Dechlorane Plus in paired hair and serum samples from e-waste workers: Correlation and differences

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HIGHLIGHTS

• Elevated serum and hair DP levels were found in e-waste workers.
• Hair DP levels positively correlated with serum DP levels in paired samples.
• Hair showed different DP isomer composition with serum.
• The correlation between hair and serum DP levels in female was weaker than in male.

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ABSTRACT

Dechlorane Plus (DP) and a dechlorinated product of DP were measured in 34 matched human hair and serum samples (19 males and 15 females) collected from e-waste recycling workers in South China. The DP (sum of syn- and anti-DP) concentrations in hair and serum samples ranged from 6.3 to 1100 ng g⁻¹ dry weight and from 22 to 1400 ng g⁻¹ lipid weight (lw). The levels of anti-Cl₁₁-DP ranged from 0.02 to 1.8 ng g⁻¹ in hair and from not detected to 7.9 ng g⁻¹ lw in serum. Significant positive correlations for both DP and anti-Cl₁₁-DP concentrations between hair and serum samples were found (p < 0.05), indicating hair to be a suitable matrix for human DP exposure. However, a significant difference was found in the DP isomer composition between hair and serum, suggesting stereoselective bioaccumulation during the absorption of DP into hair. A sharp gender difference was found in the levels of DP in hair. Moreover, syn-DP, anti-DP and anti-Cl₁₁-DP in hair significantly correlated with those in serum for male samples, but not for female samples. The observed gender differences in the present study may be, in part, ascribed to the much longer hair exposure time for females than males due to the difference in sampling distance from the scalp.

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1. Introduction

Dechlorane Plus (DP, C₁₈H₁₂Cl₁₂), developed by Hooker Chemical in the 1960s as a substitute for Dechlorane, is widely used as an additive flame retardant in the coatings of electrical wires and cables, computer and television connectors, and plastic roofing materials (Bettes, 2006; Sverko et al., 2011). Commercial DP comes as three technical products, DP-25, DP-35, and DP-515, which differ in particle size but are similar in composition. Each of them consists of two isomers, syn and anti-DP, in a ratio of 1:3 (Hob et al., 2006). DP has been categorized as a high production volume chemical by the U.S. Environmental Protection Agency (Xian et al., 2011). The usage of DP is projected to rise as it has been identified by European Commission as a possible replacement for the restricted decabromodiphenyl ether flame retardant (Sverko et al., 2011). Previous studies have suggested that DP and its analogs may be persistent, bioaccumulative, and subject to long-range transport, which can be characterized as persistent organic pollutants (Sverko et al., 2011). It was also found that DP exposure induced oxidative hepatic damage and led to an alteration of gene
expression involved in carbohydrate, lipid, nucleotide, and energy metabolism in rats and mice (Wu et al., 2012; Li et al., 2013).

Several sources, including industrial use of DP technical mixtures and the use/disposal of consumable products containing DP, have been identified as contributing to the occurrence of DP in the environment (Wang et al., 2010). In China, the demand for flame retardants, including DP, has grown dramatically over the past decades due to the increasing use of textiles and plastics in houses and offices (Wang et al., 2010). There is a DP manufacturing plant located in Hua’ian City (Jiangsu Province, China) with an annual DP production estimated in 2010 to be 2100–7000 tons (Wang et al., 2010). In addition to the emissions generated by productive processes, e-waste is another important source of DP in China due to intensive e-waste recycling activities conducted in various, unspecified locations throughout China (Ren et al., 2008). As a result of these e-waste recycling activities, elevated DP levels have been identified in abiota, biota and human samples taken from e-waste recycling regions (Ren et al., 2009; Zheng et al., 2010; Xian et al., 2011; Feo et al., 2012; Ben et al., 2013).

The identification of suitable biomonitoring indicators for the assessment of human exposure to chemicals is essential. Blood is an ideal matrix for human contaminants biomonitoring, but it is not always available in sufficient amount for reliable analysis, especially for children. Hair is a keratinous matrix and contains 3–4% lipids (Altschul et al., 2004). It can be conveniently collected, transported, and stored. Thus, human hair is a suitable matrix for the analysis of organic pollutants. In fact, several previous studies have used hair analysis to report human exposure to organic pollutants such as PCDD/PCDFs, OCPs, PCB, PBDEs and PAHs (Schramm et al., 1992; Schramm, 1997; Covaci et al., 2002; Toriba et al., 2003; Nakao et al., 2005; Chan et al., 2007; Zhang et al., 2007; Wen et al., 2008; Tadeo et al., 2009). In a previous study, Zheng et al. (2010) reported human DP exposure in populations located in an e-waste recycling area, a rural region and an urban region using hair as biomonitoring matrix. However, the correlation between hair and internal human matrices has not yet been clearly demonstrated.

To our best knowledge, only one study has investigated the correlation of DP levels between hair and blood of occupationally exposed workers in a DP manufacturing plant (Zhang et al., 2013). A significant positive correlation (r < 0.05) was obtained between the paired blood and hair samples. However, the difference between hair and blood in reflecting human DP exposure, and the factors which might influence the correlation between hair DP and serum DP, were not discussed. Though a correlation between hair and blood DP levels has been tentatively found, further insight into how different factors affect this relationship is still limited, and the differences between hair and blood in reflecting human DP levels and composition have rarely been taken into consideration.

In the present study, 34 matched hair and serum samples, including 19 paired male and 15 paired female samples, were collected from an e-waste recycling area in South China. The objective of this study was to investigate the correlation between the two important matrices (hair and serum) in indicating human DP levels. Moreover, we also investigated the effect of gender in the use of hair as a bioindicator of human DP exposure.

2. Materials and methods

2.1. Sample collection

A total of 34 matched human hair and serum samples (19 male and 15 female) were collected from e-waste recycling workers from Longtang, Qingyuan city in Guangdong province. This study was approved by the Ethics Committee of School of Life Sciences, Sun Yat-sen University. Consent was obtained from all participants after they were clearly informed of the study's objectives. A short questionnaire and general physical examination were completed, in which data on age, gender, weight, height, and occupational history of each participant were compiled. An approximately 8–10 mL venous blood sample was collected from each volunteer in an anti-coagulant-free tube by medical professionals in a local hospital. The serum was isolated from the blood by centrifugation at 3000 rpm for 5 min and kept at −80 °C prior to chemical analysis. Hair samples were also collected from these volunteers using stainless steel scissors in a local barbershop. Hair samples were wrapped in aluminum foil, sealed in polyethylene zip bags, and kept at −20 °C prior to chemical analysis.

2.2. Chemicals

Anti-DP, syn-DP, and 1,6,7,8,9,14,15,16,17,17-octadeca-7,15-diene (anti-C11-DP, lot NO. a-C11,DP 0708) standards were purchased from Wellington Laboratories (Ontario, Canada). BDE128 and BDE181 were obtained from AccuStandard Inc (New Haven, US). Organic solvents were redistilled using a glass system.

2.3. Sample cleanup and analysis

The procedures used for the extraction and cleanup of the hair and blood samples in the present study were the same as those previously used for our work on polybrominated diphenyl ethers (Zheng et al., 2014a). These methods are briefly described below. Hair samples were purified by rinsing with Milli-Q water, freeze-dried and cut into small pieces (2–3 mm) with scissors. Approximately 2 g of hair from each sample was weighed and spiked with an internal standard, BDE 128. The hair samples were then incubated for 12 h with hydrochloric acid (4 M) and a hexane/dichloromethane mixture (4:1, v/v), followed by liquid–liquid extraction. Serum samples were denatured using hydrochloric acid (6 M) and 2-propanol, and subsequently extracted with hexane/methyl-tert-butyl ether mixture (1:1, v/v). Concentrated sulfuric acid was used to remove the lipids from the serum extraction. Both hair and serum extracts were purified with a multilayer silica/alumina column. Finally, the cleaned extracts were condensed to a volume of 100 μL under a gentle stream of N2. Before instrument analysis, known amount of BDE 181 was added to each sample as a recovery standard. The total lipid content was calculated from the total triglyceride and cholesterol values measured in the serum (Rylander et al., 2006).

DP was analyzed by a Shimadzu 2010 gas chromatograph coupled with a mass spectrometer with electron-capture negative ionization in selected ion monitoring mode. The target chemicals were separated by a DB-XLB (30 m × 0.25 mm × 0.25 μm) capillary column. Each sample (1 μL) was manually injected in splitless mode. The column temperature program was as follows: hold at 110 °C for one min, then increased to 180 °C at 8 °C min⁻¹ and held for one min, then to 240 °C at 2 °C min⁻¹ and held for 5 min, before being increased to 280 °C at 2 °C min⁻¹ and held for 15 min, and finally, to 310 °C at 10 °C min⁻¹ and held for 5 min. The ions monitored were m/z 653.8 and 651.8 for DP isomers, m/z 618.0 and 620.0 for anti-C11-DP, and m/z 79 and 81 for BDE 128 and BDE 181.

2.4. Quality assurance and quality control (QA/QC)

The QA/QC measures in this study were the same as those in our recent study on PBDEs, including the use of recovery standard, procedural blanks, spiked blanks, and spiked matrices. The recovery of the internal standard, BDE 128 was in the range of 72–113% for the hair samples and 71–110% for the serum samples. Recoveries of syn-DP, anti-DP, and anti-C11-DP in the spiked blanks were in