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Temporal Trends in Gas-Phase Concentrations of Chlorinated Pesticides Measured at the Shores of the Great Lakes

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Multiple regression was used to examine the temperature dependence and to elucidate temporal trends of atmospheric gas-phase partial pressures of 10 organochlorine pesticides at five sites near the Great Lakes. The relationship of temperature to gas-phase partial pressures was examined using the Clausius−Clapeyron equation, and environmental phase-transition energies were calculated for each of the pesticides. A first-order rate constant for the decline in gas-phase partial pressures was estimated from the regression, and corresponding regional atmospheric half-lives were determined. The atmospheric half-lives of the hexachlorocyclohexanes ranged from 2.2 yr for γ-HCH at Lake Michigan to 7.3 yr for γ-HCH at Lake Ontario. The half-life for hexachlorobenzene ranged from 3.3 yr at Lake Michigan to 12 yr at Lake Superior. The half-life for *p,p*′-DDT was less than 3 yr at Lakes Superior, Michigan, and Erie. A decreasing trend for chlordanes could only be discerned at Lakes Michigan, Erie, and Ontario, where half-lives ranged from 3.2 yr for γ-chlordane at Lake Michigan and Lake Erie to 9.2 yr for *trans*-nonachlor at Lake Ontario. Using these half-lives and atmospheric concentrations, virtual elimination dates were estimated for the pesticides in the atmosphere. These virtual elimination dates ranged from about 2010 for *p,p*′-DDT to about 2060 for hexachlorobenzene. This study provides evidence that regulatory controls on pesticides have been effective in reducing the concentration of organochlorine pesticides in the environment.

Introduction

The widespread use of environmentally persistent, chlorinated organic pesticides since the 1940s is responsible for the relatively high levels of these compounds still found in many environmental compartments. Although the use of these pesticides has been banned or restricted, their presence in the Laurentian Great Lakes remains a concern, and research suggests that long-range atmospheric transport and deposition are responsible for much of the current contamination (*1*−*3*).

To quantify and monitor the atmospheric deposition of toxic organic compounds to the Great Lakes, the United States and Canada operate air sampling sites on the shores of each lake; this set of sampling sites is collectively known as the Integrated Atmospheric Deposition Network (IADN). It was mandated by the 1987 amendment to the Great Lakes Water Quality Agreement of 1978 (*4*), and it has been in operation for over 7 yr. The data obtained in this long-term study provide a unique opportunity to explore temporal trends in atmospheric, gas-phase concentrations of organochlorine pesticides near a limnetic environment. This paper examines the temporal behavior of the following organochlorine pesticides: *p,p*′-DDT, *p,p*′-DDD, *p,p*′-DDE, α- and γ-hexachlorocyclohexane (HCH), hexachlorobenzene (HCB), α- and γ-chlordane, *trans*-nonachlor, and dieldrin. The period covered by this study is from November 1990 to January 1996, with the data available for each site ranging from 3 to 5 yr.

Experimental Section

Sampling Methodology. Figure 1 shows the location of the five IADN sampling stations that provided data in this study. Sites were chosen to be representative of the regional atmospheric environment near the Great Lakes, while minimizing influence from local pollution sources. In addition to air samplers, each site is equipped with a 10 m tall meteorological tower that records average hourly values of air temperature, wind speed, wind direction, and relative humidity. In addition, solar radiation and total precipitation are measured hourly at each site.

A summary of the sampling and analytical procedures is presented here, but full details are reported elsewhere (*5, 6*). Although Indiana University and the Atmospheric Environment Service used similar methodology, there were some important differences. At the U.S. sites, air was pulled through a modified Anderson high-volume air sampler (General Metal Works, model GS2310) at a rate that gave an 820 m^3 sample in 24 h. Sampling events occurred every 12 days. Particles were collected on quartz fiber filters (Whatman QM-A), and gas-phase organic compounds were collected on XAD-2 (Sigma, Amerlite 20−60 mesh) resin. Prior to May 1992, polyurethane foam was used to collect gas-phase compounds.

At the Canadian sites, a General Metal Works PS-1 high-volume sampler was used to collect air volumes of approximately 350 m^3 over a 24-h period. The sample head employed a 10.2 cm diameter glass fiber filter (GFF, Gelman A/E Microfiber) for particle collection followed by a 7.5 cm × 6.2 cm diameter polyurethane foam (PUF, Levitt Safety) plug for vapor absorption. Sampling events occurred every 6 days through April 1994, when the schedule was changed to every 12 days.

Analytical Methodology at Indiana University. The XAD-2 resin was Soxhlet extracted using 50% hexane in acetone for 24 h. The extract was reduced by rotary evaporation, exchanged to hexane, and then fractionated on 3.5% w/w water-deactivated silica gel to remove interferences. Hexane was used to elute HCB and DDE. Subsequent elution with 50% hexane in dichloromethane was used to collect the remaining pesticides. The final extracts were concentrated under a stream of nitrogen and spiked with quantitation standards prior to gas chromatographic analysis. Analysis was performed using a Hewlett-Packard 5890 gas chromatograph with an ^{63}Ni electron capture detector in splitless

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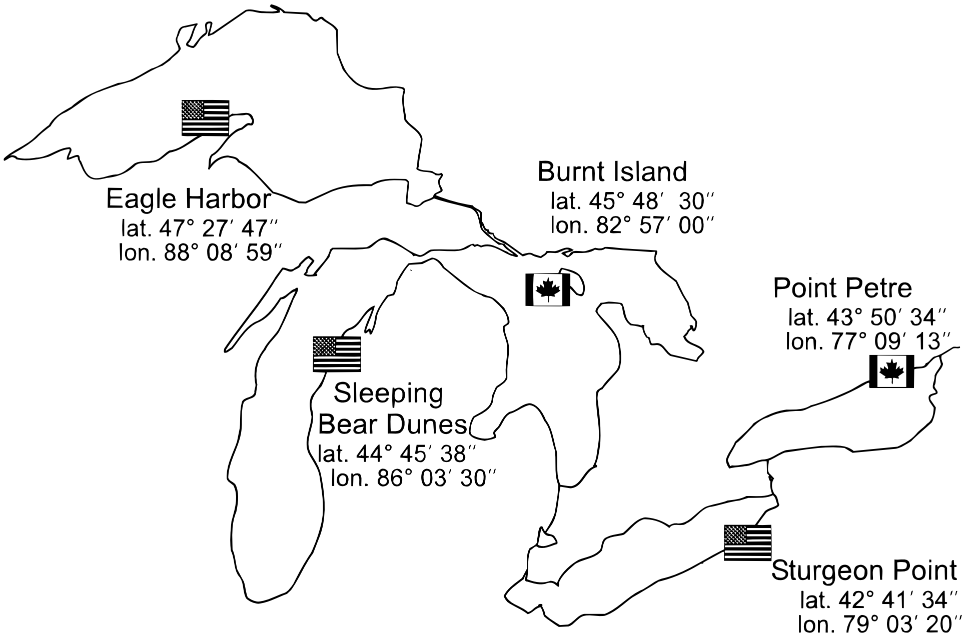

FIGURE 1. Location of primary IADN sampling stations, in latitude and longitude. U.S. and Canadian sites are indicated by their respective flags.

injection mode. Separation was achieved using 30 m × 0.25 mm i.d. (film thickness 0.25 μm) DB-5 columns until August 1994. Since then, 60 m × 0.25 mm i.d. (film thickness 0.10 μm) DB-5 columns have been used.

Extensive quality control was performed to monitor the analytical process (*7*). Extraction efficiencies were monitored by including a matrix spike for all pesticides with each extraction batch (approximately 10 samples) and a surrogate standard (added prior to extraction) in each sample. Average matrix spike recoveries were between 70% and 100% for all pesticides with standard deviations of approximately 20% or less (*8*). The primary exception was DDT, which had a standard deviation of approximately 30%. The average recovery of the surrogate standard was 102%, and no recovery correction was performed. Site-specific and matrix-specific field blanks were collected, and they were usually less than 20% of the sample mass. Laboratory blank values were below the method detection limit, and blank corrections were not performed.

Analytical Methodology at Atmospheric Environment Service. The PUF was Soxhlet extracted using hexane for 24 h, and the extract was then dried using anhydrous granular sodium sulfate (12−60 mesh) and filtered (Whatman glass-fiber, 934-AH). Volume reduction and exchange into isooctane was performed using either rotary evaporation followed by nitrogen evaporation or by closed-cell concentrator procedures. Florisil column chromatography (60−100 mesh, calcined at 600 °C and then deactivated with 3% w/w water) was used to remove interferences and to fractionate the sample into three fractions: The first fraction (eluted with hexane) contained HCB, *p,p′*-DDE, *trans*-nonachlor (partial), and *p,p′*-DDT (partial). The second fraction (eluted with 15% dichloromethane in hexane) contained α- and γ-HCH, α- and γ-chlordane, *p,p′*-DDD, *trans*-nonachlor (partial), and *p,p′*-DDT (partial). The third fraction (eluted with 60% dichloromethane in hexane and then dichloromethane alone) contained dieldrin. The final fractions were concentrated by nitrogen evaporation, accurately adjusted to a volume of 1 cm^3, and then transferred to automatic sampler vials. Analysis was performed using a Hewlett-Packard 5890 gas chromatograph equipped with dual ^{63}Ni electron capture detectors and dual heated splitless/split injection ports. Column lengths were 30 m (1990 samples) or 60 m; in both cases, the column inner diameters were 0.25 mm, the film thickness was 0.25 μm, and the stationary phase was DB-5 (J & W Scientific).

To provide confirmatory analysis and to enhance separation for certain of the coeluting compounds on the DB-5 column, a 30 m × 0.25 mm i.d. (film thickness 0.25 μm) DB-17 column was also used. Splitless-mode injections of 1 μL (purge on at 2.0 min) were made separately onto both columns using an automatic sampler (HP 7673 series). Ultra-high-purity (UHP) helium (Praxair) was used as the carrier gas in constant-pressure mode, with initial column flow rates of approximately 1.3 mL/min. The injection port and detector were held at 200 and 350 °C, respectively. The detector makeup gas was UHP nitrogen (Praxair) at 70 mL/min. External standard calibrated methods were used for quantitation.

Extraction efficiencies were monitored on an “in-batch” basis by including a matrix spike with each extraction batch (approximately six samples). The matrix spike involved the full range of the organochlorine pesticides to give matrix loadings representative of those found in actual air samples. Recoveries of these target species consistently ranged from 60 to 110%. Data for those samples with observed processing anomalies (for example, volume reduction to dryness) were rejected. No attempt was made to apply recovery corrections to data for “valid” samples. Laboratory extraction blanks were also run with every second batch of samples to track possible contamination issues. Matrix-specific field blanks were also regularly collected and analyzed as part of the regular sample stream. Depending upon the analyte, the levels in the field blanks were generally well below those found in the “real” samples. For the purposes of this paper, no attempt has been made to correct the data for the matrix blank contribution, although the IADN quality assurance program plan (QAPP) does recommend such a procedure (*9*).

Data Analysis. The period of study varied from site to site. At Burnt Island, data were available from January 1992 to December 1994. At Point Petre, data from January 1990 through December 1994 were used. Data from December 1991 to January 1996 were used for Sleeping Bear Dunes and Sturgeon Point, with the chlordane data starting in July 1992. Data from November 1990 to January 1996 were used for

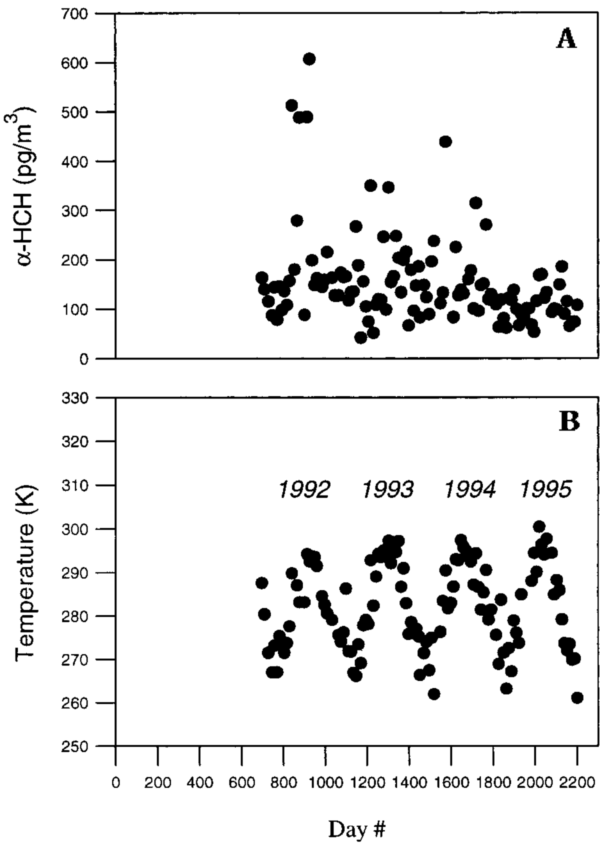

FIGURE 2. Atmospheric concentrations of α-HCH (A) and air temperature (B) at Sturgeon Point from 1992 through 1995. Each point represents a 24-h sampling period.

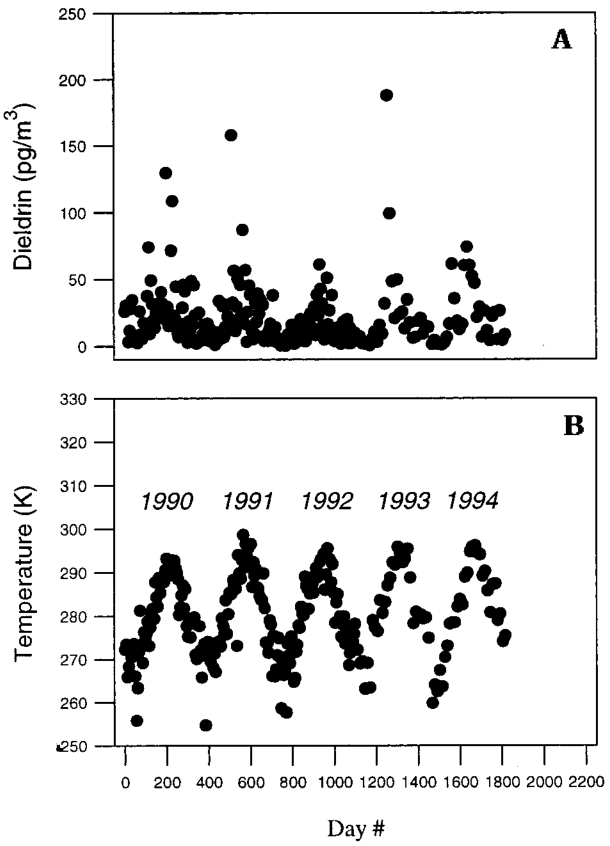

FIGURE 3. Atmospheric concentrations of dieldrin (A) and air temperature (B) at Point Petre from 1990 through 1994. Each point represents a 24-h sampling period.

Eagle Harbor, again with the chlordane data starting in July 1992.

Because the filters used to collect particles had been composited prior to analysis in order to enhance detectability, the particles portion of the sample could not be included in the data analysis, which relied on the high temporal resolution of the temperature and analytical data. This is not a problem for HCB and α- and γ-HCH, where the particle-phase fraction was less than 5% in all seasons except winter, when the ratio was less than 10%. For *trans*-nonachlor and α- and γ-chlordane compounds, this ratio was less than 10% in the nonwinter seasons and less than 22% during the winter months. For dieldrin and the DDT compounds, the ratio was generally less than 25% in all seasons but has occasionally reached 50% in the winter season.

Results from duplicate and triplicate samples were averaged, and a single value was used for all subsequent calculations. Concentrations in air were determined by dividing the total mass measured by the total air volume collected during the sampling period. Additionally, partial pressures were calculated using the ideal gas law, which incorporates the molecular weight of the compound and the average air temperature during the 24-h period. Nondetects were infrequent in this study, and they were not included in the determination of temporal trends.

Results and Discussion

Prior to examination of temporal trends, it was necessary to remove variations in the data that can be attributed to known causes. Atmospheric concentrations of semivolatile organic compounds vary seasonally (*10–13*), with concentrations reaching a maximum in the warmer months. Examples are shown in Figure 2 for α-HCH at Sturgeon Point and in Figure 3 for dieldrin at Point Petre. Note that, in both cases, the highest concentrations usually occur in the warmer summer months (April through October). If these pesticides were still in widespread use, this seasonal behavior might be related to the crop planting cycle. However, at the time these samples were collected, the use of most of these pesticides had been banned or use-restricted; therefore, other influences must be considered.

The Clausius–Clapeyron equation describes the relationship between temperature and the gas-phase partial pressures of semivolatile organic compounds:

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

where P is the partial pressure of the compound (in atm), ΔH is a characteristic phase-transition energy of the compound (in kJ/mol), R is the gas constant, and T is temperature (in Kelvin). Application of this equation requires that atmospheric concentrations be expressed as partial pressures, which can be obtained using the ideal gas law. Although conversion of concentrations in air to partial pressures involves a temperature correction, this correction is minor as compared to the exponential function implied by eq 1.

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

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

where time is the day number (in relative Julian days) of the sample and the a values are constants. The parameters a_1 and a_2, which can be estimated using multiple linear

TABLE 1. Parameters Determined by Multiple Linear Regression and Coefficient of Determination (r^2)[a]

	Eagle Harbor	$P < \|t\|$	Burnt Island	$P < \|t\|$	Sleeping Bear	$P < \|t\|$	Sturgeon Point	$P < \|t\|$	Point Petre	$P < \|t\|$
DDT										
a_0	−21.74	0.0001	−25.81	0.0001	−13.04	0.0001	−9.88	0.0002	−10.53	0.0001
a_1	−3961	0.0001	−3226	0.0001	−6322	0.0001	−7058	0.0001	−7236	0.0001
a_2	−0.00077	0.0001	*−0.00035*	*0.1830*	−0.00084	0.0002	−0.00071	0.0009	*−0.00021*	*0.1886*
r^2	0.305		0.239		0.432		0.510		0.396	
DDE										
a_0	−22.51	0.0001	−21.61	0.0001	−9.92	0.0001	−6.61	0.0001	−13.12	0.0001
a_1	−3882	0.0001	−4094	0.0001	−6963	0.0001	−7802	0.0001	−6029	0.0001
a_2	−0.00037	0.0002	*−0.00009*	*0.6587*	−0.00072	0.0001	−0.00027	0.0188	−0.00021	0.0290
r^2	0.450		0.456		0.626		0.790		0.512	
DDD										
a_0	−29.73	0.0001	−26.62	0.0001	−21.55	0.0001	−17.9	0.0001	−20.86	0.0001
a_1	−1991	0.0299	−3335	0.0001	−4521	0.0001	−5014	0.0001	−4750	0.0001
a_2	−0.00071	0.0001	*−0.00045*	*0.1217*	−0.00074	0.0012	−0.00108	0.0001	−0.00024	0.0425
r^2	0.188		0.271		0.313		0.445		0.341	
α-HCH										
a_0	−22.44	0.0001	−23.25	0.0001	−28.46	0.0001	−25.13	0.0001	−26.59	0.0001
a_1	−2521	0.0001	−2799	0.0001	−942.1	0.0328	−1894	0.0001	−1743	0.0001
a_2	−0.00066	0.0001	*−0.00017*	*0.1347*	−0.00072	0.0001	−0.00039	0.0001	−0.00038	0.0001
r^2	0.550		0.535		0.274		0.332		0.227	
γ-HCH										
a_0	−17.03	0.0001	−17.37	0.0001	−7.48	0.0050	−12.95	0.0001	−19.12	0.0001
a_1	−4638	0.0001	−4868	0.0001	−7191	0.0001	−5756	0.0001	−4268	0.0001
a_2	−0.00057	0.0001	*−0.00016*	*0.3534*	−0.00088	0.0001	−0.00059	0.0001	−0.00026	0.0001
r^2	0.586		0.620		0.519		0.608		0.378	
HCB										
a_0	−30.45	0.0001	*b*	*b*	−29.33	0.0001	−26.80	0.0001	*b*	*b*
a_1	−601.2	0.0220	*b*	*b*	−819.2	0.0001	−1569	0.0001	*b*	*b*
a_2	−0.00015	0.0142	*b*	*b*	−0.00057	0.0001	−0.00028	0.0001	*b*	*b*
r^2	0.082				0.340		0.507			
α-Chlordane										
a_0	−18.47	0.0001	−12.98	0.0001	−16.51	0.0001	−12.96	0.0001	−14.34	0.0001
a_1	−5062	0.0001	−6630	0.0001	−5349	0.0001	−6143	0.0001	−6025	0.0001
a_2	*0.00024*	*0.1677*	*−0.00011*	*0.5470*	*−0.00020*	*0.3166*	−0.00047	0.0043	−0.00031	0.0007
r^2	0.534		0.725		0.466		0.678		0.554	
γ-Chlordane										
a_0	−22.66	0.0001	−14.64	0.0001	−15.80	0.0001	−14.62	0.0001	−18.05	0.0001
a_1	−3855	0.0001	−6185	0.0001	−5477	0.0001	−5729	0.0001	−4986	0.0001
a_2	*0.00006*	*0.7645*	*−0.00023*	*0.2953*	−0.00060	0.0195	−0.00060	0.0023	−0.00029	0.0007
r^2	0.340		0.622		0.397		0.575		0.415	
trans-nonachlor										
a_0	−14.14	0.0001	−13.65	0.0001	−12.49	0.0001	*−4.43*	*0.1120*	−16.51	0.0001
a_1	−6336	0.0001	−6424	0.0001	−6542	0.0001	−8721	0.0001	−5429	0.0001
a_2	*−0.00009*	*0.6581*	*−0.00009*	*0.6510*	−0.00054	0.0189	*−0.00034*	*0.2096*	−0.00021	0.0384
r^2	0.563		0.685		0.526		0.591		0.427	
dieldrin										
a_0	−4.92	0.0435	9.34	0.0001	*−0.72*	*0.8066*	−4.58	0.0289	−9.54	0.0001
a_1	−8406	0.0001	−7261	0.0001	−9281	0.0001	−8291	0.0001	−6993	0.0001
a_2	−0.00036	0.0210	*−0.00012*	*0.5485*	−0.00126	0.0001	−0.00065	0.0001	−0.00040	0.0001
r^2	0.578		0.717		0.595		0.670		0.532	

[a] Parameters that are significant at the 95% confidence level are in normal font, and those not significant are in italics. [b] Data for HCB at Burnt Island and Point Petre were considered unreliable and therefore are not included.

regression, represent $-\Delta H/R$, from the Clausius−Clapeyron equation (see eq 1), and $-k$ (a first-order elimination rate constant), respectively. This regression method was used by Hillery et al. (*10*) to determine a rate constant for the decrease in atmospheric concentrations of polychlorinated biphenyls at Sleeping Bear Dunes and Sturgeon Point. These authors also investigated wind speed and wind direction in their analysis, but they found that both of these variables contributed little to the explained variance of the data. The actual relationship between wind speed, wind direction, and partial pressure will vary from site to site, and thus, it is difficult to adequately represent their influence at all sites using a general equation. Also, it is difficult to meaningfully average wind direction, a circular function and a diurnal phenomenon, over a 24-h sampling period. For these reasons, we did not include the influence of wind in this study.

The parameters in eq 2 were estimated using the general linear model procedure in SAS (SAS Institute, Inc., Cary, NC). The results are presented in Table 1. Nearly all of the coefficients of temperature (a_1) were statistically significant at the 99.99% confidence level, and about 70% of the coefficients of time (a_2) were statistically significant at the 95% confidence level. The Burnt Island site stands out for its lack of significant temporal trends (see a_2), probably because only 3 yr of data were available at this site. Temperature and time alone were found to explain more than 50% of the variance (measured as r^2) for over half of the pesticide/site combinations.

The Clausius−Clapeyron relationship can be represented graphically as a plot of $\ln P$ versus $(1/T)$. Examples for α-HCH at Sturgeon Point and dieldrin at Point Petre are given in Figure 4. In these plots, a negative slope was found for all of the pesticides, indicating that gas-phase concentrations increase with increasing temperature. The slope of a line fit to these data (equivalent to a_1 in Table 1) multiplied by the negative universal gas constant ($-R$) gives a chemical's phase-

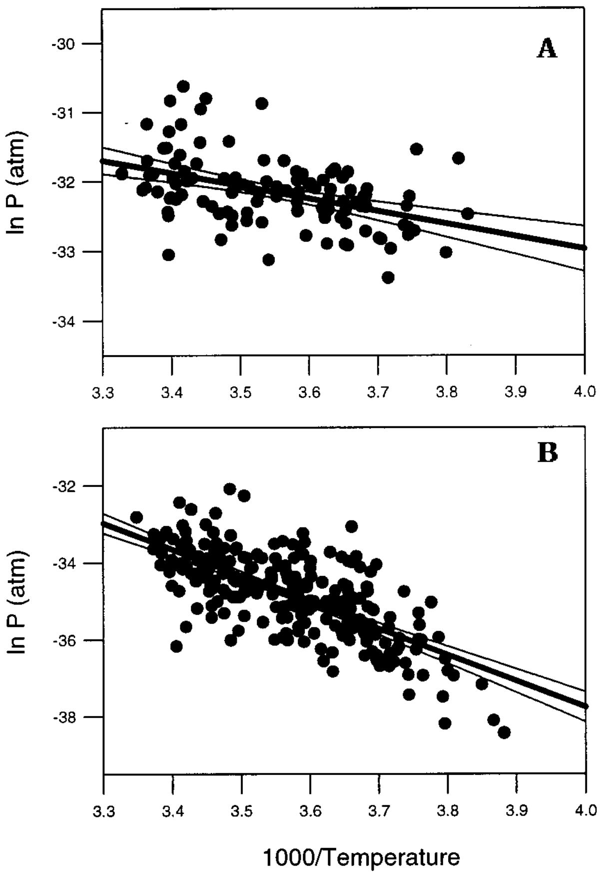

FIGURE 4. Clausius−Clapeyron plot of α-HCH at Sturgeon Point (A) and dieldrin at Point Petre (B). Line determined using least-squares fit; the 95% confidence intervals are shown.

transition energy (Δ*H*). This is the energy necessary to overcome the chemical's own attractive forces to convert 1 mol from the dissolved or liquid phase to the gas phase. In a dynamic environment, an increase in temperature can affect other processes that will lead to an increase or decrease in atmospheric gas-phase concentrations of pesticides, such as transfer across the air/water interface and partitioning from terrestrial surfaces. Despite confounding effects, calculation of Δ*H* can give some insight into environmental behavior; thus, Δ*H* was calculated for the pesticides measured in this study. The results are presented in Table 2, Section A.

The average Δ*H* determined in this study for α- and γ-chlordane is 48 and 44 kJ/mol, respectively, with no apparent spatial trend. The Δ*H* for *trans*-nonachlor ranges from 45 kJ/mol at Point Petre to 73 kJ/mol at Sturgeon Point. However Δ*H* for *trans*-nonachlor is very similar at the western sites (Eagle Harbor, Burnt Island, and Sleeping Bear Dunes) where it is 53, 53, and 54 kJ/mol, respectively. The Δ*H* for dieldrin ranges from 58 kJ/mol at Point Petre to 77 kJ/mol at Sleeping Bear Dunes, with substantial variation among the sites. The average Δ*H* for *p,p*′-DDT and *p,p*′-DDE is 30 and 33 kJ/mol at the two more northern sites (Eagle Harbor and Burnt Island), while at Sleeping Bear Dunes, Sturgeon Point, and Point Petre, the average Δ*H* is 57 kJ/mol for both compounds. *p,p*′-DDD shows a similar spatial trend, but with a lower average Δ*H* at all sites. The opposite trend is found for α-HCH, which had a Δ*H* of 21 and 23 kJ/mol at the two more northern sites and ranged from 7.8 to 16 at the lower sites. The different Δ*H* values among the sites may reflect the different processes that control the concentrations of these compounds. While a strong temperature dependence is indicative of partitioning between surfaces and the atmosphere and can be indicative of seasonal pesticide use, a weaker dependence may be due to processes that have an opposite correlation with temperature, for example, long-range transport or the direction of local winds.

The Δ*H* values for γ-HCH, which range between 35 and 60 kJ/mol, are much higher than for the α-HCH isomer. This difference in temperature dependence between the α- and γ-HCH isomers has been found in other studies (*14*−*16*) and is most likely due to temporal and spatial differences in usage. γ-HCH (lindane) is currently used in many countries, including North America. α-HCH makes up less than 1% of lindane (*17*) but is the primary component of technical HCH, which had been used globally until the last 20 yr, when its use was banned in many countries. As of 1990, the use of technical HCH has continued in a few countries, notably India, Mexico, Ukraine, and Algeria (*18*). In their study, Haugen et al. suggest that the steeper slope (thus a greater Δ*H*) for γ-HCH is due to temperature-dependent re-evaporation from the local surroundings, whereas the weaker dependence for α-HCH is due to advection from outside the local area.

Hoff et al. measured the concentrations and temperature dependence of these same pesticides in Egbert, Ontario (*15*). Although these researchers examined temperature dependence using an Antoine-type relationship, we converted their reported slopes to obtain Δ*H* for all of the pesticides. With the exception of dieldrin, their Δ*H* values were much higher than those determined in our study. This phenomenon was also noted in a study of PCBs at the same three U.S. sites (*10*), where it was found that the Δ*H* of PCBs were lower than those calculated in overland studies by about a factor of 2. Unlike Egbert, the sites in our study are near the lakeshore, where the presence of the large bodies of water may dampen the influence of temperature on the pesticide concentrations. The lake may act as a local source or sink, and in general, temperature is expected to have a smaller effect on the rate of volatilization and deposition from bodies of water than on the volatilization from particles and terrestrial surfaces. In addition, the seasonal variability of the boundary layer over the lake will influence the relationship between temperature and atmospheric concentrations of PCBs measured at the Eagle Harbor site (*19*).

Nearly all of the a_2 parameters determined for time in eq 2 are negative and of about the same magnitude. This indicates that the partial pressures of these pesticides are decreasing over time at about the same rate. To obtain a graphic representation of temperature-adjusted pesticide concentrations over time, partial pressures were corrected by removing the effect of temperature from the data as follows:

$$P_{288} = P_{\mathrm{meas}} \exp\left[-\frac{\Delta H}{R}\left(\frac{1}{288} - \frac{1}{T_{\mathrm{meas}}}\right)\right] \qquad (3)$$

where P_{288} is the partial pressure of each sample adjusted to a reference temperature of 288 K, P_{meas} is the measured partial pressure, T_{meas} is the 24-h average temperature measured at the site when the sample was taken, and Δ*H* is determined from the a_1 parameter in eq 2. These temperature-adjusted temporal trends are illustrated in Figure 5 for α-HCH at Sturgeon Point and for γ-HCH and dieldrin at Point Petre. Rate constants were determined from these temperature-corrected plots and compared to those determined from the multiple linear regression. These two methods would not necessarily yield the same results. In the temperature-corrected plots, the rate constant is determined after the influence of temperature is removed. In the multiple linear regression method, the rate constant and temperature parameter are statistically estimated together. Since the variation due to temperature is much greater than variation

TABLE 2. Phase Transition Energies (Section A) and Atmospheric Half-Lives of Pesticides (Section B) Determined from Regression Parameters[a]

Section A

	Eagle Harbor		Burnt Island		Sleeping Bear Dunes		Sturgeon Point		Point Petre	
	ΔH (kJ/mol)	relative std error (%)	ΔH (kJ/mol)	relative std error (%)	ΔH (kJ/mol)	relative std error (%)	ΔH (kJ/mol)	relative std error (%)	ΔH (kJ/mol)	relative std error (%)
DDT	33	23	27	18	53	13	59	10	60	9
DDE	32	11	34	10	58	8	65	5	50	6
DDD	17	45	28	21	38	19	42	15	40	11
α-HCH	21	12	23	9	7.8	46	16	17	14	15
γ-HCH	39	8	40	7	60	10	48	8	35	8
HCB	5.0	43	*b*	*b*	6.8	37	13	11	*b*	*b*
α-chlordane	42	11	55	6	44	11	51	8	50	6
γ-chlordane	32	16	51	7	46	14	48	10	41	8
trans-nonachlor	53	10	53	6	54	11	73	9	45	8
dieldrin	70	8	60	6	77	9	69	7	58	14

Section B

	Eagle Harbor		Burnt Island		Sleeping Bear Dunes		Sturgeon Point		Point Petre	
	$t_{1/2}$ (yr)	relative std error (%)	$t_{1/2}$ (yr)	relative std error (%)	$t_{1/2}$ (yr)	relative std error (%)	$t_{1/2}$ (yr)	relative std error (%)	$t_{1/2}$ (yr)	relative std error (%)
DDT	2.5	25	*5.4*	*75*	2.3	26	2.7	29	*9.3*	*76*
DDE	5.1	26	*22*	*230*	2.6	21	7.1	42	9.2	46
DDD	2.7	24	*4.2*	*64*	2.6	30	1.8	20	8.0	49
α-HCH	2.9	10	*11*	*66*	2.7	16	4.9	24	5.0	17
γ-HCH	3.4	15	*12*	*110*	2.2	22	3.2	23	7.3	34
HCB	12.4	40	*b*	*b*	3.3	14	6.8	18	*b*	*b*
α-chlordane	*b*	*b*	*17*	*170*	*9.4*	*99*	4.1	34	6.2	29
γ-chlordane	*b*	*b*	*8.4*	*95*	3.2	42	3.2	32	6.5	33
trans-nonachlor	*21.1*	*220*	*22*	*220*	3.5	42	*5.6*	*79*	9.2	48
dieldrin	5.2	43	*16*	*170*	1.5	17	2.9	25	4.8	26

[a] Half-lives calculated from parameters that are significant at the 95% confidence level (refer to Table 1 for *P* values) are in normal font, and those not significant are in italics. [b] Data for HCB at Burnt Island and Point Petre were considered unreliable and therefore are not included. Chlordane-related compounds at Eagle Harbor have negative rate constants.

due to time, removing the temperature component first could significantly bias the remaining temporal component. It is important that nearly all of the rate constants determined using both methods were the same. This increases our confidence in the results obtained by the multiple linear regression.

Atmospheric half-lives were determined by dividing the rate constants into the natural logarithm of 2 (see Table 2, Section B). The decreasing trend is significant for all HCH and *p,p′*-DDT related compounds at all sites, except for Burnt Island and for *p,p′*-DDT only at Point Petre. At the three sites where the half-lives of *p,p′*-DDT are significant, the half-lives range from 2.5 to 2.7 yr. *p,p′*-DDE, the primary metabolite of *p,p′*-DDT, is not declining as rapidly at Eagle Harbor, Sturgeon Point, or Point Petre, where half-lives are 5.1, 7.1, and 9.2 yr, respectively.

The half-lives of α-HCH at the eastern sites (Sturgeon Point and Point Petre) are similar to those found in the Arctic air from 1979 to 1993 by Bidleman et al. (*20*) and to those found in Lista, south Norway, from 1991 to 1995 by Haugen et al. (*14*). Although a temperature correction was not employed in either study, the seasonal variability was reduced prior to examining temporal trends. Bidleman et al. separated the data into a June through November (summer−fall) data set and a December through May (winter−spring) data set, which had the effect of removing temperature-dependent seasonal variability. Haugen et al. considered only annual geometric means in determining temporal trends, which had the effect of reducing the intra-annual variability while preserving inter-annual trends. Bidleman et al. found a 50% decrease in α-HCH over 4 yr in the summer−fall data set and 6 yr in the winter−spring data set. Haugen et al. found a 50% decrease in 4 yr. We applied an exponential fit to their data in order to compare the half-lives with our results. For the Arctic air, we calculated a half-life of 4.2 yr for summer−fall and 6.3 yr for winter−spring. For Norway, we calculated 4.6 yr. These times compare well with half-lives at Sturgeon Point of 4.9 yr and at Point Petre of 5.0 yr. However, the half-lives for the western sites (Eagle Harbor and Sleeping Bear Dunes) were almost half of this value. This is similar to the spatial trend of ΔH at these sites. Because fluctuations in α-HCH concentrations are probably not due to local usage, the spatial trend in both ΔH and temporal trends may be related to different air masses that frequent the sites. The atmosphere at Sturgeon Point and Point Petre is more frequently influenced by maritime air from the southeast than is the atmosphere at Eagle Harbor and Sleeping Bear Dunes, which is most frequently influenced by continental air from the northwest.

As was the case for ΔH, the temporal trend behavior of γ-HCH does not appear to mimic that of α-HCH. The most notable difference is between Point Petre, where the half-life is 7.3 yr, and the other sites where the half-lives are under 4 yr (where temporal trends are significant). It is important to note that γ-HCH may be used near Point Petre (*11*), and in fact, this compound shows a seasonal cycle that is not accounted for by temperature (see Figure 5B).

The half-life of hexachlorobenzene is longer than that of the HCH isomers at all sites, ranging from 3.3 yr at Sleeping Bear Dunes to 12 yr at Eagle Harbor, the longest significant half-life determined in this study. Although the use of HCB as a fungicide in Canada was discontinued in the 1970s, it has not been banned in the United States and is also used as an industrial solvent; thus, it may continue to enter the

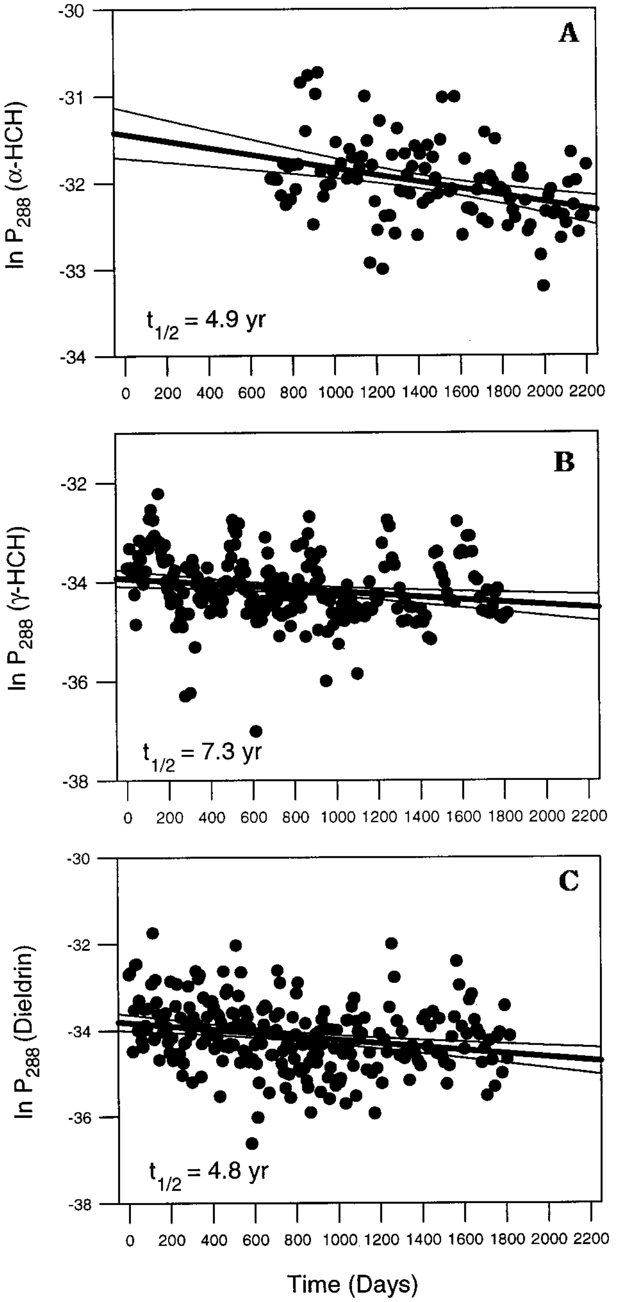

FIGURE 5. First-order decay of α-HCH at Sturgeon Point (A) and γ-HCH and dieldrin at Point Petre (B and C, respectively). Partial pressures adjusted to a reference temperature of 288 K. The 95% confidence intervals are shown.

environment. The temporal parameters for the chlordane compounds are only significant at Sleeping Bear Dunes, Sturgeon Point, and Point Petre, where half-lives range from 3.2 yr for γ-chlordane to 9.2 yr for *trans*-nonachlor. Dieldrin was found to be significantly decreasing at all sites except Burnt Island, with half-lives ranging from 1.5 yr at Sleeping Bear Dunes to 5.2 yr at Eagle Harbor.

For the pesticides that have been banned in both Canada and the United States, the half-lives determined at the U.S. sites are under 4 yr in most cases. In comparison, a study of PCBs at the same sites shows that PCBs are decreasing with half-lives of 6−8 yr (*10*). While the introduction of pesticides into the environment has been severely curtailed in the past few decades, PCBs remain in current use as dielectric fluids in capacitors and transformers and as ballasts in fluorescent lights (*21*). The longer atmospheric half-life of PCBs may be due to their continued use and releases to the environment from disposal. This illustrates the important distinction between restricting the use of a chemical and only banning its production.

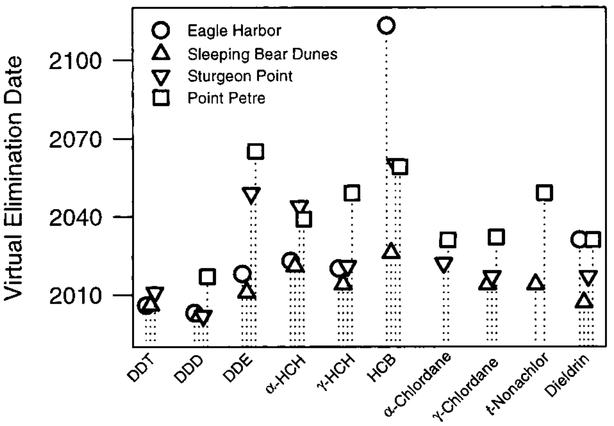

FIGURE 6. Estimated virtual elimination dates. No virtual elimination dates were calculated where rate constants are not significant (refer to Table 1 for *P* values).

The loss rates for these pesticides from the atmosphere are a combination of decay rates in several environmental compartments and input rates from other environmental compartments. For example, the atmospheric half-lives for some of these pesticides due to reactions with hydroxyl radicals are on the order of days to months (*22*−*24*). On the other hand, transformation times for these pesticides in soil range from 4 months to over 10 yr, and reactions in surface water fall somewhere in between (*23*). Partitioning rates between different compartments (including in this case, a large body of water) will have an effect on the half-lives as compared to those obtained over land. In addition, loading studies indicate that some of the pesticides are volatilizing from the lakes into the atmosphere (*25*, *26*). In this case, the continual dilution of the air over the lakes by advective processes is an important part of the rate at which the pesticides disappear.

The results of this study are relevant to the Great Lakes Binational Toxic Strategy, which was signed by the United States and Canada in April 1997. The purpose of this strategy is to facilitate virtual elimination of persistent toxic substances in the Great Lakes Basin. This elimination was called for by the 1987 amendment to the Great Lakes Water Quality Agreement of 1978. The Binational Strategy sets milestones from 1997 to 2006 in order to achieve specific reductions in the use and discharge of targeted toxic substances, a substantial number of which are the pesticides examined in this study. Because most of these pesticides are no longer in widespread use and the atmosphere is considered to be the primary contributor of current contamination to the Great Lakes, the estimation of regional atmospheric virtual elimination dates is relevant to the strategy.

Decrease in the atmospheric concentrations is not strictly first-order; the pesticides partition from other environmental compartments where degradation occurs by different mechanisms, and the new introduction of these pesticides into the environment has not entirely ceased. However, by assuming that decay is approximately first-order and that future inputs will continue to be small relative to atmospheric loads, we can estimate a virtual elimination date for these pesticides in the regional atmosphere using the rate constants determined in this study. These estimates are represented in Figure 6 to allow comparison of dates among the sites. Annex I of the Great Lakes Water Quality Agreement defines "absent" as the detection limit using best available technology; thus, we used a minimum instrument response level of roughly 0.1 pg/m^3 as the definition of "absent". New technology and improved methodology will almost certainly cause lower detection limits as environmental concentrations decrease, so these are minimum virtual elimination dates.

In general, DDT and DDD will be the first to disappear at all sites, in about 2010. This is primarily due to current, low atmospheric concentrations. This is logical, since DDT was the first pesticide to be banned and probably has the fewest current sources in the environment. Virtual elimination dates for *p,p′*-DDE occur later at all sites, due to its higher atmospheric concentrations and longer half-life. Virtual elimination dates for the HCH isomers average about 2030 at all sites. While half-lives of the HCH isomers are close to those determined for *p,p′*-DDT and *p,p′*-DDD, their higher atmospheric concentrations account for their longer continued existence. HCB will remain in the atmosphere the longest of the pesticides at all sites until, on average, 2060. However, approximation of first-order decay for HCB may not be valid due to the previously mentioned current sources. Virtual elimination dates for the chlordane compounds and dieldrin generally fall between *p,p′*-DDT related compounds and HCH isomers, although fewer significant trends are present. Overall, it appears that the virtual elimination date for most of the pesticides will occur by the middle of the next century, which is encouraging. From a spatial perspective, these data suggest that the atmosphere at Sleeping Bear Dunes will be the first to be cleaned and that the atmosphere at Point Petre will remain contaminated the longest.

Using data from a study of loading rates to the Great Lakes (*26*), MacKay and Bentzen point out that atmospheric and water concentrations for many of these compounds are approaching equilibrium, which implies that water concentrations are dependent primarily on atmospheric concentrations (*27*). Therefore, for the pesticides that are near equilibrium, knowledge of the Henry's law constants should allow the determination of concentrations in water at any future date. Although calculations of these concentrations are beyond the scope of this study, it is important to note that analytical detection limits in water are worse those in air by orders of magnitude. Therefore, virtual elimination of these compounds in water will occur prior to virtual elimination in air. Therefore, virtual elimination in the Great Lakes should consider not only aqueous measurements, but atmospheric measurements as well.

The results of this study indicate that gas-phase concentrations of the pesticides studied here are declining at all sites for which a long enough record exists to determine trends with good statistical confidence. At Burnt Island, a nonsignificant negative trend also exists. For chlordanes at Eagle Harbor on Lake Superior, no significant decreasing trend is seen, and this is similar to the result for PCBs found by Hillery et al. (*10*). Considering the length of time some of the pesticides have been restricted, their continuing decline in the environment is encouraging. When viewed in the context of atmospheric loading studies, these results indicate that concentrations of organochlorine pesticides in the Great Lakes water should also continue to decrease.

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