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Exposure of Electronics Dismantling Workers to Polybrominated Diphenyl Ethers, Polychlorinated Biphenyls, and Organochlorine Pesticides in South China

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In P.R. China, electronic waste (e-waste) from across the world is dismantled and discarded. Concentrations of polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) were measured in serum from residents of an e-waste dismantling region (Guiyu, South China), where 80% of families work in e-waste recycling, and compared to a matching cohort from a nearby region where the fishing industry dominates (Haojiang). Serum concentrations of PBDEs and OCPs, but not PCBs, were significantly different in the two regions: the median ΣPBDE concentration was 3 times higher in Guiyu than Haojiang, whereas the opposite was true for dichloro-diphenyl-trichloroethane (DDT). PBDEs typically accounted for 46% of the total organohalogen chemicals in samples from Guiyu, but 8.7% in Haojiang. The median BDE-209 concentration in Guiyu was 50−200 times higher than previously reported in occupationally exposed populations. The highest BDE-209 concentration was 3100 ng/g lipid, the highest yet reported in humans. Serum PBDE concentrations did not correlate with PCBs or OCPs, whereas PCBs and OCPs showed positive correlations, suggesting that sources of PBDEs to humans are different from PCBs and OCPs. The levels of PBDEs in individuals from Haojiang are possibly related to the recycling activity at Guiyu, through atmospheric transport.

Introduction

Exposure levels of persistent organic pollutants (POPs) continue to come under considerable scrutiny from researchers, legislators, and the general public because they are widespread and may have toxic effects in humans and wildlife (*1*, *2*). There is an international agreement to reduce and eliminate several POPs, namely polychlorinated biphenyls (PCBs) and some organochlorine pesticides (OCPs) [including hexachlorobenzene (HCB), dichloro-diphenyl-trichloroethane (DDT), and chlordane (CHL)] in the environment. Although the agricultural use of some OCPs has been banned in China for two decades, high levels of DDTs can still be observed in human samples (*3*, *4*). In addition, other chemicals such as PentaBDE, chlordecone, hexabromobiphenyl, lindane, and perfluorooctane sulfonate (PFOS) are also under consideration for inclusion in this agreement.

Polybrominated diphenyl ethers (PBDEs) are used extensively as flame retardants. Because of large production volumes, widespread usage, and their persistence, PBDEs are now ubiquitous environmental pollutants (*5*, *6*). Moreover, PBDE concentrations/burdens have increased in environmental media (*7*, *8*) and humans in some regions of the world over recent years (*9*, *10*). Occupational exposure has been reported to result from the repair and maintenance of computers (*11*), dismantling electronics (*12*) and recycling printed circuit boards (*13*), commercial decabromidiphenyl ether (DecaBDE) flame-retarded rubber manufacture (*14*), and handling electric cables using the same rubber (*14*). Different PBDE patterns have been observed between occupationally exposed and non-occupationally exposed populations (*10*, *12*, *14*, *15*). Low to medium-brominated PBDEs (tri- to hexa-) are generally the major congeners in nonoccupationally exposed humans (*10*, *15*, *16*), while higher-brominated PBDEs are often elevated in electronics-dismantling workers (*12*, *14*, *17*). BDE-153 is often now the major PBDE congener in nonoccupationally exposed populations, such as in The Netherlands (*18*), the United Kingdom (*19*), Sweden (*14*), and China (*20*). BDE-209 and BDE-183 have been specifically related to occupational exposure (*12*, *14*, *17*).

The majority of studies on occupational exposure to PBDEs are from Europe and America; no such reports have been conducted in China. However, the electronics industry is the world's largest and fastest growing manufacturing industry, and as a consequence of this growth, electrical and electronic waste (e-waste) such as computers, printers, mobile phones, television sets, stereos, radios, etc., is generated in large quantities around the world. The e-waste generated throughout the world is being transported to developing countries. It is reported that about 80% of computer e-waste is exported to Asia, and 90% of these exports have been sent to China, illegally, for "recycling" (*21*). Large quantities of organic compounds generated during e-waste disposal are released into the surrounding area, resulting in high environmental levels of POPs (*22*, *23*). Local residents are exposed to these toxic pollutants through inhalation, dermal exposure, and oral intake. This study was performed to help assess exposure to lipophilic contaminants in south China by determining PBDE, PCB, and OCP concentrations in two different cohorts of inhabitants. Examination of the concentrations and congener profiles in serum lipid of e-waste dismantlers may provide important information for the subsequent evaluation of health effects.

Experimental Section

Subjects. Blood samples were taken from two cohorts (see Table S1, Supporting Information). The first consisted of 26 inhabitants of Guiyu town, Shantou City, Guangdong Province, with a total area of 52 km^2 and a population of 150 000. In this town, 80% of families are engaged in, and nearly

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10 000 migrants are employed in, recycling work. The methods used to dismantle the electronic equipment are primitive (including chipping and melting plastics without proper ventilation, burning coated wire to recover copper, removing electronic components from printed circuit boards, and burning unsalvageable materials in the open air) with little or no safety measures (e.g., gloves, respirators) or attempts to control exposure to chemicals present in the waste (*22*, *24*). Because of the primitive methods of e-waste processing in this town, a lot of potential carcinogenic and hazardous substances such as toxic metals (e.g., mercury, lead, and cadmium) and POPs (e.g., dioxins/furans and PBDEs) are released into the environment (*22*, *24*), which pose a threat to the health of local residents and workers.

The second cohort consisted of 21 inhabitants of Haojiang district, Shantou City, Guangdong Province, about 50 km east of Guiyu, where the fishing industry predominates. Shantou City has a subtropical climate, and atmospheric conditions are strongly influenced by the Asian monsoon system, with southwesterly monsoons in summer and northeasterly winds in winter. The winter seasons have characteristic strong winds and dry weather, whereas the summer seasons are hot and humid due to occasional showers and thunderstorms.

All subjects participating in this study were informed volunteers and gave written consent. Whole blood samples (10 mL) were taken from each volunteer by medical professionals in August 2005 using BD Vacutainer serum tubes (with clotting agent and polymer separator). After coagulation, samples were centrifuged to separate the serum which was immediately frozen and transported to the laboratory. All samples were still frozen upon receipt in the laboratory, after which they were defrosted and the serum transferred to clean glass containers and stored at −20 °C until analysis. The volunteers were aged between 18 y and 81 y, and 64% were male (36% female).

Sample Cleanup and Analysis. A detailed description of the methods used for extraction and gravimetric lipid weight determination have been published elsewhere (*19*, *25*). Briefly, this entailed denaturation of the sample with hydrochloric acid and propan-2-ol, followed by extraction with a hexane: MTBE mixture. Samples were then cleaned using concentrated sulfuric acid, followed by gel permeation chromatography (Biobeads S-X3), before the addition of internal standards (CB30, $^{13}C_{12}$-labeled CB141 and $^{13}C_{12}$-labeled CB208, BDE-69 and BDE-181), final volume reduction, and analysis by GC-MS.

Samples were analyzed for 43 PCBs and 12 OCPs pesticides using a Finnigan TRACE GC-MS. The gas chromatograph used splitless injection and was fitted with a 50 m CP-Sil8 capillary column. The mass spectrometer used electron impact ionization (EI+), and selected ion monitoring (SIM) mode. PBDEs were analyzed using a Fisons MD800 GC-MS with splitless injection and a 30 m DB5 capillary column. The MS was operated in electron capture negative ion (ECNI) mode and SIM. Ammonia was used as the reagent gas. BDEs-196, -197, -206, -207, -208 and -209 were analyzed using a Micromass Autospec Ultima GC-HRMS, using a resolution of at least 10 000 tuned using perfluorokerosene (PFK). The GC used cool on-column injection and was fitted with a 15 m DB5 capillary column. The MS used an EI+ source in SIM mode.

Quality Control. PCBs and OCPs were analyzed using CB30 and ^{13}C-CB141 as internal standards, while PBDEs were analyzed using ^{13}C-CB141 and ^{13}C-CB208 as internal standards. All samples were spiked with ^{13}C-labeled recovery standards. ^{13}C-labeled PCB recoveries averaged 102−112%, and ^{13}C-labeled BDE-209 recovery averaged 116%. Laboratory blanks, consisting of purified water, were treated and analyzed as regular samples constituting about 20% of total samples analyzed, and average blank concentrations were subtracted from the concentrations found in each sample before application of the detection limit.

Detection Limits. For chemicals detected in the blank samples, the method detection limit was defined as three times the standard deviation of the blank value. In the absence of detectable concentrations in the blank samples, the method detection limit was defined as the instrument detection limit. Method detection limits were typically (in ng/g lipid) 0.3 for PCBs, 0.6 for OCPs, 0.2 for PBDEs (excluding BDE209), and 64 for BDE-209. The relatively high detection limit obtained for BDE-209 is due to a combination of the instrument detection limit and the concentrations which were found in the analytical blanks.

Statistics. Correlations between individual compounds, between target compounds and age or body weight were tested using the Pearson coefficient of determination. The Mann−Whitney U test was employed to detect the differences between POPs concentrations in samples from Guiyu and Haojiang. A p value of <0.05 was considered to indicate statistical significance. Because of the small sample size in this study, the conclusions reached must be treated with some caution. The levels of all compounds were log transformed to obtain a normal distribution, and data were analyzed using the SPSS software package. Values below the LOD are treated as being zero for calculating total chemical group concentrations such as ΣPCBs and ΣPBDEs. However, when performing statistical analyses, those congeners below the LOD were taken as 1/2 LODs.

Results and Discussion

Polybrominated Diphenyl Ethers. Sixteen PBDE congeners were identified in the serum samples. One congener (an octa-BDE) was unidentified, because of the lack of pure reference standards, but its fragment ions and the ratios were characteristic of a BDE. Octa- to decabrominated diphenyl ethers were detected frequently in the samples from Guiyu (91%) and Haojiang (80%), while the other PBDE congeners were detected in 51% of the samples from Guiyu and a smaller number (24%) from Haojiang. Total concentrations of tri- through deca-BDE congeners ranged from 140 to 8500 ng/g lipid (median: 600 ng/g lipid), and 16 to 490 ng/g lipid (median: 170 ng/g lipid), in the serum samples from Guiyu and Haojiang, respectively (Tables 1 and S3). The median concentration of ΣPBDEs (defined as the sum of all congeners detected) was 3 times higher in Guiyu than Haojiang, consistent with the expected elevated exposures through dismantling e-waste products (*12*).

When the data were compared with serum concentrations in Europe and North America, the average concentrations of tri- to hexa-BDEs (Guiyu: 91 ng/g lipid; Haojiang: 11 ng/g lipid) were much higher than those reported for European populations, such as the UK (4.7 ng/g lipid) (*19*), Romania (1.04 ng/g lipid) (*26*), and Norway and Germany (3.9 ng/g lipid) (*27*). Levels in Guiyu were also rather higher than those reported in the American population (61 ng/g lipid) (*10*). To date, the highest-reported PBDE concentration of 9630 ng/g lipid was found in an adipose tissue sample from New York (*28*), where 11 PBDE congeners (di- to hexa-BDEs) were identified. However, the concentrations of higher-brominated PBDEs (hepta- to deca-BDEs) observed in this study were among the highest reported in humans.

In Figure 1, the occupational exposures to PBDEs from different studies are compared. It can be seen that the e-waste workers from south China were by far the most exposed to highly brominated PBDEs. Further, highly brominated PBDEs (except BDE-197) showed a strong relationship between Guiyu and Haojiang (Figure S1), implying that individual residents in Haojiang may have had exposures arising from

TABLE 1. Organohalogen Concentrations in Serum Samples from E-waste Dismantling Regions (Guiyu) and a Nearby Region (Haojiang)

		concentration, ng/g lipid weight							
		median		mean[b]		minimum		maximum	
compound	*p* value[a]	Guiyu	Haojiang	Guiyu	Haojiang	Guiyu	Haojiang	Guiyu	Haojiang
ΣPCBs[c]	0.82	52	63	69	65	17	22	180	140
HCB	0.08	39	31	44	33	14	8.1	130	66
ΣHCHs	0.01	12	39	28	86	2.2	5.6	280	540
Σchlordane	0.45	2.2	2.5	2.4	3.3	0.92	0.47	5.0	15
ΣDDTs[d]	0.00	600	2300	650	2400	210	380	1800	5100
BDE-209	0.00	310	86	340	130	ND	ND	3100	370
ΣPBDEs	0.00	600	170	580	190	140	16	8500	490

[a] Mann−Whitney *U* test (for PBDEs after removal of an outlier). [b] For nondetected congeners 1/2 LODs were used for mean calculation; PBDE mean was calculated after removal of an outlier. [c] ΣPCBs(or ΣPBDEs) is the sum of all PCB (or PBDE) congeners analyzed, for nondetected congeners zero was used for the sum of PCBs/PBDEs calculations. [d] ΣDDTs is the sum of *o,p*′-DDE, *p,p*′-DDE, *o,p*′-DDD, *p,p*′-DDD, *o,p*′-DDT, *p,p*′-DDT.

TABLE 2. Concentrations of Organochlorine Compounds in Non-occupationally Exposed Populations (ng/g Lipid) Collected from Other Regions or Countries

country	year	*n*	PCBs	HCB	HCHs	DDTs	CHLs	reference
China								
Hong Kong	1999	132	42		950[b]	2870[c]		[4]
Guangzhou	2000	54	33		1110[b]	3550[c]		[4]
Shanghai	2001	5	70	64	7400	7600[d]	42[e]	[33]
Guizhou	2002	34	31	40	630	5700[d]	4.4[e]	[34]
Dalian	2002	20	42	81	1400	2100[d]	16[e]	[3]
Shengyang	2002	20	28	56	550	870[d]	6.7[e]	[3]
Guiyu	2005	21	69	51	28	650	2.4[a]	this study
Haojiang	2005	26	65	33	86	2400	3.3[a]	this study
Canada	1994/5	63	181	57	9.6	145[c]	74[e]	[38]
Sweden	1995/6	40	592	34		424		[39]
Russia	1996	51	235	63	223	464[c]	24[e]	[38]
Japan	1998	22	1700	41	330	780	230[e]	[46]
Belgium[g]	1999	44	380	41		432[f]		[36]
Slovakia	2001	1038	871	829	52.4	1804[c]		[37]
UK	2003	154	170	14	15	100		[19]
Romania	2005	142	550	30	1750	3480[c]		[26]

[a] The sum of *trans*-chlordane and *cis*-chlordane. [b] β-HCH. [c] The sum of *p,p*′-DDE and *p,p*′-DDT. [d]the sum of *p,p*′-DDE, *p,p*′-DDD, *p,p*′-DDT [e] The sum of *trans*-nonachlor, *cis*-nonachlor, *trans*-CHL, *cis*-CHL, oxychlordane [f] *p,p*′-DDE. [g] Calculated using 0.5% lipid in blood.

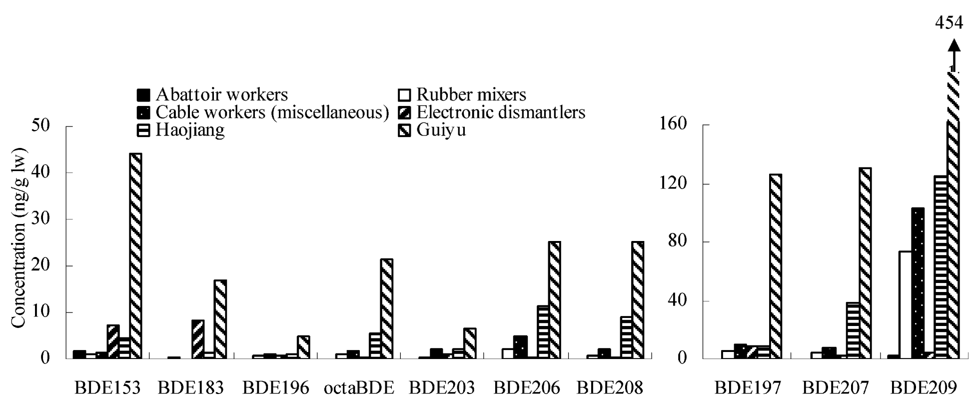

FIGURE 1. Average concentrations of ten PBDE congeners (ng/g lipid) in serum from several populations: Abattoir workers (ref *14*); rubber mixers (ref *14*); cable workers (miscellaneous) (ref *14*); electronic dismantlers (day 0) (ref *30*): in Sweden; Haojiang and Guiyu (this study). Average BDE-209 concentration in Guiyu is given as a numerial value, because it is off the scale of this diagram. Since BDE-197, -207, and -209 were present at high concentrations in most samples, they are presented with a different concentration (*y*) axis.

Guiyu through transport of PBDEs by particles in the atmosphere or through other environmental processes across the 50 km separating both regions (*29*).

Of the PBDE homologues, the dominant PBDEs detected in this study were octa- to deca-BDEs, accounting for 82% and 91% of total PBDEs in Guiyu and Haojiang, respectively. Low- to medium-brominated diphenyl ethers were detected at relatively low concentrations in this study, but they are the dominant congeners in non-occupationally exposed subjects (*19*, *30*). A result similar to our study was also observed in rubber workers exposed to commercial DecaBDE in Sweden (*14*), which is different from the personnel at an e-waste dismantling plant where BDE-183 was the major contaminant (*12*). The elevated levels of octa- to deca-BDE in the e-waste dismantlers in this study imply that the commercial DecaBDE formula is widely present in

Guiyu. The median concentration of BDE-209 in Guiyu was 50- to 200-fold higher than in previously reported occupationally exposed populations (*14*, *31*). This suggests that the residents in Guiyu must be continuously exposed to BDE-209 to maintain such relatively high levels in serum, since BDE-209 has a short half-life (estimated to be about 15 days) (*32*). The highest BDE-209 concentration, of 3100 ng/g lipid, was detected in a male subject aged 32 and is higher than in any other report in the literature to date.

Further comparison with rubber workers in Sweden showed that the residents in Guiyu had high nona-BDE concentrations relative to octa- and deca-BDE concentrations. The ratios of mean BDE-197 (octa-BDE) to -207 (nona-BDE) and BDE-209 to -207 were 0.24 and 3.2 in Guiyu, and 1.4 and 19 in rubber mixers (calculated from ref *14*). The rubber workers did not handle DecaBDE every day and they were sampled immediately after exposure to DecaBDE, while people in Guiyu are believed to have continuous high exposure to PBDEs. Generally, the half-lives of PBDE congeners in human blood decreases with increasing number of bromines (*32*). BDE-209 has a short half-life (as noted above) in human blood, while octa- (18−39 days) and nona-BDEs (37−91 days) have longer half-lives (*32*), which is likely to lead to preferential accumulation of octa- and nona-BDEs. It is also possible that octa- and nona-BDEs are formed within the body by metabolic debromination of BDE-209 (*14*). The continuous chronic exposure and the longer half-lives of nona-BDEs appear to result in relatively high concentrations of nona-BDEs in Guiyu.

Serum PBDE concentrations did not correlate with age in Guiyu. A similar lack of correlation was found in other studies (*10*, *12*, *28*). In contrast, highly brominated PBDE congeners such as BDE-197, -207, and -209 had a positive relationship with age (significant at the 95% level) in Haojiang (see Figure S2, Supporting Information). The lack of a correlation with age in Guiyu may be partially related to the fact that PBDE exposure is predominantly due to the recent expansion (in the last 10 y) of the e-waste industry in this region, and therefore that people of all ages have been exposed for a similar period. However, this is also likely to be the case for Haojiang, where the heavier PBDEs may be substantially supplied by environmental transport from Guiyu. An important factor in the lack of age correlation with PBDE concentration in Guiyu may be that most e-waste dismantlers are temporary migrant workers, from other parts of China, of various ages, who have lived in the region (and worked with e-waste) for different lengths of time. BDE-153 did not follow this trend and showed a negative relationship with age (Figure S2), which may be explained by the fact that younger people are likely to have more contact, in general, with consumer electronic products (that may contain octa-BDE, a dominant source of BDE153) than older people. It is important to note that, since the number of participants in this study was relatively small, these associations must be interpreted with caution.

PCBs. In contrast to the PBDEs, no difference was observed in PCB concentrations between the two regions. The total PCB concentrations ranged from 17 to 180 ng/g lipid and 22 to 140 ng/g lipid, with a median value of 52 and 63 for Guiyu and Haojiang, respectively. Published studies of PCBs in the Chinese population and other countries are summarized in Table 2. It can be seen that the median total PCB concentrations in this study are very close to those found in other parts of China (*3*, *4*, *33*, *34*) and about 25 times lower than found in Japan (*35*). Compared to other European countries, the range of concentrations in this study has the same lower limit as the UK (*19*) but a substantially (approximately one order) smaller upper limit than in other European studies (*19*, *26*, *36*−*39*). Lower residues of PCBs were also reported in the environment of South China (*40*), which support the hypothesis of lower PCB usage in China.

It is well-known that higher-chlorinated congeners become increasingly important in the PCB congener patterns in organisms as trophic level increases. As expected, the most abundant PCB congeners in this study were CB-138, and CB-153, accounting for 34% and 45% of the sum of PCBs in Guiyu and Haojiang, respectively. Additionally, Pearson's correlation coefficient was calculated to determine the degree of linear dependence between the most abundant PCB congeners in serum samples. A strong correlation was observed between CB-153 and other PCB congeners (e.g., Haojiang: r 153/138 = 0.964, r 153/187 = 0.974, r 153/180 = 0.970, r 153/ΣPCBs = 0.989). As found in other studies, CB-153 is therefore a good indicator for general PCB exposure in human samples in this study.

PCBs were present at similar concentrations in men and women ($p > 0.05$). A general trend of increasing PCB concentrations with age was observed in some studies (*12*, *28*). However, levels of most PCBs did not correlate with age in Guiyu (at the 95% level), except for a weak positive age-associated correlation for the samples from Haojiang (Figure S3, Supporting Information).

OCPs. The most frequently detected OCPs were HCBs, β-hexachlorocyclohexane (HCH), *p,p*′-DDE, and *p,p*′-DDT. The range of concentrations found for HCB was relatively small, while the range of DDE levels was the largest. The median HCHs and DDTs concentrations in samples from Guiyu are more than three times lower than Haojiang (12 vs 39 ng/g lipid, and 610 vs 2300 ng/g lipid). It has been reported that significant positive correlations were found between frequencies of seafood consumption and OCP levels in human breast milk (*4*). Fishing is the main source of income in Haojiang, and seafood consumption by residents in Haojiang is likely to be high. Most of the people in Guiyu were migrant workers, whose seafood consumption is generally low.

Very few data are available for pesticides in serum from China, although there have been several studies of breast-milk samples. The concentrations of DDTs in Guiyu were similar to Shengyang (*3*) but significantly lower than in Haojiang; this was similar to Hong Kong (*4*) and the northern Chinese city of Dalian (*3*) but lower than Guangzhou, Guizhou, and Shanghai (*4*, *33*, *34*). HCB has a similar level among the different regions in China (*3*, *4*, *33*, *34*), which suggests that this arises from background exposure. The median concentrations of *p,p*′-DDE, *p,p*′-DDT and β-HCH were much higher than in Japan and most European countries (*19*, *41*−*43*) but lower than some highly contaminated areas in Eastern Romania (*26*), Slovakia (*37*), and Thailand (*44*).

The major contributor (>77%) to ΣDDTs was *p,p*′-DDE, which was found at a median value of 540 ng/g lipid, with a range between 81 and 1500 ng/g lipid in Guiyu (median value of 1800 ng/g lipid) compared to a range from 320 to 3900 ng/ g lipid in Haojiang. The *p,p*′-isomers were detected in all subjects, and the *o,p*′-isomers were also detected in most of the study population. In all cases, the *p,p*′-isomers were present at much higher levels than *o,p*′-isomers because technical grade DDT contains approximately 80% of *p,p*′-DDT and *p,p*′-isomers also have long half-lives. DDT is converted to DDE over time. The *p,p*′-DDE/*p,p*′-DDT ratio, an indicator of the historical accumulation of *p,p*′-DDT, was about 13 and 4.9 in Guiyu and Haojiang, respectively. The lower *p,p*′-DDE/*p,p*′-DDT ratio (<10) suggests relatively recent use of *p,p*′-DDT in Haojiang, although DDT has been banned in China for some two decades.

China is the world's largest producer and user of HCHs. At present, two HCH formulations are used: lindane, containing only the γ-HCH isomer; and technical lindane, which consists of a mixture of HCH isomers (60−70% α-HCH,

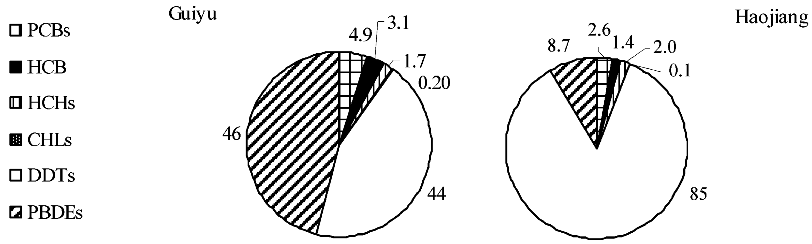

FIGURE 2. Average percentage distribution of PCBs, HCB, HCHs, CHLs, DDTs, and PBDEs in serum from Guiyu and Haojiang.

5−12% β-HCH, and 10−12% γ-HCH (*45*)). β-HCH was the dominant HCH isomer in this study, with a median value of 11 ng/g lipid in Guiyu and 38 ng/g lipid in Haojiang, accounting for 93% and 96% of total HCH concentrations, respectively. The presence of α-HCH in measurable amounts, and the high levels of β-HCH, suggests exposure to technical lindane.

Total CHL concentrations were 2.2 and 2.5 ng/g in Guiyu and Haojiang, respectively. The most abundant compound was γ-CHL, accounting for over 57% of the total CHLs. In general, CHL residues in south China inhabitants were considerably lower than those in industrialized regions, such as Japan (230 ng/g lipid) (*46*) and Shanghai (42 ng/g lipid) (*33*) although only two congeners were analyzed in this study. The low concentrations indicate a low usage of CHL in south China. Levels of HCB were similar to other regions of the globe, consistent with a rather uniform global distribution of this compound.

Linear regression analyses showed that there is a tendency for increasing concentration with age for ΣDDTs, CHLs, and ΣHCHs in Haojiang (Figure S3), while no such age-related increase was noted for HCB. There were no significant differences for OCP concentrations by gender. Similar correlation coefficients between pollutants and age have recently been observed for the general population of UK (*19*) and Romania (*26*).

Distribution of the Organohalogen Compounds. The nonparametric Mann−Whitney *U* test confirmed that there were significant differences between concentrations of PBDEs, β-HCH, DDE, and DDT between Guiyu and Haojiang (Table S2). No difference was observed between women and men except for BDE-153 ($p = 0.009$) and BDE-183 ($p = 0.046$) in Haojiang, women showing higher concentrations than men. It is likely that the sample population in this study, however, is too small to reliably identify any gender-associated differences.

The relative size of each class of halogenated compounds analyzed in the serum samples is illustrated in Figure 2. The congener profiles were quite different between Guiyu and Haojiang. In Haojiang, DDTs were the main contaminants (85%) followed by PBDEs (8.7%) while in Guiyu, the order was PBDEs (46%) > DDTs (44%) > PCBs (4.9%) > HCB (3.1%) > HCHs (1.7%) > CHLs (0.2%). Obviously, PBDEs constituted a large fraction of the total contaminant load exceeding DDTs in Guiyu, which was dramatically different from other countries (*19*, *41*).

Significant correlations were found between PCBs and OCPs (Pearson correlation coefficients 0.52−0.80, significant at the 95% level in Haojiang). This implies that PCBs and OCPs had similar exposure pathways, which are likely to be dominated by dietary exposure. No significant correlation was found between PBDEs and either PCBs or pesticide concentrations in samples from Guiyu and Haojiang (Table S3), which may suggest there are different sources of human exposures for PBDEs and either PCBs or OCPs. Diet, inhalation and dermal absorption may all contribute to exposure to PBDEs; the magnitude of overall exposure and the relative importance of each of these exposure routes will be heavily dependent on individual lifestyles. For example, it has been suggested that inhalation may make an appreciable contribution to PBDE exposure for some individuals (*47*). Recently, elevated levels of PBDEs have been found in the air at an electronics recycling plant compared to other workplaces (*48*). At this plant, workers had significantly higher levels of PBDEs in their blood (*12*). In Haojiang, it is possible that atmospheric transport of PBDEs from Guiyu may make a significant contribution through inhalation but that ingestion may still be a dominant exposure route-the lack of correlation between PBDEs with PCBs and OCPs may be due to different sources (relatively local emission vs long-range transport or agricultural application to food crops and animals).

Further work should focus on the health effects of higher-brominated congeners, qualifying and quantifying their sources of exposure to such inhabitants, and investigating the metabolites of the congeners present at high levels in this study.

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Supporting Information Available

Participant personal statistics, chemical concentration data, and statistical test results (including graphs). This material is available free of charge via the Internet at http://pubs.acs.org.

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