Organic flame retardants in offices, taxis and outsides in China: hand wipes, surface wipes and dust

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Introduction

Organic flame retardants (FRs), including brominated flame retardants (BFRs), organophosphorus flame retardants (OPFRs), chlorinated flame retardants are a class of chemicals with wide concerns. Among which, polybrominated diphenyl ethers (PBDEs) are the most popular one due to their adverse health effects, persistence and bioaccumulation. These chemicals are widely used in various products, such as building materials, consumer products, electronics, etc [1]. and can be easily released into the environment though vitalization and abrasion processes [2].

Indoor dust is considered as a good sample type to characterize FRs exposure in a microenvironment. Hence, there are a large number of literatures reported FRs in floor dust collected from homes, offices, cars, daycare centers, etc [3-5]. Hand wipes sample has been reported as a good indicator to characterize personal exposure to FRs [6, 7]. FRs on hands are likely to resulted from dust adherence or contact with contaminated surfaces. However, there are limited studies measured FR levels in contaminated surfaces which may more relevant to exposure than floor dust.

In this study, three typical occupation populations in indoor, vehicle and outdoor, namely white-collar workers, taxi drivers and outdoor securities were selected. We aimed to investigate the associations between hand wipes, surface wipes and dust. By examining the relationships, we hope to determine the pathway of FRs from environment to human skin surface. Such information is needed for exposure assessment of dermal absorption or hand-to-mouth ingestion by using environmental sample types.

Methods and materials

Participants

We recruited three populations through oral communication in Beijing from March to August in 2016. Group 1 includes 25 volunteers who work in offices with computers. Group 2 includes 20 taxi drivers. Group 3 contains 23 outside workers. They all stayed in their work places for at least 8 h per day. Participants worked in offices and outside located in different areas of Beijing. Participants were required to fill a short questionnaire about their gender, age, height, Prior to participation, verbal consent was obtained from each participant.

Sample collection

The hand wipe and surface wipe procedure has been described before [8]. Briefly, gauze pads

(7.5*7.5 cm) were cleaned by using ultrasonic extraction in hexane/acetone mixture (v : v=3:1) for 30 min (10 min for each time). Before collection, each dried gauze pad was immersed in 5 mL isopropyl alcohol. The entire surface of one hand was wiped from the finger to the wrist by one wipe, and then another wipe was used for the other hand. After collection, two wipes from the same participant were put together into a 60 ml precleaned (combusted at 450 °C for 6 h) brown glass vial, sealed in a sealing bag, and stored at -20 °C until analysis. Surface wipes were collected from offices and taxis. A measured touch area (about 500 cm^2) of participants' table in offices were wiped thoroughly. The surface of circular ring of steering wheels in taxis were wipes by using gauze pads. These surface wipes were also stored in brown glass vials as hand wipes. Field blanks were collected by taking out the immersed pads in air for 2-3 seconds and placing back into the glass vials.

Office dust was collected by using a commercial vacuum cleaner with a 25 mm nylon sampling sock (cleaned with a hexane/acetone solution) placed in the suction nozzle. Outside dust were collected in the nearest roadside of participants by using cleaned brushes. After collection, dust samples were wrapped with aluminum foil, sealed in polyethylene zip bags, and back to the lab. Before stored at -20 °C, dust samples were sieved through stainless sieves (< 50 μm).

Samples analysis

A total of 8 PBDEs (BDE28, 47, 99, 100, 154, 153, 183 and 209), 2 DP isomers (syn-DP and anti-DP), 2 NBFRs (Decabromodiphenylethane (DBDPE), 1, 2-Bis (2, 4, 6-tribromophenoxy) ethane (BTBPE)), and 10 PFRs ((triethyl phosphate (TEP), tri-n-propyl phosphate (TPP), tri-iso-butyl phosphate (TIBP), tri-n-butyl phosphate (TNBP), tricresyl phosphate isomers (∑TMPP, mixture of 4 isomers), Tris(chloropropyl) phosphate isomers (∑TCPP, mixture of 3 isomers), tris(2-butoxyethyl) phosphate (TBOEP), tris(2-chloroethyl) phosphate (TCEP) and triphenyl phosphate (TPHP) and tris(1, 3-dichloro-2-propyl) phosphate (TDCIPP)) were analyzed. BDE77, BDE 128, ^{13}C-BDE209, triamyl phosphate (TAP) and triphenyl phosphate-d15 (TPHP-d15) were used as internal standards. The analysis method for the determination of FRs in hand wipes, surface wipes and dust, as well as the information on chemicals, reagents, and instrument were clearly described in our previous literatures [8, 9].

Quality control and quality assurance

The removal efficiencies of hand wipes were reported in our previous literature [8]. Only BDE209, TCEP and TCPP were detected in filed blank and procedure blank samples (<1% than concentrations of samples). All samples were corrected by subtracting the mean of the respective blanks. Limit of detection (LOD) were determined as three times the standard deviation of the blanks. For those not detected in blanks, ten times signal-to-noise ratio was used as LOD. Recoveries of internal standards were ranged from 50-150%. The recoveries of the analytical procedure were achieved by adding standard mixtures (low, median and high) into blank wipes and dust, and the mean recoveries were ranged from 70-120% for each compound.

Statistical analyses

SPSS 16.0 software was used for statistical analysis. Non-parametric tests were used since some data was neither normally distributed nor log-normally distributed. Data below detection methods were replaced by half of LOD.

Results and discussion

FRs in dust, hand wipes and surface wipes

Summary of FRs in hand wipe, surface wipe and dust samples is shown in Table 1. PFRs concentrations in the office samples were previously described [8]. BDE209, DBDPE, BTBPE, BDE47, TCEP, ∑TCPP and TPHP were frequently detected in all type of samples with detection frequencies higher than 90%. TDCPP and TNBP were only frequently detected in taxi samples. In all kinds of samples, PFR compounds had a major contribution (> 70%) compared to PBDEs, NBFRs and DPs. BDE209 and DBDPE were the main BFRs in all kinds of samples, which was consistent with their high production volumes in China [10]. The low detection frequencies and low concentrations of other PBDEs might be due to their global phase-out. DPs presented low concentrations in any samples than other FRs, and the highest mean concentration was observed in office dust (49 ng/g) and outdoor handwipes (16 ng/m^2).

Comparisons between three kinds of samples

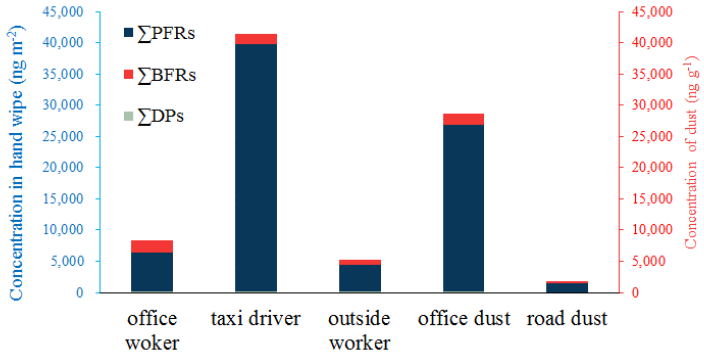

Figure 1 Concentration of FRs in hand wipes collected from office workers, taxi drivers and outside workers, and in dust samples collected from office and outside

Geometric mean concentrations of hand wipes from three populations and two types of dust is shown in Figure 1. Kruskal-Wallis and Mann-Whitney Test were used for statistical comparisons. Concentrations of ∑BFRs in hand wipes from both taxi drivers and office workers were significantly higher than those of outdoor workers, but no statistical difference was observed between taxi drivers and office workers. There are also no statistical differences between concentrations of ∑BFRs and BDE209 in office surface wipes and taxi surface wipes. A similar situation was found in Harrad et al. [4], which reported that DecaBDEs was consistent in dust collected from cars and offices. There are no significant differences between concentrations of ∑DPs in three types of hand wipes, which may due to their low detection frequency. As for ∑PFRs, concentrations in hand wipes ranked as: taxi drivers > office workers > outside workers ($p < 0.05$). The higher concentrations of TCEP, TCPP and TDCIPP on the skin surface of taxi drivers suggested these PFRs are widely used in vehicles, such as cars interiors [11], and may have a strong release. These results were in consistent with the concentrations measured in dust from Netherland [12] and the UK [5] with car dust had much higher PFR concentrations than dust from houses and offices. In addition, TNBP, a pressure additive in hydraulic fluid [11], was detected in all hand wipe and surface wipe samples from taxis, but seldom detected in other samples.

Associations between hand wipes, surface wipes and dust

To investigate factors that influencing the pathways that FRs from dust to surfaces and onto human hand surface, ultimately affecting human exposure. Associations between individual FRs in dust, surface wipes and hand wipes in the same microenvironments were investigated by using Spearman tests. No significant correlations were observed between FR levels in outdoor dust and outdoor workers' handwipes. There were also no correlations between PFR levels in dust and

handwipes from offices. Only the levels of syn-DP, anti-DP and BDE99 in dust from offices were moderately correlated with the levels on office workers' hands. These results suggested outdoor dust and indoor dust contributed a little to the FRs on participants' hands. Levels of PFR, BFR and DP compounds in surface wipes were not associated with levels in handwipes in offices. However, hand wipe levels were associated with surface wipes in taxis for most compounds. TCEP (r = 0.568), ∑TCPP (r = 0.701), TDCIPP (r = 0.598), TPHP (r = 0.855), DBDPE(r = 0.765), BTBPE (r = 0.577), BDE99 (r = 0.758), BDE209 (r = 0.803) and BDE183 (r = 0.767) in hand wipes were significantly correlated with surface wipes. These correlations may due to the direct touch of steering wheels for taxi drivers. The associations between dust, surface wipes and handwipes suggested collecting dust may not be a proper method of characterizing human exposure, while collecting samples from contaminated surface which were frequently touched might be a convenient method for personal exposure assessment.

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Table 1 FR concentrations (geometric mean (range)) in dust, surface wipe and hand wipe samples from offices, taxis and outdoor

compounds	Office			Taxi		Outdoor	
	dust (n=17, ng/g)	surface wipe (n=16, ng/m^2)	hand wipe (n=28, ng/m^2)	surface wipe (n=17, ng/m^2)	hand wipe (n=20, ng/m^2)	dust (n=15, ng/g)	hand wipe (n=22, ng/m^2)
BDE28	0.2(<LOD-1.4)	0.2(<LOD-1.2)	0.8(<LOD-3.3)	0.6(<LOD-9.2)	1.9(<LOD-27.8)	NA(<LOD-0.7)	1.5(<LOD-6.8)
BDE47	1.3(<LOD-3.8)	0.6(<LOD-7.6)	2.4(<LOD-25.2)	2.0(0.1-16.6)	4.2(1.0-51.9)	0.37(<LOD-6.2)	4.2(1.6-35.7)
BDE100	NA(<LOD-1.3)	<LOD	<LOD	<LOD	<LOD	NA(<LOD-1.0)	NA(<LOD-2.5)
BDE99	1(<LOD-3.4)	0.5(<LOD-3.0)	0.7(<LOD-20.7)	1.0(<LOD-7.3)	2.1(<LOD-24.5)	NA(<LOD-7.1)	2.6(<LOD-48.7)
BDE154	0.2(<LOD-1.6)	0.1(<LOD-0.4)	NA(<LOD-2.6)	NA(<LOD-0.6)	NA(<LOD-1.1)	NA(<LOD-0.5)	0.4(<LOD-10.6)
BDE153	0.9(<LOD-5.1)	0.2(<LOD-1.8)	NA(<LOD-5.0)	0.5(<LOD-2.9)	NA(<LOD-2.9)	NA(<LOD-1.6)	0.9(<LOD-21.3)
BDE183	2.5(<LOD-5.9)	0.9(<LOD-6.5)	4.3(1.1-25.7)	0.8(<LOD-9.5)	1.9(<LOD-12.9)	0.9(<LOD-2.7)	4.8(<LOD-120)
BDE209	1375(290.4-146373)	456(12.4-7873)	1478(209.0-16970)	857.4(133.6-18612)	1114(187.7-17047)	254.7(23.9-1979.1)	460.3(24.0-13951)
syn-DP	8.8(<LOD-141.7)	1.5(<LOD-16.5)	4.8(<LOD-112.9)	2.6(<LOD-10)	3.7(<LOD-53.3)	NA(<LOD-7.1)	6.1(<LOD-386)
anti-DP	40.3(<LOD-370)	3.9(<LOD-55.7)	10.9(<LOD-517.4)	8.9(<LOD-206)	10(<LOD-306)	NA(<LOD-19.5)	10.4(<LOD-726.8)
DBDPE	376.1(113.8-1061)	99.5(8.3-510.8)	442(78.0-4782)	372.8(89-8710)	568.2(26.9-16078)	71.1(15.5-235.5)	260.7(<LOD-18124.6)
BTBPE	4.0(1.0-10.3)	2.8(<LOD-84.8)	8.0(1.3-138.2)	1.2(<LOD-7.6)	2.6(<LOD-12.2)	4.0(0.1-54.8)	4.3(<LOD-233.9)
TNBP	—	—	—	136(<LOD-863)	265(41-708)	<LOD	NA(<LOD-333.5)
TCEP	—	—	—	28841(1804-141265)	19997(2815-81593)	615(46.5-5706)	1578(<LOD-46954)
∑TCPP	—	—	—	29061(1424-41192)	13253(979-27813)	678(141.1-3940)	1259(207-11692)
TDCPP	—	—	—	4451(321-15225)	4497(971-20566)	82.3(34-312)	387(<LOD-10669)
TPHP	—	—	—	3141(168-43430)	1655(299-9107)	69.8(6.8-427)	1203(360-4446)
TBOEP	—	—	—	NA(<LOD-64812)	NA(<LOD-46420)	NA(<LOD-708)	NA(<LOD-1171)

NA = not detected due to detection frequency lower than 50%.