JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Polybrominated Diphenyl Ethers in Retail Fish and Shellfish Samples Purchased from Canadian Markets

SHERYL A. TITTLEMIER,*,† DON FORSYTH,† KENNETH BREAKELL,§ VICTOR VERIGIN,§ JOHN JAKE RYAN,† AND STEPHEN HAYWARD#

Food Research Division and Division of Biostatistics and Epidemiology, Banting Research Centre 2203D, Health Canada, Ottawa, Ontario, Canada, K1A 0L2, and Western Region Laboratory, Health Products and Food Branch, Health Canada, Burnaby, British Columbia, Canada, V5G 4P2

Fish and shellfish retail samples ($n = 122$) were purchased from three Canadian cities in the winter of 2002 and analyzed for a total of 18 polybrominated diphenyl ether (PBDE) congeners. The samples (salmon, trout, tilapia, Arctic char, mussels, oysters, shrimp, and crab) represented the range of fish and shellfish commercially available to Canadian consumers at the time of purchase. Trout and salmon (geometric mean ΣPBDE = 1600 and 1500 pg/g, wet weight, respectively) were found to contain significantly higher amounts of PBDEs than the mussel, tilapia, and shrimp groups (geometric mean ΣPBDE = 260, 180, and 48 pg/g, wet weight, respectively). These differences in ΣPBDE concentrations among fish and shellfish products were partly driven by differences in lipid content among the samples. Mean ΣPBDE concentrations in domestic samples were also significantly greater than in imported samples, possibly reflecting global environmental distribution of PBDEs. These concentration differences will contribute to variations in dietary exposure to PBDEs when assorted fish and shellfish items from various origins are consumed.

KEYWORDS: Dietary exposure; PBDE; organohalogen; aquaculture; food

INTRODUCTION

Polybrominated diphenyl ethers (PBDEs) are globally distributed in the environment and in human populations. These compounds, used as flame retardants in polyurethane foam and rigid plastics, have been detected in human blood, milk, and tissues dating back to the 1970s (*1*, *2*). Over the past three decades, PBDE concentrations in humans have increased by factors of 10−100 (*3*). However, concentrations in the Canadian population appear to have increased to a greater amount than those in northern Europe (*4*). There are also indications that PBDE levels in human milk, and thus body burdens, are decreasing in Sweden after reaching a peak of 4.0 ng of PBDEs/g of lipid in the late 1990s (*2*, *5*−*7*). Concentrations of PBDEs in the Canadian population appear to be still increasing; human milk samples collected in 2001 and 2002 contained a median concentration of 22 ng of PBDEs/g of lipid (*4*).

Differences in PBDE body burdens between Canadian and European populations are attributed to two main factors. The first is the continued use of the pentabrominated diphenyl ether technical formulation in North America. The use of this product was voluntarily phased out in Sweden and Germany beginning in the early 1990s (*8*). The greater use of two other technical formulations (deca- and octabrominated) in North America as compared to Europe will also contribute to the disparity between Canadian and European PBDE body burdens.

Diet is an important route of exposure to PBDEs, as with other persistent hydrophobic organohalogen compounds. One study has estimated the median daily exposure of PBDEs via dietary sources to be ∼13 times greater than exposure via inhalation (*9*). The same study compared omnivorous and vegan diets using a duplicate diet approach and demonstrated that animal-derived foods, such as meat, fish, and dairy products, are the largest contributors to dietary PBDE exposure (*9*). Other surveys that examined PBDEs in foods have shown that consumption of fish is the main, or at least a major, dietary source of PBDEs for Japanese, Dutch, Catalonian, and Swedish populations (*6*, *10*−*12*). The situation is somewhat different in Canada because fish is not a major dietary item for the average Canadian. Even though marine and freshwater fish Canadian Total Diet Study composite samples contained the highest concentrations of PBDEs, the larger consumption of meat and dairy products over fish reduces the relative contribution of fish to dietary PBDE intake to ∼5% (*13*). However, the relative importance of fish as a dietary source of PBDEs will vary among individual Canadians and will increase for those consuming more fish.

The purpose of this survey was to examine congener-specific PBDE concentrations in a variety of fish and shellfish readily available to Canadian consumers and to provide these data for use in dietary exposure and risk assessments.

† Food Research Division.
§ Western Region Laboratory.
# Division of Biostatistics and Epidemiology.

10.1021/jf048665y CCC: $27.50 Published 2004 by the American Chemical Society
Published on Web 11/16/2004

Table 1. Origin (Farmed or Wild) and Source (Domestic or Import, and Importing Country) of Fish and Shellfish Products Purchased from Canadian Markets and Analyzed for Polybrominated Diphenyl Ethers (PBDEs)

		origin		source	
fish/shellfish product	total (*n*)	farmed (*n*)	wild (*n*)	domestic (*n*)	import (*n*)
trout	16	16	0	16	0
salmon	22	19	3	21	1 (Chile)
char	11	6	5	11	0
tilapia	15	12	3	5	10 (Ecuador, Taiwan, Jamaica, U.S.)
crab	16	0	16	16	0
shrimp	17	13	4	2	15 (Thailand, Ecuador, U.S.)
oysters	15	11	4	15	0
mussels	10	10	0	10	0

MATERIALS AND METHODS

Chemicals. The following 18 brominated diphenyl ether (BDE) congeners were used as external standards to quantitate PBDEs in all samples: BDE-15, BDE-17, BDE-28, BDE-47, BDE-66, BDE-71, BDE-75, BDE-77, BDE-85, BDE-99, BDE-100, BDE-119, BDE-126, BDE-138, BDE-153, BDE-154, BDE-183, and BDE-190. Numbering of the congeners is based on the scheme developed by Ballschmiter and Zell for PCBs (*14*). Six $^{13}C_{12}$-labeled BDE congeners were used as recovery internal standards: $^{13}C_{12}$-BDE-28, $^{13}C_{12}$-BDE-47, $^{13}C_{12}$-BDE-99, $^{13}C_{12}$-BDE-153, $^{13}C_{12}$-BDE-154, and $^{13}C_{12}$-BDE-183. Three polychlorinated compounds were used as instrument performance internal standards: PCB-200, PCB-209, and decachlorodiphenyl ether (CDE-209).

All ^{13}C-labeled PBDEs were supplied by Wellington Laboratories (Guelph, ON, Canada). Native PBDEs, PCBs, and CDE-209 were obtained from Wellington Laboratories, Cambridge Isotope Laboratories (Andover, MA), or AccuStandard (New Haven, CT).

All solvents were of distilled-in-glass grade, Omnisolve/BDH, or equivalent (EM Science, Gibbstown, NJ). Silicic acid (silica gel) was of chromatographic grade, 100/200 mesh, and supplied by either Bio-Rad (Bio-Sil A; Hercules, CA) or Sigma-Aldrich (SIL-350; Oakville, ON, Canada). Florisil PR was of pesticide grade, 60/100 mesh, and supplied by Supelco (Oakville, ON, Canada). Celite 545 was supplied by Fisher Scientific (Ottawa, ON, Canada). Carbopack C (graphitized carbon, 80/100 mesh) was supplied by Supelco. Anhydrous sodium sulfate was of ACS grade; potassium hydroxide and sodium hydroxide pellets were of reagent grade. Glass wool was pre-extracted with dichloromethane by Soxhlet. Ultrahigh-purity nitrogen gas was used during the sample preparation (99.999%).

Samples. Fish and shellfish retail samples ($n = 122$) were purchased from three Canadian cities (Vancouver, BC; Halifax, NS; Toronto, ON) in the winter of 2002 for analysis of various chemical contaminants, including PBDEs. The samples were purchased at the retail level by a contracted organization with experience in food market and consumer activities and represented the range of fish and shellfish commercially available to Canadian consumers. Samples purchased included fish (salmon, trout, tilapia, Arctic char), molluscs (mussels, oysters), and crustaceans (shrimp, crab). The sampling regimen consisted of making purchases of identical fish and shellfish species from the same market to obtain an edible portion of ~450 g; however, in certain cases, only smaller amounts were available for collection. Thus, individual samples prepared and analyzed do not necessarily contain tissue from a single organism, but rather a single species from a single market. At least 10 different markets were visited in each city. Samples originated from farmed and wild sources and included both domestic and imported products. **Table 1** lists sample origin and source information. This information was obtained from the retailers at the markets visited and was verified for some samples via consultation with the Canadian Food Inspection Agency.

After purchase, the samples were immediately frozen or refrigerated and shipped to a central facility for preparation. After any necessary thawing, the inedible portions of the samples were removed (skin, associated lipid-rich layer, and bones from fish; shells, veins, and digestive tracts from oysters, mussels, shrimp, and crab). The remaining edible portions were homogenized in commercial blenders, placed in chemically cleaned glass jars with polyethylene lids [and poly(tetrafluoroethylene) lid liners], and kept at −20 °C until analysis.

Extraction and Isolation of PBDEs. The determination of PBDE concentrations in all samples followed a slightly modified version of the method described by Ryan and Patry (*15*). Thawed sample homogenates (~25 g, wet weight) were spiked with ^{13}C-labeled recovery internal standards and allowed to stand for 15−30 min. Samples were then extracted with 200 mL of acetone/hexane (2:1 v/v) by mixing with a Polytron homogenizer.

Acetone was removed from the extract with a wash of Milli-Q water. The hexane extract was then filtered using glass wool, dried over anhydrous sodium sulfate, and evaporated under vacuum to dryness on a rotary evaporator. The lipid residue was dried under nitrogen until a constant weight was obtained. The lipid content of the samples was determined gravimetrically.

Lipids were then removed by dissolving the residues in dichloromethane and separating with size exclusion chromatography using two Waters Envirogel (cross-linked styrene−divinylbenzene, 100 Å, 15 μm) gel permeation columns connected in series and attached to a Waters HPLC model 600 isocratic pump, a Waters 717 autosampler, and a Millipore fraction collector. The defatted extracts were purified by passing through silicate/sulfuric acid/silicic acid (4 g of 44% w/w concentrated sulfuric acid/silica packed in a 10 mL disposable serological pipet eluted with 50 mL of hexane) and activated Florisil columns (1.5 g of deactivated Florisil packed in a 5 mL disposable serological pipet, activated at 150 °C overnight) in series. The PBDEs and coeluting polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and coplanar PCBs were eluted with dichloromethane off of the Florisil column after an initial PCB fraction (eluted with hexane) was collected. The dichloromethane fraction was evaporated, dissolved in hexane, and then passed through a Carbopack C activated carbon column (250 mg of Carbopack C 80/100 mesh in a 5 mL disposable serological pipet). The PBDEs are not absorbed to carbon and were thus washed off the activated carbon column using 4 × 1 mL of hexane and 2 × 1 mL of 2:1 v/v cyclohexane/dichloromethane. The eluate was concentrated on a rotary evaporator, and instrument performance internal standard was added prior to analysis by gas chromatography−high-resolution mass spectrometry (GC-HRMS).

Analysis of PBDEs. Analyses were performed using a VG AutoSpec Q high-resolution mass spectrometer (Micromass, Manchester, U.K.) linked to a Hewlett-Packard 5890 series II gas chromatograph (Palo Alto, CA) via direct capillary interface. The gas chromatograph was fitted with a 1 m × 0.53 mm deactivated fused silica retention gap (J&W Scientific, Folsom, CA) and a 30 m × 0.25 mm DB-5MS capillary column (J&W Scientific) with a 0.25 μm film thickness. The two columns were connected using a fused silica universal butt-connector (Restek, Bellefonte, PA).

Samples (2.0 μL) were injected in the splitless mode using a CTC A200S Fisons autosampler. The injection port was held at a temperature of 300 °C. The initial oven temperature of 110 °C was held for 1.5 min prior to an increase of 30.0 °C/min to 240 °C. The oven temperature was then increased at a rate of 3.0 °C/min to 300 °C and held at 300 °C for 5.0 min. The final step of the GC oven temperature program was an increase of 30.0 °C/min to 315 °C with a hold time of 15.0 min. The capillary interface between the GC and HRMS instruments was held at 260 °C, the re-entrant temperature at 270 °C, and the perfluorokerosene septum temperature at 160 °C.

The GC-HRMS system was operated in the positive electron impact ionization mode at a resolution of 10000 (10% valley) and controlled using the provided OPUS 3.1 software. The source temperature was kept at 260 °C, electron energy at 50 eV, trap current at 550 μA, and multiplier voltage at 370 V.

Up to 10 masses were monitored in each window in the selected ion monitoring mode, usually with two masses for each homologue group plus a lock mass. The molecular ions $[M^{\bullet+}]$ and $[M + 2^{\bullet+}]$ were monitored for all native and ^{13}C-labeled standards and analytes. Identification of each compound was based on its GC retention time

(within 1.2 s of the standard), correct ion ratio (within 15% of the standard), and a signal-to-noise ratio of at least 3:1.

Quantification of PBDEs. Standard curves consisting of eight concentration levels of native analytes with constant concentrations of ^{13}C-labeled isotopomers were established. Concentrations in the sample were calculated from the standard curve using the isotope dilution internal standard method. Recoveries of the ^{13}C-labeled recovery internal standards added at the beginning of the extraction were calculated using response factors relative to the instrument performance internal standards added just prior to analysis. The sum of all PBDE congener concentrations (with congeners at concentrations less than the method detection limit assigned a concentration of 0 ng/g) was designated ΣPBDE.

Quality Control Measures. Twelve of 19 sample batches processed contained a laboratory blank of 25 g of Milli-Q water to measure the contribution of laboratory background PBDE concentrations. The amount of PBDEs in a blank sample was subtracted from the total PBDE amount in samples analyzed in the same GC-MS sequence (12 sequences were run in total), prior to calculation of concentration. The average amount of congeners detected in the blanks was <15% of the mean congener amounts in samples for the majority of the 10 most abundant PBDEs (BDE-47, -99, -100, -154, -183, -28, -153, -66, -17, and -85, comprising >94% of the ΣPBDEs in the samples). Average contributions from the blanks to congener amounts in samples were higher for BDE-99 (24%), BDE-183 (39%), BDE-153 (24%), and BDE-85 (35%). Because there were quantifiable amounts of several PBDE congeners in all laboratory blanks, the data from the blank samples adversely affected the limits of detection for the majority of congeners.

Statistical Analyses. One-way and two-way analysis of variance (ANOVA) models were used to assess the effects of species, origin (domestic vs imported), and source (farmed vs wild) on the logarithmic transformation of the sum total of PBDE congener concentrations. For the statistical analyses, values were imputed for PBDE congener concentrations less than the method detection limit (MDL) by sampling from fitted log-normal distributions truncated at the MDL. The use of the sum total of PBDE congener concentrations calculated in this manner as opposed to ΣPBDE values (i.e., where congener concentrations less than the MDL were assigned a value of 0 ng/g) did not affect the outcomes of the analyses because the contribution from undetected congeners to the overall sum total PBDE concentration was small. All congeners aside from BDEs-71, -126, and -190 were detected above the MDL in >50% of the samples. The correlations of PBDE concentrations and lipid content were calculated, and the effect of lipid content on the results was assessed by adding log % lipid levels as a covariate to the models. SAS system software, version 8.2, was used to analyze the data.

RESULTS

PBDE Concentrations in Fish and Shellfish. PBDEs were detected in all individual samples. The average recovery and standard deviation of the ^{13}C-labeled PBDE surrogate standards added to all samples and blanks was 66 ± 22%. The recovery-corrected ΣPBDE geometric mean and range for each product group are given in **Table 2**. The highest concentrations were found in salmonid fish (salmon, trout, char), followed by crab, oysters, mussels, tilapia, and shrimp. Some of the differences in ΣPBDE concentrations among the fish and shellfish product groups were statistically significant ($p < 0.001$, Kruskal−Wallis one-way ANOVA). Trout and salmon median ΣPBDE concentrations were significantly greater than those for mussels, tilapia, and shrimp.

PBDE Concentrations in Farmed and Wild Samples. Differences in ΣPBDE concentrations between samples with farmed and wild origins were examined. Only five product groups (salmon, tilapia, shrimp, char, oysters) contained samples with farmed and wild origins and were included in this analysis. The remaining samples in the other three product groups were exclusively farmed (trout and mussels) or wild (crab). **Figure 1** contrasts the ΣPBDE concentrations in the wild and farmed samples. There was no significant difference in ΣPBDE concentrations between samples originating from farms and the wild ($p = 0.099$, two-way ANOVA).

Table 2. Geometric Mean ± Standard Error of Sample Lipid Percentages and Geometric Mean and Ranges of ΣPBDE Concentrations in Fish and Shellfish Products Purchased from Canadian Markets

fish/shellfish product	*n*	geometric mean (% lipid)	geometric mean ΣPBDE (pg/g, wet wt)	range ΣPBDE (pg/g, wet wt)
trout	16	8 ± 1	1600	570–3900
salmon	22	11 ± 1	1500	140–5500
char	11	7.9 ± 0.9	620	310–2700
crab	16	1.4 ± 0.3	470	46–2000
oysters	15	1.1 ± 0.2	380	5.7–1400
mussels	10	1.1 ± 0.1	260	45–630
tilapia	15	2.5 ± 0.4	180	9.6–5000
shrimp	17	0.8 ± 0.1	48	1.3–680

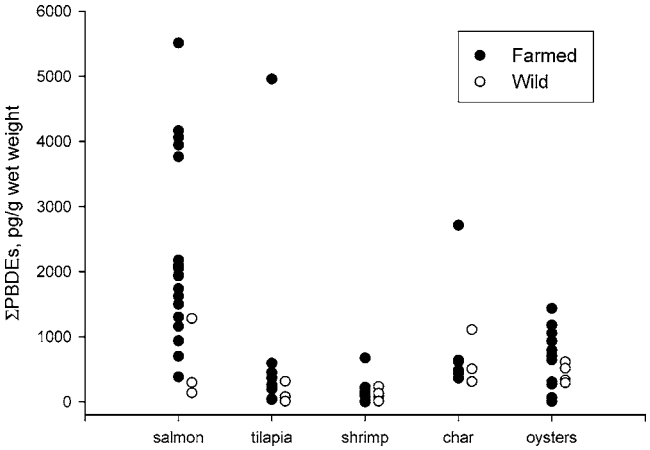

Figure 1. Total polybrominated diphenyl ether (ΣPBDE) concentrations in samples originating from farmed or wild sources.

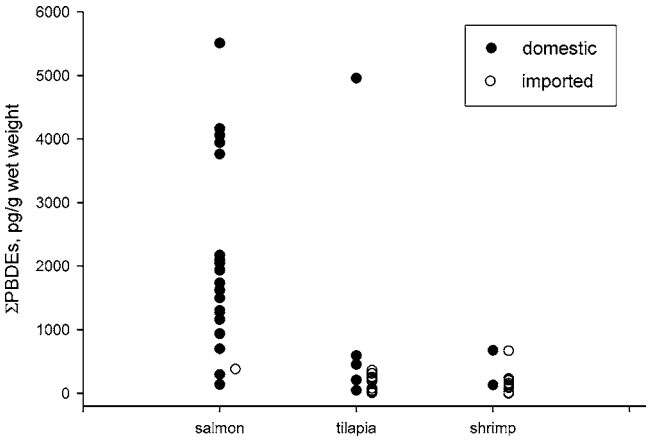

Figure 2. Total polybrominated diphenyl ether (ΣPBDE) concentrations in domestic and imported samples.

PBDE Concentrations in Domestic and Imported Samples. Differences in ΣPBDE concentrations between domestic and imported samples were examined for the salmon, tilapia, and shrimp product groups. All other product groups were exclusively from domestic sources. Differences in ΣPBDE concentrations between domestic and imported samples are shown in **Figure 2**. After allowing for effects of product group differences, mean ΣPBDE concentrations for domestic samples were sig-

nificantly greater than imported samples by a factor of ~3 ($p = 0.027$, two-way ANOVA).

PBDE Congener Distributions in Fish and Shellfish. The most abundant congener present was BDE-47, followed by BDE-99 (the average percentage of each congener as part of the total PBDEs is given in Table 1 of the Supporting Information). These two congeners on average accounted for 48% (BDE-47) and 24% (BDE-99) of the total measured PBDEs and are also the most abundant congeners observed in human milk (*15*) and other fish (*16*−*18*). For most of the product groups, BDE-100 was the next most abundant congener, then BDE-28, -153, -154, and -183 at similar levels. Exceptions to this rank order occurred in oysters, shrimp, and tilapia, for which the third most abundant congener was BDE-183 for shrimp and BDE-154 for oysters and tilapia. The least abundant congeners were BDE-190 (not detected in any samples) and BDE-126. The pentabrominated BDE-126 was detected in only one tilapia (0.19 pg/g) and two shrimp samples (0.4 and 0.6 pg/g) above the limit of detection.The PBDE congener distributions observed in the fish and shellfish are different from those observed in commercial mixtures (*19*). This difference indicates that degradation, biotransformation, differential uptake or excretion, or a combination of these processes has acted upon the commercial mixtures to alter their original congener profiles.

DISCUSSION

Dietary Exposure to PBDEs. Results of this survey demonstrate that Canadians are exposed to PBDEs via consumption of fish and shellfish. Out of the eight product groups analyzed, the salmonid fish—salmon, trout, and char—contained the highest levels of PBDEs. Geometric mean ΣPBDE concentrations in these products ranged from 620 pg/g in char to 1600 pg/g in salmon. These levels of total PBDEs are similar to others reported for salmon filets obtained in Japan (593−1040 pg/g) (*10*), The Netherlands (3400 pg/g) (*20*), and British Columbia, Canada (39−4147 pg/g) (*21*). The ΣPBDE concentrations observed in the fish product groups in this study are also comparable to those found in the edible portions of other fish aside from salmon, such as cod, herring, and whiting from the North Sea (307−7630 pg/g) (*16*) and yellowtail, mackerel, and yellow tuna from Japan (17.7−1720 pg/g) (*10*).

The shellfish items—crab, oysters, mussels, and shrimp—generally contained lower levels of PBDEs than the fish products analyzed. However, the ΣPBDE concentrations are also similar to others reported for shrimp (70 pg/g) and mussels (330−340 pg/g) (*20*).

It should be noted that use of data generated in this survey to estimate dietary exposure to PBDEs will likely overestimate the actual dietary exposure, because concentrations were determined in raw samples. Aside from oysters, the fish and shellfish analyzed in this study are generally consumed cooked. Cooking processes have been shown to lead to losses of ~30% for total PCBs and other organochlorines in trout, via the loss of fat (*22*). Similarities between PCB and PBDE physical properties suggest that losses of PBDEs will also occur during cooking processes (*23*, *24*). The removal of skin and its associated lipid-rich layer from the fish during sample processing did remove a substantial portion of fat, but not as much as would be lost during preparation and cooking.

The similarities in PBDE concentrations among Canadian, European, and Japanese fish and shellfish dietary items are consistent with previous reports that dietary exposure to PBDEs among these populations is comparable (*11*). These current results lend further support to the hypothesis that differences in PBDE human body burdens between North American and other populations are due to exposure via routes other than diet (*9*, *25*).

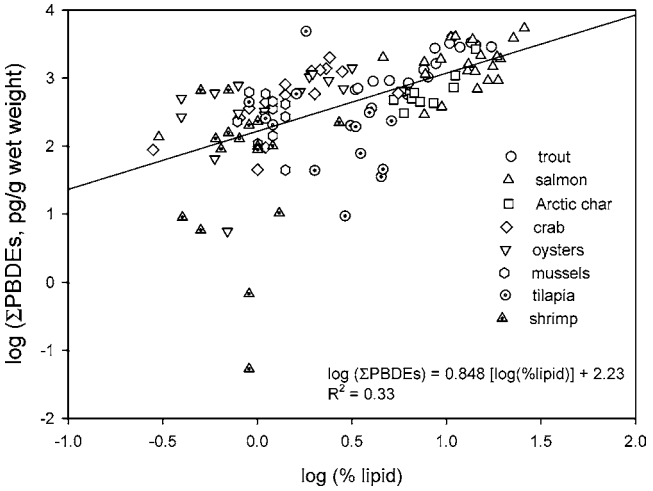

Figure 3. Correlation between total polybrominated diphenyl ether (ΣPBDE) concentrations and lipid content (% lipid) of individual fish and shellfish samples.

Differences in PBDE Dietary Exposure among Product Groups. The effects of three factors on ΣPBDE concentrations were examined in an attempt to account for the observed differences in ΣPBDE concentrations among the product groups. Lipid content of samples, source (i.e., whether the samples were from a farmed or wild source), and origin (i.e., domestic vs imported origin) were studied with respect to their effects on ΣPBDE concentrations.

Lipid content of samples was significantly positively correlated to log transformed ΣPBDE concentrations (**Figure 3**, $p < 0.001$, one-way ANOVA). Because PBDEs are hydrophobic compounds with relatively high octanol/water partition coefficients (*24*), they will tend to partition into lipid-rich tissues. Thus, samples with higher lipid contents have a greater capacity to sequester PBDEs. In this survey, the samples with higher lipid contents (salmon, trout, char) also contained the greatest amounts of PBDEs. It is also likely that higher concentrations of PBDEs would have been observed had the skin and associated lipid-rich layer been kept and analyzed along with the edible tissue of the fish samples.

As opposed to lipid content, sample source did not significantly affect ΣPBDE concentrations. Average ΣPBDE concentrations in farmed samples were higher than those in wild samples. The outliers at the upper end of the ΣPBDE concentration range were also all farmed samples. However, the difference in ΣPBDE concentrations was not statistically significant, although this may be due to the small sample numbers analyzed for wild samples. Significant differences between concentrations of hydrophobic persistent organochlorines in wild and farmed fish have been observed in another study analyzing a much larger number of samples (*26*). The concentration differences observed by Hites et al. were attributed to the use of fish oil and fish meal containing hydrophobic persistent organochlorine contaminants in feed.

Two other studies that analyzed a smaller number of farmed and wild samples for PBDEs also suggested that farmed salmon, but not farmed yellowtail, may contain higher levels of PBDEs (*10*, *21*). However, the results were not subjected to statistical analyses.

Sample origin was found to significantly affect ΣPBDE concentrations. Mean ΣPBDE concentrations were higher in

domestic samples as compared to imported samples. Because numbers of imported and domestic samples analyzed were unequal (**Table 1**), these results need to be interpreted cautiously. The differences were not due to variations in lipid content of the domestic and imported samples; when lipid-normalized ΣPBDE concentrations are included in the statistical analysis, the significant effect of sample source remains.

Differences in the imported and domestic samples may be reflecting the global distribution of PBDEs. Levels are generally highest in biota sampled near industrialized areas of North America (*3*), such as the urban areas on the Great Lakes (*27*), and appear to be lower in the southern hemisphere (*28*). This global distribution is mainly due to the geographical use pattern of PBDEs as flame retardants in fabrics and foams. Use, and thus environmental levels, is highest in North American areas of intensive consumer and industrial activity. On the other hand, the use of one PBDE formulation ("penta-BDE") is already in the process of being phased out in Europe. Most imported samples (70%) originated from countries in the southern hemisphere (Ecuador and Chile) and less industrialized areas in the northern hemisphere (Thailand) where use of PBDEs is likely lower than in North America.

Unfortunately, the relative importance of these factors affecting ΣPBDE concentrations cannot be determined because the data set generated by this survey is sparse with respect to combinations of factors. Sampling was performed to allow the analysis of fish and shellfish that was commercially available to Canadians; thus, products with specific sources and origins (e.g., wild domestic salmon) were generally unavailable at the time of sampling. However, because the samples obtained represent the fish and shellfish available in winter to Canadians in southern urban centers, the data generated in this survey provide a general overview of the PBDE levels to which the majority of Canadian consumers of fish and shellfish are exposed.

ACKNOWLEDGMENT

Patrick Laffey assisted with the statistical analyses and Helen Nicolidakis helped in the preparation of the manuscript.

Supporting Information Available: PBDEs in fish and shellfish. This material is available free of charge via the Internet at http://pubs.acs.org.

LITERATURE CITED

(1) Choi, J. W.; Fujimaki, T. S.; Kitamura, K.; Hashimoto, S.; Ito, H.; Suzuki, N.; Sakai, S.; Morita, M. Polybrominated dibenzo-p-dioxins, dibenzofurans, and diphenyl ethers in Japanese human adipose tissue. *Environ. Sci. Technol.* **2003**, *37*, 817−821.

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

(3) Hites, R. A. Polybrominated diphenyl ethers in the environment and in people: a meta-analysis of concentrations. *Environ. Sci. Technol.* **2004**, *38*, 945−956.

(4) Ryan, J. J. Polybrominated diphenyl ethers (PBDEs) in human milk: occurrence worldwide. Presented at the Third International Workshop on Brominated Flame Retardants, Toronto, ON, Canada, June 6−9, 2004; pp 17−21.

(5) Norén, K.; Meironyté, D. Certain organochlorine and organobromine contaminants in Swedish human milk in perspective of past 20−30 years. *Chemosphere* **2000**, *40*, 1111−1123.

(6) Lind, Y.; Darnerud, P. O.; Atuma, S.; Aune, M.; Becker, W.; Bjerselius, R.; Cnattingius, S.; Glynn, A. Polybrominated diphenyl ethers in breast milk from Uppsala County, Sweden. *Environ. Res.* **2003**, *93*, 186−194.

(7) Guvenius, D. M.; Aronsson, A.; Ekman-Ordeberg, G.; Bergman, A.; Noren, K. Human prenatal and postnatal exposure to polybrominated diphenyl ethers, polychlorinated biphenyls, polychlorobiphenylols, and pentachlorophenol. *Environ. Health Perspect.* **2003**, *111*, 1235−1241.

(8) Bergman, Å. BFRs—with focus on environmental fate and risks of decabromodiphenyl ether and hexabromocyclododecane. Presented at the Third International Workshop on Brominated Flame Retardants, Toronto, ON, Canada, June 6−9, 2004; pp 1−5.

(9) Harrad, S.; Wijesekera, R.; Hunter, S.; Halliwell, C.; Baker, R. Preliminary assessment of U.K. human dietary and inhalation exposure to polybrominated diphenyl ethers. *Environ. Sci. Technol.* **2004**, *38*, 2345−2350.

(10) Ohta, S.; Ishizuka, D.; Nishimura, H.; Nakao, T.; Aozasa, O.; Shimidzu, Y.; Ochiai, F.; Kida, T.; Nishi, M.; Miyata, H. Comparison of polybrominated diphenyl ethers in fish, vegetables, and meats and levels in human milk of nursing women in Japan. *Chemosphere* **2002**, *46*, 689−696.

(11) de Winter-Sorkina, R.; Bakker, M. I.; van Donkersgoed, G.; van Klaveren, J. D. *Dietary Intake of Brominated Flame Retardants by the Dutch Population*; RIVM Report 310305001; Inspectorate for Health Protection and Veterinary Public Health: The Hague, The Netherlands, 2003.

(12) 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.

(13) Ryan, J. J.; Patry, B. Body burdens and food exposure in Canada for polybrominated diphenyl ethers (BDEs). *Org. Comp.* **2001**, *51*, 226−229.

(14) Ballschmiter, K.; Zell, M. Analysis of polychlorinated biphenyls (PCB) by glass capillary gas chromatography. *Fresenius' Z. Anal. Chem.* **1980**, *302*, 20−31.

(15) Ryan, J. J.; Patry, B. Determination of brominated diphenyl ethers (BDEs) and levels in Canadian human milks. *Org. Comp.* **2000**, *47*, 57−60.

(16) Boon, J.; Lewis, W. E.; Tjoen-A-Choy, M. R.; Allchin, C. R.; Law, R. J.; de Boer, J.; Hallers-Tjabbes, C. C. T.; Zegers, B. N. Levels of polybrominated diphenyl ether (PBDE) flame retardants in animals representing different trophic levels of the North Sea food web. *Environ. Sci. Technol.* **2002**, *36*, 4025−4032.

(17) Dodder, N. G.; Strandberg, B.; Hites, R. A. Concentrations and spatial variations of polybrominated diphenyl ethers and several organochlorine compounds in fishes from the northeastern United States. *Environ. Sci. Technol.* **2002**, *36*, 146−151.

(18) 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.

(19) Sjödin, A.; Jakobsson, E.; Kierkegaard, A.; Marsh, G.; Sellström, U. Gas chromatographic identification and quantification of polybrominated diphenyl ethers in a commercial product, Bromkal 70-5DE. *J. Chromatogr.* **1998**, *822*, 83−89.

(20) Leonards, P.; Brandsma, S.; Kruijt, A.; Lohman, M.; Van Hesselingen, J.; de Boer, J. *Background Values of Brominated Flame Retardants in Food Products*; Institute for Fisheries Research: Umuiden, The Netherlands, 2002.

(21) Easton, M. D. L.; Luszniak, D.; Von der Geest, E. Preliminary examination of contaminant loadings in farmed salmon, wild salmon and commercial salmon feed. *Chemosphere* **2002**, *46*, 1053−1074.

(22) Zabik, M. E.; Booren, A. M.; Zabik, M. J.; Welch, R.; Humphrey, H. Pesticide residues, PCBs and PAHs in baked, charbroiled, salt boiled and smoked Great Lakes lake trout. *Food Chem.* **1996**, *55*, 231−239.

(23) Tittlemier, S. A.; Halldorson, T.; Stern, G. A.; Tomy, G. T. Vapour pressures, aqueous solubilities, and Henry's law constants of some brominated flame retardants. *Environ. Toxicol. Chem.* **2002**, *21*, 1804−1810.

(24) Braekevelt, E.; Tittlemier, S. A.; Tomy, G. T. Determination of octanol/water partition coefficients of some brominated flame retardants by the slow-stirring method. *Chemosphere* **2003**, *51*, 563−567.

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

(26) Hites, R. A.; Foran, J. A.; Carpenter, D. O.; Hamilton, M. C.; Knuth, B. A.; Schwager, S. J. Global assessment of organic contaminants in farmed salmon. *Science* **2004**, *303*, 226−229.

(27) Norstrom, R. J.; Simon, M.; Moisey, J.; Wakeford, B. J.; Weseloh, D. V. Geographical distribution 2000 and temporal trends (1981−2000) of brominated diphenyl ethers in Great Lakes herring gull eggs. *Environ. Sci. Technol.* **2002**, *36*, 4783−4789.

(28) Ueno, D.; Kajiwara, N.; Tanaka, H.; Subramanian, A.; Fillmann, G.; Lam, P. K. S.; Zheng, G. J.; Muchitar, M.; Razak, H.; Prudente, M.; Chung, K.-H.; Tanabe, S. Global pollution monitoring of polybrominated diphenyl ethers using skipjack tuna as a bioindicator. *Environ. Sci. Technol.* **2004**, *38*, 2312−2316.

Received for review August 6, 2004. Revised manuscript received September 13, 2004. Accepted September 28, 2004.

JF048665Y