Organophosphate Esters Levels in House Dust samples from Canada, Egypt and Turkey

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Introduction

Organophosphate esters (OPEs) are high-production-volume chemicals used as plasticizers and flame retardants in many products such as spray foam insulation, polyurethane foam, furniture, plastics, electronics equipment and textiles[1]. The recent phase-out of the Penta and Octa polybrominated diphenyl eithers (PBDEs) formulations, have led to the increased use of alternate flame retardants (FRs), including OPEs, to meet flammability standards. Similar to PBDEs, OPEs are 'additive', as opposed to 'reactive' FRs, allowing them to migrate out of the material into the environment via volatilization, abrasion, and dissolution [2, 3]. Measurements of OPEs confirmed their widespread presence throughout the environment in levels that generally exceeding those of PBDEs [4, 5]. Since OPEs are used in a wide array of household consumer products their presence in indoor dust is expected. OPEs have been detected in household and office dust at levels up to several mg/kg [6, 7]. Studies point out that indoor dust serves as an important exposure pathway for humans especially for toddlers who ingest larger quantities of dust compared to adults because of increased hand-to-mouth contact and related behaviors.
The objectives of this study were 1) to investigate the occurrence and distribution of OPEs in house dust from different countries that possess different flammability regulations and house characteristics including the type of construction and insulation 3) to assess the relative intake of OPEs compared to PBDEs and other currently used flame retardant from the same indoor dust samples

Materials and methods

Chemicals
The target analytes included: six non-halogenated OPEs [(tri-phenyl phosphate (TPhP), tris (2-ethylhexyl) phosphate (TEHP + its metabolite bis(2-ethyl hexyl) phosphate (BEHP)),: tris (cresyl) phosphate (TCP, isomers o, m and p), tris (2-butoxyethyl) phosphate (TBEP), ethyl-hexyl-diphenyl phosphate (EHDPP), tris (2-isopropyl phenyl) phosphate (TPPP)], three chlorinated OPEs [(tris (2-chloropropyl) phosphate (TCPP, sum of TCiPP1 + TCPP2), tris (2-chloroethyl) phosphate (TCEP), tris (1,3-dichloro-2-propyl) phosphate (TDCiPP)] and one brominated OPEs: tris (2,3-dibromo-2-propyl) phosphate (TDBPP).

Sample Collection
Dust was collected by obtaining whole vacuum cleaner bags, or by subsampling the contents of canisters from bag-less or central vacuums from houses of three cities of Vancouver, Canada (n=92) during 2007-2008, Istanbul, Turkey (n=39) during February-March 2012 and Cairo, Egypt (n=17) during December 2013 and January 2014.

Sample extraction and analysis
Around 0.1g of dust sample, homogenized, sieved with mesh size of 150 □m, weighed in a glass test tube and then spiked with three labeled OPEs: d-tri-ethyl phosphate, d-tributyl phosphate and d-tri-propyl phosphate prior to extraction. Spiked dust was vortexed for one min and left for a few hours to complete absorption of the labelled compounds. Extraction was conducted by sonication with 3ml of dichloromethane (DCM) mixture for 10 minutes, and then centrifuged for 3 minutes. This extraction step was repeated 3 times with fresh DCM. Supernatants from each extraction were combined and the volume was reduced to 1 mL under a gentle stream of nitrogen and solvent exchanged into iso-octane. Extracts were cleaned up by Florisil, the column was washed with 8 mL of methanol followed by 8 mL of hexane. Extracts were eluted with 7 ml hexane followed by 8 mL of ethyl acetate. Florisil fractions were concentrated to a final volume of 1 mL under a gentle stream of nitrogen and solvent exchanged into iso-octane as the keep solvent. A 100 ng of mirex was added as an internal standard to each sample prior to analysis.

Instrumental Analysis

Analyses of OPEs were performed using an Agilent 5980 gas chromatograph coupled to an Agilent 5973 mass selective detector (Mississauga, ON). Separations of analytes were performed on 30 m DB-5 capillary column (0.25 µm film thickness, 0.25 mm i.d. (J &W Scientific, Folsom, CA) with injector temperature set at 200 ºC. The source and quadrupole temperatures were set to 230 ºC (EI) or 150ºC (NCI).

Results and discussion

Concentrations and distribution of OPEs in house dust

The highest Σ_{12}OPEs concentrations (ng/g) observed in the Canadian houses (ranged from 2,600 to 733,000; median 43,300), while concentrations in dust from Turkey and Egypt were lower (ranging from 750 to 26,600; median 2,700) and (7,300 to 99,500; median 14,000), respectively. The substantial differences between OPEs concentrations in houses from the three cities likely reflect differences in the extent to which OPEs are used in indoor applications, flammability standards and possible differences in environmental persistence.

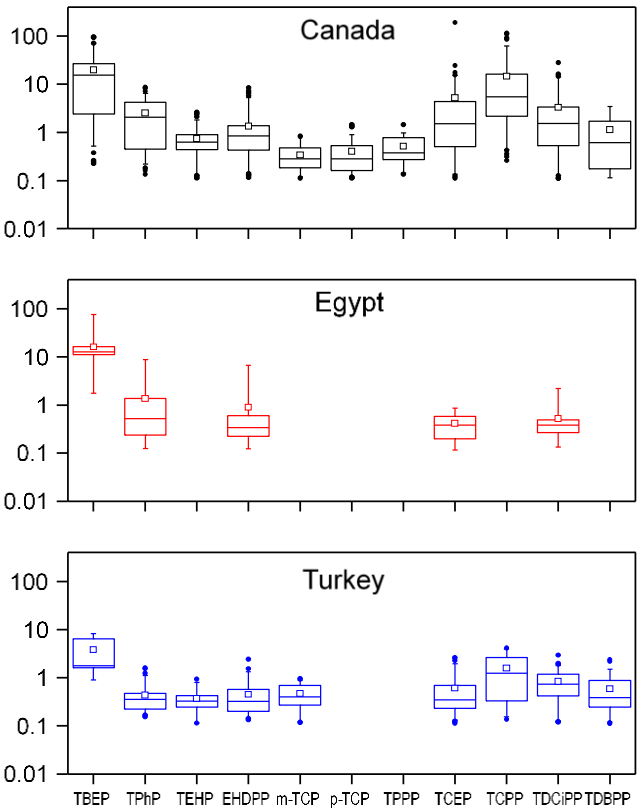

Figure 1. Box and whisker plot summarizing the concentrations of OPFRs (ng/g) in house dust samples from Vancouver, Canada (Top), Cairo, Egypt (middle) and Istanbul, Turkey (bottom). The lower and upper ends of the box represents the 25th and 75th percentiles of the data. The line and square symbols represent the median and arithmetic mean, respectively. The whiskers define the 5th and 95th percentile. Dots show data outside the 5th and 95th percentiles. (Results are not shown for OPFRs compounds that were detected in less than 50% of samples)

The large variability observed within the same city (represented by high standard deviation for the OPEs concentrations) may indicate fresh and varied inputs or release of these compounds into homes, for example houses recently insulated with spray foam insulation will probably have very high levels of TCPP as that is the FR commonly added

Relative Distribution of OPEs in dust from different countries

TBEP was the most abundant non-halogenated OPE in all house dusts, representing 53%, 40% and 92% of total analyzed OPEs in Canada, Turkey and Egypt respectively. TBEP was detected in 100% of the dust collected from Canada and Egypt, while in only 5% of the dust collected from Turkey. The median concentrations (ng/g) in the Canadian and Egyptian houses dust were 22,984 and 12,916 respectively, while the concentrations in dust from Turkey ranging from 1,755 to 8,283. TBEP is used in many applications in homes, for example in floor polishes, where it acts both as a plasticizer and leveling agent, as a plasticizer in vinyl plastics, rubbers and water based

acrylic coatings, as a temporary de-foaming agent and as a flame retardant [8]. The high level and dominance of TBEP in the dust from Egypt could be related to the common practice of polishing the hard wood flooring rather than its application as flame retardant. The chlorinated OPEs, TCPP, TCEP and TDCiPP were detected in 91% to 100% of Canadian dusts, 35% to 100% of Turkish dusts and 100% in Egyptian dusts (except for TCPP which was detected in 6% of the samples). The distribution of individual Cl-OPEs to ΣCl-OPEs in the dust from Turkey were 35% for TCPP, 11% for TCEP and 29% for TDCiPP with ΣCl-OPEs concentration ranging from 420 to 21,700 ng/g with a median value of 1,400 ng/g.

Human exposure via dust ingestion

Human exposure of OPEs via dust ingestion was estimated for toddlers and adults using the following equation .

$$EDI_i = \frac{C_i \times I_{dust} \times \lambda_i}{1000}$$

where EDIi (ng/d) = expected daily intake of target OPEs; Ci (ng/g) = OPEs concentrations measured in house indoor dust ; I_{dust} (mg/d) = dust ingestion rate; λi (dimensionless) = the absorption efficiency of target OPEs. Mean and high dust ingestion rates were used for toddler (i.e., 50 and 200 mg/d, respectively) and adult (i.e., 20 and 50 mg/d, respectively) [9]. We assumed an average body weight (bw) of 70 kg for adults and12 kg for toddlers (http://www.disabled-world.com). The total daily intake EDIi (ng/d) of ΣOPEs was calculated using median scenario which is applicable to most of the population (i.e. using median ΣOPEs concentration and mean dust ingestion rate and a high scenario applicable to 5% of the population (using 95th percentile and high dust ingestion rate). EDI was calculated for toddlers and adults using both exposure senarios. PBDEs and non-PBDE brominated novel flame retardants (NFRs) data were also available for the samples of the current study, therefore, comparison of exposure to these flame retardants also assessed and results are shown in Figure 2.

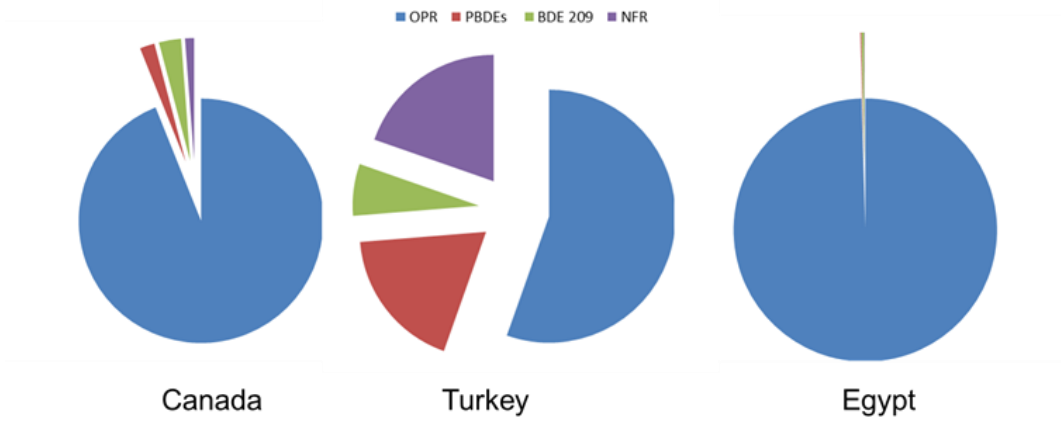

Figure 2. Relative intake for toddler of OPRs, PBDEs, BDE 209 and new flame retardants (median scenario)

The overall concentrations of ΣOPEs in dust were approximately 1 to 2 orders of magnitude higher than those of ΣPBDEs and Σcurrently used alternative flame retardant previously reported for the same dust samples. The higher levels of OPEs, in the three cities studied, compared to PBDEs and alternative flame retardant in dust were consistent with the literature. Our results add to the increasing evidence of indoor contamination and showed that toddlers are highly exposed to these chemicals via dust ingestion. Results suggest that people in the developed countries (e.g. Canada) were more exposed to indoor contaminants including FRs in dust than in the less developed countries (Turkey and Egypt). The difference in the building characteristics (e.g insulations, carpeting and ventilation) and fire regulations could also contribute to the higher exposure found in Canada compare to Turkey and Egypt.

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