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ORGANOPHOSPHATE FLAME RETARDANTS IN THE GREAT LAKES ATMOSPHERE

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Introduction

Organophosphate esters (OPEs) are used in many consumer and industrial products to delay ignition and slow the spread of fire in order to comply with flammability regulations. Polybrominated diphenyl ethers (PBDEs) have historically been the most widely used brominated flame retardants, but these compounds now are off the market globally due to their persistence, bioaccumulation, and toxicity. Because of these restrictions on PBDEs, the production and use of OPEs have increased during recent years.¹ Halogenated (mainly chlorinated) OPEs, such as tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCIPP) and tris(1,3-dichloropropyl) phosphate (TDCIPP), as well as non-halogenated aryl OPEs, such as triphenyl phosphate (TPHP), are used as flame retardants (FRs) in building materials, electronics, plastics, furniture, and textiles. The majority of non-halogenated alkyl OPEs are used as plasticizers and anti-foaming agents in hydraulic fluids, lacquers, and floor polishes.² Consequently, OPEs have been detected throughout the environment, including in water,³ sediment,⁴ indoor air,⁵ biota,⁶ and human milk and urine.^{7,8} However, data on their environmental concentrations, persistence, bioaccumulation, toxicity, and long-range atmospheric transport are still limited.

There have been only a handful of measurements of these chemicals in the ambient atmosphere, but the data that exist suggests that these compounds can undergo long-range atmospheric transport.⁹⁻¹¹ Specifically, OPEs were detected at concentrations of about 1 ng/m³ in aerosols from Antarctica in 1994.⁹ It has been suggested that the elevated levels of OPEs in pine needles from the Sierra Nevada Mountains, United States (up to 1950 ng/g),¹⁰ and in Finnish remote air (up to 12 ng/m³)¹¹ are also due to long-range atmospheric transport. More recently, Möller et al. reported OPE concentrations up to 3 ng/m³ in airborne particles over the Pacific, Indian, Arctic, and Southern Oceans,¹² as well as over the North Sea,¹³ demonstrating the widespread global occurrence of these chemicals.

In this study, we present our measurements of several halogenated and non-halogenated OPEs in particle, vapor and precipitation samples collected as part of the Integrated Atmospheric Deposition Network (IADN). We sampled at five sites in the United States Great Lakes basin every 12 days from March 2012 to December 2014 (inclusive). This is the first comprehensive report on atmospheric OPE concentrations in all three atmospheric phases, and on the spatial and temporal variations of these concentrations.

Materials and methods

Atmospheric vapor, particle and precipitation samples were collected at the five United States Integrated Atmospheric Deposition Network (IADN) sampling sites. The locations include urban sites in Chicago, IL (41.8344 N, -87.6247 W) and Cleveland, OH (41.4921 N, -81.6785 W), a rural site at Sturgeon Point, NY (42.6931 N, -79.0550 W), and remote sites at Sleeping Bear Dunes, MI (44.7611 N, -86.0586 W) and Eagle Harbor, MI (47.4631 N, -88.1497 W). The IADN website provides detailed information on air sampling procedures and site operations (www.msc.ec.gc.ca/iadn). The samples discussed here were collected during the period of March 2012 through December 2014 for the particle samples and during January 2014 through December 2014 for the vapor and precipitation samples.

A modified Anderson high-volume air sampler (General Metal Works, model GS2310) was used to collect air samples for 24 hours every 12 days at a flow rate giving a total sample volume of about 820 m³. Particles were collected on Whatman quartz fiber filters (QM-A, 20.3 × 25.4 cm) and vapor was collected on XAD-2 resin. 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. Precipitation samples are integrated over a month. Details of the sampling procedures and site operations can be found elsewhere.¹⁴

A detailed description of the sample treatment and chemical analysis procedures for the particle samples has been given elsewhere.¹⁵ In summary, the samples were spiked with known amounts of d^{12} -tris(2-chloroethyl) phosphate and $^{13}C_{18}$ triphenyl phosphate as surrogate standards and Soxhlet extracted for 24 h with a 1:1 acetone hexane mixture. The extract was reduced in volume by rotary evaporation, the solvent was exchanged to hexane, and fractionated on a column containing 3.5% w/w water deactivated silica gel (3% for precipitation samples). The column was eluted with 25 mL of hexane, 25 mL of 1:1 hexane in dichloro-methane, and 25 mL of 7:3 acetone in dichloromethane mixture. The OPEs eluted in the third fraction. After N_2 blow down, the samples were spiked with the quantitation internal standards (d_{10} -anthracene, d_{12} -benz[a]anthracene, and d_{12} -perylene). The samples were analyzed by electron impact gas chromatographic mass spectrometry for three chlorinated OPEs [tris(2-chloroethyl) phosphate (TCEP), tris(1-chloro-2-propyl) phosphate (TCPP), and tris(1,3-dichloro-2-propyl) phosphate (TDCPP)]; for one alkyl phosphate [tri-n-butyl phosphate (TnBP); and 2 aryl phosphates [triphenyl phosphate (TPhP) and ethylhexyl diphenyl phosphate (EHDP)]. The details on the instrumental analyses can be found elsewhere.^{16,17}

Results and discussion

Particulate OPE concentrations. Overall, total organophosphate (notated as Σ OPE, the sum of the six OPEs) concentrations range from 239 ± 16 pg/m^3 at Sleeping Bear Dunes to 1650 ± 120 pg/m^3 at Cleveland. As expected, OPEs were generally more abundant at the urban sites (Chicago and Cleveland) than at the rural and remote sites (Sturgeon Point, Eagle Harbor, and Sleeping Bear Dunes). A one-way analysis of variance showed that the levels of Σ OPEs at Chicago and Cleveland were significantly higher ($P < 0.001$) than those at Sturgeon Point, Sleeping Bear Dunes, and Eagle Harbor. This spatial distribution pattern has been shown previously for brominated flame retardants (BFRs)¹⁸ and is not surprising considering that OPEs are used for similar purposes. Figure 1A shows the concentrations of OPEs at each site in the particle phase. Among chlorinated OPEs, either TCIPP or TCEP were the most abundant chlorinated OPE at all the sites. Interestingly, the composition profile for Σ OPE concentrations was different at Sleeping Bear Dunes and Eagle Harbor, our remote sites. The concentrations of the three non-halogenated OPE compounds, TPHP, TnBP, and EHDP, were major contributors to Σ OPE concentrations at these two sites, and their concentrations were statistically indistinguishable from the concentrations of the halogenated OPEs.

Vapor OPE concentrations. Overall, Σ OPE concentrations ranged from 345 ± 39 pg/m^3 at Eagle Harbor to 1250 ± 150 pg/m^3 at Cleveland. As observed in the particle phase, OPEs were generally more abundant at the urban sites than at the rural and remote sites. A one-way analysis of variance showed that the levels of Σ OPEs at Chicago and Cleveland were significantly higher ($P < 0.001$) than those at Sturgeon Point, Sleeping Bear Dunes, and Eagle Harbor; the latter three had statically indistinguishable Σ OPE concentrations. Figure 1B shows the concentrations of OPEs at each site in the vapor phase. Among chlorinated OPEs, TCIPP and TCEP were the most abundant chlorinated OPE at most of the sites. At our most remote site, Eagle Harbor, the levels of non-chlorinated OPEs were statistically indistinguishable from the levels of the chlorinated OPEs. Interestingly, some of the vapor concentrations were higher or similar to particle concentrations. Figure 2 shows the ratio of the vapor concentrations to particle concentrations for each of the six OPEs at each site (leftmost) and the vapor to particle concentrations ratio averaged for all the sites for each OPE (rightmost). It is clear, that TPHP, EHDP, TDCIPP, and TCEP are mostly present in the vapor phase, while TnBP and TCIPP are mostly present in the particle phase.

Precipitation OPE concentrations. Overall, Σ OPE concentrations range from $23,300 \pm 6,900$ pg/L at Sleeping Bear Dunes to $220,000 \pm 38,000$ pg/L at Eagle Harbor. Surprisingly, the spatial distribution in precipitation is different from that in the particle and vapor samples. For precipitation, the highest levels were observed at Eagle Harbor, our most remote site, mostly due to very high TPHP levels at this site. With the exception of Eagle Harbor, the next most elevated levels are observed at our urban

sites, Chicago and Cleveland. Figure 1C shows the concentrations of OPEs at each site in precipitation. Among chlorinated OPEs, either TCIPP or TDCIPP were the dominant chlorinated OPE at most of the sites. TPHP levels were not statistically different from the levels of the chlorinated OPEs at all the sites, with the highest TPHP levels detected at Eagle Harbor.

Summary. Overall, our data clearly show that OPEs are widely present in all phases of the atmosphere at both urban and remote location and that they may undergo long range atmospheric transport.

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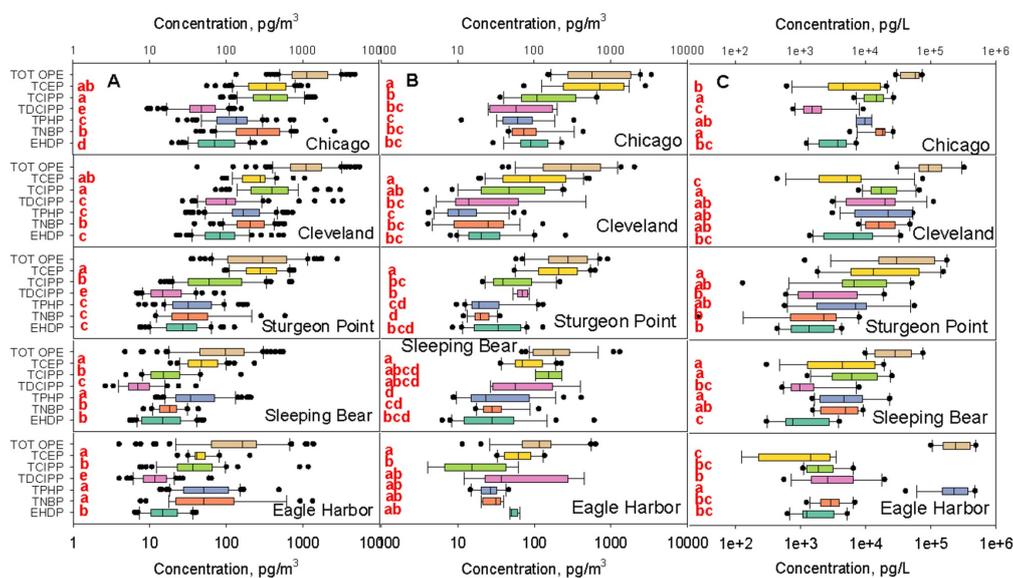


FIGURE 1. Concentrations of OPEs in particles (A, pg/m^3), vapor (B, pg/m^3) and in precipitation (C, pg/L) at the five North American Great Lakes IADN sites. The black line inside each box represents the median, the boxes represent the 25th and 75th percentiles. ANOVA results using logarithmically transformed concentrations are shown; the concentration distributions sharing the same letter are not statistically different at $P < 0.05$.

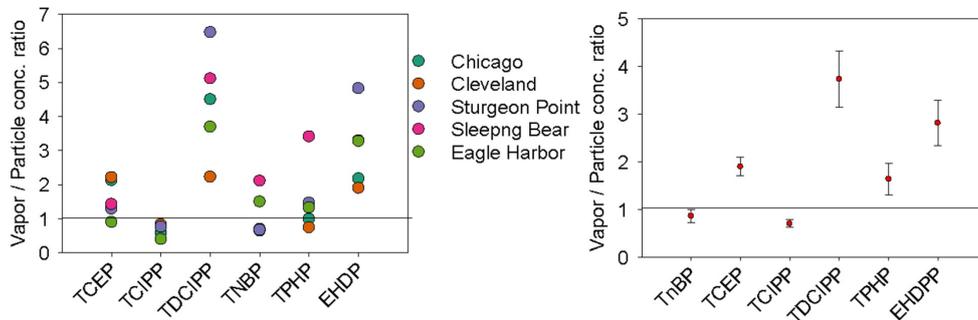


FIGURE 2. Vapor / particle concentrations ratio for the six OPEs at each IADN site (leftmost) and the average vapor / particle concentration ratio for all IADN sites together for each of the six OPEs (rightmost).