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Polybrominated diphenyl ethers (PBDEs) in plasma from E-waste recyclers, outdoor and indoor workers in the Puget Sound, WA region

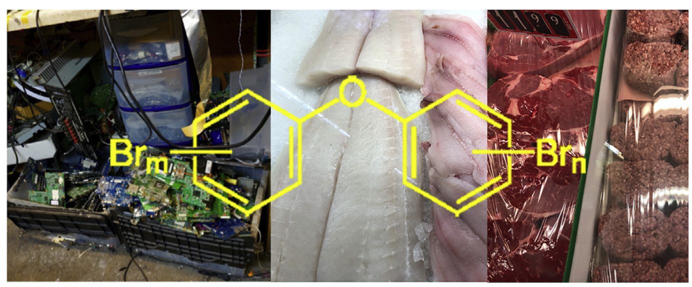
Li-Jung Kuo [a, *], Sara E. Cade [a], Valerie Cullinan [a], Irvin R. Schultz [a, b, **]

[a] *Pacific Northwest National Laboratory, Marine Sciences Laboratory, 1529 W Sequim Bay Rd, Sequim, WA 98382, USA*
[b] *NOAA - National Marine Fisheries Service, Lynker Tech & NW Fisheries Science Center, 2725 Montlake Boulevard East, Seattle, WA, 98112, USA*

HIGHLIGHTS

- High seafood eaters had higher plasma ∑PBDE levels than low seafood eaters.
- E-waste workers had plasma PBDE levels similar to non-E-waste indoor workers.
- Male volunteers had higher plasma ∑PBDEs and BDE-153 than female volunteers.
- Dust PBDEs was 32–39 times higher at E-waste sites than home or non-E-waste sites.

GRAPHICAL ABSTRACT



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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) were widely used as flame retardants in consumer products including electronic devices. Important routes of human exposure are contaminated food and contact with dust. In this study, we measured twelve PBDEs in household/workplace dust and blood plasma samples provided by 113 volunteers living in the Puget Sound region, WA and working at electronic waste (E-waste) recycling sites ($n = 29$) or non-specific indoor ($n = 57$) or outdoor occupations ($n = 27$). The volunteers in the outdoor group were also selected because of a history of high seafood consumption habits. Results indicated the sum PBDE levels varied between <2.5 and up to 310 ng g^{-1} lipid. E-waste recyclers were predominantly men, generally consumed low amounts of seafood, and had PBDE blood levels (geometric mean, GM = 26.56 ng g^{-1} lipid) that were similar to indoor workers (GM = 27.17 ng g^{-1} lipid). The sum PBDE levels were highest in the outdoor group (GM = 50.63 ng g^{-1} lipid). Dust samples from E-waste sites were highly enriched with BDE-209 and BDE-153 relative to non-E-waste businesses and homes. The concentrations of these BDE congeners in dust at E-waste sites were ~32–39 times higher than in dust from other sites. However, the detection rate of BDE-209 in plasma was low across all groups (13%) and no statistical comparisons were made. Our results suggest that E-waste recyclers in this study population did not have elevated PBDE levels in comparison to volunteers working in other types of occupations.

1. Introduction

Electronic waste (E-waste) is any type of electronic equipment that has reached the end of its useful life. Common items considered a part of E-waste include: computers, printers, monitors and

* Corresponding author.
** Corresponding author. NOAA - National Marine Fisheries Service, Lynker Tech & NW Fisheries Science Center, 2725 Montlake Boulevard East, Seattle, WA, 98112, USA.
E-mail addresses: Li-Jung.Kuo@pnnl.gov (L.-J. Kuo), irvin.schultz@noaa.gov (I.R. Schultz).

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televisions, electronic storage devices, cell phones, sound recorders/players and cameras. The generation of E-waste from both residential and commercial use is rapidly increasing in the U.S. with approximately 3.4 million tons produced in 2014 (USEPA, 2016a, b). Of this amount, approximately 1.4 million tons was recycled domestically, which represents more than a two-fold increase since 2009 (USEPA, 2014) and indicates the rapid expansion of the U.S. E-waste recycling industry. Domestic E-waste recycling is also being encouraged by state and local legislation with 28 states and the District of Columbia currently adopting consumer electronics recycling laws (www.electronicstakeback.com). For example, in 2006, the State of Washington created a mandatory E-waste program (E-cycleWashington). Since this law was enacted, the number of E-waste recyclers in the greater Seattle metropolitan area has increased more than four-fold (Lee et al., 2010; Leigh et al., 2012).

Most electronic equipment contains relatively high levels of flame retardants, which are considered necessary to meet fire safety standards. Polybrominated diphenyl ethers (PBDEs) have been the most widely used chemicals in flame retardants, although, they are now largely replaced by newer types of brominated flame retardants and organophosphate flame retardants. In recent years, there has been a gradual reduction in the commercial use of PBDEs in part due to recent bans on specific types of PBDE mixtures (Betts, 2008). Monitoring of PBDEs in blood and breast milk suggests U.S. exposures can be high relative to levels observed in other countries (Castorina et al., 2011; Fromme et al., 2016; Gill et al., 2004). A disturbing trend was the nearly 90-fold increase in human blood levels of PBDEs measured in the U.S. over the time period of 1973–2003 and 1994–2005 (Schecter et al., 2005; Turyk et al., 2010). More recent surveys in North America indicate exposure levels have leveled off or are declining, with a shift away from lower molecular weight PBDE congeners towards the more highly brominated forms (Guo et al., 2016; Law et al., 2014; Ma et al., 2013; Parry et al., 2018; Zota et al., 2013). This appears to be a consequence of the U.S. ban on penta-PBDEs in 2005 and the more recent ban on deca-PBDE in 2013 (USEPA, 2014). With regard to E-waste recycling, studies from outside the U.S. suggest the primary source for occupational exposure comes from dust generated during storage and dismantling, which may be ingested or inhaled (Jiang et al., 2014; Song and Li, 2014). However, many of these contaminants are environmentally persistent and bioaccumulate in fish and other food, so non-occupational exposure via food is also possible (Cade et al., 2018; Frederiksen et al., 2009). Occupational monitoring studies need to also consider the influence of diet in addition to dust as potential sources of PBDEs.

Past monitoring studies of E-waste recyclers have focused on workers in Europe and developing countries, with little attention to exposure of workers in the expanding U.S. E-waste recycling industry. This study focused on E-waste recyclers in the Puget Sound region of the U.S. where volunteers were recruited according to three occupational and/or dietary characteristics: E-waste recycling, non-specific office/indoor occupations and outdoor occupations. Volunteers in the outdoor group were questioned before the study to establish a history of high seafood consumption. The indoor group was included to provide reference for indoor dust exposure. Workplace and household dust samples from a subset of sites in the groups were collected and analyzed for PBDE content. The key objectives of this study were to investigate if E-waste recyclers have elevated plasma PBDE levels relative to non-E-waste workers and to gain insights into the importance of dust exposure and diet as sources of PBDEs.

2. Experimental methods

2.1. Human volunteers and collection of plasma samples

All interactions with volunteers were approved by the Institutional Review Board (IRB) at Pacific Northwest National Laboratory (PNNL) and informed consent was obtained from all volunteers prior to their participation. A total of 113 adult volunteers residing in the Puget Sound region of Washington State were recruited between December 2013 and August 2015. Volunteer recruitment primarily employed a targeted approach through advertisements in commercial and tribal fishing trade publications and organizations along with direct visits to regional E-waste recycling businesses and posted advertisements at the job site in break rooms or common areas. In addition, we posted local Craigslist advertisements for recruiting of indoor workers. The 113 male and female volunteers represented 29 E-waste workers employed at dismantling and material recovery facilities, 57 indoor workers, and 27 outdoor workers employed as commercial or subsistence fisherman and day laborers. The individuals in the outdoor worker group were interviewed before the study to establish a history of above average seafood consumption. An overview of experimental design of this study is provided in Fig. S1. A blood sample was obtained from each volunteer using glass BD vacutainer® tubes with EDTA as an anticoagulant. Plasma was obtained via centrifugation of whole blood for 15 min at 1,500x g. The plasma samples were initially stored on ice for approximately 2–3 h and then stored at −80 °C until analysis. To encourage participation, blood collection occurred at a location convenient for each volunteer and was typically done at home after work. All E-waste volunteers were actively employed at time of sampling. Prior to collection of a blood sample, a two-week dietary history was obtained along with voluntary reporting of sex, age, height, weight and race. The dietary history included information on the number of seafood, meat and dairy servings consumed per day. All volunteers received modest compensation for their time, which was approved by the PNNL IRB. A summary of demographic information and diet habits associated with these volunteers is shown in Table 1.

2.2. Dust collection

A total of 21 dust samples were collected, which included samples ($n = 8$) from the majority of E-waste sites with volunteer participation along with a random sampling of homes of volunteers in indoor and outdoor worker groups ($n = 7$). We also collected dust samples from computer repair businesses ($n = 6$) to assess similarity with E-waste sites. A previous study observed that PBDE levels in airborne particulates at a computer repair site were very low and comparable to dust from homes (Sjödin et al., 2001). However, no volunteers in the present study worked at these computer repair businesses. All dust samples were collected using a small portable vacuum cleaner (Dewalt DC515K) fitted with a cellulose extraction thimble. We used a standardized approach for the dust collection, similar to that used by other investigators (Allen et al., 2008; Watkins et al., 2012). Cross-contamination was prevented by using a new thimble for each sample and thoroughly cleaning the vacuum using isopropanol swabs between sampling. For each sample, we vacuumed a 2 m × 2 m area for approximately 5 min capturing dust from the entire surface area of the accessible floor space. After sample collection, thimbles were removed and wrapped in aluminum foil (previously baked overnight at 450 °C), sealed in polypropylene bags and transported at room temperature

Table 1
Characteristics of volunteers.

		E-waste recyclers	Outdoor worker	Indoor worker	Male	Female
n		29	27	57	61	52
Age		31 ± 9	43 ± 15	33 ± 11	35 ± 13	35 ± 13
Race/Ethnicity	White	20	17	38		
	Other	9	10	19		
BMI		27 ± 6	27 ± 6	26 ± 6	27 ± 5	26 ± 7
Gender	Male	26	17	18		
	Female	3	10	39		
Seafood serving[a]	<1/week	8	1	15	13	11
	1-10/week	20	9	26	29	26
	>10	1	17	16	19	15
Meat serving[a]	<1/week	1	5	18	7	17
(all non-seafood)	1-10/week	5	7	10	12	10
	>10/week	23	15	29	42	25
Dairy serving[a]	<1/week	2	4	5	3	8
	1-10/week	9	6	22	21	16
	>10/week	18	17	30	37	28

[a] one serving is 4 oz.

to the laboratory where samples were stored at −80 °C until processing. Blank dust samples were obtained by vacuuming sodium sulfate powder from a sheet of pre-ashed aluminum foil. Upon analysis, dust samples were sieved through an ASTM certified metal sieves 500 μm in size to remove larger particulates. Between each sample the sieve was cleaned thoroughly with neutral detergent, followed by sequential solvent rinses (methanol, dichloromethane, hexane) to prevent contamination carryover from prior sample.

2.3. Sample preparation and extraction

Extraction protocol for human plasma samples was modified from Hovander et al. (2002) and Dahlberg et al. (2014). Briefly, 5 g of the plasma was spiked with recovery surrogate standards BDE-77, 4′-Fluoro-2,2′,3,3′,4,5,5′,6,6′-nonabromodiphenyl ether (F-BDE-208) and denatured using 2-propanol and 6 M HCl. Samples were then extracted with Hexane/MTBE (1:1, v/v) three times and the organic layers were pooled followed by washing with 1% KCl solution. The washed extracts were transferred to pre-weighed glass tubes and evaporated under a gentle stream of ultra-high purity nitrogen for lipid weight determination. After being reconstituted in hexane, the samples were further cleaned up by an activated silica-acid silica column (Sjödin et al., 2004) and concentrated to ~200 μL in hexane. The samples were spiked with internal standard BDE-166 and stored at −20°C until GC-MS analysis. All target PBDE standards, including internal standards BDE-77, BDE-166, and F-BDE-208, were purchased from AccuStandard Inc. (New Haven, CT, USA).

Dust samples were spiked with recovery surrogate standards BDE-77, F-BDE-208 and extracted with Hexane/acetone (3:1, v/v) via ultrasonication followed by centrifugation to separate supernatant and dust (Van den Eede et al., 2012). The extraction was repeated twice and the supernatants were pooled and concentrated by a gentle stream of ultra-high purity nitrogen. The extracts were cleaned up by an activated silica-acid silica column and concentrated to ~500 μL in hexane. The samples were spiked with internal standard BDE-166 and stored at −20 °C until GC-MS analysis.

2.4. Instrumental analysis

The samples were analyzed by a gas chromatography/mass spectrometry (GC/MS) system (Agilent 7890 GC/5975 MSD, Santa Clara, CA, USA) fitted with a fused silica column (HP5-MS UI, 30 m, 0.25 mm i.d., 0.25 μm film thickness) and operated in electron capture negative ionization (ECNI) mode. The ion source temperature and the MS quad temperature were set to 200 °C and 150 °C, respectively. Each sample was injected under splitless mode, with helium as the carrier gas (1.5 mL min^{-1}). The GC oven was programmed from 80 °C (held for 2 min) to 200 °C at 25 °C min^{-1}, 200 °C–250 °C at 2.5 °C min^{-1}, 250 °C–300 °C at 5 °C min^{-1} followed by 300 °C isotemp for 30 min. The GC injector and GC/MS interface were maintained at 285 °C and 300 °C, respectively. The analyses were performed using selected ion monitoring (SIM), scanning for bromine ions 79 and 81 m/z. Compound identification was performed using GC retention times by comparison to the commercially available standards. The target PBDE congeners are BDE-17, 28, 47, 66, 71, 99, 100, 138, 153, 154, 183, 209. BDE-209 analysis was conducted separately from other BDE congeners. BDE-209 was analyzed in 95 samples ($n = 22$ from E-waste workers; $n = 22$ from outdoor workers; $n = 51$ from indoor/office workers) due to insufficient sample volume from some volunteers.

2.5. Quality control

The 5-point calibration curve for each target PBDE was constructed using authentic standards. Recoveries for the surrogate standard BDE-77 and F-BDE-208 relative to internal standard BDE-166 were 94 ± 25% and 108 ± 16%, respectively. Recoveries of the target BDE congeners in the matrix spike (known amounts of target PBDEs spiked in plasma samples) range from 86% to 104%. Duplicate analysis of plasma samples have a relative percentage difference (RPD) < 25%. A procedural blank prepared with deionized water was processed concurrently with each analytical batch. The limit of detection (LOD) was determined for each congener and considered to be three times the background area observed in procedural blanks. Only measurements greater than the LOD are reported. The LODs for most PBDEs ranged from 1.5 to 5.1 pg g^{-1} (ww) with BDE-47, 99 and 183 being higher at 16, 18 and 44 pg g^{-1} respectively. The LOD for BDE-209 was 480 pg g^{-1}.

2.6. Data analysis

A general linear model (GLM; $\alpha = 0.05$) was fitted to the PBDE plasma levels and examined sex, race, and occupation as the main variables and then age, body mass index (BMI), and dietary habits as additional covariates. Plasma results were lipid normalized and transformed to the $\log_{10}$ concentration plus 1 to reduce within class heterogeneity. The addition of 1 allowed the log transformation of values less than detection to be included, as they were set to zero.

When the interactions between main effects were not significant, Tukey's all pairwise comparison was used to compare levels of main factors. When the interaction between main effects was significant, analysis of variance or the Kruskal-Wallis test followed by all pairwise comparisons was used to compare combined categories such as sex and occupation. The nonparametric Kruskal-Wallis test was used when data transformation did not meet the normal assumptions or when sample sizes were small for categories. For the descriptive statistics, only those values greater than the detection limit were used. Dietary habits were categorized into low (<1 serving), moderate (1–10 servings), and high (>10 servings) numbers of servings and the numbers in each category were evaluated for their association with occupation using a Chi-square test ($\alpha = 0.05$). All statistical analyses were conducted using Minitab 17.1.0 (Minitab Inc., 2013).

3. Results and discussion

3.1. Plasma levels of PBDEs

A summary of PBDE concentrations detected in plasma samples from all 113 volunteers is listed in Table 2. The median and geometric mean (GM) of lipid normalized concentrations for the sum of 11 congeners (∑PBDEs, without BDE-209) was 28.70 ng g^{-1} lipid and 31.34 ng g^{-1} lipid, respectively. The most common PBDEs were BDE-47 (GM 12.58 ng g^{-1} lipid), BDE-153 (7.32 ng g^{-1} lipid) and BDE-100 (2.91 ng g^{-1} lipid), which were detected in approximately 90% of the volunteers. BDE-99 was also abundant (6.45 ng g^{-1} lipid) with relatively high detection rate (~60%). These four congeners are widely reported as the dominate BDE congeners in human serum or plasma (Cequier et al., 2015; Fraser et al., 2009; Fromme et al., 2015; Fromme et al., 2016; Hurley et al., 2017; Kim et al., 2012; Sjödin et al., 2008). The distribution pattern (BDE-47 ≫ BDE-153>BDE-99>BDE-100) was also observed in other U.S. studies (Fraser et al., 2009; Fromme et al., 2016). The GM of BDE-47 and BDE-100 in our study are lower than the values reported in the 2003–2004 National Health and Nutrition Examination Survey (NHANES; 20.5 and 3.93 ng g^{-1} lipid, respectively), while BDE-153 in our study is higher than the NHANES value (5.69 ng g^{-1} lipid; CDC, 2018; NIOSH et al., 2018). Several studies in Europe and Korea observed BDE-153 as more abundant than BDE-47 (Cequier et al., 2015; Fromme et al., 2009; Kalantzi et al., 2011; Kim et al., 2012).

The detection rate of BDE-209 was low (13%), with 617.07 ng g^{-1} lipid being the highest measured level in the present study. The low detection frequency is likely influenced by the relatively high MDL for BDE-209, which prevented detection at levels comparable to other PBDEs. However, our BDE-209 detection rate is consistent with findings obtained from other U.S. studies including results from NHANES (Horton et al., 2013; Johnson et al., 2010; Sjödin et al., 2001), which appear to be generally low and similar to levels reported from other world regions with the exception of several studies conducted in China (Fig. S2).

Table 2
Summary statistics for PBDEs in plasma from 113 volunteers. For congeners with detection rate <50%, only minimum and maximum values are reported.

Plasma (pg g^{-1})	Geometric mean	Median	Min	Max	% detect
BDE-17			1.58	70.91	33
BDE-28	6.01	5.23	1.60	44.16	79
BDE-71			2.27	164.8	13
BDE-47	85.24	80.51	16.55	1598	97
BDE-66			1.31	28.19	35
BDE-100	20.06	17.42	3.50	332.7	91
BDE-99	45.66	32.56	18.57	437.2	59
BDE-154	8.04	4.99	2.50	93.52	51
BDE-153	49.69	47.88	6.03	1148	88
BDE-138			13.42	763.3	4
BDE-183			44.69	287.2	24
BDE-209			800.0	2530	13
∑PBDEs[a]	212.4	209.1	22.51	2738	
Plasma (ng g^{-1} lipid)	**Geometric mean**	**Median**	**Min**	**Max**	
BDE-17			0.19	10.65	
BDE-28	0.89	0.83	0.23	6.29	
BDE-71			0.20	24.74	
BDE-47	12.58	12.21	1.66	170.5	
BDE-66			0.15	3.53	
BDE-100	2.91	2.88	0.45	35.48	
BDE-99	6.45	4.78	1.44	87.96	
BDE-154	1.19	0.79	0.30	17.34	
BDE-153	7.32	6.91	0.95	86.47	
BDE-138			1.43	117.5	
BDE-183			6.31	38.91	
BDE-209			70.18	617.1	
∑PBDEs[a]	31.34	28.70	2.30	305.8	

[a] Sum of BDE 17, 28, 47, 66, 71, 99, 100, 138, 153, 154, and 183.

3.2. PBDEs in dust

Analysis of dust samples collected from residences and various E-waste locations are shown in Fig. 1. The highest PBDE levels were observed in dust collected from E-waste sites followed by computer repair locations and then homes or offices. Dust from E-waste facilities had approximately 32–39 times higher levels of these PBDE congeners than dust from other sampling sites. BDE-153 and BDE-209 stand out as the predominant PBDEs in dust with levels at E-waste facilities greatly exceeding levels in dust from other locations (Fig. 1). The relative similarity in PBDE content of dust from

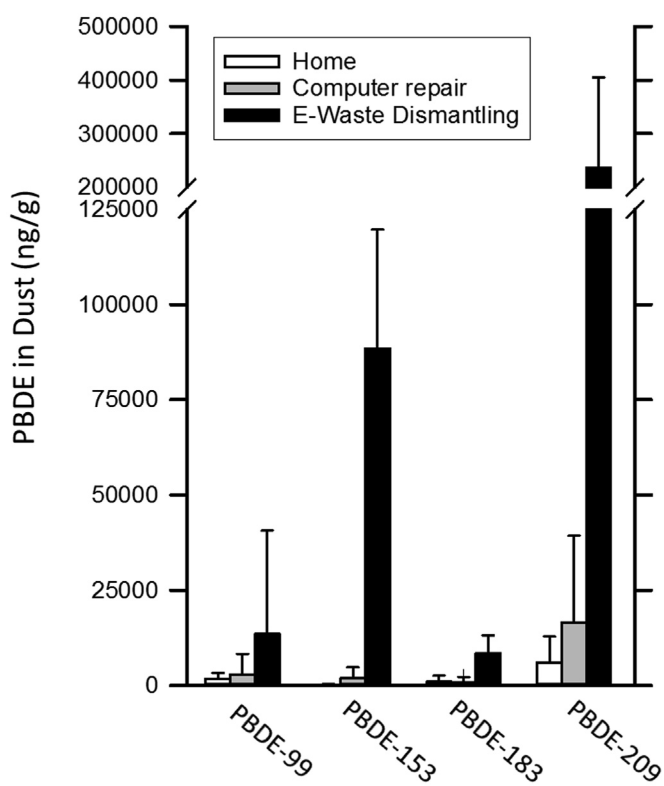

Fig. 1. PBDE congener profiles in dust samples collected from a subset of volunteer homes and E-waste job sites where volunteers worked. Computer repair locations were included for comparison. These four congeners accounted for 65–99% of the total PBDEs measured in dust. Mean ± SD, n = 7, 6, 8 for home, computer repair, and E-waste, respectively.

computer repair businesses and homes was surprising. It is normal for limited dismantling of computers and related equipment to occur during repair, which might generate PBDE enriched dust similar to E-waste recycling locations. However, the results shown in Fig. 1 suggest otherwise with the more aggressive dismantling and material recovery that occurs at E-waste sites producing dust far more enriched with PBDEs. Our data is also consistent with the finding from Sjödin et al. (2001), who reported relatively low PBDE concentrations in airborne particulates from a computer repair site.

3.3. Occupation and PBDE exposure

Summaries of PBDE concentrations in three occupation categories, E-waste workers, indoor workers, and outdoor workers, are listed in Tables S1–S3. The values for ∑PBDEs and select congeners are shown for each occupation type in Fig. 2A. The highest ∑PBDE levels were observed in the outdoor group who consumed on average, nine 4-oz servings of seafood per week compared to five and two servings on average for indoor and E-waste workers, respectively (Table 1). In addition, among all volunteers tested in this study, we found that volunteers with >10 servings of seafood per week have significantly higher ∑PBDE than those with <1 serving per week (Kruskal-Wallis; $p = 0.03$). Past studies have shown seafood and seafood related products often contain the highest PBDE levels compared to other food products (Cade et al., 2018; Costa et al., 2016; Law et al., 2014; Lyche et al., 2015; Schecter et al., 2010a, b). The higher ∑PBDE levels associated with higher seafood consumption points toward the importance of dietary sources in PBDE exposure. However, when dietary habits within a study population are less distinct, it can be difficult to establish the role of seafood consumption on PBDE exposure (Anderson et al., 2008; Costa et al., 2016; Horton et al., 2013; Ohta et al., 2002; Qin et al., 2011; Sjödin et al., 2000; Stasinska et al., 2014; Thomsen et al., 2008). It is also worth noting the GM of ∑PBDE levels observed in the outdoor workers group (50.63 ng g^{-1} lipid) is among the highest observed in recent studies from the USA and other regions (reviewed in Fromme et al., 2016). The GM of BDE-100 and BDE-153 in the outdoor group are also higher than the values reported in the recent NHANES report (Fig. 2A, CDC, 2018).

PBDE levels in E-waste workers are similar to indoor workers (GM = 26.56 and 27.17 ng g^{-1} lipid for E-waste workers and indoor workers, respectively; Fig. 2A) and comparable to levels recently reported from E-waste sites in China, India and Vietnam (Eguchi et al., 2012, 2015; Hearn et al., 2013; Quan-Xia et al., 2015). One exception is the much higher ∑PBDE levels reported by (Bi et al., 2007) from Guiyu, a China E-waste site. They reported very high BDE-209 levels (78% of total ∑PBDE measured), which was not observed in our E-waste volunteers. However, if only tri-to hexa-BDEs are considered, the ∑PBDE from Bi et al. (2007) is 91 ng g^{-1} lipid, which is closer to the values observed in other studies. The median ∑PBDE levels of both indoor workers and E-waste workers in the present study are comparable to the previous reported values (tri-to hexa-BDEs) from North America (9.5–21.1 ng g^{-1} lipid) but much higher than Asia/Australia (1.0–8.1 ng g^{-1} lipid) and Europe (0.9–11.5 ng g^{-1} lipid) (Fromme et al., 2016). The ∑PBDE levels for indoor workers are comparable to reported levels of office workers in Massachusetts, USA (GM 27.7 ng g^{-1} lipid, Watkins et al. (2011)).

The U.S. National Institute for Occupational Safety and Health (NIOSH) recently published a Health Hazard Evaluation (HHE) on the exposure of flame retardants at an E-waste recycle company (NIOSH et al., 2018). The evaluation reported BDEs-47, 100, 153 to have the highest detection rate in serum samples ($n = 12$), matching our observations (Table S1). The GM of BDEs-47, 100, 153 in our E-waste recyclers (11.22, 2.54, 7.53 ng g^{-1} lipid) are all lower than the reported values in the HHE report (13.5, 3.31, 8.39 ng g^{-1}

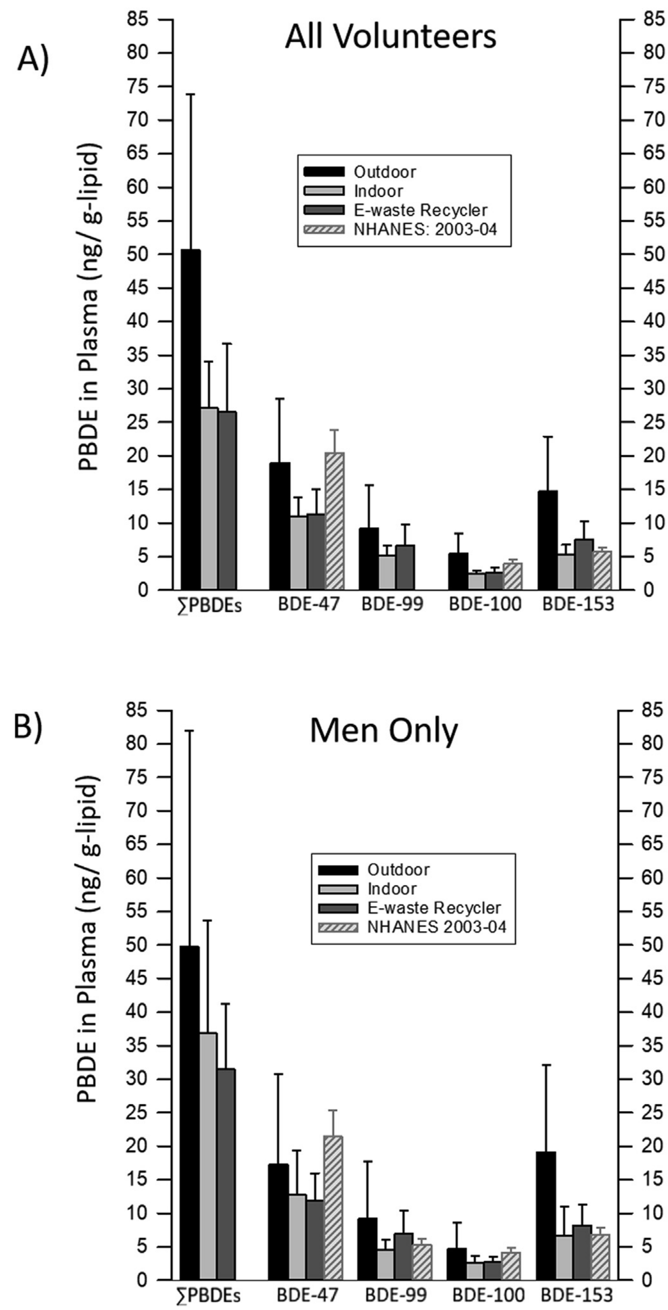

Fig. 2. Geometric mean + upper 95% CL for total PBDEs and select congeners in plasma from Puget Sound region volunteers. These four congeners accounted for >80% of the total PBDEs quantified in plasma. A) Results sorted by occupational class. B) Results for men sorted by occupational class. Supplementary Tables S1–S3 summarize all PBDE measurements by occupational class. NHANES values (CDC, 2018) are included for comparison.

lipid respectively). BDE-209 was detected at a higher rate (≥50%) in the HHE volunteers and the GM was 8.10 ng g^{-1} lipid. Compared to NHANES data (GM = 20.5, 3.93, 5.69 ng g^{-1} lipid for BDEs-47, 100, and 153, respectively), both indoor and E-waste groups in our study have lower BDE-47 and BDE-100; while E-waste recyclers have higher BDE-153 (Fig. 2A, Tables S1 and S2; CDC, 2018).

The outdoor group consistently had the highest levels of all PBDE congeners compared to indoor and E-waste workers (Fig. 2A). This was particularly noticeable for BDE-47 and BDE-153. High levels of BDE-47 in volunteers is often associated with seafood consumption (Anderson et al., 2008; Costa et al., 2016; Spliethoff et al., 2008), which reflects this congener's abundance in diverse types of seafood (Cade et al., 2018). However, the two-fold higher levels of BDE-153 in outdoor workers was surprising given its abundance in dust (Fig. 1) and other non-seafood exposure sources (Bramwell et al., 2017; Fraser et al., 2009). Although outdoor workers were a male dominant group who also consumed relatively high levels of dairy, poultry and red meat (all non-seafood meat in Table 1), the same is also true for the E-waste workers. Thus, it is not clear what factors other than seafood consumption would cause the higher BDE-153 levels in the outdoor workers.

3.4. *Influence of sex and other covariates*

Statistical analysis of the plasma levels indicated the only non-dietary variable that showed a significant correlation was sex (Table 3). Other covariates such as age, body mass index (BMI), and second order interactions were not significantly associated with PBDE levels (Table 3). The majority of the volunteers in this study were white (Table 1), which limits analysis of race. It is worth noting that white volunteers tended to have higher levels of BDE-100 and BDE-153 (Table 3). Additionally, the geometric mean values for the more abundant PBDEs were consistently higher in male volunteers compared to females (combined from all occupational groups) with significantly higher levels of total PBDEs (Kruskal-Wallis; $p = 0.03$) and BDE-153 observed (Fig. 3, Table 3). The explanation for sex differences in PBDE levels appears due in part to dietary differences other than seafood consumption. Overall seafood and dairy consumption was not significantly different among men and women (Kruskal-Wallis; $p = 0.90$ and $p = 0.25$ respectively), however, meat consumption was significantly greater in males than in females (Kruskal-Wallis; $p < 0.001$; Table S4). Poultry and red meat consumption has been suggested to be a determinant of BDE-153 exposure in the U.S. and U.K. (Fraser et al., 2009; Bramwell et al., 2017). Among volunteers in the E-waste and outdoor categories, male volunteers outnumbered female volunteers while the reverse was true for the indoor worker group (Table 1). The sex difference in dietary habits combined with the gender distribution in each occupation category would provide additional explanation for the observed differences in PBDE levels between occupation categories, particularly when comparing E-waste workers to indoor workers (Fig. 2A and B).

The similarity in PBDE profiles between male E-waste and indoor workers (Fig. 2B) was surprising given the high BDE-153 and 209 content of E-waste dust (Fig. 1). However, several studies have suggested that PBDE levels in dust may not directly correlate to

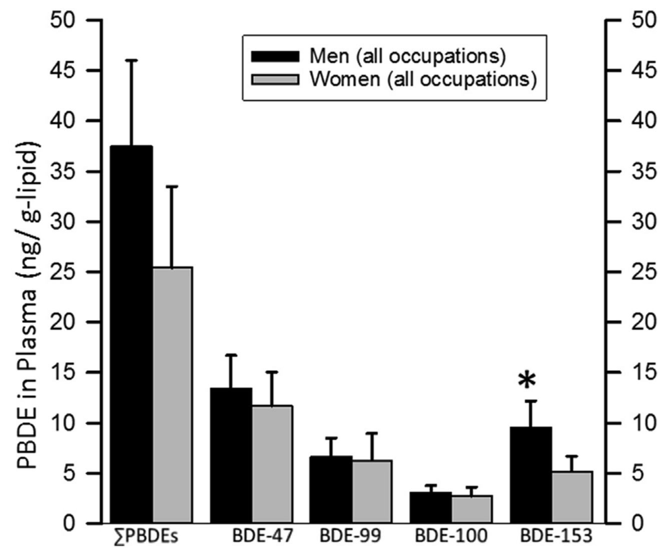

Fig. 3. Comparison of total PBDEs and select congeners between all male and female. Values are geometric mean + upper 95% CL. * = significantly greater (GLM; p = 0.01). See Table 1 for sample sizes.

PBDEs in blood (Cequier et al., 2015; Fromme et al., 2009; Johnson et al., 2010). We also observed a poor correlation between dust vs. plasma in the E-waste group ($r < 0.55$). This may be due to bioaccessibility limitations of BDE-153 and BDE-209 and/or ingestion of E-waste dust during the workday may not provide significant PBDE exposure relative to other sources. Our reliance on vacuumed floor dust may not have been the best predictor of indoor exposure to PBDEs either. Other studies have reported good correlation between handwipes and blood levels of PBDEs, presumably because handwipe sampling can integrate multiple microenvironments and may be more representative of the dust humans are in contact with (Stapleton et al., 2008; Watkins et al., 2011).

4. Conclusions

Our results suggest diet was the most important source of PBDEs to volunteers who participated in this study. We observed that, among all volunteers, people with very high seafood consumption (>10 servings of seafood per week) have significantly higher ∑PBDE than those with very low seafood consumption (<1 serving per week). Although E-waste recycling workplaces contain dust

Table 3
Summary of GLM and Kruskal-Wallis Tests. p-values and conclusions are shown; comparisons were made using lipid adjusted PBDE values.

Variable	BDE-28	BDE-47	BDE-99	BDE-100	BDE-153	∑PBDEs
Age	0.26	0.12	0.17	0.21	0.72	0.66
BMI	0.12	0.56	0.18	0.27	0.72	0.72
Race	0.74	0.81	0.37	0.07 (W tend to be > NW)[a]	0.08 (W tend to be > NW)[a]	0.44
Sex	0.36	0.24	0.26	0.23	0.01* (M > F)[b]	0.06 (M tend to be > F)[b]
Seafood Consumption	0.25	0.29	0.56	0.03* (>10 Serving greater than < 1 serving)[c]	0.37	0.03* (>10 Serving greater than < 1 serving)[c]
Race*Sex	0.051 (K–W, p = 0.40)[d]	0.49	0.08	0.83	0.69	0.25
Race*Seafood	0.19	0.33	0.52	0.75	0.82	0.80
Sex * Seafood	0.30	0.29	0.95	0.13	0.83	0.70

[a] W = white; NW = not white.
[b] M = male; F = female.
[c] one serving is 4 oz.
[d] K-W = Kruskal-Wallis test.

with significantly higher levels of BDE-153 and BDE-209, E-waste workers did not have higher levels of these PBDE congeners in their plasma. E-waste recycling is currently a male dominated industry and 90% of the E-waste volunteers in our study were men. This complicates analysis, as men in general had higher PBDE levels then women (Fig. 3). After considering the male bias in the number of E-waste volunteers, it was evident that PBDE levels in E-waste workers were not significantly different from levels observed in male volunteers in other indoor occupations (Fig. 2B). One limitation of our study is the relatively high analytical detection level for BDE-209, which prevented quantification in the majority of volunteers. Dust is potentially an important source of exposure for BDE-209, which is not routinely found in seafood (Aznar-Alemany et al., 2017; Cade et al., 2018). Since E-waste dust is especially enriched in BDE-209, plasma or serum levels of this congener could be useful for assessing occupational exposures. However, higher detection frequencies will be needed to better assess the contribution of occupational dust exposure to the overall PBDE exposure.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2018.12.006.

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