FLAME RETARDANTS TRIS (1,3-DICHLOROISOPROPYL) PHOSPHATE (TDCPP) AND TRIPHENYL PHOSPHATE IN RECREATIONAL EQUIPMENT: A MINI CASE STUDY

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Introduction

Tris (1,3-dichloro-2-propyl) phosphate (TDCPP) and triphenyl phosphate (TPP) are widely used organophosphate flame retardants (OPFRs) commonly applied to foams, upholstery and related products. With the recent phase-out of flame retardant mixtures PentaBDE and OctaBDE, reliance on OPFRs is likely to increase. Much recent research has focused on TDCPP and TPP in foam-containing products in the home and workplace[1-3]. Currently, there are many other products for which little or nothing is known with regard to the levels of TDCPP and TPP. The objective of this study was to determine if recreational camping equipment could be a source of exposure to flame retardant chemicals. In a mini-case study, we examined potential exposure to TDCPP and TPP associated with camping equipment by measuring these chemicals on hands of volunteers using the equipment as well as measurements of the OPFR metabolites bis (1,3-dichloro-2-propyl) phosphate (BDCPP) and diphenyl phosphate (DPP) in volunteers' urine before and after use.

Materials and Methods

TDCPP and TPP were obtained from Sigma (St. Louis, MO, USA). Deuterated TPP (dTPP, Sigma) was used as a recovery standard for the OPFRs, and 2,2',3,4,5,5'-hexachloro[$^{13}C_{12}$]diphenyl ether (^{13}C-CDE-141, Wellington Laboratories, Guelph, ON, Canada) was used as a second internal standard for OPFRs added just prior to analysis. BDCPP was synthesized by Wellington. DPP and deuterated internal standards d_{10}-BDCPP and d_{10}-DPP were synthesized by Dr. Vladimir Belov (Max Planck Institute for Biophysical Chemistry, Goettingen, Germany). Recreational products tested included a four-person dome tent and an aluminum frame picnic shelter purchased in North Carolina, USA.

Exposure to TDCPP and TPP was examined during a 3 day camping trip. Equipment and automobile surfaces were examined for OPFRs, air samples were collected, and hand wipes were collected from two volunteers during the trip. Prior to the trip, TDCPP and TPP on equipment and automobile surfaces were sampled using wipes consisting of sterile cotton gauze pads soaked in isopropyl alcohol, and stored in glass vials on ice. Wipes of both volunteers' palms were collected in a similar manner prior to departure, after setting up camp, and upon returning from the trip. Air was sampled using glass samplers packed with pre-cleaned XAD-2 resin and polyurethane foam. Air samples were collected in the automobile during the entire time the campers were in the vehicle (13.4 h), and under the picnic shelter and inside the tent for 8.8 h. Urine samples were collected before departure and upon return to monitor flame retardant metabolites BDCPP and DPP. A follow-up study focused on potential exposure from the picnic shelter. Air samples were collected over 12 h with samplers placed next to the shelter fabric and suspended approximately 30 cm below the shelter's center. Hand wipes were collected before and immediately after shelter assembly. Urine samples were collected before assembly, and periodically for 1 day following assembly.

Wipes and air samples were spiked with dTPP and extracted 8h on a Soxhlet apparatus followed by florisil cleanup. Samples were concentrated under N_2, exchanged to hexane, spiked with ^{13}C-CDE-141 and analyzed by gas chromatography (model 6890N, Agilent, Wilmington, DE, USA) with mass spectrometry (Agilent model 5975) (GC-MS) with electron impact ionization using a column and oven temperature program as previously described (Stapleton et al., 2009).

Urine samples were extracted using anion exchange solid phase extraction (SPE; Strata X-AW, Phenomenex, CA, USA). Urine was spiked with d_{10}-BDCPP and d_{10}-DPP, diluted 1:1 *v/v* with HPLC-grade water and acidified to pH 6.5. The sample was loaded onto an SPE cartridge conditioned with methanol and water. The cartridge was washed with water, dried under vacuum and eluted with acetonitrile containing 5% pyrrolidine. Extracts were concentrated to dryness under N_2, resuspended in 4:1 water:methanol, and filtered through a 0.2 µm nylon membrane.

BDCPP and DPP were analyzed by LC/MS-MS on an Agilent 1200 series LC connected to an Agilent 6410B triple quadrupole MS detector with multimode source. Chromatographic separation of the extracts was performed on a Kinetex XBC18 column (Phenomenex) using a gradient of water and methanol. BDCPP and DPP were detected by atmospheric pressure chemical ionization operating in negative ionization mode using multiple reaction monitoring.

Results and Discussion

TDCPP was detected in all vehicle surfaces, tent fabric, and picnic shelter components, whereas TPP was only detected in wipes of the vehicle dash, and picnic shelter fabric and frame at levels lower than those of TDCPP (Table 1). The picnic shelter fabric contained the highest amounts of both TDCPP (18,035 ng per wipe, or 143ng cm^{-2}) and TPP (587 ng per wipe, or 5 ng cm^{-2}).

Table 1. TDCPP and TPP measured in wipes of vehicle surfaces and camping equipment.

Sample	**Area Sampled**	**TDCPP** (ng/wipe)	**TPP** (ng/wipe)
Vehicle components			
Shifter	Entire knob	42	bd[1]
Wheel	Entire wheel	1,635	bd
Windshield	126 cm^2	36	bd
Dash	126 cm^2	398	8.0
Tent fabric	126 cm^2	595	bd
Picnic shelter fabric	126 cm^2	18,035	587
Picnic shelter frame	0.5 m section	1,632	6.0

[1]bd = below detection.

In hand wipes collected before departure, after camp setup involving assembly of the tent and picnic shelter, and after return from the trip, TDCPP was greatly elevated on hands of both volunteers following camp setup (Figure 2a). This finding suggests that handling of the picnic shelter, which contained the highest TDCPP level (Table 1), was a pathway of dermal exposure to TDCPP. Highest levels of TPP, however, were observed at different sampling times for each volunteer and were not associated with camp setup (Figure 2b). These results suggest that the camping equipment was not the primary source of TPP exposure, and that the sources of exposure to TPP varied between the volunteers.

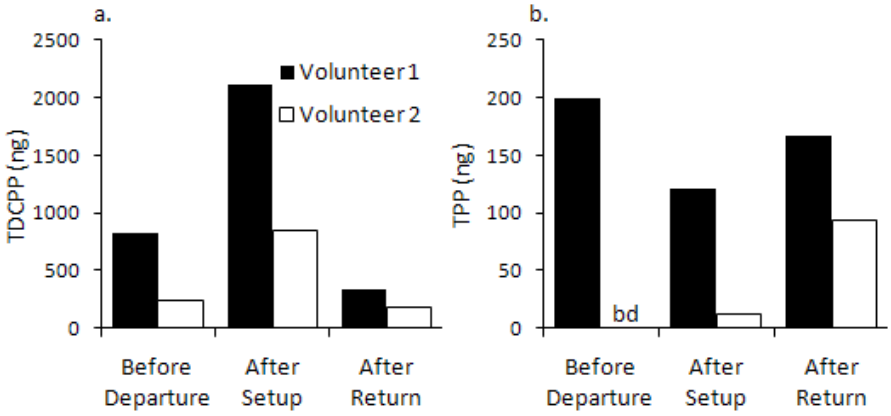

Figure 1. TDCPP (a) and TPP (b) measured on palms of volunteers before departing for the camping trip, after setting up camp, and upon returning from the trip. bd=below detection.

Highest levels of TDCPP in air samples were found in samples collected under the picnic shelter (14 ng m^{-3}) compared to those collected in the car (3.0 ng m^{-3}) and tent (3.0 ng m^{-3}). A similar trend was observed for TPP. TDCPP levels up to150 ng m^{-3} have been reported for indoor air[4], however most reported values are well below that observed for TDCPP in air sampled under the shelter. Flame retardant metabolites BDCPP and DPP measured in urine upon returning from the trip were elevated for both volunteers compared to levels measured before the trip. At 24 h after returning from the trip, metabolite levels were relatively unchanged or had increased with the exception of a decrease in BDCPP for one volunteer. Despite the observation of greater TDCPP than TPP in surface and hand wipes, urinary DPP was higher than BDCPP in all but one sample, suggesting that sources of exposure other than those sampled in this study were present, or that these flame retardants are metabolized at different rates. Further research is needed to better understand human metabolism of TDCPP and TPP.

To further evaluate potential exposure to TDCPP and TPP from the picnic shelter, levels of TDCPP and TPP in hand wipes were elevated following setup of the shelter, which took less than 10 min. This effect was most striking for TDCPP, which increased from 71 ng to 3087 ng on the volunteer's palms. In urine samples collected before shelter setup and periodically for 24 h following setup, BDCPP and DPP reached maximum levels at approximately 9 h and 8.5 h, respectively (Figure 2). As observed in Figure 2, levels of DPP were consistently higher than those of BDCPP. Although the volunteer may have been exposed to TDCPP and TPP from sources other than the shelter throughout the day, these results suggest that these flame retardants are metabolized and/or eliminated at different rates. Levels of TDCPP and TPP in air samples were higher for the sample collected close to the fabric and frame (25 ng TDCPP m^{-3}; 2.0 ng TPP m^{-3}) compared to the sample collected at approximately 30 cm suspended from the shelter center ($\leq$ 1 .0 ng m^{-3} for both TDCPP and TPP).The greater levels of TDCPP than TPP in air is consistent with greater TDCPP levels in surface wipes.

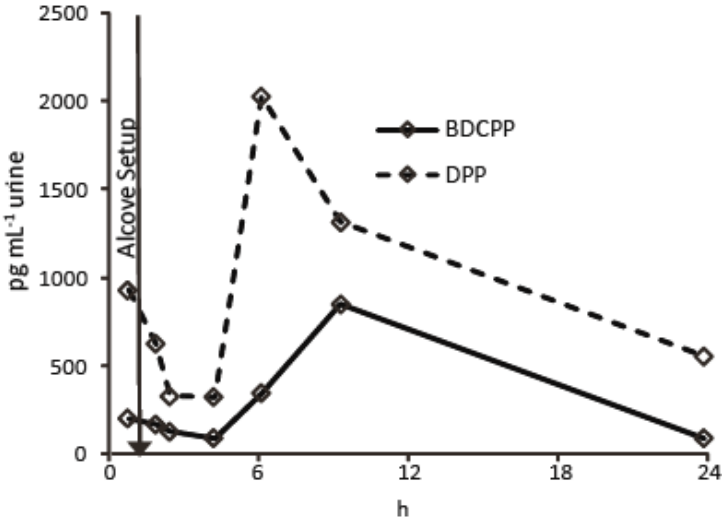

Figure 2. BDCPP and DPP measured in urine collected before picnic shelter setup and periodically after setup for one day. Values are normalized to urine specific gravity.

These results indicate that recreational equipment such as tents and shelters may contain high levels of OPFRs, particularly TDCPP, and that contact with this equipment, even briefly, may be an important source of dermal exposure to these compounds. Further research is needed to expand our currently limited understanding of levels of and exposures to OPFRs in recreational equipment.

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