

2. Workplan

2.a. Proposed Work

2.a.i. Introduction. The Great Lakes have been contaminated with many toxic organic contaminants over the past few decades. Industrial chemicals such as polychlorinated biphenyls, combustion related pollutants such as polycyclic aromatic hydrocarbons, and many chlorinated pesticides, both banned and currently in use, are some of the pollutants of interest. The atmosphere represents the major pathway by which most of these organic contaminants enter the Great Lakes. In an effort to determine the status and trends of atmospheric loadings of toxic organic contaminants, the Integrated Atmospheric Deposition Network (IADN) was established by an agreement between the United States and Canadian governments through the International Joint Commission. IADN was created in response to the Great Lakes Water Quality Agreement (Annex 15). In addition, directives for IADN come from the Clean Air Act Amendments of 1990. Section 112(m) of these Amendments directs the Environmental Protection Agency, in cooperation with the National Oceanic and Atmospheric Administration, to identify and assess the extent of atmospheric deposition of toxic pollutants to the Great Waters.

This network was initiated in late 1990. From 1990 to 1994, the Illinois State Water Survey was in charge, but in 1994, Prof. Hites at Indiana University (IU) became the principal investigator for the United States component of IADN. Dr. Ilora Basu is the deputy principal investigator, and she has been with the project since its inception in 1990.

The intent of IADN is to measure and evaluate pollutant concentrations in the atmosphere (airborne vapor, airborne particles, and precipitation) at a regional level of detail. Air and precipitation samples have been taken at five master sites near each of the Great Lakes. Three of the master sites and two of the satellite sites are located in the United States on Lakes Superior, Michigan, and Erie. Organic toxics of interest are chlorinated pesticides, polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAH), and more

recently, polybrominated diphenyl ethers (PBDEs).

We use these measurements to calculate loadings of selected toxic organic contaminants to the Great Lakes and to explore spatiotemporal trends in their atmospheric and precipitation concentrations. Over the years, we have increased the number of analytes we measure (for example, we are now including polybrominated diphenyl ether flame retardants as regular analytes). We also are exploring the relative importance of short vs. long-range transport and of agricultural inputs of in-use pesticides.

Since 1994, IADN results have been presented at numerous national and international scientific conferences as well as in 47 peer-reviewed publications. These publications are listed in Appendix 1.

2.a.ii. Sampling sites. Samples have been collected continuously at five master sites and at several satellite sites by both the United States and Canadian investigators; see Figure 1 for the site locations. The United States (specifically Indiana University) is responsible for three master stations: Eagle Harbor on Lake Superior, Sleeping Bear Dunes on Lake Michigan, and Sturgeon Point on Lake Erie. Indiana University is also responsible for two satellite stations, which are now located in Cleveland, Ohio on Lake Erie and in downtown Chicago near Lake Michigan. For inter-comparison with the data obtained by the Canadians, Indiana University also measures samples acquired at Point Petre on Lake Ontario.

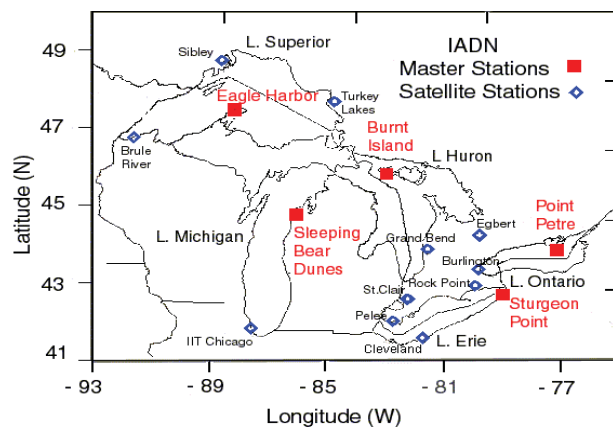


Figure 1. Map of IADN sites. Master stations are the main sites in the network. Satellite stations have been added or adopted throughout the project to augment the master stations.

2.a.iii. Sampling methods. Air samples are taken every 12 days for 24 hours using a Graseby high volume air sampler fitted with a Whatman quartz fiber filter and an Amberlite XAD-2 polymer resin cartridge to collect the particle and vapor phase contaminants, respectively. The samplers are operated at 34 m³/hour and calibrated with a variable resistance kit every four months by an orifice calibrator. At Point Petre, the samples are collected every 24 days for 24 hours. In all cases, the total volume of air sampled is ~815 m³.

Precipitation is sampled using MIC automated wet-only samplers. Each sampler consists of a 46 × 46 cm shallow funnel connected to a 30 cm long by 1.5 cm i.d. glass column packed with XAD-2 resin suspended in HPLC grade water. The sampler is normally covered, but it is opened automatically during a precipitation event, which is sensed by a conductivity grid. This grid is heated to prevent condensation, ice build-up, and prolonged sampling after the precipitation event. The funnel and the interior of the sampler are also heated to melt any snow that falls into the sampler and to keep the XAD-2 column from freezing. The precipitation flows by gravity from the funnel through the XAD-2 filled column and into a large carboy to measure the total precipitation volume. Because there is no filter in the system, the XAD-2 column collects both particulate and dissolved phase contaminants. Contaminants from the precipitation are integrated for one month regardless

of the amount of precipitation occurring during that period.

In addition to sampling organic contaminants in the atmosphere, a meteorological tower is located at each site. Wind speed and wind direction are measured at 10 meters; air temperature, barometric pressure, relative humidity, and solar radiation are measured at 2 meters. Meteorological measurements are taken every 6 seconds, but the data are recorded as hourly averages in a data logger, which is downloaded over phone lines or transferred through a data storage module to our laboratory.

2.a.iv. Compounds measured

2.a.iv.1. Current analyte list. IADN is currently measuring four groups of organic compounds in air and precipitation samples. The full list of analytes is given in the sample preparation Standard Operation Procedure (updated in April, 2007) is at:

<http://www.msc-smc.ec.gc.ca/iadn/resources/iu/sampleprep07.pdf>

As of 2005, we are measuring 84 individual PCB congeners, which elute from the gas chromatograph as 55 separate peaks and 29 unresolved peaks because of some unavoidable chromatographic overlaps. We report these latter peaks as the total concentrations of 2-3 congeners. We sum all PCB concentrations to get total PCBs, which is usually expressed as ΣPCB. We also report “suite PCBs”, which is the sum of those 83 PCB congeners selected to be compatible between the United States and Canadian laboratories. PCBs are measured in all vapor phase and precipitation samples. We stopped measuring PCBs in particle samples, with GLNPO’s permission, in October 1996. PCBs measurements of precipitation samples from remote sites were stopped, with GLNPO’s permission, in June 2006.

We are measuring 22 pesticides. Some of them are still in use (such as endosulfan), some are banned (such as DDT), and some have restricted use (such as lindane, also called γ-HCH). At the beginning of the project only seven pesticides

were measured. Gradually more pesticides were added to the list, and we routinely developed quantitation methods for these compounds. Pesticides are measured in both the vapor and particle phases and in precipitation. Analysis of pesticides in the particle phase from remote sites was stopped in May 2003.

We are measuring 43 polybrominated diphenyl ether (PBDE) congeners and six other flame retardants in both particle and vapor phases and in precipitation. We added these analytes to the IADN list at no additional cost to the project in January 2004. These compounds are of concern because their concentrations are generally increasing in the environment.

We are measuring 16 PAH with carbon numbers ranging from 13 to 24 in both the particle and vapor phases and in precipitation.

2.a.iv.2. Changes to the analyte list. Based on the technical review of November 2008, the following compounds have been dropped from the analyte list: methoxychlor, aldrin, endrin, Mirex, and octachlorostyrene. That review also recommended that we add measurements of PCBs on particles in Chicago and Cleveland -- measurements that had been stopped (with permission) in October 1996. We argue that that is not necessary. Recent work in our laboratory (reported to the Steering Committee) has shown that the fraction of PCBs on particles relative to the total in both particle and vapor phases, averages ~5%; thus, the benefit of including these measurements relative to their cost is low. We suggest that the resources that might be devoted to measuring PCBs on particulates should be better invested in emerging pollutants; see just below.

2.a.iv.3. Search for additional compounds. It is important to make sure that the compounds on the IADN analyte list are up to date. For example, when it became apparent the PBDEs were significant new POPs, they were immediately added to the list. When we noticed a large, unidentified gas chromatographic peak in several Sturgeon Point samples, we worked to identify it as Dechlorane Plus. We plan to continue and enlarge these qualitative efforts in the future. One graduate student will spend at least half of his or her time working

with pooled extracts (initially from Chicago and Cleveland) trying to identify all of the compounds in these extracts (with an emphasis on halogenated compounds). The Hites Laboratory has 40 years of experience with this sort of work, which is made possible by our expertise in mass spectrometry. One does not need to have a target compound in order to identify it by mass spectrometry.

We will also maintain close contact with the GLNPO fish program in New York. Given that fishes often bioaccumulate lipophilic POPs, it is sometime easier to identify new compounds in fishes first. We plan on an exchange of extracts to facilitate this communication.

2.a.iv.4. Methods development. Our laboratory at Indiana University has 30 years of experience in developing analytical methods for the quantitation of low levels of organic pollutants in the environment. Here are a few examples:

In 1990, IADN started with seven pesticides, but it is now 22. Each time new pesticides were added, we modified the analytical methods to quantitate them. This required developing a calibration system, improving the clean-up and gas chromatographic separations, and modifying the data handling procedures.

We have had a long history of measuring toxaphene in water, tree bark, and air. Toxaphene is a very complex mixture of hundreds of chlorinated bornanes and bornenes. About the only way to make these measurements reliably is with electron capture negative ionization gas chromatographic mass spectrometry. We developed such a method and used it for several years. We even developed freely available QBasic program to make the data processing reproducible.

When we added brominated flame retardants and Dechlorane Plus to the IADN analyte list, the instrumental part of the analytical procedure took 3-4 hours per sample. We modified that method by a clever GC column selection and temperature program so that this analysis now only takes 40 minutes per sample. At the same time, we were able to include several newer flame retardants, such as decabromodiphenyle-

thane and Dechlorane Plus in the same 40 minute analysis.

2.a.v. Sample extraction and clean-up. The organic compounds are removed from the XAD-2 absorbent media by a 24-hour Soxhlet extraction using 1:1 acetone-hexane. Surrogate recovery standards for PCBs, pesticides, PBDEs, and PAH are added just before extraction. The extracts are concentrated by rotary evaporation, and the solvent is exchanged to hexane. Silica gel, deactivated with 3.5% water, is used to fractionate the concentrated hexane extract. This column is eluted with 25 mL of hexane followed by 25 mL of 1:1 dichloromethane-hexane. The PCBs along with 5 pesticides (HCB, aldrin, *p,p'*-DDE, octachlorostyrene, and *o,p'*-DDT) elute in the hexane fraction; most of the other pesticides and all of the PAH elute in the 1:1 dichloromethane-hexane fraction. The PBDEs, *p,p'*-DDT, and *trans*-nonachlor elute in both fractions. The cleaned-up samples are further concentrated by rotary evaporation and N₂ blow-down before addition of quantitation internal standards and injection into the gas chromatograph or gas chromatographic mass spectrometer.

2.a.vi. Instrumental analysis. The PCBs and pesticides are analyzed by gas chromatography on Agilent 6890 instruments. Chromatography is done on 60-m long DB-5 and DB-1701 columns. The GCs are equipped with ⁶³Ni micro electron capture detectors. Injections are made with Agilent 7683 auto-samplers in the splitless mode. The carrier gas is H₂, and the detector make-up gas is N₂.

PAH and PBDE are analyzed on Agilent 5973 gas chromatographic mass spectrometers in the selected ion-monitoring mode. A DB-5 30-m long column is used for the separation of PAH, and a RTX-1614 15-m long column is used for the PBDEs. Data analysis is done with HP ChemStation software, and quantitation is based on the internal PAH and PBDE standards.

2.a.vii. Data handling and reporting procedures. For the GC-ECD data, peaks are identified by GC retention times compared to calibration standards. Quantitation is done by the internal standard method. When GC/MS is used, a primary

ion is used for quantitation and a secondary ion is used for confirmation. Quantitation by the internal standard procedure automatically corrects for the dilution factor, for detector response, and for other systematic quantitation variables. Surrogate standards are used to estimate recoveries of each compound in each sample. Recoveries of each compound per batch are determined by matrix spike experiments. Each sample is checked and validated for recovery, contamination, and outliers.

After calculation of the masses of all compounds, the data are tabulated in master spreadsheets with field comments, laboratory comments, sampling dates and times, analytical dates, average atmospheric temperature, average wind speed, and average wind direction. Separate spreadsheets are generated for the different sites and for different groups of compounds. These spreadsheets, with the absolute amount of each compound in each sample (in nanograms), are then reported to the IADN Database Manager for further quality checking and for appropriate flagging by the Research Data Management and Quality Control System (RDMQ). After the RDMQ validation and the calculation of annual averages and seasonal averages, the data come back again to Indiana University for further checking and confirmation. After the deputy-PI confirms the data, the spreadsheets are resubmitted to the Database Manager. All quality assured data at this point are ready to be used for trend and loading calculations. The data are finally posted on the IADN Web site, and they become available to the public.

For our own information, we also calculate the concentrations of each compound in picograms per cubic meter of air or in picograms per liter of precipitation. Finally Indiana University students and post-doctoral associates interpret that data and publish articles in the peer-reviewed literature.

Indiana University also prepares annual QC reports describing the detection limits, linearity, average blank values, percent recoveries, etc. for all matrices and for all of the compounds of interest. The field completeness, site-specific recoveries of surrogate standards, and various con-

trol charts are generated. These reports are submitted annually to GLNPO and to the Database Manager.

We have provided valid data (as Excel spreadsheets) to the IADN Database Manager within 10 months after the acquisition of the last sample in a given year. For example, all of the 2009 data will be delivered by October 2010.

Meteorological data are downloaded every two weeks to an Indiana University computer system as hourly averages. A QBasic program processes these raw data to give a recognizable format. The meteorological data are then imported into an Excel spreadsheet and tabulated in master spreadsheets. The data from each site are checked for outliers. The average temperature, wind speed, and wind direction for each 24-hour period are calculated, along with their standard deviations. The spreadsheets for different sites are reported to the IADN Database Manager.

2.a.viii. Summary of the project's QA/QC approach.

2.a.viii.1. Approved SOPs and QAPP. At the beginning of the IADN project, Clyde Sweet and Ilora Basu, at the Illinois State Water Survey, developed the Standard Operating Procedures (SOPs). In 1994, the project came to Indiana University, and the methods were adjusted and modified for the new laboratory. In 1995, Dr. Basu revised all the SOPs and submitted them to the Environmental Protection Agency. Since then, we have modified the SOPs several times whenever we improved the methods, added new analytes, bought new instruments, or upgraded the data system. The final versions for the SOPs were written in December 2005 and in April and May 2007. All complete SOPs are submitted to the Environmental Protection Agency and the IADN Database Manager. They are posted on IADN Web site at <http://www.msc-smc.ec.gc.ca/iadn/resources/iu/FieldSOP2005.pdf> <http://www.msc-smc.ec.gc.ca/iadn/resources/iu/sampleprep07.pdf> <http://www.msc-smc.ec.gc.ca/iadn/resources/iu/GCSOP2007.pdf>

Currently, we are operating under Version 5 of the QAPjP revised in November, 2006 and submitted to EPA. The detailed document is at: <http://www.msc-smc.ec.gc.ca/iadn/resources/iu/Qapjp06.pdf>

2.a.viii.2. Intercomparisons with Environment Canada. In 1998, Indiana University installed a high-volume air sampler and a MIC precipitation sampler at Point Petre, which is a Canadian Master Station. We have collected and analyzed samples from there ever since, but on a 24-day cycle rather than on the normal 12-day cycle. The point is to compare our results with those of our Canadian colleagues, who use somewhat different sampling and analytical methods. The results of these intercomparison analyses have recently been published by Wu et al.¹ and a brief summary of that paper follows:

A series of experiments were conducted among the laboratories participating in the IADN monitoring program to evaluate comparability of the reported persistent organic pollutant concentrations. The experiments included analyses of a common reference standard (CRS), analyses of split samples, and analyses of samples collected with co-located samplers at the Point Petre IADN measurement station. The analytes included polycyclic aromatic hydrocarbons (PAHs), organochlorine pesticides (OCPs), and polychlorinated biphenyls (PCBs).

For virtually all compounds, the laboratories produced generally comparable results for the CRS samples, the split samples, and the collocation samples, although some differences were observed. Analysis of the methods may pinpoint areas where variations in the methods will result in the differences observed in the reported data. These differences can be due to the field sampling process, the analytical method, field blank values, or a combination of all these factors. This study pointed out the importance of QA activities at every step of an environmen-

¹ Wu, R.; Backus, S.; Basu, I.; Blanchard, P.; Brice, K. A.; Dryfhout-Clark, H.; Fowlie, P.; Hulting, M. L.; Hites, R. A.; Findings from quality assurance activities of the Integrated Atmospheric Deposition Network. *J. Environ. Monit.* **2009**, *11*, 277-296.

tal monitoring process so that areas where improvements may be needed or where inconsistencies may exist can be identified.

We suggest that many of the differences that we did observe could be eliminated by completely harmonizing the United States and Canadian sampling and analysis methodologies. In general, the existing measurements are of good quality. Several QA/QC audits have verified that the laboratory and field SOPs are being followed correctly. The internal blank and recovery experiments verify that the sampling and measurement systems are working properly.

In 2006, we participated in an Interlaboratory Study, conducted by Terry F. Bidleman and Fiona Wong of Environment Canada. The participants were twelve different laboratories -- three from Canada, two from the United States, six from Mexico, and one from China. We compared three sets of common reference standards (CRS) for PCBs, pesticides, and PAHs. We also analyzed an air sample collected from Veracruz, Mexico in 2004. The agreement with the certified target values was generally good for the CRS, but the interlaboratory agreement was less satisfactory for the Veracruz air extract. In 2008, we participated in another Interlaboratory Study conducted by Yushan Su of Environment Canada. In this study, we analyzed two sets of reference standards (one high and one low dilution) for PCBs, pesticides, PAHs, and PBDEs. We also analyzed one air sample extract and one blind sample prepared to mimic the air extract. These results are not available yet.

2.a.ix. Overall program management.

2.a.ix.1. Internal organization and people. The IADN program at Indiana University will continue to be managed using the structure outlined in the organization chart shown in Figure 2. This has worked well in the past, and we plan no changes.

It is important to emphasize that most of this project’s staff has been with IADN for several years; this is very helpful to ensure continuity and efficiency. Prof. Hites has been the Principal Investigator since 1994, and Ilora Basu has been his deputy since 1994. In fact, Dr. Basu was actually involved with IADN since its inception in 1990 at

the Illinois State Water Survey. Karen Arnold (senior technician) has been with us since 1995, Jennifer Kelley (technician) has been with us since 1999, and James Bays (site operations) has been with us since 2005. They will all continue as 100% FTE employees. Ilora Basu is currently working at 75% FTE.

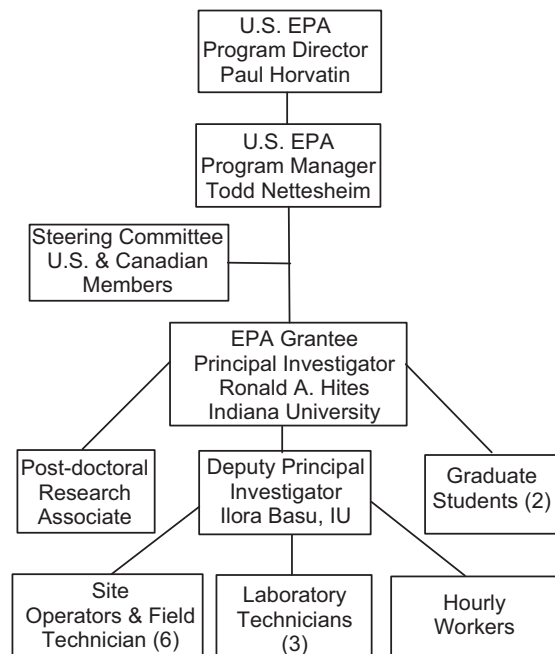


Figure 2. Organizational chart for the management of the IADN project at Indiana University. Year 1 only is shown.

Virginia Thomas (since 2007) will likely continue as a laboratory assistant for 30-40 hours a week. Don Keith (since 1996) and Tom Van Zoeren (since 1990) will continue as site operators. Jim Osborne (since 1991) will continue as a part-time, on-call field technician. Marta Venier (since 2004) will continue as a full-time post-doctoral research associate, and Amina Salamova (since 2007) and Yuning Ma (since 2008) will continue as doctoral students on this project.

2.a.ix.2. Steering Committee participation. Prof. Hites (and Drs. Basu and Venier as needed) will participate in Steering Committee activities, which include monthly conference calls and face-to-face meetings once or twice per year. The Steering Committee is responsible for

determining the future direction of IADN and assessing and improving the quality of the present network through quality assurance, methods comparability studies, reporting, etc. As a participant on the Steering Committee, Prof. Hites will be involved in evaluation of data quality indicators, revision of the target analyte list, assessing the adequacy of the measurement process, network-wide results reporting and outreach, development of trend and loading estimates and models, and assessing the degree of accuracy of trend and loading estimates.

Cooperation and communication with Environmental Protection Agency employees and participants from other monitoring programs is also beneficial in order to provide a full picture of toxic contaminants in the Great Lakes basin, as well as to properly inform policy and regulatory decisions regarding toxics reduction. For example, we will help develop the report for SOLEC (State of the Lakes Ecosystem Conference) Indicator #117, Atmospheric Deposition of Toxic Chemicals, and we will interface closely with the GLNPO fish program as we look for previously unidentified contaminants.

2.a.x. Site operations. Three master stations and two satellite stations are presently in operation for the IADN project in the United States. Each site is equipped with air samplers, precipitation samplers, and a meteorological tower with data logger. Master stations have duplicate air and precipitation samplers, and the satellite stations have only one of each type. In July of 2006, one precipitation sampler was moved from Eagle Harbor to Chicago. Field technicians go to the sites three times a year to calibrate the equipment, replace parts as needed, and perform seasonal maintenance. In case of an emergency repair, a technician can make a special trip to the site.

There is one local site operator at each site for sample collection, field data collection, weekly

maintenance of the equipment, and mailing the samples. Indiana University directly hires local individuals for this work. For Chicago and Sturgeon Point, we pay graduate students through the Illinois Institute of Technology and the State University of New York at Buffalo, respectively. The site operator at Cleveland is appointed by the Ohio State Environmental Protection Agency, Division of Air Quality, City of Cleveland. Sampling media such as XAD-2 cartridges, quartz fiber filters, and rain columns are prepared at Indiana University and sent to the sites on a monthly basis along with the sampling schedule. The site operators go to the site once a week, change the cartridges at the proper time, note all of the field conditions on prescribed forms, set the timer for sampling, collect samples, and mail them to the Indiana University laboratory. The Ontario Ministry of the Environment appoints the site operator at Point Petre. In 1998, Indiana University installed one high-volume air sampler and one MIC precipitation sampler at this site for measuring data comparability between Indiana University and Canada. Indiana University will continue to collect air and precipitation samples from this site.

2.a.xi. Proposed sample numbers and schedule. At the regular United States IADN sites, air samples are collected every 12 days for 24 hours, and precipitation samples are integrated over one month. In addition, 5% field blanks and 5% field duplicates are collected from master stations for both types of samples. Air samples are collected every 24 days at Point Petre. The annual total number of proposed samples is outlined in Table 1. The data for all samples will be delivered within 10 months of taking the last sample of the year; for example, the entire data set for 2009 will be delivered by October 31, 2010. We have had no trouble meeting this schedule in the past.

Table 1. Numbers of proposed samples to be acquired and analyzed each year; note that we have added a few extra samples in addition to the minimum requirement to make up for any losses during transportation or because of laboratory accidents.

	Regular Sites	Point Petre	Total
Air vapor-phase samples	180	16	196
Air particle-phase samples	180	16	196
Precipitation samples	80	13	93
Laboratory QC samples	<u>80</u>	<u>0</u>	<u>80</u>
Total for analysis	520	45	565

2.a.xii. Explicitly ensure continuity of quality data. Because one of the goals of this project is to compare concentrations over a long time scale, it is important to have long-term continuity of the measurements. For example, if the analytical methods were to change part way through the project, and one observed a change in concentrations at that time it would be difficult to attribute that change to actual changes in the environment or to changes in the analytical methods. For this reason, we have made great efforts to ensure continuity of the data stream from this project.

The most important mechanism for ensuring continuity is our extensive QA/QC program. About 10-15% of the sample analysis funds go toward QA/QC. We are proud of this program, and we are confident that it has helped maintain the output of high quality data from this program over the 15 years it has operated at Indiana University.

IADN's institutional stability has also helped maintain continuity. The simple fact that this program has been operated at one institution (Indiana University) for the last 15 years has generated strong institutional support and memory. Perhaps the most important factor in maintaining continuity of data quality has been the presence of Dr. Ilora Basu since the inception of this project. Dr. Basu worked on this project when it was first funded at the Illinois State Water Survey (ISWS) in 1990. When the project moved to Indiana University in 1994, Dr. Basu came with it. She drafted and implemented the original Standard Operating Procedures and the QA/QC protocols at the ISWS, and when IADN moved to Indiana, she made sure that there was no disruption in the implementation of these procedures and protocols.

2.b. Project goals/outcomes/benefits. This project is generally aimed at the Environmental Protection Agency's strategic goal of preventing water pollution and protecting aquatic systems so that the overall ecosystem health of the Great Lakes is improved (sub-objective 4.3.3). The strategic target most related to IADN is to maintain or improve an average 7% annual decline for the long-term trend in average concentrations of toxic chemicals (PCBs) from the air from the Great Lakes Basin.

The expected outcomes from this project are, but are not limited to:

- Improved understanding of the atmospheric fate and cycling of priority toxic chemicals in the Great Lakes region;
- Improved understanding of the sources, trends, and loadings of chemicals of emerging concern entering the Great Lakes; and
- Better decisions by environmental managers in development and implementation of strategies to reduce the presence of priority toxic chemicals in Great Lakes air, water, sediment, fish, and other wildlife.

2.c. Project benefits/outputs. The expected outputs from this project are, but are not limited to:

- Acquiring quality-assured air and precipitation concentrations measurements, with attention to continuity and consistency of those measurements, so that trend data are not biased by changes in network operations or personnel;
- Determining, 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; and

- Publishing and presenting:
 - Several scientific peer reviewed journal articles;
 - Several talks at regional, national, and international scientific conferences;
 - IADN trends and loadings reports; and
 - Technical summary of progress of IADN in 2013.

We believe that our past performance on this project amply demonstrates our ability to deliver these outputs.

2.d. Project eligibility. One point of IADN is to understand the extent of atmospheric deposition of toxic organic compounds into the Great Lakes. It is largely this deposition that is driving the exposure of sport fishes to these organic compounds and thus restricting the human consumption of these fishes. For example, in the last IADN loading report, it was estimated that about 40 tons/yr of polycyclic aromatic hydrocarbons (PAH) are entering the Great Lakes from the atmosphere.² Given the relatively high levels of PAH in air from urban centers (see below), it is likely that cities are the main source of PAH to the Lakes and that control measures should be focused in the cities. IADN also measures spatiotemporal trends, and for PAH, these data indicate a minimal decline in these levels as a function of time – not an optimistic finding.

We should also mention that Indiana University is an educational institution and that IADN has supported the research of several doctoral students. These are:

- Stephanie Buehler, now at the Battelle Memorial Institution
- Donald Cortes, now at STAT Analysis Corp. in Chicago

- Susan Glassmeyer, now with the United States Environmental Protection Agency laboratory in Cincinnati
- William Hafner, now in Kenmore, Washington
- Eunha Hoh, now in the School of Public Health at California State University-San Diego
- Marta Venier, now a post-doctoral associate at Indiana University

Several post-doctoral associates acquired valuable scientific training while working on the IADN project. These include:

- Dan Carlson, now at the University of Minnesota
- Barbara Hillery, now at the State University of New York in Old Westbury
- Matt Simcik, now in the School of Public Health at the University of Minnesota
- Bo Strandberg, now in Göteborg, Sweden
- Ping Sun, now at the Proctor and Gamble Corp. in Cincinnati

2.e. Collaboration, stakeholders, and leveraging. Our most important collaborators on this project are our Canadian colleagues at Environment Canada. They operate the sites on Lake Huron (at Burnt Island) and on Lake Ontario (at Point Petre), and they analyze all of the samples from these sites. We have periodic conference phone calls and meetings with these colleagues. We have done extensive QA/QC work centered at Point Petre to understand the differences in our methodology, if any. Periodically, we collaborate with them in writing various documents; for example, we all worked hard together to generate the five-year technical summary report for the review that was conducted in Tampa in November 2008. We also collaborate in the preparation of the periodic trends and loadings reports. Perhaps more significantly, over the last three years we worked closely with these colleagues in the preparation and publication of six papers in *Environmental Science and Technology*, which presented detailed spatiotemporal trend analyses of all of the IADN data (United States and Canadian) collected from 1990 through 2003.

² Blanchard, P.; Audette, C.; Hulting, M. L.; Basu, I.; Brice, K. A.; Backus, S. M.; Dryfhout-Clark, H.; Froude, F.; Hites, R. A.; Neilson, M.; Wu, R. *Atmospheric deposition of toxic substances to the Great Lakes: IADN results through 2005*. October 2008, p. 59.

We are frequently asked for IADN data by other investigators, and although these requests do not result in publications with Indiana University as a co-author, we are happy to help these other groups. These requestors have included:

- Mark Cohen in the National Oceanic and Atmospheric Administration
- Brian Eitzer at the Connecticut Agricultural Experiment Station
- Tom Holsen at Clarkson University
- Keri Hornbuckle at the University of Iowa
- Jerry Keeler at the University of Michigan
- Judith Perlinger at Michigan Technological University
- Lisa Rodenberg at Rutgers University
- Yushan Su of Environment Canada

We have also given technical assistance to the graduate students of:

- Steve Eisenreich at Rutgers University
- Keri Hornbuckle at the University of Iowa
- William Mills at the University of Illinois-Chicago
- Judith Perlinger at the Michigan Technological University
- Staci Simonich at Oregon State University
- Deb Swackhamer at the University of Minnesota

We also have provided assistance by way of e-mail to a few scientists from outside of the United States: Geoff Mills from New Zealand and Raphael Navarra from Mexico.

With one exception, in the past, we have communicated indirectly with stakeholders. The one exception was a presentation Prof. Hites gave at the SOLEC meeting in Milwaukee in 2007. He would be very pleased to do this again.

The funding for this project is leveraged by cost-sharing funding from Indiana University. The budget (see below) shows ~9% in matching money provided by Indiana University. This funding is provided in the form of Prof. Hites' salary during the academic year, when he will spend at least 20% of his time on this project without charging for that time. This is the same type and level of cost-sharing that Indiana University has provided to GLNPO since 1994.

2.f. Measuring progress. We will measure the success of this project by several factors:

- *Timeliness.* The data for all samples will be delivered within 10 months of taking the last sample of the year; for example, the entire data set for 2009 will be delivered by October 31, 2010. We have had no problem meeting this schedule in the past.
- *Dissemination of data.* We expect to publish about five peer-reviewed papers per year in good journals, such as *Environmental Science and Technology*, *Atmospheric Environment*, the *Journal of Great Lakes Research*, or *Chemosphere*. We also expect to give about three talks (and occasionally posters) annually at regional, national, and international scientific conferences. These include the annual meetings of the International Association for Great Lakes Research, the Society for Environmental Toxicology and Chemistry, and the International Conference on Dioxins and Halogenated Compounds.
- *Training new scientists.* We will continue to train doctoral students and post-doctoral associates with the expectation that, on average, one or two such people will “graduate” each year.

2.g. Project tasks/schedule. The schedule of the tasks is implicit in the “deliverables”:

- The data for all samples will be delivered within 10 months of taking the last sample of the year; see above.
- We will publish about five peer-reviewed papers per year in good journals, and we will present about three talks at regional, national, and international scientific conferences. These papers and presentations are our “communication plan.”
- We will continue to train doctoral students and post-doctoral associates with the expectation that, on average, one or two such people will “graduate” each year.
- We will continue to supply raw data to colleagues at other institutions for use in their own research. We will not attach “strings” to these data; that is, we will not require or even request, co-authorship on papers using these data. After all, these data belong to

the American public, and other scientists should be able to use these data as they see fit.

- We will continue to give technical support to research scientists at other universities and agencies.
- A final report will be generated six months after the termination of this project.

2.h. Programmatic capability and past performance

2.h.i. Data production. From 1994 until today, we have taken and analyzed over 6,600 samples; see Table 2. These data have been quality assured and submitted to the United States Environmental Protection Agency and others for inclusion in the IADN master database. In addition, dozens of papers and reports have been prepared from these data.

Table 2. Number of samples analyzed as of December, 2008

Sites	Number received	Number extracted	Samples analyzed			
			PCB	Pesticides	PAH	PBDE
Eagle Harbor	1375	1363	838	1143	1340	195
Sleeping Bear	1462	1450	881	1218	1424	198
Sturgeon Point	1396	1385	842	1168	1362	198
Chicago	984	971	592	956	961	187
Cleveland	455	435	250	424	432	188
Brule River	493	493	308	493	493	---
Point Petre	<u>524</u>	<u>517</u>	<u>325</u>	<u>391</u>	<u>506</u>	---
Total	6689	6614	4036	5793	6518	966
Timeliness	Dec. 2008	Dec. 2008	Dec. 2008	Dec. 2008	Dec. 2008	Dec. 2007

2.h.ii. Data interpretation as evidenced by publications and presentations. We have consistently published the results of the IADN project in high quality journals. The publications resulting directly or indirectly from IADN support are indicated in Appendix 1 (see below). At the present time 47 such papers have been published, and most of them have been published in the premier environmental chemistry journal, *Environmental Science and Technology*, the highest ranked journal in environmental chemistry. IADN projects have formed the base for numerous doctoral and masters theses, which have been submitted to Indiana University for academic credit. Thus, IADN is contributing to the training of future environmental scientists. Prof. Hites, his associates, and his students have presented lectures about the IADN project at over 70 regional, national, and international meetings.

Numerous quality assurance plans and reports, standard operating procedures, and data reports

have been submitted to the Environmental Protection Agency. These are too numerous to list here.

2.h.iii. Spatiotemporal trend analyses. IADN data indicate that gas-phase atmospheric partial pressures of semi-volatile organic compounds strongly depend on atmospheric temperature and that this dependence can be modeled by the integrated form of the Clausius-Clapeyron equation:

$$\ln P = a_0 - \frac{\Delta H_{SA}}{RT} \quad (1)$$

where P is the partial pressure of the analyte (in atm), ΔH_{SA} is the energy necessary to move a mole of a substance from an environmental surface (soil, water, vegetation, etc.) to the gas-phase (in kJ/mol), T is the atmospheric temperature at the sampling site when the sample was collected (in K), R is the gas constant (0.0083 kJ/mol), and a_0 is an intercept that resolves the units.

To look for spatiotemporal trends in the IADN data, we have introduced the idea of temperature corrected partial pressures, which are given by

$$\ln P_{288} = \ln P - a_1 \left(\frac{1}{288} - \frac{1}{T} \right) \quad (2)$$

where a_1 is $\Delta H_{SA}/R$ and P_{288} is the partial pressure corrected to an atmospheric temperature of 288 K. A plot of $\ln(P_{288})$ vs. time allows us to determine a first order rate constant (b_1)

$$\ln(P_{288}) = b_0 + b_1 t \quad (3)$$

where t is the sampling date in Julian days relative to January 1, 1990.

In addition to temperature and time, we have also shown that the partial pressures of several POPs strongly depend on the human population living and working near the sampling site, a concept we have parameterized as

$$\ln P = c_0 + c_1 \log(\text{pop}) \quad (4)$$

where pop is the population within a 25 km radius of the site. High correlations have been found for PAHs from sampling sites around the world,³ for polybrominated diphenyl ethers at the IADN sites,⁴ and for polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in North America (see below).⁵ All of these correlations, however, showed systematic residuals; see Figure 3. The concentrations at low and high populations were usually above the regression line, indicating significant non-linearity in this relationship. To compensate for this non-

³ Hafner, W. D.; Carlson, D. L.; Hites, R. A., Influence of local human population on atmospheric polycyclic aromatic hydrocarbon concentrations. *Environ. Sci. Technol.* **2005**, *39*, (19), 7374-7379.

⁴ Venier, M.; Hites, R. A., Flame retardants in the atmosphere near the Great Lakes. *Environ. Sci. Technol.* **2008**, *42*, (13), 4745-4751.

⁵ Venier, M.; Ferrario, J.; Hites, R. A., Polychlorinated dibenzo-*p*-dioxins and dibenzofurans in the atmosphere around the Great Lakes. *Environ. Sci. Technol.* **2009**, *43*, (4), 1036-1041.

linearity we will use here a slightly different form for this parameter

$$\ln P = c'_0 + c'_1 \log^2 \text{pop} \quad (5)$$

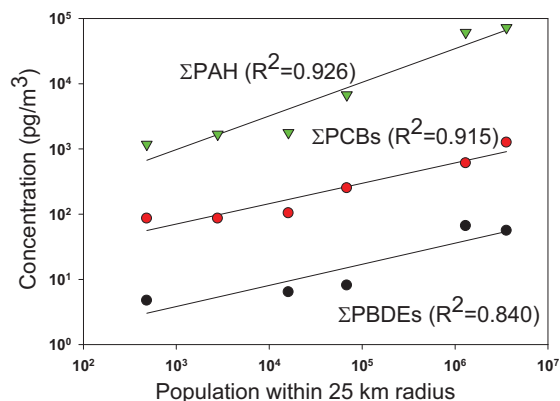


Figure 3. Relationship between the logarithm of the total PAH, PCB, and PBDE concentrations (in pg/m^3) and the logarithm of the human population within a 25 km radius of each United States sampling site.

In previous studies from our laboratory, we have also investigated the effect of directional meteorological parameters, such as wind direction and backward air trajectories, on measured partial pressures. In one study, we determined that PAH concentrations at Sturgeon Point were higher when the air was coming to the site from the south.⁶ In another study, we used wind directions measured at the site and 4-day average backward trajectories to determine that these directional parameters were relatively unimportant in explaining the variability of atmospheric partial pressures.⁷ In a third study, we used the potential source contribution function (PSCF) model to determine the sources of several chemicals (PAH, PCBs, and some pesticides) using

⁶ Cortes, D. R.; Basu, I.; Sweet, C. W.; Hites, R. A., Temporal trends in and influence of wind on PAH concentrations measured near the Great Lakes. *Environ. Sci. Technol.* **2000**, *34*, (3), 356-360.

⁷ Hafner, W. D.; Hites, R. A., Effects of wind and air trajectory directions on atmospheric concentrations of persistent organic pollutants near the Great Lakes. *Environ. Sci. Technol.* **2005**, *39*, (20), 7817-7825.

backward air trajectories.⁸ In general, most pollutants were coming to the Great Lakes from southern sources.

We have suggested a new model that combines equations 1 to 5 plus wind speed and wind direction, and we have applied it to data from the IADN sites to determine the corresponding regression coefficients. The natural logarithms of the atmospheric partial pressures ($\ln P$) were then fitted using following equation:

$$\ln P = d_0 + d_1 t + d_2 \left(\frac{1000}{T} \right) + d_3 \log^2 \text{pop} \quad (6) \\ + d_4 (\text{WS}) + d_5 \cos(\text{WD})$$

where d_0 is an intercept, d_1 is a first-order rate constant (in days⁻¹), d_2 is the Clausius-Clapeyron slope (in K), d_3 (unitless) describes the change of P as a function of population squared, and d_4 and d_5 describe the dependence of the partial pressure on wind speed (in mph) and wind direction, expressed on the cosine of the angle (in radians).

The model was applied to the gas-phase concentration of the following chemicals: Σ PCB (suite of 83 congeners that includes the toxicologically relevant ones), Σ PAH (sum of ~16 compounds), α - and γ -HCH, Σ DDT = p,p' -DDT + p,p' -DDD + p,p' -DDE, Σ Chlor = α - + γ -chlordane + *trans*-nonachlor, and Σ Endo = endosulfan I + II+ endosulfan sulphate.

Temporal trends. All seven of the chemicals or groups of chemicals showed a significant decrease in their partial pressures over time. These rates of decrease can be conveniently expressed as half-lives

$$t_{1/2} = \frac{\ln(2)}{-d_1} \quad (7)$$

⁸ Hafner, W. D.; Hites, R. A., Potential sources of pesticides, PCBs, and PAHs to the atmosphere of the Great Lakes. *Environ. Sci. Technol.* **2003**, *37*, (17), 3764-3773.

The longest half-life was for Σ PAH (~20 years), and the shortest was for α - and γ -HCH (3-4 years).

Given that PAH are produced by combustion of every type, it is not surprising that they showed the slowest rate of decrease (19 ± 2 years). Although the Toxic Release Inventory shows a general decrease of PAH emissions over the last decade in the Great Lakes region, the atmospheric concentrations of PAHs are still relatively high. This regression, where all of the sites were combined together, produced results similar to those reported by Sun et al. on a site-by-site basis; these earlier half-lives averaged 14 ± 4 years,⁹ confirming that the atmospheric concentrations of PAHs are slowly decreasing in the Great Lakes region.

Despite being banned in the United States since the late 1970s, PCBs are still ubiquitous, and their atmospheric levels are declining slowly, as shown by their relatively long half-life of 13 ± 1 years in the Great Lakes region. In 2007, Sun et al. reported an average PCB half-life of 14 ± 4 years for the same IADN sites.¹⁰ This is a surprisingly slow rate of decrease for compounds that have not been produced in North America since the late 1970s; on the other hand, there are still large amounts of PCBs that have not been permanently removed from the environment, such as in electrical gear. In addition, "decommissioned" PCBs have not really been removed from the environment either; rather, they have been placed in landfills and in other disposal facilities that may well be leaking into the atmosphere.

Among the OC pesticides, the atmospheric partial pressures of α - and γ -HCH are declining most rapidly (half-lives of 3.3 ± 0.1 and $3.8 \pm$

⁹ Sun, P.; Blanchard, P.; Brice, K. A.; Hites, R. A., Trends in polycyclic aromatic hydrocarbon concentrations in the Great Lakes atmosphere. *Environ. Sci. Technol.* **2006**, *40*, (20), 6221-6227.

¹⁰ Sun, P.; Basu, I.; Blanchard, P.; Brice, K. A.; Hites, R. A., Temporal and spatial trends of atmospheric polychlorinated biphenyl concentrations near the Great Lakes. *Environ. Sci. Technol.* **2007**, *41*, (4), 1131-1136.

0.1 years, respectively). The α isomer constituted 60-70% of the technical HCH product, which was banned in the 1970s and replaced by lindane, the purified γ isomer. The latter was phased out in Canada in 2004, and it will be phased out in the United States in 2009. The short half-life of α -HCH observed here is similar to the average half-life of 3.8 ± 0.3 years reported by Sun et al.¹¹ It is interesting that, despite its ban ~40 years ago, this insecticide is still being eliminated rapidly from the environment. Conversely, the half-life of γ -HCH reported here is somewhat less than that reported by Sun et al. for data covering up to 2003 (an average half-life of 6.1 ± 2.1 years).¹¹ The more rapid decline observed in this study, which expanded the dataset until 2007 and merged all the sites together, could reflect the ban on lindane's use that took place in Canada starting in 2004. An even more rapid loss rate might be expected in the next 5-10 years, once the ban on this compound in the United States becomes effective.

Although the United States Environmental Protection Agency is reviewing its use, endosulfan is currently used as an agricultural pesticide. Our study showed a half-life of 12 ± 1 years (calculated as Σ Endo), which is somewhat higher than the previously reported average for IADN sites (5.9 ± 2.6 years).¹¹ The National Water-Quality Assessment (NAWQA) Program estimated a decrease in endosulfan's use in the United States from 1997 to 2002, but current use estimates are not available. Therefore, we are reluctant in making any connection between use and the observed spatiotemporal trend.

Σ DDT and Σ Chlor, which are all components of banned products, showed half-lives of 7.8 ± 0.3 and 10.0 ± 0.5 years, respectively; these values are in good agreement with those previously reported by Sun et al. (8.0 ± 2.9 and 9.6 ± 2.0 years).¹¹ These relatively slow rates of decline, despite bans on these products over 20 years

ago, may indicate that there are large reservoirs of these compounds in agricultural and urban soils that are only slowly being depleted.

Seasonality. In equation 6, the third term (d_2) describes the relationship between ambient temperature and the gas-phase partial pressure of these semi-volatile organic compounds. All the compounds showed a statistically significant ($P < 0.05$) negative dependence on reciprocal temperature, indicating that gas-phase partial pressures increase with increasing temperatures. Ultimately, the absolute value of the d_2 coefficient describes the importance of seasonality for a specific compound. As such, it is reasonable that the highest seasonal value was found for Σ Endo ($-d_2 = 12 \pm 1$), a pesticide that is mainly applied in the spring and summer, when atmospheric temperatures are highest. The value of $-d_2$ was lowest for Σ PAH (2.5 ± 0.1), compounds whose atmospheric concentrations tend to peak in the winter as combustion for space heating increases.

Urbanization. The fourth term (d_3) in equation 6 describes the dependence of the gas-phase partial pressures on the squared logarithm of the local human population. The coefficients for this population term ranged from 0.12 ± 0.01 for Σ PAH (indicating a strong relationship to urbanization) to 0.018 ± 0.001 for γ -HCH (indicating almost no relationship with urbanization). The low coefficient for γ -HCH is probably because this compound is used almost exclusively in agriculture.

Directional terms. In equation 6, the last two terms describe the relationship between partial pressure and wind speed (d_4) and wind direction (d_5). Wind speed was a statistically significant term ($P < 0.05$) for all compounds except Σ DDT and Σ Chlor, and wind direction was significant for all compounds except α -HCH. The wind speed coefficient was always negative, indicating an inverse relationship between the partial pressures the intensity of the wind. The highest values for d_4 were for Σ PAH and Σ Endo (both 0.033 ± 0.008), while the lowest was for Σ PCB (0.0075 ± 0.0013). The coefficient for the cosine of the wind direction, d_5 , was negative for all compounds. Keeping in mind the properties

¹¹ Sun, P.; Blanchard, P.; Brice, K.; Hites, R. A., Atmospheric organochlorine pesticide concentrations near the Great Lakes: temporal and spatial trends. *Environ. Sci. Technol.* **2006**, *40*, (21), 6587-6593.

of the cosine function and given the negative sign of d_5 , this regression indicates that the partial pressures are relatively high on days when the winds come from the south. The strongest dependence on wind direction was found for Σ PAH and the weakest for γ -HCH. The importance of wind in explaining the partial pressures for Σ PAH has been previously observed by Cortes et al.⁶ and by Hafner and Hites.⁷

Importance of each term. The importance of each of the five regression parameters in explaining their variability of the partial pressures was estimated by calculating the relative contribution of each term to the total variability. This value is reported as the percentage of the sequential sum of squares attributed to each factor relative to the total sum of squares. This procedure is equivalent to calculating the portion of the overall variability, given as r^2 , that can be attributed to each term in the regression. These contributions are shown in Figure 4.

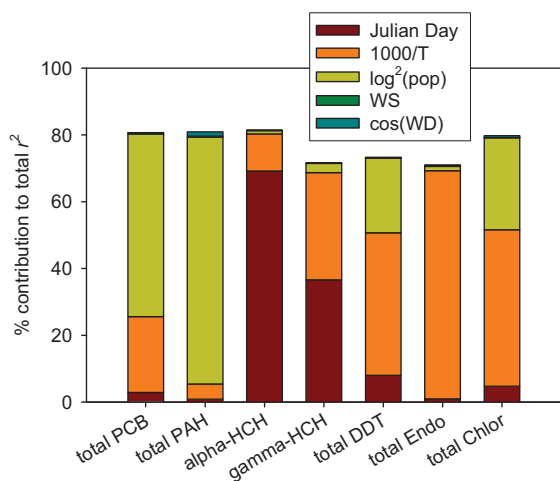


Figure 4. Relative contribution of each of the five terms in equation 6 to the total variability of the regression.

The partial pressures of Σ PCB and Σ PAH were mainly controlled by the local human population; the coefficients of this term accounted for 55 and 74% of the total variability, respectively. Temperature, expressed as $1000/T$, played a significant role in explaining the Σ PCB partial pressures, accounting for 23% of the total variability. This finding confirms the seasonal character of atmospheric partial pressures of PCBs,

as well as their strong relationship to human activities. It is surprising that time plays so little role for PCBs, which have been regulated since the 1970s. Given the long half-life we observe for PCBs, and given the strong dependence on anthropogenic activities, it is fair to say the PCBs will be with us for decades to come. Conversely, temperature played a minor role in the regression for Σ PAH, with the coefficient of the $1000/T$ term accounting for < 5% of the total variability. This result confirms the strong link of PAHs atmospheric levels to anthropogenic combustion activities, such as coal and natural gas combustion, coke production, and vehicle emissions, most of which do not have a strong seasonal aspect.

The HCHs were the only two chemicals in this study where time represented the most important factor in explaining their observed partial pressures. α -HCH was almost exclusively controlled by time (69%), and γ -HCH was controlled almost equally by time and temperature (37 and 32%, respectively). This time dependence seems to track the regulatory histories of these two chemicals: α -HCH has been banned since the 1980s, and γ -HCH has been banned in Canada since 2004 and in the United States since 2009.

For the other pesticides included in this analysis, atmospheric temperature was the primary factor in explaining the observed partial pressures. These contributions were 43% for Σ DDT, 68% for Σ Endo, and 47% for Σ Chlor. However, unlike Σ PAH, it was also possible to identify a secondary controlling factor for two of them. For Σ DDT and Σ Chlor, population explained 22% and 28%, respectively, of the partial pressure variabilities. This strong dependence of these pesticides' partial pressures on temperature suggests that these agrochemicals are used predominantly during the growing season -- primarily in the warmer spring and summer months. The contribution of the urbanization term to the total variability of the Σ DDT and Σ Chlor data might be related to the historic use of these chemicals in urban environments; for example, DDT was used to protect cities' roadside shade trees, and chlordane was used extensively to protect wooden houses against termites.

For all the studied compounds, neither of the two directional parameters (wind speed nor wind direction) played an important role in explaining the observed partial pressures, with percentages ranging from < 0.01 to 0.32 for wind speed and from 0.02 to 1.3 for the cosine of wind direction. This result is somewhat counterintuitive, and it may indicate that local sources, some of which are characterized by an elevated population, and agricultural sources, some of which are highly seasonal, simply overwhelm other, more distant sources.

2.h.iv. Dioxins in the Great Lakes Atmosphere. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) were never produced intentionally; rather, they are formed as trace impurities in the manufacturing of other chlorinated chemicals and as toxic by-products from the combustion of selected fuels, such as municipal solid waste. PCDD/Fs are now ubiquitous in the environment and find their way up the food chain, ultimately reaching man. Because PCDD/Fs are chemically stable, once they are released into the atmosphere, they can be transported by the winds to remote regions.

With the goal of investigating the spatiotemporal concentration trends of PCDD/Fs in the Great Lakes airshed, we began a series of monthly measurements at four sites on the shores of three of the lakes in mid-2004. Here, we report these results from one urban and three rural or remote sites from this network for the period between November 2004 and December 2007.

Samples were collected at the IADN sites of Chicago, Eagle Harbor, Sleeping Bear Dunes and Sturgeon Point according to the IADN procedure described before, only for an extended time (168 hours at the rural or remote sites and 48 hours at Chicago). Also, unlike IADN, XAD-2 resin and filters for each sample were combined before analysis. Samples were analyzed for PCDD/Fs at the United States Environmental Protection Agency's laboratory at the Stennis Space Center in Mississippi, using high resolution mass spectrometry, by Joseph Ferrario. This work was funded by the Great Lakes

Atmospheric Deposition program operated by the Great Lakes Commission.

The average total PCDD/F and toxic equivalent (TEQ) concentrations were highest at the urban site of Chicago (1300 fg/m^3 and 35 fg TEQ/m^3 , respectively), followed by the rural site of Sturgeon Point (740 fg/m^3 and 13 fg TEQ/m^3) and the two remote sites of Sleeping Bear Dunes and Eagle Harbor (400 fg/m^3 and 7.4 fg TEQ/m^3 and 120 fg/m^3 and 2.3 fg TEQ/m^3 , respectively). The statistically supported sequence was: Chicago > Sturgeon Point > Sleeping Bear Dunes > Eagle Harbor (Tukey's post hoc test, $P < 0.05$).

These results agree with similar data collected at rural or remote United States locations by the National Dioxin Air Monitoring Network (NDAMN)¹² in 2002 when the mean concentrations ranged from 6.4 to $15 \text{ fg WHO-TEQ/m}^3$ in rural areas and from 0.1 to 3 fg WHO TEQ/m^3 in remote areas. Considering the four years difference between the two datasets, all of these results are in good agreement with one another. Similarly, 2005 average PCDD/F TEQ concentrations for sites included in Canada's National Air Pollution Surveillance Network are in good agreement with the data presented here. Rural or remote locations in Ontario (the Canadian region bordering the Great Lakes) such as Egbert, Point Petre, and Burnt Island showed PCDD/F average concentrations of 14 , 21 , and 7.9 fg TEQ/m^3 , respectively.¹³

A sinusoidal model of the logarithmically transformed concentrations of total PCDD/F of the 17 toxic congeners (in fg/m^3) was used to account for the periodicity of the observations. All of the sites showed a significant periodicity ($P < 0.05$), with the exception of Chicago. This lack of periodicity at an urban site may be related to

¹² Cleverly, D.; Ferrario, J.; Byrne, C.; Riggs, K.; Joseph, D.; Hartford, P., A general indication of the contemporary background levels of PCDDs, PCDFs, and coplanar PCBs in the ambient air over rural and remote areas of the United States. *Environmental Science & Technology* **2007**, *41*, 1537-1544.

¹³ National Air Pollution Surveillance (NAPS) Network, Environment Canada. Available at: <http://www.etc-cte.ec.gc.ca/NapsAnnualRawData>.

the shorter sampling time at this site (48 hours vs. 168 hours) or to the time invariance of the PCDD/F sources in this city. At all the rural and remote sites, the maximum TEQ concentrations were in winter: October 29 at Eagle Harbor, November 28 at Sleeping Bear Dunes, and January 20 at Sturgeon Point. The shift in the dates of maximum concentration from late fall at Eagle Harbor to mid winter at Sturgeon Point may be related to the decreasing latitude of these sites, which determines the start of the coldest months. Given that space heating energy requirements are highest in the winter, these dates substantiate the hypothesis that combustion (particularly of fuel used for space heating) is a principal source of PCDD/Fs to the atmosphere.

None of the data from any of the sites showed a significant decrease or increase over time. Considering that the data reported here cover a time span of only two years, we consider it unlikely that we would see any change in concentration as a function of time for analytes, such as PCDD/Fs, that are expected to have relatively long atmospheric residence times.

To verify the hypothesis that urban centers are sources of atmospheric PCDD/Fs, we analyzed the relationship between local population (as a surrogate for total combustion in an urban center) and Σ PCDD/F concentration. In addition to the results reported here, several other locations were included in this analysis. This analysis was restricted to the North American region, and only results from large sampling networks were included. The following sources were employed: the Environmental Protection Agency National Dioxin Monitoring Network (NDAMN) which deployed samplers mainly in rural and remote locations around the United States;¹² the California Ambient Dioxin Air Monitoring Program (CADAMP) which collected samples predominantly in heavily populated areas of California;¹⁴ and the Canadian National Air Pollution Surveillance Network (NAPS),¹⁴ which sampled air

throughout Canada. For consistency among the data sets, only data collected in 2002 were used, with the exception of the IADN data reported here.

The plot of the logarithm of the population within a 25-km radius vs. the logarithm of the concentration of Σ PCDD/Fs (in fg/m^3) for the 60 continental sites is shown in Figure 5. A linear regression of these two variables was statistically significant ($P < 0.0001$), indicating that concentrations of Σ PCDD/Fs increase exponentially with the logarithm of the local population. When the local population doubles, the atmospheric Σ PCDD/F concentration more than doubles.

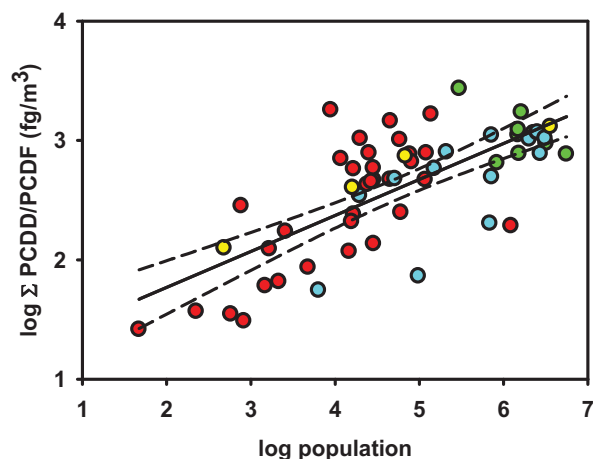


Figure 5. Atmospheric Σ PCDD/F concentrations (fg/m^3) as a function of human population within a 25-km radius of the sampling site in North America ($n = 60$). The black straight line is the linear regression of the equation: $\log(\text{PCDD}/\text{F}) = 0.30 + 1.17 \log(\text{pop})$, and $r^2 = 0.536$. The symbols are color coded as follows: red = National Dioxin Monitoring Network sites, cyan = Canadian National Air Pollution Surveillance Network sites, green = California Ambient Dioxin Air Monitoring Program sites, and yellow = sites reported here. The black dotted lines represent the 95% confidence limits.

Given the evidence discussed here, we suggest that large urban areas and industrialized centers, which are highly populated, act as sources of PCDD/Fs to the atmosphere. Long range transport, together with relatively small local sources,

¹⁴ California Ambient Dioxin Air Monitoring Program (CADAMP). Available at <http://www.arb.ca.gov/aaqm/qmosopas/dioxins/dioxins.htm>

are responsible for the concentrations observed in rural and remote places.

2.h.v. Flame retardants in the Great Lakes atmosphere. Polybrominated diphenyl ethers (PBDEs) are flame retardants used in a variety of commercial products such as furniture, electronics, and textiles. As a result of their heavy use, they have become ubiquitous in the environment.¹⁵ In 2004, concurrent with the European Union ban, the Great Lakes Chemical Corp. voluntarily stopped the production of two of the three commercially available mixtures: Penta-BDE and octa-BDE. The third commercial PBDE product, deca-BDE is not yet regulated in the United States.¹⁶

Because of the importance of these compounds as “emerging” POPs, we added them to IADN in January 2004. Air samples were collected at Cleveland, Chicago, Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point in 2005-2006 to determine the concentrations of PBDEs, 1,2-*bis*(2,4,6-tribromophenoxy) ethane (TBE), decabromodiphenyl ethane (DBDPE), and Dechlorane Plus (DP). The highest mean concentrations of total PBDEs were found at the urban sites in Chicago and Cleveland (65 ± 4 and 87 ± 8 pg/m^3 , respectively). The mean concentrations at the rural sites of Sturgeon Point (SP) and Sleeping Bear Dunes (SB) were 9.2 ± 0.6 pg/m^3 and 8.4 ± 0.8 pg/m^3 , respectively. The lowest Σ PBDE concentrations were found at the remote site of Eagle Harbor (EH) with mean concentrations of 5.8 ± 0.4 pg/m^3 .

BDE-47, 99, 100, and 209 comprised 70-80% of the Σ PBDE mixture in these samples. The patterns of the congener distributions did not show any consistent changes as a function of time and were similar at all sites, except Cleveland. At

most sites, BDE-47 was the most abundant congener, and BDE-99 and 209 were the second or third most abundant. It is widely known that BDE-47 and 99 are markers for the commercial Penta-BDE product, and BDE-209 is a marker for the commercial Deca-BDE product. Since the current United States production is dominated by Deca-BDE, our findings suggest that either BDE-209 is undergoing photolytic degradation in the environment, as suggested by Stapleton et al. in a recent study of house dust¹⁷ or that the patterns we are now seeing are the reflection of both past and current production, use, and disposal of the two mixtures.¹⁸ The low concentrations and few detects of congeners 197 and 201, which are the main degradation products of BDE-209, did not allow us to draw any conclusions about the atmospheric degradation of Deca-209. The different congener pattern found in Cleveland is probably a consequence of a few high concentrations, which were generally characterized by high concentrations of BDE-209.

To further explore the spatiotemporal trends of PBDEs, we focused on two abundant and representative congeners, BDE-47 and 209, which represent the main components of the Penta-BDE and Deca-BDE commercial mixtures. With the exception of Chicago, the atmospheric concentrations of BDE-47 (sum of gas and particle phase concentrations) are decreasing rapidly with half-lives of about 2 years, but the concentration of BDE-209 is not decreasing at any of the five sites; see Figure 6. The much shorter half-life of PBDEs compared to PCBs and PAHs might be the result of the recent widespread ban on the manufacture of some of these flame retardants and efforts by the flame retardant industry to develop alternatives.

¹⁵ Hites, R. A., Polybrominated diphenyl ethers in the environment and in people: A meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, (4), 945-956.

¹⁶ Darnerud, P. O.; Eriksen, G. S.; Johannesson, T.; Larsen, P. B.; Viluksela, M., Polybrominated diphenyl ethers: Occurrence, dietary exposure, and toxicology. *Environmental Health Perspectives* **2001**, *109*, 49-68.

¹⁷ Stapleton, H. M.; Dodder, N. G., Photodegradation of decabromodiphenyl ether in house dust by natural sunlight. *Environmental Toxicology and Chemistry* **2008**, *27*, (2), 306-312.

¹⁸ deBoer, J.; Boer, K. d.; Boon, J. P., Polybrominated Biphenyls and Diphenylethers. *The Handbook of Environmental Chemistry* **2000**, Vol. 3, Part K, 61-95.

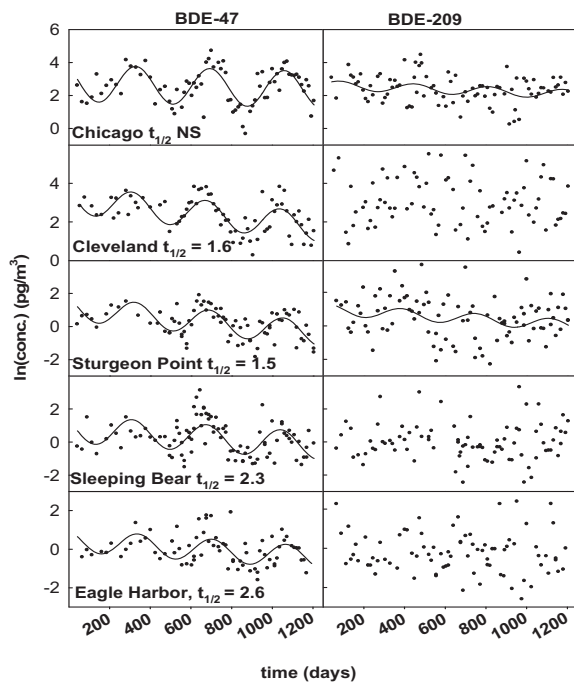
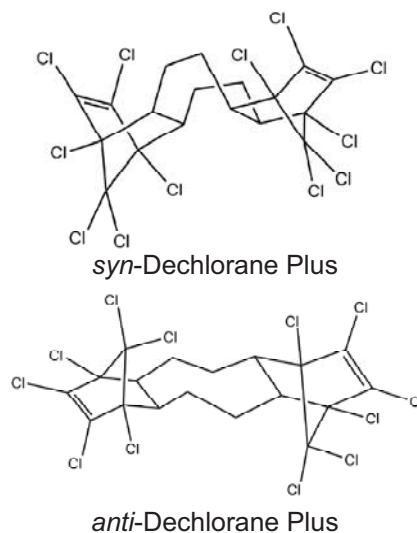


Figure 6. Temporal trends of BDE-47 and BDE-209 (sum of gas and particle phase concentrations) in pg/m^3 at the five IADN sites investigated in this study.

TBE, DBDPE and DP were detected at all sites, but there is insufficient data to determine spatiotemporal trends for these compounds. At all the sites, the concentrations of TBE were generally low and comparable with those of octa-BDE congeners. The highest average TBE concentration was found in Chicago ($1.2 \pm 0.3 \text{ pg}/\text{m}^3$) and the lowest in Eagle Harbor ($0.5 \pm 0.3 \text{ pg}/\text{m}^3$). The concentrations of DBDPE were generally higher than those for TBE, with a maximum average concentration of $22 \pm 13 \text{ pg}/\text{m}^3$ in Cleveland and a minimum average concentration of $1.0 \pm 0.5 \text{ pg}/\text{m}^3$ in Eagle Harbor. In Cleveland, the concentrations of DBDPE roughly tracked those of BDE-209 ($r^2 = 0.325$, $P < 0.001$). This observation suggests that DBDPE and BDE-209 were likely coming from the same sources. We measured the highest average concentration of DP in ambient air from Sturgeon Point ($20 \pm 6 \text{ pg}/\text{m}^3$), followed by Cleveland and Chicago (7.2 ± 1.2 and $2.4 \pm 0.3 \text{ pg}/\text{m}^3$, respectively) and Sleeping Bear Dunes and Eagle Harbor (0.8 ± 0.3 and $0.8 \pm 0.6 \text{ pg}/\text{m}^3$, respectively).

A strong positive correlation ($P < 0.05$) was observed between the geometric mean of the total PBDEs concentration at each site and the human population within a 25 km radius of each site; see Figure 3. The same correlation was significant for BDE-47 and BDE-99 but not for BDE-209, TBE, DP, and DBDPE. It is not surprising that large industrial or urban centers such as Chicago and Cleveland represent sources of PBDEs to the atmosphere, as previously demonstrated for PAHs and PCBs.

2.h.vi. Dechlorane Plus. As an example of our continuing efforts to identify new compounds (emerging pollutants), we will summarize our finding of Dechlorane Plus (DP) in the Great Lakes in the following paragraphs. This compound is a highly chlorinated flame retardant, and we detected and identified it in ambient air, fish, and sediment samples from the Great Lakes region in 2006.¹⁹ The identity of this compound was confirmed by comparing its gas chromatographic retention times and mass spectra with those of authentic material. This compound exists as two gas chromatographically separable conformers (*syn* and *anti*), the structures of which were characterized by one- and two-dimensional proton nuclear magnetic resonance.



¹⁹ Hoh, E.; Zhu, L. Y.; Hites, R. A., Dechlorane plus, a chlorinated flame retardant, in the Great Lakes. *Environ. Sci. Technol.* **2006**, *40*, (4), 1184-1189.

DP was detected in most air samples, even at Eagle Harbor. The atmospheric DP concentrations were higher at the eastern Great Lakes sites (Sturgeon Point and Cleveland) than at the western Great Lakes sites (Eagle Harbor, Chicago, and Sleeping Bear Dunes). At the Sturgeon Point site, DP concentrations once reached 490 pg/m³. DP atmospheric concentrations were comparable to those of BDE-209 at the eastern Great Lakes sites. DP was also found in sediment cores from Lakes Michigan and Erie.¹⁹ The peak DP concentrations were comparable to BDE-209 concentrations in the sediment core from Lake Erie, but were about 20 times lower than BDE-209 concentrations in the core from Lake Michigan. In the sediment cores, the DP concentrations peaked around 1975-1980, and the surficial concentrations were 10-80% of peak concentrations. Higher DP concentrations in air samples from Sturgeon Point, New York and in the sediment core from Lake Erie suggest that DP's manufacturing facility in Niagara Falls, New York, may be a source. DP was also detected in archived fish (walleye) from Lake Erie, suggesting that this compound is, at least partially, biologically available.¹⁹

This finding has been picked up by several other Great Lakes scientists, and at least 26 papers have already cited our Hoh et al. paper. Of course, we have added Dechlorane Plus to the regular list of flame retardants that we now measure in all IADN samples.

2.h.vii. Tree Bark as a passive sampling medium. The use of passive samplers was investigated to expand the spatial coverage of the IADN program. Additional active samplers are expensive and require a permanent site, a site operator, and sample collection over a long time. Polyurethane foam (PUF) or XAD-2 passive samplers have been shown to be effective, although they require deployment for several months. Alternatively, tree bark is an easy and inexpensive monitor of persistent organic pollutants that is easy to collect over a wide spatial range. Previous work has shown that tree bark is a good passive sampler for semi-volatile organic compounds with high K_{oa} values. Such analytes include organochlorine pesticides, PCBs, PAHs, and polychlorinated dibenzo-*p*-

dioxins and dibenzofurans. The following paragraphs demonstrate this approach for two types of polyhalogenated flame retardants.

In our first study, BFRs were measured in 87 tree bark samples from 29 locations in North America.²⁰ The concentrations of total PBDEs ranged from 2.3 to 5700 ng/g lipid weight, with the highest concentrations found around Arkansas. A simple radial dilution model described the distribution of total PBDE concentrations in these samples and indicated the likely sources of these chemicals were emissions from the two BFR manufacturing facilities, operated by Great Lakes Chemicals and Albemarle, located in southern Arkansas. Two unusual BFRs were also detected in tree bark samples collected in Arkansas, suggesting the two manufacturing facilities are the sources of these compounds as well. A polybrominated biphenyl congener (BB-153) was also present in most tree bark samples at low levels relative to the PBDEs.²⁰

Our second tree bark study focused on Dechlorane Plus and other flame retardants in trees from the northeastern United States. Previous work had shown that certain parts of the Great Lakes region are polluted with Dechlorane Plus (DP), a highly chlorinated flame retardant that was used as a replacement for Dechlorane (also known as Mirex). It was suspected that a source of DP to the environment might be its manufacturing facility located in the city of Niagara Falls, New York. To confirm this source location and to determine DP's spatial distribution, 26 tree bark samples were collected in triplicate from the northeastern United States, and the concentrations of DP and several BFRs were measured in these samples.²¹ The highest DP concentrations were >100 ng/g bark in the city of Niagara Falls, dropping rapidly with distance from the potential source; see Figure 7. A simple one-dimensional, Gaussian diffusion model

²⁰ Zhu, L. Y.; Hites, R. A., Brominated flame retardants in tree bark from North America. *Environ. Sci. Technol.* **2006**, *40*, (12), 3711-3716.

²¹ Qiu, X.; Hites, R. A., Dechlorane Plus and Other Flame Retardants in Tree Bark from the Northeastern United States. *Environ. Sci. Technol.* **2008**, *42* (1), 1 31-361.

was used to explain the spatial distribution of DP and to locate the source. The calculated source location was ~7 km away from the DP manufacturing plant in Niagara Falls, New York.²¹

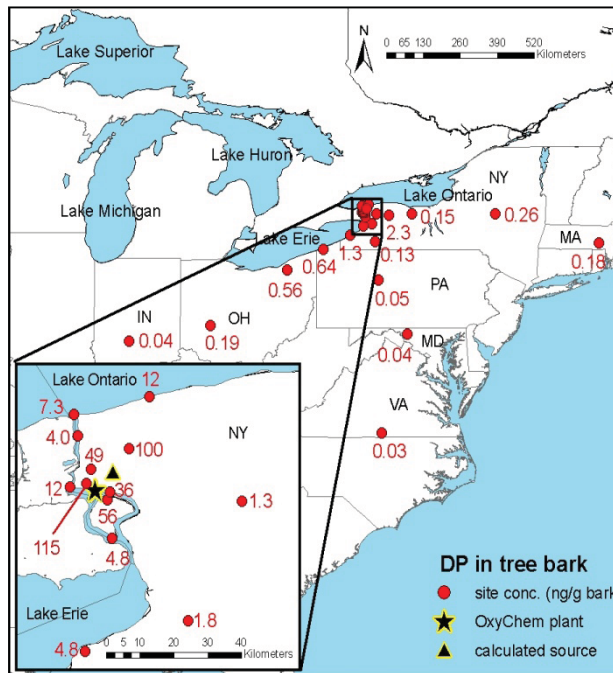


Figure 7. Map of tree bark sampling sites and the corresponding DP concentration (ng/g bark). The star represents the Dechlorane Plus manufacturing plant located in Niagara Falls, New York. The triangle represents the calculated source location.

2.h.viii. Things we have done well in the past.

We are proud of our performance as the United States' principal investigator for the Integrated Atmospheric Deposition Network. We will summarize here some of the items about which we are most pleased.

We have published the results of this project in 47 papers in high quality peer-reviewed journals (such as *Environmental Science and Technology*). These papers have been widely cited, and we know from interactions with our colleagues at other institutions that these papers are having a major effect on the study of atmospheric concentrations of persistent organic pollutants. For example, temperature correction, which we have

demonstrated to be very significant, is now becoming routine.

We have presented these results at about 70 national and international conferences. The latter have included conferences in the Netherlands, Greece, England, France, India, Switzerland, and Sweden. Thus, we are “getting the word out” about this project in high quality forums.

The project has had excellent continuity, which is important when we are determining trends from time series data. In part, this continuity has been due to the participation of Dr. Ilora Basu in the project from its inception. Dr. Basu was first employed by IADN when the project started at the Illinois State Water Survey. When the project moved to Indiana University (IU) in 1994, Dr. Basu came with it. At that time, she transferred and implemented the SOPs at IU, and generally made sure that the post-1994 data was of the same high quality as before. In addition, we have had a rigorous QA/QC program in place during the entire project.

We have reported the data in a timely fashion. For example, all of the data for all of the samples taken in 2007 were reported to the Environmental Protection Agency and to the Canadian database manager by September 2008, and we have already started reporting the 2008 data. Other parts of the project have occasionally been as much as three years late with their data reporting.

The students and post-doctoral associates who have worked on this project have received valuable training in an important area of environmental science. For example, Eunha Hoh is now an assistant professor in the School of Public Health at California State University-San Diego; it is unlikely that she would have had this opportunity if she had not worked on this project. Another example is Stephanie Buehler, who is now with Battelle Memorial Laboratories in Columbus, Ohio; again it is unlikely that she would have had this opportunity if she had not worked on this project.

On an informal basis we have also helped other investigators from around the nation and world

set up laboratories to measure trace levels of POPs in environmental samples. For example, we helped Keri Hornbuckle at the University of Iowa set up an air sampling system and Judith Perlinger at the Michigan Technological University implement analytical methods. We also have provided help to Laura McConnell of the U.S. Department of Agriculture and Staci Simonich at Oregon State University. Our general mode of help has been our willingness to answer questions and to supply copies of our SOPs and other documentation. IADN also has served as a model for a similar network operating in New Jersey called the New Jersey Atmospheric Deposition Network (NJADN) and operated by Rutgers University.

2.i. Special studies and enhancements. In years 2 to 5 of this project we plan to implement additional tasks that are intended to enhance the overall output and status of IADN. Extra personnel have been budgeted to carry out his work. It is our intention to engage in a dialog with GLNPO each year to define exactly what enhancements we will pursue in the following year. The following paragraphs are examples of such enhancements.

2.i.i. Cooperative Science and Monitoring Initiative (CSMI). This program is a joint effort between Canada and the United States to provide the environmental managers of each Great Lake with an enhanced science program that addresses their informational needs. CSMI includes all of the Great Lakes in a five year rotational cycle targeting specific years for intensive field studies. Priorities are identified by the Lakewide Management Plan Management Committees and coordinated through a binational steering committee. In 2010, CSMI will be focused on Lake Michigan. In subsequent years (2011 through 2014), CSMI will focus on Lakes Superior, Huron, Ontario, and Erie.

We have flexibility in our year one budget to collect samples from Lake Michigan in the summer of 2010, with analyses in year 2. In addition we will propose in year 2 to year 5 to collaborate with Keri Hornbuckle at the University of Iowa. Prof. Hornbuckle has provided the fol-

lowing ideas for some IADN project enhancements in years 2 to 5:

Objective 1. To evaluate the impact of spatially distributed sources of POPs in Chicago on the deposition of POPs into Lake Michigan. This objective would require analyzing previously collected air samples for the IADN POPs and modeling of transport and deposition from the 40 sites to Lake Michigan. This objective would include measurements of POPs aboard the *Lake Guardian*.

Objective 2. To evaluate the relative importance of East Chicago air as a source of POPs to Lake Michigan compared to the East Chicago tributary (Indiana Harbor) as a source of POPs to Lake Michigan. This objective would require analysis of previously collected POPs in samples collected in Indiana Harbor and Ship Canal and in the residential areas of East Chicago. This objective could require collection of air and water samples aboard the *Lake Guardian* at sites near East Chicago.

Objective 3. To evaluate the utility of passive air sampling relative to high-volume air samplers for long-term monitoring of POPs at the IADN master sites. The objective would require placement of passive air samplers at the IADN site and measurements of the POPs collected by the two methods. This objective would tie in to our existing program of tree bark measurement at the five United States sites.

Objective 4. To evaluate the spatial distribution of POPs within urban areas. This objective would require the analysis of previously collected air samples from Cleveland (August 2008) for IADN POPs. This objective might include the deployment of passive samplers in other Great Lakes cities, such as Milwaukee, Detroit, and Buffalo.

2.i.ii. Additional chemicals. The IADN chemical list may also be revised and/or expanded in the future depending on available resources, method availability, and the priorities of the program and grantee. In fact, as outlined above, it is our intent to aggressively look at air samples with qualitative tools in order to identify conta-

minants that are present in the air at significant levels but that are not now recognized as important. This is exactly how we found Dechlorane Plus.

At the moment, the most important list of chemicals to be covered is the one (including the recent additions) promulgated by the Stockholm Convention. We now cover all of these chemicals, except toxaphene (too expensive to measure routinely), pentachlorobenzene (which we will add), and perfluorinated sulfonic acid (we do not have the required instrumentation).

We are also interacting with efforts lead by Derek Muir and others to symmetrically look for high production volume chemicals with relatively high lipophilicities. In addition, we will work with the GLNPO fish program to identify new contaminants in the fishes from the Great Lakes.

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[REDACTED]

APPENDICES

A1. List of peer-reviewed publications on IADN from Indiana University

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