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Dichloro-diphenyl-trichloroethanes (DDTs) in human hair and serum in rural and urban areas in South China☆

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ABSTRACT

Human hair has been employed as a biomarker for exposure to persistent organic pollutants (POPs), but information on the source of dichloro-diphenyl-trichloroethane (DDT) and its metabolites in hair is limited. The present study investigated the contamination of DDTs in human hair from a rural area and an urban area of South China and compared with those in human serum and indoor dust. The concentrations of ∑DDTs ranged from 2.30 to 489 ng/g, with a median of 21.8 ng/g in human hair. The ∑DDT concentrations (median=40.8 ng/g) in female hair were significantly higher than those in male hair (median=20.6 ng/g). There were significantly positive correlations between the concentrations of DDTs and ages in both the female and male hair, but the age-dependence for DDTs in serum was less significant. The profile of DDT analogues in female hair, differing from that in the male hair, was more similar to that in the indoor dust, suggesting a more important role of exogenous exposure in female hair. We estimated that exogenous source is responsible for approximately 11% and 20% of the burden of DDTs in the male and female hair, respectively. Adjusted multiple linear regression model showed significantly positive association between the *p,p′*-DDE concentrations in the paired hair and serum samples, indicating that endogenous origins are the primary sources of DDTs in the hair of the residents in the study areas. Our findings demonstrated that human hair is a reliable biomarker for body burden of DDTs and can be used in epidemiology research and retrospective assessment of DDT exposure.

1. Introduction

Persistent organic pollutants (POPs) are an important class of environmental toxicants for wildlife and humans. Epidemiological studies linking POPs to disease have been conducted (Magliano et al., 2014). Serum, urine, and breast milk are common exposure biomarkers used in epidemiology research (Anand et al., 2008; Butt et al., 2014; Park et al., 2011; Zheng et al., 2016). However, collection and storage of blood samples have limited its application for POP monitoring in humans. As useful non-invasive biomarkers, urine was only applicable for specific chemicals or their metabolites and breast milk is restricted to the particular cohort of lactating women. In addition to these biological media, hair has been employed as a promising biomarker with advantages such as non-invasive, easily collected, low-cost, easily transported, and stored (D'Have et al., 2005; Gill et al., 2004). Therefore, these remarkable preferences of hair as a biomarker for epidemiology have brought its extensive applications as a complement in assessment of human exposure to POPs (Covaci et al., 2008; Esteban and Castano, 2009; Park et al., 2011; Zota et al., 2013).

Dichloro-diphenyl-trichloroethane (DDT) is an organochlorine pesticide that has been extensively used in agriculture in the 1950s–1980s before its restriction in the Stockholm Convention on Persistent Organic Pollutants (UNEP, 2009). However, the Convention has given an exemption for the production and public health use of DDT for vector-borne disease control because of the absence of equally effective and efficient alternatives (UNEP, 2009). Nowadays, about 3000–4000

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metric tons of DDT are produced annually for vector control (WHO, 2011). Besides, DDT is being produced for agricultural use of DDTs in some developing countries such as India and North Korea (Berg, 2010). Although the agricultural use of DDT was banned since 1983 in China, DDT may be still used for Dicofol (an acaricide) production (Berg, 2010). Use of DDT in some regions in the world leads to ongoing emission of this pesticide to the environment and human exposure. As a result, contamination of DDT and its primary metabolites in various environmental media across the world was still observed in recent years (Chen et al., 2011; Shen et al., 2013; Syed and Malik, 2010; Yohannes et al., 2014) because of the persistence and long range transport properties.

DDT and its metabolites have been found related to human diseases, such as breast cancer (Anand et al., 2008; Cioroiu et al., 2010), prostatic cancer (Kumar et al., 2010), and androgen interference (Dalvie et al., 2004; Martenies and Perry, 2013). Human exposure to DDTs has been investigated through monitoring of serum, milk and hair. Elevated levels of DDTs in hair and serum were reported in areas with continuous DDT usage (Covaci et al., 2008; Martinez et al., 2012). Although numerous previous studies have demonstrated DDT contamination in human hair (Covaci et al., 2008; Dahmardeh Behrooz et al., 2012; Lu et al., 2014; Tsatsakis et al., 2008), few studies have explored the internal and external sources of DDTs in hair. Identifying the sources in human hair is important for its utility in biomonitoring and epidemiological research.

In the present study, occurrence of DDT and its primary metabolites (DDTs) was investigated in hair and serum of residents in a rural area of South China. Potential factors influencing the contamination of DDTs were explored. The associations between concentrations of DDT in the hair and serum were examined to reveal the feasibility of hair in biomonitoring human exposure to these organochlorine compounds. As comparison, levels of DDTs in hair and serum from a neighboring city in South China were also investigated. Indoor dust samples were also obtained to identify the exogenous and endogenous sources of DDTs in human hair.

2. Materials and methods

2.1. Sampling

Sample collection was conducted in a rural area (Qingyuan) with common agricultural activities and a highly urbanized area (Guangzhou) in Guangdong Province in South China during October 2010 to June 2011. The distance between the two areas is approximately 75 km (Fig. S1, Supplementary Material).

Hair samples of residents from the rural area (n=140, 113 male and 27 female) and urban area (n =27, male hair) were obtained. Serum samples from the rural area (n=71, 44 male and 27 female) and from the urban area (n=7 male) were also collected. Among them, 30 serum-hair paired samples (19 males and 11 females) from the rural area were included. Besides, indoor dust samples were also collected from the rural (n=23) and urban (n=26) areas, with a pre-cleaned brush which was soaked overnight in alcohol and dried.

Hair without dyeing and perm was sampled with stainless-steel scissors. About 8–10 mL venous blood was collected from each participant with an anticoagulant-free tube by medical professionals at a local hospital and transported to the laboratory on ice packs. Serum was isolated at 3000 rpm for 5 min and stored in Teflon bottles at −80 °C in laboratory. Consent was obtained from all participants after they were clearly informed of the objectives of the study. A brief questionnaire and general physical examination were completed by participants, covering their personal information about age, gender, weight, and height, which is given in Table S1.

2.2. Sample preparation and analysis

Details of the extraction and cleanup for hair samples have been reported elsewhere (Zheng et al., 2011, 2013), and those for serum samples have been provided in the study of Yan et al. (2012). The procedures are briefly described below.

Hair samples were washed in Milli-Q water with a shaking incubator (1 h, 40 °C) twice to efficiently remove external contamination (e.g., fine soil particles, dust), as validated by SEM images in our previous study (Zheng et al., 2013). Then, hair samples were freeze-dried and cut into small pieces (2–3 mm). Approximately 2 g of hair samples were spiked with surrogate polychlorinated biphenyl (PCB) standards (PCB 30, PCB 65, and PCB 204) incubated overnight (12 h) at 40 °C with 40 mL of hydrochloric acid (4 M) and 40 mL of hexane/dichloromethane (4:1, v/v). Extraction of target analytes from the incubation medium was performed by a liquid-liquid extraction (LLE) with 3×40 mL of hexane/dichloromethane (4:1, v/v). The extracts were further cleaned by a multi-layer silica/alumina column and finally condensed to 1 mL under a gentle stream of N_2. Serum samples were denatured with hydrochloric acid (6 M) and 2-propanol and extracted with a mixture of hexane/methyltert-butyl ether (MTBE) (1:1, v/v). Lipids were removed by concentrated sulfuric acid. The combined extracts were subsequently further purified by a multilayer silica/alumina column. The total lipid content was calculated from the total triglyceride and cholesterol values measured in the serum (Rylander et al., 2006). Before injection, extractions were finally condensed to 100 μL with known amounts of internal standards (PCB 24, PCB 82, and PCB 198) added. Dust samples were sieved through a stainless steel sieve (500 mm) to remove large debris before analysis. The samples (0.05 g) were spiked with surrogate standards and extracted by Soxhlet extraction with a mixture of acetone and hexane (1:1, v/v) for 48 h. Procedures similar to hair samples were adopted for the preparation of dust samples. Known amounts of internal standards were added to each sample which was finally condensed to 200 μL.

DDTs were quantified by an Agilent 6890 gas chromatograph coupled to a 5975B mass spectrometer with an electron impact (EI) ion source (GC–EI-MS). A DB-5MS (60 m×0.25 mm i.d., 0.25 μm film thickness; J & W Scientific, Folsom, CA) capillary column was employed to separate the DDT analogues. The GC-oven temperature was programmed from an initial temperature of 80–240 °C at a rate of 6 °C/min, then finally ramped to 295 °C at a rate of 1 °C/min, and held for 15 min. Samples (1 μL) were manually injected in splitless mode.

2.3. Quality control

Quality control was assessed with surrogate standards, procedural blanks, spiked blanks, and spiked hair matrices. The mean recoveries of six individual DDT analogues (*o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT, *p,p′*-DDT) ranged from 65% to 105% in spiked blanks and from 58% to 107% in spiked matrices. The recoveries of surrogate standards PCB 30, PCB 65, and PCB 204 were in the range of 58–99%, 57–120%, and 50–129% in hair samples, and 62%–109%, 67–115%, and 76–121% in serum samples, and 58–98%, 60–129%, and 55–129% in dust samples, respectively.

The final results were not recovery-corrected. Only trace amounts of *p,p′*-DDE or *p,p′*-DDT (< 0.5 ng) were detected in procedure blanks, and the mean concentrations of the blanks were not subtracted from the concentrations of the sample extracts. The limit of detection (LOD) was defined as a signal-to-noise ratio of five. LODs for *o,p′*-DDE, *p,p′*-DDE, *o,p′*-DDD, *p,p′*-DDD, *o,p′*-DDT and *p,p′*-DDT were 0.001, 0.006, 0.006, 0.010, 0.006, and 0.013 ng/g (dry weight) for hair on a basis of average hair mass of 0.2 g. Corresponding LODs were 2.6, 7.4, 10.6, 11.1, 10.3, and 25.5 ng/g (lipid weight) for serum on a basis of average serum mass of 0.019 g.