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ORIGINAL PAPER

Polychlorinated biphenyls and their hydroxylated metabolites in the serum of e-waste dismantling workers from eastern China

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Abstract A number of studies have reported on the exposure of e-waste dismantling workers to significantly high concentrations of halogenated organic pollutants such as polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers. Such exposure can have adverse health effects. However, little information on the metabolites of these contaminants exists. In this study, we investigated PCBs levels and their hydroxylated metabolites (OH-PCB) in the serum of e-waste workers in Taizhou in eastern China. Our results indicate elevated PCB and OH-PCB levels in the serum of the workers, with medians of 443.7 and 133.9 ng/g lw, respectively. Tri- to hexachlorinated PCB congeners were the dominant homologue groups in all of the samples. 4-OH-CB107 was the predominant homologue among the hydroxylated metabolites, accounting for 88.9% of the total OH-PCB concentrations. While dietary sources (e.g., fish) appear to be an important route for PCB accumulation in non-occupational exposure groups, exposure via ingestion of house dust and inhalation of pollutants derived from the recycling of PCB-containing e-wastes may primarily contribute to the high body burden observed in the occupational groups. Since we found concentrations of metabolites higher than those of their parent compounds, further studies need to pay more attention to their bioaccumulation and toxicity.

Keywords Polychlorinated biphenyls · Hydroxylated metabolites · Serum · Biotransformation

Introduction

Polychlorinated biphenyls (PCBs) are used extensively as insulating oils in electrical components such as transformers and capacitors. Because of their environmental toxicity, persistence, and accumulation in animal and humans, PCBs have been classified as persistent organic pollutants (Ross 2004); their production has been banned by the US Congress in 1979 and by the Stockholm Convention on Persistent Organic Pollutants in 2001. However, PCBs can persist for years as they are very resistant to chemical and biological degradation.

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In China, production of PCBs from 1965 to 1974 reached approximately 10,000 tons, which consisted of 9000 tons of trichlorobiphenyl and 1000 tons of pentachlorobiphenyl (Ren et al. 2007). Taizhou, in eastern China, is one of the major areas for the dismantling of PCB-containing e-wastes (Ni et al. 2010). High concentrations of PCBs in air (Han et al. 2010), soil (Liu and Liu 2009), as well as sediments and foodstuffs (Zhao et al. 2006; Xing et al. 2010) from this area have been reported. High body burden of PCBs in local residents near e-waste sites has also been reported in recent studies (Zhao et al. 2007a; Wen et al. 2008; Zhao et al. 2008, 2010). PCBs can be biotransformed by cytochrome P450 enzymes. Major metabolic pathways lead to the formation of hydroxylated PCB metabolites (OH-PCBs) and methylsulfone PCB metabolites. OH-PCBs retained in plasma or serum are hydroxylated preferentially at the *para*- or *meta*-position into congeners having chlorine atoms adjacent to the carbon atoms (Letcher et al. 2000). OH-PCBs have some structural resemblance to thyroxine (T_4) and have stronger affinity to the thyroid hormone transporter protein than to its natural ligand, thus, they can impair thyroid hormone functions (Malmberg et al. 2004). Previous studies have shown that OH-PCB concentrations in blood may constitute 10–30% of the total PCB levels in humans (Fängström et al. 2002; Park et al. 2007). Exposure to these metabolites can have multiple adverse health effects such as neurodevelopment effects (Park et al. 2009a). They are also associated with adverse effects on motor development in infants (Berghuis et al. 2013). Recent evidence indicates that some OH-PCBs are more toxic than their parent compounds (Dreiem et al. 2009). Nevertheless, no data are available concerning levels of OH-PCB exposure of e-waste recycling workers in China, despite reports of high body burden of PCBs (Zhao et al. 2007b, 2008, 2010; Lv et al. 2015).

PCB patterns may vary among individuals, depending on proximity to specific sources. For example, study cohorts from the Faroe islands, the Baltic Sea, and the Great Lakes, all of whom have high consumption of fatty fish, have shown preferred accumulation of higher chlorinated PCBs (hexa- to octa-PCBs; Sjödin et al. 2000; Fängström et al. 2002; Fängström et al. 2005). Construction workers engaged in the removal of PCB-containing materials have been reported to have relatively high blood concentrations of the lighter chlorinated congeners (Herrick et al. 2007). Congener patterns of OH-PCBs identified across a population have considerable variability due to the selective retention or the formation of metabolites (Malmberg et al. 2004). 2,2′,3,4′,5,5′,6-Heptachlorobiphenyl-4-ol (4-OH-CB187) has been reported as the major OH-PCB in human blood in most cases (Soechitram et al. 2004; Park et al. 2009a; Grimm et al. 2015; Koh et al. 2016). Several studies, however, have observed the dominant contribution of the congener 2,3,3′,4′,5-pentachlorobiphenyl-4-ol (4-OH-CB107; Sandau et al. 2000; Sjödin et al. 2000). Studies have indicated that e-waste dismantling workers in Taizhou are constantly exposed to remarkably high levels of halogenated organic contaminants (e.g., dioxins, PCBs, and polybrominated diphenyl ethers) through inhalation and skin contact (Zhao et al. 2006, 2010; Wen et al. 2008; Ni et al. 2010). Nevertheless, little is known about the metabolism of PCBs in humans. More research is thus needed in order to determine the fate of OH-PCBs in e-waste workers.

Overall, very little information is available concerning PCB exposure of populations related to e-waste processing in China, and data on the occurrence and fate of OH-PCBs are not yet available. As part of our ongoing research into the exposure of e-waste dismantling workers to halogenated organic contaminants, we aimed to investigate the distribution of selected PCBs and OH-PCBs in the serum of e-waste workers.

Materials and methods

Sample collection

Twenty-four blood samples were collected from male workers who were involved at least 6-month regular experience in the e-waste dismantling activities from Luqiao town of Taizhou city, in September 2008. Before collection, all volunteers were informed about the objectives of the study and agreed to participate. The informed consent as well as one questionnaire sheet containing the possible exposure history and health status was provided by each participant. With the help of healthcare professionals, at least 10 mL of blood was collected from each donor via venipuncture. After collection, the samples were centrifuged, frozen immediately in a precleaned brown glass bottle with a

Teflon-lined cap, and then sent to our laboratory for storage at −80 °C until analysis.

Chemicals

Standards for PCBs (C-QME-01, which contains 41 PCB congeners with IUPAC Nos. 17, 18, 28, 31, 33, 44, 49, 52, 70, 74, 82, 87, 95, 99, 101, 105, 110, 118, 128, 132, 138, 149, 151, 153, 156, 158, 169, 170, 171, 177, 180, 183, 187, 191, 194, 195, 199/201, 205, 206, 208, 209) were purchased from AccuStandard (New Haven, CT, USA). Seven OH-PCB standards were obtained from Wellington Laboratory (Guelph, ON, Canada): 2,3,3′,4′,5-pentachlorobiphenyl-4-ol (4-OH-CB107), 2,2′,3,3′,4′,5-hexachlorobiphenyl-4-ol (4′-OH-CB130), 2,2′,3′,4,4′,5-hexachlorobiphenyl-3-ol (3′-OH-CB138), 2,2′,3,4′,5,5′-hexachlorobiphenyl-4-ol (4-OH-CB146), 2,2′,3,3′,4′,5,5′-heptachlorobiphenyl-4-ol (4′-OH-CB172), 2,2′,3′,4,4′,5,5′-heptachlorobiphenyl-3-ol (3′-OH-CB180) and 2,2′,3,4′,5,5′,6-heptachlorobiphenyl-4-ol (4-OH-CB187). ^{13}C-labeled 4-hydroxy-2,2′,3,4′,5,5′,6-heptachlorobiphenyl ($^{13}C_{12}$-4-OH-CB 187, isotopic purity 99% or greater, 50 μg/mL in toluene) used as surrogate standard was obtained from Wellington Laboratories Inc. ^{13}C-BDE-209, ^{13}C-PCB-141, PCB-209, and ^{13}C-PCB-208 were obtained from Cambridge Isotope Laboratories (Andover, MA, USA) and were used as surrogate and internal standards, respectively.

Sample analysis

The extraction and cleanup procedure applied in this study were identical to the method described by Hovander and coworkers (Hovander et al. 2000). Before extraction, about 3–5 mL serum was thawed and homogenized in a Teflon tube with surrogate standards (400 pg of PCB-209, 400 pg of ^{13}C-PCB-141, 1 ng of ^{13}C-4-OH-CB187, and 1 ng of ^{13}C-BDE-209). Hydrochloric acid (1 mL, 6 M) and 2-propanol (6 mL) were added to denature the proteins. The samples were then extracted with 6 mL of a hexane/methyl tert-butyl ether (MTBE) mixture (1:1 by volume). This procedure was repeated twice more, and the organic phases were combined and later dried under high-purity nitrogen. The lipids were then determined gravimetrically. The extracted lipids were redissolved in 4 mL of hexane, and the neutral and phenolic compounds were separated using a basic aqueous solution (0.5 M KOH in 50% ethanol). The aqueous solution was extracted with hexane three times to separate the neutral compounds, and then the remaining protonated phenolic analytes were acidified with hydrochloric acid (2 mL, 6 M). The phenolic compounds in aqueous solution were extracted three times with a hexane/MTBE mixture (9:1 by volume).

The neutral components (containing PCBs and PBDEs) were treated twice with 5 mL of concentrated sulfuric acid to destroy the lipids and then passed through columns packed with silica gel impregnated with sulfuric acid (1 g; silica/sulfuric acid 2:1 by weight) using 8 mL of hexane and 10 mL of hexane/dichloromethane solution (1:1 by volume) as the eluents. The phenolic fractions (containing OH-PCBs) were derivatized with diazomethane to methyl esters, and the extracts were purified by acidic-silica-gel column chromatography. The eluents from two fractions were concentrated to 20 μL under a gentle stream of nitrogen gas, and 400 pg of ^{13}C-PCB-208 was added as injection standard for gas chromatography–mass spectrometry (GC/MS) analysis.

The instrumental analysis of PCBs was performed in gas chromatograph mass spectrometer (Agilent 7890A/5975C) with electron ionization/selective ion monitoring (EI/SIM) mode. The instrumental setup is as follows: temperatures for the GC injection port, ion source, and interface were set at 280, 230, and 300 °C, respectively. Helium was used as a carrier gas and was introduced at a flow rate of 1.0 mL/min. Manual injection (1 μL) was done in pulsed splitless mode at a pulse pressure of 50 psi. Gas chromatographic separations were achieved using two different capillary columns (DB-XLB and DB-5MS, 30 m × 0.25 mm × 0.25 μm). The GC oven temperature program was set as follows: holding at 80 °C for 2 min; increasing to 160 °C at 15 °C/min, to 280 °C at 3 °C/min, and then to 300 °C at 10 °C/min; and holding at 300 °C for 10 min. The following ions were monitored for quantitative/qualitative analysis: *m/z* 256/258 and 186 for tri-CBs, *m/z* 292/290 and 220 for tetra-CBs, *m/z* 326/324 and 254 for penta-CBs, *m/z* 360/362 and 290 for hexa-CBs, *m/z* 394/396 and 324 for hepta-CBs, *m/z* 430/432 and 360 for octa-CBs, *m/z* 464/462 and 392 for nona-CBs, *m/z* 498/500 and 428 for PCB-209, *m/z* 372 and 374 for ^{13}C-PCB-141, and *m/z* 474/476 for ^{13}C-PCB-208 (internal standard).

For the analysis of methylated derivatives of OH-PCBs, an Agilent 7890A/5975C was operated in

electron capture negative ionization mode. Methane gas was used as a chemical ionization reagent, and helium was used as the carrier gas (1.0 mL/min flow rate). The GC oven temperature program was set as follows: holding at 80 °C for 1 min, increasing to 180 °C at 20 °C/min and holding for 5 min, increasing to 280 °C at 5 °C/min, and increasing to 300 °C at 20 °C/min and holding for 20 min. The following ions were monitored for quantitative and qualitative analysis: *m/z* 341/343 and 356 for 4-MeO-CB-107, *m/z* 375/377 and 390 for 4-MeO-CB-130 and 4-MeO-CB-146, *m/z* 354/356 and 390 for 3′-MeO-CB138, *m/z* 388/390 and 424 for 4′-MeO-CB-172, *m/z* 409/411 and 424 for 3′-MeO-CB-180 and 4-MeO-CB-187, *m/z* 475.7 and 473.7 for the internal standard (^{13}C-PCB-208), and *m/z* 421 and 423 for $^{13}C_{12}$-4-MeO-CB187.

Quality assurance

Multilevel calibration curves that include the total concentration range for detection in the serum samples were constructed for quantification, good correlation ($R > 0.999$) was achieved. Identification of the target analytes was based on the GC retention time and ion-abundance ratio of two exact *m/z* ratios. Procedural blanks of 5 mL fetal bovine serum were analyzed concurrently to check for contamination. None of the target PCBs was detected. A quality control standard was analyzed per day to confirm the measurements, as well as to check the instrumental sensitivity and stability. The percent recoveries of PCBs in the spiked fetal bovine serum varied from 75 to 103%, and the relative recoveries for OH-PCBs were 68–84%. The limits of quantification (LOQs) was defined as ten times the S/N. They ranged from 0.18 to 0.39 pg per injection for tri- to hepta-CBs and ranged from 0.38 to 0.52 pg per injection for MeO-PCBs, respectively.

Statistical analysis

Mean values with standard errors are presented in the tables. Residual values below the detection limits for the samples were treated as zero in order to calculate the total PCBs. The distribution of data was tested using the Kolmogorov–Smirnov test. Spearman rank correlations were also used to examine the strength of associations between parameters. *P* values lower than 0.01 were considered statistically significant.

Results and discussion

PCBs in the serum of e-waste workers

PCBs were found in all serum samples from the workers (results are listed in Table 1), and 24 PCB congeners with at least 50% detection rate are listed in Table S1. The median concentration of PCBs in serum is 443.7 ng/g lipid weight (range of 24.7–1943.3 ng/g lw). The OH-PCB concentrations varied from 25.0 to 947.2 ng/g lw and had a median value of 133.9 ng/g lw (0.794 ng/mL wet weight). The PCB level in our study is consistent with previously reported levels in Luqiao residents (Zhao et al. 2010). It was significantly higher than the level reported from e-waste workers from Wenling (an e-waste recycling area near Luqiao) (Ashauer et al. 2012; Lv et al. 2015) and from Guiyu (median 52 ng/g lw) in southern China (Bi et al. 2007). Zhang et al. reported a substantially higher body burden of PCBs in e-waste workers from eastern China as compared with that in workers from a reference area (Zhang et al. 2010). PCB concentrations in the occupationally exposed group in our research were substantially higher than those reported for general populations in China, such as pregnant women in Shanghai (Cao et al. 2011) and in Hong Kong (Tsang et al. 2011). Children's blood (Shen et al. 2010) and cord blood (Zhao et al. 2007b) from infants of residents in an e-waste site in Luqiao were found to have significantly higher concentrations of PCBs compared to control areas. As mentioned, China has a shorter history of PCB usage and production as compared with those in Western countries. Results from our study thus confirm that the unregulated e-waste recycling activities in Taizhou have resulted in elevated body burdens in the dismantling workers, as reported previously by Zhao et al. (2010).

When compared with those of European countries and the USA, median concentrations of PCBs in this study are comparable to those in general populations in the Netherlands (Soechitram et al. 2004), Madrid (Gómara et al. 2011), and California (Park et al. 2009b). They are lower than those in general populations in Faroe Islands (Fängström et al. 2002), Sweden, and Latvia (Sjödin et al. 2000), where consumption of contaminated fatty fish is believed to be high. In addition, the median PCB levels in our study fall at the lower end of the reported concentration ranges for heavily exposed groups, such as people

Table 1 Concentrations (ng/g lipid weight and ng/mL wet weight) of PCBs and its related metabolites in sera from e-waste dismantling workers ($n = 24$)

Item	Concentration (ng/g lipid weight)				Concentration (ng/mL wet weight)			
	Mean ± SD[a]	Min	Median	Max	Mean ± SD[a]	Min	Median	Max
PCB-28	81.0 ± 38.3	15.0	74.0	170.3	0.414 ± 0.200	0.066	0.393	0.750
PCB-52	21.0 ± 14.5	<LOQ	19.4	53.7	0.108 ± 0.080	<LOQ	0.098	0.294
PCB-101	13.7 ± 9.0	<LOQ	12.4	32.5	0.071 ± 0.049	<LOQ	0.066	0.181
PCB-118	70.4 ± 59.6	<LOQ	44.1	245.8	0.357 ± 0.308	<LOQ	0.274	1.373
PCB-138	59.2 ± 65.4	<LOQ	44.7	289.8	0.299 ± 0.342	<LOQ	0.226	1.619
PCB-153[b]	63.4 ± 74.2	<LOQ	49.1	339.3	0.322 ± 0.392	<LOQ	0.245	1.895
PCB-180	19.2 ± 23.8	<LOQ	13.4	103.8	0.098 ± 0.126	<LOQ	0.073	0.580
tri-PCBs	91.2 ± 44.4	15.0	97.6	213.8	0.467 ± 0.230	0.067	0.460	0.919
tetra-PCBs	110.6 ± 66.4	9.7	104.1	289.9	0.561 ± 0.347	0.042	0.559	1.620
penta-PCBs	170.9 ± 132.5	<LOQ	122.0	553.1	0.872 ± 0.688	<LOQ	0.720	3.088
hexa-PCBs	144.6 ± 163.3	<LOQ	116.5	731.5	0.736 ± 0.857	<LOQ	0.583	4.085
hepta-PCBs	40.2 ± 51.9	<LOQ	29.2	216.0	0.204 ± 0.270	<LOQ	0.160	1.206
$\sum_{id}$PCBs[c]	327.8 ± 257.4	15.0	259.0	1165.8	1.669 ± 1.341	0.070	1.452	6.512
$\sum_{all}$PCBs[c]	559.1 ± 436.4	24.7	443.7	1943.3	2.845 ± 2.259	0.108	2.559	10.787
4-OH-CB107	212.7 ± 221.0	17.5	117.5	835.0	1.028 ± 1.016	0.077	0.663	3.591
4-OH-CB146	12.7 ± 12.6	1.1	7.4	56.0	0.061 ± 0.057	0.006	0.038	0.241
3′-OH-CB138	8.7 ± 5.7	3.3	6.7	22.1	0.042 ± 0.025	0.018	0.032	0.105
4′-OH-CB172	1.1 ± 2.2	<LOQ	0.4	10.6	0.005 ± 0.010	<LOQ	0.002	0.046
4-OH-CB187	4.5 ± 5.7	<LOQ	2.8	23.5	0.022 ± 0.027	<LOQ	0.014	0.101
3′-OH-CB180	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
4-OH-CB130	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
$\sum_{all}$OH-PCBs[c]	239.3 ± 244.0	25.0	133.9	947.2	1.158 ± 1.119	0.110	0.794	4.074

[a] Values below the LOQ were set to 0 in calculation

[b] Concentrations reported for PCB-153 include co-eluting of PCB-132

[c] $\sum_{id}$PCBs = sum of indicator PCBs (PCB-28, 52, 101, 118, 138, 153, and 180). $\sum_{all}$PCBs = sum of all target PCBs; $\sum_{all}$OH-PCBs = sum of all target OH-PCBs; mean = arithmetic mean; SD = standard deviation; < LOQ means not detected

from polluted areas in eastern Slovakia (Park et al. 2007) and in northwestern Italy (Turrio-Baldassarri et al. 2008). Median PCB concentrations in our study are higher than those of the general population in Japan (Kawashiro et al. 2008; Hisada et al. 2013).

Of the PCB homologues in the serum samples, tri- to hexachlorinated congeners PCB-28, -118, -74, -153/-132, and -138 were the predominant compounds; they were detected in more than 95% of the serum samples. The three most predominant PCB congeners (PCB-28, -118, and -74) accounted for 43% of the total PCB concentration. Seven of the most commonly reported indicator PCBs (i.e., PCB-28, -52, -101, -118, -138, -153, and -180) contributed a large proportion (58%) of the total concentrations. When the congener profiles were compared with those in other populations around the world, the serum compositions of the more volatile, lighter PCBs (tri- and tetrachloro-PCBs) in the workers were found to be substantially higher. This is consistent with previous investigations into PCB exposure during e-waste dismantling in the same area (Shen et al. 2010). Relatively high proportions of the lower chlorinated isomers were detected in human milk samples from females living around an e-waste recycling site in Vietnam (Tue et al. 2010). This might have been due to constant exposure via inhalation of contaminated air or dermal contact with contaminated transformer metal surfaces. Previous studies have similarly shown that the major PCB homologues in Chinese transformer oil are tri- and tetra-PCBs (Jiang

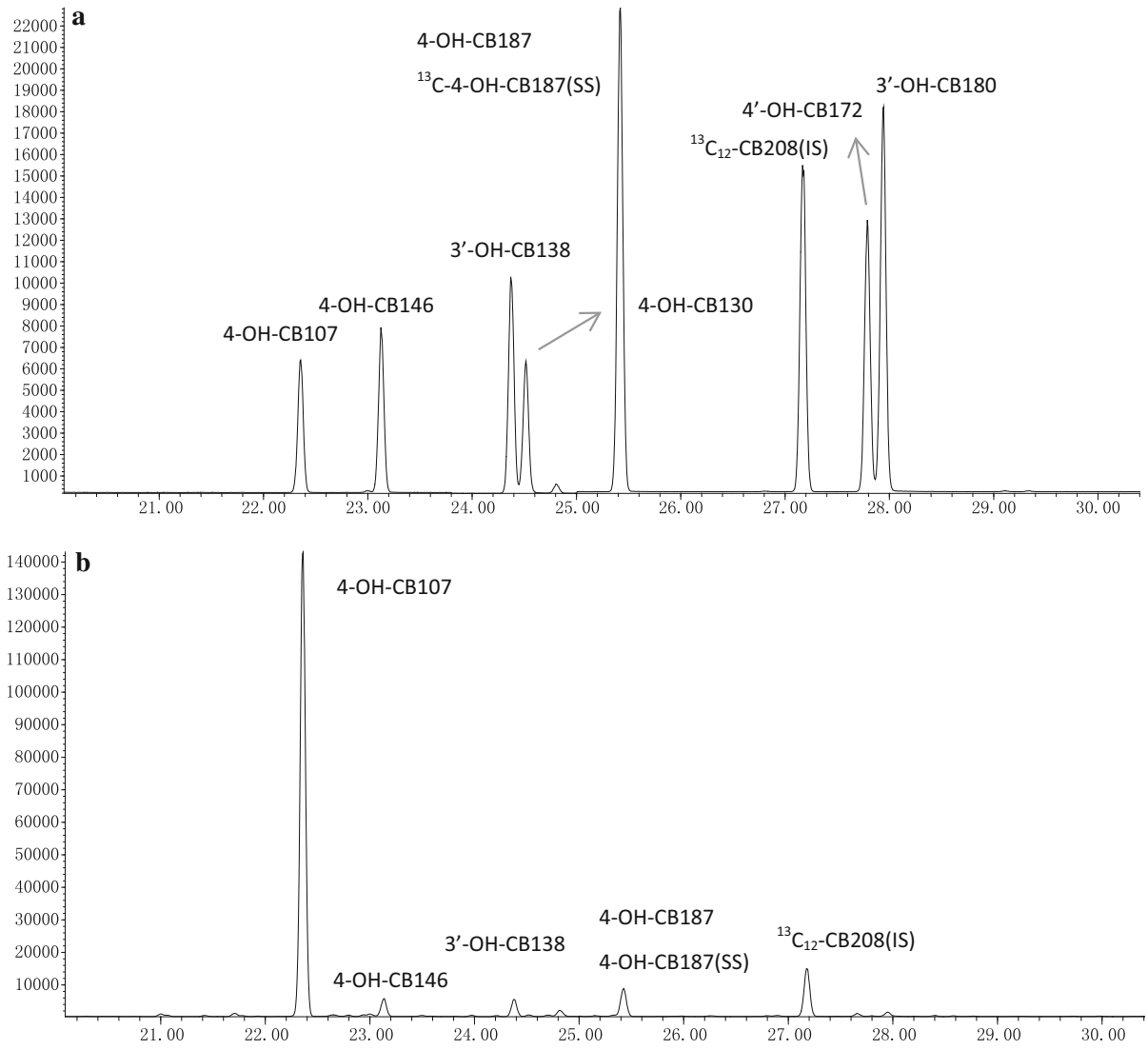
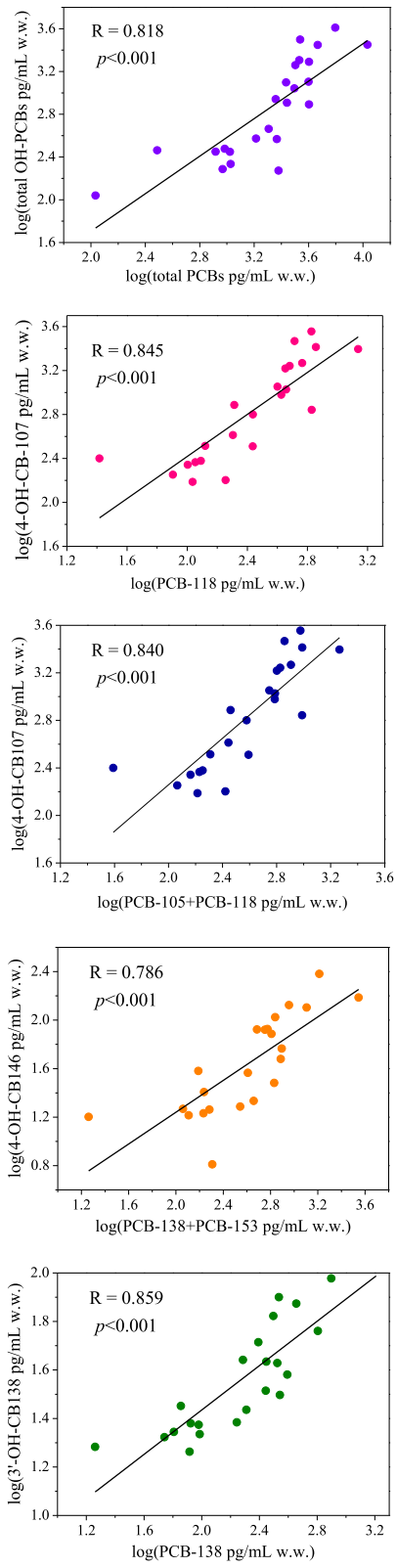


Fig. 1 Typical GC-ECNI-MS SIM chromatogram of **a** 50 ppb OH-PCBs standards and **b** OH-PCBs detected in serum from e-waste dismantling workers

et al. 2007). Nevertheless, 90% of the average human intake of PCBs originates from contaminated foods such as fish, meat, and seafood (Guo et al. 2010). Heavier PCBs have a strong tendency to bind to lipid components and to accumulate in organisms as a consequence of slow metabolism and high persistence. The general population may thus be more likely exposed to the heavier PCBs. Much higher levels of less-chlorinated PCBs in occupationally exposed individuals such as construction workers (Herrick et al. 2007) and teachers in PCB-contaminated buildings (Herrick et al. 2011), as compared with reference populations, have also been reported in several studies. Since we did not include reference participants, further investigations are required to establish the profiles of congeners used as biomarkers and thus to distinguish different exposure groups.

OH-PCBs in serum of e-waste workers

OH-PCBs were found in all serum samples from the workers (results are listed in Table 1). A typical total ion chromatogram of OH-PCBs in a serum sample is shown in Fig. 1. Table 1 and Fig. 1 show that among



◀**Fig. 2** Pearson correlations between log-transformed total PCBs and total OH-PCBs concentrations in serum samples from e-waste dismantling workers

the OH-PCBs isomers identified, 4-OH-CB107 was the predominant congener in the serum samples, having a median concentration of 0.663 ng/mL wet weight and comprising 85.8% of the total OH-PCB. The other isomers 4-OH-CB146 and 3′-OH-CB138, which were detected in all samples that were analyzed, accounted for 12.3% of the total OH-PCBs. In contrast, 3′-OH-CB180 and 4-OH-CB130 were not detected in any of the serum samples. 4-OH-CB187 and 4′-OH-CB172 were, respectively, found to be present in about 70.8% and 58.3% of the samples. 4-OH-CB187 has typically been reported to be a prevalent metabolite congener in human blood (Park et al. 2007; Gómara et al. 2011). However, we observed a unique profile of OH-PCBs in the present study. 4-OH-CB107, which may have been derived from oxidative hydroxylation of PCB-118 and PCB-105, was almost exclusively detected as a major metabolite in the serum of the workers. 4-OH-CB107 has been hypothesized to have a half-life shorter than that of 4-OH-CB187 (3.8 days vs. 15 days) in rats (Malmberg et al. 2004). The high 4-OH-CB107 concentrations in the e-waste workers may have resulted from the preferential metabolism of penta-CB precursors via enzymatic transformation, since we found relatively high concentrations of PCB-118 and PCB-105 in the workers. A similar result has been reported for e-waste workers from India (Eguchi et al. 2012). 4-OH-CB107 has been observed to be the predominant OH-PCB in populations from Inuit (Sandau et al. 2000), Latvia (Sjödin et al. 2000), Belgium (Dirtu et al. 2010), as well as in children from Faroe Islands (Fängström et al. 2005). Notably, OH-PCB formation in humans is also influenced by other factors such as sex, induction of hepatic enzymes, and TTR-binding specificity of blood proteins (Letcher et al. 2000; Nomiyama et al. 2009). Further animal and/or human studies are thus needed to elucidate the possible mechanism of OH-PCB biotransformation.

Relationships between PCBs and OH-PCBs

The relationships between the log-transformed concentrations of the precursor PCBs and their

corresponding hydroxylated metabolites, as well as the total PCBs and OH-PCBs, were investigated. Our results indicate that the majority of metabolites are highly related to their possible precursor congeners (Fig. 2). For example, the total OH-PCBs were significantly correlated with the sum of PCBs ($R = 0.818$, $P < 0.001$), and 4-OH-CB107 was significantly correlated with both PCB-105 and PCB-118 ($R = 0.845$ and 0.825, $P < 0.001$). Other pairs of possible PCB precursors and OH-PCB metabolites also showed good correlations (4-OH-CB146 and PCB-138 and PCB-153, $R = 0.840$, $P < 0.001$; 3′-OH-CB138 and PCB-138, $R = 0.859$, $P < 0.001$). This observation is consistent with previous reports (Sjödin et al. 2000; Park et al. 2009b). The results may be explained by the rapid and extensive enzymatic metabolism of lower chlorinated PCBs in the workers. In addition, no significant relationship was observed between the total concentrations of PCBs and OH-PCBs and age or duration of work (in years).

The average OH-PCB/PCB concentration ratio was 0.42, ranging from 0.08 to 1.01. This ratio is higher than the highest ratio reported, which is for a Yusho population (mean value of 0.35) (Linderholm et al. 2007). A relatively high OH-PCB/PCB ratio has similarly been observed in Latvian men, the body burdens of whom are largely due to fish consumption (Sjödin et al. 2000). The ratio of 4-OH-CB107 to PCB-118 and PCB-105 ranged from 0.6 to 6.4, having an average value of 2.1. This ratio is unexpectedly high because concentrations of OH-PCBs are usually lower than those of their potential parent PCBs (Nomiyama et al. 2009). The cause of this high rate of biotransformation remains unknown, but it may be derived from exposure to high proportions of the precursor penta-PCBs. The metabolites might have large metabolite enrichment factors and reach concentrations higher than those of their parent compounds (Ashauer et al. 2012; Grimm et al. 2015). For example, 4-OH-CB107 may be selectively retained in plasma (bound to transthyretin) or converted to either its glucuronide conjugate or sulfate conjugate and then distributed to sensitive tissues (Meerts et al. 2002).

Conclusion

This study advances knowledge on the burden of halogenated compounds in occupational groups in eastern China. We found significant higher concentrations of PCBs and OH-PCBs in the workers, with the concentration of OH-PCBs being twice that of their parent PCBs; thus, PCBs may pose great health risks to e-waste workers.

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