

## Short-term Fluctuations within Long-term Atmospheric Declines of Chlorinated Pesticide Concentrations in the Great Lakes Region

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### Introduction

Two frequently characterized features in atmospheric measurements of pesticides sets are seasonal variability and temporal trends (1, 2, 3, 4, 5). While temporal trends can be difficult to extract, seasonal variance is usually substantial and is often attributed to temperature in accordance with the Clausius-Clapeyron relationship:

$$\ln P = \frac{\Delta H_{\phi}}{R} \left( \frac{1}{T} \right) + const \quad (1)$$

where  $P$  is the atmospheric concentration expressed as partial pressure,  $\Delta H_{\phi}$  is enthalpy of phase change,  $R$  is the gas constant, and  $T$  is temperature. However, two additional features were observed for atmospheric concentrations of  $\gamma$ -hexachlorocyclohexane ( $\gamma$ -HCH) measured at sampling sites located in the Laurentian Great Lakes region. We believe that these features are indicative of current use of lindane, a pesticide primarily composed of  $\gamma$ -HCH (6). This paper examines a potential signature of current pesticide use, shows that seasonality in atmospheric pesticide concentrations is not always primarily due to temperature, and demonstrates how these features may give new insight into environmental decay rates.

### Materials and Methods

Samples were collected as part of the Integrated Atmospheric Deposition Network effort, a long term sampling campaign sponsored by the United States and Canadian governments in order to monitor and estimate deposition of toxic chemicals to the Great Lakes. Sampling sites are located at Eagle Harbor on Lake Superior, Sleeping Bear Dunes on Lake Michigan, Sturgeon Point on Lake Erie, Burnt Island on Lake Huron, and Point Petre on Lake Ontario. These sites were chosen to be representative of the regional atmospheric environment near the Lakes, while

minimizing influence from local pollution sources. Each site is equipped with a 10 m meteorological tower which 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.

Only a summary of sampling and analytical procedures is presented here, but full details are reported elsewhere (7, 8). At the U.S. sites, air was pulled through a modified Anderson high-volume air sampler at a rate that gave 820 m<sup>3</sup> in 24 hours. Sampling events occurred every 12 days. Particles were collected on quartz fiber filters and gas-phase organic compounds were collected on XAD-2 resin. Prior to May of 1992, polyurethane foam was used to collect gas-phase compounds. At the Canadian sites, 350 m<sup>3</sup> of air was collected over a 24 hour period. Polyurethane foam was used to collect gas-phase compounds. Particles were collected on glass fiber filters. Sampling events occurred every 6 days through April 1994, when the schedule was changed to every 12 days.

For samples analyzed at Indiana University (the U.S. sites), the XAD-2 resin was Soxhlet extracted using 50% hexane in acetone for 24 hours. After reduction by rotary evaporation and hexane exchange, the extract was fractionated on deactivated silica gel in order to remove interferences. 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 <sup>63</sup>Ni electron capture detector. 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.

For samples analyzed at Atmospheric Environment Service (Canadian sites), the PUF was Soxhlet extracted using hexane for 24 hours. After reduction by rotary evaporation or closed-cell concentrator procedures and *iso*-octane exchange, the extract was fractionated on Florisil columns in order to remove interferences. 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 <sup>63</sup>Ni electron capture detector. Separation was achieved using 30 m × 0.25 mm i.d. (film thickness 0.25 μm) (1990 samples) or 60 m × 0.25 mm i.d. (film thickness 0.25 μm) DB-5 columns.

## Results and Discussion

As part of another project to examine temporal trends in the data (9), we determined  $\Delta H_\phi$  for each of the pesticides using simple linear regression. We then removed the influence of temperature from the data as follows:

$$P_{288} = P_{act} \times \exp \left[ \frac{\Delta H_\phi}{R} \times \left( \frac{1}{288} - \frac{1}{T_{act}} \right) \right] \quad (2)$$

where  $P_{288}$  is the partial pressure adjusted to a reference temperature of 288 K,  $P_{act}$  is the actual partial pressure, and  $T_{act}$  is the actual air temperature. This transformation effectively removed

the seasonality for most of the pesticides, and made temporal trends more apparent. However, for  $\gamma$ -HCH measured at Point Petre, a strong seasonal cycle remained after correction. We fit a periodic with exponential decay function to this data:

$$\ln \hat{P} = \ln \bar{P} - A \cos(2\pi ft + \phi) - kt \quad (3)$$

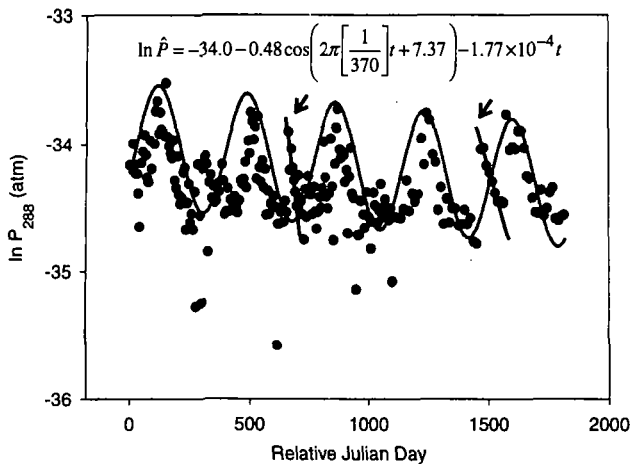
where the  $P$ s are the fitted and average partial pressures (in atm),  $A$  is an amplitude factor,  $f$  is a frequency,  $t$  is time in Julian days from 1/1/90,  $\phi$  is a phase shift factor, and  $k$  is a rate constant (in days<sup>-1</sup>). The fit of this equation to the temperature adjusted data is given in Figure 1. Note that the frequency corresponds to a seasonal cycle of about 1 year, with the maximum concentration occurring in May. McConnell *et al.* (10) suggest that higher levels of  $\gamma$ -HCH in the spring in this region of Canada may be due to this pesticide's use in the prairie provinces as a seed dressing. Based on this suggestion and on our data, we conclude that for lindane at Point Petre, seasonal usage is a major component of the seasonal variability. Although a residual seasonal cycle was not seen for lindane at other sites, the non-temperature corrected data appear to be offset from the temperature cycle in some cases, implying a seasonal use component. An example where the original data are offset from the temperature cycle is given in Figure 2 for Sturgeon Point.

Other interesting features in the residual data for  $\gamma$ -HCH at Point Petre are high concentration events that are followed by exponential decay. These events are marked by arrows in Figure 1. In both cases, the temperature is increasing but the  $\gamma$ -HCH concentrations are rapidly decreasing. An exponential fit applied to these data gives half-lives of 21 days ( $r^2 = 0.836$ ) and 48 days ( $r^2 = 0.973$ ) for these two events, respectively. These half-lives are similar to half-lives due to atmospheric oxidation (11, 12). Although residual cycles were not observed for the other pesticides in our study, high concentration events are evident in the non-temperature adjusted data. Two such events are illustrated in Figure 2 for  $\gamma$ -HCH at Sturgeon Point; see the two arrows. An exponential fit applied to these data gives half-lives of 44 days ( $r^2 = 0.902$ ) and 28 days ( $r^2 = 0.990$ ) for the two events, respectively.

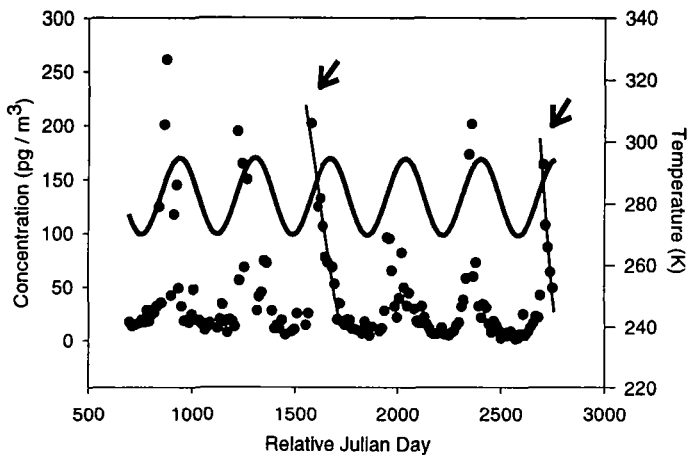
These fast-events probably correspond to regional applications of the pesticide, with a subsequent decrease due primarily to atmospheric oxidation, dilution, air-to-water, and air-to-soil partitioning.

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**Figure 1:** Time series of  $\gamma$ -HCH data at Point Petre after temperature adjustment. A seasonal cycle is evident in the residual data. The line represents the best fit of the periodic function. Arrows indicate high concentration events with subsequent first order decay.



**Figure 2:** Time series of non-temperature adjusted data for  $\gamma$ -HCH at Sturgeon Point (left scale) and the best fit of atmospheric temperature measurements taken at the site (right scale). The periodicity in  $\gamma$ -HCH data is offset to the left of the temperature cycle. Arrows indicate high concentration events followed by first order decay.

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