

# A NATIONAL SURVEY OF ORGANOPHOSPHATE ESTER FLAME RETARDANTS IN CANADIAN HOUSE DUST

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## Introduction

Organophosphate esters (OPEs), in particular triesters, represent an important class of commercial additives used as flame retardants, plasticizers, hydraulic fluids, solvents, extraction agents, antifoam agents, adhesives, and coatings for electronic devices. The chemical structures of organophosphate esters used as flame retardants and plasticizers are similar to those of organophosphorus insecticides, which are designed to affect the nervous system of insects. There are indications that some OPEs, particularly chlorinated OPEs such as tris(dichloro-isopropyl) phosphate (TDCPP), tris(2-chloroethyl) phosphate (TCEP), and tris(chloropropyl) phosphate (TCPP), could have adverse health effects<sup>1,2</sup>. House dust is known to be a repository for semi-volatile organic compounds and particle-bound organic matter and thus may be a significant source of human exposure to some environmental pollutants, including OPEs. The objective of this study was to generate exposure data for these emerging flame retardants using house dust samples collected for the Canadian House Dust Study (CHDS). A large sample size (n = 818) of house dust was analyzed to provide a nationally representative urban house estimate for 13 organophosphate ester concentrations ( $\mu\text{g/g}$ ).

## Materials and methods

### Chemicals

Target OPEs included trimethyl phosphate (TMP), triethyl phosphate (TEP), tripropyl phosphate (TPrP), tri-isobutyl phosphate (TiBP), tri-n-butyl phosphate (TnBP), TCPP, tripentyl phosphate (TPeP), TCEP, tributoxyethyl phosphate (TBEP), 2-ethylhexyl-diphenyl phosphate (EHDPP), triphenyl phosphate (TPhP), TDCPP, and tricresyl phosphate (TCrP). Individual OPE standards were purchased from TCI America (Portland, OR) except TPrP and TCPP (Sigma-Aldrich, Oakville, ON, Canada). Deuterated internal standards (i.e., TMP-d<sub>9</sub>, TEP-d<sub>15</sub>, TPrP-d<sub>21</sub>, TnBP-d<sub>27</sub>) were purchased from CDN Isotopes Inc. (Pointe-Claire, QC, Canada). Diphenyl methyl phosphate (DPhMP) was purchased from Chem Service (West Chester, PA) and <sup>13</sup>C<sub>18</sub>-TPhP from Wellington Laboratory (Guelph, ON, Canada).

### Sample collection

Two types of vacuum samples were collected from randomly selected urban Canadian single family dwellings under Health Canada's Canadian House Dust Study as previously described<sup>3,4</sup> and briefly summarized here. Household vacuum dust (HD) samples were obtained from the vacuum systems used by the study participants as part of their regular housecleaning routine. Fresh dust (FD) sampling was conducted by trained technicians following protocols developed for the CHDS<sup>4</sup>. FD samples were collected in living areas (bedrooms, living rooms, hallways, offices) using a Pullman Holt (model 102 ASB-12PD) vacuum sampler, in which dust particles follow a direct pathway from the floor to the vacuum bag, without contacting the internal mechanical parts, thus avoiding potential contamination. The areas sampled to collect the FD samples consisted of "active" dust and minimized the inclusion of old house dust found in joints and cracks in flooring or in areas where the householder did not vacuum on a regular basis. Wet areas in the home (kitchens, bathrooms, laundry rooms) were avoided to protect the integrity of the FD sample. The home owner was asked not to vacuum the sampling areas for a period of one week before the scheduled FD sampling. The samples were collected in the winter season.

### Sample extraction and cleanup

Dust samples (0.06 g  $\pm$  0.003 g), spiked with internal standard mixture solution (200 ng each for TMP-d<sub>9</sub>, TEP-d<sub>15</sub>, TPrP-d<sub>21</sub>, and TnBP-d<sub>27</sub>, DPhMP, and <sup>13</sup>C<sub>18</sub>-TPhP in toluene), were sonicated in hexane/acetone (3 x 1.5 mL, 1:1, v/v) for 15 min and centrifuged for 5 min at 1500 rpm. The clear supernatant was transferred to a 7-mL

amber vial, concentrated and then solvent exchanged to hexane. HLB SPE cartridges, preconditioned with acetone, dichloromethane (DCM) and hexane, were used for sample cleanup. One milliliter of the extract was loaded onto the cartridge. The cartridge was first eluted with 3 x 3.5 mL of hexane. This fraction was saved for other uses and will not be discussed here. Target OPEs were then eluted with 2 x 3 mL of hexane/DCM (1:1). The eluates were evaporated to just dryness at room temperature and then reconstituted in 200  $\mu$ L of toluene.

#### GC/MS/MS analysis

Sample extracts were analyzed using a Varian GC (CP-3800) coupled with a Varian Saturn 2200 ion trap mass spectrometer (Palo Alto, CA). The GC column was a DB-1701 (30 m x 0.25 mm i.d., 0.25  $\mu$ m film thickness) from J&W Scientific (Folsom, CA). The ion trap MS was operated in positive chemical ionization (PCI) mode using methanol as reactant gas. The MS conditions for the monitoring of target analytes are listed in Table 1.

**Table 1.** Target OPEs, molecular weights (MW), precursor ions, collision energies, product ions, method detection limit (MDL), limit of quantitation (LOQ), and average recovery (Ave. Rec., %).

Compound	Acronym	MW	Precursor Ion (m/z)	CID <sup>a</sup> (V)	Product ion (m/z)			MDL ( $\mu$ g/g)	LOQ ( $\mu$ g/g)	Ave. Rec. (%)
					(Q/q/q) <sup>b</sup>					
Trimethyl-	TMP	140	141	0.56	<b>127</b>	109	99	0.08	0.28	118
Triethyl-	TEP	182	183	0.43	<b>155</b>	127	99	0.09	0.29	111
Tripropyl-	TPrP	224	225	0.33	<b>183</b>	141	99	0.20	0.68	90
Tri-iso-butyl-	TiBP	266	267	0.36	<b>99</b>	211	155	0.40	1.32	79
Tri-n-butyl-	TnBP	266	267	0.36	<b>211</b>	155	99	0.07	0.23	83
Tri(chloropropyl)-	TCPP	326	327	0.30	<b>251</b>	175	99	0.11	0.35	94
Tripentyl-	TPeP	308	309	0.40	<b>239</b>	169	99	0.07	0.23	92
Tri(2-chloroethyl)-	TCEP	284	285	0.46	<b>223</b>	161	99	0.16	0.53	83
Tributoxyethyl-	TBEP	398	399	0.43	<b>299</b>	199	99	0.43	1.43	88
2-Ethylhexyl-diphenyl-	EHDPP	362	251	0.46	<b>247</b>	233	153	0.16	0.55	60
Triphenyl-	TPhP	326	327	0.46	<b>247</b>	251	233	0.13	0.42	104
Tris(dichloro-isopropyl)-	TDCPP	430	431	0.46	<b>319</b>	211	209	0.08	0.28	102
Tricresyl-	TCrP	368	369	0.10	<b>369</b>	370	355	0.03	0.12	112

<sup>a</sup>Collision induced dissociation (CID, V)

<sup>b</sup>Q = quantifying ion, q = qualifier ion

## Results and discussion

### Method performance

The method detection limit (MDL) and limit of quantitation (LOQ), calculated using the procedure outlined in the US EPA Regulation 40 CFR part 136<sup>5</sup>, ranged from 0.03  $\mu$ g/g for TCrP to 0.43  $\mu$ g/g for TBEP. The method demonstrated good recoveries, ranging from 60% for EHDPP to 118% for TMP.

### Comparison of HD and FD samples

Concentration ranges for the 8 OPEs detected (TnBP, TCPP, TCEP, TBEP, EHDPP, TPhP, TDCPP, and TCrP) in 134 pairs of household vacuum dust (HD) and fresh "active" dust (FD) are listed in Table 2. Results for all 8 OPEs obtained from the two sampling methods (HD vs FD) demonstrated significant ( $p < 0.001$ ) positive correlations based on Spearman Ranking (Table 2), indicating that analysis of organophosphate esters using HD

samples is a cost-effective and informative alternative to the expensive fresh dust samples collected by trained technicians.

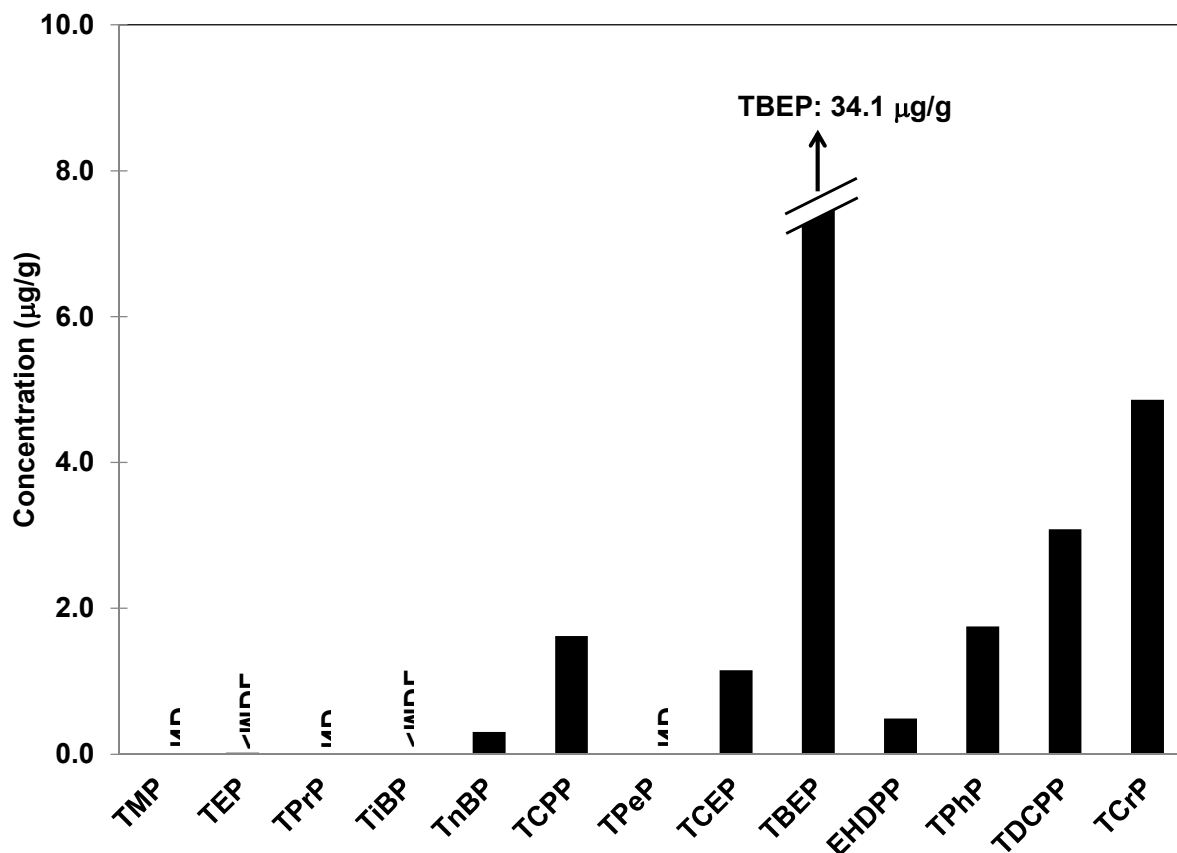
**Table 2.** Summary data (concentrations in  $\mu\text{g/g}$ ) and Spearman rank correlation coefficients of paired samples (FD vs HD) for eight detected analytes ( $p < 0.001$  for all 8 analytes).

Sample		TnBP	TCPP	TCEP	TBEP	EHDPP	TPhP	TDCPP	TCrP
<b>FD</b> (n=134)	Median	0.25	1.36	0.80	31.9	0.54	1.75	2.73	2.61
	Min	<MDL	<MDL	<MDL	3.58	<MDL	0.26	0.12	0.08
	Max	7.13	55.9	32.8	143	105	63.4	76.6	62.2
	95th PCTL <sup>a</sup>	1.45	12.7	4.36	105	2.08	8.92	8.97	14.8
	DF (%) <sup>b</sup>	87.3	97.0	95.5	100	88.8	100	100	100
<b>HD</b> (n=134)	Median	0.26	1.12	0.60	22.77	1.02	1.60	2.01	0.99
	Min	<MDL	<MDL	<MDL	2.42	<MDL	<MDL	0.11	0.05
	Max	4.42	49.4	7.04	236	15.13	95.0	101	75.2
	95th PCTL <sup>a</sup>	1.36	9.58	3.73	115	6.12	12.1	11.9	6.90
	DF (%) <sup>b</sup>	89.6	95.5	94.8	100	91.8	99.3	100	100
Spearman's rank coefficient $r_s$		0.632	0.736	0.558	0.655	0.353	0.497	0.523	0.536

<sup>a</sup>95th percentile, <sup>b</sup>DF = detection frequency (%)

#### National OPE baseline values

Median concentration values of OPEs from 818 dust samples are presented in Figure 1. TMP, TPrP, and TPeP were not detected in any dust samples. TEP and TiBP were only detected in 15.5% and 13.3% of the samples, respectively. The median concentrations of these two OPEs were below their respective method detection limits. Among the OPEs detected, the most dominant was TBEP with median concentrations of 34.1  $\mu\text{g/g}$ . Other OPEs such as TnBP, TCPP, TBEP, EHDPP, TPhP, TDCPP and TCrP, were present at high detection frequencies in the dust samples. Widely scattered concentration levels were observed for target OPEs detected in dust samples, indicating a potentially wide variability in Canadian household exposures to these chemicals. The association of home characteristics and OPE exposure has not been analyzed yet. Data from this study will inform risk assessment and risk management of these organophosphate flame retardants.



**Figure 1.** Median OPE concentrations ( $\mu\text{g/g}$ ) in 818 urban house dust samples

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