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Brominated flame retardant (BFRs) and Dechlorane Plus (DP) in paired human serum and segmented hair

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ABSTRACT

Brominated flame retardants (BFRs) and Dechlorane Plus (DP) were measured in both human hair and paired serum samples from a cohort of university students in South China. Segmental analysis was conducted to explore gender difference and the relationships between the hair and serum. The concentrations of total PBDEs in the hair and serum samples were in a range of 0.28–34.1 ng/g dry weight (dw) and 0.16–156 ng/g lipid weight (lw), respectively. Concentrations of ΣDPs (sum of the *syn*-DP and *anti*-DP isomers) in all hair samples ranged from nd-5.45 ng/g dry weight. Concentrations of most PBDEs and decabromodiphenylethane (DBDPE) in distal segments (5–10 cm from the scalp) were higher than those in the proximal segments (0–5 cm from the scalp) (*t*-test, $p < 0.05$), which could be due to the longer exposure time of distal segments. The proximal segments exhibited a unique congener profile, more close to that in the serum rather than the distal segments of hair. An obvious gender difference was found in the levels of ΣPBDEs using integrated hair samples, while the difference disappeared when considering alone the proximal segments of hair (0–5 cm from scalp) for both genders. This paper provides supplement to the current knowledge on sources of BFRs and DPs in hair and declares the importance of segmental analysis.

1. Introduction

Polybrominated diphenyl ethers (PBDEs), which used to be among the most widely used brominated flame retardants (BFRs), have been manufactured commercially from the 1970s to add in building materials, plastics, polyurethane foams, furniture, textiles, and electronics (Alaee et al., 2003). They are available in three technical mixtures: Penta-, Octa- and Deca-BDEs depending on the degree of bromination (Norrgran et al., 2015), and they can leach out of the products over time and accumulate in environment. Although PBDEs have now been banned in many countries (Van der Veen and de Boer, 2012) because of their adverse effects on human health, they will remain in our environment and organisms for years due to their persistence and bioaccumulation. Lots of studies have reported that PBDEs were present in human serum (Garí et al., 2013), feces (Sahlström et al., 2014), hair (Zheng et al., 2011) and breast milk (Chao et al., 2007). With the phasing out of PBDEs, several new brominated flame retardants have been put into use because of their similarity in properties to PBDEs. For example, decabromodiphenylethane (DBDPE) replaced decabromodiphenyl ether (BDE-209), and 1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE) replaced the octa-BDEs. At the same time, the production of Dechlorane Plus (DP) has risen a lot because they are possible replacements for the deca-BDE (Sverko et al., 2011).

It might be prudent to choose hair as a biomarker to monitor human exposure, as hair can be non-invasively collected, and the transport and store of hair are convenient. As the growth rate of hair is 0.6–1.4 cm/month (Pragst and Balikova, 2006), analysis of hair samples could provide information on retrospective exposure. Also, due to hair is simultaneously exposed to chemicals from external environments (air/dust) and internal tissues (blood), this brings difficulties in distinguishing the exogenous and endogenous contamination. In order to investigate whether externally adsorbed and internally deposited flame retardants (FRs) in hair could be distinguished, researchers have made two attempts: try to remove all the external contaminants in sample preparation, or try to figure out relationships between contaminants in hair and serum. However, in sample preparation, Poon et al. (2015)

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found that water and shampoo could not sufficiently remove all external contamination, while solvents (such as *n*-hexane, dichloromethane and methanol) might penetrate to the inner part of the hair and can extract compounds from the inner structure of hair. Kucharska et al. (2015) also concluded that there is no washing medium being able to entirely and exclusively remove external contaminants. On the other hand, in the only four studies concentrating on association between PBDE concentrations in hair and serum by Zheng et al. (2013), Poon et al. (2014), Liu et al. (2016) and Liang et al. (2016), inconsistent results were obtained in the relationships of some important congeners between hair and serum. A significant increase ($p < 0.0001$) in total PBDEs from proximal (root end) to distal segments along the hair shaft was observed (Carnevale et al., 2014). Meanwhile, our previous study (Qiao et al., 2016) got controversy results in gender differences of organophosphate flame retardant (PFR) levels when using the integrated hair, comparing to use the same position of hair (0–5 cm from scalp) of both genders. The experimental design did not consider the position and length of hair in the above-stated four studies (Zheng et al., 2013; Poon et al., 2014, Liu et al., 2016; Liang et al., 2016), which might explain why they did not reach the same conclusion on the relationship of PBDEs between hair and serum. As the relationship between contaminants in hair and serum was not clear, and the controversy results on the gender difference were reached, segmental analysis for hair might help to solve the two questions.

In the present study, serum and segmented hair of university students in South China were sampled and PBDEs, DPBDE, BTBPE and DPs in the samples were detected. The relationship between these compounds in hair and serum specially focused segmental analysis of hair. It is hypothesized that the results obtained from the segmented hair would be more reasonable than those from the integrated hair for explaining the relationships in concentration and composition of the pollutants between hair and serum. It is also expected that the results will help us to better characterize the gender difference.

2. Materials and methods

2.1. Sample collection

Human hair and serum samples were collected from volunteer participants in Sun Yat-sen University located in Guangzhou, China in April, 2014. This research was launched with authorization of the Ethics Committee in School of Life Science, Sun Yat-sen University. The participants included 26 males and 17 females (21–25 years old), and all of them have not used any coloring agents in last 2 years. All the samples were cut on the posterior vertex as closely to the scalp as possible and the whole length were collected. Male hair length was 0–5 cm from the hair shaft. In order to perform segmental analysis of hair, and also to facilitate the comparison between genders, we cut 12 female hair (more than 5 cm) samples into two segments: the proximal segment (0–5 cm from the root) and the distal segment (5–10 cm from the root). The hair samples were wrapped in aluminum foil, sealed in polyethylene zip bags, and kept at −80 °C prior to chemical analysis. Paired 10–15 mL of venous blood samples of the participants were collected in anticoagulant-free tubes. The serum was isolated from the blood by centrifugation at 1680 × *g* for 5 min and kept at −80 °C prior to analysis.

2.2. Sample cleanup and analysis

The sample cleanup procedures were developed on the basis of the method reported by Kucharska et al. (2014). Hair samples were purified by rinsing with Milli-Q water, freeze-dried and cut into small pieces (2–3 mm). After spiking with surrogate standards (BDE-77, -181, -205, and ^{13}C-BDE-209), approximately 2 g of hair was Soxhlet-extracted with a mixture of acetone and hexane (1:3, v/v) for 48 h. The extracts were concentrated to 1 mL, solvent-exchanged to hexane, and purified by florisil cartridge (Supelclean ENVI-Florisil, 3 mL 500 mg, Supelco, USA). The cartridge was pre-cleaned with 8 mL of ethyl acetate and 6 mL of hexane, then eluted with 10 mL of hexane. The elution was collected and concentrated to near dryness under a gentle nitrogen steam before finally dissolving in 50 μL of isooctane. Prior to instrumental analysis, the extract was spiked with known amounts of the internal standards BDE-118, BDE-128, 4-F-BDE-67, and 3-F-BDE-153. For serum analysis, approximately 5 mL of each sample were extracted using diatomite-Soxhlet method, and then purified using the same method as hair samples.

We analyzed PBDEs, DPs, BTBPE, and DBDPE by gas chromatograph-electron capture negative-ionization mass spectrometry (GC/ECNI-MS) in selected ion monitoring (SIM) mode. For tri- to hepta-BDE congeners (BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183), a 30 m × 0.25 mm i.d. × 0.25 mm DB-XLB capillary column (J & W Scientific, CA) was used. A 15 m × 0.25 mm i.d. × 0.10 mm DB-5HT capillary column (J & W Scientific, CA) was used for the determination of octa- to deca-BDEs (BDE-196, BDE-197, BDE-202, BDE-203, BDE-206, BDE-207, BDE-208, BDE-209), DPs, BTBPE and DBDPE. Detailed information about analytical parameters was provided previously (Luo et al., 2009). Hair BFR and DP concentrations were corrected with the dry weight of each sample, and serum BFR and DP concentrations were corrected for lipid weight. The total lipid content was calculated from the total triglyceride and cholesterol values measured in the serum (Rylander et al., 2006).

2.3. Quality control

Analyte recoveries were assessed by spiking 30 ng of the target compounds (BDE-28, BDE-47, BDE-66, BDE-85, BDE-99, BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-202, BDE-203, BDE-206, BDE-207, BDE-208, BDE-209, BTBPE and DBDPE) into 2 g hair (n = 5) and 5 mL serum (n = 5). Mean recoveries of BFRs were in the range of 47.8 ± 2.9% to 130 ± 7.1% for hair, and 77.3 ± 15.9% to 163 ± 21.2% for serum, respectively. Procedural blanks (n = 5 for serum and n = 6 for hair) were conducted in each batch of sample preparation. All target analytes were blank-corrected. The limits of quantification (LOQs) were calculated as the mean values plus three times standard deviations of analytes in blanks. For the undetected compounds in blanks, the LOQs were estimated as a signal to noise ratio of 10. The LOQs of BFRs and DPs in hair ranged from 0.001 to 0.27 ng/g dry weight (dw). The LOQs of BFRs and DPs in serum ranged from 0.0001 to 16.7 ng/g lipid weight (lw) (except for BDE-206, BDE-207, BDE-209 and BTBPE, Table 1).

2.4. Statistical analysis

All statistical analyses were performed using SPSS Statistics 19.0 (SPSS, Inc., Chicago, IL). ΣPBDEs were defined as the sum of 18 PBDE congeners including BDE-28, BDE-47, BDE-66, BDE-85, BDE-99,BDE-100, BDE-138, BDE-153, BDE-154, BDE-183, BDE-196, BDE-197, BDE-202, BDE-203, BDE-206, BDE-207, BDE-208, and BDE-209. Summary statistics were only computed for congeners with detection frequencies of ≥ 50%. BFR and DP levels were log-transformed to obtain normal distributions, and concentrations less than the LOQs were assigned a value equal to half of LOQ for statistical analyses. The gender and segmental differences of BFR levels in hair were performed by *t*-test. The correlations between hair and serum were assessed using Spearman correlation analysis. The level of significance was set as $p = 0.05$ throughout the study.

3. Results and discussion

3.1. BFRs and DPs in integrated hair and paired serum

Eighteen PBDE congeners were identified in the integrated hair