Environment International 112 (2018) 41–48

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Organophosphate flame retardants in dust collected from United States fire stations

Beverly Shen[a,*], Todd P. Whitehead[a], Ranjit Gill[b], Joginder Dhaliwal[b], F. Reber Brown[b], Myrto Petreas[b], Sharyle Patton[c], S. Katharine Hammond[a]

[a] School of Public Health, University of California, 50 University Hall, Berkeley, CA, USA
[b] Environmental Chemistry Laboratory, California Department of Toxic Substances Control, 700 Heinz Avenue, Berkeley, CA, USA
[c] Biomonitoring Resource Center, Commonweal, 451 Mesa Road, Bolinas, CA, USA

ABSTRACT

Firefighters are exposed to chemicals during fire events and we previously demonstrated that fire station dust has high levels of polybrominated diphenyl ethers (PBDEs). In conducting the Fire Station Dust Study, we sought to further characterize the chemicals to which firefighters could be exposed – measuring the emerging class of phosphorous-containing flame retardants (PFRs) in fire stations, for the first time, as well as PBDEs. Dust samples from 26 fire stations in five states were collected from vacuum-cleaner bags and analyzed for PFRs and PBDEs. PFR concentrations were found to be on the same order of magnitude as PBDE concentrations (maximum PFR: 218,000 ng/g; maximum PBDE: 351,000 ng/g). Median concentrations of tri-n-butyl phosphate (TNBP), tris (2-chloroisopropyl) phosphate (TCIPP), and tris(1,3-dichloroisopropyl)phosphate (TDCIPP) in dust from fire stations were higher than those previously reported in homes and other occupational settings around the world. Total PFR levels did not vary significantly among states. Levels of TDCIPP were higher in stations where vacuum cleaners were used to clean surfaces other than the floor. PBDE levels were comparable to those found in our previous study of 20 California fire stations and much higher than levels in California residences. PFR and PBDE levels in fire station dust are higher than in other occupational and residential settings, underscoring the need to identify and control sources of this contamination.

1. Introduction

Flame retardants have been used widely in United States consumer products such as furniture foam, plastic electronics casings, and even clothing since the 1970s with the intention of delaying the ignition of fire (U. S. EPA, 2014). Concern over adverse health effects, persistence, and bioaccumulation has led to the phase-out of one class of flame retardants known as polybrominated diphenyl ethers (PBDEs) (U. S. EPA, 2014) and phosphorous-containing flame retardants (PFRs) have emerged as replacements in the commercial market (Dodson et al., 2012; Stapleton et al., 2012). The effects of PFRs on human health have not been well described, though animal research suggests these chemicals may act as endocrine disruptors (Liu et al., 2012; Chen et al., 2015). The chlorinated PFRs tris(chloroethyl)phosphate (TCEP) and tris (1,3-dichloroisopropyl)phosphate (TDCIPP) have been associated with carcinogenicity in animals (van der Veen and de Boer, 2012; CA EPA, 2017a); rats fed TCEP for two years developed kidney tumors and rats fed TDCIPP for two years developed tumors of the kidney, liver, testis, and adrenal gland (Agency for Toxic Substances and Disease Registry, 2012). PFRs have been found in the indoor air(Sjödin et al., 2001; Bradman et al., 2014) and dust(Bradman et al., 2014; Stapleton et al., 2009) of multiple microenvironments (van der Veen and de Boer, 2012), including work environments; however, PFRs have not been previously measured in fire stations.

Firefighters experience a wide range of occupational health hazards, from ergonomic hazards (Walton et al., 2003; Chiou et al., 2012; Plat et al., 2012) to post-traumatic stress (Plat et al., 2012; Berninger et al., 2010; Webber et al., 2011; Fushimi, 2012) to overexertion (Walton et al., 2003). They also may be at increased risk for leukemia (Daniels et al., 2015), testicular cancer (Bates et al., 2001; LeMasters et al., 2006; Bates, 2007), prostate cancer (LeMasters et al., 2006; Bates, 2007), multiple myeloma (LeMasters et al., 2006), and malignant mesothelioma (Daniels et al., 2014). Firefighters are exposed to a wide range of chemicals including flame retardants (Horn et al., 2016; Jayatilaka et al., 2017) while they actively suppress fires (Jankovic et al., 1991; McDiarmid et al., 1991; Fent and Evans, 2011; Laitinen et al., 2012;

* Corresponding author.
E-mail address: beverlyshen@berkeley.edu (B. Shen).

https://doi.org/10.1016/j.envint.2017.12.009
Received 19 August 2017; Received in revised form 5 December 2017; Accepted 6 December 2017

McNamara et al., 2012; Fent et al., 2014; Evans and Fent, 2015) or check for hidden fires after completing fire suppression (Wobst et al., 1999; Bolstad-Johnson et al., 2000; Burgess et al., 2001; Baxter et al., 2014). However, firefighters spend a considerable amount of on-shift downtime at their fire stations, where their exposures to chemicals have not been well characterized.

In 2010–2011, as part of the Firefighter Occupational Exposures (FOX) study, concentrations of PBDEs, novel brominated flame retardants, polycyclic aromatic hydrocarbons (PAHs), and polychlorinated biphenyls were measured in dust samples collected from the vacuum cleaner bags of 20 fire stations in Southern California (Shen et al., 2015; Brown et al., 2014). The FOX study found elevated levels of BDE-209, in particular, when compared to other occupational and residential settings. Specifically, the FOX study found that median BDE-209 concentrations were 18-fold higher in dust from fire stations than in dust collected during the same time period from California residences and analyzed by the same methodologies (Shen et al., 2015). This, along with the elevated PBDE concentrations in the blood of FOX participants (Shaw et al., 2013; Park et al., 2015), indicates that California firefighters are exposed to higher levels of certain PBDEs than the general population.

In this follow-up study of 26 additional fire stations from five states, concentrations of PFRs were measured in fire station dust for the first time. The presence of high levels of PBDEs in dust from California homes has been reported in multiple studies (Dodson et al., 2012; Zota et al., 2008), likely as a result of California's unique flammability standards. Correspondingly, this study sought to evaluate whether California fire stations had uniquely high levels of PBDEs or if elevated PBDE levels were also present in fire stations located in other states.

2. Materials and methods

2.1. Fire station recruitment

In 2015, the Fire Station Dust Study (FSDS) worked with the International Association of Fire Fighters (IAFF) to recruit five fire stations from each of five states (California, Minnesota, New Hampshire, New York, Texas). An additional pilot fire station from California was used to refine sampling protocols prior to launching the study.

2.2. Dust sampling

We collected bags from vacuum cleaners used for routine dust removal in the living quarters of 26 fire stations in 2015. We mailed sampling packets to each fire station and included: 1) a sampling protocol describing how to seal and ship the vacuum bag; 2) a re-sealable 36 cm × 61 cm × 0.2-mm thick polyethylene bag to contain the vacuum cleaner bag; 3) a questionnaire acquiring general fire station information and fire station cleaning practices; and 4) a preaddressed, prepaid envelope in which to mail the vacuum-cleaner bag to the Environmental Chemistry Laboratory at the California Department of Toxic Substances Control (DTSC) in Berkeley, California. We received a total of 26 vacuum-cleaner bags, including the vacuum-cleaner bag from the pilot fire station. Samples remained in the polyethylene bag at room temperature at DTSC until analysis.

2.3. Surveys

Fire station personnel completed a survey about the brand and model of their vacuum cleaner as well as the cleaning protocols they use for fire engines, fire stations, and turnout gear in an attempt to capture potential determinants of flame retardant concentrations.

2.4. Chemical analysis

Dust samples were sieved to remove fibers and debris larger than 150 μm. The extraction method was adapted from a previously described method (Van den Eede et al., 2012). Briefly, we weighed approximately 50 mg of the resulting fine-dust fraction, spiked it with a mixture of labeled internal standards (Supporting Information, Table S1) and extracted the analytes by sonication in a 3:1 hexane:acetone solution. The extracts were cleaned using Florisil column chromatography, then solvent-exchanged into isooctane and spiked with two labeled injection standards (Supporting Information, Table S1) yielding final extract volumes of 100 μL for the PBDE fraction and 1 mL for the PFR fraction. We analyzed the samples in three sample batches: the first two batches contained nine dust samples and the third batch contained eight dust samples. Each sample batch also contained a duplicate, two method blanks, a laboratory control, and a standard reference material (NIST SRM No. 2585; Supporting Information, Table S2). We analyzed the extracts for five PFRs using electron impact ionization mode gas chromatography-tandem mass spectrometry (CA EPA, 2017b). We also analyzed 18 PBDEs via high-resolution gas chromatography–mass spectrometry operated in electron impact ionization mode, following the same analytical protocols we described in the FOX study for dust samples collected from Southern California fire stations (Shen et al., 2015) and reference California homes (Whitehead et al., 2013). We calculated method reporting limits (MRLs) as three times the standard deviation of the method blank values for each analyte from three sample batches.

2.5. Statistical methods

Summary statistics and figures were generated using Microsoft Excel (Microsoft Office 2011 for Mac OS X). Statistical analyses were performed in R (R Core Team. 2016. *R: A language and environment for statistical computing*. Vienna, Austria: R Foundation for Statistical Computing). Pearson correlation coefficients were used to evaluate the relationships between analytes. To characterize the geographic variability of the flame retardants, we estimated within-state (σ_w^2) and between-state (σ_b^2) variance components and then calculated two descriptive ratios using the following equations:

$$\text{Lambda, } \lambda = \frac{\sigma^2{}_w}{\sigma^2{}_b} \tag{1}$$

$$\text{Intraclass correlation coefficient, } \rho = \frac{\sigma^2{}_b}{\sigma^2{}_b + \sigma^2{}_w} \tag{2}$$

We tested for differences in flame retardant levels by other explanatory factors (including age of building, turnout gear cleaning policies, turnout gear storage policies, and vacuum cleaner usage) using ANOVA. Chemical concentrations were log transformed prior to analysis. Significant associations were determined at $\alpha \le 0.05$.

3. Results and discussion

3.1. Characteristics of fire stations

A survey was returned by 25 of the 26 fire stations (6 of 6 from California, 5 of 5 from Minnesota, 5 of 5 from New Hampshire, 5 of 5 from New York, 4 of 5 from Texas). About half (56%) of the fire stations were built before 1970 and the rest (44%) were built after 1970. Most of the fire stations had turnout gear cleaning policies (80%) and designated areas for turnout gear storage (92%). In 68% of fire stations turnout gear was stored in the apparatus bay, in 4% in the living quarters, and in 12% in another space (16% of fire stations did not respond to this question). Turnout gear was stored in an enclosed area in 65% of the fire stations, but only 45% of the fire stations had ventilated storage areas. Turnout gear was explicitly banned from 92% of