Organophosphorus flame retardants in children's car seats: Implications for vehicle air quality

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Abstract. Flame retardants (FRs) are used in many consumer products for fire safety reasons. Their use in children's car seats may result in children's and vehicle occupants' exposure to these compounds including inhalation exposure through poor vehicle air quality. We have tested several children's car seats from local retailers for the presence of FRs. A number of organophosphorus flame retardants (OPFRs) were identified in the extracts (dichloromethane) of eight foam materials taken from the seats. They included several organophosphates (triethyl phosphate (TEP) (detected in all 8 samples) followed by tris(butoxyethyl) phosphate (2), triphenyl phosphate (1), di-(t-butylphenyl) phenyl phosphate (1) butyl diethyl phosphate (1) and tris(4-tert-butylphenyl) phosphate (1)) and organophosphonates (two isomers of 5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphinan-5-yl)methyl methyl methylphosphonate (PMMMP) (detected in 5 of the 8 samples) followed by diethyl ethylphosphonate (1) and 4-methoxy-2-methylbutyl ethyl butylphosphonate (1)). TEP was the most frequently detected among these OPFRs. Due to its relatively high vapour pressure (0.39 mm Hg at 25 °C) among detected OPFRs, TEP is most likely to emit into vehicle interior air during product use, which could result in inhalation exposure for the children using the car seat and other passengers. We therefore have tested the emission rate of TEP in a micro-chamber at 40 °C for estimating potential exposure of vehicle occupants. The emission profile shows the concentrations of TEP in the chamber reached a maximum within the first few hours and then decreased over time. There was a lack of correlation between 24-hour average emission rate and concentrations of TEP in the product. The exact health risk to children and other vehicle occupants in this case requires further research to quantify.

1 Introduction

Flame retardants are widely used in consumer products and building materials to curb the spread of fire and save lives. Organophosphorus flame retardants (OPFRs) are one of the major groups of flame retardants. It includes many individual OPFRs or mixtures of OPFRs [1]. Use of OPFRs in consumer products and building materials have already resulted in their presence in the environment [2] and in humans [3]. A recent survey measuring 21 OPFRs in 178 milk products purchased from 30 countries covering five continents shows the presence of OPFRs in food on a global scale [4]. OPFRs reported in these studies are mostly organophosphates such as triphenylphosphate and chlorinated alkylphosphates; no organophosphonates have been reported.

OPFRs are also detected in the dust of vehicle interiors [5] as well as in children's car seats [6, 7]. In this study, we investigated the presence of OPFRs in polyurethane panels used as cushions in children's car seats sold in Canada and determined emissions of triethylphosphate (TEP), the most volatile OPFR found in the samples. The objective of the study was to identify a wide range of OPFRs used in children's car seats and use TEP as a model compound to demonstrate potential release of OPFRs in vehicles through desorption.

2 Experimental

2.1 Materials and standards

Four children's car seats were purchased from either local stores in Ottawa, Canada or obtained on-line from Canadian retailers. Eight foam samples were cut from different sections of each car seat using a pre-cleaned sharp blade, and were further cut into approximately 2 x 2 x 2 mm cubes using pre-cleaned scissors. The cut material was then wrapped in aluminium foil and sealed inside Ziploc bags for later use.

Standards of several commercially available organophosphates, namely triethyl phosphate (TEP; Reagent Plus; $\geq$ 99.8%), tributyl phosphate (TBP; $\geq$ 99%), tris(2-butoxyethyl) phosphate (TBOEP; 94%), triphenyl phosphate (TPP) and tris(2-ethyl hexyl) phosphate (TEHP; 97%) were purchased from Millipore-Sigma (Oakville, ON, Canada). Methylene chloride (DCM; $\geq$ 99.9%) was obtained from Fisher Scientific (Ottawa, Canada) whereas n-nonane was obtained from Millipore-Sigma (99%; Oakville, ON, Canada). Two deuterated internal standards in n-nonane, namely tributyl phosphate-d^{27} (d^{27}-TBP) and di-n-nonane phthalate-d^4 (d^4-DNNP) were obtained from Cambridge Isotope Laboratories Inc.; MA, USA).

Standard solutions for calibrations were prepared by dissolving appropriate amounts of the organophosphate standards along with the two internal standards in DCM.

2.2 Solvent extraction of samples

A cut foam sample was accurately weighed (around 100 mg) into a 22 mL amber glass vial fitted with a Teflon-lined cap. 10 mL of DCM was then added and the vial was sonicated for 3 hrs in a bath sonicator loaded with ice-cold water. The vial was kept closed during the sonication. After sonication the samples were allowed to stand overnight. 100 μL of the extract was then filtered through a 0.2 μm (pore size) syringe filter into a GC vial fitted with a 200-μL insert for GC/MS analysis (see Section 2.4).

2.3 Micro-chamber tests of emissions

A micro-chamber (μ-CTE^{TM}, Markes International, UK) was used for the chamber tests. The micro-chamber had six equal cells where samples can be placed for testing; each cell was made of stainless steel in a cylinder shape with a volume of 44 mL and a diameter of 0.045 m. The cell can be heated incrementally up to 120 ºC. Each polyurethane foam panel was cut into a circular form to be fitted onto the bottom of the cell (0.0016 m^2) for tests. Air flow was set by adjusting the pressure valve that controls the supply of pure air. The outlet of each cell was fitted with an ORBO-605 (6 mm outer-diameters and 100 mm in length), packed with 100 mg of Amberlite and 50 mg of XAD-2 #20049, Millipore-Sigma; Oakville, ON, Canada) for sample collection. Actual sampling rate was measured using a digital flow-meter (model 4100, TSI Inc., USA). Prior to each test, test cells were washed with acetone, and flushed with clean air overnight at the test temperature.

The ORBO tube was removed from the micro-chamber outlet after sample collection was completed and then the chemicals in the tube were eluted into a vial with 5mL of DCM. The samples were first evaporated to ~500 μL under a gentle stream of N$_2$ and then transferred into a GC vial. The residual was washed with small volume of DCM and added to the GC vial. The solution in the GC vial was evaporated to about 100 μL and further transferred to another GC vial fitted with a 200-μL insert. The residual in the GC vial was washed with small volume of DCM and added to the insert. The solution in the insert was spiked with internal standards and further evaporated to 50 μL for GC/MS analysis (see section 2.4).

2.4 GC/MS analysis

The samples prepared according to sections 2.2 and 2.3 were analysed using an Agilent 7890 GC/7200 Q-TOF gas chromatograph/mass spectrometer (GC-TOF/MS, Agilent Technologies, CA, USA) that was coupled with a CTC-PAL Multi-Purpose autosampler (Agilent Technologies, CA, USA). A DB-5 MS UI column (30 m length, 0.25 mm, outer-diameter and 0.25 μm film thickness, Agilent Technologies, CA, USA) was used for the separation of chemical components. Oven temperature was programmed as follows: initial temperature of 40 ºC for 5 min, increased at 15 ºC/min to 220 ºC followed by increasing at 10 ºC/min to 300 ºC and kept at that temperature for 10 min. Temperature of both the injector port and transfer line was maintained at 280 ºC. The GC was operated in the splitless mode with helium as the carrier gas. The MS was operated in electron impact ionization mode and the ions were scanned in the range of m/z 30 to m/z 600 at an acquisition rate of 4 spectra/sec. The source temperature was set at 230 ºC. Emission current and energy of filament was set at 3.0 mA and 70 eV, respectively.

3 Results and Discussion

3.1 Identification of organophosphates and organophosphonates in foam materials

Several chemicals that belong to the two sub-groups of organophosphorus flame retardants (OPFR), organophosphate and organophosphonate (Fig. 1), were identified in the foam materials used in children's car seats. These two sub-groups of OPFRs differ from each other with the latter group having one P-C bond and two P-O bonds, while the former has three P-O bonds.
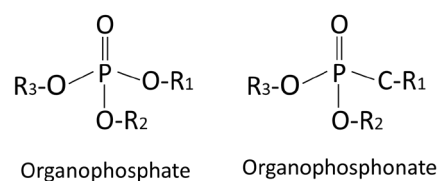
Fig. 1. General structure of organophosphate and organophosphonate.

The identification of OPFRs was initially conducted based on the match of mass spectra with those available in NIST library. Three organophosphates, namely triethylphosphate (TEP), tris(butoxyethyl) phosphate (TBOEP) and triphenylphosphate (TPhP) were further confirmed with analytical standards (Table 1). Among the phosphonates, TEP was detected in all eight samples, while TBOEP and TPhP was found only in one sample each.

Several organophosphonates wer also detected in the samples. Mass spectra of these organophosphonate peaks are characterized by the fragments of m/z 111 ($C_2H_8O_3P^+$), m/z 93 ($C_2H_6O_2P^+$) and m/z 79 ($CH_4O_2P^+$). All these three fragments can be seen in the mass spectrum of methylphosphonates and ethylphosphonates in the NIST library. On the other hand, m/z 99 ($H_4O_4P^+$), which is one of the characteristic fragments of organophosphates such as TEP, is absent in the spectrum of these organophosphonate peaks. Two isomers of PMMMP (CAS: 41203-81-0, molecular weight: 286.2, and chemical structure: 5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphinan-5-yl)methyl methyl methylphosphonate) eluted at 19.695 min and 19.912 min with very similar mass spectrum were further confirmed by their near identical mass spectra to reported ones [7]. PMMMP isomers were presently in

high frequency (five out of eight samples) in the samples. PMMMP isomers were first reported in a Japanese study on window curtains [8] and also recently found in children's car seats [7]. Although production of several other alkylphosphonates including dimethyl methylphosphonate and diethyl ethylphosphonate has been reported [1], their presence in consumer products or in the environment has not been widely reported.

Table 1. Organophosphate and organophosphonate flame retardants identified in eight children's car seat samples.

Chemical	# of Samples
Triethyl phosphate*	8
Tris(butoxyethyl) phosphate*	1
Triphenyl phosphate*	1
Di-(t-butylphenyl) phenyl phosphate	1
Butyl diethyl phosphate	1
Tris(4-tert-butylphenyl) phosphate	1
PMMMP isomer-1**	5
PMMMP isomer-2**	5
Diethyl ethylphosphonate	1
4-Methoxy-2-methylbutyl ethyl butylphosphonate	1

*: Structure confirmed with authentic standards.
**PMMMP = 5-ethyl-2-methyl-2-oxido-1,3,2-dioxaphosphinan-5-yl)methyl methyl methylphosphonate; Structure confirmed by comparing MS spectrum in [7].

3.2 Emission profile of triethylphosphate in chamber tests.

Among the identified OPFRs, triethylphosphate (TEP) has the highest vapour pressure (0.39 mm Hg at 25 °C). Presence of TEP in all samples and its relatively high vapour pressure means that TEP will likely emit into vehicle interior air during product use. We therefore focused on TEP to demonstrate possible emissions of OPFRs from children's car seats and potential inhalation exposure of passengers to these chemicals in vehicles. Six of the eight foam samples were also subjected to emission tests, covering a wide range of TEP concentrations from 280 µg/g to 2352 µg/g (Table 2).

Table 2. Estimation of percentage of TEP emitted in the first 24 hours.

Sample	Test specimen amount (g)	Test specimen thickness (mm)	TEP Conc. in specimen (µg/g)	% TEP emitted in first 24hrs
1	0.52	20	280	22.3
2	0.28	7	428	34.1
3	0.25	7	2352	6.3
4	0.53	11	2126	2.3
5	0.49	12	2174	3.8
6	0.95	20	872	1.1

The chamber tests for emission characterization were conducted in a micro-chamber at 40 °C with the following considerations. The first is that by increasing the test temperature from room temperature we can shorten the required experiment time. The second is that

the interior temperature of a vehicle parked under the sun can easily reach 40 °C [9].

Since the volume of chamber emission cell is very small (44 ml) and flow of clean air was set at 50 ml/min, the air exchange rate per hour for the chamber was 68. In order to collect sufficient amount of TEP for subsequent GC/MS analysis, the sampling time for each tube was set at 2 hours. Since the full chamber exiting air volume passed through the collection tube, the amount of TEP collected in the tube equals to the amount of TEP emitted in the 2 hour time period. The emission rate (ER, µg/h) therefore can be calculated by measured TEP amount in the sample tube divided by the sample collection time (2 hours).

ERs of TEP at the later chamber testing times (23 h and 26 h) were lower than those in early chamber test time (1 h and 3 h data) (Table 3), indicating a depleting source strength over the testing time as TEP emitted from test specimen. We assumed that such decrease is linear, and therefore used the average of the two emission times to calculate the average ER in the first 24 hours. The average ERs from the six test specimens ranged from 1.07 µg/h to 1.70 µg/h, except for one sample at 0.37 µg/h (Table 3). Considering the emission surface area of the specimen in the chamber cell (0.0016 m^2), the emission factors of TEP at 40 °C was in the range of 670 – 1100 µg/(h×m^2).

Table 3. Emission rate (ER, µg/h) of TEP from six samples. The time is the mid-point of time of the 2 hour sampling.

Sample	ER at 1 h	ER at 3 h	ER at 23 h	ER at 26 h	ER average
1	2.00	1.67	1.14	0.61	1.36
2	3.18	2.50	0.62	0.49	1.70
3	2.86	2.43	0.45	0.40	1.54
4	1.42	NA	NA	0.73	1.07
5	2.59	1.93	1.13	1.11	1.69
6	0.77	0.33	0.19	0.18	0.37

The foam materials taken from the car seats have different thickness ranging from 7 mm to 20 mm. The foam was cut circular to fit the bottom of the emission cell but no attempt was made to trim the circular specimen to the same thickness. The non-uniform weight of test specimens (Table 2) were largely a result of different thicknesses of the foam panels. TEP concentrations in the specimens were in the sub-percentage range (0.03% - 0.2% or 280 – 2400 µg/g (Table 2)). Therefore, the difference in emission values among the six samples is likely due to a combination of TEP concentration in the specimen and the thickness of the specimens used in the chamber tests. Estimates of the percentage of TEP emitted from the foam material in the first 24 hours were calculated by multiplying the average ER by 24 hours and then dividing by the amount of TEP present in the specimen (Table 3). Depending on the materials, the estimated emitted amount of TEP at 40 °C ranged from 1.1 % (sample 1) to 34.1 % (sample 2) in the first 24 hours. The two highest percentages of emitted amount were associated with two specimens that had the lowest TEP concentrations.

It was also observed that the average ERs of TEP among the test specimens in the first 24 hours were relatively similar and were not concentration dependant (Fig. 2). Excluding one specimen (sample 6 with data point marked by a solid triangle in Fig. 2), the ERs were approximately in the range of 1-2 µg/h for all specimens. The reason for the low ER of TEP from sample 6 is unclear.
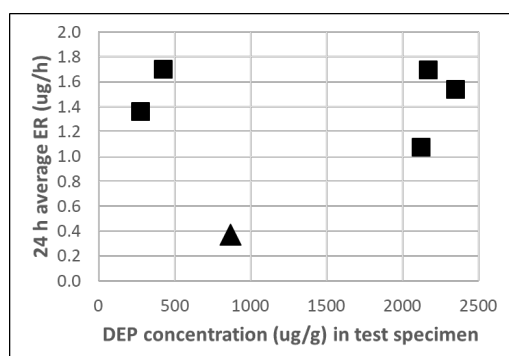
Fig. 2. Emission rate of TEP as a function of TEP concentration in the test specimen.

3.3 Influence of emissions of OPFRs from car seats on indoor air quality in vehicles.

Use of children's car seats is mandated for the safety of children and manufacturing them with materials containing flame retardants can provide additional safety benefits. However, one also has to recognize that added flame retardants may emit from materials during use and impact indoor air quality in vehicles. This is particularly true if such additive flame retardants have relatively high vapour pressure.

One such OPFRs is TEP. The boiling point of TEP (215 °C) is at the higher end of the boiling point range of volatile organic compounds (VOCs), which is generally considered to be in the range of 50 °C – 250 °C as defined by World Health Organization. The boiling point of TEP is in fact almost the same as boiling point of dodecane (216 °C, a C12 alkane VOC). Therefore, emissions of TEP from children's car seat may have a significant impact on the indoor air quality in vehicles.

This study demonstrated potential release of TEP in children's car seats through desorption by simple chamber tests. Both Chen at al. [10] and Xiong et al. [11] have studied emission of VOCs such as benzene and toluene in vehicles at various temperatures of 22.5 – 35.6 °C and 24 – 35 °C, respectively. They found that in general, when temperature is lowered by about 10 °C, the concentrations of VOCs in the vehicle are roughly reduced by half. Although the tests were carried out at 40 °C, emissions of TEP at lower temperatures may also be expected. Our results are considered relevant to real-life exposures, as car seats are subjected to a wide temperature range during use in various weather conditions [9].

4 Conclusions

This study has generated scientific data on the presence of OPFRs used in the foam materials in children's car seats. In addition to organophosphates, several organophosphonates including two PMMMP isomers have also been detected. In addition, emission rate of TEP, a relatively volatile OPFR, was determined at 40 °C using a micro-chamber. These data may be used to assess inhalation exposure to OPFRs emitted from children's car seats in vehicles.

Acknowledgements

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