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Elevated Levels of Urinary 8-Hydroxy-2#-deoxyguanosine in Male Electrical and Electronic Equipment Dismantling Workers Exposed to High Concentrations of Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, Polybrominated Diphenyl Ethers, and Polychlorinated Biphenyls

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Environ. Sci. Technol., 2008, 42 (11), 4202-4207 DOI: 10.1021/es800044m • Publication Date (Web): 01 May 2008

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Elevated Levels of Urinary 8-Hydroxy-2'-deoxyquanosine in **Male Electrical and Electronic Equipment Dismantling Workers Exposed to High Concentrations of** Polychlorinated Dibenzo-p-dioxins and Dibenzofurans, Polybrominated **Diphenyl Ethers, and Polychlorinated Biphenvls**

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Received January 7, 2008. Revised manuscript received March 10, 2008. Accepted March 18, 2008.

To investigate the occupational exposure levels to polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs), indoor dust (n = 3) in workshops and hair samples from male workers (n = 64) were collected at two electrical and electronic equipment waste (E-waste) dismantling factories located in the LO area in east China in July 11-13, 2006. Pre- and postworkshift urines (64 of each) were also collected from the workers to study oxidative damage to DNA using 8-hydroxy-2'-deoxyguanosine (8-OHdG) as a biomarker. The concentrations of PCDD/Fs, PCDD/F-WHO-TEQs, PBDEs, PCBs and PCB-WHO-TEQs were (50.0 \pm 8.1) \times 10³, 724.1 \pm 249.6, (27.5 \pm 5.8) \times 10^6 , (1.6 \pm 0.4) \times 10^9 , (26.2 \pm 3.0) \times 10^3 pg/g dry weight (dw) in dust, and (2.6 \pm 0.6) \times 10 3 , 42.4 \pm 9.3, (870.8 \pm 205.4) \times 10^3 , (1.6 \pm 0.2) \times 10⁶, 41.5 \pm 5.5 pg/g dw in hair, respectively. The homologue and congener profiles in the samples demonstrated that high concentrations of PCDD/Fs, PBDEs, and PCBs were originated from open burning of E-waste. The 8-OHdG levels were detected at 6.40 \pm 1.64 μ mol/mol

creatinine in preworkshift urines. However, the levels significantly increased to 24.55 \pm 5.96 μ mol/mol creatinine in postworkshift urines (p < 0.05). Then, it is concluded that there is a high cancer risk originated from oxidative stress indicated by the elevated 8-OHdG levels in the E-waste dismantling workers exposed to high concentrations of PCDD/Fs, PBDEs, and PCBs.

Introduction

Waste electrical and electronic equipment (WEEE or E-waste) is becoming a major environmental concern, particularly in developing countries in recent years (1-4). The UN Environment Programme has estimated that 20-50 million metric tons of E-waste are produced worldwide each year, and the number is rapidly increasing (5). Most the E-waste is transported to developing countries for "recycling" (5). E-waste recycling has already become an industry in the southeast coast of China, in areas such as LQ and Guiyu (2, 4). Unfortunately, due to the crude recycling process such as open burning of E-waste in those places, a lot of contaminants are released into the environment, including persistent organic pollutants (POPs), especially polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and polychlorinated biphenyls (PCBs) (4), which have been reported to cause a range of health problems in the immune, endocrine, nervous, and reproductive system of humans and animals (6-8).

PCDD/Fs, PBDEs, and PCBs have recently been detected in many environmental and human samples in the areas contaminated by E-waste, such as air, soil, dust, sediment, freshwater, fish, cow milk, human milk, blood, umbilical cord blood, and newborn meconium (1-4, 9-14). The concentrations of PCDD/Fs, PBDEs, and PCBs in soil were detected in the range of 30.9×10^3 to 967.5×10^3 , 2.9×10^6 to 44.5×10^6 , and 73.8×10^3 to 1.4×10^6 pg/g dry weight (dw), respectively. However, to our knowledge, few studies have focused on the potential health impacts of these contaminants in local humans. Besides normal digestant exposure like local residents, the E-waste dismantling workers accumulate more contaminants during their work time by inhalation and dermal contact and may be under the risk of exposure to PCDD/Fs, PBDEs, and PCBs.

Many studies have confirmed that PCDD/Fs, PBDEs, and PCBs can induce oxygen radicals that subsequently lead to oxidative damage to DNA (15-19). Oxidative DNA lesions are supposed to play important roles in various diseases, including cancer and premature aging (20). 8-Hydroxy-2'deoxyguanosine (8-OHdG) is an important product from oxidative damage to DNA and is formed in a promutagenic DNA lesion induced by the reaction of hydroxyl radicals with guanosine at the C8 site in DNA (21); thus, the presence of 8-OHdG may lead to mutagenesis. Moreover, the repair process for damage inflicted by 8-OHdG results in excised 8-OHdG adduct being excreted into the urine (22-24). Therefore, 8-OHdG has been proposed to assess individual cancer risk originated from oxidative stress (21).

To investigate the occupational exposure levels to PCDD/ Fs, PBDEs, and PCBs and the accumulation in the human body, indoor dust in workshops and hair samples from male workers were collected and analyzed at two E-waste dismantling factories located in the LQ area, which is one of the largest sites for dismantling E-waste in China. In addition, the pre- and postworkshift urines of the workers were also

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collected to compare differences in 8-OHdG levels and to assess the health impact of these contaminants on the human body.

Materials and Methods

Sampling. Sixty-four male workers, aged from 18 to 60 and employed for at least one year, were randomly selected to participate in the study from two big E-waste dismantling factories in the LQ area in July 11-13, 2006. After providing their written informed consent to participate in this study, all individuals were interviewed at enrollment; and a questionnaire was used to elicit their health status, occupational history, and so on. The pre- and postworkshift urine (10 mL each) were collected before and after their work at the same day. Their hair samples (3-5 g each) were also collected along with the preworkshift urines. Three indoor dust samples (10 g each) were collected at corners of the three workshops where most participants worked. The sampled workshops were 6-8 years in age (average 7.3 years). All of the samples were frozen immediately after collection and stored at −20 °C until chemical analysis.

Chemical Reagents and Standard Solutions. All solvents were pesticide residue grade and were purchased from J.T. Baker (J.T. Baker, Inc., NJ, USA). Silica gel (100–200 mesh) and basic aluminum (Alumina B Super I) were purchased from ICN (Eschwege, Germany). Florisil was obtained from LGC Promochem (Hadfield, UK). Bio-Beams SX-3 was purchased from Bio-Rad. Standard solutions of PCDD/Fs (1613-LCS, 1613-IS) (25), PBDEs (1614-LCS, 1668A-IS) (26), and PCBs (1668A-LCS, 1668A-IS) (27) were obtained from Cambridge Isotope Laboratories Inc., USA. 8-OHdG of analytical grade was obtained from Sigma (St. Louis, MO, USA). Bond Elut LCR SPE columns (10 mL/500 mg; C18 OH) were purchased from Varian (Harbor City, CA, USA). All solutions were prepared with ultrapure water from a Milli-Q water system (Millipore Corp., Bedford, MA, USA).

Measurement of PCDD/Fs, PBDEs, and PCBs. Hair samples were washed with 1% (v/v) commercial shampoo in water for 5 min, followed by ultrapure water to remove on-surface impurities. They were then oven-dried at 70 °C and cut into 1-2 mm-long pieces. The dust samples were freeze-dried, ground, and homogenized by sieving through a stainless steel 60-mesh sieve.

The analytical procedure are summarized in Supporting Information Figure S1. Briefly, approximately 0.1 g of the dust or 2 g of the hair sample was spiked with ^{13}C -labeled surrogate standards and then extracted with a Soxhlet apparatus for 48 h with 250 mL of toluene for dust or dichloromethane for hair. The concentrated extract was sequentially subjected to multilayer silica gel, florisil, AgNO₃-silica, basic alumina chromatography columns and gel permeation chromatography (GPC) for further cleanup and being separated into three groups of chemicals. The last eluted sample was collected in three fractions, which were concentrated to 10 μ L. Then, 13 C-labeled internal standards (IS), 1668A-IS (for PCBs and PBDEs fractions) and 1613-IS (for PCDD/Fs), were added prior to GC injection.

The quantification was performed on a high resolution gas chromatography (HRGC) coupled with high resolution mass spectrometer (HRMS) (Finnigan MAT 95xp, Thermo Electron) with an electron impact (EI) ion source. Exactly 1 μ L of sample solution was injected by an autosampler (AS2000, Thermo Electron) in splitless mode. The exact instrumental conditions for the analysis of PCDD/Fs, PBDEs, and PCBs are listed in Supporting Information Table S1.

Measurement of Urinary 8-OHdG. The cleanup treatment of urines and analysis of urinary 8-OHdG were carried out according to the method described by Liu et al. (24). The details were shown in the Supporting Information. The

concentration of urinary 8-OHdG was presented as micromoles per mole creatinine (μ mol/mol creatinine).

Quality Assurance and Quality Control. To ensure quality of analysis, blank samples covering the whole analytical procedures were analyzed every ninth samples. The average amount of blank samples was subtracted from the amount of samples. Recoveries of all ¹³C₁₂-labeled surrogates were in the range of 35%–110% for all samples, which is in the acceptable range established by the USEPA 1613B, 1614, and 1668A. The laboratory has successfully participated in an interlaboratory comparison study of PCDD/Fs, PBDEs, and PCBs in different matrices organized by the Norway Institute of Public Health (Norwegain Institute of Public Health, 2005) (28, 29).

Data Analysis. The Statistical Package for Social Sciences (SPSS for Windows, version 11.0; SPSS Inc., Chicago, IL) was used for the quantitative data analysis. The differences among groups were assessed by the paired samples t-test or analysis of variance (ANOVA). The significance level was p < 0.05 and two-tailed. Data are presented as means \pm SEM (standard error of the mean). When calculating the toxic equivalency quantities (TEQs) of samples, the concentrations of undetected congeners were set to their limit of determination (LOD, S/N = 3).

Results and Discussion

Concentrations of PCDD/Fs, PBDEs, and PCBs. Almost all targeted congeners of PCDD/Fs, PBDEs, and PCBs were found in all samples except that PCB104, 169 and 188 were not detected in several hair samples. The concentrations of PCDD/Fs, PBDEs, and PCBs were in the range of 139 to 21.5 \times 10³, 18.1 \times 10³ to 9.4 \times 10⁶, and 55.4 \times 10³ to 7.2 \times 10⁶ pg/g dw in hair, respectively. Their average concentrations were 2.6×10^3 , 870.8×10^3 , and 1.6×10^3 pg/g dw in hair, respectively (Table S2, Supporting Information). In dust, the average concentrations were 50.0×10^3 pg/g dw for PCDD/ Fs, 27.5×10^6 pg/g dw for PBDEs, and 1.6×10^9 pg/g dw for PCBs. In addition, PCDD/F-WHO-TEQs (30), PCB-WHO-TEQs, and total dioxin-like TEQs were also calculated. Their levels were found to be 42.4, 41.5, and 83.9 pg/g dw in hair, and 724.1, 26.2 \times 10³, and 26.9 \times 10³ pg/g dw in dust, respectively (Table S2, Supporting Information). The levels of homologues and congeners of PCDD/Fs, PBDEs, and PCBs detected in dust and hair were separately summarized in Supporting Information Tables S3-5.

PCDD/Fs, PBDEs, and PCBs have been reported in dust and hair by previous studies (Table S6, Supporting Information). But, suprisingly, their concentrations were found to be much lower in dust than in the present study. The PCDD/Fs TEQ levels in our study were up to 724.1 pg WHO-TEQ/g dw and were about 500 times higher than those found in house dust from Japan (31) or even nearly 5-10 times higher than those found in electrostatic precipitator (ESP) dust from sinter plants (32, 33). For total PCBs, the levels detected in the present study were almost 3 orders of magnitude greater than the highest ones in indoor dust from USA (34). The PBDEs concentrations were 2-fold higher than the highest concentrations in indoor dust from Washington, DC, USA (35). It is obvious that the indoor dust in the workshops from LQ area contains much higher levels of PCDD/Fs, PBDEs, PCBs, and total TEQ. The dust should be regarded as a hazardous waste and disposed of appropriately.

Data on PCDD/Fs, PBDEs, and PCBs in hair are very limited. Comparing the available data in human hair, the concentrations of PCDD/Fs in hair in this study were 40 times higher than those collected from residents living close to contaminated Ya-Er Lake (36), about 20 times higher than the upper limit of the concentration in healthy subjects in Japan (37), and even slightly higher than those of lying-in women in the study area (2). As for PCBs, the levels were

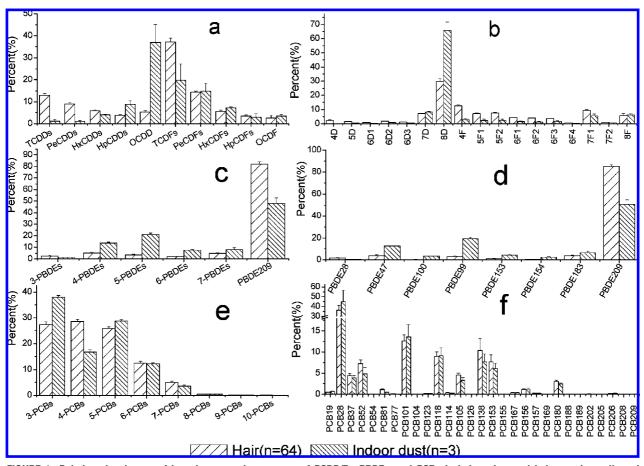


FIGURE 1. Relative abundances of homologues and congeners of PCDD/Fs, PBDEs, and PCBs in indoor dust and hair samples collected from the LQ area. (The data were normalized to the summation mass of homologues and congeners, respectively) In the figure, panels a—f refer to PCDD/Fs homologues, PCDD/Fs congeners, PBDEs homologues, PBDEs congeners, PCBs homologues, and PCBs congeners, respectively. In the *x*-axis of panel b, D refers to PCDDs and F refers to PCDFs. The details were shown as below: 4D: 2,3,7,8-TCDD; 5D: 1,2,3,7,8-PeCDD; 6D1: 1,2,3,4,7,8-HxCDD; 6D2: 1,2,3,6,7,8-HxCDD; 6D3: 1,2,3,7,8,9-HxCDD; 7D: 1,2,3,4,6,7,8-HpCDD; 8D: OCDD; 4F: 2,3,7,8-TCDF; 5F1: 1,2,3,7,8-PeCDF; 5F2: 2,3,4,7,8-PeCDF; 6F1: 1,2,3,4,7,8-HxCDF; 6F2: 1,2,3,6,7,8-HxCDF; 6F3: 2,3,4,6,7,8-HxCDF; 6F4: 1,2,3,7,8,9-HxCDF; 7F1: 1,2,3,4,6,7,8-HpCDF; 7F2: 1,2,3,4,7,8,9-HpCDF; 8F: OCDF.

nearly 2 orders of magnitude greater than those of hair samples in Japan and Belgium (37, 38). The mean PCB-TEQ concentration in hair from the LQ area was nearly 40 times higher than those previously reported in hair of the workers occupationally exposed to municipal solid-waste (MSW) incineration (39). The results showed that the hair in the LQ area was highly polluted with PCDD/Fs, PBDEs, and PCBs. The highest values of these compounds in hair were found by the present study. Because hair can reflect the body's integral exposure to POPs from endogenous and exogenous sources (2, 39), the results showed that the E-waste dismantling workers in the LQ area heavily accumulated PCDD/Fs, PBDEs, and PCBs in their bodies.

Homologue and Congener Profiles of PCDD/Fs, PBDEs, and PCBs and Their Sources. Relative abundances of homologues and congeners of PCDD/Fs, PBDEs, and PCBs in dust and hair were calculated and shown in Figure 1. Generally, the concentrations of PCDF homologues in all samples were higher than those of PCDD homologues with the same degree of chlorination, except OCDD and OCDF. OCDD contributed to nearly 70% of total PCDD/Fs in dust. 1,2,3,4,6,7,8-HpCDD, OCDF, and 1,2,3,4,6,7,8-HpCDF were other main congeners. Otherwise, the ratio of OCDD to PCDD/Fs decreased to 30% in hair. Other dominating congeners included 2,3,7,8-TCDF, 2,3,4,7,8-PeCDF, and 1,2,3,7,8-PeCDF. According to TEQs in all samples, three congeners—2,3,4,7,8-PeCDF, 1,2,3,7,8-PeCDD, and 2,3,7,8-TCDD—were about 70% of the total WHO-TEQs. Among them, 2,3,4,7,8-PeCDF was predominant and contributed

nearly 40%. Many studies have reported that the PCDD/Fs congener patterns of thermal processes by combustion processes are similar (40, 41). Thus, it can be concluded that PCDD/Fs in all samples from the LQ area in this work were mainly from open burning of E-waste.

Of PBDE homologues, deca-BDE accounted for 48.5-81.9% and was the most abundant homologue in all samples (Figure 1). The ratios of deca-BDE to total PBDEs in hair were also found to be statistically higher than those in dust. Penta- and tetra-BDEs were found to be another two major homologues, but their contributions to total PBDEs were much less than that of deca-BDE, especially in hair. The observation may be a consequence of wide commercial use of deca-BDE as the most common PBDE flame retardant (42). As for congeners, an order of abundance was detected in all samples as follows: PBDE209 > 47 > 99 > 183 > 153. The similar congener profiles suggested a similar source of PBDEs in the samples (Figure 1). The congener composition of PBDE47, 99, 100, 153, and 154 revealed that the PBDE profiles in hair and dust were similar to that of Bromkal 70–5DE (Figure S2, Supporting Information) (43). Only trace quantities of PBDE183 were detected in penta-BDE commercial products, but it has not been reported in deca-BDE commercial products. Consequently, PBDE183 could be a marker for the commercial octa-BDE products (43). In this study, PBDE183 was found to be a major constituent of PBDEs in all samples (Figure 1). Then, octa-BDE was supposed to be another commercial mixture of PBDEs used in electronic equipments dismantled in the LQ area besides penta-BDE

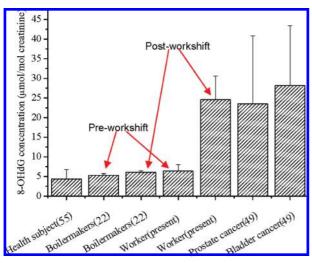


FIGURE 2. Comparison of the concentrations of urinary 8-OHdG from different studies (μ mol/mol creatinine) (1): Zhang 2006 (55). (2): Kim et al. 2004 (22). (3): Wu et al. 2004 (49).

and deca-BDE commercial products. PBDEs can be released from plastics containing brominated flame retardants when heating (e.g., melting of polymers) (44). Open burning of E-waste is believed to be one of the most important sources of PBDEs in the LQ area.

For PCBs, low chlorinated PCBs (3–5 Cl) accounted for $81.70\pm1.01\%$ (51.89-90.75%) of total PCBs in all samples. Indicator PCBs including PCB28, 101, 118, 138, 153, 52, and 180 were determined as the major congeners (Figure 1). As for TEQs, PCB126 was the main constituent among the 12 dioxin-like PCBs. PCB118, 156, and 105 were other major contributors. In the past decades, approximately 10 000 tons of trichlorobiphenyl and pentachlorobiphenyl were applied in transformer capacitors in China (45). The homologue and congener profiles of PCBs found in this study reflected the historical use of PCBs because many of the transformer capacitors were dismantled in the LQ area.

As for homologue and congener compositions of PCDD/Fs, PBDEs, and PCBs, similar profiles were found between the hair and the dust. The results suggested that PCDD/Fs, PBDEs, and PCBs in both hair and dust should originate from the same source, which probably was open burning of E-waste.

Urinary 8-OHdG. 8-OHdG levels were detected and ranged from 0.64 to 95.74 and from 0.37 to 343.17 μ mol/mol creatinine in the pre- and postworkshift urines, respectively. The levels of urinary 8-OHdG and creatinine in dismantling workers were shown in Supporting Information Table S7. The concentrations were $6.40 \pm 1.64 \, \mu$ mol/mol creatinine in the preworkshift urines. However, a significant increase of 8-OHdG levels (p < 0.05), reaching $24.55 \pm 5.96 \, \mu$ mol/mol creatinine, was detected in the postworkshift urines. Interestingly, there was a significant linear correlation observed between 8-OHdG concentrations of the preworkshift urines and those of the postworkshift urines from the workers (Figure S3, Supporting Information: y = 3.142x + 4.429, R = 0.8622, p < 0.0001).

It is well-known that 8-OHdG is a biomarker for oxidative damage to DNA, which has been proposed to assess individual cancer risk originated from oxidative stress (21–23, 46–50). Sharp increases of 8-OHdG levels in the postworkshift urines compared with those in the preworkshift urines indicated the oxidative stress on workers during their work time. Kim et al. (22) have reported an increase of 0.78 μ mol/mol creatinine in urine from boilermakers during their work time (Figure 2). Surprisingly, the increase of 8-OHdG was detected to be 18 μ mol/mol creatinine in the present study. PCDD/Fs, PBDEs, and PCBs have been reported to

possess the ability to induce oxygen radicals that may lead to oxidative damage to DNA (15–19). Moreover, Nishimura et al. (15) have reported significant increases of 8-OHdG levels in rats exposed to 2,3,7,8-TCDD. Therefore, PCDD/Fs, PBDEs, and PCBs should result in the increase of 8-OHdG levels found in the present study. Although, besides PCDD/Fs, PBDEs, and PCBs, some of other contaminants have also been found in E-waste dismantling areas, such as heavy metals and volatile organic compounds (4, 51, 52), which can induce 8-OHdG slightly (23, 24, 48, 53, 54). But, PCDD/Fs, PBDEs, and PCBs were found at much higher concentrations in both hair and dust in this study. Therefore, PCDD/Fs, PBDEs, and PCBs are believed to be one of the most important contributors to the elevated 8-OHdG levels in the present study.

The urinary 8-OHdG levels in the preworkshift urines were found to be higher than those in healthy Chinese (4.39 \pm 2.40 μ mol/mol creatinine) (55). Furthermore, the levels of 8-OHdG in the postworkshift urines (24.55 \pm 5.97 μ mol/mol creatinine) were much higher than those in other occupational exposure workers (22, 24, 47, 48, 50, 56–58), even close to the concentrations in cancer patients such as prostate cancer and bladder cancer (Figure 2) (49). Although no tumor or cancer has been found in the workers yet, it is undoubted that there is a high cancer risk originated from the oxidative stress indicated by the elevated urinary 8-OHdG levels in the E-waste dismantling workers exposed to high concentrations of PCDD/Fs, PBDEs, and PCBs.

Acknowledgments

We appreciate the local CDC employee for their help in the sampling. This research is supported by National Natural Scientific Foundation of China (No. 40590390), National High-Tech Research Program of China (2006AA06Z403), and National Natural Scientific Foundation of China (No. 20607030).

Supporting Information Available

Measurement of Urinary 8-OHdG, Tables S1-S7, and Figures S1-S3. This material is available free of charge via the Internet at http://pubs.acs.org.

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