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CAUSES OF VARIABILITY IN PESTICIDE AND PCB CONCENTRATIONS IN AIR NEAR THE GREAT LAKES

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Introduction

The Integrated Atmospheric Deposition Network (IADN) began in 1990 as a joint effort between the United States and Canada to monitor the atmospheric deposition of persistent organic pollutants (POPs) to the Laurentian Great Lakes. IADN consists of five master stations, one near each of the lakes. This network measures the atmospheric concentrations of several polychlorinated pollutants at each site every 12 days (or 30 times per year).

Previous IADN publications have investigated the temporal trends of many of the gas-phase pesticide and polychlorinated biphenyl (PCB) concentrations using the following multiple linear regression:[1-3]

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

where P is the partial pressure of the compound in atmospheres, a_0 is a constant, a_1 is the slope ($-\Delta H/R$) of the Clausius-Clapeyron equation,[1-3] T is the 24 hr average air temperature at the site in Kelvin, a_2 is a first-order rate constant, and *time* is the day of sampling. While based on the known behavior of gas-phase POPs in the environment, this equation assumes that temperature and time correctly account for almost all of the variability in the partial pressures of each compound. In fact, when wind speed and direction have been added to this equation, these parameters were found to be not significant,[1, 3] thus supporting the use of Equation 1. However, Cortes et al.[4] found significant agricultural application effects for γ-HCH (lindane), a currently-used pesticide, at a Canadian-operated master station near Lake Ontario. In this case, it was shown that the use of this pesticide during the spring planting season caused an elevation in the atmospheric concentrations measured hundreds of kilometers away. Thus, Equation 1 was modified to include a Lorentzian agricultural application term:

$$\ln P = a_0 + a_1\left(\frac{1}{T}\right) + a_2\ time + \frac{a_3}{1+\left(\frac{(time\ MOD\ a_4)-a_5}{a_6}\right)^2} \tag{2}$$

where a_3 is an amplitude factor, a_4 is the periodicity (typically 365 days), a_5 is an offset (typically day 140, corresponding to May planting), a_6 is the half-width of the planting season (typically 30-40 days), and MOD is the modulus function.

We now have about 10 years of data, and it seemed appropriate to re-investigate the causes of variability in the gas-phase pesticide and total PCB (ΣPCB) concentrations at IADN's U.S. master stations to determine if Equation 2 was appropriately accounting for the variability in these concentrations.

Methods and Materials

Indiana University operates three IADN master stations: Sleeping Bear Dunes near Lake Michigan, Eagle Harbor near Lake Superior, and Sturgeon Point near Lake Erie. Data through 2001 were used from each station. Each site is equipped with a meteorological tower that records an hourly average for wind speed and wind direction at an elevation of 10 m and air temperature, relative humidity, and solar radiation at 2 m. Air samples were collected using a high-volume sampler that pulls air through a filter and XAD-2 absorbent at a rate of 34 m^3/h. Sampling occurred every 12 days and lasted 24 hours. The XAD-2 resin was Soxhlet extracted with a mixture of 50% acetone in hexane for 24 hours. The extracts were then concentrated and solvent-exchanged to hexane by rotary evaporation and subsequently fractionated with silica gel. PCBs, hexachlorobenzene (HCB), and DDE were eluted with hexane while the remaining pesticides were eluted using 50% dichloromethane in hexane. The extracts were then concentrated under a stream of nitrogen, spiked with internal standards, and analyzed on a Hewlett-Packard 5890 gas chromatograph with a ^{63}Ni electron capture detector.[5]

Results and Discussion

IADN monitors both currently-used and banned pesticides at its U.S. master stations. Our hypothesis is that the multiple linear regression (see Equation 2) used to evaluate trends in IADN data is adequately accounting for the variability in partial pressures of currently-used pesticides but not of banned pesticides. The best way to explore this hypothesis is to look at plots of the natural logarithm of partial pressure (ln P) vs. time at varying stages of the analysis along with autocorrelation plots of the data for each stage.

Autocorrelation is the correlation of a variable to itself separated by a given lag, or in our case by a given number of sampling intervals. Brunciak et al.[6] have explored the autocorrelation of atmospheric ΣPCB concentrations at Chesapeake Bay and used this approach to describe the buffering of PCB concentrations in the atmosphere by the Bay. While such an analysis could be applicable in this study, our main use of autocorrelation here is to help to verify whether or not Equation 2 is adequately describing the variability of the data. As a rule, residuals from a properly specified linear regression should not contain autocorrelation. By exploring the autocorrelation in the residuals at various stages of the analysis, we will better understand how to account for the variability in each compound concentration. We will explain this process by using γ-HCH at Sturgeon Point as an example. The corresponding plots are given in Figure 1.

We will start by examining the unadjusted partial pressures against time. Figure 1A shows such a plot. Here we clearly see the annual cycling of γ-HCH at Sturgeon Point. We assume this cycling is because of temperature effects.[1, 2] The corresponding autocorrelation plot for Figure 1A (Figure 1B) is simply the autocorrelation of ln P as a function of successive lags. Not unexpectedly, we find significant autocorrelation with a periodicity of 30 lags, corresponding to 360 days. Such strong autocorrelation, showing oscillations corresponding to seasonal frequencies, is indicative of seasonal temperature effects.

To remove this seasonal periodicity, and thus remove the temperature effects, we corrected the partial pressures to a reference temperature of 288 K to obtain ln P_{288}.[2] Figure 1C shows the resulting data. Clearly, there is significant periodicity remaining in the temperature-corrected data, as highlighted by the LOESS function shown in Figure 1C. The autocorrelation plot in Figure 1D (which is for the residuals of Equation 1) shows strong autocorrelation with an oscillating pattern similar to Figure 1B, indicating that some of the seasonal periodicity remains in the data. Since we have removed the temperature effects from the data, the remaining periodicity must be from the agricultural application of γ-HCH.

To visualize the removal of the agricultural application cycle, the resulting Lorentzian function for each sampling day (the third term in Equation 2) was subtracted from ln P_{288} for that sample to give ln P_{Lorentz}, a plot of which is shown in Figure 1E. The autocorrelation plot of the residuals for Equation 2 is shown in Figure 1F. Here we see that not only has all of the remaining periodicity been removed, but the overall variability in the data has decreased dramatically, indicating that the addition of the use of Equation 2 is crucial to fully describe the variability in γ-HCH concentrations at Sturgeon Point. In fact, the r^2-value increased significantly from 0.63 to 0.83 when using Equation 1 vs. 2, respectively. Similar results were found for γ-HCH at the other U.S. sites. Because γ-HCH has been banned in the U.S., the discovery of agricultural application effects not only in Canada[4] but also at the U.S. sampling sites is significant and unexpected. These results clearly indicate the importance of long-range transport in the contamination of the Great Lakes.

To contrast the γ-HCH example, Σchlordane (α-chlordane + γ-chlordane + *trans*-nonachlor), all of which are banned pesticides, at Sleeping Bear Dunes was examined using the same method. Temporal and autocorrelation plots of unadjusted ln *P* showed clear seasonal patterns. However, unlike γ-HCH, when the residuals from Equation 1 were examined, there was no periodicity in the autocorrelation. In other words, temperature and time fully account for the variability in the atmospheric concentrations of this banned pesticide. Similar results were found at all sites for other banned pesticides, while other currently-used pesticides behaved similarly to γ-HCH. The one oddity was ΣPCB, a chemical that has banned for over 25 years. Autocorrelation plots of Equation 1 ΣPCB residuals showed significant autocorrelation across many lags in a pattern quite different from γ-HCH but still indicative of unaccounted variability. Autocorrelation analysis will not only help to identify and remove variability in the IADN data by helping us to properly specify the regression equation, but it will also allow us to have full confidence in our parameter results.

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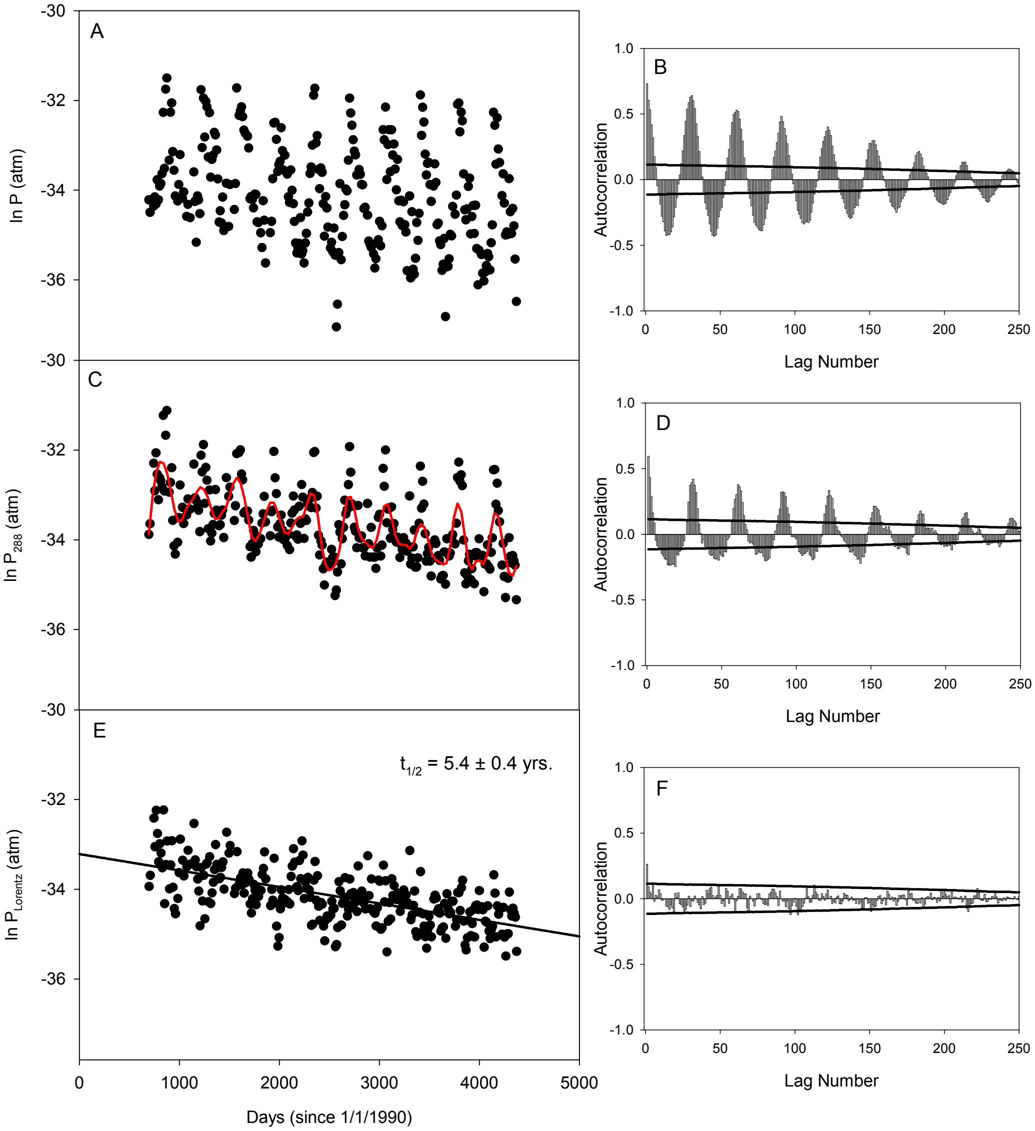

Figure 1. Sturgeon Point γ-HCH partial pressures vs. time for (*A*) unadjusted partial pressures, (*C*) temperature corrected partial pressures, and (*E*) temperature and agricultural application corrected partial pressures with corresponding autocorrelation plots (*B*, *D*, and *F*). The horizontal lines on plots *B*, *D*, and *F* represent the 95% confidence limits, above which the autocorrelations are significant. A LOESS smoothing function has been fitted to Figure 1C to highlight the periodicity. A half-life ($t_{1/2}$) is given for the regression line plotted in Figure 1E.