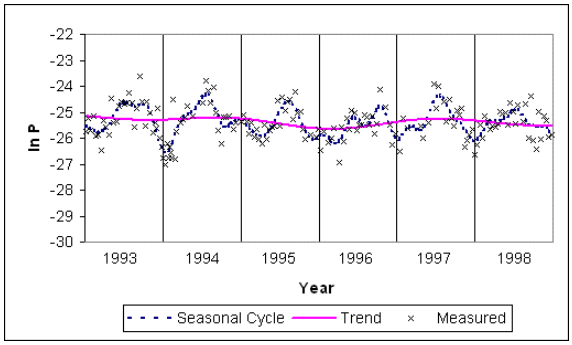
Using the rate constants from the curves in Figure 4, we can calculate half-lives for ΣPCB in air near each lake. ΣPCB in Lake Michigan's atmosphere has a half-life of 10.0 ± 1.8 years, while Lake Superior's data indicate a half-life of 5.7 ± 0.7 years. These values are in contrast to the half-lives of approximately 20 years found using IADN data through 2000. The half-lives of 6-10 years, however, compare well with PCB half-lives found in other media at both lakes. In this historical context, the apparent increases in ΣPCB shown in the IADN data from 1998-1999 are most likely temporary, and in fact, the average ΣPCB concentration in 2000 *decreased* from that in 1999. The cause of this temporary elevation is currently unknown.

Another trend analysis technique has recently been applied to IADN PCB data (Hung et al., in preparation) to determine whether atmospheric concentrations are declining at two sites: Burnt Island and Point Petre. This analysis was conducted on PCB data from 1992 to 1998 for Point Petre and from 1993 to 1998 for Burnt Island. As we discussed with pesticides, PCBs also exhibit seasonality. For the determination of a temporal trend, the intra-annual variability must be reduced. A statistical time series analysis technique (digital filtration, DF) was employed to smooth any seasonality in the air data (Nakazawa et al., 1997). This technique has been successfully used in determining the trends of PCBs (Hung et al., 2001) and organochlorines in Arctic air (Hung et al., 2002), as well as in atmospheric levels of trace gases, e.g. methane and carbon dioxide (Nakazawa et al., 1997; Worthy et al., 1998). For each compound, an approximate long-term trend and an average seasonal cycle were estimated by fitting a smoothing Reinsch-type cubic spline and Fourier components to the data, respectively (Nakazawa et al., 1997). Long- and short-term variations of the trend and the seasonal cycle were then extracted using iterative digital filters with two cut-off periods: a short term cut-off period, set to 4 months, and a long term cut-off period, set to 24 months. The variabilities longer than 4 months and shorter than 2 years were extracted to obtain the overall seasonal cycle and the variabilities longer than 2 years were extracted to obtain the final long-term trend. The cut-off periods, which produce the "best fit" to the specific dataset, have been chosen by trial-and-error based on visual inspection of the fitted seasonal cycle. Outliers, which were data larger than 3 standard errors of fit away from the fitted curve, were successively rejected after each iterative fit (Hung et al., 2001, 2002).

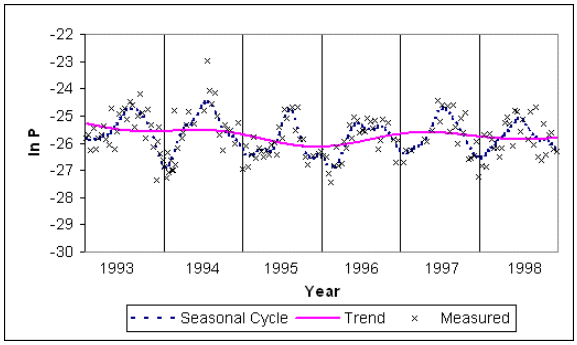
Examples of the seasonal cycles and trends estimated by the DF techniques are shown in Figure 5 for PCBs 44 and 101 at Point Petre and Burnt Island. Trends and seasonal cycles were also generated for Sleeping Bear Dunes using all available data up to the end of 1998 for comparison. Trends were also derived for other PCB congeners.

Burnt Island

PCB 44

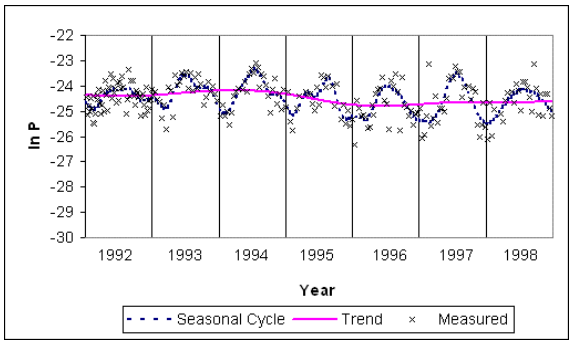


PCB 101

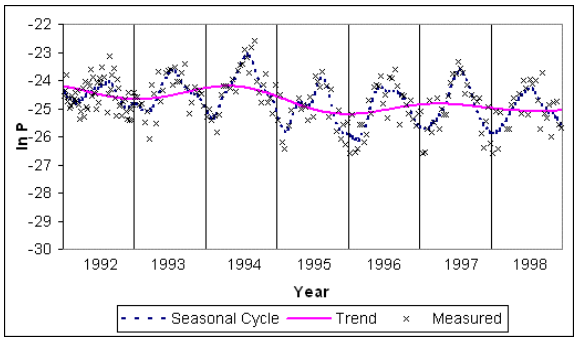


Point Petre

PCB 44

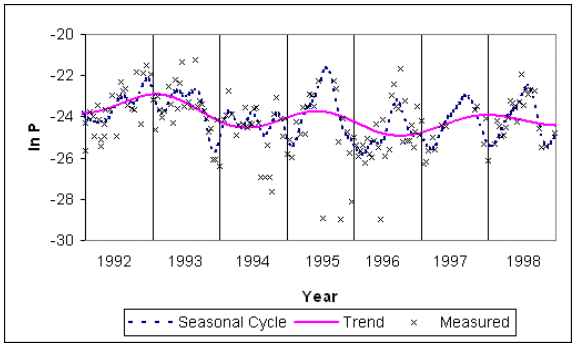


PCB 101



Sleeping Bear Dunes

PCB 44



PCB 101

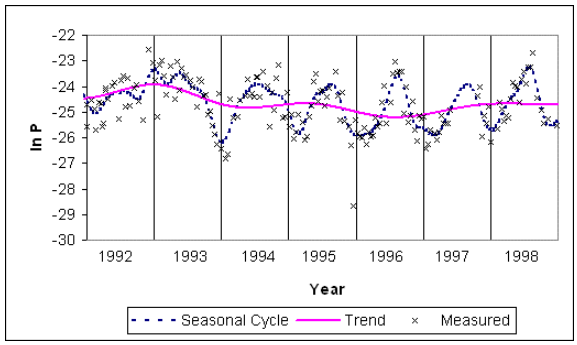


Figure 5. Trends and seasonal cycles derived using the digital filtration technique for PCBs 44 and 101 at Burnt Island, Point Petre, and Sleeping Bear Dunes. The trends were statistically significant with a confidence of 95 % determined with F-tests against de-seasoned data.

It was observed that for both Point Petre and Burnt Island, higher chlorinated congeners generally decline faster than the lower chlorinated congeners. Since lower chlorinated congeners are more volatile and mobile, volatilization of these congeners from lake water (Buehler et al., 2001b) and atmospheric transport from nearby sources might sustain the levels of these compounds in the air. On the other hand, higher chlorinated congeners, which are heavier and more lipophilic, are subjected to removal by precipitation or scavenging processes, accelerating the decline of their concentrations in the atmosphere.

To access the relative decline rates of different congeners, apparent first-order half-lives, $t_{1/2}$, were estimated by dividing ln 2 by the regression slopes of the trend lines. The regression results for selected congeners are presented in Table 5. Half-lives were also determined for Sleeping Bear Dunes using the DF technique with all available data up to the end of 1998 for comparison. The half-lives for this site determined here are quite different from those determined by Simcik et al. (1999) using the multiple linear regression technique. This is mainly because Simcik et al. have segregated the data by the origin of the air mass. In their study, half-lives were determined for samples with air mass originating over land surface and over water surface separately. Those samples with air masses originating over both lake and land were not included in the determination of half-lives. The half-lives generated with the DF technique were determined with all available data without segregation, and it has extended the time series of Simcik et al. (1999) with the addition of the 1998 data, totaling 166 to 177 samples. These two types of analyses provide two different perspectives of the atmospheric concentration data. By segregating the data according to air mass origin, Simcik et al. (1999) emphasized the effect of sources on the concentrations recorded at these relatively rural sites. On the other hand, the use of all available data in this study focuses on the overall rate of decline in air concentrations over the lakes.

From Table 5, it is apparent that for Burnt Island and Point Petre, the lower chlorinated congeners generally showed longer half-lives than higher chlorinated ones. This pattern is less prominent at Burnt Island than at Point Petre. Also, half-lives for the same congener at Burnt Island are generally longer and the correlations are usually poorer (smaller r^2) than those observed at Point Petre. While Point Petre is influenced by large urban developments, such as Toronto and Buffalo, Burnt Island is remote from such source regions. Without the influence of large urban sources, most of the lighter PCBs might be closer to air-water equilibrium at Lake Huron than at Lake Ontario, resulting in longer atmospheric half-lives.

Table 5. Half-lives ($t_{1/2}$) and *r*-squared values determined by linear regression of trends from the digital filtration technique.

PCB #	Burnt Island			Point Petre			Sleeping Bear Dunes		
	$t_{1/2}$	r^2	n[a]	$t_{1/2}$	r^2	n[a]	$t_{1/2}$	r^2	n[a]
18	47	0.03	170	24	0.43	232	13	0.11	177
44	19	0.21	166	9.3	0.53	230	4.5	0.35	166
101	12	0.22	168	6.0	0.56	230	6.4	0.42	177
180	4.1	0.35	161	8.4	0.34	226	3.1	0.79	168

[a] n = number of samples used in regression

It can be seen that the same PCB congeners decline at different rates at the three sites presented in Table 5. Various factors may contribute to this difference, for example, ambient conditions, water concentrations in the vicinity of the site, influence of prevailing air mass, precipitation rates, etc. Further study should be performed to investigate the relationships between these factors and the rates of change of various congeners at different sites.

3. 1. 3. PAH

Equation 2 was used to estimate half-lives for individual gas-phase PAHs at Sleeping Bear Dunes, Eagle Harbor, and Sturgeon Point. Data for phenanthrene, fluoranthene, pyrene, and chrysene through 2000 were used at each site. All PAHs showed statistically significant declining trends at the 90% confidence level or better. Phenanthrene tended to have the highest half-life at all sites, ranging from 14 to 18 years. The half-life for fluoranthene had a broader range among the three sites and increased from west to east across the basin. This may be related to increased population or industrialization from west to east across the Great Lakes. The half-life for fluoranthene was 11 years over Lake Superior, 13 years over Lake Michigan, and 16 years over Lake Erie. Pyrene half-lives were approximately half of those found for fluoranthene, averaging around 6 years. Chrysene showed the least variation in declining rates across the basin with a half-life of 4 years at Eagle Harbor and Sleeping Bear Dunes and around 6 years at Sturgeon Point.

Many PAHs occur mainly in the particle phase. A study by Cortes et al. (2000) found that at Sturgeon Point a significant declining trend could not be found for PAHs in this phase. In this case, Cortes et al. (2000) discovered that PAH concentrations at this master station were influenced by wind direction during sampling.

Hourly wind directions were incorporated into a linear regression model that divided the wind into four sectors based on the predominant wind patterns at each site (see equation 4).

$$conc = a_0 + a_1 f_{wd,1} + a_2 f_{wd,2} + a_3 f_{wd,3} + a_4 f_{wd,4} \quad (4)$$

where *conc* is the total gas-phase concentrations for the 24-hour sampling period and $f_{wd,i}$ is the fraction of the 24-h period during which the wind was blowing from sector *i*.

The model statistics and fitted parameters for each site show that the model is only significant for the Sturgeon Point site, where wind direction alone explains 29% of the variance in gas-phase PAH concentrations. This indicates that regional PAH sources are present. The model parameters also indicate how the wind direction influences PAH concentrations at the site. Wind that is consistently from the Buffalo region produces a concentration of 10,000 pg/m^3 while wind consistently off the lake produces a concentration of 3000 or 1600 pg/m^3, depending if the wind is from the north or west. Our results thus indicate that winds from the Buffalo region are a source of PAH to Sturgeon Point.

Sturgeon Point is not the only site where we have found regional PAH sources. IADN operates two stations on Lake Superior, a master station at Eagle Harbor and a satellite station at Brule River. These stations are approximately 400 km apart, with Brule River sitting 40 km southeast of Duluth, MN, a city with a population of about 100,000. A recent comparison of PCB, PAH, and pesticide concentrations at these two sites by Buehler et al. (2001a) indicated that while PCB and pesticide concentrations were comparable at the two sites, PAH concentrations at Brule River were on average up to 3 times greater than levels at Eagle Harbor, and on some individual days 10 time greater. A back trajectory analysis showed that winds generally came to Brule River from the northwest, or the direction of Duluth, MN. The lack of other prospective cities in the area coupled with the wind patterns indicated that Duluth was a source of PAH contamination to the Brule River site, indicating that even a relatively small city can impact PAH levels at a rural sampling site.

3. 2. Precipitation

Temporal and spatial analyses were conducted basin-wide for OCs and PAHs in precipitation (Chan et al., in press). Hexachlorocyclohexane (HCHs) and dieldrin in Great Lakes precipitation continued their decline. Figure 6 shows the global use of technical hexachlorocyclohexane (HCH) for the period 1950 to 1995 (Li, 1999) along with the annual volume weighted mean concentration of α-HCH (the dominant isomer in technical HCH) in precipitation at Sibley for the period 1985 to 1998. Global use of α-HCH peaked in 1980 and dropped significantly in the early 1980s. The significant decline in precipitation concentrations at Sibley from 15-25 ng/L in the mid-eighties to 2-3 ng/L in the late nineties coincides well with the reduction in global use. A plot of the α-HCH to γ -HCH ratio over the years is shown in Figure 7. This ratio has gradually declined from 3.5 to 0.7 indicating usage of an HCH mixture richer in lindane, which is to be expected given the ban on the use of the technical mixture that was dominated by the alpha isomer.

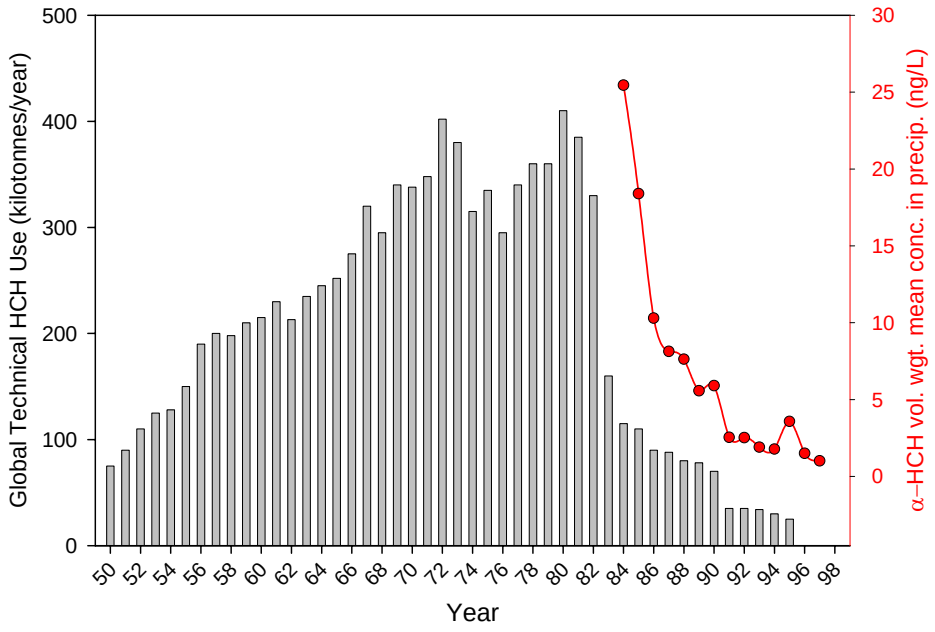


Figure 6. Long-term trends (1950-1996) in the global use of technical hexachlorocyclohexane (HCH) and the volume weighted mean concentration of α-HCH in precipitation (in ng/L) at Sibley, Ontario, Canada.

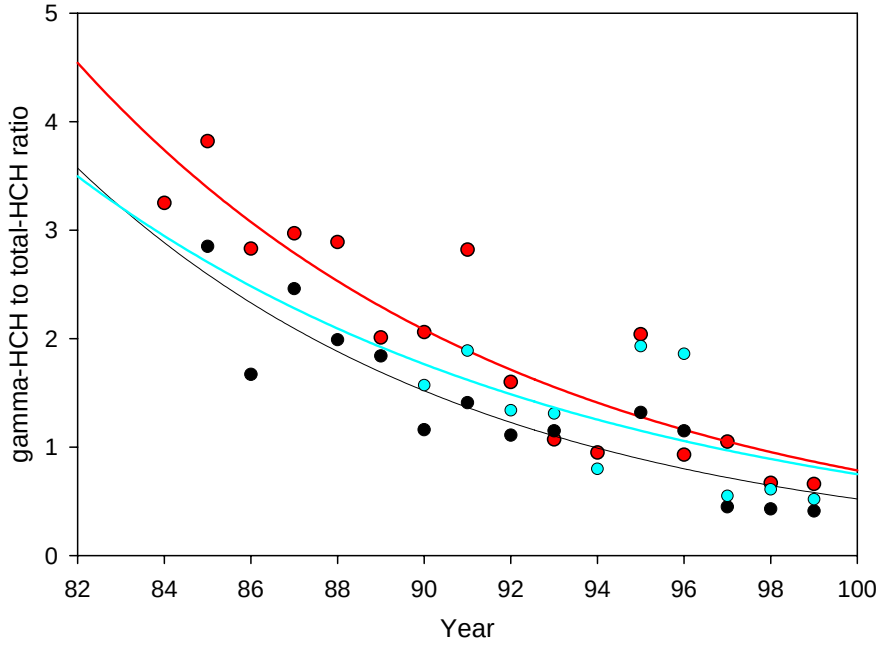


Figure 7. Ratio of α-HCH to γ-HCH (lindane) in precipitation samples from Sibley (red), Pelee (black), and Point Petre (blue), 1984-1999.

A non-parametric analysis was used to evaluate the spatial trends of several persistent organic pollutants in Great Lakes precipitation. For each of the five years, each of the nine stations was ranked in order of concentration for each contaminant, with 1 being the lowest concentration and 9 being the highest. The average rank for each station for each contaminant over the five-year period was then tested for statistical significance. The relevant *t*-distribution (N = 5) had a mean of 5.0, a standard deviation of 2.7, and upper and lower 95% confidence limits of 7.6 and 2.4, respectively. Stations with contaminant ranks falling outside these confidence limits were considered to be statistically different. The results are shown in Table 6. Results found to be statistically different for each contaminant have been given in a bold font.

There was a distinct north to south difference in precipitation contaminant concentrations in the Great Lakes Basin. The three northern stations had significantly lower concentrations of most contaminants, while significantly higher concentrations were observed at stations in the southern portion of the Basin. α-HCH was the exception, with no statistical difference in concentrations among all nine stations. The highest concentrations of DDE in precipitation for all five years were measured at the Point Pelee site. DDE concentrations at Pelee remained well above those measured at the other sites. Subsequent investigation has revealed that the whole Pelee Peninsula is heavily contaminated with DDT as a result of heavy past use.

Stations on the same lake had significantly different concentrations of some contaminants. For example, the difference in PAH concentrations between Burlington and Point Petre, and the difference in DDE and dieldrin concentrations between Point Pelee and Rock Point were both statistically significant. Burlington always had significantly higher concentrations of α- and β-endosulfan than the other stations.

Table 6. Average station ranking of selected organochlorine pesticides and polycyclic aromatic hydrocarbons in Great Lakes precipitation

	α-HCH	γ-HCH	DDE	Dieldrin	α-Endo.	β-Endo.	Phen.	Fluoran.	Pyrene	2-Me-Naph.
Sibley	3.0	**2.2**	**1.6**	**1.8**	**1.2**	**2.4**	4.4	**1.2**	**1.0**	**1.0**
Turkey Lakes	3.8	**2.0**	**2.2**	3.0	**1.8**	**1.8**	**1.2**	**2.4**	**2.4**	**2.4**
Burnt Is.	5.6	4.0	**2.2**	4.6	3.2	**2.0**	**2.4**	2.8	3.4	3.4
Grand Bend	5.8	6.6	5.0	6.2	6.4	6.2	3.4	4.6	5.0	5.0
St. Clair	3.8	7.2	6.6	7.2	6.6	6.2	**8.2**	**8.2**	7.4	7.4
Pelee	4.8	6.4	**9.0**	**8.8**	5.0	5.4	7.2	7.0	6.6	6.6
Rock Pt.	7	5.8	5.4	3.8	5.6	4.8	6.0	5.6	5.6	5.6
Burlington	4.8	7.6	7.0	6.4	**8.8**	**9.0**	**7.8**	**8.4**	**8.6**	**8.6**
Pt. Petre	6.4	3.2	6.0	3.2	6.4	7.2	4.4	4.8	5.0	5.0

4. Loadings

An International Joint Commission (IJC) workshop in 1986 culminated in the first-ever atmospheric loading estimates to the Great Lakes based on data from 1980-1985 (Strachan and Eisenreich, 1988). Four years after that first report, an update to the loadings was prepared (Eisenreich and Strachan, 1992) in which many needed improvements were implemented. Although IADN in its current form was taking shape, mass loading estimates were still only available for wet and dry particle deposition. In 1996, the first set of loading estimates using IADN data and including gas exchange and using measured values of gas and particle-phase concentrations in air was published (Hoff et al., 1996). This was followed by the first formal IADN biennial loadings report for the period 1993-1994 (Hillery et al., 1998). In accordance with Annex 15, IADN has continued producing biennial loadings estimates with the release of two more reports for the periods of 1995-1996 (Galarneau et al., 2000) and 1997-1998 (Buehler et al., 2001b).

Detailed descriptions of the loadings calculations were presented in early publications of the estimates (Hoff, 1994; Hoff et al., 1996; Hillery et al., 1998). In general, loadings estimates (L, in kg/yr) are based on three processes: wet deposition, dry deposition, and net gas exchange. They are represented by the equation:

$$L = C_p R_p A + C_a \phi_a v_d A + [k_{ol}(1-\phi_a)C_a(RT/H)A - k_{ol}(1-\phi_w)C_w A] \qquad (5)$$

Wet deposition is the product of the volume-weighted mean precipitation-phase concentration, C_p (kg/m^3), the rate of precipitation, R_p (m/yr), and the area of the lake, A (m^2). In a similar manner, dry deposition is the product of the total atmospheric concentration of the pollutant, C_a (kg/m^3), the fraction of the compound in the particle phase, ϕ_a, the deposition velocity of the particles, v_d (m/yr), and the area of the lake. Gas transfer is divided into two components: volatilization and absorption. The variable, k_{ol} (m/yr), is the overall air-water mass transfer coefficient, R (atm m^3 K^{-1} mol^{-1}) is the ideal gas constant, T (K) is the temperature at the air-water interface, H (mol atm^{-1} m^{-3}) is the Henry's Law constant, and C_w (kg/m^3) is the concentration of the compound in the water. For absorption, $(1-\phi_a)C_a$ is the concentration of the compound in the gas phase. Absorption is the transfer of the compound in the gas phase from air to water. For volatilization, ϕ_w is the fraction of the compound on the particle phase in the water, thus making $(1-\phi_w)C_w$ the dissolved concentration of the compound of interest. Volatilization is then the transfer of the compound from water to air. Net gas exchange is the sum of the absorption and volatilization estimates. Positive net gas exchange indicates absorption, while negative net gas exchange indicates volatilization. While IADN directly measures pollutant concentrations in the gas, precipitation, and particle phases, it must rely on other researchers for water concentration measurements and Henry's Law constant estimates.

The Henry's Law constant (HLC, Pa m^3/mol) is a critical parameter which describes equilibrium partitioning of trace gases between air and water. It is extensively used to estimate scavenging of gaseous compounds by precipitation and their exchange with lakes and oceans. Gas exchange is the dominant process in the loadings of gas phase chemicals

to the Great Lakes. For slightly soluble compounds, the HLC can be approximated by the ratio of vapor pressure to water solubility, although due to uncertainties in literature values for these properties it is desirable to measure the HLC directly. Most of the HLC used in past loadings reports have been measured directly and some are temperature dependent. For some substances, the temperature dependencies have been applied using a PCB slope (Tateya et al., 1988).

A large source of error to the loadings calculations is the error associated with the HLC, and in the last technical summary report more accurate air-water partition coefficients were included as a recommendation. Since the last technical summary report, many of the HLC have been updated and now include experimentally determined temperature dependencies, but some critical values are still missing, for example β-endosulfan. These corrected values are given in Table 7.

Table 7. Corrected Henry's Law constants as a function of temperature.

Substance	Log H = m/T + b		Reference
	M	b	
α-HCH [a]	-3268	10.722	Sahsuvar et al., 2002
γ-HCH (Lindane) [a]	-3334	10.552	Sahsuvar et al., 2002
Dieldrin [c]	-3416	12.2	Cotham and Bidleman, 1991
trans-Chlordane [b]	-1760	7.36	Jantunen and Bidleman, in prep.
cis-Chlordane [b]	-1994	8.11	Jantunen and Bidleman, in prep.
trans-Nonachlor [b]	-2317	9.28	Jantunen and Bidleman, in prep.
p,p'-DDD [c]	-3416	11.3	Suntio et al., 1987; Tateya et al., 1988; Hoff et al., 1996
p,p'-DDE [b]	-2297	9.22	Jantunen and Bidleman, in prep.
p,p'-DDT [c]	-3416	11.7	Cotham and Bidleman, 1991
α-Endosulfan	-1001	4.26	Rice et al., 1997
HCB [b]	-3094	11.92	Jantunen and Bidleman, 2002
PCB 18 (tri) [b]	-1823	4.13	Bamford et al., 2000
PCB 44 (tetra) [b]	-1347	2.56	Bamford et al., 2000
PCB 52 (tetra) [b]	-1593	3.45	Bamford et al., 2000
PCB 101 (penta) [b]	-1551	3.45	Bamford et al., 2000
Phenanthrene	-2469	8.89	Bamford et al., 1999
Pyrene	-2239	7.59	Bamford et al., 1999
Benzo[*b*]fluoranthene [c]	-3416	10.4	Ten Hulscher et al., 1992
Benzo[*k*]fluoranthene [c]	-3416	10.7	Ten Hulscher et al., 1992
Benzo[*a*]pyrene [c]	-3416	10.8	Ten Hulscher et al., 1992
Indeno[*1,2,3-cd*]pyrene [c]	-3416	6.95	Ten Hulscher et al., 1992

a: The HCH have been updated using only the most reliable data currently available, with experimentally determined temperature dependency.
b: Update with experimentally determined temperature dependent values.
c: Temperature dependency applied using the PCB slope (-3416, Tateya et al., 1988)

The 1995-1996 loadings report made a few changes to the calculations used in estimating the loadings. First, eight more substances were added to the original list of 20 pollutants reported. Henry's Law constants were updated to include recently determined temperature-dependent estimates. Measured wind speeds were used in determining the gas exchange term of the fluxes rather than the constant wind speed of 5 m/s that was used in previous calculations. Also, mass transfer calculations used in the gas exchange model calculations were simplified. These changes were carried through into the 1997-1998 report.

The 1997-1998 loadings report (Buehler et al., 2001b) presented annual loading estimates to the Lakes spanning seven years (1992-1998) of IADN data. Though this report followed those before it by presenting annual loadings to each of the five Great Lakes as determined from IADN master station concentration data, it also used a new approach to analyze long-term loading trends. Buehler et al. (2001b) looked at loadings estimates throughout the history of IADN by using a basin-wide approach. This system-wide estimate was obtained by summing the loadings for each substance across all five lakes (when available) for each year. Figure 8 shows these total regional loadings for α-HCH, a banned pesticide; γ-HCH (lindane), a currently used though heavily restricted pesticide; and total PCBs, banned industrial chemicals.

Figure 8 shows that the loadings of α- and γ-HCH into the Great Lakes has generally decreased since 1992. Despite such a decrease, however, γ-HCH, a currently-used pesticide, has almost always had the highest regional loading values other than the currently-emitted PAHs and metals. Region-wide loading estimates for these in-use chemicals (PAHs and metals), however, show no real declining trend. Such chemicals continue to have many anthropogenic sources, allowing them to directly enter the atmosphere, which transports them to the Great Lakes, where they deposit.

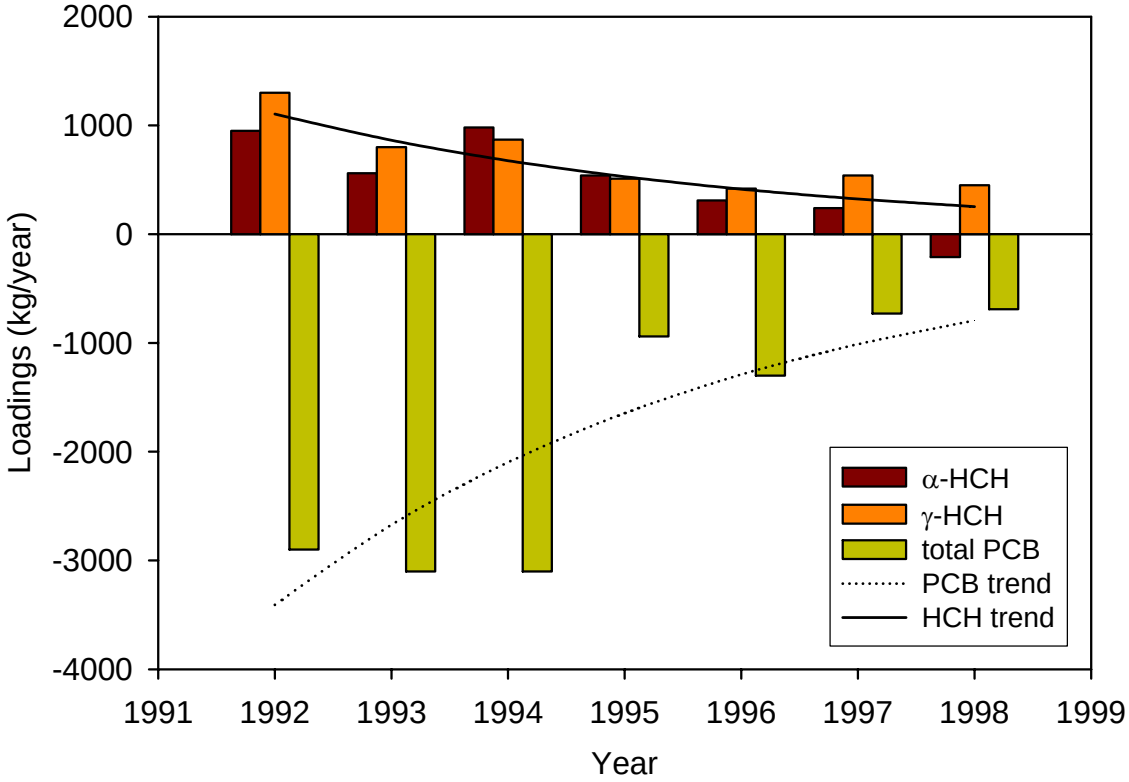


Figure 8. Annual loadings for α-HCH, γ-HCH (lindane), and total PCBs into or out of the five Great Lakes collectively. The two curves indicate general trends in the HCH (average of α- and γ-isomers) and PCB loadings. The fitted exponential curves have correlation coefficients (r^2) of 0.833 and 0.744 for the HCH and PCB loadings, respectively; both are statistically significant with 99% confidence.

PCB loadings to the Great Lakes as a function of time are also shown in Figure 8. In this case, we find that the waters of the Great Lakes have been volatilizing PCBs into the atmosphere for at least 7 years (this is the meaning of negative loadings) and that the rate of volatilization has generally decreased with time. Clearly, when PCBs had been in use in the 1960s, there were substantial inputs of these compounds into the Lakes. Now that PCBs have been banned and the atmospheric concentrations have decreased (Hillery et al., 1997), the air-water equilibrium has shifted, and the water is releasing its stores of PCBs back into the atmosphere. Regional loadings for the banned chemicals dieldrin, *p,p′*-DDE, and HCB are also mostly negative across time. In fact, dieldrin regional flows have been negative in all years and have decreased by approximately a third from 1992 to 1998, similar to PCBs in Figure 8.

As indicated by the two curves in Figure 8, the deposition of HCHs into the Lakes and the evaporation of PCBs from the Lakes seem to be approaching zero. Because these compounds are relatively volatile and have little or no dry or wet deposition into the Lakes (Buehler et al., 2001b), we know that the total deposition shown in Figure 8 is driven almost entirely by air-water exchange. This observation suggests that air-water partitioning for these compounds is approaching equilibrium. In fact, loadings estimates indicate that most banned compounds IADN measures are moving towards equilibrium.

Large potential for error in the IADN loadings calculations exists in the use of data from one remote sampling site to characterize each lake (Hoff, 1994; Hillery et al., 1998). Research suggests that spatial variability exists for many compounds across any one lake (Achman et al., 1993; Monosmith and Hermanson, 1996). In particular, it has been shown that urban areas have increased levels of deposition to the Great Lakes as compared to background levels (Offenberg et al., 1997; Simcik et al., 1997; Franz et al., 1998; Zhang et al., 1999). This implies that loadings calculated using only data from a remote sampling site might grossly underestimate the true deposition to the entire lake. Given the many urban centers that exist in the Great Lakes region, there is the potential for many urban impacts on loadings estimates to the Great Lakes. Since the characterization of such sources was deemed necessary to the original long-term design of the network, (Voldner and Eisenreich, 1987) the 1995-1996 (Galarneau et al., 2000) and 1997-1998 (Buehler et al., 2001b) loadings reports assessed whether the IADN approach can be used to estimate the significance of these concentrated inputs to the lakes.

The assessment compares data collected at Sleeping Bear Dunes (IADN's Master Station on Lake Michigan) and at Chicago (IADN's satellite station at the Illinois Institute of Technology). To assess whether the larger Chicago fluxes were significant across the entire lake, the impact Chicago might have over the whole lake was estimated by using an urban plume effect that assumes deposition from Chicago extends only over a small sub-area of Lake Michigan. This sub-area corresponds to 1.7% of the total lake area for wet and dry deposition, and 3.5% of the total lake area for gas exchange (Galarneau et al., 2000). A temporal component was also added to account for the time that air is flowing from the city over the lake and can thus impact loadings. Then, the increase in lake-wide flows as a result of the inclusion of the urban flows with the regional data was calculated as a percent (urban effect). The results of these calculations are shown in Table 8. Negative urban effect percentages indicate that the background (BG) lake-wide volatilization flows are decreased by including the urban inputs. Background (BG) flows refer to Sleeping Bear Dunes data.

Table 8. The effect on lake-wide loadings of adding flows from Chicago to master station estimates of regional background (BG) flows from Sleeping Bear Dunes.

Species	Year	Wet Deposition			Dry Deposition			Net Gas Exchange			Total Mass Flows		
		BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect
α-HCH	1996	15	0.41	2.7%	-	-	-	300	8	2.7%	320	8.4	2.6%
	1997	40	0.37	0.9%	3.4	0.0028	0.1%	300	4.2	1.4%	340	4.6	1.4%
	1998	17	0.24	1.4%	0.91	0.0022	0.2%	200	1.5	0.8%	220	1.7	0.8%
γ-HCH	1996	6.6	0.34	5.2%	-	-	-	110	3.2	2.9%	120	3.5	2.9%
	1997	31	0.51	1.6%	2.3	0.029	1.3%	150	2.4	1.6%	180	2.9	1.6%
	1998	13	0.47	3.6%	1.9	0.011	0.6%	190	2.5	1.3%	200	3	1.5%
dieldrin	1996	30	0.52	1.7%	-	-	-	-220	1.6	-0.7%	-190	2.1	-1.1%
	1997	24	0.85	3.5%	15	0.63	4.2%	-150	2.4	-1.6%	-110	3.9	-3.5%
	1998	31	0.53	1.7%	18	0.53	2.9%	-210	0.41	-0.2%	-160	1.5	-0.9%
α-endosulfan	1996	14	0.16	1.1%	-	-	-	360	5	1.4%	370	5.2	1.4%
	1997	15	0.28	1.9%	36	0.15	0.4%	830	5.7	0.7%	880	6.1	0.7%
	1998	10	0.45	4.5%	140	0.12	0.1%	830	8.3	1.0%	980	8.9	0.9%
cis-chlordane	1996	3.9	0.012	0.3%	-	-	-	-3.3	1.3	-39.4%	0.6	1.3	216.7%
	1997	9.9	0.88	8.9%	2.5	0.31	12.4%	2.2	1.6	72.7%	15	2.8	18.7%
	1998	11	0.12	1.1%	3.2	0.31	9.7%	-4.5	1	-22.2%	9.7	1.4	14.4%
trans-chlordane	1996	9.6	0.16	1.7%	-	-	-	-3	1.2	-40.0%	6.6	1.4	21.2%
	1997	1.1	0.1	9.1%	1.5	0.075	5.0%	-0.36	1.2	-333.3%	2.2	1.4	63.6%
	1998	1.2	0.17	14.2%	1.8	0.075	4.2%	-4.9	0.85	-17.3%	-1.9	1.1	-57.9%
trans-nonachlor	1996	0.95	0.064	6.7%	-	-	-	-15	0.023	-0.2%	-14	0.087	-0.6%
	1997	0.78	0.068	8.7%	1.1	0.027	2.5%	-16	-0.0048	0.0%	-14	0.09	-0.6%
	1998	0.89	0.04	4.5%	0.82	0.017	2.1%	-17	-0.049	0.3%	-15	0.008	-0.1%
p,p'-DDD	1996	1.8	0.05	2.8%	-	-	-	4.7	0.2	4.3%	6.5	0.25	3.8%
	1997	0.36	0.1	27.8%	0.76	0.015	2.0%	3.5	0.3	8.6%	4.6	0.42	9.1%
	1998	2.9	0.029	1.0%	0.99	0.016	1.6%	5.3	0.31	5.8%	9.2	0.36	3.9%
p,p'-DDE	1996	3.9	0.16	4.1%	-	-	-	-2.7	1	-37.0%	1.2	1.2	100.0%
	1997	2.5	0.12	4.8%	-	-	-	-1.5	0.74	-49.3%	1	0.86	86.0%
	1998	2.7	0.14	5.2%	-	-	-	-12	0.71	-5.9%	-9.3	0.85	-9.1%
p,p'-DDT	1996	9	0.53	5.9%	-	-	-	5.6	1.8	32.1%	15	2.3	15.3%
	1997	4.3	0.42	9.8%	1.1	0.17	15.5%	13	1.2	9.2%	18	1.8	10.0%
	1998	3	0.43	14.3%	2	0.092	4.6%	14	1.1	7.9%	19	1.6	8.4%
HCB	1996	0.91	0.014	1.5%	-	-	-	8.3	0.66	8.0%	9.2	0.67	7.3%
	1997	0.75	0.018	2.4%	-	-	-	16	0.46	2.9%	17	0.48	2.8%
	1998	0.83	0.021	2.5%	-	-	-	26	0.33	1.3%	27	0.35	1.3%

Table 8. The effect on lake-wide loadings of adding flows from Chicago to master station estimates of regional background (BG) flows from Sleeping Bear Dunes.

Species	Year	Wet Deposition			Dry Deposition			Net Gas Exchange			Total Mass Flows		
		BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect	BG (kg/yr)	Chicago (kg/yr)	Urban Effect
PCB18	1996	1.7	0.029	1.7%	-	-	-	-24	0.45	-1.9%	-22	0.48	-2.2%
	1997	0.82	0.03	3.7%	-	-	-	-6.2	0.53	-8.5%	-5.4	0.56	-10.4%
	1998	1.4	0.075	5.4%	-	-	-	-5.5	0.52	-9.5%	-4.1	0.6	-14.6%
PCB44	1996	0.97	0.033	3.4%	-	-	-	-22	1.4	-6.4%	-21	1.4	-6.7%
	1997	1.3	0.057	4.4%	-	-	-	-8.20	1.4	-17.1%	-6.9	1.5	-21.7%
	1998	2.8	0.11	3.9%	-	-	-	-11	0.9	-8.2%	-8.2	1	-12.2%
PCB52	1996	2.2	0.047	2.1%	-	-	-	2.2	1.9	86.4%	4.4	1.9	43.2%
	1997	1.7	0.054	3.2%	-	-	-	7.10	1.9	26.8%	8.8	2	22.7%
	1998	1.9	0.11	5.8%	-	-	-	11	1.7	15.5%	13	1.8	13.8%
PCB101	1996	1.4	0.056	4.0%	-	-	-	-9.1	0.98	-10.8%	-7.7	1	-13.0%
	1997	1.1	0.063	5.7%	-	-	-	-3.79	1.1	-29.0%	-2.7	1.2	-44.4%
	1998	1.7	0.15	8.8%	-	-	-	-4.3	1.1	-25.6%	-2.6	1.3	-50.0%
suite-PCB	1996	48	1.6	3.3%	-	-	-	-320	22	-6.9%	-270	24	-8.9%
	1997	25	1.3	5.2%	-	-	-	-51.4	19	-37.0%	-26	20	-76.9%
	1998	38	3.4	8.9%	-	-	-	-34	18	-52.9%	4	21	525.0%
phenan-threne	1996	220	46	20.9%	100	23	23.0%	-7200	3800	-52.8%	-6900	3900	-56.5%
	1997	320	95	29.7%	97	26	26.8%	700	2000	285.7%	1100	2100	190.9%
	1998	180	100	55.6%	120	16	13.3%	-310	1500	-483.9%	-10	1600	-16000.0%
pyrene	1996	140	57	40.7%	110	43	39.1%	-950	500	-52.6%	-700	600	-85.7%
	1997	220	99	45.0%	99	39	39.4%	-18	300	-1666.7%	300	440	146.7%
	1998	130	98	75.4%	150	24	16.0%	18	230	1277.8%	300	350	116.7%
B[*b*+*k*]F	1996	258	53	20.5%	197	42	21.3%	55	18	32.7%	510	110	21.6%
	1997	338	99	29.3%	180	39	21.3%	86	19	22.1%	610	160	26.2%
	1998	278	118	42.4%	288	35.8	12.4%	100	5.7	5.7%	670	160	23.9%
B[*a*]P	1996	84	29	34.5%	41	15	36.6%	-2.4	4.6	-191.7%	120	49	40.8%
	1997	120	57	47.5%	48	18	37.5%	14	5.5	39.3%	180	81	45.0%
	1998	89	58	65.2%	86	12	14.0%	10	1.6	16.0%	190	72	37.9%
I[1,2,3-*cd*]P	1996	130	32	24.6%	100	22	22.0%	20	6.3	31.5%	250	60	24.0%
	1997	200	47	23.5%	85	21	24.7%	27	4.9	18.1%	310	73	23.5%
	1998	140	51	36.4%	180	21	11.7%	37	1.8	4.9%	360	74	20.6%
sum-PAH	1996	480	110	22.9%	340	79	23.2%	72	29	40.3%	890	220	24.7%
	1997	650	200	30.8%	320	79	24.7%	130	29	22.3%	1100	310	28.2%
	1998	510	230	45.1%	550	68	12.4%	150	9.1	6.1%	1200	310	25.8%

Urban inputs have a minor lake-wide effect for most pesticides. There does seem to be a large effect, however, on *cis*- and *trans*-chlordane net gas exchange and total mass flows. Net gas exchange of *trans*-chlordane over the Chicago lake sub-area will drastically change lake-wide volatilization and markedly increase total mass flows. The same is true for *cis*-chlordane, though to a lesser extent. *p,p′*-DDE also shows strong urban effects, with lake-wide volatilization being greatly reduced and total mass flows being increased.

PCBs show a varied urban effect. While urban inputs do not impressively affect wet deposition flows, stronger effects are seen in gas exchange and total mass flows. For example, in 1998, inclusion of Chicago flows will decrease suite-PCB volatilization by as much as 53% while they will increase total flows to the entire lake by over 500%. In the same year, wet deposition flows will only increase 8.9% by incorporating Chicago into the lake-wide loadings. Similar disparities in depositional effects are seen in 1996 and 1997, though not to the same extent as total flow increases in 1998. Since PCBs had mainly urban uses, it is not surprising that an urban site would affect PCB flows to such a great extent. PAHs, which have many current sources in Chicago, show large urban effects in all deposition categories as compared to other chemicals.

Loadings estimates from 1996-1998 show that an urban center can have a significant impact on lake-wide loadings for certain chemicals. These results further encourage the use of urban data for future reports and also signal the need for more urban satellite stations in the IADN program. Having precise measurements from urban centers on all lakes will hopefully facilitate the calculation of better, more exact loadings so that a more complete picture of the Great Lakes can be formed.

5. Extensions to IADN Activities

There have been many requests for IADN data. Through the use of the web site, individuals have been requesting IADN data for their research. From the inception of the web site to the present, IADN has received at least 33 data requests from internal and external researchers in provincial, national and international organizations and universities. Hundreds of other scientists have used the data and results from the IADN network. Some examples of IADN-related research from our and other laboratories are described below.

5. 1. Potential Source Contribution Function (PSCF) Analysis

An important part of Annex 15 of the GLWQA is the determination of the sources of the persistent organic pollutants that are measured. Source-receptor work was recognized by the last peer-review panel through a recommendation to implement this type of research. In the past, the general direction and location of the source was ascertained by regression analysis of the wind speed and direction measurements made at the sampling site (Hillery et al., 1997, Cortes et al., 2000) and through simple trajectory analysis. Using a large amount of trajectories in a probabilistic model called Potential Source Contribution Function (PSCF), the geographic location of these sources can be estimated.

PSCF was originally developed and used for acid rain producing aerosols (Malm et al., 1986, Zeng et al., 1989) and heavy metals. The model uses back trajectories calculated using NOAA's HYSPLIT program. Back trajectories are composed of hourly points, which are meant to approximate the location of the air mass a given number of hours back in time from the sampling site, which in this case optimally extend back 96 hours. Often this single coordinate may not be a adequate representation of the entire air mass. To account for this, multiple trajectories were calculated each day. The first trajectory was made when the sampling period started at 9:00 AM, three more were then made at 6 hour increments. To further increase the volume of hourly points, each of these four start times consisted of three trajectories calculated at starting altitudes of 10, 100, and 500 meters above ground level.

All of the concentration data for the samples were converted to partial pressures and temperature corrected, and when necessary, corrected for temporal trends. The average of these partial pressures was used as a dividing line to determine what trajectories (and their representative hourly points) would be given a classification of "high" and which would be "low". The area around the Great Lakes was divided into a grid of $0.5^\circ \times 0.5^\circ$ latitude/longitude cells. All the hourly points were then placed in their respective cell depending upon their coordinates. The value of the PSCF is simply the quotient of high hourly points in each of the cells over the total number of points. A higher PSCF value would then indicate the odds that a trajectory passing through that cell would be carrying a high concentration of a given pollutant to the sampling site. To improve the significance of the model, only cells with 25 or more hourly points per cell appear in the final plot, which corresponds to at least 3-4 trajectories per cell.

Figure 9 (top) depicts the PSCF plot for total PCBs arriving at the Eagle Harbor site on Lake Superior and at the Sturgeon Point site (bottom) on Lake Erie. A significant amount of data was needed for each of these plots, 263 and 242 measurements respectively. The Eagle Harbor plot indicates that the urban area of Chicago and Northwestern Indiana is serving as a source of PCBs to Lake Superior. Using IADN data, the overall average air concentration at both Eagle Harbor and the satellite site at Chicago (Illinois Institute of Technology) were calculated. There is a considerable difference between the 1600 ± 40 pg/m^3 measured at Chicago and the 100 ± 7 pg/m^3 found at Eagle Harbor. This gradient reinforces the evidence for the source region seen in the plot. A similar scenario is seen in the Sturgeon Point map. (Figure 9, bottom). Despite the proximity of the city of Buffalo, NY, it would seem that the predominant source is located farther east, beginning around the Hudson River and extending east through Massachusetts to the Atlantic. The Hudson river is known to contain over 500 metric tons of PCBs (US EPA, 2000), which may constitute a significant source to the atmosphere. Also, the concentrations of PCBs over New York Harbor have been reported to be about 3000 pg/m^3 (Totten et al., 2001). This is over a factor of 10 difference from the 280 ± 15 pg/m^3 measured at Sturgeon Point.

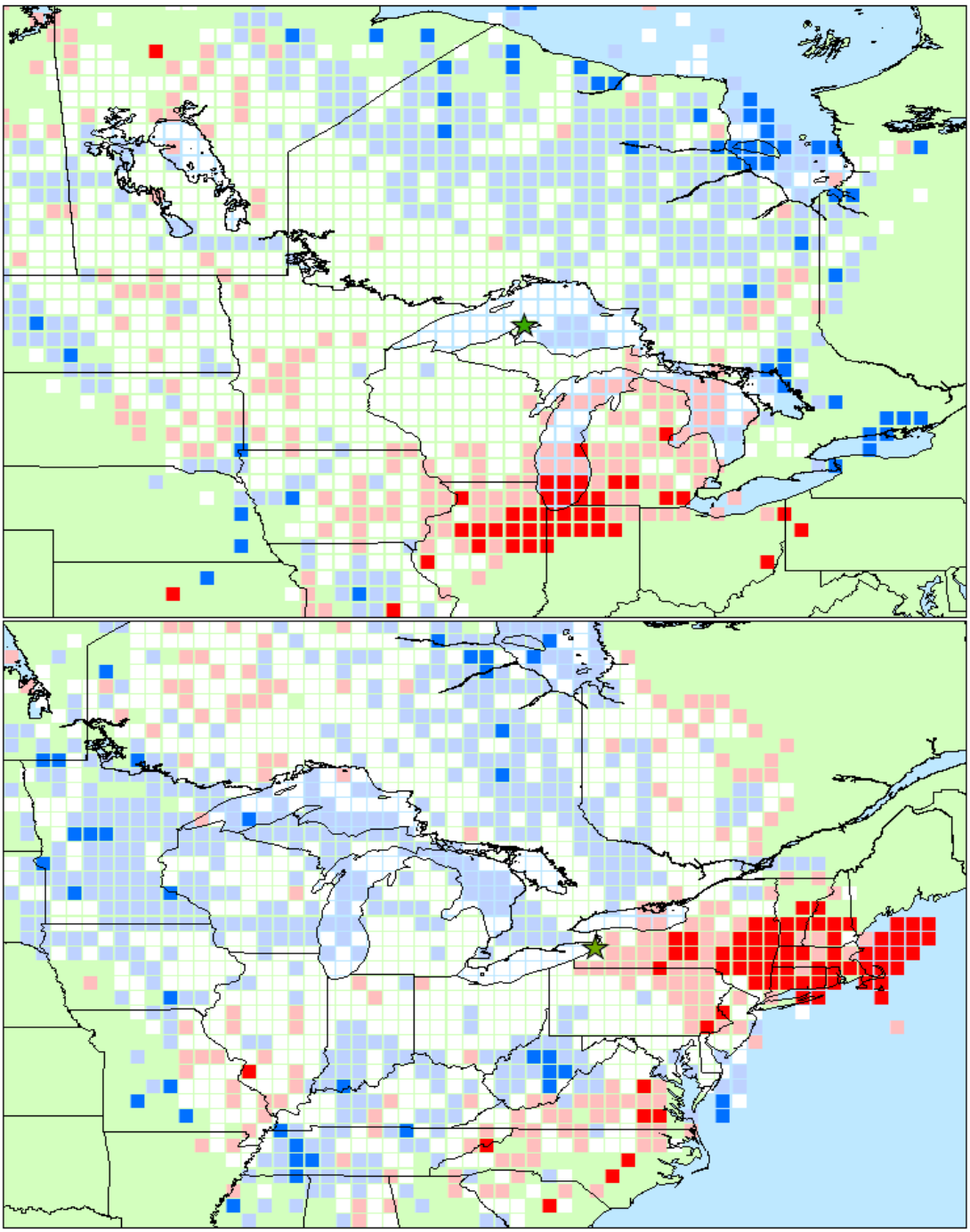


Figure 9. Potential source contribution function (PSCF) maps of total PCBs at Eagle Harbor on Lake Michigan (top) and Sturgeon Point on Lake Erie (bottom). Dark blue represents probabilities from 0.00-0.20; light blue, 0.21-0.40; white, 0.41-0.60; pink, 0.61-0.80; and red, 0.81-1.00. Ungrouped red and blue dots are noise.

These PSCF plots will provide new insights into the how atmospheric transports functions in the Great Lakes Basin. Because the number of trajectories needed to produce them is so large, they also stress the importance of a long term sampling network such as IADN.

5. 2. Atmospheric Concentrations of Toxaphene

Toxaphene is one of the substances targeted by the GLWQA (among other agreements dealing with persistent toxic substances) and was listed on the suggested IADN chemical lists in both IP1 and IP2. IADN researchers have conducted method development and limited monitoring activities for this substance. Thirty-seven air samples were collected from September 1996 through December 1997 at Eagle Harbor, Michigan to determine the atmospheric concentration of toxaphene near Lake Superior. The concentrations ranged between 0 and 63 pg/m^3, with most under 20 pg/m^3, which agreed well with concurrent measurements over the lake and near Lake Michigan made by other research groups. These concentrations are significantly lower than those measured in 1988 and 1989 in Egbert, a village in southern Ontario (Hoff et al., 1993). The phase transition energy was calculated to be 47 kJ/mol, half the value calculated for the Egbert site; this disparity has been seen in comparisons of lakeshore and over-land values for other compounds. If temperature effects are removed, the average toxaphene concentration for the Eagle Harbor samples was 6.4 ± 2.2 pg/m^3, which was lower than the 16 pg/m^3 average at Egbert, Ontario. This difference in concentration may (or may not) be due to differences in sampling dates or locations or in measurement techniques. This work was published by Glassmeyer et al. (1999).

5. 2. 1. Toxaphene Measurements from the South to the North of the U.S.

In a more recent study designed to track the movement of toxaphene from the southern U.S. to the Great Lakes, James and Hites (2002) implemented a sampling network to measure the gas-phase concentrations of toxaphene near Lake Michigan at Sleeping Bear Dunes, Michigan (the IADN site); Bloomington, Indiana; Lubbock, Texas; and Rohwer, Arkansas. Clausius-Clapeyron plots for all of the data at all four sites are given in Figure 10. The toxaphene concentrations referenced to 288 K were 11 ± 1, 25 ± 1, 150 ± 3, and 960 ± 30 pg/m^3, respectively. James and Hites combined these concentration data with a non-parametric, backward trajectory, multiple regression model of the form:

$$\ln(P) = a_0 + a_1/T + a_2\theta \qquad (6)$$

where P is the partial pressure of toxaphene (in atm) in a given sample, T is the atmospheric temperature at the sampling site during sampling (in degrees Kelvin), and θ is 0 if the backward trajectory comes from the north and 1 if the trajectory comes from the south. The parameters of this model were generally significant, giving a temperature coefficient (a_1) corresponding to 45 ± 8 kJ/mol and a positive directional coefficient (a_2) of 0.6 ± 0.2 (except for Texas, which was not significant). The positive sign and magnitude

of the directional coefficient indicates that the sources of toxaphene are located south of the sampling sites.

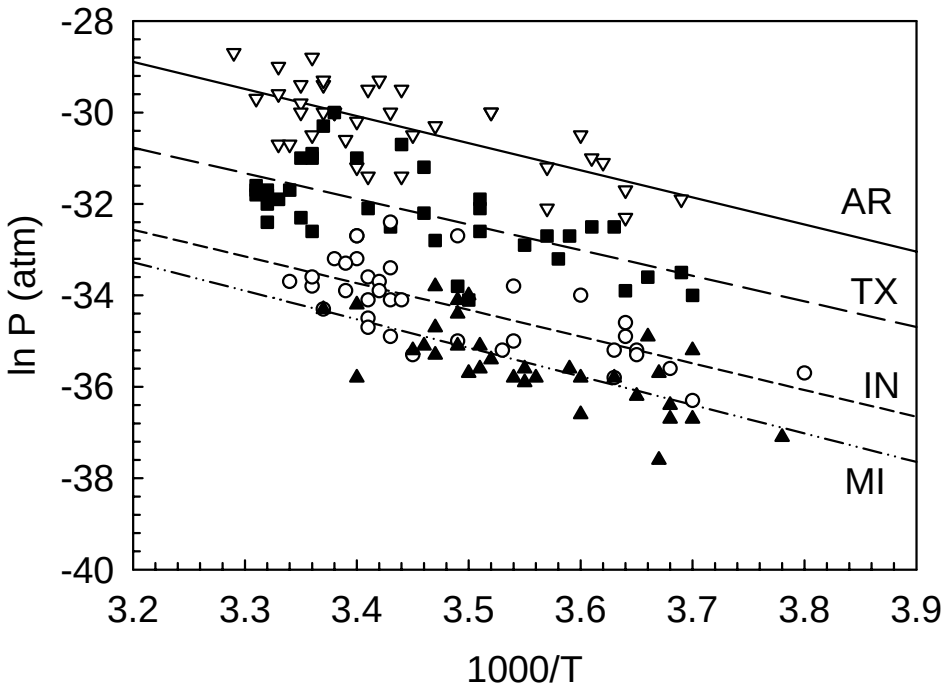


Figure 10. Gas-phase temperature dependence of toxaphene partial pressure (in atm) at the four sampling sites. Each sampling site is represented by a different symbol and line pattern; the "MI" data are obtained at the Sleeping Bear Dunes IADN site.

5. 2. 2. Measurements of Airborne Toxaphene at Point Petre

In 1992, the Meteorological Service of Canada (MSC) commenced work on the development of a reliable analytical method using GC-ECNI-MS for the determination of individual toxaphene congeners in ambient air. To allow a reasonable comparison with previous data for toxaphene reported by Muir and coworkers using GC-ECD (e.g. Muir et al., 1988; Hoff et al. 1993), this method has adopted their approach of focusing upon the identification and quantification of the specific, dominant peaks or clusters ("T" species) typically observed in environmental samples, with the sum of these "T" species then being reported as "total toxaphene". Technical toxaphene has been used as the analytical standard, but independent response factors have been assigned to the target peaks and clusters. Because of the appreciable variability in ECNI-MS response shown by individual toxaphene congeners, this is considered to be a reasonable and potentially more accurate procedure than the application of a "single response factor" used by many other workers. Furthermore, this approach overcomes any possible errors arising from the significant compositional differences that are found to exist between technical toxaphene and typical air samples.

The methodology was initially applied to some archived extracts derived from multi-day samples collected at Point Petre in 1992. Dedicated multi-day sampling for toxaphene at Point Petre began in October 1995 and is continuing. The methodology and results to September 1997 have been described in detail by Shoeib et al. (1999).

Figure 11 shows the airborne vapor-phase concentrations for toxaphene components T2 (7Cl), T2 (8Cl), T12B and total toxaphene (defined as the sum of calibrated components, with non-detects assigned a zero value) at Point Petre for the 1992 and 1995-1999 sampling periods. The particle-phase samples gave toxaphene component responses that were above the detection limit in only a few samples, so they are not considered here. Field blanks (PUF and GFF) also showed negligible toxaphene content and consequently blank correction of the sample composition values has not been necessary. Airborne concentrations of total toxaphene (as the sum of the calibrated components) range from 0.9 pg/m^3 to 10.1 pg/m^3.

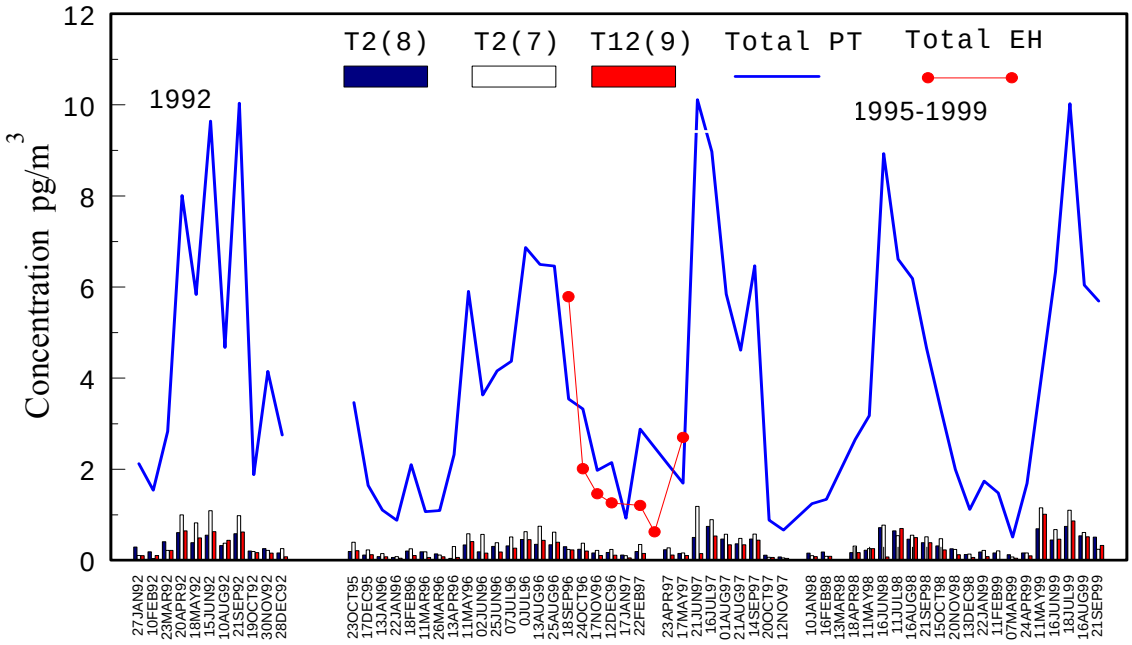


Figure 11. Vapor-phase airborne toxaphene concentration at Point Petre during 1992 and 1995-99

A clear seasonality appears to be present in the data, with a summer to winter ratio of about 6. The concentrations of the three individual species shown in Figure 11 also tend to track the pattern for total toxaphene and appear in all the samples, but together contribute only about 10% of the total toxaphene in air.

Also shown in the figure are corresponding total toxaphene values for air samples collected at Eagle Harbor from September 1996 to May 1997 and analyzed at MSC. The concentrations are remarkably similar to those observed at Point Petre, suggesting that a significant spatial variability does not exist for this species in the Great Lakes background air.

Figure 12 presents plots of the logarithm of the toxaphene concentration vs. reciprocal absolute temperature for samples collected in 1992 and then in 1995-99. The slopes of the two correlations are remarkably similar, although there seems to be a small absolute difference in the concentrations seen in the two sampling periods. However, this could be easily accounted for by calibration uncertainties or even small differences in the peak acceptance/rejection criteria or real difference in source and transport between the two periods.

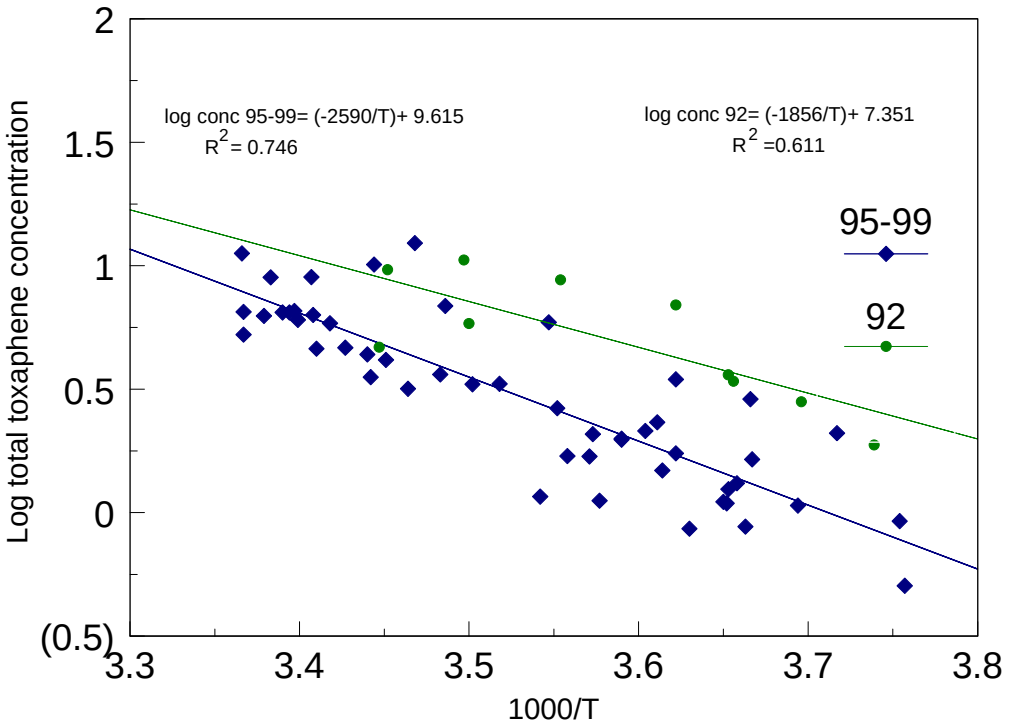


Figure 12. Total toxaphene concentration vs inverse mean temperature

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Table 9 compares the Clausius-Clapeyron plot regression parameters reported for toxaphene by other workers: the current data have lower slope values than that seen earlier at Egbert, Ontario in 1988 and in Columbia, South Carolina from 1977 to 1985 (both data sets were incidentally obtained using single-column GC-ECD analytical methods), but they appear similar to those found in 1994-95 at the Columbia site (using GC-ECNI-MS) and also recent measurements on the Lake Superior shoreline at Eagle Harbor. Hoff *et al.* (1998) have discussed possible interpretations of the Clausius-

Clapeyron slopes in terms of the interaction of various source influences e.g. long-range transport vs. local air-surface exchange. Generally, a lower slope is associated with a greater influence of long-range transport on the atmospheric concentrations.

Table 9. Regression parameters for Clausius-Clapeyron plots of $\log_{10}$ of total toxaphene (in pg/m^3) vs. 1/T (in K).

	Slope	Intercept	r^2	Num. Samples	Ref.
Point Petre, Ontario					
1992	-1856	7.3	0.61	10	This work
1995-1999	-2590	9.6	0.75	50	This work
Eagle Harbor, Michigan					
Sep 1996-Dec 1997	-2439	6.9	0.45	36	Glassmeyer et al.(1999)
Egbert, Ontario					
1988	-4780	17.8	0.3	118	Hoff et al. (193)
Columbia, South Carolina					
1977-1985	-4783	19.7	0.34	32	Bidleman et al. (1998)
1994-1995	-2308	10.13	0.36	21	Bidleman et al. (1998)

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5. 3. Enantiomeric Ratios of Chlordane-Related Compounds

Some important environmental contaminants are chiral; therefore, enantiomeric ratios (ER) of these compounds can provide useful insights into their environmental fates. In this study (Ulrich and Hites, 1998), permethylated α- and γ-cyclodextrin gas chromatographic columns combined with electron capture, negative ionization, mass spectrometry were used to measure the ER values of chlordane and related compounds. These techniques provided the selectivity and sensitivity necessary for these low-level environmental determinations. Studies using racemic and enriched standards confirmed that this analytical system gave reproducible and accurate ER measurements. From August 1994 through September 1995, 48 air samples were taken near Lake Erie at the Sturgeon Point station, 5 air samples were taken near Lake Michigan at the Sleeping Bear Dunes station, and 6 air samples were taken near Lake Superior at the Eagle Harbor station. These samples were analyzed to determine the spatial trends in ER values. While there were slight differences between the various sites, there were considerable differences between the compounds. The overall ER for α-chlordane was 1.05 ± 0.02, which is close to racemic. The overall ER for γ-chlordane was 0.88 ± 0.02, which is significantly different than racemic and from the measured α-chlordane value. This discrepancy suggests that α- and γ-chlordane are metabolized differently in the environment. The overall ER of heptachlor

epoxide was 1.99 ± 0.04; this large deviation from racemic indicates that this compound is an enzymatic degradation product of heptachlor.

5. 4. Chlorothalonil and Dacthal in Great Lakes Air and Precipitation Samples

Two chlorinated pesticides, chlorothalonil and Dacthal, have been found at relatively high concentrations in air and precipitation samples taken from around the Great Lakes (James and Hites, 1998). Chlorothalonil is a fungicide used mainly on peanuts and potatoes; Dacthal is a pre-emergence herbicide used primarily on onions and broccoli. These compounds were identified using electron capture, negative ionization gas chromatographic mass spectrometry, and their mass spectra are given in Figure 13. These compounds were subsequently quantitated by electron capture gas chromatography. The concentrations of these compounds in Great Lakes air and precipitation were as high as or higher than those of other organochlorine pesticides now being measured by the Integrated Atmospheric Deposition Network. Long-term measurements of the atmospheric and precipitation concentrations of these two compounds are being considered by the IADN Steering Committee.

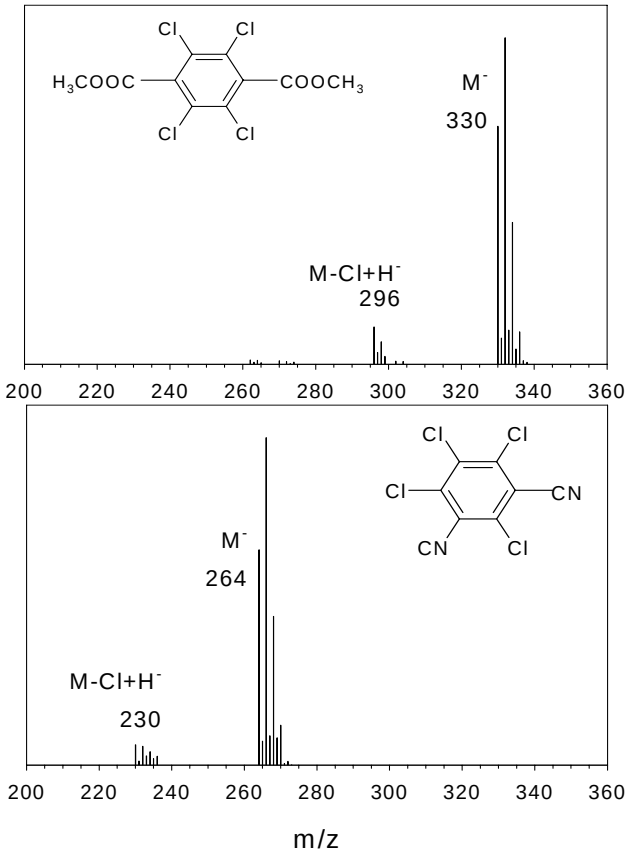

Figure 13. Electron capture negative ionization mass spectra of Dacthal (top) and chlorothalonil (bottom), compounds found in at relatively high abundance in IADN air samples.

5. 5. Polybrominated Diphenyl Ethers in Great Lakes Air

Polybrominated diphenyl ethers are widely-used flame retardants whose concentrations are increasing in the environment and that appear to be bioaccumulative. IADN air samples were analyzed from urban, rural, and remote sites near the Great Lakes to investigate the occurrence, concentrations, and spatial and temporal differences of polybrominated diphenyl ethers (PBDE) in air (Strandberg et al., 2001). The concentrations of PBDEs were compared to those of other organohalogen compounds such as PCBs and organochlorine pesticides. The samples were collected in 1997-1999, and in order to minimize the variability of the data, we chose only samples taken when the atmospheric temperature was 20 ± 3°C. PBDEs were found in all samples, indicating that these compounds are widely distributed and that they can be transported through the atmosphere to remote areas. The total concentrations of PBDEs were similar to some of the organochlorine pesticides such as ΣDDT and ranged from 5 pg/m^3 near Lake Superior to about 52 pg/m^3 in Chicago. In fact, the spatial trend was well correlated to those of ΣPCB; see Figure 14. Our results indicate a relatively constant level from mid-1997 to mid-1999. At 20 ± 3 ^{o}C, about 80 % of the tetrabromo homologues are in the gas-phase, and about 70% of the hexabromo homologues are associated with the particle-phase. Thus, particle-to-gas partitioning in the atmosphere is an important process for these compounds. The IADN laboratories are currently studying PBDE concentrations in both air and precipitation for samples collected in 2002-2003. Based on these and other data, the IADN Steering Committee may expand the analyte list to include PBDE.

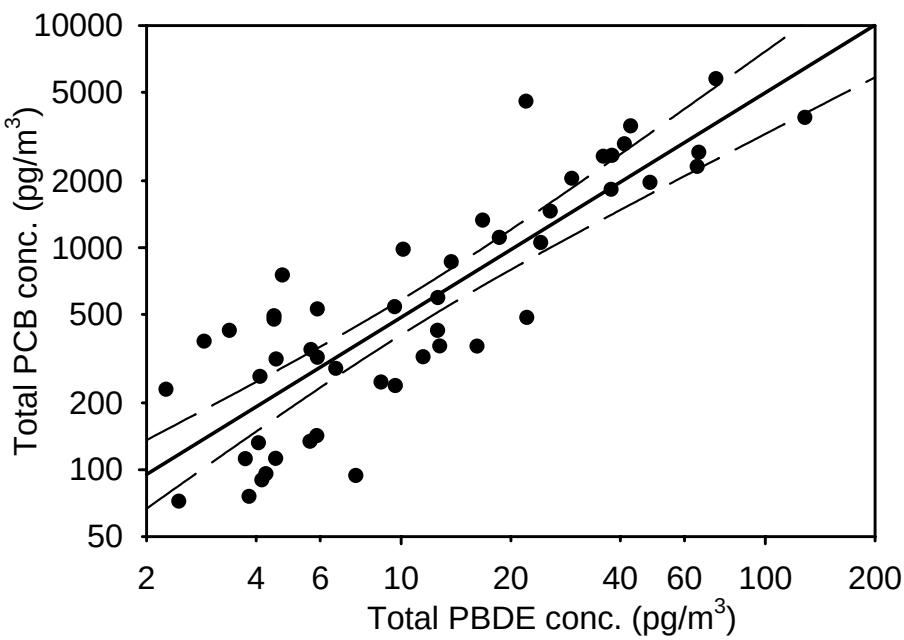

Figure 14. Concentrations of polybrominated diphenyl ethers in IADN samples collected near the Great Lakes as a function of ΣPCB concentrations in these samples. The correlation coefficient (*r*) is 0.856, and the 95% confidence limits of the regression are shown.

5. 6. Mercury in Air

Mercury exists in the atmosphere predominantly in its elemental form (Hg^0). Due to its stability, mercury has a residence time of the order of about one year and therefore can undergo long range transport (Schroeder and Munthe, 1998). Following deposition, mercury can be converted to methyl mercury, a highly toxic mercury species, which has been found to bioaccumulate in aquatic biota, especially fish. Along with PCBs, mercury remains a contaminant of concern in fish in the Great Lakes (Scheider et al., 1998). To obtain spatial and temporal distribution of total gaseous mercury (TGM) levels on the Canadian side of the Great Lakes, a measurement campaign was started in 1997 at IADN sites. TGM has been measured at Point Petre since January 1997, at Burnt Island since April 1998, and at the satellite station of Egbert since January 1997. At all stations, the measurements were made using Tekran™ 2537A mercury vapor analyzers. Briefly, after TGM is collected on a gold cartridge, it is thermally desorbed and detected by cold vapor atomic fluorescence spectroscopy (Schroeder et al., 1995). Two cartridges provided continuous measurements with integration times of 15 minutes. The instrument was calibrated daily using an internal mercury source verified quarterly by manual injections (Steffen and Schroeder, 1999). The data are quality controlled using RDMQ™ (Environment Canada, 1995) and were hourly averaged. Recent results from these stations have been summarized in Blanchard et al. (2002) and will be briefly described here.

Statistical analysis of the data by digital filtration (Hung et al., 2001) demonstrated that over the 4 years of data at Point Petre and Egbert, clear temporal trends in the TGM data could not be observed. This is in agreement with current Canadian emissions which have remained stable between 1996 and 2000 at around 10 t/yr (Pilgrim et al., 2000). Monthly TGM and temperature means are presented in Figure 15 for Egbert, Burnt Island and Point Petre. Seasonal cycles with maxima in winter and minima in summer can be observed for the sites of Egbert and Burnt Island. This seasonal pattern could be the result of several factors including: differences in meteorological conditions between summer and winter such as reduced mixing heights, higher wind speeds in winter, and larger removal from the atmosphere by wet and dry deposition during warmer months; a northern hemispherical wintertime increase in coal combustion for domestic heating purposes (Rotty, 1987); the seasonal cycle of atmospheric oxidants (e.g. ozone); and possibly the behavior of TGM on a hemispherical scale such as exemplified by recent data of TGM vertical profiles (Banic et al., 2001) which indicate that the Arctic springtime TGM depletion episodes could result in a significant hemispherical sink of TGM annually.

Throughout the period, measurements of several trace metals have been conducted at the three sites as part of IADN and results were available for 1997-1998 for Point Petre. Principal component analysis (Henry et al., 1984) was used to identify potential sources of metals to the two sites. This was done in conjunction with air parcel back-trajectories (Olson et al., 1978) incorporating geographical information to the statistical analysis. The results of the analysis (Table 10) are similar to what has been obtained previously (Blanchard et al., 1997). The results include a crustal component (PC1), a general oil

combustion component (PC2), a coal combustion component (PC3), and a smelter component (PC4). PC3 is particularly interesting since it has a high loading for TGM associated with Ag, Cd, Cr, Mn, Mo, Se, Sn and Zn. For this component, three days Lagrangian back-trajectories associated with the highest 10% of the scores were calculated corresponding to the mid-point of the sampling period. These indicate air parcels passing over the heavily populated and industrialized areas of the lower Great Lakes to the Southwest of the site.

Table 10. Varimax rotated principal components analysis of 1997-1998 Point Petre trace elements and total gaseous mercury data.

	PC1	PC2	PC3	PC4	PC5
Ag			0.48		
Al	0.90				
As				0.92	
Ba	0.65				
Cd		0.66	0.31	0.41	
Co		0.84			
Cr	0.36		0.65		
Cu					0.87
Fe	0.88				
Hg		–0.14	0.73		
Mo	0.41	0.39	0.69		
Ni		0.85			
Pb				0.92	
Sb				0.82	
Se	0.33		0.79		
Sr	0.83				
Sn		0.50	0.35	0.54	
Ti	0.76				
V	0.35	0.81			
Zn	0.34	0.38	0.67		
Eigenvalues	8.5	3.2	1.7	1.5	1.1
%Variance Explained	40.6	15.4	8.0	7.0	5.3

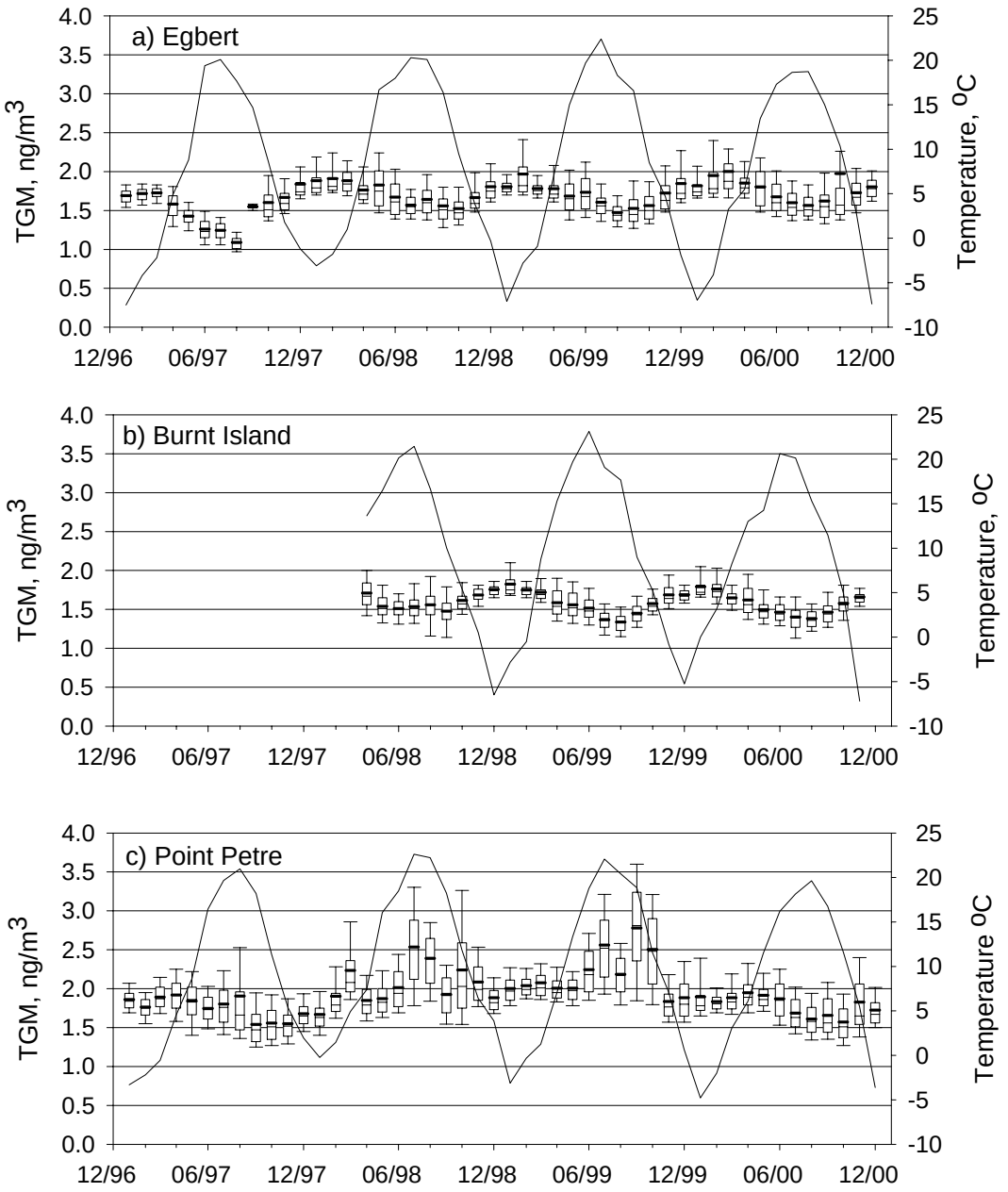

Figure 15. Monthly total gaseous mercury (TGM) and temperature means for (A) Egbert, (B) Burnt Island, and (C) Point Petre. The boxes represent the 25th and 75th percentiles. The thick line is the mean and the fine line is the median. The error bars are the 10th and 90th percentiles.

Atmospheric mercury loading estimates have been calculated for Lake Superior and the results reported in Hoff et al. (1996). There is now a larger number of atmospheric data available. The mercury deposition network (MDN), which monitors mercury in wet deposition, started operating sites around the Great Lakes as far back as 1995; its URL is: http://nadp.sws.uiuc.edu/mdn/. The two Canadian IADN master stations and one satellite site (Egbert) are now part of MDN. Further, in recent years several campaigns have been conducted to measure particulate and reactive mercury. All of these data will be used to calculate updated loading estimates for the Great Lakes for the next IADN loadings report.

5. 7. Measurements of Airborne Atrazine at Canadian IADN Sites

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is used to improve resource availability to agricultural crops by eliminating competing annual broadleaf and grass weeds. In North America, it is employed primarily in the cultivation of corn, with extensive applications in the Midwestern United States. Official estimates for the United States show atrazine as second only to alachlor in application tonnage, with almost 30 million kilograms applied annually. Based upon its physical properties, it has been predicted that most of the atrazine applied to an agricultural area will be constrained to the aquatic environment and bound in soil residues rather than being subject to movement through the atmosphere. However, the presence of atrazine in background air has been reported by other researchers, although the amount of data available has been limited.

In an effort to examine the presence of atrazine in the vapor-phase and particulate-phase samples collected at Canadian IADN sites, the clean-up procedures employed for these samples required modification to also allow isolation of atrazine. Extraction efficiencies were evaluated using spiked matrix samples and a working analytical finish established using gas-chromatography (GC) combined with electron impact, mass spectrometry (EIMS) on a vintage (1983) HP5970. The overall method developed has been applied to identify the presence of atrazine in air samples at Point Petre, Burnt Island and Egbert sites.

Figure 16 shows some typical (unpublished) ambient values and patterns observed at one of the sites (Point Petre) from 1996 to 1999. Similar data plots are available for the Burnt Island and Egbert sites.

Some of the data-points are still under review to interpret some questionable matrix-spike recovery values and also evaluate observations of apparent interference in the MS qualifier ions, most significantly for low winter values in the vapor-phase. Similar interference anomalies have also been found to be present in the field blanks. To provide the fairest "raw" representation of the data, these "interfered values" have not been rejected, but the mean field blank values have also been plotted for comparison.

Some notable features of the data are:

1) Atrazine occurs at elevated levels in the air over a limited Spring/Summer timeframe;

2) During these periods of increased concentrations, both vapor-and-particle-phases are involved;
3) The MSC method currently seems to have some problem with detecting low vapor-phase atrazine due to an interferent that appears to be PUF related. Chromatographic changes and the use of a new Agilent 5973 GC-MS are planned to investigate this more fully.

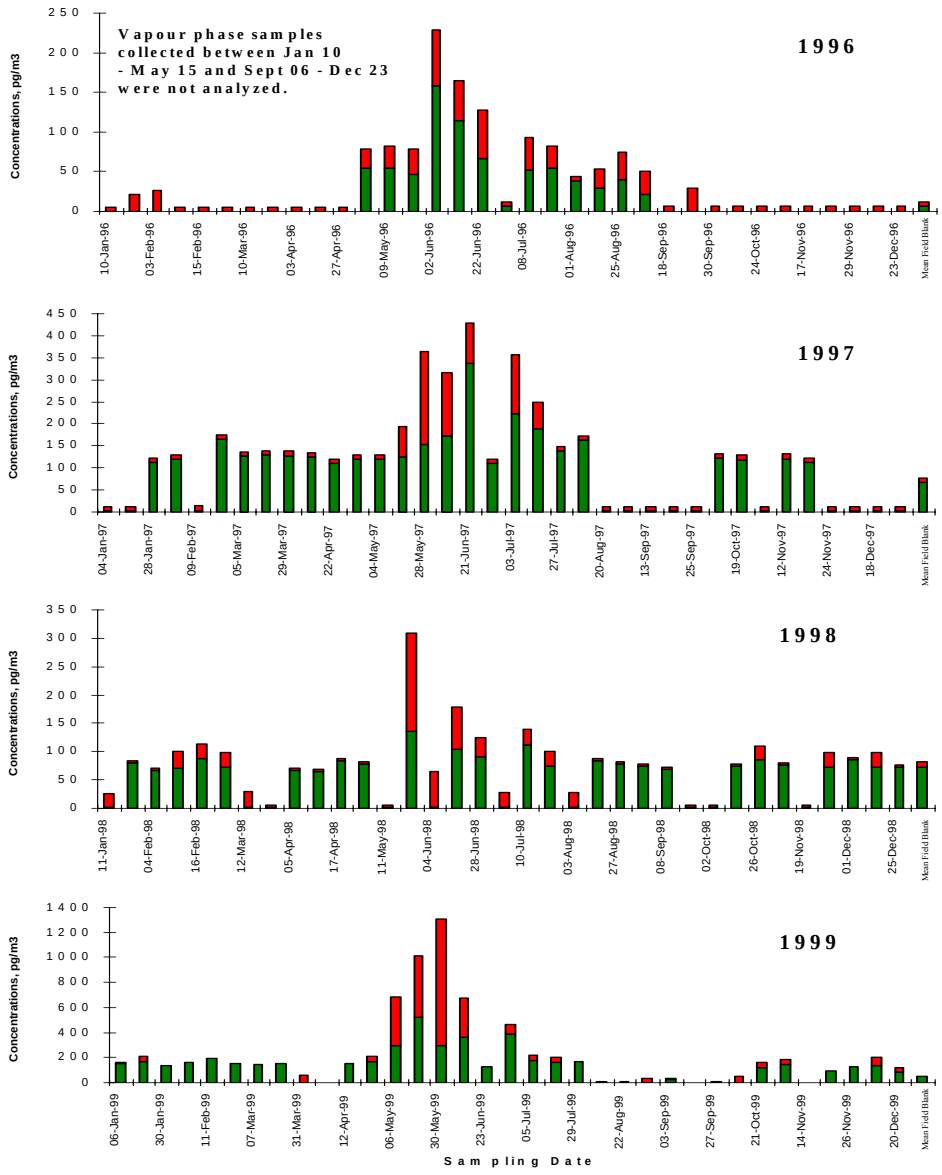

Figure 16. Atrazine in the ambient air at Point Petre from January 1996 to December 1999. Green bars represent the vapor phase concentrations, and the red bars represent the particle phase concentrations.

5. 8. Lake Ontario Atmospheric Deposition Study (LOADS)

LOADS is a research initiative launched in 2001 that is of interest to IADN. The goal of the project is to provide estimates of loadings of a number of critical pollutants identified in the Lake Ontario Lake Management Plan (LaMP) as well as several additional chemicals. Sources of these pollutants are to be identified using advanced source-receptor models. The sampling includes the collection of ambient air samples for the measurement of Hg (both elemental and reactive gaseous), PCBs, DDE, Mirex, HCB and dioxin/furans every six days for a period of approximately one year at Sterling, New York on the south shore of Lake Ontario. Wet deposition samples for the measurement of Hg, PCBs, DDE, Mirex, HCB and dioxin/furans and direct dry deposition samples for the measurement of PCBs, DDE, Mirex, and HCB were also collected at the same location. Samples were also collected for 1 week each in the spring (April) and fall (September) aboard the US EPA's Research Vessel *Lake Guardian*. During each week on the ship, coupled air and water concentrations were measured and several wet and dry deposition samples were obtained. While sampling was taking place on the ship, intensive daily samples were also obtained at the land-based site. MSC collected additional samples at the IADN Point Petre and at the mid-lake research buoy sites during the *Lake Guardian* cruises to inter-compare LOADS data with IADN data. MSC also collected total gaseous mercury data onboard the *Lake Guardian* during both cruises. This project is under the direction of Prof. Thomas M. Holsen in the Department of Civil and Environmental Engineering at Clarkson University. IADN Technical team members provided input during the design phase of the LOADS sampling program. The 1997 peer-review panel had recommended explicit collaboration as a means of extending IADN activities, and the LOADS experiment is a good example of such collaboration.

5. 9. Canada-Germany Intercomparison at Point Petre

Under the framework of the Oslo-Paris Convention for the Prevention of Marine Pollution of the North Sea and the North East Atlantic (OSPAR), a Comprehensive Atmospheric Monitoring Programme (CAMP) exists which measures atmospheric inputs of selected contaminants in air and precipitation. Although analysis of PAHs in air and precipitation has been carried out by CAMP for many years, there are no harmonized methods. In the late 1990's, the OSPAR working group undertook an intercomparison study with Belgium, Denmark, the Netherlands, Sweden, Norway, Germany, and the United Kingdom as part of a PAH pilot study. This OSPAR intercomparison was the first and most comprehensive one with respect to the determination of PAHs in atmospheric samples in the OSPAR region and in Europe.

At the 1999 WMO/EMEP/UNEP Workshop on Modeling of Atmospheric Transport and Deposition of Persistent Organic Pollutants (POPs) and Heavy Metals, it was decided to extend this study beyond the European continent. The German Federal Environmental Agency (FEA) has thus approached Environment Canada to participate in a joint study to determine if PAHs in air and precipitation can be determined with different sampling and analytical methods with sufficient accuracy.

To this end, FEA will be shipping two air and precipitation collectors to Canada, to be installed at the Point Petre Master Station on Lake Ontario. For a period of one year, replicate air (gaseous, particulate) and precipitation samples will be collected and analyzed by each country for a range of PAHs, as well as lindane. At the conclusion of the study, data (including additional IADN data collected at the Point Petre site during this timeframe) will be shared among agencies, and a joint report will be issued. The Meteorological Synthesizing Center East of EMEP (in Russia) will be hosting a workshop to model the resultant data.

5. 10. ECO-1 Research Buoy

Environment Canada's ECO-1 research buoy has been developed since 1996 as a novel over-water sampling platform. Over-water sampling was also recommended by the last peer-review panel. The buoy is 12 meters in diameter and 10 m above the waterline. It has been outfitted with meteorological and air quality monitoring equipment. It is currently located at a mid-lake site in the western end of Lake Ontario, approximately 12 km south of Toronto, Ontario, Canada. It now serves as a self-contained monitoring laboratory. The research buoy is maintained by the Meteorological Service of Canada out of Downsview, Ontario and as a research effort in support of the Integrated Atmospheric Deposition Network. Staff of the Centre for Atmospheric Research Experiments oversees the Scientific Program, which operates the buoy in support for MSC researchers and collaborating scientists.

The buoy has three rooms within its hull, which are accessed from the deck through a watertight door in the conning tower. The buoy is powered by two 8 kW diesel generators and outfitted with a computer network connected to shore by two-way radio communications and satellite phone. The state of the buoy (power, electrical loads, and internal temperatures), as well as the state of ongoing experiments and measurements, can be monitored from shore. The conning tower carries meteorological sensors for measuring wind speed and direction, air temperature, humidity, and atmospheric pressure, some of which are reported hourly by satellite as part of the operational MSC weather network. Also on the tower are input lines for air sampling and a funnel type precipitation collector.

In 1999 and 2000, the buoy communications system was upgraded to monitor conditions on the buoy and interrogate sample collection operations from onshore and to peruse their data in near real time. During this time, the high volume air sampling system for organic contaminants was redesigned for greater flow rates and improved calibration and control. The buoy represents a unique capability for IADN using recent advances in sensors, computer systems and communications, and is a state-of-the-art platform from which to collect samples of Lake Ontario air.

The buoy also serves as an over-water sampling platform in western Lake Ontario, a site which is influenced by the large urban centers in the region including Toronto, Hamilton, and Buffalo. The buoy has been used for continuous monitoring of greenhouse gases (NO_x, ozone) and total gaseous mercury (TGM). In the fall of 2000, a large plume of gaseous mercury was detected from the buoy, corroborated by similar signals detected at Egbert and Point Petre, Ontario (Blanchard et al., 2002). With respect to persistent or-

ganic pollutants, results from simultaneous high volume sampling at the buoy and at Point Petre show concentrations of chlordanes, dieldrin, and total DDT that were 1.5-5 times higher than at the Point Petre site. Elevated values of these contaminants may represent inputs to Lake Ontario from regional sources, since concentrations of other contaminants such as γ-HCH, which is derived from long-range transport, were similar between sites. Regional sources could include the Niagara fruit belt, the nearby urban centers and the agricultural zones of southwest Ontario and mid-western U.S.. Most recently, the buoy has been used in support of a Canadian Toxic Substances Research Initiative to measure the air-water gas exchange of banned and current use pesticides. Air samples were collected in August to November, 2001 and these results will be compared with results from the Point Petre site.

5. 11. Other Ongoing Research

One of the recommendations of the 1997 peer-review panel was to "support research in support of IADN activities". The establishment of passive air samplers at IADN sites is one example of such research activities. Passive air samplers were deployed during the summer of 2002 at approximately 20 locations in the Great Lakes Basin to map concentrations of air toxics.

The samplers consist of a polyurethane foam disk that is mounted in a stainless steel deployment chamber. Calibration studies (Harner and Shoeib, submitted) indicate that these devices sample air at a rate of approximately 8 m^3/day. Thus, a two month deployment period will represent approximately 500 m^3 air. This is consistent with air sample volumes for the IADN program. The samplers will be deployed for two month integration periods according to the following schedule:

- Summer: July-Sept., 2002
- Winter: January-March, 2003
- Spring: April, 2003.

The sites include several IADN master and satellite stations, the Lake Ontario buoy, and several other urban and rural locations. Target chemicals will include PCBs, organochlorine pesticides, and PBDEs. The results from this study will be used to assess the spatial and temporal distribution of persistent organic pollutants (POPs) in the Great Lakes basin. This information may provide insight into the sources and transport behavior of the target chemicals. These data will also serve as an interesting comparison with ongoing air sampling under IADN.

The IADN data are also being used in conjunction with the data from Canada's Arctic network in the University of Toronto global POPs model (Wania and Mackay, 1999). The aim is to identify major removal processes for atmospheric PCBs using a fugacity-based global transport model. The results will be used to explain the differences in atmospheric PCB trends observed in the Arctic and temperate sites, such as sites around the Great Lakes. This work is being done by Dr. Hayley Hung (of MSC) in collaboration with Prof. Frank Wania and his students. This modeling project is another example of

the kind of research collaboration recommended by the last review panel. Another project is the development of a global mercury model by Dr. Ashu Dastoor at MSC using atmospheric mercury data from IADN sites.

6. Where do we go from here?

The Steering Committee feels that the network has, for the most part, fulfilled the goals of IADN set forth in IP2 (to determine loadings and trends, acquire quality-assured measurements, and help determine sources). Journal publications and loadings reports by members of the Steering Committee have explored interpretation of loadings and concentrations. Quality assurance has been a major focus during the second implementation period. The least amount of work has probably occurred in the area of source determination, though modeling and back-trajectory techniques have been applied to IADN data to ascertain general regions where sources are located. Pinpointing sources requires measurements taken at a finer scale than monitoring in remote areas to obtain a regional signal, as intended by IADN's design. However, IADN data remains available to those performing modeling and source determination studies; use of the data for such purposes must continue to be encouraged.

The IADN program has implemented many of the recommendations set forth in the last Technical Summary and IP2. A centralized database was established and a database manager was hired. A Quality Assurance Officer is in place, and a series of audits and round robins have been conducted. Collocated sampling was re-established and continues at the Point Petre site. A QA workgroup has been formed to review the results of these activities and make suggestions for improvement. Data turnaround time has been shortened since the program began. A shortened list of common PCB congeners to be monitored by all participating agencies (the "PCB Suite") was developed based on past detection and toxicological importance. A network website was created that provides background information on IADN, station locations, a data request form, and a resource page linking users to method documentation and other reports. The IADN chemical list was reviewed, and a dossier for nominating new chemicals was developed. Paired urban and rural monitoring continues at Chicago and Sleeping Bear Dunes on Lake Michigan, and Indiana University and U.S. EPA are currently establishing another urban station in Cleveland, Ohio. Improved Henry's Law Constants were determined. IADN Steering Committee members continue to form and maintain ties to other monitoring and toxics programs. As shown in the "Extensions to IADN Activities" section, IADN-affiliated research resulted in monitoring of additional chemicals like PBDEs and mercury, passive and over-water sampling, and source region determination.

While IADN has succeeded in fulfilling its primary goals, the network's results and research must continue to be of high quality and relevant to the public domain. The following are suggestions and recommendations for the future of IADN. They are preliminary, and final recommendations for incorporation into IP3 will be determined based on expert input from the scientific peer review panel as well as further discussion by the IADN Steering Committee. Some are dependent on resource availability while others require

increased or improved communication with various stakeholders. Recommendations relevant to IADN's core work in surveillance and monitoring function come first, followed by those of a more research-oriented nature.

Surveillance and Monitoring

- Be responsive to the goals of the U.S. Great Lakes Strategy and the Canada-Ontario Agreement. For example, we may need to make additions to the analyte list and to increase the number of urban sampling sites.

- Contribute to national and international monitoring and assessment efforts for persistent bioaccumulative toxic (PBT) substances. These include, but are not limited to, the Commission on Environmental Cooperation's Environmental Monitoring and Assessment plan and the US EPA's nationwide PBT monitoring strategy.

- Improve the distribution of our results to policymakers and to the public through briefings and publications aimed at stakeholders with a less technical background. In addition, we will continue to also report results to the scientific community through the peer-reviewed literature.

- Speed up data output and reporting and report loading results within 2 years of the sampling time. This might require resource commitment from participating agencies, particularly Canada.

- Support and encourage water monitoring efforts. For example, U.S. EPA should reinitiate water monitoring for persistent toxics in Lake Michigan.

- Continue to compare our measurements and loadings for the Great Lakes to those for other regions of the North America and the world, particularly to those for Europe and Russia.

- Continue and intensify our efforts to systematically and periodically report quality assurance data; to automate laboratory data intercomparison; and to take corrective actions as a result of these comparisons. Further on-site audits by the QA Officer may be needed to determine possible causes of interagency data differences.

Research Relevant to Annex 15

IADN satisfies the surveillance and monitoring portion of Annex 15 of the GLWQA. Other research on atmospheric deposition and persistent toxic substances is being conducted in government, private industry, and academia. IADN staff must strive to maintain awareness of this research and improve cooperation and communication with those doing such work. The IADN Steering Committee should aim to:

- Be aware of information on new and emerging PBT chemicals and their potential addition to IADN by encouraging and promoting the use of the Nomination Dossier on the IADN web site.

- Involve other researchers to participate by using data from other programs and projects to examine concentrations and calculate loadings. For example, future loadings may use CAMNet and MDN data, passive sampler data, and buoy-based measurements.

- Continue to collaborate with other scientists to obtain more accurate physical properties such as Henry's Law Constants and mass transfer coefficients and to study environmental transformation processes that affect the fate of toxic substances in the Great Lakes.

- Initiate collaborative studies featuring simultaneous air-water measurements of the IADN toxic substances.

- Collaborate on projects that examine tributary loadings to better understand their relative contribution to lake-wide loadings.

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8. Appendices

8. 1. Annex 15 - Airborne Toxic Substances

1. **Purpose.** The Parties, in cooperation with State and Provincial Governments, shall conduct research, surveillance and monitoring and implement pollution control measures for the purpose of reducing atmospheric deposition of toxic substances, particularly persistent toxic substances, to the Great Lakes Basin Ecosystem.
2. **Research.** Research activities shall be conducted to determine pathways, fate and effects of such toxic substances for the protection of the Great Lakes System. In particular, research shall be conducted to:
   a) understand the processes of wet and dry deposition and those associated with the vapor exchange of toxic substances;
   b) understand the effects of persistent toxic substances, singly or in synergistic or additive combination with other substances, through aquatic exposure routes on the health of humans and the quality and health of aquatic life where a significant source of these substances is the atmosphere, in accordance with sub-paragraph 4(b) of Annex 12;
   c) develop models of the intermediate and long-range movement and transformation of toxic substances to determine;
      i) the significance of atmospheric loadings to the Great Lakes System relative to other pathways; and
      ii) the sources of such substances from outside the Great Lakes System.
3. **Surveillance and Monitoring.** The Parties shall:
   a) establish, as part of the Great Lakes International Surveillance Plan (GLISP) instituted under Annex 11, an Integrated Atmospheric Deposition Network in accordance with paragraph 4 below;
   b) identify, by means of this Network, toxic substances and, in particular, persistent toxic substances, appearing on List No. 1 described in Annex 1, of those designated as Critical Pollutants pursuant to Annex 2 and their significant sources in accordance with sub-paragraph 4(c) of Annex 12, and to track their movements; and
   c) utilize this Network in order to:
      i) determine atmospheric loadings of toxic substances to the Great Lakes System by quantifying the total and net atmospheric input of these same contaminants, pursuant to sub-paragraph 3(a) of Annex 11;
      ii) define the temporal and spatial trends in the atmospheric deposition of such toxic substances in accordance with sub-paragraph 4(a) of Annex 12; and
      iii) develop Remedial Action Plans and Lakewide Management Plans pursuant to Annex 2.

4. **Components of the Integrated Atmospheric Deposition Network.** The Parties shall confer on or before October 1, 1988, regarding;
   a) the identity of the toxic substances to be monitored;
   b) the number of monitoring and surveillance stations;
   c) the locations of such stations;
   d) the equipment at such stations;
   e) quality control and quality assurance procedures; and
   f) a schedule for the construction and commencement of the operation of the stations.
5. **Pollution Control Measures.** The Parties, in cooperation with State and Provincial Governments, shall develop, adopt and implement measures for the control of the sources of emissions of toxic substances and the elimination of the sources of emissions of persistent toxic substances in cases where atmospheric deposition of these substances, singly or in synergistic or additive combination with other substances, significantly contributes to pollution of the Great Lakes System. Where such contributions arise from sources beyond the jurisdiction of the Parties,
   a) the Parties shall notify the responsible jurisdiction and the Commission of the problem and seek a suitable response.
   b) The Parties shall also assess and encourage the development of pollution control technologies and alternative products to reduce the effect of airborne toxic substances on the Great Lakes System.
6. **Reporting.** The Parties shall report their progress in implementing this Annex to the Commission biennially, commencing with a report no later than December 31, 1988.

8. 2. Complete Publication List

8. 2. 1. Peer-Reviewed Publications

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