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Temporal trends of persistent organic pollutant concentrations in precipitation around the Great Lakes[☆]

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ABSTRACT

The concentrations of polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs), and several chlorinated insecticides in precipitation have been measured in samples collected every month since 1997 at six sites on the shores of the North American Great Lakes. We report here the geometric mean concentrations for each of these compounds for each year and at each site. Assuming a first-order rate decline for these data, we have calculated the time it takes for these concentrations to decrease by half. The halving times are not statistically distinguishable among the sites. Overall, the observed halving times are 11 ± 2 years for the PCBs, 14 ± 3 years for the PAHs, 4.0 ± 0.2 for the hexachlorocyclohexanes, 8.0 ± 0.9 for the DDTs, 5.1 ± 0.8 for the chlordanes, and 8.4 ± 0.6 for the endosulfans. In general, the halving times calculated from precipitation concentrations agree with those calculated from atmospheric vapor and particle phase concentrations.

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1. Introduction

Tracking the effectiveness of the Stockholm Convention (SC) requires careful measurements of the environmental concentrations of persistent organic pollutants (POPs). In a recent paper, we used the vapor and particle phase atmospheric concentrations of several POPs measured at six sites on the shores of the North American Great Lakes to investigate the rate at which these compounds were disappearing from the environment (Salamova et al., 2015). In that paper, we reported that the atmospheric concentrations of polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAHs) were decreasing with halving times (the time it takes for the concentration of that chemical to decrease by a factor of two) of 10–15 years; those of the hexachlorocyclohexanes were decreasing with halving times of 3–4 years; and those of other chlorinated pesticides were decreasing with halving times of 8–10 years. All of these halving times were based on atmospheric concentrations measured once every 12 days from 1 January 1991 until 31 December 2013. This atmospheric measurement campaign is part of the Integrated Atmospheric Deposition Network (IADN), a joint United States–Canadian effort.

This paper is a companion paper to this previous publication (Salamova et al., 2015). Here, we will focus on the same pollutants, and ask the same question: How fast are the concentrations of these compounds decreasing? But in this paper, we will base this analysis on measurements of these compounds in precipitation collected monthly at the same six sites around the Great Lakes. These measurements cover the period 1 January 1997 until 31 December 2013. We have previously presented the temporal trends of precipitation concentrations of these compounds in a series of papers using earlier data. Using data from 1997 to 2002, Carlson et al. (2004) found few significant temporal trends in the concentrations of these compounds in precipitation. Later, using data from 1997 to 2003, Sun et al. (2006a, 2006b, 2006c) found a few concentration trends, but with one exception, most of these concentrations in precipitation were not decreasing significantly. The one exception was for PCBs in Chicago, where a halving time of 6.8 ± 3.1 years was observed (Sun et al., 2006b). More recently, using data from only Point Petre over the period 2000–2011 (inclusive), Liu et al. (2014) reported halving times of 12–19 years for PCBs, 3.5–4.6 years for the HCHs, 7.1–13 years for DDTs, chlordanes, and endosulfans.

This paper brings those earlier analyses forward in time and uses a new statistical approach that we have used earlier for the atmospheric vapor and particle phase concentrations; namely, temporal regressions based on annual geometric means (Salamova et al., 2015). This paper also fully integrates our data at all six

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sampling sites and includes almost all of the compounds measured by IADN (except flame retardants), a list which has evolved over time. A guide showing the data coverage for the different compound types and sampling sites as a function of year is shown in Fig. S1. We will also compare trend measurements based on precipitation versus those based on the atmospheric vapor and particle phases.

2. Experimental section

Samples were collected from six sites on the shores of the Great Lakes: Eagle Harbor, near Lake Superior; Sleeping Bear Dunes and Chicago, near Lake Michigan; Sturgeon Point and Cleveland, near Lake Erie, and Point Petre, near Lake Ontario. The last site is co-located with one operated by Environment Canada, but the data reported here are from an Indiana University sampler. Details of these sites can be found on the IADN website (<https://www.ec.gc.ca/rs-mn/default.asp?lang=En&n=BFE9D3A3-1>). Precipitation samples were integrated over an entire month, and the total amount of precipitation in that month was measured. Although some periods were slightly longer or shorter, we usually collected 12 samples per year.

Precipitation was sampled using MIC automated wet-only samplers (MIC Co., Thornhill, ON). Each sampler consists of a 46 by 46 cm shallow funnel connected to a 30-cm long by 1.5 cm i.d. glass column (ACE Glass, Vineland, NJ) packed with XAD-2 resin. The sampler is normally covered, but it is opened automatically during a precipitation event, which is sensed by a conductivity grid. This grid is heated to prevent condensation, ice build-up, and prolonged sampling after the end of a precipitation event. The funnel and the interior of the sampler are also heated to melt any snow that falls into the sampler and to keep the XAD-2 resin column from freezing.

The precipitation flows by gravity from the funnel through the XAD-2 resin column and into a large carboy, which is used to measure the total precipitation volume associated with a given sample. Because there is no filter in the system, the XAD-2 resin column collects both particulate and dissolved phase contaminants in precipitation. These columns were prepared at our Indiana University laboratory and sent to the sites for sample collection. After sampling, the cartridges from all six sites were sent back to Indiana University and stored at 5 °C until extraction. The XAD resin was removed from the column and extracted in a Soxhlet apparatus with a 1:1 (v:v) acetone hexane mixture (OmniSolv, EM Science, Gibbstown, NJ). Twenty-five mL of HPLC-grade water was added to the Soxhlet extract immediately after completion of the extraction but before separation of the phases by a separatory funnel. The organic phase was then evaporated and exchanged to hexane. The sample was cleaned by silica (Aldrich, silica gel) column chromatography after separation of the water layer. More details, including information on surrogates, internal standards, recoveries, and the collection of the vapor and particle phase samples can be found elsewhere (Sun et al., 2006a, 2006b, 2006c).

The PCBs and organochlorine insecticides were measured with electron capture gas chromatography with a 60-m column. The GC peak identifications were occasionally verified by gas chromatographic mass spectrometry (Wu et al., 2009). The PAHs were measured with isotope dilution gas chromatographic mass spectrometry in the electron impact mode. All analyses are based on internal calibration compounds. All concentrations are given in pg/L of precipitation. Extensive QA/QC procedures have been implemented (Wu et al., 2009). None of the concentrations reported here have been blank or recovery corrected.

3. Results and discussion

With the exception of Cleveland, where sampling started in 2003, most of the sites have full data sets from 1997 to 2013 (inclusive). The following discussion will focus on the following compounds or compound groups: “Total PCBs” include about 80 PCB congeners that were present in the various Aroclor commercial mixtures. In addition, we are presenting individual precipitation concentrations of PCB-18, PCB-52, and PCB-101; these congeners have 3, 4 and 5 chlorines, respectively. We selected these 3 congeners because they are considered “indicator PCBs” (Castro-Jiménez et al., 2008), they were relatively abundant, and they were measured as isomerically clean GC peaks. Because of resource limitations, we do not have PCB precipitation data for Sturgeon Point, Sleeping Bear Dunes, or Eagle Harbor. Among the PAHs we measured, we are focusing here only on the concentrations of phenanthrene, benzo[a]pyrene, and total PAHs (defined as the sum of the concentrations of the 22 PAHs measured). We selected these compounds because phenanthrene was the most abundant PAH measured and because benzo[a]pyrene is a well-known carcinogen. Among the chlorinated insecticides, we are focusing here on the concentrations of α - and γ -HCH (the latter was also known as lindane), “total DDTs” (the sum of the concentrations of *p,p'*-DDT, *p,p'*-DDE, and *p,p'*-DDD), “total chlordanes” (the sum of the concentrations of α - and γ -chlordane and *trans*-nonachlor), and “total endosulfans” (the sum of the concentrations of endosulfan-I, endosulfan-II, and endosulfan sulfate).

Because environmental concentration measurements are log-normally distributed (Hites, 2015), all averages presented here are geometric means. Data over an entire year were averaged to eliminate seasonal effects, which are large (Sun et al., 2006c). The resulting data are included in the Supplementary Information. We assumed a first-order decline such that

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

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

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

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

Polychlorinated biphenyls (PCBs). The concentrations of PCBs in precipitation in Chicago are decreasing with halving times of 7.9–10.6 years and at Point Petre with halving times of 5.3–13.5 years, depending on the congener. These values in Chicago are similar to those reported previously by Sun et al. (2006b). In Cleveland, the situation is anomalous; here the halving times of PCB-18, 52, and 101 range from –5.6 (a negative halving time means that the concentrations are actually doubling) to 10.3 years, with no significant trend detected for total PCB levels. For PCB-18, the concentrations are doubling every 5.6 years but it is not clear why this one congener at this one site should show such a different behavior. These results may suggest that the dataset at Cleveland is not yet long enough to indicate clear temporal trends.

Our previously reported atmospheric measurements (based on the vapor phase PCB concentrations) (Salamova et al., 2015) are also summarized in Table 1. With the exception of total PCBs and PCB-18 at Cleveland and PCB-52 at Point Petre, the halving times determined from the atmospheric vapor phase and from precipitation are not significantly different and do not vary systematically among sites. Looking at the averages across sites and at both the

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