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Temporal Trends of Semivolatile Organic Contaminants in Great Lakes Precipitation

MATT F. SIMCIK,^{†,‡} RAYMOND M. HOFF,[§]
WILLIAM M. J. STRACHAN,^{||}
CLYDE W. SWEET,[⊥] ILORA BASU,[‡] AND
RONALD A. HITES^{*,‡}

*School of Public and Environmental Affairs and
Department of Chemistry, Indiana University,
Bloomington, Indiana 47405, Centre for Atmospheric
Research Experiments, Atmospheric Environment Service,
RR#1, Egbert, Ontario, Canada L0L 1N0, National Water
Research Institute, Canada Centre for Inland Waters,
P.O. Box 5050, Burlington, Ontario, Canada L7R 4A6,
and Illinois State Water Survey, 2204 Griffith Drive,
Champaign, Illinois 61820*

Precipitation was sampled around the Great Lakes as part of the Integrated Atmospheric Deposition Network (IADN) from 1991 to 1997. Many of the monthly volume weighted mean concentrations of the analytes have significantly decreased during the last 6 years with first-order half-lives on the order of 3 ± 2 years. There was little, if any, spatial variability in the observed half-lives, suggesting similar loss processes for the various lakes and suggesting that the decrease in precipitation concentrations reflects a regional decrease in environmental levels. The first-order half-lives of organochlorine pesticide concentrations in Great Lakes precipitation were not significantly different than the corresponding atmospheric gas-phase, lake water, and biota half-lives, suggesting that the entire system is at or near long-term equilibrium.

Introduction

The deposition of rain and snow (so-called wet deposition) is a major pathway by which semivolatile organic compounds pollute the Great Lakes. Wet deposition is a particularly important contamination pathway for polychlorinated biphenyls (PCBs), organochlorine pesticides, and polycyclic aromatic hydrocarbons (PAH) (1–10). As a result, the governments of the United States and Canada have recognized the need to measure the wet deposition of toxic substances to the Great Lakes. They have codified this intent in the 1987 amendments of the Great Lakes Water Quality Agreement (Annex 15), which called for the formation of an Integrated Atmospheric Deposition Network to measure wet deposition and air concentrations of several semivolatile organic compounds and trace elements. Subsequently, the U.S. EPA made the IADN program a core activity in their

Great Waters Program, which was mandated by the U.S. Clean Air Act. IADN now has one master station per lake; each station is located in a rural area remote from urban influences. IADN measures the concentrations of 98 PCB congeners, 17 PAH, and 10 organochlorine pesticides in precipitation about 13 times per year at these five master stations.

Many of the organochlorine compounds IADN measures in wet deposition have been banned for years. Thus, their concentrations in many environmental compartments have decreased over time. In particular, polychlorinated biphenyl (PCB) concentrations have decreased in Great lakes fish (11–15), water (16, 17), and air (18, 19). Unfortunately, most of the wet deposition measurements of organic contaminants have been on a short term (7, 8, 10) or on a single year (2–6) basis. In an attempt to determine if the wet deposition of semivolatile organic compounds has decreased at the same rate as concentrations have decreased in fish, water, and air, we have analyzed the long-term IADN precipitation data for PCBs, organochlorine pesticides, and PAH in terms of the temporal distribution of these compounds.

Experimental Methods

The Lake Superior master station is located at Eagle Harbor (47°27'47"N, 88°08'59"W) on the Keweenaw Peninsula of Michigan's Upper Peninsula. Sampling there began in November of 1990. The Lake Michigan master station is located at Sleeping Bear Dunes (44°45'38"N, 86°03'30"W), and it has been in operation since December of 1991. The Lake Huron master station is located on Burnt Island (45°48'30"N, 82°57'00"W), and it has sampled precipitation since February 1992. The Lake Erie master station is located at Sturgeon Point (42°41'34"N, 79°03'20"W), and it has been in operation since December 1991. The Lake Ontario master station is located at Point Petre (43°50'34"N, 77°09'13"W), and it has been in operation since May 1991. Data for the Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point sites are available from their inception through 1997. Burnt Island data are available from its inception through 1994, except for PAH, which are not available at all. Point Petre data are available from its inception through 1996, except for PAH, which are only available for 1995 and 1996.

Precipitation was sampled using MIC automated wet-only samplers (MIC Co., Thornhill, ON) at each of the five IADN master stations. Each sampler consists of a 46 × 46 cm shallow stainless steel funnel connected to either a 30 cm long × 1.5 cm i.d. glass tube (ACE Glass, Vineland, NJ) for the U.S. sampling or a 30 cm long × 2 cm i.d. Teflon tube for the Canadian sampling; both tubes were packed with XAD-2 resin. The sampler was normally covered, but it was opened during a precipitation event, which was sensed by a conductivity grid. This grid was heated to prevent condensation, ice build-up, and prolonged sampling after the end of a precipitation event. The funnel and the interior of the sampler were also heated to melt any snow that fell into the sampler and to keep the XAD-2 tube from freezing. The precipitation flowed by gravity from the funnel through the XAD-2 filled tube and into a large carboy to measure the total precipitation volume. The plumbing from the XAD-2 tube to the carboy was arranged to keep the XAD-2 wet at all times. Because there was no filter in the system, the XAD-2 tube collected both particulate and dissolved phase contaminants from the precipitation. At the three U.S. sites, precipitation was passed through the same XAD-2 cartridge for 28 days regardless of the amount of precipitation that occurred during that period. This sampling strategy was also used at the two Canadian sites after 1994. Prior to this time,

* Corresponding author e-mail: hitesr@indiana.edu.

[†] Present address: Division of Environmental and Occupational Health, School of Public Health, University of Minnesota, Minneapolis, MN 55455.

[‡] Indiana University.

[§] Atmospheric Environment Service.

^{||} Canada Centre for Inland Waters.

[⊥] Illinois State Water Survey.

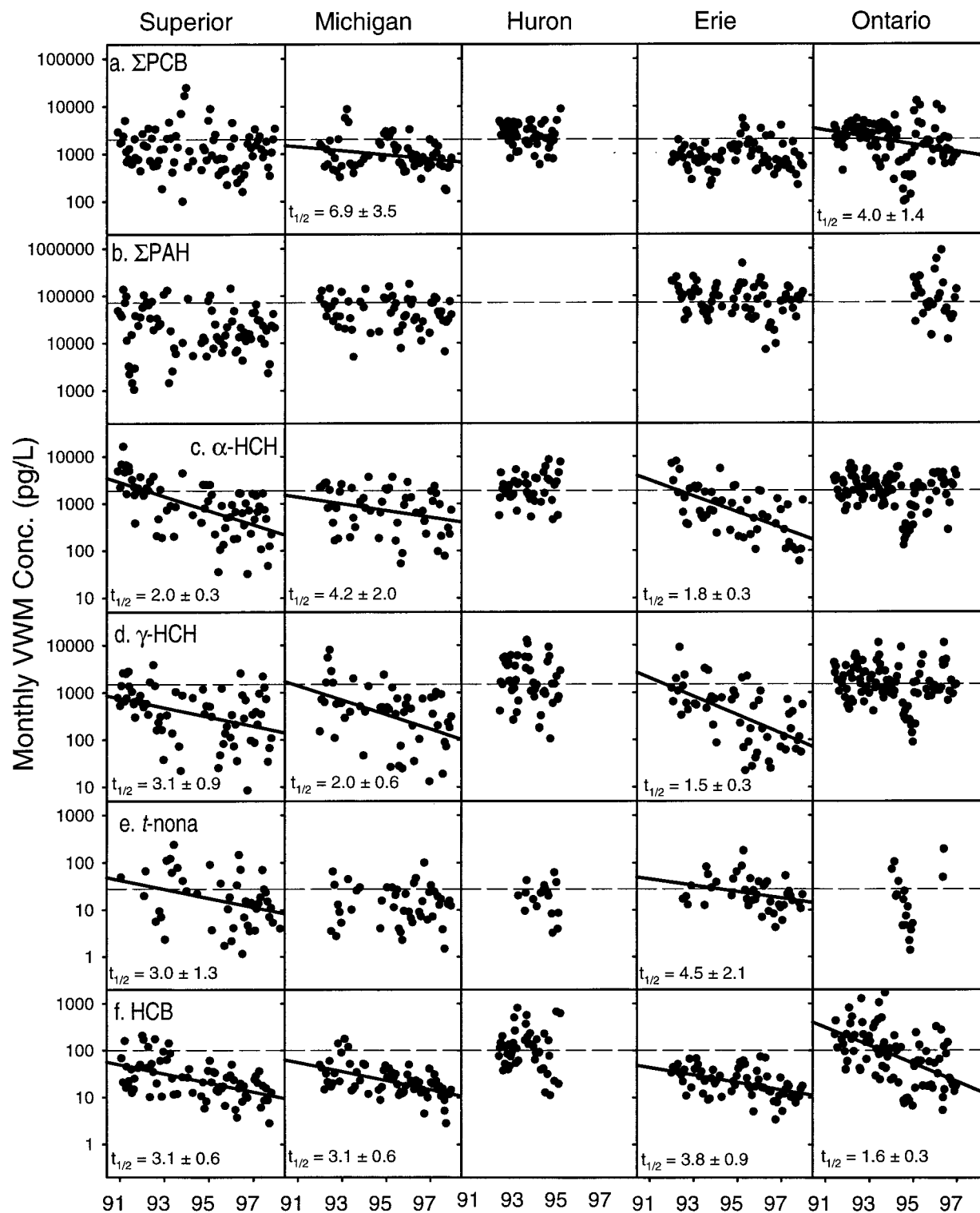


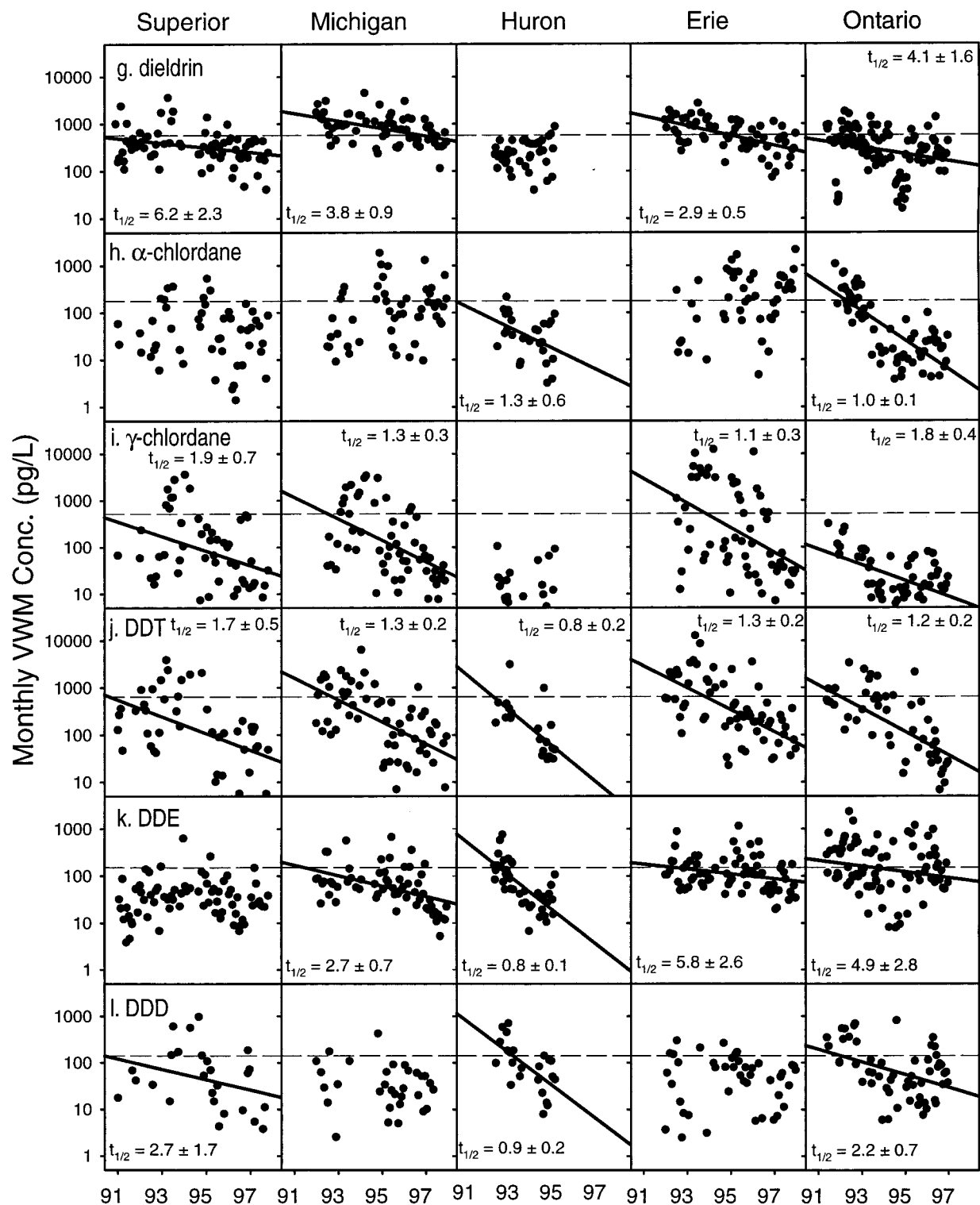
FIGURE 1. Monthly VWM wet precipitation concentrations of (a) Σ PCB, (b) Σ PAH, (c) α -HCH, (d) γ -HCH, (e) *trans*-nonachlor, (f) hexachlorobenzene, (g) dieldrin, (h) α -chlordane, (i) γ -chlordane, (j) DDT, (k) DDE, and (l) DDD near each of the five Great Lakes. The trend

precipitation was integrated for 14 days; in these cases, we composited the data from these samples as 28-day averages.

After return to the laboratory, the United States XAD-2 cartridges were emptied, and the XAD-2 was spiked with surrogate standards and extracted in a Soxhlet apparatus for 24 h using 50% acetone in hexane. The Canadian XAD-2 cartridges were spiked with surrogate standards prior to their deployment in the field. Back in the laboratory, these cartridges were extracted by passing methanol and dichloromethane sequentially through the cartridge. The combined

Canadian eluent was then treated with 3% NaCl solution to separate the aqueous phase. This aqueous phase was back extracted twice with dichloromethane, which was added to the original extract.

The Indiana University surrogate standard consisted of PCB congeners 14, 65, and 166; dibutylchlorodate; and d_{10} -phenanthrene. The Canadian surrogate standard consisted of PCB congeners 30 and 166, δ -hexachlorocyclohexane, and tribromobenzene. In both countries, the extracts were reduced in volume by rotary evaporation, and the solvent



lines indicate significant (> 90% confidence) first-order decreases in concentrations, and the dashed lines indicate the ensemble average from Table 3.

was exchanged to hexane. Sometimes in switching to hexane, two separate phases were created, one of hexane and one of an emulsion. In these cases, the emulsion layer was back extracted twice with hexane, and the organic layer was added to the hexane phase each time; the hexane phase was then back extracted with water. In all cases, the samples were reduced in volume and cleaned up to remove chromatographic interfering compounds by silica column chromatography. The sample was charged to the top of the column and eluted in three fractions. The first fraction used hexane

as the eluent, and it contained the PCBs, DDE, and HCB. The second fraction used 50% hexane in dichloromethane as the eluent, and it contained the remaining pesticides and all PAH. The samples were then reduced under a gentle stream of prepurified nitrogen. In the United States, internal standards were added at this point. The internal standard for PCB analysis consisted of PCB congeners 30 and 204. The PAH internal standard consisted of d_{10} -anthracene, d_{12} -benz[a]anthracene, and d_{12} -perylene. The pesticide internal standard consisted of PCB congeners 65 and 155.

PCB congeners and organochlorine pesticides were determined on a Hewlett Packard 5890 gas chromatograph equipped with an electron capture detector. PAH were determined by gas chromatographic mass spectrometry on either a Hewlett Packard 5989, 5973, or 5971 mass spectrometer by electron impact in the selected ion mode. Detailed information on the Indiana University GC conditions can be found elsewhere (18). In Canada, the GC conditions were: 30 m, 250 μ m i.d., 0.25 μ m film thickness, DB-1 column; programmed from 80 °C (held for 1 min) to 280 °C (held for 5 min) at 3.5 °C per min; carrier gas, He at 1 mL/min; injection port temperature, 220 °C; splitless injection mode with purge vent off for 30 s; detector temperature, 350 °C; and detector make-up gas, N₂ at 29 mL/min.

Several techniques were employed to ensure the highest standards for data integrity. Surrogate recoveries were high for all sites, with those for PCBs ranging from 87 to 97%, those for pesticide ranging from 81 to 85%, and those for PAHs ranging from 52 to 88%. Because of the high surrogate recoveries, the concentrations of analytes were not corrected for surrogate recoveries. Both lab and field blanks were analyzed to ensure that there was no contamination of the samples during sampling or analytical workup in the laboratory. PAH lab blanks averaged less than ~0.8 ng per sample of each PAH analyzed. PAH field blanks averaged less than ~3 ng per sample per PAH. PCB lab blanks averaged less than ~5 ng per sample for Σ PCBs, and field blanks averaged less than ~7 ng per sample for Σ PCBs. Pesticide lab blanks averaged less than ~0.08 ng per sample for each pesticide and field blanks less than ~0.7 ng per sample. Because of the low levels measured in both laboratory and field blanks, the data presented here have not been corrected for blanks.

Results and Discussion

Because all of the precipitation during a given 28-day period was passed through an XAD-2 cartridge, the individual measurements in this study can be considered to be monthly volume weighted mean (VWM) concentrations. VWM concentrations are useful because they minimize the bias of high concentrations observed during short rain events; these high concentrations result from the effective washout of contaminants in the first moments of a precipitation event (20). Annual VWM concentrations with associated uncertainties are given in the Supporting Information. In this case, the annual VWM concentration is the total mass of analyte for a given year divided by the total volume of rain collected in that year. The uncertainties in the VWM concentrations are calculated according to the method of Hawley et al. (21), who gives the standard error as

$$SE = \frac{(\sum (v_i / \sum v_i)^2 \text{var}(c_i))^{1/2}}{\sqrt{n}} \quad (1)$$

where v_i is the rain volume in sample i (in L), c_i is the analyte concentration in that sample (in pg/L), and n is the number of samples. The variances of the concentrations were calculated from the variance of duplicate or triplicate samples that were measured from side-by-side samplers in the field (21).

We present results here for 12 analytes: Σ PCBs (the sum of 98 congeners), Σ PAH [sum of acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, retene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[e]pyrene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenzo[a,h]anthracene, benzo[ghi]perylene, and coronene], α - and γ -HCH, *trans*-nonachlor, hexachlorobenzene (HCB), dieldrin, α - and γ -chlordane, DDT, DDE, and DDD. The monthly VWM concentrations for these 12 analytes are shown as a function

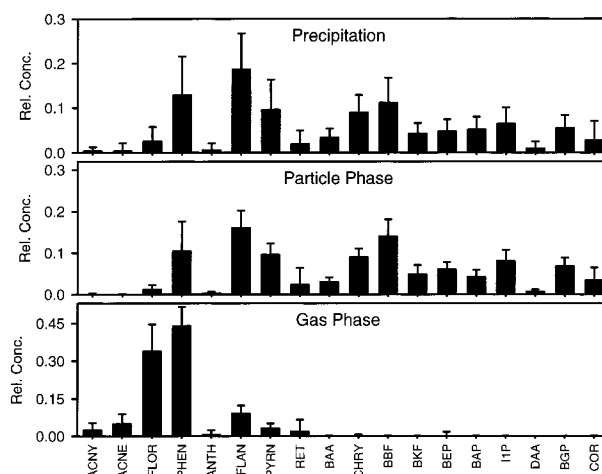


FIGURE 2. Normalized PAH profiles for precipitation, particle, and gas phases near Lake Superior, Michigan, and Erie. Bars represent mean fraction of total \pm 1 SD.

of sampling date in Figure 1 for each of the five Great Lakes. Note that Figure 1 uses a logarithmic scale for the concentrations and that the scatter in these data is high. This latter feature is surprising given that the equivalent gas-phase concentrations show very much less scatter (18, 22). The reason for this large observed variability in precipitation concentrations, compared to other atmospheric compartments, is not clear.

Temporal Trends. Many PCB congeners and chlorinated pesticides have shown significant decreases in atmospheric gas-phase concentrations at these same IADN sites over the last 6 years (19, 22). To determine if these compounds showed similar trends in their precipitation concentrations, we regressed the logarithm of their monthly VWM concentrations vs time. Assuming first-order kinetics, the slope of the regression line (after correction to natural logarithms) divided into $\ln(2)$ gives a half-life. The error of the regression establishes the error of the half-life. The regressions for those compounds and locations for which they were significant at the 90% confidence limit are shown in Figure 1 as straight lines. Except for Lake Huron, for which the data set spanned only 3 years, 32 out of the 48 remaining data sets showed statistically significant half-lives. This demonstrates the power of this regression analysis when one has a large number (up to 121) of samples.

The observed half-lives for the gas-phase concentrations of Σ PCBs near Lakes Michigan and Erie were about 3 years (19). The monthly VWM concentrations of Σ PCB in precipitation collected near Lakes Michigan and Ontario showed half-lives of 6.9 ± 3.5 and 4.0 ± 1.4 years, respectively (see Figure 1a). Given the substantial errors (about $\pm 50\%$) associated with all of these values, we conclude that the precipitation and gas-phase half-lives of Σ PCB are all about the same, ranging between about 2 and 6 years. Lake Superior did not show a significant decrease in gas-phase PCB concentrations, and it does not show one in precipitation concentrations either. For reasons that are not clear, Lake Erie showed a half-life of 3.3 ± 1.0 years for Σ PCB gas-phase concentrations, but it does not show a significant decrease in precipitation concentrations.

Unlike PCBs and many organochlorine pesticides, PAH have continuing sources, and one would not expect to see a significant decrease in PAH precipitation concentrations. This supposition is born out for the PAH in precipitation collected near Lakes Superior, Michigan, and Erie; see Figure 1b. (There are not enough data near Lake Ontario to allow us to draw any conclusions.) In contrast to precipitation, which shows no significant decrease in Σ PAH concentrations,

TABLE 1. Comparison of First-Order Half-Lives (Years) in Great Lakes Precipitation and Atmospheric Gas-Phase^a

	Lake Superior		Lake Michigan		Lake Huron		Lake Erie		Lake Ontario	
	precipitation	gas	precipitation	gas	precipitation	gas	precipitation	gas	precipitation	gas
ΣPCBs	NS	NS	6.9 ± 3.5	2.8 ± 0.7	NS		NS	3.3 ± 1.0	4.0 ± 1.4	
ΣPAH	NS	3 to 8	NS	3 to 9			NS	2 to 7	NS	
α-HCH	2.0 ± 0.3	2.9 ± 0.3	4.2 ± 2.0	2.7 ± 0.4	NS	NS	1.8 ± 0.3	4.9 ± 1.2	NS	5.0 ± 0.8
γ-HCH	3.1 ± 0.9	3.4 ± 0.5	2.0 ± 0.6	2.2 ± 0.5	NS	NS	1.5 ± 0.3	3.2 ± 0.7	NS	7.3 ± 2.5
trans-nona	3.0 ± 1.3	NS	NS	3.5 ± 1.5	NS	NS	4.5 ± 2.1	NS	NS	9.2 ± 4.4
HCB	3.1 ± 0.6	12 ± 5	3.1 ± 0.6	3.3 ± 0.5	NS	NS	3.8 ± 0.9	6.8 ± 1.2	1.6 ± 0.3	
dieldrin	6.2 ± 2.3	5.2 ± 2.2	3.8 ± 0.9	1.5 ± 0.7	NS	NS	2.9 ± 0.5	2.9 ± 0.7	4.1 ± 1.6	4.8 ± 1.2
α-chlordane	NS	NS	NS	NS	1.3 ± 0.6	NS	NS	4.9 ± 1.2	1.0 ± 0.1	6.2 ± 1.8
γ-chlordane	1.9 ± 0.7	NS	1.3 ± 0.3	3.2 ± 1.3	NS	NS	1.1 ± 0.3	3.2 ± 0.7	1.8 ± 0.4	6.5 ± 2.1
DDT	1.7 ± 0.5	2.5 ± 0.6	1.3 ± 0.2	2.3 ± 0.6	0.8 ± 0.2	NS	1.3 ± 0.2	2.7 ± 0.8	1.2 ± 0.2	NS
DDE	NS	5.1 ± 1.3	2.7 ± 0.7	2.6 ± 0.5	0.8 ± 0.1	NS	5.8 ± 2.6	7.1 ± 3.0	4.9 ± 2.8	9.2 ± 4.2
DDD	2.7 ± 1.7	2.7 ± 0.6	NS	2.6 ± 0.8	0.9 ± 0.2	NS	NS	1.8 ± 0.4	2.2 ± 0.7	8.0 ± 3.9

^a All uncertainties represent standard errors. All half-lives presented are significant at the $p < 0.10$ level; pesticide half-lives in air from Cortes et al. (22), PCB half-lives in air from Simcik et al. (19), and PAH half-lives in air from Cortes et al. (23).

some of these compounds did show significant decreases in their atmospheric gas-phase concentrations, with half-lives ranging from 2 to 9 years at each of the U.S. IADN sites (23). PAHs, however, are present in the atmosphere in both the gas and particle phases, and, in fact, it was only the gas-phase PAH concentrations that showed a decrease with time. The particle-bound PAH concentrations showed no decrease with time just like the PAH in precipitation showed no decrease. A comparison of the PAH profiles (see Figure 2) shows that the PAH distribution in precipitation resembles ($r^2 = 0.925$) that of the particle phase but not that of the gas phase ($r^2 = 0.085$). This implies that precipitation is an effective scavenger of the particle-phase PAH in the atmosphere, and since the particle-phase PAH concentrations did not decrease with time (23), the PAH concentrations in precipitation did not decrease with time either. The temporal observations reported here are for total PAHs, but the same trends were observed for each of the individual PAH.

The monthly VWM concentrations for most of the organochlorine pesticides exhibited significant half-lives for most of the sites (see Figure 1c-l). With the exceptions of Lake Huron and α-chlordane, the observed half-lives in VWM precipitation concentration of the pesticides averaged 2.7 ± 1.4 years. Of those pesticides that exhibited significant decreases in concentration, the half-lives were similar at the various sites (see Figure 1). This spatial homogeneity in the rate at which pesticide concentrations decrease in precipitation suggests that similar loss processes are active over the entire Great Lakes region and that there has been a regional decrease in environmental levels of these compounds. To further explore this hypothesis, it is helpful to compare the observed half-lives in precipitation to that of other media from around the Great Lakes.

The concentration half-lives for these compounds observed in precipitation are compared to atmospheric gas-phase concentration half-lives in Table 1. With a few exceptions, whenever there is a significant half-life for both the precipitation and gas-phase concentrations, the half-lives agree with 95% confidence. This similarity in half-lives suggests that the same loss process is acting on these two atmospheric media.

These precipitation half-lives can also be compared to a few measurements in Great Lakes water. Jeremiason et al. (16) reported a half-life of 3.5 years for PCBs in Lake Superior water (dissolved phase), and in a later study, Jeremiason et al. (24) reported a half-life of 2.7 years for PCBs in settling particles in Lake Superior. Pearson et al. (17) reported a half-life of 8.9 years for PCB in water (dissolved phase) from Lake Michigan. These values agree well with the PCB gas-phase half-lives (about 3 years) from the IADN study (19) and with

the precipitation half-lives (6.9 ± 3.5 near L. Michigan and 4.0 ± 1.4 years near Lake Ontario). The only available half-life for dissolved phase pesticide concentrations was obtained for α-HCH and γ-HCH in Lake Ontario from Ridal et al. (25). The half-lives calculated from these reported concentrations are 2.6 ± 0.1 years for α-HCH and 3.5 ± 0.1 years for γ-HCH. These values agree well with the observed half-lives of α-HCH in precipitation from around the Great Lakes which exhibited a range of 1.8 to 4.2 years and γ-HCH in precipitation which exhibited a range of 1.5 to 3.1 years (see Table 1).

Many more long-term studies have been conducted on biota. Table 2 presents half-lives of PCBs and organochlorine pesticides in herring gull eggs, lake trout, and spottail shiners from around the Great Lakes. In general, the PCB concentration half-lives range from 2 to 35 years, but most reported values are on the order of 8 ± 2 years. These half-lives agree with the observed precipitation half-lives. The observed half-lives for organochlorine pesticides in biota range from 2 to 37 years, but again most are on the order of 7 ± 3 years. The significant precipitation half-lives of the same compounds ranged from 1 to 7 years (see Table 1).

The similarity of the concentration half-lives measured in Great Lakes precipitation, air, water, and biota suggest that most of these hydrophobic organic contaminants are at a long-term equilibrium. Based on these data, we suggest that this equilibrium extends not just across the air–water interface, as indicated by Mackay and Bentzen (26) and Hillery et al. (27), but among all the compartments. This means that the deposition rate from the atmosphere to the lakes for these compounds is, over an annual cycle, about equal to the evaporation of these compounds from the lakes to the atmosphere and that the rate at which equilibrium is achieved between the air and precipitation and between the water and biota is also rapid, probably on the order of a few months.

Spatial Trends. In an attempt to isolate any spatial differences, we did the following: First we, averaged all monthly concentrations for a given compound for a given location and calculated the associated standard error of that concentration; this gave 59 such averages and errors (see Table 3). Since we are averaging over all years, it is likely that the volumes of the rain events will average to a similar value, and thus, we can assume that the arithmetic mean of the concentrations is about the same as their volume weighted mean. Second, we calculated the mean of the average concentrations by averaging across the (usually) 5 locations; this is an ensemble average, also depicted by the dashed lines in Figure 1. In this case, we calculated the standard error by taking the square root of the sum of the squares of the individual errors divided by the square root of the number of locations. These averages and errors are given in Table 3.

TABLE 2. Temporal Trends from Biota around the Great Lakes^a

	lake	half-life (yr)	time frame	ref		lake	half-life (yr)	time frame	ref
PCBs in HGE	Superior	6	1974–1983	(28)	DDE in HGE	Superior	3–4	1974–1983	(28)
	Superior	6–10	1979–1996	(29)		Superior	15–22	1979–1996	(29)
	Michigan	~12	1979–1996	(29)		Michigan	NS	1979–1996	(29)
	Huron	8–13	1979–1996	(29)		Huron	~14	1979–1996	(29)
	Erie	7–16	1979–1996	(29)		Erie	7–37	1979–1996	(29)
PCBs in LT	Ontario	7 ± 1	1979–1996	(29)	dieldrin in HGE	Ontario	10–11	1979–1996	(29)
	Superior	7	1977–1990	(30)		Ontario	22 ± 8	1977–1993	(31)
	Michigan	6	1977–1990	(30)		Superior	NS	1974–1983	(28)
	Huron	8	1977–1990	(30)		Ontario	6 ± 1	1981–1992	(32)
	Erie	35	1977–1990	(30)	dieldrin in LT	Superior	35	1977–1990	(30)
PCBs in SS	Ontario	7 ± 1	1977–1993	(31)		Michigan	12	1977–1990	(30)
	Superior	NS	1975–1990	(14)		Huron	7	1977–1990	(30)
	Huron	NS	1975–1990	(14)		Erie	6	1977–1990	(30)
	Erie	2–6	1975–1990	(14)		Ontario	9	1977–1990	(30)
	Ontario	3–7	1975–1990	(14)	HCB in HGE	Ontario	10 ± 1	1977–1993	(31)
DDT in LT	Superior	4	1977–1990	(30)		Superior	4–9	1974–1983	(28)
	Michigan	5	1977–1990	(30)		Ontario	4 ± 1	1981–1992	(32)
	Huron	5	1977–1990	(30)		Ontario	5 ± 1	1977–1993	(31)
	Erie	12	1977–1990	(30)		Superior	NS	1974–1983	(28)
	Ontario	8	1977–1990	(30)	α-chlordane in HGE	Ontario	2 ± 1	1981–1992	(32)
α-HCH in HGE	Ontario	NS	1977–1993	(31)		Superior	12 ± 2	1977–1993	(31)
	Superior	NS	1974–1983	(28)		Superior	NS	1974–1983	(28)
	Ontario	4 ± 0.2	1977–1993	(31)		Ontario	2 ± 16	1981–1992	(32)
						Ontario	9 ± 2	1977–1993	(31)

^a HGE = herring gull eggs, LT = lake trout, SS = spottail shiner.TABLE 3. Site Specific Averages (in pg/L) and Ensemble Averages for All IADN Analytes^a

	Superior			Michigan			Huron			Erie			Ontario			ensemble mean ± SE
	mean ± SE	<i>t</i>		mean ± SE	<i>t</i>		mean ± SE	<i>t</i>		mean ± SE	<i>t</i>		mean ± SE	<i>t</i>		
PCB	2011 ± 356	0.08		1300 ± 166	-2.39	2794 ± 221	2.57			1138 ± 111	-3.29		2635 ± 215	2.10		1976 ± 229
PAH	32 220 ± 3820	-2.63		56 160 ± 5070	-1.41					102 500 ± 9421	0.82		147 800 ± 37 440	1.49		84 670 ± 19 560
α-HCH	1750 ± 288	-0.18		1154 ± 135	-2.57	2551 ± 259	2.17			1318 ± 227	-1.58		2305 ± 139	1.89		1816 ± 219
γ-HCH	694 ± 95	-2.89		801 ± 182	-2.10	2748 ± 401	2.84			803 ± 187	-2.08		2088 ± 196	2.16		1427 ± 235
<i>t</i> -nona	34 ± 7	0.63		19 ± 3	-1.16	22 ± 4	-0.72			30 ± 5	0.26		34 ± 12	0.45		28 ± 7
HCB	37 ± 5	-2.31		30 ± 4	-2.60	167 ± 27	1.91			26 ± 2	-2.78		222 ± 49	2.28		96 ± 25
dieldrin	478 ± 64	-1.05		993 ± 100	3.55	265 ± 26	-4.49			720 ± 64	1.63		408 ± 35	-2.28		573 ± 63
α-chlor	82 ± 16	-2.15		231 ± 50	0.92	50 ± 9	3.07			374 ± 65	2.66		126 ± 23	-1.03		173 ± 39
γ-chlor	354 ± 98	-0.51		458 ± 106	0.03	21 ± 6	-2.61			1384 ± 339	2.47		44 ± 8	-2.47		452 ± 165
DDT	470 ± 119	-0.54		555 ± 124	-0.11	351 ± 154	-1.02			1023 ± 252	1.49		488 ± 100	-0.48		577 ± 159
DDE	53 ± 10	-3.36		96 ± 16	-1.52	112 ± 23	-0.83			162 ± 22	0.70		274 ± 38	3.00		139 ± 24
DDD	133 ± 45	-0.12		221 ± 166	0.42	155 ± 39	0.12			73 ± 11	-0.88		139 ± 25	-0.06		144 ± 80

^a *t*-values in bold are significant with 95% confidence; those in bold and underscored are significant at 99% confidence.

Third, we calculated a *t*-test value for each of the 59 averages to determine if the concentration for that location and compound were significantly above or below the ensemble average; see Table 3. Using a critical *t*-test value of ± 1.96 for 95% confidence and ± 2.58 for 99% confidence, we have marked the significantly high and low average concentrations in Table 3.

ΣPCB precipitation concentrations are lower than average near Lakes Michigan and Erie and higher than average near Lakes Huron and Ontario. This is surprising given that the watershed of Lakes Erie and Ontario are both highly populated, usually an indication of high PCB concentrations. ΣPAH concentrations were lower than average near Lake Superior, which is not surprising given the slight industrialization in the watershed of this lake. The HCHs and HCB concentrations were generally higher than average near Lakes Huron and Ontario but lower than average at the other locations. Perhaps this is a result of Canada's continuing use of γ-HCH (lindane) as a pesticide. It is not clear why the HCB concentrations in precipitation would be higher than average near Lakes Huron and Ontario. The concentrations of dieldrin and the chlordanes were generally above average in precipitation collected near Lake Erie and to some extent near Lake Michigan but below average at the other locations. The

cause of this effect is not clear. All of the DDT related compounds were close to their average concentration except for DDE, which was below average near Lake Superior and above average near Lake Ontario. Perhaps this difference relates to the different historical uses of DDT in these two regions.

Looking at these data by lake, we see that the concentrations in precipitation collected near Lakes Superior and northern Michigan were often significantly below average and rarely above average, but the concentrations at the other locations were often above average. This is expected given the low levels of anthropogenic activity near Lakes Superior and northern Lake Michigan and the high levels near Lakes Erie and Ontario. It is surprising that the samples collected near Lake Huron show that three compounds have above average concentrations despite this particular sampler being located in a remote part of this lake's watershed.

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Supporting Information Available

The annual volume weighted mean concentrations of Σ PCBs, Σ PAH, and 10 organochlorine pesticides in precipitation collected near each of the five Great Lakes is available free of charge via the Internet at <http://pubs.acs.org>.

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