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Residues of Polybrominated Diphenyl Ethers in Honeys from Different Geographic Regions

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Polybrominated diphenyl ethers (PBDEs) are a class of widely used flame-retardants. Fifty honey samples labeled as being from different countries and regions were analyzed for 27 PBDE congeners. The concentrations of the 26 PBDEs, excluding BDE-209, ranged from 300 to 10,550 pg/g while the concentrations of BDE-209 ranged from nondetected to 9,260 pg/g. The honey samples labeled as originating in developed countries generally displayed higher concentrations of the total 27 PBDEs than those labeled as being from developing countries. Concentrations of 26 PBDEs ranged from 2,720 to 10,550 pg/g in honeys originating in developed countries and ranged from 1,030 to 3,470 pg/g in those from developing countries. BDE-209 was a dominant PBDE congener in all honey samples, on average accounting for 16% and 65% of the total 27 PBDEs in honeys from developed and developing countries, respectively. Honeys originating in developing countries, however, showed much higher BDE-209 levels and higher ratios of BDE-209 relative to the other PBDE congeners. In addition, some highly brominated PBDE congeners such as BDE-196, -197, -206, and -207 showed elevated concentrations in honeys from developing countries. The findings were in agreement with the long, heavy historical uses of PBDE products in developed countries and the current, heavy uses of BDE-209 in developing countries. When BDE-209 was fortified in honey and incubated in the dark for four weeks at 25 or 60 °C, BDE-153, -183, -206, and -207 were detected as debromination products of BDE-209. Less brominated congeners in honeys may primarily come from the environment. Debromination of BDE-209 is also a source of less brominated congeners in honeys. The detection of PBDEs in honeys suggests that human exposure to PBDEs occurs as a result of honey consumption.

KEYWORDS: Honey; polybrominated diphenyl ethers (PBDEs); food contamination; food safety

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are used extensively as flame retardants. Because of large production volumes, widespread usage, and their persistence, PBDEs are now widespread in the environment (*1*−*3*). The most common commercial PBDE products worldwide are the penta-, octa- and deca-BDE mixtures. The total world PBDE production was approximately 67,000 t in 2001 (*4*), of which deca-BDE mixtures accounted for 75% of the total PBDE production (*3*). The commercial deca-BDE product consists mainly (>95%) of the deca-congener (BDE-209) (*5*). Previous reports have shown that PBDEs can enter the ambient environment during production, use, disposal, and recycling processes (*6*). PBDEs have been detected in virtually all environmental media such as air, water, sediment, soil and plants (*1*−*3*,*7*,*8*). PBDE contamination has become an emerging environmental concern in recent years, which is attracting attention from the public and environmental community.

PBDEs can enter into the food chain *via* bioaccumulation in fats or nonfatty products (*9*) and, thus, may present a potential threat to human health. PBDEs have been detected in human fat tissues, blood, and breast milk (*10*). PBDE concentrations in the environment and humans have increased rapidly in the past two decades (*11*). The main route of exposure to PBDEs in the general human population is through consumption of PBDE-contaminated food (*12*) and inhalation of vapor-phase chemicals in contaminated indoor environments (*13*). PBDE-contaminated food includes fish, dairy products, meat, eggs, and vegetables (*14*). Dietary exposure is a very important route of exposure to PBDEs (*15*).

PBDE residues in various foods have been documented. For example, market basket surveys were performed for the content of PBDEs in food items in Europe and North America (*1*,*9*,*16*,*17*). The main PBDE congeners included BDE-47, -99, -100, -153, and -209 in fish, meat, dairy products, vegetables, and other food items. BDE-47 was the most dominant, and its concentration was 5−46000, 3−740, 6−240, 4−120, and nd−90 pg/g wet weight (ww), respectively (*9*, *16*, *17*). Due to highly bioaccumulative potential of PBDEs, fish is believed to be the main contributor of PBDEs to human exposure (*18*,*19*) and thus it has been analyzed to a greater extent than other food groups. The mean reported total PBDE content (∑PBDE) in fish was approximately 4200 pg/g ww

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while the median of the reported ∑PBDE was 1100 pg/g ww worldwide (*18*). High concentrations of PBDEs were found in fatty products such as butter, fats and oils (∑PBDE, 119−569 pg/g ww) (*16*, *20*, *21*). Solid milk products like cheese also contained relatively high amounts of PBDEs (18−34 pg/g ww), while liquid milk products contained very low concentrations of PBDEs (0.8 pg/g ww) (*22*). Concentrations of ∑PBDEs in fast food and beverages were found to be 39−52 and 76 pg/g ww, respectively, in Europe and North America (*17*, *23*). There have been no studies of PBDEs in honey although honey is one of the most popular foods in the world. Honey is often consumed by children and elderly and ill people, particularly in developing countries. Therefore, honey should be free of any chemical contamination and be safe for human consumption.

Honeybees travel long distances and are likely exposed to PBDEs deposited on plants and vegetations *via* atmospheric transfer. Honey, therefore, may contain PBDE residues that would correlate with the PBDE usages and pollution status in a particular region. The objectives of this study were to determine residual levels, compositions and distribution of PBDEs in honey samples from different geographic regions, and to investigate their possible pollution sources.

MATERIALS AND METHODS

Sample Collection. Fifty honey samples were purchased directly from the retail stores or mailed from different regions worldwide. These honeys were labeled with the geographic regions and origin of the country (**Table 1**). They were grouped into developed and developing countries based on the current approximate economic status of the countries. For discussion purposes, New Zealand, Hawaii and Alaska were referred to as background regions due to their geographical isolation and lower populations. All honey samples were stored at −20 °C until extraction and analysis.

Sample Extraction, Cleanup and Fractionation. A mixture of surrogate standards of $^{13}C_{12}$-BDE-3, -15, -28, -47, -99, -153, -154, and -183 was added to 20 g of blank honey samples for recovery studies. The blank honey samples were two honey samples labeled as originating in Hawaii, in which PBDEs were not detected (**Figure 1**). All commercial honey samples and recovery samples (20 g) were mixed with a 3-fold amount of anhydrous sodium sulfate, wrapped with a filter paper, and placed in a 64 mL extraction cell. The remaining volume of the cell was filled up with clean Ottawa sand (20−30 mesh). The sample cell was loaded onto an accelerated solvent extractor (ASE) 200 system (Dionex, Sunnyvale, CA). The extraction was performed with a mixture of equal volumes of acetone and methylene chloride at a pressure of 1500 psi and temperature of 100 °C for three static cycles, a flush volume of 60% of the cell volume and a N_2 purge time of 5 s. Each honey sample was extracted in triplicate, and an equal weight mixture of anhydrous sodium sulfate and Ottawa sand was extracted as the blank control.

After the extract was dried with 30 g of anhydrous sodium sulfate and rinsed with hexane (3 mL), it was concentrated to approximately 3 mL by using a rotary evaporator. The concentrated extract in hexane was cleaned up on an 8 mm i.d. aluminum/silica column. The column was packed, from the bottom to the top, with neutral alumina (6 cm, 3% deactivated), neutral silica gel (10 cm, 3% deactivated), 50% sulfuric acid silica (10 cm), and anhydrous sodium sulfate. The column was eluted with 30 mL of methylene chloride and hexane (1:1, v/v) to yield the PBDE fraction. The fraction was concentrated to 20 μL under a gentle stream of high purity nitrogen after an aliquot of 20 μL of dodecane was added as trapping solvent. A known quantity of $^{13}C_{12}$-PBDE-139 was then added as an internal standard prior to the chemical analysis.

Degradation of BDE-209 in Honey. Solutions of freshly purchased BDE-209 dissolved in acetone were added to aliquots of the same blank honey sample used in recovery tests at a concentration of 20 ng/g. One group of honey samples, fortified with BDE-209 standard, was allowed to incubate at 60 °C in the dark in an oven for four weeks. The incubation temperature was set at 60 °C because honey is often processed at between 60 and 65 °C. Another group of the BDE-209 fortified honey samples was placed at 25 °C in the dark in an oven for four weeks. Each group had triplicate samples. After four weeks, two groups of the honey samples were extracted, cleaned up and fractionated according to the aforementioned method.

Table 1. Geographical Origin Information of the 50 Honey Samples

country	no. of samples	location
	Developed Countries	
USA	13	California, Kansas, Maryland, Virginia, Washington, Wisconsin, North Dakota
U.K.	3	Kent
Canada	2	Ontario
Japan	3	Tokyo
	Developing Countries	
China	2	North Eastern region
India	2	New Delhi
Thailand	2	North Thailand
Indonesia	2	Jakarta
Vietnam	2	South region
Bhutan	2	Bhumtang
Mexico	2	Mexico City
Argentina	1	Buenos Aires
	Background Regions	
USA	10	Oahu and the Big Island, Hawaii
USA	2	Central region, Alaska
New Zealand	2	West coast

Instrumental Analysis. PBDEs were analyzed on a Varian 3800 gas chromatograph (GC) connected with a electron capture detector (ECD) and Saturn 2000 ion trap mass spectrometer (ITMS) (Varian, Walnut Creek, CA). An aliquot of 2.0 μL of sample was injected in splitless mode with an AS8400 autosampler. The purge valve was activated 3 min after the sample injection. The column flow rate was 2 mL/min of carrier gas (helium). Temperatures of the injector and ion trap were 300 and 250 °C, respectively. A 30 m DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used for the separation of BDE-3, -7, -15, -17, -28, -47, -49, -66, -71, -77, -85, -99, -100, -119, -126, -138, -153, -154, -156, -183, -184, and -191. The column temperature was started at 100 °C for 2 min and increased to 250 at 10 °C/min, 265 at 1 °C/min, 300 at 20 °C/min and then was held at 300 °C for 10 min. BDE-196, -197, -207, -206, and -209 were separated on a 15 m DB-5MS column (15 m × 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was programmed from 150 to 300 °C at a rate of 10 °C/min and then held at 300 °C for 10 min. The ITMS was operated under the conditions previously described (*24*, *25*). GC/ITMS parameters were also the same as previously described (*24*, *25*) except that the precursor ion for BDE-196 and 197 and BDE-209 was 642. Because highly brominated PBDEs show higher sensitivity on the ECD than on the MS, GC/ECD was used to monitor BDE-209 degradation in honey.

Quality Control and Quality Assurance. All analytical procedures were performed under quality assurance and quality control protocols. PBDEs were not detected in the three blank controls. The limits of detection (LODs) were determined as signals 3 times the background signals. Peaks that were smaller than 3 times the signal-to-noise ratio were considered nondetected. The LOD of individual PBDE congeners ranged from 1 to 10 pg/g for all PBDE congeners except for BDE-209 (**Table 2**). The LOD for BDE-209 was 30 pg/g. Recoveries of the surrogate standards averaged between 60% and 120% (**Table 2**). Reported values are recovery-corrected.

RESULTS AND DISCUSSION

Fifty honey samples labeled from different countries and regions were analyzed for 27 PBDE congeners. The PBDE congeners were detected in all honey samples except two honey samples labeled from Hawaii. **Table 3** shows the average concentrations and concentration ranges of the PBDEs in honey samples grouped according to the labels as originating in developed and developing countries and background regions.

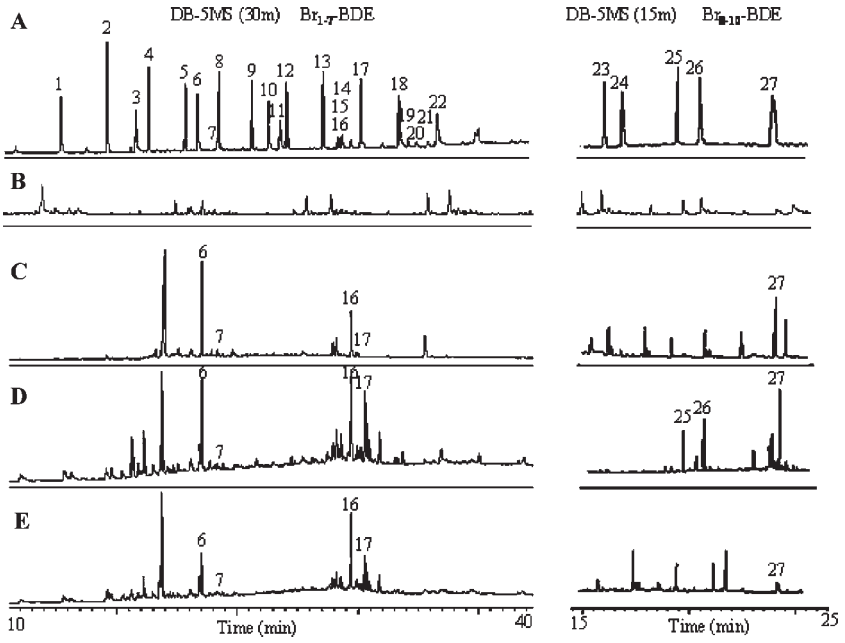

Figure 1. Typical GC/ITMS chromatograms of PBDEs in a standard mixture (50 ppb each congener) (**A**), chromatograms of extracts of a blank control honey sample (**B**) and honey samples from a developed country (**C**), developing country (**D**), and a background region (**E**). Peak 1 (BDE-3), 2 (BDE-7), 3 (BDE-15), 4 (BDE-17), 5 (BDE-28), 6 (BDE-47), 7 (BDE-49), 8 (BDE-71), 9 (BDE-66), 10 (BDE-77), 11 (BDE-85), 12 (BDE-99), 13 (BDE-100), 14 (BDE-119), 15 (BDE-126), 16 (BDE-153), 17 (BDE-154), 18 (BDE-138), 19 (BDE-156), 20 (BDE-183), 21 (BDE-184), 22 (BDE-191), 23 (BDE-196), 24 (BDE-197), 25 (BDE-206), 26 (BDE-207), and 27 (BDE-209).

Table 2. Recoveries, Relative Standard Deviations (RSD) of Recoveries, and Limits of Detection (LODs) of 27 PBDE Congeners in Honey Samples

BDE congeners (homologues)	recoveries (%)	RSD (%)	LODs (pg/g ww)
BDE-3 (Br_1)	75	10	0.6
BDE-7 (Br_2)	80	15	0.6
BDE-15 (Br_2)	85	15	1.50
BDE-17 (Br_3)	93	20	2.3
BDE-28 (Br_3)	110	20	2.0
BDE-47 (Br_4)	105	20	1.5
BDE-49 (Br_4)	101	10	0.8
BDE-71 (Br_4)	120	10	0.7
BDE-66 (Br_4)	98	18	0.6
BDE-77 (Br_4)	89	18	0.8
BDE-85 (Br_5)	98	13	3.8
BDE-99 (Br_5)	113	14	1.2
BDE-100 (Br_5)	85	11	0.81
BDE-119 (Br_5)	110	15	1.6
BDE-126 (Br_5)	73	18	4.0
BDE-153 (Br_6)	90	13	9.2
BDE-154 (Br_6)	120	15	8.6
BDE-138 (Br_6)	106	10	5.5
BDE-156 (Br_6)	96	19	5
BDE-183 (Br_7)	96	10	9
BDE-184 (Br_7)	96	9	10
BDE-191 (Br_7)	91	10	10
BDE-196 (Br_8)	70	15	10
BDE-197 (Br_8)	60	11	13
BDE-206 (Br_9)	69	13	5
BDE-207 (Br_9)	68	5	14
BDE-209 (Br_{10})	82	9	30

Figure 1 shows typical GC/ITMS chromatograms of PBDEs in honey samples from different countries and regions. BDE-47, -49, -138, and -153 are most commonly monitored congeners in biological and environmental samples (*26*). They were found to be major congeners in honey samples in the present study (**Figures 1** and **2**). Profiles of the 26 PBDEs ($\sum PBDE_{26}$) except BDE-209 differed obviously in honeys from developing and developed countries. All the 27 congeners were quite evenly present in honeys originating in developed countries while the highly brominated PBDEs were more, and in higher concentrations, than less brominated congeners in honeys originating in developing countries. Such results may be due to the long history of PBDE uses in developed countries and decomposition of highly brominated congeners to less brominated ones under natural conditions. Electronics industries are rapidly changing in developing countries such as China and India and the amount of PBDE products such as deca-BDE mixtures used has been dramatically increasing. This may relate to the detection of more highly brominated PBDEs in honeys from developing countries.

The average concentrations of $\sum PBDE_{26}$ were 5950, 1870, and 640 pg/g ww in honey samples originating in developed countries, developing countries and background regions, respectively. The average concentrations of BDE-209 were 1170, 3390, and 450 pg/g ww in honey samples originating in developed countries, developing countries and background regions, respectively. The concentrations of $\sum PBDE_{26}$ (excluding BDE-209) ranged from 2,720 to10,550 pg/g in the 21 honey samples originating in developed countries. The concentrations of $\sum PBDE_{26}$ ranged from 1,030 to 3,470 pg/g in the 15 honey samples originating in developing countries and ranged from 300 to 850 pg/g in the honey samples labeled as originating in background regions. The concentrations of the four main congeners BDE-47, -49, -138, and -153 ($\sum PBDE_4$) ranged from 630 to 7,520 pg/g, from 230 to 1,920 pg/g, and from 100 to 600 pg/g in honey samples originating in developed countries, developing countries, background regions, respectively. It is interesting that the average concentrations of hepta- to deca-BDEs in honey samples originating in India, China and Thailand were approximately 3−5 times those in honeys originating in developed countries (data not shown). The average level of the total 27 PBDEs in honey samples from background regions was approximately 5 and 7 times lower than that in honey samples from developing countries and

Table 3. Average Concentrations of PBDEs in the Honey Samples from Different Countries

	av concns ± std dev and concn ranges (pg/g ww)					
	developed countries (n = 21)		developing countries (n = 15)		background regions (n = 14)	
PBDE congeners	mean	range	mean	range	mean	range
BDE-3	260 ± 250	35−790	50 ± 40	6−120	20 ± 10	nd[a]−40
BDE-7	200 ± 205	20−580	50 ± 30	10−120	10 ± 10	nd−40
BDE-15	95 ± 60	20−210	50 ± 40	10−150	25 ± 40	nd−150
BDE-17	260 ± 210	20−580	70 ± 50	10−205	30 ± 20	nd−70
BDE-28	220 ± 200	10−560	60 ± 60	10−240	20 ± 20	nd−60
BDE-47	420 ± 560	20−1800	230 ± 250	nd−910	110 ± 110	10−410
BDE-49	210 ± 170	20−510	80 ± 80	nd−350	30 ± 50	nd−210
BDE-66	260 ± 170	30−550	80 ± 70	10−290	10 ± 10	nd−30
BDE-71	50 ± 20	20−100	35 ± 30	10−100	10 ± 10	nd−20
BDE-77	30 ± 20	nd−70	20 ± 30	nd−140	10 ± 10	nd−30
BDE-85	210 ± 200	10−590	40 ± 30	nd−140	10 ± 10	nd−30
BDE-99	180 ± 180	10−500	50 ± 50	10−200	10 ± 10	nd−20
BDE-100	60 ± 50	10−170	20 ± 20	nd−60	10 ± 10	nd−10
BDE-119	20 ± 10	nd−40	10 ± 10	nd−30	10 ± 10	nd−10
BDE-126	50 ± 90	nd−330	20 ± 30	nd−100	10 ± 10	nd−20
BDE-138	460 ± 360	20−1100	150 ± 140	10−450	80 ± 40	20−140
BDE-153	1520 ± 1730	110−6170	360 ± 440	20−1700	140 ± 120	10−500
BDE-154	260 ± 230	10−690	80 ± 60	10−260	20 ± 20	10−70
BDE-156	10 ± 10	nd−410	5 ± 10	nd−20	10 ± 10	nd−20
BDE-183	100 ± 70	40−250	80 ± 120	10−480	30 ± 30	10−120
BDE-184	230 ± 350	nd−1240	50 ± 110	nd−510	10 ± 10	nd−20
BDE-191	290 ± 290	10−860	60 ± 90	nd−340	20 ± 20	nd−80
BDE-196	120 ± 180	nd−650	50 ± 80	nd−320	10 ± 10	nd−10
BDE-197	110 ± 90	10−280	40 ± 70	nd−320	20 ± 20	nd−80
BDE-206	200 ± 490	nd−1740	40 ± 90	nd−410	5 ± 5	nd−20
BDE-207	120 ± 100	nd−330	80 ± 100	nd−400	20 ± 20	nd−70
BDE-209	1170 ± 860	180−3360	3390 ± 2820	550−9260	450 ± 320	nd−1170
$\sum PBDE_4$[b]	2620 ± 1870	630−7520	810 ± 4802	230−1920	360 ± 140	100−600
$\sum PBDE_{26}$[c]	5950 ± 2820	2720−10550	1870 ± 670	1030−3470	640 ± 170	300−850

[a] Not detected. [b] Sum concentrations of BDE-47, -49, -138 and -153. [c] Sum concentrations of the 26 PBDEs except BDE-209.

developed countries, respectively (**Table 3**). The large data dispersions may be attributed to different origins of the honey samples, PBDE exposures in different regions, storage conditions and time, honey processing and treatment variations, and uncertainty of the actual origin of the honey samples. There was no significant difference in concentrations of the total PBDEs and congener profiles in the honey samples originating in developing countries, developed countries and background regions. However, the average concentrations and congener profiles of PBDEs indicate general trends of exposures to, and sources of, PBDEs in honey.

The average concentration of BDE-209 in honeys labeled as originating in developing countries was approximately 3-fold of that in honeys originating in developed countries (**Table 3**). BDE-209 was the dominant congener among all PBDE congeners detected in honey samples. It averaged approximately 25% of the $\sum PBDE_{26}$ in samples originating in developed countries and was approximately 2-fold of the $\sum PBDE_{26}$ in samples originating in developing countries (**Table 3**). The honey samples from the background regions, i.e., Alaska, Hawaii and New Zealand, contained very low concentrations of BDE-209 as well as the other PBDEs. These findings indicate an agreement between PBDE usages and their presence in honeys. Heavy uses of deca-BDE mixtures are a primary suspected source of BDE-209 in the honeys.

High concentrations of BDE-209 in various environmental media raised concerns about whether BDE-209 in the environment was transformed into less brominated congeners. Studies showed debromination of BDE-209 in the environment (*1*−*3*, *27*). A number of recent studies have also shown that BDE-209 is susceptible to breakdown under sunlight (*28*, *29*). However, no report of BDE-209 degradation in honey was found in the published literature. A preliminary study was conducted to understand whether BDE-209 degrades in honey, which may be a source of less brominated congeners in honey. **Figure 3** shows GC−ECD chromatograms of extracts of the BDE-209 fortified honey samples after 4 weeks of incubation at 25 and 60 °C. The chromatograms show degradation of BDE-209 in honey at 25 and 60 °C for 4 weeks. Four debromination products of BDE-209 are BDE-153, -183, -206 and -207, which were identified by matching their mass spectra and GC retention times with those of respective BDE congener standards. The peaks of BDE-206 and BDE-207 in **Figure 3D** are relatively smaller than the corresponding peaks in **Figure 3C** while the peaks of BDE-153 and -183 in **Figure 3D** are relatively larger than the corresponding peaks in **Figure 3C**. It is noteworthy that **Figure 3A** is a GC−ECD chromatogram of an extract of a blank control honey sample without any incubation and **Figure 3B** is a GC−ECD chromatogram of a recently purchased BDE-209 standard (unincubated standard solutions). The three small peaks labeled as 2, 3, and 4 (unknown, BDE-207 and BDE-206, respectively) were impurities in the standards. The abundance of these three impurities was less than 3% based on the percentage of peak areas in **Figure 3B**. The abundance of these three compounds was more than 25% based on the percentage of peak areas in **Figure 3C**. Impurities in the standard did not affect the analytical results.

The results shown in **Figure 3** suggest that BDE-209 may undergo stepwise debromination to produce less brominated congeners in honey. Debromination of BDE-209 in other matrices also occurs under photochemical, hydrothermal and reductive treatments (*1*, *2*, *28*−*31*). The results show that debromination of BDE-209 is a source of less brominated congeners in

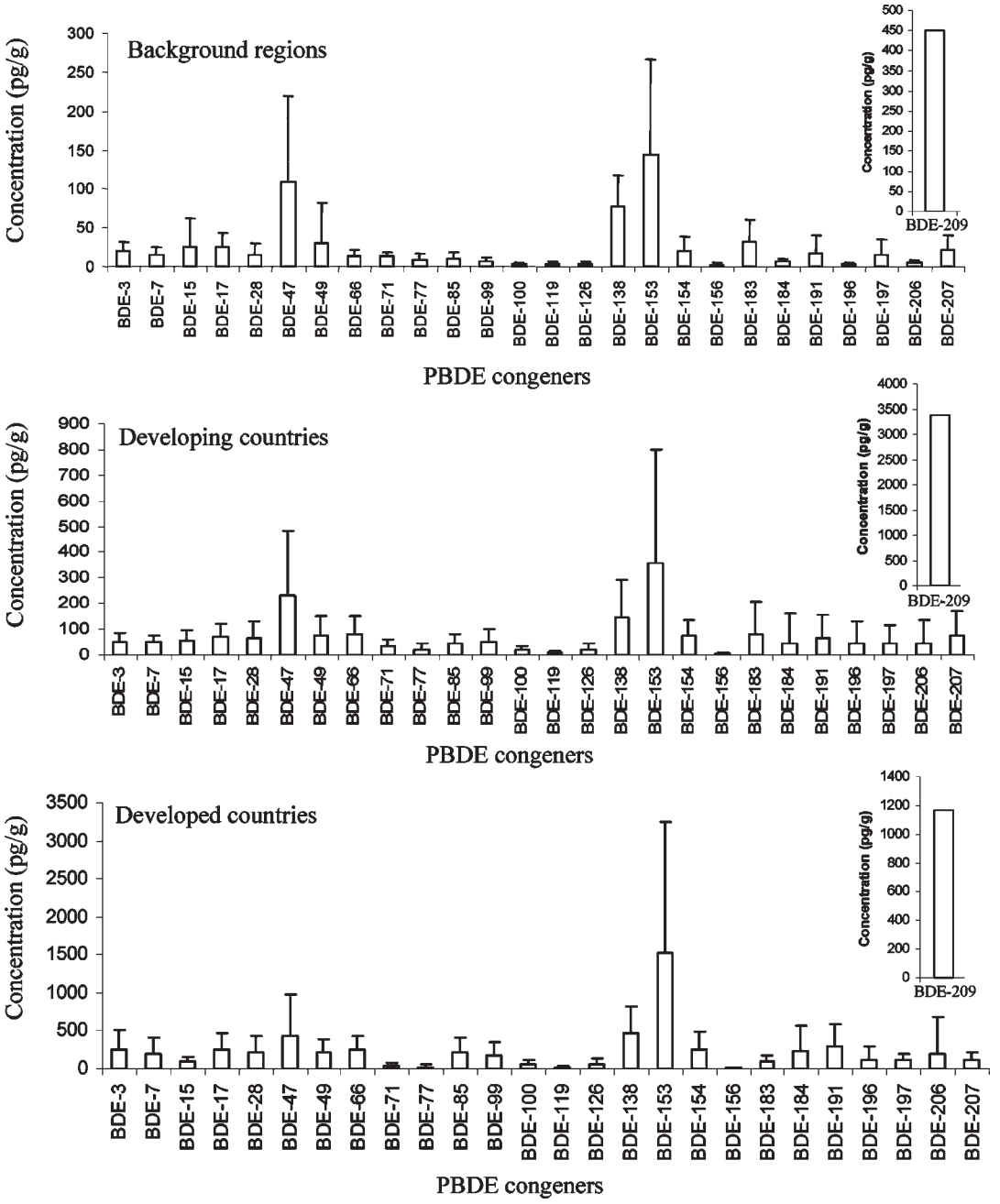

Figure 2. Average profiles of 27 PBDE congeners (pg/g ww) in the honey samples labeled from the background regions, developing countries and developed countries.

honey. Degradation of BDE-209 in honey warrants further investigation, particularly on degradation products and kinetics. Information of BDE-209 degradation rates, products and pathways is important for understanding the sources of PBDEs in honey. Such information is also significant for assessing human exposures and risks associated with PBDEs (*32*, *33*).

Overall, the four main PBDE congeners, BDE-47, -49, -138 and -153, had an accumulative abundance of greater than 50% of $\sum PBDE_{26}$ in all honey samples (**Table 3**), being similar to the composition of the penta-BDE commercial formula (*23*). The penta-BDE commercial mixture was a major brominated fire retardant (BFR) product used in some developing countries (*23*), in addition to the deca-BDE mixture (*17*). It is noteworthy that the proportion of low molecular weight congeners detected in honey samples from different countries was relatively greater than that of high molecular weight congeners except for BDE-209. This may be attributed to the higher tendency of lower brominated congeners to vaporize relative to higher brominated congeners and the potential decomposition of higher brominated congeners to lower brominated ones. Honey samples from background regions displayed different PBDE compositional patterns that had relatively lower abundance of higher brominated congeners than those in honey samples from developing countries. The PBDEs in honeys from background regions may be partially from long-range transport (*34*−*37*) rather than local sources. Assuming all honey samples have been similarly aged and not contaminated with additional PBDEs during transportation and treatment processes, the fact that the concentrations of low brominated congeners in honeys from developed countries were higher than those from developing countries implies that the lower levels of brominated congeners in honeys from developed countries would primarily come from the environment.

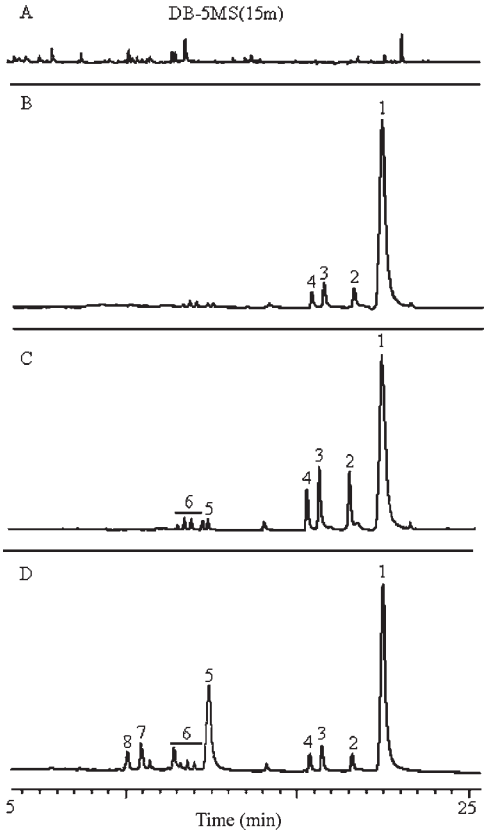

Figure 3. GC−ECD chromatograms of an extract of a blank control honey sample (**A**), and a recently purchased BDE-209 standard (50 ng/mL) (**B**) and extracts of the BDE-209 fortified honey samples after 4 weeks of incubation at 25 °C (**C**) and 60 °C (**D**). Peak 1 is BDE-209. Peaks 3, 4, 5, and 7 are BDE-207, BDE-206, BDE-183, and BDE-153, respectively, which are degradation products of BDE-209. Other peaks (e.g., 2, 6, and 8) are also possible degradation products of BDE-209.

In summary, this study investigated the concentrations of 27 PBDEs in honey samples labeled as originating in 17 countries and regions. The results from this data set showed higher levels of the $\sum PBDE_{26}$, excluding BDE-209, in honey samples from developed countries in comparison with those from developing countries, or background regions. The concentrations of the $\sum PBDE_{27}$ ranged from 2,900 to 13,910 pg/g in honey samples originating in developed countries and from 1,580 to 12,730 pg/g in those originating in developing countries. BDE-209 was the most dominant congener in all honey samples. BDE-47, -49, -138, and -153 were also dominant congeners and accounted for approximate 50% of the $\sum PBDE_{26}$ (excluding BDE-209). The findings are consistent with long, heavy historical uses of PBDE products in developed countries and current, heavy uses of BDE-209 in developing countries. BDE-209 can be degraded to less brominated congeners in honey.

LITERATURE CITED

(1) Brooke, D. N.; Burns, J.; Crookes, M. J.; Dungey, S. M. *Environmental risk evaluation report: Decabromodiphenyl ether* (*CAS no. 1163-19-5*); http://publications.environment-agency.gov.uk/pdf/SCHO0909BQYZ-e-e.pdf. ISBN: 978-1-84911-112-6. Environment Agency: U.K., 2009.

(2) Wang, D.; Li, Q. X. Application of mass spectrometry in the analysis of polybrominated diphenyl ether. *Mass Spectrom. Rev* **2009**, *28*, 1–39.

(3) de Wit, C. A. An overview of brominated flame retardants in the environment. *Chemosphere* **2002**, *46*, 583–624.

(4) Alaee, M.; Arias, P.; Sjödin, A.; Bergman, A. An overview of commercially used brominated flame retardants (BFRs) and their applications changes in their use pattern in different countries/regions over time and possible modes of release. *Environ. Int.* **2003**, *29*, 683–689.

(5) Rahman, F.; Langford, K. H.; Scrimshaw, M. D.; Lester, J. N. Polybrominated diphenyl ether (PBDE) flame retardants. *Sci. Total Environ.* **2001**, *275*, 1–17.

(6) Watanabe, I.; Sakai, S. Environmental release and behavior of brominated flame retardants. *Environ. Int.* **2003**, *29*, 665–682.

(7) Ward, J.; Mohapatra, S. P.; Mitchell, A. An overview of policies for managing polybrominated diphenyl ethers (PBDEs) in the Great Lakes basin. *Environ. Int.* **2008**, *34*, 1148–1156.

(8) Zhu, L. Y.; Hites, R. A. Brominated flame retardants in tree bark from North America. *Environ. Sci. Technol.* **2006**, *40*, 3711–3716.

(9) Schecter, A.; Päpke, O.; Harris, T. R.; Tung, K. C.; Musumba, A.; Olson, J.; Birnbaum, L. Polybrominated diphenyl ether (PBDE) levels in an expanded market basket survey of U.S. food and estimated PBDE dietary intake by age and sex. *Environ. Health Perspect.* **2006**, *114*, 1515–1520.

(10) Qu, W. Y.; Bi, X. H.; Sheng, G. Y.; Lu, S. Y.; Fu, J. M.; Yuan, J.; Li, L. P. Exposure to polybrominated diphenyl ethers among workers at an electronic waste dismantling region in Guangdong, China. *Environ. Int.* **2007**, *33*, 1029–1034.

(11) Koizumi, A.; Yoshinaga, T.; Harada, K; Inoue, K; Morikawa, A; Muroi, J. Assessment of human exposure to polychlorinated biphenyls and polybrominated diphenyl ethers in Japan using archived samples from the early 1980s and mid-1990s. *Environ Res.* **2005**, *99*, 31–39.

(12) Meironyté, D.; Norén, K.; Bergman, A. Analysis of polybrominated diphenyl ethers in Swedish human milk. A time-related trend study, 1972−1997. *J. Toxicol. Environ. Health.* **1999**, *58*, 329–341.

(13) Jakobsson, K.; Thuresson, K.; Rylander, L.; Sjödin, A.; Hagmar, L.; Bergman, A. Exposure to polybrominated diphenyl ethers and tetrabromobisphenol A among computer technicians. *Chemosphere* **2002**, *46*, 709–716.

(14) Frederiksen, M.; Vorkamp, K.; Thomsen, M.; Knudsen, L. E. Human internal and external exposure to PBDEs - A review of levels and sources. *Int. J. Hyg. Environ. Health* **2009**, *212*, 109–134.

(15) Kalantzi, O. I.; Martin, F. L.; Thomas, G. O.; Alcock, R. E.; Tang, H. R.; Drury, S. C.; Carmichael, P. L.; Nicholson, J. K.; Jones, K. C. Different levels of polybrominated diphenyl ethers (PBDEs) and chlorinated compounds in breast milk from two U.K. regions. *Environ. Health Perspect.* **2004**, *112*, 1085–1091.

(16) Gomara, B.; Herrero, L.; Gonzalez, M. J. Survey of polybrominated diphenyl ether levels in Spanish commercial foodstuffs. *Environ. Sci. Technol.* **2006**, *40*, 7541–7547.

(17) Voorspoels, S.; Covaci, A.; Neels, H.; Schepens, P. Dietary PBDE intake: a market-basket study in Belgium. *Environ. Int.* **2007**, *33*, 93–97.

(18) Bragigand, V.; miard-Triquet, C.; Parlier, E.; Boury, P.; Marchand, P.; El Hourch, M. Influence of biological and ecological factors on the bioaccumulation of poly- brominated diphenyl ethers in aquatic food webs from French estuaries. *Sci. Total Environ.* **2006**, *368*, 615–626.

(19) Tomy, G. T.; Palace, V. P.; Halldorson, T.; Braekevelt, E.; Danell, R.; Wautier, K.; Evans, B.; Brinkworth, L.; Fisk, A. T. Bioaccumulation, biotransformation, and biochemical effects of brominated diphenyl ethers in Juvenile LakeTrout (*Salvelinus namaycush*). *Environ. Sci. Technol.* **2004**, *38*, 1496–1504.

(20) Bocio, A.; Llobet, J. M.; Domingo, J. L.; Corbella, J.; Teixido, A.; Casas, C. Polybrominated diphenyl ethers (PBDEs) in foodstuffs: human exposure through the diet. *J. Agric. Food Chem.* **2003**, *51*, 3191–3195.

(21) Darnerud, P. O.; Eriksen, G. S.; Jóhannesson, T.; Larsen, P. B.; Viluksela, M. Polybrominated diphenyl ethers: occurrence, dietary exposure, and toxicology. *Environ. Health Perspect.* **2001**, *109*, 49–68.

(22) Kiviranta, H.; Ovaskainen, M. L.; Vartiainen, T. Market basket study on dietary intake of PCDD/Fs, PCBs, and PBDEs in Finland. *Environ. Int.* **2004**, *30*, 923–932.

(23) Huwe, J. K.; Larsen, G. L. Polychlorinated dioxins, furans, and biphenyls, and polybrominated diphenyl ethers in a US meat market basket and estimates of dietary intake. *Environ. Sci. Technol.* **2005**, *39*, 5606–5611.
(24) Wang, D. L.; Atkinson, S.; Hoover-Miller, A.; Shelver, W. L.; Li, Q. X. Simultaneous use of gas chromatography/ion trap mass spectrometry-electron capture detector to improve the analysis of bromodiphenyl ethers in biological and environmental samples. *Rapid Commun. Mass Spectrom.* **2008**, *22*, 647–656.
(25) Xu, T.; Cho, I. K.; Wang, D. L.; Rubio, F. M.; Shelver, W. L.; Gasc, A. M. E.; Li, J.; Li, Q. X. Suitability of a magnetic particle immunoassay for the analysis of PBDEs in Hawaiian euryhaline fish and crabs in comparison with gas chromatography/electron capture detection-ion trap mass spectrometry. *Environ. Pollut.* **2009**, *157*, 417–422.
(26) Ikonomou, M. G.; Rayne, S.; Fischer, M.; Fernandez, M. P.; Cretney, W. Occurrence and congener profiles of polybrominated diphenyl ethers (PBDEs) in environmental samples from coastal British Columbia, Canada. *Chemosphere* **2002**, *46*, 694–663.
(27) van Den Steen, E.; Covaci, A.; Jaspers, V. L. B.; Dauwe, T.; Voorspoels, S.; Eens, M.; Pinxten, R. Accumulation, tissue-specific distribution and debromination of decabromodiphenyl ether (BDE-209) in European starlings (*Sturnus vulgaris*). *Environ. Pollut.* **2007**, *148*, 648–653.
(28) Bezares-Cruz, J.; Jafvert, C. T.; Hua, I. Solar photodecomposition of decabromodiphenyl ether: Products and quantum yield. *Environ. Sci. Technol.* **2004**, *38*, 4149–4156.
(29) Söderström, G.; Sellström, U.; de Wit, C. A.; Tysklind, M. Photolytic debromination of decabromodiphenyl ether (BDE-209). *Environ. Sci. Technol.* **2004**, *38*, 127–132.
(30) Nose, K.; Hashimoto, S.; Takahashi, S.; Noma, Y.; Sakai, S. I. Degradation pathways of decabromodiphenyl ether during hydrothermal treatment. *Chemosphere* **2007**, *68*, 120–125.
(31) Keum, Y.-S.; Li, Q. X. Reductive debromination of polybrominated diphenyl ethers by zero-valent Iron. *Environ. Sci. Technol.* **2005**, *39*, 2280–2286.
(32) US Environmental Protection Agency (US EPA). *Toxicological Profile for Decabromodiphenyl ether* (*BDE-209*), *Integrated Risk Information System*, June **2008**.
(33) US Environmental Protection Agency (EPA). *Toxicological Profile for Pentabromodiphenyl ether* (*BDE-47*), *Integrated Risk Information System*, June **2008**.
(34) Noël, M.; Dangerfield, N.; Hourston, R. A.; Belzer, W.; Shaw, P.; Yunker, M. B.; Ross, P. S. Do trans-Pacific air masses deliver PBDEs to coastal British Columbia, Canada? *Environ. Pollut.* **2009**, *157*, 3404–3412.
(35) Hoh, E.; Hites, R. A. Brominated flame retardants in the atmosphere of the East-Central United States. *Environ. Sci. Technol.* **2005**, *39*, 7794–7802.
(36) Iacovidou, E.; Mandalakis, M.; Stephanou, E. G. Occurrence and diurnal variation of polychlorinated biphenyls and polybrominated diphenyl ethers in the background atmosphere of Eastern Mediterranean. *Chemosphere* **2009**, *77*, 1161–1167.
(37) de Wit, C. A.; Herzke, D.; Vorkamp, K. Brominated flame retardants in the Arctic environment - trends and new candidates. *Sci. Total Environ.*, in press, doi:10.1016/j.scitotenv.2009.08.037.

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