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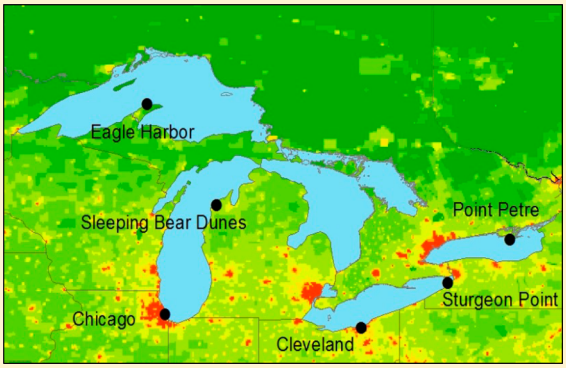
# Revised Temporal Trends of Persistent Organic Pollutant Concentrations in Air around the Great Lakes

Amina Salamova, Marta Venier, and Ronald A. Hites*

School of Public and Environmental Affairs, Indiana University, Bloomington, Indiana 47405, United States

Supporting Information

**ABSTRACT:** The concentrations of polychlorinated biphenyls, polycyclic aromatic hydrocarbons (PAH), and several chlorinated insecticides in air have been measured every 12 days since 1991 at several sites on the shores of the North American Great Lakes. We give here the geometric mean concentrations for each of these compounds for each year and at each site. In most cases, these concentrations have been measured in both the vapor and particle phases; if concentrations were available for both phases, the two concentrations were summed, and those data are presented here. Assuming a first-order rate model for these data, we have calculated the time it takes for the concentrations to decrease by half. For most compounds, the halving times are the same for the vapor phase and for the vapor and particle phase concentrations summed together. The halving times are generally not distinguishable among the sites. Overall, the observed halving times are 8−15 years, except for that of lindane, which is disappearing with a halving time of ∼4 years.




## INTRODUCTION

After the implementation of regulations designed to reduce the environmental concentration of some pollutant, it is essential to measure its concentration in the environmental compartments of interest as a function of time to determine if the regulation has been effective and to determine how fast the concentration in the environment is (presumably) decreasing. In this paper, we will focus on several persistent organic pollutants (POPs) in the atmosphere around the North American Great Lakes. The pollutants of interest here are (a) polychlorinated biphenyls (PCBs), the production and use of which were eliminated in North America in 1976, (b) several chlorinated insecticides, the most well-known of which is DDT, the North American use of which was eliminated in 1972, and (c) the polycyclic aromatic hydrocarbons, which continue to be released into the environment from numerous stationary and mobile combustion sources. The concentrations of these and other such compounds in the atmosphere have been measured at six locations (see the map in the abstract) on the shores of the Great Lakes once every 12 days since 1991 as part of the Integrated Atmospheric Deposition Network (IADN).

We have previously presented the temporal trends of these concentrations in a series of papers using more and more data covering increasingly longer time scales and using a series of increasingly complex regression methods. Our first paper on these data used vapor phase PCB data from only 1991−1995 and regressed logarithmically transformed concentrations as a function of sampling date and atmospheric temperature on that date.[1] This early paper showed that the PCB concentrations were decreasing with halving times (the time it takes for the concentrations to decrease by a factor of 2) of 6−7 years, depending on the location. Subsequent papers expanded this coverage to include several chlorinated insecticides and polycyclic aromatic hydrocarbons in both the vapor and particle phases (collected between 1991 and 1997, but analyzed separately).[2,3]

This work was eventually updated to include samples collected through 2003;[4−6] in this case, the vapor and particle phase data were analyzed separately using two different statistical models. Later, four more years of data were added, and we used a partial harmonic regression method to combine the time trend analyses of the vapor and particle phases at all sites.[7] More recently, we presented time trends for PCBs and organochlorine insecticides using only vapor phase data from 1992 to 2010 at three sites;[8] in this case, the statistical analyses were based on annual averages. We have also reported time trends for all compounds in all phases at only Point Petre using a harmonic regression method for data analysis.[9] Adding more years of data to our analyses yielded longer halving times, suggesting that environmental levels may be stabilizing with time.

This paper gives atmospheric concentration data through December 2013 and, for the first time, fully integrates our data at Point Petre with those from the other five sites. In addition, we have, for the first time, added the vapor phase and particle phase concentrations together before proceeding with the statistical

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**Table 1. Halving Times (in years) with Their Standard Errors for the Atmospheric Concentrations of the Various Compounds and Compound Groups Measured at Six IADN Sites on the Shores of the North American Great Lakes[a]**

| | phase | Chicago | Cleveland | Sturgeon Point | Sleeping Bear | Eagle Harbor | Point Petre |
|---|---|---|---|---|---|---|---|
| total PCBs | vapor | 11.9 ± 2.7 | 18.6 ± 8.6 | 15.3 ± 2.6 | 12.9 ± 2.6 | 13.2 ± 1.8 | 16.3 ± 7.1 |
| PCB-18 | vapor | 8.9 ± 1.1 | NS | 8.9 ± 1.0 | 9.8 ± 1.3 | 11.3 ± 1.7 | 8.2 ± 2.3 |
| PCB-52 | vapor | 12.8 ± 3.3 | 13.2 ± 3.8 | 19.6 ± 4.8 | 12.5 ± 2.3 | 13.8 ± 2.5 | NS |
| PCB-101 | vapor | 12.7 ± 3.9 | 11.6 ± 3.5 | 22.4 ± 6.1 | 12.8 ± 2.2 | 10.5 ± 1.3 | 12.2 ± 3.8 |
| total PAH | vapor + particle | 10.4 ± 1.4 | 7.6 ± 1.9 | 13.9 ± 4.3 | NS | 17.2 ± 5.1 | 24.1 ± 10.9 |
| phenanthrene | vapor + particle | 10.8 ± 1.6 | 6.4 ± 1.7 | 12.6 ± 3.9 | NS | 13.8 ± 3.6 | NS |
| benzo[*a*]pyrene | vapor + particle | 6.6 ± 0.6 | NS | 14.7 ± 4.0 | NS | NS | NS |
| $\alpha$-HCH | vapor | 3.9 ± 0.3 | 4.1 ± 0.6 | 3.5 ± 0.2 | 3.9 ± 0.2 | 4.3 ± 0.2 | 4.4 ± 0.5 |
| $\alpha$-HCH | vapor + particle | 4.0 ± 0.4 | 4.0 ± 0.6 | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ |
| $\gamma$-HCH | vapor | 4.3 ± 0.3 | 4.2 ± 0.5 | 3.6 ± 0.2 | 3.7 ± 0.2 | 4.5 ± 0.2 | 3.9 ± 0.3 |
| $\gamma$-HCH | vapor + particle | 4.2 ± 0.4 | 4.3 ± 0.5 | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ |
| total DDTs | vapor | 11.9 ± 2.3 | 9.1 ± 2.3 | 10.4 ± 1.0 | 9.3 ± 1.0 | 10.5 ± 1.4 | 12.6 ± 3.5 |
| total DDTs | vapor + particle | 9.9 ± 1.7 | 7.7 ± 1.4 | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ |
| total chlordanes | vapor | 11.6 ± 2.1 | 9.0 ± 2.4 | 8.7 ± 0.7 | 9.5 ± 1.1 | 10.2 ± 1.2 | 11.7 ± 3.7 |
| total chlordanes | vapor + particle | 10.3 ± 1.7 | 9.2 ± 2.2 | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ |
| total endosulfans | vapor | 8.0 ± 1.4 | 7.6 ± 2.1 | 8.0 ± 1.2 | 8.1 ± 1.6 | 8.9 ± 1.2 | 7.1 ± 1.6 |
| total endosulfans | vapor + particle | 8.3 ± 1.1 | 6.4 ± 1.5 | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ | $N \leq 6$ |

[a]All data for each compound at each site in each year are given in the Supporting Information. Some of the regressions are shown in Figure 1.

analyses, and we have included all of the compounds measured by IADN, a list that has evolved over time. A guide showing the data coverage for the different compound types and sampling sites as a function of year and atmospheric phase is shown in Figure S1 of the Supporting Information. We are also presenting for the first time the annual geometric mean concentrations for each compound or compound group at each of the six sites for each of the 20 years of the project. Furthermore, we have based the new time trend analyses on these annual geometric mean concentrations, and all of these regression results are presented.

## EXPERIMENTAL SECTION

The details of the sample collection and chemical analyses have been published previously;[1−9] thus, only a summary is given here. The samples are collected at each of the six sampling sites for 24 h once every 12 days (every 24 days at Point Petre). A summary of sampling years and data availability is given in Figure S1 of the Supporting Information. The air is sampled by a high-volume sampler at a flow rate such that ∼820 $m^3$ is sampled over the 24 h period. The air is first pumped through a 2.2 $\mu$m filter to collect the particles and then through a bed of XAD-2 resin to collect the vapor phase components. Once returned to the laboratory, the particle and vapor phase media are extracted separately, and the extracts are cleaned up and analyzed separately. The PCBs and organochlorine insecticides are measured with electron capture gas chromatography with a 60 m column. The PAH are measured via isotope dilution gas chromatographic mass spectrometry in the electron impact ionization mode. All analyses are based on internal calibration compounds. Extensive QA/QC procedures have been implemented.[1−10]

## RESULTS AND DISCUSSION

We are using here the following compounds or compound classes. "Total PCBs" include ∼80 PCB congeners that were present in the various Aroclor commercial mixtures. In addition, we are presenting individual concentrations of PCB-18, PCB-52, and PCB-101, which have three, four, and five chlorines, respectively. We selected these three congeners because they are considered "indicator PCBs",[11] they were relatively abundant, and they were measured as isomerically clean GC peaks. PCBs were measured only in the vapor phase at all sites. Of the 22 PAH we measured, we are giving here the concentrations of phenanthrene, benzo[*a*]pyrene, and total PAH. We selected these compounds because phenanthrene was the most abundant PAH and because benzo[*a*]pyrene is a well-known carcinogen. In all of these cases, the PAH concentrations given here are the sum of those in the vapor and particle phases. For PAH, this summation is important because they are abundant in both phases, although in different proportions based on their molecular weight. For example, ∼95% of the atmospheric load of phenanthrene is in the vapor phase, but only ∼20% of that of benzo[*a*]pyrene is in the vapor phase. Among the chlorinated insecticides, we are presenting here the concentrations of $\alpha$- and $\gamma$-HCH (the latter was also known as lindane) in both the vapor plus particle phases and in the vapor phase alone. Because our measurements of chlorinated insecticides in the particle phase at Sturgeon Point, Sleeping Bear Dunes, Eagle Harbor, and Point Petre stopped in mid-2003, only insecticide data for Chicago and Cleveland are given as the sum of the vapor and particles phases. We are presenting here the sum of the concentrations of *p*,*p*′-DDT, *p*,*p*′-DDE, and *p*,*p*′-DDD as "total DDTs"; the sum of the concentrations of $\alpha$- and $\gamma$-chlordane and *trans*-nonachlor as 'total chlordanes', and the sum of the concentrations of endosulfan-I, endosulfan-II, and endosulfan sulfate as 'total endosulfans'. In these three cases, we are presenting vapor phase concentrations at all six sites and vapor plus particle phase concentrations at Chicago and Cleveland.

Because environmental concentration measurements are log-normally distributed,[12] all averages presented here are geometric means. Data over an entire year were averaged to eliminate seasonal effects, which are large. If the data did not cover an entire year, they were not included. All of the resulting data are included in the Supporting Information. We assumed a first-order model such that

$$\ln(\overline{C}) = a_0 + a_1 t \quad (1)$$

where $\overline{C}$ is the geometric mean concentration in year $t$ and $a_0$ and $a_1$ are fitted constants. A halving time was calculated from



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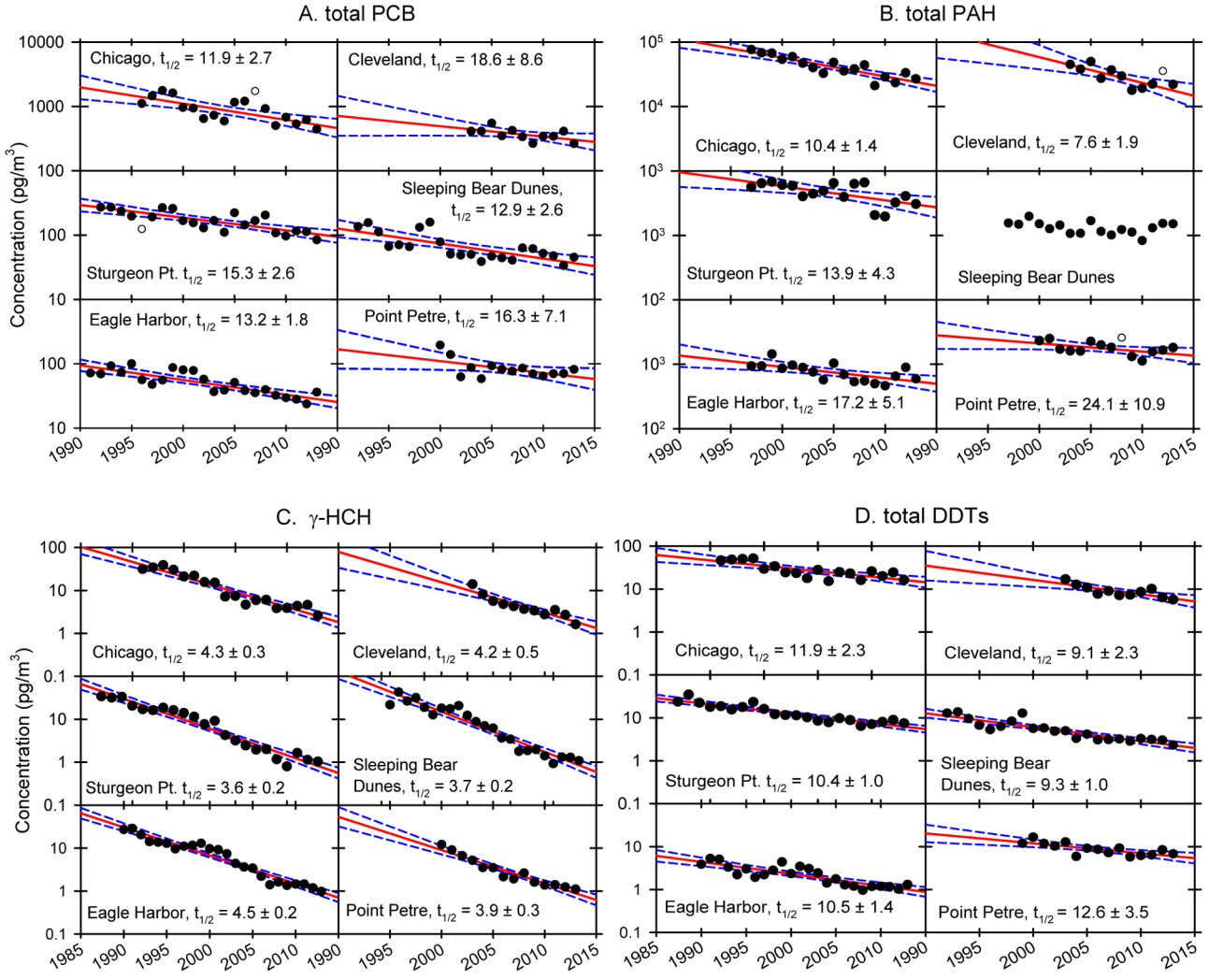


**Figure 1.** (A) Annual, geometric average, vapor phase concentrations of all measured PCB congeners summed together and plotted as a function of sampling year. The empty circles in the Chicago (2007) and Sturgeon Point (1996) panels represent outliers and were not used for the regressions shown here. Note the concentration scales for the Chicago and Cleveland data are 10 times higher than for the other sites. (B) Annual geometric average, vapor and particle phase, concentrations of all the measured polycyclic aromatic hydrocarbons (PAH) summed together and plotted as a function of sampling year. The empty circles in the Cleveland (2012) and Point Petre (2008) panels represent outliers and were not used for the regressions shown here. The regression for the Sleeping Bear Dunes data was not statistically significant at $P < 0.05$. Note the concentration scales for the Chicago and Cleveland data are 10 times higher than for the other sites. (C) Annual geometric average, vapor phase, concentrations of $\gamma$-HCH (also known as lindane) plotted as a function of sampling year. (D) Annual geometric average, vapor phase, concentrations of *p,p′*-DDT, *p,p′*-DDE and *p,p′*-DDD summed together and plotted as a function of sampling year. In all cases, the blue dashed lines represent the 95% confidence limits of the regressions, and the halving times (and their standard errors) are given in each plot.

$$t_{1/2} = \frac{-\ln(2)}{a_1} \quad (2)$$

Regression analyses gave the standard error of the $a_1$ parameter from which the standard error of $t_{1/2}$ was calculated. All of the statistical results are included in the Supporting Information, and the halving times are summarized in Table 1.

**Polychlorinated Biphenyls (PCBs).** These compounds were banned from production and use in the United States in 1976, and their concentrations in the environment decreased rapidly starting at that time. For example, the PCB concentrations in lake trout from Lake Michigan decreased 6-fold between 1975 and 1985[13] but have decreased much more slowly since that time.[8,13] Our atmospheric measurements also indicate a slow rate of decrease, with halving times ranging from 11.9 ± 2.7 years (Chicago) to 18.6 ± 8.6 years (Cleveland) (see Figure 1A). An overall halving time for PCB concentrations in the Great Lakes' atmosphere of ∼15 years suggests that there are still sources of PCBs leaking into the air even 40 years after they were banned. Clearly, it will take a long time for these compounds to completely disappear from the environment.

There were no differences in the halving times of PCBs among the six sites, suggesting a relatively homogeneous decrease rate in the Great Lakes region. The only exception was PCB-101 at Sturgeon Point, the halving time of which was about twice that at Eagle Harbor. Within each site, the halving times for PCB-18, -52, and -101 were statistically indistinguishable from one another and from those of total PCBs (see Table 1), with one exception. The sole exception was at Sturgeon Point, where the halving time of PCB-18 (8.9 ± 1.0 years) was significantly faster than those of total PCBs, PCB-52, and PCB-101. This result may indicate that this trichloro congener is more rapidly removed from the atmosphere than other congeners or that PCB-52 and PCB-101 have unusually long halving times at this particular site,


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perhaps suggesting larger reservoirs of these two congeners near this site.

The concentrations for all PCBs measured during 2007 at Chicago were unusually high, and these data were omitted from the regressions. These high PCBs concentrations have been noticed before and were attributed to building construction in the vicinity of the sampling site on the Illinois Institute of Technology campus.[14] The unusually low concentrations at Sturgeon Point in 1996 are inexplicable.

**Polycyclic Aromatic Hydrocarbons (PAHs).** These compounds are not manufactured intentionally as commercial products; rather, they are produced by the incomplete combustion of any carbon-based fuel. Outside of general restrictions on the emissions of particles from large-scale combustion systems, there have been no bans on the production of PAH. Nevertheless, our data for total PAH concentrations (see Figure 1B) show some significant decreases over time, with halving times ranging from 7.6 ± 1.9 to 24.1 ± 10.9 years. The levels of PAH at Chicago and Cleveland are relatively high, but these concentrations are decreasing most rapidly, probably because of the controls on particle emissions from combustion sources imposed over the last 30−40 years, especially in cities. It is encouraging that PAH levels are also decreasing significantly at Eagle Harbor, our most remote site. Concentrations of phenanthrene are decreasing at approximately the same rate as total PAH concentrations except at Sleeping Bear Dunes and Point Petre, where no significant decreases were observed. Significantly decreasing rates for benzo[*a*]pyrene were detected only at Chicago and Sturgeon Point, and the halving time at Chicago was approximately half that at Sturgeon Point. The unusually high total PAH concentrations observed at Cleveland in 2012 and at Point Petre in 2008 suggest that there might have been elevated PAH sources at these sites at these times.

**Hexachlorocyclohexanes ($\alpha$- and $\gamma$-HCHs).** These two compounds were widely released into the environment as insecticides even though only the $\gamma$-isomer had insecticidal properties. This practice changed in 1942, when the $\gamma$-isomer was purified and marketed under the name "lindane". The use of this compound was restricted in Canada in 2004 and in the United States in 2009. Our data (see Table 1 and Figure 1C) indicate that the concentrations of both of these compounds have halving times in the atmosphere of ∼4 years. This is the most rapid halving time we have observed for any compound in our study. The HCHs are the most volatile of the compounds we have studied, and this may explain their relatively rapid atmospheric loss rate. For Chicago and Cleveland, we have 17 and 11 years, respectively, of overlapping vapor and particle phase data from which we can calculate the halving time for the concentrations of these two compounds in these two phases added together. The vapor phase and the vapor and particle phase halving times were indistinguishable from each other. The halving times for $\alpha$- and $\gamma$-HCH in the vapor phase at Eagle Harbor were significantly ($P < 0.01$) slower than those at Surgeon Point and Sleeping Bear Dunes. The relatively slow halving times for the HCHs measured at Eagle Harbor were indistinguishable from those at the urban sites. This is a somewhat surprising result, which would not have been uncovered without the relatively high precision of these regressions.

**Total DDTs.** DDT itself has been banned in North America since 1972. It degrades in the environment to DDE and DDD, so we are presenting the concentrations of these three compounds summed together. The range of halving times in the vapor phase is relatively small, from 9.1 ± 2.3 years at Cleveland to 12.6 ± 3.5 years at Point Petre (see Table 1 and Figure 1D). For compounds that have been off the market for more than 40 years, it is remarkable that they are still present in the environment, but it is gratifying that their concentrations are decreasing, albeit at a decadal rate. The vapor phase only versus the vapor and particle phase rates at Chicago and Cleveland are statistically indistinguishable from one another. This is expected given that ∼79% of the atmospheric load of these compounds is associated with the vapor phase. DDT was heavily used for an extended period of time. In the 30 years before its ban, more than 600 million kg of DDT was used in the United States,[15] creating a large environmental reservoir that is taking a long time to dissipate.

**Total Chlordanes.** These insecticides were widely used for termite control around homes and other wooden structures. Chlordane's use in the United States was restricted in 1988, well after the bans on DDT and PCBs. Our measured halving times for these compounds in the vapor phase (8.7 ± 0.7 to 11.7 ± 3.7 years) are similar to those of the DDTs with no significant differences at any site or for any phase (see Table 1). Approximately 87% of the atmospheric load of these compounds is associated with the vapor phase, a value similar to that of total DDTs. The similarities of the environmental halving times and vapor−particle partitioning behavior of the DDTs and chlordanes suggest that these two groups of pollutants are both leaking from similar sources into the atmosphere at approximately the same rates.

**Total Endosulfans.** This insecticide is still on the market, but it is slated for complete elimination in 2016. Even though it is currently in use, it is interesting that its vapor phase atmospheric concentrations around the Great Lakes are decreasing with halving times ranging from 7.1 ± 1.6 years at Point Petre to 8.9 ± 1.2 years at Eagle Harbor. The vapor only versus the vapor and particle rates in Chicago and Cleveland are indistinguishable from one another even though, in this case, only 59% of the atmospheric load is associated with the vapor phase.

Given that endosulfan is still in use, its halving time is a combination of the rate at which its use is being restricted and its environmental degradation rate. We estimated the rate at which the use of endosulfan is decreasing from its usage data in the United States each year from 1997 to 2009.[16] These data indicate a usage halving time of ∼9 years. This can be added to the measured average atmospheric halving time to give a chemical degradation halving time:[17]

$$t_{\text{chem}} = \left( \frac{1}{t_{\text{atms}}} + \frac{1}{t_{\text{use}}} \right)^{-1} \tag{3}$$

where $t_i$ is the halving time in either the atmosphere (8 years) or due to usage restrictions (9 years) or chemical degradation (unknown). This result suggests an atmospheric chemical degradation halving time of ∼4 years. This halving time is significantly less than those for total DDTs and total chlordanes, suggesting that endosulfan is less environmentally persistent than these other compounds. This reduced environmental persistence is likely related to the more polar functionality of the sulfur heterocyclic substructure (see Scheme 1).

**Significance.** This study presents temporal trends for the POPs measured by the Integrated Atmospheric Deposition Network; these trends have been calculated from annual geometric mean concentrations for each chemical or chemical group for the vapor phase and for the vapor plus particle phase at each site. Previous studies used several different and complex



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**Table 2. Halving Times (in years) Observed in Previous Studies of the Integrated Atmospheric Deposition Network Data Set Compared to Those Reported Here[a]**

| demographics | | | | | compound | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| first author and ref | years of data | no. of sites | phase(s) | method[b] | ΣPCB | α-HCH | γ-HCH | ΣDDT | ΣChlor | ΣEndo | Phen | BaP | ΣPAH |
| Hillery et al.[1] | 1991−1995 | 3 | vapor | CC reg | 5.8 ns | | | | | | | | |
| Cortes et al.[2] | 1991−1995 | 5 | vapor | CC reg | | 2.7−4.9 | 2.2−3.4 | 1.8−7.1 | 1.5 ns | | | | |
| Cortes et al.[3] | 1991−1997 | 3 | particle | 1st ord | | | | | | | 9.6 ns | 4.9 ns | |
| Cortes and Hites[18] | 1991−1997 | 3 | vapor | CC reg | | 3.0−3.2 | 3.4−4.4 | 3.5−6.2 | 2.4 ns | | | | |
| Buehler et al.[19] | 1991−2000 | 3 | vapor | CC reg | 8.3−18 | 3.3−4.4 | 4.3−7.9 | 7.4−17 | 6.8−16 | | | | |
| Sun et al.[4] | 1991−2003 | 7 | vapor | CC reg | | | | | | | 8.8−13 | | 8.7−19 |
| Sun et al.[4] | 1991−2003 | 7 | particle | sine reg | | | | | | | 4.8 ns | 4.8 ns | 5.6 ns |
| Sun et al.[5] | 1991−2003 | 7 | vapor | CC reg | | 3.8−4.2 | 4.2−5.9 | 5.0−16 | 4.9−13 | 3.2 ns | | | |
| Sun et al.[5] | 1991−2003 | 7 | particle | sine reg | | 1.7 ns | 3.1−5.1 | 3.8 ns | 3.9 ns | 3.0 ns | | | |
| Sun et al.[6] | 1991−2003 | 7 | vapor | CC reg | 7.7−26 | | | | | | | | |
| Venier and Hites[20] | 1991−2007 | 6 | vapor | CC reg | 13 ± 1 | 3.3 ± 0.1 | 3.8 ± 0.1 | 7.8 ± 0.3 | 10. ± 0.5 | 11 ± 1 | | | 19 ± 2 |
| Venier and Hites[7] | 1991−2007 | 6 | all phases | partial | 17 ± 2 | 3.3 ± 0.1 | 3.5 ± 0.1 | 8.6 ± 0.4 | 6.4 ± 0.3 | 13 ± 1 | 11 ± 1 | | |
| Venier et al.[14] | 1991−2008 | 2 | vapor | 4 ways | 8−19 | 3−4 | 4 | | | | 9−12 | | |
| Salamova et al.[8] | 1991−2010 | 3 | vapor | annual | 12−23 | 2.9−3.9 | 2.5−3.1 | 8.4−10 | 8.1−10 | | | | |
| this work | 1991−2013 | 6 | vapor | annual | 12−19 | 3.5−4.3 | 3.6−4.6 | 9.1−13 | 8.7−12 | 7.1−8.9 | − | − | − |
| this work | 1991−2013 | 6 | vap+part | annual | − | 4.0 | 4.2−4.3 | 7.7−9.9 | 9.2−10 | 6.4−8.3 | 6.4 ns | 6.6 ns | 7.6 ns |

[a]Where ranges are given, the times are the minimal and maximal halving times observed at the various sites studied. When times are given with errors, the data from the various sites had been combined in the regression analysis. [b]Abbreviations: CC reg, Clausius−Clapeyron regression; 1st ord, first-order model; sine reg, harmonic regression using only the sine function; partial, regression of the residuals after correction for seasonality and population density; 4 ways, four regressions based on the Clausius−Clapeyron equation, on a sine- and cosine-based model, on digital filtration, and on dynamic harmonic regression.



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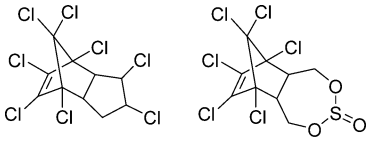
trend analysis methods (which were often different for each phase) and have used shorter (in some cases, much shorter) data sets. The results of the trends reported here are compared to those reported in previous studies in Table 2. The data in Table 1 were collapsed into ranges for Table 2 because our analysis of

**Scheme 1. Structures of Chlordane and Endosulfan**




these data did not indicate site specific differences. In general, the simple statistical approach used here gives results comparable to those that were obtained in previous studies, especially when data from more than 10 years were included. These findings confirm the reliability of this method, and they indicate that accurate temporal rates can be estimated using this relatively simple approach. Another important feature of this approach is that all of the annual geometric mean concentrations can be published (see the Supporting Information) as opposed to regression equations that require the users to calculate the concentrations themselves.

Although there are no clear spatial trends in the halving times given in Table 1, Cleveland and Point Petre usually have higher errors associated with their times, probably because the time series covers fewer years at these two sites than at the other four. Adding more data to the time series analyses for all the sites has decreased and will continue to decrease the standard errors for the calculated halving times, and this has improved the precision of the results.

## ■ ASSOCIATED CONTENT

### Supporting Information

Summary of the availability of the data from the Integrated Atmospheric Deposition Network (Figure S1) and all of the annual geometric mean concentrations (in picograms per cubic meter) for all of the compounds discussed here for all of the sampling years and for all of the six sites, along with the regression results using eqs 1 and 2 (Table S1). This material is available free of charge via the Internet at http://pubs.acs.org.

## ■ AUTHOR INFORMATION

### Corresponding Author

*E-mail: hitesr@indiana.edu. Phone: (812) 855-0193. Fax: (812) 555-0193.

### Notes

The authors declare no competing financial interest.

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