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Brominated Flame Retardants, Polychlorinated Biphenyls, and Organochlorine Pesticides in Captive Giant Panda (*Ailuropoda melanoleuca*) and Red Panda (*Ailurus fulgens*) from China

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Organochlorine pesticides (OCPs), polychlorinated biphenyls (PCBs), and brominated flame retardants (BFRs) were investigated in captive giant and red panda tissues from China. The total concentrations of OCPs, PCBs, and polybrominated diphenyl ethers (PBDEs) in tissues ranged from 16.3 to 888 ng/g lipid weight (lw), 24.8 to 854 ng/g lw, and 16.4 to 2158 ng/g lw, respectively. *p,p*′-DDE and β-HCH were major OCP contaminants. PCBs 99, 118, 153/132, 170, 180, and 209 were the major contributing congeners determined. Among PBDEs, congener BDE-209 was the most frequent and abundant, followed by BDE-206, BDE-208, BDE-207, BDE-203, BDE-47, and BDE-153. Decabromodiphenyl ethane (DeBDethane) was detected in 87 and 71% of the giant and red panda samples with concentrations up to 863 ng/g lw, respectively. The remarkable levels and dominance of BDE-209 and DeBDethane may relate to significant production, usage, or disposal of BFRs in China. The positive significant correlation between concentrations of PBDEs and PCBs in captive pandas may suggest that the exposure routes of PBDEs and PCBs to panda are similar. To our knowledge, this is the first report of the occurrence of DeBDethane in captive wildlife samples. Therefore, further studies are warranted to better understand DeBDethane production, transport, uptake, and toxicological effect.

Introduction

Over the past several decades, the bioaccumulation of anthropogenically produced halogenated contaminants such as polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls (PCBs), and organochlorine pesticides (OCPs) has been raised as a concern for the health of both human and wildlife (*1*). PBDEs are a group of brominated flame retardant (BFR) chemicals that are added to manufactured products including paints, plastics, textiles, and electronic appliances (*2*). In view of PBDE bioaccumulation in human and wildlife, the European Community introduced a new regulation to ban the usage of penta-BDE and octa-BDE technical mixtures (*3*). American manufacturers also voluntarily halted production of these in December 2004 (*4*). However, the production and usage of deca-BDE mixtures is on the rise (*5*). The deca-BDE formulation made up 83.3% of the PBDE global demand in 2001. In China, the domestic production of deca-BDE was approximately 25 000 t in 2004 (*6*). Decabromodiphenyl ethane (DeBDethane) was produced in the early 1990s by Albemarle Corporation, which is currently used to replace deca-BDE by many industries since only trace quantities of dioxin-compounds are produced under pyrolysis conditions. Information on recent production amounts of DeBDethane is limited in China; one report lists its estimated production for the year 2006 at 12 000 t (*7*). The production of DeBDethane in China is expected to exponentially increase at rates up to 85% per year (*8*). PCBs have been widely used as dielectric fluids in transformers and capacitors, heat exchange fluids, and as additives in pesticides, adhesives, plastics, and paints because of their insulating and nonflammable properties (*9*). In China, the total amount of technical PCBs, called PCB3 and PCB5, produced from 1965 to 1974 was approximately 10 000 t, accounting for 0.6% of the total global production (*10*). But PCBs still leak from old capacitors and transformers. OCPs also still exist widely in various environmental matrices because of their persistence, bioaccumulation, and long-distance transport, although many countries have banned the use of OCPs during the last 30 years. Dichlorodiphenytrichloroethanes (DDTs) and hexachlorocyclohexane (HCHs) have been used for agriculture since 1960s, and have been banned since 1983 in China (*11*).

PBDEs, PCBs, and OCPs have been identified worldwide in environmental and biological matrices, such as air (*12*), water (*13*), sediment (*14*), wildlife (*15, 16*), human blood, and breast milk (*17*). However, few studies have reported on the occurrence of organohalogen contaminants in terrestrial mammals (*16*). PBDEs and PCBs can severely affect the physiological functions of wildlife and human health. The toxic effects include immunotoxicity, reproductive effects, teratogenicity, endocrine disruption, and carcinogenicity (*18*). Exposure to OCPs has been implicated in the etiologies of various cancers, miscarriage, reproductive disorders, and behavioral abnormalities (*19*).

The giant panda (*Ailuropoda melanoleuca*) and the red panda (*Ailurus fulgens*) are endemic to the Himalayan Hengduan Mountains in China, with population totals around 1000 and 8000 individuals, respectively (*20*). They are confronted with environmental and genetic pressures. Both species belong to the order Carnivora, but bamboo forms 80% of the diet of wild and captive pandas, with the remaining 20% being eggs, rodents, insects, and other protein sources. Monitoring the concentrations of organohalogen contaminants in panda tissues is important for understanding the distribution and potential impact of these compounds on these species. It is also important to assess the potential

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sources by investigating organohalogen contamination in terrestrial species. Recent studies of organohalogen compounds in polar bears have indicated associations with toxic effects on several organ systems (*21*), chronic exposure to organohalogen compounds may also associated with pandas' health. However, there is little information on the distribution and degree of contamination of organohalogen compounds, particularly in wildlife, in China (*22*).

Our main objective was to assess the concentrations of organohalogen compounds (OCPs, PCBs, PBDEs, and other two BFRs) in giant and red pandas. Special emphasis was focused on BDE-209 and DeBDethane because consumption of these BFRs is continuously increasing in China and certain studies have suggested their potential bioaccumulation in higher trophic level animals. These data will provide information on the concentrations of persistent organic pollutants in captive wildlife in China. This study is the first to report on BFRs in the giant and red pandas and contributes to a better understanding of the levels, tissue distribution of PBDEs and other BFRs in captive terrestrial mammals.

Experimental Section

Sample Collection. Details of sample information and sampling locations are given in the Supporting Information (SI; Table S1 and Figure S1). All sampled individuals were found dead from disease. No panda was killed for the purpose of this study. The collected tissue samples were packed using aluminum foil and sealed in two polyethylene bags, and then frozen at −20 °C until further analysis.

Sample Preparation and Analysis. The procedure for sample extraction was similar to that described previously (*15*). About 1.0 g of freeze-dried tissue was spiked with surrogate standards ($^{13}C_{12}$−BDE-209, CDE-99, $^{13}C_{12}$−PCB-141, PCB-65, and PCB-204) and was Soxhlet extracted with 50% acetone in hexane for 48 h. The lipid content was determined by gravimetric measurement from an aliquot of extract. Another aliquot of extract was subjected to gel permeation chromatography. Eluate from 90 to 280 mL containing organohalogen compounds was collected and concentrated. This fraction was purified on a 2-g silica gel solid-phase extraction column (Isolute, International Sorbent Technology, UK), then concentrated and spiked with internal standards (BDE-118, BDE-128, and $^{13}C_{12}$−PCB-208 for PBDEs, PCB-82 and PCB-189 for PCBs and OCPs).

PBDEs (BDE-28, -47, -66, -99, -100, -153, -154, -183, -196, -203, -206, -207, -208, and -209), PBB-153, and DeBDethane were analyzed using a Shimadzu model 2010 gas chromatograph (GC) coupled with a model QP2010 mass spectrometer (Shimadzu, Japan) under electron capture negative ionization (ECNI) in the selected ion monitoring (SIM) mode. Identification of DeBDethane in tissue samples was confirmed with an Agilent 6890 GC/5975B mass selective detector (MSD) in electronic impact ionization mode (EI). Twenty-one PCB congeners, with three pairs of coeluting congeners (PCB-18, -74, -66, -99, -118, -105, -153/132, -141, -164/163, -138, -128, -187, -180, -170, -199, -203/196, -206, and -209) and 18 OCPs (α-, *β*-, *γ*-, *δ*-HCH and *p, p'*-DDE, *p, p*-DDD, *p, p'*-DDT, heptachlor, heptachlor epoxide, aldrin, dieldrin, endrin, endrin ketone, endrin aldehyde, endosulfan I, endlsulfan II, endosulfan sulfate, and methoxychlor) were analyzed by Agilent 6890 GC/5975B MSD using EI mode. Detailed analytical procedure and instrumental analysis conditions are given in the SI. The limit of detection (LOD), defined as a signal/noise ratio (S/N) = 3, ranged from 0.001 to 1.45 ng/g lw for PBDEs, 0.006 to 0.27 ng/g for PBB-153, 0.053 to 2.49 ng/g for DeBDethane, 0.02 to 3.82 ng/g for PCBs, and 0.01 to 9.16 ng/g for OCPs, respectively.

Quality Assurance (QA)/Quality Control (QC). Instrumental QC included regular injection of solvent blanks and standard solutions. For methods QC, three procedural blanks, triplicate spiked blanks, and triplicate spiked matrices were analyzed. Only trace levels of BDE-47 and -99 were detected in blanks and the mean concentrations were subtracted from those in samples. BDE-153 and -209 and PCB-153, -138, -128, -187, and -209 were also detected in blanks, but at nonquantifiable (S/N < 3) levels.

The surrogate standard recoveries in 26 samples were 65.4−102% for $^{13}C_{12}$−PCB-141, 72.0−113% for CDE-99, 83.9−113% for PCB-65, 72.1−130% for PCB-204 (relative standard deviations [RSD] < 15.0%), and 47.9−128% for ^{13}C-BDE-209 (RSD = 26.2%). Details of recoveries of individual PBDE and PCB congeners in triplicate spiked blanks and triplicate spiked matrices are given in the SI. Reported concentrations were not surrogate recovery corrected in the present study.

Data Analysis. For samples with concentration below LOD, zero was used for the calculations. All levels are presented on a lipid weight (lw) basis. ΣPBDEs is defined as the sum of the 12 most frequently detected congeners (BDE-28, -47, -99, -100, -153, -183, -196, -203, -206, -207, -208, and -209). ΣPCBs is defined as the sum of 21 congeners. ΣHCHs and ΣDDTs are defined as the sum of α-, *β*-, *γ*-, and *δ*-HCHs and the sum of *p, p'*-DDE, *p, p'*-DDD, and *p, p'*-DDT, respectively. Spearman rank correlations were calculated between the ΣPBDEs and ΣPCBs. The size of samples of giant panda is small and hampered the comparison among tissues, while the differences of contaminants among tissues of red panda were analyzed using one-way analysis of variance (ANOVA). Statistical analysis was performed using SPSS 11.5 for Windows (SPSS Inc., Chicago, IL). The level of significance was set at $\alpha = 0.05$ throughout this study.

Results and Discussion

OCPs in Panda Tissues. Among OCPs analyzed, DDTs were the most prevalent contaminants in panda tissues (Table S2). *p,p'*-DDE and *p,p'*-DDD were detected in all samples and *p,p'*-DDT was detected in 80% of samples. The mean concentrations of DDTs in giant and red panda livers were not significantly different ($p > 0.05$). However, the mean concentrations of DDTs in giant panda livers were higher than those in red pandas, indicating that these sample regions experience different sources of input. For red pandas, no significant difference ($p > 0.05$) has been found among various tissues, and the general order of increasing concentrations is kidney ≤ adipose < liver < muscle (Table 1). The concentrations of DDTs in giant panda and red panda livers were lower than those in raccoon dogs (*Nyctereutes procyonoides*) from Japan (*23*). The concentrations of DDTs in panda livers were similar to those in polar bears from Alaska (*24*) and grizzly bears from British Columbia (*25*). The concentrations of DDTs in red panda adipose tissues were lower than in those of pork adipose from Romania (*26*).

p, p'-DDE was the predominant compound in panda tissues, accounting for more than 50% of total DDT concentrations in various tissues (Figure 1). The high *p, p'*-DDE levels detected in this study were not particularly surprising as many previous studies have shown that *p, p'*-DDT can be biodegraded to *p, p'*-DDE under aerobic condition and to *p, p'*-DDD under anaerobic condition; this suggests that the aged DDTs residues from the environment might be major exposure sources of DDTs (*27*). In addition, the contribution of *p, p'*-DDT to the total DDT concentrations in giant panda livers (26%) was higher than in corresponding tissues of red panda (9.17%, Figure 1). This result may reflect different metabolic reactions to DDTs of giant panda and red panda, or of pandas exposed to different contamination sources.

HCHs were the second most prevalent OCP compound in panda tissue samples. The concentration of ΣHCHs ranged from not detectable (under the LOD) to 282 ng/g lw. *β*-HCH was the only HCH isomer detected in giant panda tissues,

TABLE 1. Orgnohalogen Compound Levels (ng/g lw) and Lipid% in Various Tissues of Giant Panda and Red Panda

tissue	lipid % (SD)	ΣHCHs	ΣDDTs	ΣPCBs	ΣPBDEs	PBB153	DeBDethane
			Giant Panda				
liver	18.5	nd-92.7	16.3−83.2	24.8−697	38.4−742	nd-0.3	1.60−21.2
(n = 4)	(10.7)[a]	(24.3)[b,c]	(41.9)	(289)	(228)	(0.1)	(11.8)
kidney (n = 2)	76.5	46.7−192	25.5−29.2	29.9−35.3	62.4−68.7	nd	nd-2.98
brain (n = 1)	74.9	138	26.5	27.6	83.0	nd	0.1
gonad (n = 1)	1.28	n.d	888	402	2158	nd	863
			Red Panda				
liver	23.1	25.3−99.7	14.6−56.2	53.1−551	52.6−581	nd-0.397	5.97−10.3
(n = 4)	(7.03)	(56.9)	(36.3)	(221)	(211)	(0.1)	(8.05)
kidney	31.6	nd	16.5−30.5	68.5−107	68.4−227	nd	nd-18.3
(n = 3)	(10.3)		(25.2)	(84.7)	(131.8)		(7.43)
muscle	12.9	nd-282	26.1−238	34.2−854	25.3−2045	nd-0.367	nd-40.9
(n = 6)	(7.91)	(87.2)	(90.1)	(206)	(434)	(0.063)	(13.3)
adipose	83.3	25.2−40.0	20.7−33.5	43.7−80.7	16.4−279	nd	nd-8.36
(n = 4)	(10.9)	(33.7)	(25.2)	(60.5)	(91.7)		(3.01)

[a] Values in parentheses are the relative standard deviations for lipid contents and the mean concentrations for others. [b] Values in parentheses are the relative standard deviations for lipid contents and the mean concentrations for others. [c] nd, Below the limit of detection.

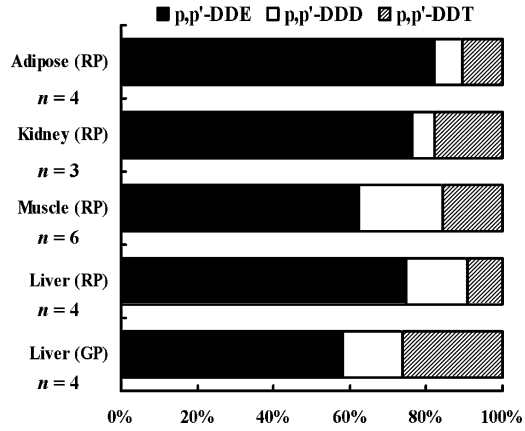

FIGURE 1. Composition (%) of DDT compounds in various tissues of giant panda (GP) and red panda (RP).

except for one brain sample with trace amounts of α-HCH and δ-HCH. For red panda tissues, β-HCH was also the predominant isomer, accounting for 55.2−100% of total HCH concentrations in most samples (Table S2). This β-HCH dominating profile in pandas is in accordance with the earlier findings that β-HCH is the most persistent isomer in environment (*28*) and has higher biomagnification capability than other isomers (*29*). However, two red panda muscle samples showed relatively high concentrations of γ-HCH (110 ng/g lw and 211 ng/g lw), suggesting exposure to technical lindane in some individuals analyzed in this study. The concentrations of HCHs in tissues of giant and red panda were lower than those in birds inhabiting areas of Shanghai City, respectively (*30*). The concentrations of HCHs in red panda adipose tissues were higher than those in pork adipose from Romania (*26*).

PCBs in Panda Tissues. The concentration of PCBs ranged from 24.8 to 697 ng/g lw (mean 289 ng/g lw) in giant panda livers, and 53.1 to 551 ng/g lw (mean 221 ng/g lw) in red pandas (Table 1 and Table S3). For red pandas, concentrations of PCBs were not significantly different among the tissue samples (p > 0.05). The mean concentrations of PCBs in livers and muscles were almost similar and were 2- to 3-fold higher than those in adipose tissues and kidneys. Compared with the PCB levels of pork tissues from Romania, the levels in corresponding tissues of giant and red panda were higher (*26*).

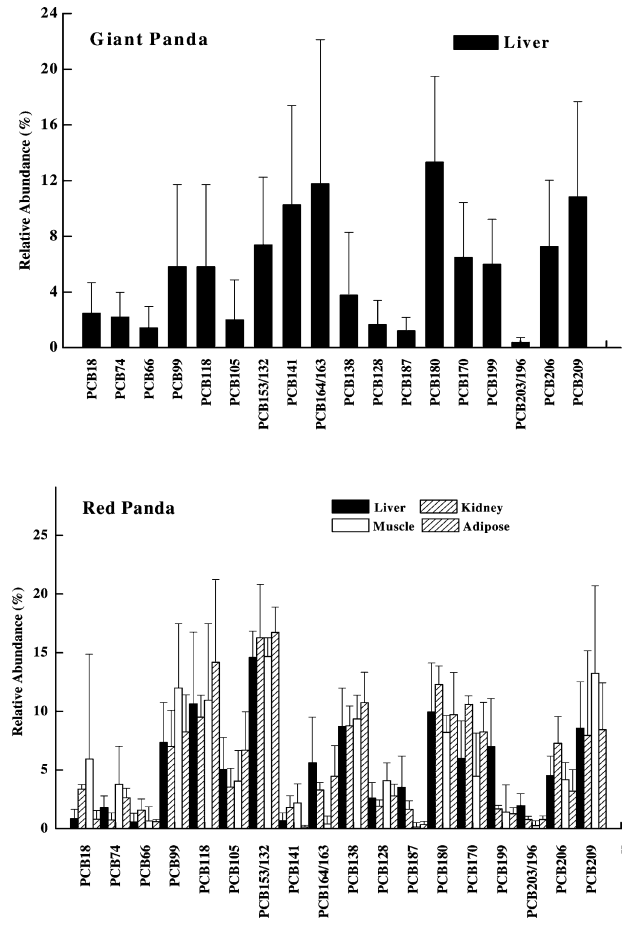

FIGURE 2. PCB congener profiles in various tissues of individual giant and red pandas.

PCB congener profiles in panda tissues showed that PCBs 99, 118, 153/132, 170, 180, and 209 were the major contributing congeners (Figure 2). The Σ(PCBs 99, 118, 153/132, 170, 180, and 209) accounted for 54 and 63% of the total congener concentrations for giant panda and red panda, respectively. These congeners shared the characteristic of having chlorine atoms in both ortho positions and in positions 2 and 5 in one (PCBs 99, 118, and 170) or both (PCBs 153/132, 180, and 209) rings. Di-ortho PCB congeners with chlorine substitution at para and meta positions in both rings

are hard to metabolize (*31*). Higher contributions of PCB 141 and 164/163 to the total PCBs for giant panda livers were observed, which indicated that different metabolism activity of PCBs between giant panda and red panda (Figure 2).

The relative toxic potential of coplanar PCBs in tissues was calculated using the World Health Organization toxic equivalency factors (*32*). The dioxin-like PCB congeners, including 118 and 105, were used to calculate the total toxic equivalent (TEQ) in the present study. The TEQ varied from 0.05 pg/g lw to 10.7 pg/g lw in panda tissues (Table S3). For giant panda, the concentration of TEQ in liver was 1.61 pg/g lw. For red panda, the lowest and highest concentrations of TEQ were found 0.64 pg/g lw for adipose tissues and 10.7 pg/g lw for muscles. PCB 118 has greater contribution of TEQ and accounted for 71% of the total TEQ in tissue samples of pandas in the study. Although the TEQ concentrations in pandas in the present study were low, the cocktail effects of other contaminants such as DDTs, HCHs, PBDEs and species-specific sensitivity should not be ignored.

PBDEs in Pandas Tissues. With the exception of BDE-66 and BDE-154, 12 other PBDE congeners were detected in at least 70% of all tissue samples (Table S4). The total PBDE concentrations in giant panda tissue samples ranged from 38.4 to 2158 ng/g lw. The highest PBDE concentration was found in gonad adipose tissue from individual male pandas, while the lowest PBDE concentration was found in the brain tissues of individual females. No comparison was performed among the various tissues of giant panda due to small sample sizes. Although no significant differences were observed for the total PBDE concentrations among various red panda tissues, the mean total concentrations of PBDEs in various red panda tissues generally decreased in order of muscle > liver > kidney > adipose (Table 1). The total concentrations of PBDEs in giant panda livers were similar to that of red panda.

In general, the concentrations of PBDEs in giant panda are 1−3 orders of magnitude higher than concentrations reported for polar bears from Alaska (*24*), and 1−2 orders of magnitude lower than concentrations in common kestrels (*Falco tinnunculus*) from the central areas of Beijing assayed in a previous study (*15*). The concentrations of PBDEs in livers of giant and red panda were higher than those of common buzzards (*Buteo buteo*) from Beijing areas (*15*) and lower than those of hens from Taizhou, Zhejiang Province (*33*). The concentrations of PBDEs in muscles and adipose tissues of red panda were also lower than those of hens from Zhejiang Province (*33*).

The percent congener contributions to the sum of PBDEs (12 BDEs) were calculated for livers in giant panda and various tissues in red panda (Figure 3). BDE-209, with levels from 5.09 to 1479 ng/g lw, was the major BDE congener in this study, accounting for 51.6 and 42.5% of the sum of PBDEs in giant and red pandas, respectively. It was followed by BDE-206, BDE-208, BDE-207, BDE-203, BDE-47, and BDE-153 (Figure 3). The liver PBDE congener patterns in giant and red pandas were similar to each other, even though their absolute concentrations were different. The congener-specific pattern observed in this study was in accordance with several studies on terrestrial biota, such as foxes (*16*), birds of prey (*15*), and polar bears (*34*), which showed that BDE-209 has been the dominant congener in several specimens. These results suggest that terrestrial biota may accumulate highly brominated congeners to higher levels than do aquatic biota. For less brominated congeners, BDE-47 and BDE-153 were the predominant in this study, which was similar to other studies on tissues of hens from Taizhou, Zhejiang province (*33*).

It was worthwhile to note that all the samples contained very high concentrations of octa- and nona-BDEs (BDE-196, 203, 206, 207, and 208), which are thought to degrade from

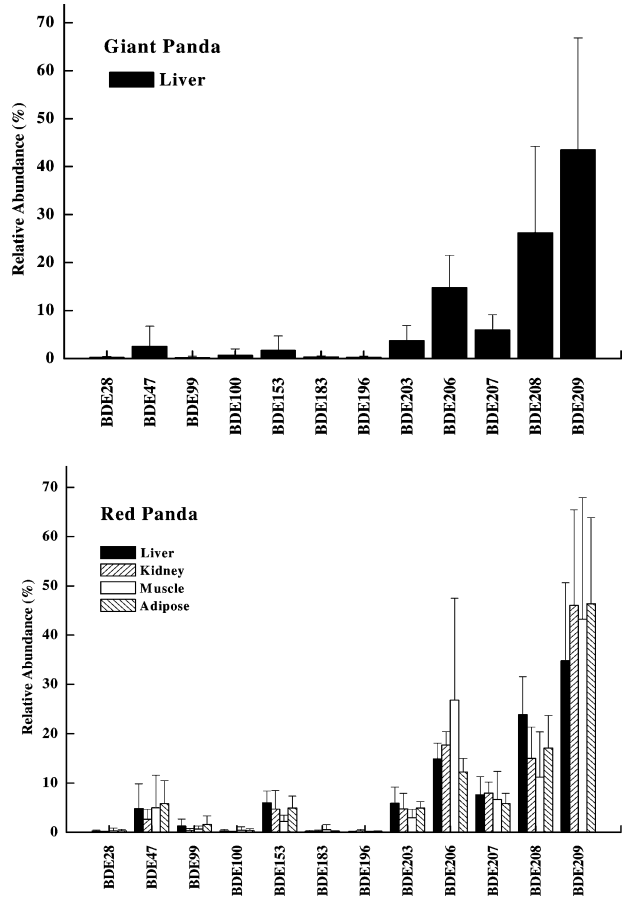

FIGURE 3. PBDE congener profiles in various tissues of individual giant and red pandas. BDE-66 was excluded from these profiles due to modest contributions levels.

deca-BDE technical products. Figure S2 displays a comparison among the profiles of octa- through deca-BDE congeners found in pandas and technical deca-BDE mixtures from Europe (Bromkal 82−0DE), North America (Saytex 102E), and China (Deca-1 and Deca-2) (*35*). It is obvious that the contributions of octa- to nona-BDEs in panda tissues were significantly higher than those in technical mixtures, which could be attributed to the preferential accumulation of octa- and nona-BDEs as expected by their longer half-lives (*36*). An alternative explanation for this is that BDE-209 could metabolically debrominate to octa- and nona-BDEs. Further comparison of the PBDE profiles in livers between giant and red panda showed that the octa- to nona-BDEs and other two dominant low brominated congeners (BDE-47 and -153) had higher abundances in red pandas than in giant pandas (Figure 3). Specifically, the average Σ(octa- to nona-BDEs)/Σ(octa- to deca-BDEs) ratios in giant pandas were 0.5 for liver; for red pandas, ratios were greater and remarkably constant (0.6, 0.5, 0.5, and 0.5 for liver, kidney, muscle, and adipose, respectively). This suggests that the metabolic turnover of BDE-209 in red pandas is higher than in giant pandas. The mean age of the giant pandas sampled (14.5 years) was greater than that of red pandas (3∼4 years), which may have impacted PBDEs accumulation. In addition, the energy digestibility and assimilation rates for red panda are much higher than those of giant panda, which could contribute to the differences (*37*). However, differences in the exposure concentrations and elimination half-lives among congeners between giant panda and red panda cannot be ruled out due to differences in the sampling locations and dietary compositions (Table S1).

The origin of the BDE-209 contamination in pandas is intriguing. The most deca-BDE in the surface water and air

originated from the textile industry, chemical industry, electronics, plastics industries (*38*), and wastewater treatment plant (*39*). No comparable data are available for China, but all these industries are substantial in China. In addition, it has been reported that BDE-209 levels in urban air samples from China were higher than those in North American and European studies (*40*). The pandas in the present study were captive in zoos in relatively urbanized and industrialized areas, and were offered milk and cakes made of rice, corn, soybeans, and honey, as a part of their diet. The giant panda in captivity was surrounded by iron bars and brick wall. The cages of pandas in captivity were disinfected with a solution of sodium hypochlorite at one time per week in summer and two weeks in winter. The expected sources might be due to the consumption of the contaminated food, ingestion of dusts from environment, and exposure to the detergent during cleaning the cages. In addition, status of sickness may be influence on metabolism of PBDEs (*41*). This suggests that the higher burdens of the more brominated congeners, including BDE-209, may originate from urban PBDE sources at these different locations. Uptake can be considered as main routes via exposure to products or degradates or via the food. Although so far very few data exist on the ability of different species to debrominate/metabolize BDE-209, these results indicate that significant bioaccumulation of BDE-209 can occur in terrestrial mammals (*42*). Clearly, the number of samples obtained in this study is not enough to indicate precisely the main sources of deca-BDE in captive pandas.

DeBDethane and PBBs. PBB153 was detected at a detection frequency of 60% in samples, but the concentrations of PBB153 were very low, ranging from not detectable to 0.397 ng/g lw. PBBs were introduced as flame retardants in the early 1970s, but their production was banned in the U.S. in 1976. PBBs have been extensively reported in various biota samples (*43*). However, most of the data on PBBs exposure comes from aquatic biota, hampering comparison with the present measurements in terrestrial animals. It is not known whether the low current PBBs concentrations observed in pandas are the result of natural decay. The source of PBB 153 in pandas is unclear.

DeBDethane was detected at a detection frequency of 87% for giant panda tissues and 71% for red pandas tissues (Figure S3). The highest DeBDethane concentration (863 ng/g lw) was found in giant panda gonad tissue and was at least 20-fold higher than in other giant and red panda tissues. The average DeBDethane concentrations in giant panda livers were greater than those in red panda (Table 1). The DeBDethane/BDE-209 ratio ranged from 0.01 to 1.67, where the highest ratios were found in samples with low to medium levels of BDE-209. Although all samples in which DeBDethane was detected also contained BDE-209, the differing DeBDethane/BDE-209 ratio supports the assumption that the products are used independently. DeBDethane is only sporadically detected in the environment because it has been used as an additive flame retardant to replace the deca-BDE mixture from the early 1990s. It is only recently that DeBDethane has been found in air, sediment, sewage sludge, and household dust at the same concentrations as several of the most abundant BDEs (*44*). Since DeBDethane has the same applications as BDE-209, it may be used in many different types of products. In addition to leakage during industrial production/application of the chemical, consumer products are potential sources of DeBDethane to the environment. DeBDethane uptake via air may be an important exposure route for pandas, although only sparse information concerning DeBDethane production in China is available.

DeBDethane is of special interest because it, like deca-BDE, is believed to be nonbioavailable and to be a virtually harmless compound due to its large molecular size and low water solubility. Our reports suggest that the high DeBDethane levels could occur in the captive wildlife samples. In addition, the results of analyses of environmental matrices also showed that DeBDethane is widespread in the environment in China (data not shown). To our knowledge, this is the first report that DeBDethane occurs in captive wildlife samples. Therefore, further studies are warranted to better understand DeBDethane production, transport, uptake, and toxicological effects on terrestrial mammals.

Relationships between Brominated and Chlorinated Organic Compounds. Significant correlation was found between PBDE and PCB concentrations in giant and red panda tissue samples ($p < 0.01$, Figure S4), while no significant correlation was observed between PBDE/PCB and DDT concentrations. This result suggests that PBDEs occur with PCBs, and that the sources of PBDE and PCB exposure may be similar in Beijing and Chongqing. Inhalation of air as well as diet may be potential sources (*45, 34*), including uptake from environmental dust (*46*). This result indicates that the exposure sources of OCPs might be different from those of PCBs and PBDEs. On the other hand, the important toxicokinetics factors pertaining to the absorption, assimilation, oxidative metabolism (CYP-mediated), protection from phase II enzymes, and excretion cannot be excluded, which may differ between structurally diverse contaminant classes, species, and sex. Therefore, it is difficult to readily interpret the relationships among different contaminants in the present study.

Our study provides pandas BFRs exposure data and increases the number of observed BFRs accumulation trends in captive terrestrial mammals. However, since the number of panda samples in our current study was small, and samples were from zoos, the results may not reflect BFRs accumulation in the wild animal population. Risk assessments for BFRs are not available at present, because information on physiological, toxicological, and ecological effects of BRFs is rare. Therefore, only when more species-specific information on BFRs becomes available will risk assessments for captive wildlife be possible. Although our findings provide significant information on PBDEs and DeBDethane in pandas, further studies with larger numbers of samples are necessary to further understand their sources and accumulation routes and to evaluate their potential toxic effects to captive wildlife.

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Supporting Information Available

Additional sampling information and locations is in Table S1 and Figure S1, DDT concentrations in Table S2, PCB concentrations in Table S3, PBDE concentrations in Table S4, a comparison of octa- through deca-BDE congeners in Figure S2, of DeBDethane and BDE-209 in Figure S3, and correlation between PBDE and PCB concentrations in Figure S4. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945–956.
(2) Van Esch, G. Environmental Health Criteria 162: Brominated diphenyl ethers; World Health Organization: Geneva, Switzerland; 1994; http://www.inchem.org/documents/ehc/ehc162.htm.
(3) Directive 2003/11/EC of the European parliament and of the council amending for the 24th time council directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (pentabromodiphenylether, octabromodiphenyl ether).

(4) Renner, R. In U.S., flame-retardants will be voluntarily phased out. *Environ. Sci. Technol.* **2004**, *38* (1), 14A
(5) Law, R. J.; Allchin, C. R.; de Boer, J.; Covaci, A.; Herzke, D.; Lepom, P.; Morris, S.; Tronczynski, J.; de Wit, C. A. Levels and trends of brominated flame retardants in the European environment. *Chemosphere* **2006**, *64*, 187–208.
(6) http://www.fireren.com/article/lunwen/200485142302.htm.
(7) http://soci.com.cn/resource/2610.htm.
(8) http://www.taixinghuagong.com/forum/index.php?action=vthread&forum=4&topic=9.
(9) De Voogt, P.; Wells, D. E.; Reutergardh, L.; Brinkman, U. A. Th. Review: biological activity, determination and occurrence of planar, mono- and di-ortho PCBs. *Int. J. Environ. Anal. Chem.* **1990**, *40*, 1–46.
(10) Mai, B.; Zeng, E.; Luo, X.; Yang, Q.; Zhang, G.; Li, X.; Sheng, G.; Fu, J. Abundances, depositional fluxes, and homologue patterns of polychlorinated biphenyls in dated sediment cores from the Pearl River Delta, China. *Environ. Sci. Technol.* **2005**, *39*, 49–56.
(11) Zhang, G.; Parker, A.; House, A.; Mai, B.; Li, X.; Kang, Y.; Wang, Z. Sedimentary records of DDT and HCH in the Pearl River Delta, South China. *Environ. Sci. Technol.* **2002**, *36*, 3671–3677.
(12) Lee, R. G. M.; Thomas, G. O.; Jones, K. C. PBDEs in the atmosphere of three locations in Western Europe. *Environ. Sci. Technol.* **2004**, *38*, 699–706.
(13) Litten, S.; McChesney, D. J.; Hamilton, M. C.; Fowler, B. Destruction of the World Trade Center and PCBs, PBDEs, PCDD/Fs, PBDD/Fs, and chlorinated biphenylenes in water, sediment, and sewage sludge. *Environ. Sci. Technol.* **2003**, *37*, 5502–5510.
(14) Mai, B.; Chen, S.; Luo, X.; Chen, L.; Yang, Q.; Sheng, G.; Peng, P.; Fu, J.; Zeng, E. Distribution of polybrominated diphenyl ethers in sediments of the Pearl River Delta and adjacent South China Sea. *Environ. Sci. Technol.* **2005**, *39*, 3521–3527.
(15) Chen, D.; Mai, B.; Song, J.; Sun, Q.; Luo, Y.; Luo, X.; Zeng, E.; Hale, R. C. Polybrominated diphenyl ethers in birds of prey from Northern China. *Environ. Sci. Technol.* **2007**, *41*, 1828–1833.
(16) Voorspoels, S.; Covaci, A.; Lepom, P.; Escutenaire, S.; Schepens, P. Remarkable findings concerning PBDEs in the terrestrial top-predator red fox (*Vulpes vulpes*). *Environ. Sci. Technol.* **2006**, *40*, 2937–2943.
(17) Bi, X.; Qu, W.; Sheng, G.; Zhang, W.; Mai, B.; Chen, D.; Yu, L.; Fu, J. Polybrominated diphenyl ethers in South China maternal and fetal blood and breast milk. *Environ. Pollut.* **2006**, *144*, 1024–1030.
(18) Darnerud, P. O. Toxic effects of brominated flame retardants in man and in wildlife. *Environ. Int.* **2003**, *29*, 841–853.
(19) Zala, S. M.; Penn, D. J. Abnormal behaviors induced by chemical pollution: a review of the evidence and new challenges. *Anim. Behav.* **2004**, *68*, 649–664.
(20) Wei, F.; Feng, Z.; Wang, Z.; Hu, J. Current distribution, status and conservation of wild red pandas *Ailurus fulgens* in China. *Biol. Conserv.* **1999**, *89*, 285–291.
(21) Sonne, C.; Dietz, R.; Leifsson, P. S.; Born, E. W.; Letcher, R. J.; Kirkegaard, M.; Muir, D. C.; Riget, F. F.; Hyldstrup, L. Do organohalogen contaminants contribute to histopathology in liver from East Greenland polar bears (*Ursus maritimus*). *Environ. Health Perspect* **2005**, *113*, 1569–1574.
(22) Yeung, L. W.; So, M. K.; Jiang, G.; Taniyasu, S.; Yamashita, N.; Song, M.; Wu, Y.; Li, J.; Giesy, J. P.; Guruge, K. S.; Lam, P. K. Perfluorooctanesulfonate and related fluorochemicals in human blood samples from China. *Environ. Sci. Technol.* **2006**, *40*, 715–720.
(23) Kunisue, T.; Takayanagi, N.; Tsubota, T.; Tanabe, S. Persistent organochlorines in raccoon dogs (*Nyctereutes procyonoides*) from Japan: Hepatic sequestration of oxychlordane. *Chemosphere* **2007**, *66*, 203–211.
(24) Kurunthachalam, K.; Se, H. Y.; Thomas, J. E. Chlorinated, brominated, and perfluorinated contaminants in livers of polar bears from Alaska. *Environ. Sci. Technol.* **2005**, *39*, 9057–9063.
(25) Christensen, J. R.; MacDuffee, M.; Yunker, M. B.; Ross, P. S. Hibernation-associated changes in persistent organic pollutant (POP) levels and patterns in British Columbia grizzly bears (*Ursus arctos horribilis*). *Environ. Sci. Technol.* **2007**, *41*, 1834–1840.
(26) Covaci, A.; Adriana Gheorghe, A.; Schepens, P. Distribution of organochlorine pesticides, polychlorinated biphenyls and α-HCH enantiomers in pork tissues. *Chemosphere* **2004**, *56*, 757–766.
(27) Kalantzi, Q. I.; Alcock, R. E.; Joheston, P. A.; Santillo, D.; Stringer, R. L.; Thomas, G. O.; Jones, K. C. The global distribution of PCBs and organochlorine pesticides in butter. *Environ. Sci. Technol.* **2001**, *35*, 1013–1018.
(28) Mohn, W. M.; Tiedje, J. M. Microbial reductive dechlorination. *Microbiol. Rev.* **1992**, *56*, 482–507.
(29) Lundstedt-Enkel, K.; Tysklind, M.; Trygg, J.; Schüller, P.; Asplund, L.; Eriksson, U.; Häggberg, L.; Odsjö, T.; Hjelmberg, M.; Olsson, M.; Örberg, J. A statistical resampling method to calculate biomagnification factors exemplified with organochlorine data from herring (*Clupea harengus*) muscle and guillemot (*Uria aalge*) egg from the Baltic Sea. *Environ. Sci. Technol.* **2005**, *39*, 8395–8402.
(30) Nakata, H.; Hirakawa, Y.; Masahiro Kawazoe, M.; Nakabo, T.; Arizono, K.; Abea, S.; Kitano, T.; Shimada, H.; Watanabe, I.; Li, W.; Ding, X. Concentrations and compositions of organochlorine contaminants in sediments, soils, crustaceans, fishes and birds collected from Lake Tai, Hangzhou Bay and Shanghai city region, China. *Environ. Pollut.* **2005**, *133*, 415–429.
(31) Kannan, N.; Reusch, T. B. H.; Schulz-Bull, D. E.; Petrick, G.; Duinker, J. C. Chlorobiphenyls: model compounds for metabolism in food chain organisms and their potential use as ecotoxicological stress indicators by application of the metabolic slope concept. *Environ. Sci. Technol.* **1995**, *29*, 1851–1859.
(32) Van den Berg, M.; Birnbaum, L.; Bosveld, A. T.; Brunström, B.; Cook, P.; Feeley, M.; Giesy, J. P.; Hanberg, A.; Hasegawa, R.; Kennedy, S. W.; Kubiak, T.; Larsen, J. C.; van Leeuwen, F. X.; Liem, A. K.; Nolt, C.; Peterson, R. E.; Poellinger, L.; Safe, S.; Schrenk, D.; Tillitt, D.; Tysklind, M.; Younes, M.; Waern, F.; Zacharewski, T. Toxic equivalency factors (TEFs) for PCBs,PCDDs, PCDFs for humans and wildlife. *Environ. Health Perspect* **1998**, *106*, 775–792.
(33) Liang, S.; Zhao Q.; Qin, Z.; Zhao, X.; Yang, Z.; Xu, X. Levels and distribution of polybrominated diphenyl ethers in various tissues of foraged hens from an electronic wastes recycling area in South China. *Environ. Toxicol. Chem.* **2008**, DOI: 10.1897/07−518.
(34) Christensen, J. R.; MacDuffee, M.; Macdonald, R. W.; Whiticar, M.; Ross, P. S. Persistent organic pollutants in British Columbia grizzly bears: consequence of divergent diets. *Environ. Sci. Technol.* **2005**, *39*, 6952–6960.
(35) La Guardia, M. J.; Hale, R. C.; Harvey, E. Detailed polybrominated diphenyl ether (PBDE) congener composition of the widely used penta-, octa-, and deca-PBDE technical flame-retardant mixtures. *Environ. Sci. Technol.* **2006**, *40*, 6247–6254.
(36) Thuresson, K.; Hoglund, P.; Hagmar, L.; Sjodin, A.; Bergman, A.; Jakobsson, K. Apparent half-lives of hepta- to deca-brominated diphenyl ethers in human serum as determined in occupationally exposed workers. *Environ. Health Perspect* **2006**, *114*, 176–181.
(37) Wei, F.; Wang, Z.; Feng, Z.; Li, M.; Zhou, A. Seasonal energy utilization in bamboo by the red panda (*Ailurus fulgens*). *Zoo Biol.* **2000**, *19*, 27–33.
(38) Hale, R. C.; La Guardia, M. J.; Harvey, E.; Gaylor, M. O.; Mainor, T. M. Brominated flame retardant concentrations and trends in abiotic media. *Chemosphere* **2006**, *64*, 181–186.
(39) La Guardia, M.; Hale, R. C.; Harvey, E. Evidence of debromination of decabromodiphenyl ether (BDE-209) in biota from a wastewater receiving stream. *Environ. Sci. Technol.* **2007**, *41*, 6663–6670.
(40) Chen, L.; Mai, B.; Bi, X.; Chen, S.; Wang, X.; Ran, Y.; Luo, X.; Sheng, G.; Fu, J.; Zeng, E. Concentration levels, compositional profiles, and gas-particle partitioning of polybrominated diphenyl ethers in the atmosphere of an urban city in South China. *Environ. Sci. Technol.* **2006**, *40*, 1190–1196.
(41) Dye, J. A.; Venier, M.; Zhu, L.; Ward, C.; Hites, R. A.; Birnbaum, L. S. Elevated PBDE levels in pet cats: sentinels for humans. *Environ. Sci. Technol.* **2007**, *41*, 6350–6356.
(42) Herzke, D.; Berger, U.; Kallenborn, R.; Nygard, T.; Vetter, W. Brominated flame retardants and other organobromines in Norwegian predatory bird eggs. *Chemosphere* **2005**, *61*, 441–449.
(43) Zhu, L.; Hites, R. A. Temporal trends and spatial distributions of brominated flame retardants in archived fishes from the Great Lakes. *Environ. Sci. Technol.* **2004**, *38*, 2779–2784.
(44) Kierkegaard, A.; Bjorklund, J.; Friden, U. Identification of the flame retardant decabromodiphenyl ethane in the environment. *Environ. Sci. Technol.* **2004**, *38*, 3247–3253.
(45) Jones-Otazo, H. A.; Clarke, J. P.; Diamond, M. L.; Archbold, J. A.; Ferguson, G.; Harner, T.; Richardson, G. M.; Ryan, J. J.; Wilford, B. Is house dust the missing exposure pathway for PBDEs? An analysis of the urban fate and human exposure to PBDEs. *Environ. Sci. Technol.* **2005**, *39*, 5121–5130.
(46) Shoeib, M.; Harner, T.; Ikonomou, M.; Kannan, K. Indoor and outdoor air concentrations and phase partitioning of perfluoroalkyl sulfonamides and polybrominated diphenyl ethers. *Environ. Sci. Technol.* **2004**, *38*, 1313–1320.

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