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Current halogenated flame retardant concentrations in serum from residents of Shandong Province, China, and temporal changes in the concentrations

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ABSTRACT

The residents of Shandong Province, China, are exposed to high concentrations of halogenated flame retardants because large amounts of halogenated flame retardants are produced in the province. We determined the concentrations of eight polybrominated diphenyl ether congeners (PBDEs), seven novel brominated flame retardants (NBFRs), and the two dechlorane plus isomers (DPs) in serum from residents of Shandong Province. The aim was to identify temporal trends in the concentrations of these pollutants. The mean total concentrations of PBDEs, NBFRs and DPs were 41, 2.2 and 2.1 ng/g lipid in pooled serum samples collected in 2014, and were 32, 3.5 and 3.1 ng/g lipid in pooled serum samples collected in 2015, respectively. Decabromodiphenyl ether was the dominant PBDE congener in all of the samples. The novel brominated flame retardant and dechlorane plus concentrations were between one and two orders of magnitude lower than the PBDE concentrations. The PBDE concentrations in serum decreased significantly between 2007 and 2015, but the pentabromobenzene, pentabromotoluene, and dechlorane plus concentrations were relatively stable.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) have been used as flame retardants in many types of product (including plastic, electronic, and textile products) for decades (Trudel et al., 2011; Wang et al., 2014; Müller et al., 2016). The widespread use of PBDEs has contaminated the environment and caused a great deal of concern about their effect on human health (Chen et al., 2012; Law et al., 2014). Restrictions have been placed on the production and use of PBDEs to protect the environment and human health (Ma et al., 2013; Wang et al., 2014), and PBDEs have been replaced with alternative flame retardants, such as novel brominated flame retardants (NBFRs) and dechlorane plus (DP) (Covaci et al., 2011; Xian et al., 2011). However, some alternative flame retardants have been found to be persistent, bioaccumulative, and toxic pollutants (Gramatica et al., 2016), and there is a great deal of concern about the environmental and human health problems that may be caused by these chemicals (He et al., 2013; Su et al., 2014; Chen et al., 2015; Kim et al., 2016; Müller et al., 2016).

The current concentrations of PBDEs, NBFRs, and DP and temporal trends in the concentrations of these pollutants in environmental media, and particularly in human tissues, are poorly understood even though the pollutants are widespread and pose risks to human and environmental health. Temporal trends in PBDE concentrations in tissues of human living in different countries have been examined in several previous studies (Koizumi et al., 2005; Fangstrom et al., 2008; Toms et al., 2012; Ma et al., 2013). In those studies, it appeared that temporal changes in PBDE concentrations in human tissues were associated with temporal changes in the amounts of PBDEs produced and used. For example, PBDE concentrations in blood from newborn babies in New York decreased sharply after 2004, reflecting the phasing out of the production and using of the pentabromodiphenyl ether and octabromodiphenyl ether commercial mixtures in the USA at that time (Ma et al., 2013). It has been suggested that humans may be exposed to PBDEs from different sources in different areas (Toms et al., 2012), and this could mean that PBDE concentrations in human tissues will follow different temporal trends in different areas. Few studies of NBFRs and DPs in human tissues are performed, and temporal trends in the concentrations of these pollutants are poorly understood.

The octabromodiphenyl ether commercial product has never been produced in China, and the production and use of the pentabromodiphenyl ether commercial product were phased out in China in 2007. However, the decabromodiphenyl ether commercial product is still

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produced and used in China. Large amounts of flame retardants are produced in Shandong Province, in China, and the residents of the province have been exposed to high concentrations of flame retardants for some years (Jin et al., 2009; He et al., 2013). However, temporal trends in the concentrations of flame retardants in the tissues of people living in Shandong Province have not been studied.

In the present study, we determined the concentrations of eight PBDEs (2,4,4′-tribromodiphenyl ether (BDE-28); 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47); 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99); 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100); 2,2′,4,4′,5,5′-hexabromodiphenyl ether (BDE-153); 2,2′,4,4′,5,6′-hexabromodiphenyl ether (BDE-154); 2,2′,3,4,4′,5′,6-heptabromodiphenyl ether (BDE-183); decabromodiphenyl ether (BDE-209)), seven NBFRs (pentabromobenzene (PBBz), pentabromotoluene (PBT), hexabromobenzene (HBB), 2,3,5,6-tetrabromo-*p*-xylene, pentabromoethylbenzene, pentabromobenzyl acrylate, and di(2-ethylhexyl)tetrabromophthalate), and the two DP isomers (syn-DP and anti-DP) in serum from residents of Shandong Province and attempted to identify temporal trends in the concentrations of these pollutants in serum in the residents of the province. The aim of this was to improve our understanding of the occurrences and behaviors of flame retardants in humans in Shandong Province. To the best of our knowledge, this is the first study in which temporal trends in NBFR and DP concentrations in human serum in China have been studied.

2. Materials and methods

2.1. Sample information

Serum samples were collected from residents of Weifang City, Shandong Province (a brief introduction of Weifang is included in the Supplementary Data). A 0.50 mL serum sample was collected from each of 490 people in July 2014 and 452 people in July 2015. The samples were stratified according to age, sex, and sampling time, then the grouped samples were combined to give 20 pooled samples. The numbers and mean ages of the people who supplied the samples in each pooled sample are shown in Table 1. The pooled samples were transported to the laboratories in which the analyses were performed and then stored at −20 °C until they were analyzed. None of the donors had liver disease, and all of the donors gave informed consent after we had clearly explained the project to them.

2.2. Sample preparation and analysis

The chemicals and other materials used in the sample preparation methods and during the instrumental analyses are described in the Supplementary Data. The pooled serum samples were extracted and cleaned following a method that has been described previously (He et al., 2012). Briefly, a 3 mL aliquot of each pooled serum sample was spiked with 4 ng ^{13}C-labeled BDE-139, 40 ng ^{13}C-labeled BDE-209, 2 ng ^{13}C-labeled syn-DP, and 4 ng ^{13}C-labeled HBB. Hydrochloric acid, isopropanol, and a 1:1 v/v mixture of hexane and methyl *tert*-butyl ether were added to each sample, then the sample was centrifuged and the organic phase was transferred to a glass tube containing 4 mL aqueous KCl (1% w/w). The mixture was shaken, the organic phase removed, and the KCl was extracted twice with 3 mL of a 1:1 v/v mixture of hexane and methyl *tert*-butyl ether. The organic extracts were mixed, then evaporated to dryness to allow the extracted lipid to be gravimetrically determined. The residue was then dissolved in 4 mL hexane, and 2 mL 0.5 M $KOH_{(aq)}$ were added. The hexane was then removed, concentrated, and cleaned by passing it through a gel permeation chromatography column and a multilayer silica gel column. The clean extract was then evaporated to 80 μL for instrumental analysis (a glass tube with a capacity of 100 μL was used to determine the evaporated volume). The sample preparation method is described in detail in the Supplementary Data.

The PBDEs in the extracts were determined by gas chromatography negative chemical ionization tandem mass spectrometry using a Trace 1310 gas chromatograph and a TSQ 8000 Evo mass spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). BDE-28, BDE-47, BDE-99, BDE-100, BDE-153, BDE-154, and BDE-183 were separated using a TG-5HT column (30 m×0.25 mm, 0.10 μm film thickness; Thermo Fisher Scientific) and analyzed in selected ion monitoring mode. BDE-209 was separated using a different TG-5HT column (15 m×0.25 mm, 0.10 μm film thickness; Thermo Fisher Scientific) and analyzed in selective reaction monitoring mode. The NBFRs and DP isomers in the extracts were determined by gas chromatography negative chemical ionization mass spectrometry using a 6890N gas chromatograph and a 5975N mass spectrometer (Agilent Technologies, Santa Clara, CA, USA). The NBFRs and DP isomers were separated using a J & W Scientific DB-5MS column (30 m×0.25 mm, 0.10 μm film thickness; Agilent Technologies) and analyzed in selected ion monitoring mode. The instrumental parameters that were used are described in the Supplementary Data.

2.3. Quality assurance and quality control

The limit of detection was defined as the concentration giving a signal to noise ratio of 3, and the limit of quantitation was defined as the concentration giving a signal to noise ratio of 10. The limits of detection for the PBDE congeners, NBFRs, and DP isomers that were analyzed were 0.02 – 5, 0.1 – 5, and 0.1 – 0.5 pg, respectively. The limits of quantitation for the PBDE congeners, NBFRs, and DP isomers that were analyzed were 0.05 – 20, 0.5 – 10, and 0.5 – 2 pg, respectively. The ^{13}C-labeled BDE-139, ^{13}C-labeled BDE-209, ^{13}C-labeled syn-DP, and ^{13}C-labeled HBB recoveries were 79–109%, 55–88%, 82–113%, and 67–92%, respectively. A method blank sample was analyzed with every batch of serum samples. The concentrations of the analytes in the blank samples were very low (< 10% of the concentrations in the samples), with signal/noise ratios being consistently less than 10, so the concentrations of the analytes in the samples were not blank-corrected (this was also the same method implemented in previous analysis of these compounds (Jin et al., 2009; He et al., 2013; Wang et al., 2014; Li, 2016)).

2.4. Statistical analyses

Statistical analyses were performed using SPSS 22.0 software (IBM, Armonk, NY, USA). Differences between the analyte concentrations in different pooled samples were identified using independent-samples *t*-test. Bivariate Spearman correlation tests were performed on the

Table 1
Age ranges and mean ages of the donors who supplied the serum samples that were combined to give each pooled sample in 2014 and 2015 and the number of samples combined to give each pooled sample. The donors were all residents of Shandong Province, China.

Pooled sample		Age range	Number of donors		Mean age (y)	
		(y)	2014	2015	2014	2015
Male-1		20 – 29	53	25	26	27
Male-2		30 – 39	80	80	35	35
Male-3		40 – 49	80	80	44	44
Male-4		50 – 59	34	52	53	53
Male-5		≥ 60	38	40	71	73
	All males	≥ 20	285	277	43	46
Female-1		20 – 29	21	17	26	26
Female-2		30 – 39	58	32	35	36
Female-3		40 – 49	66	56	44	44
Female-4		50 – 59	20	30	54	55
Female-5		≥ 60	40	40	69	69
	All females	≥ 20	205	175	45	48