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Burdens of PBBs, PBDEs, and PCBs in tissues of the cancer patients in the e-waste disassembly sites in Zhejiang, China

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ABSTRACT

This study was conducted to explore the burdens of PBBs, PBDEs, and PCBs among cancer patients living in the e-waste disassembly sites. The contents of 23 PBB congeners, 12 PBDE congeners, and 27 PCB congeners in kidney, liver, and lung samples were measured by GC–MS. The results showed that low-brominated PBBs and PBB153 were the predominant congeners. PBDE47 were the most predominant PBDE congeners. PBDE209 were detected in >70% of the samples, with geometric means ranging from 64.2 to 113.9 ng g^{-1} lipid. Among the three subfamilies of PHAHs, PCB concentrations were the highest. The detected levels of PHAHs were in the same order of magnitude in the three tissues, which indicated that any of the three tissues could be the suitable indicator for assessing body burdens of PHAHs. PBB contents (181–192 ng g^{-1} lipid) were obviously higher than those reported in the general USA population (3–8 ng g^{-1} lipid). PBDE levels (174.1–182.3 ng g^{-1} lipid) were comparable to those reported in the USA population, but significantly higher than those of the European population. PCBs levels were comparable to those of the European population. The high cancer incidence in the disassembly sites may be related to higher burdens of PBBs, PBDEs, and PCBs in tissues.

1. Introduction

Waste electrical and electronic equipment, or “e-waste” for short, has become the fastest growing stream of all solid waste found in China in that huge amounts of such waste are constantly being generated from (legal or illegal) imports and domestic use (Hicks et al., 2005). A cluster of small villages in the littoral zone in the Zhejiang province has become a booming recycling center for e-waste, but nonetheless at the expense of having thousands of village workers engaged in primitive recycling operations without the use of adequate protective equipment (Zhao et al., 2008). Such primitive operations include, but are not limited to, stripping of metals in open pit acid baths, removing electronic components from circuit boards by heating over a grill, and recovering metals by burning cables in (or near) the cropland (Deng et al., 2007). Yet as a result of these operations and through leakage, evaporation, runoff, and leaching, many toxic chemicals, such as polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and polychlorinated biphenyls (PCBs), have been reported to be released into the local environmental and human matrices such as air (Deng et al., 2007), sediment (Wang et al., 2005; Luo et al., 2007), soil (Liu et al., 2006; Zhao et al., 2008), cord blood (Qu et al., 2007), and milk (Zhao et al., 2007a). These pollutants can be bioaccumulated in the aquatic and the terrestrial food chains and biomagnified in humans via food due to their lipophilicity (Zhao et al., 2007a,b). These earlier findings suggest that the residents living near the e-waste disassembly site might be at high health risk.

Polyhalogenated aromatic hydrocarbons (PHAHs) represent a large family of highly lipophilic and environmentally persistent substances, of which PBBs, PBDEs, and PCBs are three subfamilies that were of great concern in the present study. All three PHAHs subfamilies are notably toxic and bioaccumulative (Hardy, 2000; McDonald, 2002). Animal studies (WHO, 1994a,b) showed that the PHAHs in these three subfamilies not only were they capable of disrupting endocrine functions but could also induce carcinogenicity.

An increasing incidence of cancer (such as liver cancer, and lung cancer) has been found around the e-waste disassembly sites during the last decades. However, there is still no report on body burdens of PHAHs among these local cancer patients in the disassembly sites. Accordingly, the present study had its focus on assessing body burden (or internal exposure) of local cancer patients to the 62 PHAHs that were deemed likely present in e-waste. Human tissue samples can reflect steady-state concentrations of lipophilic chemicals, which is considered as a suitable indicator for the study of environmental or occupational exposure to many chemical pollutants including PBDEs and PCBs (Meironyté Guvenius et al., 2001; Petreas et al., 2004; Johnson-Restrepo et al., 2005; Naert et al., 2006;Covaci et al., 2008). Therefore, tissue samples (kidney, liver, and lung) were collected for

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assessing body burdens of PHAHs. This exploration represented the first of its kind in reporting extensively the recent levels of PBBs, PBDEs, and PCBs in tissues of local cancer patients. Information obtained from this type of exploration may also be useful for subsequent evaluation of the health risks at issue.

2. Materials and methods

2.1. Sample collection and storage

After obtained consent from participants according to procedures approved by the Ethics Committees of Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, kidney ($n=19$), liver ($n=55$), and lung ($n=7$) tissue samples (each of ~10–50 g) were collected from these surgical patients who were newly diagnosed for cancer from April 2007 to January 2008 at the First Hospital of Wenling and the Second Hospital of Wenling, with each sample placed into a separate chemically-cleaned glass bottle, and labeled with a unique code and the proper sampling date. The mean age of the individuals was 65 years ranging from 32 to 94 years. All samples were transported to the analytical laboratory as soon as possible in ice boxes and continued to be stored in the dark at −20 °C until analysis.

2.2. Materials and chemicals

The following standards were obtained from the Cambridge Isotope Laboratory (USA): 12 native PBDE congeners; 7 $^{13}C_{12}$-labeled PBDEs (PBDE15, 28, 47, 99, 153, 154, and 183); 23 PBB congeners; 27 PCB congeners; and surrogate standards pentachloro-nitrobenzene (PCNB), 2,4,5,6-tetrachloro-m-xylene (TMX), and PCB209. All solvents used (hexane, acetone, and methylene chloride) were of pesticide grade (Promochem, Germany). Silica gel (100–200 mesh) was purchased from Promochem (Germany). Aluminum foil was rinsed with acetone and dried at ambient temperature prior to use. Sodium sulfate (granular, anhydrous) was pre-cleaned with methylene chloride and purified by heating at 450 °C for 8 h in a shallow metallic enamel tray. Cellulose extraction thimbles of 33 mm i.d. and 94 mm in length were from Schleicher & Schuell (Germany); these thimbles were pre-cleaned by Soxhlet extraction with *n*-hexane: acetone (3:1, v/v) for 4 h before use. Glassware was soaked, cleaned with chromic solution, rinsed thoroughly with distilled water and acetone, and finally heated in a baking oven (Heraeus, Germany) at temperatures programmed from 40 °C to 420 °C at a rate of 15 °C min^{-1} for 16 h.

2.3. Sample preparation and clean-up

The tissue samples were first individually pulverized by a stainless-steel machine, then, were all freeze-dried. About 2–5 g of these dried tissue residues from each sample was introduced into a pre-cleaned thimble and Soxhlet extracted for 24 h using 180 mL *n*-hexane/acetone (3:1, v/v) solution. For this preparation process, TMX, PCNB, and PCB209 were added to each sample as surrogate congener standards. The extract from each sample was then concentrated to about 1 mL by rotary evaporation (550 mbar, 60 °C). After gravimetrical lipid determination, the concentrated extracts were further cleaned individually by a multilayer silica gel column containing: 2 g of anhydrous sodium sulfate; 8 g of silver nitrate ($AgNO_3$) silica (10%, $AgNO_3$ w/w); 2 g of deactivated silica (3.3% organic-free reagent water w/w); 15 g of acidic silica (44% conc. sulphuric acid w/w); 1 g of deactivated silica (3.3% organic-free reagent water w/w); and 2 g of anhydrous sodium sulfate. The silica gel column was wrapped in aluminum foil throughout clean up, to protect samples from debromination induced from UV-light, and pre-eluted with 80 mL of hexane prior to adding to the extract. The first fraction eluted with *n*-hexane (100 mL) was used to concentrate the PCB congeners, with the second fraction (eluted with 10% methylene chloride in 80 ml *n*-hexane) intended for collection of the PBB and PBDE congeners (US EPA, 1996). The eluants were concentrated separately to about 1 mL, again by rotary evaporation. The solvent of each sample was evaporated to dryness by gentle nitrogen stream at 25 °C and redissolved in 200 µL hexane.

2.4. Chemical analysis

The chemical analysis was performed using an Agilent 5975 GC–MS system equipped with a capillary DB-5MS column (5% phenyl/95% methyl silicone, 30 m, 0.25 mm i.d., and 0.25 µm film thickness, from J&W Scientific, Folsom, California, USA). The column oven temperature was programmed from 90 °C (initial time, 1 min) to 250 °C at a rate of 4 °C min^{-1}, then from 250 °C to 300 °C at a rate of 25 °C min^{-1}, and held for 5 min. The GC injector temperature was maintained at 260 °C, with the temperatures of the MS ion source and of the transfer line being kept at 230 °C and 300 °C, respectively. The carrier gas was helium at a constant flow rate of 1.5 mL min^{-1}. The mass spectrometer was operated in the electron impact (EI) ionization mode with an electron energy of 70 eV. Samples (1 µl) were injected in the splitless mode with a solvent delay set at 4 min. The molecular ions ($[M]^+$ or $[M+2]^+$) and the fragment ions resulting from the loss of X_2 (i.e., $[M-X_2+2]^+$ or $[M-X_2+4]^+$, where X = chlorine or bromine) were selected as the precursor ions for mass spectrometric analysis. Quantitative analyses of PBB209 and PBDE209 were performed on the Agilent 5975 GC–MS equipped with a DB-5MS (5% phenyl/95% methyl silicone, 15 m, 0.25 mm i.d., and 0.1 µm film thickness, from J&W Scientific, Folsom, California, USA), at temperatures programmed from 90 °C (initial time, 1 min) to 250 °C at a rate of 10 °C min^{-1}, then from 250 °C to 300 °C at 15 °C min^{-1}, and finally held for 8 min. Mass spectrometer condition was performed by EI (70 eV) and selected ion monitoring of high abundance (m/z 943 and m/z 799 for PBB209 and PBDE209, respectively).

2.5. Quality assurance/quality control

For every batch of 10 samples, a solvent blank and a procedural blank were added to ensure that the samples and the analysis process were free of contamination. The detection limits (LOD) of the targeted compounds were defined as 3 times the signal to noise (S/N) ratio, ranged from 0.08 to 0.24 ng g^{-1} lipid for PBB congeners, from 0.08 to 0.32 ng g^{-1} lipid for PBDE congeners, from 0.02 to 0.12 ng g^{-1} lipid for PCB congeners, and from 0.80 to 1 ng g^{-1} lipid for PBB209 and PBDE209. Spike recoveries for $^{13}C_{12}$-labeled PBDEs (at 10 ng) ranged from 75.2 to 96.5%; and those for TMX, PCNB, and PCB209 ranged from 70.4 to 92.5%, 81.6 to 107.4%, and 90.8 to 112.6%, respectively. Triplicate analysis of six diluted standard solutions (1.0, 5.0, 10.0, 25.0, 50.0, and 100.0 ng mL^{-1}) was performed for each selected standard mixture. Multi-level calibration curves were constructed for the quantification; and good to excellent linearity ($r^2>0.99$) was achieved.

2.6. Data analysis

A value of half LOD was given to the samples in which the contents of PBBs, PBDEs or PCBs were not detectable. Descriptive statistics (mean, range, etc.) were computed to characterize the concentrations of PBBs, PBDEs, and PCBs in the samples. All statistical analyses were performed for congeners for which more than 50% of the samples were above the LOD, using the Statistical Package for the Social Sciences (SPSS for Windows ver. 11.5) where applicable. The (statistical) term mean used throughout this paper referred to *geometric* mean. The levels of PBB209 and PBDE209, though measured and considered duly, were not included in calculating the total concentrations of PBBs and PBDEs. Nonparametric methods (Mann–