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Determination of Temporal Trends in Atmospheric Concentrations of Selected Organochlorine Pesticides Measured near the Great Lakes

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Abstract

As a participant in the Integrated Atmospheric Deposition Network, Indiana University measures atmospheric concentrations of toxic organic compounds near the Great Lakes. A multiple regression technique was used to examine the temporal trends in concentration of three general classes of organochlorine pesticides. Atmospheric half-lives of hexachlorocyclohexane related compounds range from 2.2 years for γ -HCH at Sleeping Bear Dunes to 12 years for hexachlorobenzene at Eagle Harbor. DDT is decreasing with a half-life of less than 3 years at all sites examined in this study. A decreasing trend for chlordane could only be discerned at Sleeping Bear Dunes and Sturgeon Point, where half-lives ranged from 3.2 years for γ -chlordane at both sites to 9.4 years for α -chlordane at Sleeping Bear Dunes.

Introduction

The widespread use of environmentally persistent, chlorinated organic pesticides since the 1940's is responsible for the relatively high levels still found in many environmental compartments. Although many of these compounds have been banned or severely restricted, their presence in the Great Lakes remains a current concern, and research suggests atmospheric transport and deposition are responsible for much of the current contamination^{1,2}. In order to quantify and monitor the atmospheric deposition of toxic organic compounds to the Great Lakes, the United States and Canada operate air sampling sites along the lake shores. This Integrated Atmospheric Deposition Network, called for in the 1987 amendment to the Great Lakes Water Quality Agreement of 1972³, has been in operation for over five years. The data provided by this long-term study provide a unique opportunity to explore temporal trends in atmospheric, gas-phase concentrations of organochlorine pesticides at the lake shore. In this study, the atmospheric half-lives of three general classes of organochlorine pesticides were determined.

Experimental Methods

Indiana University operates three air sampling stations: Eagle Harbor on Lakes Superior, Sleeping Bear Dunes on Lake Michigan, and Sturgeon Point on Lake Erie. Each site is equipped with a 10 m meteorological tower which records hourly values of air temperature, solar radiation, wind speed, wind direction, relative humidity, and total rainfall. For the samples used in this study, air was pulled through a high-volume air sampler at a rate of 34 m³/hr for 24 hours, with sampling

events occurring every 12 days. Particle fractions were collected on a quartz fiber filter prior to collection of gas-phase compounds in a vapor trap containing between 35 and 45 g of pre-cleaned XAD-2 resin.

The XAD-2 resin was Soxhlet extracted using a hexane/acetone (50:50) solution for 24 hours. The extract was reduced by rotary evaporation and exchanged to hexane, and then fractionated with silica gel in order to remove interferences. Hexane was used to elute PCBs and the pesticides hexachlorobenzene and DDE. Subsequent elution with dichloromethane/acetone (50:50) was used to capture the remaining pesticides. The final extracts were concentrated under a steady 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 electron capture detector. Separation was achieved using a 60 m × 0.25 mm i.d. (d_f = 0.10 μ m) DB-5 column⁴.

Results and Discussion

Environmental concentrations of semi-volatile organic compounds are commonly found to vary seasonally⁵⁻⁸. A plot of concentration vs. time for each of the pesticides in this study indicate a definite seasonal trend, with concentrations reaching a maximum in the warmer months. This is shown in Figure 1 for DDT at Sturgeon Point. In order to characterize the variability of atmospheric pesticide concentrations as a function of time and temperature, a multiple linear regression was performed using the following equation:

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

where P is partial pressure of the pesticide in atmospheres, T is air temperature in Kelvin, and *time* is the number of days from the date of the first sample taken. Parameters were estimated using the general linear model procedure in SAS (SAS Institute, Inc., Cary, North Carolina). The parameters for temperature were statistically significant (P < 0.0001) for 29 out of 30 pesticide/site combinations, and the parameters for time were significant (P < 0.05) for 19 out of 30 pesticide/site combinations. Temperature and time were found to explain more than 50% of the variance (measured as r^2) for 17 out of 30 pesticide/site combinations.

In order to obtain a graphic representation of decreasing trends over time, concentrations were normalized to a reference temperature as follows:

$$P = P_{act} \times \exp\left[\frac{\Delta H_{\bullet}}{R} \times \left(\frac{1}{280} - \frac{1}{T_{act}}\right)\right]$$
(2)

where P is the partial pressure adjusted to a reference temperature of 280 Kelvin, P_{act} is the actual partial pressure, and T_{act} is the actual air temperature. A decreasing trend was apparent for the hexachlorocyclohexane (HCH) related compounds, the DDT related compounds, and dieldrin. While the chlordane related compounds appear to be decreasing at Sleeping Bear Dunes and Sturgeon Point, they appear to be increasing at Eagle Harbor. A plot of the hexachlorocyclohexanes and hexachlorobenzene vs. time is shown in Figure 2.





Figure 1: Atmospheric concentrations of DDT and air temperature at Sturgeon Point from 1991 through 1995. Each point represents a 24 hour average.

Figure 2: Temperature adjusted concentrations of the hexachlorocyclohexanes and hexachlorobenzene. Each bar represents an annual average (December through November) with corresponding standard error indicated.

TRANSPORT AND FATE

The parameter for time in Eq.1, which is a rate constant, was used to calculate atmospheric halflives for each pesticide (see Table 1). The temporal parameter for all HCH and DDT related compounds at all sites is significant. The half-lives of DDT are remarkably similar at all sites, ranging between 2.5 and 2.7 years. The hexachlorocyclohexanes are decreasing with a half-life of less than 5 years at all sites, but hexachlorobenzene is not declining as quickly at Sturgeon Point and Eagle Harbor, where half-lives are 6.8 and 12.4 years, respectively. γ -Chlordane is decreasing with a half-life of 3.2 years at both Eagle Harbor and Sturgeon Point. The temporal parameter for α -chlordane was only significant at Sturgeon Point, where the half-life is 4.1 years. The shortest half-life is found for dieldrin at Sleeping Bear Dunes, with a half-life of 1.5 years. At Eagle Harbor, the half-life for dieldrin is much longer, at 5.2 years.

	Eagle Harbor		Sleeping Bear Dunes		Sturgeon Point	
	t _{1/2} (yrs)	Std Error	t _{1/2} (yrs)	Std Error	t _{1/2} (yrs)	Std Error
DDF	E 1	2(0)	27	210/		429/
	25	20%	2.0	21%	27	42%
DDD	2.7	24%	2.6	30%	1.8	20%
α-ΗСΗ	2.9	10%	2.7	16%	4.9	24%
у-НСН	3.4	15%	2.2	22%	3.2	23%
HCB	12.4	40%	3,3	14%	6.8	18%
α-Chlordane	*	*	9.4	99%	4.1	34%
y-Chlordane	*	*	3.2	42%	3.2	32%
t-Nonachlor	*	*	3.5	42%	5.6	79%
Dieldrin	5.2	43%	1.5	17%	2.9	25%

Table 1: Atmospheric half-lives of pesticides determined from regression parameters. The parameters were significant at the 95% confidence level for all pesticides except two which are in italics. * Chlordane related compounds at Eagle Harbor have positive rate constants.

It is important to distinguish atmospheric half-lives of the pesticides measured in this study from theoretical atmospheric half-lives due solely to hydroxyl radical reactions, which are on the order of days⁹. Environmental decay rates fall somewhere between a minimum decay rate in any compartment and an upper value determined as a weighted average in all compartments¹⁰, and these pesticides are transformed much more slowly in soil and water than in air. Partitioning rates between different compartments, and in this case the large body of water, will certainly have an effect on the half-lives compared to those obtained over land. Finally, loading studies indicate that some of the pesticides are volatilizing from the lake into the cleaner atmosphere^{11,12}, and in this case, the continual dilution of the air by advective processes is an important part of the rate at which the pesticides disappear. Nevertheless, the declining atmospheric levels indicated in this study are encouraging. These results should have important implications in continuing research on atmospheric processes and removal mechanisms occurring in the limetic environment.

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