SUPPORTING INFORMATION

High Levels of Organophosphorus Flame Retardants in the Great Lakes Atmosphere

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Experimental Details

Instrumental Analyses. The samples were analyzed for the following compounds:

Chlorinated phosphate esters:	
tris(2-chloroethyl)phosphate	(TCEP)
tris(1-chloro-2-propyl)-phosphate	(TCPP)
tris(1,3-dichloro-2-propyl)phosphate	(TDCPP)
Alkyl phosphate esters:	
tri-*n*-butyl phosphate	(TnBP)
tri(butoxyethyl)phosphate	(TBEP)
tris(2-ethylhexyl)phosphate	(TEHP)
Aryl phosphate esters:	
triphenyl phosphate	(TPP)
tri-*o*-tolyl-phosphate	(TOTP)
tri-*p*-tolyl-phosphate	(TPTP)
tris(3,5-dimethylphenyl)-phosphate	(TDMPP)
tris(2-isopropylphenyl)phosphate	(TIPPP)
tris(4-butylphenyl) phosphate	(TBPP)

Analyses were performed on an Agilent 7890 series gas chromatograph coupled to an Agilent 5973 mass spectrometer operating in the electron impact mode. Chromatographic separations were achieved using a DB-5MS Ultra Inert capillary column (30 m × 250 µm film thickness, Agilent Technologies, Santa Clara, CA). Injections (2 µL) were made in the pulsed splitless mode, and the injection port was held at 280 ºC. The GC oven temperature was programmed as follows: 70 ºC for 3 min, 10 ºC/min to 170 ºC, held for 5 min, 10 ºC/min to 230 ºC, held for 5 min, 5 ºC/min to 250 ºC, and then 10 ºC/min to 300 ºC, held for 3 min. The total run time was 41 minutes. The helium carrier gas (99.999%; Liquid Carbonic, Chicago) was used at a constant flow rate of 1.5 mL/min. The temperature of the GC-MS transfer line was maintained at 280 ºC. The electron energy was set at 70 eV, and the ion source temperature was set at 230 °C. Selected ion monitoring of the following ions was used to detect and quantitate these compounds:

Compound	m/z
TnBP	99
TEHP	99
TCEP	249
TCPP	125
TDCPP	191
TPP	326
TBEP	85
TOTP	368
TPTP	368
TIPPP	452
TDMPP	410
TBPP	479

Quality Control and Quality Assurance. Details on IADN quality control and quality assurance procedures are described in the IADN Quality Assurance Program Plan (U.S. EPA 2001). Briefly, four quality control criteria were used to ensure the correct identification and quantitation of the target compounds: (*a*) The gas chromatographic retention times matched those of the standard compounds within ± 0.1 minutes. (*b*) The signal-to-noise ratio was greater than 3:1. (*c*) The isotopic ratios for selected ion pairs were within ± 15% of the theoretical values. *(d)* The recoveries of recovery standards [d_{12}-*tris*(2-chloroethyl)phosphate (TCEP) and $^{13}C_{18}$ triphenyl phosphate] were between 50% and 130%. The average surrogate recoveries were in the range of 70-100%.

Either a laboratory blank (a quartz fiber filter or a XAD-2 cartridge extracted in the laboratory the same way as the samples) or an OP spike recovery sample was run with every batch of 6-10 samples. In total, 11 laboratory blanks were extracted, and the average total ΣOP mass in these blanks were 6.3 ± 2.1 ng. Only TnBP and TPP were detected in the laboratory blanks with the average levels of 3.7 ± 2.0 ng and 2.6 ± 0.4 ng, respectively. These masses in the blanks correspond to < 10% of the mass collected in any of the rural or remote air samples and < 2% of the mass collected in either of the urban samples. The average recoveries for the spiked samples were ~75%.

Field blanks were collected at every site seasonally and were used to assess the extent of background contamination present in the field. Field blanks were collected using the same type of quartz fiber filters and XAD-2 resin cartridges. The blanks were installed and kept in a collocated sampler for the same period of time as regular samples without turning on the sampler motor. ΣOPs concentrations in the field blanks comprised ~8% , 12%, 23%, 14%, and 7% of these concentrations in Chicago, Cleveland, Eagle Harbor, Sleeping Bear Dunes, and Sturgeon Point samples, respectively. On average, ΣOPs concentrations in the field blanks comprised 13 ± 3% of these concentrations in all of the samples. TnBP, TDCPP, TCEP, and TPP were the most abundant OPs in these blanks and comprised 23 ± 7%, 18 ± 15%, 15 ± 7 %, and 9.7 ± 2.8% of average sample levels, respectively. TCPP, TBEP, TEHP, and TBPP were detected in blanks at < 5% of average sample levels. The rest of the OPs were not detected in the field blanks. Concentrations below the annual field blank site-by-site averages were treated as non-detects.

Materials. TnBP was purchased from Acros Organics, distributed by Fisher Scientific, Pittsburgh, PA. TCEP, TCPP, and were purchased from AccuStandard, New Haven, CT. TPP, TOTP, TPTP, TDMPP, and TIPPP were purchased from Wellington Laboratories, Guelph, ON. TBEP and TEHP were from MP Biomedicals, Santa Ana, CA. TBPP was from Sigma-Aldrich, St. Louis, MO. All solvents used for the extraction and cleanup procedures were residue-analysis grade. Glassware was baked at 500 ^{0}C for at least 6 hours prior to use.

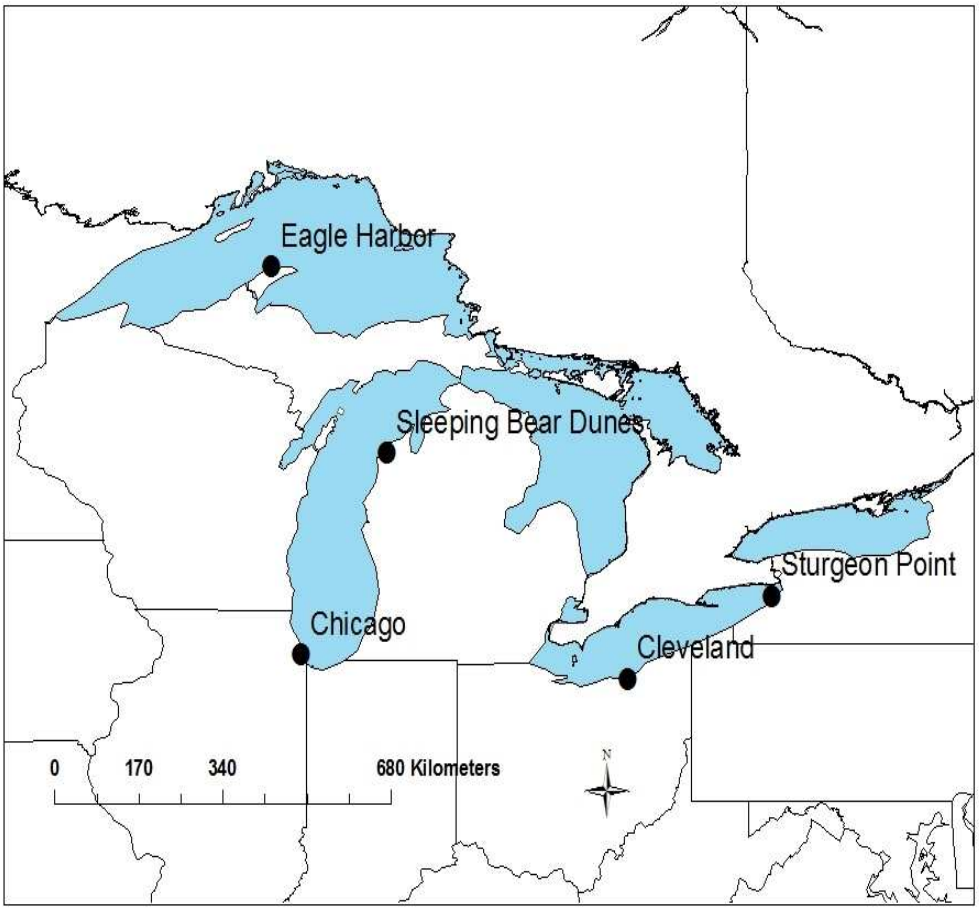

FIGURE S1. Locations of the United States' Integrated Atmospheric Deposition Network (IADN) sampling sites.

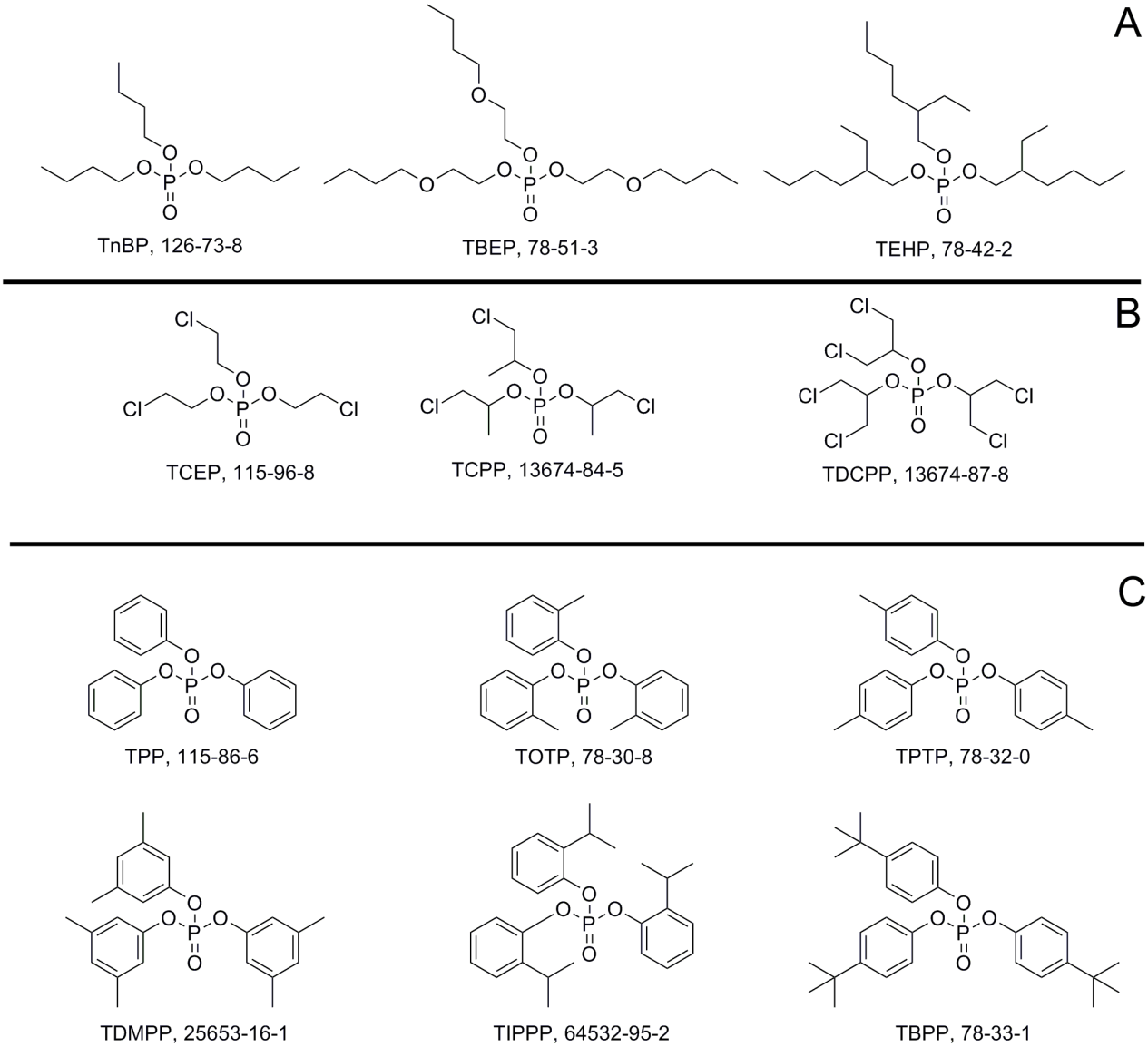

Figure S2. Structures of the compounds discussed in the text, their abbreviations, and their *Chemical Abstracts* Registry Numbers. Section **A** represents alkyl phosphate esters, section **B** represents chloroalkyl phosphate esters, and section **C** represents aromatic phosphate esters.

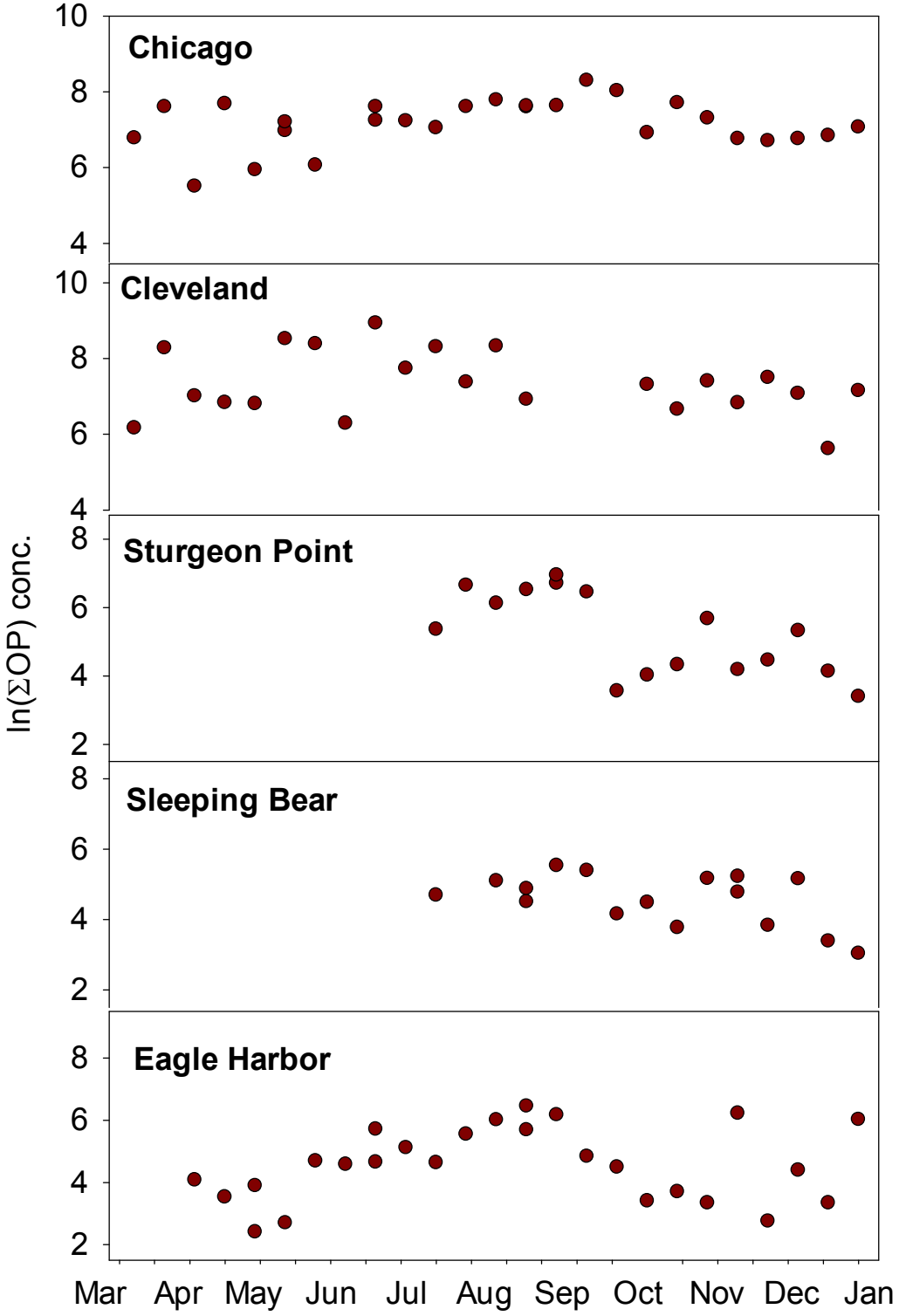

FIGURE S3. Seasonal variations in ΣOP concentrations (plotted as the natural logarithms of their concentrations in pg/m^3) at the five IADN sites.

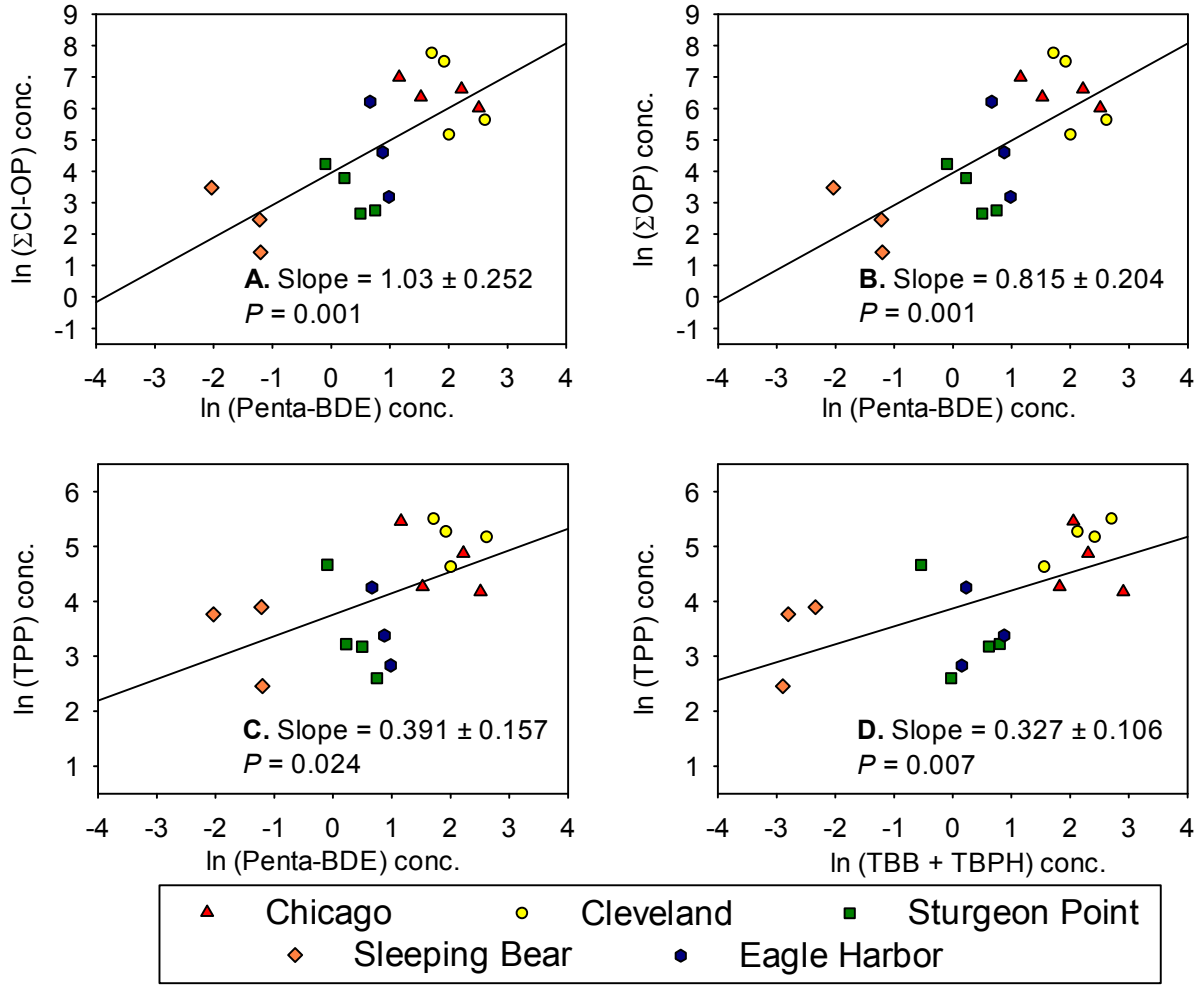

FIGURE S4. Pairwise correlations of the natural logarithms of the seasonally averaged concentrations (in pg/m^3) for: (A) Penta-BDE and ΣCl-OPs; (B) Penta-BDE and ΣOPs; (C) Penta-BDE and TPP; and (D) TBB+TBPH and TPP at the five IADN sites. The regression lines (in black), the probabilities of the regressions being not significant (*P*), and the slopes are given in each plot.